n-Butyl acrylate zwitterionomers of the ammonioethoxydicyanoethenolate type: 1. Synthesis

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Radical copolymerization of n-butyl acrylate (A) and 2,2-dicyano-1-[2-(2-(acryloyloxy)ethyl)dimethylammonioethoxy] ethenolate (B) initiated at 60°C by 4,4'-azobis-4-cyanovaleric acid (ACVA) was studied in two complementary systems: homogeneous phase in dimethylformamide (DMF) and heterogeneous phase in aqueous ethanol (water volume fraction 0.4). In DMF ($[A+B] \sim 0.6$–$1\ mol\ l^{-1}$, $[ACVA]/[A+B] = 5 \times 10^{-3}$, molar fraction of monomer B in the comonomer feed $f_B \leqslant 0.7$), the copolymerization obeys the terminal unit model and the two monomers of identical acrylate structure behave as an ideal azeotropic comonomer pair: reactivity ratios $r_A \sim r_B \sim 1$. In aqueous ethanol ($[A+B] \sim 0.6$–$2\ mol\ l^{-1}$, $[ACVA]/[A+B] = 5 \times 10^{-3}$, $f_B \leqslant 0.8$), the unusual composition diagram (apparent reactivity ratios $r_A, r_B > 1$) probably results from preferential sorption of either monomer by the insoluble growing macroradicals: the experimental data may be reconciled with the terminal unit model and with invariant 'intrinsic' reactivity ratios ($r_A \sim r_B \sim 1$) within the simplified framework that stresses the major importance of the ratio of the binding constants of monomers A and B to the growing chain ($K = k_{AA}/k_{BB} \sim 0.49$). Moreover, copolymerization in heterogeneous phase leads to higher molecular weights. The zwitterionic units significantly increase the copolymer chain sensitivity towards thermal degradation: an irreversible and rather slow first-order rearrangement of the zwitterionic structure occurs for temperatures higher than 150°C ($K \sim 2.8 \times 10^{-6}\ s^{-1}$ at 160°C), well before the initial weight loss observed at about 260°C under nitrogen.

(Keywords: zwitterionomers; radical copolymerization; n-butyl acrylate)

INTRODUCTION

According to previous work in our laboratory, amorphous statistical copolymers of n-butyl acrylate (A) containing low to moderate amounts (molar fraction ~0.04–0.35) of zwitterionic units bearing a quaternary ammoniopropanesulfonate side group ($-N^+-(CH_2)_3-SO_3^-$) are easily synthesized by free-radical copolymerization[1] and show a very typical two-phase morphology. It is characterized by the dispersion of zwitterion-rich and 'hard' microdomains in a nearly pure butyl acrylate 'soft' matrix. This heterogeneous structure was derived without any ambiguity from a number of salient experimental features, such as:

(i) the identification of two well defined glass transitions (differential scanning calorimetry) supported by the analysis of chain dynamics through ^1H broad-line nuclear magnetic resonance spectroscopy[2];

(ii) the presence of the so-called 'ionic peak' in the small-angle X-ray scattering patterns[2];

(iii) the occurrence of spin diffusion over rigid microdomains observed through ^{13}C dipolar-decoupled magic-angle spinning n.m.r. spectroscopy[3];

(iv) the enhanced dynamic mechanical properties, similar to those of a thermoplastic elastomer[4]; and

(v) the possibility of preferential or selective plasticization of this two-phase material by additives of well adjusted polarity[5].

The close analogy with the well known ionomers[6–10] is quite evident, and the recent structural model proposed by Eisenberg *et al.*[11] may be easily transposed to these zwitterionomers. Strong dipole–dipole interactions between the zwitterionic units[12] within the very mobile and weakly polar butyl acrylate matrix are the main driving force for the primary aggregation of the zwitterions in 'multiplets'. The overlap of regions of reduced mobility anchored to the multiplets, which occurs progressively as the zwitterion content of the material increases, results in the emergence of rigid 'clusters' of sufficient size to show their own glass transition.

The general purpose of the present series of communications is the comprehensive analysis of the structure–property correlations for new amorphous zwitterionomers of potential enhanced properties considered either as bulk materials or as functionalized latexes (arising from emulsion polymerization).

