Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 7379–7387 **7379**
DOI: 10.1021/ma900535e

Grafting Polyisobutylene from Nanoparticle Surfaces: Concentration and Surface Effects on Livingness

Wolfgang H. Binder,*,† Ronald Zirbs,† Doris Machl,‡ and Markus Gahleitner‡

†*Institute of Chemistry, Division of Technical and Macromolecular Chemistry, Lehrstuhl für Makromolekulare Chemie, Martin-Luther Universität Halle-Wittenberg, D-06120 Halle (Saale), Germany, and* ‡*Borealis GmbH, Ahrensfelder Dreieck 19, D-16356 Ahrensfelde, Germany*

Received March 12, 2009; Revised Manuscript Received August 20, 2009

ABSTRACT: We report on the grafting-from living cationic polymerization of isobutylene from SiO_2-nanoparticles surfaces. After modification of the NP-surfaces (SiO_2; 6 nm) initiators (I) for the cationic polymerization of isobutylene (IB) were grafted onto the NP surface in variable densities (0.1−0.85 molecules initiator/nm^2). With densely packed initiators (0.85 molecules initiator/nm^2) PIB-brushes with controlled molecular weights (5000−50 000 g mol^{-1}) could be obtained. Various concentration-ranges of initiator-moieties in solution as well as isobutylene were studied, revealing a controlled polymerization process only in the range between [I] = 0.4−30 mM and [IB] = ∼0.04−3.3 M without the use of sacrificial soluble initiating systems, thus enabling a high-volume density polymerization of grafted nanoparticles without homopolymer formation. At high grafting densities (0.6−0.8 initiator molecules/nm^2), the polymerization proceeded with three different rate-constants, with a slower polymerization at the beginning and increasing rates of polymerization after ∼300 and 600 s, respectively. With reduced initiators densities (below 0.4 molecules initiator/nm^2) loss of control over the polymerization process and a significant change of the polymerization kinetics was observed.

Introduction

Surface-induced polymerization reactions (grafting-from-methods)[1−5] often constitute an important and fruitful combination of controlled polymerization methods with surface and interface functionalization.[4,6] Thus, a large variety of polymerization reactions from surfaces have been described generating polymer brushes in variable density, taking advantage of the use of controlled radical polymerization (such as ATRP,[2,3,7−12] NMP,[12,13] RAFT[12]), living anionic[14] or living cationic polymerization.[14] Planar surfaces (such as Au−,[15] SiO_2[16]), or curved surfaces (i.e.: those originating from nanoparticles (Au−,[17,18] SiO_2−,[9] Fe_2O_3−[13]) have been used as structural surfaces, generating core−shell nanoparticles or polymer-brushes[19] on surfaces in variable densities.[20]

Besides other methods, the ATRP- and cationic-polymerization methods in particular have been shown to display highly efficient results (with respect to grafting-density,[21] brush-properties), being restricted only by the limited amount of polymerizable monomers via these methods. When compared to anionic-grafting-from methods, the equilibrium between active and dormant species in controlled radical and cationic polymerization methods allows the efficient control of the amount of active species on the surface, thus eliminating many side-reactions or density limitations present in anionic polymerization due to charge-repulsion of the active species. However, in order to efficiently control the equilibrium between active and dormant species,[22] soluble initiators (also termed sacrificial initiator) have been used, to effect a sufficient amount of counterreactive molecules, thus leading to the presence of the equilibrium and thus avoid fast loss of the active species from the surface during the polymerization reaction.

In early work, we[23,24] and others[25,26] have been exploiting cationic polymerization of polyisobutylene or poly(styrene) to effect the grafting from the surface of silica-nanoparticles, thus generating defined SiO_2-nanoparticles with grafted PIB-chains of controlled chain length. In contrast to the work of Faust et al.[25] and Brittain et al.,[26] who reported on the grafting-from-polymerization of PIB and PS from planar surfaces, we are focusing on grafting-from living cationic polymerization-reactions from nanoparticle surfaces. As the grafting-from polymerization of PIB offers the generation of nanocomposite-materials with highly valuable properties, the question of a concentration dependent synthesis of the final nanocomposites in various concentration ranges is crucial. Furthermore, the development of reaction systems devoid of sacrificial initiator molecules in solution arose, thus optimizing the amount of graft-product in one single-batch-reaction system without the need to separate soluble homopolymer from the grafted-product. However, in this respect two questions occurred:

(1) What is the minimum and maximum concentration of initiator on a nanoparticles surface able to initiate a living polymerization of PIB[27,28] during a grafting-from procedure? As most living polymerization reactions of polyisobutylene are conducted within a relatively limited range of monomer, initiator, and co-initiator concentrations,[29−36] the increase of the monomer concentration to achieve an amount of polymer of more than 10% in the reaction mixture can lead to a loss of livingness in the reaction system. A compilation of the conditions of concentrations in polyisobutylene polymerization over the past decades (see Figure 1 for a diagram on the commonly used [isobutylene], [initiator] concentrations reveals relatively small borders, limiting the absolute concentrations of [IB][25,34,37−43] between 0.2 and 2 M and the concentration of initiator [initiator] = 2−30 mM. At concentrations above and below, only a

---

*Corresponding author. E-mail: wolfgang.binder@chemie.uni-halle.de.

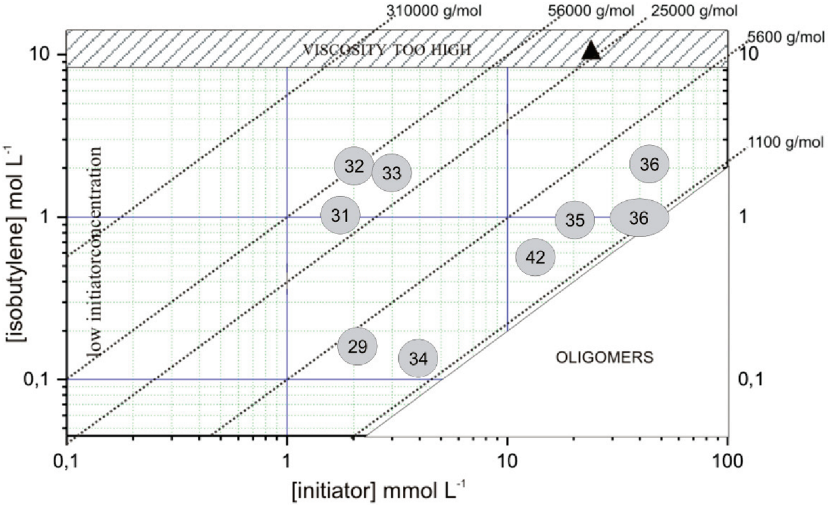


Figure 1. Overview on the living cationic polymerization of isobutylene in selected examples, citing representative references with respect to the used concentrations of initiator (I) and isobutylene (IB) and the achieved molecular weight. The diagram gives the citations within the brackets.

few results for a truly living cationic polymerization of PIB have been reported.

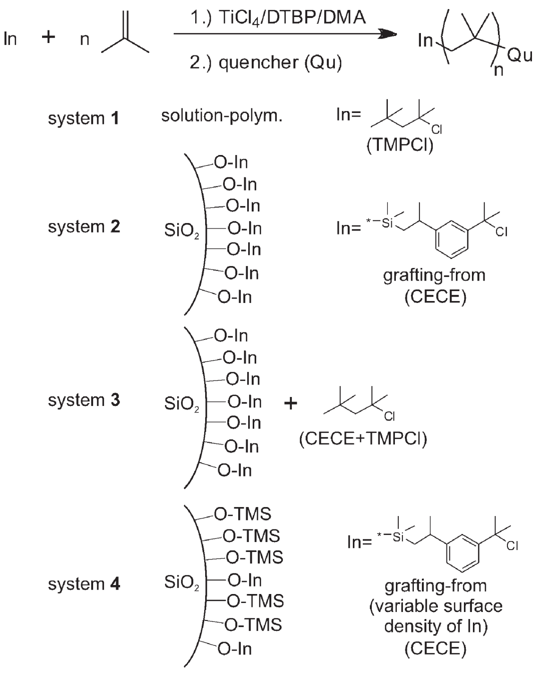
(2) How does the density of initiator molecules on the surface of the SiO_2-nanoparticles influence the livingness of the subsequent polymerization process *without* the use of a sacrificial initiator molecules present in solution? For instance, the grafting-from methods in the case of ATRP requires a delicate balance between the active and dormant species often controlled by the addition of Cu(II) species used to drive the equilibrium to the inactive (dormant) species in order to achieve a uniform polymer brush.[8,10] Recently, Vancso et al.[44] have demonstrated significant kinetic effects when using different grafting-densities in the ATRP of PMMA from surfaces, demonstrating effects of "crowded" initiators on the surfaces, leading to an increase of termination reactions with increasing amounts of initiators or the surfaces. In the case of living cationic polymerization the equilibrium between active and dormant species are more complex, including multiple Lewis acid molecules (i.e.: $[Ti_2Cl_9]^-$ complexes, according to the model of Storey[36] or the model of Puskas et al.[45,46]).

