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Surface initiated polymerization of isoprene from silica nano- and glass particles via living anionic and controlled radical polymerization techniques

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Finally, very special debt of gratitude goes to my parents and my sister (Hilal) for all their love and support and I dedicate this thesis to them.

Abstract

In this thesis the preparation of polyisoprene-silica (PI-SiO_2) composites via surface initiated polymerization (SIP) method is targeted. Polyisoprene (PI) is grafted from initiator/additive functionalized silica nano- (SA15 from Sigma Aldrich and AE200 from Evonik) and glass particles (K3 and B-K3 from Trovotech) via living anionic surface initiated polymerization (LASIP) and surface initiated controlled radical polymerization (SI-CRP) techniques. The particle surfaces are functionalized with three types of coupling agents, *i)* three diphenyl ethylene (DPE) derivatives with different alkyl-spacer lengths, thus separating the DPE moiety in different distances from the particles' surfaces for LASIP, *ii)* a chain transfer agent (CTA) derivative for surface initiated reversible addition fragmentation chain transfer (SI-RAFT) polymerization and *iii)* an AIBN (conventional azo initiator) derivative for SI-RAFT and surface initiated nitroxide mediated polymerization (SI-NMP) depending on the additive ((2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) and 2,2,5-tri-methyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) for SI-NMP and a suitable CTA for SI-RAFT).

LASIP of isoprene from DPE-functionalized nano- and glass particle surfaces is conducted by using *n*-BuLi/*sec*-BuLi to activate the ethylene moiety on the DPE units in different solvent systems and at various temperatures depending on the solvent. Grafted PI-silica composites are analyzed via TGA, resulting in grafting densities (σ_{PI}) of the produced inorganic-polymer composites in the range from 0.10 to 0.24 PI-chains/nm^2. GPC analysis reveals that the polydispersity (PDI) values ranging from M_w/M_n= 1.1 to M_w/M_n= 1.7. The final microstructure of the grafted polyisoprene is investigated via NMR, revealing that 15% *1,2*, 35% *cis-1,4* and 50% *trans-1,4*. DLS measurements show that obtained composites have a shell thickness of 3-5 nm.

SI-RAFT of isoprene is conducted by initiating the polymerization with the addition of azobisisobutyronitrile (AIBN) or dicumyl peroxide (DCP) from CTA-functionalized silica nanoparticles (NPs) and also with the addition of a suitable CTA from azo-functionalized silica NPs. SI-NMP of isoprene is carried out in the presence of a stable radical (TEMPO or TIPNO) from azo-functionalized silica NPs. GPC analysis reveals that the SI-CRP of isoprene was not as successful as LASIP reactions, as PDI values were relatively high (up to M_w/M_n= 2.3) for a controlled radical polymerization. The grafting density values of the produced composites were also lower than the ones which were prepared via LASIP.

List of Abbreviations

AIBN	Azobisisobutyronitrile
ATRP	Atom transfer radical polymerization
CB	Carbon black
CRP	Controlled radical polymerization
CTA	Chain transfer agent
DCC	N,N'Dicyclohexylcarbodiimide
DCP	Dicumyl peroxide
DCM	Dichloromethane
DLS	Dynamic light scattering
DMAP	4-Dimethylaminopyridine
DMF	Dimethylformamide
DP	Degree of polymerization
DPE	Diphenylethylene
EO	Ethylene oxide
GP	Glass particle
GPC	Gel permeation chromatography
HF	Hydrofluoric acid
ITO	Indium tin oxide
LAP	Living anionic polymerization
LASIP	Living anionic surface initiated polymerization
LCP	Living cationic polymerization
LCSIP	Living cationic surface initiated polymerization
MALDI-tof	Matrix assisted laser dissorption ionization time of flight spectroscopy
MWCN	Multi-walled carbon nanotube
NC	Nanocomposite
NMP	Nitroxide mediated polymerization
NMR	Nuclear magnetic resonance
NP	Nanoparticle
PDI	Polydispersity index
PI	Polyisoprene
RAFT	Reversible addition fragmentation chain transfer
ROMP	Ring opening metathesis polymerization
ROP	Ring opening polymerization
SIP	Surface initiated polymerization
SIIP	Surface initiated ionic polymerization
SI-ATRP	Surface initiated atom transfer radical polymerization
SI-CRP	Surface initiated controlled radical polymerization
SI-FRP	Surface initiated free radical polymerization
SI-NMP	Surface initiated nitroxide mediated polymerization
SI-RAFT	Surface initiated reversible addition fragmentation chain transfer
SI-RATRP	Surface initiated reverse atom transfer radical polymerization
SI-ROP	Surface initiated ring opening polymerization
TEMPO	2,2,6,6-tetramethylPIeridinyloxy
TEOS	Tetraethyl orthosilicate
TGA	Thermo gravimetric analysis
THF	Tetrahydrofurane
TIPNO	2,2,5-tri-methyl-4-phenyl-3-azahexane-3-nitroxide
TLC	Thin layer chromatography
TMEDA	Tetramethylethylenediamine
TMSiCl	Trimethylsilyl chloride
TSPA	4-trimethoxysilyl-1,2,5,6-tetrahydrophthalic

Index

1. Introduction

1.1. Polymer-inorganic nanocomposites

Polymer-inorganic composites have attracted great attention due to their wide range of applications[1-10] as these composites have use in various fields such as electronics,[9-10] rubber technology[11-13] and engineering[7,14-18]. Polymer-inorganic composites can most simply be defined as polymeric materials at one end attached to a solid inorganic substrate (spherical, flat or porous structure from nano to micro size) either through covalent or physical interactions[1]. These composite materials provide great opportunities for constructing functional materials[1,14,16,19-20] as they can combine fascinating electrical, optical and magnetic properties of the inorganic core and the desired properties of a polymer such as solubility, film formation, processability and compatibility to the environment[3,14-15,20-21]. Since 1990's the investigations of polymer-inorganic nanocomposites have increased dramatically in order to be able to design polymer thin films with controlled molecular weight and architecture and incorporate this polymers with suitable inorganic substances to exploit their properties in various applications[1,22-23]. Today polymer-inorganic nanocomposites are not only a research area for polymer science but also for material science and engineering[24-25].

According to the size of the inorganic substance these composites can be classified as nano-, micro- and macrocomposites. As the size of the inorganic particle decreases to the nanoscale the specific surface area that interacts with the organic macromolecule (polymer) increases (see **Figure 1.1**). This amplified interaction at nanoscale results in surprising mechanical, magnetic and electro-optical behavior at macroscale[2]. Although there has been a large volume of published literature about the relationships between nanoscale structure and macroscale properties, the understanding of the basic physical origin of large property changes has still been unknown[1-3]. One of the many affected macroscopic properties is the glass transition temperature (T_g). Changes in T_g are in direct correlation with diverse transport phenomena and chain relaxation[26-27]. Depending on the nature of the interactions between the polymer and NP being attractive or repulsive, T_g tends to either increase or decrease, respectively[28]. Other criteria at the nanoscale which make an impact at macroscale are dispersion of the NPs in polymer matrix and the geometry of the NPs[28-29].

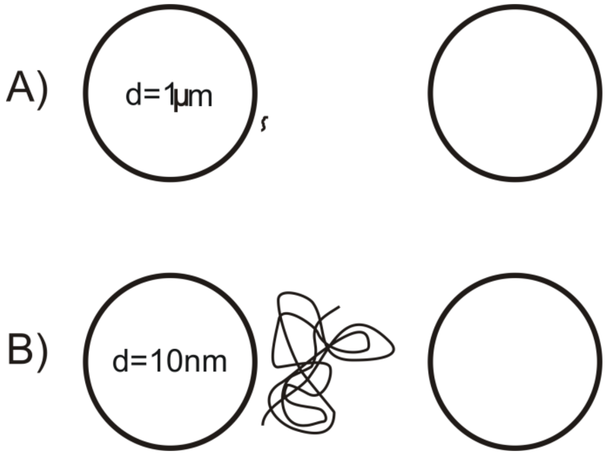


Figure 1.1 Graphical representation of the interaction of a polymer chain with A) a micro-sized particle and B) a nano-sized particle (Figure taken from literature[2]).

Researchers have not only investigated the structure property relationship of the nanocomposites (NCs), but also tried to produce such NCs with controlled surface architecture[19,21-23,30-36]. One way of producing polymer-inorganic NPs is so called 'physisorption'. In this method polymer and inorganic substrate interact with each other via secondary binding forces (van-der-Waals, dipolar, hydrogen bonding), thus the binding energy is low[37-39]. The low binding energy between the organic and inorganic content may cause obstacles during processing and application[2-3].

Another way of producing such composites is so called 'chemisorption'. In this method the interaction between the organic polymer shell and the inorganic core is chemical (either covalent or ionic)[19,32,40-42], therefore the binding energy between the polymer shell and the inorganic core is higher when compared to the physisorption method. Chemical grafting methods are more advantageous and preferred for producing polymer-inorganic composites[8] in comparison to physisorption, especially when the binding forces are considered for specific applications and processing issues.

Chemisorption can also be divided into two: *grafting onto*[19,43-44] and *grafting from*[19,32,42,45-46]. In the former a previously produced polymer (with a desired end group) is attached to the functionalized surface of an inorganic particle (*grafting onto*) whereas in the latter the polymer is grown from the inorganic particle's surface which is functionalized with a suitable initiating group that allows polymerization (*grafting from*) via various polymerization techniques[19,21,30,32,47-49]. (See **Figure 1.2**)

Among those two, *grafting from* method (also known as 'surface initiated polymerization' (SIP)) is more advantageous than the *grafting onto* method especially when the grafting density is considered. In the *grafting onto* method the approach of the polymers (macromolecules) to the surface of the particle causes steric hindrance, hence the grafting density value of the polymers on the surface in *grafting onto* methods is significantly lower than the one in *grafting from* method[8]. There are also strict limitations on the choice of functional groups for incorporation into the polymer. The reason for this limitation is that the functional groups on the polymer can compete with the anchoring group, thus reducing the grafting density[50]. Therefore SIP is one of the most useful methods for producing these polymer-inorganic NCs[8,21,51]. SIP will be explained in more detail in the following section.

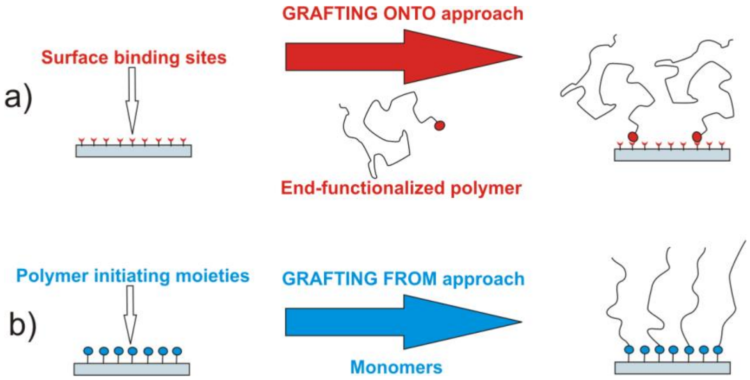


Figure 1.2 Schematic representation of chemisorption methods; a) grafting onto approach, b) grafting from approach

Depending on the grafting density (σ_i) of the polymers which are attached to the surface of the inorganic substrate, these composites can be named as polymer brushes in case of high grafting density as the polymer chains are stretched away from the surface of the inorganic core[1,19,21,30,50]. However a brush conformation is not the only physical state that these composites can display. Lower grafting density values result in crossover and mushroom regimes, as the polymer chains overlap with each other instead of stretching away from the surface (see **Figure 1.3**). When the grafting density is high, the polymer chains are closer to each other; therefore the chains have to be stretched away from the surface of the inorganic particle. When the grafting density values of the surface-attached polymers are lower, the polymer chains are found to be more relaxed state; therefore they form either mushroom or crossover regimes in which they may overlap on each other[50]. In 2007 Brittain and Minko introduced a single parameter (the reduced tethered density, Σ) to distinguish a brush from other conformation states. The reduced tethered density is defined as $\Sigma = \sigma \pi R_g^2$, where R_g is radius of gyration of a tethered chain at specific experimental conditions of solvent and temperature[52]. Based on the equation above the mushroom regime occurs when $\Sigma < 1$, the crossover regime occurs at $\Sigma \approx 1$ and the brush regime occurs at $\Sigma > 1$[52]. Schematic representation of these three physical states is shown in **Figure 1.3** below.

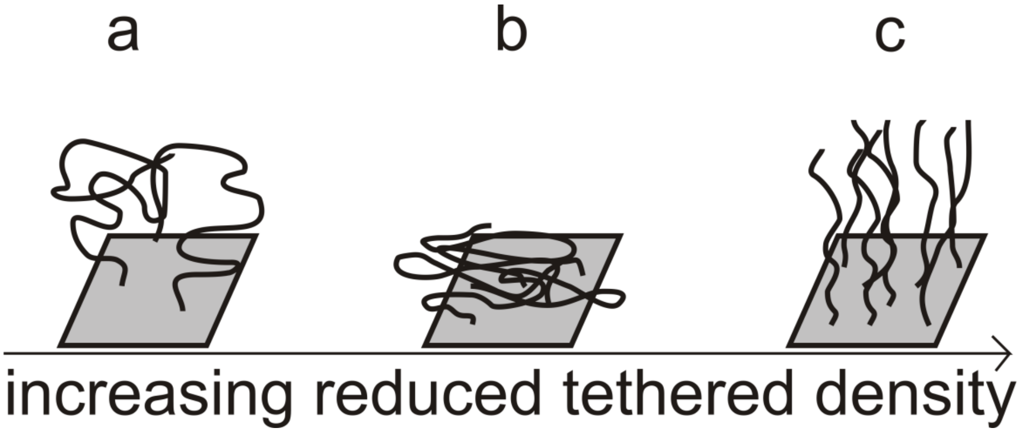


Figure 1.3 Conformation of polymer chains depending on the grafting density; a) mushroom regime, b) crossover regime, c) brush conformation.

1.2. Surface initiated polymerization (SIP)

As it is mentioned earlier surface initiated polymerization (SIP) is one of the most useful methods for producing polymer brushes (polymer-inorganic composites)[8,19,21,32,42,45-46,51,53-55] due to its availability to combine favorable properties of inorganic solid substrates with the desired properties of polymers. SIP can simply be defined as the polymerization of monomers directly from the initiator sites which are already immobilized on the surface of the substrate[19,21].

In SIP techniques the surface of the substrate (organic or inorganic) is mostly functionalized with a suitable surface modifying group which can subsequently initiate a polymerization with the addition of a monomer and necessary reagents or the polymerization is directly initiated from the functional groups on the particle surface with the addition of a monomer and necessary reagents depending on the polymerization technique. Since small monomers are polymerized from the previously initiator functionalized surface of the substrate (or directly from the surface), the steric hindrance is lower when compared to the *grafting onto* method, hence higher grafting density values can be achieved with SIP technique[50]. High grafting densities ($\Sigma > 1$) allow a polymer brush regime which forces polymers chains to adopt an entropically unfavorable stretched state thus providing relatively thick films[56]. It has been previously reported that many specific properties of polymer-inorganic NCs such as protein resistance[57-58] and lubricity[59] can only be obtained by achieving a high grafting density. The advances in polymer sciences (especially the developments in living/controlled polymerization methods) have increased the number of researches on SIP of various polymers; hence the applications of these resulting composites have been significantly widened.

SIP procedures that have been reported so far mostly require surface functionalization of the inorganic substance by using small initiator molecules (surface modifying groups) as shown in **Figure 1.2b**. These surface modifying groups form self assembled monolayers (SAMs) which can be defined as organic molecules that arrange themselves spontaneously on the surface of solid (mostly metal) and liquid substrates[60-62] prior to SIP. Due to SAMs' low cost of production and versatile surface coating they have been used in various application areas such as electronics[62-63], adhesion[64], and molecular recognition for biosensors[64] and nano fabrication[60-61].

In order to prepare SAMs on inorganic particle surfaces prior to SIP mainly two types of bonding systems have been used: thiol-noble metal[19,21,49,65-66] (mostly gold) for SIP from metal substrates or silane-silanol bonding[8,19-20,32,41,67-72] for SIP from silica (SiO_2) substrates. However some obstacles about these bonding systems have been reported as well. It has been reported the Au-S bonds might go into redox cleavage over time and using thiol initiators might cause problems for technical applications[73]. On the other hand, chlorosilane or alkoxysilane initiators are synthesized by using expensive and toxic reagents and they have relatively short shelf life due to moisture contamination[56].

In order to overcome such obstacles alternative routes have been explored. (3-Aminopropyl) triethoxysilane was reacted with 2-bromoisobutyryl bromide to obtain an amide-based initiator for ATRP. However, amide-based ATRP initiators were found to be less active when compared to ester-based ATRP initiators[74-75].

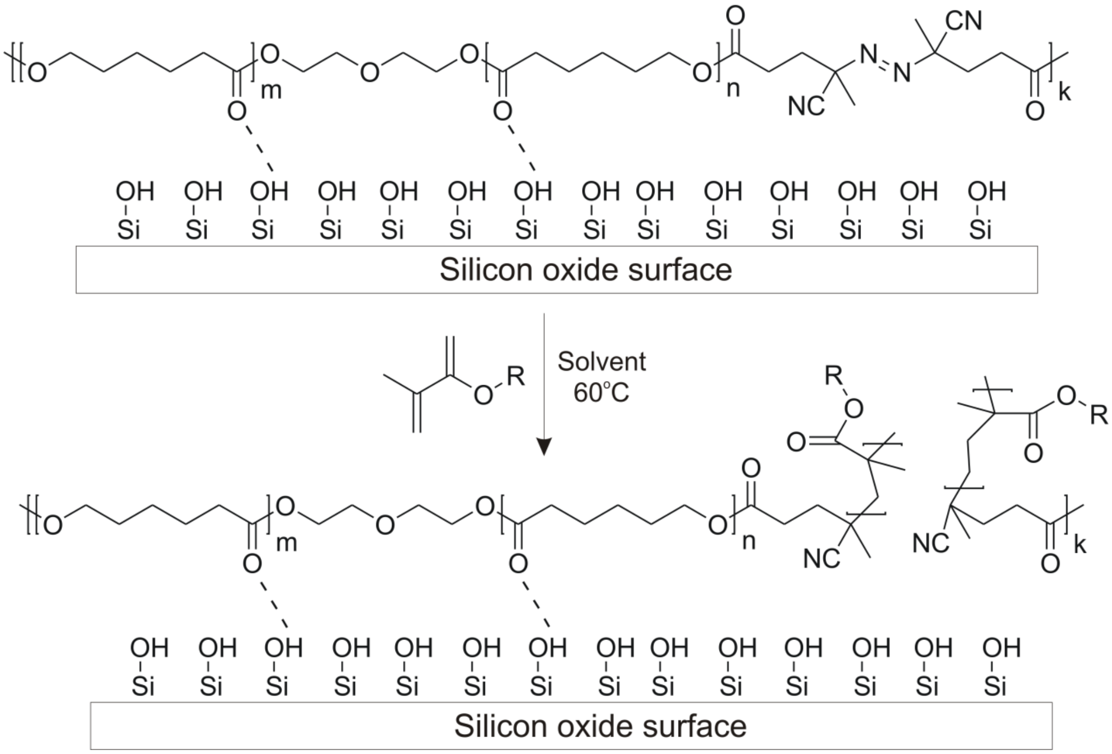


Figure 1.4 Adsorption of poly(ε-caprolactone) macro-initiotor and subsequent free radical polymerization of n-alkyl methacrylate[56]

Due to the limitations of small-molecule initiators (surface modifying groups), macro-initiators which are bulkier than surface modifying groups have been introduced as an alternative strategy. Several research groups have tried to replace the strong covalent grafting by the small-molecule initiator with weaker non-covalent binding of macro initiators to the surface (hydrogen bonding or electrostatic interactions)[56,76-77]. The most important point was the selection of solvent as a non-solvent for the macro-initiator must be chosen as a good solvent for the macro-initiator might cause the reduction in film thickness[76]. A macro-initiator which was introduced by Rühe *et al.*[76] contained a diazo moiety and interacted with the particle surface via hydrogen bonding in order to conduct surface initiated free radical polymerization of n-alkyl methacrylate from this macro-initiator functionalized surface (See **Figure 1.4**). This specific strategy basically combines the physisorption (physical attachment of the macro-initiator) and chemisorption (grafting of covalently bonded polymer to the macro-initiator).

Up to now various polymers were grafted from several inorganic substrates. In this thesis SIP from silica (SiO_2) NPs (spherical or flat substrates) will mainly be focused and details will be given in following sections. Beside silica particles, SIP studies have also been reported on gold[21,49,65-66], metal oxides (iron oxide[54], indium tin oxide (ITO)[78], zinc oxide[79]), metal (CdSe[80-81], iron and stainless steel[82-83]) and carbon black[33-34,84] particles. Some specific examples of SIP from different particle surfaces will also be mentioned in the following sections.

1.2.1. SIP from silica substrates

Silica (SiO_2) substrates (flat or spherical) have been extensively studied for polymer-inorganic composites produced via SIP techniques[8,20,41,69-70,72,85-86]. Up to now many studies on SIP from silica substrates have been reported by using different living/controlled polymerization methods[8,20-21,30-32,40,69,71,86-89]. Silica nanoparticles (NPs) have been intensely used as filler materials because they have various applications in paint and rubber industry for producing organic-inorganic hybrid materials[8]. Another reason for this high interest towards silica particles as filler materials beside their wide application area is their easy synthesis which results in uniform shaped and sized particles due to the precise control during synthesis[90]. The Si-OH (silanol) functional groups on the surface of the particles allow surface functionalization of these particles with desired functional groups for various applications[88]. Although more specific examples will be given in the corresponding sections it is useful to present some important studies on SIP from silica particles below.

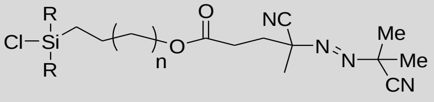
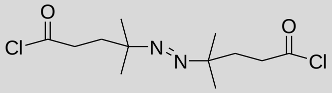
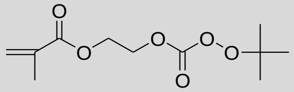
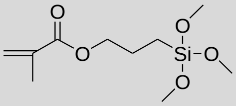
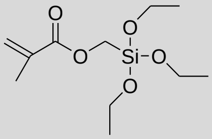
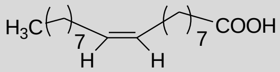
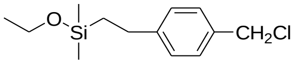
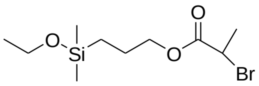
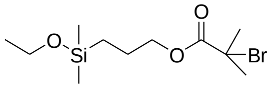
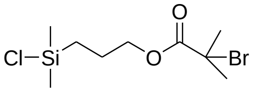
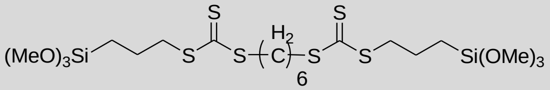
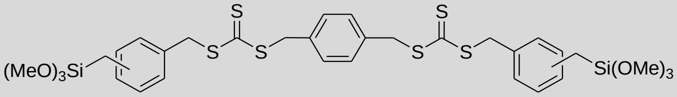
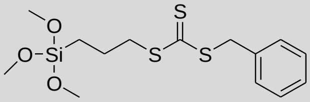
The main types of chemical bonding between the silica surface and the surface modifying groups are silane-silanol types of bondings which can be obtained by treating the surface silanol groups of the silica substrate with either chlorosilanes[19,68,91-93] or alkoxysilanes[89,94-95] end-functionalized surface modifying groups (different examples can be seen in **Table 1.1**). Formation of an ester by treating the silanol groups on the silica surface with a carboxylic acid (or carboxylic acid chloride) is another method of immobilizing surface modifying group on the silica substrate[96-97].

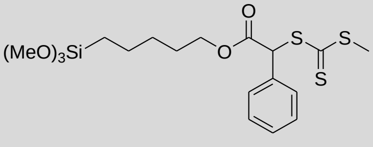
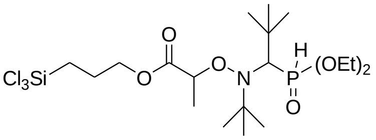
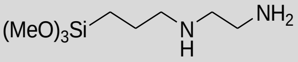
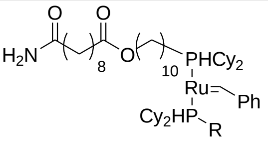
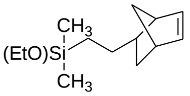
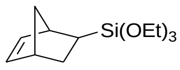
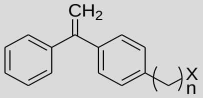
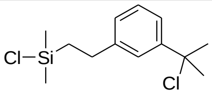
Conventional free radical polymerization method has been one of the most studied systems as an SIP technique for producing silica-polymer composite materials due to its tolerance towards various functional groups and impurities[87,96-102]. Besides, the conventional free radical polymerization has always been a leading industrial method for producing polymers[8] therefore the reason of these intensive studies on the surface initiated free radical polymerization (SI-FRP) from silica substrates could be understood easily, especially when it is considered that the laboratory scale production is to be applied in industrial scale. One of the first examples of SI-FRP from silica was reported by Rühe *et al.*[87]. Polystyrene was grafted from the surface of silica gel which was functionalized with an azo initiator via free radical polymerization. A self assembled monolayer (SAM) of a conventional azo-initiator was immobilized on the silica gel surface and used as initiator for SIP of styrene subsequently. The grafting density could be controlled by controlling the amount of the azo-initiator bearing a monochlorosilane anchoring group which was immobilized on the silica gel surface[87,99].

Another early attempt on SIP from the surface of a silica substrate was done by Oosterling *et al.*[71] who reported grafting of polyisoprene from nanosized silica particles and micro sized glass slides as a block-copolymer. ***A-B-A*** type triblock poly(styrene-*block*-isoprene-*block*-styrene) was grafted from functionalized surfaces of silica and glass substrates via living anionic polymerization. Monomer conversion of the *grafting from* polymerization was investigated under different conditions and the produced nanocomposite materials were characterized via elemental analysis. The surface of the silica NPs (12 nm in size) was functionalized with p-vinylbenzylthrichlorosilane (VBS). SIP was initiated by the addition of *n*-BuLi and the addition of more styrene (and isoprene for block copolymer) resulted in propagation of the polymer chain. The kinetic studies revealed that the polymerization had pseudo-living character, however the grafting density was extremely low and SIP of block copolymer was not reproducible.

Beside these two early examples of SIP from silica above, various polymerization techniques and various types of silica substrates (flat, spherical, porous structures) have been used for producing polymer-silica composite materials. More details on SIP from silica particles will be given in the corresponding sections. **Table 1.1** shows examples of the research on SIP from silica particles via numerous polymerization techniques by using different coupling agents and additives.

Table1.1 Examples of coupling agents used for SIP of various monomers from silica particles via different polymerization techniques

entry	coupling agent	polymerization method	polymer	grafting data	reference
1	 n= 1, 9	FRP	PS	0.05 g/g of silica	87,99
2	 	FRP	PA-*co*-PAC	0.11 g/g of silica	96
3		FRP	PS, PMMA, PS-co-PBuA	0.10 g/g of silica	98,101-102
4		FRP	PS	0.1 chains/nm^2	100
5		FRP	PS	n.a.	97
6		ATRP	PS	2.6 chains/nm^2	103
7	 	ATRP	PS, PMMA, POEGMA, PMEMA	2-5 chains/nm^2	104-105
8		ATRP	PS, PMMA, P(n-BuA)	1000 chains/particle	106
9	 	RAFT	PMA	0.6 chains/nm^2	107
10		RAFT	PMA	14.2-58.2 μmol/g silica	94

11		RAFT	PMMA, PNIPAM, P(n-BuA)	0.3 chains/nm^2	94,108
12		NMP	PS, P(n-BuA)	0.95-1.1 chains/nm^2	91-92
13		ROP	P(ε-CL)	0.10 g/g of silica	109
14	  , 	ROMP	PNB	0.01-0.03 chains/nm^2	110-111
15		LAP	PS	0.3 chains/nm^2	19-21,112
16		LCP	PIB	0.6-0.8 chains/nm^2	40

FRP: Free radical Polymerization, ATRP: Atom Transfer Radical Polymerization, RAFT: Reversible Addition Fragmentation Chain Transfer, NMP: Nitroxide Mediated Polymerization, ROP: Ring Opening Polymerization, ROMP: Ring Opening Metathesis Polymerization, LAP: Living Anionic Polymerization, LCP: Living Cationic Polymerization

1.2.2. SIP from different surfaces

As it was briefly mentioned earlier silica substrates are not the only inorganic substrates which have been used to graft polymers to produce polymer-inorganic composites. Silicon is another inorganic substrate which has been used for SIP processes[68,113-115]. The main difference between SIP from silica and silicon is the type of bond between the particle surface and the surface modifying group. In silica particles surface silanol groups (Si-OH) are treated with chlorosilane (or alkoxysilane) end-functionalized modifying groups to form Si-Si bond between the particle surface and the surface modifying group. On the other hand, surface Si-H functional groups of the silicon substrates which are obtained by treating the silicon oxide substrate with dilute hydrofluoric acid (HF) can be homolytically dissociated by UV irradiation to form a radical site which reacts readily with an alkene (forming a robust Si-C bond) to give rise to a surface-tethered alkyl radical on the β-carbon[116]. Silicon surfaces are mostly functionalized with chloromethylbenzyl bearing surface modifying groups prior to surface initiated-controlled radical polymerization (SI-CRP) methods[117].

Another type of substrates which has been used for SIP processes is metal oxide substrates. Many of the examples of SIP from metal oxide surfaces have employed aluminum[118] (Al_2O_3), titanium[119-121] (TiO_2) and iron oxides[54] (Fe_3O_4). There are also reports on SIP from other metal oxide surfaces such as indium tin oxide[78] (ITO), copper oxide[122] (CuO_x), zinc oxide[123] (ZnO), nickel oxide[122] (NiO_x) and magnesium hydroxide[124] ($Mg(OH)_2$). The surface of metal oxides are generally functionalized with surface modifying groups bearing chlorosilane and alkoxysilanes anchoring moieties to form metal-O-Si bonds between the metal oxide substrate and the surface modifying group. Metal-O-Si bonds are generally weaker than the Si-O-Si bonds, however among those metal-O-Si bonds, the Al-O-Si bonds are the strongest[116]. There are also reports on SIP from iron and titanium oxides by using surface modifying groups which were end functionalized with phosphoric acid moiety forming metal(Fe/Ti)-O-P series[120,125]. It has been shown that the bonding between Ti-O-P (or Fe-O-P) is stronger than Ti-O-Si (or Fe-O-Si) due to the strong interaction between metal oxide and phosphoric acid and also the instability of metal-O-Si bonds[120,123-125]. Additionally the surface modification of copper and nickel oxides can only be done by using alkoxysilane bearing surface modifying groups as chlorosilane causes extensive corrosion[122].

Gold substrates have been extensively used to graft polymers via various SIP techniques[21,49,62,65-66,73,116,126-127]. There are two types of gold substrates used for polymer grafting: i) gold films deposited on flat surfaces such as silicon-wafers[128], glass[49] and quartz slides[21] and ii) gold nanoparticles[66,126-127]. Mainly disulfides and thiols are used as anchoring groups to form Au-S bonded SAMs on the surface of the gold substrates. The initiating moiety of the surface modifying group is separated from the thiol and/or the disulfide anchoring group by an alkyl spacer in order to reduce the steric hindrance during the polymerization[116]. Ligand exchange reactions have also been used as an alternative surface functionalization strategy for citrate-stabilized gold substrates by exchanging the citrate with thiol end-functionalized surface modifying group as the Au-S bond is stronger than the Au-citrate interaction[129].

The last type of inorganic substrates which has been used to graft polymers is metals and semiconductors. Although metal oxides as substrates are mentioned above, these specific types of substrates require different anchoring groups to form SAMs prior to SIP processes[116]. Cadmium selenide (CdSe)[81], cadmium sulfide (CdS) and Fe (stainless steel as well) are the three main examples of this kind of substrates. For the immobilization of surface modifying group on the CdSe and CdS nanoparticles ligand exchange strategy has used by replacing the ligand-stabilized NP (mostly pyridine) with phosphine oxide ligand bearing surface modifying group[80-81]. In order to graft polymers from planar iron and stainless steel substrates the initiating groups are immobilized on the surface via electrografting[83].

1.3. SIP via different polymerization techniques from various surfaces

1.3.1. Surface Initiated Ionic Polymerization (SIIP)

Ionic polymerization methods have been used extensively to synthesize nearly monodisperse linear homopolymers and block copolymers[22]. More complex structured polymers (star shaped, graft copolymer architectures) have also been prepared via living ionic polymerization methods[21-22,48,112]. The fascinating properties of polymer-inorganic composites lead researchers to synthesize those composites via living ionic polymerization techniques.

However, living cationic and living anionic surface initiated polymerization methods show differences when compared to conventional cationic and anionic polymerization procedures. The right selection of solvent, monomer and initiator is essential[19]. Due to the intolerance of both polymerization methods to impurities such as moisture and oxygen SIP procedure requires extreme inert conditions[19,130-131]. For the control of molecular weight it is extremely important to consider the efficiency and the reactivity of the initiator as well as the effect of solvent[19-20,50,112].

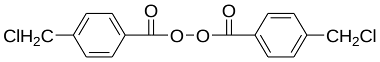
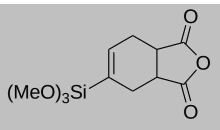
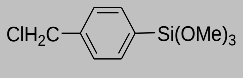
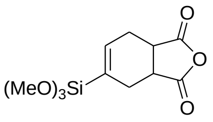
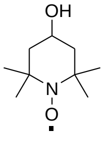
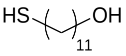
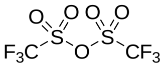
One of the main obstacles in surface initiated ionic polymerization (SIIP) is that the corresponding inorganic substances (silica nanoparticles, clay particles) contain inevitably moisture which can terminate a living ionic polymerization, thus the livingness of the polymerization is endangered[16,112]. In order to overcome this problem high vacuum techniques were applied by Hadjichristidis *et al.*[21,130] to conduct living anionic surface initiated polymerization (LASIP) from planar silica and gold surfaces. Diphenylethylene (DPE) based surface modifying groups were used and SIP was initiated by the addition of *n*-BuLi[21]. The high vacuum techniques are also helpful to keep the polymerization system inert so that the living anionic polymerization which is intolerable to any kind of impurity would not be disturbed.

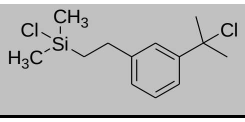
Another disadvantage of surface initiated polymerization processes is the agglomeration of particles especially when the size of the particles is in the nanoscale. This issue has been reported previously by Ohno *et al.*[70] and Hübner *et al.*[132]. A solution to overcome this is to ultrasonicate the particle/solvent mixture before both the surface functionalization and surface initiated polymerization reaction in order to achieve full dispersion.

1.3.1.1. Living cationic surface initiated polymerization (LCSIP)

Living cationic polymerization (LCP) is one of the polymerization techniques which has been applied to produce polymer-inorganic composites as a SIP method[133]. **Table 1.2**, below, shows some examples of living cationic surface initiated polymerization (LCSIP) of various monomers from various substrate surfaces.

Table 1.2 Examples of LCSIP of various monomers from different particle surfaces

entry	coupling agent	additive	particle	monomers	reference
1	-	-	carbon black	vinyl ethers, indene, acetylnaphthalene, N-vinyl carbazole, N-vinyl-2-pyrrolidine	134-138
2		$AgClO_4$	carbon black	cyclic ethers and cyclic esters, vinyl monomers	139
3	 	H_2O, $SOCl_2$, $AgClO_4$	ultrafine silica	cyclic ethers and cyclic esters, vinyl monomers	140-141
4		DCC +  + $HClO_4$	ultrafine silica	iso-butyl vinyl ether, N-vinylcarbazole, 2,3-dihydrofuran, γ-butyrolactone	142
5	-	$ZnCl_2$	carbon black	iso-butyl vinyl ether	143
6			gold NP	2-oxazoline	127

7		$TiCl_4$	silica NP	isobutylene	113
8	-	$SOCl_2$, $AgClO_4$	graphite	styrene	144
9		$TiCl_4$	silica NP	isobutylene	40

One of the first attempts on LCSIP was reported by Tsubokawa *et al.*[134-138] who produced polymer grafted carbon black (CB) particles by polymerizing various monomers (vinyl monomers, vinyl ethers, indene, acenaphtylene, N-vinyl carbazole, N-vinyl-2-pyrrolidine) via LCSIP (entry 1, **Table 1.2**). The common characteristic of these LCSIP processes was that no surface modifying group was used in order to functionalize the surface. The polymers of the corresponding monomers were directly grafted from the carboxylic acid functional groups which were already present on the CB surface. In these experiments livingness of the polymerization, conversion of monomers, the grafting ratio and effect of time and temperature on the LCSIP were investigated. The results indicated that SIP had a living character and the grafting density was dependent on both the polymerization time and temperature. The increase in polymerization temperature resulted in increase in polymerization rate; however the high reaction temperature also caused a decrease in grafting density due to the increase in chain transfer reactions between the growing polymer chains.

A surface modifying group for cationic ring opening SIP of cyclic ethers and cyclic esters was later introduced (entry 2, **Table 1.2**)[139]. The polymerization of the corresponding monomers was initiated by an acylium perchlorate based surface modifying group which was used to functionalize the surface of CB particles. 3,3 '-Bischloromethylbenzoyl peroxide was used to functionalize the surface of the CB resulting in CB-Ph-CH_2Cl. This benzyl chloride functional group was treated with $AgClO_4$ to obtain initiating benzyl cation:CB-Ph-$CH_2^+ClO_4^-$. With this strategy THF, epichlorohydrin, ε-caprolactone, δ-valerolactone were successfully grafted from CB surface. LCSIP of the other vinyl monomers which were polymerized with LCSIP (without using a surface modifying group) were also investigated with this method and yielded satisfactory results. The effect of polymerization time and temperature were similar to the LCSIP reactions which were previously conducted in the absence of a surface modifying group.

Acylium perchlorate based surface modifying groups were also applied on ultrafine silica particles (entry 3, **Table 1.2**)[140]. Due to the different surface chemistry of the silica particles a new synthetic strategy was developed (see **Figure 1.5**). 4-trimethoxysilyl tetrahydrophtalic anhydride was used to functionalize the surface silanol groups and then the anhydride was first hydrolyzed and the resulting carboxylic acid was converted to acid chloride before treating with $AgClO_4$. A direct surface modifying group (4-(chloromethyl)phenyltrimethoxysilane) was later used in order to avoid hydrolysis of the anhydride and the subsequent chlorination of the carboxylic acid[141].

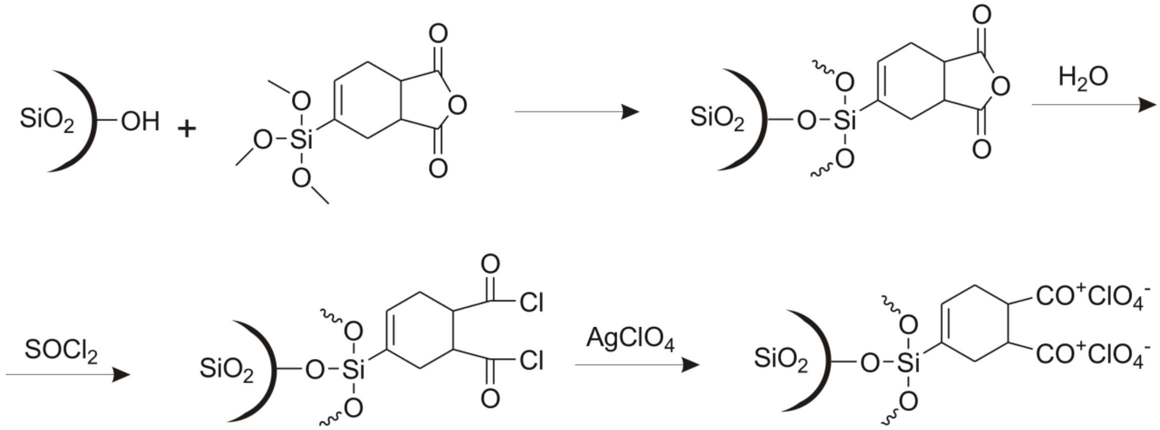


Figure 1.5 Synthetic pathway to surface modification of the silica particles and activation of the initiator group[140]

LCSIP of styrene from silica particles by using these surface modifying groups and initiating systems resulted in surface grafted polymer with high monomer conversion at high temperature (94.7% at 20^{o}C) but low grafting percentage (17.3% at 20^{o}C). Increase in temperature caused decrease in grafting density but increase in monomer conversion, while decrease in temperature caused decrease in monomer conversion but increase in grafting percentage[141].

LCSIP of vinyl monomers were also investigated by using oxoammonium perchlorate initiating groups[142]. The functional groups were introduced by treating silica particles first with 4-trimethoxysilyl-1,2,5,6-tetrahydrophthalic (TSPA) anhydride and then with 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy radical (4-hydroxy TEMPO). Finally treating the resulting surface functionalized particles with $HClO_4$ provided the initiating oxoammonium perchlorate groups (see **Figure 1.6**).

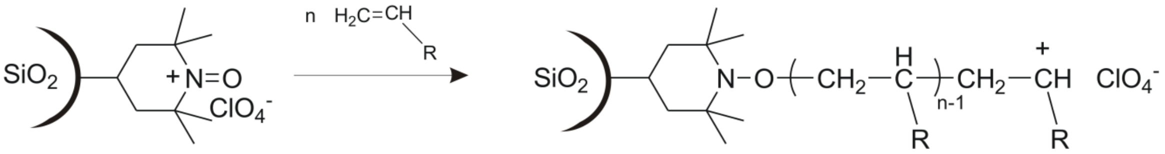


Figure 1.6 LCSIP of vinyl monomers from silica particles by using oxoammonium perchlorate initiating group[142]

LCSIP of iso-butyl vinyl ether was also tried in the presence of zinc chloride ($ZnCl_2$)[143]. Previous attempts on the LCSIP of iso-butyl vinyl ether resulted surface grafted polymers with low monomer conversion and broad molecular weight distributions. The introduction of $ZnCl_2$ dramatically increased the conversion (100% conversion in 15 minutes) and polymers with low polydispersity values (1.25) were obtained. The role of $ZnCl_2$ was to prevent chain transfer reaction which had caused the reformation of carboxylic acid on CB surface.

LCSIP of isobutylene from surface functionalized silica particles was also investigated by researchers. The LCSIP of isobutylene as both homo- and copolymer, grafted from functionalized silica nanoparticles (NPs) was reported (entry 7, **Table 1.2**)[113]. Titanium tetrachloride ($TiCl_4$) was used as free initiator in solution in order to start the polymerization after the surface functionalisation of the silica NPs. The entry 9 in **Table 1.2** also shows the LCSIP of isobutylene from 3-(1-chlorodimethylsi-lylmethyl)ethyl-1-(1-chloro-1-methyl)ethylbenzene (CECE) functionalized silica NPs[40]. In this SIP system, the polymerization was initiated by the addition of free initiator $TiCl_4$ at a temperature ranging from -80°C to -65°C after the surface functionalization of the silica NPs, resulting in densely grafted PIB (σ_{PIB}= 0.8 chains/nm^2) on the surface of the NPs with low polydispersity values (M_w/M_n= 1.4) and high molecular weight (M_n= 62000 g/mol). LCSIP of styrene directly from –COOH functional groups of the graphite surface was also reported[144]. These surface carboxylic acid groups were first converted to acid chloride with $SOCl_2$ and then the polymerization was carried out in the presence of $AgClO_4$ as an additive to form the cationic active group. The polymerization was carried out at 30°C resulting in 86% monomer conversion, 10-11% of grafting ratio and the grafted PS with a PDI value of M_w/M_n= 1.4 (entry 8, **Table 1.2**).

