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Heterografted PEO–P*n*BA brush copolymers

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Abstract

A series of P[(HEMA-TMS)-*co*-PEOMA] graft copolymers with different amounts of incorporated macromonomer grafts were prepared by copolymerization of a PEO macromonomer (PEOMA, $MW_{av} = 1100$ g/mol, $DP_{PEO} = 23$) with 2-(trimethylsilyloxy)ethyl methacrylate (HEMA-TMS) using various initial ratios of the comonomers via atom transfer radical polymerization. After transformation of the HEMA-TMS units to 2-(2-bromopropionyloxy)ethyl methacrylate (BPEM), the resulting P(BPEM-*co*-PEOMA) copolymers were used as macroinitiators for the controlled polymerization of *n*BA in a 'grafting from' reaction. The resulting densely heterografted brush copolymers with a uniform length of PEO grafts ($DP_{PEO} = 23$) and a range of lengths for the P*n*BA side chains ($DP_{PnBA} = 15-60$) depending solely on the reaction time. Analysis of the bulk properties showed that the specific architecture of the copolymers suppresses crystallization of the PEO, and consequently leads to amorphous, homogeneous materials.

Keywords: Molecular brushes; Atom transfer radical polymerization; Controlled radical polymerization

1. Introduction

Polymer brushes can be grafted from flat, colloidal, and irregular surfaces and also from each repeat unit of a polymer backbone, generating molecular, 'bottle-brush' structures [1]. Their properties depend on a variety of molecular parameters including the degrees of polymerization of the main (DP_n) and side chains (DP_{sc}), graft density, main chain topology, and chemical composition.

Three preparation methods for graft copolymers were reported, 'grafting to', where a side chains are preformed and then attached to the backbone, 'grafting through' by (co)polymerization of macromonomer(s), and 'grafting from', when monomer is grafted from the backbone [2].

Atom transfer radical polymerization (ATRP) [3–5] has been employed to prepare well-defined polymers with controlled molecular weight, composition and functionality [6], which was also adopted to the synthesis of brushes. 'Grafting through' approach was successful for a number of macromonomers, including poly(methyl methacrylate) (PMMA) [7] or polyethylene (PE) with butyl acrylate [8], polydimethylsiloxane (PDMS) [9], poly(lactic acid) (PLA) [10], poly(ethylene glycol) methyl ether methacrylate (PEOMA) [11], poly(isobutylvinyl ether) (PiBVE) [12] and polystyrene (PS) with poly(ethylene oxide) (PEO) [13]. 'Grafting from' a polymeric macroinitiator was reported for brushes with homopolymer side chains consisting of polystyrene (PS) [14,15], polyacrylates (methyl (PMA) [16], *n*-butyl (P*n*BA) [14,15,17], *t*-butyl acrylate (P*t*BA) [16,18]), and polymethacrylates (*n*-butyl (P*n*BMA) [19], PMMA [19], PEO macromonomer (PEOMA) [11]). *n*BA was also 'grafted from' three and four-armed multifunctional macroinitiators to yield star brushes [20]. Dendrigraft polymers were prepared, when styrene and *n*BMA were polymerized by TEMPO-macroinitiator [21]. Side chains in brushes were extended by ATRP to yield block copolymer side chains (PS-*b*-P*n*BA, P*n*BA-*b*-PS) [15,18]. Similar block bottle-brush copolymers were formed directly by conventional free radical polymerization of block copolymer macromonomers consisting of styrene and 2-vinylpyridine (PS-*b*-PVP) [22]. Both approaches resulted in macromolecules with cylindrical, core–shell structures. In addition, AB and ABA block copolymers, containing

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PBPEM and poly(octadecyl methacrylate) (PODMA) densely grafted segment were synthesized [23]. Molecular brushes with various composition were also prepared by using as ATRP macroinitiators, random [16] and gradient copolymers [24] of 2-(2-bromopropionyloxy)ethyl methacrylate (BPEM) and MMA. Recently, heterografted brush with poly(2-vinylpyridine) (PVP) and PMMA side chains was prepared by free radical copolymerization of two macromonomers [25].

In this paper, we report the synthesis of copolymers of 2-(trimethylsilyloxy)ethyl methacrylate (HEMA-TMS) and a relatively high molecular weight PEO macromonomer (PEOMA, $\mathrm{MW_{av}} = 1100$ g/mol, $\mathrm{DP_{PEO}} = 23$) by ATRP. The resulting loosely grafted copolymers, P[(HEMA-TMS)-*co*-PEOMA] were transformed to macroinitiators P(BPEM-*co*-PEOMA) and used for the controlled polymerization of *n*BA to yield densely heterografted brushes with PEO and P*n*BA side chains.

The mechanical properties of the PEO–P*n*BA heterografted brushes were studied by dynamic mechanical spectroscopy and their morphologies by wide angle X-ray scattering (WAXS), small angle X-ray scattering (SAXS), and differential scanning calorimetry (DSC). The heterografted copolymers were compared with densely homografted P*n*BA and PPEOMA brush copolymers.

