

Synthesis of Alternating Polystyrene/Poly(ethyleneoxide) Branched Polymacromonomers

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Abstract: Newly designed PS/PEO alternating branched polymacromonomers have been obtained by polycondensation of α -dicarboxy-functionalized polystyrene and α -dihydroxy-functionalized polyethyleneoxide. 4-[3,5-Bis(methoxycarbonyl)phenoxyethyl]benzyl bromide was used as atom-transfer radical polymerization (ATRP) initiator for the synthesis of α -dicarboxy functionalized polystyrenes. These macromonomers possess low polydispersities

and molecular weights in the range of 7000 to 100000, as proved by gel permeation chromatography (GPC) and ^1H NMR. α -Dihydroxy functionalized polyethyleneoxide (PEO) was synthesized by treatment of monofunctionalized PEO with 3,5-bis(benzyloxy)benzoyl chloride. Polycondensation of the

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α -dicarboxy PS with the α -dihydroxy PEO in solution or in bulk resulted in alternating PS/PEO polymacromonomers, which were effectively purified from the unreacted macromonomers and characterized by using ^1H NMR, GPC, thermal analysis, and optical microscopy. Light-scattering measurements in organic solvents like THF or dioxane have shown that these polymacromonomers form stable micelles.

Introduction

A particularly challenging aspect of polymer synthesis concerns the development of techniques for the preparation of macromolecular materials with well-defined structures. Polymacromonomers represent an important class of branched polymers with interesting molecular and bulk properties that are associated with the tethered branch chains around the backbone chain. A large number of studies have addressed the polymerization of end-functionalized homomacromonomers with a terminal group that yield mostly spherical or star-like architectures.^[1] In cases in which high degrees of polymerization are attained, the interaction between the side chains forces the polymacromonomer to gradually adopt a cylindrical shape.^[2–3] Various properly end-functionalized macromonomers have been polymerized and result in polymacromonomers with a vinylic backbone.^[3–8] In order to control the chain-length homogeneity in polymacromonomers, living anionic polymerization has mainly been

used for the macromonomer synthesis.^[9–11] Recent reports have shown that controlled radical polymerization techniques like atom transfer radical polymerization (ATRP), could be used for the polymer synthesis; they offer the advantage of being applicable to a wide range of monomers and result in polymers with low molecular-weight polydispersity and well-defined architecture.^[12] Additionally, controlled polymeric structures can be obtained by using proper macroinitiators.^[13–14]

Macromonomers composed from amphiphilic block copolymers have also been polymerized; this resulted in very interesting cylindrical structures.^[15] The amphiphilic nature of block copolymers composed of incompatible blocks has long been recognized and has become a popular research topic because of the ability of these polymers to aggregate into micelles in selective solvents^[16] and also due to their surface properties. These two features have been thoroughly investigated in miscellaneous applications.^[17]

Apart from the synthesis of linear amphiphilic structures, attempts have been made to design new amphiphilic branched PS/PEO copolymers.^[18] This interest emerges from the quite different behavior observed for these branched polymers from the linear homologues. The challenge however lies into controlling both the functionality and the degree of branching of these copolymers (meaning the compositional and topological homogeneity), which are critical factors for the better understanding of the influence of the topology on the properties of amphiphilic species.^[18–19] Recently, novel amphiphilic PS/PEO architectures^[20] have been reported, the

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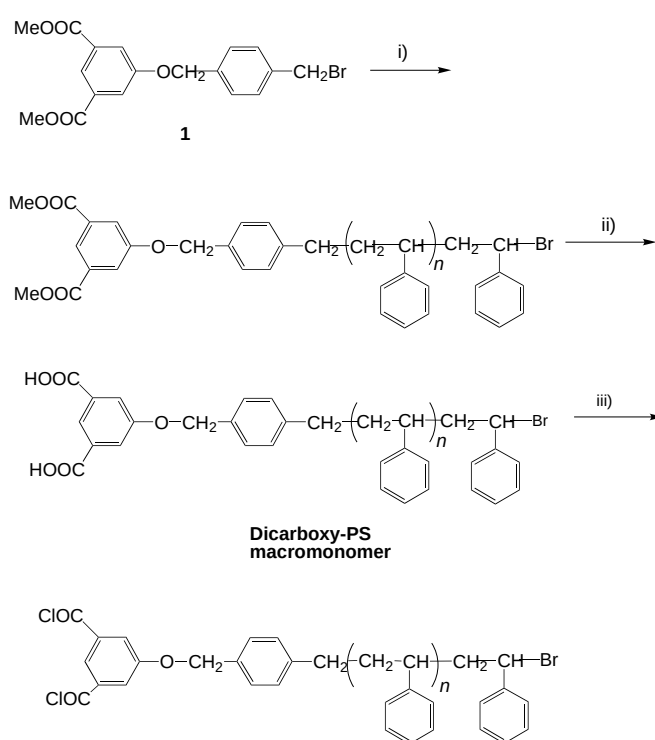
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study of which will hopefully help to elucidate the effect of topology on the self-organized properties of these polymers.

