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PDMS−PEO Densely Grafted Copolymers

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ABSTRACT: Molecular brushes with poly(dimethylsiloxane) (PDMS) side chains were prepared by atom transfer radical polymerization (ATRP) conditions via macromonomer method (*grafting through*). The well-defined polymers with molecular weight distribution $M_w/M_n = 1.22-1.35$ and with up to 350 repeating units of macromonomers with methacrylate functionality (PDMSMA, MW = 1000 g/mol, $DP_{PDMS} = 10$) were formed in the presence of CuCl/Me$_6$TREN catalyst. Similar conditions were used for copolymerization with another macromonomer, i.e. poly(ethylene glycol) methyl ether methacrylate (PEOMA, MW = 1100 g/mol, $DP_{PEO} = 23$). The comparable reactivities of both methacrylates resulted in heterografted brush copolymers with random composition and with narrow molecular distribution ($M_w/M_n = 1.07-1.18$). The obtained molecular brushes, consisting of amorphous PDMS fraction and crystallizable PEO segments, after annealing at high temperature had properties characteristic for soft gels ($G' \ll 10^4$ Pa).

Introduction

Densely grafted copolymers, also termed molecular brushes, can be obtained by several grafting techniques using atom transfer radical polymerization (ATRP).[1−4] One of them, *grafting from*, typically proceeds via the initial preparation of well-defined multifunctional macroinitiators with a high degree of polymerization ($DP_n > 400$) and narrow molecular weight distribution ($M_w/M_n \sim 1.2$), which is subsequently used for the growth of side chains.[5−13] Because of the large amounts of initiating sites and high probability of cross-linking, the polymerization is usually limited to low monomer conversion (<20%). This route is preferable for incorporation of low molecular weight (meth)acrylate monomers to side chains.

The alternative technique is *grafting through*, i.e., a macromonomer method, which might also lead to a well-defined polymer backbone. The degree of polymerization of side chains (DP_{sc}) is predefined by the macromonomer. Using this approach, homografted brushes with poly(vinyl ether) ($DP_n < 180$, $DP_{PIBVE} = 10$; $DP_n < 100$, $DP_{PIBVE} = 20$ and $DP_n < 10$, $DP_{PIBVE} = 40$)[14] and polyethylenoxy grafts ($DP_n \leq 425$, $DP_{PEO} = 5$ and $DP_n \leq 200$, $DP_{PEO} = 23$)[9] were prepared by ATRP. In the case of methacryloyl macromonomer containing two chains of the same length of polystyrene (PS) or poly(*tert*-butyl acrylate) (PtBA), very dense brushes were formed.[15] The copolymerization of macromonomer with low molecular weight monomer leads to the formation of copolymers with loosely distributed grafts. Previously, the ATRP of polystyrene macromonomer with *N*-vinylpyrrolidone,[16,17] poly(dimethylsiloxane) (PDMS) or polylactide macromonomer (PLA) with methyl methacrylate (MMA),[18,19] PMMA or polyethylene macromonomer with *n*-butyl acrylate (BA),[20−22] and PEO macromonomer with 2-(trimethylsilyloxyl)ethyl methacrylate (HEMA-TMS)[23] were reported. The loosely grafted statistical PEO copolymers with HEMA-TMS, after transformation of trimethylsilyloxy groups to 2-bromopropionate groups, were used as a macroinitiators for polymerization of BA.

The combination of *grafting through* and *grafting from* methods resulted in densely heterografted PBA−PEO brushes.[23] A similar example was reported for block copolymers with PPEOMA-*bl*-PHEMA, where the OH group in each repeat unit of HEMA was converted to an initiating group and next grafted by HEMA.[24] The polymerization of two comonomers by *grafting from* a multifunctional macroinitiator, e.g., copolymerization of aniline-2-sulfonic acid and aniline initiated by poly[4-(4-vinylbenzoxyl)phenylamine[25] or 1-octene and methyl acrylate by poly(2-(2-bromoisobutyryloxy)ethyl methacrylate (PBIEM),[10] generated densely grafted brushes with random copolymer side chains. Brushes with block copolymer grafts, PS-*bl*-PBA[6,26] and PS-*bl*-PtBA,[11] were obtained by preparation of brush with the first block via *grafting from* macroinitiator (poly(2-(2-bromopropionyloxy)ethyl methacrylate (PBPEM),[6] PBIEM,[11] polyisocyamide[26]) and then extended by polymerization of the second monomer.

The composition and microstructure of graft copolymers depend on selection of co(macro)monomers, i.e., two methacrylates or methacrylate/acrylate pair, which can have either similar or different reactivity ratios, yielding either statistical or gradient distributions, respectively. Such effects were described for the copolymers containing PEO/octadecyl methacrylate heterografts[27] and for gradient copolymer consisting of three components PMMA-*g*-PLA/PDMS.[28]

This paper describes the successful ATRP of PDMS macromonomer (MW = 1000 g/mol, $DP_{PDMS} = 10$) via *grafting through* using ethyl 2-bromoisobutyrate (Et-Br*i*Bu) as an initiator and copper(I) chloride/tris(2-dimethylaminoethyl)amine (CuCl/Me$_6$TREN) as a catalyst/ligand system in organic solvent. The hydrophobic

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PDMSMA with low T_g was copolymerized with crystallizable hydrophilic PEO macromonomer (MW = 1100 g/mol, DP_{PEO} = 23), yielding statistical heterografted brushes. They were obtained by a convenient one pot procedure that avoided additional synthetic steps, such as synthesis of macroinitiator required for the *grafting from* method. The incorporation of crystalline PEO macromonomer among chains of PPDMSMA modified glassy properties of pure homopolymer PPDMSMA generating soft gel behavior in the final polymeric material.

