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Polymer 43 (2002) 3139–3145

polymer

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Block copolymers comprising poly(ethylene oxide) and poly(hydroxyethyl methacrylate) blocks: synthesis and characterization

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Abstract

Monofunctional poly(ethylene oxide) macroinitiators with a molecular weight of 2000, 5000, 10 000, 20 000 and bifunctional poly-(ethylene oxide) macroinitiators with a molecular weight of 20 000 were used for the atom transfer radical polymerisation (ATRP) of hydroxyethyl methacrylate (HEMA) in ethylene glycol as a solvent. The polymerisation proceeds in a controlled way up to high conversions. The molecular weight of the obtained copolymers increases linearly with conversion. A high rate of polymerisation was observed for the ATRP of HEMA. The effect of the poly(ethylene oxide) moiety on the course of the reaction is limited to solvating effects. The surface analysis of poly(ethylene oxide)/poly(hydroxyethyl methacrylate) block copolymers by means of atomic force microscopy in tapping mode using phase imaging shows phase separated domains with characteristic features related to the volume fraction of the respective blocks.

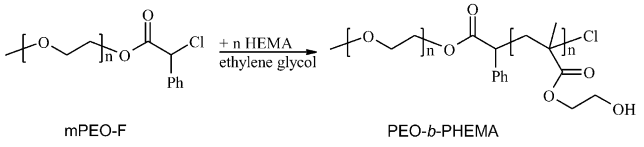
Keywords: Poly(ethylene oxide)-*block*-poly(hydroxyethyl methacrylate); Kinetics of the ATRP of HEMA with poly(ethylene oxide) macroinitiators; Surface morphology studied by atomic force microscopy

1. Introduction

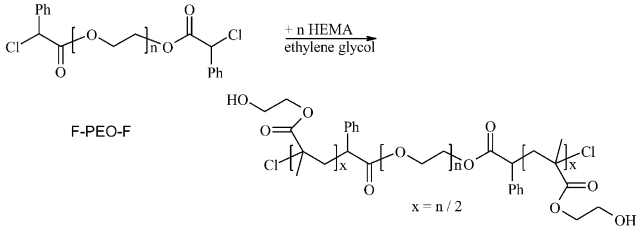
Poly(ethylene oxide) (PEO) has found wide application in biotechnology and for medical purposes [1]. Telechelic PEOs with suitable end groups were used for the preparation of PEO–protein adducts [2–4], as coatings for biologically active surfaces [5,6], or as spacers for the binding of active components onto surfaces [7–10]. Hydroxyethyl methacrylate (HEMA) is an important component (building block) for the preparation of hydrogels, of materials suitable for active component carriers (drug delivery systems), and especially for the preparation of contact lenses [11,12]. For block copolymers with PEO and PHEMA—two polar blocks—synergetic effects are expected with a high potential of application.

The synthesis of PEO/PHEMA block copolymers, however, is not trivial as living ionic or group transfer polymerisation is not compatible with free hydroxyl groups present in one of the monomers. HEMA was polymerised for the first time under controlled conditions by atom transfer radical polymerisation (ATRP) [13]. The polymerisation was carried out in solution (ethylmethylketone/1-propanol 70/30 v/v) using a bromo-substituted initiator in combination with copper chloride. The first PEO macroinitiators used for the ATRP of styrene were reported by Kops et al. [14].

This paper presents the first synthesis of PEO-*b*-PHEMA and PHEMA-*b*-PEO-*b*-PHEMA by using mono- and bifunctional PEO macroinitiators for the ATRP of HEMA in ethylene glycol solution (Eqs. (1) and (2)).



mPEO-F PEO-*b*-PHEMA (1)



F-PEO-F PHEMA-*b*-PEO-*b*-PHEMA (2)

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PII: S0032-3861(02)00130-1

2. Experimental

2.1. Materials

Monohydroxy-functional poly(ethylene oxide)s (mPEO) with a molecular weight of 2000, 5000, 10 000, and 20 000 and hydroxytelechelic poly(ethylene oxide) with a molecular weight of 20 000 (from Shearwater Polymers Inc.) were dried before use by means of azeotropic distillation with toluene in a water separator. The preparation of PEO-macroinitiators (mPEO–F, F–PEO–F) was performed according to Ref. [15].

A solution of HEMA in distilled water (25 vol.%) was extracted four times with hexane. The solution was then saturated with NaCl, the resulting HEMA phase was separated from the brine, dried with Na_2SO_4 and distilled in HV. HEMA was stored in nitrogen atmosphere at −78 °C.

Ethylene glycol (>99%, Aldrich) was dried according to standard laboratory methods, CuCl (98%, Aldrich) and 2,2′-bipyridine (bipy) (ABCR) were used as received. Polymerisations were carried out in an inert gas atmosphere. Nitrogen (Linde) was passed over molecular sieves (4 Å) and finely distributed potassium on aluminium oxide. (The preparation of PEO-macroinitiators (mPEO–F, F–PEO–F) and the polymerisation of HEMA with these macroinitiators in ethylene glycol was performed according to Ref. [15].)

