

Amphiphilic block copolymers comprising poly(ethylene oxide) and poly(styrene) blocks: synthesis and surface morphology

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Dedicated to Professor Roderic P. Quirk in friendship and appreciation of his scientific achievements

Abstract

Monofunctional PEO-macroinitiators (mPEO-F) were prepared from monohydroxyfunctional poly(ethylene oxide)s and 2-chloro-2-phenylacetylchloride. In order to synthesise poly(ethylene oxide)-*block*-poly(styrene) (PEO-*b*-PS) the macroinitiators were applied to the atom transfer radical polymerisation (ATRP) of styrene in the bulk. Well-defined block copolymers were obtained with predetermined molecular weight and narrow molecular weight distribution. Kinetic aspects of ATRP of styrene depending on the molecular weight of the macroinitiator are discussed. Surface analysis by means of atomic force microscopy in tapping mode using phase imaging reveals characteristic morphologies as a function of the volume fraction of PEO. The higher the PEO content the more PEO is found at the polymer/air interface. The preparation of the samples has a main impact on the observed morphology. The polymer films are hygroscopic and alter their morphology being exposed to air. © 2002 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

Amphiphilic block copolymers are used in a variety of applications, e.g. as stabilisers for emulsions and dispersions or as compatibilisers in polymer blends. Especially block copolymers with a hydrophobic polystyrene and a hydrophilic poly(ethylene oxide) block have been studied lately with respect to their phase behaviour in aqueous solution and their properties as polymeric emulgators [1–3].

Diblock copolymers poly(styrene)-*block*-poly(ethylene oxide) (PS-*b*-PEO) were originally prepared by sequential living anionic polymerisation of styrene and ethylene oxide [4–6]. Triblock copolymers poly(ethylene oxide)-*block*-poly(styrene)-*block*-poly(ethylene oxide) (PEO-*b*-PS-*b*-PEO) were synthesised via living anionic polymerisation of styrene initiated with a bifunctional initiator and subsequent addition of ethylene oxide [7]. Triblock copolymers with a PEO sequence as the middle block were obtained by coupling reactions of PS-*b*-PEO [4].

A new method for the preparation of these block copolymers by using PEO macroinitiators in ATRP of

styrene was first published by Kops et al. [8]. We reported the preparation of a PEO macroinitiator with a novel initiating end group on the basis of 2-chloro-2-phenyl acetate and its initiating properties in the ATRP of styrene [9]. In the present paper we focus on the preparation of well defined block copolymers over a wide range of composition, with special emphasis on the kinetics of styrene polymerisation with poly(ethylene oxide) macroinitiators of different molecular weights and the investigation of the surface morphology of these block copolymers.

2. Experimental

Materials. Monohydroxy-functional poly(ethylene oxide)s (mPEO) with molecular weights of 2000, 5000, 10,000, and 20,000 (from Shearwater Polymers Inc.) were dried before use by azeotropic distillation with toluene using a water separator. The molecular weights of monohydroxy-functional mPEO 2000 and mPEO 5000 was checked by means of MALDI-TOF and corresponds with the values given by the manufacturer. α -Chlorophenylacetyl chloride (95%, Fluka) was distilled over a Vigreux column before

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use. Inhibitors in styrene (S) were removed by passing the monomer over an aluminium oxide column. CuCl (98%, Aldrich) and 2,2'-bipyridine (bipy) (ABCR) were used as received without purification. 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) and the polymerisation of styrene with these macroinitiators in bulk was performed according to Ref. [9].

Kinetics. Each data point in the kinetic plots represents a single experiment.

Measurements. The details of the NMR, GPC, MALDI-TOF and AFM measurements were described in Ref. [10].

Preparation of the polymer samples for AFM-measurements. Foils of PEO-*b*-PS block copolymers were prepared starting with a 5 wt% solution of the block copolymer in methylene chloride.

Variation 1. The polymer solution was spread on a silicon wafer and the solvent was evaporated. The polymer film was dried and annealed at 160 °C in high vacuum for 100 h.

Variation 2. The polymer solution was placed in a Schlenk flask and the solvent was evaporated in a stream of dry nitrogen. The polymer film was dried in high vacuum.

Variation 3. Pieces of polymer films were placed on a silicon wafer and annealed at 160 °C in high vacuum.

Variation 4. The polymer solution was spread on a cellophane foil and the solvent was evaporated under dry nitrogen. The polymer film was dried for 100 h in vacuum.

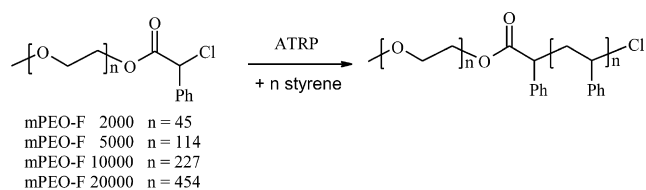
All samples were kept under dry nitrogen in a desiccator over phosphorus pentoxide.