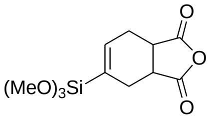
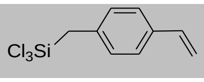
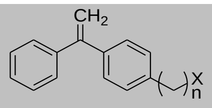
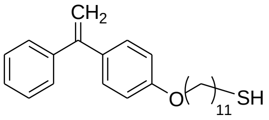
1.3.1.2. Living anionic surface initiated polymerization (LASIP)

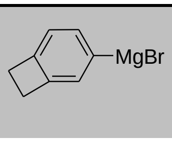
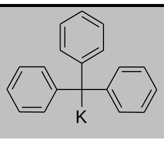
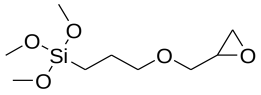
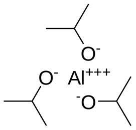
Living anionic surface initiated polymerization (LASIP) has been one of the most used methods for producing polymer-inorganic comoposites[19-21,42,49,112]. Advincula *et al.*[20-21,112] and

Quirk *et al.*[145-146] developed and used a surface modifying group system which can be activated by alkyl lithium compounds; a 1,1-diphenyl ethylene (DPE) derivative (entry 15, **Table 1.1**). The ethylene group between two phenyl rings provides an optimum initiating system for living anionic polymerization. The side chain attached to this DPE group helps the surface modifying group to attach to any inorganic substance with a suitable anchoring end group depending on the surface functional groups of the inorganic substance. The alkyl spacer length of the surface modifying group which is shown by “n” in entry 15 (**Table 1.1**) determines the distance between functional end groups of the surface modifying group and the surface of the inorganic substance. As n increases the polymerization is initiated from a longer distance from the inorganic particle surface, hence resulting in better polymerization (low polydispersity, accurate molecular weight prediction) due to reduced steric hindrance effect and increased space.

Unlike LCSIP, LASIP cannot be initiated directly from the surface of the corresponding particles due to the high negative charge density. Therefore in all cases use of a surface modifying group is required. **Table 1.3** shows some examples of LASIP of various polymers from different particles by using various surface modifying groups.

Table 1.3 Examples of LASIP of various monomers from different particle surfaces

entry	surface modifying group	additive	particle	monomer	reference
1	n-BuLi	TMEDA	graphite	styrene, MMA	35,147
2		KOH	SiO$_x$, TiO$_x$, Ni-Zn ferrite	epoxides, cyclic acid anhydrides	35
3		t-BuLi	silica NP	sytrene, isoprene, vinyl pyridine	71
4	n-BuLi	crown ethers	graphite, carbon black	styrene, MMA	148
5	 X= -Si(CH$_3$)$_2$Cl, -Si(OCH$_3$)	BuLi	silica NP, silicon-wafers flat surface (clay), gold NP	styrene, MMA isoprene ethylene oxide	19-21,112,145-146
6		BuLi	gold NP	styrene, isoprene, MMA, ethylene oxide	49

7			multi walled carbon naotube (MWCN)	ethylene oxide	[42,51]
8			silica	ethylene oxide	[149]

The first four entries of **Table 1.3** show early examples of LASIP processes in order to produce polymer-inorganic composite materials[35,71,147-148]. In these studies the anchoring moiety of the surface modifying group varies from organiolithium to organosilanes. Polystyrene (PS) and polymethyl methacrylate (PMMA) was grafted from metalized (via treating with n-BuLi) surface of graphite powder (4 μm particle size) in the presence of tetramethylethylenediamine (TMEDA) as an additive[147] (entry 1, **Table 1.3**). Although the attempt was to conduct SIP anionically the results indicated that the polymerization did not have a living character. The grafting percentage of the produced composites was relatively high (between 85% and 99%). Anionic ring opening polymerization of epoxides and cyclic acid anhydrides from inorganic SiO_x, TiO_x, Ni-Zn ferrite particles was also tried as a LASIP method[35] (entry 2, **Table 1.3**). Alkoxysilane bearing surface modifying groups (anhydride) are immobilized on the particle surfaces and the functional anhydride groups were hydrolyzed with the addition of KOH to form carboxylate anions to initiate anionic ring opening polymerization. Up to 90% of monomer conversion and surface grafted polymers with low PDI values (1.15) were achieved.

Entry 3 of **Table 1.3** shows another LASIP example in which poly(styrene-*b*-isoprene) was grafted from silica particles (12 nm particle size) by using a methylene trichlorosilyl anchoring group which is attached to styrene on the *para* position[71] which is then initiated by subsequent addition of *tert*-BuLi and styrene and isoprene. The percentage of grafting increased with the monomer loading, so did the free polymer in the reaction solution. The polymerization had a living character and homo and block copolymer grafted silica particles were obtained. A similar example to entry 1 in **Table 1.3** shows LASIP of styrene and MMA from graphite and carbon black (CB) surfaces in the presence n-BuLi and crown ether instead of TMEDA[148]. The use of crown ether dramatically increased the monomer conversion (100%) and grafting ratio (entry 4, **Table 1.3**).

As it was mentioned earlier, the introduction of 1,1-diphenylethylene (DPE) based surface modifying group for LASIP by Advincula *et al.*[112] and Quirk *et al.*[145] increased the amount of researches which were done on LASIP from various substrates, therefore the DPE type surface modifying group might be considered as a breakthrough for LASIP (entry 5, **Table 1.3**). The ethylene moiety on the DPE can be activated by the addition of an alkyl lithium and the length of the side chain can be adjusted in order to increase the distance between the particle surface and the active site where the polymerization is started (see **Figure 1.7**). This allows researchers to overcome the surface charge density issue as well. It has been used for spherical[20] and flat surfaces[19,21]. One of the main advantages of this DPE based surface modifying group is that of it reacts quantitatively with the alkyl lithium type initiator which is added to activate the DPE groups, hence the homopolymerization in solution during the LASIP process was minimized[19]. More control over the polymerization lead researchers to control the molecular weight and the polymer thickness on the particle surface and eventually this resulted in a better control of physical and thermal properties, composition and morphology of the grafted polymer as well[146].

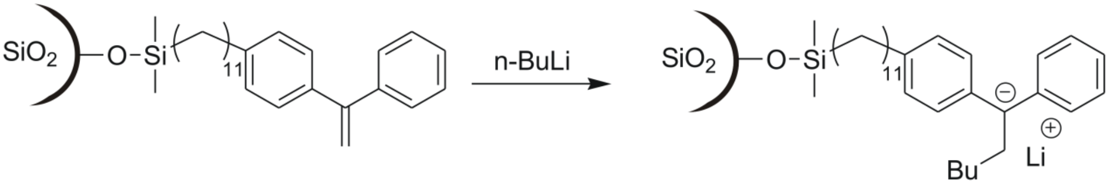


Figure 1.7 Schematic representation of the activation of surface immobilized DPE by the addition of n-BuLi[112]

The DPE based surface modifying groups have been mostly used for LASIP of styrene and methyl methacrylate both as homopolymer and block copolymer[19-20,112]. The anchoring moiety attached to the DPE groups has been mostly organosilanes (dimethylchlorosilane or alkoxysilane)[20,112]. Control over molecular weight and narrow polydispersity values (M_n/M_w= 1.2) were achieved in these researches. There are also reports on LASIP of styrene from negatively charged flat clay particles by using a DPE derivative bearing a positively charged quaternary ammonium as anchoring group[21]. Additionally poly(isoprene-b-ethylene oxide) was grafted from silicon-wafers via LASIP by using dimethylchlorosilyl attached DPE derivative as surface modifying group[146]. However in this system the anchoring group is directly attached to the DPE, therefore the initiating moiety was relatively close to the surface of the substrate which resulted in a broadening of the polydispersity of the grafted polymers, M_n/M_w= 2.4.

1.3.2. Surface Initiated Controlled Radical Polymerization (SI-CRP)

Due to recent advances in controlled/living radical polymerization techniques researchers could build more complex architecture via these polymerization methods[150-151]. Controlled/living radical polymerization techniques (also free radical polymerization (FRP) technique) have been used as surface initiated polymerization methods in order to prepare polymer-inorganic composite materials[30-32,47,54-55,107,152].

Before going into details of surface initiated controlled radical polymerization (SI-CRP) some specific examples of surface initiated free radical polymerization (SI-FRP) will be given briefly. A few examples of SI-FRP from silica particles are already shown in **Table 1.1**. As an early attempt on SI-FRP (entry 1, **Table 1.1**) a dimethylchlorosilyl bearing conventional azo initiator (AIBN) derivative was attached to the surface silanol groups of silica particles and FRP of styrene was conducted[87,99]. High molecular weight (M_n= 10kg/mol to 274 kg/mol) polymer brushes with high grafting density (σ= 1.82 µmol/m^2) were obtained with this method. The kinetic studies showed that the initiation and propagation of the polymer at low conversion was similar to that of solution polymerization[87]. The kinetic studies also showed that the termination reactions were significantly reduced in SI-FRP when compared to solution polymerization because free chains had to diffuse against a concentration gradient into the film to terminate the polymerization which was not possible due to the steric hindrance occurred on the particle surface because of the growing polymer chain[8,87,99]. Later, a new synthetic route for SI-FRP of vinyl monomers from silica surfaces was developed[96]. The silanol groups on the particle surface were converted to $-NH_2$ by treating with 3-aminopropyltriethoxysilane and then these amino functionalized particles were treated with t-butylperoxy-2-methacryloyloxyethylcarbonate in order to bind peroxycarbonate groups which can initiate a FRP (entry 2, **Table 1.1**). This treatment reduced the amount of non-grafted homopolymer in the SI-FRP process and increased the grafting ratio up to 90% with respect to the SI-FRP experiments which were done by immobilizing an azo-initiator on the particle surface.

A novel strategy was later introduced by different research groups for SI-FRP[98,100-102]. In this strategy alkoxysilyl bearing monomers were attached to silica surfaces (120 nm particle size) and FRP was initiated with the addition of a conventional azo- or peroxy-initiator and further monomer (entry 3-4, **Table 1.1**). The advantage of this method was to control the grafted polymer thickness on the particle surface with the amount of added monomer (see **Figure 1.8**). A linear growth on the shell thickness is observed with the monomer loading up to a certain degree. For this specific work[102], no significant increase in shell thickness was observed after 13 ml of styrene (per 1.2 g of surface functionalized silica) addition.

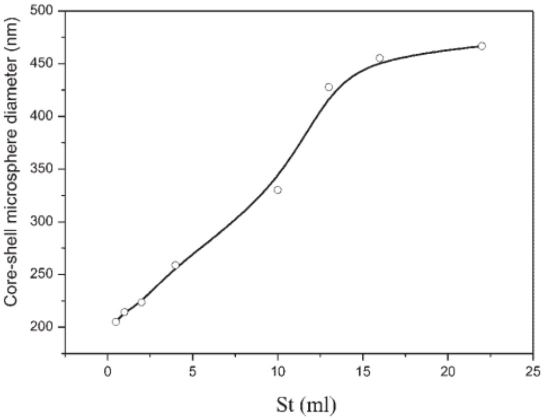
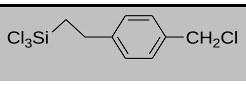
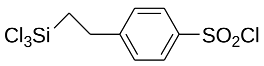
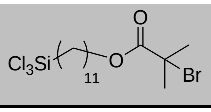
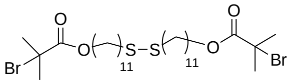
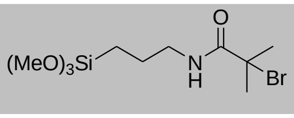
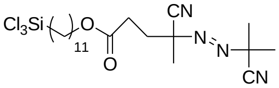
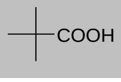
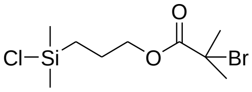
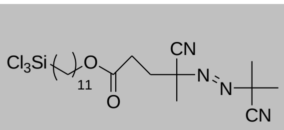
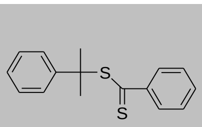
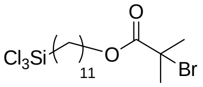
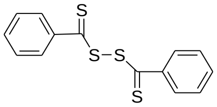
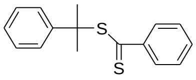
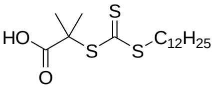
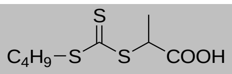
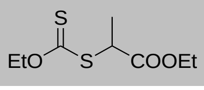
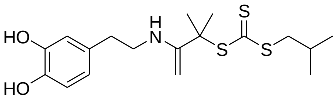
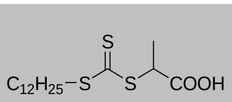
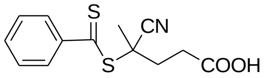
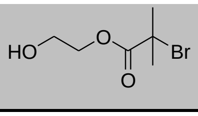


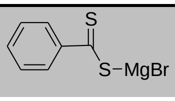
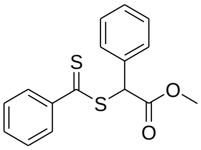
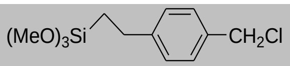
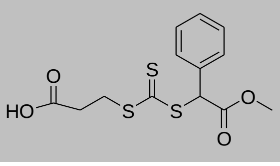
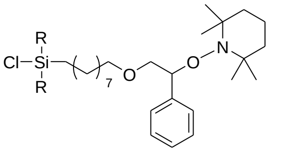
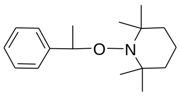
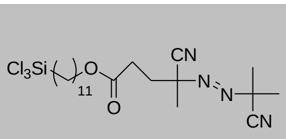
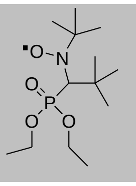
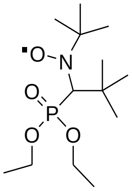
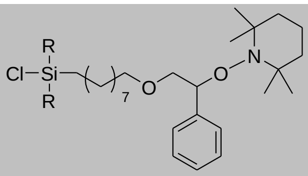
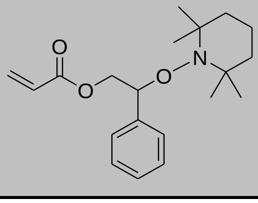
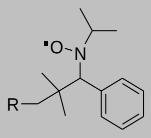
Figure 1.8 The effect of monomer loading on polymer thickness[102].

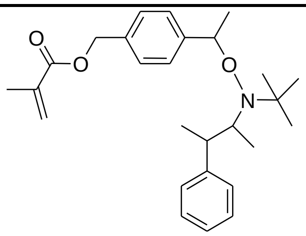
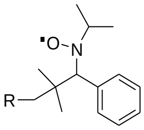
Table 1.4 shows some examples of SI-CRP of various monomers from different particles via different CRP techniques by using various surface modifying groups depending on the desired polymerization method and anchoring groups depending on the substrate surface. Each example in **Table 1.4** will be explained in detail in the regarding section.

Table 1.4 Examples of SICRP from various surfaces

entry	surface modifying group	additive	SIP technique	particle	monomer	grafting density	reference
1		CuCl/Bipy	ATRP	silica	acrylamide	114.8 μmol/m^2	153
2		CuBr/dHbipy *p*-toluenesulfonyl chloride	ATRP	silica	MMA	2.9 chains/nm^2	154
3		CuBr/dnNbpy $CuBr_2(dnNbpy)_2$	ATRP	silica	styrene t-butyl acrylate	n.a.	155

4		CuBr/bipy CuCl/CuBr$_2$/bipy	ATRP	gold	MMA glycid MA 2-hydroxyethyl MA n-butyl acrylate	0.55 chains/nm^2	156-159
5		CuBr/PMDETA	ATRP	iron oxide	styrene	0.24-0.34 g/g particle	31,54
6		CuBr$_2$/bipy	R-ATRP	silica	styrene MMA	n.a.	160
7	SOCl$_2$ + 	CuCl$_2$/bipy	R-ATRP	silica	MMA	n.a.	161
8		CuCl$_2$/TPMA tin(II) 2-ethylhexanoate	A(R)GET-ATRP	silica imogolite cellulose	n-BuA VC MMA HEMA	n.a.	55,162-163
9			RAFT	silicate	styrene MMA N,N-dimethylacrylamide (2-dimethylamino) ethyl methacrylate	0.68 chains/nm^2	30,164
10	 + 	AIBN  	RAFT	flat silica	styrene MMA MA DMAEMA	n.a.	115
11	 	AIBN	RAFT	titania	acrylic acid	0.48 g/g particle	165
12		AIBN	RAFT	titania	styrene t-BA NIPAM	0.04-0.12 chains/nm^2	121
13		AIBN	RAFT	CdS	styrene MA MMA BA	n.a.	81
14		AIBN	RAFT	gold NP	*N*-isopropylacrylamide	0.27 g/g particle	126
15		AIBN	RAFT	MWCN	*N*-isopropylacrylamide	n.a.	166

							
16		AIBN	RAFT	PS-based resin	MA	0.39 chains/nm^2	167
17	 	AIBN	RAFT	silica	MA, MMA styrene, n-BuA HEMA, DMEMA	0.38 chains/nm^2	114,168
18			NMP	silicon-wafers, glass, titana NP, PA, MWCN	styrene, oligo(ethylene glycol) 3-vinyl pyridine 4-vinyl pyridine	1.7 chains/nm^2	120,169-172
19			NMP	silica	Styrene n-BA EA	0.28-0.37 µmol/m^2	93,173
20		-	NMP	polymer substrate	styrene n-BA DMAEA	0.08-0.32 g/g particle	174-175
21	 		NMP	silica steel	DMAEA	0.15-0.72 µg/cm^2	82,176

22			NMP	polymer substrate	styrene MMA HEMA	n.a.	177

1.3.2.1. Surface initiated atom transfer radical polymerization (SI-ATRP)

Atom transfer radical polymerization (ATRP) has been one of the most used controlled/living radical polymerization methods for SIP processes[54-55,103-106,153-161,178-180]. A surface modifying group containing an ATRP initiator functional group or conventional FRP initiator is immobilized on the surface of the inorganic substrate followed by the addition of monomer and other additives. Some examples of SI-ATRP (from silica particles) are already listed in **Table 1.1** (entries 6-8) and in **Table 1.4** (entries 1-8).

The first research on SI-ATRP in literature[153] reports on the grafting of poly(acrylamide) (PAAm) from porous silica particles (5μm diameter size). A trichlorosilyl bearing benzylchloride derivative was attached to the surface of the silica particles and SI-ATRP was conducted with the addition of CuCl and bipyridine (entry 1, **Table 1.4**). In this first attempt, a polymer film with a thickness of 10 nm was achieved. However the actual M_n value of the surface grafted polymer was found to be higher than the theoretical value (M_n(theo)= 7400 g/mol) proving that the efficiency of the initiator was less than 100%.

In another early attempt on SI-ATRP 2-(4-chlorosulfonylphenyl) ethyl trimethoxysilane was used to functionalize the surface of silicon-wafers to bind a chlorosulfonylphenyl group (an effective ATRP initiator)[154]. SI-ATRP of MMA was conducted by the addition of CuBr and bipyridine (entry 2, **Table 1.4**). This research is also known as the first SI-ATRP in which sacrificial initiator (p-toluenesulfonyl chloride) was used in order to control the livingness of the process. The use of sacrificial initiator allowed better control over the polymerization so that more accurate M_n values were achieved[8,154] because in the absence of free/sacrificial initiator, the concentration of the initiator and the concentration of the deactivating species (Cu^{II}) were too low to allow a controlled polymerization[116], thus the molecular weight control and narrow molecular weight distribution could not be achieved. The increase in the amount of homopolymer (non-grafted) can be noted as a disadvantage of the sacrificial initiator concept[155]. Therefore Matyjasewski *et al.*[155] used another strategy to control the SI-ATRP.

Instead of using sacrificial initiator to overcome the low concentration of deactivating Cu^{II} species, extra Cu^{II} was directly added to the polymerization mixture as an additive. With this strategy PS was successfully grafted from bromoisobutyrate functionalized silicon-wafers (entry 3, **Table 1.4**). However addition of extra Cu^{II} species to the process limited the application area of this method especially when biological applications are considered.

After overcoming basic obstacles researchers tried to perform SI-ATRP of different monomers in different reaction media. 50 nm thick PMMA brushes was successfully grafted from bromoisobutyrate attached gold coated silica particles in aqueous media (water/methanol)[156]. Later, 700 nm polymer thickness in pure aqueous media was reached[158]. Poly(2-hydroxy-ethyl methacrylate) (PHEMA) (a hydrophilic polymer) was grafted from bromoisobutyrate functionalized gold particles by using a mixed halide (CuCl/$CuBr_2$/bipy) catalyst system which was reported earlier[159]. (Entry 7 in **Table 1.1** and entry 4 in **Table 1.4**) (See **Figure 1.9**).

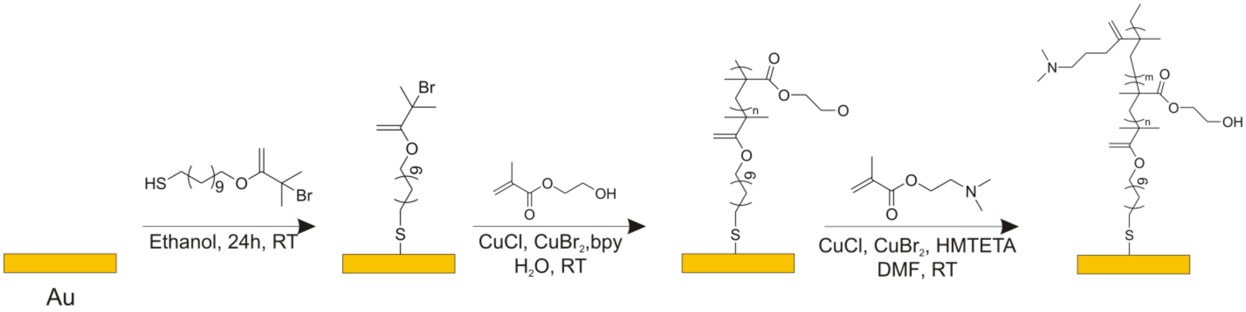


Figure 1.9 Schematic representation of SI-ATRP of PHEMA-b-PDMAEMA from bromoisobutyrate functionalized gold surface.

Grafting of polystyrene (PS) from iron oxide magnetic NPs could be given as an example of SI-ATRP from metal oxide surfaces[54]. In this particular work a triethoxysilane bearing amide based ATR initiator was attached to the surface of magnetic Fe_3O_4 NPs and SI-ATRP was performed in the presence of CuBr/PMDETA initiating system and styrene as monomer. PS was successfully grafted with high molecular weight (M_n= 45000 g/mol) and relatively low molecular weight distribution (M_w/M_n= 1.5). A novel route for SI-ATRP was later developed[31]: in situ synthesis of the surface functionalized silica nanoparticles by treating the ethoxysilyl bearing bromoisobutyrate ATRP surface modifying group with tetraethoxysilane (TEOS) to form ATR initiator functionalized silica particles whose size could also be controlled by adjusting parameters (entry 5, **Table 1.4**). Homo- and block-copolymers of PS, poly(methyl acrylate) (PMA) and poly(*t*-butyl acrylate) P(*t*-BuA) were grafted from these surface functionalized NPs with high molecular weight (Mn= 37100 g/mol for PMA-b-PS) and low molecular weight distribution values (M_w/M_n= 1.2). An alternative approach to SI-ATRP was tried by immobilizing a conventional azo-initiator via trichlorosilane anchoring moiety on the surface of flat silicon substrate[160]. PS and PS-b-PMMA were successfully grafted from these azo-functionalized silicon substrates in the presence of $CuBr_2$/bipy catalyst system via SI-ATRP. This SIP system is also called as reverse ATRP (R-ATRP). The preparation of PMMA brushes from peroxide functionalized silica particles in the presence of $CuCl_2$/bipy catalyst system can also be given as an example for SI-RATRP[161] (entries 6-7, **Table 1.4**.).

However the use of Cu catalyst causes limitations to SI-ATRP for certain applications especially when the produced composites are intended to be used for biomedical purposes. In order to overcome this concerns a new strategy[55] was developed, enabling researchers to reduce the amount of toxic Cu metal catalyst to a few ppm. This is done by adding a reducing agent (ascorbic acid, Sn^{II} 2-ethylhexanoate or Cu^0) to the reaction media in order to regenerate the activator[116]. This system is called activator (re)generated electron transfer ATRP (A(R)GET ATRP) (entry 8, **Table 1.4**). Especially biocompatible polymers such as poly(hydroxyethyl methacrylate) (PHEMA) have been grafted from cellulose substrates for biomedical application with this method[162]. This technique also increased the tolerance of ATRP towards oxygen and other impurities.

As it can be seen from **Table 1.4** (entries 1-8), mostly styrene and acrylic monomers bearing different functional groups depending on the application have been polymerized with ATRP for SIP processes. To sum up, SI-ATRP (and derivatives) has been an excellent tool to produce polymer brushes from inorganic particles due to its tolerance towards monomers bearing various functional groups[116]. Most of the initiators (even the ones bearing surface binding groups) are commercially available or can be easily synthesized[116]. The limitations due to applications have been overcome with novel approaches (use of sacrificial initiator[154], deactivator[155], R-ATRP[160-161,181] to reduce the catalyst amount) in order to widen the application area of SI-ATRP processes.

1.3.2.2. Surface initiated reversible addition-fragmentation chain transfer (SI-RAFT) polymerization

Reversible addition-fragmentation chain transfer (RAFT) polymerization has been a useful controlled/living polymerization technique since its discovery[182]. A distinctive advantage of RAFT when compared to ATRP is that RAFT does not require a specific initiator and any free radical polymerization (FRP) can easily be converted to RAFT by adding a chain transfer agent (CTA) such as a dithioester, a dithiocarbamate or a trithiocarbonate while other parameters (monomer, initiator and solvent) can be kept constant[116].

RAFT has also been used to produce polymer brushes from particles' surfaces[30,47,70,81,85,94,107-108,114-115,121,126,131,151,164-168,183-188]. Due to the nature of RAFT two different approaches have been applied. The first approach involved attaching a conventional FR initiator to the surface of the substrate and conduct SI-RAFT by adding monomer and a suitable CTA (**Figure 1.11-A**). This strategy was used to produce PS, PMMA and poly(dimethyl acrylamide) (PDMA) brushes from azo-functionalized silicate substrate by adding 2-phenylprop-2-yl dithiobenzoate as CTA[30]. Later, poly(2-hydroxyethyl methacrylate) brushes were also grafted from peroxide-functionalized polymer substrate surface[183]. Addition of free/sacrificial initiator was also tested and the results showed that the sacrificial initiator not only improved the polymer growth but also prevented the early termination by CTA capping by increasing the amount of radicals in the solution[116]. Several other research groups have used this approach to produce various polymer brushes[164].

The second approach to produce polymer brushes via SI-RAFT was to attach a CTA derivative to particle surface and initiate the polymerization by subsequent addition of a monomer and a conventional FR initiator. This approach can also be divided into two: R-group approach (**Figure 1.11-B**) and Z-group approach (**Figure 1.11-C**). The R-group and the Z-group are the functional groups attached to the thiocarbonate in a chain transfer agent as shown in **Figure 1.10-A**[182]. According to the mechanism of the RAFT polymerization (**Figure 1.10-B**) the R-group reversibly leaves during the polymerization and lets the polymerization propagate then the R-group recombines with the propagating chain in order to keep the concentration of the active species low, thus the polymerization gains living/controlled nature. Therefore the R-group should be a good free-radical leaving group such as cumyl, cyanoisopropyl[182]. The Z-group on the other hand determines the activity of the CTA upon selection. Mostly aryl and alkyl groups are used as a suitable Z-group[182]. The choice of Z-group is also important for the functional end group selection of the polymer for the further post-polymerization treatments[189].

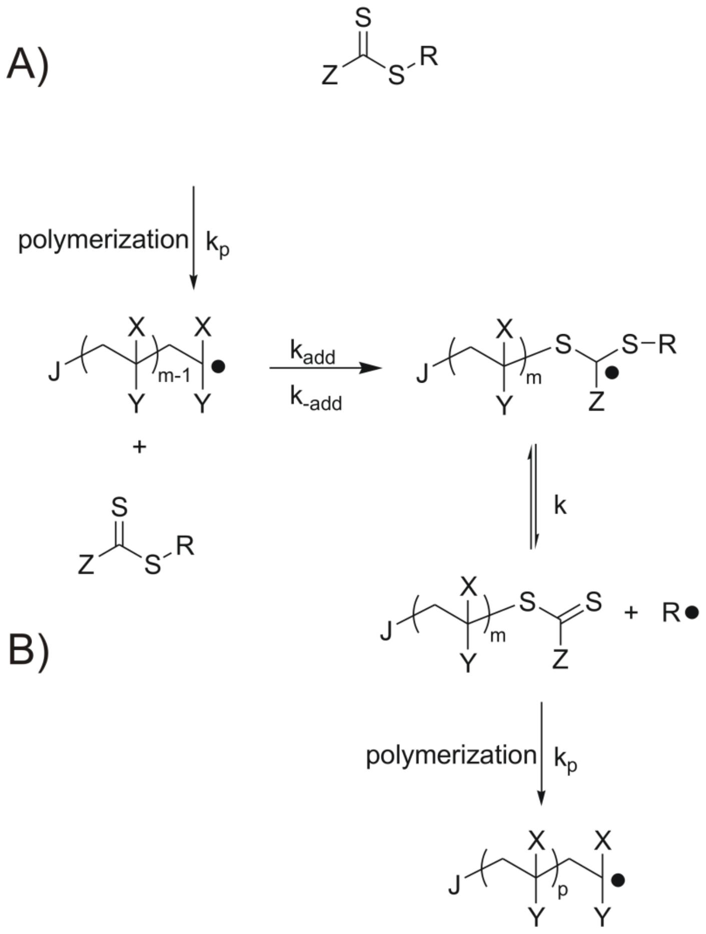


Figure 1.10: A) Basic chemical structure of a chain transfer agent (CTA), B) mechanism of RAFT polymerization

Based on the explanation above, the R-group and the Z-group approaches of SI-RAFT follow separate fashions. When the CTA binds to the surface of the substrate from the R-group site[47], the polymerization follows a "*grafting-from*" fashion as the polymer grows directly from the surface of the substrate (**Figure 1.11-B**). When the CTA binds to the surface of the substrate from the Z-group site[94], "*grafting onto*" fashion is followed as the polymer basically grows in the solution, and attaches to the thiocarbonate reversibly (**Figure 1.11-C**).

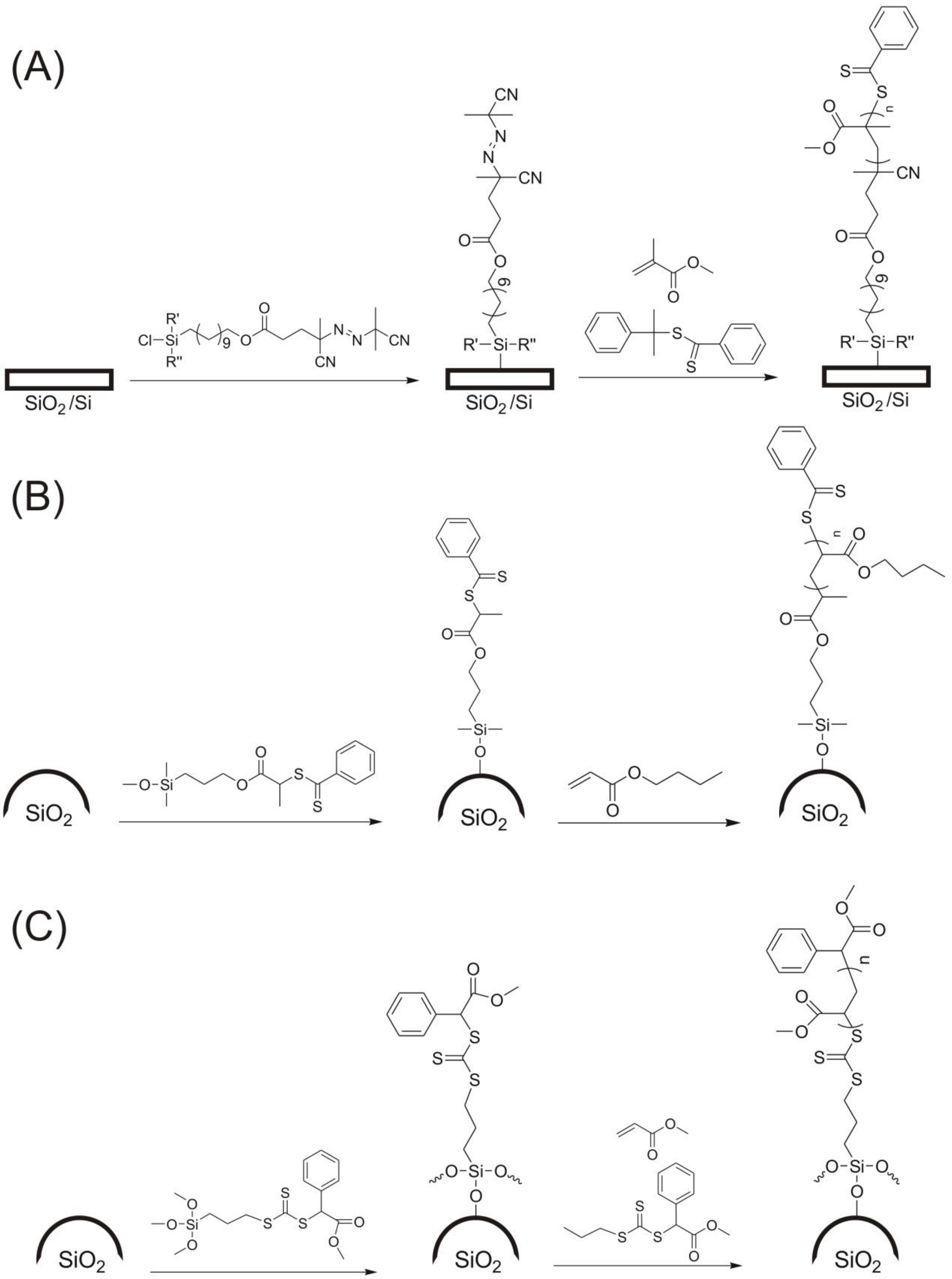


Figure 1.11 Schematic representations of three different approaches on SI-RAFT A) conventional radical initiator binding[30], B) R-group binding[47] and C) Z-group binding[94] approaches

Boyes *et al.*[115] used the R-group approach to produce various homo- and block copolymer brushes from flat silica surfaces (see **Figure 1.12**). The surface of the silica substrate was first functionalized with bromoisobutyrate derivative and then with dithiobenzoyl disulfide. SI-

RAFT was started with the addition of AIBN and monomer in the presence of free/sacrificial CTA (entry 10, **Table 1.4**). GPC analysis of the grafted polymers proved high control over polymerization, resulting in accurate molecular weight projection and low PDI values (between M_w/M_n= 1.06 and M_w/M_n= 1.17). Vana et al.[86] designed and used surface modifying groups bearing trithiocarbonate as a chain transfer agent and trimethoxysilyl as an anchoring group. By using this surface modifying system, poly(methyl acrylate) could be grafted from silica NPs with relatively low PDI values (M_w/M_n= 1.3) and accurate molecular weight projections.

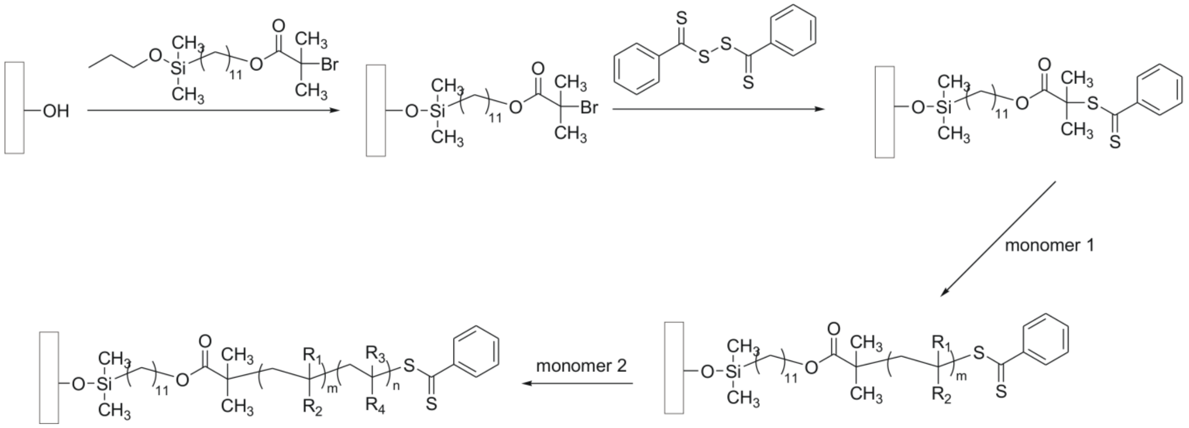


Figure 1.12 Schematic representation of surface modification with CTA agent (R-group approach) and subsequent SI-RAFT polymerization[115]

The R-group approach has been intensively used to produce polymer brushes not only from silica[47,70,85,94,107-108,184] (entries 9-11, **Table 1.1**) but also from titania[121,165] (entries 11-12, **Table 1.4**), CdS[81] (entry 13, **Table 1.4**), gold NPs[126] (entry 14, **Table 1.4**) and multiwalled carbon nanotubes (MWCN)[166] (entry 15, **Table 1.4**). The Z-group approach has also been used to produce brushes of corresponding polymers of acrylic, styrenic and acrylamide based monomers[114,167-168] (entries 16-17, **Table 1.4**).

SI-RAFT can be considered as a quite useful tool to produce surface initiated polymer brushes due to its tolerance towards many functional groups and common impurities[8,56,116]. However, the difference between R-group and Z-group approaches must be noted in order to clearly understand the concept of SI-RAFT polymerization. As mentioned earlier The R-group approach follows a “*grafting from*” fashion as it involves the detachment of the CTA during the polymerization which might broaden the molecular weight due to the termination of the highly active radical species. On the other hand the Z-group approach follows a "*grafting to*" fashion, thus the propagation of the polymer in the solution causes a decrease in the grafting density due to steric hindrance especially when high molecular weight polymer brushes are desired[94].

1.3.2.3. Surface initiated nitroxide mediated polymerization (SI-NMP)

Ever since the discovery of nitroxide mediated polymerization (NMP) by Hawker et al.[190] it has been used as a significant tool for producing various polymers with controlled structure and molecular weight. NMP has also been used as a SI-CRP method [41,69,191-192]. NMP basically follows a similar principle to ATRP in which a dormant species is formed (by using a stable nitroxide radical as an additive) during the polymerization to keep the concentration of the active species low, thus the polymerization has living/controlled nature[190]. Unlike ATRP, NMP does not require a special initiator therefore any FRP reaction can be converted to NMP by adding an adequate amount of a stable nitroxide radical[116,130,190].

In 1999 Husemann and Hawker et al.[169] developed a synthetic route to conduct SI-NMP of styrene from 2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy (TEMPO) functionalized silicon-wafers (entry 18, **Table 1.4**). Up to 120 nm film (PS) thickness with monomer loading control was achieved. However due to the low concentration of radicals in the reaction solution, reversible capping (formation of dormant species) became less effective. This issue was overcome by adding sacrificial/free alkoxyamine to the reaction media[169]. This strategy resembles the addition of sacrificial/free initiator in ATRP in order to balance the concentration of the active radical species[157]. In the absence of free alkoxyamine the concentration of the radical species is too low, thus the molecular weight control is significantly reduced[193]. On the other hand addition of free alkoxyamine leads to formation of non-grafted homopolymer in the solution which requires an extra separation process to remove homopolymer from the surface grafted polymer[116]. Many research groups applied this strategy to produce polymer brushes of various monomers from functionalized surfaces of silica/glass slides[170], titanium[120], polymer substrates[171] and multi-walled carbon nanotubes (MWCN)[172].

As a disadvantage of this strategy, it is limited to styrenic monomers as the attempts on acrylic polymer brushes via NMP yielded low M_n and high PDI values[193]. In order to overcome this problem scientists designed a new alkoxyamine: N-tert-butyl-N-[1-

diethylphosphono-(2,2-dimethylpropyl)] nitroxide (DEPN)[174] (entry 19, **Table 1.4**). In 2004 Parvole et al.[93] used DEPN based alkoxide to prepare poly(n-butyl acrylate) (PBA) and poly(ethyl acrylate) PEA brushes from azo functionalized silica particles in which DEPN acted as chain growth moderator (so called bimolecular polymerization system). However DEPN mediated polymerizations of styrenic monomers yielded polymers with broader molecular weight distributions due to possibly a higher percentage of termination reactions[174].

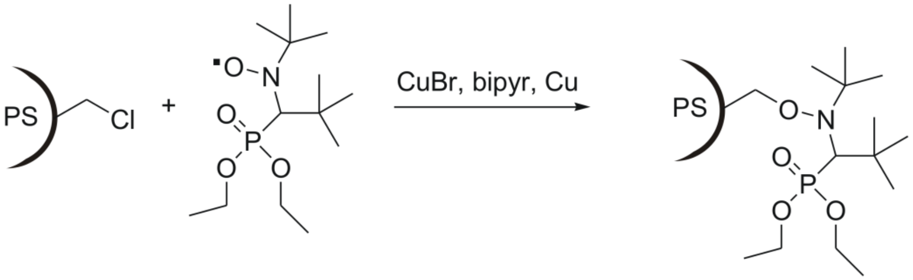


Figure 1.13 Immobilization of DPEN on chloro-functionalized polymer substrate[175]

Instead of using conventional radical initiator derivatives as surface modifying groups for SI-NMP, DEPN derivatives have also been used as surface modifying groups by researchers as an alternative strategy. PS, PBA, poly(2-(dimethylamino ethyl)acrylate) (PDMAEA) brushes were successfully prepared with this strategy by reasearchers[173,175] (see **Figure 1.13**). Another strategy for NMP was later developed by using α-hydrido nitroxide (a universal alkoxyamine) as a free initiator to moderate the polymerization[194]. This strategy was applied to SIP to prepare poly(*t*-butyl acrulate) (PtBA) and poly(acrylic acid) (PAA) brushes from TEMPO functionalized silica substrates[176]. PDMAEA brushes were also grafted from TEMPO functionalized (via electrografting) stainless steel (see **Figure 1.14**) as random copolymer[82]. α-Hydrido nitroxide was also used as both surface modifying group and initiator by researchers. PS, PMMA and PHEMA were grafted from α-hydrido nitroxide-functionalized polymer substrates in the presence of α-hydrido nitroxide as a free initiator[177]. Later PS from α-hydrido nitroxide-functionalized silica particles was prepared in the presence of α-hydrido nitroxide as a free initiator as well[69].

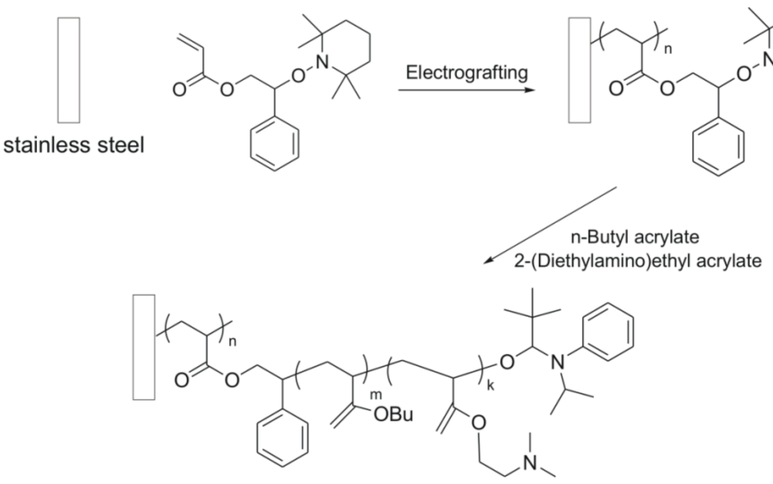


Figure 1.14 Surface modification of stainless steel with TEMPO bearing surface modifying group (electrografting) and subsequent surface initiated copolymerization of DMAEA and n-BA[82]

To summarize, NMP has been a useful tool to prepare homo- and block copolymers with controlled architecture and molecular weight since its discovery[190] due to its ease and the fact that it does not require any further catalyst which is also tempting for certain biomedical applications. However the necessity of specific mediating nitroxide for specific monomers could be considered as a disadvantage of SI-NMP process as most of these nitroxide compounds are not commercially available[8,116,133].

A main obstacle in the SI-CRP techniques is that the radicals on the particle surface which are formed in the primary steps of SIP process tend to recombine due to their spatial proximity especially when the initial grafting density of the surface modifying groups is high[195]. The recombination reactions which take place during SIP limit the polymer film growth on the surface of the particle. The agglomeration problem which was mentioned in section **1.3.2.2** also applies for SI-CRP methods.

