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SYNTHESIS AND COLLOIDAL BEHAVIOUR OF A POLYSTYRENE-b-POLY(ETHYLENE OXIDE) BLOCK COPOLYMER

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Abstract—A convenient route was established for synthesizing a polystyrene-b-poly(ethylene oxide) block copolymer. Polystyryl lithium, prepared by initiating the polymerization of styrene with sec-butyl lithium, was end-capped by reaction with ethylene oxide. After isolation and characterization, the product was reacted with potassium methoxide to give a polymeric anion with a potassium counterion. The system was then used to initiate the polymerization of ethylene oxide to form the second block. Micellar aggregates formed by the polystyrene-b-poly(ethylene oxide) block copolymer in water were investigated by transmission electron microscopy using a phosphotungstic acid stain for the polyether component. Two types of colloidal particle differing greatly in average size were shown to be present in solution.

INTRODUCTION

Studies of block copolymers prepared from styrene and ethylene oxide (oxirane) have been reported by a number of laboratories [1–6]. Because the block copolymers contain both hydrophilic and hydrophobic blocks, they can associate in aqueous media to form colloidally stable aggregates [5, 6]. An interesting feature of the "micellar" aggregates is that the hydrophobic component, polystyrene, remains glassy up to temperatures approaching the boiling point of water. For this reason the block copolymers are potentially useful for encapsulating materials and holding them in aqueous suspension.

In the present paper we report a more convenient method of synthesizing polystyrene-b-poly(ethylene oxide) than has been used hitherto. We also report a method of staining the aggregates formed in aqueous media with a heavy metal so that they may be usefully studied by electron microscopy.

SYNTHESIS OF THE BLOCK COPOLYMER

Literature accounts [7–13] of the anionic preparation of diblock polystyrene-b-poly(ethylene oxide) copolymers and analogous triblock systems indicated that the use of a potassium counterion and reaction temperature of up to 70°C were required, if the addition of ethylene oxide to polystyryl anion was to proceed at a reasonable rate to give a copolymer containing only small amounts of homopolymer contaminants. In a preliminary investigation we therefore chose to prepare polystyrene-b-poly(ethylene oxide) using cumyl potassium as the styrene block initiator. The preparation and purification of methyl cumyl ether [14, 15] and its conversion to cumyl potassium [16, 17] were found to be both tedious and time consuming. We therefore decided to investigate an alternative synthetic route.

The chosen route involved the preparation of polystyryl lithium using commercially available sec-butyl lithium, followed by end-capping of the polymer with ethylene oxide [7]. The hydroxyl terminated product was converted to a polymeric anion with the required potassium counterion by reaction with potassium methoxide and then this polymeric anion was used to initiate the polymerization of ethylene oxide.

EXPERIMENTAL

Materials

Styrene (BDH, 99.5%) was stirred *in vacuo* over calcium hydride for 72 hr, then distilled from a Na mirror and sealed in calibrated break-seal ampoules.

Tetrahydrofuran (Fisons SLR grade) was stirred over calcium hydride for 48 hr, then distilled through a 30 cm Vigreaux column, collecting material b.p. 65.5°C. Anhydrous benzophenone (0.6 g) was added, followed by Na wire, and the whole was degassed on the vacuum line. After 1–2 days the solvent assumed an intense purple colour. Quantities were then removed by vacuum transfer as required.

Ethylene oxide (BDH, LR grade) was stirred over crushed calcium hydride at 0°C for 8 hr/day over 4 days (while being stored unstirred at −78°C overnight). It was then distilled through a column containing successively NaOH and molecular sieve 3 Å pellets onto calcium hydride. It was stirred at 0°C for a further 8 hr before vacuum transfer to calibrated break-seal ampoules.

Toluene (BDH, AR grade) was stirred over calcium hydride *in vacuo*, with periodic degassing for 2–3 days.

Sec-butyl lithium (Aldrich 1.4 M solution in heptane) was filtered under N_2 through a porosity 1 sinter then analysed by the method of Gilman and Haubein [18] immediately prior to use.

Polymerizations

(i) *End-capped polystyryl lithium.* This was prepared in toluene solution by anionic polymerization under vacuum before addition of solvent and monomer. The inside of the polymerization vessel was prewashed with a solution of polystyryl lithium in toluene and then rinsed with toluene distilled from the polystyryl lithium solution.

Styrene (4 g) was added from a break-seal ampoule to toluene, followed by sec-butyl lithium solution (0.80 cm^3 of a 0.535 M solution) at ambient temperature with stirring.

After 22 hr a sample was removed and then ethylene oxide in excess (16 g) was added from a break-seal ampoule which had been cooled in solid CO_2. The mixture was then allowed to warm to room temperature during which time the orange-red colour faded. The solution was stirred for 10 days at room temperature before methanol was added from a break-seal ampoule to terminate any living ends. The polymer was precipitated in hexane, and then freeze dried from benzene to give a white solid. Despite the use of a large excess of ethylene oxide, it was found that only end-capping had occurred.

