Random ethylacrylate–sulphonatopropylbetaine copolymers. 1. Synthesis and characterization

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(*Received 9 June 1987; accepted 8 September 1987*)

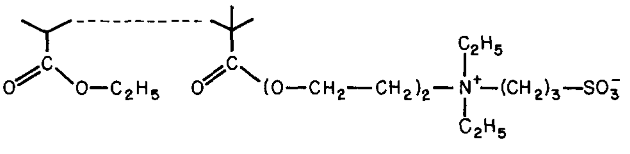
Radical copolymerization of ethylacrylate (A) and 3-[diethyl-2-(2-methacryloyloxyethoxy)ethylammonio]-propanesulphonate (B) initiated by azo-bis-isobutyronitrile (AIBN) was studied in ethanol solution at 60°C: $0.5<[A+B]<1\ \mathrm{mol\,l^{-1}}$, $[AIBN]/[A+B]=10^{-2}$. The copolymerization process obeys the terminal unit model over the whole composition range: $r_A=0.242$, $r_B=3.93$. The weight average degree of polymerization, $4\times10^2<\overline{DP}_w<4\times10^4$, is an increasing function of the molar fraction of monomer B in the monomer feed, f_B, up to $f_B\sim0.7$ and then tends to level off. The AB copolymers are able to dissolve $LiClO_4$ in stoichiometric amounts ($[LiClO_4]/[B]=1$) to yield amorphous AB′ blends which show a slightly increased glass transition temperature with respect to those of their precursors. In all cases, the composition dependence of the glass transition temperature of the AB or AB′ systems obeys the Fox equation: $T_g^{-1}=\Sigma w_i\ T_{g,i}^{-1}$ with $T_g(\mathrm{An})=-13°\mathrm{C}$, $T_g(\mathrm{Bn})=133°\mathrm{C}$ and $T_g(\mathrm{B'n})=144°\mathrm{C}$.

(Keywords: radical copolymerization; ethylacrylate; 3-[diethyl-2-(2-methacryloyloxyethoxy)ethylammonio]-propanesulphonate; reactivity ratios; molecular weights; LiClO$_4$ solvation; glass transition temperatures)

INTRODUCTION

We recently described the synthesis[1], the dilute solution[2,3] and the bulk properties[4,5] of a series of aliphatic and aromatic atactic poly(sulphopropylbetaines) which display unusual and unique behaviour: increasing chain expansion in water solution with increasing ionic strength[2], high efficiency in binding 'soft' polarizable anions[3], strong bulk polarity and the ability to dissolve stoichiometric amounts of mineral salts of widely different lattice energies to yield amorphous ionic blends[4,5]. These very typical properties arise from the highly dipolar structure of the zwitterionic lateral groups and from the strong specific interactions they can exchange with a variety of dipolar and ionic species. Random copolymerization of zwitterionic and relatively apolar monomers may thus appear as a general and versatile way of synthesizing a wide variety of new functional polymeric materials where some interesting properties could easily be monitored in a controlled manner by composition. More precisely, a recent preliminary study[6] has already suggested that ethylacrylate copolymers of low zwitterionic content could more or less mimic the well-known ionomers[7] through association of the dipolar segments in multiplets.

This paper reports the preparation and characterization of random copolymers of ethylacrylate (A) and of 3-[diethyl-2-(2-methacryloyloxyethoxy)ethylammonio] propanesulphonate (B). These were selected as a simple model system for the study of their bulk properties because of some favourable factors: the parent homopolymers show a large enough difference in polarity and glass transition temperatures ($T_g(\mathrm{An})=-13°\mathrm{C}$, $T_g(\mathrm{Bn})=133°\mathrm{C}$[5]) and the copolymers are expected to be amorphous over the whole composition range.



(A) (B)

Scheme I

The following topics are reviewed: copolymerization kinetics, reactivity ratios, compositional polydispersity and unit distribution; molecular weights; and glass transition of the copolymers and their amorphous blends with $LiClO_4$. In the following text, f_i and F_i refer to the molar fractions of monomer i (molar mass $\mathcal{M}_i$) in the monomer feed and in the copolymer respectively.

EXPERIMENTAL

Monomers, reagents and solvents

Ethylacrylate was purified by vacuum distillation over CaH_2 and safely stored at −15°C without any autopolymerization. Monomer B was synthesized and purified as previously described[1] and azo-bis-isobutyronitrile (AIBN) was recrystallized from toluene solution. The solvents and anhydrous lithium perchlorate of the best reagent grade were used without further purification.

