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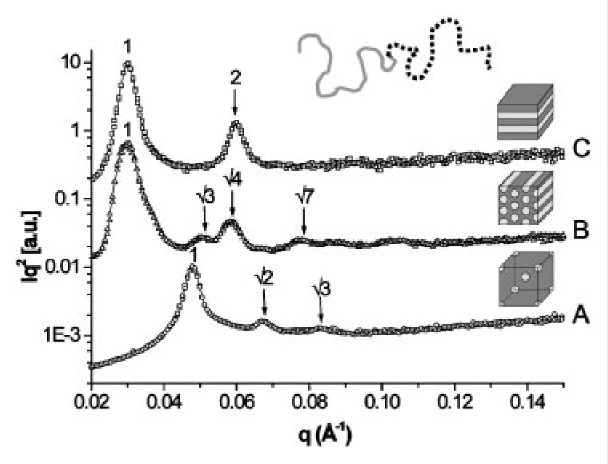
Full Paper: We describe the preparation of amphiphilic diblock copolymers made of poly(ethylene oxide) (PEO) and poly(hexyl methacrylate) (PHMA) synthesized by anionic polymerization of ethylene oxide and subsequent atom transfer radical polymerization (ATRP) of hexyl methacrylate (HMA). The first block, PEO, is prepared by anionic polymerization of ethylene oxide in tetrahydrofuran. End capping is achieved by treatment of living PEO chain ends with 2-bromoisobutyryl bromide to yield a macroinitiator for ATRP. The second block is added by polymerization of HMA, using the PEO macroinitiator in the presence of dibromobis(triphenylphosphine) nickel(II), $NiBr_2(PPh_3)_2$, as the catalyst. Kinetics studies reveal absence of termination consistent with controlled polymerization of HMA. GPC data show low polydispersities of the corresponding diblock copolymers. The microdomain structure of selected PEO-*block*-PHMA block copolymers is investigated by small angle X-ray scattering experiments, revealing behavior expected from known diblock copolymer phase diagrams.



SAXS diffractograms of PEO-*block*-PHMA diblock copolymers with 16, 44, 68 wt.-% PEO showing spherical (A), cylindrical (B), and lamellae (C) morphologies, respectively.

Synthesis and Characterization of Amphiphilic Poly(ethylene oxide)-*block*-poly(hexyl methacrylate) Copolymers[a]

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Introduction

Poly(ethylene oxide) (PEO) based amphiphilic block copolymers exhibit interesting self assembling properties both in solution[1] as well as in bulk.[2] The hydrophobic sequences in these polymers are generally based on styrene,[3] dienes[4] or hydrogenated aliphatic polyolefin blocks.[5] These amphiphiles typically find applications in stabilization of dispersions,[6] encapsulation of drugs and surfactant enhancers. More recently, these polymers have been used as structure directing agents for the formation of nanostructured silica-based materials. Amphiphiles like polyisoprene-*block*-poly(ethylene oxide),[7] polybutadiene-*block*-poly(ethylene oxide),[8] polystyrene-*block*-poly(ethylene oxide),[9,10] poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide)[11] and alkyl-PEO alcohols[12] have been used in conjunction with ceramic precursors in sol-gel processes to obtain arrays of nanocomposite morphologies. These composites can subsequently be employed to generate, e.g., mesoporous

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materials or nanoparticles of different shapes and sizes.[13] Because of the enormous scientific and technological promise these materials hold in a broad range of areas it is interesting to expand the set of amphiphilic block copolymers and thus derive nanostructured hybrid materials with novel property profiles.

To this end here we report about the synthesis of amphiphilic poly(ethylene oxide)-*block*-poly(hexyl methacrylate), PEO-*block*-PHMA. There are several reasons that make this choice of blocks attractive. First, PEO as well as PHMA have glass transition temperatures well below room temperature (T_g(PEO) = −60 °C; T_g(PHMA) = −5 °C). It has been suggested that the mobility provided through a low T_g of the structure directing agents in the structure formation process of block copolymer directed nanocomposites is important for obtaining well developed morphologies.[8,13] Second, hydrophobic blocks made from the family of esters of methacrylic acid are of particular interest because of special features of their local dynamics, i.e., highly anisoptropic motions well above the glass transition.[14]

The most widely used technique for the preparation of block copolymers is living anionic polymerization, which involves sequential addition of monomers. For a block copolymer involving PEO and an alkyl methacrylate sequential anionic polymerization is not possible as the addition of ethylene oxide to living poly(alkyl methacrylate) anions bears potential complications.[15] Side reactions between living poly(ethylene oxide) and the alkyl ester group of the poly(alkyl methacrylate) block cause the formation of inhomogeneous block copolymers.[16] The synthesis of block copolymers through addition of alkyl methacrylate to living PEO involves difficulties, too. The low solubility of PEO sequences in tetrahydrofuran permits polymerization of methacrylates only at temperatures above 20 °C, whereas anionic polymerization of methacrylates proceeds easily only below −75 °C.[17] At elevated temperatures transfer and termination reactions cannot be prevented during the methacrylate polymerization.

