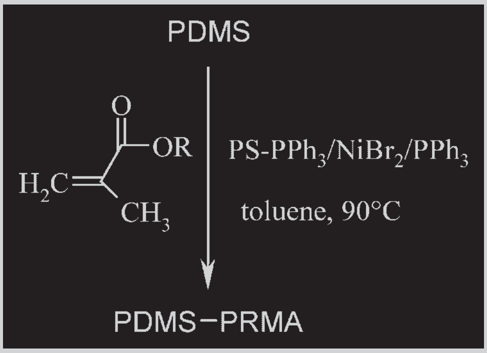
Summary: A nickel (II) bromide catalyst immobilized onto crosslinked diphenylphosphinopolystyrene (PS-PPh_3/$NiBr_2$) was used for the synthesis of silicone-methacrylate copolymers by atom transfer radical polymerization (ATRP) of various methacrylate monomers using ω-bromide silicone chains as macroinitiator. The polymerization proved to be very well-controlled when a sufficient amount of soluble ligand, i.e., triphenylphosphine (PPh_3), was added to the polymerization medium. Under these conditions, this technique efficiently led to the production of different copolymers with controlled compositions and molecular weights as well as narrow polydispersity indices ($\overline{M}_w/\overline{M}_n < 1.5$). The recovered copolymers proved to be almost free of catalyst residues. Indeed, inductively coupled plasma (ICP) analysis revealed a metal content lower than 100 ppm, representing only a few percent of the initial metal content in the polymerization medium.



Synthesis of PDMS block copolymer in toluene catalyzed by PS-PPh_3/$NiBr_2$ in the presence of soluble PPh_3 at 90 °C.

Synthesis of Silicone-Methacrylate Copolymers by ATRP Using a Nickel-Based Supported Catalyst

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Introduction

Controlled radical polymerization (CRP) is a very efficient technique for synthesizing under rather conventional conditions copolymers of tunable composition, molecular weight, and topology allowing the synthesis of polymers with highly complex architectures.[1,2] In particular, atom transfer radical polymerization (ATRP) has opened the way to a real macromolecular engineering of polymeric materials.[3] In this field, silicone-based copolymers have been successfully synthesized by ATRP. In most of the cases, silicones are used as coatings or additives because of their unique surface properties. For instance, silicones are used as paper release or metal protector in the case of coating applications, or as additives in the fields of antifoams and paints.[4] Polydimethylsiloxane (PDMS) is undoubtedly the most widely used silicone, which is characterized by a unique combination of properties such as low surface tension, low glass transition temperature, high permeability to gas, and excellent weather resistance. Its wide range of applications such as polyurethane foam stabilization, release coatings, and pressure-sensitive adhesives illustrates the versatility of this inorganic polymer. However, since PDMS is a fluid at room temperature, the homopolymer lacks dimensional stability. In order to produce silicone-based materials with more desirable mechanical properties, block, graft, and network copolymers containing PDMS segments have been investigated.[5–8] Such block and graft copolymers have been prepared using free radical polymerization. For example, PDMS containing internal tetraphenylethylene moieties was used for the synthesis of segmented multiblock copolymers with various vinyl monomers.[9,10] While the use of macroinitiators for free radical polymerization appeared to be very promising, conventional methods introduced problems such as limited end-group functionalization, incomplete initiation efficiency, and homopolymer formation.[11,12] A significant improvement to those systems was brought up by the advent of CRP. Interestingly enough, ATRP starting from PDMS macroinitiators, which carry active alkyl halide end-group(s), has been studied to synthesize well-defined block copolymers.[13–17] However, because of the low

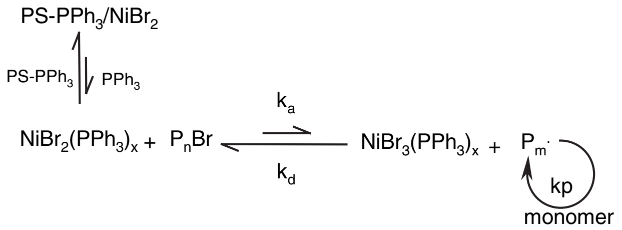

Figure 1. Sketch of the proposed SATRP mechanism.

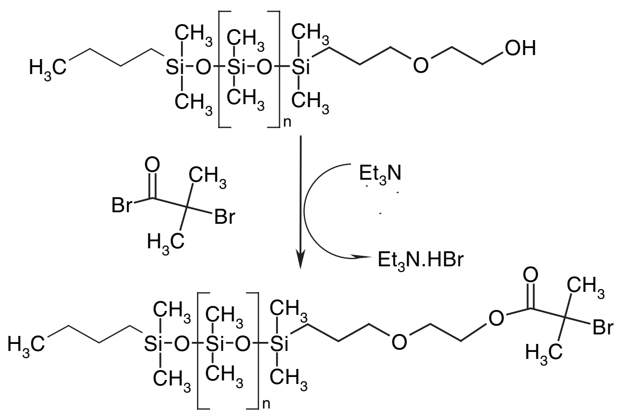

Figure 2. Synthesis of α-bromo PDMS macroinitiator from a α-hydroxyl terminated PDMS.

catalyst activity, ATRP processes performed in homogeneous conditions (i.e., using soluble ligated catalysts) lead to the production of copolymers contaminated with high residual catalyst contents. A potential way to overcome this drawback is the use of supported catalytic systems that can be recycled and reused. Several efficient supported catalytic systems in ATRP have been reported so far by Shen,[18] Zhu,[19] and Matyjaszewski.[20] Very recently, our group has reported on the use of a nickel(II) bromide catalyst ligated on to crosslinked diphenylphosphinopolystyrene resins (PS-PPh_3/$NiBr_2$).[21] When added with a sufficient amount of a soluble ligand such as triphenylphosphine (PPh_3), the PS-PPh_3/$NiBr_2$ supported catalyst actually proved to be highly efficient in ATRP of methyl methacrylate (MMA) initiated by ethyl-2-bromoisobutyrate (EBr^{i}B). The poly(methyl methacrylate) (PMMA) samples, recovered simply by filtration of the supported catalyst and precipitation in a non-solvent, were characterized by controlled molecular weights and polydispersity indices as low as 1.1. Moreover, the so-isolated polymer chains were almost free of catalyst residues as attested by inductively coupled plasma (ICP) measurements (ca. 1% of the starting metal content under the investigated experimental conditions, i.e., ≈35 ppm in residual Ni). The proposed mechanism was based on a reversible equilibrium between soluble and immobilized catalysts (Figure 1).[22] The supported catalyst was supposed to act as a reservoir that delivers the catalyst reversibly in solution allowing a controlled ATRP while maintaining a very low catalyst content in the polymer. Consequently, this system has been reused successfully without any loss in catalytic activity or

