Random ethylacrylate zwitterionic copolymers: 3. Microphase separation as a function of the zwitterion structure

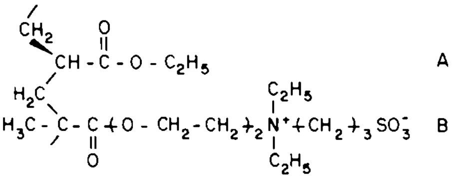
A. Mathis, Y.-L. Zheng and J. C. Galin*
Institut Charles Sadron (CRM-EAHP), CNRS-ULP, 6 rue Boussingault, 67083 Strasbourg-Cedex, France
(*Received 13 September 1990; accepted 5 November 1990*)

The structural characteristics of a series of statistical ethylacrylate (A) copolymers bearing a wide variety of zwitterionic units (B) (i.e. quaternary ammonium carboxy or sulphonato betaine, dicyanomethylid and dicyanoethenolate), were analysed by differential scanning calorimetry and small angle X-ray scattering (SAXS, 20–100°C). For low to moderate B content (0.07 < molar fraction, $F_B < 0.20$) all the copolymers and their stoichiometric amorphous blends with $LiClO_4$ ($[LiClO_4]/[B] = 1$) show a single glass transition temperature (T_g) and a very characteristic SAXS peak, still present in the liquid state ($T_g + 50°C$) which corresponds to correlation distances in the range 30–50 Å. Microphase separation of the zwitterionic units B, in dipolar domains dispersed in the weakly polar A matrix, occurs systematically whatever the structure of the zwitterion (dipole moment in the range $3–10 \times 10^{-29}$ C m) and its relative position with respect to the chain backbone.

(Keywords: ethylacrylate zwitterionic copolymers; ammonium carboxy and sulphonato betaines; ylid and dicyanoethenolate; glass transition temperature; SAXS analysis; microphase separation)

INTRODUCTION

In three preceding papers we described the synthesis[1] and the characterization[2,3] of a series of statistical copolymers of ethylacrylate (A) and 3-[diethyl-2-(2-methacryloyloxyethoxy)ethylammonio]propanesulphonate (B) of the following structure:



Structural studies by small angle X-ray scattering (SAXS)[2] and by dynamic mechanical spectroscopy[3] have clearly shown that these quasi-Bernoullian copolymers (product of reactivity ratios $r_A \times r_B = 0.95$) for low to moderate B content (molar fraction, $F_B < 0.36$) and their amorphous stoichiometric blends with $LiClO_4$ ($[LiClO_4]/[B] = 1$) display a very characteristic two-phase structure; zwitterionic units B segregate in microdomains of about 20 Å diameter dispersed in the A matrix according to a liquid-type order. The dipolar microdomains, specially in the presence of salt, behave as relatively stable physical cross-links which lead to an increase of the rubbery plateau modulus and to a strongly extended rubbery zone with respect to poly(ethylacrylate). By analogy with the well-known ionomers[4–6], the main driving force of the observed microphase separation has to be found in the strong specific dipole–dipole interactions between the zwitterionic B units (and additionally ion–dipole interactions in presence of $LiClO_4$) within the liquid A matrix ($T_g(An) = -13°C$). This matrix has no true solvation properties towards the highly dipolar B units[3] in spite of its weak polarity (for An, average dipole moment[7] per monomeric unit $(\bar{\mu}^2/N)^{0.5} = 3.40 \times 10^{-30}$ C m; dielectric permittivity[8], $\varepsilon = 7$ at 20°C). For a given A matrix, microphase separation should obviously be dependent on structural features of the zwitterionic B unit. In the previous case, it is probably favoured by two complementary factors: (i) the very high dipole moment of the quaternary ammonium sulphonatopropylbetaine: 8.7×10^{-29} C m as measured in water solution for triethylammonium propylsulphonate[9] *versus* 6.9 and 9.2×10^{-29} C m for the theoretically calculated values of the more stable curled and the extended conformations respectively[10]; (ii) the presence of a flexible spacer of two oxyethylene units between the chain backbone and the zwitterionic moiety which avoids steric hindrance and thus optimizes the possibilities of intra- and intermolecular dipolar interactions between B units.

