Preparation and properties of stat-copoly(oxyethylene–oxypropylene)-block-poly(oxyethylene): 1. Use of crown ether in the anionic copolymerization of propylene oxide and ethylene oxide

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Stat-copoly(oxyethylene–oxypropylene)s were prepared by anionic polymerization initiated by potassium methoxypropanol in the presence of 18-crown-6 ether, and were characterized by g.p.c. and n.m.r. Molecular weight distributions were narrow. Reactivity ratios, determined from composition and from sequence distribution, were $r_E = 3.1–3.3$ and $r_P = 0.31–0.33$, in good agreement with reactivity ratios determined for polymerization without added crown ether. Diblock copolymers with one stat-copoly(oxyethylene–oxypropylene) block and one poly(oxyethylene) block were prepared by sequential polymerization, and were characterized by g.p.c. and n.m.r.

(Keywords: diblock copolymers; anionic polymerization; characterization; crown ether; reactivity ratio; statistical copolymers)

INTRODUCTION

Block copolymers of propylene oxide and ethylene oxide are well-known examples of aqueous surfactants. A number of triblock copolymers, both $E_xP_yE_x$ and $P_yE_xP_y$, are available commercially (e.g. Pluronics from BASF, Synperonics from ICI). (Here E represents an oxyethylene chain unit and P an oxypropylene chain unit). Diblock copolymers of propylene oxide and ethylene oxide are not readily available.

The properties of a block copolymer are determined by its overall composition and overall chain length. The commercially available triblock E–P copolymers cover a wide range of compositions and lengths (from 20 to 80 wt% E with chain lengths from 60 to 250 units, E and P, and P-block lengths of up to 60 units), and this allows control of properties (e.g. surface activity in aqueous solution). Nevertheless, a greater variation of properties can be achieved by varying the chemical nature of the blocks.

A statistical oxyethylene–oxypropylene block can be substituted for the oxypropylene block. Potentially this allows fine control over the hydrophobicity of the copolymer, and close control of properties in aqueous solution becomes possible. No detailed study of the preparation and properties of well-defined statistical–block copolymers of moderate molecular weight has apparently been reported previously. This paper reports the preparation of such diblock copolymers by anionic polymerization in the presence of a crown ether. Part 2 will describe an investigation of the micellization and gelation properties of the prepared copolymers in aqueous solution.

COPOLYMERIZATION

Anionic polymerization was used to prepare stat-copoly(oxyethylene–oxypropylene) and, from this precursor, copolymers with oxyethylene blocks of various lengths. The initiator used was the potassium salt of 1-methoxy-2-propanol: e.g. for polymerization of propylene oxide (PO),

$$RO^- + PO \rightarrow RP_1O^- \rightarrow\rightarrow\rightarrow\rightarrow RP_nO^- \quad (1)$$

where $R = CH_3OCH_2CH(CH_3)–$ and $P = –OCH_2CH(CH_3)–$. It was intended to prepare block copolymers with narrow block-length distributions. In this respect, a problem in the anionic polymerization of propylene oxide is the proton abstraction reaction

$$CH_3OCH_2CH(CH_3)P_nO^- + PO \rightarrow CH_3OCH_2CH(CH_3)P_nOH + CH_2{=}CHCH_2O^- \quad (2)$$

which leads to initiation of a new chain via the allyl alcoholate, as well as continued growth of the original chain, since all species are rapidly equilibrated:

$$RP_nOH + RP_mO^- \leftrightarrows RP_nO^- + RP_mOH \quad (3)$$

Since new chains are initiated through the reaction, the abstraction reaction leads to a broadened chain length distribution. Investigations have shown[1–4] that addition of a crown ether and polymerization at low temperature alleviate the problem. In the present work, anionic polymerizations were carried out in the presence of

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18-crown-6 ether at 40°C. Fortunately for the preparation of diblock copolymers, the product of reaction (2) is a new monofunctional chain.