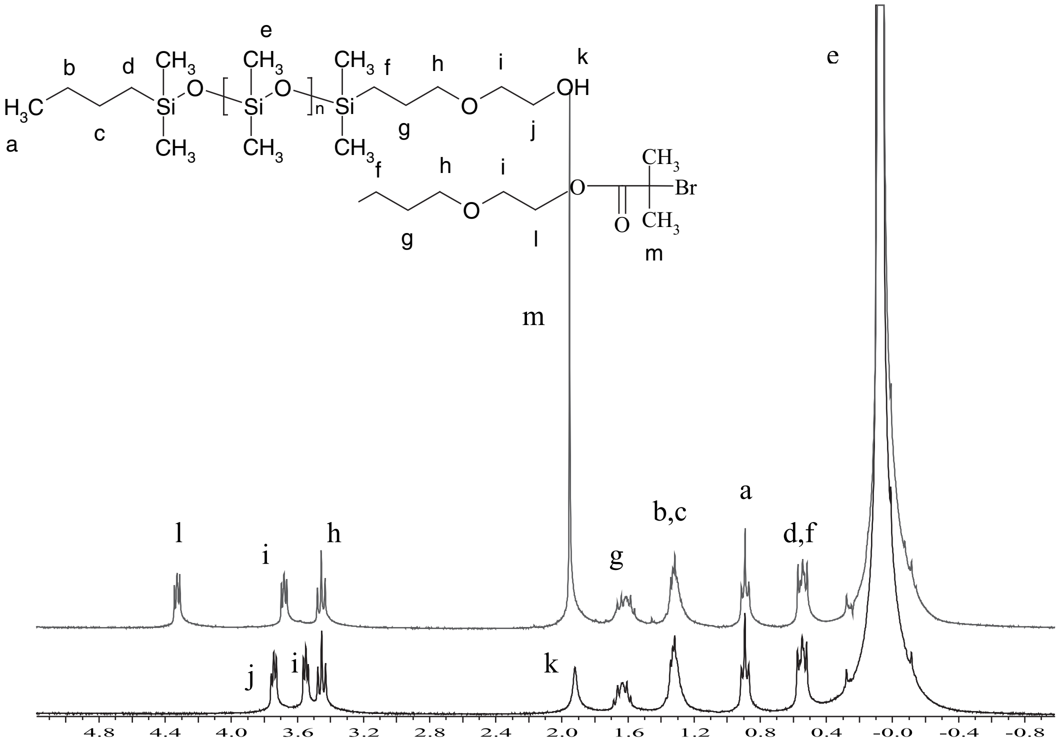

Figure 3. ^{1}H NMR spectra of α-hydroxy PDMS (top spectrum) and the resulting α-bromo PDMS.

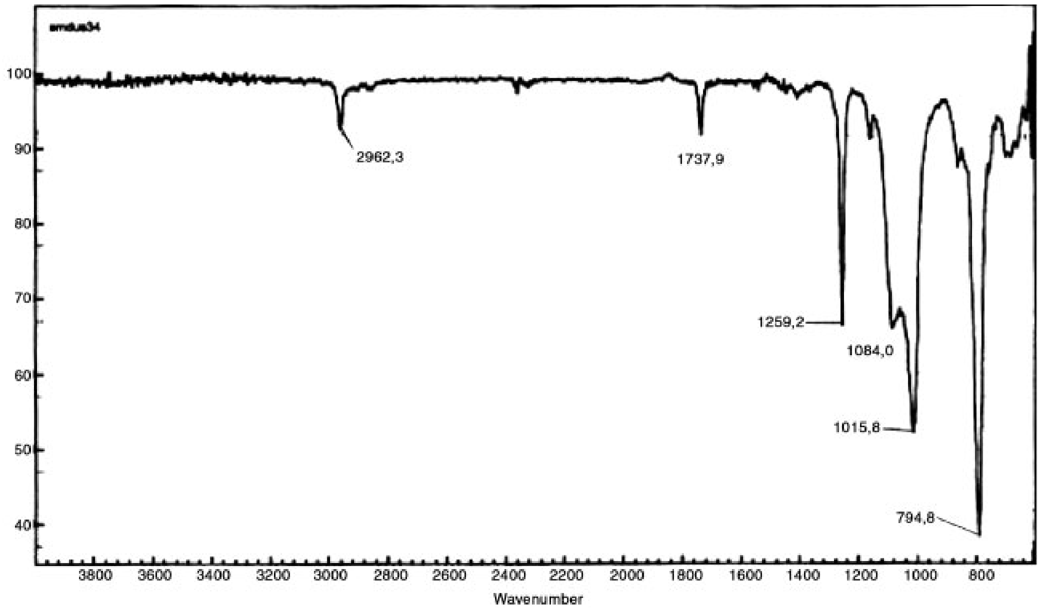

Figure 4. FTIR spectrum of the α-bromo PDMS macroinitiator.

polymerization control. In this paper, the PS-PPh_3/$NiBr_2$ supported catalytic system used in the presence of soluble PPh_3 has been investigated to prepare silicone-organic block copolymers starting from an ω-bromo PDMS macroinitiator. Several methacrylic monomers such as MMA, dimethylaminoethyl methacrylate (DMAEMA), butyl methacrylate (BuMA) or 2-ethylhexyl methacrylate (EHMA) have been considered.