The two comonomers depicted, n-butyl acrylate (A) and 2,2-dicyano-1-[2-(2-(acryloyloxy)ethyl)dimethylammonioethoxy] ethenolate (B), were selected in order to fulfil essentially two complementary requirements:

(i) The presence of a weakly polar butyl acrylate matrix of high mobility is a decisive factor for the development

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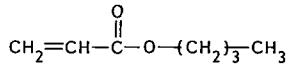
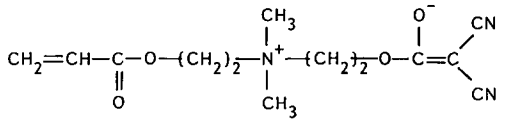


A



B

of a two-phase morphology: compare, for instance, microphase separation, restricted to multiplet aggregation in ethyl acrylate zwitterionomers ($T_g(A_n) = -13°C$) bearing a variety of dipolar units[13], with the two-phase (clustered) structure of n-butyl acrylate zwitterionomers[2] ($T_g(A_n) = -46°C$).

(ii) The presence of zwitterionic units of high dipole moment but of rather low hydrophilicity favours the emergence of rigid domains showing less sensitivity to potential selective plasticization by moisture[5]. The ammonioethoxydicyanoethenolate structure, recently introduced in macromolecular chemistry[14], appears very promising with respect to both requirements: compare, for instance, the dipole moments $\mu = 24.0$ and 25.9 D ($1\ D = 3.336 \times 10^{-30}$ C m) for the triethylammoniopropanesulfonate and ethoxydicyanoethenolate model compounds[15], respectively, and the number of site-bound water molecules per zwitterionic unit, $n \sim 2.0$[16] and 0.45[17], in the corresponding methacrylic polymers, respectively.

The first part of this series of communications is devoted to the synthesis, the molecular characterization and the thermal stability of the zwitterionomers, with special emphasis on the comparison of the free-radical copolymerization of the two comonomers in homogeneous and heterogeneous phase: solution of the monomers in dimethylformamide (DMF) and in aqueous ethanol, respectively. The first process was assumed to allow the calculations of reliable values of the characteristic reactivity ratios r_A and r_B, while the second one was considered in a first approach as 'intermediate' between homogeneous solution copolymerization and emulsion copolymerization, which will be described elsewhere.

In all the following text A and B will refer to the non-polar and zwitterionic monomers, respectively; f_i and F_i to the molar fraction of monomer i (A or B) of molar mass M_i in the monomer feed and in the corresponding copolymer, respectively.

EXPERIMENTAL

Monomers, reagents and solvents

n-Butyl acrylate was purified by vacuum distillation over CaH_2 and safely stored at 5°C without autopolymerization. The zwitterionic monomer (monomer B) was prepared as previously described[14]. 4,4'-Azobis-4-cyanovaleric acid (ACVA) was recrystallized according to a literature procedure[18] without separating its two isomers, which do not show a significant difference in their rate of thermal decomposition[19]. Dimethylformamide (DMF) was purified by vacuum distillation over CaH_2, and all the other solvents (96 vol% ethanol,...) and reagents of the best reagent grade were used without further purification.

Free-radical copolymerizations

The monomers and the solvents were introduced in a Pyrex glass double-walled reactor fitted with a magnetic stirrer and connected with an external Lauda thermostat allowing the temperature to be monitored within ± 0.1°C. The system was degassed at room temperature by three successive vacuum–argon sweeping cycles and then heated at 60°C. The initiator was added all at once as soon as the polymerization temperature was reached. The copolymerization was carried out at a constant temperature of 60°C for a given time under a slight pressure of argon and then stopped by addition of a small amount of hydroquinone. Copolymer recovery depends on the solvent used. In DMF, the copolymer was recovered by precipitation of its homogeneous solution into distilled water (6 vol. H_2O for 1 vol. DMF, monomer B remains soluble in this binary mixture), thoroughly washed with water, and then dried under 10^{-2} Torr (1.3 Pa) at 50°C for 24 h. It was purified by reprecipitation from DMF solution into water under identical experimental conditions. In some cases, the copolymer was further suspended in water and stirred overnight for quantitative elimination of residual DMF. In water–ethanol binary mixtures, the insoluble copolymer was recovered by simple filtration of the reaction mixture when still warm and purified as previously described. In all cases, the lack of any residual monomer B was checked by thin-layer chromatography (silica gel, Merck 60 F_{254}) using DMF as deposition solvent and methanol as the eluting one: $R_F(B) = 0.82$ and R_F(copolymers) ~ 0. The copolymers were systematically dried overnight under 10^{-2} Torr at 50°C before any analysis or physical measurement.

