An improved technique of the cumylpotassium preparation: application in the synthesis of spectroscopically pure polystyrene–poly(ethylene oxide) diblock copolymers

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A series of AB-type diblock copolymers composed of polystyrene (PS) as the A block and poly(ethylene oxide) (PEO) as the B block was synthesized by sequential anionic polymerization. The prepared copolymers had fixed molecular weights for the PS blocks and varying lengths for the PEO chains. Problems connected with the preparation of the initiator, cumylpotassium, were analysed and a new synthetic approach for its preparation proposed. Our synthetic procedure enables spectroscopically pure PS–PEO diblock copolymers free of high molecular weight impurities to be prepared.

(Keywords: cumylpotassium; PS–PEO diblock copolymers)

Introduction

Block copolymers consisting of two types of incompatible polymer blocks have a variety of industrial and research applications[1,2]. Among the many known copolymers, the polystyrene–poly(ethylene oxide) (PS–PEO) block copolymers have a special place. Because of the hydrophilic nature of the PEO blocks, PS–PEO copolymers containing >50% PEO are soluble in water. In aqueous media the copolymers associate to form colloidally stable aggregates or micelles. The colloidal behaviour of PS–PEO copolymers has been investigated by many authors[3–11]. In general, one of the most important features of micelle behaviour in aqueous solutions arises from their ability to solubilize hydrophobic molecules. Many experiments[3,4] have been carried out in order to determine the onset of PS–PEO micellization (the critical micelle concentration, *CMC*). Recently[8,9] we have found a convenient method for the determination of the *CMC* for PS–PEO block copolymers using pyrene as a fluorescent probe. We have studied about 10 copolymer samples with different PEO contents. Unfortunately all the copolymers had different lengths of the PS part as well. It would be interesting to examine copolymers having fixed molecular weights for one block. We therefore decided to prepare a set of copolymer samples having the same molecular weight for the PS blocks. We intend to study the *CMC* of these samples as a function of the PEO content.

Several preparation routes have been used to synthesize PS–PEO diblock copolymers. Khan *et al.*[6] used hydroxy-terminated PS which was reactivated with potassium methoxide and formed an anion which was used for the subsequent polymerization of ethylene oxide. After polymerization, the copolymers had to be carefully purified in order to remove the homopolymers. Another route leading to PS–PEO diblock copolymers via the coupling of two preformed homopolymers gives only low yields while introducing another moiety at the junction between the two blocks[12].

Sequential anionic polymerization, e.g. the polymerization of ethylene oxide initiated by the PS anion, is probably the most commonly used method. It requires the presence of a strongly solvated counterion. Only the potassium cation associated with the propagating chain makes the polymerization of ethylene oxide in solvents of moderate polarity (such as tetrahydrofuran, THF) feasible. The use of sodium requires high pressures and longer polymerization times[12]. Lithium can start the initiation of ethylene oxide in THF but the propagation process does not occur[13,14].

The usual techniques for anionic preparation of the PS–PEO block copolymers use diphenylmethyl potassium or cumylpotassium (α,α′-dimethyl benzyl potassium) as the initiators[12,13,15–18]. The preparation of diphenylmethyl potassium from diphenylmethane and naphthyl potassium is not difficult. However, one cannot avoid the production of difunctional by-products and the resulting copolymers show higher polydispersity[12]. The use of cumylpotassium leads to particular problems. The prepared copolymers often contain high molecular impurities (triblock PEO–PS–PEO copolymers) and are not spectroscopically pure[19]. We improved the currently used technique of cumylpotassium preparation in order to minimize the impurities in the copolymer samples.

Experimental

Materials. Styrene (Aldrich) was washed with aqueous NaOH to remove inhibitors, followed by water, then dried with $CaCl_2$ and distilled under reduced pressure. The distillate was stirred overnight with a piece of sodium and distilled in a vacuum line just before use.

α-Methylstyrene (Aldrich) was washed with aqueous NaOH, followed by water, dried with $CaCl_2$ and distilled. The distillate was used immediately for the preparation of cumyl methyl ether.