The mechanical properties of the PDMS−PEO brushes were studied by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Their morphologies were characterized by X-ray scattering techniques (WAXS, SAXS). The heterografted copolymers were compared with densely homografted PPDMSMA and PPEOMA brush polymers.

Experimental Section

Materials. Poly(ethylene glycol) methyl ether methacrylate, (Aldrich, PEOMA, MW_{av} = 1100 g/mol) and monomethacryloxypropyl poly(dimethylsilyloxane) (Gelest, PDMSMA, MCR-M11, MW_{av} = 1000 g/mol) were used as a macromonomers. Before polymerization, PEOMA, solid at room temperature, was dissolved in THF and passed through an alumina column to remove the antioxidant inhibitor (MEHQ and BHT), then the solvent was evaporated and the macromonomer was dried under vacuum to a constant mass. Liquid PDMSMA was passed through an alumina column. Copper(I) chloride (CuCl, Acros, 95%) was purified by stirring with glacial acetic acid (Fisher Scientific), followed by filtration and washing the solid three times with ethanol and twice with diethyl ether. The solid was dried under vacuum (1×10^{-2} mbar) for 2 days. Tris(2-dimethylaminoethyl)amine (Me_6TREN)[29] was prepared as previously described. Ethyl 2-bromoisobutyrate (EtBriBu, Aldrich, 99%) and all other solvents were used without purification.

Synthesis. General Procedure for ATRP of PDMSMA Macromonomer (Example). The solution of PDMSMA (2 g, 2 mmol) in xylene (3 mL) and Me_6TREN (2.1 μL, 8×10^{-3} mmol) was degassed by three freeze−pump−thaw cycles. CuCl (0.79 mg, 8×10^{-3} mmol) was added, and the mixture was stirred for 30 min at room temperature. Next, the Schlenk flask was placed in a thermostated oil bath at 70 °C. After 1 min, EtBr*i*Bu (0.78 mg, 4×10^{-3} mmol) was added to start the reaction. The polymerization was stopped by exposing the solution to air, and then the mixture was diluted with THF and filtered through an activated (neutral) alumina column to remove the copper catalyst. The remaining unreacted macromonomer was removed by ultrafiltration in THF solution using a membrane (Millipore, Regenerated Cellulose, YM10, NMWL: 10 000). The polymers were dried under vacuum at room temperature to a constant mass.

The same procedure was also applied for the copolymerization with PEO macromonomer, which was dissolved in solvent at the beginning of preparation.

Characterization. Gel permeation chromatography (GPC) measurements were conducted in THF and toluene at 30 °C using a Waters 515 liquid chromatograph pump (1 mL/min) and four Polymer Standards Service columns (guard, 10^5, 10^4, 10^3 Å) in series with three detection systems: a differential refractometer (Waters model 410), multiangle laser light scattering (MALLS) detector (DAWN model F), and a differential viscometer (Viscotek model H502). The determination of apparent molecular weights for the homopolymers was based on the low polydispersity index of linear polystyrene (PS) standards. The refractive index increment d*n*/d*c* was determined with an Otsuka Photal RM-102 differential refractometer.

^{1}H nuclear magnetic resonance (NMR) spectroscopy was performed on a Brüker 300 MHz spectrometer in chloroform-*d* at room temperature.

Characterization of Macromonomers and (Co)polymers. ^{1}H NMR PDMSMA, MW = 1000 g/mol ($CDCl_3$) δ (ppm): 6.02 (s, 1H, CHH=), 5.46 (s, 1H, CHH=) 4.02 (t, 2H, $-OC\mathit{H}_2-$, J = 6.97 Hz), 1.9 (s, 3H, $-CH_2{=}CC\mathit{H}_3$), 1.6 (m, 2H, $-OCH_2-C\mathit{H}_2-$), 1.2 (m, 4H, $CH_3\text{-}(C\mathit{H}_2)_2$), 0.8 (t, 3H, $C\mathit{H}_3-(CH_2)_2-$, J = 6.97 Hz), 0.5 (m, 4H, $-C\mathit{H}_2-Si$), 0.0 (m, 6H × degree of polymerization (DP_n), $C\mathit{H}_3-Si-C\mathit{H}_3$).

^{1}H NMR PEOMA, MW = 1100 g/mol ($CDCl_3$) δ (ppm): 6.05 (s, 1H, CHH=), 5.50 (s, 1H, CHH=), 4.25 (t, 2H, $-O-C\mathit{H}_2-CH_2-O$-, J = 4.86 Hz), 3.42−3.75 (m, 4H × degree of polymerization (DP_n)-2, $-O-C\mathit{H}_2-C\mathit{H}_2-O$), 3.35 (s, 3H, $-O-C\mathit{H}_3$), 1.9 (s, 3H, $=CC\mathit{H}_3$).