N,N-*Dimethylaminoethylpropionate.* This ester was prepared at a 0.1 mol scale from propionyl chloride and *N,N*-dimethylaminoethanol by direct transposition of the literature experimental procedure described for *N,N*-diethylaminoethoxyethyl methacrylate[20]. Yield 66%. ^{1}H n.m.r. ($CDCl_3$): δ (ppm) 4.18 (2H, CO–OCH_2), 2.55 (2H, CH_2N), 2.35 (2H, CH_2CO), 2.29 (6H, N(CH_3)$_2$), 1.14 (3H, CH_3). Anal. calc. for $C_7H_{15}NO_2$: C, 57.90%; H, 10.41%; N, 9.65%; O, 22.04%. Found: C, 57.68%; H, 10.52%; N, 9.69%; O, 22.10%.

2,2-Dicyano-1-[2-((propionyloxy)ethyl)dimethylammonioethoxyl] ethenolate. This zwitterion was prepared at a 0.04 mol scale through ring opening of dicyanoketene ethylene acetal by *N,N*-dimethylaminoethyl propionate by direct transposition of the literature experimental procedure given for monomer B[14]. Yield: 88%. ^{1}H n.m.r. (DMSO-d_6): δ (ppm) 4.43 (2H, CO–O–CH_2), 4.33 (2H, CH_2–O–CO–C(CN)$_2$), 3.62–3.72 (4H, H_2C–N^+–CH_2), 3.12 (6H, –N^+–(CH_3)$_2$), 2.35 (2H, CH_2–CO–O), 1.03 (3H, CH_3). Anal. calc. for $C_{13}H_{19}N_3O_4$: C, 55.50%; H, 6.81%; N, 14.94%; O, 22.75%. Found: C, 55.58%; H, 6.64%, N, 14.85%; O, 22.72%. $T_m = 141.5$–142°C.

Potentiometry

Potentiometric titration of the zwitterionic units in the copolymer was performed on a Mettler DL.21 potentiometric device fitted with a Metrohm 6.020 3.000 glass electrode, using a binary mixture of acetic anhydride–acetic acid (Ac_2O–AcOH) (9:1, v/v) as solvent and

trifluoromethanesulfonic acid 0.1 N in acetic acid as titrating reagent (protonation of the anionic site of the zwitterion[14,15]).

^{13}C n.m.r., infra-red and ultra-violet spectroscopies

^{13}C n.m.r. spectra of monomers were recorded at room temperature on a Bruker AC200 spectrometer operating at 50.3 MHz. Measurements were performed on 15–20 wt% solutions in DMSO-d_6 or binary mixtures trifluoroethanol–trifluoroethanol-d_3 (8:2, v/v): the chemical shifts δ are given with respect to the dimethylsulfoxide (DMSO) septet fixed at 39.7 ppm and to the trifluoroethanol (TFE) CH_2 quadruplet fixed at 126.3 ppm, respectively. ^{13}C n.m.r. spectra of copolymers and of the parent homopolymers were recorded on a Bruker AM-400 spectrometer operating at 100.6 MHz. Measurements were performed on 20 wt% solutions in DMSO-d_6 at 120°C. Deconvolution of the carbonyl pattern was carried out using the LINESIM program (Bruker).

I.r. spectra (KBr pellets) were recorded on an *FT*i.r. spectrometer BOMEM-Michelson MB-155.

U.v. spectra were recorded on a Shimadzu UV-2101 PC spectrometer using polymer solutions in trifluoroethanol. The determination of the zwitterion content in the copolymers relies on the characteristic absorption of the delocalized anionic site of the B units at 236 nm[14] where the contribution of the n-butyl acrylate units A may be safely neglected: molar absorption $\varepsilon(A_n) = 26\,1\,mol^{-1}\,cm^{-1}$ *versus* $\varepsilon(B) = 17\,550$ and $\varepsilon(B_n) = 16\,760\,1\,mol^{-1}\,cm^{-1}$.

Molecular-weight measurements

Refractive-index increments, dn/dc, were measured at room temperature on a Brice Phoenix BP 1000V differential refractometer using a neon laser beam of $\lambda = 632$ nm. Measurements were performed either in DMF or TFE solution; the copolymers obey the expected additivity relationship $dn/dc = \Sigma_i W_i (dn/dc)_i$ with $dn/dc = 0.035$ and $0.107\,ml\,g^{-1}$ for A_n and B_n, respectively, in DMF solution, and $dn/dc = 0.157$ and $0.211\,ml\,g^{-1}$ for A_n and B_n, respectively, in TFE solution. Light scattering experiments were carried out at room temperature on a Sofica 42000 or on a Sematech 633 apparatus at the same wavelength.

Isothermal degradation and thermogravimetric analysis (t.g.a.)