2. Experimental

2.1. Materials

HEMA-TMS (97.4% by GC) was prepared as described in the Supporting Information for Ref. [14]. Poly(ethylene glycol) methyl ether methacrylate, $H_2C{=}C(CH_3)COO{-}(CH_2CH_2O)_nCH_3$ (PEOMA, $\mathrm{MW_{av}} = 1100$ g/mol, $\mathrm{DP_{PEO}} = 23$) was obtained from Aldrich. The macromonomer, which is a solid at room temperature (rt), was purified by dissolving in THF and passing through an alumina column. Next, the solvent was evaporated, and the macromonomer was dried under vacuum to a constant mass. *n*-Butyl acrylate (*n*BA, Aldrich, 98%) was stirred over calcium hydride for 2 h and distilled under vacuum (1×10^{-2} mbar). All monomers were stored at -15 °C under an inert gas atmosphere. *p*-Toluenesulfonyl chloride (TosCl, Aldrich, 99 + %) was recrystallized from hexane, filtered, and dried. Copper(I) bromide (CuBr, Aldrich, 98%) was purified by stirring with glacial acetic acid (Fisher Scientific), followed by filtration and successive washing of the solid three times with ethanol and twice with diethyl ether. The solid was dried under vacuum (1×10^{-2} mbar) for 2 days. Copper(II) bromide ($CuBr_2$, Acros, 99 + %) was used as received. 4,4′-Di(5-nonyl)-2,2′-bipyridyne (dNbpy) was prepared as previously described [26]. All solvents and internal standards were used without further purification.

2.2. Measurements

Gel permeation chromatography (GPC) measurements were conducted in THF at 30 °C using a Waters 515 liquid chromatograph pump (1 ml/min) and four Polymer Standards Service columns (guard, 10^5, 10^4, and 10^3 Å) in series with three detection systems by, a differential refractometer (Waters Model 410). The molecular weights of the copolymers were determined based on low polydispersity linear PMMA standards using toluene as an internal standard.

The conversion of PEOMA was determined by monitoring the reduction in the monomer peak area.

Gas chromatography (GC) was performed using a Shimadzu GC-14A equipped with a FID detector and a widebore capillary column (30 m, DB-Wax, J&W Sci.) in order to determine conversion of HEMA-TMS and *n*BA. Methyl ethyl ketone (MEK) was used as an internal standard. Injector and detector temperature: 250 °C; start column temperature: 40 °C, isotherm 0 min, heating 20 °C/min, final temperature of column: 190 °C, isotherm 3 min. The conversion of HEMA-TMS and BA was calculated by observing the decrease in the monomer peak area relative to that of the standard. GC measurements were repeated five times for each sample to reduce error.

^{1}H nuclear magnetic resonance (NMR) spectroscopy was performed in chloroform-*d* with a Bruker 300 MHz spectrometer. The cumulative conversion of HEMA-TMS and PEOMA were determined by comparing the peak area of signals assigned to the unsaturated protons of the comonomers $CH_2{=}C(CH_3){-}$ ($\delta_{CH2} = 5.48$; 6.04 ppm) and the methylene protons in the copolymer $-CH_2{-}C(CH_3){-}$ ($\delta_{CH2} = 1.8$ ppm).

WAXS and SAXS were used to characterize the structure of the bulk materials. In both cases, the X-ray source was Cu Kα radiation ($\lambda = 0.154$ nm) with a pinhole collimation and 2D position sensitive detectors (Bruker) were used. 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). Frequency dependencies of the complex shear modulus at a reference temperature (master curves) were determined from frequency sweeps measured with a small amplitude sinusoidal deformation at various temperatures under a dry nitrogen atmosphere. Independently, temperature dependencies at a constant deformation rate were measured.

DSC was performed with a Metler 30 calorimeter to determine the glass transition temperatures. Heating and cooling runs were performed at a rate of 10 °C/min.

2.3. Synthesis

2.3.1. Preparation of macroinitiators—loosely grafted PEO copolymers P[(HEMA-TMS)-co-PEOMA]

The general procedure is described below for the synthesis of copolymers with ratio of comonomers, HEMA-TMS:PEOMA = 63:37 (wt%) (90:10, mol%). TosCl (0.004 g, 0.021 mmol) was dissolved in HEMA-TMS (0.5 ml) and toluene (0.2 ml) in a 10 ml round-bottomed flask, and the solution was purged with nitrogen for 10 min at 0 °C. In a 25 ml Schlenk flask, dNbpy (0.017 g, 0.042 mmol), PEOMA (2.7 g, 2.4 mmol), the remaining HEMA-TMS (0.4 g, total 4.4 mmol) and solvent (1.0 ml) were combined and degassed by three freeze-pump–thaw cycles. CuBr (0.003 g, 0.021 mmol) was added and the mixture was stirred for 10 min at rt. The Schlenk flask was placed in a thermostated oil bath at 90 °C. After 3 min the initiating system was transferred to the Schlenk flask and an initial sample was taken. During polymerization, samples were taken periodically for the determination of the molecular weight by GPC and conversion by GPC or NMR. The reaction was stopped by exposing the solution to air, diluting with CH_2Cl_2, and filtering through an activated (neutral) alumina column to remove the copper catalyst. The remaining PEOMA macromonomer was removed by ultrafiltration in MeOH/THF (50/50, vol%) solution using an ultrafiltration membrane (Millipore, Regenerated Cellulose, YM10, 76 mm, NMWL: 10,000). The graft copolymer was dried under vacuum to a constant mass.