3. Results and discussion

3.1. Macroinitiators

In order to prepare PEO-*b*-PS block copolymers within a wide range of composition, monohydroxy-functional poly(ethylene oxide)s (mPEO) with a molecular weight of 2000, 5000, 10,000, and 20,000 were endcapped with 2-chloro-2-phenylacetyl chloride to yield the respective functionalised macroinitiators (mPEO-F) (Scheme 1). Macroinitiators mPEO-F 2000 and mPEO-F 5000 were characterised by means of ¹H NMR spectroscopy, MALDI-TOF MS, and GPC. The molecular weights of the macroinitiators mPEO-F 2000 and mPEO-F 5000 determined by means of GPC in DMAc using poly(styrene) standards (5300 and 11,600, respectively), are largely overestimated. These results have to be taken into consideration when PEO/PS block copolymers are characterised by means of GPC.

The molecular weights found by MALDI-TOF MS (experimental mass in the peak maximum 2160.2 and



Scheme 1. Polymerisation of styrene using different poly(ethylene oxide) macroinitiators mPEO-F.

5599.2 amu) are in good agreement with the theoretical values.

The high molecular weight macroinitiators, i.e. mPEO-F 10,000 and mPEO-F 20,000 were characterised indirectly by investigating the molecular weight and composition of the block copolymers obtained with these macroinitiators.

3.2. Polymerisations

The atom transfer radical polymerisation (ATRP) of styrene in bulk using four macroinitiators was carried out at 130 °C with a molar ratio initiator/CuCl/bipy of 1/1/2. The degree of polymerisation P_n of the polystyrene block at complete conversion was designed to be the same as that of the corresponding PEO macroinitiator (styrene monomer/EO-repeating units = 1) (Scheme 1).

At the end of the reaction, the reaction mixture was dissolved in CCl₄ and stirred in air until the copper catalyst was completely oxidised. The resulting copper(II) complex is insoluble in the polymer solution and is easily removed by filtration. The conversion was determined by means of ¹H NMR spectroscopy of the filtrate. The solvent and the monomer still present in the filtrate were then evaporated and the crude product was dried to constant weight. The molecular weight and the molecular weight distribution of the obtained products were determined by means of GPC and the composition of the products was determined by means of ¹H NMR spectroscopy.

The structural evidence for the existence of block copolymers PEO-*b*-PS was given by selective extraction of the copolymers with water and cyclohexane and by reductive cleavage of the ester bond between the two blocks, separation of the resulting poly(styrene) from poly(ethylene oxide) and subsequent analysis of the resulting blocks as reported earlier [9].

The extraction of the block copolymers with water and cyclohexane was carried out in order to remove PEO homopolymer from the block copolymer if present in the crude product because of incomplete functionalisation of hydroxy-PEO or due to combination reactions in the early phases of the polymerisation and to remove poly(styrene) homopolymer formed by thermal polymerisation. A quantitative determination of the homopolymers removed by this procedure could not be achieved. The yield of recovered block copolymers was in any case higher than 80 wt%. The characteristics of the extracted block polymers were compared to those of the crude products.

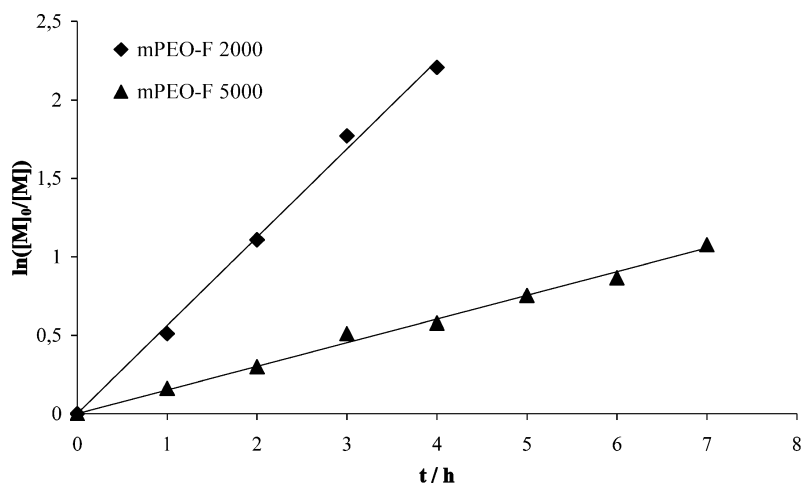


Fig. 1. First order plot of the polymerisation of styrene with mPEO-F 2000 and mPEO-F 5000 (styrene/initiator/CuCl/bipy = 45/1/1/2 (mPEO-F 2000) and 114/1/1/2 (mPEO-F 5000), $T = 130\text{ }^{\circ}\text{C}$).

3.3. Kinetics

3.3.1. Polymerisation of styrene with mPEO-F 2000 and mPEO-F 5000

The first order plots of the polymerisation of styrene with the macroinitiators mPEO-F 2000 and mPEO-F 5000 are shown in Fig. 1. Each data point represents a single experiment reproducibility is thus given. From the slope of the straight line obtained up to high conversions by linear regression the apparent rate constants $k_{app} = k_p[P.]$ as a direct measure of the concentration of the radicals was determined. For the polymerisation with mPEO-F 2000 as the initiator $k_{app} = 1.56 \times 10^{-4} \text{ s}^{-1}$ and for that with mPEO-F 5000 $k_{app} = 0.42 \times 10^{-4} \text{ s}^{-1}$ was found. The ratio of the apparent rate constants corresponds to the ratio of initiating end groups introduced into the feed.