It was also intended to prepare statistical blocks with uniform composition along their lengths. Values of the reactivity ratios for ethylene oxide and propylene oxide in anionic copolymerization without crown ether have been determined[5]: over the temperature range 0–80°C acceptable values (to $\pm 20\%$) are $r_E = 3.0$ and $r_P = 0.28$. Consequently ethylene oxide is incorporated into the statistical copolymer more rapidly than propylene oxide, leading to composition drift during the copolymerization. Reactivity ratios for copolymerization at 40°C in the presence of crown ether were determined in the present work, with similar results. In practice the effect of composition drift was minimized by stopping the copolymerizations at low conversions (generally $< 10\%$).

Notation

A statistical copolymer of composition 30 mol% oxyethylene (E) and 70 mol% oxypropylene (P) and block length 73 chain units (counting both E and P) is denoted $(E/P\text{-}30/70)_{73}$. A diblock copolymer prepared from the statistical copolymer by adding 60 oxyethylene units is denoted $(E/P\text{-}30/70)_{73}E_{60}$.

EXPERIMENTAL

Materials

1-Methoxy-2-propanol (Aldrich, 98%) was stirred over anhydrous $MgSO_4$ under dry nitrogen for 24 h and then fractionally distilled (mid-point cut, b.p. 119°C) under dry nitrogen on to type-4A molecular sieves and stored in a desiccator. Potassium metal (BDH, laboratory reagent grade) was freshly cut before use. 18-Crown-6 ether (Fluka, 98%) was vacuum-dried ($< 10^{-3}$ mbar, ≈ 6 h) before use. Petroleum ether (b.p. 100–120°C) was stirred over CaH_2 and then distilled on to and stored over sodium wire. Propylene oxide (PO, BDH, 99.5%) was stirred over CaH_2 under dry nitrogen for ≈ 48 h. Ethylene oxide (EO, Fluka, 98%) was stirred over CaH_2 under vacuum ($< 10^{-3}$ mbar) at 0°C for at least 8 h.

Copolymerization

Copolymerization was carried out in an ampoule which could be sealed by a Teflon tap, and which was oven-dried and flamed on the vacuum line before use. A solution of the 18-crown-6 ether (18C6) in THF was used to transfer the required amount into the ampoule under dry nitrogen; the THF was carefully pumped off, leaving the dry 18C6 behind. The ratio of 18C6 to potassium cation in the copolymerization (r) was within the range 1.1–1.5. The initiator was a mixture of 1-methoxy-2-propanol and its potassium salt at a ratio of molar concentrations $[RO^-K^+]/[ROH] \approx 0.33$. It was prepared by allowing potassium metal (freshly cut under dry petroleum ether) to react completely with 1-methoxy-2-propanol in a flask under nitrogen, and was transferred into the ampoule by syringe. Dry monomers were distilled into the ampoule via the vacuum line. The exact amount of each reactant in the recipe was determined by detaching and weighing the ampoule at each stage. The total weight of monomers distilled into the ampoule ranged from 50 to 500 g; the total amounts of initiator ($[I] = [ROH] + [RO^-K^+]$) used were such that the calculated number-average molecular weights of the copolymers (for 100% conversion, ignoring reaction (2)) were in the range 30 000–50 000.

The sealed ampoule was immersed in a water bath at 40°C. The extent of copolymerization was estimated from the liquid level in the ampoule and the copolymerization was stopped at a low conversion by cooling the ampoule with solid CO_2 and acetone before removal of the unconverted monomers by evacuation. The product was weighed to determine the exact conversion. A portion of the copolymer for analysis by g.p.c. and n.m.r. was neutralized by shaking or stirring for about 8 h with a few drops of concentrated hydrochloric acid, and dried on the vacuum line ($< 10^{-4}$ mmHg, 70°C, 24 h).

The remaining 'living' statistical copolymer was subdivided by transferring it by syringe into small ampoules under a dry nitrogen atmosphere. Each weighed ampoule was then in turn attached to the vacuum line and exhaustively evacuated to remove any traces of water before the required amount of EO was distilled in. Polymerization was carried out initially at 40°C and finally at 80°C, the higher temperature being required in order to prevent crystallization of the growing oxyethylene block. The time allowed for polymerization was about 2 weeks; the conversion was 100%. The resulting block copolymer was neutralized and dried, as described above, and stored in the dark at low temperature.