Copolymerizations with 50:50 (wt%) (84:16, mol%) and 30:70 (wt%) (70:30, mol%) initial ratios of HEMA-TMS to PEOMA were conducted according to the above procedure.

2.3.2. Transformation of the HEMA-TMS units in the random graft copolymer to BPEM (2-(2-bromopropionyloxy)ethyl methacrylate)

P[(HEMA-TMS)-*co*-PEOMA] $DP_{PEOMA}/DP_{HEMA-TM} = 29/256$, $M_{n,ap} = 21 \times 10^3$ g/mol, $M_w/M_n = 1.67$, $M_{n,th} = 84 \times 10^3$ g/mol (3.35 g, 16.36 mmol HEMA-TMS units) was dissolved in dry THF (45 ml) under nitrogen. Potassium fluoride (0.95 g, 16.36 mmol) was added, followed by slow addition of 1 M tetrabutylammonium fluoride in THF (0.16 ml, 0.16 mmol). 2-Bromopropionyl bromide (2.6 ml, 24.5 mmol) was added dropwise over the course of 15 min. The reaction mixture was stirred at rt for 4 h, exposed to air, precipitated into methanol/ice (50/50, v/v), dissolved in $CHCl_3$ (200 ml), and passed through an activated (basic) alumina column. The polymer was reprecipitated three times in hexane and dried under vacuum at 25 °C for 24 h.

Copolymers with 50:50 (wt%) (84:16, mol%) and 30:70 (wt%) (70:30, mol%) initial ratios of HEMA-TMS to PEOMA were transformed in the same way.

2.3.3. Heterografted brush P(BPEM-co-PEOMA)-graft-PnBA

One of the macroinitiators **I**, **II**, or **III** (0.1 g, which contains 0.063, 0.05, or 0.03 g Br end groups, respectively), dNbpy (1 equiv.), $CuBr_2$ (0.025 equiv., 5% of CuBr), *n*BA (400 equiv.) and MEK (4 vol% of monomer) were added to a 50 ml Schlenk flask and degassed by three freeze-pump–thaw cycles. After stirring the mixture at rt for 1 h, CuBr (0.5 equiv.) was added, and the flask was placed in a thermostated oil bath at 70 °C.

After various reaction times, the polymerizations were stopped by cooling to rt and opening the flask to air. GPC was used to determine the molecular weight and the polydispersity. The polymers were purified by distilling off the solvent and monomer under high vacuum at rt, dissolving the crude polymers in chloroform, and passing through an activated (neutral) alumina column. Finally, the polymers were dried under vacuum to a constant mass.

3. Results and discussion

3.1. Copolymerization of HEMA-TMS with PEOMA

Loosely grafted copolymers P[(HEMA-TMS)-*co*-PEOMA] were prepared by a ‘grafting through’ copolymerization of PEOMA ($MW_{av} = 1100$ g/mol, $DP_{PEO} = 23$) with HEMA-TMS under typical ATRP conditions (Scheme 1a, Table 1).

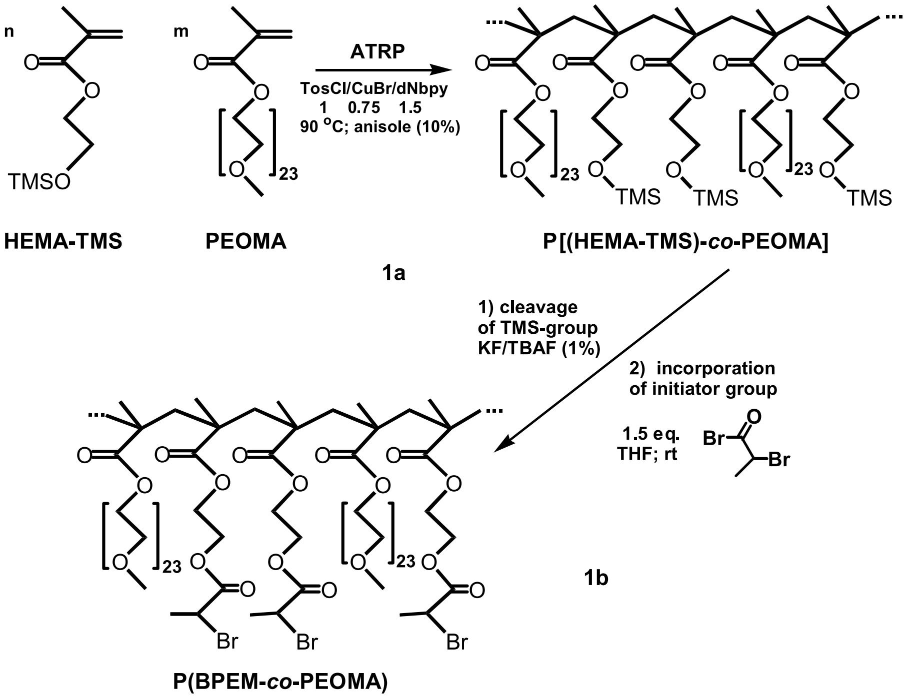
The copolymer composition was controlled by the comonomer feed, although the PEO macromonomer was slightly more reactive than HEMA-TMS. The kinetic results are presented in Fig. 1 as conversion-time plots. The reactivity ratios were estimated by the Jaacks method [27] at high and low comonomer feed ratios, [HEMA-TMS]:[PEOMA] = 9 and 0.11, respectively. Fig. 2(a) and (b) show double logarithmic plots of fractional comonomer conversions $x_{HEMA-TMS}$ and x_{PEO-MA}. Slopes provide reactivity ratios $r_{HEMA-TMS} = 0.77 \pm 0.02$ (Fig. 2(a)) and $r_{PEOMA} = 1.22 \pm 0.02$ (Fig. 2(b))). This indicates the formation of copolymers P[(HEMA-TMS)-*co*-PEOMA] with a slight gradient in composition along the backbone of the copolymer.