The present publication investigates concentration effects in the living carbocationic polymerization of isobutylene, comparing concentration effects in solution as well as via grafting-from polymerization from nanoparticles surfaces. Moreover, effects of either the concentration of initiating moieties on a surface, or of the absolute concentration of initiating moieties in solution are studied (see Scheme 1), thus investigating three different polymerization systems to nail down the borders of minimal- and maximal initiator concentrations to still effect a living polymerization of isobutylene from nanoparticle surfaces. Kinetic experiments monitoring the consumption of isobutylene are conducted to study the effects of monomer and initiator concentrations on the polymerization process.

Experimental Section

General Data. ^1H and ^{13}C spectra were recorded at room temperature on a Varian Gemini 2000 (400 MHz) and a Varian Unity Inova 500 (500 MHz) FT-NMR spectrometer. $CDCl_3$ (Isotec Inc. 99.8 atom % D) was used as solvent for NMR-spectroscopy. Chemical shifts were recorded in parts per million (δ) and referenced to residual protonated solvent ($CDCl_3$: 7.26 ppm (^1H) and 77.0 ppm (^{13}C)). GPC analysis was performed on a Viscothek VE 2001 system using a Styragel linear column GMH_{HR}; THF was used as carrier-solvent at 1 mL/min at RT. Polystyrene standards (M_p = 1050−1 870 000 g/mol) and polyisobutylene standards (PSS 340−374 000 g/mol) were used for conventional external calibration using a Waters RI 3580 refractive index detector.

Scheme 1



Solvents/Reagents. The silica nanoparticles (Degussa Aerosil AE200; r = 6 nm, surface = 200 m^2/g; Degussa Aerosil OX50; r = 20 nm, surface 50 m^2/g) were used as purchased. The NP's were dried in high vacuum at 0.1 mbar and 50 °C for 48 h and used immediately after drying. Dichloromethane was dried over CaH_2 refluxing for 24 h hours and distilled directly prior use. Hexane used for the polymerization reactions was distilled under reduced pressure and then refluxed in a mixture of concentrated sulfuric acid (98%; 50 mL/L hexane) and oleum (10 mL/L hexane) under continuous stirring for 48 h to remove olefins. After cooling to room temperature, the hexane was washed 5 times with water, dried with sodiumsulfate (anhydrous), refluxed with CaH_2 for 48 h and purified by distillation. Titaniumtetrachloride was distilled under reduced pressure and stored in a cap-seal flask until use. Di-*tert*-butylpyridine (DtBP) and *N,N*-dimethylacetamide (DMA) were used as purchased (SigmaAldrich, p.a. chemicals, dried, cap-seal flasks). 2-Chloro-2,4,4-trimethylpentane (TMPCl)[37] and 3-(1-chlorodimethylsilylmethyl)ethyl-1-(1-chloro-1-methyl)ethylbenzene (CECE)[25] were synthesized according to the literature and stored at −24 °C before use.

Polymerization of Isobutylene in Solution. The exact polymerization process in solution is analogous to the "grafting-from"-polymerization part. In a typical experiment, the polymerization of IB was carried out in *n*-hexane/DCM 65/35 (v/v) at a temperature of −80 to −65 °C using following concentrations: $[\text{initiator}] = 0.1$ to $40\ \text{mmol L}^{-1}$, $[\text{DTBP}] = 3\ \text{mmol L}^{-1}$, $[\text{IB}] = 0.1$ to $10\ \text{mol L}^{-1}$, $[TiCl_4] = 80\ \text{mmol L}^{-1}$ and $[\text{DMA}] = 5\ \text{mmol L}^{-1}$. The resulting polymers were isolated by precipitation in methanol, dried, and then analyzed.

Polymerizations were conducted in a HighTec-Zhang glass-reactor (200 mL), including automatic cooling via an external cryostat under an argon atmosphere and a FT-IR spectrometer VERTEX 70 (Bruker), coupled to a fiber-module MIR, 5 H, which was used to collect IR spectra during the polymerization-process (9 s/spectra, 4 scans/spectrum). Each spectrum was collected over the spectral range of 3000−800 cm^{-1}. The conversions of the polymerizations were determined by monitoring the intensity of the absorbance of the C−C double-bond-deformation−oscillation (910−880 cm^{-1}).

The temperature during the polymerization was monitored, revealing changes from −80 to −65 °C (see temperature-profile in the Supporting Information). Despite the use of a highly potent cryostat, this temperature profile proved to be the same, irrespective whether grafting-from or pure solution polymerization was conducted. The temperature of the polymerization is thus defined by the profile shown, ranging between −80 to −65 °C.

Synthesis of Initiator-Modified SiO_2−NPs[25]. The dried NPs (under Ar atmosphere) were dispersed in dichloromethane (30 mL/g NP), DTBP (0.3 mL/g NP), CECE (varying concentrations) and trimethylchlorosilane (TMSCl) (sum of CECE and TMSCl: 7 mmol/g NPs, which corresponds to ∼10 equiv of the theoretical amount of Si−OH binding sites on the NP surface) were added and the mixture was stirred at +4 °C for 24 h. The initiator-modified NPs were separated via ultracentrifugation (5000 U/min). Several redispersion (cold, dry dichloromethane) and centrifugation steps (5000 U/min) provided pure initiator-modified NPs without any residual, soluble initiator. The NPs were dispersed in dry dichloromethane and stored at (−24) °C until use. The density of bound initiator could be determined using solid-state^{29}Si NMR and TGA methods (see Supporting Information).

Synthesis of Polyisobutylene-Grafted NPs. The following polymerization procedure describes a typical way for the production of a fully PIB-covered (0.85 PIB chains per nm^2) 12 nm silica−NP core−shell nanoparticle. All used glassware and stirrers are dried at 100 °C under vacuum, fitted in hot condition and cooled under a constant flow of dry argon. To ensure a controlled character of the polymerization all polymerization steps were performed under a dry argon atmosphere. The polymerization was done in a 250 mL three-necked-flask fitted with a mechanical stirrer, an Ar inlet and a rubber septum. Then 70 mL of purified *n*-hexane, 200 μL of *N,N*-dimethylacetamide (DMA), and 200 μL of di-*tert*-butylpyridine (DtBP) were put inside the three-necked flask and cooled to −80 °C. At this temperature, the initiator-modified NPs were dispersed in 35 mL of dichloromethane and added to the reaction mixture. In the meantime, the isobutylene gas was dried with sodium hydroxide and condensed into a second flask at −80 °C. After addition of 3 mL of titanium tetrachloride into the reaction flask, the liquid isobutylene (31 mL) was added rapidly into the polymerization flask using a syringe. After 30 min at −80 °C, the polymerization was quenched by adding dry methanol (15 mL). The solution was stirred again at −80 °C for 30 min. Subsequently, the polymerization solution was concentrated under reduced pressure to about one-third of the starting volume and slowly poured into a heavily stirred 1:1 mixture of methanol and acetone (800 mL). After 10 min, the stirring was stopped and the products were collected by decanting the solvent. Cleaning was performed by dissolving the product in a small amount of hexane (10 mL/g) and precipitate again in a 1:1 mixture of methanol and acetone. Further separation of the soluble polyisobutylene and the core−shell nanoparticles could be achieved by dissolving the product in pure hexane (100 mL/g) and use centrifugation or sedimentation to separate the PIB-grafted nanoparticles. This method allowed separation of the modified NPs from the soluble PIB in a reproducible manner. In a typical experiment, the polymerization of IB via a grafting-from technique was carried out in *n*-hexane/DCM 65/35 (v/v) at −80 °C using the following concentrations: $[\text{initiator}] = 0.1{-}40\ \text{mmol L}^{-1}$, $[\text{DTBP}] = 3\ \text{mmol L}^{-1}$, $[\text{IB}] = 0.1{-}10\ \text{mol L}^{-1}$, $[TiCl_4] = 80\ \text{mmol L}^{-1}$, and $[\text{DMA}] = 5\ \text{mmol L}^{-1}$.