^{1}H NMR PPDMSMA ($CDCl_3$) δ (ppm): 3.8 (broad peak, 2H, $-OC\mathit{H}_2-CH_2-$), 1.63 and 1.45 (broad peak, $-C\mathit{H}_2-C(CH_3)-$), 1.6 (broad peak, 2H, $-OCH_2-C\mathit{H}_2-$), 1.23 (broad peak, 3H, $-CH_2-C(C\mathit{H}_3)-$), 1.2 (m, 4H, $CH_3-(C\mathit{H}_2)_2$), 0.8 (t, 3H, $C\mathit{H}_3-(CH_2)_2$, J = 6.97 Hz), 0.5 (m, 4H, $-C\mathit{H}_2-Si$), 0.0 (m, 6H × degree of polymerization (DP_n), $C\mathit{H}_3-Si-C\mathit{H}_3$).

^{1}H NMR P(PDMSMA-*co*-PEOMA) ($CDCl_3$) δ (ppm): backbone, 1.23 (broad peak, 3H, $-CH_2-C(C\mathit{H}_3)-$), 1.63 and 1.45 (broad peak, $-C\mathit{H}_2-C(CH_3)-$); PDMS side chains, 3.8 (broad peak, 2H, $-OC\mathit{H}_2$), 1.6 (m, 2H, $-OCH_2-C\mathit{H}_2-$), 1.2 (m, 4H, $CH_3-(C\mathit{H}_2)_2$), 0.8 (t, 3H, $C\mathit{H}_3-(CH_2)_2$, J = 6.97 Hz), 0.5 (m, 4H, $-C\mathit{H}_2-Si$), 0.0 (m, 6H × degree of polymerization (DP_n), $C\mathit{H}_3-Si-C\mathit{H}_3$); PEO side chains, 4.13 (t, 2H, $-O-C\mathit{H}_2-CH_2-O-$, J = 4.86 Hz), 3.42−3.75 (m, 4H × degree of polymerization (DP_n)-2, $-O-C\mathit{H}_2-C\mathit{H}_2-O$), 3.35 (s, 3H, $-O-C\mathit{H}_3$).

Differential scanning calorimetry (DSC) was performed with a Metler 30 calorimeter to determine the glass transition temperatures and the melting (or crystallization) points. Heating and cooling runs were performed at a rate of 10 °C/min in the temperature range from −140 to 75 °C.

Wide-angle X-ray diffraction (WAXS) and small-angle X-ray scattering (SAXS) were used to characterize the structure of the bulk materials. In both cases, the X-ray source was the Cu Kα radiation (λ = 0.154 nm) with a pinhole collimation, and 2D position-sensitive detectors (Bruker) were used. Measurements were performed at various temperatures. The recorded 2D scattered intensity distributions were integrated over the azimuthal angle and are presented as functions of the scattering vector ($s = 2 \sin \theta/\lambda$, where θ is the scattering angle).

Dynamic mechanical analysis (DMA) was performed using a mechanical spectrometer (RMS 800, Rheometic Scientific). Temperature dependencies vs shear modulus were measured at a constant deformation frequency of 10 rad/s. The results were obtained under cooling or heating with the rate 2 °C/min.

Results and Discussion

Polymerization of PDMS Macromonomer. The preparation of poly(PDMS macromonomer) brush (Scheme 1a) in the presence of CuCl/dNbpy as a catalyst/ligand system and xylene solvent was not efficient and reached very low conversion, below 2%, after 5 days. However, the replacement of dNbpy by another ligand Me_6TREN[30] significantly increased the activity of the catalyst, yielding higher conversion, up to 50%, after 21 h (**I** in Table 1). The polymerization rate was enhanced by introducing larger amount of catalyst/ligand (2 equiv to initiator), which resulted in polymers **II** and **III** with almost 70% conversion at higher ratio of monomer/initiator after 21 h. The detailed data are presented in Table 1.

The polymerization was followed by ^{1}H NMR (Figure 1). The peak areas of signal assigned to the methylenoxy protons $-O-C\mathit{H}_2$ at 4.02 ppm (*c*) or the vinyl protons $C\mathit{H}_2{=}C-$ at 5.46 and 6.02 ppm (*a*) in PDMSMA macromonomer were compared with the signal at 3.8 ppm ascribed to the methylenoxy protons in polymer (*k*), which appeared after starting the reaction and was increasing with time. This enabled calculation of con-