Experimental Part

Materials

Crosslinked PS-PPh_3/$NiBr_2$ resin beads (PS-PPh_3; 2.18 mmol $P \cdot g^{-1}$; 1% crosslinked, Argonaut Technology), triethylamine (NEt_3, 99%, Acros), bromoisobutyryl bromide (98%, Aldrich), $MgSO_4$ (99%, Aldrich), $NaHCO_3$ (99%, Aldrich), and $NiBr_2$ (98%, Aldrich) were used as received without any further

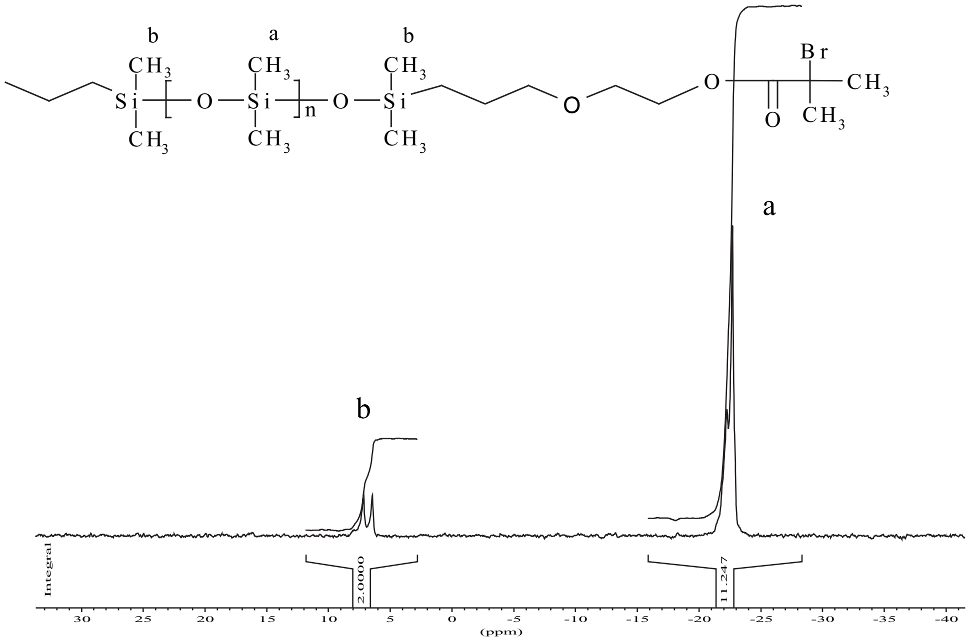

Figure 5. ^{29}Si-NMR spectrum of α-bromo PDMS macroinitiator in $CDCl_3$.

Table 1. Synthesis of silicone-organic block copolymers via homogeneous ATRP in toluene (monomer/solvent; 1/1 vol.), at 90 °C and initiated by the α-bromo PDMS macroinitiator ($\overline{DP} \approx 12$).

Entry	t	Monomer	Conversion[a]	$\overline{DP}$ theoretical[b]	$\overline{DP}$ experimental[a]	$f = \overline{DP}_{th}/\overline{DP}_{exp}$	$\bar{M}_n$ exp[c]	$\bar{M}_w/\bar{M}_n$[c]
	h		%					
1	4	MMA	55	110	128	0.86	15 700	1.17
2	24		96	192	272	0.71	25 100	1.40
3	4	DMAEMA	47	94	320	0.29	45 400	1.40
4	24		97	194	478	0.41	61 000	1.36

[a] Determined by ^{1}H NMR spectra.
[b] $\overline{DP}$ theoretical = [Monomer]$_0$/[PDMS-Br]$_0$ × conversion.
[c] Determined by SEC using PMMA standards.

purification. PPh$_3$ (99%, Acros) was recrystallized from ethanol. Toluene (99.5+%, Acros), tetrahydrofuran (THF, 99.9+%, Acros), dichloromethane (99+%, Acros), MMA (99%, Acros), DMAEMA (98%, Aldrich), BuMA (99%, Acros), and EHMA (99%, Acros) were passed through a column of basic alumina (Aldrich) to remove the stabilizers (inhibitors), bubbled with nitrogen and stored under nitrogen with a slight overpressure. The α-OH functionalized PDMS was supplied by ABCR Gelest and used after drying under vacuum.

Characterization

NMR spectra were recorded on a 300 MHz Bruker spectrometer. Molecular weights and molecular weight distributions were measured in THF at 35 °C using size exclusion chromatography (SEC) on a Polymer Lab system equipped with a Basic-Marathon Autosampler, a guard column (PLgel 10 µm 50 × 7.5 mm), two mixed-B columns (PLgel 10 µm; 300 × 7.5 mm), and a differential refractive index detector (PL-RI). Molecular weights were calibrated using linear PMMA standards in the range of 600–1 700 000 g · mol^{-1}. ICP measurements were performed on a Jobin–Yvon 35+ ICP atomic emission spectrophotometer calibrated with Jobin–Yvon ICP standards in toluene solution. Samples were prepared by dissolving approximately 50 mg of polymer sample in toluene and then diluting the solution up to 50 ml with toluene.

Synthesis of the PDMS Macroinitiator

Carbinol-terminated PDMS [degree of polymerization ($\overline{DP}$) ≈ 12] dissolved in THF ([PDMS-OH]$_0$ = 0.16 M, [NEt$_3$]$_0$ = 0.33 M) was added to the stirred solution followed by an excess of 2-bromoisobutyryl bromide ([Br^{i}BBr]$_0$ = 0.22 M). The reaction was allowed to react for 72 h at room temperature under agitation. In order to ensure complete conversion of the hydroxyl groups, the temperature was increased and maintained at 60 °C for 1 h. The solution was filtered off to eliminate the insoluble salts and the solvent was removed under vacuum. The resulting oil was taken up in dichloromethane and washed with saturated sodium hydrogenocarbonate solution and water. The organic layer was isolated and dried over magnesium sulfate, filtered off, and the solvent removed under vacuum to give the desired product (yield ≈ 80%).

General Supported ATRP (SATRP) Polymerization Procedure

Typically, the polystyrene support (PS-PPh$_3$), the catalyst and a magnetic stirring bar were introduced in a glass tube reactor equipped with a three-way stopcock. Three nitrogen/vacuum cycles were performed. Solvent, monomer, initiator, and soluble ligand were added in a separated flask and bubbled with nitrogen before being transferred in to the glass tube reactor by using a previously flame-dried stainless steel cannula. The mixture was subsequently heated up to the desired temperature under magnetic stirring. Samples were withdrawn at different time intervals to determine the monomer conversion and copolymer composition (by ^{1}H NMR), number average molecular weight ($\bar{M}_n$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) (by SEC). The polymerization reaction was stopped by cooling down the glass tube reactor in liquid nitrogen, and after the support settling, the polymer solution was removed under a slight nitrogen overpressure via a stainless steel cannula. The catalytic support was washed with extra solvent and dried under vacuum while the copolymer solution was poured into a large volume of heptane (a good solvent of PDMS macroinitiator and non-solvent of recovered diblock copolymers). After polymer precipitation, filtration, and drying under reduced pressure, the as-recovered copolymer was characterized by both SEC and ^{1}H NMR spectra.