Polymerisation of HEMA procedure I. Into a Schlenk-tube one equivalent of Cu(I)Cl, two equivalents of 2,2′-bipyridine and one equivalent of macroinitiator are placed and the tube is evacuated and then filled with nitrogen. Ethylene glycol 2 g (32.2 mmol) and HEMA 2 g (15.4 mmol) are added under nitrogen and the reaction mixture is degassed via three freeze–thaw cycles and afterwards again filled with nitrogen. The polymerisation is carried out at 80 °C and terminated by rapidly cooling to room temperature. Samples of the reaction mixture are taken and investigated by means of ^{1}H NMR and GPC. The crude product is then dissolved in a mixture of aqua dest. and acetone (1/1 v/v) and purified by means of dialysis. The residual water is removed by freeze drying.

Polymerisation of HEMA procedure II. Into a Schlenk-tube one equivalent of macroinitiator is placed and the tube is evacuated, then filled with nitrogen. Ethylene glycol 2 g (32.2 mmol) and HEMA 2 g (15.4 mmol) are added under nitrogen. The mixture is then heated to 40–50 °C in order to homogenise it. One equivalent of Cu(I)Cl and two equivalents of 2,2′-bipyridine are added under nitrogen and the reaction mixture is degassed by three freeze–thaw cycles and again filled with nitrogen. The polymerisation is carried out as described above.

2.2. Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 and 75 MHz, respectively. Dimethylsulfoxide (DMSO-d_6) was used as a solvent, and tetramethylsilane (TMS) served as an internal standard.

Gel permeation chromatography (GPC) analyses were carried out using a high pressure liquid chromatography pump (Bischoff), a refractive index detector (Waters), and a UV-detector (Carlo Erba at $\lambda = 264$ nm). The eluting solvent was dimethylacetamide (DMAc) with 0.12 wt% LiCl and with a flow rate of 0.5 ml min^{-1}. Four columns with Jordi Gel DVB were applied: length of each column: 250 mm, diameter 10 mm, diameter of gel particles 5 μm, nominal pore width 100, 500, 10^3 and 10^4 Å. Calibration with polystyrene standards was used for the estimation of the molecular weights of poly(ethylene oxide)/poly(hydroxyethyl methacrylate) block copolymers.

Images of the polymer surfaces were obtained with an Extended Multimode NanoScope IIIa atomic force microscope (AFM, from Digital Instruments Inc.) at room temperature in air. A Vertical Engaged 120 μm Scanner (JV-Scanner) was used. Measurements in Tapping-Mode were performed with 125 μm TESP Si-tips from digital Instruments at frequencies of 200–400 kHz and spring constants of 20–100 N/m.

Preparation of the polymer samples for AFM-measurements. Foils of PEO-*b*-PHEMA block copolymers were prepared starting with a 5 wt% solution of the block copolymer in methanol. The polymer solution was spread on a silicium wafer and the solvent was evaporated in a nitrogen atmosphere. The polymer film was dried and annealed at 160 °C in high vacuum for 100 h.

3. Results and discussion

In order to prepare PEO-*b*-PHEMA and PHEMA-*b*-PEO-*b*-PHEMA block copolymers within a wide range of composition, mPEO with a molecular weight of 2000, 5000, 10 000, and 20 000 and hydroxytelechelic PEO with a molecular weight of 20 000 were endcapped with 2-chloro-2-phenylacetyl chloride to yield the respective functionalised macroinitiators mPEO–F and F–PEO–F. These macroinitiators were characterized by means of ^{1}H NMR, MALDI-ToF and GPC (Ref. [15]).

3.1. Polymerisations

Preliminary experiments in which HEMA was subjected to ATRP in the bulk polymerisation at 130 °C revealed that even after short reaction times an insoluble, probably crosslinked polymer was obtained. As the HEMA was purified before use, the crosslinking might have been caused by the high polymerisation temperature and by the presence of the catalyst which may have favoured transesterification reactions. In order to decrease the rate of polymerisation the temperature was lowered to 80 °C and the monomer concentration was decreased by polymerisation in solution. Ethylene glycol was chosen as the solvent to eliminate the possibility of a change in the microstructure of the polymer

Table 1
Polymerisation of HEMA with mPEO–F and F–PEO–F macroinitiators in 50 wt% solution of ethylene glycol (initiator/CuCl/bipy = 1/1/2, $T = 80$ °C)

