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I. Controlled Radical Polimerization

Trithiocarbonates Containing Trimethoxysilyl Functionalities as Mediating Agents in Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization of Methyl Acrylate

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Summary: Reversible addition-fragmentation chain transfer (RAFT) polymerization with benzyl(3-trimethoxylsilylpropyl)trithiocarbonate (BTPT) and 1,4-bis(3′-trimethoxysilylpropyltrithiocarbonylmethyl)benzene (TPTB) as mediators was performed to produce branched poly(methyl acrylate) (pMA). The deviation of the experimental number average molecular weights towards higher values and the size exclusion chromatography (SEC) traces measured at distinct time instants after polymerization indicated a coupling of the trimethoxysilyl end-groups to form terminal-linked pMA of high molecular weight. The trimethoxysilyl moieties also caused the unusual creation of doubly ionized pMA chains in electrospray ionization mass spectrometry (ESI-MS). BTPT was furthermore anchored onto fumed silica to carry out a RAFT graft polymerization with benzylpropyltrithiocarbonate as additional RAFT agent in solution to afford well-defined pMA chains fixed to silica nanoparticles. A block copolymerization of the living anchored pMA chains with styrene (Sty) produced grafted pMA-*b*-pSty chains with good agreement between experimental and theoretical molecular weights.

Keywords: crosslinking; nanoparticles; poly(methyl acrylate); reversible addition-fragmentation chain transfer (RAFT); silica

Introduction

The advent of controlled radical polymerization techniques such as nitroxide mediated polymerization (NMP),[1] atom transfer radical polymerization (ATRP)[2,3] and reversible addition-fragmentation chain transfer (RAFT) polymerization[4–7] has enabled the design of customized macromolecules in a relatively simple and straightforward manner. Especially the RAFT process has proven to be a very suitable technique for synthesizing polymers with complex architectures not only due to its versatility towards monomers and reaction conditions, but also because various macromolecular architectures, as for example block copolymers, star and comb polymers, have already been successfully synthesized.[8,9] Since the polymer properties are also largely governed by its topology, it is crucial to predefine the macromolecular structure by applying specific RAFT agents that act as scaffolds for the desired polymer architecture. With this approach, various types of macromolecular topologies can be obtained with relative ease.

Material properties of polymers are not only affected by the variety of accessible architectures, but also by the addition of reinforcing inorganic fillers such as silica, alumina and carbon black.[10] In particular

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nanocomposites have recently received increasing interest due to their unique and tunably properties, which are the result of the extremely high surface-to-volume ratio of the nanoparticles that can effect a large volume fraction of the polymer matrix. However, these particles also tend to strongly agglomerate, and this, on the other hand, causes degradation of the mechanical and optical properties of the resulting nanocomposites as the particles are not evenly dispersed throughout the hybrid material.[11] This problem can be overcome by covering the nanoparticles with polymer chains using surface-initiated controlled radical polymerization. In this case, solid-supported RAFT polymerization has again turned out to be a very powerful alternative to other controlled radical polymerization techniques. In principle, three approaches can be considered when performing a RAFT graft polymerization. First, a surface-tethered initiator may be combined with a RAFT agent in solution.[12–17] This approach, however, does not lead to a good control over molecular weight as the surface-bound chains represent only the fraction that originates from the continuous initiation process. Second, the RAFT agent can be anchored to the particle surface via its Z-group, known as the "Z-group approach". In this case the active dithio moiety is always linked close to the surface, which enables the isolation of sulfur-free polymer and at the same time recovery of the RAFT agent via cleavage with excess amounts of AIBN, which might be of interest for technical applications.[8,18,19] Under optimized conditions, especially regarding grafting density of RAFT agents and type and amount of additional RAFT agent in solution, the Z-group approach provides well-defined surface-confined polymer with monomodal molecular weight distributions.[18–22] The location of the active RAFT-group near by the surface, however, somewhat limits the grafting density of polymer chains due to shielding effects, which can be circumvented by anchoring the RAFT agent via its R-group, designated as the "R-group approach". In this case the dithio moiety departs from the surface during chain growth, which lowers the sterical hindrances and hence allows the formation of dense polymer brushes grafted onto solid support.[23–26] The downside of this approach is the fact that the RAFT agent is easily detached by radicals in solution and thus after polymerization living polymer chains containing RAFT endgroups are found both on the surface and in solution.

This work presents how specially designed trithiocarbonates offer a simple path to highly branched polymers and to silica-polymer hybrids synthesized in a controlled fashion. RAFT agents containing trimethoxysilyl moieties were applied in RAFT polymerization without surface-attachment, resulting in polymer networks with uniform bridging lengths. This result was evident from the characterization of the resulting pMA via SEC and ESI-MS compared to the pMA produced with a similar RAFT agent without trimethoxysilyl moieties. Furthermore, surface-confined pMA chains were synthesized via the Z-group approach using fumed silica as the solid substrate and analyzed via attenuated total reflection infrared (ATR-IR) spectroscopy. The resulting living chains were also used to conduct a block copolymerization with styrene, affording silica modified with block copolymer chains, an approach which allows a very fine tuning of the chemical composition of the polymer film.