The purpose of this paper is to present a screening study of the influence of the structure of the zwitterionic monomer B on the microphase separation in the ethylacrylate statistical copolymers. Small angle X-ray scattering measurements were systematically performed on a single sample for every zwitterionic structure on copolymers of low to moderate B content ($0.05 < F_B < 0.20$), in either the absence or presence of added salt ($[LiClO_4]/[B] = 1$): the occurrence of a characteristic and well defined scattering peak was considered as unambiguous proof of a biphasic structure. The comonomer B was varied over a wide range of structures to allow a first evaluation of the role of the position of the zwitterion with respect to the main chain, of its dipole moment and of the polarizability of its anionic site. The various zwitterionic structures are depicted in *Table 1*.

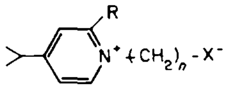
---

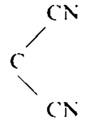
* To whom correspondence should be addressed

0032-3861/91/173080-06

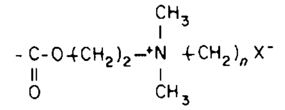
Table 1 Structure of the various zwitterionic units B

Vinylpyridine (VP) series

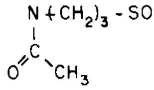
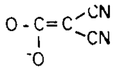


X	n	Isomer	R	Symbol
SO_3	3	2-vinyl	H	2VPSB(3)
SO_3	3	5-vinyl	CH_3	2M5VPSB(3)
SO_3^-	3	4-vinyl	H	4VPSB(3)
	0	4-vinyl	H	4VPY(0)

Dimethylaminoethylmethacrylate (M) series



$$-\underset{\underset{O}{\|}}{C}-O-(CH_2)_2-{}^{+}\underset{CH_3}{\overset{CH_3}{N}}-(CH_2)_n X^-$$

X	n	Symbol
CO_2^-	1	MCB(1)
CO_2	2	MCB(2)
SO_3	2	MSB(2)
SO_3^-	3	MSB(3)
SO_3^-	4	MSB(4)
	2	MSB(6)
	2 3	MCN(3) MCN(4)

The nomenclature of B units recalls the aminoprecursor and the chemical structure of the zwitterion using an integer within brackets related to the number of carbon or heteroatoms between the opposite charges: for instance, 2M5VPSB(3) stands for 2-methyl-5-vinylpyridinium sulphonatopropylbetaine.

EXPERIMENTAL

Solvents and monomers

Solvents (dimethylformamide, DMF; acetonitrile, ACN; tetramethylenesulphone, $TMSO_2$; acetone; isopropanol, iPrOH; methanol) were purified by distillation over convenient drying reagents (H_2Ca for DMF, P_2O_5 for ACN) according to literature procedures[11]. Ethylacrylate (A) was vacuum distilled over H_2Ca and all the sulphonatopropylbetaine monomers were synthesized and purified as previously described[12]. β-[N,N-dimethyl-N-(β-methacryloyloxyethyl)]propiobetaine, MCB(2), was obtained through ring-opening of β-propiolactone by N,N-dimethylaminoethylmethacrylate[13].

Quaternization reagents

Sodium bromoacetate (BANa) and sodium 2-bromoethanesulphonate (BESNa) were prepared by neutralization of the corresponding acids in aqueous solution followed by freeze-drying. Tetracyanoethyleneoxide (TCNEO)[14], dicyanoethylene or propylene keteneacetals (DCKEA and DCKPA respectively)[15], (methyl-2-oxazolinium-1,3)-3 propanesulphonate[16] (MOXZPS) were obtained according to literature procedures. Propane and butane sultones (PS and BS respectively) were purified by vacuum distillation.

Synthesis of the zwitterionic copolymers

The experimental device and the general procedures are similar to those previously described[1,12]. Copolymerizations were carried out at 60°C in ethanol solution, in the presence of azo-bis-isobutyronitrile (AIBN) as radical initiator, as detailed later. The copolymers were recovered by rotary evaporation of the solvent and of monomer A, solubilization of the residue in ethanol and precipitation into a large excess of water. The quaternization reactions of the amino polymeric precursors (initial polymer concentration of 8% w/v) were performed under a variety of experimental conditions adjusted to the nature of the quaternization reagent. The copolymer recovery and purification were carried out according to the following procedures: for runs 1 to 3, precipitation in ethylether, solubilization of the residue in ethanol and reprecipitation into ethylether; for runs 4, 5 and 7, precipitation into water; for run 6, precipitation into ethylether, dispersion of the residue into water–ethanol mixture (9:1 v/v), dialysis for 48 h repeated three times (cellulosic Spectrapor membranes of molecular weight cut-off 3500) followed by freeze-drying; for runs 8 and 9, rotary evaporation of the solvent, dispersion of the residue in water, dialysis for 48 h followed by freeze-drying.