This paper deals with the synthesis and characterization of PS/PEO alternating branched polymacromonomers. In particular, these polymacromonomers are constituted of alternating PS and PEO branches of controlled length, attached as side moieties to an aromatic polyester backbone. This amphiphilic architecture was built by polycondensation of a newly synthesized dicarboxy end-functionalized PS with a dihydroxy end-functionalized PEO. The dicarboxy end-functionalized PS was synthesized by atom-transfer radical polymerization of styrene with 4-[3,5-bis(methoxycarbonyl)-phenoxy]methyl benzyl bromide (**1**) as initiator, while mono-hydroxy end-functionalized PEO was prepared by using hydroxy-terminated PEO. The resulting polymacromonomers were characterized by ^1H NMR, size exclusion chromatography, thermal analysis, static light scattering, and optical microscopy.

Results and Discussion

α -Dicarboxy end-functionalized PS macromonomers were prepared by using ATRP according to Scheme 1. The characterization data of dicarboxylic acid methyl ester macromonomers are summarized in Table 1. Gel permeation chromatography (GPC) measurements were used to determine the molecular weight of the synthesized macromonomers. A wide range of M_w was obtained, depending mainly on the catalytic system used, as shown in Table 1. Although bipyridine gave lower polydispersities, higher M_w macromonomers were obtained with PMDETA. N,N,N',N',N'' -pentamethyldiethylenetriamine^[21] or tris[2-(dimethylamino)ethyl]amine (Me_6TREN)^[22] as ligands. In the cases in which PMDETA and Me_6TREN were used, the polymerization was very fast but with a broad molecular-weight distribution. The molecular weights of macromonomers vary between 7000–100 000. More information about the molecular weight of the synthesized macromonomers can be derived from ^1H NMR. A representative ^1H NMR spectrum of an



Scheme 1. i) St, CuBr, Ph_2O , 110°C ; ii) 10N KOH, acetone, HCl, 37%; iii) SOCl_2 , reflux.

Table 1. Molecular Weight Characteristics of the synthesized PS macromonomers

Polymer	NMR results		GPC results		PDI
	M_n		M_n	M_w	
PS₁ ^[a]	8700		7700	9600	1.25
PS₂ ^[a]	7400		6100	8100	1.33
PS₃ ^[a]	6900		6700	9200	1.37
PS₄ ^[a]	10800		8700	11800	1.35
PS₅ ^[b]	53200		51500	65500	1.27
PS₆ ^[b]	106200		104700	155900	1.48
PS₇ ^[c]	49000		48000	75800	1.58

Catalytic system used: [a] CuBr, bipy. [b] CuBr, PMDETA. [c] CuBr, Me_6TREN .

α -dicarboxylic acid methyl ester PS macromonomer with the assignment of the peaks is depicted in Figure 1. The molecular weight calculations were based on either the methyl protons (H_a) at $\delta = 3.9$ of the ester before hydrolysis or the signal at $\delta = 5.1$ corresponding to methylene protons (H_d) in the α -position to the oxygen of the initiator and in the aromatic region between $\delta = 6.2$ –7.2 of polystyrene. The aromatic protons H_c , H_b with an integration ratio of 2:1 are located at $\delta = 7.8$ and 8.3, respectively. The calculated molecular weights in some cases are in excellent agreement with the results obtained by GPC, as shown in Table 1. Attempts to determine the absolute molar mass by MALDI-TOF analysis were unsuccessful.