Experimental Part

Materials

The fumed silica with 7 nm of nominal particle size, a surface area of 390 $m^2 \cdot g^{-1}$, and a bulk density of 36.8 $g \cdot L^{-1}$ was purchased from Aldrich. Particle sizes are given for primary particles, which form branched, chain-like aggregates of some tenths of micrometers. Sodium methoxide (30 wt.-% in methanol, Fluka), carbon disulfide (Fluka), 3-mercaptopropyltrimethoxysilane (mixed *m,p*-isomers, ABCR), and benzyl chloride (Fluka) were used as received. To remove inhibitor, styrene (Fluka) and methyl acrylate (Fluka) were passed through a basic alumina (Merck) column before use. 2,2′-Azo-bis-isobutyronitrile (AIBN, AKZO) was recrystallized from methanol. Tetrahydrofuran (THF) used as the eluent in size exclusion chromatography (Carl Roth, stabilized with 2,6-di-*tert*-butyl-4-methylphenol) was used as received. Unless otherwise specified, all other chemicals were purchased from Merck and used without further purification.

Instrumentation

Molecular weight distributions were determined by means of size exclusion chromatography (SEC) using a JASCO AS-2055-plus autosampler, a Waters 515 HPLC pump, three PSS-SDV columns with nominal 5-μm particle size and pore sizes of 10^5, 10^3 and 10^2 Å, a Waters 2410 refractive index detector, and THF at 35 °C as the eluent at a flow rate of 1 $\text{mL} \cdot \text{min}^{-1}$. The SEC set-up was calibrated against polystyrene and poly(methyl methacrylate) standards of narrow polydispersity from Polymer Standards Service (PSS). Mark-Houwink parameters for poly(MA) in THF ($K = 1.68 \cdot 10^{-2}$ $\text{mL} \cdot \text{g}^{-1}$, $a = 0.696$)[27] provided access to absolute molecular weights according to the principles of universal calibration.

NMR spectra were recorded on a Varian Mercury 200 spectrometer using $CDCl_3$ as a solvent.

Elemental analyses (C,H,N,S) were carried out on a Elementar Vario El III elemental analyzer.

Electrospray ionization mass spectrometry (ESI-MS) was performed on a Finnigan LCQ ion trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operated in the nebulizer-assisted electrospray mode. The spectrum was obtained in the positive ion mode within the *m*/*z* range 100 to 2000 at a spray voltage of 4.5 kV and a capillary temperature of 200 °C. The polymer sample was dissolved in a mixture of dichloromethane and methanol at a concentration of about 100 $\mu\text{g} \cdot \text{mL}^{-1}$. The presented ESI-MS spectrum results from co-addition of about 200 individual spectral traces.

Attenuated Total Reflectance Fourier Transform Infrared (ATR/FT-IR) spectrometry was performed using an A 529-HD MVP-Star (diamond, single reflection) unit by Harrick within a Bruker IFS 88 FT-IR spectrometer.

RAFT Agents

Benzylpropyltrithiocarbonate (BPT) and 1,4-Bis(3′-trimethoxysilylpropyltrithiocarbonylmethyl)benzene (TPTB) were synthesized according to a procedure recently published by our group.[28] Benzyl(3-trimethoxylsilylpropyl)trithiocarbonate (BTPT) was synthesized in a similar manner: to a solution of sodium methoxide (18.0 g, 0.10 mol, 30 wt.-% in methanol) in methanol (30 mL) 3-mercaptopropyltrimethoxysilane (19.6 g, 0.10 mol) was added dropwise at 0 °C under a nitrogen atmosphere. The mixture was stirred for 2 hours and carbon disulfide (7.6 g, 0.10 mol) was added dropwise to the solution at ambient temperature. After 3 hours benzyl chloride (12.6 g, 0.10 mol) was added and the mixture was stirred for 12 hours. The solvent was removed in vacuo and the crude product was purified via column chromatography (silica, pentane: dichloromethane = 9: 1, *R*f = 0.47) affording yellow oily BTPT (5.2 g, 14 mmol, 14%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 0.8 (t, 2 H, CH_2–Si), 1.8 (q, 2 H, CH_2–CH_2–Si), 3.4 (t, 2 H, CH_2–CH_2–CH_2–Si), 3.6 (s, 9 H, $3 \times CH_3$), 4.6 (s, 2 H, S–CH_2–Ph), 7.2–7.4 (m, 5 H, C_6H_5).

^{13}C-NMR (300 MHz, $CDCl_3$) δ (ppm): 8.7 (CH_2-Si), 21.6 (CH_2–CH_2–Si), 39.3 (CH_2–CH_2–CH_2–Si), 41.3 (S–CH_2–Ph), 127.6, 128.6, 129.1, 134.9 (C_6H_5), 223.4 (C(=S)S).