Polymerization and kinetic measurements

The monomers, solvent and initiator were introduced into a Pyrex glass double-wall reactor fitted with a magnetic stirrer and connected to an external Lauda

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thermostat, allowing the temperature to be monitored within ±0.1°C. The system was degassed by three successive vacuum–argon sweeping cycles and the reaction was then carried out at a constant temperature of 60°C under a slight pressure of argon. After addition of a small amount of hydroquinone to stop the polymerization, the solvent and residual monomer A were stripped off by rotary evaporation and the copolymer was recovered in two different ways according to its B content: for $F_B < 0.25$ the copolymer was dissolved in methanol and reprecipitated in water; for higher F_B values, the copolymer was dissolved in water or water–methanol mixtures and the solution was exhaustively dialysed for 48 h using cellulosic Spectrapor membranes of molecular weight cut-off 3500 and finally freeze-dried. The lack of any residual monomer B was checked by thin-layer chromatography (silica gel Merck 60-F-254), using methanol as solvent: $R_F(B) \sim 0.39$, $R_F(\text{copolymers}) \sim 0$. The copolymers are very hygroscopic, especially those of high B content. They were dried at 80°C under 10^{-2} torr (1.3 Pa) for at least 24 h and then stored in a dessicator; they were further dried overnight in the same conditions before any analysis or physical measurement.

For kinetic measurements, the ethylacrylate consumption was monitored by gas–liquid chromatography: a Perkin–Elmer 900 gas chromatograph fitted with a dual flame ionization detector and connected to a Hewlett–Packard 3370 B integrator. Separation was performed at 80°C on a column of poly(dimethylsiloxane) (0.300 g) deposited on Chromsorb W ($l = 1.50$ m, $\phi = \frac{1}{8}''$).

Lithium perchlorate–copolymer blends

Stoichiometric $LiClO_4$–copolymer blends ($[LiClO_4]/[B] = 1$) were obtained either by evaporation of their solution in trifluoroethanol or methanol for $F_B < 0.60$ or by freeze-drying of their aqueous solution for higher B content. They were dried as for the pure copolymers.

Molecular weight measurements

Refractive index increments, d*n*/d*c*, were measured at room temperature on a Brice–Phoenix BP 10004 differential refractometer using a neon laser beam of $\lambda = 632$ nm. The results were $dn/dc(\text{An}) = 0.129$ and $0.141\ \text{ml g}^{-1}$ in methanol and 2,2,3,3-tetrafluoropropanol (TFP), respectively; $dn/dc(\text{Bn}) = 0.144$ (ref. 2) and $0.164\ \text{ml g}^{-1}$ in 0.1 M H_2O–NaCl and TFP, respectively. Light scattering experiments were carried out at room temperature on a Fica PGD 420,0M apparatus at the same wavelength. Gel permeation chromatography (g.p.c.) was performed either with a laboratory-built apparatus fitted with Sephacryl S-200 gel columns and calibrated with poly(oxyethylene) standards for water solutions (0.1 M NaCl) or with a Waters 200 device fitted with Styragel columns and calibrated with polystyrene standards for tetrahydrofuran (THF) solutions.

Differential scanning calorimetry (d.s.c.)

D.s.c. experiments were performed on Perkin–Elmer DSC-2 or DSC-4 apparatus monitored by a microprocessor and interfaced with a computer data station, using 10–15 mg samples. The following heating–cooling sequences were systematically repeated until reproducible scans were obtained (most often the third scan): heating to $T_g + 50$°C at a rate of $20°\text{C min}^{-1}$, annealing for 5 min at this temperature, cooling to a temperature depending on the polymer at a rate of $40°\text{C min}^{-1}$ and annealing for 5 min. The glass transition temperature was measured at the midpoint of the base line shift ($\Delta C_p/2$) with an accuracy of about ±1.5°C. The width of the transition was estimated by the ΔT value, $\Delta T = T_2 - T_1$, where T_1 and T_2 are the intersections of the tangent at the thermogram inflection point with the extrapolated glassy and liquid base lines.

RESULTS AND DISCUSSION

Copolymerization kinetics, reactivity ratios, compositional heterogeneity and unit distribution

Because of the very dissimilar solubility properties of monomers A and B and of their corresponding homopolymers, only water, ethanol and their mixtures (γ_H = volume fraction of water) appear as potential non-exotic copolymerization solvents, as shown in *Table 1*.