Characterization of Grafted Chains. After centrifugation, the amount of soluble PIB and the amount of modified NPs was determined gravimetrically. For GPC analysis of the bound PIB, 0.5 g of PIB-grafted NP's were dissolved in 5 mL of hexane, 5 mL of water, and 5−10 drops of concentrated hydrofluoric acid, and the resulting mixture was shaken for 15 min. Afterward, the hexane phase was separated, a small amount of potassium carbonate was added, and the solution was evaporated under reduced pressure. The residue was dissolved in THF, filtered through a syringe filter (0.2 μm), and measured via SEC.

Furthermore, all samples were also subjected to TGA, DLS, and NMR analyses, in order to achieve a calculation of the surface coverage:

(a) Calculation of initiator-grafted nanoparticles: the initiator modified NP's were characterized using TGA and solid state ^{29}Si NMR (Supporting Information). The data obtained from the ^{29}Si NMR clearly indicate that at least 50% and 60% of all available Si−OH binding sites on the SiO_2 surface are modified. These results could be supported via TGA-measurements. The total amount of initiator-moieties present on the SiO_2 surface could be calculated as 0.8−0.85 mmol of initiator bound to 1 g of the AE200 silica nanopowder. The theoretical amount of Si−OH groups of a silicondioxide surface was calculated (and described in the literature) to be approximately 1.2 mmol/g of SiO_2−NP.

(b) PIB-grafted SiO_2−NP: to estimate the amount of binding sites on the surface which initiates a polymerization, a series of polymerizations have been conducted. Via a combination of SEC (yielding M_n of the cleaved PIB chains from the NP-surface) and TGA (total amount of grafted organic material) the number of polymer chains grafted to the surface could be identified.

TEM. Samples were measured using a Tecnai 12 (FEI) 120 KV equipped with a CCD-Camera (Gatan Bioscan 792) at 100 KV. The samples were dissolved in *n*-heptane and 1 drop of this solution was placed together with one drop of acetone onto a Pioloform coated 3.05 mm grid (AGAR, hexagonal 100 mesh, copper) and measured directly.

TGA. Samples were measured using a NETZSCH TG 209C equipped with a NETZSCH TASC 414/4 controller. The temperature range was 30 to 900 °C and the heating rate used was 10 K/min in all cases. The samples (∼15 mg) were weighted into a platinum cup and heated under a constant flow of synthetic air of 25 mL/min. Data interpretation was done using NETZSCH Proteus software.

Results and Discussion

The basic investigations rely on four different polymerization systems to study concentration effects of isobutylene and initiator moieties, all based on the living cationic polymerization of isobutylene (see Scheme 1). System 1: the conventional solution polymerization of isobutylene (using TMPCl as initiator). This system served as control experiment to study major effects of the concentration on the quality of the polymerization process. System 2: the *grafting-from* polymerization using modified SiO_2-nanoparticles, with a complete-dense layer of grafted initiator moiety. System 3: the same polymerization as in system 2, but investigated with additionally added soluble initiator in order to check for effects on the necessity of this soluble initiator. System 4: the *grafting-from* polymerization with a variable density of initiator moieties, varying between ~0.1 to 0.85 molecules of initiator/nm^2 (SiO_2−NP).

Table 1. Results for the Surface Modification of SiO_2 Nanoparticle (r = 6 nm) with Initiator (CECE) and Trimethylsilyl Chloride (TMSCl)

	content of CECE [mol %]	CECE/TMSCl [mmol/mmol]	weight loss[b] (TGA) [%]	titration experiments[a] [initiator/nm^2]	TGA experiments[a] [initiator/nm^2]
NP1	100	7.4/0	7	0.85	0.8
NP2	75	5.5/1.9	6	0.6	0.6
NP3	50	3.7/3.7	5	0.4	0.4
NP4	25	1.8/5.6	4	0.25	0.2
NP5	10	0.7/6.7	2	0.1	< 0.1[c]
NP6	1	0.07/7.3	2	< 0.1[c]	< 0.1[c]
NP7	0	0/7.4	< 2[c]	0	0

[a] For calculations and exact data, see Supporting Information. [b] Weight %. [c] Below the detection limit of the instrument.

The current paper is divided into four parts, starting with the preparation of surface-bound initiator in variable concentration, the grafting-from polymerization under increasing amounts of nanoparticles in solution, as well as the variation of initiator-density on the nanoparticle surface. Subsequently, kinetic investigations of the grafting-from process via IR monitoring are provided.

Synthesis of Initiators and Surface-Bound Initiator Nanoparticles. The generation of surface-bound initiator was accomplished according to a procedure of Faust et al.[25] by immobilizing CECE initiator to SiO_2−NP's from Degussa-AG, sized 6 nm. Efficient drying conditions were necessary in order to achieve complete reaction on the NP-surfaces. A detailed quantification via TGA measurements (see Table 1) revealed the generation of surfaces with amounts corresponding to the maximum-coverage with initiator molecules (**NP1**: 0.85 molecules/nm^2). Moreover, additional solid-state ^{29}Si NMR-spectroscopy via integration of the respective surface bound Q^1, Q^2, and Q^3 sites allowed confirming the chemical structure of the bound initiator (see Supporting Information). Values from TGA were additionally checked by titration experiments (checking for active *tertiary* chlorine), revealing values in accordance with the TGA measurements. The generation of reduced densities of initiator molecules on the surface was achieved by coreaction of CECE−Cl with trimethylsilyl chloride (TMS−Cl) in variable amounts, leading to grafted amounts of initiator ranging from 0.6 initiator molecules to ~0.1 initiator molecules/nm^2. The determination of

Table 2. Results for the Living Cationic Polymerization of Isobutylene in Solution and via *Grafting-from* Using NP1[a]