Synthesis of Grafted RAFT Agent

To a suspension of silica nanoparticles (6.9 g) in toluene benzyl(3-trimethoxylsilylpropyl)trithiocarbonate (0.12 g, 0.33 mmol) and maleic anhydride (10 mg, 0.1 mmol, diluted in 0.1 mL water) were added under vigorous stirring. The mixture was stirred at 60 °C for 3 hours, cooled to room temperature and filtered. The resulting modified silica was washed with dichloromethane in a Soxhlet apparatus for 12 h to remove residuals and dried under vacuum at room temperature over night. The grafting density of RAFT agent on the silica surface was determined via elemental analysis (mass content of sulfur: 0.4%, 0.06 molecules $\cdot$ nm^{-2}).

Polymerization of MA Mediated by Free RAFT Agent

In a typical experiment a solution of AIBN and RAFT reagent in MA (30 g, 0.35 mol) was degassed via three freeze-pump-thaw cycles and channeled to an argon-filled glove box. The mixture was then evenly portioned to glass vials that were sealed with Teflon septa and subsequently heated to 60 °C. Polymerizations were stopped by cooling the vials in ice water after distinct time periods. Monomer conversion was determined gravimetrically by removing the residual monomer under reduced pressure.

Polymerization of MA Mediated by Anchored BTPT

In a typical run a solution of MA (6 g, 0.070 mol) and toluene (24 g, 0.26 mol) was subjected to three freeze-pump-thaw cycles and channeled to an argon-filled glove box. AIBN (1.2 mmol $\cdot$ L^{-1}) and BPT (7.1 mmol $\cdot$ L^{-1}) were added and the mixture was then evenly divided to glass vials that contained distinct amounts of silica-immobilized BTPT (5.0 mmol $\cdot$ L^{-1}). The vials were then sealed, heated to 60 °C and stirred vigorously during polymerization. The reaction was stopped by cooling the vials in ice water. Residuals were evaporated under reduced pressure and total monomer conversion was determined by gravimetry. The resulting solid was washed in a Soxhlet apparatus with dichloromethane for 12 h and the free polymer was analyzed via size exclusion chromatography.

Synthesis of Surface-Tethered Block Copolymer

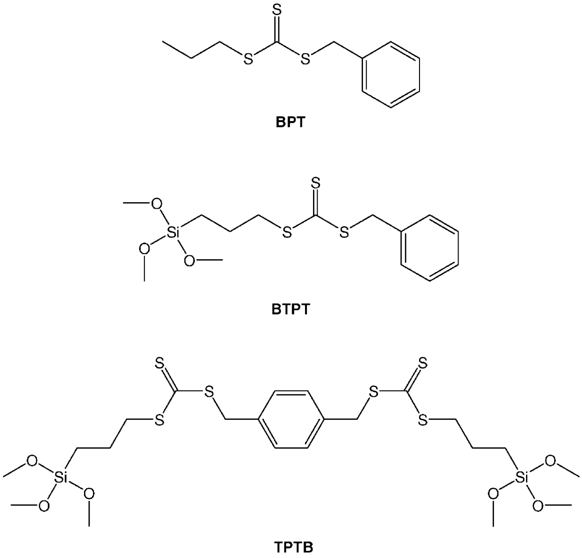
A solution of styrene (6 g, 0.058 mol) and toluene (24 g, 0.26 mol) was degassed via three freeze-pump-thaw cycles and mixed with AIBN (1.2 mmol $\cdot$ L^{-1}) and BPT (4.9 mmol $\cdot$ L^{-1}) inside an argon-filled glove box. The mixture was evenly divided to two glass vials containing a well-defined amount of surface-bound and free pMA. Polymerization and characterization procedures are identical to the polymerization with BTPT described above.

Cleavage of Surface-Bound Polymer

In an argon-filled glove box a solution of AIBN (0.5 mol $\cdot$ L^{-1}) in toluene, which was subjected to three freeze-pump-thaw cycles, was added to glass vials containing silica-bound polymer. The vials were sealed and heated to 80 °C and stirred intensively for 3 hours. After reaction the silica particles were filtrated and the filtrate was analyzed via SEC.