The molecular weight of the polystyrene blocks in the obtained block copolymers determined by means of ^1H

NMR spectroscopy increases linearly with conversion and is in good agreement with the theoretical one (Fig. 2).

The plot of the molecular weight of the block copolymers determined by means of GPC versus conversion reveals a linear dependence as well. The polydispersity indices of the block copolymers obtained with mPEO-F 2000 as initiator have values between 1.05 and 1.10 while those of the block copolymers obtained with mPEO-F 5000 are slightly higher and have values around 1.15.

The GPC traces of the block copolymers obtained with mPEO-F 2000 are symmetrical and move with increasing conversion towards lower elution volume, i.e. higher molecular weights (Fig. 3). A slight tailing of the peaks towards lower molecular weights—probably due to thermal self initiation of styrene taking place during the course of the polymerisation is noted.

As a result, with the macroinitiators mPEO-F 2000 and mPEO-F 5000 well defined block copolymers in controlled

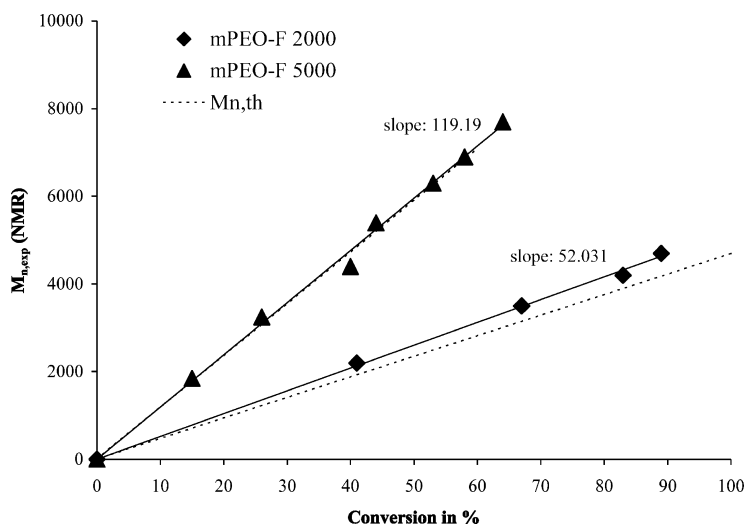


Fig. 2. Plot of $M_{n,exp}$ (NMR) of the polystyrene block against conversion (styrene/initiator/CuCl/bipy = 45/1/1/2 (mPEO-F 2000) and 114/1/1/2 (mPEO-F 5000), $T = 130\text{ }^{\circ}\text{C}$).

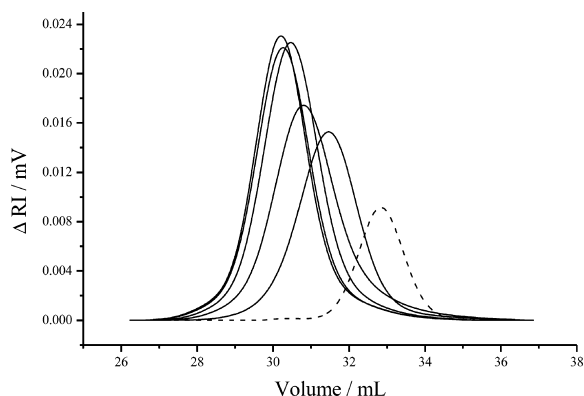


Fig. 3. GPC traces of the block copolymers obtained with mPEO-F 2000 (eluent: DMAc with 2.441 g LiCl l⁻¹, 80 °C).

polymerisation reactions were obtained under the described polymerisation conditions.

3.3.2. Polymerisation of styrene with mPEO-F 10,000

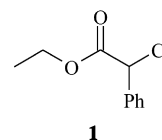
The polymerisation mixtures with mPEO-F 10,000 exhibit a higher viscosity than those with the lower molecular weight initiators mPEO-F 2000 and mPEO-F 5000. During the course of the reaction the polymerisation mixture became turbid indicating a change in the polymerisation conditions (Table 1).

As seen from the data in Table 1, the conversion of styrene in the polymerisation with mPEO-F 10,000 as initiator does not increase in a reproducible way with time: some disturbance seems to take place in the course of the polymerisation.

From the kinetic plot of those experiments which attained only small conversions within the respective

reaction times (Table 1, No. 6, 7, 10, 12, and 14), a value of $k_{app} = 0.17 \times 10^{-4} \text{ s}^{-1}$ in accordance with the concentration of initiating end groups was found. The conversions attained in the other experiments suggest a higher apparent rate of polymerisation and thus a higher concentration of radicals in the polymerisation mixture than expected.

In order to ensure that initiator mPEO-F 10,000 introduces the expected amount of initiating end groups into the feed, a control experiment was carried out: In analogy to the polymerisation of styrene with mPEO-F 10,000, a polymerisation with a low molecular weight model initiator **1** representing the end groups in the presence of the respective amount of unfunctionalised mPEO 10,000 was carried out. Considering the limits of experimental error, the obtained value of $k_{app} = 0.11 \times 10^{-4} \text{ s}^{-1}$ is in agreement with the value for the polymerisation of styrene with mPEO-F 10,000 found earlier; deficient initiator functionalisation or end group effects are thus excluded.



Although the conditions change during polymerisation with mPEO-F 10,000 as initiator the polymerisation still seems to be controlled as can be deduced from the characteristics of the polymerisation.