All the copolymer samples were dried at 60°C under 1.3 Pa for at least 24 h and stored in a desiccator; they were further dried overnight in the same conditions before any measurement. Copolymer composition was derived from N and S elemental analyses and from potentiometric measurements according to literature[17] using $HClO_4$ as titrating reagent in acetic acid as solvent. This system allows quantitative titration of the more basic functions such as free amino functions or the carboxylate anion of the ammonium carboxybetaines:

$$>N^+-(CH_2)_n-CO_2^- \quad (n=1,2)$$

Lithium perchlorate–zwitterionic copolymer blends

Stoichiometric amorphous $LiClO_4$–copolymer blends ($[LiClO_4]/[B] = 1$) were obtained by evaporation of their solution in trifluoroethanol[1,2] and were dried as the pure copolymers.

Physical characterization of the copolymers

Weight average molecular weights, $\bar{M}_w$ were derived from light scattering measurements at room temperature (Fica PGD 420, OM apparatus, $\lambda = 632$ nm, methanol or trifluoroethanol as solvents[1]). Differential scanning calorimetry (d.s.c.) measurements (Perkin-Elmer DSC-2 or DSC-4 apparatus, 10–15 mg samples) involved repetition of the following heating–cooling sequences until reproducible scans were obtained[1] (usually after the third time): heating to $T_g + 50°C$ at a rate of $20°C\,min^{-1}$, annealing for 5 min at this temperature, cooling to $T_g - 70°C$ at a rate of $40°C\,min^{-1}$ and annealing for 5 min. The glass transition temperature T_g was measured at the midpoint of the base line shift ($\Delta C_p/2$, ΔC_p being the heat capacity increment) with an accuracy of $\pm 1.5°C$. Wide and small angle X-ray scattering (WAXS and SAXS respectively) measurements were carried out as previously described[2] (X-ray beam wavelength $\lambda = 1.54$ Å, linear detector for quantitative analysis) between room temperature and 100°C. Films of poly(ethylacrylate) doped with known amounts (0.005–0.05 molar fraction) of 4-ethylpyridinium dicyanomethylide[18] were obtained by slow evaporation of their dilute solution in trifluoroethanol deposited on a quartz plate, and their u.v. spectra were directly recorded on a Cary 2300 spectrometer.

Dipole moments of some zwitterionic model compounds

Dipole moments were calculated from dielectric measurements in dilute solution, as detailed elsewhere[9]: pyridinium, 2-ethylpyridinium and triethylammonium sulphopropylbetaines in water solution; triethylammonium sulphoethyl and sulphobutylbetaines in water solution; triethylammonium *N*-ethoxy and *N*-propoxy dicyanoethenolates in trifluoroethanol solution.

RESULTS AND DISCUSSION

Synthesis of the ethylacrylate zwitterionic copolymers

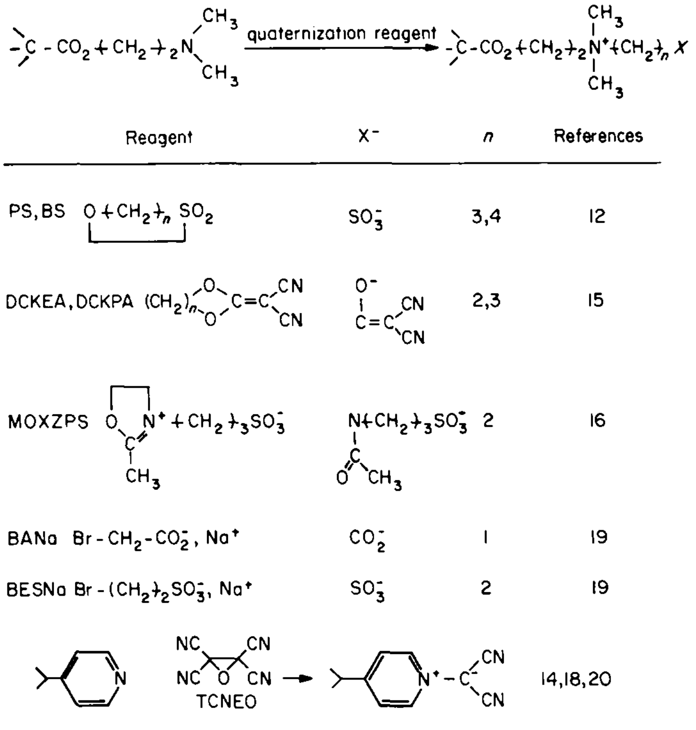
All the copolymers were synthesized either by direct radical copolymerization of ethylacrylate (A) with zwitterionic comonomers or by functionalization of statistical ethylacrylate copolymers bearing tertiary amino functions (from 4-vinylpyridine, 4VP, or dimethylaminoethyl methacrylate, M) through quaternization by suitable electrophilic reagents.