The initiation efficiency in this system was further proved by the absence of the signals at $\delta = 4.4$ due to methylene protons at the active end of the initiator. As shown in Figure 1, the signals of the methylene protons H_d , H_e of the initiator are located at $\delta = 5.1$ and 4.4, respectively. The peaks at $\delta = 7.7$

Abstract in Greek:

Στην εργασία αυτή παρουσιάζεται η σύνθεση νέων εναλλασσόμενων διακλαδισμένων πολυμακρομοномерών. Τα πολυμακρομοномерή αυτά αποτελούνται από εναλλασσόμενες πλευρικές αλυσίδες πολυστυρολίου και πολυαιθυλενοξειδίου σε έναν αρωματικό πολυμερικό σκελετό. Τα α -δικαρβοξυ-μακρομοномерή του πολυστυρολίου συντέθηκαν με ελεγχόμενο πολυμερισμό ελευθέρων ριζών, χρησιμοποιώντας κατάλληλο εκκινητή που φέρει τις δραστικές ομάδες. Με τη μέθοδο αυτή έγινε δυνατή η σύνθεση μακρομοномерών που παρουσιάζουν χαμηλή διασπορά μοριακών βαρών και μοριακά βάρη στην περιοχή των 7000–100 000. Συντέθηκαν επίσης α -διυδροξυ τροποποιημένα πολυαιθυλενοξείδια με τη χρήση του μονουδροξυ-πολυαιθυλενοξειδίου. Με αντίδραση πολυεστεροποίησης των α -διυδροξυ-πολυαιθυλενοξειδίων και α -δικαρβοξυ-πολυστυρολίων συντέθηκαν τα προσχεδιασμένα πολυμακρομοномерή, τα οποία χαρακτηρίστηκαν με τεχνικές όπως NMR, χρωματογραφία αποκλεισμού μεγεθών, θερμική ανάλυση και οπτική μικροσκοπία. Διαλύματα των πολυμακρομοномерών αυτών παρουσιάζουν λυοτροπική συμπεριφορά, ενώ η μελέτη αραιών διαλυμάτων με στατική σκέδαση φωτός έδειξε την δημιουργία σταθερών μικκυλίων.

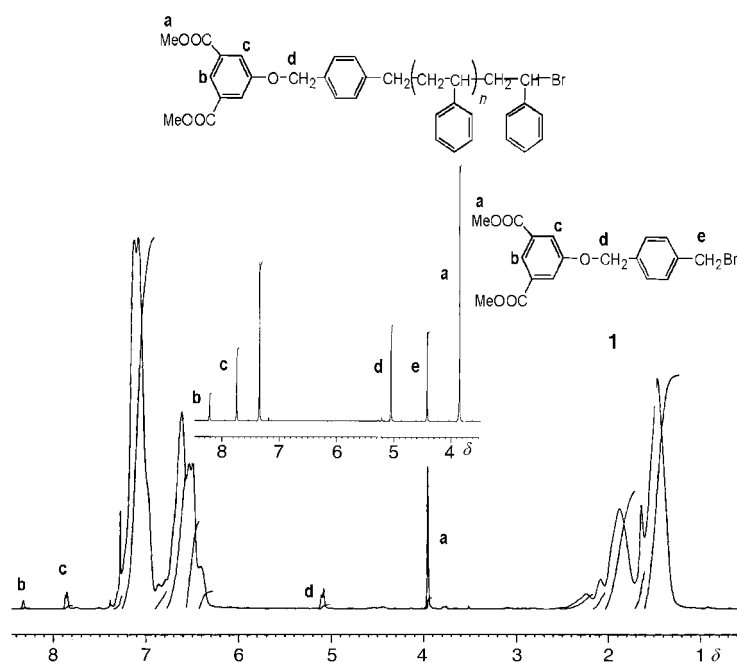


Figure 1. ^1H NMR spectra of the initiator (**1**) and the α -dicarboxylic acid methyl ester PS macromonomer (**PS₃**) with the assignment of the peaks.

and 8.2 correspond to the aromatic protons H_c and H_b with an integration ratio of 2:1. Comparison of the NMR spectra of the initiator and the macromonomer shows that effective initiation was successful, since the methylene protons (H_e) on the active site of the initiator disappeared after polymerization, while all other protons mentioned above are present in the correct integration rate. Hydrolysis of the α -dicarboxylic acid methyl ester PS macromonomer with KOH (10N) resulted in α -dicarboxylic acid PS macromonomer. The ^1H NMR spectrum of this macromonomer is shown in Figure 2; here the methyl protons H_a of the carboxy methyl groups observed at $\delta = 3.95$ disappeared after hydrolysis.

The preparation of the PEO macromonomer was performed by reaction of the monohydroxy terminated PEO as shown in Scheme 2. In Figure 3 the ^1H NMR spectrum of the

of integrated peak intensities in the area around $\delta = 3.6\text{--}3.4$ that were attributed to the methylene protons of the ethylene oxide backbone and at $\delta = 5.15$ corresponding to the CH_2 protons of the benzyl groups. The integral ratio obtained is very close to the theoretical value related to the number of repeated units of PEO 2000, $n = 45.4$.