No.	Initiator	HEMA/initiator[a]	t (min)	X_p (%)[b]	$M_{n,\,th}$[c]	$M_{n,exp}$[d]	M_w/M_n[d]
1[e]	mPEO–F 2000	45	8	97	5700	20 700	1.47
1[f]	mPEO–F 2000	45	7	98	5900	25 500	1.36
2[e]	mPEO–F 5000	114	10	89	13 200	47 200	1.20
2[f]	mPEO–F 5000	114	10	95	14 100	48 500	1.20
3[e]	mPEO–F 10 000	227	15	77	22 700	67 000	1.36
3[f]	mPEO–F 10 000	227	14	67	19 800	61 000	1.28
4[e]	F–PEO–F 20 000	454	12	73	21 200	80 700	1.40
5[e]	mPEO–F 20 000	454	15	55	32 500	102 000	1.35

[a] Molar ratio.
[b] Conversion determined by means of ^{1}H NMR spectroscopy (300 MHz).
[c] M_n value of the PHEMA block: $M_{n,th} = [M]/[I]X_pM_{monomer}$.
[d] M_n value of the block copolymer evaluated by means of GPC in DMAc with 2.441 g/l LiCl, 80 °C, PS-standards.
[e] Polymerisation procedure I: all components were mixed, degassed, and heated to 80 °C.
[f] Polymerisation procedure II: ethylene glycol, HEMA, and the macroinitiator were heated to 40–50 °C to dissolve the macroinitiator. The catalyst was added, the mixture degassed and then heated to 80 °C.

by transesterification reactions. In order to dissolve the PEO macroinitiators in the reaction medium within a reasonable period of time the temperature had to be adjusted to 80 °C. The higher rate of polymerisation of HEMA compared with that of methyl methacrylate or styrene ($k_{p(HEMA)} = 1000$ l/mol s at 30 °C [16], $k_{p(MMA)} = 248$ l/mol s at 30 °C [17], $k_{p(styrene)} = 52$ l/mol s at 30 °C [18] is due to the polar nature of the monomer and the solvents required to dissolve the polymer which dramatically affects the solubility (Matyjaszewski) and/or the structure (Haddleton) of the catalytic species [19–21].

In procedure I HEMA was polymerised in 50 wt% ethylene glycol solution using the monofunctional PEO macroinitiators mPEO–F 2000, 5000, 10 000 and 20 000 and the bifunctional PEO macroinitiator F–PEO–F 20 000. The degassed mixture of all components including the catalyst was heated to 80 °C and polymerisation was allowed for a certain time (t). The macroinitiators were not dissolved instantaneously in the reaction mixture. In order to prevent the disadvantages of slow initiation (slow solubilisation of the PEO macroinitiators) an alternative procedure was employed. In procedure II the macroinitiator, HEMA and ethylene glycol were mixed and heated to 40–50 °C to dissolve the macroinitiator and to obtain a homogeneous solution before the catalyst was added. Then the mixture was degassed, the catalyst was added and the mixture was heated to 80 °C for polymerisation. The molar ratio initiator/CuCl/bipy was 1/1/2. The theoretical value of the number average degree of polymerisation at full conversion of HEMA was chosen to be equal to the number average degree of polymerisation of the respective macroinitiator (Table 1). It is thus expected that at full conversion the molar ratio of repeating units HEMA/EO in the copolymer is 1. The block copolymers were isolated by dissolution of the crude products in an acetone/water mixture, removal of low molecular weight material including the catalyst by dialysis and removal of water by freeze drying. According to GPC during dialysis no fractionation of the copolymers occurred. The monomer conversion was determined by means of ^{1}H NMR spectroscopy, the molecular weight and the polydispersity index were estimated by means of GPC. The results obtained are summarised in Table 1. For the lower molecular weight initiators mPEO–F 2000 and 5000 high yields of block copolymers were obtained after ca. 10 min. For the higher molecular weight initiators mPEO–F 10 000 and 20 000 and F–PEO–F 20 000 the yields obtained after ca. 15 min are between 55 and 77%. This decrease in the rate of polymerisation is due to the lower concentration of initiating species with increasing molecular weight of the PEO macroinitiator. For a specific macroinitiator the M_n values of the resulting block copolymers estimated by means of GPC are independent of the procedure used for the polymerisation. However, a tendency to lower M_w/M_n values is observed for the second polymerisation procedure (cf. runs 1–3 procedures e and f in Table 1).