The sample of polystyrene which was removed before treatment of the bulk with ethylene oxide was isolated in a similar manner to the copolymer. GPC analysis of the polystyrene sample showed a single peak indicating $\bar{M}_n = 9300$ g mol^{-1}, $\bar{M}_w = 10{,}800$ g mol^{-1} and $\bar{M}_w/\bar{M}_n = 1.15$.

(ii) *Polystyrene-b-poly(ethylene oxide)*. A Pyrex ampoule (65 cm^3 volume, 2.75 mm wall thickness) was baked out at *ca* 10^{-4} mmHg then filled with dry N_2. Part of the polymer (1 g) prepared in (i) was added rapidly to the ampoule which was attached to the vacuum line and pumped down. Purified tetrahydrofuran (30 cm^3) was added by vacuum transfer and N_2 was readmitted, followed by 3.00 cm^3 of a 0.033 M solution of potassium methoxide in tetrahydrofuran. The ampoule was re-attached to the line, evacuated and then residual solvent was removed slowly by vacuum transfer. Finally, the residue was pumped on at high vacuum before tetrahydrofuran (16 cm^3) and ethylene oxide (7.5 g at −78°C) were added by vacuum transfer and the ampoule was sealed.

The ampoule was heated progressively from 30° to 70° over 7 days and was then held at 70° for a further 4 days. When cooled the contents formed a stiff gel. The product was isolated as an off-white solid by removal of solvent *in vacuo*. The yield (8.40 g) indicated essentially 100% conversion of the ethylene oxide to polymer.

(iii) *Fractionation and characterization of the product.* GPC analysis of the reaction product showed a main peak arising from the elution of the polystyrene-b-poly(ethylene oxide) block copolymer and two very minor peaks attributed to the presence of small proportions of polystyrene and poly(ethylene oxide) homopolymers. The material of the main peak had by GPC, $\bar{M}_n = 55{,}000$ g mol^{-1}, $\bar{M}_w = 63{,}600$ g mol^{-1} and $\bar{M}_w/\bar{M}_n = 1.15$ (using a calibration established with poly(ethylene oxide) standards).

The polystyrene homopolymer (~3% by weight of the reaction product) was successively removed by dissolving batches of the sample (1 g) in warm toluene (40 cm^3) and then adding anhydrous diethyl ether dropwise to the vigorously stirred solution. The resultant precipitate was isolated after allowing the cooled solution to stand overnight. It was dried *in vacuo* to give 0.973 g of material.

The poly(ethylene oxide) impurity was separated using preparative GPC using a 700 × 25 mm column packed with Sephadex G100 and using a differential refractometer as detector. Separations were carried out using 20 cm^3 batches of 2% w/v aqueous solutions. The block copolymer in micellar form emerged first from the columns. However, this occurred above the upper resolution limit of the columns (which corresponded to a molecular weight of 8×10^4 g mol^{-1} for poly(ethylene oxide)) and so no useful analytical information could be extracted from the elution data. The poly(ethylene oxide) impurity (3% by weight of the reaction product) emerged at an elution volume corresponding to a molecular weight of approximately 400 g mol^{-1} and it could therefore be readily separated from the main product.

The composition of the purified polystyrene-b-poly(ethylene oxide) was determined using both ^{1}H-NMR and u.v. spectroscopy assuming that, for spectroscopic purposes, the copolymer could be treated as if it were a mixture of the two homopolymers. The two results were in fair accord. ^{1}H-NMR (60 MHz) gave $C_4H_9(CH_2CHPh)_{90}(CH_2CH_2O)_{1460}H$ corresponding to $\bar{M}_n = 73{,}700$ g mol^{-1} and u.v. (at 262 nm) gave $C_4H_9(CH_2CHPh)_{90}(CH_2CH_2O)_{1370}H$ corresponding to $\bar{M}_n = 69{,}000$ g mol^{-1},

ELECTRON MICROSCOPY

Phosphotungstic acid ($H_3PW_{12}O_{40}$) precipitates many polar polymers from aqueous solution at low pH due to the formation of a salt-like complex [19]. This has led to its use as a positive stain in electron microscopy studies particularly for polysaccharides (although it is not now generally regarded as a specific stain for the latter). Other systems investigated include polyethers and polyamides [19]. In the present study we have used phosphotungstic acid to stain positively the polyether component of the micelles formed by the polystyrene-b-poly(ethylene oxide) block copolymer in water.

EXPERIMENTAL

Solutions covering the concentration range, 10^{-2}–10^{-1} g dm^{-3} were prepared by dissolving samples of the block copolymer in water at 85°C. The solutions were degassed sealed in glass ampoules and heated to 120°C for a short period (~10 min). They were then cooled down to 85°C and left at this temperature for 30 min. All the solutions were clear, but had a bluish cast.