The GPC traces in Fig. 3 show that the copolymer molecular weight increased with the conversion of HEMA-TMS and the macromonomer. The low molecular weight tail in the final copolymer may indicate the occurrence of termination reactions and could explain the higher polydispersity index.

The resulting graft copolymers (**I**–**III**) with various graft density (10–30 mol%, 37–70 wt%) are shown in Scheme 2. The values of molecular weights ($M_{n,ap}$) determined by GPC (PMMA standards) are lower than the theoretical values ($M_{n,th}$), as observed previously for other densely homografted brushes due to the highly compact structure of brushes [15].

Final conversions of each monomer reached 45–55% (HEMA-TMS by GC and PEOMA by GPC). These values are similar to the total conversion determined by NMR which indicated 45–52% of both comonomers and allowed the calculation of backbones length, $DP_{HEMA-TMS+PEOMA} = 225–260$.

The graft copolymer precursors P[(HEMA-TMS)-*co*-PEOMA] were transformed to ATRP macroinitiators by



Scheme 1. Synthesis of macroinitiator.

cleavage of the TMS protecting groups and esterification with 2-bromopropionyl bromide (Scheme 1b).

Molecular weights and polydispersity indices for the copolymers after transformation are presented in Table 1 and show no significant change in the values of M_w/M_n (1.3–1.5).

3.2. Synthesis of heterografted brushes

The macroinitiators were used for the 'grafting from' polymerization of *n*BA by ATRP [15] to form a series of heterografted brush copolymers. These brushes contain PEO side chains with uniform length ($DP_{PEOMA} = 23$) and P*n*BA side chains with variable chain length (Scheme 3).

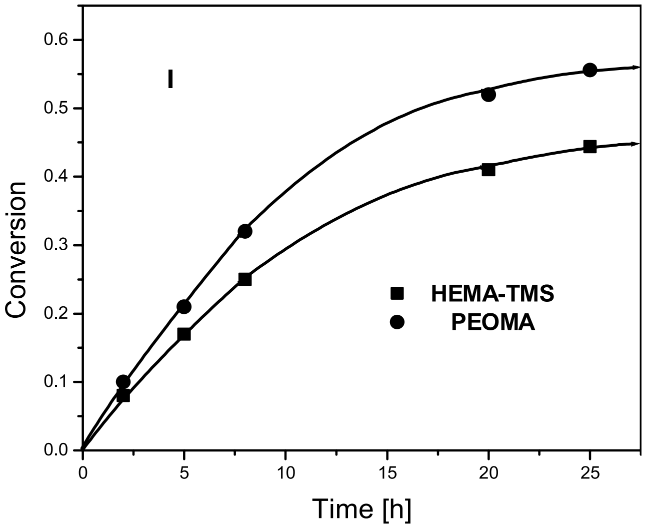


Fig. 1. Conversion vs. time plot for the copolymerization of HEMA-TMS and PEOMA (**I**). Initial conditions presented in Table 1.

The 'grafting from' process with copolymers containing 10 mol% (**I**) or 16 mol% (**II**) of macromonomer were performed under standard ATRP conditions (Tables 2 and 3). The targeted monomer conversion was low, usually 5–15%, yielding brushes with $DP_{nBA} = 17–63$. The degree of polymerization of the side chains determined by gravimetry was in the range 15–59, which is in good agreement with that determined by GC. The apparent molecular weight increased linearly with reaction time (Fig. 4). This allows one to obtain different lengths of the P*n*BA side chains merely by stopping the reaction after various times while employing the same initial conditions for the synthesis of polymers (**IA–C** or **IIA–C**). The molecular weights determined by GPC ($M_{n,ap}$; solid line in Fig. 4) are significantly lower than the theoretical values calculated from the monomer conversion determined by GC ($M_{n,th}$; dash line). The polydispersity indices of brushes (**IA–C**) were higher, because of the broader molecular weight distribution of macroinitiator (**I**) as compared to macroinitiator (**II**). The GPC traces for macroinitiator (**II**) and heterografted brushes (**IIA–C**) are shown in Fig. 5.