1.3.3. Surface initiated ring opening polymerization (SI-ROP)

Both LISIP and SI-CRP have been very useful methods for producing polymer brushes from surfaces, however they are mostly limited to vinyl monomers. In order to synthesize biocompatible and biodegradable polymers for certain biomedical applications ring opening polymerization techniques are essential[8].

As an early attempt on SI-ROP, Tsubokawa *et al.*[140] designed a surface modifying group containing acylium perchlorate and polymerized ε-caprolactone in the presence of $AgClO_4$. (entry 2, **Table 1.2**). Another example of SI-ROP was also listed in entry 13 in **Table 1**. Poly(ε-caprolactone) was grafted from hydroxyl and/or amine functionalized silica and CdS NPs[109]. The polymerization was acid catalyzed in the presence of triethyl aluminium ($AlEt_3$) and followed a coordination insertion mechanism due to the presence of $AlEt_3$. Molecular weight control was achieved as the monomer to amine ratio determined the molecular weight (see **Figure 1.15**).

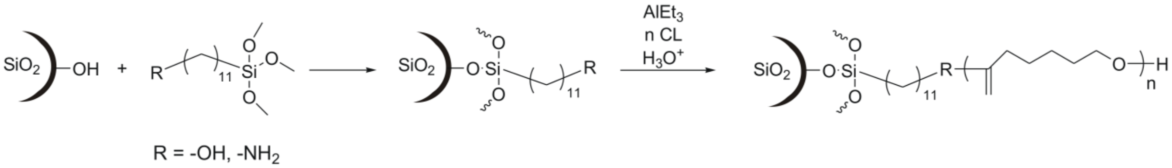


Figure 1.15 Schematic illustration of ROP of ε-CL from silica substrates[109]

In 2001 Jordan *et al.*[127] grafted poly(2-oxazoline) from trifluoromethyl thiolate functionalized gold particles via cationic ring opening polymerization. The resulting composite was found to be thermally stable and the ex-situ analysis (FT-IR, MALDI-*tof*) proved that the polymerization had living character (entry 6, **Table 1.2**). Poly(L-glutamate) was later grafted directly from amine functionalized silicon-wafers surface achieving up to 40 nm brush thickness in a couple of hours[196].

Poly(*p*-dioxane) with a brush thickness of 140 nm was directly grafted from the silanol groups on the silica NPs via SI-ROP in the presence of tin(II)octoate in order to investigate the effect of tin(II)octoate[197]. With a similar strategy poly(ε-caprolactone) and poly(L-lactide) grafted silica NPs were prepared via SI-ROP by first functionalizing the surface of silica NPs with prehydrolized-3-glycidoxypropyl trimethocysilane and subsequent catalytic ring opening polymerization[198]. Metal alkoxides of aluminium, tin and yttrium were also introduced as additives. The presence of tin(II)octoate provided high grafting density while in the presence of yttrium alkoxide almost no polymer was grafted from the surface. Later the approach on SI-ROP of ethylene oxide (EO) was improved by introducing aluminium isopropoxide ($Al(O^iPr)_3$) as the initiator (entry 8, **Table 1.3**)[149]. However the monomer conversion was found to be relatively low (24% maximum) and the film thickness on the silica surface was only 4 nm.

1.4. Monomers used for SIP processes

As it can be seen from previous tables among many monomers styrene has been mostly studied monomer in SIP reactions[45,71,100-101,103-104,112,199]. In the literature styrene and acrylates[86,92,152,180,200-202] have been grafted from different particles' surfaces via LASIP[20,112], SI-RAFT[30,199], SI-NMP[45] and SI-ATRP[200] not only as homopolymers but also in block copolymer brushes which were grafted from the surfaces of inorganic substrates. Due to the advances in controlled/living polymerization techniques hydrophilic monomers could also be grafted from particle surfaces to obtain poly(oligo(ethylene glycol) methacrylate) (POEGMA) and poly(2-(N-morpholino)-ethyl methacrylate) (PMEMA)[105] for various applications[119].

Isoprene[203-206] and butadiene[205,207-208] have mostly been studied via living anionic polymerization in solution resulting in polyisoprene and polybutadiene being either natural or synthetic rubber. However there are only a few researches reported on SIP of isoprene/butadiene from inorganic substances. SIP of isoprene from styrene attached (by trichlorosilyl anchoring group on the *para* position) silica and glass slides via anionic polymerization could be given as the first example[71]. In this work poly(styrene-*block*-isoprene) was grafted from the functionalized surface of silica and glass slides. Later, LASIP of isoprene was conducted from DPE functionalized surfaces of silicon wafers by using DPE based surface modifying groups[145-146]. The surface modifying group with dimethylchlorosilyl anchoring moiety did not have any alkyl spacer therefore the initiating group was directly bonded to the substrate surface resulting in moderate molecular weight control and broad molecular weight distribution.

As it was mentioned above isoprene was mostly polymerized in solution via living anionic polymerization under different conditions by using different initiator systems[203,206,209]. There are also a few reports on the synthesis of PI in solution via living/controlled radical polymerization techniques. Solution and bulk polymerization of isoprene via NMP[210-211] by using a nitroxide bearing macro initiator to prepare PEO-*b*-PI and RAFT[189,212] by using a trithiocarbonate bearing CTA in the presence of *t*-butyl peroxide as a conventional free radical initiator was reported. Both attempts provided promising results, such as polymers with controllable molecular weight and narrow molecular weight distribution (M_w/M_n= 1.13[210]) values and the monomer conversion in both cases was found to be low (34% at most).

1.5. Objective

The main objective of this thesis is to prepare covalently attached polyisoprene (PI) silica composites via surface initiated polymerization (SIP) method. In this regard, the surfaces of silica nano- and glass particles are to be functionalized with surface modifying groups bearing a moiety that has ability to initiate the polymerization of isoprene with a desired polymerization technique.

For the polymerization of isoprene from functionalized surfaces of the silica particles, living anionic polymerization and controlled radical polymerization (reversible addition-fragmentation chain transfer (RAFT) and nitroxide mediated polymerization (NMP)) techniques are chosen. Therefore several surface modifying groups are to be prepared in order to functionalize the surfaces of the silica particles prior to SIP (see **Figure 2.1**).

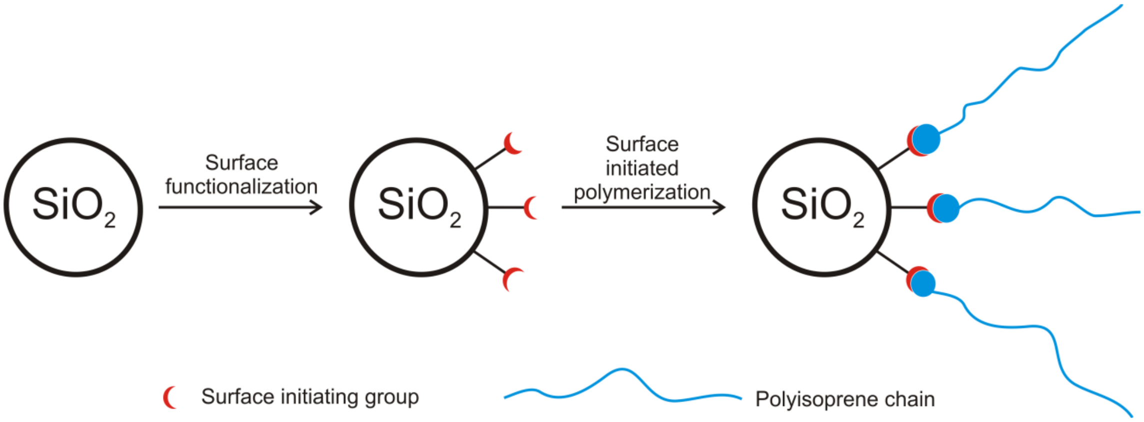


Figure 1.16 Graphical illustration of surface functionalization of the silica particles and subsequent surface initiated polymerization of isoprene

In order to investigate different parameters (solvent, temperature, initial grafting density of the surface initiating groups, alkyl spacer length of the surface initiating groups), SIP of isoprene from silica particles are conducted under different conditions. Produced composites are characterized via TGA in order to determine the grafting density of PI chains and via DLS in order to determine the size of the composites, whereas the grafted PI is characterized via GPC in order to determine the polymerization quality and via NMR spectroscopy in order to determine the microstructure of the polymer.

2. Synthetic concept

The aim of this thesis is to prepare polyisoprene grafted silica (PI-SiO_2) nano- (SA15, AE200) and glass particles (K3, B-K3) via living anionic surface initiated polymerization (LASIP) and surface initiated controlled radical polymerization (SI-CRP) methods (RAFT and NMP). For this purpose a series of surface modifying groups which have the initiating ability for specific polymerization technique and bear an anchoring group (chlorosilane and alkoxysilane) should be synthesized and used for the functionalization of the particle surfaces (see **Figure 2.1**).

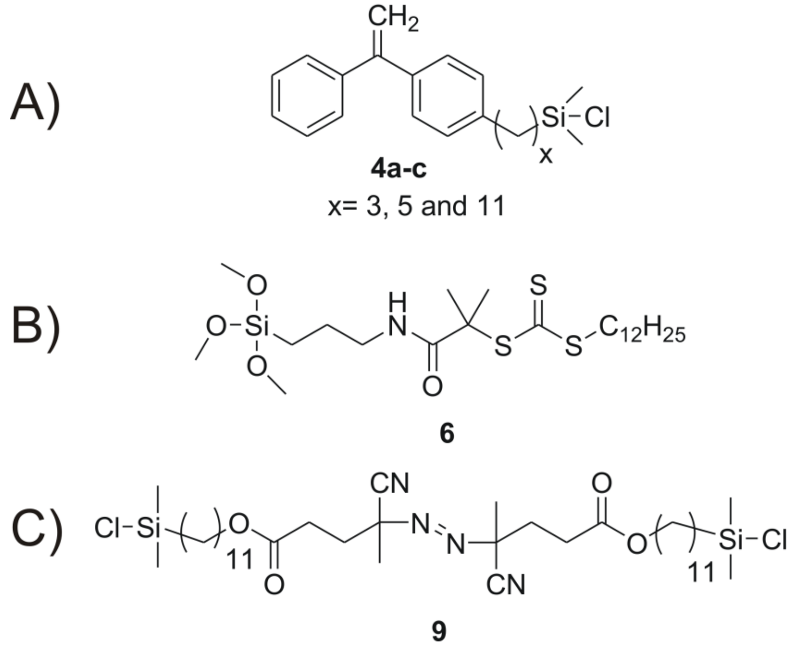
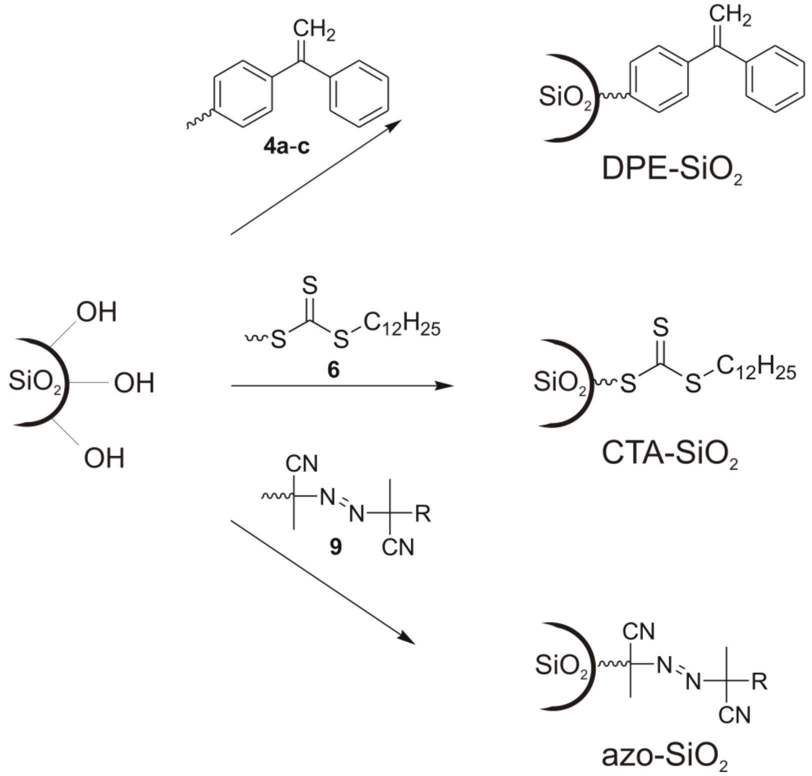


Figure 2.1 Chemical structures of the surface modifying groups A) DPE based surface modifying group for LASIP, B) CTA based surface modifying group for SI-RAFT and C) AIBN based surface modifying group for SI-NMP and SI-RAFT (depending on the additive)

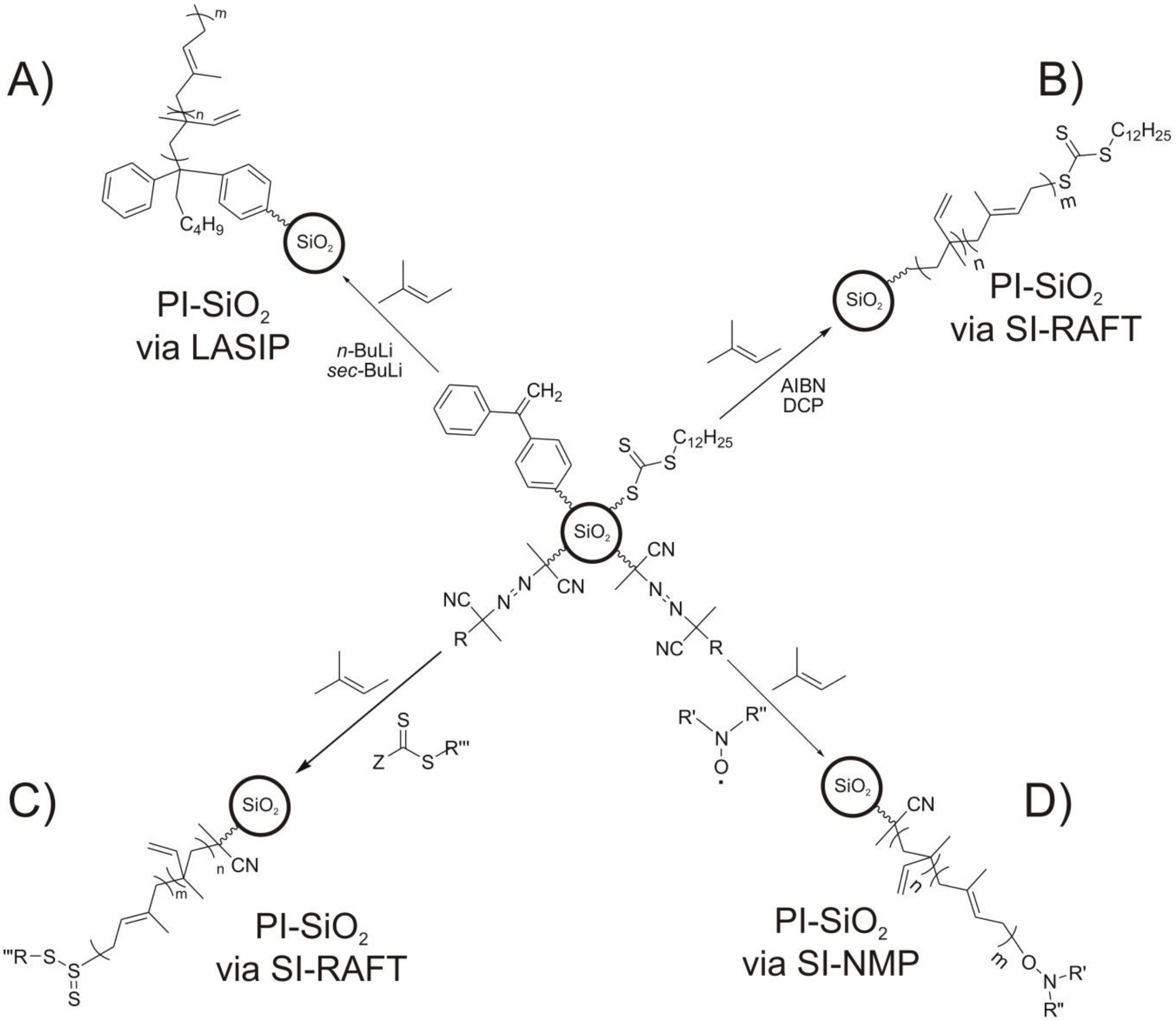
For the LASIP of isoprene dimethylchlorosilyl anchoring group bearing DPE derivatives with different spacer length (3, 5 and 11 -CH_2-) are chosen (**4a-c**, **Figure 2.1**). For the SI-CRP of isoprene two different surface modifying groups are selected; i) a chain transfer agent (CTA) derivative bearing an alkoxysilane anchoring moiety to conduct SI-RAFT with the addition of the monomer (isoprene) and a conventional free radical initiator and ii) a conventional azo initiator derivative bearing a dimethylchlorosilyl anchoring group to conduct SI-RAFT with the addition of a suitable chain transfer agent (CTA) and SI-NMP with the addition of suitable alkoxyamines.

Prior to surface initiated polymerization (SIP) of isoprene, surface functionalization of the nano- and glass SiO_2 particles with these surface modifying groups should be carried out in order to obtain DPE-functionalized SiO_2 particles, CTA-functionalized SiO_2 particles and azo-functionalized SiO_2 particles (see **Scheme 2.1**). Surface functionalization reactions should be carried out under different reaction conditions by using different amount of the corresponding surface modifying group in order to find the optimum conditions for the surface functionalization and investigate the effect of these parameters on the functionalization reaction.



Scheme 2.1 Schematic illustration of the surface functionalization of the SiO2 particles with surface modifying groups

Surface initiated polymerization (SIP) of isoprene should be performed by using these surface functionalized NPs and GPs by using necessary additives/reagents, such as *n*-BuLi/*sec*-BuLi in order to activate the DPE initiating groups for LASIP from DPE-functionalized particles (**Scheme 2.2A**), a conventional free radical initiator (AIBN or DCP) to conduct SI-RAFT from CTA-functionalized particles (**Scheme 2.2B**), a suitable CTA (S-1-dodecyl-S’-(α,α’-dimethyl-α’’-acetic acid)trithiocarbonate) to conduct SI-RAFT from azo-functionalized particles (see **Scheme 2.2C**) and a suitable alkoxyamine ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) or 2,2,5-tri-methyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO)) for SI-NMP (see **Scheme 2.2D**).



Scheme 2.2 Schematic representation of the surface initiated polymerization of isoprene from surface functionalized SiO_2 particles via A) LASIP, B) SI-RAFT and C) SI-RAFT (with the addition of a CTA) and D) SI-NMP (with the addition of alkoxyamine)

Figure 2.2 shows the chemical structures of the free radical initiators, the CTA and the stable radicals which were used for the SI-CRP of isoprene. AIBN and DCP are chosen as free radical initiators for both SI-RAFT and SI-NMP, whereas TEMPO and TIPNO are chosen as stable radicals to form dormant species by attaching to the growing polymer chain in order to keep the active radical concentration low, hence the polymerization is controlled. For SI-RAFT of isoprene, this specific CTA (**Figure 2.2c**) is chosen as it has been proven to be a powerful and efficient CTA for RAFT polymerization of isoprene[189].

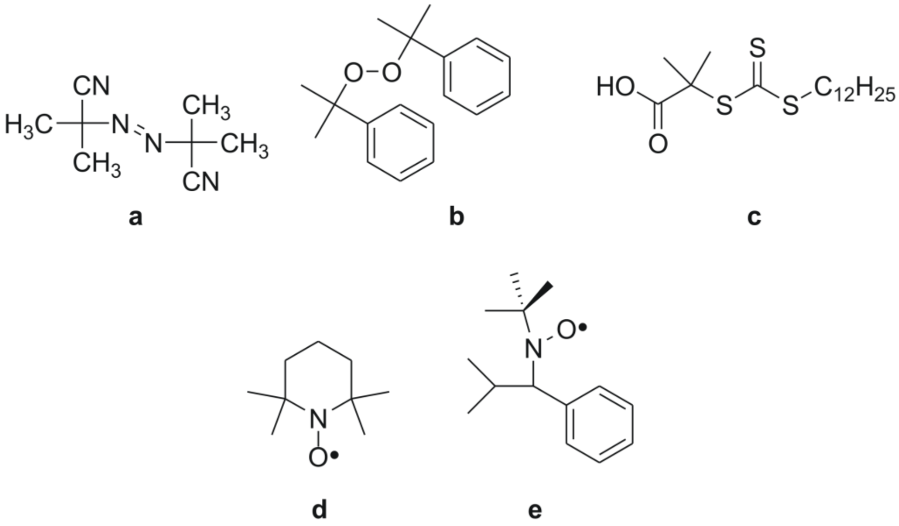


Figure 2.2 The chemical structures of free radical initiators a) azobisisobutyronitrile (AIBN), b) dicumyl peroxide (DCP), the CTA c) S-1-dodecyl-S'-(α,α'-dimethyl-α''-acetic acid)trithiocarbonate, the alkoxyamines d) (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and e) 2,2,5-tri-methyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO)

3. Results and Discussion

3.1. The concept of SIP of isoprene via LASIP and SI-CRP

The aim of this thesis is to conduct surface initiated polymerization of isoprene from surface functionalized SiO_2 (silica) nano- and glass particles via living anionic surface initiated polymerization (LASIP) and surface initiated controlled radical polymerization (SI-CRP) as Surface initiated polymerization (SIP) has been a powerful tool to prepare covalently attached polymer-inorganic composite materials[8].

In order to conduct SIP of isoprene from silica particles, surface modifying groups bearing initiating moieties of the desired polymerization techniques are required in order to functionalize the surface of the inorganic substrate prior to SIP[19,50]. The surface modifying groups are immobilized on the surface of the silica particles to form SAMs and the polymer (PI) is grafted from these functionalized surfaces of the silica particles with the addition of isoprene and necessary additives.

For the LASIP of isoprene diphenylethylene (DPE) based surface modifying groups are proven to be the best for producing polymer-inorganic composite materials[20,145-146]. The ethylene group on DPE can be activated with the addition of an alkyl lithium (*n*-BuLi, *sec*-BuLi) to initiate the polymerization after immobilizing the DPE precursor on the surface via an anchoring group (mostly chlorosilane and alkoxysilane for silica). The grafting density of the prepared composite can be controlled by the initial grafting density of the surface modifying group (σ_{MG}) as the polymer grows from such initiating groups which are already immobilized on the particle surface. However high grafting of surface modifying groups on the particle surface can risk the polymerization quality due to the steric hindrance which occurs on the particle surface during the polymerization and the reduced spatial proximity of the initiated chains would not allow a living polymerization[8]. In order to overcome this obstacle DPE derivatives with different alkyl spacer length can be used in order to separate the active end from the surface of the particle[20]. In this thesis three DPE derivatives with different alkyl spacer length (x= 3, 5 and 11) are synthesized and immobilized on silica surface by using different amount (1, 2, 3 and 4 equivalents with respect to the number of the surface silanol groups) of the surface modifying groups prior to LASIP in order to investigate the effect of the alkyl spacer length and the initial surface modifying group grafting density on LASIP (see **Scheme 2.1**). LASIP of isoprene was performed by using these DPE-functionalized silica nano- and glass particles (with different initial surface modifying group grafting density) under different conditions (the activating compound, solvent, temperature) (see **Scheme 2.2A**).

The high moisture content of the silica particles is one of the main obstacles of LASIP process from silica particles. In order to overcome this issue each particle is dried under vacuum at $90^{o}C$ for 24 hours in order to remove water content before both the surface modification and polymerization reactions. Another issue regarding the silica particles is their tendency to agglomerate in suspension reducing the specific surface area thus jeopardizing the LASIP process. Prior to the surface functionalization reactions and SIP reactions, a suspension of the silica particles is ultrasonicated for at least 15 minutes in order to avoid agglomeration of the particles. There are also obstacles related to living anionic polymerization. Although living anionic polymerization has been a powerful tool to polymerize various monomers, it requires extreme inert conditions as it does not have tolerance towards impurities such as moisture, oxygen and many functional groups[213-215].

In the literature there are reports on polymerization of isoprene via nitroxide mediated polymerization[211] (NMP) and reversible addition fragmentation chain transfer (RAFT) polymerization[189,212,216] techniques. Therefore SI-NMP and SI RAFT are chosen as SIP methods to produce PI-SiO_2 composites. For the SI-CRP from silica nanoparticles (NPs) two main strategies can be applied: immobilization of a conventional free radical initiator[217] (leading both SI-NMP and SI-RAFT) and immobilization of a chain transfer agent[86] (CTA) (leading SI-RAFT) on the particle surface. In this thesis for the SI-CRP of isoprene from silica NPs the surface modifying groups (shown in **Figure 2.1B** and **2.1C**) are prepared and used for the surface functionalization of the silica NPs: an azo-initiator derivative bearing a trichlorosilane anchoring group and a chain transfer agent (CTA) derivative bearing a triethoxysilane anchoring group are prepared and immobilized on the surface of the silica NPs with different initial surface modifying group densities prior to SI-CRP (see **Scheme 2.1**).

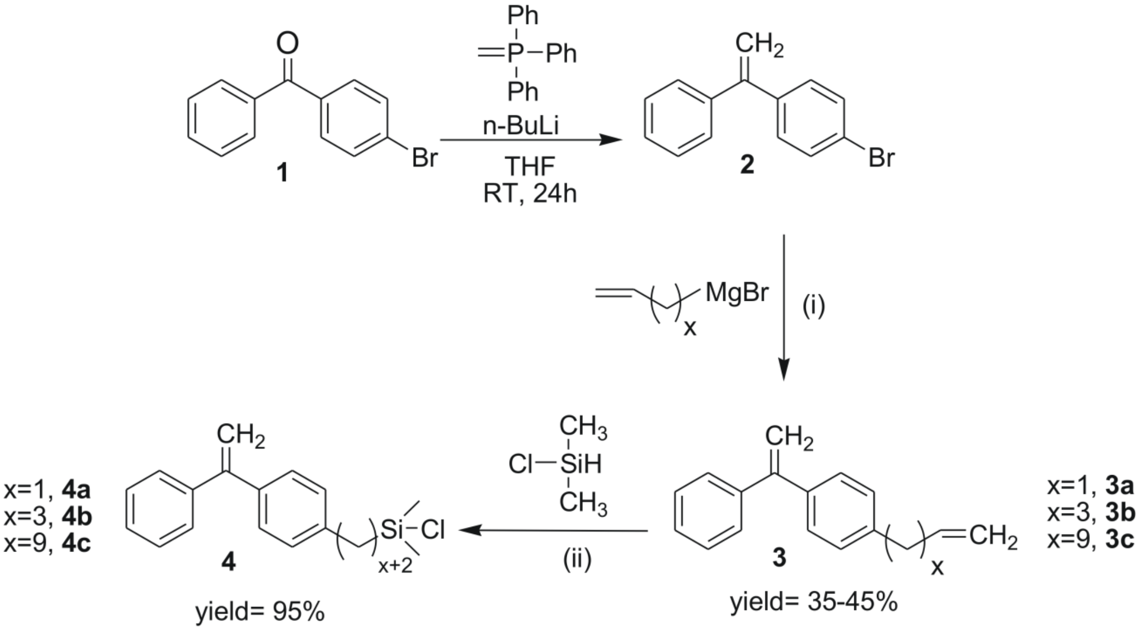
SI-RAFT polymerization of isoprene from CTA-functionalized silica NPs is performed with the addition of monomer and a conventional free radical initiator (azobisisobutyronitrile (AIBN) or dicumyl peroxide (DCP)) (see **Scheme 2.2B**). SI-RAFT polymerization of isoprene is also performed with the addition of a suitable CTA from azo-functionalized NPs (see **Scheme 2.2C**), whereas SI-NMP of isoprene from azo-functionalized NPs is conducted with the addition of monomer and a suitable stable radical ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl

(TEMPO) and 2,2,5-tri-methyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO)) (see **Scheme 2.2D**). Similar to LASIP experiments SI-CRP reactions are carried under different conditions in order to investigate the effect of different polymerization parameters (initial surface modifying group grafting density and free/sacrificial initiator).

The overall grafting density of the PI-silica composite can be controlled by the initial grafting density of the surface modifying groups (σ_{MG}). However the radicals which are formed during the early stages of the polymerization tend to recombine, thus the termination of the polymerization occur, especially when the initial grafting of surface modifying groups is high as the active radicals are closer to each other[158]. The low monomer conversion can be noted as a disadvantage of CRP of isoprene(up to 30%)[189]. On the other hand CRP is a relatively simple process to handle when compared to living anionic polymerization.

3.2. Synthesis of surface modifying groups for LASIP

The synthetic procedure of the surface modifying groups for LASIP (**4b** and **4c**), was adopted from the literature by Advincula *et al.*[20] (see **Scheme 3.1**). Compound **4a** was obtained from Merseburger Spezialchemikalien. The synthesis was completed in three steps. In the first step, 4-bromo-benzophenone (**1**) was converted to 4-bromo-diphenylethylene (DPE) (**2**) via a Wittig reaction with a yield of 79%. In the second step, a Grignard reagent from the corresponding bromo-alkene was formed and used to substitute the bromine atom in compound **2** resulting in the corresponding alkenyl derivatives of DPE (**3b** and **3c**) with relatively low yields (40%). Finally the DPE derivatives were selectively converted to the corresponding monochlorosilane compounds via hydrosilylation reactions with the addition of Karstedt catalyst and dimethylchlorosilane (**4b** and **4c**) in quantitative yields. The critical point for this step was to avoid the silylation of the ethylene moiety of DPE instead of the terminal ethylene moiety on the side chain (see **Scheme 3.1**). Excess of dimethylchlorosilane (more than 1 equivalent with respect to the corresponding DPE derivative) might have caused the silylation of the ethylene group on the DPE moiety, therefore the amount of dimethylchlorosilane was strictly kept to 1 equivalent with respect to the corresponding DPE derivative (**3b** or **3c**).



Scheme 3.1 Schematic pathway to DPE based surface modifying groups for LASIP (i) in diethyl ether for at room temperature for 4 hours, (ii) in toluene at room temperature for 24 hours

Figure 3.1 shows the ^{1}H-NMR spectra of the compounds **3b** and **4b**. ^{1}H NMR spectrum of **2**, **3c** and **4c** was already reported by Advincula *et al.*[20] (see **Appendix** for further detail). **Figure 3.1a** shows the ^{1}H -NMR spectrum of **3b** indicating that new vinyl protons have emerged due to the pentenyl group attached to the DPE. Aliphatic hydrogens on the pentenyl group were assigned to the peaks at low ppm range (from 1.7 ppm to 2.7 ppm). After the hydrosilylation reaction the signals of the vinyl protons which emerged after the Grignard reaction disappeared due to being converted to dimethylchlorosilane. The only vinyl proton signal left at 5.5 ppm is assigned to the ethylene unit on the DPE moiety. The singlet at 0.6 ppm is assigned to the six hydrogens of the two methyl groups attached to the silicon atom (see **Figure 3.1b**). The integral values of the corresponding peaks prove that no silylation of the ethylene moiety on the DPE occurred, hence the success of hydrosilylation reaction as well. Additionally an increase in the J coupling constants of the aromatic hydrogen resonances, vinyl hydrogen resonances and the alkyl spacer hydrogen resonances was observed after the silylation reaction: J= 8.3 Hz for Ar-H, J= 3.2 Hz for $=CH_2$ and J= 3.0 Hz for $-CH_2-$ in **3b** whereas J= 10.5 Hz for Ar-H, J= 3.6 Hz for $=CH_2$ and J= 3.6 Hz for $-CH_2-$ in **4b**. ^{13}C NMR analysis also proved the success of silylation reaction as new peaks at 2.4 ppm and 14.9 ppm emerged due to the hydrosilylation. ^{29}Si NMR analysis of the DPE based surface modifying agents (**4b-c**) displayed single peaks at 31.9 ppm and 32.0 ppm respectively (see **Appendix**).

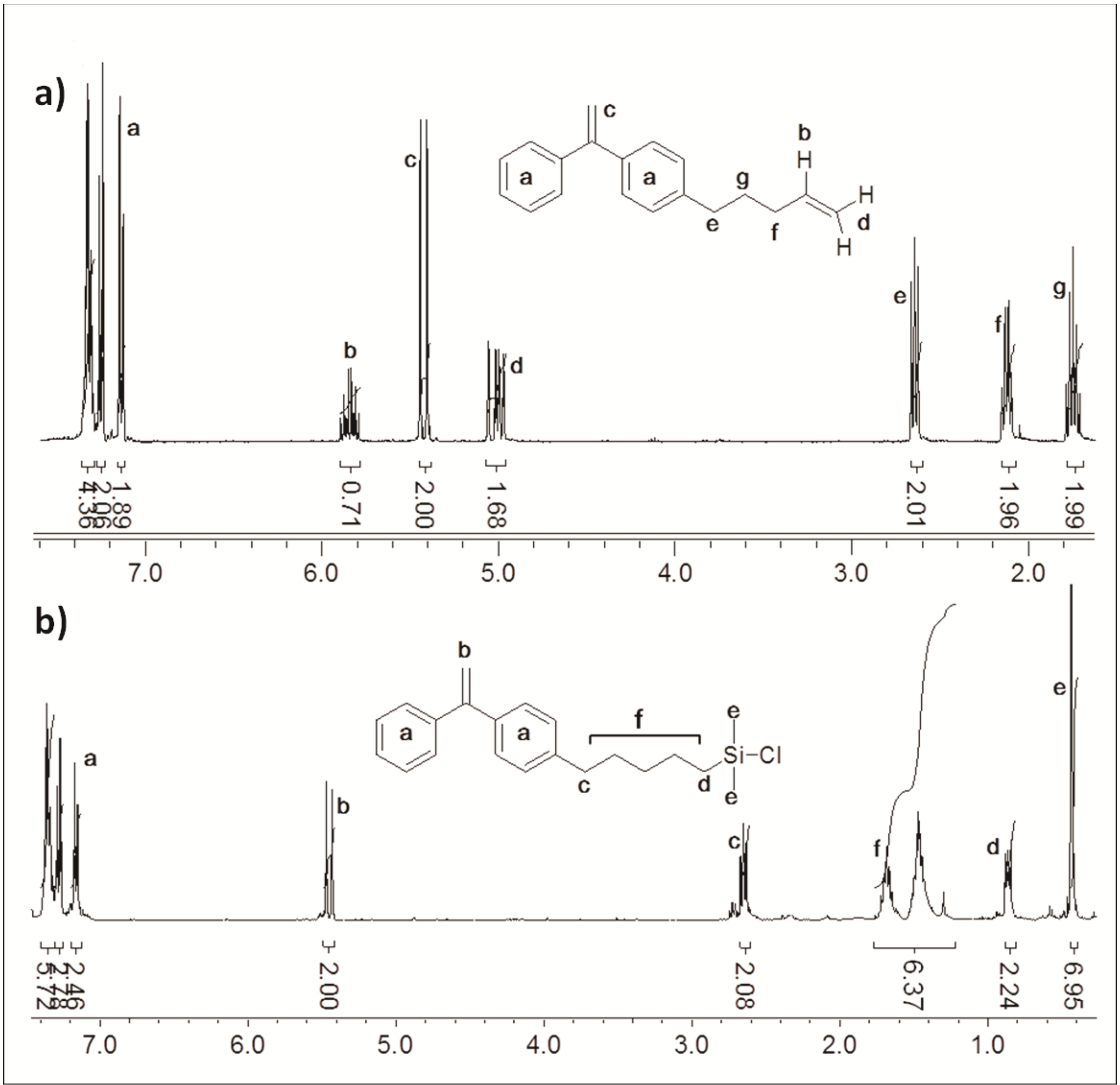


FIGURE 3.1 ^{1}H NMR spectra of a) **3b**, b) **4b**

3.3. Synthesis of surface modifying groups for SI-CRP

In order to carry out a surface initiated polymerization of isoprene via controlled radical polymerization methods (RAFT and NMP) surface modifying groups bearing initiator and/or chain transfer agent had to be chosen carefully. In 2007 Germack *et al.*[189] reported polymerization of isoprene via RAFT by using a trithiocarbonate containing chain transfer agent; S-1-dodecyl-S’-(α,α’-dimethyl-α’’-acetic acid)trithiocarbonate (**5**) (See **Figure 3.2**). Although monomer conversion in polymerization was low, this specific chain transfer agent (CTA) was found to be the best for the polymerization of isoprene via RAFT. S-1-dodecyl-S’-(α,α’-dimethyl-α’’-acetic acid)trithiocarbonate was synthesized as described earlier by Lai *et al.*[218]. The carboxylic acid group on one end of the CTA allowed an appropriate modification to attach an anchoring group so that the surface modifying agent can be immobilized on the particle surface (see **Figure 3.2a**).

The synthetic procedure of the AIBN-based surface modifying group which was used both for SI-NMP and SI-RAFT was adopted from the work of Czaun *et al.*[217]. 4,4′-Azobis(4-cyanovaleric acid) (**7**) which is a derivative of free radical initiator (AIBN) was end functionalized with an alkyl spacer and a chlorosilane anchoring group so that it could also be attached to surface of the silica NPs (see **Figure 3.2b**).

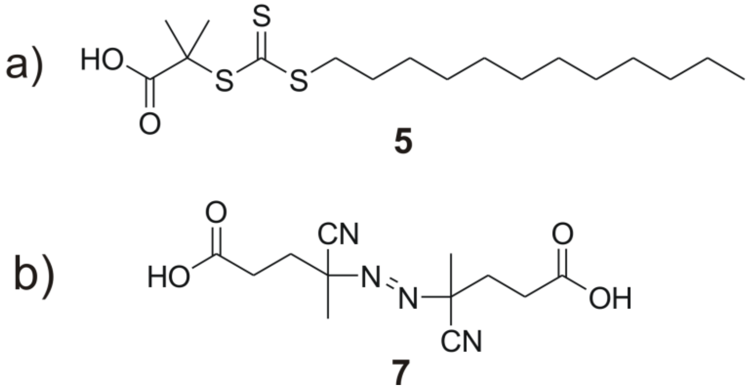
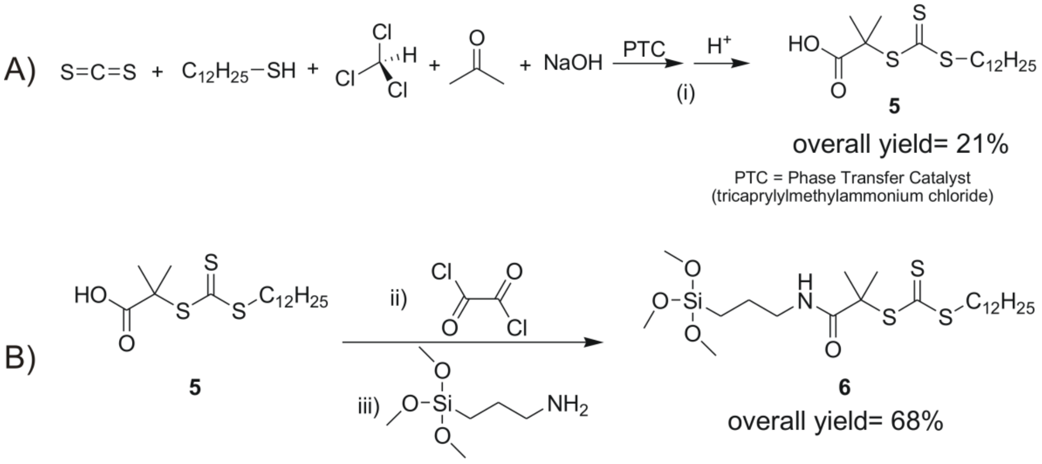


Figure 3.2 The chemical structure of a) S-1-dodecyl-S’-(α,α’-dimethyl-α’’-acetic acid)trithiocarbonate, b) 4,4′-azobis(4-cyanovaleric acid).

3.3.1. Synthesis of triethoxysilyl attached chain transfer agent

S-1-dodecyl-S’-(α,α’-dimethyl-α’’-acetic acid)trithiocarbonate (**5**) was used both as a chain transfer agent (CTA) in SI-RAFT polymerization experiments and for the preparation of CTA derivative surface modifying agent. The trithiocarbonate (**5**) was obtained with a yield of 21% as yellow solid by reacting dodecanethiol and carbon disulfide (CS_2) with sodium hydroxide and followed by the addition of chloroform and acetone and finally via acidification (see **Scheme 3.2a**).

In order to use the compound **5** as a surface modifying group for the SI-RAFT experiments an anchoring group should have been attached. The first trial was the esterification of the carboxylic acid moiety with an alcohol which bears a vinyl group (allowing a further hydrosilylation reaction with an organosilane) in one end in the presence of DCC and DMAP. However the attempt was not successful as esterification did not occur. Another attempt was to chlorinate the carboxylic acid moiety of **5** with thionyl chloride in order to attach (3-aminopropyl)trimethoxysilane to form an amide based surface modifying group. The use of thionyl chloride was not successful either, because the trithiocarbonate moiety also reacted with the thionyl chloride.



Scheme 3.2 Schematic pathway to synthesis of A) CTA (5), B) CTA-based surface modifying agent (**6**) (i) in acetone at room temperature for 4 hours (ii) at room temperature for 24 hours, (iii) in toluene at room temperature for 24 hours

A successful synthetic route was then achieved by using oxalyl chloride to chlorinate the carboxylic acid functional group on compound **5** instead of thionyl chloride. The two step synthetic procedure (see **Scheme 3.2b**) is as follows: in the first step compound **5** was converted to the corresponding acid chloride by treating it with oxalyl chloride in the presence of catalytic amount of DMF (2-3 drops). Then the acid chloride was reacted with (3-aminopropyl)trimethoxysilane in toluene in the presence of pyridine for amidation reaction to obtain CTA derivative bearing a trimethoxysilane anchoring group (**6**). The pyridine salt which was formed during the reaction was removed by filtration and evaporating the solvent and excess pyridine under reduced pressure gave crude product with a yield of 68% as yellow solid. Flash column chromatography attempt (SiO_2, eluent: CH_2Cl_2) caused loss of most of the product, therefore the crude product was used as it was for the surface functionalization reactions.