Recent reports demonstrate that the combination of anionic polymerization of ethylene oxide and subsequent controlled radical polymerization of vinylic monomers[18] is not only a viable as well as a simpler alternative to a purely anionic route, but it also allows the preparation of unprecedented copolymer structures. Atom Transfer Radical Polymerization (ATRP)[19] has been used to prepare a wide range of architectures including block, star gradient and statistical copolymers, as well as well-defined macromonomers.[20] Herein, we describe the synthesis of a new set of amphiphilic PEO-*block*-PHMA block copolymers with well defined molecular weights and block weight fractions by combination of anionic and ATRP synthesis techniques. The switch from the first mechanism to the second is achieved by transformation of PEO oxanionic "living" sites into macroinitiators for ATRP. Commercially available dibromobis(triphenylphosphine) nickel(II), $NiBr_2(PPh_3)_2$, introduced by Sawamoto and coworkers[21] and used extensively by Jérôme et al.,[22] is employed as the catalyst. The effects of monomer concentrations are investigated and kinetic experiments are performed to determine the extent to which polymerizations are controlled. GPC data of the resulting PEO-*block*-PHMA diblock copolymers show narrow molecular weight distributions. Finally, first small angle X-ray scattering (SAXS) studies on selected PEO-*block*-PHMA block copolymers are undertaken to elucidate microphase separation and morphologies in this system.

Experimental Part

Materials

Potassium ethoxide (KOEt), potassium *tert*-butoxide (KO^{t}Bu), 2-bromoisobutyryl bromide (98%), ethyl 2-bromoisobutyrate (2-(EiB)Br, $(CH_3)_2CBrCO_2C_2H_5$) (98%), $[NiBr_2(PPh_3)_2]$ (99%) (all from Aldrich), methanol and hexane (both from Mallinckrodt) were used as received. Tetrahydrofuran (THF) and toluene (both from Mallinckrodt) were purified from the deep red 1,1-diphenylethylene and butyllithium adduct. Ethylene oxide (Aldrich, 99.5+%) was allowed to stand over butyllithium and was degassed a few times before distillation into a graduated ampoule. The monomer hexyl methacrylate (Röhm GmbH) was stirred over CaH_2 and distilled under high vacuum.

Instrumentation

^{1}H NMR (400 MHz) spectra were recorded on a Varian INOVA 400 spectrometer using $CDCl_3$ signal ($\delta = 7.27$ ppm) as an internal standard. GPC measurements were performed in 98% THF and 2% *N*,*N*-dimethylacetamide[4] at room temperature using 5 μ Waters Styragel columns (10^3, 10^4, 10^5, 10^6 Å, 30 cm each; Waters Corporation, Milford, MA) at a flow rate of 1.0 ml/min. A waters 490 programmable multiwavelength UV diode array detector (operated at $\lambda = 260$ nm and a Waters 410 RI detector operated at a temperature of 25 °C) were used. Raw data were processed using PSS-Win GPC V6.2 (Polymer Standards Service, Mainz, Germany) software. The molecular weights were calculated using a polystyrene calibration curve.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker-Reflex spectrometer equipped with a nitrogen laser source operating at a wavelength of 337 nm and a pulse rate of 3–5 Hz. The accelerating voltage and the reflector voltage were 20 kV and 30 kV, respectively. The samples were prepared by dissolving 2 mg polymer in 1 ml of THF. Dithranol was used as the matrix. The addition of a cationization agent was not necessary for the polymers under study. Polystyrene was used as an external standard. Analysis was done on Bruker XMASS software.

The SAXS setup consisted of a Rigaku rotating anode X-ray source (Cu K_α, $\lambda = 1.54$), typically operated at 40 kV, 50 mA. The X-rays were nearly monochromatized by Ni filtering followed by focusing onto the detector using a pair of crossed Franks mirrors. A 2-dimensional CCD detector[23] (512 × 512 pixels) at a typical sample to detector distance of 60 cm was used to record the diffraction patterns. The powder pattern rings were azimuthally integrated around the incident beam direction to yield 1-dimensional traces of diffracted intensity vs $q = 4\pi \sin\theta/\lambda$, where 2θ is the angle between the incident and scattered beam directions. These traces were divided by q to normalize to X-rays per unit area in the detector plane. The polymer samples were annealed in a brass ring overnight at a temperature of 150 °C and quenched to room temperature. Prior to recording the scattering data the samples were heated to 50 °C to melt the PEO block.

Synthesis

The general synthetic procedures are outlined in Scheme 1 and 2.