An attempt to graft *n*BA from macroinitiator (**III**) was unsuccessful. This could be explained by steric hindrance effects, since the amount of incorporated macromonomer was relatively larger (30 mol%) and the highly dense PEO grafts may shield access to the bromopropionate groups,

Table 1

Synthesis of copolymers P[(HEMA-TMS)-*co*-PEOMA] and transformation to P(BPEM-*co*-PEOMA)

No.	Ratio A:B mol% (wt%)	Time (h)	Total conv. (NMR) (%)	A conv. (GC) (%)	B conv. (GPC) (%)	DP_A, DP_B	Copolymerizatioan[a]			Esterification		
							$M_{n,th}$ ($\times 10^{-3}$ g/mol)	$M_{n,ap}$ ($\times 10^{-3}$ g/mol)	M_w/M_n	$M_{n,th}$ ($\times 10^{-3}$ g/mol)	$M_{n,ap}$ ($\times 10^{-3}$ g/mol)	M_w/M_n
I	90:10 (63:37)	25	45.0	44.4	55.5	203, 22	65.2	21	1.67	77.8	45	1.51
II	84:16 (50:50)	48	51.1	47.7	52.0	212, 44	91.2	16	1.41	104.4	37	1.33
III	70:30 (30:70)	48	52.1	46.0	54.0	173, 87	130.6	27	1.47	141.4	39	1.41

A—HEMA-TMS → BPEM, **B**—PEOMA ($MW_{av} = 1100$ g/mol; $DP_{PEO} = 23$).

[a] Cond.: $[(A + B)]_0$:$[TosCl]_0$:$[CuBr]_0$:$[dNbpy]_0 = 500:1:0.75:1.5$; toluene 30%; $T = 90$ °C.

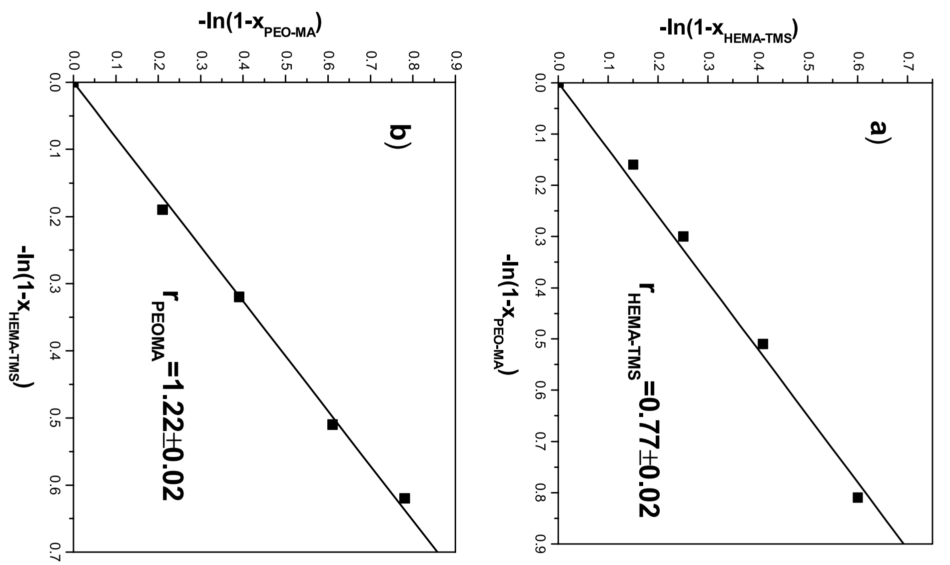


Fig. 2. Jaacks plots of the ATRP at comonomer ratios (a) $[HEMA\text{-}TMS]_0$:$[PEOMA]_0 = 9$ and (b) $[HEMA\text{-}TMS]_0$:$[PEO\text{-}MA]_0 = 0.11$. Cond.:$[A + B]_0$:$[TosCl]_0$:$[CuBr]_0$:$[dNbpy]_0 = 500:1:0.75: 1.5$; toluene 30%; $T = 90$ °C (x : comonomer fractional conversion).