The solutions were mixed with equal volumes of phosphotungstic acid solution (10^{-2}–10^{-1} g dm^{-3}). Small drops of solution were then allowed to drain and evaporate on carbon substrates mounted on copper grids. Electron microscopy studies were made using a JEOL 100 CX electron microscope operating at 80 kV.

RESULTS AND DISCUSSION

Electron microscopy showed that two types of particle differing greatly in average size were present in all the aqueous solutions examined. Figure 1 shows an electron micrograph containing both types of particle. These were isolated from a copolymer solution of concentration 0.05 g dm^{-3}.

In aqueous solution the small particles most probably consisted of a compact polystyrene core surrounded by a highly swollen flexible fringe of poly(ethylene oxide). After staining and drying, the poly(ethylene oxide) can be expected to have collapsed on to the polystyrene core to form a dense outer shell. Some flattening out of the spherically shaped particles on the carbon substrate would also have occurred during this process.

Because the boundaries of the small particles in the micrographs were rather diffuse, it was difficult to size them accurately. The number-average radius of the small particles isolated from the solution of concentration 0.05 g dm^{-3} was 5.4 nm, which within the uncertainty of the measurements is the same as that for the other concentrations studied.

If the small particles in the micrographs are treated as spheres, the ratio of their weight-average to number-average molecular weights, $\bar{M}_w/\bar{M}_n$, is found to be 1.67; if they are treated as discs, $\bar{M}_w/\bar{M}_n = 1.12$. The actual value of $\bar{M}_w/\bar{M}_n$ for the small particles in solution will be somewhere between these two limits.

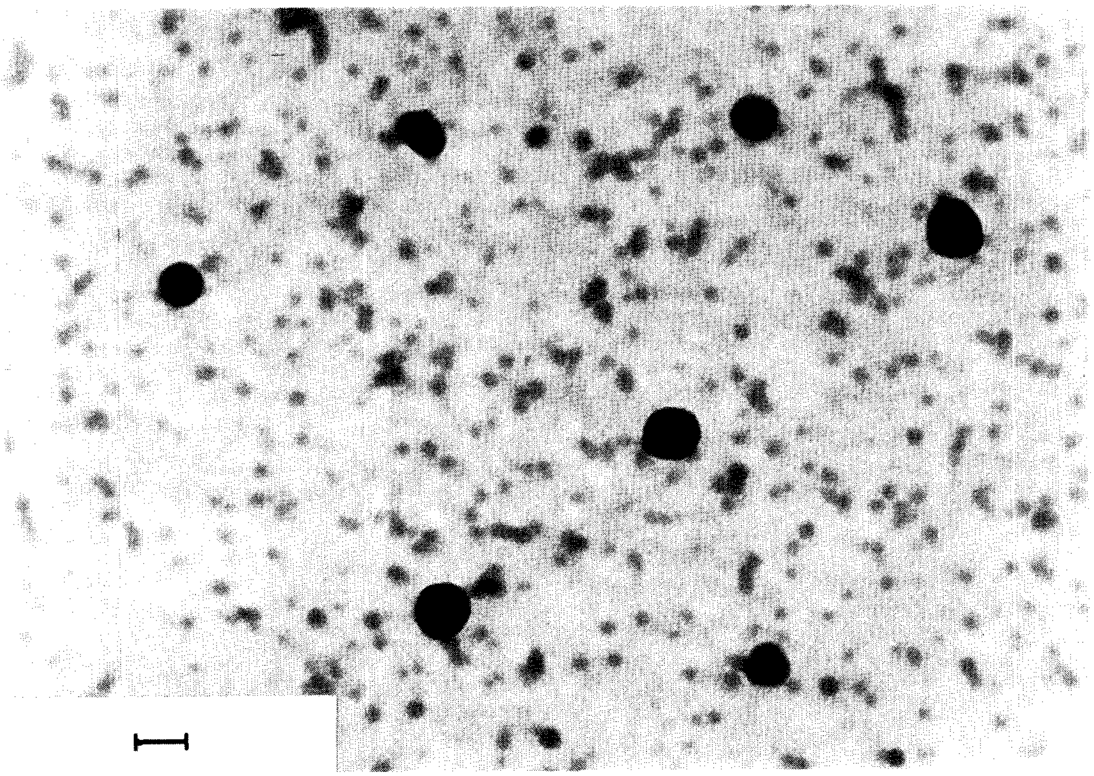

Fig. 1. Electron micrograph of colloidal particles isolated from a solution of the polystyrene-b-poly(ethylene oxide) block copolymer. The scale bar is 50 nm.