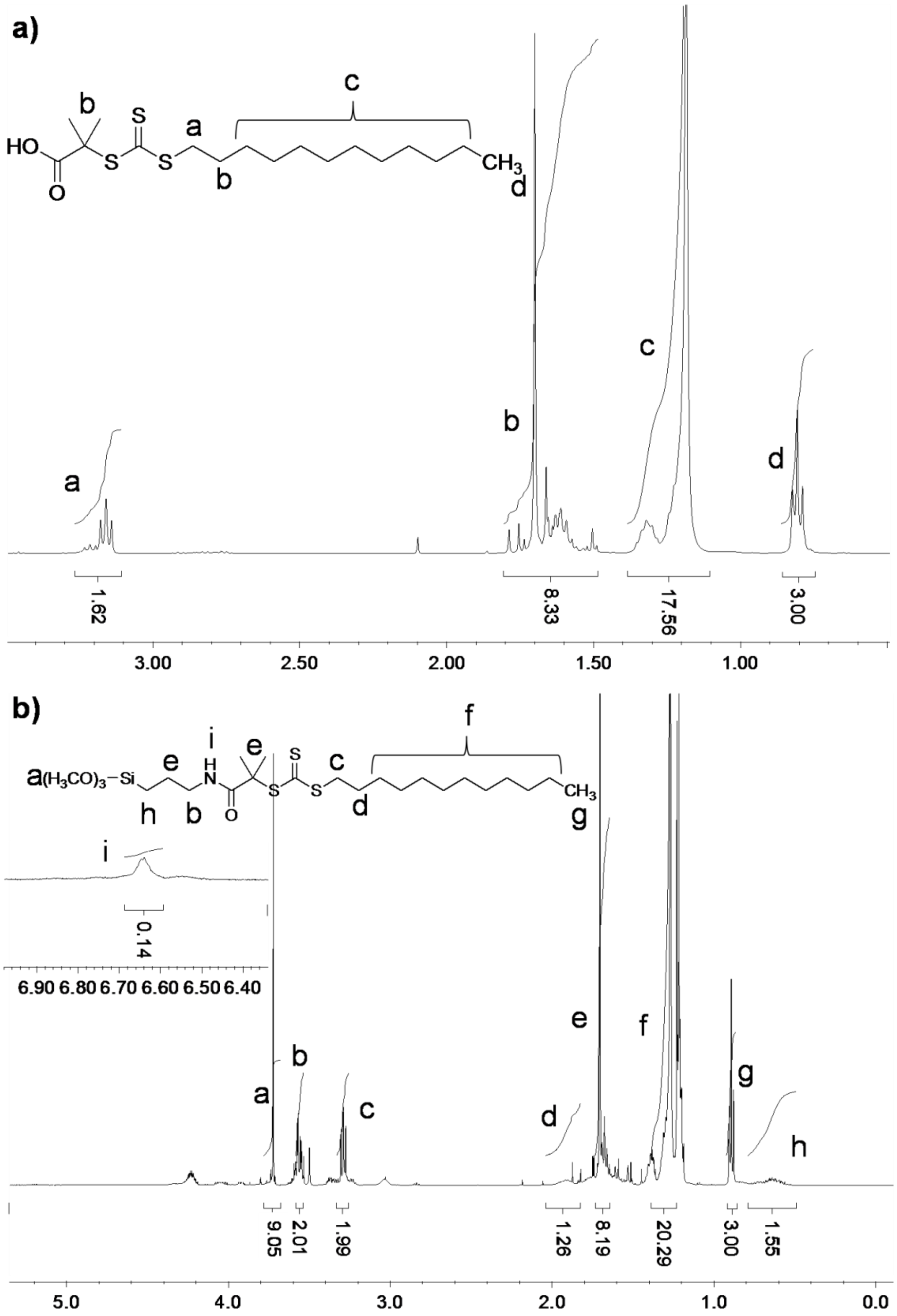
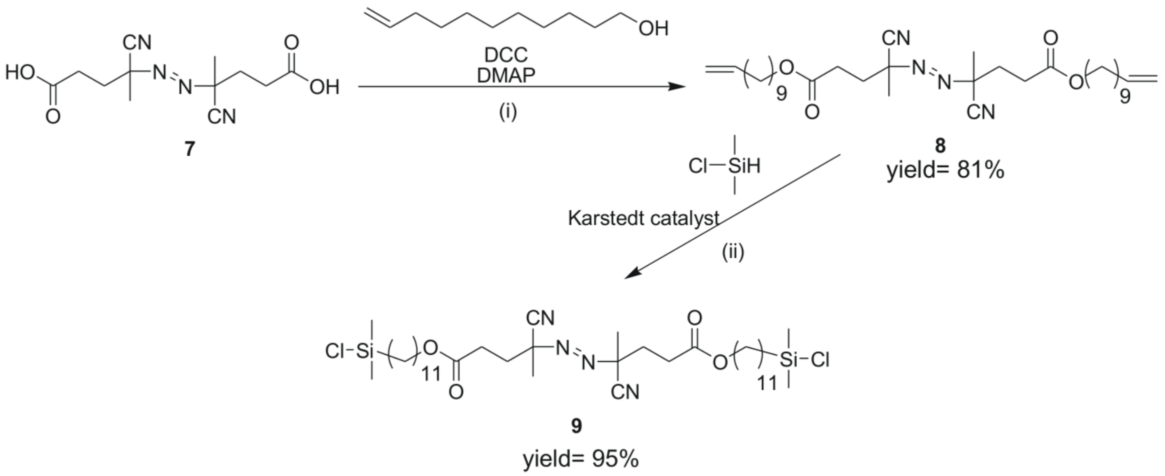


Figure 3.3 ^{1}H NMR spectra of a) **5** and b) **6**

Figure 3.3 shows the ^{1}H NMR spectra of the compounds **5** and **6**. The triplet at 0.8 ppm in **Figure 3.3a** was assigned to the terminal $–CH_3$ group on the compound **5** whereas the other aliphatic hydrogens' (including the two $–CH_3$ attached to the carbon atom next to the trithiocarbonate unit) peaks appeared between 1.6 ppm and 1.2 ppm. The triplet at 3.2 ppm was assigned to the two hydrogens attached to the carbon next to the trithiocarbonate moiety. After the amidation reaction the emergence of new peaks was observed as expected. As it was mentioned earlier flash column chromatography purification of the compound **6** was not successful, thus resulting in an unclear spectrum (see **Figure 3.3b**). The singlet at 3.7 ppm was assigned to the nine hydrogens of the three methoxy groups which are attached to the silicon atom. The multiplet at 3.5 ppm was assigned to the $–CH_2$ unit next to the nitrogen atom. The amide hydrogen peak was found to be at 6.6 ppm with an integral value of 0.14 with respect to the other assigned hydrogens. Another peak at 0.6 ppm was assigned to the two hydrogens of the $–CH_2$ group next to the silicon atom. The ^{29}Si NMR analysis of **6** displayed a single peak at -38.3 ppm (see **Appendix**).

3.3.2. Synthesis of monochlorosilane attached AIBN derivative

The synthesis of monochlorosilane attached AIBN derivative (**9**) was carried out in a two-step synthetic procedure (see **Scheme 3.3**). In the first step a diacid derivative of AIBN was converted to a diester by treating 4,4′-azobis(4-cyanovaleric acid) (**7**) with 10-undecen-1-ol in the presence of DCC and DMAP with a yield of 81% as pale yellow solid. The diester (**8**) was then treated with dimethylchlorosilane in order to attach the dimethylchlorosilyl group onto the alkenyl end groups of **8** in the presence of a Karstedt catalyst giving the monochlorosilane attached AIBN derivative (**9**) with a yield of 95% as pale yellow oil. The whole synthetic procedures which involved 4,4′-azobis(4-cyanovaleric acid) and its derivatives were carried out in dark conditions in order to keep the AIBN moiety intact.



Scheme 3.3 Schematic pathway to synthesis of **9** (i) in dichloromethane (DCM) at room temperature for 24 hours in dark, (ii) in toluene at room temperature for 24 hours in dark

^{1}H-NMR spectra analysis of compound **8** (see **Figure 3.4a**) indicated that the esterification of 4,4′-azobis(4-cyanovaleric acid) was successfully managed. The vinyl protons were assigned to the peaks at 4.9 ppm and 5.8 ppm with the expected integral values. The corresponding peaks of the aliphatic hydrogens were found to be between 1.2 ppm and 2.6 ppm. After the hydrosilylation reaction (see **Figure 3.4b**) the vinyl proton peaks at 5.8 ppm and 4.9 ppm disappeared as expected, whereas a peak at 0.10 ppm corresponding to the six hydrogens of two methyl groups attached to silicon atom emerged as a result of silylation. A decrease in the coupling constant of the aliphatic –CH_2– hydrogens after the silylation reaction also proved the conversion of the undecene to the corresponding dimethylchlorosilyl derivative: J= 6.7 Hz for -CH_2- in compound **8** whereas J= 4.9 Hz for -CH_2- in compound **9**. ^{13}C NMR analysis of compound **8** and **9** (see **Figure 3.5**) also proved the success of Karstedt reaction as the peaks of the vinyl carbons (139 ppm) disappeared while new peaks which were assigned to the carbon atom (1.4 ppm) attached to the silicon atom emerged. ^{29}Si NMR analysis of **9** also displayed a single peak at 32.0 ppm (see **Appendix**).

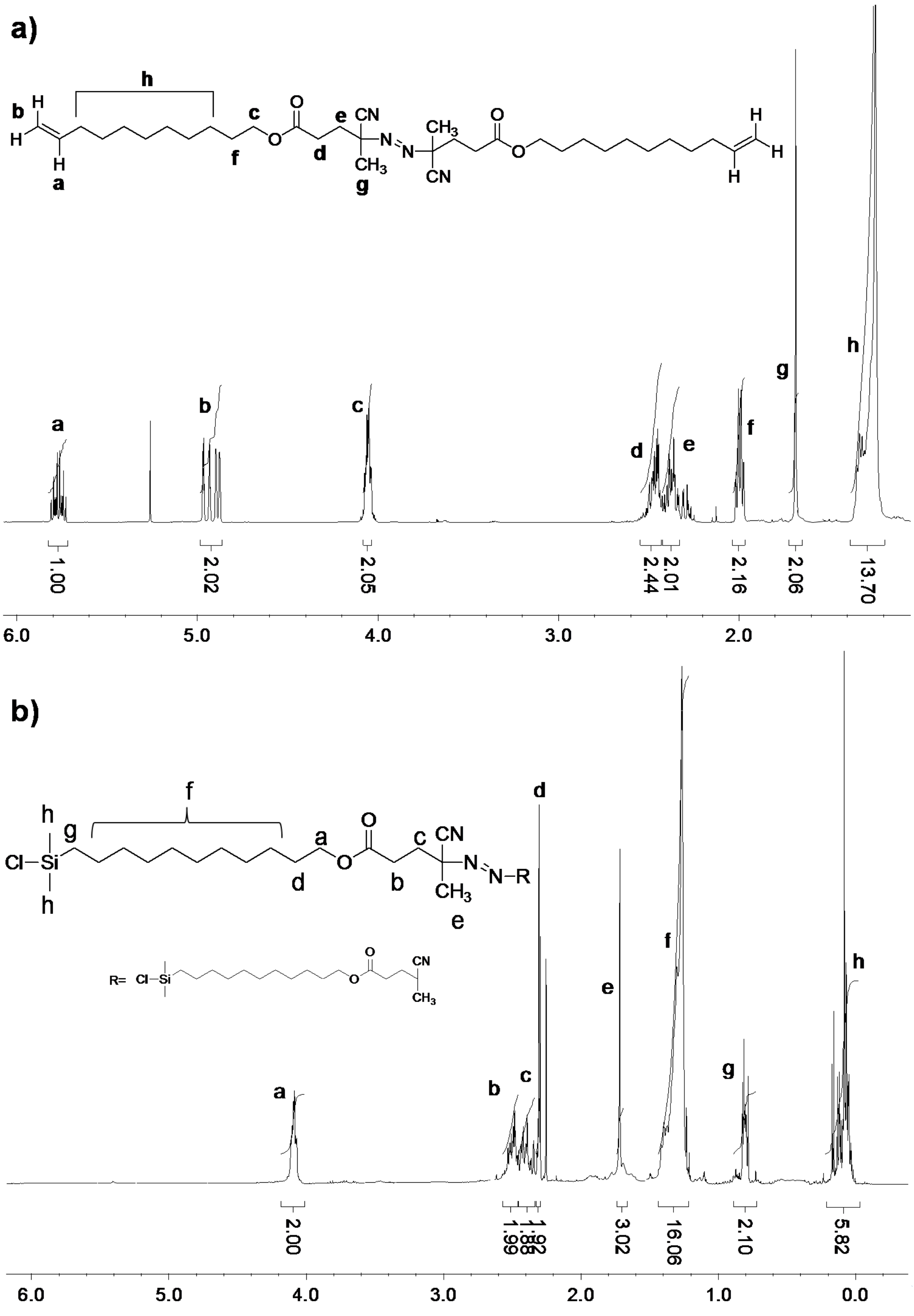


Figure 3.4 ^{1}H NMR spectra of a) **8** and b) **9**

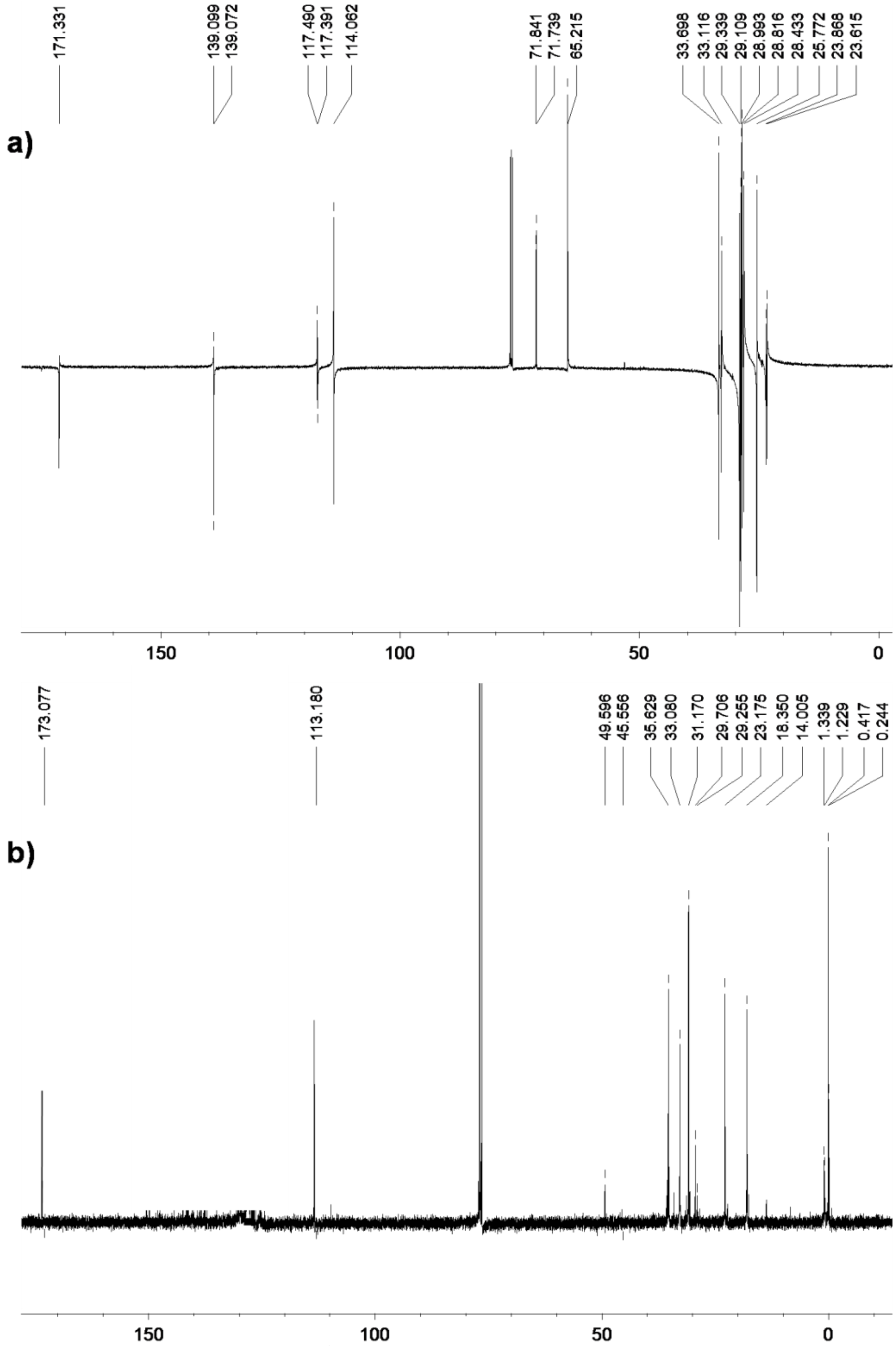


Figure 3.5 ^{13}C NMR spectra of a) **8** and b) **9**

3.4. Surface functionalization reactions with 4a-c for LASIP

The silica particles which were used for surface functionalization and surface initiated polymerizations subsequently were SA15 NPs, K3 and B-K3 GPs. SA15 NPs were spherically shaped nanoparticles with a diameter size of 15 nm, whereas K3 and B-K3 (containing boron atom) GPs were randomly shaped, porous glass particles with a random size distribution (see **Table 3.1** for more detailed information).

Table 3.1 The list of silica particles used for LASIP reactions and their physical properties

particle	size	shape	content	BET surface area[a] (m^2/g)	pH[a]	conductivity[a] (mS)	accessible numer of silanol groups[b] (mmol/g)
SA15	15 nm	spherical	SiO_2	150+/-25	3.7-4.5	n.a.	1.19
AE200[c]	12 nm	spherical	SiO_2	200+/-25	3.7-4.5	n.a.	1.57
K3	3 µm	porous	silicate	1.0-1.5	11.7	1.3	0.21
B-K3	3µm	porous	boron-silicate	1.0-1.5	10.5	0.5	0.83

[a] taken from the data sheet of the corresponding particle, [b] calculated after TGA measurements according to ***equation 3.1***, [c] used only for SI-CRP reactions

Before the surface modification reactions the number of accessible surface silanol groups of the particles which are to be functionalized with the prepared surface modifying agents had to be determined. This was done because not all of the surface silanol groups could be functionalized due to the bulky structure of the surface modifying agents due to steric hindrance. Therefore the surface of the particles were first functionalized with excess amount of trimethylsilyl chloride (TMSiCl) which is a smaller molecule than the surface modifying groups and can also be attached to the surface of the particles with the same synthetic procedure. It was assumed that all the accessible surface silanol groups were functionalized by using an excess amount of TMSiCl.

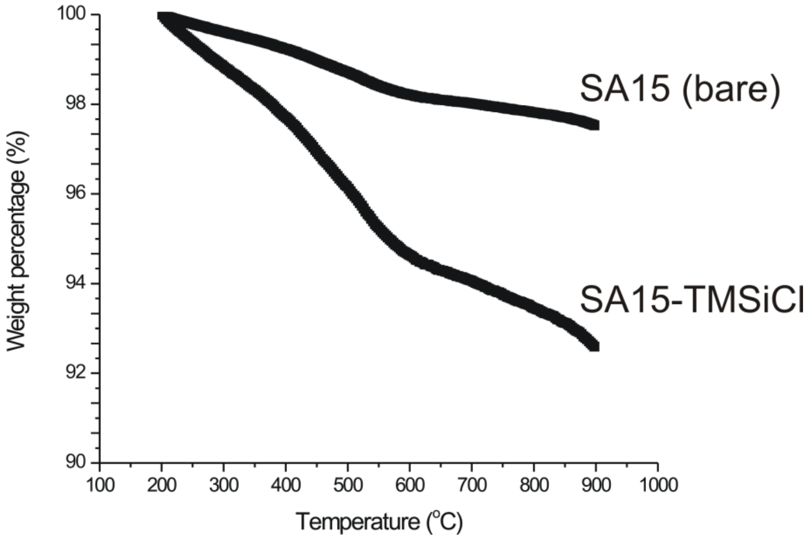
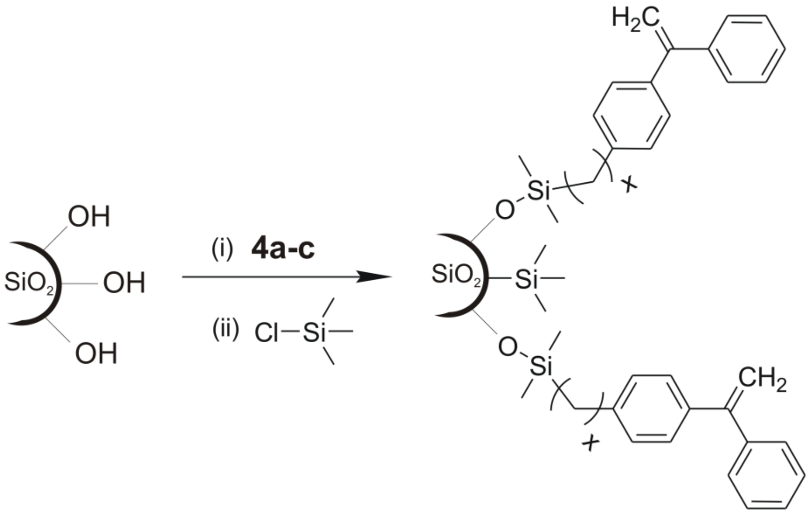


Figure 3.6 TGA curves of bare SA15 NP and TMSiCl-functionalized SA15 NP (excess amount of TMSiCl with respect to the number of surface silanol groups of the SA15 NP)

The surface functionalized nano- and glass particles were characterized by thermo gravimetrical analysis (TGA) in order to determine the number of functionalized silanol groups. The TGA curves of bare silica particle (SA15) and TMSiCl-functionalized particle are shown for comparison in **Figure 3.6**. Due to volatile content on the bare SA15 NP 2% weight loss was observed, whereas a weight loss of 7.5% was detected in TMSiCl-functionalized SA15 NP. The measurement parameters were as follows: temperature from 32^{o}C to 900^{o}C, under N_2 atmosphere, with 5 K/min heating rate. The number of silanol groups per 1 g of particle was calculated by using ***equation 3.1*** below.

$$n_{MG} \ / \ 1 \ g \ particle = \frac{W_1 - W_2}{M_{MG} W_2} \qquad \textbf{\textit{Equation 3.1}}$$

In ***equation 3.1*** n_{MG} */ 1 g particle* is the number of functionalized surface silanol groups per 1 g of particle, W_1 is the sample weight, W_2 is the residual weight and M_{MG} is the molecular weight of the surface modifying group. As the surface modifying group was TMSiCl for the determination of the number of accessible surface silanol groups, M_{MG} was taken as 108.6 g/mol. In order to exclude the error which could have been occurred because of the volatile content (water, solvent), the sample weight was taken as the weight at T= 100^{o}C. According to the TGA measurements and the calculations based on the above equation the number of moles of surface silanol groups per 1 g of particle is shown in **Table 3.1**.



Scheme 3.4 Schematic illustration of surface modification of particles with LASIP surface modifying groups (**4a**-**c**) (i) in toluene at room temperature for 3 days in the presence of pyridine as base (ii) in toluene at room temperature for 3 days in the presence of pyridine as base

After the accessible number of the silanol groups for each particle was determined, the surface functionalization reactions were carried out. The synthetic procedure will be explained in more detail in the **Experimental** section. However different sets of experiments were performed in order to find out the optimum conditions for surface modification reactions. The particles were functionalized with 1, 2, 3 or 4 equivalents of DPE based surface modifying group with the longest alkyl side chain (**4c**) with respect to the accessible number of surface silanol groups in order to investigate the effect of the surface initiator grafting density on the LASIP reactions. The surface functionalized particles were investigated via TGA and the surface functionalization values (as percentage and number of moles of surface modifying group per 1 gram of particle) were calculated according to ***equation 3.1***, and the grafting density of the surface modifying groups (σ_{MG}) were calculated according to ***equation 3.2***, by using the molecular weight of the corresponding surface modifying group (see **Table 3.2**).

Table 3.2 TGA results of the surface functionalization reactions of NPs and GPs. The surface functionalization reactions were performed in toluene as solvent in the presence of pyridine as base by using 1, 2, 3 or 4 equivalents of the surface modifying group (**4c**) with respect to the accessible surface silanol groups* for three days at room temperature.

entry	particle	amount of surface modifying group (**4c**)	functionalization percentage[a] (%)	n_{MG}/g particle[b] (mmol/g)	σ_{MG}[c] (molecule/nm^2)
1	**SA15**	1 eq	10.1	0.12	0.03
2	**SA15**	2 eq	33.6	0.40	0.10
3	**SA15**	3 eq	52.4	0.62	0.15
4	**SA15**	4 eq	89.1	1.06	0.26
5	**K3**	1 eq	21.8	0.05	0.07
6	**K3**	2 eq	39.5	0.08	0.11
7	**K3**	3 eq	58.0	0.08	0.11
8	**K3**	4 eq	64.7	0.09	0.12
9	**B-K3**	1 eq	19.9	0.16	0.05
10	**B-K3**	2 eq	35.1	0.29	0.09
11	**B-K3**	3 eq	51.3	0.42	0.14
12	**B-K3**	4 eq	55.4	0.46	0.15

[a] calculated by the ratio of the functionalized silanol groups with respect to the accessible silanol groups on the particle surface, [b] calculated according to ***equation 3.1***, [c] calculated according to ***equation 3.2***
* The number of moles of the accessibel silanol groups for each particle: n_{SiOH}(SA15)= 1.19 mmol/g particle, n_{SiOH}(K3)= 0.21 mmol/g particle and n_{SiOH}(B-K3)= 0.83 mmol/g particle.

According to **Table 3.2**, functionalization success increased with the increasing amount of the loaded surface modifying group as expected. Among the silica particles SA15 NPs were found to be functionalized in a higher success with higher loading (up to 89.1% of the accessible surface, **entry 4**). The K3 and B-K3 GPs could only be functionalized to an extent (up to 64.7% of the accessible surface for K3, **entry 8**; up to 55.4% of the accessible surface for B-K3, **entry 12**), with these specific surface modifying groups. This can be explained by the porous structure of the glass particles. Because bulkier molecules such as the surface modifying groups could not penetrate into the pores of the GPs, the functionalization success reduced. The results presented in **Table 3.2** also indicated that even in the best case there remained ≈10% of the surface silanol groups unfunctionalized due to steric hindrance (**entry 4**). As these unfunctionalized silanol groups would cause the termination of living anionic polymerization they had to be blocked by further functionalizing the already surfaced functionalized particles with TMSiCl. When the surface modifying group grafting density values are compared with literature values (σ_i= 0.3 molecules/nm^2) it was confirmed that the best results which were obtained with SA15 NPs are in an acceptable range[20-21,112].

Beside the examples of surface modification experiments shown in **Table 3.2**, other experiments were conducted by using triethylamine as base instead of pyridine. However the presence of triethylamine significantly reduced the functionalization success both for SA15 NPs and K3, B-K3 GPs. Surface functionalization experiments were also carried out for longer reaction time (up to one week) however no significant increase in functionalization success was observed. The reaction temperature did not have an important effect on the modification success either as the surface modification experiments which were carried out at 50^{o}C resulted in only 89.5% functionalization of the accessible surface for SA15 NPs when the other parameters (reaction time (three days) and base (pyridine)) were kept same. Therefore the rest of the surface functionalization reactions were conducted for three days at room temperature and by using pyridine as base.

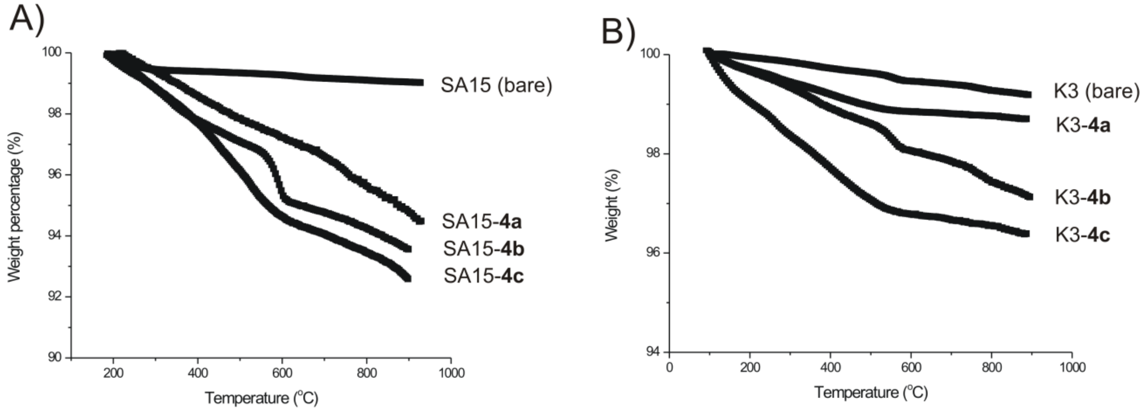


Figure 3.7 TGA curves of a) bare silica particles SA15 NP and **4c**-functionalized SA15 NP, b) K3 GP and **4c**-functionalized K3 GP

The surface functionalization experiments were also performed with other LASIP initiators (**4a** and **4b**) in order to see the effect of the spacer length (side chain length) on both the surface functionalization reactions and subsequent LASIP reactions by using only 4 equivalents of the surface modifying groups with respect to the number of moles of accessible surface silanol groups of the corresponding particle. **Table 3.3** shows TGA results of these surface modification reactions. Some of the selected TGA curves of bare silica particles and functionalized silica particles are also shown in **Figure 3.7** for comparison. Due to the high surface coverage of SA15 NPs the weight loss percentage values observed in DPE-functionalized SA15 NPs (6-8%) were more than DPE-functionalized K3 GPs (1-4%). An unexpected sharp weight loss in **4b**-functionalized SA15

NPs and K3 GPs (SA15-**4b** and K3-**4b** in **Figure 3.7**) was observed both around 550°C which can only be explained by an experimental error as a similar behavior was not observed in any of the other measurements.

Table 3.3 indicated that as the spacer length of the surface modifying group increased the modification success decreased due to the growing size of the surface modifying group. Regardless of the size of the surface modifying group, SA15 NPs (entries 1 and 2 in **Table 3.3** and entry 4 in **Table 3.2**) were functionalized more easily than the K3 and B-K3 GPs (entries 3-6 in Table 3.3 and entries 8, 12 in **Table 3.2**) due to the porous structure of the GPs as explained above.

Table 3.3 TGA results of the surface functionalization reactions of NPs and GPs. The surface functionalization reactions were performed in toluene as solvent in the presence of pyridine as base by using 4 equivalents of surface modifying agents (**4a-c**) with respect to the accessible surface silanol groups for three days at room temperature for maximum functionalization.

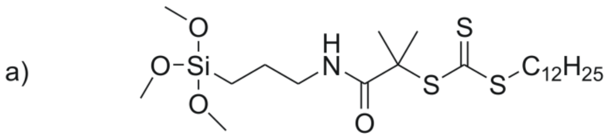
entry	particle	coupling agent	functionalization success[a] (%)	n_{MG}/g particle[b] (mmol/g)	σ_i[c] (molecule/nm^2)
1	SA15	**4a**	97	1.15	0.28
2	SA15	**4b**	95	1.13	0.27
3	K3	**4a**	82.8	0.17	0.24
4	K3	**4b**	69.8	0.15	0.21
5	B-K3	**4a**	76.1	0.63	0.20
6	B-K3	**4b**	61.9	0.51	0.17

[a] calculated by the ratio of the functionalized silanol groups with respect to the accessible silanol groups on the particle surface, [b] calculated by ***equation 3.1***, [c] calculated by ***equation 3.2***

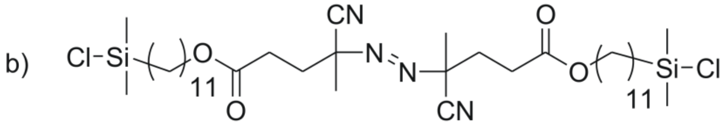
3.5. Surface functionalization reactions with 6 and 9 for SI-CRP

For surface initiated controlled radical polymerization (SI-CRP) reactions, two different silica NPs were functionalized with the CRP surface modifying groups (**6** and **9**). The first silica nanoparticle was SA15 NPs which was also used for LASIP reactions. The second particle was AE200 NPs which was also spherically shaped nanoparticle with 12 nm diameter size and narrow size distribution.

The surface of the above mentioned NPs were functionalized with CRP surface modifying groups in a similar synthetic manner. Although the details will be explained in **Experimental** section, the surface functionalization of the NPs with the CTA-based surface modification group was carried out in toluene at room temperature and in the presence of catalytic amount of maleic anhydride and water, whereas surface functionalization of the NPs with the AIBN-based surface modification group was carried out in toluene at room temperature, in dark (the dissociation of AIBN occurs at 65^{o}C) and in the presence of pyridine as base. The CRP surface modifying groups (**6** and **9**) have more than one surface binding functional group per molecule (see **Figure 3.8**). The trimethoxysilyl anchoring group on **6** provides three binding groups per molecule, whereas dimethylsilyl chloride moiety on both ends of **9** provides two binding groups per molecule, therefore while functionalizing the surface of the particles only 1 and 2 equivalents of the surface modifying groups (shown in **Table 3.4**) with respect to the number of moles of the accessible surface silanol groups were used. The functionalized particles were investigated via TGA and ***equation 3.1*** was used to calculate the surface initiator groups after modification whereas ***equation 3.2*** was used to calculate the grafting density of surface modifying groups (σ_{MG}).



6

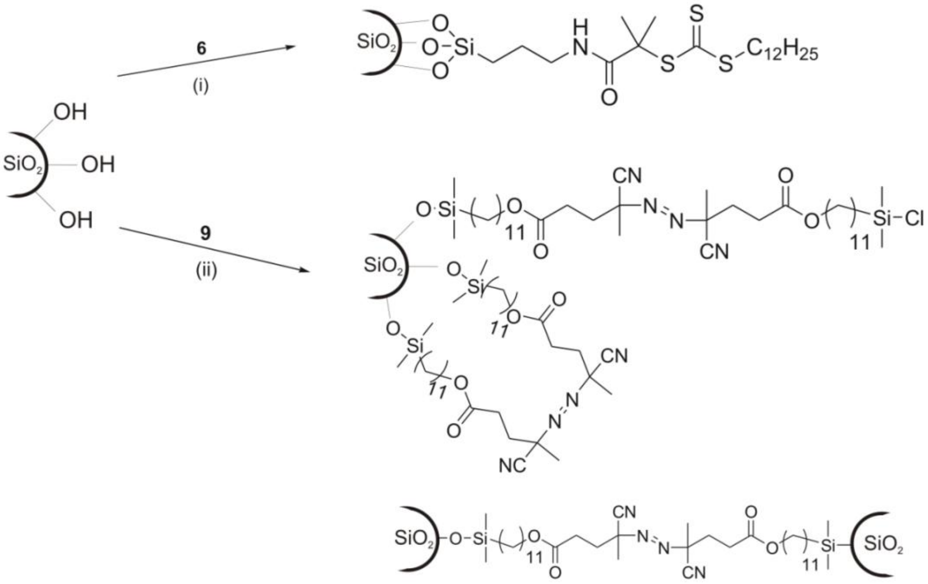


9

Figure 3.8 Chemical structures of a) CTA-based surface modifying group (**6**) and b) AIBN-based surface modifying group (**9**)

When the chemical structures of the CRP surface modifying groups are considered, possible side reactions might have occurred. The trimethoxysilyl anchoring group on CTA based surface modifying group (**6**) had the possibility to react with moisture to yield methanol and CTA-Si-$(OH)_3$ which could not bind to the surface of the silica NPs. Therefore compound **6** was kept under inert conditions after preparation. Another unwanted side reaction of **6** could have been self condensation of the amide yielding back to the compound **5** and (3-aminopropyl)trimethoxysilane. As maleic anhydride was proven to prevent such side reactions, a catalytic amount of maleic anhydride was added to the reaction mixture for the surface functionalization of NPs with CTA based surface modifying group.

As for the AIBN based surface modifying agent (**9**) the most significant issue which had to be taken into consideration was the possible dissociation of the azo group. Therefore compound **9** was kept in the freezer (-20^{o}C) in dark after preparation and the surface functionalization reactions were also carried out at room temperature and in dark. An unwanted side reaction during the surface functionalization of the silica NPs with compound **9** was bridging of the compound between two NPs due to the presence of the functional groups on both ends of the compound. In order to reduce the possibility of this bridging reaction, the NP suspension (in toluene, 15 ml/g particle) was ultrasonicated for a longer time than the other surface functionalization reactions (30 minutes).



Scheme 3.5 Schematic illustration of the surface modification reactions of silica NPs (SA15, AE200) with SI-CRP surface modifying agents (1 and 2 equivalents with respect to the number of accessible surface silanol groups) (i) in toluene at room temperature for 24 hours in the presence of catalytic amount maleic anhydride and water in dark, (ii) in toluene at room temperature for 3 days in the presence of pyridine as a base

Table 3.4 TGA results of the surface functionalization reactions of SA15 and AE200 (by using 1 and 2 equivalents of the SI-CRP surface modifying groups (**6**, **9**) with respect to the surface silanol groups). The surface functionalization reactions were performed in anhydrous toluene as solvent and a catalytic amount of maleic anhydride and H_2O for one day when the particle surface was functionalized with **6**, whereas in the presence of pyridine for three days when the particle surface was functionalized with **9**.

entry	particle	surface modifying group / amount[a]	n_{MG}/g particle[b] (mmol)	σ_{MG}[c] (molecule/nm^2)
1	AE200	**6** / 1 eq.	0.12	0.10
2	AE200	**9** / 1 eq.	0.17	0.14
3	SA15	**6** / 1 eq.	0.09	0.11

4	SA15	**9** / 1 eq.	0.14	0.15
5	AE200	**6** / 2 eq.	0.16	0.15
6	AE200	**9** / 2 eq.	0.22	0.19
7	SA15	**6** / 2 eq.	0.13	0.14
8	SA15	**9** / 2 eq.	0.19	0.19

[a] calculated according to the results of the previous TGA measurements [b] calculated according to ***equation 3.1***, [c] calculated according to ***equation 3.2***

When two equivalents of the surface modifying groups with respect to the number of moles of the accessible surface silanol groups were used, the grafting density of surface modifying groups (σ_{MG}) was found to be higher as expected (entries 5-8 in **Table 3.4**). This was done intentionally in order to see the effect of the initial surface initiator grafting density on the SI-CRP, because it has been reported that high surface density of the radical initiator groups on the surface caused recombination of the radicals which were formed during radical polymerization[195]. The TGA curves of bare SA15 NP and CRP initiator (**6**, **9**)-functionalized SA15 NPs are also shown in **Figure 3.9** for comparison. TGA indicated a weight loss of 3.6% for CTA-functionalized SA15 NP (SA15-**6**), whereas the weight loss of the AIBN-functionalized SA15 NP (SA15-**9**) was 5%.

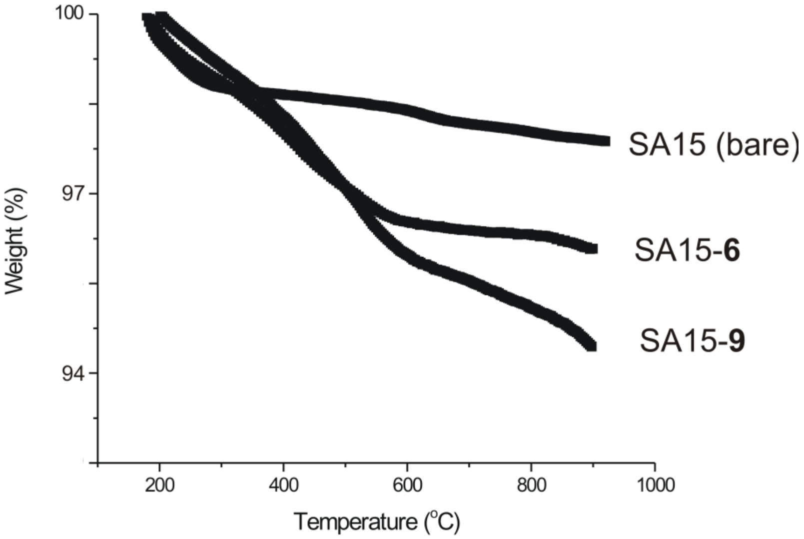
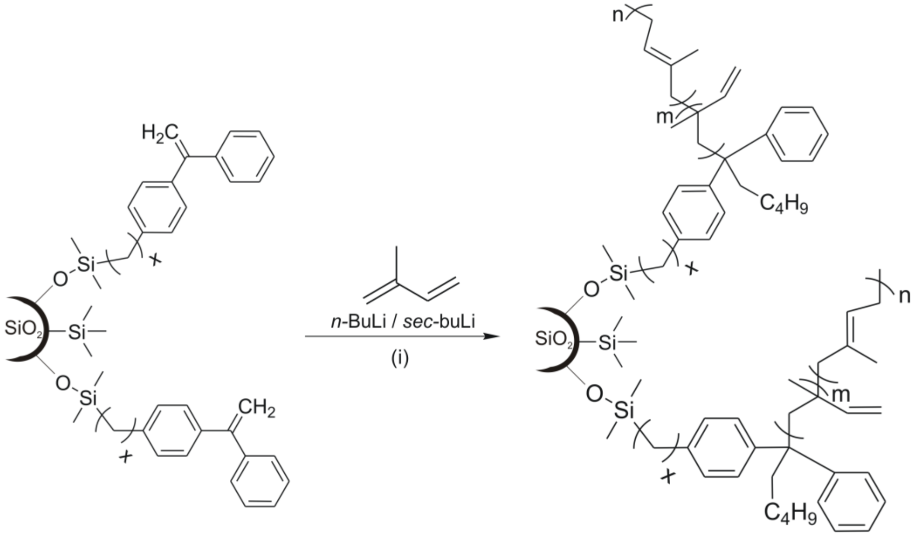


Figure 3.9 TGA curves of SA15 NPs and CRP initiator (**6**, **9**)-functionalized SA15 NPs (The TGA curves shown here belong to the samples of entries 3 and 4 in **Table 3.4**)

3.6. Living anionic surface initiated polymerization (LASIP) reactions

LASIP of isoprene from DPE-functionalized SA15 NPs and K3 and B-K3 GPs were carried out under extremely inert conditions as mentioned earlier. The DPE-functionalized particles were further functionalized with TMSiCl in order to prevent unreacted surface silanol groups from interfering with the living anionic polymerization process due to its sensitivity towards –OH (hydroxyl) groups. The DPE-functionalized NPs and GPs were stored in the glovebox after purification in order to keep them in inert conditions. The solvents (benzene, toluene and n-hexane) were purified according to the procedure reported in literature[130], and also stored in the glovebox after it was degassed by purging with N_2. The DPE moiety on the surface initiating group was activated by the addition of *n*-BuLi or *sec*-BuLi (1.1 equivalent with respect to the number of the surface modifying groups) and the LASIP was started with the addition of isoprene monomer which was also purified according to the literature (see **Scheme 3.6**)[130]. The LASIP reactions were quenched with the addition of excess methanol (1 ml).



Scheme 3.6 Schematic illustration of SI-CRP reactions

After the polymerization was completed, surface grafted polymer and non-grafted homopolymer were present in the reaction mixture. In order to separate the surface grafted polymer and the homopolymer, the following separation procedure was applied (see also **Figure 3.10**):

Firstly, the reaction mixture was transferred into a round bottom flask and concentrated under reduced pressure in order to remove the solvent. The crude product was then precipitated in methanol in which both homopolymer and surface grafted polymer were insoluble. The precipitate was centrifuged and the aliquot was decanted. Then the precipitate was dispersed in cold anhydrous toluene in which the homopolymer was dissolved whereas the surface grafted polymer remained as precipitate. The dispersion was then centrifuged and the aliquot was decanted and kept for the analysis of the non-grafted homopolymer. This dispersion/centrifugation cycle was repeated for two more times in order to separate the whole surface grafted polymer from the homopolymer.

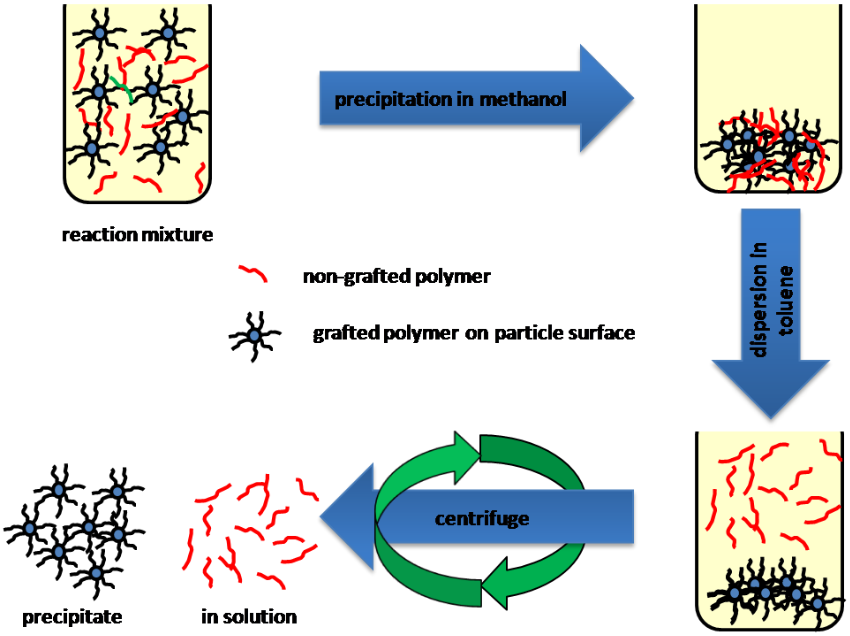


Figure 3.10 Graphical illustration of separation process of the surface grafted polymer

In order to analyze the surface grafted polymers via GPC, the organic content (polymer) had to be cleaved off from the surface of the silica particles. This was done by treating a small amount of surface grafted polymer with a couple of drops of aqueous KOH solution (saturated) in THF at reflux conditions for 30 minutes. The surface grafted polymers were also investigated via TGA in order to determine the grafting density and via NMR to investigate the microstructure of the surface grafted polymers. In order to investigate the effect of different parameters on the LASIP process several sets of experiments were conducted by altering those parameters.

3.6.1. Investigation of the living character of SIP

In this set of reactions the livingness of the LASIP process was investigated by adding different amount of monomer with respect to the number of moles of surface initiating groups in order to obtain polymers with different degree of polymerization (DP) values. The particles which were functionalized by using 4 equivalents of **4c** with respect to the number of accessible silanol groups on the particle surface were used to graft PI for this set of experiments. The surface initiating groups were activated with n-BuLi and benzene was used as solvent. The polymerization times were determined depending on the desired degree of polymerization; 1 hour for DP= 25, 2 hours for DP= 50, 3 hours for DP= 75 and 4 hours for DP= 100. **Table 3.5** shows the results of the first set of LASIP reactions.