Results and Discussion

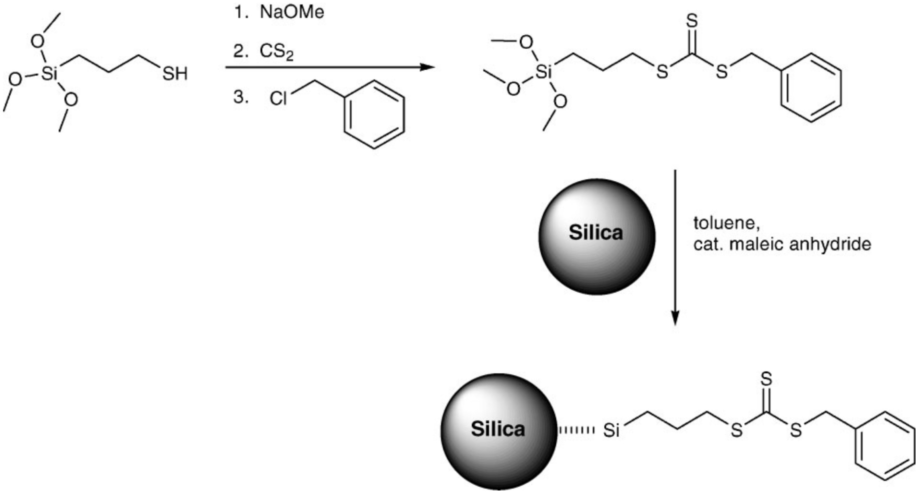
In this work the use of the trithiocarbonates illustrated in Scheme 1 as mediators in RAFT polymerization of MA is presented. BTPT was furthermore attached to silica nanoparticles to perform a controlled graft polymerization and a successive block copolymerization with styrene as the comonomer. The synthesis and grafting procedure depicted in Scheme 2 consists of a simple one-pot reaction sequence followed by reaction with fumed silica in toluene under catalysis of maleic anhydride to form modified silica nanoparticles. This synthesis strategy allows the isolation of pure RAFT agent before immobilization so that the resulting grafting density of RAFT agent on the silica can be easily tuned. The application of silica-confined BTPT has already been investigated by Perrier and co-workers with respect to grafting density, types of free RAFT agents and reaction media.[22] However, there have not been any reports on the use of these trithiocar-



Scheme 1.
RAFT agents used in this work: benzylpropyltrithiocarbonate (BPT), benzyl(3-trimethoxylsilylpropyl)trithiocarbonate (BTPT) and 1,4-Bis(3′-trimethoxysilyl-propyltrithiocarbonylmethyl)benzene (TPTB).

bonates containing trimethoxysilyl moieties as free mediators, that is without surface-attachment, in RAFT polymerization so far. TPTB has recently been used in our group to produce surface-bound polymer loops via the RAFT process.[28] The employment of BTPT and TPTB as free mediators, in comparison, provides easy access to end-group-linked polymer synthesized in a controlled fashion.

As can be seen in Figure 1, BPT effectively controls the polymerization of MA producing narrow molecular weight distributions with *PDI* values below 1.25 and an increase in the average molecular weight with monomer conversion. Theore-



Scheme 2.
Synthesis and grafting procedure of BTPT.

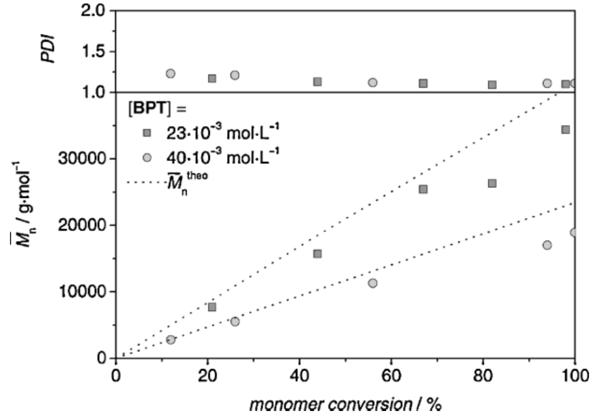


Figure 1.

Number average molecular weight, $\overline{M}_n$, and polydispersity index, *PDI*, versus monomer conversion for the polymerization of MA mediated by BPT and initiated by AIBN (4.7 mmol · L^{-1}) at 60 °C. The dotted lines indicate the theoretical molecular weight, $\overline{M}_n^{\text{theo}}$.

tical average molecular weights were calculated via Eq. (1), which accounts for the increase of the number of chains in the system due to continuous initiation[29]:

$$\overline{M}_n^{\text{theo}} = \frac{X \cdot c_M^0 \cdot M_{\text{monomer}}}{c_{\text{RAFT}}^0 + c_I^0 \cdot d \cdot f \cdot (1 - e^{-k_d \cdot t})} \qquad (1)$$

with the monomer to polymer conversion, X, the initial monomer concentration, c_M^0, the initial RAFT agent concentration, c_{RAFT}^0, the initial initiator concentration, c_I^0, the molecular weight of monomer, M_{monomer}, with d being the number of chains that are generated in the termination process ($d \approx 1$ for MA), with the initiator decomposition rate coefficient, k_d ($k_d = 1.10 \times 10^{-5}$ s^{-1} for AIBN at 60 °C[30]), and the initiator efficiency $f = 0.72$.[31] The experimental molecular weights deviate slightly to smaller values at high conversion, which may well be due to uncertainties either of the Mark-Houwink coefficients that were used for universal SEC calibration or of the kinetic parameters that enter Equation (1). The efficiency of AIBN, for instance, is only available for styrene solution and may be slightly different in MA solution.