Ethanol was selected as the solvent in spite of the insolubility of the poly(zwitterion) Bn and all the copolymerizations were carried out under the following conditions:

$$0.5 \leqslant [A + B] \leqslant 1\ \text{mol l}^{-1}, \qquad [\text{AIBN}]/[A + B] = 10^{-2}, \qquad T = 60°\text{C}$$

The reaction medium remains homogeneous throughout the copolymerization only for low monomer B contents, $f_B < 0.1$; the copolymer precipitates in the other cases. Conversion was limited to about 30% to avoid too high a compositional heterogeneity of the resulting copolymers, except for the kinetic experiments.

The consumption of ethylacrylate obeys first-order kinetics up to a conversion of about 60% over the whole composition range, as shown in *Figure 1* for different f_A values. This allows the definition of an *apparent* pseudo first-order rate constant K:

$$\ln([A]_0/[A]_t) = K[\text{AIBN}]_0^{0.5} t$$

K is a strongly decreasing function of f_B for $f_B < 0.25$, and then tends to level off for higher f_B: see *Figure 2*. The occurrence of two domains where the reactivity of the system with respect to monomer A shows widely different sensitivity to monomer feed composition cannot be exactly correlated with the transition from homogeneous to heterogeneous copolymerization, but the possible influence of such a physical factor cannot be ruled out.

Direct potentiometric titration of the very weakly basic sulphonate anion in the zwitterionic copolymers requires the use of CF_3SO_3H as titrating reagent and of acetic anhydride–acetic acid, 9:1 by volume, as solvent[1]. Because of solubility limitations, this method is restricted

Table 1

	Monomer		Polymer	
Solvent	A	B	An	Bn
H_2O	−	+	−	+
EtOH	+	+	+	−
H_2O + EtOH	+ if $\gamma_H < 0.90$	+	+ if $\gamma_H < 0.27$	+ if $\gamma_H > 0.64$

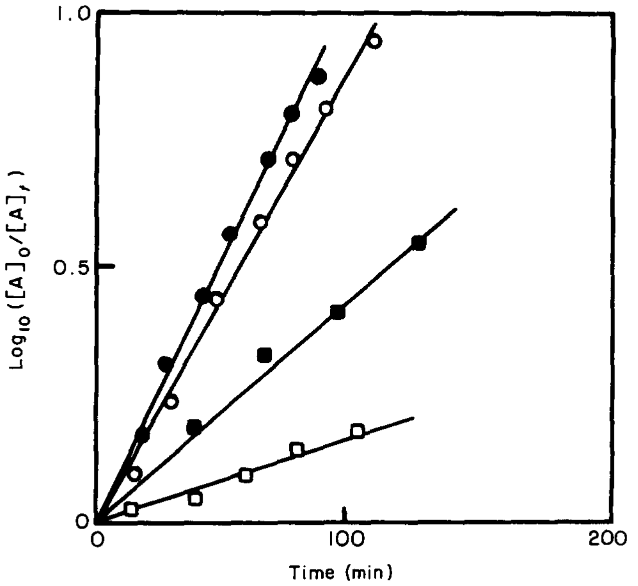

Figure 1 First-order consumption of ethylacrylate in copolymerization for various initial monomer feed compositions, f_B: 0 (●); 0.05 (○); 0.34 (■); 0.60 (□)

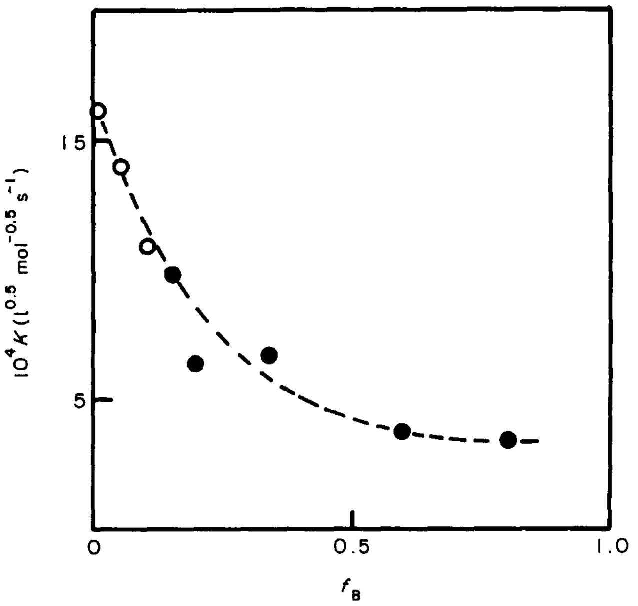

Figure 2 Variation of the apparent first-order rate constant K of ethylacrylate consumption with initial monomer feed composition: homogeneous phase (○); heterogeneous phase (●)

to copolymers of low B content, $F_B < 0.1$. Copolymer composition was thus derived from elemental analysis, and in spite of the hydrophilicity of the samples (see 'Experimental' section), self-consistent and reliable values were obtained from both nitrogen and sulphur microanalysis as shown below:

F_B(S): 0.115 0.364 0.850
F_B(N): 0.120 0.336 0.820

The experimental results of a series of copolymerizations carried out over the whole range of monomer feed compositions are given in *Table 1*. The reactivity ratios were calculated according to the Kelen–Tüdos method, which takes into account the degree of conversion τ (ref. 8). Calculations show that there is no reason to consider separately the homogeneous and heterogeneous reactions, and all the data are reasonably linearized (correlation coefficient $R(14) = 0.9504$), leading to the following reactivity ratios: $r_A = 0.242$, $r_B = 3.93$; see *Figure 3*. The system is not significantly different from the so-called 'ideal' copolymerization: $r_A r_B = 0.95$ *versus* 1. The relative rates of incorporation of the two monomers A and B are independent of the nature of the terminal unit of the propagating macro-radicals. Moreover, knowledge of the Q_A and e_A values from the literature[9] and of the preceding reactivity ratios allows the derivation of two sets of the corresponding Q_B and e_B values, the most probable being $Q_B = 1.49$ and $e_B = 0.31$. These values should be considered approximate since they are calculated from only a single copolymerization system; they are, however, compatible with those of methacrylic acid aliphatic esters[9], showing that the highly dipolar zwitterion, which is completely disconnected from the polymerizable double bond by a two oxyethylene unit spacer, has no influence on the monomer reactivity.

The variation of the compositional heterogeneity of the samples with conversion was analysed in the usual way.

Table 2 Copolymerization of A and B monomers in ethanol solution at 60°C

Run	[A+B]	f_B	$[I] \times 10^2$ (mol l^{-1})	Time (min)	Yield (wt%)	$\bar{F}_B$
1	0.491	0	0.550	50		0
12	0.994	0.026	0.869	30	19.8	0.07
20	1.000	0.050	0.907	25	15.0	0.12
21	0.497	0.079	0.540	35	21.9	0.23
9	0.979	0.102	0.848	20	11.2	0.31
10	0.995	0.147	0.980	40	36.0	0.36
3	0.495	0.202	0.490	75	22.8	0.43
27	0.503	0.245	0.250	120	19.4	0.61
16	0.740	0.297	0.480	50	14.7	0.66
13	0.498	0.404	0.504	80	27.0	0.73
15	0.661	0.480	0.516	60	4.0	0.78
17	0.514	0.590	0.580	55	19.6	0.82
24	0.468	0.684	0.546	60	31.0	0.86
25	0.443	0.900	0.563	60	49.0	0.97

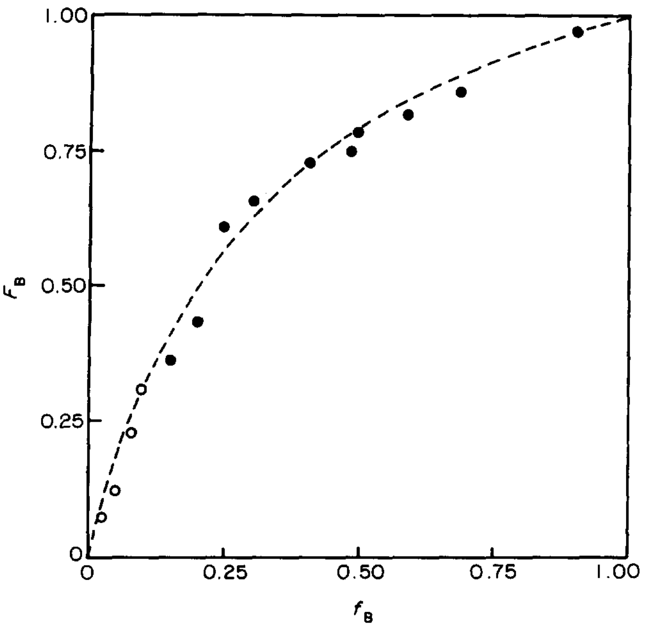

Figure 3 Composition diagram of the A–B copolymerization system: homogeneous phase (○); heterogeneous phase (●). Instantaneous composition curve is calculated for $r_A = 0.242$ and $r_B = 3.93$ (-----)

The integrated form of the Skeist equation was used, as proposed by Meyer and Lowry[10], which allows the calculation of the instantaneous F_B and the cumulative $\bar{F}_B$ composition of the copolymers as a function of the total mole conversion $\tau = 1 - [M]/[M]_0$ for any initial monomer feed composition; see the curves of *Figure 4*, which are related to some of the copolymerization systems defined in *Table 1*. The ratio of the rate of consumption of monomer B to that of monomer A is as high as 4. This leads to strong drifts in composition even for moderate conversion, especially for monomer feeds of low B content. For instance, for a monomer feed composition corresponding to $f_B^0 = 0.079$, the cumulative $\bar{F}_B$ value is decreased by a factor of 0.8 for conversion of only 0.20, and monomer B is exhausted before conversion reaches about 0.9.