According to the results shown in **Table 3.5**, LASIP of isoprene from the surface functionalized silica NPs and GPs was successfully conducted. The percentage of the non-grafted homopolymer was less than 10% in each case; in other words more than 90% of the isoprene which was added to the polymerization was grafted from the initiator functionalized surface of the particles. The reason of the existence of homopolymer was that some of the *n*-BuLi which was added to activate the surface modifying groups initiated the monomer (isoprene) itself before activating the surface modifying group. This might be explained by the presence of possible chain transfer reactions and the 0.1 equivalent excess (with respect to the surface initiating groups) use of *n*-BuLi in case that some of the *n*-BuLi could be killed by the moisture which could have been present due to the high absorptive character of the silica particles.

GPC analysis revealed that the number average molecular weight (M_n) of the degrafted polymers exceeded the theoretical molecular weight (calculated by [M]/[I]) and the PDI values were found to be relatively high for a living polymerization; in the range between M_w/M_n= 1.4 and M_w/M_n= 1.7 for **entries 2-5**. This could be explained by the initial high grafting density of the surface modifying groups in the case of SA15 NPs as the high grafting density might have caused steric hindrance. This assumption was confirmed with the GPC results of the polymers which had been grafted from K3 and B-K3 GPs on whose surface the initiator grafting density was lower when compared to SA15 NPs. The PDI values for the polymers which were grafted from GPs (**entries 6-13**) were found to be around M_w/M_n= 1.1 which was more likely a value for a living anionic polymerization. The GPC analysis which were done on these non-grafted homo-PI indicated that the number average molecular weight values were closer to the calculated molecular weight (via [M]/[I]) and the molecular weight distribution values were also lower than the surface grafted polymers because SIP on the particle surface occurred in the presence of steric hindrance and charge repulsion whereas homopolymer grew in solution with an enough space yielding results which could be achieved with a controlled polymerization.

Table 3.5 Results of LASIP reactions – investigation of livingness of LASIP. LASIP reactions were performed in benzene as solvent at 0°C and n-BuLi (1.1 equivalents with respect to the number of surface initiating groups*) was used to activate the ethylene moiety on DPE to initiate polymerization. Depending on the projected degree of polymerization, the reactions were carried out for 1, 2, 3, and 4 hours.

entry	polymer	[M]/[I]	$Mn_{calc.}$ (g/mol)	surface grafted polymer		homopolymer		grafting ratio[a] (%)	microstructure[b] (%)			σ_{PI}[c] (chains/nm^2)	size[d] (nm)
				Mn_{GPC} (g/mol)	PDI	Mn_{GPC} (g/mol)	PDI		1,2	cis-1,4	trans-1,4		
1	PI	100	6800	-	-	8100	1.09		15	33	52	-	-
2	SA15-**4c**-$(PI)_{25}$	25	1700	2200	1.43	1900	1.35	94	-	-	-	0.19	21.0
3	SA15-**4c**-$(PI)_{50}$	50	3400	4900	1.48	3800	1.32	92	-	-	-	0.20	22.6
4	SA15-**4c**-$(PI)_{75}$	75	5100	6300	1.55	5700	1.44	91	-	-	-	0.23	23.2
5	SA15-**4c**-$(PI)_{100}$	100	6800	10500	1.68	8300	1.36	93	17	34	49	0.21	24.7
6	K3-**4c** -$(PI)_{25}$	25	1700	3100	1.11	2200	1.09	96	-	-	-	0.09	n.a.
7	K3-**4c** -$(PI)_{50}$	50	3400	5900	1.08	4100	1.08	92	-	-	-	0.11	n.a.
8	K3-**4c** -$(PI)_{75}$	75	5100	9000	1.11	7300	1.08	95	-	-	-	0.10	n.a.
9	K3-**4c** -$(PI)_{100}$	100	6800	11600	1.14	8900	1.12	91	16	33	51	0.10	n.a.
10	B-K3-**4c** -$(PI)_{25}$	25	1700	2900	1.12	2400	1.1	96	-	-	-	0.11	n.a.
11	B-K3-**4c** -$(PI)_{50}$	50	3400	6100	1.11	4500	1.1	93	-	-	-	0.14	n.a.
12	B-K3-**4c** -$(PI)_{75}$	75	5100	9200	1.14	7900	1.11	90	-	-	-	0.12	n.a.
13	B-K3-**4c** -$(PI)_{100}$	100	6800	11500	1.14	10200	1.12	91	14	32	54	0.13	n.a.

[a] determined by calculating the percentage of the amount of grafted polymer to the amount of the added monomer [b] determined by NMR investigations, [c] calculated according to ***Equation 3.2***, [d] diameter size of the PI grafted particles determined via DLS measurements.

* The initial amount of the surface modifying group on the particles from which PI was grafted from are; n_{MG} = 1.06 mmol/g particle for SA15-**4c**, n_{MG} = 0.09 mmol/g particle for K3-**4c**, n_{MG} = 0.15 mmol/g particle for B-K3-**4c**

The increase in the molecular weight with the increasing projected degree of polymerization indicated the living behavior of the performed polymerization reactions although the actual molecular weight of the obtained surface grafted polymers exceeded the projected molecular weights. This suggestion applied for both SA15 NPs and K3, B-K3 GPs. The surface grafted polymers were investigated via TGA in order to determine the grafting densities of the produced composites. The grafting density values (σ_{PI}) were calculated by using the formula below where A_S is the surface area of the silica particle, R is geometric size, ρ_{SiO2} is mass density of the bare particle, N_A is the Avogadro's number and M_{PI} is the molecular weight of the surface grafted polymer. **Table 3.5** indicated that the highest grafting density values were achieved for the composites in which SA15 NPs (around σ_{PI}= 0.23 chains/nm^2) were used for the LASIP process (entries 2-5, **Table 3.5**), due to its size and the initial high grafting density of the surface modifying groups (σ_{MG}) which had been confirmed with previous TGA measurements (**Table 3.4**). The grafting density values of the composites when the polyisoprene was grafted from K3 and B-K3 GPs were found to be ≈0.1 chains/nm^2 (entries 6-13, **Table 3.5**). This value actually indicated that the produced composite cannot display a brush-like conformation due to low grafting density.

$$A_S = 3\frac{W_2}{R\rho_{SiO_2}} \qquad \textbf{Equation 3.2a}$$

$$\sigma_{PI} = \frac{(W_1 - W_2)N_A}{A_S M_{PI}} \qquad \textbf{Equation 3.2b}$$

The microstructure of the surface grafted polymers was determined via NMR analysis. The results shown in **Table 3.5** indicated that the microstructure of the polymers which were grafted from silica particles did not depend on the type of the particle. Additionally the microstructure of the homopolymer which was synthesized as a control experiment and the surface grafted polymers were similar; 15% *1,2*, 35% *cis-1,4* and 50% *trans-1,4* (**entries 1, 5, 9** and **13**). Hence it can be concluded that the LASIP itself did not have a role on the microstructure.

The sizes of the PI grafted silica NPs (SA15) were determined via DLS analysis. Due to their initial random shape and porous structure of the GPs it was not possible to obtain an accurate size determination for PI grafted GPs. The size of the particles depends on both the grafting density (as the polymer chains are stretched away from the surface in case of high grafting or they tend to overlap in case of low grafting) and the length of the surface grafted polymer. The obtained results (entries 2-6, **Table 3.5**) confirmed this argument as the largest size was determined (d= 24.7 nm) for SA15-**4c**-(PI)$_{100}$ (entry 5, **Table 3.5**) which had the longest PI chain (M_n= 10500 g/mol) and second highest grafting density (σ_{PI}= 0.21). The diameter sizes of the other PI grafted NPs were also in the range between 21.0 nm and 23.2 nm. As the measured size is the diameter size it is concluded that there is only 4.9 nm shell (PI) thickness on the inorganic core (SA15 NP).

3.6.2. *Effect of the initiator density on the particle surface on LASIP*

Another set of LASIP experiments was conducted to investigate the effect of the initial surface modifying group grafting density (σ_{MG}) on the particle surface on the LASIP reactions. In **Table 3.2** the results of the surface functionalization reactions by using different amount of surface modifying groups were already shown. For this set of experiments those surface functionalized particles were used and isoprene was polymerized via LASIP. LASIP experiments were carried out in an ice bath at 0^{o}C, in benzene as solvent and *n*-BuLi (1.1 equivalents with respect to the surface initiating groups) was used in order to activate the surface modifying groups. The surface initiated polymers were characterized via TGA, NMR, DLS and GPC. The results are shown in **Table 3.6**.

GPC analysis indicated that the polymers grafted from the particles which were functionalized by using only 1 equivalent of the surface modifying group with respect to the number of the surface silanol groups had the lowest PDI values M_w/M_n= 1.07 for SA15-**4c**-(1)-PI$_{100}$ and M_w/M_n= 1.06 for K3-**4c**-(1)-PI$_{100}$ and also the most accurate molecular weight control (entries 1 and 5, **Table 3.6**). As the grafting density of the surface modifying groups (σ_{MG}) increased, the PDI values of the grafted polymers increased as well and the accuracy of the molecular weight projection decreased. The PDI value for the polymer which was grafted from SA15 NP which had been functionalized with 4 equivalents of surface modifying group with respect to the surface silanol groups increased up to M_w/M_n= 1.68 (SA15-**4c**-(4)-PI$_{100}$) from M_w/M_n= 1.07 (SA15-**4c**-(1)-PI$_{100}$) (entries 1 and 4, **Table 2.6**). The effect of the initial surface modifying group grafting density on the K3 GPs was not that intense as the PDI value increased up to M_w/M_n= 1.14 (K3-**4c**-(4)-PI$_{100}$) from M_w/M_n= 1.06 (K3-**4c**-(1)-PI$_{100}$) (entries 5 and 8, **Table 3.6**). This could be explained by lower surface coverage of the K3 GPs due to low amount of silanol groups on the particle surface originally. Thus it could be concluded that as the grafting density of the surface initiating groups increased the polymerization quality decreased due to steric hindrance.

Table 3.6 Results of LASIP reactions – investigating the effect of the initiator density on the particle surface. LASIP reactions were performed in benzene as solvent at 0^{o}C an n-BuLi (1.1 equivalents with respect to the number of surface initiating groups) was used to activate the ethylene moiety on DPE based surface modifying group (**4c**) to initiate polymerization.

entry	polymer[a]	n_{MG} (mmol/g particle)	surface grafted polymer		homopolymer		grafting ratio[b] (%)	microstructure[c] (%)			σ_{PI}[d] (chains/nm^2)	size[e] (nm)
			Mn_{GPC}	PDI	Mn_{GPC}	PDI		1,2	cis-1,4	trans-1,4		
1	*SA15-**4c**-(1)-PI$_{100}$	0.12	7100	1.07	7000	1.08	91	17	37	46	0.03	3.2
2	*SA15-**4c**-(2)- PI$_{100}$	0.40	7300	1.18	7400	1.17	93	15	34	51	0.08	9.1

3	*SA15-**4c**-(3)- PI$_{100}$	0.62	8100	1.24	8200	1.22	95	13	33	54	0.12	13.8
4	*SA15-**4c**-(4)- PI$_{100}$	1.06	10500	1.68	8300	1.36	93	17	34	49	0.21	24.7
5	*K3-**4c**-(1)- PI$_{100}$	0.05	7400	1.06	7000	1.07	90	16	35	49	0.03	n.a.
6	*K3-**4c**-(2)- PI$_{100}$	0.08	7300	1.12	7100	1.09	92	15	29	56	0.06	n.a.
7	*K3-**4c**-(3)- PI$_{100}$	0.08	8600	1.15	8300	1.13	93	14	34	52	0.08	n.a.
8	*K3-**4c**-(4)- PI$_{100}$	0.09	11600	1.14	8900	1.12	95	16	33	51	0.10	n.a.

[a] Projected molecular weight for each polymer was 6800 g/mol, [M]/[I]= 100 [b] determined by calculating the percentage of the amount of grafted polymer to the amount of the added monomer [c] determined by NMR investigations, [d] calculated according to ***Equation 3.2*** [e] diameter size of the PI grafted particles determined via DLS measurements.

* The number in bracket in the name of the polymer represents the amount of surface modifying group used for surface modification reaction.

NMR analysis showed that the microstructure was not affected by the density of the initiating groups on the surface of the particles. The average percentage of the microstructure conformations were found to be 15% *1,2*, 35% *cis-1,4* and 50% *trans-1,4*.

The grafting density values of the grafted polymer (σ_{PI}) were found to be consistent with the results of surface functionalization reactions which were shown in **Table 3.2**. An increase in σ_{PI} values which was calculated by using ***equation 3.2*** after the TGA measurements can be observed according to the initial grafting density of the surface initiating group. For SA15 NPs the grafting density value increased from 0.03 chains/nm^2 (SA15-**4c**-(1)-PI$_{100}$) to 0.21 chains/nm^2 (SA15-**4c**-(4)-PI$_{100}$) (entries 1-4, **Table 3.6**), whereas the grafting density for the composites with K3 GPs increased from 0.03 chains/nm^2 (K3-**4c**-(1)-PI$_{100}$) to 0.10 chains/nm^2 (entries 5-8, **Table 3.6**). The diameter size of the PI grafted NPs increased with the increasing surface modifying group grafting density as expected due to the stretching away of the polymer chains from the surface because of high grafting density of the initiating groups on the particle surface.

3.6.3. Effect of solvent on LASIP

LASIP reactions were also carried out in different solvents such as toluene and n-hexane. For these polymerization reactions the particles which were functionalized with 4 equivalents of **4c** with respect to the number of accessible surface silanol groups of the corresponding particle were used and LASIP was initiated by activating the DPE units with the addition of *n*-BuLi. The projected molecular weight for each polymer was M_n= 6800 g/mol for 100 isoprene units (calculated according to [M]/[I]). The surface grafted polymers were analyzed via GPC after they had been cleaved off from the particle surfaces and the results are shown in **Table 3.7**.

Table 3.7 Results of LASIP reactions – investigating the effect of the solvent. LASIP reactions were performed in toluene as solvent at -70°C and at -50°C and in n-hexane as solvent at -70°C. n-BuLi (1.1 equivalents with respect to the number of surface initiating groups*) was used to activate the ethylene moiety on DPE based surface modifying group (**4c**) to initiate polymerization. For each polymerization, the degree of polymerization was 100, [M]/[I]= 100.

				grafted polymer		homopolymer		grafting ratio[a]
entry	polymer	solvent	temperature (°C)	Mn_{GPC}	PDI	Mn_{GPC}	PDI	
1	PI	toluene	-70	-	-	17300	2.1	
2	SA15-**4c**-PI_{100}	toluene	-70	22000	2.4	24200	2.7	72
3	K3-**4c**-PI_{100}	toluene	-70	17600	2.3	19300	2.4	83
4	B-K3-**4c**-PI_{100}	toluene	-70	18300	2.2	21400	2.3	76
5	PI	n-hexane	-70	-	-	-	-	-
6	SA15-**4c**-PI_{100}	n-hexane	-70	-	-	-	-	-
7	K3-**4c**-PI_{100}	n-hexane	-70	-	-	-	-	-
8	B-K3-**4c**-PI_{100}	n-hexane	-70	-	-	-	-	-
9	SA15-**4c**-PI_{100}	toluene	-50	23200	2.7	23500	2.6	68
10	K3-**4c**-PI_{100}	toluene	-50	18400	2.5	19100	2.6	71
11	B-K3-**4c**-PI_{100}	toluene	-50	19100	2.3	20300	2.5	59

[a] determined by calculating the percentage of the amount of grafted polymer to the amount of the added monomer

* The initial amount of the surface modifying group on the particles from which PI was grafted from are; n_{MG} = 1.06 mmol/g particle for SA15-**4c**, n_{MG} = 0.09 mmol/g particle for K3-**4c**, n_{MG} = 0.15 mmol/g particle for B-K3-**4c**

GPC results showed that LASIP in toluene (entries 1-5 and 9-11, **Table 3.7**) resulted in surface grafted polymers with high PDI values between M_w/M_n= 2.2 and M_w/M_n= 2.7 and exceeded molecular weight values between M_n= 17600 g/mol and M_n= 23200 g/mol than the calculated molecular weight (entries 2-4 and 9-11, **Table 3.7**). Therefore it can be concluded that the surface initiated polymerization of isoprene in toluene did not have a living character. On the other hand neither grafted polymer nor homopolymer (non-grafted) were found in the reaction mixture when SIP was carried out in n-hexane. The grafting ratio (determined by calculating the percentage of the amount of grafted polymer to the amount of the added monomer) was also decreased when the LASIP was carried out in toluene (59%, entry 11, **Table 3.7**).

3.6.4. Effect of activating compound on LASIP

LASIP reactions were also carried out by using *sec*-BuLi (instead of *n*-BuLi) to activate the surface modifying groups of the functionalized particles in order to see the effect of the activating compound on LASIP reactions. These set of experiments were done by using the **4a**- and **4b**-functionalized silica particles in benzene as solvent at 0^{o}C. The projected molecular weight for each polymer was M_n(theo)= 6800 g/mol for 100 isoprene unit (calculated according to [M]/[I]). The results are presented in **Table 3.8**.

Table 3.8 Results of LASIP reactions – investigating the effect of initiator. LASIP reactions were performed in benzene as solvent at 0^{o}C. *n*-BuLi and *sec*-BuLi (both 1.1 equivalents with respect to the number of surface initiating groups) were used to activate the ethylene moiety on DPE based surface modifying groups (**4a-c**) to initiate polymerization. For each polymerization, the degree of polymerization was 100, [M]/[I]= 100.

	entry	polymer*	n_{MG} (mmol/g particle)	surface grafted polymer		homopolymer		grafting ratio^a (%)	σ_{PI}^{b} (chains/nm^2)	size^c (nm)
				Mn$_{GPC}$	PDI	Mn$_{GPC}$	PDI			
n-BuLi	1	SA15-**4a**-PI$_{100}$	1.15	10500	1.68	8300	1.36	91	0.20	23.8
	2	K3-**4a**-PI$_{100}$	0.17	11600	1.14	8900	1.12	94	0.16	n.a.
	3	B-K3-**4a**-PI$_{100}$	0.63	11500	1.14	10200	1.12	92	0.16	n.a.
	4	SA15-**4b**-PI$_{100}$	1.13	9400	1.46	7900	1.22	90	0.19	22.6
	5	K3-**4b**-PI$_{100}$	0.15	10700	1.09	8100	1.09	94	0.16	n.a.
	6	B-K3-**4b**-PI$_{100}$	0.51	11000	1.12	9500	1.10	93	0.14	n.a.
sec-BuLi	7	SA15-**4a**-PI$_{100}$	1.15	8100	1.56	7200	1.36	92	0.21	22.1
	8	K3-**4a**-PI$_{100}$	0.17	7900	1.13	7100	1.12	95	0.17	n.a.
	9	B-K3-**4a**-PI$_{100}$	0.63	8300	1.14	7400	1.12	93	0.17	n.a.
	10	SA15-**4b**-PI$_{100}$	1.13	7500	1.39	6900	1.28	91	0.19	21.9
	11	K3-**4b**-PI$_{100}$	0.15	7200	1.11	6400	1.16	96	0.16	n.a.
	12	B-K3-**4b**-PI$_{100}$	0.51	6900	1.09	7000	1.11	94	0.15	n.a.

[a] determined by calculating the percentage of the amount of grafted polymer to the amount of the added monomer [b] calculated according to ***euation 3.2*** [c] diameter size of the PI grafted particles determined via DLS measurements.

GPC analysis after cleaving off the surface grafted polymer from the surface of inorganic particle revealed that polyisoprene which was grafted from the surface of the particles by activating the DPE moiety on the surface modifying groups with *sec*-BuLi had slightly lower PDI values and more accurate molecular weight control (entries 7-12, **Table 3.8**).

The effect of the activating group was more distinctive when the polyisoprene was grafted from SA15 NPs (entries 1 and 7, **Table 3.8**) when compared to the ones grafted from K3 and B-K3 GPs as the PDI values decreased to M_w/M_n= 1.56 from M_w/M_n= 1.68 for SA15-**4a**-

PI_{100} (entries 1 and 7, **Table 3.8**) and to M_w/M_n= 1.39 from M_w/M_n= 1.46 for SA15-**4b**-PI_{100} (entries 4 and 10, **Table 3.8**) when LASIP was activated with *sec*-BuLi. The difference in the PDI values for the polymers which were grafted from GPs was almost negligible.

The same behavior was observed when the actual molecular weight values were considered. The actual molecular weight of the obtained polymers when the LASIP was activated with *sec*-BuLi (M_n= 8100 g/mol for SA15-**4a**-PI_{100} and M_n= 7500 g/mol for SA15-**4b**-PI_{100}) was closer to the projected molecular weight value; M_n(theo)= 6800 g/mol (entries 11 and 12, **Table 3.8**). This behavior was also observed for the polymers which were grafted from GPs. The actual molecular weights (M_n= 7200 g/mol for K3-**4b**-PI_{100} and M_n= 6900 g/mol for B-K3-**4b**-PI_{100}) were closer to the projected molecular weight when LASIP was activated with *sec*-BuLi (entries 11 and 12, **Table 3.8**).

TGA measurements of the produced composites revealed that the activating group did not have much effect on the grafting density of the polymer as the grafting density values of the produced polymers when activated with *n*-BuLi and *sec*-BuLi were found to be either same or very close to each other both for the polymers grafted from SA15 NPs and K3, B-K3 GPs.

DLS measurements showed that the sizes of the composites are slightly larger when PI was grafted in the presence of *n*-BuLi (d= 23.8, 22.6 nm for entries 1 and 4, **Table 3.8**). However the reason for this is only the polymerization was less controlled in the presence of n-BuLi, thus the molecular weight of the PI was higher and the polymer chain was longer as the same surface functionalized NPs with the same initial surface modifying group grafting density values were used.

3.6.5. Effect of the spacer length of the surface modifying group on LASIP

The final set of experiments was conducted to investigate the effect of the spacer length of the surface modifying groups which were used to functionalize the surface silanol groups on LASIP. The experiments were carried out in benzene at 0^{o}C by using *n*-BuLi to activate surface modifying groups and particles which were functionalized with **4a**, **4b** and **4c**. The projected molecular weight was M_n(theo)= 6800 g/mol for the polymers which were grafted from the **4a**- and **4b**-functionalized particles and M_n(theo)= 68000 g/mol for the polymers which were grafted from the **4c**-functionalized particles. The produced polymers were analyzed via GPC, NMR, DLS and TGA in order to investigate the quality of the living anionic polymerization, microstructure and the grafting densities respectively.

Table 3.9 The results of LASIP reactions – investigating the effect of the spacer length of the surface modifying group. LASIP reactions were performed in benzene as solvent at 0^{o}C. n-BuLi (1.1 equivalents with respect to the number of surface initiating groups) was used to activate the ethylene moiety on DPE based surface modifying groups (**4a-c**) to initiate polymerization.

entry	polymer	n_{MG} (mmol/g particle)	[M]/[I]	$Mn_{(calc.)}$ g/mol	surface grafted polymer		homopolymer		grafting ratio^a (%)	σ_{PI}^{b} (chains/nm^2)	size^c (nm)
					Mn_{GPC}	PDI	Mn_{GPC}	PDI			
1	PI_{100}		100	6800	-	-	8100	1.09		-	n.a.
2	SA15-**4a**-PI_{100}	1.15	100	6800	10500	1.68	8300	1.36		0.24	23.8
3	K3-**4a**-PI_{100}	0.17	100	6800	11600	1.14	8900	1.12		0.17	n.a.
4	B-K3-**4a**-PI_{100}	0.63	100	6800	11500	1.14	10200	1.12		0.19	n.a.
5	SA15-**4b**- PI_{100}	1.13	100	6800	9400	1.46	7900	1.22		0.23	21.9
6	K3-**4b**- PI_{100}	0.15	100	6800	10700	1.09	8100	1.09		0.14	n.a.
7	B-K3-**4b**- PI_{100}	0.51	100	6800	11000	1.12	9500	1.12		0.16	n.a.
8	SA15-**4c**-PI_{1000}	1.06	1000	68000	49400	1.24	n.a.	n.a.		0.21	35.6
9	K3-**4c**-PI_{1000}	0.09	1000	68000	52100	1.10	n.a.	n.a.		0.10	n.a.
10	B-K3-**4c**-PI_{1000}	0.46	1000	68000	54800	1.10	n.a.	n.a.		0.13	n.a.

[a] determined by calculating the percentage of the amount of grafted polymer to the amount of the added monomer [b] calculated according to ***equation 3.2*** [c] diameter size of the PI grafted particles determined via DLS measurements.

When the initial surface modifying group grafting densities on the particle surfaces are considered, it could be assumed that the polymers which were grafted from **4c**-functionalized particles were expected to have lower PDI values and more accurate molecular weight values due the decreased steric hindrance effect and charge repulsion. When the active chain ends (DPE moiety) are closer to each other (in the case of **4a**-functionalzied silica particles) due to the high grafting of the surface modifying group, the charge repulsion between these active chain ends increases as the magnitude of the electrostatics force of interaction between two point charges is directly proportional to the scalar multiplication of the magnitudes of charges and inversely proportional to the square of the distances between them. High grafting of the surface initiating groups also increases the possibility of unwanted side reactions such as chain transfer which could result in broadening in PDI and exceeded molecular weight values. Another assumption was that LASIP of isoprene from **4c**-functionalized particles should have occurred in better polymerization conditions due to the increased distance between the active chain end and the particle surface. This assumption can also be supported by the length of the DPE based surface modifying groups. The length of **4a** was estimated 1 nm whereas the length of **4c** was estimated 2 nm by Chem3D software. The increased length of the surface initiating group not only increases the distance between the active chain end and the particle surface, but also increases the distance between active chain ends themselves (d_2>d_1 in **Figure 3.11**), hence reducing the charge repulsion as well. The graphical illustration of these assumptions is presented in **Figure 3.11**. The result shown in **Table 3.9** confirmed these assumptions.

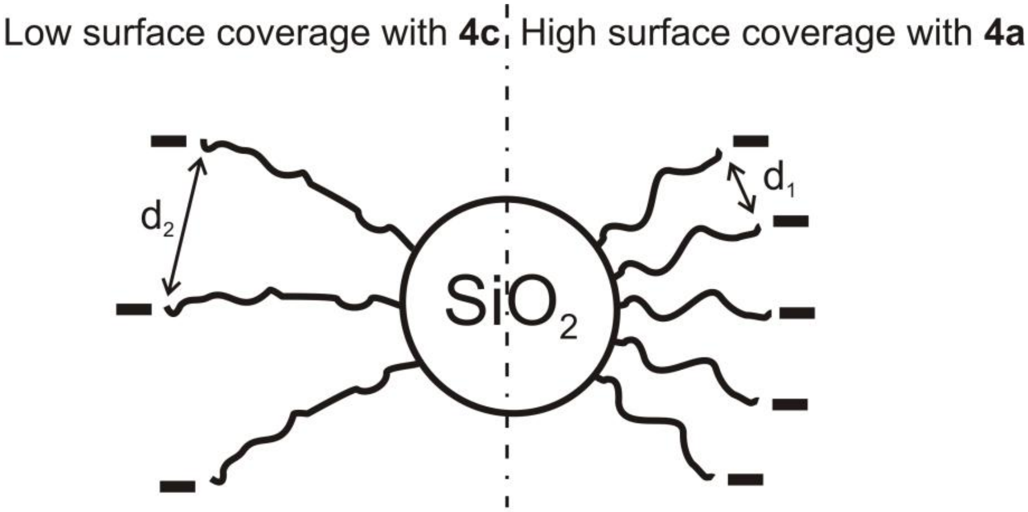


Figure 3.11 Graphical illustration of the effect of spacer length on LASIP

According to the GPC analysis, lower PDI values (M_w/M_n= 1.24 for SA15-**4c**-PI_{1000} and M_w/M_n= 1.10 for K3-**4c**-PI_{1000} and B-K3-**4c**-PI_{1000}, entries 8-10, **Table 3.9**) were achieved for the polymers grafted from the particles on which **4c** (the surface modifying group with the longest side chain) had been immobilized. More accurate molecular weight projection was also achieved for the same grafted polymers although the actual molecular weight values exceeded the projected molecular weights (except for entries 8-10; due to increase in viscosity which was caused by the high molecular weight, the polymerization stopped after a certain time). This could be explained by the longer distance between the initiating moiety of the surface modifying group and the particle surface when the surface of the particles was functionalized with **4c**. Hence the polymerization could take place without any disturbance which might have caused by steric hindrance or charge repulsion as shown in **Figure 3.11**.

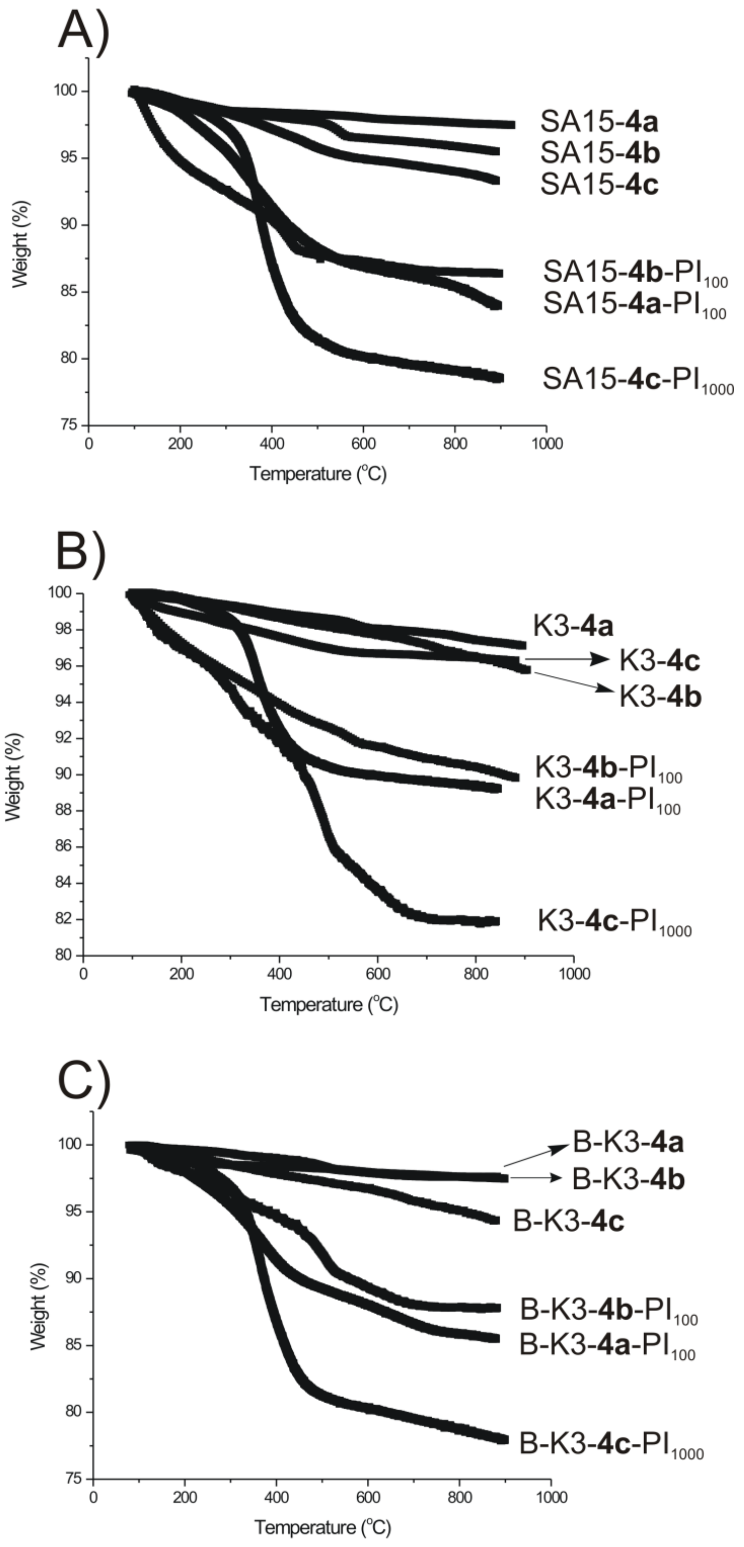


Figure 3.12 TGA curves of A) DPE-functionalized SA15 NPs and PI-grafted SA15 NPs, B) DPE-functionalized K3 GPs and PI-grafted K3 GPs and C) DPE-functionalized B-K3 GPs and PI-grafted B-K3 GPs

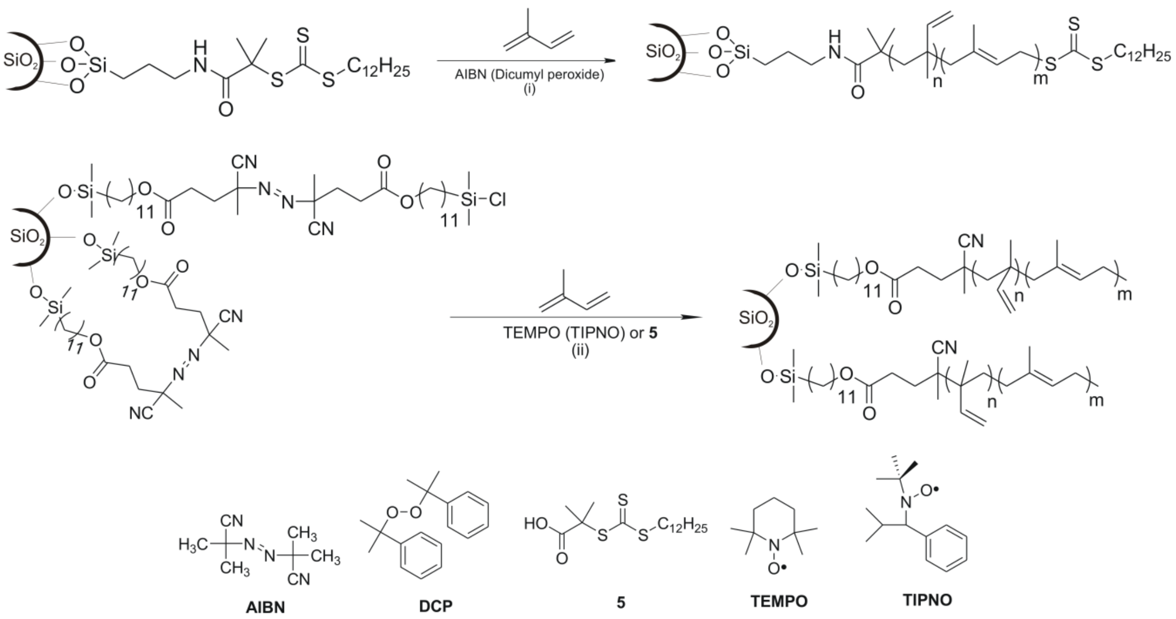
TGA measurements revealed that the grafting density values increased when the polyisoprene was grafted from the **4a**-functionalized particles (the surface modifying group with the shortest spacer length). The highest grafting density values (σ_{PI}) were obtained when the polyisoprene was grafted from SA15 NPs (entries 2, 5 and 8, **Table 3.9**; σ_{PI}= 0.24 chains/nm^2 for SA15-**4a**-PI$_{100}$, σ_{PI}= 0.23 chains/nm^2 for SA15-**4b**-PI$_{100}$ and σ_{PI}= 0.21 chains/nm^2 for SA15-**4c**-PI$_{1000}$) as a result of having high initial grafting density of surface initiating group (σ_{MG}). Even in the case of GPs (K3, B-K3), the grafting density values (σ_{PI}) up to σ_{PI}= 0.17 chains/nm^2 and σ_{PI}= 0.19 chains/nm^2 were achieved when the **4a**-functionalized particles were used for LASIP of isoprene (entries 3-4, **Table 3.9**). The TGA curves of the surface functionalized particles and PI grafted particles are also shown in **Figure 3.12** for comparison.

The grafted polymers were also investigated via NMR which showed that the spacer length did not have much effect on the microstructure of the grafted polymer, as the average percentage values for the microstructure types were found to be constant: 15% *1,2*, 35% *cis-1,4* and 50% *trans-1,4*, irrespective of the used surface modifying group with different spacer length.

Due to the initial high grafting density of the surface modifying group on the particle surface, the size of the PI which was grafted from **4a**-functionalzied SA15 NPs (SA15-**4a**-PI$_{100}$, d= 23.8 nm entry 2, **Table 3.9**) was found to be higher than that of the one which was grafted from **4b**-functionalized particle (SA15-**4b**-PI$_{100}$, d= 21.9 nm, entry 5, **Table 3.9**). The number molecular weight of the PI on SA15-**4a**-PI$_{100}$ was also higher than the one on SA15-4b-PI$_{100}$; this also confirms the DLS result. As the degree of polymerization (DP) of the PI on the third sample (SA15-**4c**-PI$_{1000}$, d= 35.6 nm, entry 5, **Table 3.9**) was projected to be [M]/[I]= 1000, it is not possible to make a comparison with the others. However the data obtained (d= 35.6 nm) form the DLS analysis indicated that after a certain amount of surface coverage there might be no linear increase on the shell thickness. According to the molecular weight of the third sample (M_n= 49400 g/mol) the diameter size of the polymer grafted NP should have been larger than the actual one especially when the initial grafting density of the surface modifying groups are equal (see entry 5, **Table 3.5** for comparison). This proves that there is no linear increase on the particle size with the degree of polymerization even if the initial grafting density of the surface modifying groups is equal.

3.7. Surface initiated controlled radical polymerization (SI-CRP) reactions

Polyisoprene was also grafted from surface functionalized silica NPs via controlled radical polymerization methods such as RAFT and NMP. As it was mentioned earlier two different surface modifying groups (a CTA derivative for RAFT and an AIBN derivative for RAFT and NMP) for this purpose were synthesized and the surfaces of the silica nanoparticles (SA15 and AE200 NPs) were functionalized with these surface modifying groups prior to SI-CRP reactions.



Scheme 3.7 Schematic illustration of SI-CRP reactions (i) in 1,2-dichlorobenzene at 130oC for 24 hours, (ii) in 1,2-dichlorobenzene at 130^{o}C for 24 hours

Polymerization reactions were carried out under different conditions and in the presence of different additives in order to investigate the effect of different parameters on SI-CRP reactions. The general polymerization procedure could be described as follows: an adequate amount of the surface functionalized particles was placed in a Schlenk flask equipped with a magnetic stirring bar and a rubber septum. To the flask, initiator/additive (depending on the surface modifying group used), isoprene (purified as described in **Section 3.5**) and 1,2-dichlorobenzene as solvent were added and freeze thaw cycle was applied three times in order to evacuate O_2. The polymerization was started by placing the flask in an oil bath at 130^{o}C as the dissociation of the dormant species (PI-ON-R_2 and PI-CS_2) takes place at 123^{o}C^{193}. The SI-CRP polymerizations were carried out both in the absence and in the presence of free/sacrificial initiator and/or CTA in order to investigate the effect of the free/sacrificial initiator and/or CTA on the SI-CRP reactions. The purification of the produced composites for characterization was performed as described in **Section 3.5**.

3.7.1. Effect of the initiator density on the particle surface on SI-CRP

The first set of reactions was carried out to investigate the effect of the initial grafting density of the surface modifying groups on SI-CRP. For these reactions, the surface functionalized particles which were presented in **Table 3.4** were used. SI-CRP reactions were carried out in toluene as solvent at 130°C and the solvent/initiator volume ratio was kept 1/1. AIBN and DCP were used as free radical initiators for the CTA derivative (**6**)-functionalized particles in order to perform SI-RAFT whereas SI-NMP was conducted by using AIBN derivative (**9**)-functionalized particles in the presence of TEMPO and TIPNO as alkoxyamines and SI-RAFT was conducted in the presence of compound **5** as a chain transfer agent. The chemical structures of the free radical initiators, alkoxyamines and the chain transfer agent are shown in **Scheme 3.7**. The projected molecular weight for each polymer was M_n(theo)= 6800 g/mol for 100 isoprene unit (calculated by [M]/[I]). The produced composites were investigated via TGA and DLS and the surface grafted polymers (after cleavage) were investigated via GPC. Results are presented in **Table 3.10**.

Table 3.10 Results of SI-CRP reactions – investigating the effect of the surface modifying group density on the particle surface. The SI-CRP reactions were performed in 1,2-dichlorobenzene as solvent at 125°C. AIBN or DCP (1 equivalent with respect to the surface modifying group) was used as initiator when the CTA-functionalized particles were used for SI-RAFT. TEMPO, TIPNO and **5** (1 equivalent with respect to the surface modifying group) was used as additive when azo-functionalized NPs were used for SI-NMP and SI-RAFT. For each polymerization, the degree of polymerization was projected as 100, [M]/[I]= 100.

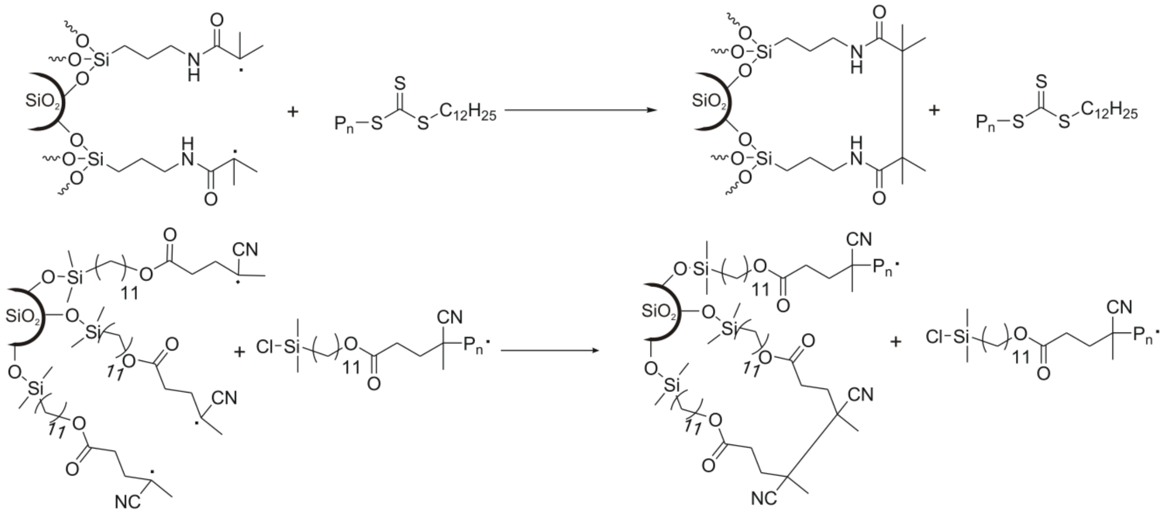
entry	functionalized particle[a]	n_{MG} (mmol/g particle)	additives	M_n (g/mol)	PDI	conversion (%)	grafting ratio[b] (%)	σ_{Mg}[c] (molecule/nm^2)	σ_{PI}[c] (PI-cahins/nm^2)	size[d] (nm)
1	SA15-**6**(1)	0.09	AIBN	4100	1.7	19	85	0.11	0.11	17.9
2	SA15-**9**(1)	0.14	**5**	3500	1.9	24	79	0.15	0.15	17.7
3	SA15-**9**(1)	0.14	TEMPO	1400	2.6	16	71	0.15	0.14	17.1
4	AE200-**6**(1)	0.12	AIBN	5100	1.6	34	83	0.10	0.10	14.6
5	AE200-**9**(1)	0.17	**5**	4800	1.8	17	78	0.14	0.14	14.9
6	AE200-**9**(1)	0.17	TEMPO	3900	2.4	12	83	0.14	0.14	14.7
7	SA15-**6**(2)	0.13	AIBN	3800	1.8	17	68	0.14	0.11	18.3
8	SA15-**9**(2)	0.19	**5**	3200	1.9	23	62	0.19	0.17	18.2

9	SA15-**9**(2)	0.19	TEMPO	1600	2.5	17	65	0.19	0.14	17.8
10	AE200-**6**(2)	0.16	AIBN	4800	1.7	26	71	0.15	0.12	16.0
11	AE200-**9**(2)	0.22	**5**	4600	1.8	16	65	0.19	0.16	15.5
12	AE200-**9**(2)	0.22	TEMPO	3700	2.5	11	69	0.19	0.17	15.2
13	SA15-**6**(2)	0.13	AIBN **5**	6800	1.7	23	59	0.14	0.14	20.3
14	SA15-**6**(2)	0.13	DCP **5**	6300	1.5	21	52	0.14	0.14	19.8
15	SA15-**9**(2)	0.19	AIBN **5**	7100	1.6	17	60	0.19	0.19	21.1
16	SA15-**9**(2)	0.19	AIBN TEMPO	-	-	-	-	0.19	-	-
17	SA15-**9**(2)	0.19	AIBN TIPNO	6400	1.8	20	49	0.19	0.18	21.9
18	AE200-**6**(2)	0.16	AIBN **5**	6600	1.4	26	52	0.15	0.14	19.7
19	AE200-**6**(2)	0.16	DCP **5**	6100	1.3	22	46	0.15	0.15	18.6
20	AE200-**9**(2)	0.22	AIBN **5**	6900	1.4	19	44	0.19	0.18	19.1
21	AE200-**9**(2)	0.22	AIBN TEMPO	-	-	-	-	0.19	-	-
22	AE200-**9**(2)	0.22	AIBN TIPNO	7200	1.5	19	54	0.19	0.19	18.4

[a] calculated according to the amount of monomer added to the SI-CRP reaction [b] The notation in bold specifies the surface modifying group used for the surface functionalization of the corresponding particle and the number in brackets specifies the amount of surface modifying agent used for surface functionalization reaction with respect to the initial surface silanol groups; [c] calculated according to ***equation 3.2***; [d] diameter size of the PI grafted particles determined via DLS measurements.