Scheme 1. ATR (Co)polymerization of PDMSMA and PEOMA

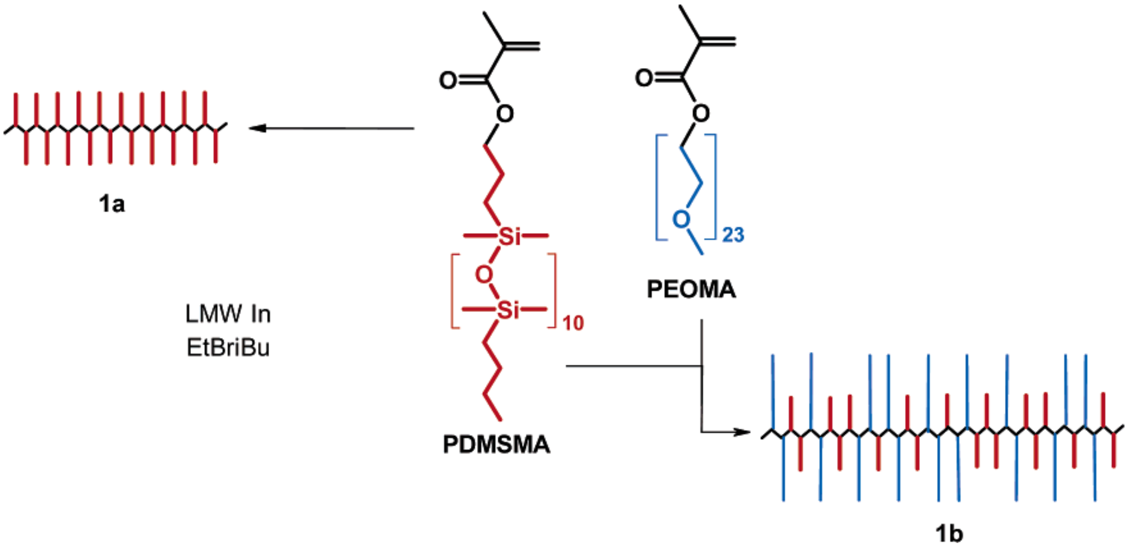

Table 1. Homopolymerization of PDMSMA

									GPC-MALLS					
			NMR		GPC (toluene)				THF			toluene		
no.	MM/EtBriBu/CuCl/Me_6TREN[a]	T (°C)	conv (%)	DP_n[b]	conv (%)	DP_n[b]	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n	dn/dc (mL/g)	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n	dn/dc (mL/g)
I	250/1/1/1	80	50.1	125	48.1	120	49.7	1.34	98.6	1.22	0.023	90.1	1.26	−0.071
II	300/1/2/2	70	67.0	201	65.5	196	54.3	1.38	204.3	1.32	0.025	150.5	1.36	−0.071
III	400/1/2/2	70	68.9	275	66.2	265	69.4	1.44	259.5	1.35	0.022	255.0	1.40	−0.071

[a] Xylene/PDMSMA = 1/1 vol/wt. [b] $M_{n,th} = DP_n \times 1000$, where 1000 is MW of PDMSMA.

sumption of PDMSMA. The conversion was also determined using GPC analysis by monitoring the decrease of the macromonomer peak area, relative to polymer peak which was shifted toward higher molecular weight with the progress of polymerization, as presented in Figure 2. The tailing in molecular weight distribution could be ascribed to termination or transfer reactions. The results obtained using both methods, NMR and GPC, showed very good agreement; the values differed less than 2−3% (Table 1).

The apparent values of molecular weights determined by conventional GPC using polystyrene standards ($M_{n,ap}$) are significantly lower than theoretical values ($M_{n,th}$) calculated from monomer conversion assuming quantitative initiation. The GPC values are underestimated by linear standards, which have larger hydrodynamic volumes than densely grafted copolymers. However, GPC-MALLS provided absolute molecular weights of the molecular brushes which agreed with theoretical values. The molecular weight distribution was in the range 1.2−1.4 and was increasing with DP_n of polymer. The measurements, performed in toluene, gave negative signals because its refractive index is higher than that of PDMSMA (dn/dc = −0.071). Although the difference in refractive index between PDMS macromonomer and THF is smaller (dn/dc = 0.023), this eluent was also chosen for the reason that the signals of later described copolymers of PDMSMA with PEOMA could not be detected in toluene. The results showed comparable values of the molecular weight of poly(PDMS macromonomers) analyzed in the presence of both eluents, and the degree of polymerization calculated from GPC-MALLS was similar to that estimated from monomer conversion by NMR and GPC. The GPC-MALLS traces

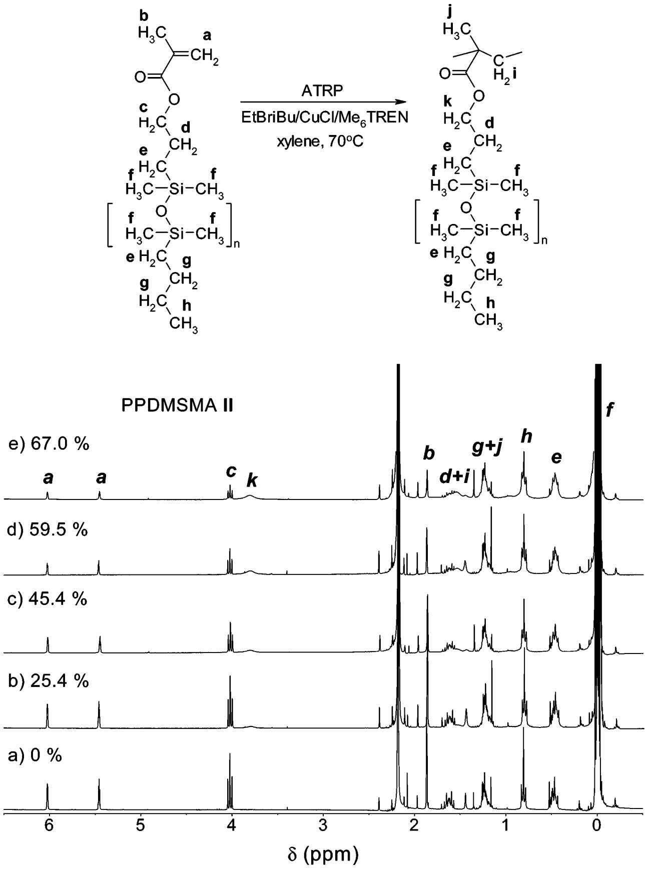

Figure 1. 300 MHz ^{1}H NMR spectra recorded during PDMSMA homopolymerization. [PDMSMA]$_0$:[EtBriBu]$_0$:[CuCl]$_0$:[Me_6TREN]$_0$ = 300:1:2:2; *o*-xylene/PDMSMA = 1/1 vol/wt. T = 70 °C.