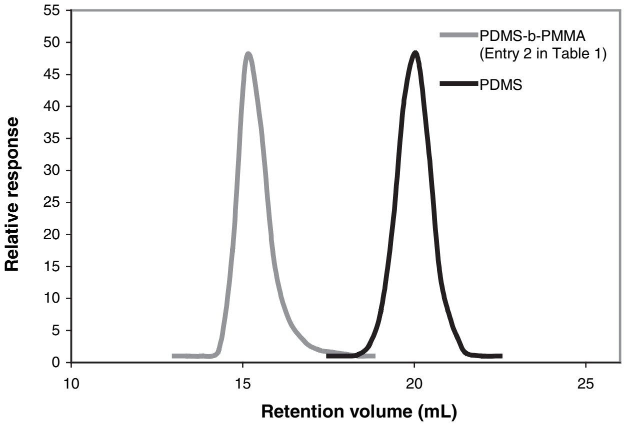

Figure 6. SEC traces of a silicone-organic block copolymer (P[MMA-*b*-DMS]) obtained by ATRP from the α-bromo PDMS macroinitiator (Table 1, entry 2).

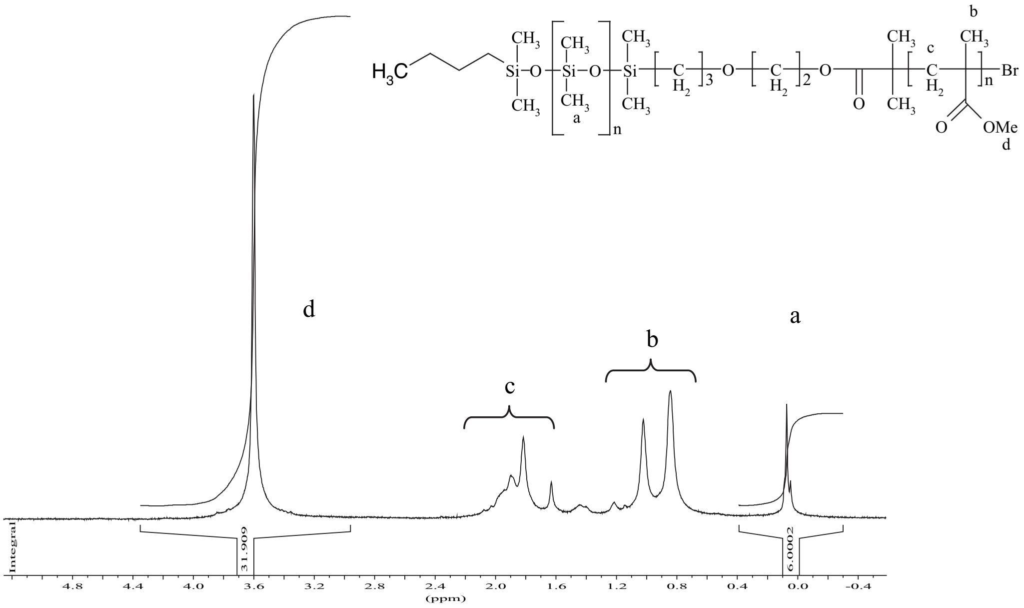

Figure 7. ^{1}H NMR spectrum of a P[DMS-*b*-MMA] block copolymer (entry 2 in Table 2) in $CDCl_3$.

Results and Discussion

Synthesis of the PDMS Macroinitiator

A nickel (II) bromide catalyst ligated onto crosslinked polystyrene resins (PS-PPh_3/$NiBr_2$) has been studied for the production of silicone-organic copolymers. This supported catalytic system has been used in the presence of at least six equivalents of soluble ligand, i.e., PPh_3. Indeed, these conditions have proved highly efficient for controlling both the polymer molar masses and molecular weight distributions in ATRP of MMA as initiated by EBr^{i}B.[22]

As the first step, it was important to confirm the efficiency of the ATRP of methacrylic monomers initiated by a PDMS macroinitiator, using the aforementioned nickel-based

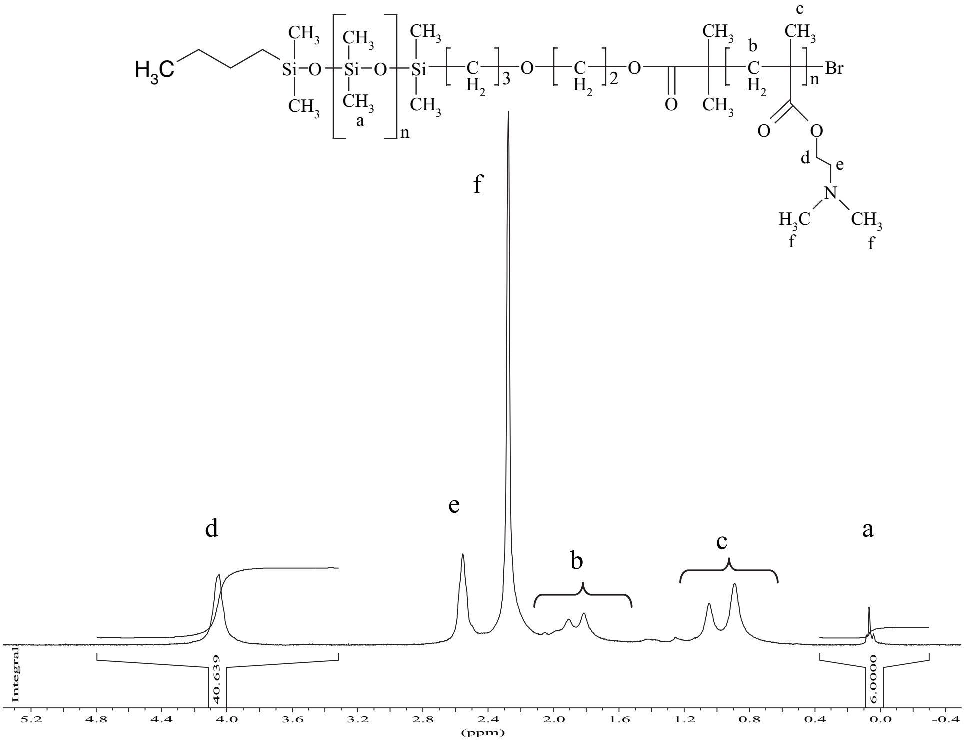

Figure 8. ^{1}H NMR spectrum of a P[DMS-*b*-DMAEMA] block copolymer (entry 4 in Table 2) in $CDCl_3$.