N.m.r. spectroscopy

^{13}C n.m.r. spectra were obtained using a Bruker AC300E spectrometer operating at 75.5 MHz and copolymer solutions of ≈ 30 wt% in $CDCl_3$. ^1H n.m.r. spectra were obtained using a Varian Associates Gemini 200 spectrometer operating at 200 MHz and copolymer solutions of ≈ 2 wt% in $CDCl_3$. The copolymer composition was determined from both ^1H and ^{13}C spectra using a pulse interval of at least 12 s in order to allow complete relaxation between pulses. The ^{13}C spectra were ^1H-decoupled throughout the acquisition.

The triad sequence distribution was obtained from ^{13}C CH and CH_2 subspectra by respectively adding and subtracting DEPT (Distortionless Enhancement by Polarization Transfer) spectra[6] obtained with final ^1H pulses of 45° and 135° flip angles. The weighting of each spectrum was adjusted empirically in order to null resonances known to be entirely of the undesired multiplicity. Details of the n.m.r. assignments are given elsewhere[7].

Gel permeation chromatography

Molecular weights and molecular weight distributions were investigated by g.p.c. The system consisted of three μ-Styragel columns (length 30 cm, internal diameter 7.5 mm, nominal pore sizes 500, 10^3 and 10^4 Å). The eluent was tetrahydrofuran at 25°C and a flow rate of 1 $cm^3\ min^{-1}$. The system was calibrated with poly(oxyethylene) standards of known molecular weights.

RESULTS AND DISCUSSION

Statistical copolymers

Preparative conditions and some characteristics of the copolymers are listed in *Table 1*.

Molecular weight. G.p.c. curves were narrow peaks with limited tailing towards high elution volume. Values

Table 1 Preparative conditions and molecular weights for statistical copolymers of ethylene oxide and propylene oxide

Copolymer	r	Conversion (wt%)	M_n (g.p.c.)[a]	M_n (n.m.r.)
$(E/P\text{-}30/70)_{73}$	1.33	8.0	4900	3900
$(E/P\text{-}30/70)_{31}$	1.40	4.4	2000	–
$(E/P\text{-}49/51)_{83}$	1.49	8.5	5000	–
$(E/P\text{-}49/51)_{119}$	1.23	28.4	6900	6100
$(E/P\text{-}57/43)_{51}$	1.48	6.4	3000	–
$(E/P\text{-}66/34)_{115}$	1.13	14.9	6700	–
$(E/P\text{-}79/21)_{220}$	1.23	9.0	–	10 300

[a] Molecular weights calculated 'as if poly(oxyethylene)'

of the number-average molecular weight (M_n) obtained by the use of the poly(oxyethylene) calibration are given in *Table 1*; the ratio of average molecular weights was in the range $M_w/M_n = 1.1\text{–}1.2$ for all samples. Small shoulders on the low-volume sides of the g.p.c. peaks of some samples indicated some initiation (<10 mol%) by adventitious water. Initiation by water first generates bifunctional ethylene glycol or propylene glycol, which then propagates from both OH groups, thus producing a polymer which is on average twice as long as a chain from the monofunctional initiator 1-methoxy-2-propanol.

^{13}C n.m.r. was used to obtain molecular weights by end-group analysis: see *Table 1*. In some samples the integrated intensities of resonances assigned to end groups[7] revealed a small excess of hydroxy terminal groups (predominantly $-OCH_2CH(CH_3)OH$) over methoxy and allyl groups originating respectively from the initiation and proton abstraction reactions, consistent with initiation by water and, possibly, isomerization of allyl to propenyl end groups and subsequent hydrolysis[8].

Values of M_n determined by g.p.c. were systematically higher (+15%) than those determined by n.m.r., consistent with early elution of the statistical copolymers compared with poly(oxyethylene) of the same molecular weight. Values of chain lengths (see molecular formulae) were based on molecular weights determined by n.m.r. or, where n.m.r. had not been used, on molecular weights determined by g.p.c. but reduced by 15% for consistency.

Unsaturation. The proportion of unsaturated ends in the statistical copolymers, monitored by ^{13}C n.m.r., was in the range 25–35%. This resulted from reaction of a small proportion, <1%, of the PO to give allyl alcoholate. Because this low level of proton abstraction is unimportant to the principal concerns of this work, no systematic study of the reaction was carried out.