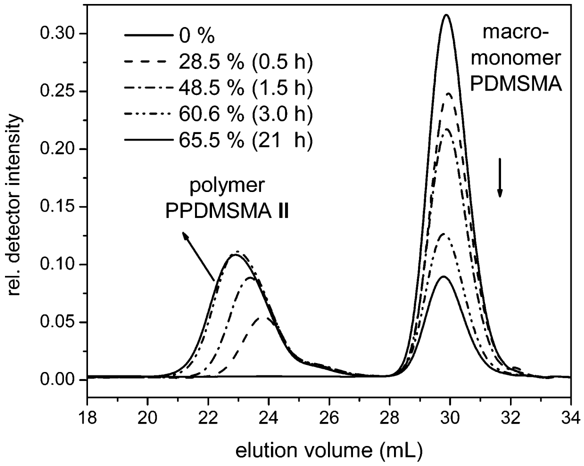

Figure 2. Toluene GPC traces for ATRP of PDMSMA (MW = 1000 g/mol). $[\mathrm{PDMSMA}]_0$:$[\mathrm{EtBr}i\mathrm{Bu}]_0$:$[\mathrm{CuCl}]_0$:$[\mathrm{Me_6TREN}]_0$ = 300:1:2:2; *o*-xylene/PDMSMA = 1/1 vol/wt; T = 70 °C.

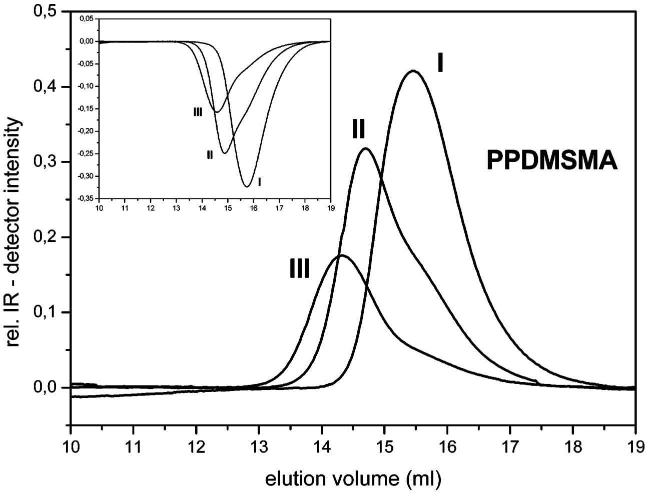

Figure 3. GPC-MALLS traces for PPDMSMA **I**–**III** in THF. The results in toluene eluent are presented in the inset. Conditions of polymerizations are described in Table 1.

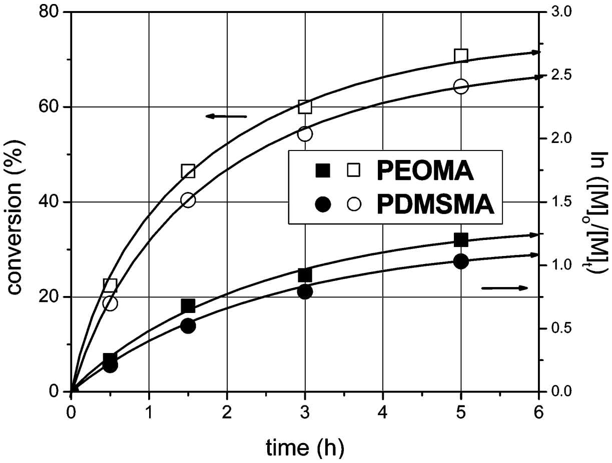

Figure 4. Plot of monomer consumption vs time for the copolymerization of PDMSMA with PEOMA (**IV**). [PEOMA + PDMSMA]$_0$/[EtBriBu]$_0$/[CuCl]$_0$/[Me$_6$TREN]$_0$ = 250/1/2/2, xylene/mon = 2/1 vol/wt, T = 70 °C.