Dihydroxy end-functionalized PEO was prepared by deprotection of the hydroxyl groups by catalytic hydrogenation. The effective removal of the benzyl groups of the PEO-macromonomer was proved by the disappearance of the signal due to the $-\text{CH}_2-$ protons of the benzyl groups of the dendritic initiator at $\delta = 5.1$ in the NMR spectrum.

Polycondensation of the α -dicarbonyl chloride PS macromonomer obtained after its treatment with thionyl chloride and the α -dihydroxy PEO macromonomer yields PS/PEO polymacromonomers as shown in Scheme 3. Polymerization experiments were performed under various experimental conditions. As reported previously,^[1a, 1b] the degree of polymerization of the polymacromonomers is controlled by both the concentration and the molecular weight of the macromonomers (slow diffusion-controlled effect). In addition, in our case, the phase separation of the two macromonomers is expected to raise more difficulties in the reaction between the α -dicarbonyl chloride and the

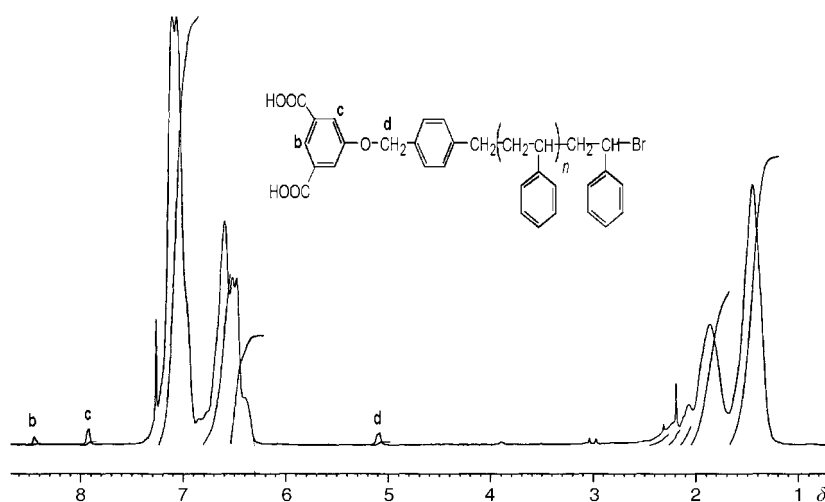
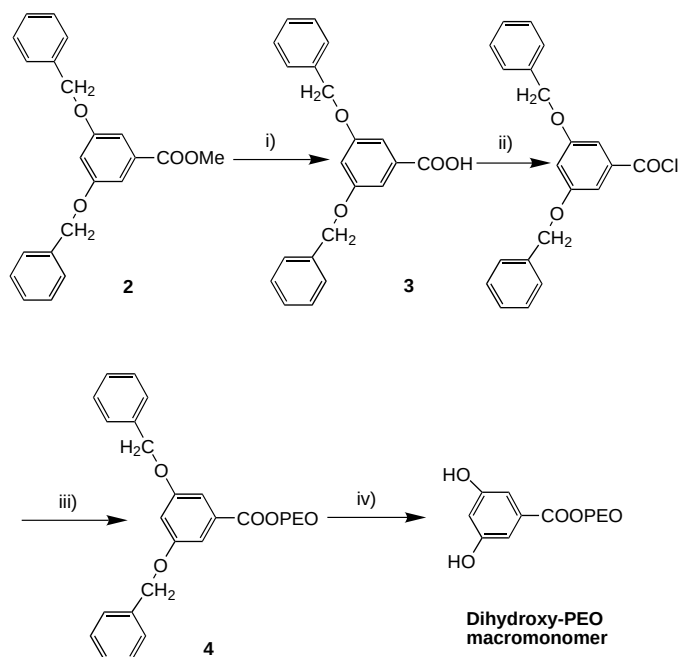


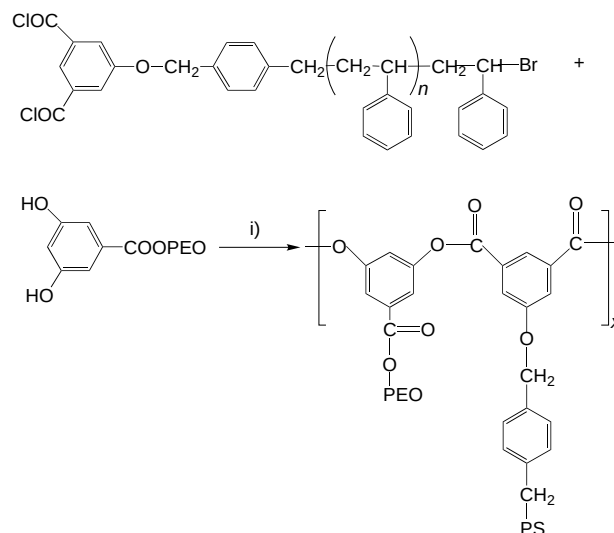
Figure 2. ^1H NMR spectrum of α -dicarboxylic acid PS macromonomer (**PS₃**) with the assignment of the peaks.