Synthesis of PEO Macroinitiator

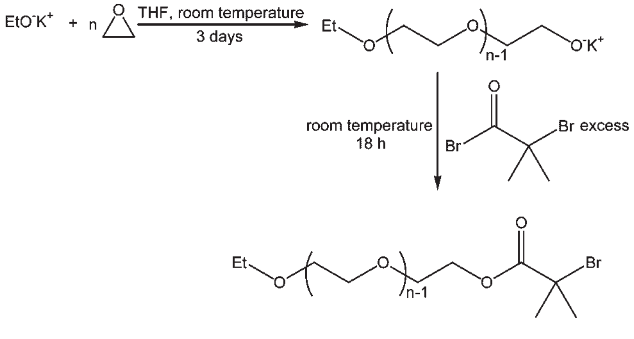
Ethylene oxide (15.0 ml, 0.35 mol) was polymerized in THF (150 ml) for three days at room temperature, using KOEt (2.1 ml, 5.52×10^{-3} mol) as initiator. The initiator was dried overnight under high vacuum conditions to remove the solvent ethyl alcohol before polymerization. The living PEO solution was added to an excess of 2-bromoisobutyryl bromide (1.8 ml, 1.46×10^{-2} mol) under inert conditions and stirred overnight. The resulting end capped PEO macroinitiator (PEOBr26) was filtered, concentrated and then precipitated in excess hexane. The polymer was recovered by decanting the solvents and drying under vacuum.

^{1}H NMR ($CDCl_3$): $\delta = 1.1$ (t, 3H, CH_3CH_2O–), 1.87 (s, 6H, –$C(Br)(CH_3)_2$), 3.4–3.8 (–CH_2CH_2O–), 4.3 (t, 2H, –$COOCH_2$-CH_2O).

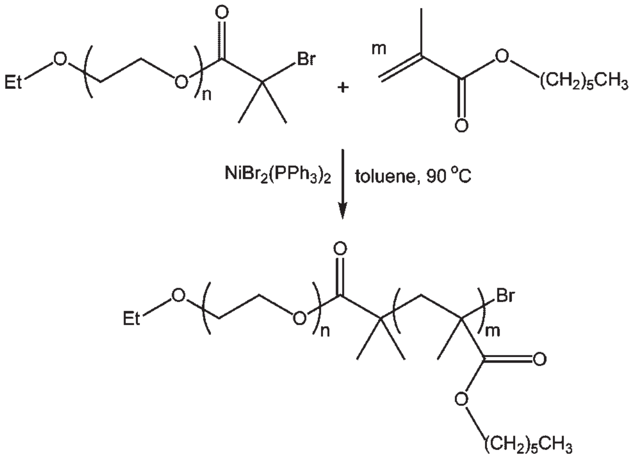
The absolute molecular weight of the macroinitiator was calculated from ^{1}H NMR results, as discussed in the next section.

Polymerization of Hexyl Methacrylate

Macroinitiator PEOBr26 $\bar{M}_n^{NMR} = 2\,800$ (0.82 g, 2.93×10^{-4} mol), $NiBr_2(PPh_3)_2$ (0.218 g, 2.93×10^{-4} mol), freshly distilled hexyl methacrylate (5.0 g, 2.9×10^{-2} mol) and toluene (6.1 ml) were added to a reaction vessel under inert conditions. The system was immersed in an oil bath set at 90 °C.[22b,24] The reaction was stirred for 7 h, and subsequently quenched by submerging the reaction vessel in an ice bath. The polymer solution was passed through a column of neutral alumina to remove the nickel catalyst before GPC and NMR analysis. The polymer was precipitated in methanol at −78 °C, recovered by centrifugation and dried under vacuum to constant weight.



Scheme 1. Synthesis of macroinitiator PEOBr.



Scheme 2. Synthesis of PEO-*block*-PHMA diblock copolymer by ATRP.

^{1}H NMR ($CDCl_3$): $\delta = 3.6$–3.7 (–CH_2CH_2O–), 3.8–4.0 (–$COOCH_2(CH_2)_4CH_3$).

Kinetics Run

Macrointiator PEOBr30 ($\bar{M}_n^{NMR} = 2\,800$, 1.495 g, 5.34×10^{-4} mol), $NiBr_2(PPh_3)_2$ (0.397 g, 5.34×10^{-4} mol), freshly distilled hexyl methacrylate (10 g, 5.88×10^{-2} mol) and toluene (12.3 ml) were added to a reaction vessel under inert conditions. The system was immersed in an oil bath set at 90 °C. The reaction mixture was stirred for 60 min. The reaction was subsequently quenched by submerging the reaction vessel in an ice bath. The reaction vessel was taken inside the glove box and a 3 ml aliquot of the reaction mixture was pipetted out while keeping the contents stirred after which it was immersed back in the oil bath. The polymerization was again quenched after another 63 min, and the procedure repeated. In total, 7 aliquots of the polymerizing solution were obtained after time intervals of 60, 123, 186, 253, 315, 378 and 443 min, respectively. During the first few minutes of the insertion of the reaction mixture into the oil bath the temperature was found to increase up to ~96 °C before it stabilized to 89–90 °C. These temperature fluctuations were observed each time the reaction mixture was immersed in the oil bath. The molecular weights of the diblock copolymers were determined by GPC and NMR after catalyst removal as described above. HMA conversion was determined from ^{1}H NMR by comparison of the PHMA block peak intensities at $\delta = 3.8$–4.0 ppm (–$COOCH_2(CH_2)_4CH_3$) to the sum of the peak intensities of the PHMA and the residual monomer HMA at $\delta = 4.15$ ppm (t, 2H, –$COOCH_2(CH_2)_4$-CH_3).