For isothermal studies, finely ground samples of about 100–150 mg were sintered under 5×10^3 bar into discs (thickness 0.8–1 mm), which were placed in a drying pistol Büchi TO-51, and then heated under vacuum at 160°C. Structural evolution of the sample was monitored by i.r. spectroscopy (see above). Dynamic t.g.a. measurements were performed on 10–70 mg samples under a constant nitrogen flow ($200\,ml\,min^{-1}$) and at a heating rate of $5\,K\,min^{-1}$ using a Mettler TA/3000 t.g.a. device.

RESULTS AND DISCUSSION

Selection of the copolymerization media, monomer reactivities and analysis of the copolymers

Because of the respective solubility properties of monomers A, B and of their corresponding homopolymers, DMF was selected as a typical dipolar aprotic solvent for copolymerization in the homogeneous phase, while aqueous ethanol appeared as the only appropriate binary solvent for copolymerization in the heterogeneous phase (precipitation of the copolymer from the homogeneous comonomer solution) as detailed below.

Solubility of the zwitterion B measured at 60°C in various water–ethanol mixtures is given in *Figure 1a*. It goes through a rather flat maximum for water volume fraction ϕ_{H_2O} of about 0.50–0.65. This very typical behaviour suggests maximum synergetic contributions of the two pure liquids to the overall solvation power of their mixtures for a fairly well defined composition. It may be tentatively correlated with some characteristic properties of the water–ethanol mixtures measured at 20–25°C, as given in *Figure 1b*. From a quantitative

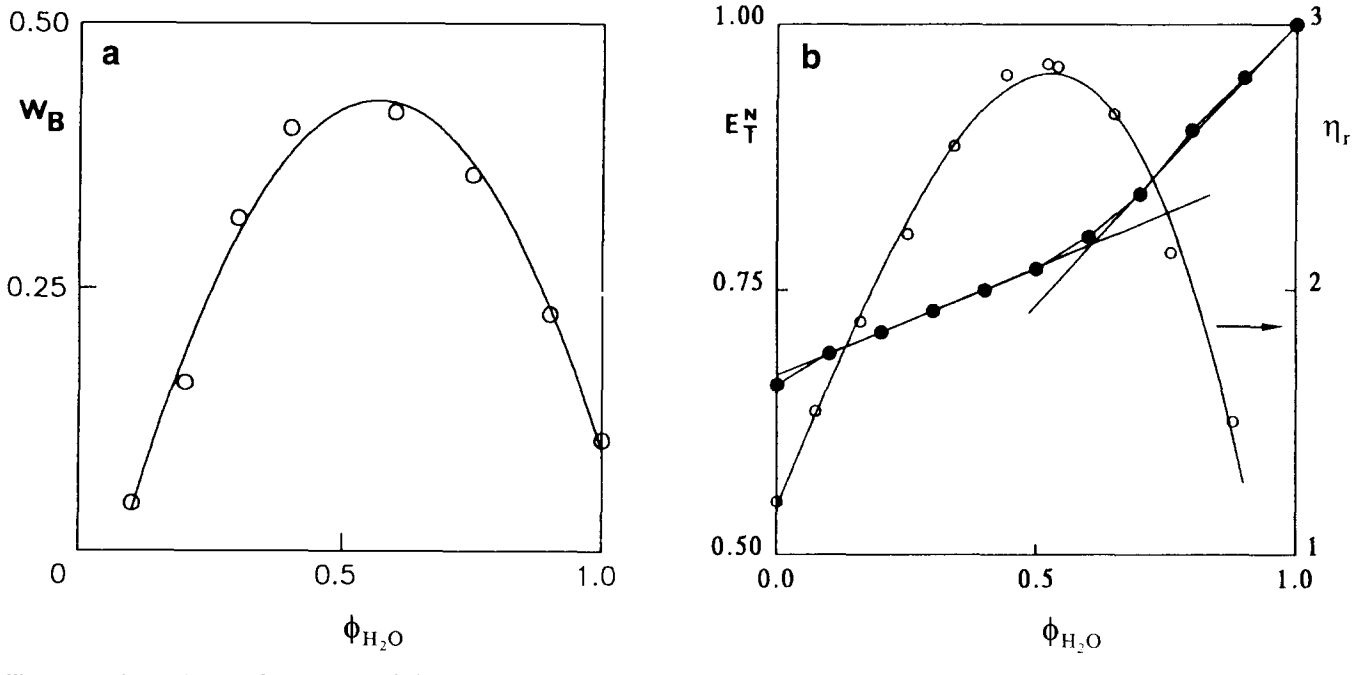


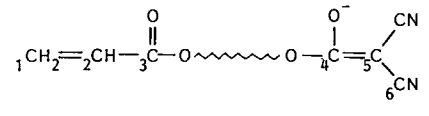
Figure 1 Phase diagram for solution of the zwitterionic monomer B in binary mixtures H_2O–C_2H_5OH: (a) variation of the solubility W_B (in weight fraction) at 60°C *versus* the volume fraction of water ϕ_{H_2O}; (b) variation of the Dimroth–Reichardt polarity parameter E_T^N (25°C) and of the relative viscosity η_r (20°C) of the binary solvent *versus* ϕ_{H_2O}