The entries 1-12 in **Table 3.10** summarize SI-CRP experiments which were conducted to investigate the effect of the initial surface modifying group grafting density on SI-RAFT and SI-NMP of isoprene. Although the GPC results indicated that the polymerization reactions were not controlled due to the absence of free/sacrificial initiator or CTA, the polymerization reactions in which the particles with lower initial surface modifying group density (σ_{MG}= 0.10 molecule/nm^2 for AE200-**6**, σ_{MG}= 0.14 molecule/nm^2 for AE200-**9**, σ_{MG}= 0.11 molecule/nm^2 for SA15-**6**, σ_{MG}= 0.15 molecule/nm^2 for SA15-**9**) were used yielded slightly better results (entries 1-6, **Table 3.10**). In some cases the higher grafting density of the surface modifying groups resulted recombination of the radicals on the surface which was formed during the polymerization reactions, thus the quality of the polymerization reactions were reduced and the living character could not be achieved. This assumption was also proven by the decrease of the grafting density of the polymer chains when compared to the initial grafting density of the surface modifying groups which were determined by TGA measurements before and after SIP reactions. Among these polymerization reactions the best results were achieved with SI-RAFT reactions in which PI was grafted from CTA-functionalized silica NPs with the addition of AIBN (entries 1, 4, 7 and 10, **Table 3.10**), while SI-NMP experiments yielded the worst results providing polymers with high PDI values and lower molecular weights than the calculated ones (especially entries 3 and 9, **Table 3.10**). This could be explained by the efficiency differences of the CTA and TEMPO as additives for CRP. It has been reported that S-1-Dodecyl-S′-(α,α′-dimethyl-α″-aceticacid)trithiocarbonate (**5**) has been an effective chain transfer agent for RAFT polymerization of isoprene in solution or bulk[189]. However NMP of isoprene has been tried by using different alkoxyamines instead of TEMPO so far[210-211]. When the two different silica particles (SA15 and AE200) are compared, SIP reactions which were initiated from the functionalized AE200 NPs yielded better results such as lower PDI values and more accurate molecular weight control (entries 4-6 and 9-12).

Monomer conversion values (determined by calculating the percentage of the amount of the polymer obtained (grafted + non-grafted) to the amount of monomer added) into the conducted SI-CRP reactions were at most 34% (entry 4, **Table 3.10**). This value was actually consistent with the literature values[189,211,216], as the highest conversion achieved for isoprene polymerization via RAFT was 27% and via NMP was 39% in solution polymerization. DLS measurements which were conducted to investigate the increase in the sizes of the particles after SI-CRP reactions resulting in a maximum of 3-4 nm PI shell thickness on the inorganic core (SA15 and AE 200) indicating that the grafted polymer chains overlapped on each other instead of stretching away from the surface to display a crossover regime.



Scheme 2.8 Schematic illustration of the recombination of the radicals which were formed during SI-CRP reactions

The most distinctive difference between the SI-CRP reactions which were conducted by using the particles with low surface modifying group density and the high surface modifying group density on the particle surface was the recombination of the radicals on the particle surface a side reaction. As it was explained earlier, the formed radicals during polymerization tend to recombine instead of taking part in the polymerization. When the surface modifying group density on the particle surface was higher, the rate of recombination reactions increased because of their spatial proximity[158]. Hence, many of the surface coupling groups was inactivated due to recombination and isoprene could not be grafted from the surface of the particles as projected. When the initial grafting density of the surface modifying groups (σ_{MG}) and the grafting density of the surface grafted polymer (σ_{PI}) shown in entries from 1 to 6 and entries from 7 to 12 in **Table 3.10** are compared, a decrease in grafting density values for the particles on which the initial surface modifying group density is higher could be observed due to these recombination reactions.

3.7.2. Effect of free/sacrificial initiator and CTA on SI-CRP

SIP reactions were also carried out in the presence of free/sacrificial initiator and CTA in order to see the effect of free/sacrificial initiator and CTA on SI-CRP of isoprene. These specific SI-CRP reactions were conducted by using NPs with higher surface modifying group grafting density. GPC results indicated that the quality of the polymerization significantly increased when sacrificial initiator and/or free CTA were used as the PDI values decreased and the projected molecular weights were achieved (entries 13-22, **Table 3.10**). However the presence of sacrificial initiator and free CTA did not have effect on the monomer conversion.

Among the SI-CRP reactions which were carried out in the presence of sacrificial initiator and free CTA the best results were obtained when isoprene was grafted from CTA-functionalized NPs via SI-RAFT and when DCP was used as initiator instead of AIBN with relatively low molecular weight distributions M_w/M_n= 1.3 and M_w/M_n= 1.5, but lower molecular weight values than the projected ones (entries 14 and 19, **Table 3.10**). The SI-CRP reactions which were initiated from CTA-functionalized NPs yielded polymers with more accurate molecular weight values (entries 13-14 and 17-18, **Table 3.10**). Similar to the SI-CRP reactions which were carried in the absence of sacrificial initiator and free CTA, lower

PDI values were achieved when surface functionalized AE200 NPs were used for SI-CRP reactions regardless of the surface modifying group (entries 18-22, **Table 3.10**).

When the initial grafting density of the surface modifying groups (σ_{MG}) and the grafting density of the surface grafted polymer (σ_{PI}) (entries 13-22, **Table 3.10**) are compared, it could be concluded that the presence of free/sacrificial initiator and/or CTA significantly reduced the recombination of the active radicals on the particle surface because no significant decrease on the grafting density values after the SI-CRP reactions was observed. This also proves that the SI-CRP reactions which were conducted in the presence of free/sacrificial initiator and/or CTA are more controlled than the ones conducted without using free/sacrificial initiator and/or CTA. Due to better molecular weight control and higher grafting density DLS analysis indicated an increase in the diameter size between 5 and 7 nm (entries 13-17, **Table 3.10**) for the PI grafted SA15 NPs via SI-CRP in the presence of free/sacrificial initiator or CTA and an increase in the diameter size between 6.6 and 7.7 nm (entries 18-22, **Table 3.10**) for the PI was grafted AE200 NPs via SI-CRP.

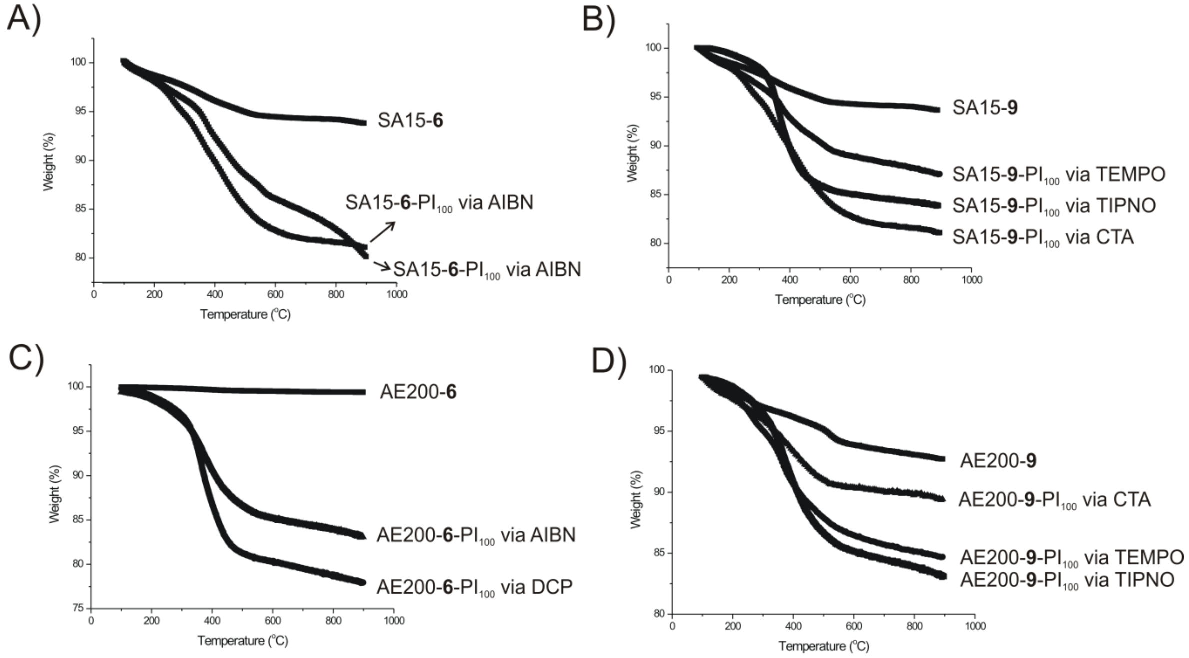


Figure 3.13 TGA curves of A) CTA-functionalized SA15 NPs and polymer grafted SA15 NPs, B) AIBN-functionalized SA15 NPs and polymer grafted SA15 NPs, C) CTA-functionalized AE200 NPs and polymer grafted AE200 NPs and D) AIBN-functionalized AE200 NPs and polymer grafted AE200 NPs

Additionally it must be noted that in all SI-CRP reactions non-grafted homopolymers were present in the reaction mixture, up to 56% (entries 13-22, **Table 3.10**). The assumption was confirmed when the grafting ratio values of the first 12 entries in **Table 3.10** (SI-CRP reactions in the absence of free/sacrificial initiator) and the other entries (entries 13-22, **Table 3.10**) (SI-CRP reactions in the presence of free/sacrificial initiator) were compared. Although the addition of free/sacrificial initiator or CTA increased the polymerization quality (lower molecular weight distribution and more accurate molecular weight control), the ratio of polymer grafting decreased. **Figure 3.13** shows the TGA curves of the CRP initiator-functionalized silica NPs and the polymer grafted particles which were produced in the presence of free/sacrificial initiator for comparison.

4. Experimental

4.1. Materials

All chemicals and reagents were purchased from Sigma Aldrich and used without further purification unless otherwise noted. Tetrahydrofurane (THF) and diethyl ether were used after distillation over sodium and benzophenone[130], whereas dichloromethane (DCM), N,N-dimethylformamide (DMF) and pyridine were distilled over CaH_2. Benzene, toluene, n-hexane and isoprene were dried according to the literature[130]. Glass particles (GP) B-K3 and K3 were obtained from *Trovotech*, silica nanoparticles (NP) SA15 (15 nm diameter size) from Sigma Aldrich and AE200 (12 nm diameter size) from Evonik. One of the surface modifying groups for LASIP (**4a**) was obtained from *Merseburger Spezialchemikalien*; compounds **4b** and **4c** were synthesized according to literature by Advincula *et al.*[21]. The synthetic procedure for CTA which was used for SI-RAFT was adopted from literature[182]. A novel synthetic route for CTA derivative surface modifying agent (**6**) was developed. The synthetic procedure of the AIBN derivative (**9**) surface modifying agent was adopted from literature[217].

4.2. Drying of solvents, monomer and silica particles

The solvents which were used for LASIP reactions such as benzene, toluene and n-hexane, were purified according to the literature[130]. The basic procedure is as follows: Firstly the solvent was stirred over concentrated sulfuric acid (1:5 volume ratio) for a week in a conical flask inside a hood in order to remove the thiophenes and substituted phenyl-compounds and vinyl compounds. Then it was washed with an aqueous solution of NaOH (1M) and then with water several times until it becomes neutral and finally was pre-dried with $CaCl_2$. Then it was transferred carefully into a round bottom flask containing finely grounded CaH_2 and a magnetic stir bar, attached to a vacuum line and degassed. It was left for reaction of CaH_2 with moisture overnight. Then it was again degassed and distilled in a round bottom flask. The freshly distilled solvent was kept in the glovebox prior to use in LASIP reactions.

Isoprene was first passed through basic alumina column in order to remove the inhibitor. Then it was dried over finely grounded CaH_2 on the vacuum line overnight. Finally it was distilled in a round bottom flask and kept in a freezer at $-20^{o}C$ and consumed in a week at most.

Due to the high moisture content of the silica nano- and glass particles they were dried under vacuum (<0.01 mbar) at 90^{o}C for 24 hours prior to use in surface modification reactions.

4.3. Measurements

Characterization of the synthesized surface modifying groups and produced polymers was done by NMR. ^{1}H NMR and ^{13}C NMR measurements were performed by using a Varian Gemini 2000 spectrometer. ^{1}H NMR analysis of the samples was performed with 400 MHz instrument while ^{13}C NMR analysis was performed with 100 MHz instrument. The measurements were performed at room temperature with $CDCl_3$ as solvent unless otherwise noted.

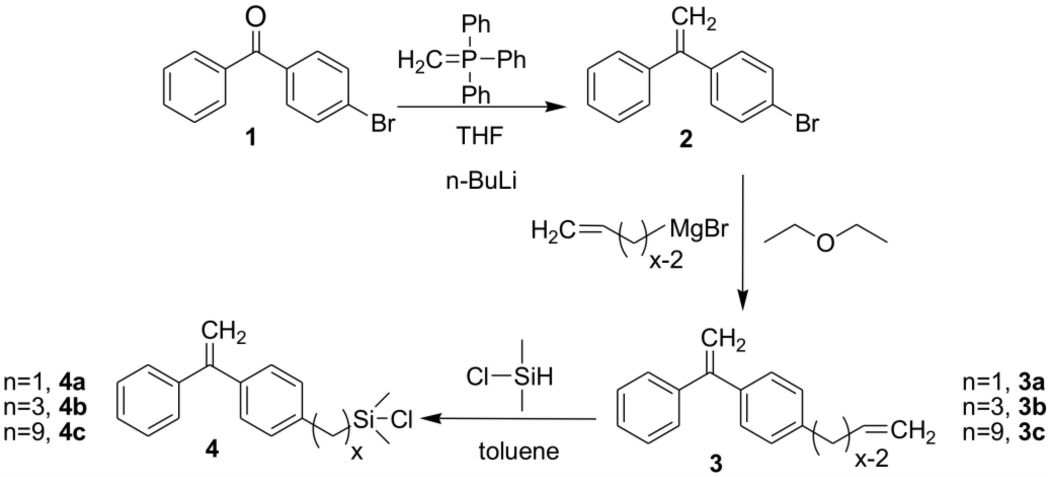
The molecular weight and the molecular weight distribution of the produced polymers were characterized by using gel permeation chromatography (GPC). The measurements were performed in a Viskotek GPCMax VE 2001 with THF (stabilizer induced) as solvent and a flow rate of 1.00 ml/min, a column temperature of 35^{o}C and a detector temperature of 35^{o}C. Calibration was done with polystyrene standards equipped with two TSK-gel columns (H_{HR}-HGuard+GMH_{HR}-N, bead size: 5 µm, M_w(polyisobutylene) < 4 x 10^{5}) and one *ViscoGel HR High Resolution* column (G2500 HR, bead size: 5 µm, M_w(polyisobutylene) < 20000) with a *TDA 302 Triple Detector Array*.

Dynamic light scattering analysis (DLS) was used to analyze the surface modifying group functionalized particles and furthermore the surface initiated polymer brushes. The measurements were performed by using Viskotek 802 DLS instrument at room temperature. Quartz cells were used as container for the dispersion of sample which was prepared in THF ([C] = 1.0x10^{-3} mg/ml).

Thermo gravimetric analysis (TGA) was performed to investigate grafting density of the produced polymer-inorganic composites, by using a Netzsch TG F3 Tarsus instrument. The measurements were conducted under an atmosphere of N_2 with temperature ranging from 32^{o}C to 900^{o}C with 10 K/min heating rate. Netzsch Proteus Analysis software was used to interpret the TGA measurements.

4.4. Synthesis of DPE-based surface modifying groups for LASIP

In order to conduct surface initiated polymerization of isoprene from the silica GPs and NPs, the surface silanol groups of the particles had to be functionalized first. For this purpose, different surface modifying groups which could initiate either living anionic polymerization or controlled radical polymerization were synthesized. The synthetic procedure of diphenyl ethylene (DPE) derivative surface modifying groups (**4a**-**4c**) for LASIP was adopted from the literature by Advincula *et al.*[20].



Scheme 4.1 Schematic pathway to DPE derivative surface modifying groups for LASIP

4.4.1. Synthesis of 4-bromo diphenylethylene (2)

To a 50 ml round bottom flask which was dried under vacuum and flushed with nitrogen, 3.1 g (7.6 mmol) of methyltriphenylphosphonium iodide were suspended in 30 ml of dry THF under an atmosphere of N_2. A turbid milky solution was formed, then 3.1 ml (2.5 M in hexane, 7.6 mmol) of n-BuLi were added to this solution. The color of the mixture turned to dark orange and was left to stir for 30 min. 2.0 g (7.6 mmol) of 4-bromo benzophenone (**1**) were dissolved in 5 ml of dry THF and added to the reaction mixture drop wise over 15 minutes. The resulting mixture which turned to yellow turbid solution was left to stir overnight for the completion of the reaction. The reaction was then checked by thin layer chromatography for completion (TLC, eluent: n-hexane, R_f = 0.66). After completion of the reaction, the mixture was diluted with 20 ml of chloroform and 20 ml of diluted HCl (0.01 N). The organic layer was collected and dried over sodium sulfate (Na_2SO_4). The solvent was evaporated and the product (**2**) was purified via column chromatography (silica, eluent: n-hexane) to yield 1.29 g of (**2**), 65%. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.44-7.46 (d, 2 H, J= 7.5 Hz, Ar-H), 7.30-7.34 (m, 5 H, J= 7.3 Hz, Ar-H), 7.19-7.24 (d, 2 H, J= 7.2 Hz, Ar-H), 5.44-5.46 (m, 2 H, J= 5.5 Hz, $C=CH_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) 149, 140.9, 140.4, 131.3, 129.8, 128.2, 128.1, 127.9, 121.8, 114.7.

4.4.2. Synthesis of 4-(5'-pentenyl)-diphenylethylene (3b)

To a three necked round bottom flask dried under vacuum and flushed with N_2, 0.25 g (10.4 mmol) of magnesium turnings, and a small iodine particle were placed. In a separate flask, 1.55 g (10.4 mmol) of 5-bromo-1-pentene were dissolved in freshly dried 10 ml of diethyl ether. The solution was added drop wise at room temperature to the three necked round bottom flask to initiate the Grignard reaction over 15 minutes. In a separate two necked flask which was dried and flushed with N_2 earlier, a solution of Ni(dppe)Cl_2 (10 mg) and 1 g (3.9 mmol) of **2** in 10 ml of dry diethyl ether was prepared. After 2 hours of stirring of the Grignard reagent (total consumption of magnesium turnings) was added drop wise to the prepared solution over 10 minutes. The reaction mixture was left to stir for 24 hours at room temperature for completion (checked by TLC, eluent: n-hexane, R_f= 0.42).

The reaction mixture was then acidified with 0.1 N HCl and extracted with diethyl ether three times. The organic parts were combined and washed with saturated Na_2CO_3 solution and dried over Na_2SO_4. After the solvent was removed by evaporation, the pure product (**3b**) was isolated via column chromatography (silica, eluent: n-hexane) to give 0.31 g of **3b** as yellow oil with a yield of 32%. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.36-7.29 (m, 5H, Ar-H), 7.27-7.23 (m, 2H, Ar-H), 7.16-7.11 (m, 2H, Ar-H), 5.89-5.78 (m, 1H, J= 6.63, 6.63, 10.21, 16.91 Hz, C=CH), 5.45-5.38 (m, 2H, J= 1.63, 1.63, 15.90 Hz, $=CH_2$), 5.06-4.95 (m, 2H, $= CH_2$), 2.66-2.60 (m, 2H, $-CH_2-$), 2.15-2.07 (m, 2H, $-CH_2-$), 1.78-1.69 (m, 2H, $-CH_2-$). ^{13}C NMR ($CDCl_3$): δ (ppm) 142.03, 138.85, 138.51, 128.16, 127.58, 114.72, 113.63, 77.38, 77.07, 76.75, 35.16, 33.46, 30.69.

4.4.3. Synthesis of 4-(11'-undecenyl)-diphenylethylene (3c)

3c was obtained by a similar synthetic procedure as described for **3b** as yellow oil with a yield of 39%. 11-bromo-1-undecene was used instead of 5-bromo-1-pentene. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.38-7.28 (m, 5H, Ar-H), 7.26-7.21 (d, 2H, J= 8.42 Hz, Ar-H), 7.14-7.10 (d, 2H, J= 8.27 Hz, Ar-H), 5.8 (m, 1H, -CH=), 5.4 (d, 2H, J= 3.21 Hz, $=CH_2$), 5.01-4.89 (m, 2H, $=CH_2$), 2.61 (t, 2H, J= 3.0 Hz, $-CH_2-$), 2.05-1.20 (m, 16H, $-(CH_2)_8-$). ^{13}C NMR ($CDCl_3$): δ (ppm) 149.9, 142.5, 141.7, 139.2, 138.7, 128.3, 128.1, 128.0, 127.6, 114.1, 113.5, 35.7, 33.8, 31.4, 29.6, 29.5, 29.4, 29.2, 29.0.

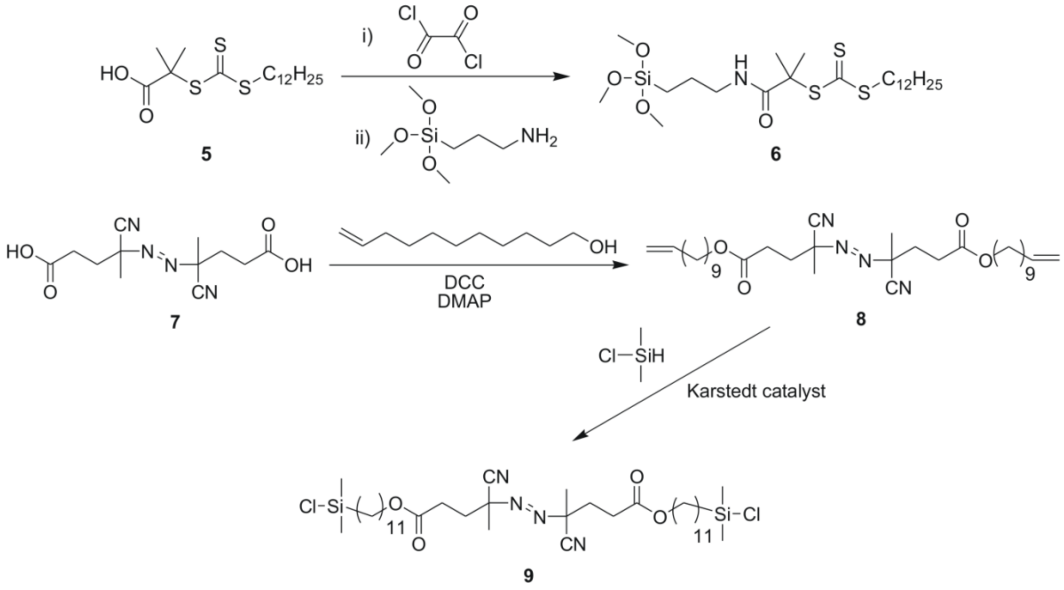
4.4.4. Synthesis of monochlorosilane attached DPE derivatives (4b-4c)

0.3 g (1.248 mmol) of **3b** were dissolved in 10 ml of freshly distilled dry toluene and 0.14 ml (1.248 mmol) of chlorodimethylsilane and three drops of the Karstedt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene) were added to this solution. The reaction mixture was stirred overnight at 60^oC under Ar atmosphere. After the completion of the reaction (checked by TLC) the solvent was removed under reduced pressure and the pure product, **4b**, was obtained with a quantitative yield. ^1H NMR ($CDCl_3$): δ (ppm) 7.40-7.31 (m, 5H, Ar-H), 7.30-7.25 (d, 2H, J=10.74 Hz, Ar-H), 7.19-7.13 (d, 2H, J=10.36 Hz, Ar-H), 5.48-5.41 (d, 2H, J=3.56 Hz, $=CH_2$), 2.67-2.60 (t, 2H, Ar-CH_2-R), 1.77-1.22 (m, 6H, $-(CH_2)_3-$), 0.88-0.81 (t, 2H, $-CH_2-Si$), 0.49-0.44 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) 149.8, 142.0, 138.8, 138.5, 128.3, 128.2, 128.1, 127.6, 114.7, 113.6, 35.2, 33.5, 30.7. ^{29}Si NMR ($CDCl_3$): (ppm) 31.9.

4c was obtained by a similar synthetic procedure as **4b** was synthesized, with a quantitative yield. 4-(11'-undecenyl) diphenylethylene (**3c**) was used instead of 4-(5'-pentenyl) diphenylethylene (**3b**). ^1H NMR ($CDCl_3$): δ (ppm) 7.36-7.31 (m, 5H, Ar-H), 7.25 (d, 2H, J=8.74 Hz, Ar-H), 7.13 (d, 2H, J=8.5 Hz, Ar-H), 5.42 (d, 2H, J=2.6 Hz, $=CH_2$), 2.72-2.55 (t, 2H, J=5.6 Hz, Ar-CH_2-R), 1.72-1.00 (m, 18H, $-(CH_2)_9-$), 0.99-0.79 (t, 2H, $-CH_2-Si$), 0.11-0.05 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) 149.7, 142.5, 141.2, 139.2, 138.7, 127.6, 114.0, 113.5, 35.7, 33.8, 31.7, 29.5, 29.2, 28.9. ^{29}Si NMR ($CDCl_3$): δ (ppm) 32.0.

4.5. Synthesis of AIBN- and CTA-based surface modifying groups for SI-CRP

A novel synthetic procedure was developed to synthesize triethoxysilyl attached trithiocarbonate surface modifying group (**6**) which acted as a chain transfer agent in SI-RAFT polymerization reactions. The AIBN derivative surface modifying group for SI-CRP (**9**), was synthesized according to the literature by Czaun *et al.*[217]. (See **Scheme 4.2**)



Scheme 4.2 Schematic pathway to surface modifying groups for SI-CRP

4.5.1. Synthesis of S-1-Dodecyl-S'-(α,α'-dimethyl-α"-aceticacid)trithiocarbonate (5)

The synthetic procedure was adopted from Lai *et al.*[218]. In a round bottom flask, 1-dodecanethiol (20.19 g, 0.10 mol), acetone (48.1 g, 0.83 mol), and Aliquot 336 (tricaprylylmethylammonium chloride, 1.62 g, 0.04 mol) were mixed under N_2 atmosphere and the round bottom flask was cooled to 10^{o}C. A NaOH solution (50%) (8.4 g, 0.1 mol) was added slowly and the mixture was stirred for 15 minutes. To this mixture, a solution of carbon disulfide (C_2S) (7.6 g, 0.1 mol) in acetone was (10.1 g, 0.28 mol) was added over 20 minutes. Ten minutes later chloroform (17.8 g, 0.15 mol) was added in one portion and then 50% (weight) NaOH solution (40 g, 0.5 mol) was added over 30 minutes. The resulting reaction mixture was stirred overnight.

After the reaction was completed 150 ml of water and 125 ml of concentrated HCl were added to acidify the reaction mixture which was then concentrated by evaporating the acetone. The solid was collected by filtration and stirred in 250 ml of isopropanol. The undissolved solid (S,S′-bis(1-dodecyl)trithiocarbonate) was filtered off and the isopropanol solution was concentrated to dryness. The resulting solid (S-1-Dodecyl-S′-(α,α′-dimethyl-α″-aceticacid)trithiocarbonate) was recrystallized from hexane to yield 20.4 g (21%) yellow powder. ^{1}H NMR ($CDCl_3$): δ (ppm), 3.26-3.11 (t, 2H, J = 7.41, 7.41 Hz, S-CH_2-), 1.81-1.48

(m, 8H, C-(CH3)$_2$ and –CH$_2$-), 1.38-1.10 (m, 18H, -(CH$_2$)$_9$-), 0.86-0.75 (t, 3H CH$_2$-CH$_3$). ^{13}C NMR (CDCl$_3$): δ (ppm) 226.2, 178.5, 55.0, 35.8, 31.9, 29.5, 29.4, 28.3, 24.8, 22.8, 14.1.

4.5.2. Synthesis of 2-(3-(trimethoxysilyl)propylcarbamoyl)propan-2-yl dodecyl carbonotrithioate (6)

The trimethoxy silyl attached chain transfer agent (**6**) was obtained via two-step synthetic procedure. Firstly 2 g (10 mmol) of S-1-Dodecyl-S′-(α,α′-dimethyl-α″-aceticacid)trithiocarbonate (**5**) was placed in a 50 ml two-necked round bottom flask, which was previously dried and then flushed with N$_2$. To the round bottom flask 8.6 ml (100 mmol) of oxalyl chloride and catalytic amount of dry DMF (3 drops) were added. The mixture was stirred at room temperature for 24 hours. After excess of oxalyl chloride was removed under reduced pressure, the resulting carboxylic acid chloride derivative of **5** was added to a round bottom flask, in which a solution of 2.2 ml (10 mmol) of (3-aminopropyl)triethoxysilane in 20 ml of dry dichloromethane (DCM) and pyridine (2 ml) was prepared earlier. The reaction mixture was then stirred at room temperature for 24 hours. The pyridine salt which was formed during reaction was filtered and compound **6** was obtained by removing the solvent and excess pyridine under reduced pressure. ^{1}H-NMR (CDCl$_3$): δ (ppm) 6.63 (t, 1H, J= 6.96 Hz, -NH), 3.72 (s, 9H, J= 4.89 Hz, Si-(OCH$_3$)$_3$), 3.56 (m, 2H, N-CH$_2$), 3.29 (m, 2H, S-CH$_2$), 1.73-1.64 (m, 8H, -CH$_2$- and –(CH$_3$)$_2$), 1.44-1.26 (m, 20H, -(CH$_2$)$_{10}$-), 1.72-1.55 (m, 3H, -CH$_3$), 0.9 (t, 3H, J= 6.96 Hz, -CH$_3$), 0.81-0.69 (m, 2H, -CH$_2$-CH$_3$). ^{13}C NMR (CDCl$_3$): δ (ppm) 226.2, 179.9, 56.2, 53.5, 43.9, 35.6, 31.7, 29.7, 29.5, 29.4, 28.3, 24.8, 22.8, 14.1, 7.0. ^{29}Si NMR (CDCl$_3$): δ (ppm) -38.3.

4.5.3. Synthesis of monochlorosilane attached AIBN (9)

The monochlorosilyl attached AIBN derivative (**9**) was obtained via two-step synthetic procedure. 2.8 g (10 mmol) of 4,4’-azobis(cyanovaleric acid) (**7**), 2.1 g (10 mmol) of DCC and 0.6 g (5 mmol) of DMAP were placed in a 100 ml three-necked round bottom flask which was dried earlier and flushed with N$_2$. To this mixture, 50 ml of freshly distilled dry DCM and 4.4 ml (20 mmol) of 10-undecen-1-ol were added. The reaction mixture was stirred at room temperature in dark for 24 hours. The reaction mixture was washed with 100 ml of distilled water (three times) and then the organic part was collected and dried over Na$_2$SO$_4$. The undecene attached AIBN derivative (**8**) was obtained by removing the solvent under reduced pressure. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.77 (t, 1H, J= 16.93 Hz, CH_2=CH), 4.99-4.86 (m, 2H, CH=CH_2), 4.08-4.03 (m, 2H, OCH_2), 2.55-2.43 (m, 2H, $COCH_2$), 2.42-2.33 (m, 2H, -CH_2-), 2.0 (m, 2H, --CH_2-), 1.72-1.55 (m, 3H, -CH_3), 1.38-1.19 (m 14H, -$(CH_2)_7$-). ^{13}C NMR ($CDCl_3$): δ ppm 171.3, 139.1, 117.5, 114.1, 71.8, 65.2, 33.7, 33.1, 29.4, 29.1, 28.8, 28.4, 25.8, 23.9, 23.6.

In the second step, 2.82 g (5 mmol) of **8** was dissolved in 10 ml of freshly distilled toluene in a previously dried two-necked round bottom flask which was equipped with a magnetic stir bar. Then 2.24 ml (20 mmol) of DMSiCl and three drops of Karstedt catalyst were added to the solution and the reaction mixture was stirred at room temperature in dark for three days. The dimethyl chlorosilyl attached AIBN derivative (**9**) was obtained by removing the solvent and excess DMSiCl under reduced pressure. ^{1}H-NMR ($CDCl_3$): δ (ppm) 4.1 (t, 2H, OCH_2), 2.35-2.52 (m, 6H, CH_2), 1.68-1.73 (3s, 3H each, C-CH_3), 1.2-1.4 (b, 18H, $(CH2)_9$), 0.1 (s, 6H, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ ppm 173.12, 127.94, 65.33, 49.41, 35.61, 33.10, 31.20, 29.70, 23.17, 14.05, 1.23. ^{29}Si NMR ($CDCl_3$): δ ppm 32.0.

4.6. Surface functionalization reactions

In order to investigate the accessible number of silanol groups on the particles surfaces, the particles were functionalized with excess TMSiCl (1.26 ml, 10 mmol) assuming that the smaller sized TMSiCl would react with all accessible silanol groups on the surface of the particles. After the particles were functionalized with TMSiCl, the surface functionalized particles were investigated via TGA and accessible number of silanol groups on the particles surfaces was calculated (see ***Equation 3.1***).

The general procedure for surface modification reactions with excess TMSiCl is as follows: 1 g of silica particles were dried under reduced pressure (<0.1 mbar) for 24 hours at 90°C. Then the dry particles were dispersed in freshly distilled anhydrous toluene (15 ml solvent/g particle) and excess amount of TMSiCl (1.26 ml, 10 mmol) was added to the dispersion together with pyridine (10 mmol). The final dispersion was vigorously stirred under an atmosphere of N_2 for 3 days. After the reaction of TMSiCl with the silanol groups on the NPs and GPs was completed, excess TMSiCl and pyridine was removed by centrifugation and dispersion into cold anhydrous toluene (20 ml). This process was repeated for three times to efficiently remove excess of all reagents. The functionalized particles were dried under vacuum for 24 hours at 90°C and finally investigated via TGA.

4.6.1. Surface functionalization of silica particles for LASIP

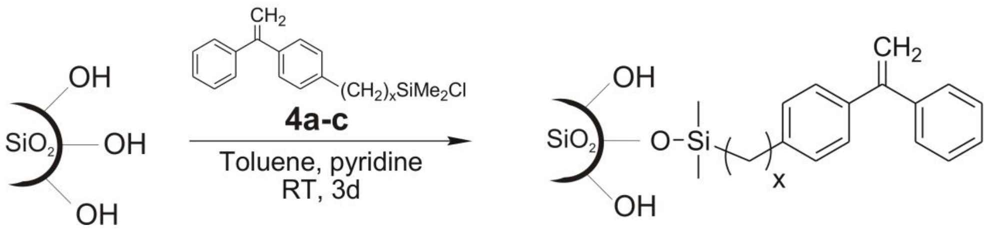
After the accessible number of silanol groups on the particle surfaces was determined, the surface functionalization reactions were conducted. The silica nano- (SA15) and glass particles (K3 and B-K3) were dried under vacuum (<0.1 mbar) at 90^{o}C for 24 hours, before the surface modification reactions. The list of all surface modification reactions including the reagents used and amounts is shown in **Table 4.1**. Detailed procedures for specific experiments will also be given below.

Table 4.1 The list of all surface modification reactions of SA15 NPs and K3, B-K3 GPs with DPE based surface modifying groups (**4a-c**) prior to LASIP reactions. The surface modification reactions were carried out in anhydrous toluene as solvent in the presence of pyridine as base at room temperature for three days, by using 1 g of corresponding particle for each experiment.

entry	particle	surface modifying group (mmol)	amount of surface modifying group		amount of pyridine	
			(mmol)	equivalent wrt* surface SiOH[a]	(mmol)	equivalent wrt surface SiOH[a]
1	SA15	**4c**	1.19	1	1.19	1
2	SA15	**4c**	2.38	2	2.38	2
3	SA15	**4c**	3.57	3	3.57	3
4	SA15	**4c**	4.76	4	4.76	4
5	K3	**4c**	0.21	1	0.21	1
6	K3	**4c**	0.42	2	0.42	2
7	K3	**4c**	0.63	3	0.63	3
8	K3	**4c**	0.84	4	0.84	4
9	SA15	**4a**	4.76	4	4.76	4
10	SA15	**4b**	4.76	4	4.76	4
11	SA15	**4c**	4.76	4	4.76	4
12	K3	**4a**	0.84	4	0.84	4
13	K3	**4b**	0.84	4	0.84	4
14	K3	**4c**	0.84	4	0.84	4
15	B-K3	**4a**	3.32	4	3.32	4
16	B-K3	**4b**	3.32	4	3.32	4
17	B-K3	**4c**	3.32	4	3.32	4

[a] according to the number of moles of surface SiOH (silanol) groups, determined by previous TGA measurements; SA15: 1.19 mmol SiOH/g particle, K3: 0.21 mmol SiOH/g particle, B-K3: 0.84 mmol SiOH/g particle.

* with respect to



Scheme 4.3 Schematic illustration of surface modification of SA15 NPs and K3, B-K3 GPs with DPE based surface modifying groups

4.6.1.1. Detailed procedure for surface functionalization of SA15 NPs with ***4a**-**c***

1 g of dried SA15 NPs (under vacuum at 90°C for 24 hours) was dispersed in 15 ml of freshly distilled anhydrous toluene in a one-necked round bottom flask. To this dispersion, an adequate amount of DPE derivative, **4a**-**4c**, (4.76 mmol, 4 equivalent with respect to the surface silanol groups) and 0.4 ml (4.76 mmol) of pyridine were added and the reaction mixture was stirred at room temperature for three days.

Surface functionalized particles were purified by repeated centrifugation and dispersion method. The reaction mixture was first centrifuged and the liquid which contained unreacted surface modifying group and pyridine was decanted. The precipitate was then dispersed in cold anhydrous toluene (≈25 ml) and centrifuged again. This process was repeated for three times in order to remove all unreacted surface modifying groups. After purification, the surface functionalized SA15 NPs were dried under vacuum at 90°C for 24 hours. The surface functionalized SA15 NPs were investigated via TGA in order to determine the amount of functionalized silanol groups.

The surface functionalized SA15 NPs were further functionalized with TMSiCl in order to block unreacted silanol groups so that they could not interfere with LASIP reactions. For this purpose, the surface functionalized SA15 NPs were dispersed in freshly distilled anhydrous toluene in a one-necked round bottom flask. To this dispersion, 0.6 ml (4.76 mmol, 4 equivalents with respect to the surface silanol groups) of TMSiCl and 0.4 ml (4.76 mmol) of freshly distilled anhydrous pyridine were added and the reaction mixture was stirred at room temperature for three days.

The purification of further functionalized SA15 NPs was done in the same way as explained above.

4.6.1.2. Detailed procedure for surface functionalization of B-K3 GPs with ***4a**-**c***

1 g of dried B-K3 GPs (under vacuum (<0.1 mbar) at 90°C for 24 hours) was dispersed in 15 ml of freshly distilled anhydrous toluene in a one-necked round bottom flask. To this dispersion, adequate amount of DPE derivative (**4a**-**4c**) (3.32 mmol, 4 equivalents with respect to the number of the surface silanol groups) and 0.3 ml (3.32 mmol) of pyridine were added and the reaction mixture was stirred at room temperature for three days.

The purification of B-K3 GPs after modification with surface modifying groups, **4a**-**4c**, and further modification with TMSiCl was done in the same way as explained under the section **4.6.1.1**.

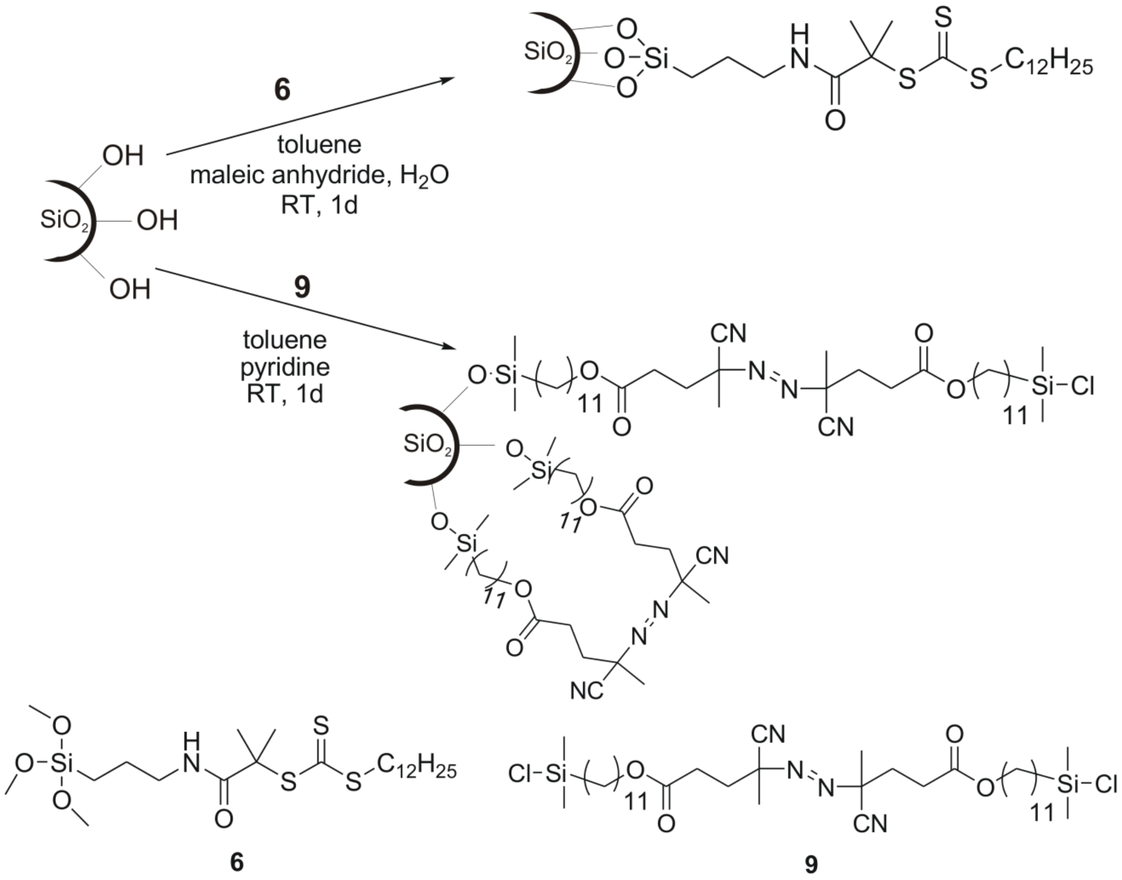
*4.6.1.3. Detailed procedure for surface functionalization of K3 GPs with **4a**-**c***

1 g of dried K3 GPs (under vacuum (<0.1 mbar) at 90^{o}C for 24 hours) was dispersed in 15 ml of freshly distilled anhydrous toluene in a one-necked round bottom flask. To this dispersion, adequate amount of DPE derivative (**4a**-**c**) (0.84 mmol, 4 equivalents with respect to the surface silanol groups) and 0.1 ml (1.1 mmol) of pyridine were added and the reaction mixture was stirred at room temperature for three days.