The molecular weight of the polystyrene blocks in the crude and the purified block copolymers increases linearly with conversion (Fig. 4). The initiation efficiency as determined by means of ¹H NMR spectroscopy from the

Table 1

Results of the polymerisation of styrene with mPEO-F 10,000 (styrene/initiator/CuCl/bipy = 227/1/1/2, $T = 130 \text{ °C}$)

No.	t/h	x_p^a (%)	$\bar{M}_{n,th}^b$	$\bar{M}_{n,exp}^c$	PDI ^c	$\bar{M}_{n,exp}^d$
1	0.5	5	1200	21,700 (20,900) ^e	1.09 (1.17) ^e	900 (1400) ^b
2	1	4	950	20,100	1.32	800
3	1	8	1900	22,000	1.09	1200
4	1	15	3500	22,600 (19,900) ^e	1.13 (1.23) ^e	2800 (3900) ^e
5	1.5	10	2700	21,800	1.08	1600 (1650) ^e
6	2	12	2800	21,900	1.11	2100
7	2.5	12	2800	23,800	1.08	2300
8	2.5	32	7600	24,100	1.29	7800
9	3	30	7100	24,000 (23,100) ^e	1.21 (1.20) ^e	6900 (8600) ^e
10	4	17	4000	23,100	1.12	3300
11	5	66	15,600	27,100 (28,600) ^e	1.35 (1.29) ^e	15,900 (22,600) ^e
12	6.5	31	7300	n.d.	n.d.	7000
13	8	81	19,100	32,000	1.31	19,500
14	10	49	11,600	25,000	1.28	11,700
15	12	89	21,000	33,100	1.33	21,600
16	16	89	21,000	32,700 (31,700) ^e	1.31 (1.26) ^e	21,700 (30,100) ^e

^a Determined by means of ¹H NMR spectroscopy.

^b $\bar{M}_{n,th} = [M]/[I]x_pM_{Monomer}$.

^c Determined by means of GPC (DMAc II mit 2.441 g LiCl l⁻¹, 80 °C, polystyrene standards).

^d Composition determined by means of ¹H NMR spectroscopy.

^e Block copolymers after extraction with aqua dest. and cyclohexane.

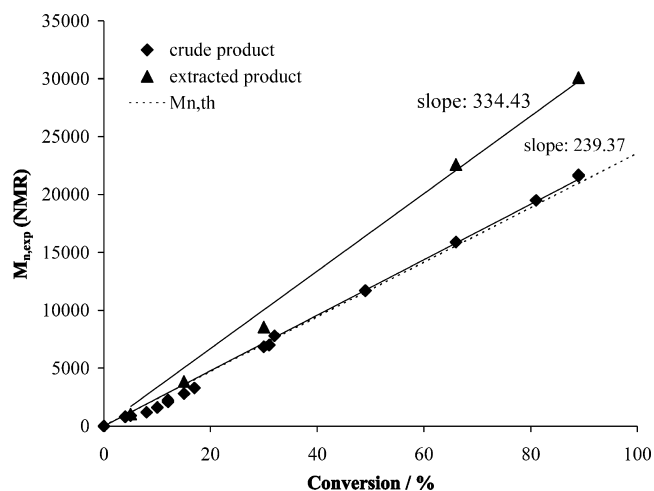


Fig. 4. Plot of $M_{n, \text{exp}}$ (NMR) of the polystyrene blocks of the crude product and the extracted block copolymer against conversion (styrene/initiator/CuCl/bipy = 227/1/1/2 (mPEO-F 10,000, $T = 130^\circ\text{C}$).

composition of the extracted block copolymers reaches ca. 80%. Considering a loss of initiator of about 6% due to combination reactions caused by the 'persistent radical effect' in the early stages of the polymerisation [11], the functionality of the mPEO-F 10,000 is supposed to be about 0.85.

The molecular weights of the block copolymers determined by means of GPC also reveal a linear dependence on conversion. The polydispersity indices of the obtained block copolymers have values of 1.1–1.2 at low conversions, at a conversion of ca. 30%, however, the polydispersity indices increase to values of 1.3. This might be correlated with the heterogeneity of the system observed at a conversion of about 30% suggesting a change in the polymerisation conditions. Because of the different physical and chemical properties of the PEO-moiety and the growing polystyrene block, phase separation during the course of the polymerisation occurs.

The copper(II) complex which is responsible for the transformation of the active species to the dormant species and which shows a higher solubility in the polar PEO-moiety might be withdrawn from the polymerisation taking place in the polystyrene/styrene phase. A deactivation reaction might then only take place at the interface of the two phases resulting in an increased concentration of radicals in the polystyrene/styrene phase and thus in an enhanced rate of polymerisation and in an increase of polydispersity indices of the obtained products.

In the polymerisation with mPEO-F 2000 and mPEO-F 5000, P_n of the two blocks is too small to cause phase separation. In order to verify this, mPEO-F 5000 was used as an initiator in the polymerisation of styrene with a corresponding predetermined P_n of 454.