analysis of a number of empirical polarity scales[21], including for instance the well known Dimroth–Reichardt E_T^N parameter[22] (solvatochromy of a zwitterionic dye of the pyridinium phenolate type) and the Winstein Y parameter (kinetics of the solvolysis of t-butyl chloride), Langhals[23] has shown the occurrence of a critical transition point at about $\phi^*_{H_2O}=0.45$ separating two domains where the variations of the polarity of the corresponding mixtures with composition are clearly differentiated ($\phi^*_{H_2O}$ does not correspond necessarily to a polarity maximum). In the same way, the relative viscosity of the binary solvent[24] reaches a maximum at $\phi^*_{H_2O}\sim 0.48$–0.54, suggesting strongest association through hydrogen bonding at this concentration. The fairly good analogy observed between the solubility of the zwitterionic monomer B and a number of physicochemical events for similar water–ethanol mixtures is probably not incidental.

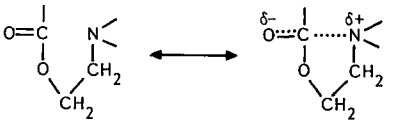
On the other hand, n-butyl acrylate is miscible in rather large amounts at 60°C with well adjusted water–ethanol mixtures. For instance in the ternary system EtOH (x vol)/H_2O (y vol)/A (n vol), phase separation occurs only for $n>4.5$ if $x=6$, $y=4$ and for $n>10$ if $x=7$, $y=3$.

Copolymerizations were thus performed at 60°C in the binary solvent H_2O–EtOH, $\phi_{H_2O}=0.4$.

An *a priori* estimation of the relative monomer reactivities was performed through ^{13}C n.m.r. spectroscopy at room temperature. Because of transparency and solvation power requirements, dimethylsulfoxide (DMSO) and trifluoroethanol (TFE) were selected as model solvents for the two copolymerization media, dimethylformamide (DMF) and aqueous ethanol respectively. The characteristic chemical shifts of the carbon atoms of the acrylic moiety (monomers A and B) and of the zwitterionic anionic site (monomer B), as identified below, are given in *Table 1*. Two typical features may be outlined.



(i) In DMSO solution, the ^{13}C n.m.r. data related to the acrylic function of the two comonomers A and B and of *N,N*-dimethylaminoethyl acrylate (DMAEA, tertiary amino precursor of the zwitterionic monomer) show only very weak and practically negligible differences. It may be noticed that the potential intramolecular donor–acceptor interaction in DMAEA, which has been postulated in the homologous methacrylic series on the basis of a reduced basicity of the tertiary amino function with respect to triethylamine[25], is not clearly seen on the ^{13}C n.m.r. spectrum. This possible interaction obviously vanishes in the zwitterionic structure.



(ii) The change from the strongly dipolar and aprotic DMSO solvent to the moderately dipolar and strongly protic TFE solvent results in a characteristic spectrum shift towards lower fields, especially for the C3, C4 and C5 carbons ($\Delta\delta\sim 3$–5 ppm). This behaviour merely arises from the strong hydrogen-bonding interactions between TFE and the ester carbonyl C3 (monomers A and B) and the C4 and C5 carbon atoms of the zwitterionic anionic site (monomer B). Moreover, the acrylic moieties of the two comonomers are more differentiated in TFE than in DMSO. The partial positive charge on carbon C1 appears slightly stronger in B, and the polarization of the polymerizable double bond, estimated in a first approach by the difference $\Delta\delta=\delta(C1)-\delta(C2)$, is nearly the same for both monomers A and B in DMSO while it becomes significantly greater for monomer B in TFE solution ($\Delta\delta\sim 7$ *versus* 3 ppm). This effect, however, has not to be overestimated, because of the high sensitivity of the ^{13}C n.m.r. spectrometry.

Thus, as long as electronic effects only (and not potential steric effects) are considered, the two comonomers A and B are expected to display fairly similar reactivities in copolymerization, more especially in DMF solution.