Results and Discussion

Synthesis of PEO Macroinitiators

The poly(ethylene oxide) was synthesized by anionic polymerization of ethylene oxide with KOEt as initiator in THF for three days at room temperature. The PEO macroinitiator was prepared by end capping of living PEO with an excess of 2-bromoisobutyryl bromide. Figure 1 shows the ^{1}H NMR spectrum of a typical PEO macroinitiator, PEOBr26, with the tertiary halide end group. From the intensity ratio of peaks (b) to (d) $\bar{M}_n^{NMR} = 2\,800$ was calculated. The percentage of end functionalization was obtained by comparison of the peak intensities between the methyl protons of the initiator (d) and the two methyl protons of the 2-bromoisobutyryl moiety (c).

Further analysis of PEO synthesized using Potassium *tert*-butoxide (KO^{t}Bu) as initiator and reacted with either methanol or 2-bromoisobutyryl bromide was performed by MALDI-TOF MS. Figure 2a shows the spectrum of a representative PEO terminated with methanol and thus having –H as the end group. Only one series of peaks is observed. The signals are separated by 44 m/z, the molecular weight of one ethylene oxide unit. Taking K$^+$ as the counter ion each individual peak can be assigned to a particular degree of polymerization of the polymer. The K$^+$ left in the polymer after workup was enough to act as a cationization agent in the ionization process of the MALDI-TOF procedure. The molar masses involved are: repeat unit, –CH_2–CH_2–O–, 44.05 g/mol, counter ion, K$^+$, 39.10 g/mol, end group, –H, 1.01 g/mol, and initiator group, –O–$C(CH_3)_3$, 73.12 g/mol. Subtracting the initiator group, end group and the counter ion masses from each of the signals and dividing the result by the repeat unit mass an integral number for the degree of polymerization was obtained, e.g.:

$$(2\,184\,\text{g/mol} - 73.12\,\text{g/mol} - 1.01\,\text{g/mol} - 39.10\,\text{g/mol})/44.05\,\text{g/mol} = 47$$

Interestingly, for PEO end capped by 2-bromoisobutyryl bromide three series of peaks are observed as shown in Figure 2b. As expected, the signals of every series are separated by 44 m/z. The most intense series corresponds to the macroinitiator PEOBr with K$^+$ as the counter ion. The series with intermediate intensity is assigned to proton terminated PEO. The least intense series (indicated by * in the inset) is consistent with a PEO end capped with an

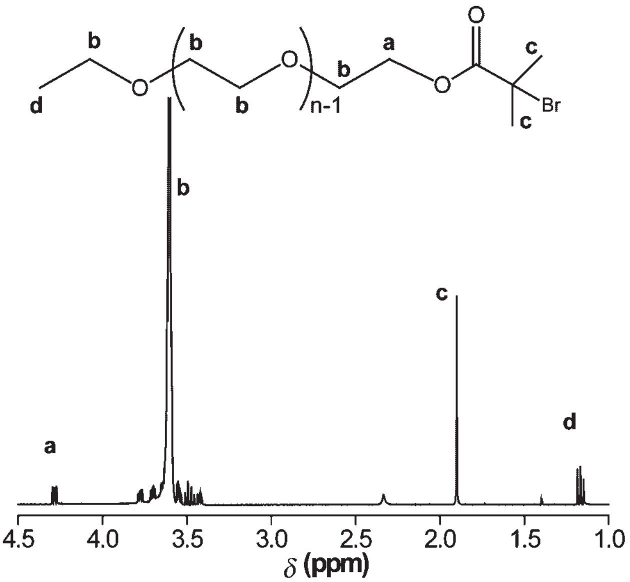


Figure 1. ^{1}H NMR spectrum of macroinitiator PEOBr13. The peak at $\delta = 2.34$ ppm is assigned to the residual water present in the polymer.