The unit distribution, calculated in the usual way from the previous reactivity ratios[11], is quite close to a Bernoullian distribution, as expected from a nearly 'ideal' copolymerization system. The fractions of the various B-centred triads may be readily approximated by: $F(\text{B}\overset{*}{\text{B}}\text{B}) = F_B^2$, $F(\text{B}\overset{*}{\text{B}}\text{A}) = 2F_B(1-F_B)$, $F(\text{A}\overset{*}{\text{B}}\text{A}) = (1-F_B)^2$.

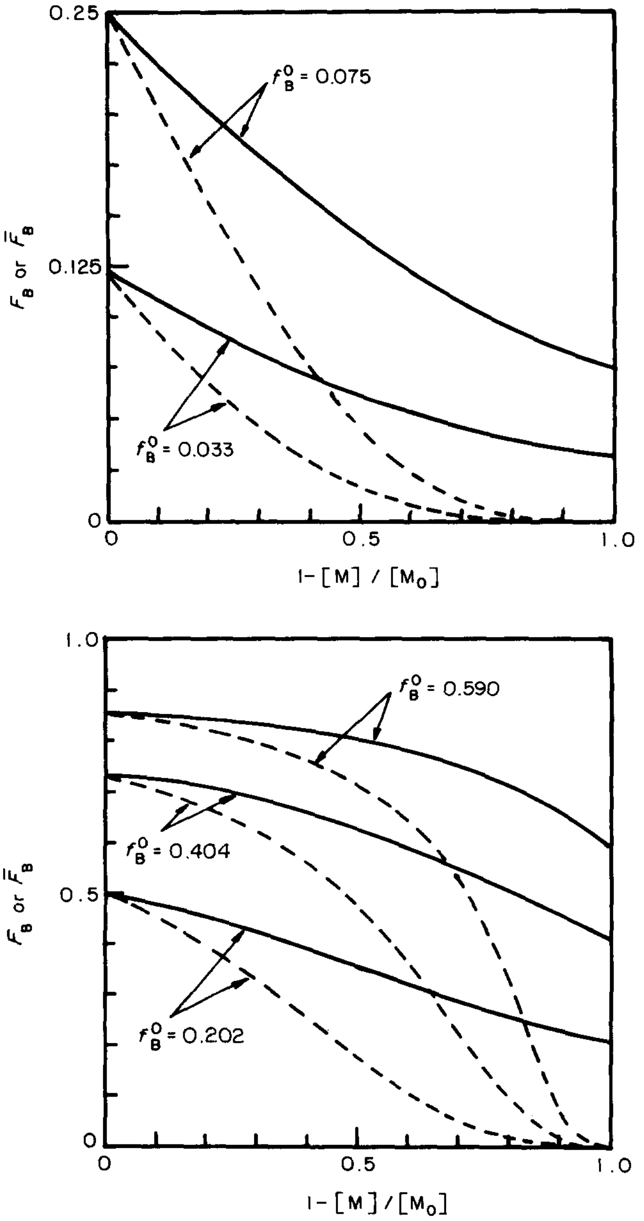

Figure 4 Variation of the instantaneous F_B(-----) and cumulative $\bar{F}_B$ (———) copolymer compositions with total mole conversion for various initial monomer feeds

Molecular weights

The copolymers retain the solubility properties of poly(ethylacrylate) in THF, methanol, ethanol, acetone etc. for $F_B < 0.25$ and become water soluble, as the poly(zwitterion), for $F_B > 0.66$. However, all the samples can be readily dissolved in fluorinated alcohols[1] such as trifluoroethanol,2,2,3,3-tetrafluoropropanol (TFP) and hexafluoroisopropanol.

For copolymers of low B content, g.p.c. experiments in THF solution were completely unreliable because of strong absorption of the samples on the Styragel columns. For copolymers of high B content, g.p.c. experiments in water solution (0.1 M NaCl) lead to a broad unimodal distribution characterized by an apparent polydispersity index $\bar{M}_w/\bar{M}_n \sim 2.5$. This value may be biased by side effects arising from compositional heterogeneity of the samples, but it appears reasonable for a radical copolymer obtained in heterogeneous phase (compare with $\bar{M}_w/\bar{M}_n \sim 1.9$ for poly(ethylacrylate) synthesized in homogeneous ethanol solution).