Radical copolymerization of ethylacrylate with amino or zwitterionic comonomers. The copolymerizations, carried out at 60°C in ethanol solution in the presence of AIBN as radical initiator, were stopped at moderate conversion (generally less than 25%) to avoid too strong a chemical heterogeneity. The experimental results given in *Table 2* suggest that copolymerization is faster with methacrylic comonomers than with the vinylpyridines, and that ethylacrylate is the less reactive species in all cases: the molar fraction of the amino or zwitterionic comonomer in the copolymer is about 2–4 times higher than its corresponding value in the monomer feed.

Quaternization of ethylacrylate precursor copolymers bearing amino functional groups. The reactions detailed in *Scheme 1* were carried out by transposition of closely related literature procedures.

Three main features may be derived from the experimental results given in *Table 3*.

First, the copolymer recovery and purification are not easy and mechanical losses may be rather high, especially



Scheme 1

Table 2 Amino (N) precursor copolymers and zwitterionic (B) copolymers obtained by copolymerization at 60°C in ethanol solution

Run	Copolymer	$[M]^a$ $(mol\,l^{-1})$	$f_N{}^b$	$f_B{}^b$	$[AIBN]10^2$ $(mol\,l^{-1})$	t (min)	Yield (%)	$F_N{}^b$	$F_B{}^b$	$\bar{M}_w \times 10^{-5c}$
1	A-M	1	0.076		0.59	60	23	0.170		0.743
2	A-M	1	0.074		0.47	85	24	0.145		0.513
3	A-4VP	1	0.076		0.79	240	20	0.194		0.344
4	A-MCB(2)	3		0.10	0.50	60	44		0.151	0.257
5	A-2VPSB(3)	1		0.023	0.47	135	11		0.095	6.13
6	A-2M5VPSB(3)	0.49		0.021	0.49	210	8		0.081	0.106

[a] [M] is related to the total monomer concentration

[b] f_i and F_i are related to the molar fraction of monomer *i* in the comonomer feed and in the copolymer respectively (N and B = amino and zwitterionic monomers respectively)

[c] $\bar{M}_w$ measured by light scattering in methanol solution

Table 3 Quaternization of the amino precursor copolymers

Run	Precursor Ref.	F_N	Reagent	R[a]	Solvent	t (°C)	Time (h)	Copolymer recovery (%)	F_B[b]	$\bar{M}_w \times 10^{-4}$ Calc.	$\bar{M}_w \times 10^{-4}$ Exp.
1	A-M1	0.170	PS	2.0	$TMSO_2$	120	6	64	0.170	8.89	8.18
2	A-4VP	0.194	PS	2.0	$TMSO_2$	120	6		0.194		
3	A-M2	0.145	BS	2.0	ACN	80	24	72	0.145	6.07	6.50
4	A-M2	0.145	DCKEA	1.2	Acetone	30	18	65	0.145	6.06	
5	A-M2	0.145	DCKPA	1.2	Acetone	30	18	93	0.145	6.16	
6	A-M1	0.170	MOXZPS	1.2	DMF	120	4	38	0.158		
7	A-4VP	0.194	TCNEO	2.5	$TMSO_2$	50	18	95	0.132	3.96	
8	A-M1	0.170	BANa	3.0	iPrOH:5 vol. MeOH:2 vol.	80	24	33	0.155	5.67	
9	A-M2	0.145	BESNa	3.0		80	24	46	0.120	5.87	5.87

[a] R = (Quaternization reagent)/(amino function)
[b] The quaternization yield is given by $(F_B/F_N) \times 100$

when dialysis is involved (runs 6, 8 and 9). In the case of MOXZPS, the quaternization reagent and the functionalized copolymer are both zwitterionic species of similar solubility properties and, in spite of repeated dialysis, the reagent identified by thin layer chromatography (R_F in $CH_3OH{=}0.51$) cannot be quantitatively eliminated.