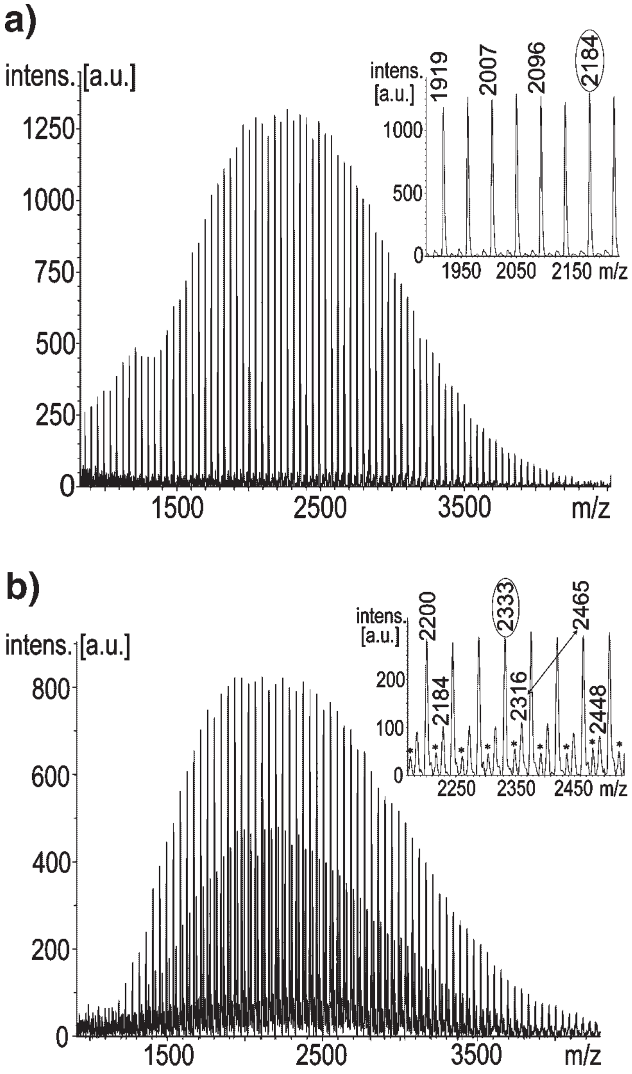


Figure 2. (a) MALDI-TOF MS spectrum of PEOH224; the inset shows a particular area of the series enlarged. (b) MALDI-TOF MS spectrum of PEOBr224; the inset shows a particular area of the series enlarged. The arrow in the inset indicates the peak correlation between the uncapped species and the end functionalized species with 50 monomer repeat units. Matrix: dithranol, without cationization reagent.

isobutyryl bromide moiety but devoid of the initiator group (here *tert*-butoxide). These peaks might result as a side product of the MALDI-TOF process where the initiator group is cleaved. After subtracting the initiator group, the end group, –(CO)–C(CH_3)$_2$Br, 150 g/mol, and the counter ion molecular weight from one of the signals of the most intense series, and dividing the resulting number by the repeat unit mass, an integral number for the degree of polymerization is obtained:

$$(2\,333\ \mathrm{g/mol} - 73.12\ \mathrm{g/mol} - 1.50\ \mathrm{g/mol} - 39.10\ \mathrm{g/mol})/44.05\ \mathrm{g/mol} = 47$$

Although non end-functionalized species are detected a quantitative percentage for the end functionalization cannot be determined from the MALDI-TOF results, as ionization and desorption is dependent on the chemical nature of the polymer.

Figure 3 shows the comparison of GPC elugrams of macroinitiators PEOBr prepared by performing the end capping reaction in 3 different ways with that of the uncapped species PEOH. First, an excess of 2-bromoisobutyryl bromide was added dropwise (PEOBr12a), or at one go (PEOBr12b) to the living PEO solution and finally, the living PEO solution was added dropwise to an excess of 2-bromoisobutyryl bromide (PEOBr12c). Both elugrams of PEOBr12a and PEOBr12b show a second peak or a shoulder at lower elution volumes, indicative of the presence of higher molecular weight side products. As the apparent molecular weight of the latter peak is roughly twice as much as that of the proton terminated species PEOH12, this may indicate the coupling of PEO chains. For the mechanism of this side reaction we propose first an elimination of the β-protons of the 2-bromoisobutyryl units followed by the coupling of PEO chain ends. This is further corroborated by the corresponding vinyl peaks in ^{1}H NMR spectra of the bimodal GPC samples (data not shown). The last method resulted in identical GPC traces of the PEO macroinitiator (PEOBr12c) and the proton terminated PEOH12 demonstrating successful end capping. Therefore the latter procedure was followed for subsequent end capping reactions. The results of the characterization of a series of macroinitiators used for the diblock copolymer synthesis described in the next paragraph are shown in Table 1. The degree of end-functionalization determined by ^{1}H NMR always exceeds 90% and approaches 100% in most cases.

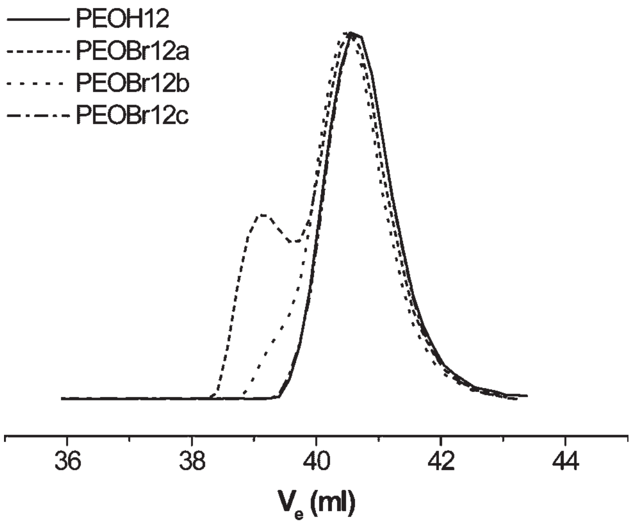


Figure 3. GPC elugrams of PEO macroinitiators PEOBr12a–c, prepared by different procedures as described in the text (V_e is the elution volume).