Ethylene oxide (Fluka) was distilled from CaH_2.

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Predried and distilled THF (SDS) was distilled from the violet solution containing anhydrous benzophenone and sodium.

Cumyl methyl ether was prepared according to Ziegler *et al.*[20] by the reaction of α-methylstyrene with methanol in the presence of $HClO_4$. The crude ether was fractionally distilled. The purity of the ether found by gas chromatography was 98%. The product was used immediately to prepare the initiator; upon standing the ether decomposes slowly back to α-methylstyrene and methanol. It is worth mentioning the importance of the purity of the starting cumyl methyl ether. Reaction of the main impurity in the cumyl methyl ether (α-methylstyrene) with potassium yields dianions which, upon the addition of styrene and ethylene oxide, can produce triblock copolymers (PEO–PS–PEO).

Initiator. The usual high vacuum technique was used during the initiator preparation as well as the polymerization. Pieces of potassium and sodium (13.7 and 9.1 g, respectively, 60% w/w potassium) were melted and filtered through a coarse fritted disc into the flask. THF (250 ml) was then cryodistilled into the flask followed by the addition of freshly prepared cumyl methyl ether (18.8 g). The solution turned red almost immediately upon the addition of the first drops of cumyl methyl ether. The reaction was completed overnight. The solution was then slowly filtered through a fritted glass filter (porosity 2) in order to remove potassium methoxide and unreacted solid K–Na alloy. The concentration of cumylpotassium was determined by the addition of a known volume of initiator solution to distilled water, followed by titration with 0.01 N HCl to the phenolphthalein end point. Although it was argued[20] that this direct method is not sufficiently precise because of the colloidal character of the titrated solution our results were quite satisfactory. The concentration of the initiator was found to be 0.41 M which gave a yield of >85% with respect to cumyl methyl ether.

Polymerization. A few millilitres of the initiator solution were added to the flask containing THF (1000 ml) at −78°C until a slightly pink colour persisted (to eliminate the impurities) and the calculated volume of the initiator solution was added. Then styrene (55 g) was added dropwise over a period of 15 min. After another 45 min, the stock solution of the PS anion was divided, under a strong stream of high quality nitrogen (Air Liquide, N45), into several flasks via a syringe. Calculated amounts of ethylene oxide were then cryodistilled into each of the flasks, and the solutions were allowed to come gradually to room temperature and left under stirring for a further 2 days. The solutions containing the highest amounts of ethylene oxide (samples 4 and 5) were kept slightly above room temperature in order to keep the polymerization mixtures liquid. The resulting solutions were concentrated *in vacuo* and the copolymers precipitated in large volumes of distilled and dried diethyl ether.

Characterization of copolymers. The g.p.c. analyses were performed on a GPC 150C chromatograph (Millipore-Waters) equipped with three HIBAR Lichrogel columns (Merck): PS 400 (10 μm), PS 40 (10 μm) and PS 4 (10 μm).

Table 1 Characteristics of the prepared PS–PEO block copolymers[a]

Sample	M_{total}	M_{PEO}	PEO (w/w%)	Polydispersity[b]
1	7950	3950	50	1.21
2	10 500	6500	62	1.15
3	15 000	11 000	73	1.20
4	23 600	19 600	83	1.17
5	34 800	30 800	89	1.25

[a] $M_{PS} = 4000$ g mol^{-1}

[b] Calculation of the polydispersity (M_w/M_n) is based on the evaluation of g.p.c. chromatograms using PS standards

The composition of the copolymers was determined by ^{1}H n.m.r. (200 MHz) using $CDCl_3$ as solvent. The PEO content was calculated from the ratio of the intensities of the CH_2CH_2 signal (at 3.6 ppm) and of the aromatic signal (at 6.4–7.2 ppm).

The sample of living PS which was removed before the addition of ethylene oxide was precipitated in methanol. The molecular weight of the PS block was found to be 4000 g mol^{-1}. This corresponds almost exactly to the theoretical value which was calculated from the amount of initiator added. The characteristics of the prepared copolymers are given in *Table 1*. (The values of polydispersity have not been corrected with respect to the zone spreading.)