Composition. ^1H and ^{13}C n.m.r. were used to obtain overall compositions: see *Table 2*. Compositions were determined by comparison of the intensity of resonances from the atoms of the methyl group of the oxypropylene chain units with that from the methylene groups (oxyethylene and oxypropylene chain units) or methine groups (oxypropylene chain units). Corrections were made for end groups and the small amounts of residual crown ether.

Sequence distribution. ^{13}C n.m.r. was used to determine the triad sequence distribution of the statistical copolymers. The results, given in *Table 3*, demonstrate the statistical nature of the copolymers. (Note that in this table, the character P denoting oxypropylene represents a unit orientated in the direction $-O-CH_2-CH(CH_3)-$.)

Reactivity ratios. Reactivity ratios may be determined either from the variation of the copolymer composition with feed composition (method I) or from the triad sequence distribution of a single copolymer (method II). Recently the authors described simple numerical implementations of both methods, and their application to the determination of reactivity ratios for the anionic copolymerizations of EO and PO over the temperature range 0 to 80°C in the absence of crown ether[5]. The numerical methods searched for reactivity ratios giving the best fit to the experimental data (copolymer composition or triad distribution) for given initial monomer feed compositions. Method I was based on the copolymerization equation

$$F_E = \frac{(r_E - 1)f_E^2 + f_E}{(r_E + r_P - 2)f_E^2 + 2(1 - r_P)f_E + r_P} \qquad (4)$$

which expresses the instantaneous mole fraction of EO in the copolymer F_E in terms of the mole fraction of EO in the monomer feed f_E and the reactivity ratios of EO and PO, r_E and r_P respectively. Method II was based on the following expressions for the probabilities of monomer triads:

$$[EEE] = w(1-u)^2/(u+w) \qquad (6a)$$

$$[EEP] = [PEE] = uw(1-u)/(u+w) \qquad (6b)$$

$$[PEP] = u^2w/(u+w) \qquad (6c)$$

$$[EPE] = uw^2/(u+w) \qquad (6d)$$

$$[EPP] = [PPE] = uw(1-w)/(u+w) \qquad (6e)$$

$$[PPP] = u(1-w)^2/(u+w) \qquad (6f)$$

where u and w are respectively the conditional probabilities of adding PO to a chain ending in an EO unit, and of adding EO to a chain ending in a PO unit. The values of u and w are related to f_E, r_E and r_P by

$$u = 1/(r_E x + 1) \qquad (7a)$$

$$w = x/(r_P + x) \qquad (7b)$$

where $x = f_E/(1 - f_E)$. In both methods, drift of the monomer feed composition during polymerization because of differential reactivity was accounted for by simulating the polymerization as a series of very small steps and adjusting the feed composition after each step according to the amount of monomer entering the polymer.

Table 2 Compositions of statistical copolymers of ethylene oxide and propylene oxide

Copolymer	Conversion (wt%)	Feed mole fraction f_E	Copolymer mole fraction F_E
$(E/P\text{-}30/70)_{73}$	8.0	0.122	0.304
$(E/P\text{-}30/70)_{31}$	4.4	0.137	0.301
$(E/P\text{-}49/51)_{83}$	8.5	0.239	0.490
$(E/P\text{-}49/51)_{119}$	28.4	0.243	0.490
$(E/P\text{-}57/43)_{51}$	6.4	0.310	0.567
$(E/P\text{-}66/34)_{115}$	14.9	0.403	0.655
$(E/P\text{-}79/21)_{220}$	9.0	0.548	0.793

Table 3 Triad sequence distribution of the statistical copolymers

	Copolymer			
Triad	$(E/P\text{-}30/70)_{73}$	$(E/P\text{-}49/51)_{119}$	$(E/P\text{-}66/34)_{115}$	$(E/P\text{-}79/21)_{220}$
[PPP]	0.335	0.143	0.051	0.008
[PPE]	0.130	0.128	0.076	0.032
[PEP]	0.149	0.154	0.094	0.035
[EPP]	0.159	0.131	0.083	0.039
[PEE]	0.065	0.113	0.151	0.135
[EPE]	0.073	0.108	0.135	0.127
[EEP]	0.067	0.141	0.154	0.140
[EEE]	0.022	0.082	0.256	0.484