Synthesis of PEO-block-PHMA Diblock Copolymers

PEO macroinitiators were used for the NiBr$_2$(PPh$_3$)$_2$ catalyzed ATRP of hexyl methacrylate in toluene at 90 °C. This resulted in diblock copolymers poly(ethylene oxide)-*block*-poly(hexyl methacrylate), PEO-*block*-PHMA. Figure 4 shows the GPC elugrams of a PEO macroinitiator PEOBr26 with $\overline{M}_n^{GPC} = 4\,200$ and a polydispersity index ($\overline{M}_w/\overline{M}_n$) = 1.09 as well as the diblock copolymer PEO-*block*-PHMA T37 with $\overline{M}_n^{GPC} = 16\,800$ and $\overline{M}_w/\overline{M}_n = 1.09$ derived from

Table 1. Characterization of macroinitiators PEOBr.

Polymer	GPC[a]		MALDI-TOF		NMR	
	$\overline{M}_n$ g/mol	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$ g/mol	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$ g/mol	Functionality
PEOBr223	1 600	1.18	1 900	1.14	2 000	0.91
PEOBr16	3 200	1.15			2 200	0.99
PEOBr224	1 900	1.16	1 800	1.08	2 550	0.96
PEOBr26	4 200	1.09			2 800	0.97
PEOBr30	3 200	1.08			2 800	0.99
PEOBr13	4 700	1.08	3 300	1.05	3 300	0.94
PEOBr12	7 200	1.07			4 700	0.92
PEOBr15	11 000	1.06			8 900	1.0

[a] Based on polystyrene calibration.

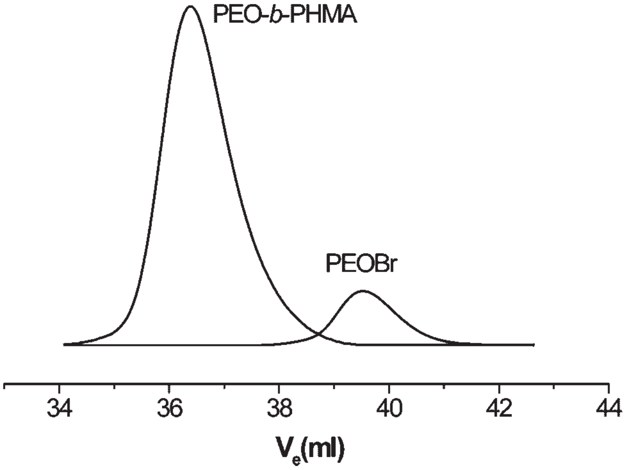


Figure 4. GPC elugrams of PEO macroinitiator PEOBr26 with $\overline{M}_n^{GPC} = 4\,200$ and $\overline{M}_w/\overline{M}_n = 1.09$ and the PEO-*block*-PHMA diblock copolymer T37 derived from it with $\overline{M}_n^{GPC} = 16\,800$ and $\overline{M}_w/\overline{M}_n = 1.09$ (from PS calibration).

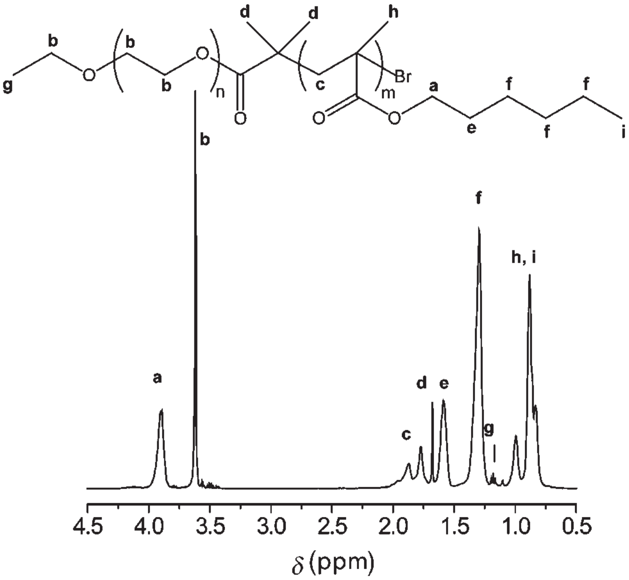


Figure 5. ^{1}H NMR spectrum of a PEO-*block*-PHMA diblock copolymer T37.

it. Both the homopolymer PEO prepared by anionic polymerization and the diblock copolymer PEO-*block*-PHMA prepared by subsequent ATRP have narrow molecular weight distributions. Figure 5 shows the ^{1}H NMR spectrum of PEO-*block*-PHMA T37. The composition in terms of block weight fractions is calculated on the basis of the ratio of the area for the PEO backbone proton signals (b) to the total area of the signals (a) + (b), where (a) is the proton signal from the hexyl side chains of the PHMA. The spectrum is further used to calculate the number average molecular weight, $\overline{M}_n$, of a PEO-*block*-PHMA diblock copolymer by using the $\overline{M}_n$ of the respective macroinitiator PEOBr as determined by ^{1}H NMR (described in the last section). The characterization results of a whole series of diblock copolymers synthesized by ATRP are summarized in Table 2. The polymerizations were carried out at different monomer concentrations. Over the concentration range examined (0.93–2.5 M) no systematic variations in, e.g., the molecular weight distributions could be observed (see Table 2).

Table 2. Characterization of PEO-*block*-PHMA diblock copolymers.