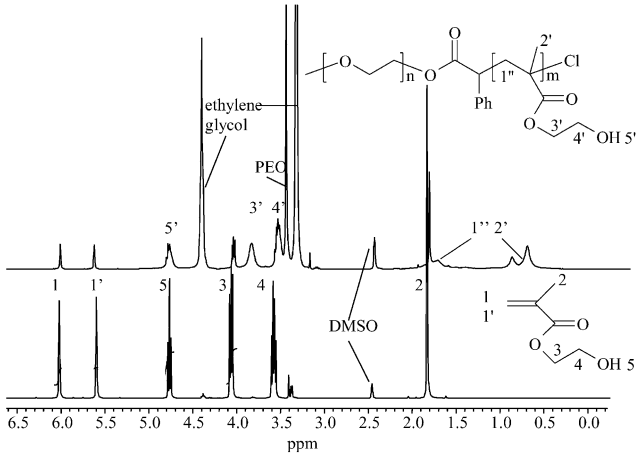

Fig. 1. ^{1}H NMR spectra of HEMA (below) and of a raw product obtained in the polymerisation of HEMA with PEO–F 2000 (above) (DMSO-d_6).

Fig. 1 shows a ^{1}H NMR spectrum of a crude reaction mixture, which was used for the determination of monomer

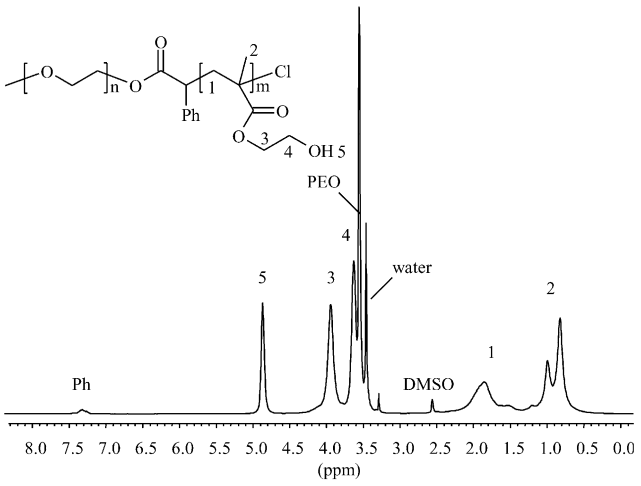

Fig. 2. ^{1}H NMR spectrum of a PEO-*b*-PHEMA block copolymer (after purification by dialysis and drying for 100 h in high vacuum, (DMSO-d_6).

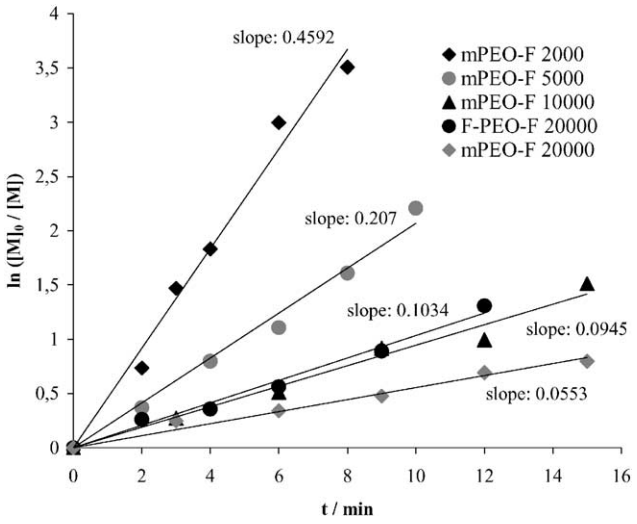

Fig. 3. First order plot of the polymerisation of HEMA with the macroinitiators mPEO–F 2000, mPEO–F 5000, mPEO–F 10 000, F–PEO–F 20 000, and mPEO–F 20 000. (Polymerisation conditions: 50 wt% ethylene glycol, HEMA/Initiator/CuCl/bipy = 45 (mPEO–F 2000), 114 (mPEO–F 5000), 227 (mPEO–F 10 000), 454 (F–PEO–F 20 000), 454 (mPEO–F 20 000)/1/1/2, for initiation the mixture of all components was heated to 80 °C).

conversion. For the sake of comparison the spectrum of HEMA is also presented. The resonance lines were assigned by comparison with spectra of authentic samples. For the determination of conversion of HEMA the resonance line H3′ of PHEMA at $\delta = 3.9$ ppm and the resonance lines of the olefinic protons H1 and H1′ of HEMA were considered.

Fig. 2 shows the ^{1}H NMR spectrum of a block copolymer after purification. The resonance lines for the methyl groups between 0.7 and 1.2 ppm can be assigned to mm, mr and rr triads of HEMA. From the intensity ratio it becomes clear that the PHEMA block is highly syndiotactic as it is expected for the radical polymerisation of methacrylates. From the ^{1}H NMR spectra the molar ratio of EO/HEMA units was also determined. However, due to the fact that the resonance lines of the $-CH_2CH_2-O-$ repeating units are not base line separated from the resonance lines of the CH_2OH group of HEMA the accuracy of the values obtained is low. In addition the quantitative determination of the EO/HEMA ratio is difficult because of residual water that could not be removed from the sample, the resonance line of the water protons overlaps with the resonance line of the EO-repeating units.