Scheme 2. EtOH 95%, KOH 10N, HCl 37%; ii) SOCl_2 , reflux; iii) PEO-OH, CH_2Cl_2 , Et_3N ; iv) H_2 , MeOH, Pd/C.

α -dihydroxy macromonomers. For these reasons, polymerizations were performed either in concentrated solutions or in bulk at high temperatures. The results for the different conditions are depicted in Table 2.

Purification of the polymacromonomers from the unreacted macromonomers was carried out by selective dissolution of the respective macromonomers. The polymerization products were extracted with MeOH for one day in order to remove possible unreacted PEO. The residues (after being dried in



Scheme 3. i) CH_2Cl_2 , Et_3N .

vacuo) were purified by extraction with diethyl ether, three or four times for six days. This purification procedure was repeated several times until the sharp peak in GPC corresponding to the unreacted PS macromonomer disappeared. The purified products were dried in vacuo at room temperature. Representative examples are given in Figure 4. Here the products after the removal of the unreacted PEO-macromonomer contain a significant amount of the PS-macromonomer, which was effectively removed after repeated extraction with diethyl ether.

A representative ^1H NMR spectrum of the corresponding PS/PEO polymacromonomer ((PS-PEO)-PM2) is depicted in Figure 5. The copolymer compositions, as well as the ratio of the molecular weights of PS/PEO, were in good agreement with the calculated ones, since the PEO molecular weight is accurately known.

The PS/PEO amphiphilic polymacromonomers obtained have number-average molar masses between 30 000 and 75 000 as determined by GPC and based on calibration with PS standards. As has been demonstrated,^[24] GPC calibrated with linear standards severely underestimates the molecular weight of a branched polymer, especially at high molecular weights. All successful experiments were made by using PS macromonomers with M_n in the range 5000–9000. PS macromonomers with $M_n = 50\,000$ were used several times for polymerization without success.

Direct determination of the molecular weight of PS/PEO polymacromonomers in THF and dioxane was attempted by using static light scattering. Different solvents were used in order to examine the influence of the

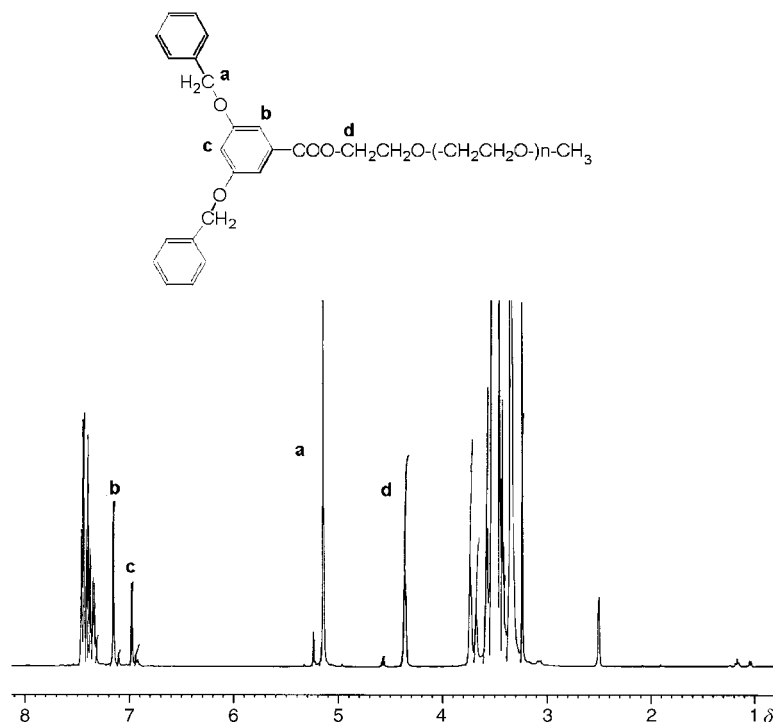
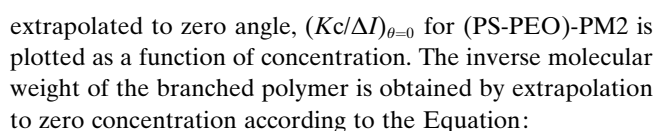


Figure 3. ^1H NMR spectrum of α -dibenzoyloxy PEO macromonomer with the assignment of the peaks.