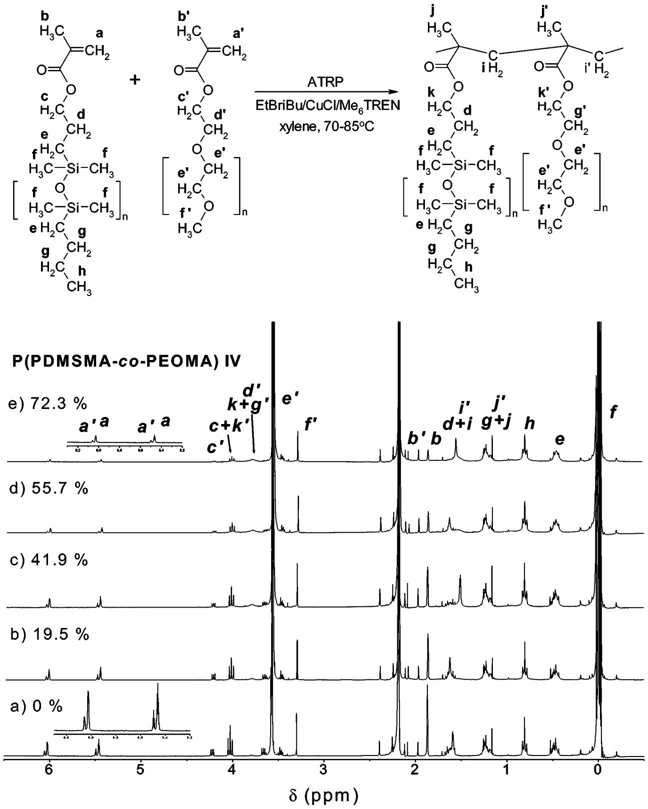

Figure 5. ^{1}H NMR spectra recorded during the copolymerization of PDMSMA and PEOMA (**IV**). $[\mathrm{PDMSMA}]_0$:$[\mathrm{PEOMA}]_0$:$[\mathrm{EtBriBu}]_0$:$[\mathrm{CuCl}]_0$:$[\mathrm{Me_6TREN}]_0$ = 250:1:2:2; xylene/PDMSMA = 2/1 vol/wt; T = 70 °C.

in THF and toluene for PPDMSMA with various degree of polymerization are presented in Figure 3.

Copolymerization of PDMS and PEO Macromonomers. The application of CuCl/dNbpy or CuBr/dNbpy catalyst/ligand systems for equimolar amounts of comonomers, the same as for PDMSMA homopolymerization, led to low conversion, below 10% after 6 days. Two equivalents of CuCl/Me$_6$TREN to 1 equiv of initiator at 70 °C provided the best conditions for copolymerization with PEOMA macromonomer (MW = 1100 g/mol, DP$_{\mathrm{PEO}}$ = 23). All copolymerizations reached more than 70% conversion in 6 h (Table 2).

As shown in the semilogarithmic kinetic plot for monomer consumption vs time (Figure 4), polymerization of two methacrylate macromonomers, PEOMA and PDMSMA, proceeded at similar rates to high conversion after 5 h ($p_{\mathrm{PEOMA}} = 0.69$ and $p_{\mathrm{PDMSMA}} = 0.65$ in the case of **IV**) for all copolymers (**IV**–**VI**, Scheme 1b). Simultaneous incorporation of two macromonomers into copolymer by the *grafting through* method yielded densely heterografted brushes. It also resulted in a similar size of side chains corresponding to the particular macromonomer (DP$_{\mathrm{PEO}}$ = 23 and DP$_{\mathrm{PDMS}}$ = 10) along the polymethacrylate backbone. The relative content of each macromonomer in the copolymers was defined by the initial ratios of comonomers used in the copolymerization.

The determination of comacromonomers conversion by ^{1}H NMR was more complicated than for PPDMSMA because some of signals overlapped in the range 3.65–4.15 ppm, which could not be distinguished as separate peaks (Figure 5). They belong to the methylenoxy protons $-\mathrm{OC}H_2$, which are present in both macromonomers and the formed copolymer (δ (ppm) = 4.13; k', 4.02; c, 3.85; d', 3.8; k, 3.7; g'). Similar case was for signals between 1.00 and 1.75 ppm. However, the comparison of the peak area of signals assigned to the methoxy protons of PEOMA in monomer and copolymer $-\mathrm{O}-\mathrm{C}H_3$

Table 2. Copolymerization of PDMSMA (A) and PEOMA (B)[a]

			NMR				GPC-MALLS (THF)				
			conv (%)		DP_n				DP_n		
	A/B	T (°C)	A	B	A	B	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n	A	B	d*n*/d*c* (mL/g)
IV	0.75/0.25	70	71.8	73.7	136	45	144.2	1.18	105	35	0.033
V[b]	0.5/0.5	85	87.6	90.5	109	113	221.8	1.07	106	106	0.046
VI	0.25/0.75	70	75.8	79.2	49	147	177.2	1.16	41	124	0.055

[a] $[PEOMA + PDMSMA]_0/[EtBriBu]_0/[CuCl]_0/[Me_6TREN]_0$ = 250/1/2/2, xylene/mon = 2/1 vol/wt. [b] Xylene/mon = 1/1 vol/wt.

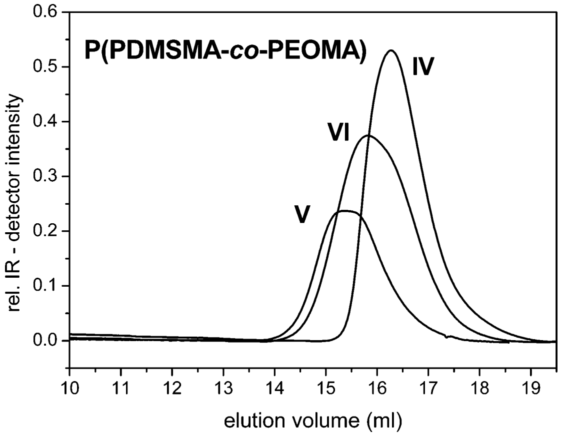

Figure 6. GPC-MALLS traces for the copolymers P(PDMS-*co*-PEOMA) **IV**−**VI**. Conditions of polymerizations are described in Table 2.