RAFT polymerization of MA with BTPT leads to a different trend of deviations in molecular weights (Figure 2). Polydispersities are all below 1.5 and therefore typical of a successful controlled radical polymerization, even though higher than with BPT. Experimental average molecular weights determined directly after polymerization, however, deviate to higher values for all RAFT agent concentrations suggesting irreversible condensation reactions caused by the trimethoxysilyl moieties of the produced polymer chains. The end-groups were confirmed by means of electrospray ionization mass spectrometry (ESI-MS). Figure 3 shows the ESI-MS spectrum of a pMA sample obtained from controlled radical polymerization with BTPT. The large peaks with a spacing of 86 mass units correspond to single ionized pMA chains containing BTPT end-groups. The second set of peaks with an interval of 43 mass units belongs to pMA chains that were ionized twice and thus contained two sodium cations. This quite unusual behavior for synthetic polymers is probably caused by a high affinity of the trimethoxysilyl groups towards sodium cations, which results in a fraction of doubly ionized pMA chains.

As a result of the trimethoxysilyl end-groups the pMA chains are able to condense with each other, catalyzed by traces of water, to form branched star polymers of high molecular weight, which is illustrated in Figure 4. The SEC curves clearly show

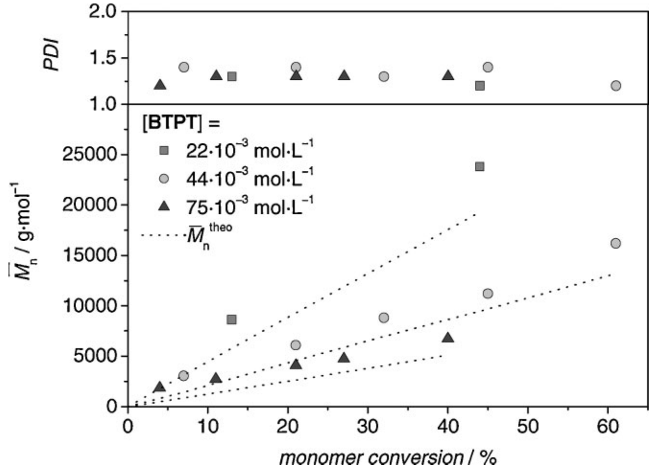


Figure 2.
Number average molecular weight, $\overline{M}_n$, and polydispersity index, *PDI*, versus monomer conversion for the polymerization of MA mediated by BTPT and initiated by AIBN (3.4 mmol · L^{-1}) at 60 °C. The dotted lines indicate the theoretical molecular weight, $\overline{M}_n^{theo}$.

the formation of condensed polymer during a period of three days, roughly doubling (one day) and quadrupling (three days) the molecular weight of the original pMA. The net effect of this post-polymerization reaction is a broadening of the molecular weight distribution and an increase in the molecular weight. This effect appears to start already during the polymerization, as indicated by the high *PDI* and M_n values observed in Figure 2.

The application of the bifunctional RAFT agent TPTB as mediating agent in the polymerization of MA leads to quite similar phenomena. Whereas the polydispersities indicate a controlled polymerization (<1.5), number average molecular weights, also measured directly after polymerization, again slightly deviate to higher values (see Figure 5). This effect also has its origin in the existence of the trimethoxysilyl end-groups, which cause the polymer

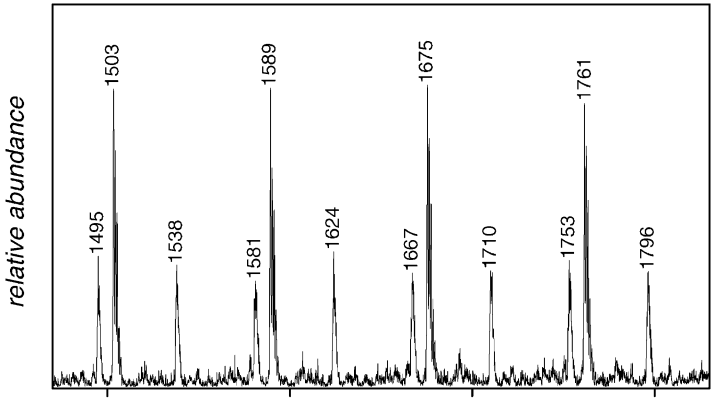


Figure 3.
ESI-MS spectrum of Na$^+$-ionized pMA generated after 20 min of polymerization mediated by of BTPT (44 mmol · L^{-1}) and initiated by AIBN (3.4 mmol · L^{-1}) at 60 °C; the monomer conversion was 6.6%.