3.2. Kinetics

The first order plots of the polymerisation of HEMA with the macroinitiators mPEO–F 2000, mPEO–F 5000, mPEO–F 10 000, F–PEO–F 20 000, mPEO–F 20 000 are shown in Fig. 3. Each data point represents a single experiment; reproducibility is thus given. The plots show straight lines up to high conversion. The ratio of the apparent rate constants $k_{app} = k_p[P^{\cdot}]$ obtained from the slopes reflects the ratio [HEMA]/[PEO–F] in the feed. The values for the apparent rate constants are summarised in Table 2.

The number average molecular weights of the PEO-*b*-PHEMA and PHEMA-*b*-PEO-b-PHEMA samples mentioned above as estimated by means of GPC show a linear increase with monomer conversion as is shown for the polymerisation of HEMA with mPEO–F 10 000 and F–PEO–F 20 000 (Fig. 4). The polydispersity indices of the samples increase with conversion from 1.2 to 1.4.

As mentioned in Section 1 the polymerisation of HEMA has a high rate constant of propagation ($k_{p(HEMA)} = 1000$ l/mol s at 30 °C [16]). For reactions with such a high polymerisation rate instantaneous initiation is not to be expected. In addition, the experimental procedure I which was followed, favours slow initiation since the macroinitiator is not dissolved in the reaction medium at room temperature and is dissolved in the HEMA/ethylene glycol mixture only upon heating to 80 °C. Time dependent GPC analysis (Fig. 5) reveals the slow consumption of the mPEO–F 10 000 macroinitiator. A decrease of the concentration of the macroinitiator is observed with time and in parallel an increase of the molecular weight of the block copolymer is observed. It is to be noted that GPC analysis of the reaction product obtained when HEMA is polymerised with the bifunctional macroinitiator does not show a bimodal distribution of the product (Fig. 6).

Table 2
Apparent rate constant of the HEMA polymerisation with PEO macroinitiators (initiator/CuCl/bipy = 1/1/2, $T = 80$ °C)

Initiator	[HEMA]/[initiator][a]	k_{app} (10^{-3} s^{-1})
mPEO–F 2000	45	7.67
mPEO–F 5000	114	3.50
mPEO–F 10 000	227	1.67
F–PEO–F 20 000	454	1.50
mPEO–F 20 000	454	1.00

[a] Molar ratio.

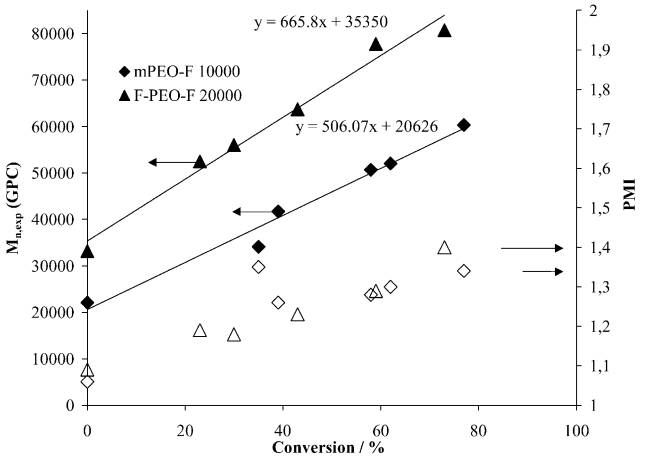

Fig. 4. $\overline{M}_{n,exp}$ (GPC) and polydispersity indices of PEO-*b*-PHEMA and PHEMA-*b*-PEO-*b*-PHEMA vs. conversion of HEMA. (Polymerisation conditions: mPEO–F 10 000 and F–PEO–F 20 000 initiators; (HEMA/Initiator/CuCl/bipy = 227 (mPEO–F 10 000), 454 (F–PEO–F 20 000)/1/1/2, $T = 80$ °C).

The GPC results of the crude reaction product show no evidence for oligomers with molecular weights lower than the molecular weight of the initiator used. This is considered as an evidence for the absence of PHEMA homopolymer from the reaction product.

In order to eliminate the influence of the solubilisation time of the macroinitiator on the initiation rate, the second experimental procedure was followed: the macroinitiators were dissolved at 40–50 °C in ethylene glycol and HEMA, then the catalyst was added, the reaction mixture was degassed and the polymerisation was started by heating to 80 °C. The polymerisation of HEMA with mPEO–F 2000 and mPEO–F 5000 under these conditions leads to a higher rate of polymerisation as compared with polymerisation procedure I (Figs. 3 and 7). The value of k_{app} increases slightly to $9.67 \times 10^{-3}\,s^{-1}$ for mPEO–F 2000 and to $4.83 \times 10^{-3}\,s^{-1}$ for mPEO–F 5000 (for comparison see