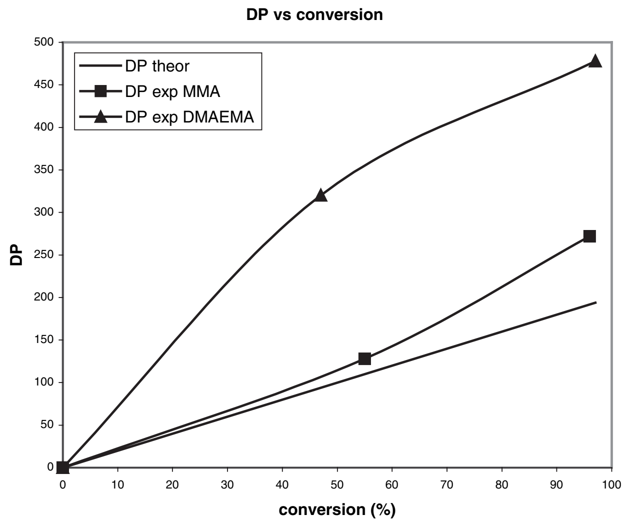

Figure 9. Evolution of $\overline{DP}$ with conversion for P[DMS-*b*-MMA] and P[DMS-*b*-DMAEMA] block copolymers as synthesized by homogeneous ATRP initiated by α-bromo PDMS.

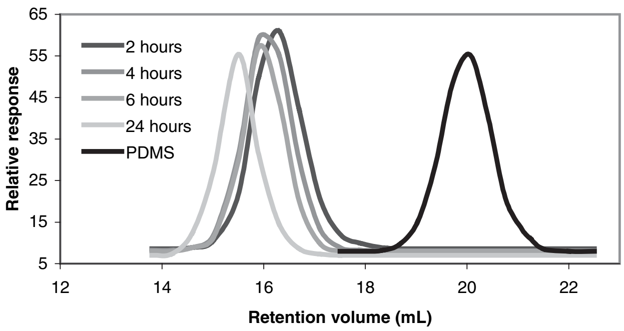

Figure 10. SEC traces of P[MMA-*b*-DMS] block copolymers as obtained by SATRP initiated by the α-bromo PDMS ($\overline{DP} \approx 12$) macroinitiator (see Table 2).

catalyst but carried out under homogeneous conditions, i.e., using $NiBr_2$ ligated by soluble PPh_3 as catalyst. Consequently, the copolymerization of methacrylic monomers was investigated after halogenation reaction of PDMS end-capped with a hydroxyl function. A well-defined α-hydroxyl terminated PDMS ($\overline{M}_w/\overline{M}_n = 1.1$ as measured by SEC in THF using PMMA standards) has been functionalized with Br^iBBr to give an α-bromo PDMS (Figure 2), which has been used in a subsequent step as the macroinitiator for the polymerization of the studied methacrylic monomers by ATRP. The PDMS samples were first characterized by ^1H NMR and FTIR spectra. ^1H NMR spectra confirmed the quantitative reaction of the hydroxyl end-groups of the α-hydroxy PDMS as evidenced by the presence of the sharp signal at about 2 ppm assigned to the $–C(Br)–(C\underline{\mathbf{H_3}})_2$ methyl protons of the α-bromo PDMS (signal m in Figure 3) and the quantitative shift of the signal at 3.7 ppm ($–C\underline{\mathbf{H_2}}–OH$; signal j in Figure 3) in favor of a new resonance centered at 4.3 ppm. FTIR spectra show the presence of the "Si–C" band at 794 cm^{-1}, the "Si–O" band at 1 015 cm^{-1}, and the "Si–CH_3" band at 1 259 cm^{-1} and the appearance of the "C=O" band at 1 738 cm^{-1}, after the reaction of the hydroxyl-terminated PDMS with Br^iBBr (Figure 4). This α-bromo PDMS macroinitiator was also characterized by ^{29}Si-NMR in order to determine the number of siloxane units in the polymer chain. Accordingly, the mean $\overline{DP}$ of the studied α-bromo PDMS has been estimated to be 12 (Figure 5).

Efficiency of α-Bromo PDMS/$NiBr_2$/PPh_3 as Macroinitiator/Ligated Catalyst in Synthesis of Silicone-Methacrylic Copolymers

First and for the sake of comparison, the studied α-bromo PDMS macroinitiator was used for the synthesis of silicone-organic copolymers via homogeneous ATRP of methacrylic monomers such as MMA and DMAEMA using $NiBr_2(PPh_3)_2$ as the catalyst. The polymerization reactions were carried out in toluene (monomer/solvent; 1/1 vol.) at 90 °C. The molecular parameters as measured by ^1H NMR and SEC are reported in Table 1.

The conversions and polymerization degrees in MMA and DMAEMA were determined by ^1H NMR from the

Table 2. Synthesis of P[MMA-*b*-DMS] block copolymers via SATRP in toluene initiated by the α-bromo PDMS macroinitiator ($\overline{DP} \approx 12$) and catalyzed by PS-PPh_3/$NiBr_2$ in the presence of soluble PPh_3. Conditions: 90 °C, $[MMA]_0 = 4.68$ M, $[M]_0/[I]_0/[C]_0/[L]_0/[L']_0 = 200/1/1/6/6$ (M, monomer; I, initiator; C, catalyst; L, ligand immobilized onto the support; L′, free PPh_3).