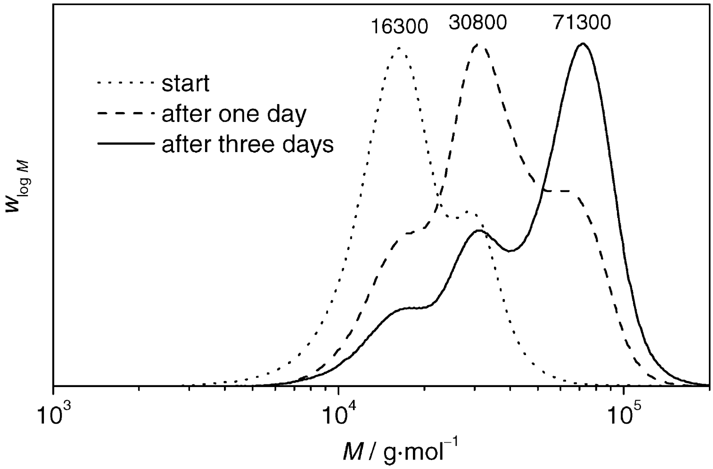


Figure 4.
Molecular weight distributions (SEC traces) of pMA measured at distinct time instants after the polymerization mediated by BTPT (44 mmol · L^{-1}) and initiated by AIBN (3.4 mmol · L^{-1}) at 60 °C. Monomer conversion was 61%; values at the top correspond to the molecular weights at the peak maximum, M_p.

chains to form terminal cross-linked networks with uniform network chain lengths. The increase of molecular weight was even so pronounced that a fraction of the resulting networks was completely insoluble in THF. Figure 6 shows the soluble fraction of one sample measured one and five days after polymerization, respectively. The increase of the high molecular weight content and the overall broadening of the molecular weight distribution are clearly visible. Since the two RAFT agents BTPT and TPTB effectively control the polymerization of MA, this pathway allows the very easy formation of polymer networks with tunable und uniform bridging lengths.

The RAFT graft polymerization of MA mediated by anchored BTPT with additional BPT in the solution phase was conducted with high contents of solvent (toluene) to assure that the viscosity of the reaction mixture stayed low and hence

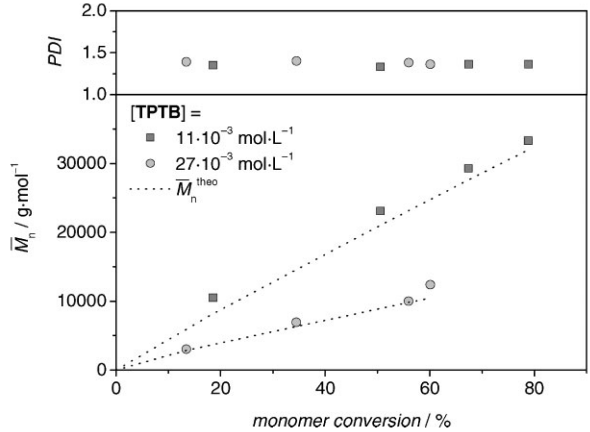


Figure 5.
Number average molecular weight, $\overline{M}_n$, and polydispersity index, PDI, versus monomer conversion for the polymerization of MA in toluene (50 wt.-%), mediated by TPTB and initiated by AIBN (4.7 mmol · L^{-1}) at 60 °C. The dotted lines indicate the theoretical molecular weight, $\overline{M}_n^{\text{theo}}$.

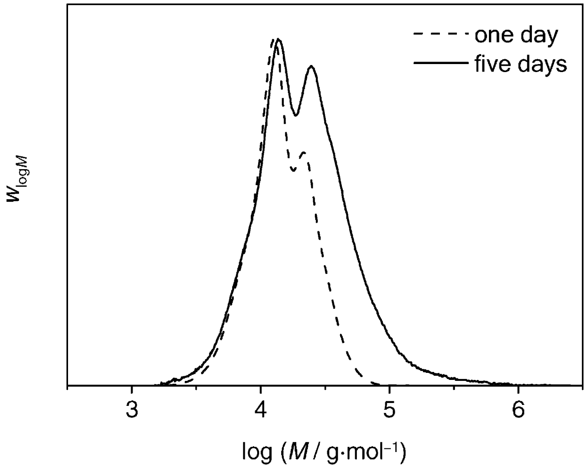


Figure 6.
Molecular weight distributions (SEC traces) of pMA measured at distinct time instants after the polymerization in toluene (50 wt.-%) mediated by TPTB (27 mmol · L^{-1}) and initiated by AIBN (4.7 mmol · L^{-1}) at 60 °C. Monomer conversion was 60%.

vigorous stirring was possible. The evolution of number average molecular weight with monomer conversion, depicted in Figure 7, shows that the polymerization both in solution and on the surface was controlled successfully. The molecular weights of the pMA formed in solution and on the surface are in good agreement with the corresponding theoretical values up to molar masses of approximately 10 000 g · mol^{-1}. From that point on the molecular weights of the grafted pMA deviate to smaller values, which can be attributed to shielding effects on the surface caused by the difficulty for growing radicals, which occur only in the interstitial solution phase,