(δ = 3.30 ppm; *f′*) with the methylenoxy protons −O−CH_2−CH$_2$− (δ = 4.22 ppm; *c′*) or with the vinyl protons CH$_2$=C− (δ = 5.50, 6.05 ppm; *a′*) in the monomer allowed to calculate PEOMA conversion. For PDMSMA, the signal of methylene protons −CH_2−Si (δ = 0.5 ppm; *e*) in monomer and copolymer was compared with monomer signals CHH=C− (δ = 5.45, 6.02 ppm; *a*).

The molecular weights of final copolymers were determined by GPC-MALLS in THF (in toluene signals were too weak to be detected). The overall refractive index of copolymer increased from 0.033 to 0.055 with initial amount of PEOMA used in copolymerization (25%−75%) because d*n*/d*c* values for homopolymers are 0.023 for PDMSMA and 0.068 for PEOMA. GPC-MALLS traces are presented in Figure 6, which show narrower molecular weight distribution for copolymers than for poly(PDMS macromonomer) (M_w/M_n = 1.05−1.18 at DP_n = 170−238).

Bulk Morphology and Mechanical Properties. The mechanical properties of prepared materials and their morphology depend on the PEO/PDMS segments ratio in copolymers. The ratio varied from 25% to 75% PEO and from 75% to 25% PDMS, respectively. PPDMSMA was a liquid with subambient T_g. The crystallinity of the heterografted brushes increased with the amount of incorporated PEO macromonomer. DSC traces presented in Figure 7b show the glass transition at −120 °C for homopolymer **I**. In the case of copolymers this T_g transition was also clearly observed for brush **VI** containing 75% of PDMSMA together with melting of PEO segments (25%) at 25 °C. The intensity of melting peak during heating cycles increased with the PEO content. The melting temperature also increased to 40 °C. This can be compared with homopolymer PPEOMA (T_m = 50 °C), which was previously determined.[9] Interestingly the sample with 75% content of PEO showed significant supercooling with crystallization temperature below 0 °C.

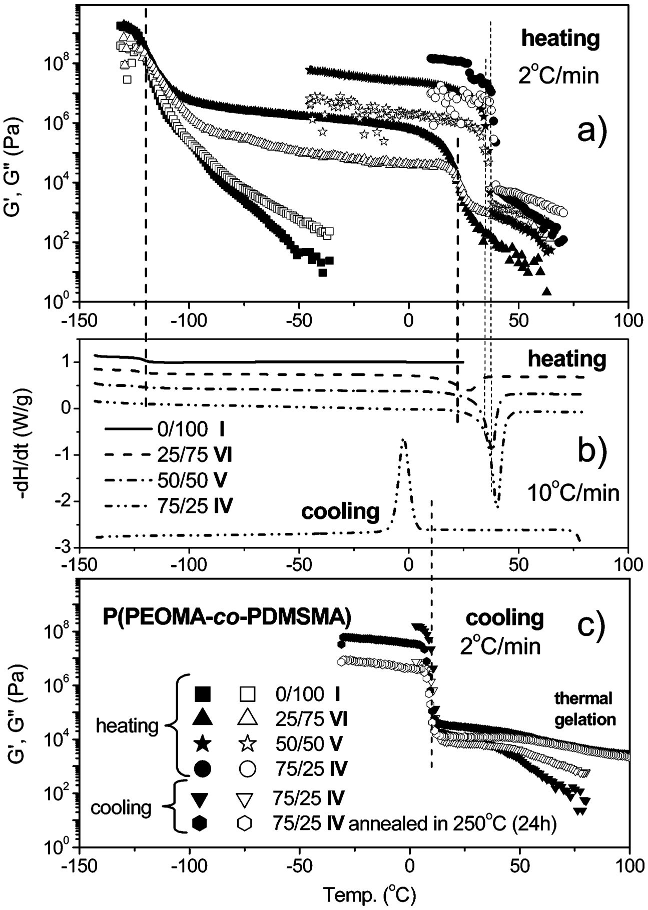

Figure 7. Thermomechanical characteristics of the heterografted PDMS−PEO brushes: (a) Isochronal mechanical characteristics of copolymers **IV**−**VI** with various distribution of grafts and homopolymer PPDMSMA (**I**), (b) DSC traces indicating the glass transition and melting or crystallization, and (c) mechanical characteristics of copolymer with 75% PEOMA (**IV**) before and after annealing at 250 °C. The vertical dashed lines mark the glass transition in homografted polymer **I** and the melting or crystallization in heterografted copolymers **IV**−**VI**.