Light scattering measurements were performed in three different solvents according to copolymer composition: methanol for $F_B < 0.25$, TFP for $0.25 < F_B < 0.60$ and H_2O–0.1 M NaCl for $F_B > 0.60$. The apparent weight average molecular weights thus obtained may be significantly higher than the actual values when compositional heterogeneity of the copolymers is relatively strong[12], but this effect is levelled when the refractive index increments of both species A and B are high[13]. This is precisely the case of the systems under study (see 'Experimental' section), and the $\bar{M}_w$ values given in *Table 2* may thus be considered as fairly representative. For the high molecular weight water-soluble polymers ($\bar{M}_w \sim 10^6$, see below) the very slight curvature of the $P(\theta)$ function observed in a number of Zimm plots suggested that the polydispersity index could be derived from analysis of the scattering pattern at high angles[14]. However, we have checked that the molecular weights and the dimensions of the copolymers are still too low to consider the experimental data obtained at high angles as the true asymptotic behaviour. Under these conditions, light scattering cannot afford any reliable information about molecular weight distribution.

Figure 5 shows the influence of initial monomer feed composition on weight average degrees of polymerization $\overline{DP}_w^*$ normalized to standard conditions ([M] = [A + B] = 1 mol l^{-1}, [AIBN] = 5×10^{-3} mol l^{-1}):

$$\overline{DP}_w^* = \frac{\bar{M}_w}{\mathcal{M}[M]}\left(\frac{[\text{AIBN}]}{0.5}\right)^{0.5}$$

with $\mathcal{M} = \mathcal{M}_A F_A + \mathcal{M}_B F_B$. $\overline{DP}_w^*$ is a strongly increasing function of the monomer B content in the monomer feed up to $f_B \sim 0.7$ and then reaches a plateau value. As for compositional data, the transition from homogeneous to heterogeneous copolymerization at $f_B \sim 0.1$ does not result in any clear discontinuity. The differences in conversion of the various runs may slightly affect the calculated $\overline{DP}_w^*$ values, but the observed trend may be considered as well ascertained.

Table 3 Molecular weights and glass transition data for AB copolymers and their stoichiometric AB′ blends with $LiClO_4$

				AB copolymers			AB′ blends
Run	W_B	$\bar{M}_w \times 10^{-5}$	$(\bar{S}_z^2)^{0.5}$ (nm)	T_g (°C)	ΔC_p ($J\ g^{-1}\ K^{-1}$)	ΔT (°C)	T_g (°C)
An	0	1.36		−13.1	0.406	8.5	
22	0.08	0.748		−11.1	0.435	12.0	−4.9
26	0.17	0.685		−2.0	0.389	21.6	
12	0.21	0.315		−3.1	0.364	21.4	
29	0.25	0.954		7.3	0.377		
20	0.32	0.461		16.6	0.360		24
11	0.48	0.546		49.7	0.331	25.1	61.9
21	0.52	0.646		49.5	0.293		59.5
33	0.54	0.470		48.4	0.339		60.0
9	0.61	1.10		57.3		25.0	82.0
10	0.66	1.35		71.3	0.314	24.8	95.0
3	0.73	3.04	78	90.8	0.264	19.0	112
16	0.87	8.63	93	103.8	0.285	18.4	124.5
13	0.90	5.50	58	–			
15	0.93	13.7	98	114.0		20.0	
8	0.94	2.83	34	–			
17	0.94	32.9	142	112.5	0.280	17.0	
19	0.95	66.5	157	114.4	0.318	24.0	133.0
18	0.95	54.3	123	116.8	0.260		
$Bn^{2,5}$	1.0	29.3	59	133.0	0.255	16.0	144.0

All $(\bar{S}_z^2)^{0.5}$ values are measured in H_2O–0.1 M NaCl except those of samples 3 and 16, which are measured in TFP solution

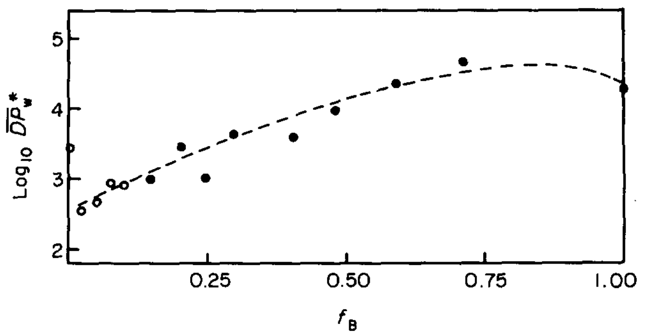

Figure 5 Variation of the normalized weight average degree of polymerization $\overline{DP}_w^*$ of the copolymers with initial monomer feed composition: homogeneous phase (○); heterogeneous phase (●)