Second, nucleophilic ring-opening of the cyclic quaternization reagent by tertiary amine in dipolar aprotic solvents (runs 1 to 7) is in most cases quantitative. The reactions involving the sodium salts of brominated acids, which proceed with elimination of sodium bromide, require alcoholic solvents to dissolve the reagents. In spite of a drastically less favourable reaction medium for amine quaternization, yields are still fairly high (runs 8 and 9) and the residual amino functions have no significant influence for the structural studies reported further.

Third, the experimental values of the weight average molecular weights of three representative zwitterionic copolymers are in very good agreement with those calculated taking into account the molecular weight increase of the quaternized unit and the quaternization yield: runs 1, 3 and 9. Even in the most drastic experimental conditions (heating for 6 h at 120°C in run 1) no degradation or cross-linking occurs[12].

Finally, the copolymers derived from a common precursor have both identical composition and identical zwitterion distribution (runs 3–5 of *Table 3*). Direct copolymerization of ethylacrylate with zwitterionic monomers does not allow such microstructure control (different reactivity ratios for every comonomer pair).

Glass transition of the zwitterionic copolymers and of their blends with $LiClO_4$

All the copolymers and their stoichiometric amorphous blends with $LiClO_4$ (see further discussion on SAXS experiments) show one single T_g and their variations from sample to sample cannot be analysed quantitatively because they obviously depend on both the zwitterion structure and on the copolymer composition (see *Table 4*). However, some general trends may be well ascertained.

The introduction of highly dipolar units in the chain significantly increases the glass transition temperatures with respect to those of the corresponding amino precursors ($T_g \simeq -12.5$°C for A-M and $T_g \simeq 10$°C for A-4VP). The strongest increase, of $\Delta T_g \simeq 100$°C, noticed for A-4VPSB(3) is consistent with the fact that the homopolymer poly[4VPSB(3)] has a very high T_g above 230°C (not accessible before decomposition), probably the highest of all the zwitterionic homopolymers already studied[22].

Within the relatively narrow composition range under study (0.17 < weight content, $W_B < 0.40$), T_g is an increasing function of W_B in zwitterionic units, whatever their structure.

The addition of stoichiometric amounts of $LiClO_4$ to the zwitterionic copolymers systematically yields a significant but relatively low increase of the glass transition temperature. This effect, in the range 3–20°C, is stronger for the systems of higher zwitterion and salt content.

These three sets of experimental data are quite consistent with those related to the series of ethylacrylate zwitterionic copolymers previously studied[1]. More especially, for aliphatic copolymers of zwitterion content $W_B = 0.26$–0.40, the T_g range observed in this work, 16–66°C, is fairly compatible with the previous range, 14–31°C, taking into account the variety of dipolar structures involved in the new samples.

X-Ray scattering patterns of the zwitterionic copolymers and of their blends with $LiClO_4$

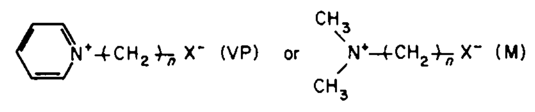
The X-ray scattering patterns are very similar to those previously observed[2].

The WAXS patterns, insensitive to the presence of salt (no trace of crystallization), show systematically a broad diffusion band at about 5 Å and, in most cases, a second broad halo in the range 8.5–9.1 Å. They are specific to poly(ethylacrylate) long blocks since such a diffusion is generally observed in amorphous polymers and may be ascribed to short range order related to the closest approach distance between the polymer chains[23].