The dynamic mechanical measurements shown in Figure 7a,c provide additional information on the melt structure of brushes with various compositions. The temperature dependencies of the real (*G′*) and imaginary (*G″*) shear modulus show softening/hardening transition in homopolymer **I**, which is related to the temperature of transition to the glassy state of PDMS at −120 °C. The copolymers with PEO grafts **IV**−**VI** indicate at higher temperature the additional transition to melt state in the range 20−35 °C during heating leading to higher value of *G″* than *G′* (Figure 7a). Moreover, the modulus of the heterografted copolymers at temperatures below the melting point increases strongly with the content of crystallizable PEO segments. Additionally, when the sample of heterografted brush containing 75% PEO (**IV**) was annealed at 250 °C for 24 h in a

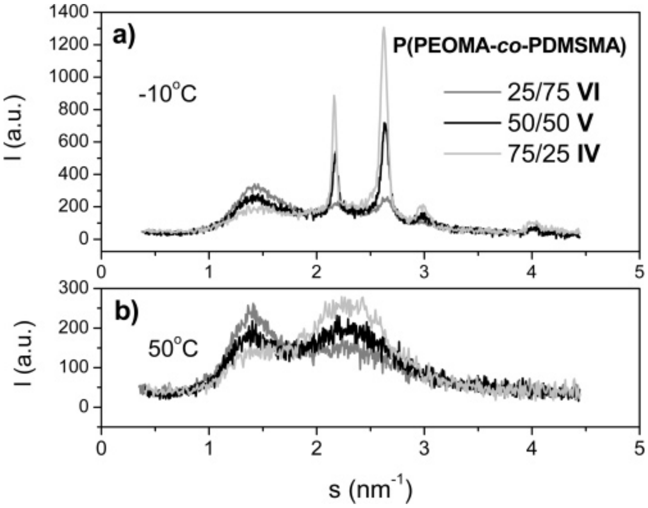

Figure 8. Wide-angle diffractograms for the heterografted PEO/PDMS brush copolymers **IV**−**VI** obtained in temperature (a) below melting point of PEO segments at −10 °C and (b) above melting point at 50 °C.

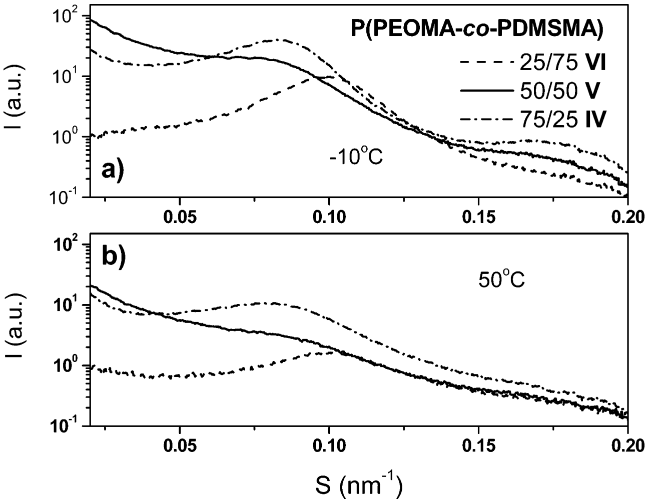

Figure 9. Small-angle X-ray scattering intensity distributions vs the wave vector for the heterografted PEO/PDMS brush copolymers **IV**−**VI** obtained at temperature (a) below melting point of PEO segments at −10 °C and (b) above melting point at 50 °C.

vacuum, the value of real shear modulus significantly increased, yielding $G' \geq G''$ ($G' \ll 10^4$ Pa). Plausibly, the soft gel behavior, presented in Figure 7c, developed by thermally induced cross-linking. All these observations suggest that the dynamics of the PEO chains control the systems.

The structure of copolymers **IV**−**VI** was also examined by X-ray diffraction. The wide-angle diffractograms presented in Figure 8a confirm DSC results, i.e., the presence of amorphous halo assigned to PDMS grafts and typical crystalline diffraction pattern for PEO segments, when the measurements were performed at −10 °C. The increase of measurement temperature to 50 °C caused melting of crystalline PEO, which became amorphous (Figure 8b). At both temperatures the proportion of PEO/PDMS intensities was changing with composition of brush copolymers.

In all samples with a variable crystallinity level, the small-angle X-ray scattering at temperature below melting point of PEO (Figure 9a) indicated an intensity maximum corresponding to distance of 10.0−12.5 nm with increasing PEO contents. These distances can be attributed to periodicity in the partially crystalline structure. The analysis of the materials at temperature above melting point of PEO is shown in Figure 9b and reveals the presence of separated phases. The dynamic mechanical measurements and DSC traces, presented in Figure 7a,b, also confirmed the biphasic character.

Conclusion

New molecular brushes were prepared via the macromonomer method, i.e., *grafting through* homo- and copolymerization. Methacrylate end-capped PDMS macromonomer (MW = 1000 g/mol) was polymerized under ATRP conditions (CuCl/Me$_6$TREN), yielding polymacromonomers with DP$_n$ in the range of 120−350 with controlled molecular weight distribution (M_w/M_n = 1.22−1.35). The same PDMS macromonomer was also used for copolymerization with the crystallizable macromonomer PEOMA (MW = 1100 g/mol), yielding densely heterografted copolymers containing ethylenoxy (DP$_{PEO}$ = 23) and dimethylsilyloxy (DP$_{PDMS}$ = 10) side chains. The copolymerization of two methacrylates resulted in copolymers with statistical composition due to similar reactivity ratios. The PEO/PDMS composition was defined by the initial ratios of comonomers (0.25/0.75, 0.5/0.5, 0.75/0.25).

Analysis of the morphology and mechanical properties of heterografted brushes showed the presence of amorphous PDMS and crystalline PEO domains. The modulus of such systems indicated the melt state described by $G'' > G'$. However, the cross-linking process, which was caused by annealing at high temperature, resulted in the formation of elastomers that display new properties for a bulk stable material. These properties are typical for a soft gel ($G' \ll 10^4$ Pa, $G' \geq G''$).

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