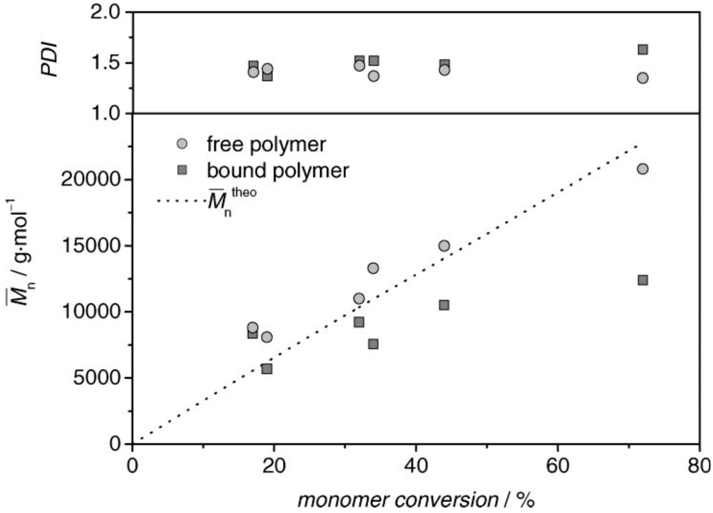


Figure 7.
Number average molecular weight, $\overline{M}_n$, and polydispersity index, *PDI*, of free and bound polymer versus monomer conversion for the polymerization of MA in toluene (70 wt.-%) mediated by free BPT (7.1 mmol · L^{-1}) and anchored BTPT (5.0 mmol · L^{-1}, 0.06 molecules · nm^{-2}) and initiated by AIBN (1.0 mmol · L^{-1}) at 60 °C. The dotted lines indicate the theoretical molecular weight, $\overline{M}_n^{theo}$.

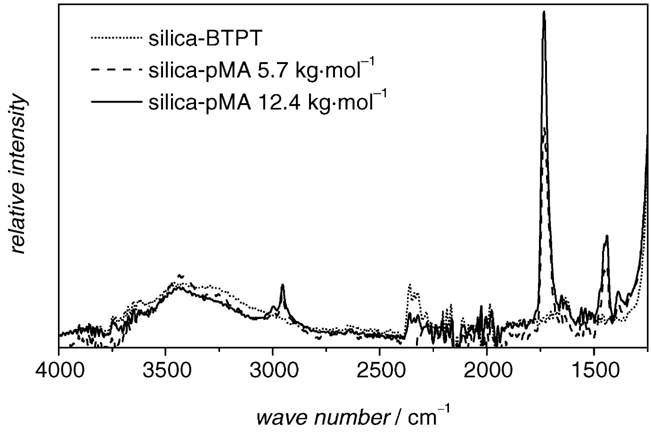
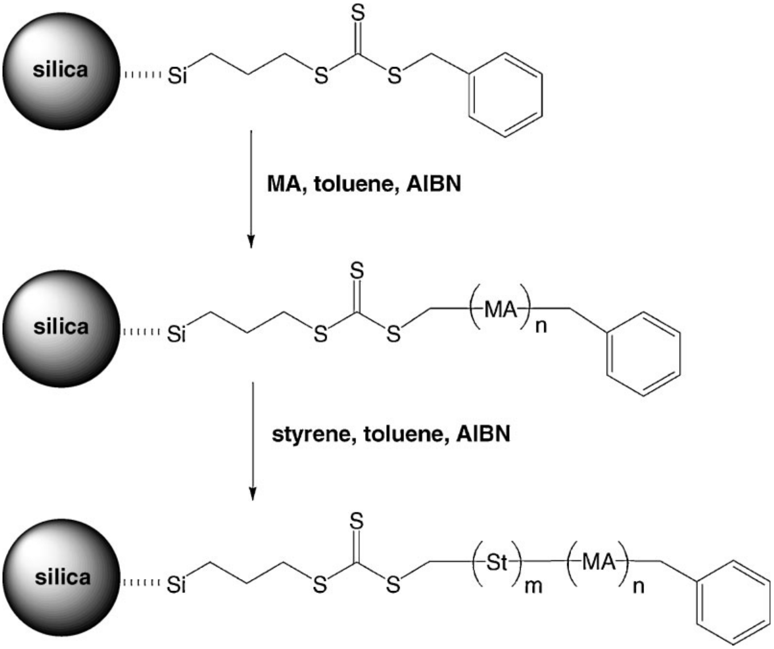


Figure 8.
ATR-FTIR spectra of modified silica before and after the polymerization with different loadings, i.e., number aver molecular weights, of pMA. The ATR-FTIR spectrum of the bound polymer shows a peak at 1734 cm^{-1} which is characteristic for the C=O double bond of MA. The signal at 2900 cm^{-1} belongs to the vibration of the C-H bond.

to reach the trithiocarbonate moieties. For this reason the molecular weight of the pMA in solution tends to increase more rapidly compared to the anchored pMA chains at high conversions, which is quite characteristic of a Z-group supported RAFT graft polymerization. The *PDI* values of free and grafted pMA chains do not differ significantly except at high conversions, which goes hand in hand with the increase in sterical hindrance described above, since at that stage the control of chain growth at the surface is also slightly hampered. The resulting silica nanoparticles modified with



Scheme 3.
Synthetic route to surface-bound block copolymer.

Table 1.