All the water-soluble polymers contain more than 0.84 weight fraction of B units, and the variations of their apparent radius of gyration with the actual degree of polymerization were tentatively analysed, neglecting in a first approach their weak fluctuations in composition:

$$(\bar{S}_z^2)^{0.5}\ (\mathrm{nm}) = 1.11 \times \overline{DP}_w^{0.50}$$

correlation coefficient $R(5) = 0.9801$.

$$(\bar{S}_z^2)^{0.5}\ (\mathrm{nm}) = 0.344 \times \overline{DP}_w^{0.57}$$

for the poly(zwitterion)[2] Bn. The decrease of the exponent from 0.57 to 0.50 (characteristic of a θ solvent) when going from the homopolymer to the copolymers is more or less expected and may be readily explained by the very weak solvation of the ethylacrylate A units in water solution. However, the copolymer chain still appears more expanded than that of the homopolymer of the same $\overline{DP}_w$. Polydispersity effects ($\bar{M}_w/\bar{M}_n \sim 2.5$ for copolymer samples, compared with 1.6 for the homopolymer fractions[2]) are not sufficient to take into account this experimental fact, which may arise from the previous assumption (too high apparent $(\bar{S}_z^2)^{0.5}$ values depending on the solvent) and also from intramolecular repulsive interactions between A and B units.

Salt solvation and glass transition in the bulk copolymers

Because of strong ion–dipole interactions between the zwitterions and the ionic species, sulphopropylbetaine homopolymers display the very scarce ability to dissolve mineral salts of widely different lattice energies (NaCl, $LiClO_4$) up to stoichiometric amounts ([salt]/[zwitterion] = 1) to yield amorphous blends[5]. The same complexation is observed for $LiClO_4$– copolymer blends ($[LiClO_4]/[B] \leqslant 1$) over the whole composition range, as checked by the lack of any characteristic diffraction of crystalline $LiClO_4$ in wide angle X-ray scattering patterns.

In d.s.c. experiments, the copolymers essentially show one single glass transition temperature, T_g; see *Table 3*. The T_g variations with composition may be analysed using either the most general Couchman equation[15,16]:

$$\ln T_g = \sum w_i \Delta C_{p,i} \ln T_{g,i} / \sum w_i \Delta C_{p,i} \qquad (1)$$

where $\Delta C_{p,i}$ is the heat capacity increment of component i (weight fraction w_i) at its glass transition temperature $T_{g,i}$, or the most classical Fox equation[17]:

$$T_g^{-1} = \sum w_i T_{g,i}^{-1} \qquad (2)$$

Equation (2) has been shown to be merely a particular form of equation (1) within the framework of simplifying assumptions[15,16] and especially of the Simha–Boyer approximation[18,19] $\Delta C_p T_g = \text{constant}$, which is fulfilled for our systems: $\Delta C_{p,A} T_{g,A} = 105.6\ J\ g^{-1}$, $\Delta C_{p,B} T_{g,B} = 103.6\ J\ g^{-1}$. *Figure 6* shows the good agreement of the experimental data with curves calculated according to both equation (1) and equation (2). The values of the transition width, as measured by $\Delta T = T_2 - T_1$ (see 'Experimental' section), are widely scattered and their variations with composition do not