The purification of K3 GPs after modification with surface modifying groups (**4a**-**4c**) and further modification with TMSiCl was done in the same way as explained under the section **4.6.1.1**.

4.6.2. Surface functionalization of silica particles for SI-CRP

Surface functionalization reactions of SA15 and AE200 NPs prior SI-CRP reactions were conducted in a similar synthetic procedure as in surface modification reactions for LASIP. The SA15 and AE200 NPs were dried under vacuum (<0.1 mbar) at 90^{o}C for 24 hours and used for the immobilization of surface modifying groups (**6** and **9**) on the surface of the particles. The list of all surface modification reactions including the reagents used and amounts is shown in **Table 4.2**. Detailed procedures for specific experiments will also be given below.



Scheme 4.4 Schematic illustration of surface modification of SA15 and AE200 NPs with CTA based (**6**) and AIBN based (**9**) surface modifying groups

Table 4.2 The list of all surface modification reactions of SA15 and AE200 NPs with CTA based (**6**) and AIBN based (**9**) surface modifying groups prior to SI-CRP reactions. The surface modification reactions of NPs with 6 were carried in anhydrous toluene as solvent in the presence of catalytic amount of maleic anhydride and H_2O at room temperature for one day, by using 1 g of corresponding particle for each experiment. The surface modification of NPs with **9** were carried out in anhydrous toluene as solvent in the presence of pyridine as base at room temperature for three days by using 1 g of corresponding particle for each experiment.

entry	**particle**	**surface modifying group**	**amount of surface modifying group**		**amount of pyridine**		**maleic anhydride (mg)**	**H_2O^b**
			(mmol)	equivalent wrt surface SiOH[a]	(mmol)	equivalent wrt surface SiOH[a]		
1	SA15	**6**	1.19	1	-	-	0.1	3 drops
2	SA15	**9**	1.19	1	1.19	1	-	-
3	SA15	**6**	2.38	2	-	-	0.1	3 drops
4	SA15	**9**	2.38	2	2.38	2	-	-
5	AE200	**6**	1.57	1	-	-	0.1	3 drops
6	AE200	**9**	1.57	1	1.57	1	-	-
7	AE200	**6**	3.14	2	-	-	0.1	3 drops
8	AE200	**9**	3.14	2	3.14	2	-	-

[a] according to the number of moles of surface SiOH (silanol) groups, determined by previous TGA measurements; SA15: 1.19 mmol SiOH/g particle, AE200: 1.57 mmol SiOH/g particle. (wrt: with respect to)

[b] deionized water

*4.6.2.1. Detailed procedure for surface functionalization of SA15 NPs with CTA based CRP initiator (**6**)*

1 g of dried SA15 NPs (under vacuum (<0.1 mbar) at 90°C for 24 hours) was dispersed in freshly distilled anhydrous toluene and the mixture was ultrasonicated for 15 minutes in order to achieve full dispersion. To this dispersion, 0.1 mg of maleic anhydride in 0.1 ml of water and 0.62 g (1.19 mmol, 1 equivalent with respect to the number of surface silanol groups) of surface modifying group **6** were added. The resulting reaction mixture was stirred at room temperature for 24 hours. Then the surface functionalized particles were isolated via repeated centrifugation/dispersion method as described under the section **4.6.1.1**.

The surface functionalized particles were dried under vacuum at room temperature for 24 hours and then kept in the glovebox prior to use in SI-CRP reactions. The surface functionalized particles were also analyzed via TGA in order to determine the number of functionalized silanol groups.

*4.6.2.2. Detailed procedure for surface functionalization of SA15 NPs with AIBN based CRP initiator (**9**)*

1 g of dried SA15 NPs (under vacuum at 90°C for 24 hours) was dispersed in freshly distilled anhydrous toluene and the mixture was ultrasonicated for 30 minutes in order to achieve full dispersion. To this dispersion, 0.92 g (1.19 mmol, 1 equivalent with respect to the number of surface silanol groups) of surface modifying group **9** and 0.1 ml (1.1 mmol) of pyridine were added. The resulting reaction mixture was stirred at room temperature for 72 hours. Then the surface functionalized particles were isolated via repeated centrifugation/dispersion method as described under the section **4.6.1.1**.

The surface functionalized particles were dried under vacuum at room temperature for 24 hours and then kept in the glovebox prior to be used in SI-CRP reactions. The surface functionalized particles were also analyzed via TGA in order to determine the number of functionalized silanol groups.

*4.6.2.3. Detailed procedure for surface functionalization of AE200 NPs with CTA based CRP initiator (**6**)*

1 g of dried AE200 NPs (under vacuum (<0.1 mbar) at 90°C for 24 hours) was dispersed in freshly distilled anhydrous toluene and the mixture was ultrasonicated for 15 minutes in

order to achieve full dispersion. To this dispersion, 0.1 mg of maleic anhydride in 0.1 ml of water and 0.97 g (1.57 mmol, 1 equivalent with respect to the number of surface silanol groups) of surface modifying group **6** were added. The resulting reaction mixture was stirred at room temperature for 24 hours. Then the surface functionalized particles were isolated via repeated centrifugation/dispersion method as described under the section **4.6.1.1**.

The surface functionalized particles were dried under vacuum at room temperature for 24 hours and then kept in the glovebox prior to use in SI-CRP reactions. The surface functionalized particles were also analyzed via TGA in order to determine the number of functionalized silanol groups.

*4.6.2.4. Detailed procedure for surface functionalization of AE200 NPs with AIBN based CRP initiator (**9**)*

1 g of dried AE200 NPs (under vacuum at 90^{o}C for 24 hours) was dispersed in freshly distilled anhydrous toluene and the mixture was ultrasonicated for 30 minutes in order to achieve full dispersion. To this dispersion, 1.21 g (1.57 mmol, 1 equivalent with respect to the number of surface silanol groups) of surface modifying group **9** and 0.15 ml (1.57 mmol) of pyridine were added. The resulting reaction mixture was stirred at room temperature for 72 hours. Then the surface functionalized particles were isolated via repeated centrifugation/dispersion method as described under the section **4.6.1.1**.

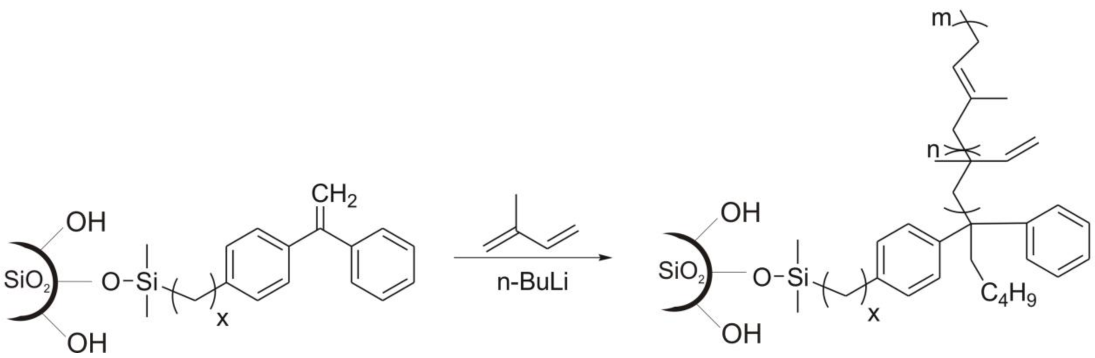
The surface functionalized particles were dried under vacuum at room temperature for 24 hours and then kept in the glovebox prior to be used in SI-CRP reactions. The surface functionalized particles were also analyzed via TGA in order to determine the number of functionalized silanol groups.

4.7. Surface initiated polymerization (SIP) reactions

4.7.1. Living anionic surface initiated polymerization (LASIP) reactions

Due to the sensitivity of living anionic polymerization to any kind of impurity (water, oxygen), LASIP reactions were carried out under extreme inert conditions. Solvent and previously functionalized and purified silica nano- and glass particles were stored in the glovebox. Isoprene was dried over calcium hydride (CaH_2) under vacuum for 24 hours and distilled into a dry round bottom flask and stored at -20^o prior to use (not more than a week).

The surface functionalized particles were dispersed in anhydrous solvent (benzene, toluene and n-hexane) inside the glovebox and sealed properly. Then the reaction vial was taken out and ultrasonicated for 15 minutes in order to achieve full dispersion. Adequate amount of initiator (*n*-BuLi or *sec*-BuLi) was added to the reaction vial to activate the DPE groups on the surface of the particle. The resulting mixture was stirred constantly in an ice bath at 0°C (when benzene was used as solvent) for 20 minutes. Finally, an adequate amount of isoprene (depending on the desired molecular weight and the number of moles of surface modifying groups determined via TGA measurements; either 4 hours (DP= 100) or 2 days (DP= 1000) was added to the reaction vial through the rubber septum of the vial via syringe. SIP reaction was quenched by the addition of excess methanol (1 ml). The list of all LASIP reactions including reagents and amounts under different reaction conditions is listed in **Table 4.3**. The details of specific experiments will also be given in the following sections.



Scheme 4.5 Schematic illustration of LASIP reactions

Table 4.3 The list of all LASIP reactions. The LASIP of isoprene was carried out in benzene, toluene and n-hexane as solvent (5 ml for each reaction listed below) at different temperatures (depending on the solvent, and the ethylene moiety on DPE was activated with the addition of either n-BuLi or sec-BuLi to initiate the polymerization.

entry	functionalized particle[a]	solvent	temperature (°C)	activating compound[b] n-BuLi (mmol)	sec-BuLi (mmol)	[M]:[DPE]:[AG][c]	M_n(calc)[d]
1	SA15-**4c**(4)	benzene	0	1.3	-	25:1.1:1	1700
2	SA15-**4c**(4)	benzene	0	1.3	-	50:1.1:1	3400
3	SA15-**4c**(4)	benzene	0	1.3	-	75:1.1:1	5100
4	SA15-**4c**(4)	benzene	0	1.3	-	100:1.1:1	6800
5	SA15-**4c**(1)	benzene	0	0.13	-	100:1.1:1	6800
6	SA15-**4c**(2)	benzene	0	0.44	-	100:1.1:1	6800
7	SA15-**4c**(3)	benzene	0	0.68	-	100:1.1:1	6800
8	SA15-**4c**(4)	toluene	-70	1.3	-	100:1.1:1	6800

9	SA15-**4c**(4)	toluene	-50	1.3	-	100:1.1:1	6800
10	SA15-**4c**(4)	n-hexane	-70	1.3	-	100:1.1:1	6800
11	SA15-**4a**(4)	benzene	0	1.3	-	100:1.1:1	6800
12	SA15-**4b**(4)	benzene	0	1.3	-	100:1.1:1	6800
13	SA15-**4a**(4)	benzene	0	-	1.4	100:1.1:1	6800
14	SA15-**4b**(4)	benzene	0	-	1.4	100:1.1:1	6800
15	SA15-**4c**(4)	benzene	0	-	1.3	100:1.1:1	6800
16	SA15-**4c**(4)	benzene	0	1.3	-	1000:1.1:1	68000
17	K3-**4c**(4)	benzene	0	0.15	-	25:1.1:1	1700
18	K3-**4c**(4)	benzene	0	0.15	-	50:1.1:1	3400
19	K3-**4c**(4)	benzene	0	0.15	-	75:1.1:1	5100
20	K3-**4c**(4)	benzene	0	0.15	-	100:1.1:1	6800
21	K3-**4c**(1)	benzene	0	0.06	-	100:1.1:1	6800
22	K3-**4c**(2)	benzene	0	0.09	-	100:1.1:1	6800
23	K3-**4c**(3)	benzene	0	0.13	-	100:1.1:1	6800
24	K3-**4c**(4)	toluene	-70	0.15	-	100:1.1:1	6800
25	K3-**4c**(4)	toluene	-50	0.15	-	100:1.1:1	6800
26	K3-**4c**(4)	n-hexane	-70	0.15	-	100:1.1:1	6800
27	K3-**4a**(4)	benzene	0	0.19	-	100:1.1:1	6800
28	K3-**4b**(4)	benzene	0	0.17	-	100:1.1:1	6800
29	K3-**4a**(4)	benzene	0	-	0.19	100:1.1:1	6800
30	K3-**4b**(4)	benzene	0	-	0.17	100:1.1:1	6800
31	K3-**4c**(4)	benzene	0	-	0.15	100:1.1:1	6800
32	K3-**4c**(4)	benzene	0	0.15	-	1000:1.1:1	68000
33	B-K3-**4c**(4)	benzene	0	0.51	-	25:1.1:1	1700
34	B-K3-**4c**(4)	benzene	0	0.51	-	50:1.1:1	3400
35	B-K3-**4c**(4)	benzene	0	0.51	-	75:1.1:1	5100
36	B-K3-**4c**(4)	benzene	0	0.51	-	100:1.1:1	6800
37	B-K3-**4c**(4)	toluene	-70	0.51	-	100:1.1:1	6800
38	B-K3-**4c**(4)	toluene	-50	0.51	-	100:1.1:1	6800
39	B-K3-**4c**(4)	n-hexane	-70	0.51	-	100:1.1:1	6800
40	B-K3-**4a**(4)	benzene	0	-	0.69	100:1.1:1	6800
41	B-K3-**4b**(4)	benzene	0	-	0.56	100:1.1:1	6800
42	B-K3-**4c**(4)	benzene	0	-	0.51	100:1.1:1	6800
43	B-K3-**4c**(4)	benzene	0	0.51	-	1000:1.1:1	68000

[a] The notation in bold specifies the surface modifying group used for the surface functionalization of the corresponding particle and the number in brackets specifies the amount of surface modifying agent used for surface functionalization reaction with respect to the initial surface silanol groups; [b] in each polymerization 1.1 equivalent of activating compound with respect to the initial surface silanol groups (determined via TGA earlier) is used; [c] [M]: concentration of monomer (isoprene); [DPE]: concentration of DPE moiety on the corresponding particle surface, [AG]: concentration of activating group; [d] calculated as [M]/[DPE]**M(*isoprene)

*4.7.1.1. Detailed procedure for the synthesis of SA15-**4a**-(PI)$_{100}$*

1 g of previously functionalized SA15 NP's with **4a** (1.18 mmol of functionalized silanol groups) were placed in a vial in the glove box. 5 ml of benzene was added and then the vial was sealed properly. The vial was removed from the glove box and ultrasonicated for 15 minutes to avoid agglomeration; afterwards the vial was placed in an ice bath at 0^o. n-BuLi (1.3 mmol, 2.5 M in hexane, 1.1 equivalent with respect to the surface DPE groups) was injected to the vial to activate the surface initiator groups. After 20 minutes, isoprene (8.8 g, 130 mmol, 100 equivalents with respect to the surface DPE groups) was injected and the reaction mixture was stirred for 4 hours. The polymerization was finally quenched with the addition of excess methanol (1ml). A detailed procedure for the separation of surface grafted polymer and the non-grafted polymer will be explained under section **4.7.3**.

*4.7.1.2. Detailed procedure for the synthesis of B-K3-**4b**-(PI)$_{100}$*

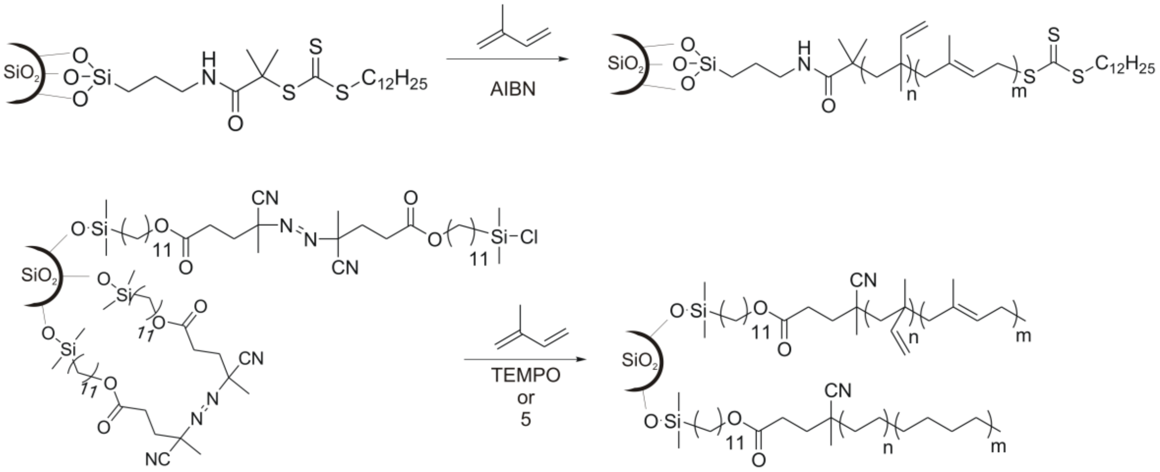
1 g of previously functionalized B-K3 glass particle with **4b** (0.51 mmol of functionalized silanol groups) was placed in a vial in the glove box. 5 ml of benzene was added and the vial was sealed. The vial was taken out from the glovebox, ultrasonicated for 15 minutes and placed in an ice bath. n-BuLi (0.56 mmol, 2.5 M in hexane, 1.1 equivalent with respect to the surface DPE groups) was injected to the vial to activate the surface initiator groups. After 20 minutes 3.4 g of (51 mmol, 100 equivalents with respect to the surface DPE groups) isoprene were injected and the reaction mixture was stirred for 4 hours. The polymerization was finally quenched with excess methanol (1ml).

*4.7.1.3. Detailed procedure for the synthesis of K3-**4c**-(PI)$_{100}$*

1 g of previously functionalized K3 glass particle with **4c** (0.09 mmol of functionalized silanol groups) was placed in a vial in the glove box. 5 ml of benzene was added and the vial was sealed. The vial was taken out from the glovebox, ultrasonicated for 15 minutes and placed in an ice bath. n-BuLi (0.11 mmol, 2.5 M in hexane, 1.1 equivalent with respect to the surface DPE groups) was injected to the vial to activate the surface initiator groups. After 20 minutes 0.75 g of (11 mmol, 100 equivalents with respect to the surface DPE groups) isoprene were injected and the reaction mixture was stirred for 4 hours. The polymerization was finally quenched with excess methanol (1ml).

4.7.2. Surface initiated controlled radical polymerization (SI-CRP) reactions

Unlike the case with LASIP reactions, two different controlled/living polymerization techniques were used in three different methods. The particles whose surface was functionalized with triethoxysilyl attached CTA (**6**) was used for SI-RAFT reactions. On the other hand, the particle whose surface was functionalized with dimethylchlorosilyl attached AIBN derivative (**9**) was used for both SI-RAFT and SI-NMP reactions depending on the additive (TEMPO, TIPNO for SI-NMP and **5** for SI-RAFT). The list of all LASIP reactions including reagents and amounts under different reaction conditions is listed in **Table 4.4**. The details of specific experiments will also be given in the following sections.



Scheme 4.6 Schematic illustration of SI-CRP reactions

Table 4.3 The list of all SI-CRP reactions. SI-CRP of isoprene was carried out in 1,2-dichlorobenzene as solvent (1:1 monomer to solvent volume ratio) at 130°C.

entry	**functionalized particle**[a]	**additives**[b]					**[M]:[MG]:[A]:[FI]**[c]	**M_n(calc)**[d]
		AIBN (mmol)	DCP (mmol)	TEMPO (mmol)	TIPNO (mmol)	**5** (mmol)		
1	SA15-**6**(1)	0.05	-	-	-	-	100:1:0.5:0	6800
2	SA15-**9**(1)	-	-	-	-	0.14	100:1.1:0	6800
3	SA15-**9**(1)	-	-	0.14	-	-	100:1:1:0	6800
4	AE200-**6**(1)	0.06	-	-	-	-	100:1:0.5:0	6800
5	AE200-**9**(1)	-	-	-	-	0.17	100:1:1:0	6800
6	AE200-**9**(1)	-	-	0.17	-	-	100:1:1:0	6800
7	SA15-**6**(2)	0.07	-	-	-	-	100:1:0.5:0	6800
8	SA15-**9**(2)	-	-	-	-	0.19	100:1:1:0	6800
9	SA15-**9**(2)	-	-	0.19	-	-	100:1:1:0	6800
10	AE200-**6**(2)	0.08	-	-	-	-	100:1:0.5:0	6800

11	AE200-**9**(2)	-	-	-	-	0.22	100:1:1:0	6800
12	AE200-**9**(2)	-	-	0.22	-	-	100:1:1:0	6800
13	SA15-**6**(2)	0.07	-	-	-	0.13	100:1:0.5:1	6800
14	SA15-**6**(2)	-	0.07	-	-	0.13	100:1:1:1	6800
15	SA15-**9**(2)	0.1	-	-	-	0.19	100:1:0.5:1	6800
16	SA15-**9**(2)	0.1	-	0.19	-	-	100:1:0.5:1	6800
17	SA15-**9**(2)	0.1	-	-	0.19	-	100:1:0.5:1	6800
18	AE200-**6**(2)	0.08	-	-	-	0.16	100:1:0.5:1	6800
19	AE200-**6**(2)	-	0.08	-	-	0.16	100:1:0.5:1	6800
20	AE200-**9**(2)	0.11	-	-	-	0.22	100:1:0.5:1	6800
21	AE200-**9**(2)	0.11	-	0.22	-	-	100:1:0.5:1	6800
22	AE200-**9**(2)	0.11	-	-	0.22	-	100:1:0.5:1	6800

[a] The notation in bold specifies the surface modifying group used for the surface functionalization of the corresponding particle and the number in brackets specifies the amount of surface modifying agent used for surface functionalization reaction with respect to the initial surface silanol groups; [b] in each polymerization 1 or 0.5 (when bifunctional free radical initiators were used) equivalent of additive with respect to the initial surface silanol groups (determined via TGA earlier) is used; [c] [M]: concentration of monomer (isoprene); [MG]: concentration of surface modifying group immobilized on the corresponding particle surface (determined via TGA measurements earlier), [A]: concentration of additive, [FI]: concentration of free/sacrificial initiator and/or CTA; [d] calculated as [M]/[MG]**M(*isoprene)

*4.7.2.1. Detailed procedure for the synthesis of SA15-**6**-(PI)$_{100}$ via SI-RAFT*

1 g of previously CTA-functionalized and purified SA15 NPs were placed in a Schlenk flask and dispersed in 1,2-dichlorobenzene and the flask was sealed properly. The monomer to solvent volume ratio was kept 1:1. The Schlenk flask was placed in the ultrasonic bath for 15 minutes and 1.3 ml of (13 mmol, 100 equivalents with respect to the number of the surface modifying group) freshly distilled isoprene and 21 mg of AIBN (0.13 mmol, 1.0 equivalent with respect to the number of the surface modifying group) were added to the flask. For the polymerization reactions which were carried out in the presence of free CTA, 47.2 mg (0.13 mmol, 1.0 equivalent with respect to the number of the surface modifying group) of CTA was added. Freeze-thaw cycle was applied to the flask for three times. Then the flask was attached to a reflux condenser and placed in an oil bath at 130^{o}C in order to start the polymerization. The resulting reaction mixture was left to stir for 16 hours for completion.

*4.7.2.2. Detailed procedure for the synthesis of SA15-**9**-(PI)$_{100}$ via SI-RAFT*

1 g of previously azo-functionalized and purified SA15 NPs were placed in a Schlenk flask and dispersed in 1,2-dichlorobenzene and the flask was sealed properly. The monomer to solvent volume ratio was kept 1:1. The flask was placed in the ultrasonic bath for 15 minutes and then 1.9 ml (19 mmol, 100 equivalents with respect to the number of the surface

modifying group) of freshly distilled isoprene and 69 mg (0.19 mmol, 1.0 equivalent with respect to the number of the surface modifying group) of chain transfer agent (**5**) were added to the flask and freeze-thaw cycle was applied for three times. For the polymerization reactions which were carried out in the presence of sacrificial initiator, 30.7 mg (0.13 mmol, 1.0 equivalent with respect to the number of the surface modifying group) of AIBN was added. Then the Schlenk flask was attached to a reflux condenser and placed in an oil bath at 130^{o}C in order to start the polymerization. The resulting reaction mixture was left to stir for 16 hours for completion.

*4.7.2.3. Detailed procedure for the synthesis of SA15-**9**-(PI)$_{100}$ via SI-NMP*

1 g of previously functionalized and purified SA15 NPs were placed in a Schlenk flask and dispersed in 1,2-dichlorobenzene and the flask was sealed properly. The Schlenk flask was taken out from the glovebox and placed in the ultrasonic bath for 15 minutes and 1.9 ml (19 mmol, 100 equivalents with respect to the number of the surface modifying group) of freshly distilled isoprene and 30 mg of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) were added to the reaction mixture and freeze-thaw cycle was applied for three times. For the polymerization reactions which were carried out in the presence of sacrificial initiator, 30.7 mg (0.13 mmol, 1.0 equivalent with respect to the number of the surface modifying group) of AIBN was added. The polymerization was started by placing the flask, which was attached to a reflux condenser, in an oil bath at 130^{o}C in order to start the polymerization. The resulting reaction mixture was left to stir for 16 hours for completion.

4.7.3. Separation of surface grafted polymers

Polymerization mixture contained surface grafted polymer, homopolymer and other impurities (additives, side products) in solvent, therefore a set of purification process had to be applied. The surface initiated polymers (regardless of SIP method) were isolated as follows:

The reaction mixture was transferred into a round bottom flask and concentrated under reduced pressure. The crude product which contained surface grafted polymer and homopolymer was then precipitated in methanol (15 ml) in which both surface grafted polymer and homopolymer precipitated, and the mixture was centrifuged for 10 minutes. The aliquot was decanted and the precipitate was dispersed in cold anhydrous toluene (20 ml) in which the homopolymer was soluble, whereas the surface grafted polymer precipitated. This dispersion was also centrifuged for 10 minutes and the aliquot was decanted and collected as the homopolymer for analysis. The precipitate was dispersed and centrifuged for a couple of times in order to remove all the homopolymer (see **Figure 4.1**).

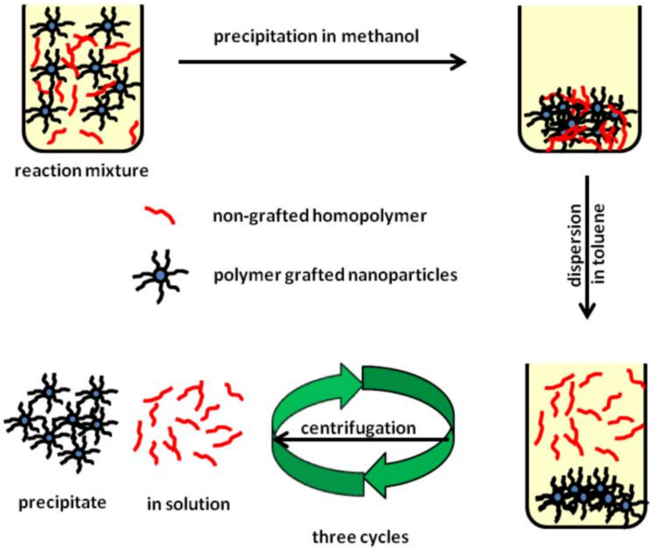


Figure 4.1 Graphical illustration of purification process of the surface grafted polymer

5. Summary

In this thesis surface initiated polymerization (SIP) of isoprene from surface functionalized silica nano- (SA15, AE200) and glass (K3, B-K3) particles was conducted via living anionic surface initiated polymerization (LASIP) and surface initiated controlled radical polymerization (SI-CRP) methods. For this purpose three different types of initiator/additive surface modifying groups were synthesized and the surfaces of these particles were functionalized with above mentioned surface modifying groups prior to SIP.

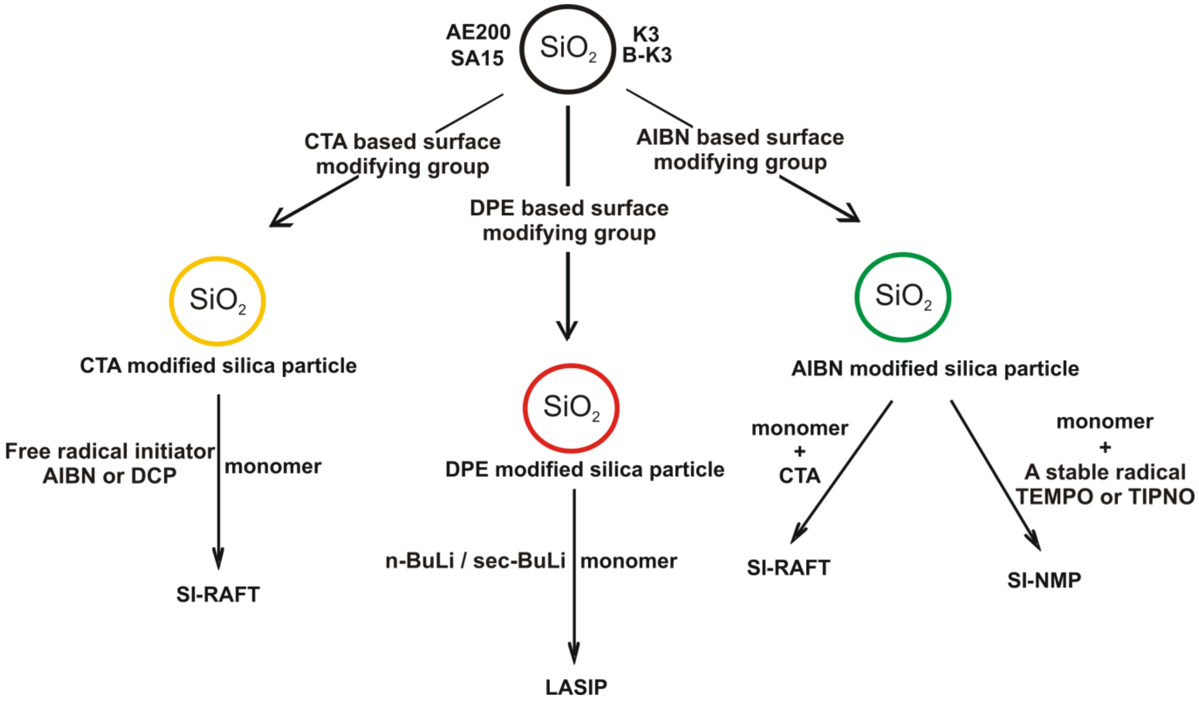


Figure 5.1 Schematic illustration of SIP of isoprene via LASIP and SI-CRP

The first type of surface modifying group was three diphenylethylene (DPE) derivatives with different alkyl-spacer lengths (**4a-c**), thus separating the DPE moiety with different distances from the particles' surfaces. The second type of surface modifying group was a trithiocarbonate bearing chain transfer agent (CTA) derivative (**6**) for surface initiated reversible addition fragmentation chain transfer (SI-RAFT) polymerization and the last type of surface modifying group was an AIBN derivative (**9**) for SI-RAFT and surface initiated nitroxide mediated polymerization (SI-NMP) reactions. (The chemical structures of the surface modifying groups are presented in **Figure 5.2**.)

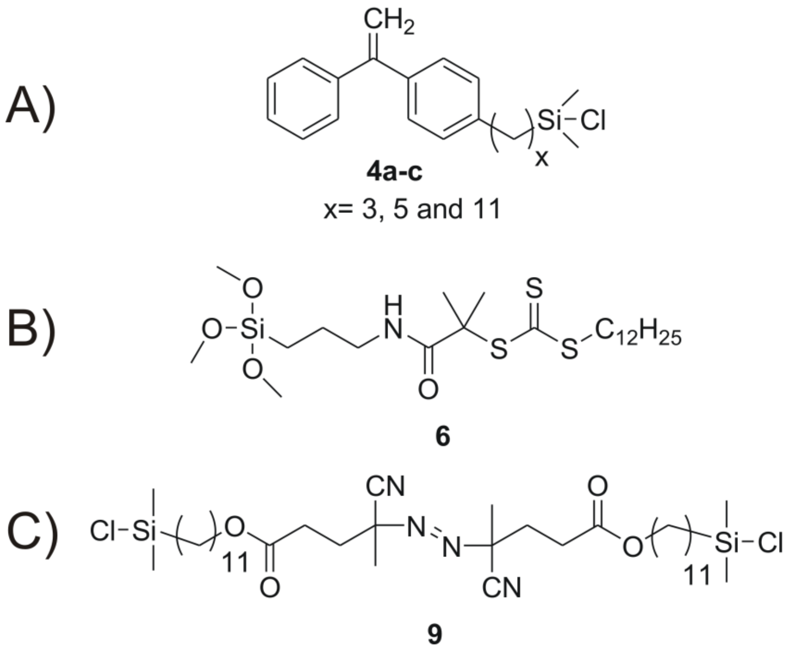
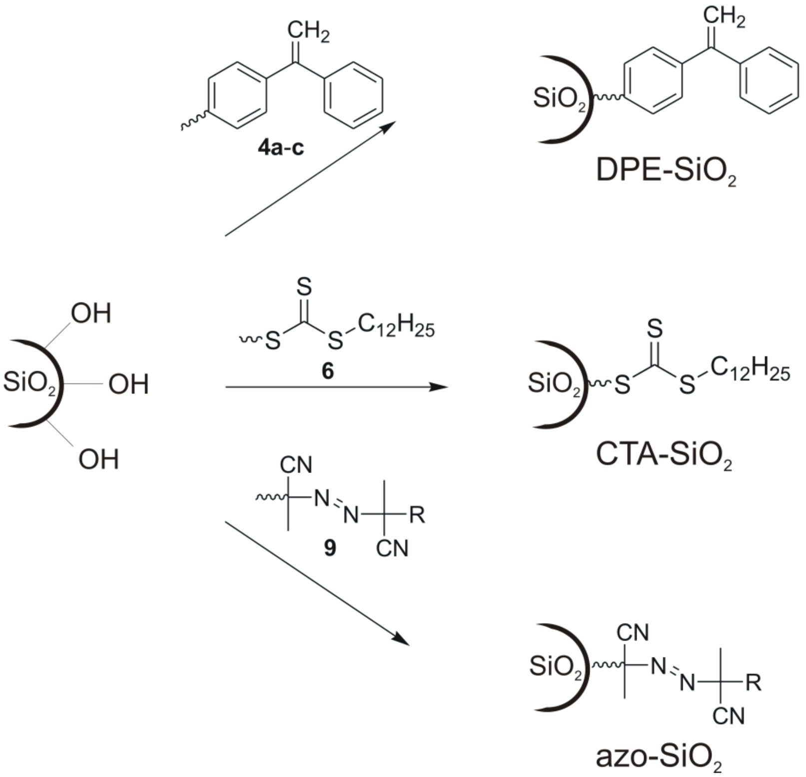


Figure 5.2 Chemical structures of the surface modifying groups A) DPE based surface modifying group for LASIP, B) CTA based surface modifying group for SI-RAFT and C) AIBN based surface modifying group for SI-NMP and SI-RAFT (depending on the additive)

For the LASIP reactions SA15 nanoparticle (NP) which is a spherically shaped nanoparticle with a diameter size of 15 nm and narrow size distribution and two different types of glass particles (GP) (K3 and B-K3) which are randomly sized and shaped porous structured particles were used. The surfaces of these particles were functionalized with above mentioned DPE derivative surface modifying groups under various conditions in order to investigate different parameters. The highest modification success was obtained when the particle surfaces were functionalized with 4 equivalents of the surface modifying groups s of the corresponding particle in the presence of pyridine (1 equivalent with respect to the number of accessible surface silanol group) and in anhydrous toluene as solvent.

The surface modification success of SA15 NPs was better than the GPs, due to the random shape, size and the porous structure of the GPs. When the surfaces of the NPs and GPs were functionalized with **4a** (the DPE derivative with the shortest spacer length), up to 97 % of the accessible surface silanol groups of the SA15 NPs could be functionalized, whereas the modification percentage of the surface silanol groups for K3 was 82.8 % and for B-K3 was 76.1 %. When the surface modifying groups with longer spacer length (**4b** and **4c**) were used, the modification percentage decreased due to the steric hindrance effect; 89.1% for SA15 NP, 42.9% for K3 GP and 55.4% for B-K3 GP. The unfunctionalized surface silanol groups were blocked by further modifying the surface of the particles with trimethylsilyl chloride (TMSiCl), so that these –OH groups would not interfere with the living anionic polymerization. The surface functionalized particles were kept in the glovebox after purification under inert conditions prior to LASIP reactions (see **Scheme 5.1**).



Scheme 5.1 Schematic illustration of the surface functionalization of the SiO2 particles with surface modifying groups

LASIP reactions were also carried out under different conditions in order to investigate the effect of different parameters to LASIP reactions. Firstly the living character of SIP reactions was investigated by planning different sets of polymerization reactions with different chain lengths (DP = 25, 50, 75 and 100). The results indicated that SIP of isoprene from SA15 NPs and K3, B-K3 GPs had living character as the increase in the actual molecular weight with increasing amount of monomer was observed.

Grafting density of the produced composites and the microstructure of the surface grafted polymers were also investigated via TGA and NMR spectroscopy respectively. As the initial number of surface silanol groups on SA15 NPs was higher than the GPs the grafting density values of the composites produced by using SA15 NPs (between σ_{PI}= 0.19 and σ_{PI}= 0.23

chains/nm^2) were higher than that of K3 (between σ_{PI}= 0.09 and σ_{PI}= 0.11 chains/nm^2) and B-K3 GPs (between σ_{PI}= 0.11 and σ_{PI}= 0.14 chains/nm^2). On the other hand the microstructure conformations of the surface grafted polymers were not affected by the type of the particle.

Another set of experiments was conducted to investigate the effect of the initiator density on the particle surface on the LASIP. For this purpose particles whose surfaces were functionalized with 1, 2, 3 and 4 equivalents of surface modifying groups with respect to the number of moles of accessible surface silanol groups were used for LASIP reactions, while the other parameters were kept constant. The results showed that the polymers grafted from the particles whose surfaces were functionalized by using 1 equivalent of the surface modifying group with respect to the number of the surface silanol groups had the lowest PDI values, M_w/M_n= 1.07 for SA15-**4c**-(1)-PI$_{100}$ and M_w/M_n= 1.06 for K3-**4c**-(1)-PI$_{100}$, and the most accurate molecular weight control. As the amount of surface modifying groups which was used to functionalize the surface of the particle increased the PDI values of the grafted polymers increased as well and the accuracy of the molecular weight projection decreased. The PDI value for the polymer grafted from SA15 NP which had been functionalized with 4 equivalents of surface modifying group with respect to the surface silanol groups increased up to M_w/M_n= 1.68 (SA15-**4c**-(1)-PI$_{100}$) from M_w/M_n= 1.07 (SA15-**4c**-(1)-PI$_{100}$).

LASIP reactions were also carried out in different solvents in order to investigate the effect of solvent on LASIP. Benzene, toluene and n-hexane were used as solvents for LASIP reactions. The results of the experiments indicated benzene to be the best solvent for these specific LASIP reactions. In the LASIP reactions in which toluene was used as solvent the PDI values were found to be too high (up to M_w/M_n= 2.7) for a living reactions and the actual molecular weight values (up to M_n= 22000 g/mol) exceeded the projected molecular weight (M_n(theo)= 6800 g/mol). When n-hexane was used as solvent for the LASIP reactions neither surface grafted polymer nor homopolymer were obtained.

The DPE moiety of the surface modifying group on the surface of the particles was activated with both *n*-BuLi and *sec*-BuLi in order to investigate the effect of the activating group to the LASIP reactions. The results showed that the polymers which were obtained by the activation of DPE moiety with *sec*-BuLi had lower PDI values and better molecular weight control could be achieved. On the other hand the activating group did not have much effect on the grafting density or the microstructure of the produced surface grafted polymer.

The last set of experiments was conducted to investigate the effect of the spacer length of the surface modifying groups which were used to modify the particle surfaces and from which the LASIP of isoprene was initiated subsequently. The DPE derivative surface modifying groups had 3, 5 and 11 $–CH_2$ groups on the side chain (**4a**, **4b** and **4c** respectively). The LASIP reactions were carried out by using NPs and GPs which were functionalized with above mentioned surface modifying groups (4 equivalents with respect to the number of moles of accessible surface silanol groups). The GPC results revealed that when the spacer length was longer the polymerization was better. The lowest PDI values were obtained for the polymers which were grafted from the particles whose surfaces were functionalized with **4c**. The polymers which were grafted from the **4a**-functinalized particles were obtained with higher PDI values and exceeded molecular weight than the projected one. On the other hand the grafting density values were higher when the LASIP isoprene was grafted from **4a**-functinalized particles, especially for GPs. This result was consistent with the surface functionalization experiments as the surface functionalization of the particles with smaller sized surface modifying group (**4a**) had been more successful. Finally the microstructure conformation of the surface grafted polymers was not affected by the spacer length of the surface modifying groups.

For the SI-CRP reactions SA15 NPs and AE200 NPs (also spherically shaped particles with 12 nm diameter size and narrow size distribution) were used. As mentioned earlier two different types of surface modifying groups for SI-CRP were synthesized, a trithiocarbonate bearing CTA derivative (**6**) and an AIBN derivative (**9**). Two sets of surface modification reactions were conducted by using these surface modifying groups to obtain functionalized particles with high and low surface modifying group grafting density on the particle surface.

After the surface modification reactions SI-CRP of isoprene from these functionalized particles was performed under different conditions in order to investigate the effect of different parameters on SI-CRP. CTA-functionalized particles were used for SI-RAFT polymerization by the addition of a free radical initiator (AIBN or DCP), whereas AIBN-functionalized particles were used for both for SI-RAFT polymerization by carrying out the polymerization in the presence of a chain transfer agent (CTA) (**5**) and for SI-NMP by carrying out the polymerization in the presence of a stable radical (TEMPO or TIPNO) (see **Figure 5.1**).

The first set of reactions was performed to investigate the effect of the initial surface modifying group density on the particle surface on SI-CRP reactions. The results revealed that the SI-CRP reactions were more successful when the polyisoprene was grafted from the particles on which the initial surface modifying group density was lower. This could be explained by tendency of the radicals which were formed during CRP reactions to recombine due their spatial proximity when the initial surface modifying group density was high. Hence polyisoprene could not be grafted from the particle surface. This result was also confirmed by the amount of homopolymer obtained in the solution. The monomer in the reaction mixture was polymerized by the initiator in the solution yielding higher amount of homopolymer than expected. Additionally the monomer conversion in the SI-CRP reactions was relatively low (28 % at most) when compared to LASIP experiments, however this result was consistent with the literature reports.

To sum up, SIP of isoprene from silica nano- and glass particles were conducted via LASIP and SI-CRP methods. Three types of surface modifying groups were synthesized and used for surface modification of these particles. According to the characterization of the produced composites, LASIP of isoprene was more successfully achieved, when compared to SI-CRP of isoprene, when the PDI, grafting ratio and grafting density values are concerned.