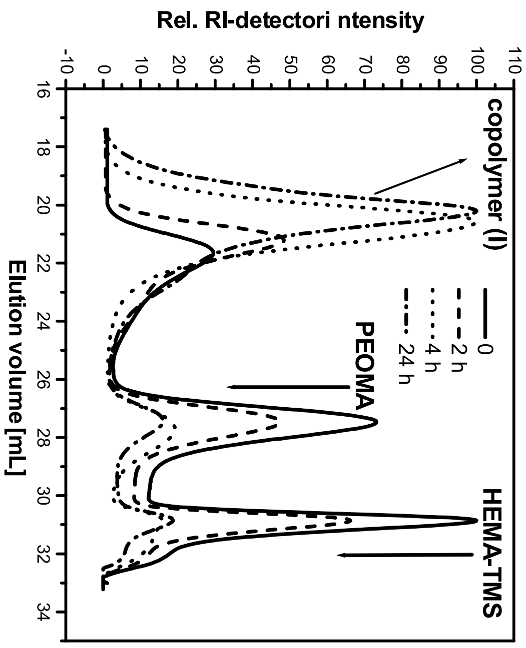
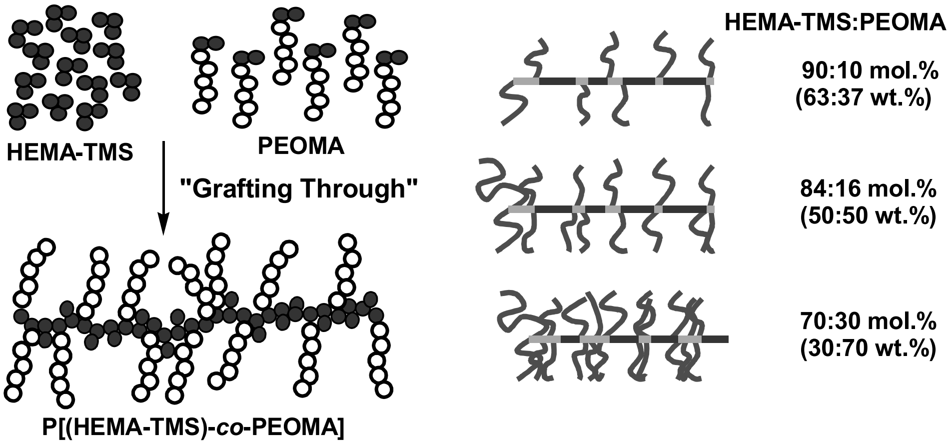


Fig. 3. GPC traces for the copolymerization of HEMA-TMS and PEOMA (90:10) (**I**). Initial conditions presented in Table 1.



Scheme 2. Copolymers with different grafting densities.

Table 2
Brush copolymers P(BPEM-*co*-PEOMA)-*graft*-P*n*BA synthesized via ‘grafting from’ macroinitiator (**I**)

Brush	Reaction time (h)	Conv. GC (%)	$M_{n,th}$ (× 10^{-6} g/mol)	M_n (× 10^{-6} g/mol) (GPC)	M_w/M_n	DP_{sc}			PEO (wt%)
						GC	Grav.	Aver.	
IA	13	4.2	0.49	0.19	1.77	17	15	16	4.9
IB	24	7.5	0.80	0.26	1.66	30	27	28	3.0
IC	39	13.7	1.40	0.45	1.77	55	47	51	1.7

$[nBA]_0$:$[MI(\mathbf{I})]_0$:$[CuBr]_0$:$[CuBr_2]_0$:$[dNbpy]_0 = 400:1:0.5:0.025:1$; MEK 4 vol%; $T = 70$ °C; MI (**I**)—BPEM:PEOMA = 90:10 (mol%) (63:37, wt%).

Table 3
Brush copolymers P(BPEM-*co*-PEOMA)-*graft*-P*n*BA synthesized via ‘grafting from’ macroinitiator (**II**)

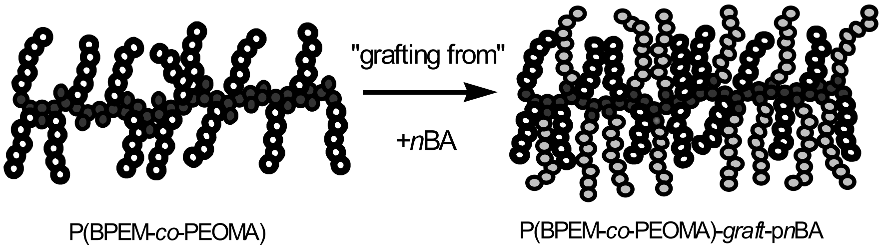
Brush	Reaction time (h)	Conv. GC (%)	$M_{n,th}$ (× 10^{-6} g/mol)	M_n (× 10^{-6} g/mol) (GPC)	M_w/M_n	DP_{sc}			PEO (wt%)
						GC	Grav.	Aver.	
IIA	7	5.1	0.70	0.18	1.35	20	23	22	6.9
IIB	13	9.1	1.05	0.26	1.32	36	33	35	4.6
IIC	25	15.7	1.70	0.42	1.41	63	55	59	2.8

$[nBA]_0$:$[MI(\mathbf{II})]_0$:$[CuBr]_0$:$[CuBr_2]_0$:$[dNbpy]_0 = 400:1:0.5:0.025:1$; MEK 4 vol%; $T = 70$ °C; MI (**II**)—BPEM:PEOMA = 84:16 (mol%) (50:50, wt%).

significantly decreasing the initiation efficiency of the ATRP process.

3.3. Structure and mechanical properties of bulk materials of heterografted brushes

The heterografted brush copolymer (**IIC**) was characterized as a bulk material. Fig. 6 shows results of the X-ray scattering experiments performed both in the wide and small angle range. Scattering typical for P*n*BA brush polymers is observed [28]. The small angle peak (a), indicating correlation distances of about 10 nm, can result from interchain backbone–backbone correlation or from correlated positions of Br atoms decorating the ends of P*n*BA arms. Both these correlations should be related to the thickness of the brush, which primarily depends on the side chain length. The two wide angle peaks (b) and (c) are attributed to the correlation distances between cores of the



Scheme 3. The preparation of P(BPEM-*co*-PEOMA)-*graft*-P*n*BA by ‘grafting from’.