	entry	initiator	[I] (mM)	[IB] (M)	[IB]/[I]	M_n(calc)[c]	M_n(SEC)	M_n(SEC)/M_n(calc)	M_w/M_n	RN
[IB] = const	1	TMPCl	0.4	0.5	1250	70 298	72 000	1.02	1.25	4.7
	2	system 1	1	0.5	500	28 215	31 000	1.1	1.2	4.7
	3		1.9	0.5	250	14 188	16 250	1.15	1.1	4.7
	4		9.6	0.5	50	2966	3200	1.08	1.1	4.7
	5		30.8	0.5	15.6	1037	2000	1.93	1.2	4.7
[I] ~ const	6	TMPCl	9.8	0.2	20	1282	1800	1.4	1.1	1.9
	7	system 1	9.8	0.3	30	1843	2000	1.08	1.1	2.8
	8		9.3	0.9	100	5771	5900	1.02	1.1	8.5
	9		8.6	1.7	200	11 382	13 500	1.19	1.2	16.0
	10		7.6	3	400	22 604	25 800	1.14	1.25	28.2
	11		7.1	3.6	500	28 215	30 000	1.06	1.3	33.8
	12		6.1	4.9	800	45 048	60 000	1.33	1.8	46.1
	13		5.6	5.6	1000	56 270	62 000	1.1	2.4	52.6
[IB]/[I] = const	14	TMPCl	0.1	0.04	443	25 017	28 000	1.12	1.85	0.4
	15	system 1	1	0.5	500	28 215	29 100	1.03	1.3	4.7
	16		1.9	0.8	443	25 017	26 100	1.04	1.25	7.5
	17		7.4	3.3	440	24 848	25 300	1.02	1.1	31.0
	18		22	9.7	443	25 017	22 000	0.88[d]	1.06	91.2
							6000		1.2	
[I] = const	19	CECE[b]	6	0.5	83	4657	4500	0.97	1.2	2.6
	20	system 2	5.4	1.7	316	17 730	45 000	2.54	1.3	8.9
	21		4.4	3.6	811	45 505	53 000	1.16	1.1	18.8
	22		3.8	4.9	1285	72 100	82 000	1.14	2.8	25.5
[IB]/[I] = const	23	CECE[b]	0.06	0.04	640	35 910	80 000	2.23	1.9	0.2
	24	system 2	0.6	0.44	704	39 501	48 000	1.22	1.3	2.3
	25		1.2	0.8	674	37 818	53 000	1.40	1.2	4.2
	26		4.6	3.3	714	40 062	45 000	1.12	1.3	17.2
	27		13.8	9.7	705	39 557	57 000	1.44	2.3	50.5
[IB] = const	28	CECE[b]	0.25	0.5	2000	112 220	110 000	0.98	1.6	2.6
		system 2								
	29	TMPCl+ CECE	0.5 + 0.5	0.5	500	28 215	30 100	1.07	1.25	[e]
	30	system 3	1 + 1	1	500	28 215	29 500	1.05	1.15	[e]
	31		5 + 5	2	200	11 382	13 200	1.16	1.15	[e]

[a] Polymerization conditions and obtained molecular weights are given for each entry. Yields in all cases are above 95% of isolated polymer. RN (run numbers) are calculated according to Storey et. al.[47] [b] Using **NP1**: (0.85 molecules of initiator/nm^2). [c] Calculated as [IB]/[I] × M(isobutylene); [I] corresponds to the experimentally determined amount of initiator bound on the surface (see Table 1). [d] Multimodal distribution. [e] Not calculated due to mixture of different initiators.

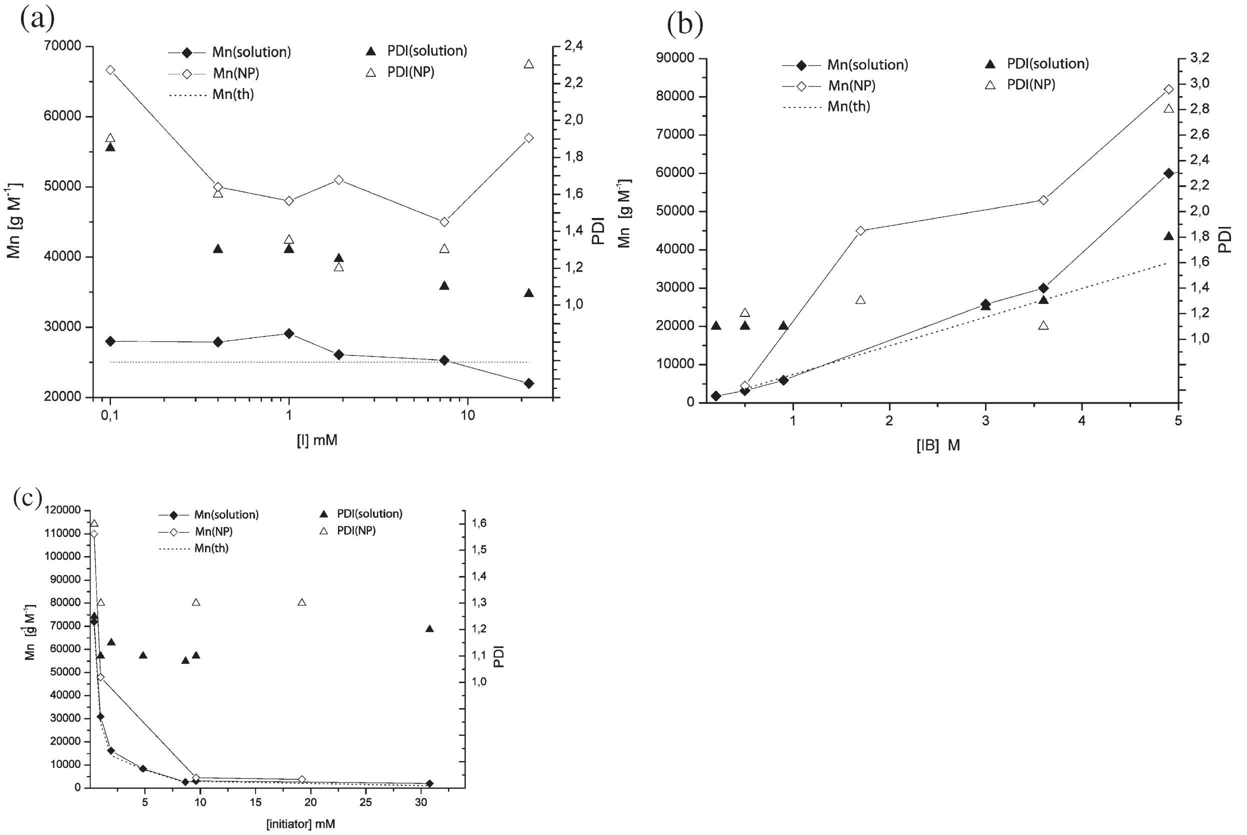


Figure 2. Results for polymerization experiments M_n and M_w/M_n = PDI (black symbols = solution polymerization, white ones = "*grafting-from*" polymerization (**NP1**)) with (a) constant [monomer]/[initiator] ratio ([IB]/[I] = 443; projected molecular weight M_n = 25 000 g·mol^{-1}); (b) with varying monomer concentration [IB] = 0.2−5.6 M^{-1} with [I] = 5.6−9.8 mM and (c) with variable initiator concentration [I] = 0.4−30.8 mM, with [IB] = 0.5 M respectively. The triangles represent the polydispersities (PDI) obtained by GPC while the squares mark the obtained M_n. [DTBP] = 0.003 M; [TiCl$_4$] = 0.08 M; [DMA] = 0.005 M; 65/35 hexane/DCM; at T = (−80 to −65 °C).

low-surface coverage however (Table 1, **NP5 − NP8**: below 10 mol % of active CECE initiator in the reaction mixture) was difficult due to the detection limit by both methods (acid-base titration and TGA). These experimentally determined values were then used as the basis for all subsequent calculations for the graft-polymerization reactions.

Polymerization of Isobutylene under Variable (Solution) Concentration. *Polymerization*. The soluble TMPCl- as well as the surface-bound CECE-initiators were used for the living cationic polymerization reactions of isobutylene, varying (a) the amount of the isobutylene-concentration and (b) the amount of the initiator-concentration as shown in Table 2. Results for the solution-polymerization are shown in entries 1−18 (*system 1, initiated by TMPCl*); those for the graft-polymerization in entries 19−27 (*system 2, initiated by surface bound CECE− NP1*). Some examples of *grafting-from* reactions in the presence of soluble initiator (soluble TMPCl plus surface bound CECE on **NP1**) are shown in Table 2, entries 28 −30 (*system 3*). The data were evaluated by comparing the calculated molecular weight (via the monomer/initiator-ratio) with the experimental M_n (SEC) and the respective polydispersity (M_w/M_n).