Polymer	M_n	M_w	PS/PEO	Temperature [°C]	Time [h]
PS₃ ^[a]	6 700	9 200	–	–	–
(PS-PEO)-PM1 ^[b,c]	50 000	143 000	0.9944	90	144
(PS-PEO)-PM2 ^[d]	30 000	86 000	1	180	3
(PS-PEO)-PM3 ^[d]	37 000	136 000	0.9994	180	3
(PS-PEO)-PM4 ^[d]	18 500	75 000	0.9964	180	22
(PS-PEO)-PM5 ^[b,c]	61 000	168 000	1	90	96
(PS-PEO)-PM6 ^[d]	75 000	285 000	1	180–200	2.5

The ^1H NMR spectrum shows peaks at $\delta \approx 7.2$ (aromatic H, PEO), $\delta \approx 6.8$ (aromatic H, PEO), $\delta \approx 6.5$ (aromatic H, PEO), $\delta \approx 6.2$ (aromatic H, PEO), $\delta \approx 5.8$ (aromatic H, PEO), $\delta \approx 5.5$ (aromatic H, PEO), $\delta \approx 5.2$ (aromatic H, PEO), $\delta \approx 4.8$ (aromatic H, PEO), $\delta \approx 4.5$ (aromatic H, PEO), $\delta \approx 4.2$ (aromatic H, PEO), $\delta \approx 3.8$ (aromatic H, PEO), $\delta \approx 3.5$ (aromatic H, PEO), $\delta \approx 3.2$ (aromatic H, PEO), $\delta \approx 2.8$ (aromatic H, PEO), $\delta \approx 2.5$ (aromatic H, PEO), $\delta \approx 2.2$ (aromatic H, PEO), $\delta \approx 1.8$ (aromatic H, PEO), $\delta \approx 1.5$ (aromatic H, PEO), $\delta \approx 1.2$ (aromatic H, PEO), $\delta \approx 0.8$ (aromatic H, PEO), $\delta \approx 0.5$ (aromatic H, PEO), $\delta \approx 0.2$ (aromatic H, PEO).

solvent quality on the PS and the PEO units. THF was first used as a good solvent for both PS and PEO units of the polymacromonomer in the concentration range $2 \times 10^{-5} \leq c \leq 2 \times 10^{-3} \text{ g mL}^{-1}$. In Figure 6, the inverse scattering intensity



in which M_w is the apparent molecular weight of the scattering particles, K is the optical constant, ΔI the difference between the scattering intensity of the solution and that of the pure solvent, P_θ the particle scattering function, A_2 the second virial coefficient, and c the polymer concentration. At high concentrations the plot is linear and the presence of micelles is

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critical micellization concentrations lie in lower concentrations that cannot be studied by using this technique.

Measurements of the intrinsic viscosity $[\eta]$ in THF resulted in very small values, about 0.1 dL g^{-1} ; this indicated that these polymacromonomers have very compact dimensions in solution.^[25] It should be noted that the viscosity values expected for linear polystyrene with the same molecular weight is much higher.

Optical examinations under cross polars of a 2.2% solution of (PS-PEO)-PM2 in dichloroethane are shown in Figure 7. Despite the relatively low M_w of this sample ($M_w = 86\,000$) relative to other polymacromonomers, lyotropic behavior was observed; this showed that the immiscibility of the two block probably enables the formation of a mesomorphic phase. Lyotropic behavior has previously been observed for polystyrene polymacromonomers^[26–27] with significantly higher molecular weights.