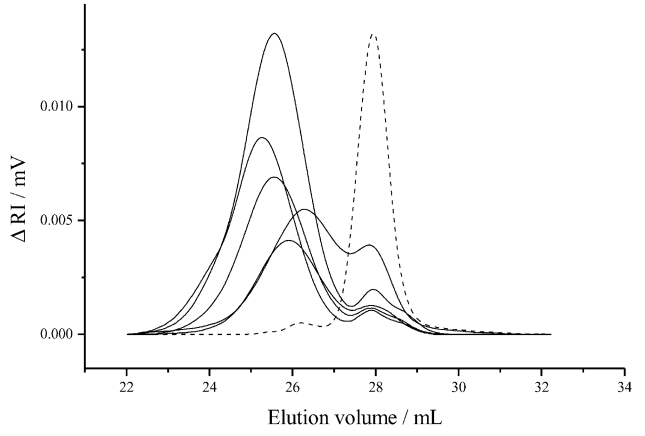

Fig. 5. GPC traces of mPEO–F 10 000 (- - -) and of respective PEO-*b*-PHEMA (—) at various polymerisation times (shown are traces at 3, 6, 9, 12, and 15 min) (DMAc with 2,441 g LiCl/ml, 80 °C, PS-standards).

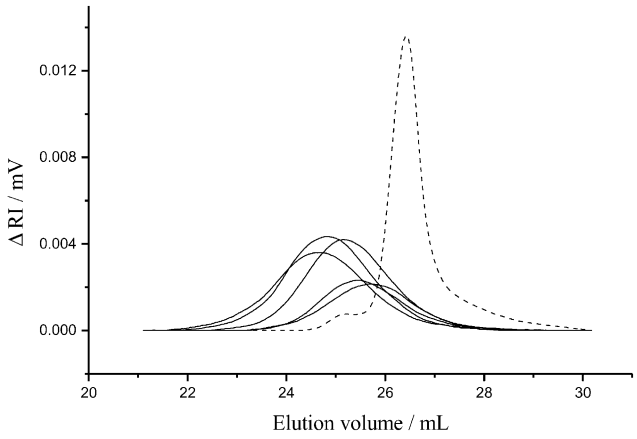

Fig. 6. GPC traces of F–PEO–F 20 000 (- - -) and of respective PHEMA-*b*-PEO-*b*-PHEMA (—) at various polymerisation times (shown are traces at 2, 4, 6, 9, and 12 min) (DMAc with 2.441 g LiCl/ml, 80 °C, PS-standards).

k_{app} values of Table 2). This procedure, however, failed for the higher molecular weight PEO macroinitiators, which form a gel during degassing of the reaction mixture. This gel is dissolved only slowly during heating to 80 °C and makes stirring impossible. We assume that the gel is caused by a physical crosslinking of the PEO-moiety, i.e. by complexation of the copper salt by the PEO in the reaction mixture. This is only observed when the Cu(I)Cl and bipy are separately added to an already dissolved PEO macroinitiator in a HEMA/ethylene glycol solution.

The first experiments in which HEMA was polymerised with mPEO–F macroinitiators revealed no influence of the PEO initiator on the course of the reaction compared to the

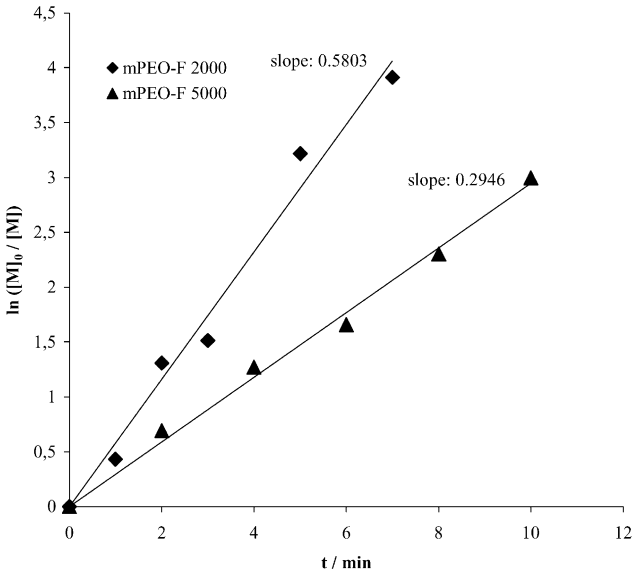

Fig. 7. Kinetic plot of the polymerisation of HEMA with the macroinitiators mPEO–F 2000 and mPEO–F 5000. (Polymerisation conditions: 50 wt% ethylene glycol, HEMA/Initiator/CuCl/bipy = 45 (mPEO–F 2000) or 114 (mPEO–F 5000)/1/1/2. The initiator was first dissolved in ethylene glycol/HEMA, then CuCl/bipy was added and the mixture was heated to 80 °C for initiation).