In conventional solution polymerization, the varied parameters concern the initiator-concentration (ranging from 0.1 to 22 mM) and the isobutylene concentration [IB] = 0.2−9.7 M^{-1}. As visible in entries 1−11, moderate and medium concentrations of initiator and isobutylene yield polyisobutylene polymers with the expected molecular weights and low polydispersities (see also Figure 2a). At [IB] above ~3.6 M (entries 12, 13 and 18), the polydispersity is strongly increased (values above 1.4), thus indicating loss of control over the polymerization reaction due to high viscosity effects. Surprisingly, the molecular weights stay within the expected range, although with broad molecular weight distribution. Similar aspects are observed at very low concentrations of initiator [I] = 0.1 mM (entry 14), leading to high PD-values, indicative of an insufficient amount of active species, leading to a disturbed equilibrium between the active/dormant species. Assuming a second-order kinetics with respect to the co-initiator ([TiCl$_4$]),[36] the run number of living cationic polymerization can be defined according to Puskas et al.[47] as follows:

$$\mathrm{RN} = k_p[\mathrm{M}]/k_{-i} \tag{1}$$

with the run number (RN), the rate of propagation (k_p) and the apparent rate of ion collapse (k_{-i}) and [M] = [IB] as the concentration of monomer in the polymerization mixture. Independently, Storey et al.,[48] Faust et al.,[49,50] and Puskas et al.[46] have determined and reported the corresponding k_p and k_{-i} values for the polymerization of isobutylene (k_p: 7 × 10^8 M^{-1}·s^{-1}; k_{-i}: 7.5 × 10^7 s^{-1}; k_i (rate of ion ionization) = 15 M^{-2}·s^{-1}). These values were used to to estimate the run number (RN) for the conditions of our grafting-from polymerizations (see Table 2). Thus, at very low concentrations of [IB], the run number would be lower than 1, at already medium concentrations of isobutylene ranging between 0.5−1 M about 4−10, and at higher concentrations of isobutylene (limiting concentration of ~3.3 M) the RN approaches 30, increasing with increasing concentration of IB. Thus, it can be concluded that, at high concentrations of IB, the polymerization is not proceeding in a controlled

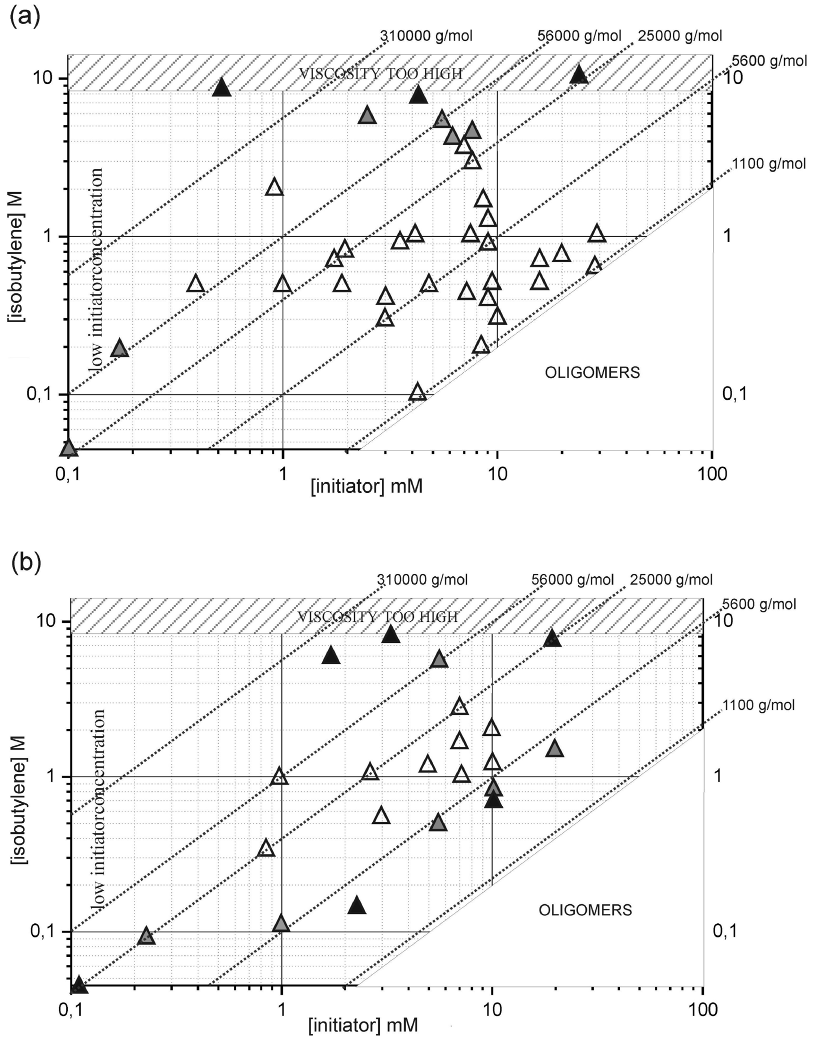


Figure 3. (a) Investigations of the polydispersity of solution polymerization with varying concentrations of [IB] and [initiator = TMPCl; system 1] The white symbols represent the polymerizations with an PDI < 1.4; the gray ones 1.4 < PDI < 1.8 and the black ones a PDI > 1.8 (PDI < 1,4 (△); 1,4 < PDI < 1,8 (gray triangle) and PDI > 1,8 (▲)) . [DTBP] = 0.003 M; [$TiCl_4$] = 0.08 M; [DMA] = 0.005 M; 65/35 hexane/DCM; at T = (−80) °C. (b) Investigations of the polydispersity of grafting from polymerization with varying concentrations of [IB] and [initiator = CECE on **NP1**; system 2] The white symbols represent the polymerizations with an PDI < 1.4; the gray ones 1.4 < PDI < 1.8 and the black ones a PDI > 1.8 (PDI < 1,4 (△); 1,4 < PDI < 1,8 (gray triangle) and PDI > 1,8 (▲)) . [DTBP] = 0.003 M; [$TiCl_4$] = 0.08 M; [DMA] = 0.005 M; 65/35 hexane/DCM; at T = (−80 to −65 °C) .

manner, thus limiting the maximum amount of the generated polymer per volume inside the reaction.

All initial *grafting-from* reactions were performed with the maximum-density of initiator [I] on the NP-surface (**NP1**; 0.85 initiator molecules/nm^2), thus varying the amount of initiator only via the amount of nanoparticles in solution during polymerization. The grafting-from polymerization reactions (*system 2*/Table 2/entries 19−27) show similar trends as the solution polymerization (see also Figure 2b). Addition of soluble initiator (see Table 2: entry 28−30 and Figure 2c) did not improve or change the results of the polymerization reaction. By comparing the results between the solution polymerization (Figure 3a) and the grafting-from polymerization (Figure 3b), it is obvious that the difference is minor with respect to the borders of isobutylene and initiator concentration limits. In both cases, isobutylene concentrations higher than [IB] $\sim$ 3.3 M^{-1} and initiator-concentrations lower than [I] $\sim$ 0.1 mM lead to uncontrolled polymerization reactions of isobutylene.

Characterization of Grafted Nanoparticles. The obtained PIB-grafted nanoparticles were characterized via TEM, DLS, and TGA in order to verify the core/shell structure and the uniform controlled polymerization process. Parts a and b of Figure 4 show the cryo-TEM-micrographs of two PIB-grafted nanoparticles with shorter (M_n = 5000 g·mol^{-1} (r (NP) = 6 nm (SiO_2 core) + 3 nm (PIB), and longer M_n = 15000 g·mol^{-1} (r(NP) = 6 nm (SiO_2 core) + 7 nm (PIB)). The core size agrees well with the expected values of ~3 nm and ~6.5 nm, respectively.[19] The nanoparticles were also characterized in solution using dynamic light scattering (DLS, Figure 4c) using tetrahydrofuran as good solvent for the PIB brush. In accordance with the theoretical predictions of Faust et al.[25] for PIB brushes, as well as the calculations of Brittain et. al,[19] comparable results are obtained with respect to the brush thickness. TGA results (see Supporting Information) confirm the grafting densities when starting the grafting-from polymerization using **NP1** as initiator.

Grafting-from Polymerization of Isobutylene with Variable Surface-Initiator Concentration. As the variation of initiator concentration in solution yielded comparable polymerization-reactions between the pure solution and grafting-from reactions, experiments with a *variable* density of initiator on the NP-surface (0.85 - 0.1 initiator molecule/nm^2), but still constant overall concentration of initiator in solution were conducted. Results of these experiments are shown in Table 3 and Figure 5.