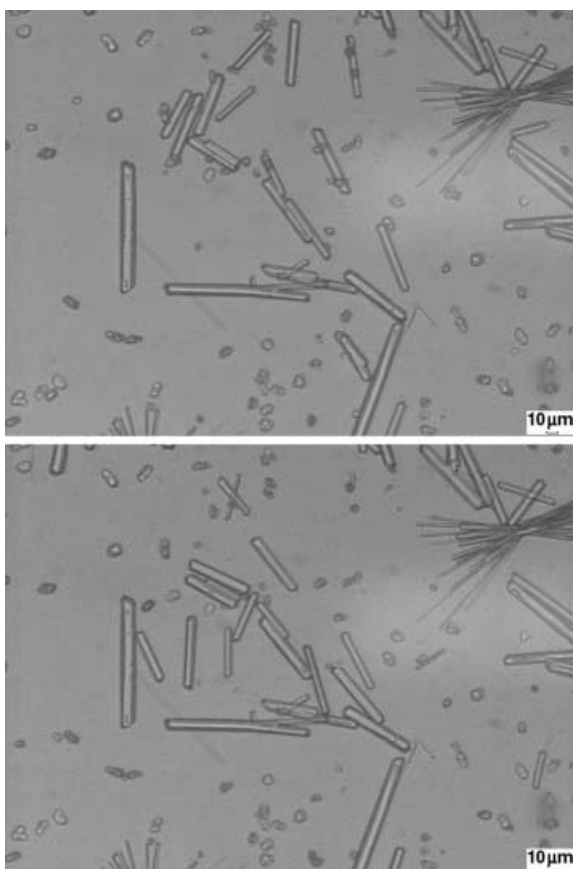


Figure 7. Two subsequent polarization micrographs of 2.2% dichloroethane solution of (PS-PEO)-PM2 polymacromonomer.

Samples cast from the same solution were examined by using differential scanning calorimetry (DSC) and the results for the first heating, the cooling, and the second heating scans are presented in Figure 8. In the first heating scan two endotherms are observed. The first one at 47°C is attributed to the PEO melting; the second at 140°C compares well with a transition observed for other polymacromonomers,^[27] although in our case polymacromonomers with completely different main-chain structure have been synthesized. α -Dicarboxylic acid PS macromonomer shows a T_g at 95°C in

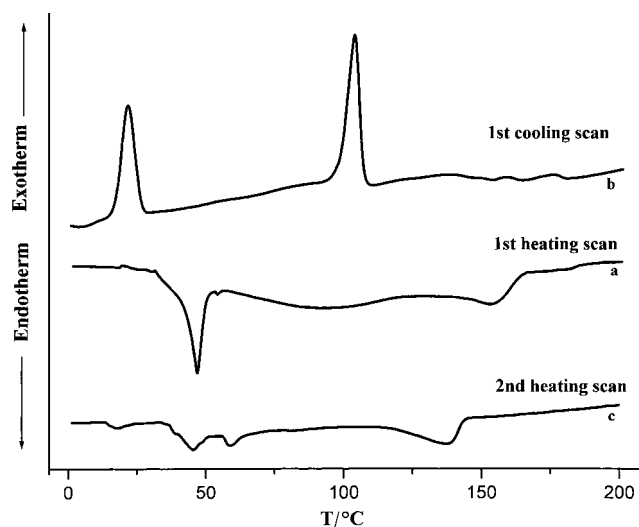


Figure 8. DSC thermograms of the solution cast (PS-PEO)-PM2 polymacromonomer.

the first heating scan. During the cooling scan for the polymacromonomer, two well-resolved exotherms were obtained, and this behavior was observed for the subsequent cooling scans. The second heating scan showed a weak double endotherm in the range in which the PEO crystallizes, while the higher temperature endotherm shifts to lower temperatures.

Conclusion

The combination of ATRP for the synthesis of PS macromonomer with polyesterification for the main chain structure was exploited to engineer alternating branched PS/PEO polymacromonomers. New α -dicarboxy-functionalized PS macromonomers have been synthesized by using the ATRP technique. Polycondensation of these macromonomers with PEO macromonomer, suitably end functionalized with two hydroxy groups, resulted in novel amphiphilic PS/PEO polymacromonomers. These polymacromonomers have been characterized by means of GPC, ^1H NMR spectroscopy, light scattering, DSC, and optical microscopy. The formation of lyotropic liquid crystals was detected by polarized-light microscopy. These amphiphilic species have a tendency to form stable micelles in THF or dioxane, as revealed by light scattering measurements.

Experimental Section

Materials: Triethylamine was heated under reflux with *p*-toluenesulfonyl chloride and distilled twice before use. Dichloroethane (DCE) was treated with P_2O_5 and distilled twice. PEG-2000 (Aldrich) was treated with toluene to remove water by azeotropic distillation and dried under vacuum. Styrene was treated over CaH_2 and vacuum distilled before polymerization. Me₆TREN was easily prepared in a one-step synthesis from commercially available tris-(2-aminoethyl)amine by following the literature procedure.^[28] 4-[3,5-Bis(methoxycarbonyl)phenoxy]methylbenzyl bromide (**1**)^[29] and 3,5-bis(benzyloxy)benzoic acid methyl ester (**2**)^[30] were synthesized according to known procedures. Hydrolysis of (**2**) in ethanol resulted in (**3**). All other reagents were obtained from Aldrich and used without further purification.