polymerisation of HEMA with a model initiator (Table 3). The polymer obtained after 16 min reaction time showed a monomodal molecular weight distribution (no oligomers are detected) and a polydispersity index of 1.3–1.5. The polymer yield was between 55 and 64%. In order to study the influence of the PEO block on the HEMA polymerisation more carefully we compared the kinetics of HEMA polymerisation with monofunctional mPEO–F macroinitiators and with α-chlorophenyl acetate as a model initiator. The [monomer]/[initiator] ratio for all experiments was constant and equal to 454. All polymerisations were performed according to procedure I. First order kinetic plots (Fig. 8) show straight lines up to high conversion. The apparent rate constants (Table 4) decrease slightly with increasing number of repeating EO-units in the macroinitiator. The polymerisation with the model initiator shows the highest apparent rate constant. Thus, the PEO moiety has only a small influence on the rate of polymerisation of HEMA.

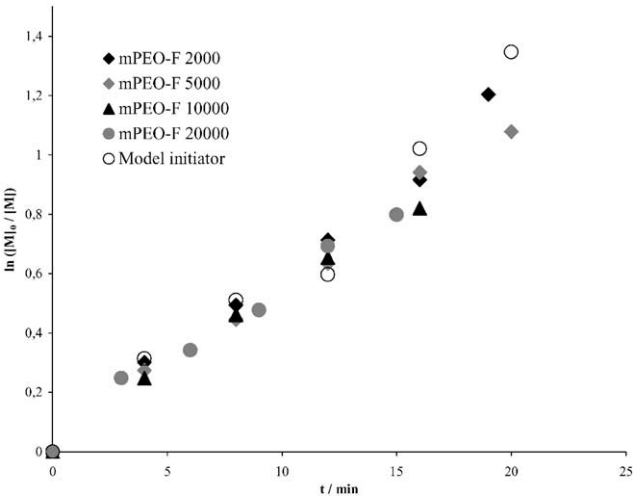

Fig. 8. First order kinetic plot of the polymerisation of HEMA with the macroinitiators mPEO–F 2000, mPEO–F 5000, mPEO–F 10 000, mPEO–F 20 000 and ethyl α-chlorophenyl acetate as a model initiator. (Polymerisation conditions: 50 wt% ethylene glycol, HEMA/initiator/CuCl/bipy = 454/1/1/2; for initiation the mixture of all components was heated to 80 °C).

3.3. Surface morphology

The morphology of block copolymers at a surface, e.g. at the interface to air or to the support, is different from the bulk morphology [22]. Due to the free surface energy of the respective components of the block copolymer [23] and the selective interactions with the interface medium—air in this case—one component of the block copolymer is preferred at the interface. The fact that the PEO component of the considered block copolymer is semi-crystalline and that the PHEMA component is amorphous is expected to have an additional effect on the surface morphology.

Crystallisation is a prominent molecular self-organisation process in nature. However, polymer crystallisation is usually kinetically hindered, due to the connectivity of the segments resulting in a lack of long-range order. In addition, non-crystallisable moieties may create entropic and steric constraints. In thin films of a block copolymer with a volume fraction $X_{V(A,B)} \approx 0.5$ and for a kinetically induced chain folded state, there is an energetically driven tendency to orientate the lamellae perpendicular to the substrate and thus to the interface. Such a behaviour was investigated for hydrogenated poly(butadiene)/PEO block copolymers [24]. We observed [25] for poly(styrene)/PEO block copolymers with a volume fraction of $X_{V(PEO)} = 0.52$ domains of ca. 30 nm diameter which also seem to broaden into gyroid structures orientated perpendicular to the surface.

In the following the atomic force microscopic image of a PEO/PHEMA block copolymer will be discussed. The block copolymer studied was prepared using the macroinitiator mPEO–F 20 000 with a molar ratio of [HEMA]/[mPEO–F] = 454. The experimental molecular weight of the PHEMA block determined by means of ^{1}H NMR spectroscopy was $M_{n,(NMR)} = 26\,900$. Based on the composition of the block copolymer and taking into account the densities of the partially crystalline PEO ($\rho_{PEO} = 1.13$ g/cm^3) and amorphous PHEMA ($\rho_{PHEMA} = 1.15$ g/cm^3) the volume fractions of the blocks were calculated to be $X_{V(PEO)} = 0.4$ and $X_{V(PHEMA)} = 0.6$. The polymer film was prepared on a silicium wafer from methanol solution in nitrogen atmosphere and was annealed at 160 °C in high vacuum. The interface to the nitrogen atmosphere was studied.