Polymer	Macroinitiator	HMA$[M]_0$	GPC[a)]		NMR	
		M	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	PEO
			g/mol		g/mol	wt.-%
T13	PEOBr13	0.93	11 400	1.10	15 300	21
T236	PEOBr224	0.93	16 500	1.19	15 300	12
T237	PEOBr224	0.93	14 300	1.14	18 700	14
T305	PEOBr223	0.93	14 000	1.13	12 900	15
T19	PEOBr16	0.95	7 180	1.18	7 900	28
T42	PEOBr15	1.01	13 500	1.13	13 000	68
T41	PEOBr15	1.13	13 100	1.07	14 500	62
T21	PEOBr16	1.36	7 300	1.16	7 800	28
T39	PEOBr15	1.49	17 200	1.06	20 300	44
T22	PEOBr16	1.77	11 500	1.10	15 800	14
T24	PEOBr13	1.77	13 900	1.14	19 700	17
T26	PEOBr13	2.11	14 000	1.12	22 100	15
T25	PEOBr13	2.5	16 400	1.11	24 200	14
T31	PEOBr26	2.5	14 800	1.11	18 700	16
T35	PEOBr26	2.5	17 300	1.11	20 700	14
T37	PEOBr26	2.5	16 800	1.09	18 750	16

[a)] Based on polystyrene calibration.

Kinetics of Polymerization of the HMA Block

For ATRP of HMA in toluene at 2.5 M concentration at 90 °C with PEOBr30 as the initiator, Figure 6a shows the time dependence of $\ln([M]_0/[M])$. Here $[M]_0$ is the initial monomer concentration and [M] is the monomer concentration at time *t*. Also shown in the same graph is the time dependence of conversion. The near linear behavior of $\ln([M]_0/[M])$ is consistent with a controlled polymerization that is first order in monomer concentration indicating absence of termination. The dependence of the molecular weight and polydispersity on the HMA conversion is illustrated in Figure 6b. Within experimental error the number average molecular weights ($\overline{M}_n$) were found to increase in direct proportion to monomer conversion. The corresponding molecular weight distributions were narrow throughout the reaction ($\overline{M}_w/\overline{M}_n < 1.2$). These results suggest that the macroinitiator PEOBr with $NiBr_2(PPh_3)_2$ as a catalyst induces a living polymerization of HMA. Kinetics studies performed at an initial monomer concentration $[M]_0 = 0.93$ M showed similar results, as did ATRP studies of HMA with the initiating system $(CH_3)_2CBrCO_2C_2H_5$/$NiBr_2(PPh_3)_2$ (see *Supporting Information*).

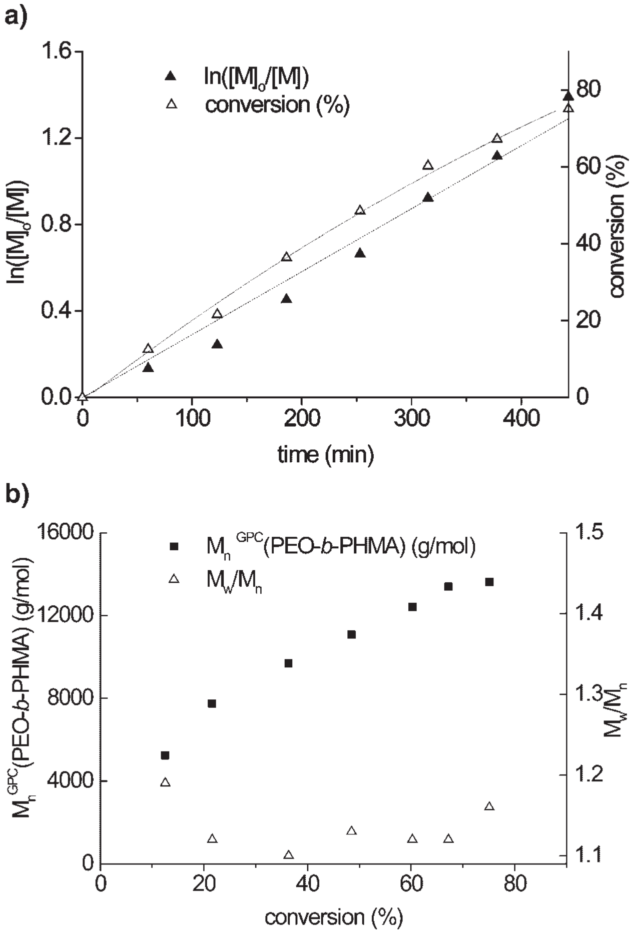


Figure 6. (a) Plots of $\ln([M]_0/[M])$ and the conversion vs time for HMA polymerization in toluene at 90 °C using macroinitiator PEOBr30 ($\overline{M}_n^{GPC} = 3\,200$). Conditions: $[HMA]_0 = 2.5$ M, $[NiBr_2(PPh_3)_2]_0 = 2.27 \times 10^{-2}$ M, $[PEOBr30]_0 = 2.27 \times 10^{-2}$ M. (b) Conversion dependence of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ for HMA polymerization using macroinitiator PEOBr30 ($\overline{M}_n^{GPC} = 3\,200$). Conditions: 90 °C in toluene, $[HMA]_0 = 2.5$ M, $[NiBr_2(PPh_3)_2]_0 = 2.27 \times 10^{-2}$ M, $[PEOBr30]_0 = 2.27 \times 10^{-2}$ M.