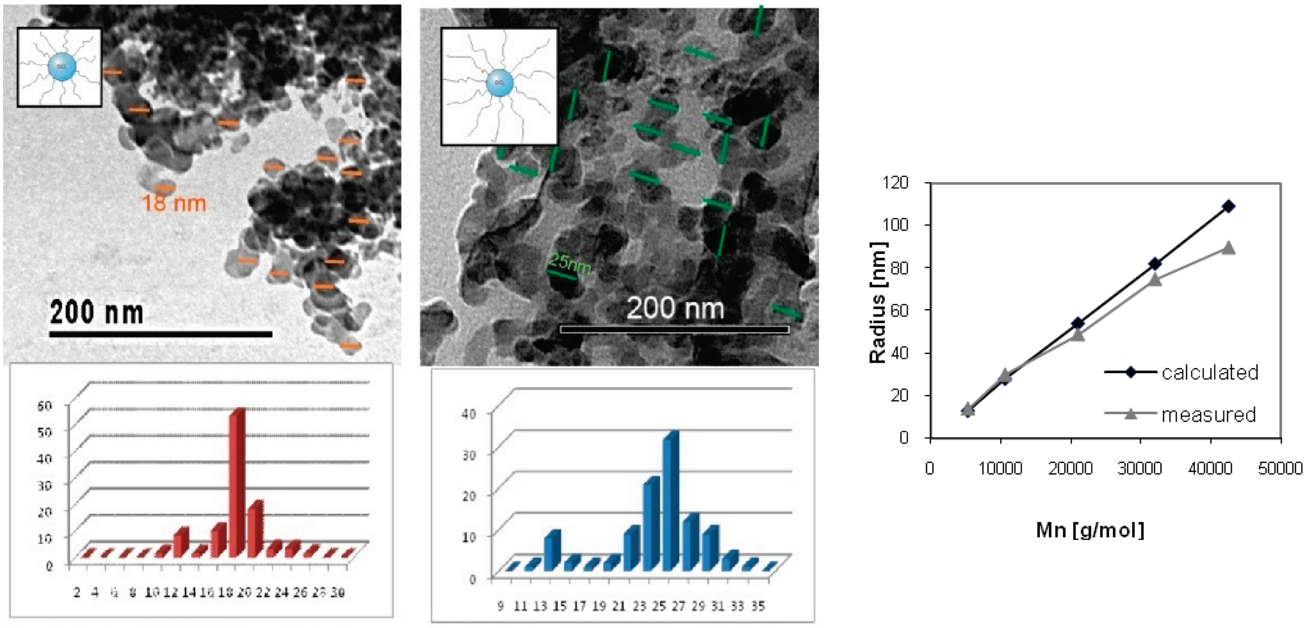


Figure 4. Cryo-TEM images and dynamic light scattering (DLS) of **NP1** grafted with with (a) 5000 g/mol PIB and (b) 15 000 g/mol PIB shells. Bottom: statistical analyses of the TEM-pictures. (c) Dynamic light scattering of **NP1** grafted with variable chain length of PIB (measured as solution in tetrahydrofuran). Samples were measured using a Tecnai 12 (FEI) 120 KV equipped with a CCD-Camera (Gatan Bioscan 792) at 100 KV. The samples were dissolved in *n*-heptane and 1 drop of this solution was placed together with one drop of acetone onto a Pioloform coated 3.05 mm grid (AGAR, hexagonal 100 mesh, cooper) and measured directly.

Table 3. *Grafting-from* Polymerization of Isobutylene Using NP1−NP6 as Initiating Systems with [I] = Constant (4 mM), but Reduced Amount of Grafted-Initiator Molecules on the NP Surface[a] (according to Table 1)

					^{1}H NMR[c]			
	M_n(calc) (g mol^{-1})	M_n(SEC) (g mol^{-1})	RN[d]	PDI	*tert*-chloride	*exo*-olefin	*endo*-olefin	M_n (g mol^{-1})[f]
NP1	50 000	58 000	5.2	1.25	50	45	5	55 000
NP2	25 000	29 000	3.2	1.3	27	38	36	25 700
NP3	55 000	62 000	[e]	1.4	25	62.5	12.5	59 600
NP4	50 000	55 000	[e]	1.8	[b]	[b]	[b]	[b]
NP5	50 000	62 000	2.6	2.3	[b]	[b]	[b]	[b]
NP6	50 000	61 000	[e]	2.8	[b]	[b]	[b]	[b]

[a] [IB] = 1.0 M; [DTBP] = 0.003 M; [TiCl$_4$] = 0.08 M; [DMA] = 0.005 M; 65/35 hexane/DCM; at T = (−80 to −65 °C). [b] Amount of polymer too low for end group-determination via ^{1}H NMR. [c] Fraction of end groups in % as determined by integration of the ^{1}H NMR. [d] RN: run number, as determined by IR-kinetic monitoring, calculated by Storey et al.[47] [e] No values determined. [f] Determined by integration of the endgroups.

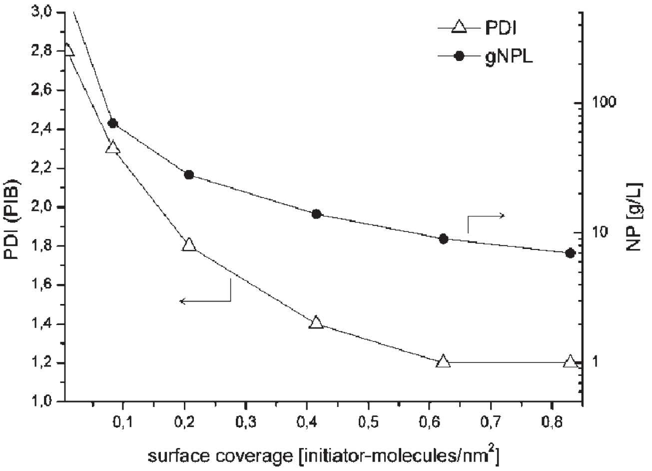


Figure 5. *Grafting-from* polymerizations of isobutylene from **NP1** to **NP6** with constant initiator concentration [CECE-surface bound = 4 mM] (△, PDI of grafted polymer; ●, g NP/L in the polymerization solution).

The initiator concentration of these polymerization reactions were held constant ([I] = 4 mM), with nanoparticles showing maximum (**NP1**), and reduced amounts of initiator on the NP surface (**NP2−NP6**). At initiator amounts of less than 0.4 molecules/nm^2 (**NP3**), the resulting grafted PIB-polymers show high polydispersities (M_w/M_n > 1.8), although with relatively good correlation to the expected molecular weights. Thus, we observed that, in contrast to the excellent comparison between solution/grafting-from polymerization in terms of absolute initiator and PIB concentration, the density of the initiator on the NP-surface strongly influenced the polymerization reaction. In order to evaluate the chemistry of the end group, the endquenched nanoparticles were directly analyzed by ^{1}H NMR spectroscopy (see supplementary). The corresponding spectra enable to analyze the fractions of monomeric *exo*- and *endo*-allyl and *tert*-chlorine end groups as estimated by integration according to the assignments by Storey et al.[42] and others.[43] It is obvious that there is only a minor change within the experimental error of integration within the different fractions of end groups, thus indicating the same mechanism for chain growth and termination during the polymerization reaction, eliminating bridging effects of the growing cations under formation of dimeric *exo*-olefinic species. Thus, despite the high grafting density of PIB-chains the probability of bridging and interference between the growing