Spherical particles with molecular weights of 69,000 g mol^{-1} and 690,000 g mol^{-1} would have radii of 3.0 nm and 6.5 nm respectively (taking the density of the particles to be 1 g cm^{-3}). Any flattening of the particles during drying would give particles with larger radii in the observation plane. The bulky nature of the staining agent could also lead to some enlargement of the particles. Since the small particles we have detected have a number-average radius of only 5.4 nm, it is clear therefore that the association number of these micelles must be quite low.

That the small particles are not simply aggregates of the phosphotoungstic acid can be ruled out on two grounds. First, a control experiment was carried out by allowing drops of phosphotungstic acid solution to evaporate on a carbon substrate in the absence of block copolymer. The micrographs obtained contained light and dark patches, but not the distinct particles shown in Fig. 1. Secondly, negative staining of specimens with uranyl acetate was also found to provide sufficient contrast to reveal the presence of small particles, although the method was not nearly as good as the use of phosphotungstic acid since it led to some clumping of the particles.

All the specimens examined by electron microscopy contained a proportion of large particles similar to those shown in Fig. 1. We believe the large particles are spherical in shape in solution and have cores which contain trapped poly(ethylene oxide) blocks as well as polystyrene blocks. The particles have colloidal stability because of the presence of an outer fringe of poly(ethylene oxide) blocks. The presence of the large particles is responsible for the solutions having a distinct bluish cast. Shadowing with C/Pt indicated that during isolation the particles flattened out on the carbon substrate. However, a distinct outer fringe of poly(ethylene oxide) blocks was maintained as seen in the micrograph in Fig. 1. The large particles have number-average inner and outer radii of 38 and 65 nm respectively when mounted on the carbon substrate.

The large particles were probably the result of incomplete dissolution of the bulk polymer. However, attempts to remove them be heating the solution to various temperatures and taking the solutions through various cycles were not successful. One of the problems encountered was that the temperature to which solutions could be usefully raised to enhance dissolution was limited because, like aqueous solutions of poly(ethylene oxide) homopolymer, the copolymer solutions exhibit lower critical solution temperature behaviour. In studies [20] of block copolymer micelles in organic solvents, we have often encountered difficulties in equilibrating systems even when the micellar cores were highly swollen with solvent. We have serious doubts therefore whether the type of block copolymer investigated here, containing relatively long highly hydrophobic blocks, can ever be fully equilibrated in an aqueous medium.

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REFERENCES

1. B. Lotz and A. Kovacs. *Kolloid Z.u.Z. Polymere* **209,** 97 (1966).
2. B. Lotz, A. Kovacs, G. A. Bassett and A. Keller. *Kolloid Z.u.Z. Polymere* **209,** 115 (1966).
3. R. G. Crystal, P. F. Erhardt and J. J. O'Malley. *Block Polymers* (Edited by S. L. Aggarwal), pp. 163–211. Plenum Press, New York (1970).
4. C. M. Barker and B. Vincent. *Colloids Surf.* **8,** 297 (1984).
5. K. Nakamura, R. Endo and M. Takeda. *J. Polym. Sci. Polym. Phys. Edn* **14,** 135 and 1287 (1976).
6. G. Riess, J. Nervo and D. Rogez. *Polym. Engng Sci.* **17,** 634 (1977).
7. D. H. Richards and M. Szwarc. *Trans. Faraday Soc.* **55,** 1644 (1959).
8. G. Finaz, P. Rempp and J. Parrod. *Bull. Soc. Chim. France* 262 (1962).
9. J. J. O'Malley, R. G. Crystal and P. F. Erhardt. *Block Polymers* (Edited by S. L. Aggarwal). Plenum Press, New York (1970).
10. J. J. O'Malley and R. H. Marchessault. *Macromolec. Synth.* **4,** 35 (1972).
11. S. Marti, J. Nervo and G. Riess. *Prog. Colloid Polym. Sci.* **58,** 114 (1975).
12. C. M. Barker and B. Vincent. *Colloid Surf.* **8,** 289 (1984).
13. Xie Hongquan and Zhou Peiguang. *Polym. Engng Sci.* **25,** 32 (1985).
14. A. Klages. *Ber.* 2638 (1902).
15. W. G. Brown, C. J. Mighton and M. Senkus. *J. Org. Chem.* **3,** 62 (1938).
16. K. Ziegler, F. Crössman, H. Kleiner and O. Schäfer. *Ann. der Chem.* **473–74,** 1 (1924).
17. K. Ziegler and H. Dislich. *Ber.* **90,** 1107 (1957).
18. H. Gilman and A. H. Haubein. *J. Am. chem. Soc.* **66,** 1515 (1944).
19. J. E. Scott. *J. Histochem. Cytochem.* **19,** 689 (1971).
20. C. Price, E. K. M. Chan, A. L. Hudd and R. B. Stubbersfield. *Polym. Commun.* **27,** 196 (1986).