Entry	*t*	Conversion[a)]	$\overline{DP}$ theoretical[b)]	$\overline{DP}$ experimental[a)]	$f = \overline{DP}_{th}/\overline{DP}_{exp}$	$\overline{M}_n$ experimental[c)]	$\overline{M}_w/\overline{M}_n$[c)]
	h	%					
1	2	12	24	38	0.63	9 150	1.36
2	4	34	68	84	0.81	12 100	1.31
3	6	44	88	99	0.89	13 800	1.31
4	24	89	178	240	0.74	25 300	1.42

[a)] Determined by ^1H NMR spectra.
[b)] $\overline{DP}$ theoretical = $[MMA]_0/[PDMS\text{-}Br]_0 \times$ conversion.
[c)] Determined by SEC using PMMA standards.

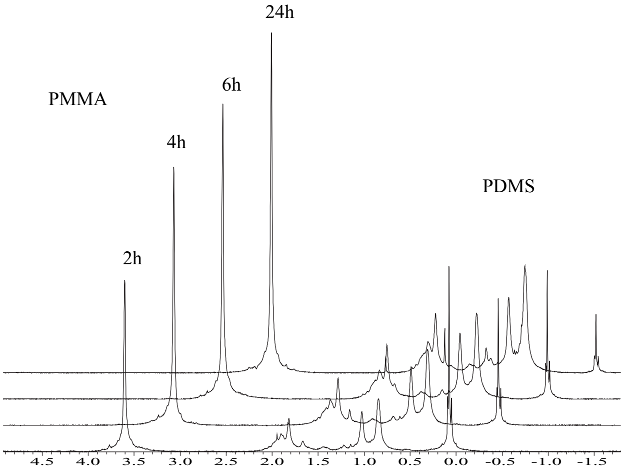

Figure 11. ^{1}H NMR spectra of the P[DMS-*b*-MMA] block copolymers in $CDCl_3$; effect of the reaction time (for conditions: see Table 2).

spectra of the crude product containing unreacted monomer using the relative intensities of the respective characteristic signals. The methacrylate content in the copolymer was determined from the relative intensities of the protons characteristic of the polymethacrylate segments and the PDMS block, respectively. Typical ^{1}H NMR spectra of P[DMS-*b*-MMA] and P[DMS-*b*-DMAEMA] block copolymers are shown in Figure 7 and 8, respectively. As observed in Table 1, as far as the MMA polymerization is concerned, the control over the molecular parameters is generally good in terms of molar masses as well as in terms of polydispersity indices. Indeed, SEC analysis shows a narrow unimodal molecular weight distribution, while the quantitative shift of the SEC trace to higher molecular weight demonstrates the high efficiency of the initiation step (70–90% of initiation efficiency, *f* in Table 1) (Figure 6). However, when the PPh_3-ligated nickel bromide catalyst is used for the polymerization of DMAEMA, the control over the $\overline{DP}$ of the methacrylate units is altered even though quite narrow molecular weight distributions are maintained. All happens as if a large part of the initiator (60–70% as attested by the low initiation efficiencies) is lost at the very beginning of the polymerization reaction probably caused by the presence of the aminated monomer units, capable of coordinating the catalyst and consequently to modify the redox potential of the transition metal. This point is clearly evidenced in Figure 9 where one can observe that the $\overline{DP}$ of the polymethacrylate segment obviously deviates from the predicted values all along the polymerization.

Synthesis of P[DMS-b-MMA] Copolymers via Supported ATRP

The α-bromo PDMS macroinitiator has thus proved highly efficient for synthesizing silicone-methacrylic copolymer via homogeneous ATRP catalyzed by PPh_3-ligated $NiBr_2$. Moreover, the use of purposely added soluble ligand such as PPh_3 has recently allowed for controlling the SATRP of MMA.[21,22] Accordingly, comparative syntheses have been attempted via SATRP by using the PS-PPh_3/$NiBr_2$ supported catalytic system in the presence of purposely added soluble PPh_3. Samples were withdrawn at determined periods of time and the copolymer compositions estimated by ^{1}H NMR spectra in $CDCl_3$ (Table 2).

Interestingly enough, a good control over the length of the PMMA block could be attained. Indeed, the polymerization degree of the PMMA segments in the copolymers increases with the monomer conversion, and whatever the studied reaction time, the molecular weight distribution remains monomodal with polydispersity indices remaining as narrow as the values obtained for SATRP of homo-PMMA initiated by EBr^{i}B.[22] Indeed, SEC chromatograms show narrow unimodal molecular weight distributions and a quantitative shift of the SEC trace to higher molecular weight with reaction time attesting for the absence of PMMA homopolymer (Figure 10). It is worth mentioning

Table 3. Synthesis of silicone-organic block copolymers via SATRP in toluene initiated by the α-bromo PDMS macroinitiator ($\overline{DP} \approx 12$) and catalyzed by PS-PPh_3/$NiBr_2$ in the presence of soluble PPh_3. Conditions: 90 °C, $[I]_0/[C]_0/[L]_0/[L']_0 = 1/1/6/12$ (M, monomer; I, initiator; C, catalyst; L, ligand immobilized onto the support; L′, free PPh_3).

Entry	Copolymer	$[MMA]_0/[PDMS\text{-}Br]_0$	$[DMAEMA]_0/[PDMS\text{-}Br]_0$	t	Conversion[a)]		$\overline{DP}_{th}$[b)]	$\overline{DP}_{exp}$[a)]	$\overline{DP}_{th}$[b)]	$\overline{DP}_{exp}$[a)]	$\bar{M}_n$ experimental[c)]	$\bar{M}_w/\bar{M}_n$[c)]	$f = \overline{DP}_{th}/\overline{DP}_{exp}$	
				h	%		MMA	MMA	DMAEMA	DMAEMA			MMA	DMAEMA
					MMA	DMAEMA								
1	P[DMS-*b*-MMA]	200	–	18	94	–	188	(456)	–	–	35 700	1.21	(0.41)	–
2	P[DMS-*b*-MMA-*b*-DMAEMA]	–	200	6	94	26	188	308	52	109	38 600	bimodal	0.61	0.48
3	P[DMS-*b*-MMA]	267	–	18	89	–	238	319	–	–	34 500	1.27	0.75	–
4	P[DMS-*b*-MMA-*b*-DMAEMA]	–	133	6	92	42	246	(510)	56	62	33 800	1.76	(0.48)	0.90
5	P[DMS-*b*-MMA]	133	-	18	88	–	117	138	–	–	13 900	1.34	0.85	–
6	P[DMS-*b*-MMA-*b*-DMAEMA]	–	267	6	83	38	110	162	101	244	32 100	bimodal	0.68	0.41

[a)] Determined by ^{1}H NMR spectra.
[b)] $\overline{DP}$ theoretical = $[Monomer]_0/[PDMS\text{-}Br]_0 \times$ conversion.
[c)] Determined by SEC using PMMA standards.