Results and discussion

In our laboratory, the standard procedure of cumylpotassium preparation consists of the reaction of cumyl methyl ether with potassium in boiling heptane[15]. At this temperature potassium is liquid and in the form of small droplets. The large available surface of potassium enables the reaction to be completed within 24 h. The heptane is then replaced by THF and the solution can be directly used to initiate the polymerization of styrene. This method, however, has a serious drawback. Relatively rough reaction conditions are favourable for radical reactions. Some radicals seem to be able to promote the fusion of two or more aromatic rings to form a fluorescent species. Copolymers prepared in this manner possess unwanted luminescent properties. We have dealt with this problem more thoroughly in a recent paper[19].

Another possibility for the preparation of cumylpotassium employs the use of K–Na alloy. In his pioneering work, Ziegler[21] used the ratio of 5:1 K–Na to prepare the alloy. The initiator was prepared from cumyl methyl ether and the alloy directly in THF at room temperature. The solution is filtered to remove insoluble potassium methoxide and used to initiate the polymerization. The resulting copolymers are spectroscopically clean. The basic problem which is encountered here is the presence of the K–Na alloy in the cumylpotassium solution – tiny droplets of liquid alloy are able to pass through the filter and their presence in the polymerization mixture causes the dimerization of styrene monomer. Prepared copolymers therefore contain a significant amount of impurities of about double the molecular weight, probably PEO–PS–PEO type copolymer (*Figure 1a*). In order to avoid this problem we looked more closely at the composition of the alloy. From the K–Na phase diagram we can see that the composition of the alloy can be adjusted over a wide range[22,23]. At room temperature, the alloy is liquid

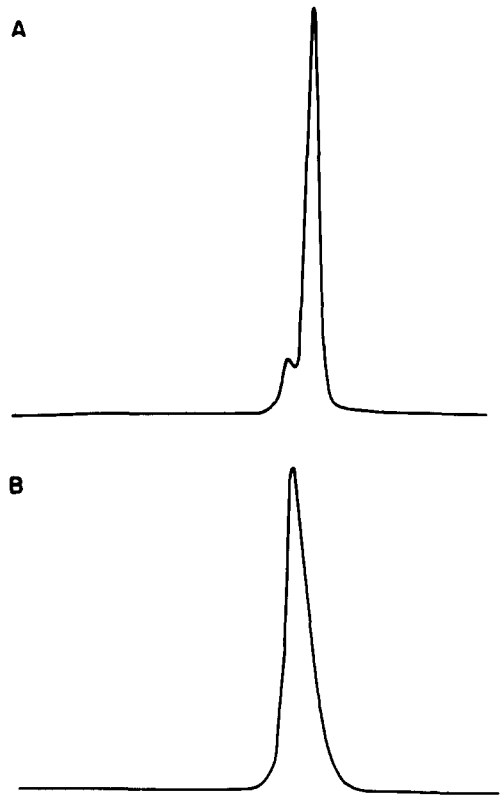

Figure 1 G.p.c. curves of the PS–PEO diblock copolymer. The initiator was prepared according to (A) Ziegler's procedure and (B) the modified procedure, see text

when it contains ~29–83% w/w potassium. We can thus prepare a liquid alloy of a suitable composition. During the reaction with cumyl methyl ether the potassium is gradually consumed to form cumylpotassium and potassium methoxide. When the potassium content in the alloy drops to <29% w/w the alloy becomes solid.

The idea of adjusting the K–Na alloy composition is novel to this work. In our approach we used an alloy containing initially 60% w/w potassium metal. After the reaction with cumyl methyl ether the remaining alloy (containing <29% w/w potassium) was solid and together with potassium methoxide was easily filtered. The copolymer samples did not contain any high molecular weight impurities (*Figure 1b*).

Conclusions

The modified technique of the initiator preparation allowed PS–PEO diblock copolymers with low polydispersity, free of triblock copolymer impurities to be prepared. The composition of the prepared copolymers is systematically varied with respect to the PEO block size. The copolymers are spectroscopically pure.

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