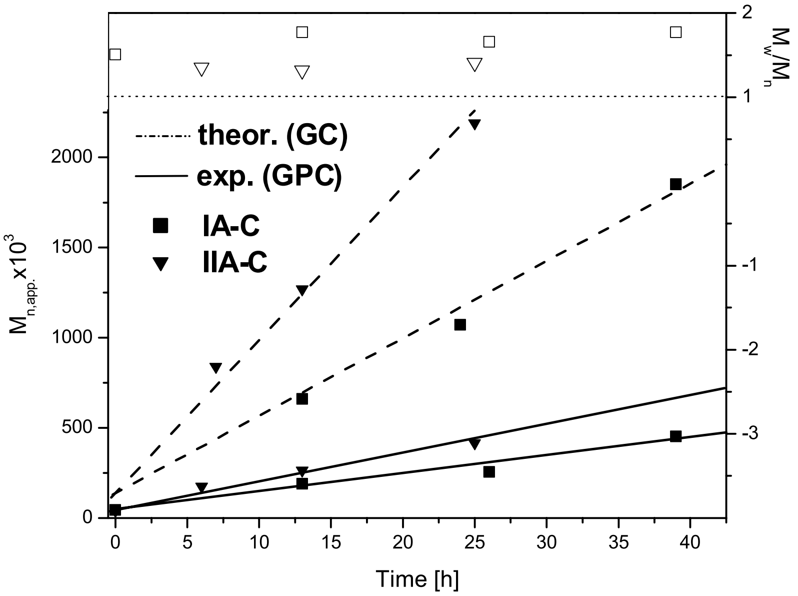


Fig. 4. Dependence of molecular weight, M_n, and molecular weight distribution, M_w/M_n, on reaction time for the polymerization of *n*BA. Polymerization conditions: $[n\mathrm{BA}]_0$:$[\mathrm{MI(I)}]_0$:$[\mathrm{CuBr}]_0$:$[\mathrm{CuBr_2}]_0$:$[\mathrm{dNbpy}]_0$ = 400:1:0.5:0.025:1; MEK 4 vol%; T = 70 °C.

*n*BA side chains and to the amorphous halo of this polymer, respectively.

Thermomechanical characterization of the material is shown in Fig. 7 in the form of frequency dependencies of the real and imaginary parts of the shear modulus within a broad frequency range (master curve at the reference temperature of 223 K). The dependencies indicate three relaxation processes which were also observed for *n*BA brush homopolymers [28], i.e. the high frequency segmental relaxation, the side chain relaxation slower by some orders of magnitude, and the global polymer relaxation controlling the melt flow observed at the lowest frequencies. The temperature dependence of the segmental relaxation times of this polymer is shown in Fig. 8(a) in comparison with the DSC heating trace indicating the glass transition (Fig. 8(b)). The temperature dependence of the relaxation times is fitted with the Williams–Landel–Flory (WLF) relation indicating the behavior of this material typical for glass-forming, macromolecular systems. The relaxation time of 100 s is also nearly achieved at the glass transitions, which is typical for many polymeric amorphous systems.

The above observations concerning both structure and dynamics show that the heterografted copolymer constitutes an amorphous, homogeneous, glass-forming material in which contains PEO, which would be capable of crystallization [11] or microphase-separation. However, the PEO

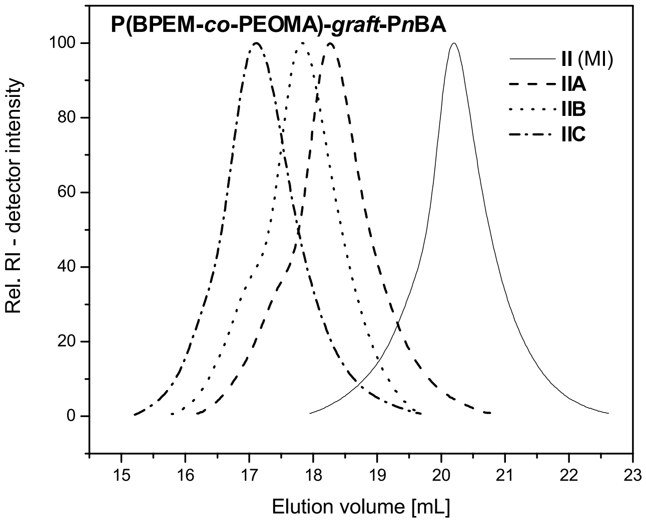


Fig. 5. GPC traces of P(BPEM-*co*-PEOMA)-*graft*-P*n*BA (**IIA–C**). Polymerization conditions $[n\mathrm{BA}]_0$:$[\mathrm{MI(I)}]_0$:$[\mathrm{CuBr}]_0$:$[\mathrm{CuBr_2}]_0$:$[\mathrm{dNbpy}]_0$ = 400:1:0.5:0.025:1; MEK 4 vol%; T = 70 °C.