Copolymer composition was derived independently from elemental analysis (N), acid–base titration by potentiometry and u.v. spectroscopy (see 'Experimental' part). Comparison of some representative measurements given in *Table 2* shows a good agreement between the three analytical methods. Potentiometric titrations are restricted to copolymers of low zwitterionic content ($F_B<0.40$) because of solubility problems in the titration solvent (Ac_2O:AcOH, 9:1 vol/vol). The self-consistency of the results derived from elemental analysis and u.v. spectroscopy over the whole composition range shows that the molar absorptivity of the zwitterionic unit is independent of its microenvironment within the chain: $\varepsilon(ABA)=\varepsilon(BBA)=\varepsilon(BBB)$. U.v. spectroscopy was thus used systematically throughout the following work.

Copolymerization in homogeneous DMF solution

Copolymerizations were performed at 60°C under the following conditions: $0.6\leqslant[A+B]\text{mol}\,l^{-1}\leqslant 1$, $[ACVA]/[A+B]=5\times10^{-3}$, $0.07\leqslant f_B\leqslant 0.70$.

Table 1 Characteristic ^{13}C n.m.r. chemical shifts δ(ppm) of typical acrylic and zwitterionic carbon atoms of the various monomers at room temperature (see carbon indexation in the text)

Monomer	Solvent	C1	C2	C3	C4	C5	C6[a]
A	DMSO	131.68	128.81	165.89			
A	TFE	132.81	129.66	170.85			
DMAEA[b]	DMSO	131.54	128.48	165.53			
B	DMSO	132.78	128.29	165.19	168.98	31.67	121.82 121.56
B	TFE	134.88	128.12	168.43	173.32	34.75	–[c]

[a] The two cyano groups are non-equivalent[14]
[b] *N,N*-Dimethylaminoethyl acrylate, tertiary amino precursor of monomer B
[c] Partly masked by the CH_2 quadruplet of the solvent

The reaction medium remained homogeneous throughout the copolymerization, and conversion (total mole fraction of transformed monomers) was systematically limited to values lower than 0.30 to avoid a too high compositional heterogeneity of the resulting copolymers.

The reactivity ratios r_A and r_B were derived from a series of experiments (see composition diagram in *Figure 2a*) according either to the Kelen–Tüdös linearization method, which takes into account the degree of conversion[26] (KT) or to the Yezriliev–Brokhina–Roskin numerical method[27] (YBR):

KT $\begin{cases} r_A = 1.12 \\ r_B = 1.13 \end{cases}$ regression coefficient over nine data points, $R(9) = 0.998$

YBR $\begin{cases} r_A = 1.11 \pm 0.28 \\ r_B = 1.12 \pm 0.66 \end{cases}$

The system obeys the simple terminal unit model and is nearly an ideal azeotropic one ($r_A = r_B = 1$); the composition diagram given in *Figure 2a* is not significantly different from the first bisectrix: $F_B = 1.022 f_B - 0.01$, $R(9) = 0.999$. In the Q–e scheme, monomer B would have identical Q and e values to monomer A[28], $Q = 0.38$ and $e = 0.55$, but the reliability of these primary values derived from a single copolymerization system has obviously to be further checked.

This typical behaviour results in two important consequences for the copolymers: a good compositional homogeneity independent of conversion (see *Table 3*), and a microstructure of the Bernoulli type. Moreover, it is self-consistent with the similar reactivity of the two comonomers suggested by ^{13}C n.m.r. spectroscopy (see above) and the lack of any perturbing physical effect in homogeneous DMF solution. The radical homopolymerization of the B analogous methacrylate is free of any template effects in such conditions, in spite of potential strong dipolar interactions between the monomer and the growing macroradical[29].

Table 2 Comparison of various analytical methods for the determination of the copolymer composition (molar fraction F_B)

Elemental analysis	Potentiometry	U.v. spectroscopy
0.116 ± 0.005	0.12 ± 0.004	0.114 ± 0.004
0.199 ± 0.010	0.196 ± 0.006	0.192 ± 0.006
0.392 ± 0.020		0.408 ± 0.012
0.640 ± 0.032		0.623 ± 0.019

Heterogeneous copolymerization in aqueous ethanol solution ($\phi_{H_2O} = 0.4$)

Copolymerizations were performed at 60°C under the following conditions: $0.6 \leqslant [A+B]\ \text{mol}\,l^{-1} \leqslant 2$, $[ACVA]/[A+B] = 5 \times 10^{-3}$, $0.1 \leqslant f_B \leqslant 0.8$.