The SAXS patterns show a scattering peak corresponding to distances d and d' within the range 30–50 Å (see *Table 4*). The peak becomes better resolved in the presence of stoichiometric amounts of $LiClO_4$ but without significant fluctuation in position, and it is barely shifted towards longer distances by a temperature increase of up to 100°C, well above the glass transition temperature (for copolymer A-MCB(1), for instance, $d = 32.5$ and 34.5 Å at 25 and 80°C respectively). This quasi-insensitivity to temperature is especially evident for copolymer A-MCB(2) where a rearrangement of the

Table 4 Dipole moments μ of the zwitterionic units, glass transition temperatures (d.s.c.) and and average correlation distances (SAXS) of the pure copolymers (T_g, d) and of their stoichiometric blends with $LiClO_4$ (T'_g, d')

Zwitterionic structures



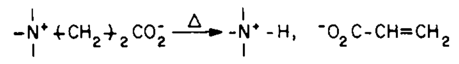
					Pure copolymers		LiClO₄ blends	
Reference	X^-	n	μ (C m)[a] ($\times 10^{-30}$)	W_B	T_g (°C)	d (Å)	T'_g (°C)	d' (Å)
A-2VPSB(3)	SO_3^-	3	85[b]	0.192				30.5
A-2M5VPSB(3)	SO_3^-	3		0.175		47.5		44.5
A-4VPSB(3)	SO_3^-	3	83[b]	0.353	108.0	30.5	126.0	30.5
A-4VPY(0)	$C(CN)_2$	0	31 (ref. 24)	0.204	22.5	30.0		
A-MCB(1)	CO_2^-	1	52[c]	0.283	16.0		26.0	33.0
A-MCB(2)	CO_2^-	2	65[c]	0.289				33.0
A-MSB(2)	SO_3^-	2	71[b]	0.265	35.5	31.0	38.5	33.0
A-MSB(3)	SO_3^-	3	83[b]	0.364	66.0	31.5	77.0	33.0
A-MSB(4)	SO_3^-	4	96[b]	0.332	57.5		77.5	38.0
A-MSB(6)	SO_3^-	6	94[b]	0.406		39.0		
A-MCN(2)	$O-C=C(CN)_2$	2	88[b]	0.332	48.0	34.5		36.0
A-MCN(3)	$-O$	3	99[b]	0.342	49.5	36.0		

[a] $1\ C\ m = 3 \times 10^{29} D$

[b] From dielectric measurements on model compounds: see Experimental

[c] μ values identified with those of the corresponding amino acids $^+NH_3-(CH_2)_n-CO_2^-$ (ref. 25)

zwitterion into an ammonium acrylate ion-pair[13] may occur above 70°C:



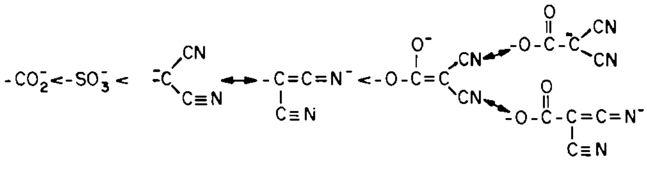
$$-\overset{|}{\underset{|}{N}}{}^+-(CH_2)_2CO_2^- \xrightarrow{\Delta} -\overset{|}{\underset{|}{N}}{}^+-H,\ {}^-O_2C-CH=CH_2$$

The limited experimental data do not allow correlation of the small variations of d and d' with the copolymer composition or with the zwitterion structure. However, comparison with the corresponding data related to the previously studied ethylacrylate zwitterionic copolymers[2] (see structural formula in the Introduction) is instructive for two reasons: (i) the correlation distances d are in fairly good agreement with the expected ones; compare for instance $d = 31.5$ Å for copolymer A-M5B(3) with $d = 36.0$ Å for the analogous sample of identical composition W_B in reference 2; (ii) the systematic decrease of the correlation distance observed in the presence of $LiClO_4$ ($d' \simeq d - 6$ Å, over a broad composition range) cannot be detected on the copolymers under study, and the reason for such a discrepancy still remains obscure.

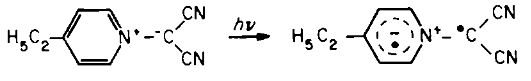
Thus all the zwitterionic copolymers show a characteristic microphase separation of the dipolar units in the apolar ethylacrylate matrix, both in the glassy and in the liquid state. The salt $LiClO_4$, selectively located in the zwitterionic microdomains (strong specific ion-dipole interactions), increases their electronic contrast with the matrix and probably improves the phase separation (sharper interface arising from enhanced interfacial tension). Microphase separation is actually observed whatever the structure and position of the zwitterionic moiety with respect to the chain backbone. These two factors are worth further discussion.