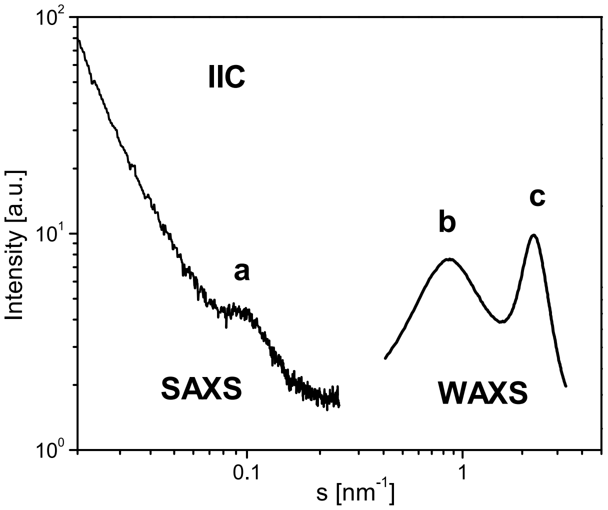


Fig. 6. X-ray scattered intensity distribution measured in the small (SAXS) and wide (WAXS) angle range for the heterografted brush polymer (**IIC**) obtained by 'grafting from' method.

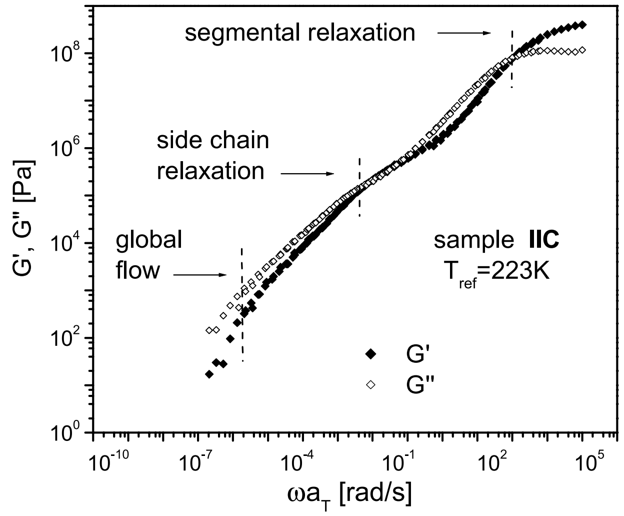


Fig. 7. Frequency dependencies of the real (G') and imaginary (G'') shear modulus components for the heterografted brushes P(BPEM-*co*-PEOMA)-*graft*-P*n*BA (**IIC**) synthesized via 'grafting from' macroinitiator (**II**).

remains well mixed with the other component (P*n*BA) due to the specific macromolecular architecture.

4. Conclusions

Copolymers of P[(HEMA-TMS)-*co*-PEOMA] with different graft densities were synthesized by ATRP using a 'grafting through' procedure. Simultaneous copolymerization of PEOMA and HEMA-TMS, resulted in faster consumption of the PEO macromonomer leading to a copolymer with a slight tendency to form a gradient composition along the copolymer backbone. The reactivity ratios of the comonomers are $r_{\mathrm{PEOMA}} = 1.2$ and $r_{\mathrm{HEMA\text{-}TMS}} = 0.8$, as calculated by the Jaacks method. These graft copolymer precursors were transformed to P(BPEM-*co*-PEOMA), macroinitiators, and then used for the 'grafting from' polymerization of *n*BA. Heterografted brush copolymers P(BPEM-*co*-PEOMA)-*graft*-P*n*BA with PEO ($\mathrm{DP_{PEO}} = 23$) and P*n*BA ($\mathrm{DP}_{n\mathrm{BA}} = 15$–$59$) side chains were prepared. The 'grafting from' macroinitiator containing >30 mol% PEOMA was not successful, presumably because the initiating groups were blocked by the high local concentration of PEO side chains.

Analysis of the structure and properties of a typical system shows that the specific macromolecular architecture consisting of a random distribution of chemically different bunches along the backbone can lead to amorphous, homogeneous bulk materials behaving like typical glass-forming systems even when one component has a tendency to crystallize.

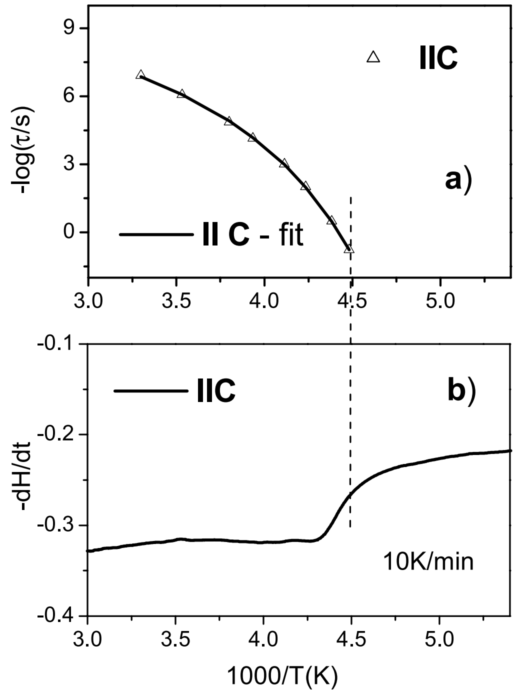


Fig. 8. (a) Temperature dependence of the segmental relaxation time and the fit with the WLF relation and (b) the DSC thermogram for sample (**IIC**).

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