The kinetic plot shows a linear dependence up to a conversion of ca. 15%. The value of $k_{\text{app}} = 0.08 \times 10^{-4} \text{ s}^{-1}$ is in accordance with the low concentration of initiating end

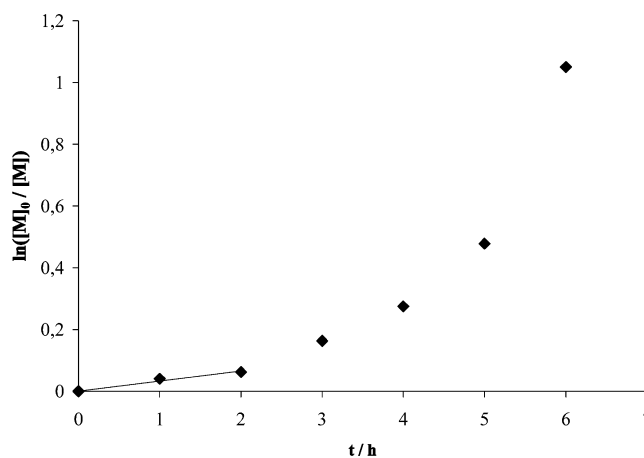


Fig. 5. First order plot of the polymerisation of styrene with mPEO-F 5000 (styrene/initiator/CuCl/bipy = 454/1/1/2 (mPEO-F 5000), $T = 130^\circ\text{C}$).

groups (Fig. 5). After 3 h of reaction time the rate of polymerisation and thus the concentration of radicals increases. As observed in the polymerisation with mPEO-F 10,000, the polydispersity indices of the obtained block copolymers increase abruptly when the polymerisation system becomes inhomogeneous (when the linear part of the first order kinetic plot is ended) (Fig. 6).

3.3.3. Polymerisation of styrene with mPEO-F 20,000

The polymerisation of styrene with mPEO-F 20,000 shows a linear kinetic plot again (Fig. 7). The value of $k_{\text{app}} = 0.56 \times 10^{-4} \text{ s}^{-1}$ is three times larger than that of the polymerisation with mPEO-F 10,000 although only half the amount of initiating end groups is present in the polymerisation mixture. Here again a phase separation occurs. The polydispersity indices of the obtained block copolymers already increase at a conversion as low as 5–10% up to values of 1.4–1.5 (Fig. 8).

It should be stressed that phase separation as a cause of the disturbances observed in the polymerisation of styrene with PEO macroinitiators is not proved yet, further investigations are necessary to entirely understand these results. However, many facts favour our interpretation of the kinetic results.

3.4. Surface morphology

Generally the structure and morphology of block copolymers at the surface, for example the interface to air or to the support, is different from the bulk morphology [12]. Examination of the surface morphology of poly(styrene)/poly(isoprene) block copolymers revealed exclusively poly(isoprene) at the surface to air while for poly(styrene)/poly(methyl methacrylate) block copolymers preferentially poly(styrene) is detected at the interface to air [13,14]. Responsible for this morphological arrangement is the surface energy of the respective domains and the interaction of the domains with the support (carrier) [15]. For poly(ethylene oxide)/poly(styrene) block copolymers it

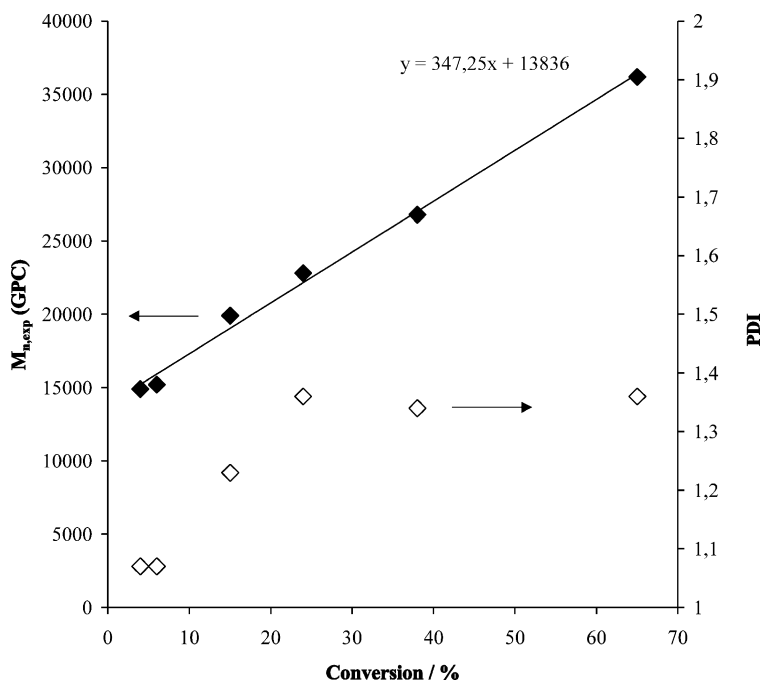


Fig. 6. Plot of $M_{n,exp}$ (GPC) and polydispersity indices of the block copolymers against conversion (styrene/initiator/CuCl/bipy = 454/1/1/2 (mPEO-F 5000), $T = 130$ °C).

was expected that the polystyrene domains are located at the interface to air, since poly(styrene) is apolar compared to poly(ethylene oxide).