For a given zwitterionic structure, such as sulphopropylbetaine SB(3), the presence of a long spacer to disconnect the dipolar moiety from the chain backbone, as in the previous series of copolymers studied[2], is unnecessary: see the vinylpyridinium and the A-MSB(3) copolymers. Moreover, steric hindrance close to the zwitterion, as in the 2-vinylpyridinium A-2VPSB(3) or in the 2-methyl-5-vinylpyridinium A-2M5VPSB(3) samples, does not sufficiently weaken the dipolar interactions between B units to inhibit microphase separation. However, steric hindrance has been recognized as a very critical factor for ion-dipole interaction in aqueous dilute solutions of poly(zwitterions) and salts[24].

In the same way, the zwitterion structure, as reflected by its anion polarizability and its dipole moment ($3 \times 10^{-29} < \mu(C\ m) < 12 \times 10^{-29}$, see measured and estimated values in *Table 4*), does not appear of major importance for the definition of SAXS patterns. The polarizabilities of the anionic sites may be ordered as follows:



The dicyanoethenolate anion shows multiple resonance structures. The electrostatic interactions with the lithium cation of the added salt are expected to depend more or less on the polarizability of the anionic site. As already noticed (see Introduction), microphase separation is favoured by zwitterionic units of very high dipole moments. Its occurrence in the pyridinium dicyanomethylide A-4VP(0) is of special interest since this zwitterion has the lowest dipole moment ($\mu = 3.1 \times 10^{-29}$ C)[25], lower than those of the classical ammonium ion pairs ($\mu \simeq 4 \times 10^{-29}$ C m)[26] found in some cationic ionomers[27–29]. The solvation power of the ethylacrylate matrix towards the dipolar units may be tested on model systems, using the solvatochromy of poly(ethylacrylate) films doped with increasing amounts of 4-ethylpyridinium dicyanomethylide. The long wavelength transition of this ylid arises from the formation of an intramolecular charge transfer complex and shows an enhanced sensitivity to its microenvironment polarity, which may be estimated by an 'apparent local dipole moment', μ^*, directly derived from the measured transition energy[18,22] E_T:



$$E_T\,(\mathrm{kJ\ mol^{-1}}) = \frac{11.964 \times 10^4}{\lambda\,(\mathrm{nm})}$$

$$\mu(\mathrm{D}) = 0.20E_T - 56.6$$

$$(1\ \mathrm{D} = 3.34 \times 10^{-30}\ \mathrm{C\ m})$$

When increasing the [ylid]/[ethylacrylate] molar ratio from 0.005 to 0.05 the visible spectrum of the doped films changes from one single well defined absorption peak at 401.4 nm ($\mu^* \simeq 9 \times 10^{-30}$ C m) to a broader band showing a maximum at 387.8 nm ($\mu^* \simeq 16 \times 10^{-30}$ C m) and a shoulder at 328.8 nm ($\mu^* \simeq 53 \times 10^{-30}$). These hypsochromic shifts are very characteristic of a strong increase of the polarity of the ylid microenvironment, and the shoulder is probably representative of ylid 'multiplets' stabilized by specific dipole–dipole interactions. The microphase separation observed in the A-4VPY(0) copolymer is thus very consistent with the segregation of the ylid in the poly(ethylacrylate) doped films.

CONCLUSION

With respect to SAXS measurements and within a relatively narrow composition range ($0.17 < W_B < 0.40$), the statistical ethylacrylate zwitterionic copolymers under study show microphase separation either in the absence or in presence of stoichiometric amounts of $LiClO_4$ ($[LiClO_4]/[B] = 1$), and either in the glassy or the liquid states. The widely varying structure of the zwitterionic units (dipole moment μ in the range $3–10 \times 10^{-29}$ C m (9–33 D)) is probably a decisive factor of the sharpness of the microphase separation and of the cohesion and stability of the dipolar microdomains dispersed in the weakly polar ethylacrylate matrix. Dynamic mechanical spectroscopy studies would be sensitive to such differences. Finally all the experimental results obtained on our copolymers or on similar systems[30–32] and the theoretical calculations on the association of low molecular weight zwitterionic species[10] suggest that statistical quaternary ammonium zwitterionic copolymers may be better candidates than their homologous cationic ionomers[27–29] for biphasic materials of potential technological interest. The possibility of structure control by selective solubilization of added salt in the dipolar microdomains is a very specific and interesting feature of these materials.

ACKNOWLEDGEMENTS

This work was supported in part by the French Government through a grant to Y.L.Z., and the authors gratefully acknowledge Mrs H. Bellissent for technical assistance in the polymer synthesis.