The copolymers are totally insoluble in the reaction medium over the whole composition range, and conversion (total mole fraction of transformed monomers) was systematically limited to values lower than 0.3, as in the previous case. The copolymerization diagram given in *Figure 2b* shows a very unusual shape where an azeotropic point at about $F_B \sim 0.33$ separates two regions where homopropagation of the predominant monomer is significantly favoured (trend towards blocky microstructure): accordingly, the r_A and r_B values should be greater than 1. Moreover, compositional heterogeneity

Table 3 Composition drift with conversion α for copolymers prepared in homogeneous or heterogeneous phase

Solvent	f_B	α	F_B
DMF	0.2	0.30	0.115
		0.46	0.117
EtOH–H_2O	0.1	0.21	0.021
		0.63	0.068
EtOH–H_2O	0.5	0.22	0.637
		0.54	0.557
		0.92	0.490

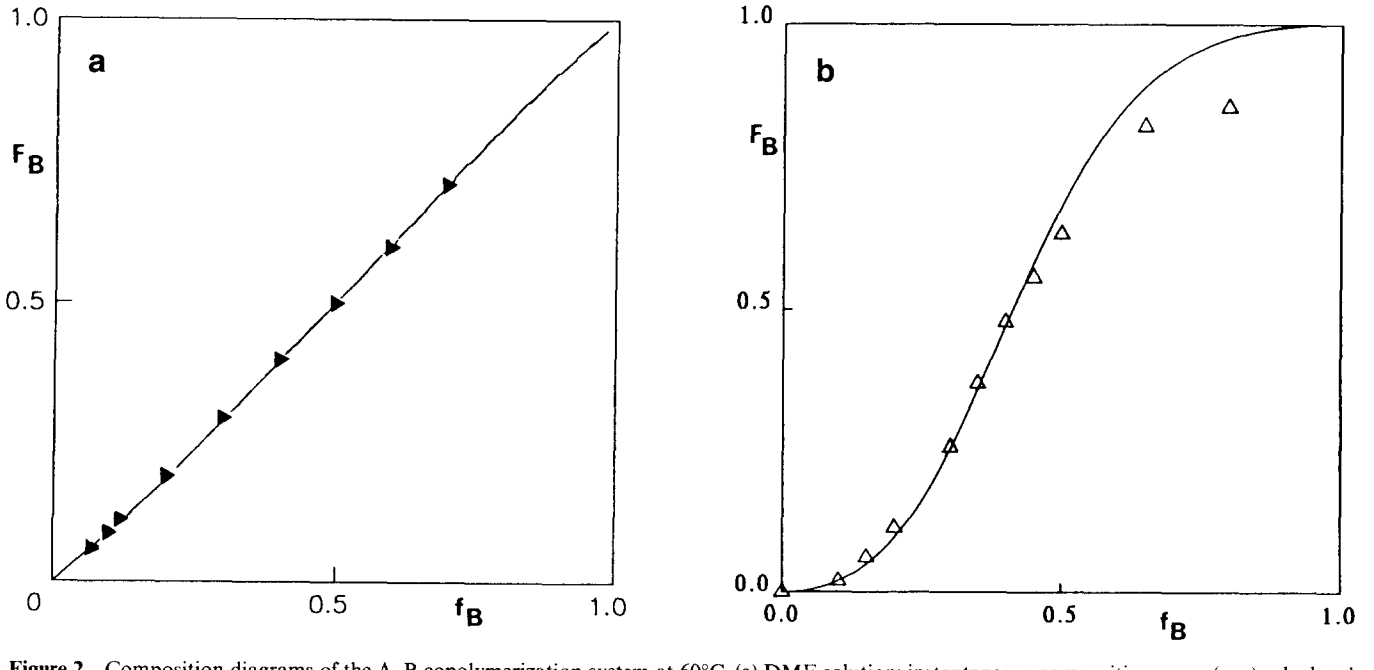


Figure 2 Composition diagrams of the A–B copolymerization system at 60°C. (a) DMF solution: instantaneous composition curve (—) calculated for $r_A = 1.12$, $r_B = 1.13$. (b) Aqueous ethanol solution: instantaneous composition curve (—) calculated for $r_A = 1.12$, $r_B = 1.13$ and $K = 0.487$ (see text)

of the copolymers should be an increasing function of conversion. The opposite composition drifts observed for two samples obtained from monomer feeds on both sides of the azeotropic point are in good agreement with the expected behaviour as shown in *Table 3*. Analysis of the experimental data according to the KT or YBR methods leads only to poorly defined reactivity ratios over limited composition range:

$$\text{KT} \quad 0.35 \leqslant F_B \leqslant 0.65 \quad \begin{cases} r_A = 2.97 \\ r_B = 6.39 \end{cases} \quad R(5) = 0.966$$

$$\text{YBR} \quad 0.10 \leqslant F_B \leqslant 0.65 \quad \begin{cases} r_A = 1.76 \pm 4.6 \\ r_B = 1.76 \pm 8.4 \end{cases}$$