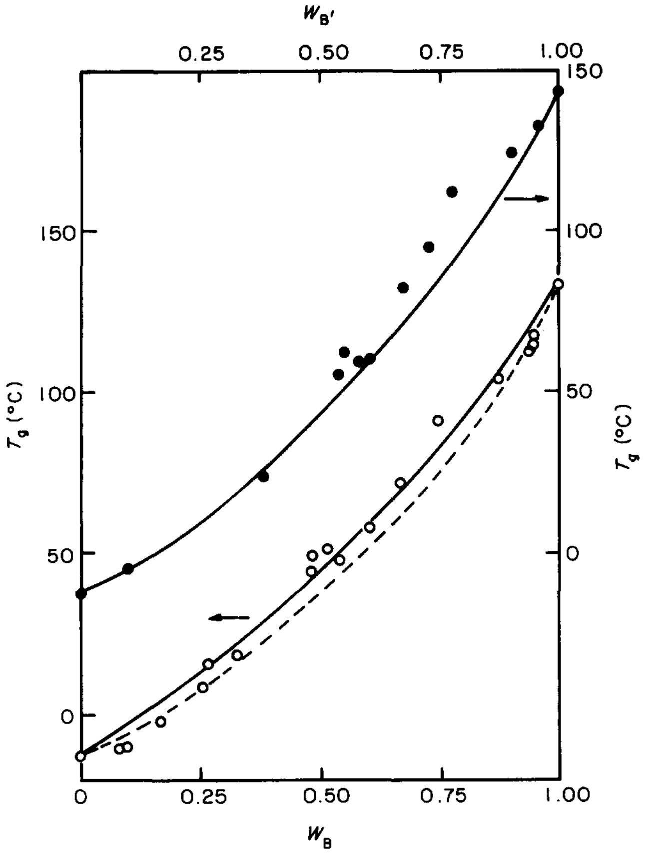

Figure 6 Composition dependence of the glass transition temperatures of the AB copolymers (○) and of their stoichiometric blends with $LiClO_4$ (●). Theoretical curves are calculated according to equation (1) (-----) and equation (2) (———) (identical at the scale of the figure for ●)

seem monotonous (see *Table 3*). However, the broadening of the transition zone with respect to the transition zone of the parent homopolymers is well ascertained, and it suggests increased heterogeneity at the level of chain segments involved in the transition: both compositional polydispersity (which may vary from sample to sample, as shown previously) and possible partial association of the zwitterionic units B in 'multiplets'[6] may contribute together to the observed broadening. Finally, as expected, the heat capacity increments at T_g of the copolymers are roughly a linear function of their weight composition (see *Table 2*):

$$\Delta C_p (\mathrm{J\,g^{-1}}) = 0.408 - 0.147\,w_B, \quad R(17) = 0.9217, \quad \sigma = 0.022$$

Addition of stoichiometric amounts of $LiClO_4$ to the AB copolymers tends to raise their T_g temperatures, as already observed for the $LiClO_4$–Bn homopolymer blends[5]. The T_g variations with composition may be tentatively analysed using the same equations as for the pure copolymers, assuming that the amorphous blends are identical to random AB′ copolymers, where the B′ unit is the stoichiometric complex $LiClO_4$–zwitterion ($w_{B'}$ is the weight fraction of B′ unit in the copolymer), with $\Delta C_p T_g = 116.4\,\mathrm{J\,g^{-1}}$ for B′n. *Figure 6* shows that the agreement between the experimental values and the calculated curves is barely less satisfactory than in the previous case. In any case, the influence of $LiClO_4$ seems definitely weaker than that observed for a number of lithium salt–polyether systems[20–22], where coordination of the cation by the ether oxygen atoms of a few monomeric units drastically increases the T_g values. Since specific interactions between the ion pairs and the zwitterions are very likely, the smoothed effect observed may be tentatively ascribed to a one-to-one interaction, which should be less efficient in decreasing the average segmental mobility. Finally, the transition widths of the AB′ systems are also widely scattered but they appear in most cases greater than those of their corresponding AB precursors: this feature is in good agreement with the increased microheterogeneity of the samples in the presence of $LiClO_4$ over the whole composition range, as suggested by small-angle X-ray scattering data[6].

CONCLUSION

The radical copolymerization of ethylacrylate (A) and 3-[diethyl-2-(2-methacryloyloxyethoxy)ethylammonio]-propanesulphonate (B) in ethanol solution at 60°C obeys the terminal unit model over the whole composition range, and the reactivity ratios are close to those of an ideal system ($r_A r_B = 1$): $r_A = 0.242$, $r_B = 3.93$. The random AB copolymers of high molecular weight thus obtained show the very unusual property of dissolving $LiClO_4$ in stoichiometric amounts ($[LiClO_4]/[B] = 1$) to yield amorphous AB′ blends. For both systems the variations of the glass transition temperature T_g with composition are in good agreement with the Fox equation, $T_g^{-1} = \sum w_i T_{g,i}^{-1}$ with $T_g = -13$, 133 and 144°C for An, Bn and B′n respectively. In spite of their apparent simplicity these zwitterionic systems are better considered as analogous to the cationic vinylpyridinium ionomers[23]. Preliminary small angle X-ray scattering results have already suggested partial association of the highly dipolar B or B′ units in 'multiplets'[6]. The strongly reinforced mechanical properties, especially in the presence of $LiClO_4$, as will be described in a forthcoming communication[24], are consistent with such a specific structure.

ACKNOWLEDGEMENTS

The authors are greatly indebted to Mrs H. Bellissent for her efficient assistance in the experimental work. This work was partly supported by the French Government through a grant to one of us (Y.L.Z.).

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