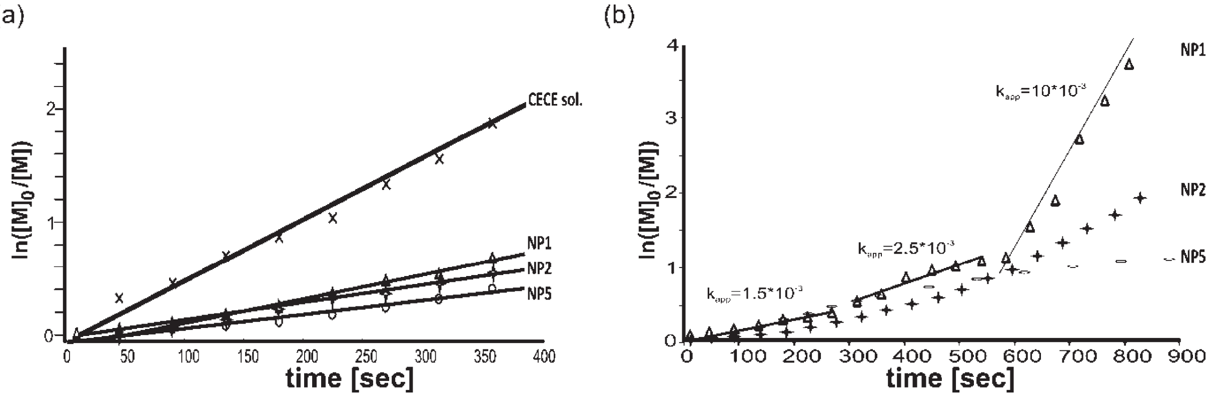


Figure 6. Kinetic investigations of the isobutylene polymerization (via inline-IR-monitoring) at various isobutylene-concentrations and during grafting-from polymerization. (a) Polymerization ln[M$_0$]/[M$_t$] vs time in the grafting-from polymerization at the following initiator concentrations: **NP1** (△) (0.85 initiator molecules/nm^2); **NP2** (four pointed star) (0.6 initiator molecules/nm^2) and **NP5** (oval) (0.1 initiator molecules/nm^2); ln[M$_0$]/[M]$_t$ in a solution polymerization. [Ini] = 0.5 mM; [IB] = 2 M; [DTBP] = 0.003 M; [TiCl$_4$] = 0.08 M; [DMA] = 0.005 M; 65/35 hexane/DCM; at T = −80 to −65 °C. (b) Expansion of the same region including the late phase of the polymerization.

chains is not observed. In contrast to polymerization in solution, where no olefinic groups were detected, the grafting-from polymeriaztions seem to involve either considerable amount of chain-transfer-reactions or carbocation-rearrangement similar to Storey et al.[42]

Kinetic Investigations: Grafting-from Polymerization of Polyisobutylene vs Solution Polymerization. Deeper insight into the polymerization was obtained by inline-IR measurements of the isobutylene polymerization relying on a method described by Storey et al.[47] Thus, the concentration of isobutylene in either the solution polymerization as well as the grafting-from polymerization of **NP1**, **NP2**, and **NP5** was measured, using the optimum conditions described before (see Figure 6).

Surprisingly, the kinetics are entirely different for the various surface-concentrations of initiator on the NP surfaces (see Figure 6, parts a and b). Thus, the monomer consumption of a polymerization initiated by **NP1** (full coverage of surface with initiators, ~ 0.85 molecules/nm^2) shows a distinct change in the kinetics after about 600 s, with a strong increase of the apparent rate of polymerization, changing from $k_{\text{app}} = 2 \times 10^{-3}\ \text{s}^{-1}$ to about $(5-10) \times 10^{-3}\ \text{s}^{-1}$ (see Figure 6b). This behavior is also observed to a lower extent with **NP2** (80% coverage of surface with initiators, leading to an absolute concentration of initiators ~ 0.6 molecules/nm^2), but not in the case of the much lower coverage of the NP-surface with initiator (**NP5** (~10% coverage of surface with initiators, leading to a concentration of initiators ~ 0.1 molecules/nm^2). The corresponding solution-polymerization using CECE as initiator yields a uniform kinetic behavior with only one apparent rate-constant ($k_{\text{app}} = 5.3 \times 10^{-3}\ \text{s}^{-1}$; corresponding to a RN of 91). To our opinion, this as a strong indication that the polymerization in the initial phase of the grafting-from process in **NP1** and—to a minor extent in **NP2**—is slowed down due to brush-effects present at the initial stages of the polymerization reaction. This effect is then reduced upon entering the brush/mushroom transition after about ~300 to 600 s, leading to an increase of the apparent rate-constant to a $k_{\text{app}} \sim 5 \times 10^{-3}\ \text{s}^{-1}$. Calculating the RN-numbers in the grafting-from polymerization, the following values are obtained for the nanoparticle surfaces with different densities (Table 3): **NP1** (RN = 5.2) and **NP2** (RN = 3.2) and **NP5** (RN = 2.6). In the case of denser grafting of initiator (**NP1** and **NP2**), a significant increase in the apparent rate of polymerization is observed during the polymerization reactions (changing from $2 \times 10^{-3}\ \text{s}^{-1}$ to $5 \times 10^{-3}\ \text{s}^{-1}$), which can be explained by the reduced steric hindrance of the growing chains, as they emerge from the curved nanoparticles surfaces. As expected, this effect is not observed in the case of **NP5** with only 10% of surface-coverage and the corresponding solution polymerization of isobutylene, using the same initiator as present on the NP surfaces.

The obtained results have revealed that there is a comparable polymerization reaction in solution and grafting-from reactions with respect to the absolute solution concentration of initiator and isobutylene, respectively. Qualitatively and quantitatively PIB-grafted silica nanoparticles with a controlled thickness of the PIB-layer can thus be obtained in high quality and in a high volume density, as the concentration of isobutylene can be increased up to ~3.3 M in the reaction medium. At higher concentrations of IB a controlled polymerization is not possible, neither in solution nor via grafting-from procedures. However, keeping the initiator concentration in a range of ([I] ~ 4 mM) (which should still lead to a controlled polymerization in solution) but reducing the number of surface-bound initiator below 0.4 initiator molecules/nm^2 results in a loss of control of the polymerization reaction. Therefore, as the formal concentration of the initiator remains constant ([I] = 4 mM), the loss of control with reduced density of initiating centers on the NP surface cannot be a consequence of disturbed activation/deactivation equilibria. Compared to planar surfaces (where the absolute concentration of initiator is too low to enable the ionization/deionization equilibrium in the quasiliving cationic or controlled radical polymerization process) the addition of soluble initiator to the polymerization system is not required. Thus, the loss of controlled polymerization can be assumed as backcoiling of the active, ionized species onto the surface of the NP, thus disturbing the equilibrium between the ionizied and the nonionized species by purely steric reasons.

However, in nearly all of our controlled grafting-from polymerizations the RN is between 5−91, which is definitely higher than i.e.: in the case of ATRP (grafting-from polymerization). We attribute this case to the much faster propagation rate constant k_{p} (PIB): $7 \times 10^8\ \text{M}^{-1}\cdot\text{s}^{-1}$ in contrast to the k_{p} (ATRP of butyl acrylate): $4 \times 10^4\ \text{M}^{-1}\cdot\text{s}^{-1}$, as reported by Matyjaszewski et al.[8] We thus conclude that the cationic polymerization can endure a much higher concentration of monomer in the *grafting-from* process than the corresponding radical polymerization reaction, thus enabling the controlled grafting-from synthesis of PIB in significant higher amounts within the reaction system.

Conclusion

We have described the preparation of PIB-grafted SiO_2 nanoparticles with uniform PIB shell via the grafting-from-living cationic polymerization of isobutylene from appropriately functionalized NP surfaces. As demonstrated by TEM, DLS, and TGA measurements, high control over the shell thickness can be obtained. Furthermore, the concentration-limits with respect to the initiator concentration and the monomer concentration (isobutylene) have been determined to be equal for the solution polymerization and the grafting-from process without the use of sacrificial initiators. The found limits of $[I] = 0.4-30$ mM; $[IB] = \sim 0.04-3.3$ M are valid if the calculated concentration of initiator form a densely packed surface on the nanoparticle, whereas in the case of less densely grafted surfaces a loss of control over the polymerization was observed.

The kinetics of the grafting-from process are slightly different for the various surface-concentrations of initiator on the NP surfaces, displaying a significant change in the rate of polymerization within the first 300−600 s in comparison to the subsequent 600−900 s of the polymerization, scaling with increasing grafting-density. As the polymerization proceeded, the rate of polymerization is increasing with a significant increase of the apparent rate constant. This as a strong indication that the polymerization in the initial phase of the grafting-from process at high initiator densities on the surfaces is slowed down due to brush effects present at the initial stages of the polymerization reaction.