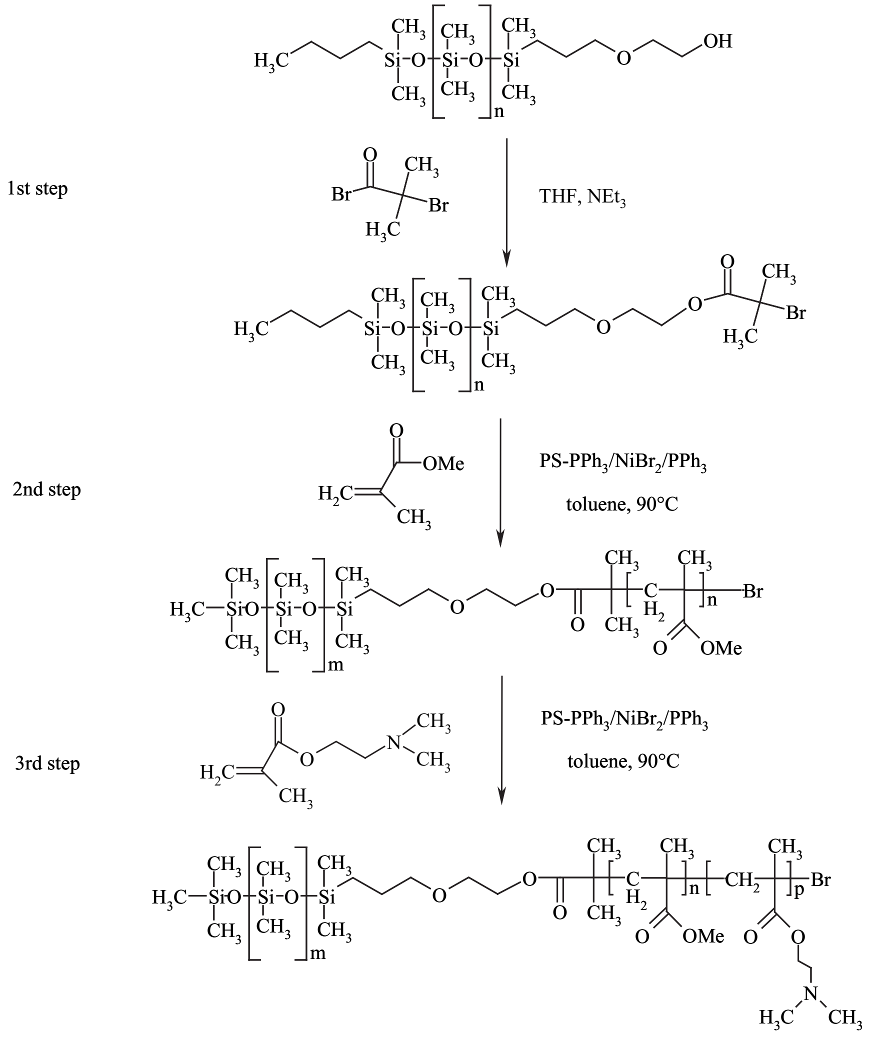

Figure 12. Synthesis of P[DMS-*b*-MMA-*b*-DMAEMA] block copolymer by supported ATRP.

that in the absence of purposely-added PPh_3, no control over the copolymerization could be achieved in perfect agreement with recently published data for the homopolymerization of MMA initiated by EBr^iB. Figure 11 shows the ^1H NMR spectra of the P[DMS-*b*-MMA] block copolymers as a function of the reaction time. The increase in the length of the polymethacrylate blocks is clearly evidenced by the relative intensities of the characteristic signal of the methyl groups (–C(O)OC**H**$_3$) from the methacrylic segment at 3.6 ppm (PMMA in Figure 11) and the methyl of the siloxane groups at ca. 0 ppm (PDMS in Figure 11) (see Figure 7 for the complete attributes of the resonance signals).

Polymerization of DMAEMA

The efficiency of the $PS\text{-}PPh_3/NiBr_2$ supported catalyst thus used in the presence of an excess of soluble PPh_3, was observed for the synthesis of PMMA homopolymers and P[DMS-*b*-MMA] block copolymers. The supported catalytic system has also been applied to other methacrylic monomers such as DMAEMA. P[DMS-*b*-MMA-*b*-DMAEMA] block copolymers with varied compositions were accordingly synthesized (Table 3). Indeed, it has been previously observed that the ATRP of DMAEMA using homogeneous PPh_3-ligated nickel bromide catalyst leads to a loss of control over the $\overline{DP}$ of the methacrylate units while a quite narrow molecular weight distribution can be preserved. In order to improve the initiation efficiency, the polymerization of MMA was first carried out until near total conversion before the addition of DMAEMA in the crude reaction medium (see Figure 12).

The introduction of DMAEMA in the reaction medium leads again to a loss of control over the molecular parameters in terms of polydispersity indices as well as of molar

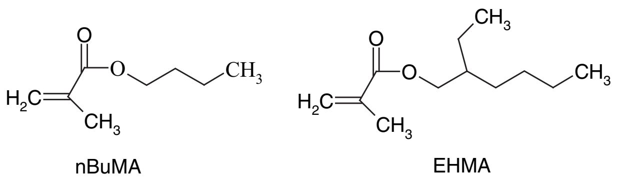

Figure 13. Investigated non-functional methacrylic monomers.

masses. Even if the control of the polymerization of MMA appears to be good as attested by the narrow molecular weight distribution and $\overline{DP}$s close to the theoretical values, the introduction of DMAEMA triggers both bimodality in the SEC chromatogram and $\overline{DP}$s higher than theoretical values. As observed in homogeneous ATRP, the presence of the amine group seems to modify the efficiency of the catalyst. Indeed, the nickel content in the P[DMS-*b*-MMA] copolymers is generally below 100 ppm except for the copolymers containing DMAEMA units which contain more than 500 ppm of residual metal as measured by ICP. This might be due to the ability of the amino-functionalized monomer to complex the nickel catalyst, displacing a phosphine ligand and tearing off part of the catalyst from the support. Consequently, it leads to a color modification of the supported catalyst from dark green to orange and a copolymer contaminated by high residual catalyst content.