Synthesis of dicarboxy end-functionalized polystyrene by using ATRP: A round-bottom flask equipped with a U-tube, a rubber septum, a magnetic stirrer, and a gas inlet/outlet was flamed under vacuum. 4-[3,5-Bis(methoxycarbonyl)phenoxyethyl]benzyl bromide (**1**) (0.1964 g, 0.5 mmol) was added to the flask containing CuBr (0.0717 g, 0.5 mmol) and bipyridine (0.234 g, 1.5 mmol). The system was degassed four times and flushed with argon. Equal volumes of the solvent and the monomer were transferred to the flask through a syringe. The reaction mixture was then immersed in an oil bath and heated at 110 °C for 24 h. After cooling to room temperature, THF (5–10 mL) was added to the reaction mixture to dissolve the polymer, then the solution was filtered in order to remove the catalyst and precipitated in a large excess of methanol. The obtained polymers were dried under vacuum at room temperature. These polymers were hydrolyzed with KOH 10N in acetone and acidified with HCl (37 %) in order to obtain the dicarboxy end-functionalized PS. The polymers were characterized by ¹H NMR and GPC; the results are given in Table 1.

Synthesis of dihydroxy end-functionalized PEO: Compound **3** (1.69 g, 5.06 mmol) was dissolved in thionyl chloride (30 mL) and heated under reflux at 85 °C under argon for 20 h. The solution was evaporated and dried under vacuum in order to remove any traces of thionyl chloride. PEG-OH-2000 (7.5 g, 3.75 mmol) was added to the same flask under argon, followed by introduction of Et₃N (0.52 mL, 3.75 mmol) and distilled dichloroethane (40 mL). The mixture was heated under reflux under argon for 22 h. It was filtered to remove the triethyl ammonium chloride, treated with MeOH (15 mL), and concentrated under reduced pressure. The obtained liquid was dissolved in toluene (25 mL), filtered, and precipitated in hexane (250 mL). The purified product **4** was dried under vacuum at room temperature. Hydrogenation of **4** in methanol solution with Pd on activated carbon gave the desired dihydroxy end-functionalized PEO. In Figure 2 shows the ¹H NMR spectrum of the PEO-macromonomer. The same procedure was adopted for the preparation of the PEO-5000 macromonomer.

Polymerization of dicarboxy-functionalized PS with dihydroxy-functionalized PEO-2000: The PS-PEO polymacromonomers were synthesized by either melt or solution polymerization. In a typical solution polymerization, a round bottom flask with dicarbonyl chloride PS (0.163 g, 0.0243 mmol) under argon was charged with dihydroxy PEO (52.6 mg, 0.0244 mmol) and distilled DCE (0.2 mL). The mixture was stirred for about 1 h, and then one drop of distilled Et₃N was added. The extremely viscous solution was refluxed at 85 °C for 5 days. In the case of melt polymerization, the mixture of macromonomers was heated at 180 °C for 2 h under argon.

Measurements: (DSC) thermograms were obtained by using an SP plus calorimeter equipped with the autocool accessory from Rheometrics Scientific Ltd. The heating rate was 20 °C min⁻¹ and the thermograms covered the range from –50 °C to 200 °C. ¹H NMR spectra were recorded with a Bruker Avance DPX 400 MHz spectrometer, by using CDCl₃ and [D₆]DMSO as solvents.

The number-average M_n and weight-average M_w molecular weights of the polymers were determined by using gel permeation chromatography apparatus (Polymer Lab, Series II Marathon) equipped with a Fama 500 UV/Vis detector and with two Ultrastaygel columns (10⁴ and 500 Å pore size). Measurements were performed in THF, and calibration was based on polystyrene standards.

Light scattering experiments were carried out by using a thermally regulated (±0.1 °C) spectrogoniometer model SEM RD (Sematech, France) equipped with a He–Ne laser (633 nm). Prior to measurements the polymer solutions were made free from foreign particles by filtration and centrifugation with 0.5 µm filters. The refractive index increment dn/dc required for the light scattering measurements, was obtained by means of a Chromatic KMX-16 differential refractometer operating at 633 nm. The refractive index of PS/PEO polymacromonomer in 1,4-dioxane was found to be 0.1111.

Acknowledgements

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