Theoretical number average molecular weights, $\overline{M}_n^{theo}$, number average molecular weights, $\overline{M}_n$, and polydispersities, *PDI*, of free and bound polymer for the block copolymerization of MA and styrene in toluene mediated by free BPT (4.9 mmol · L^{-1}) and anchored BTPT (5.0 mmol · L^{-1}, 0.06 molecules · nm^{-2}) and initiated by AIBN (1.2 mmol · L^{-1}) at 60 °C. Molecular weights of copolymers were obtained using Mark-Houwink parameters for poly(MA).

	Sty Conv.	$\overline{M}_n^{theo}$	$\overline{M}_n^{free}$	PDI^{free}	$\overline{M}_n^{bound}$	PDI^{bound}
Homo polymerization pMA		8570	8380	1.34	10900	1.25
Block copolymerization pMA-*b*-pSty	23%	14700	13900	1.42	15400	1.33
Block copolymerization pMA-*b*-pSty	41%	19400	18700	1.53	21400	1.42

pMA chains were analyzed via ATR-IR-spectroscopy (Figure 8). In comparison to the fumed silica modified only with RAFT agent BTPT, the nanocomposites exhibit strong absorption at 1734 and 2900 cm^{-1} corresponding to the C=O and C–H bonds, respectively, of the grafted pMA chains. As expected the intensity of the peaks increases with pMA loading, which moreover may allow a quantitative analysis of the spectroscopic data. Altogether this demonstrates the suitability of IR-spectroscopy as a tool for the analysis of surface-confined polymers.

After RAFT graft polymerization, the surface-tethered pMA chains can be applied to an extension polymerization to form a diblock copolymer due to the living character of the grafted polymer chains. This is demonstrated in Scheme 3 for the copolymerization of MA and styrene. The results of this approach to form surface-bound pMA-*b*-pSty, listed in Table 1, show the prosperity and straightforwardness of this synthesis route as the experimental and theoretical molecular weights of free and grafted block copolymers are in good agreement with each other and the polydispersities also indicate a successful controlled radical polymerization. The SEC traces of free and grafted pMA and pMA-*b*-pSty, illustrated in Figure 9 for the sample with 41% styrene conversion, show that the molecular weight distributions clearly shift to higher molecular weights. The SEC curve corresponding to the grafted pMA-*b*-Sty, however, also shows a very small shoulder at the low molecular weight side. This is probably caused by a small fraction of original grafted pMA chains that did not reinitiate, which is mostly due to the above-mentioned shielding effects and is hence not applicable for pMA produced in solution. However, in general this pathway

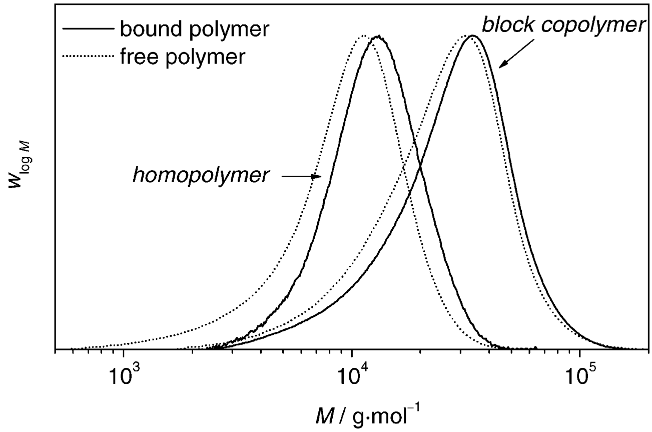


Figure 9.

Molecular weight distributions (SEC traces) of free polymer (dotted line) and bound polymer (full line) produced in a block copolymerization of MA and styrene in toluene mediated by free BPT (4.9 mmol · L^{-1}) and anchored BTPT (5.0 mmol · L^{-1}, 0.06 molecules · nm^{-2}) and initiated by AIBN (1.2 mmol · L^{-1}) at 60 °C.

enables a very fine tuning of the properties of the polymer film as not only the film thickness and density but also the chemical compostion of grafted polymer chains can be easily tuned, which may give rise to interesting nanocomposite materials.

Conclusion

An insight into the possibilities of producing new architectures and materials via RAFT polymerization has been provided. The existence of trimethoxysilyl groups in RAFT agents fundamentally alters the polymerization process as that it induces a coupling of the polymer chains, leading to branched polymers and polymer networks of high molecular weight. This fact was indicated by the evolution of molecular weights and could directly be seen in the SEC traces measured at different distinct instants in time after polymerization. In addition, the trimethoxysilyl end-groups caused the unusual formation of doubly ionized pMA chains, probably induced by the affinity towards sodium cations, which were observed in the ESI-MS spectrum. The RAFT graft polymerization of MA mediated by anchored BTPT and free BPT afforded well-defined surface-bound pMA chains, which exhibited characteristic vibrational modes detected via ATR-IR spectroscopy and were also successfully applied to a block copolymerization with styrene as the co-monomer.

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