REFERENCES

1 Zheng, Y.-L., Galin, M. and Galin, J. C. *Polymer* 1988, **29**, 724
2 Mathis, A., Zheng, Y.-L. and Galin, J. C. *Makromol. Chem., Rapid Commun.* 1986, **7**, 333
3 Bazuin, C. G., Zheng, Y.-L., Muller, R. and Galin, J. C. *Polymer* 1989, **30**, 654
4 Eisenberg, E. and King, M. 'Ion Containing Polymers', Academic Press, New York, 1977
5 MacKnight, W. J. and Earnest Jr, T. R. *J. Polym. Sci., Macromol. Rev.* 1981, **16**, 41
6 Bazuin, C. G. and Eisenberg, A. *Ind. Eng. Chem. Prod. Res. Dev.* 1981, **20**, 271
7 Pohl, H. A. and Zabusky, H. H. *J. Phys. Chem.* 1962, **66**, 1390
8 Williams, G. and Watts, D. C. *Am. Chem. Soc., Div. Polym. Chem., Polym. Prepr.* 1972, **12**(1), 79
9 Galin, M., Chapoton, A. and Galin, J. C. in preparation
10 Bredas, J. L., Chance, R. R. and Silbey, R. *Macromolecules* 1988, **21**, 1633
11 Riddick, J. A., Bunger, W. B. and Sakano, T. K. 'Organic Solvents', 4th Edn, John Wiley, New York, 1986
12 Monroy Soto, V. M. and Galin, J. C. *Polymer* 1984, **25**, 121
13 Asonova, T. A., Zezin, A. B. and Razvodovskii, Ye. F. *Polym. Sci. USSR* 1974, **16**, 896
14 Bieche, A. and Dietrich, P. *Chem. Ber.* 1963, **96**, 3044
15 Middleton, W. J. and Engelhardt, V. A. *J. Am. Chem. Soc.* 1958, **80**, 2788
16 Forestière, A. and Sillion, B. *J. Heterocyclic Chem.* 1980, **17**, 1381
17 Tamikado, T. *J. Polym. Sci.* 1960, **43**, 489
18 Lopez-Velasquez, D. and Galin, J. C. *Macromolecules* 1986, **19**, 1096
19 Bartlett, P. L. US Patent 3,839,425, 1974
20 Cottart, J. J., Loucheux, C. and Lablache-Combier, A. *J. Appl. Polym. Sci.* 1981, **26**, 1233
21 Haberfield, P., Nudelman, A., Bloom, A., Romm, R. and Giasberg, H. *J. Org. Chem.* 1971, **36**, 1792
22 Galin, M., Marchal, E., Mathis, A., Meurer, B., Monroy Soto, V. M. and Galin, J. C. *Polymer* 1987, **28**, 1937
23 Plate, N. A. and Shibaev, V. P. *J. Polym. Sci., Macromol. Rev.* 1974, **8**, 117
24 Wielema, T. A. and Engberts, J. B. F. N. *Eur. Polym. J.* 1987, **12**, 947
25 Treiner, C., Skinner, J. F. and Fuoss, R. M. *J. Phys. Chem.* 1964, **68**, 3406
26 Grunwald, E., Highsmith, S. and Ting-Po, I. in 'Ions and Ion-pairs in Organic Reactions' (Ed. M. Szwarc), John Wiley, New York, 1974, Vol. 2, p. 448
27 Gauthier, S., Duchesne, D. and Eisenberg, A. *Macromolecules* 1987, **20**, 753
28 Bazuin, C. G. and Eisenberg, A. *J. Polym. Sci. Part B Polym. Phys.* 1986, **24**, 1121
29 Duchesne, D. and Eisenberg, A. *Am. Chem. Soc. Polym. Prepr.* 1984, **25**, 116
30 Clough, S. B., Cortelek, D., Nagabhushanam, T., Salamone, J. C. and Watterson, A. C. *Polym. Eng. Sci.* 1984, **24**, 385
31 Salamone, J. C., Elayaperumal, P., Clough, S. C., Watterson, A. C. and Bibbo, M. A. *Am. Chem. Soc. Polym. Prepr.* 1986, **27**, 323
32 Neculescu, C., Clough, S. B., Elayaperumal, P., Salamone, J. C. and Watterson, A. C. *J. Polym. Sci., Polym. Lett. Edn* 1987, **25**, 201