Phase imaging is a method applied in atomic force microscopy (AFM) which is sensitive to the mechanical properties (mechanical resistance or impedance) of the surface. As a consequence, by phase imaging not only chemically different surfaces are detected but also crystalline and amorphous domains of the same material are distinguished [16]. The fact that PEO is a semicrystalline material should be observed in the surface morphology. In accordance with this expectation the phase image of a mPEO 10,000 sample (prepared according to variant 1) with a surface roughness of < 10 nm reveals a phase image with

50 nm broad lamellae. The topographical image shows these lamellae only schematically (Fig.9(a)). The conclusion of this phase image analysis is that crystalline and amorphous PEO can clearly be distinguished by AFM.

The bulk morphology of block copolymers are strongly dependent on the volume fraction of the components. If the space requirements of two blocks are equal lamellar structures are expected. As the volume fraction of one block decreases, gyroid, cylindrical and finally spherical shapes are expected.

The AFM images of surfaces of PEO/PS block copolymers were taken dependent on the volume fractions of the two components which were determined from the molar ratio of the building blocks determined by ^1H NMR

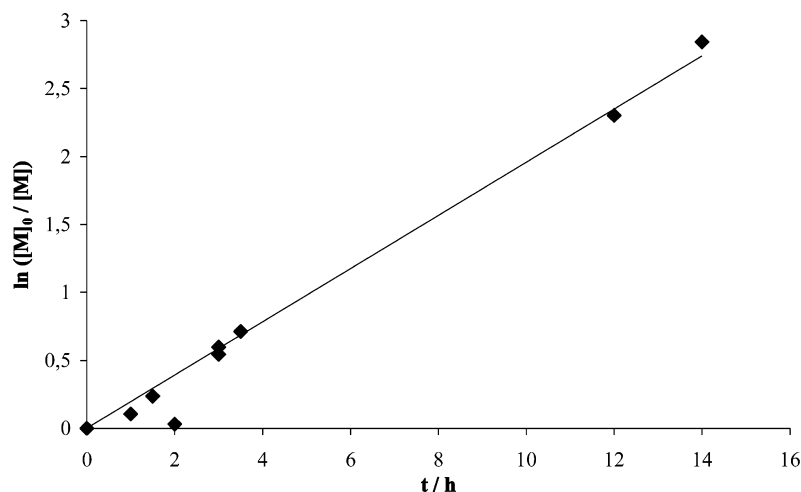


Fig. 7. First order plot of the polymerisation of styrene with mPEO-F 20,000 (styrene/initiator/CuCl/bipy = 454/1/1/2 (mPEO-F 20,000), $T = 130$ °C).

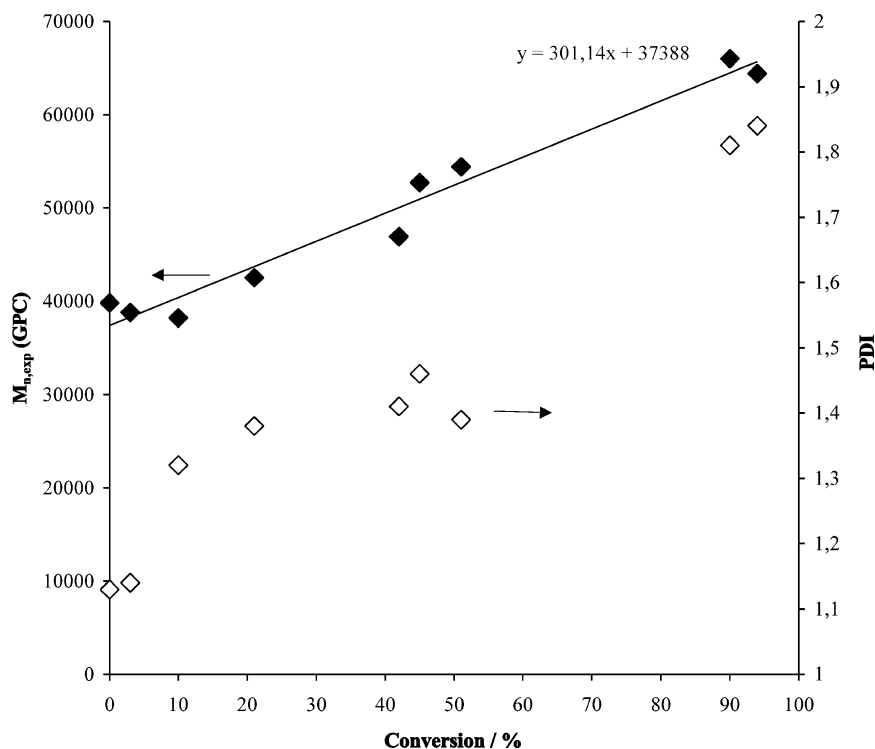


Fig. 8. Plot of $M_{n,exp}$ (GPC) and polydispersity indices of the block copolymers against conversion (styrene/initiator/CuCl/bipy = 454/1/1/2 (mPEO-F 20,000), $T = 130$ °C).

spectroscopy under consideration of the densities of partially crystalline PEO ($\rho_{PEO} = 1.13$ g/cm³) and amorphous PS ($\rho_{PS} = 1.05$ g/cm³). In the following the surface morphology of selected samples of PEO-*b*-PS will be presented and discussed.