Table 3
Polymerisation of HEMA with a model initiator—ethyl α-chlorophenyl acetate—and with mPEO–F macroinitiators in 50 wt% solution of ethylene glycol (HEMA/initiator/CuCl/bipy = 454/1/1/2, T = 80 °C)

No.	Initiator	t (min)	X_p (%)[a]	$M_{n,th}$[b]	$M_{n,exp}$[c]	M_w/M_n[c]
1	Ethyl–F[d]	16	64	37 800	91 900	1.47
2	mPEO–F 2000	16	60	35 400	86 300	1.27
3	mPEO–F 5000	16	61	36 000	88 400	1.26
4	mPEO–F 10 000	16	56	33 000	119 100	1.38
5	mPEO–F 20 000	15	55	32 500	102 000	1.35

[a] Conversion determined by means of ^{1}H NMR spectroscopy (300 MHz).
[b] M_n value of the PHEMA block: $M_{n,th} = [M]/[I]x_pM_{monomer}$.
[c] M_n value of the block copolymer determined by means of GPC in DMAc with 2.441 g/l LiCl, 80 °C, PS-standards.
[d] $C_6H_5CH(Cl)COOEt$.

Table 4
Apparent rate constant of the HEMA polymerisation with mPEO–F macroinitiators and ethyl α-chlorophenyl acetate as a model initiator. (Polymerisation conditions: HEMA/Initiator/CuCl/bipy = 454/1/1/2, T = 80 °C)

No.	Initiator	P_n (initiator)	k_{app} (10^{-3} s^{-1})
1	Ethyl–F[a]	0	1.06
2	mPEO–F 2000	45	1.02
3	mPEO–F 5000	114	0.93
4	mPEO–F 10 000	227	0.89
5	mPEO–F 20 000	454	0.92

[a] $C_6H_5CH(Cl)COOEt$.

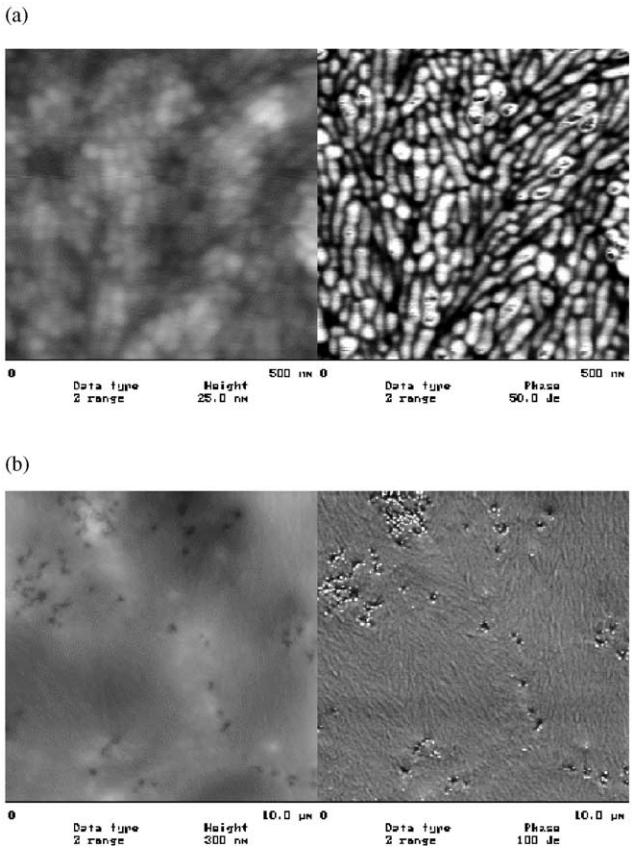

Fig. 9. Topographic (left) and phase image (right) AFM of a PEO-*b*-PHEMA block copolymer. (a) High resolution images, (b) lower resolution images. ($X_{V(PEO)} = 0.4$, $X_{V(PHEMA)} = 0.6$).

Based on the volume fractions of the components gyroid or lamellar structures are expected. The topographic image of higher resolution (Fig. 9a) reveals vague spherical and cylindrical structures. In the phase image these structures are clearly resolved. It seems that the crystalline PEO cylinders in the PHEMA matrix are partly parallel but mostly perpendicularly orientated to the surface as it was observed previously in poly(styrene/PEO block copolymers [25]. In contrast to the surface morphology of PEO-*b*-PS with a similar PEO volume fraction the PEO-b-PHEMA sample under investigation has a fish bone-like superstructure as shown in the phase image of lower resolution (Fig. 9b). These superstructures are clearly different from the PEO lamellae observed in PEO-rich block copolymers. As an explanation of this phenomenon, changes in the structure during removal of residual solvent in vacuo are considered. The phase image but also the topographic image clearly show cracks and holes which are attributed to the drying process. The surfaces of all PEO-*b*-PHEMA copolymers are highly hygroscopic and as a consequence the phase images become diffuse after a short period of time in air.

Acknowledgements

Financial support of Deutsche Forschungsgemeinschaft (Proj. Nr. Ho 772/28-1) and Fonds der chemischen Industrie is acknowledged.

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