Using method I and the data in *Table 2*, the copolymer composition F_E was reproduced with a root-mean-square error of 2.3% by the reactivity ratios $r_E = 3.3$ and $r_P = 0.33$. Using method II, the best fit to the triad distributions in *Table 3* were given by the parameters in *Table 4*. Allowing for typical uncertainties of $\approx 20\%$ in the best-fit ratios[5], there is satisfactory agreement between the two methods. In the earlier study with no crown ether[5], the reactivity ratios obtained were $r_E = 2.8 \pm 0.6$ and $r_P = 0.25 \pm 0.07$ (method I) and $r_E = 3.1 \pm 0.4$ and $r_P = 0.30 \pm 0.04$ (method II). Within experimental error therefore, crown ether has no effect on the reactivity ratios, enhancing the rate of all propagation reactions equally. The values of the product $r_E r_P$ are 1.00 (method I) and 0.93 (method II), very close to the value of 1 corresponding to Bernoullian propagation statistics in which the probability of adding a particular monomer is independent of the chain end.

Block copolymers

Block copolymers were prepared from four of the statistical copolymers, as indicated in *Table 5*. The overall compositions obtained from n.m.r. spectroscopy agreed closely with those predicted on the basis of the recipe used. The ratio of the total intensity of the resonances of the hydroxy-terminated end groups to that of the resonances of the oxypropylene groups of the statistical block was determined for both the statistical copolymers and the block copolymers. For a given series of copolymers, the ratio was the same, within experimental error, i.e. no detectable homopoly(oxyethylene) was formed by initiation by water in the second stage of the preparation.

A full end-group analysis, leading to values of M_n, was carried out only for the block copolymers of series (E/P-70/30): see *Table 5*. G.p.c. curves were obtained for all the block copolymers and showed single, narrow peaks; polymeric impurities, if present, were below the 5 wt% level. The curves of selected samples were analysed in order to gain a semiquantitative impression of the molecular weight and molecular weight distribution: see *Table 5*. For the block copolymers containing a high proportion of poly(oxyethylene), the molecular weights from g.p.c., based on the poly(oxyethylene) calibration, were consistent with the values obtained by n.m.r. or predicted from the composition. The chain lengths (i.e. molecular formulae) given in *Table 5* are based on the chain lengths and compositions of the statistical copolymers listed in *Table 1* and the compositions of the block copolymers listed in *Table 5*.

Table 4 Best-fit parameters for the triad distributions in *Table 3*

Copolymer	r_E	r_P	R.m.s. error (%)
$(E/P\text{-}30/70)_{73}$	3.0	0.28	5.6
$(E/P\text{-}49/51)_{119}$	3.0	0.29	7.5
$(E/P\text{-}66/34)_{115}$	2.8	0.36	6.2
$(E/P\text{-}79/21)_{220}$	3.2	0.29	4.7
Average	3.0	0.31	–

Table 5 Compositions and molecular weights of the block copolymers

	N.m.r.		G.p.c.[a]	
Sample	mol% E	M_n	M_w/M_n	M_n
$(E/P\text{-}30/70)_{73}E_{36}$	53.3	5500	1.2	5500
$(E/P\text{-}30/70)_{73}E_{60}$	62.0	6600	1.1	6500
$(E/P\text{-}49/51)_{119}E_{21}$	56.5	–	–	–
$(E/P\text{-}49/51)_{119}E_{79}$	69.4	–	–	–
$(E/P\text{-}49/51)_{119}E_{119}$	74.5	–	–	–
$(E/P\text{-}66/34)_{115}E_{67}$	78.5	–	–	–
$(E/P\text{-}66/34)_{115}E_{95}$	81.4	–	–	–
$(E/P\text{-}66/34)_{115}E_{120}$	83.3	–	1.2	11 000
$(E/P\text{-}66/34)_{115}E_{268}$	89.8	–	1.2	15 000
$(E/P\text{-}79/21)_{220}E_{78}$	85.6	–	–	–
$(E/P\text{-}79/21)_{220}E_{200}$	88.6	–	–	–
$(E/P\text{-}79/21)_{220}E_{271}$	90.7	–	–	–

[a] G.p.c. curves of samples were narrow: see text. Molecular weights were calculated 'as if poly(oxyethylene)'

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