For PEO-*b*-PS (prepared according to variant 1) with a volume fraction of PEO $X_{V(PEO)} = 0.90$ no PS was detected at the surface of the sample. The phase image of this copolymer is very similar to that of the earlier-mentioned PEO-homopolymer. This result is to some extent unexpected because the hydrophobic PS-blocks should be oriented towards the surface in contact with air. In the literature, however, there are reports which describe the adhesion of PEO both to hydrophobic and hydrophilic surfaces [17–21]. This phenomenon was explained by the amphiphilic character of the EO repeating units (hydrophobic ethylene groups and hydrophilic oxygen atoms). Obviously, either the hydrophobic ethylene groups or the hydrophilic oxygen atoms interact with surfaces of corresponding surface energy.

In the case of PEO-*b*-PS (prepared according to variant 2) with a volume fraction of PEO of $X_{V(PEO)} = 0.85$ the glass site of the polymer film was analysed and showed a characteristic pattern (the surface to air was not analysed because of the high roughness of this sample) (Fig. 9(b)). The topographic image shows irregularities which are due to defects in the sample preparation [16]. The phase image shows lamellae with ca. 30 nm. In addition spherical

domains of 20–30 nm diameter are observed which were assigned either to imperfections (defects) of the lamellar structure or to phase separated poly(styrene). The occurrence of phase-separated polystyrene on the hydrophilic glass is unexpected, but is explained by rapid evaporation of the solvent. As a consequence, equilibrium between phases was not attained. Not fully oriented domains were observed also in PS/PMMA block copolymers. On annealing, however, an orientation of the lamellae was achieved [14].

The surface morphology of a sample with a volume fraction of PEO of $X_{V(PEO)} = 0.52$ shows after annealing at high vacuum an irregular structure (Fig. 9(c)). The topographic image is not resolved and the phase image clearly shows bright domains of ca. 30 nm diameter which seem to broaden to form gyroid structures situated perpendicular to the surface. In thin films there is an energetically driven tendency to orient the lamellae perpendicular to the substrate and thus the surface. Such a behaviour has been reported for hydrogenated poly(butadiene)/PEO block copolymers [22].

The PEO/PS block copolymers with relative low PEO content $X_{V(PEO)} = 0.29$ are brittle materials. A film of this material was cast on a cellophane foil and carefully dried in high vacuum. The phase image of the surface to air shows cylindrical to spherical structures. Based on the copolymer composition these bright spheres or cylinders are placed in a dark PS matrix and are arranged perpendicular or parallel to the surface (Fig. 9(d)).