Polymerization of Other Non-Functional Methacrylic Monomers

In order to confirm the efficiency of the nickel-based supported catalytic system, SATRP of other non-functional methacrylic monomers such as BuMA (Figure 13) and EHMA (Figure 13) was investigated.

As expected, the control over the molecular parameters remains very good. Indeed, the $\overline{DP}$s are in the same range as the theoretical values and polydispersity indices are maintained low (Table 4).

In conclusion, the efficiency of the catalyst in SATRP has been observed to be strongly influenced by all parameters that can modify the transition metal complex. For instance, the solvent, monomer, or initiator could act as ligand(s) for the transition metal catalyst and, therefore, change the nature of the initial complex. SATRP is a difficult multicomponent system, it is therefore of prime importance to consider all of its components to reach the optimum copolymerization conditions and expected control.

Conclusion

The controlled synthesis of silicone-organic copolymer was achieved using a previously synthesized α-bromo PDMS macroinitiator and the soluble transition metal complex as ATRP catalysts. Then, silicone-organic copolymers were synthesized by SATRP catalyzed by a nickel bromide catalyst, supported onto a crosslinked PS-PPh_3/$NiBr_2$ resin, in the presence of a sufficient amount of purposely-added "free" soluble PPh_3. The synthesis of P[DMS-*b*-MMA] block copolymers was very well controlled leading to copolymers with controlled composition and narrow molecular weight distribution. SEC characterizations show efficient initiation and absence of homopolymer formation. However, the use of an amino-functionalized monomer, e.g., DMAEMA, triggers a loss of control. This lack of control has been explained by the presence of a tertiary amine capable of coordinating the transition metal of the catalytic complex and turns down its efficiency. Nevertheless, other non-functional methacrylic monomers such as BuMA and EHMA have been successfully copolymerized under the investigated experimental conditions with controlled compositions, narrow molecular weight distributions and very low residual metal content.

Table 4. Synthesis of silicone-organic block copolymers via SATRP in toluene initiated by the α-bromo PDMS macroinitiator ($\overline{DP} \approx 12$) and catalyzed by PS-PPh_3/$NiBr_2$ in the presence of soluble PPh_3. Conditions: 90 °C, $[M]_0/[I]_0/[C]_0/[L]_0/[L']_0 = 200/1/1/6/12$ (M, monomer; I, initiator; C, catalyst; L, ligand immobilized onto the support; L′, free PPh_3).

Entry	Monomer $[M]_0$	t	Conversion[a)]	$\overline{DP}$ theoretical[b)]	$\overline{DP}$ experimental[a)]	$f = \overline{DP}_{th}/\overline{DP}_{exp}$	$\bar{M}_n$ experimental[c)]	$\bar{M}_w/\bar{M}_n$[c)]
		h	%					
1	BuMA (3.13 M)	6	56	112	111	1.00	19 900	1.44
2		24	93	186	219	0.85	30 900	1.37
3	EHMA (2.23 M)	6	45	90	118	0.76	21 800	1.35
4		24	90	180	216	0.83	33 500	1.35

a) Determined by ^1H NMR spectra.
b) $\overline{DP}$ theoretical = $[\text{Monomer}]_0/[\text{PDMS-Br}]_0$ × conversion.
c) Determined by SEC using PMMA standards.

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[1] "*Controlled Radical Polymerization*", K. Matyjaszewski, Ed., American Chemical Society, Washington, DC 1998, Vol. 685.
[2] "*Controlled/living Radical Polymerization: Progress in ATRP, NMP, and RAFT*", K. Matyjaszewski, Ed., American Chemical Society, Washington, DC 2000, Vol. 768.
[3] K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921.
[4] M. J. Owen, *Chimie nouvelle* **2004**, *85*, 27.
[5] R. C. Kumar, Jr., M. H. Andrus, R. R. Dueltgen, M. H. Mazuek, *ACS Polym. Prepr.* **1994**, *35*, 786.
[6] H. Shinoda, K. Matyjaszewski, L. Okrasa, M. Mierzwa, T. Pakula, *Macromolecules* **2003**, *36*, 4772.
[7] H. Shinoda, P. J. Miller, K. Matyjaszewski, *Macromolecules* **2001**, *34*, 3186.
[8] H. Shinoda, K. Matyjaszewski, *Macromol. Rapid Commun.* **2001**, *22*, 1176.
[9] J. V. Crivello, D. A. Conlon, J. L. Lee, *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1197.
[10] J. V. Crivello, J. L. Lee, D. A. Conlon, *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1251.
[11] C. P. R. Nair, G. Clouet, *Macromolecules* **1990**, *23*, 1361.
[12] V. Harabagiu, V. Hamciuc, D. Giurgiu, *Makromol. Chem., Rapid Commun.* **1990**, *11*, 433.
[13] K. Huan, E. Khoshdel, D. M. Haddleton, *Polym. Prepr.* **2000**, *41*, 538.
[14] K. Huan, L. Bes, D. M. Haddleton, E. Khoshdel, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1833.
[15] K. Matyjaszewski, P. J. Miller, E. Fossum, Y. Nakagawa, *Appl. Organomet. Chem.* **1998**, *12*, 667.
[16] Y. Nakagawa, P. J. Miller, K. Matyjaszewski, *Polymer* **1998**, *39*, 5163.
[17] P. J. Miller, K. Matyjaszewski, *Macromolecules* **1999**, *32*, 8760.
[18] J. Yang, S. Ding, M. Radosz, Y. Shen, *Macromolecules* **2004**, *37*, 1728.
[19] Y. Shen, S. Zhu, *Macromolecules* **2001**, *34*, 8603.
[20] S. Hong, H. Paik, K. Matyjaszewski, *Macromolecules* **2001**, *34*, 5099.
[21] E. Duquesne, J. Habimana, P. Degée, P. Dubois, *Chem. Commun.* **2004**, 640.
[22] E. Duquesne, J. Habimana, P. Degée, P. Dubois, *Macromolecules* **2005**, *38*, 9999.