The results enable (a) a qualitative estimation of the range of monomer and initiators required to still run a controlled cationic polymerization in a grafting-from reaction and (b) to maximize the amount of grafted nanoparticles within one synthetic step, since for the first time, the maximum concentrations of isobutylene have been determined, still keeping control over molecular weight and polydispersity. Further results on the use of PIB-grafted SiO_2 nanoparticles will be reported soon.

Acknowledgment. We would like to express thanks for a grant from the Austrian Science Foundation FFG 811021 for financial support. Grants from the DFG INST 271/249-1; INST 271/247-1, and INST 271/248-1 are gratefully acknowledged.

Supporting Information Available: Tables giving a detailed calculation of PIB on the nanoparticle surface and figures showing ^1H NMR spectra of the compounds **NP3**, **NP1** with grafted PIB, ^{29}Si solid state NMR of pure, unmodified NP and surface-initiator-modified **NP1**, and the temperature profile during the polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) William, J.; Brittain; Minko, S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45* (16), 3505–3512.
(2) Fukuda, T.; Tsujii, Y.; Ohno, K. *Macromolecular Engineering*; Matyjaszewski, K., Gnanou, Y., Leibler, L., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2007; Vol. *2*, pp 1137−1178.
(3) Sumerlin, B. S.; Matyjaszewski, K. *Macromolecular Engineering*; Matyjaszewski, K., Gnanou, Y., Leibler, L., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2007; Vol. *2*, pp 1103−1135.
(4) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem. Soc. Rev.* **2004**, *33* (1), 14–22.
(5) Bhattacharya, A.; Misra, B. N. *Prog. Polym. Sci.* **2004**, *29*, (8).
(6) Boyes, S. G.; Granville, A. M.; Baum, M.; Akgun, B.; Mirous, B. K.; Brittain, W. J. *Surf. Sci.* **2004**, *570* (1−2), 1–12.
(7) Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 9413–9415.
(8) Sumerlin, B. S.; Neugebauer, D.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 702–708.
(9) Ohno, K.; Morinaga, T.; Koh, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2005**, *38*, 2137–2142.
(10) Matyjaszewski, K.; Dong, H.; Jakubowski, W.; Pietrasik, J.; Kusumo, A. *Langmuir* **2007**, *23*, 4528–4531.
(11) Boerner, H. G.; Duran, D.; Matyjaszewski, K.; da Silva, M.; Sheiko, S. S. *Macromolecules* **2002**, *35*, 3387–3394 .
(12) Tsujii, Y.; Ohno, K.; Yamamoto, S.; Goto, A.; Fukuda, T. Structure and Properties of High-Density Polymer Brushes Prepared by Surface-Initiated Living Radical Polymerization. In *Advances in Polymer Science: Surface-Initiated Polymerization I*; **2006**; Springer Verlag: Berlin, Heidelberg, New York, pp 1−45.
(13) Binder, W. H.; Gloger, D.; Weinstabl, H.; Allmaier, G.; Pittenauer, E. *Macromolecules* **2007**, *40*, 3097–3107.
(14) Advincula, R. *Adv. Polym. Sci.* **2006**, *197*, 107–136.
(15) Sakellariou, G.; Park, M.; Advincula, R.; Mays, J. W.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 769–782.
(16) Zhou, Q.; Wang, S.; Fan, X.; Advincula, R.; Mays, J. *Langmuir* **2002**, *18*, 3324–3331.
(17) Dong Jin Kim; Kang, S. M.; Kong, B.; Kim, W.-J.; Paik, H.-j.; Choi, H.; Choi, I. S. *Macromol. Chem. Phys.* **2005**, *206*, 1941–1946.
(18) Ignacio García; Tercjak, A.; Zafeiropoulos, N. E.; Stamm, M.; Mondragon, I. *Macromol. Rapid Commun.* **2007**, *28*, 2361–2365.
(19) Zhao, B.; Brittain, W. J. *Prog. Polym. Sci.* **2000**, *25*, 677–710.
(20) Brittain, W.; Boyes, S.; Granville, A.; Baum, M.; Mirous, B.; Akgun, B.; Zhao, B.; Blickle, C.; Foster, M., Adv. Polym. Sci.: Surface Rearrangement of Diblock Copolymer Brushes—Stimuli Responsive Films. In *Surface-Initiated Polymerization II*; **2006**; Springer Verlag: Berlin, Heidelberg, New York, pp 125−147.
(21) Lee, H.; Matyjaszewski, K.; Yu, S.; Sheiko, S. S. *Macromolecules* **2005**, *38*, 8264–8271.
(22) Litvinenko, G.; Mueller, A. H. E. *Macromolecules* **1997**, *30*, 1253–1266.
(23) Zirbs, R.; Binder, W.; Gahleitner, M.; Machl, D. *Macromol. Symp.* **2007**, *254* (1), 93–96.
(24) Zirbs, R.; Binder, W. H.; Machl, D. *Polym. Prepr.* **2006**, *47* (2), 851.
(25) Kim, I.-J.; Faust, R. *J. Macromol. Sci., Part A* **2003**, *40*, 991–1008.
(26) Brittain, W. J.; Zhao, B. *Macromolecules* **2000**, *33*, 342–348.
(27) Faust, R.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1847–1869.
(28) Faust, R.; Kennedy, J. P. *Polym. Bull.* **1986**, *15*, 317–323.
(29) Feng, D.; Higashihara, T.; Faust, R. *Polymer* **2008**, *49*, 386–393.
(30) Breland, L. K.; Storey, R. F. *Polymer* **2008**, *49*, 1154–1163.
(31) De, P.; Faust, R. *Macromolecules* **2005**, *38*, 9897–9900.
(32) Tawada, M.; Faust, R. *Macromolecules* **2005**, *38*, 4989–4995.
(33) Puskas, J. E.; Antony, P.; Kwon, Y.; Paulo, C.; Kovar, M.; Norton, P. R.; Kaszas, G.; Altstädt, V. *Macromol. Mater. Eng.* **2001**, *286*, 565–582.
(34) De, P.; Faust, R. *Macromolecules* **2006**, *39*, 6861–6870.
(35) Storey, R. F.; Curry, C. L.; Brister, L. B. *Macromolecules* **1998**, *31*, 1058–1063.
(36) Thomas, Q. A.; Storey, R. F. *Macromolecules* **2003**, *36*, 10120–10125.
(37) Kaszas, G.; Puskas, J. E.; Kennedy, J. P.; Hager, W. G. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 421–426.
(38) Robson, F.; Storey; Shoemake, K. A.; Chisholm, B. J. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2003–2017.
(39) Cao, X.; Faust, R. *Macromolecules* **1999**, *32*, 5487–5494.
(40) Keszler, B.; Fenyvesi, G.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 706–714.
(41) Puskas, J. E.; Chen, Y.; Kulbaba, K.; Kaszas, G.; Soleymannezhad, A. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1770–1776.
(42) Simison, K. L.; Stokes, C. D.; Harrison, J. J.; Storey, R. F. *Macromolecules* **2006**, *39*, 2481–2487.
(43) Cheng-Long Zhang, Wu, Y.-X.; Xu, X.; Feng, Y. L. L.; Wu, G.-Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 936–946.
(44) Benetti, E. M.; Reimhult, E.; de Bruin, J.; Zapotoczny, S.; Textor, M.; Vancso, G. J. *Macromolecules* **2009**, *42*, 1640–1647.
(45) Puskas, J. E.; Shaikh, S.; Yao, K. Z.; McAuley, K. B.; Kaszas, G. *Eur. Polym. J.* **2005**, *41* (1), 1–14.
(46) Puskas, J. E.; Chan, S. W. P.; McAuley, K. B.; Shaikh, S.; Kaszas, G. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5394–5413.
(47) Puskas, J. E.; Kaszas, G.; Litt, M. *Macromolecules* **1991**, *24*, 5278–5282.
(48) Storey, R. F.; Thomas, Q. A. *Macromolecules* **2003**, *36*, 5065–5071.
(49) Sipos, L.; De, P.; Faust, R. *Macromolecules* **2003**, *36*, 8282–8290.
(50) Kolishetti, N.; Faust, R. *Macromolecules* **2008**, *41*, 3842–3851.