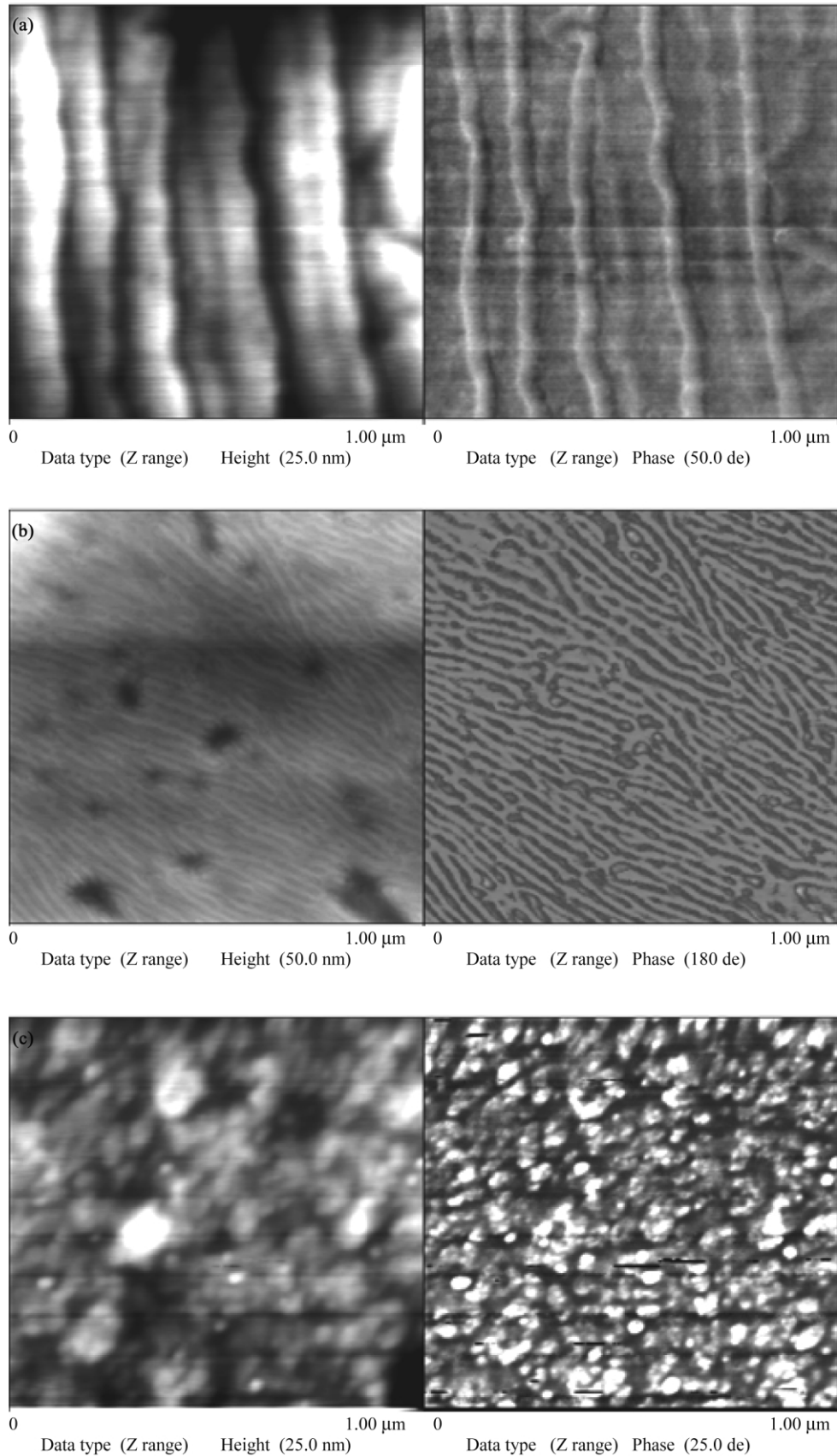


Fig. 9. Topographic (left) and phase images (right) of mPEO 10,000 and of mPEO 10,000/PS block copolymer samples (cf. Table 1): (A) mPEO 10,000 (preparation variant 1); (B) PEO-*b*-PS, Table 1, No. 5 ($X_{V(\text{PEO})} = 0.85$, preparation variant 2); (C) PEO-*b*-PS, Table 1, No. 9 ($X_{V(\text{PEO})} = 0.52$, preparation variant 3); (D) PEO-*b*-PS, Table 1, No. 5 ($X_{V(\text{PEO})} = 0.85$, preparation variant 4); (E) The sample (D) after 30 min on air.

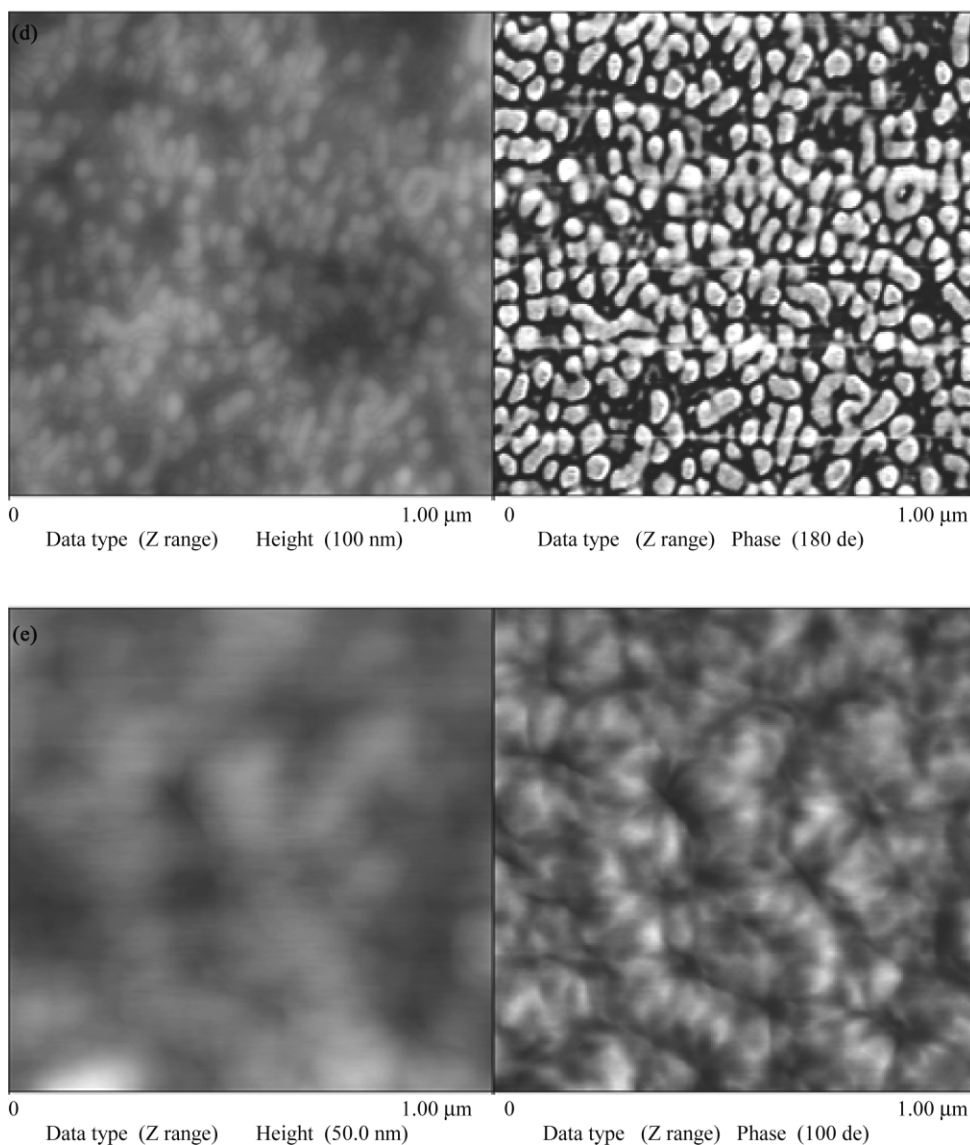


Fig. 9 (continued)

Acknowledgments

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