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7. Appendix

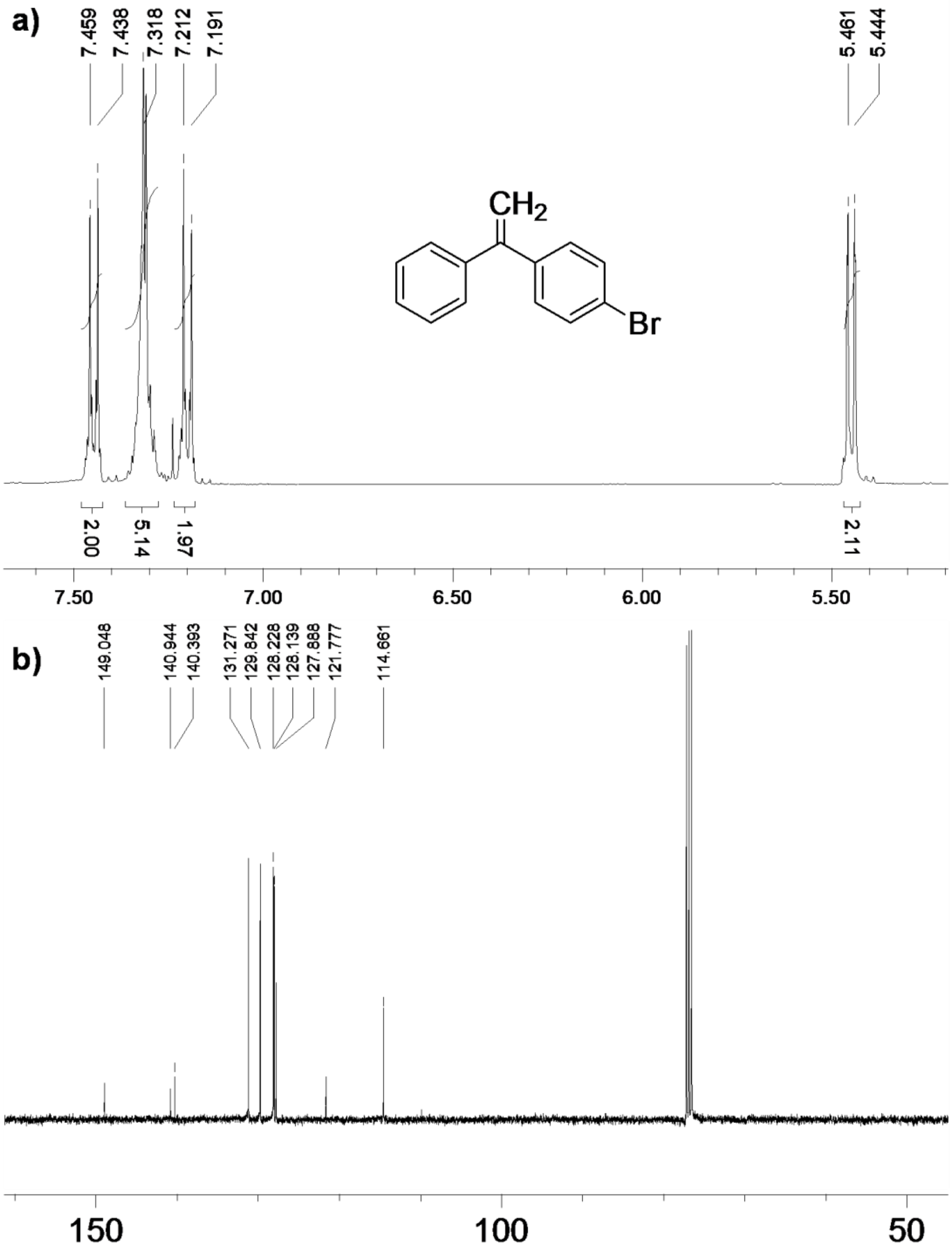


Figure A1 a) ^{1}H NMR spectrum of **2**, b) ^{13}C spectrum of **2**

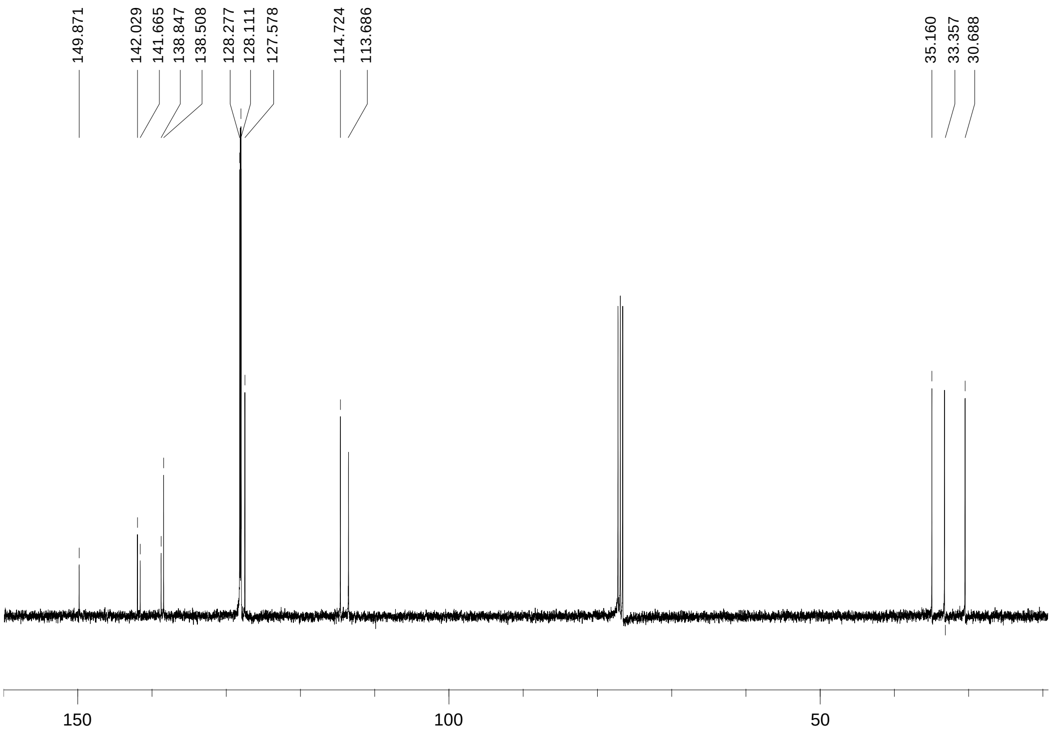


Figure A2 ^{13}C NMR spectrum of **3b**

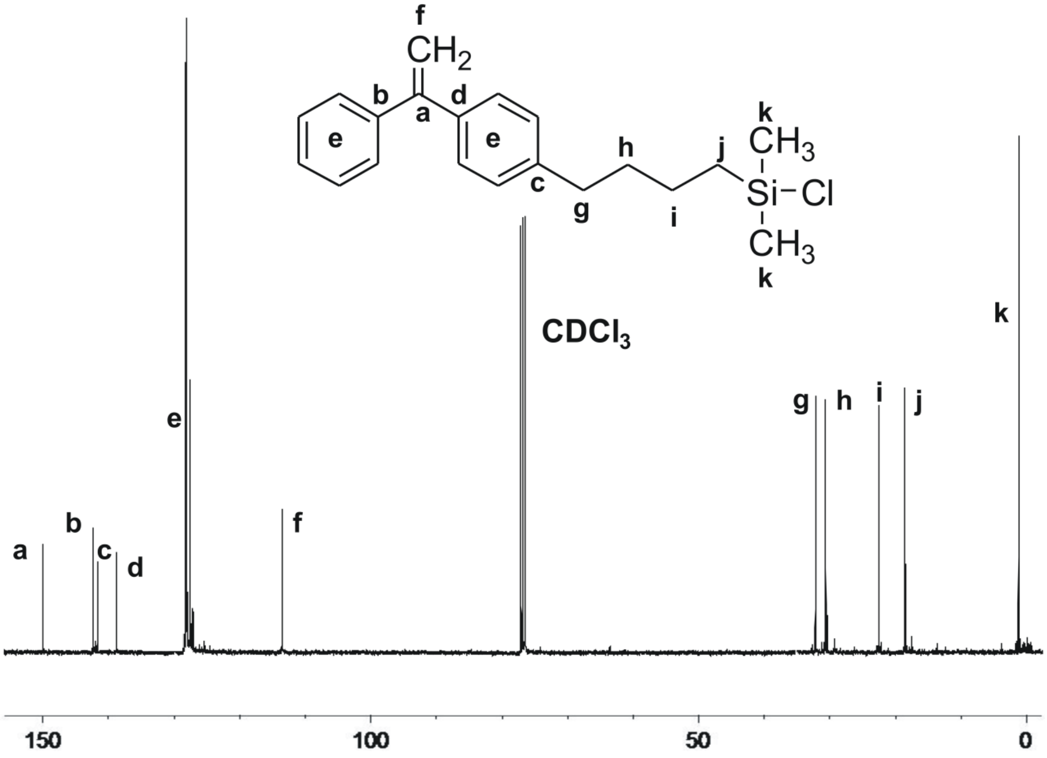


Figure A3 ^{13}C NMR spectrum of **4b**

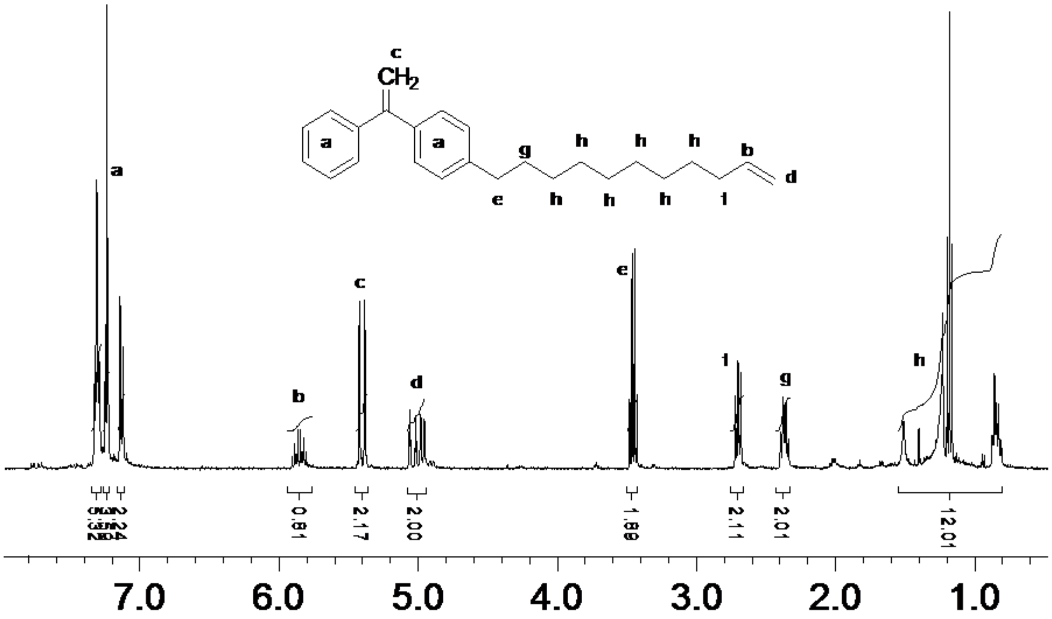


Figure A4 ^{1}H NMR spectrum of **3c**

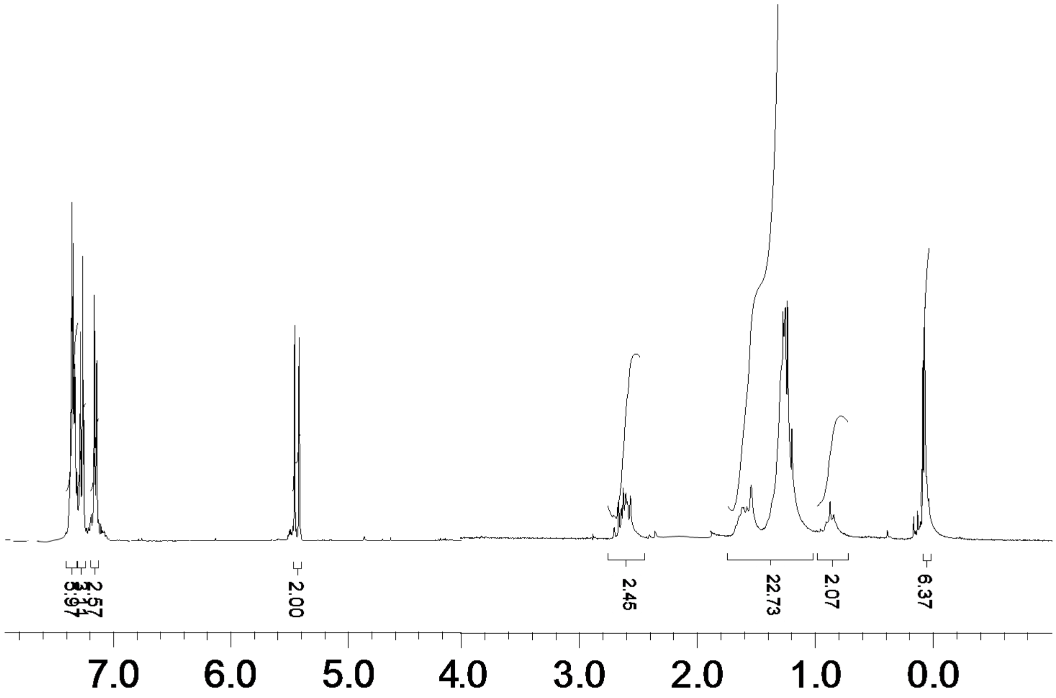


Figure A5 ^{1}H NMR spectrum of **4c**

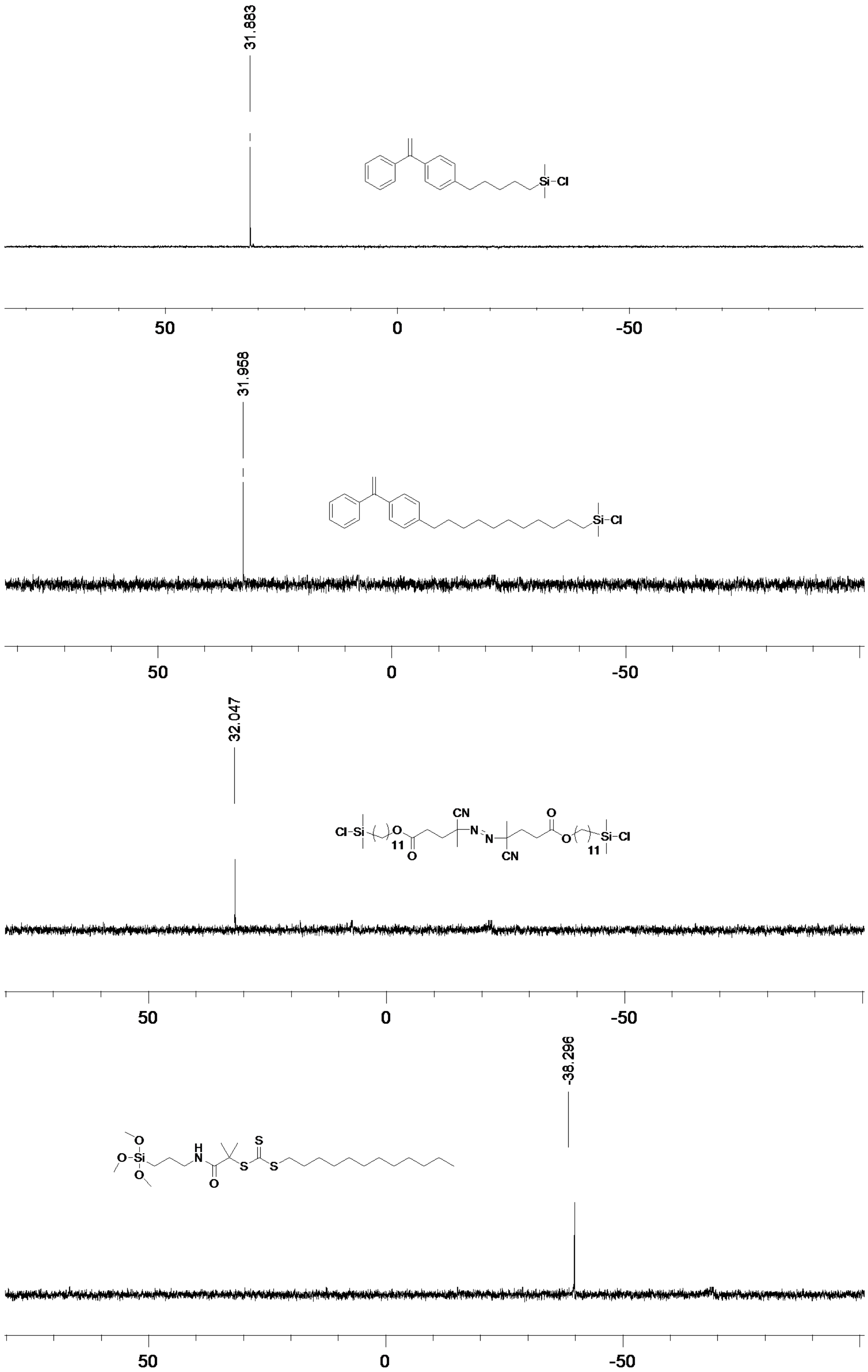
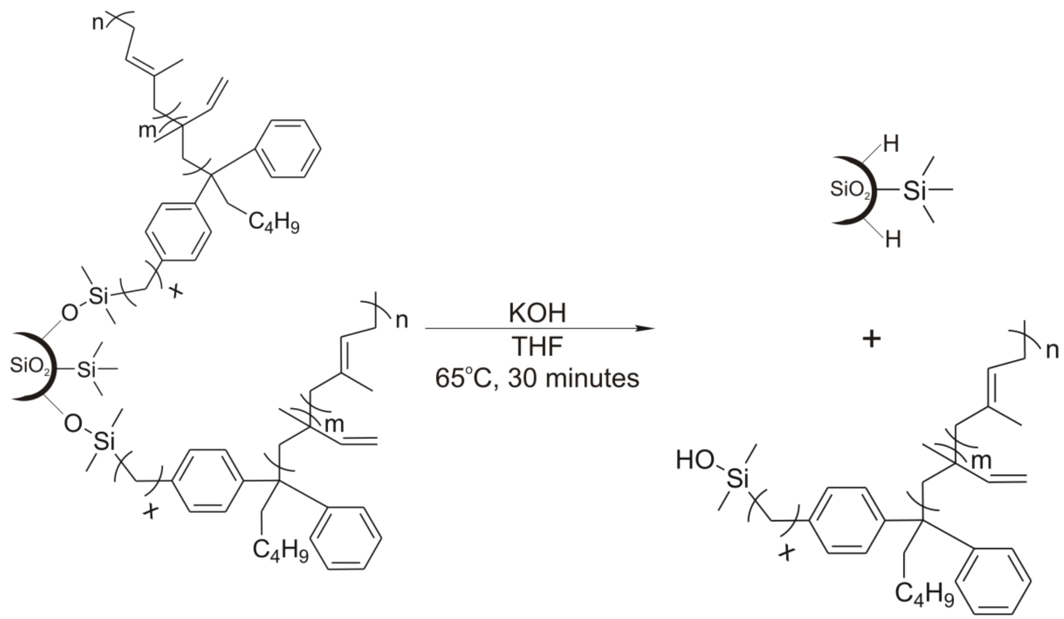


Figure A6 ^{29}Si NMR spectra of **4b**, **4c**, **6** and **9**



Scheme A1 Schematic illustration of degrafting of the surface attached polymer

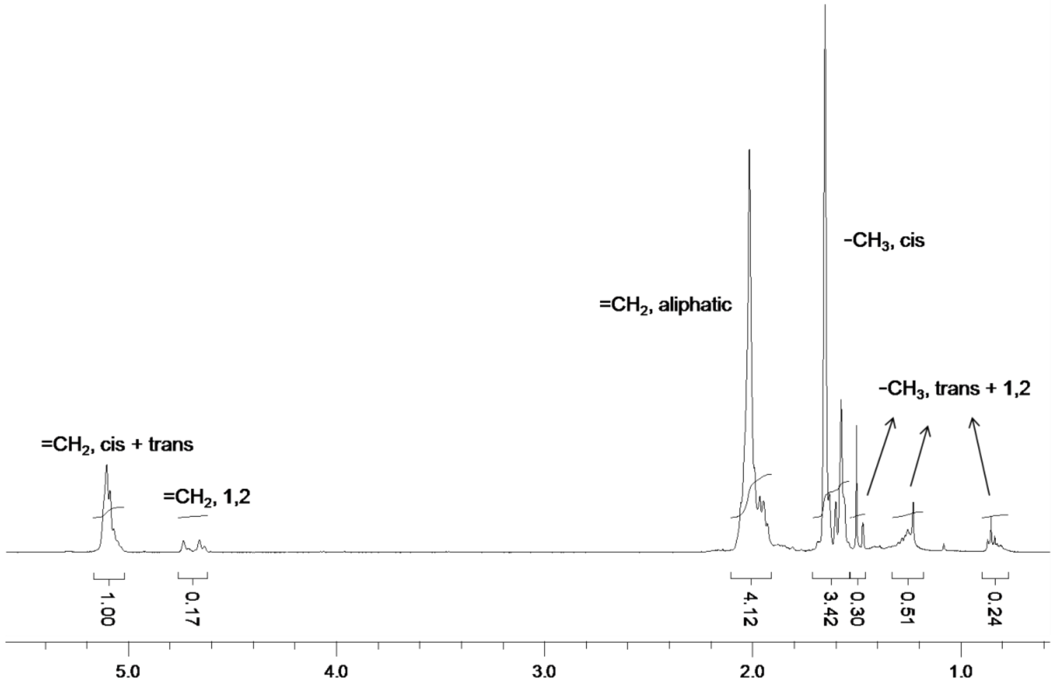


Figure A7 1H NMR spectrum of PI_{1000} (degrafted from SA15-4c-PI_{1000})

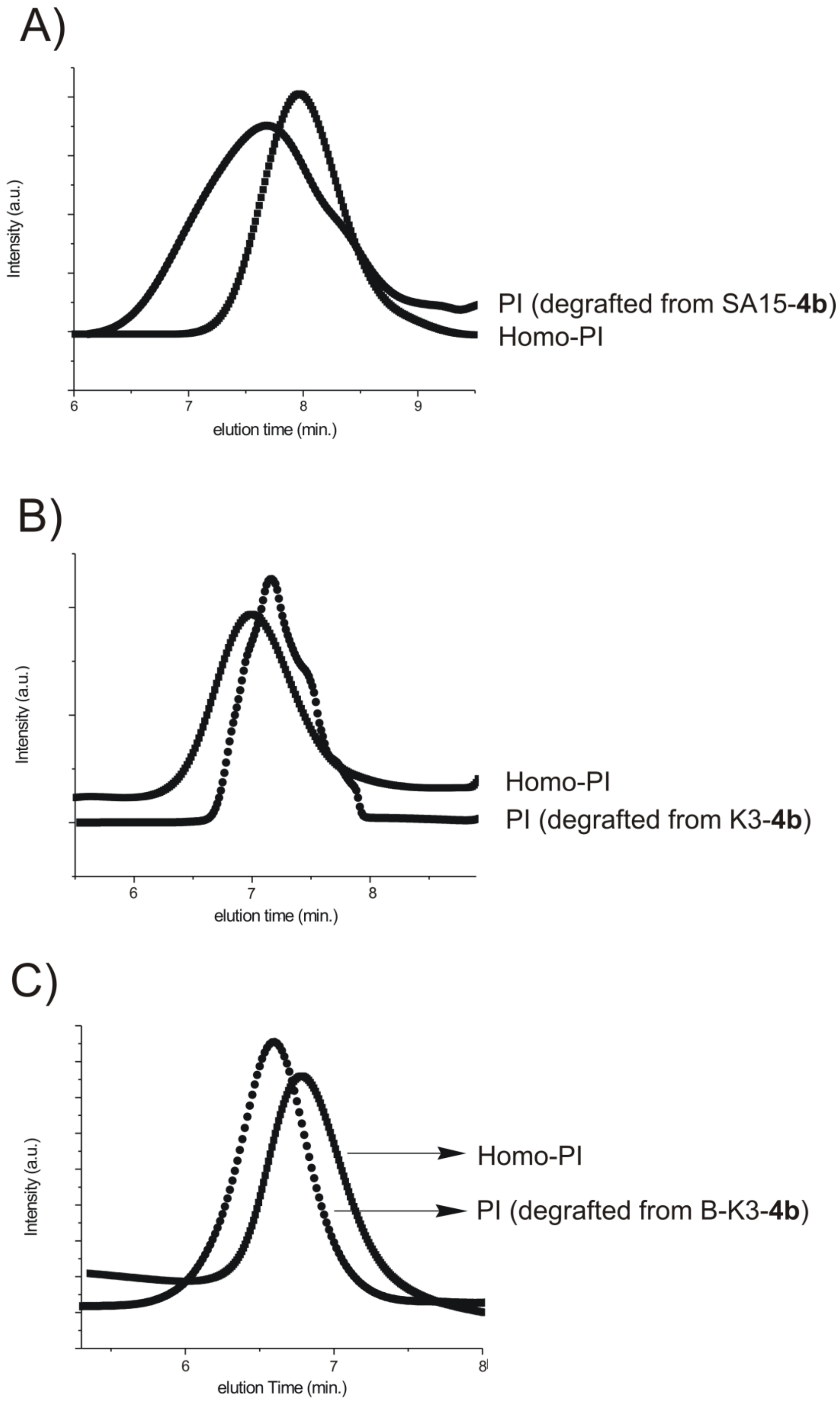


Figure A8 GPC traces of surface grafted PI and non-grafted homopolymer (LASIP experiments)

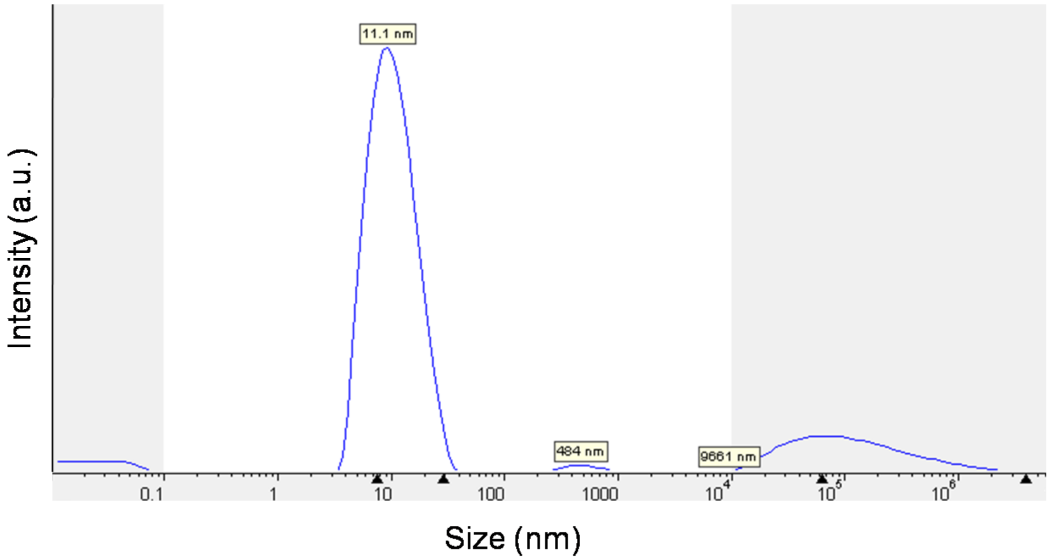


Figure A9 DLS graph of bare AE200 NP

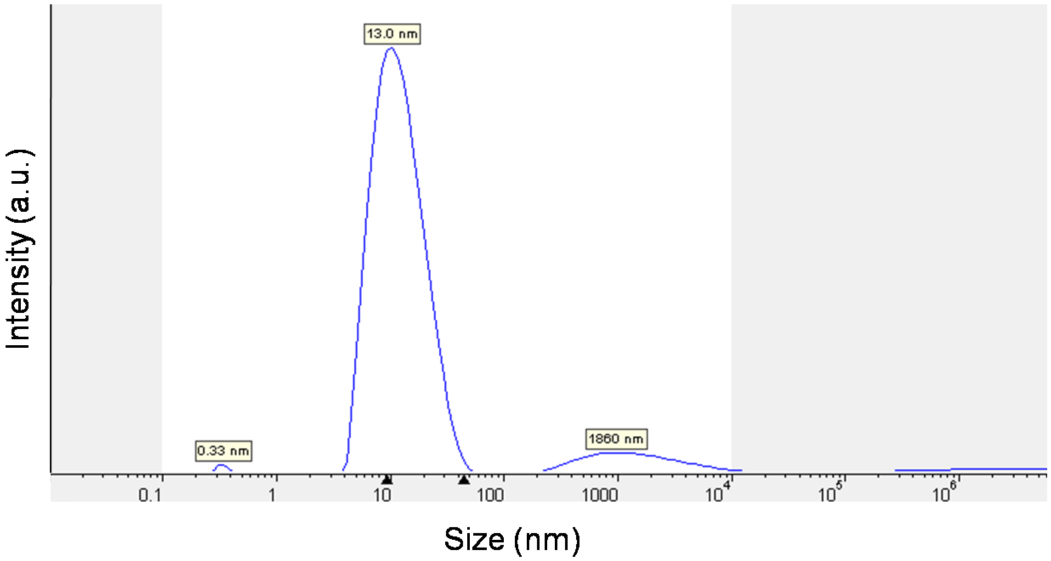


Figure A10 DLS graph of bare SA15 NP

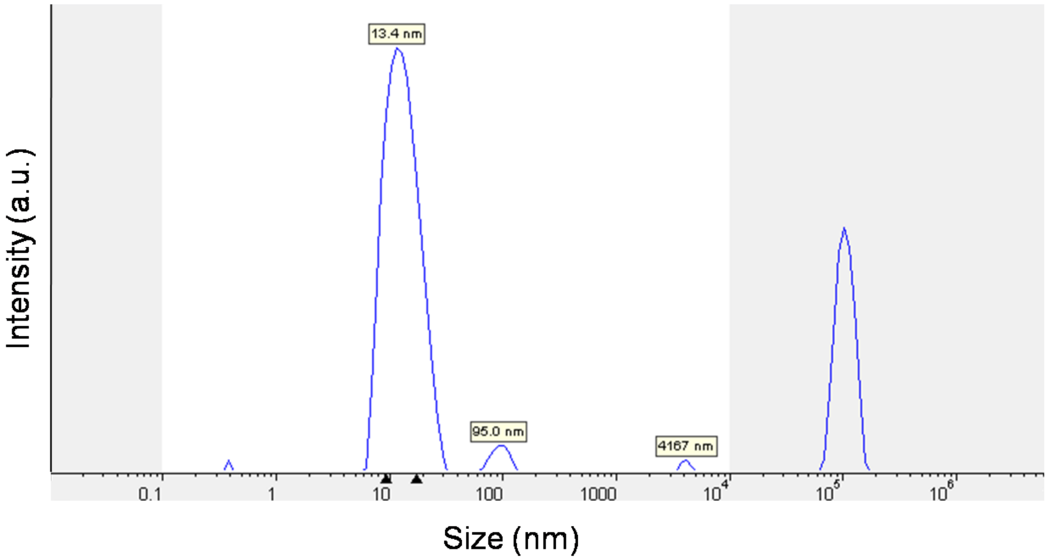


Figure A11 DLS graph of DPE-functionalized SA15 NP (SA15-**4c**)

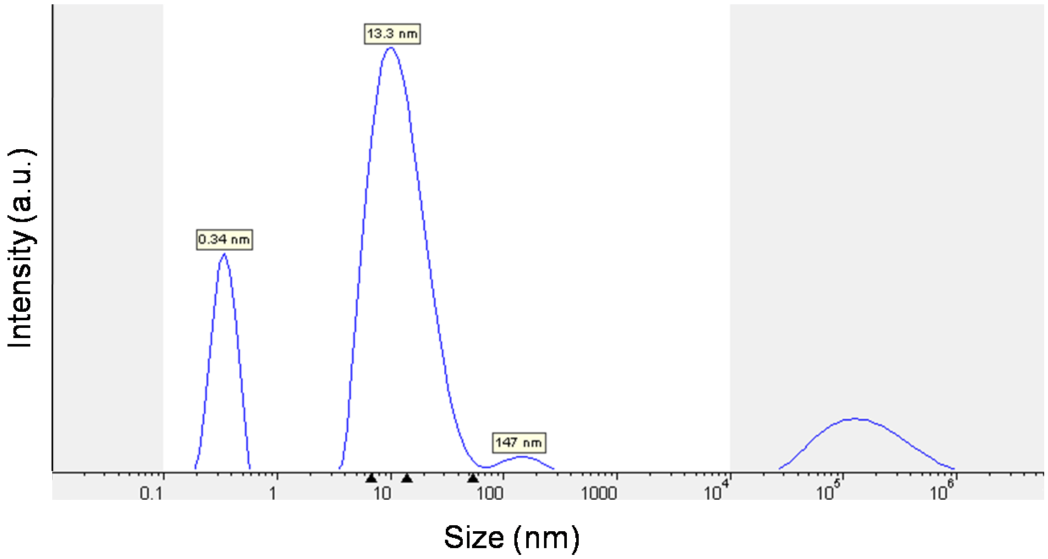


Figure A12 DLS graph of CTA-functionalized SA15 NP (SA15-**6**)

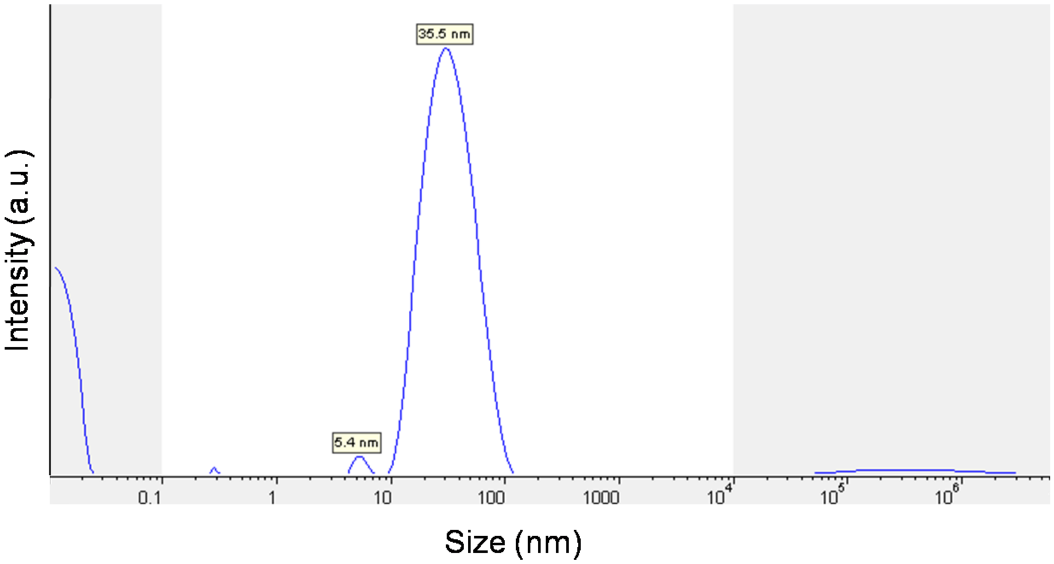


Figure A13 DLS graph of PI-grafted SA15 NP (SA15-**4c**-PI$_{1000}$)

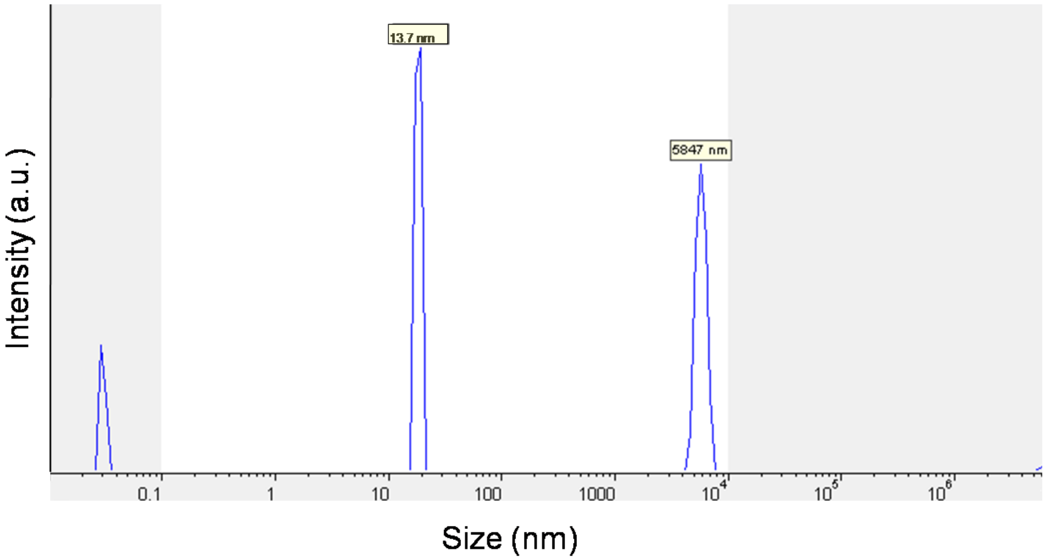


Figure A14 DLS graph of AIBN-functionalized SA15 NP (SA15-**9**)

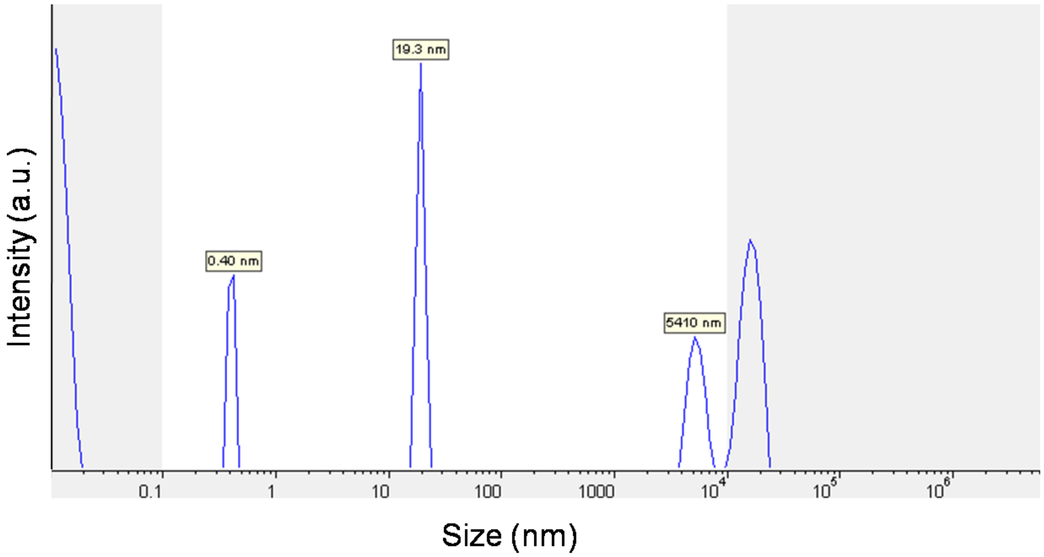


Figure A15 DLS graph of PI-grafted AE200 NP (AE200-**9** PI_{100}) with CTA in the presence of free/sacrificial initiator

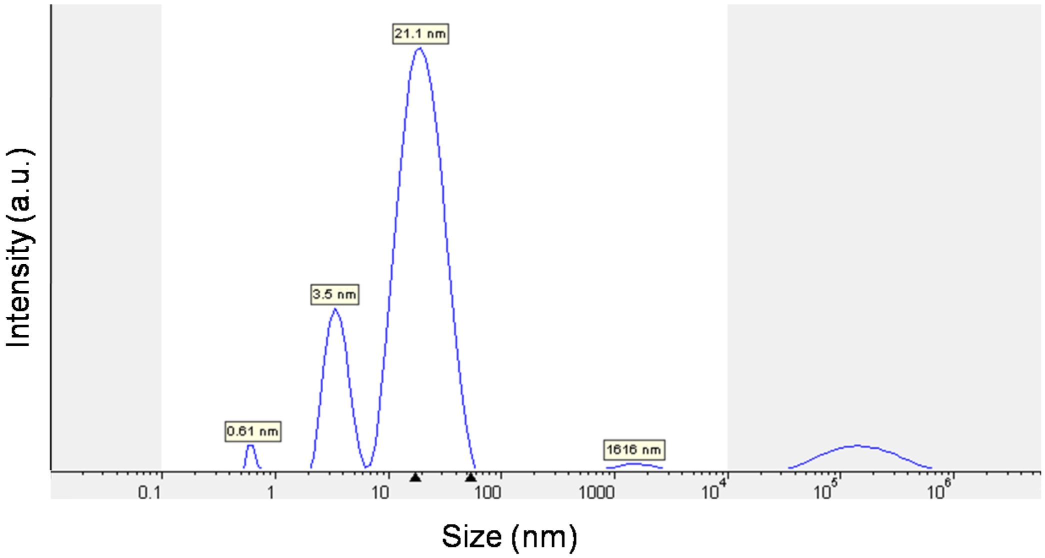


Figure A16 DLS graph of PI-grafted SA15 NP (SA15-**9**-PI_{100}) with AIBN in the presence of free/sacrificial initiator

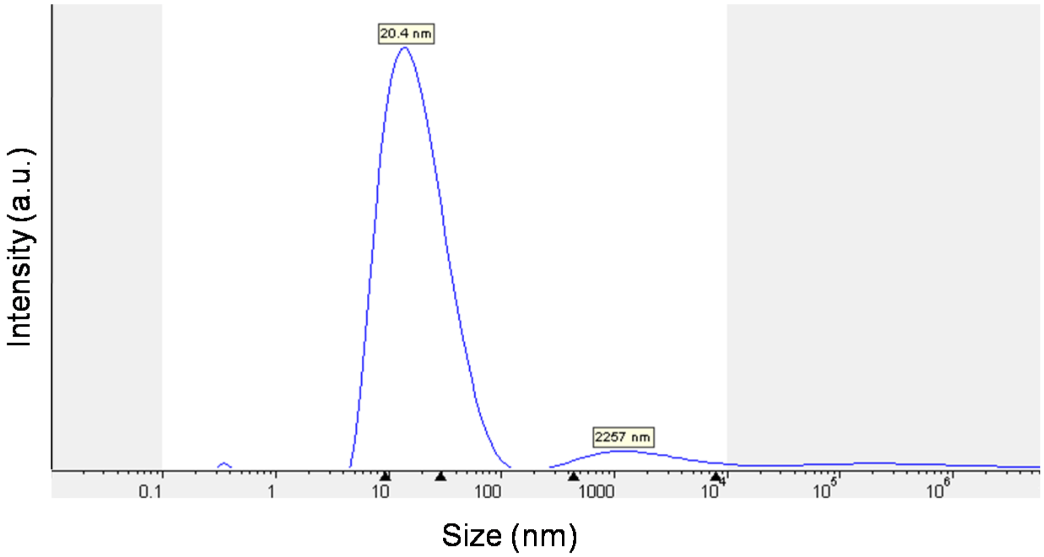


Figure A17 DLS graph of PI-grafted SA15 NP (SA15-**6**-PI$_{100}$) with AIBN in the presence of free/sacrificial initiator

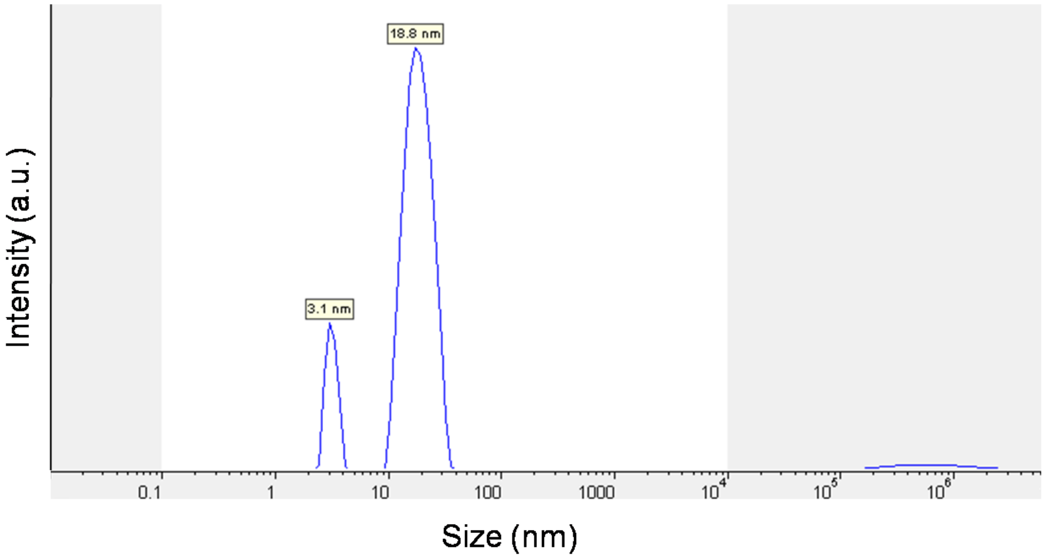


Figure A18 DLS graph of PI-grafted AE200 NP (AE200-**6**-PI$_{100}$) with DCP in the presence of free/sacrificial initiator

Halle, den 29.05.2013

Eidesstattliche Erklärung

Hiermit erkläre ich, Onur Kir, dass ich die vorliegende Arbeit selbstständig ohne fremde Hilfe angefertigt habe. Ich habe keine weiteren Quellen oder Hilfsmittel verwendet und die Werke von denen ich wörtlichen bzw. inhaltlichen Stellen entnommen habe, als solche kenntlich gemacht und angeführt.

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- Kir, O., Binder, W., H.; *Eur. Polym. J.*; **2013** (accepted, in press)
- Kir, O., Huesing, N., Enke, D., Binder, W. H.; *Macromolecular Symposia*; vol. 209 (1); **2010**; 67-70
- Binder, W. H., Pulamagatta, B., Kir, O., Kurzhals, S., Barqawi, H., Tanner, S.; *Macromolecules*; **2009**; 42 (24); pp 9457-9466

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