Small Angle X-Ray Scattering

Finally we report on first structural investigations of the PEO-*block*-PHMA diblock copolymers employing small angle X-ray scattering (SAXS). Three PEO-*block*-PHMA diblock copolymers, referred to as T37, T39, and T42, were chosen for these studies. Their PEO wt.-% are 16, 44 and 68, respectively. Spectra were taken at 50 °C, i.e., above the melting point of the semicrystalline PEO. A representative SAXS pattern obtained for T37 is shown in Figure 7A. The main peak is centered around a value for the scattering wave vector *q* corresponding to ≈12.6 nm. There are at least two higher order reflections clearly visible at angular positions of $\sqrt{2}$ and $\sqrt{3}$ of the first-order maximum. This pattern is consistent with spheres packed in a simple or body-centered cubic lattice, as expected for this weight fraction of $w_{PEO} = 0.16$.

In the SAXS pattern of T39 (Figure 7B) the main peak is located at a *q* value corresponding to ≈20.8 nm, and there are higher order reflections at angular positions of $\sqrt{3}$, $\sqrt{4}$ and $\sqrt{7}$ of this first-order maximum. This spacing is consistent with a hexagonal array of cylinders. For T42 (Figure 7C) the main peak is centered around a *q* value corresponding to ≈20.9 nm, and there is one higher order reflection clearly visible at an integral multiple 2 of this *q* value. Such a sequence is consistent with an arrangement of lamellae. These results demonstrate that for the chosen PEO weight fractions (0.16–0.68) and overall molecular weights with $\overline{M}_n$ between 10 and 20 kg/mol, see Table 2, the PEO-*block*-PHMA diblock copolymers form microphase separated structures with well detectable SAXS traces. Although a definitive lattice assignment cannot be made without more diffracted orders than are typically observed with block copolymer samples, the data are consistent with the morphologies expected from phase diagrams of similar block copolymers.[2c] These are shown as insets in Figure 7.

Conclusions

We have described the preparation of a new set of amphiphilic diblock copolymers consisting of a poly(ethylene oxide) and a poly(hexyl methacrylate) block. The synthesis combines two efficient reactions, anionic polymerization of EO and ATRP of HMA and leads to polymers with well-defined molecular weights and narrow molecular weight

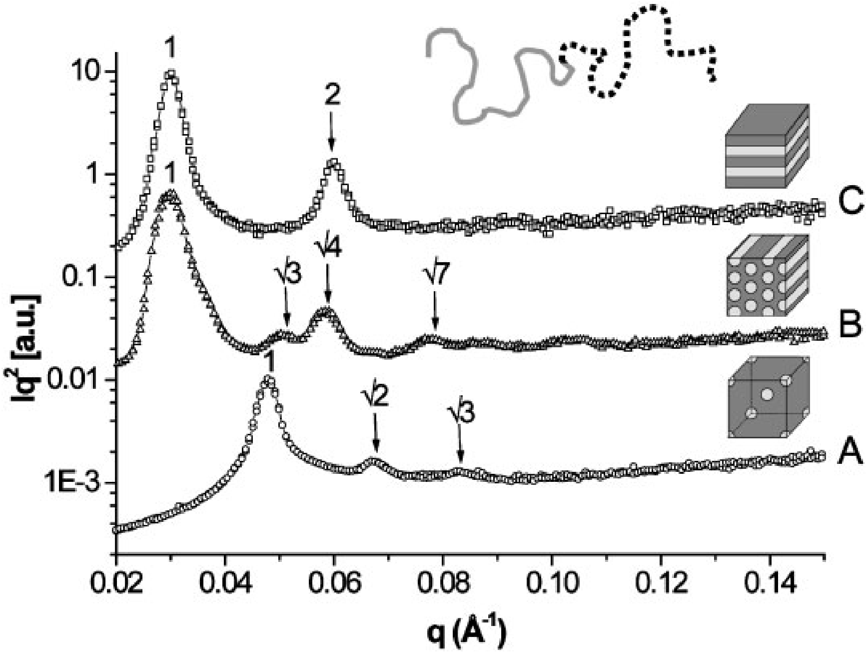


Figure 7. SAXS diffractograms of PEO-*block*-PHMA diblock copolymers T37 (A), T39 (B), and T42 (C), taken at 50 °C. Diffractograms were shifted along the *y*-axis to prevent data overlap. Positions of higher order reflections with respect to first order maximum are indicated above each spectrum. The arrows indicate the expected positions of diffracted orders of the indicated ratio of distances from the origin of diffraction.

distributions. Kinetics studies reveal a living polymerization for HMA. First microstructure investigations by SAXS show microphase separated structures as expected from existing diblock copolymer phase diagrams. These results suggest that the PEO-*block*-PHMA block copolymers may be used as novel structure directing agents for the synthesis of nanostructured polymer-ceramic hybrid materials. Work along these lines is now in progress in our laboratories.

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