The strong deviations of the r values from those determined in the 'ideal' conditions of copolymerization in homogeneous DMF solution are obviously reminiscent of a number of solvent effects described in the literature[30,31]. When copolymerization involves two monomers of strongly different polarities, in most cases their reactivity ratios are solvent-dependent, especially when the reaction occurs in the heterogeneous phase, and they may reach unrealistic values higher than 1, as in the case of the comonomer pair styrene–acrylamide[32,33], for instance. From a careful analysis of a number of such systems, Harwood has shown that the copolymers of a given composition have the same microstructure whatever the reaction medium[31]. This identity of unit distribution within the chain implies that each monomer is characterized by a unique and invariant intrinsic reactivity ratio (see, however, the alternative interpretation of Fukuda *et al.*[34], who stress that only the product of the reactivity ratios $r_A r_B$ should be constant) and that the observed solvent effects merely arise from physical factors such as preferential or selective absorption of the comonomers on the growing macroradical. These specific solvation effects control the actual local monomer feed composition in the microenvironment of the reactive site[30,31]. Harwood's model appears highly attractive and physically sound even if it is supported only by a few quantitative measurements of such adsorption phenomena in the copolymerization experimental conditions[35,36]. For the system under study, a rough quadrupole calculation shows that the energy differences between parallel and antiparallel conformations of two zwitterions ($\mu = 25.9$ D, intercharge distance 5.4 Å) placed at distances of 3 and 4 Å in a medium of dielectric permittivity of about 46 (estimated at 25°C for H_2O–EtOH, $\phi_{H2O} = 0.4$) reach values of about $2kT$ and $1.2kT$ respectively at 60°C. Potential adsorption of monomer B on B-rich growing chains may appear reasonable and cannot be ruled out *a priori*. A copolymerization scheme may be tentatively proposed within the framework of the terminal unit model with the following simplifying assumptions.

(i) The very initial propagation step is free from any perturbing preferential solvation phenomenon (very short macroradicals in homogeneous phase), and the composition of the corresponding chain is given directly by the classical equation using the 'intrinsic' reactivity ratios measured in DMF solution:

$$y_0 = \frac{F_A^0}{F_B^0} = x_0 \frac{r_A x_0 + 1}{x_0 + r_B} \qquad \text{with} \qquad x_0 = \frac{f_A^0}{f_B^0} \tag{1}$$

(ii) Cross-interactions A–B are negligible, and only A–A and B–B interactions are strong enough to be operative in the reaction medium (a very reasonable assumption taking into account the chemical structure and the immiscibility of the two comonomers). The preferential solvation process may thus be described by the two equilibria:

$$P + A \overset{k_{AA}}{\rightleftharpoons} PA \qquad P + B \overset{k_{BB}}{\rightleftharpoons} PB$$

In the case of a one-to-one interaction, the amount of sorbed monomer i (A or B) by the growing chain P will be determined by its overall concentration in the medium, the i unit content of the chain P and the equilibrium constant k_{ii}. For low conversion, the actual monomer feed composition in the chain microenvironment will take a value x^*, different from the initial values x_0 in the original bulk solution, according to:

$$x^* = \frac{f_A^*}{f_B^*} = x_0 \frac{F_A^0 k_{AA}}{F_B^0 k_{BB}} = x_0 y_0 K \qquad \text{with} \qquad K = \frac{k_{AA}}{k_{BB}} \tag{2}$$

Thus, the composition of the copolymer chain growing from a local monomer feed of composition x^* will be given by:

$$y^* = \frac{F_A^*}{F_B^*} = x^* \frac{r_A x^* + 1}{x^* + r_B}$$

$$= K x_0^2 \frac{r_A x_0 + 1}{x_0 + r_B} \frac{K r_A x_0^2 (r_A x_0 + 1)/(x_0 + r_B) + 1}{K x_0^2 (r_A x_0 + 1)/(x_0 + r_B) + r_B} \tag{3}$$

For low conversion, equation (3) allows one to analyse the variations of copolymer composition $y^* = f(x_0, r_A, r_B, K)$ using the ratio K of the equilibrium constants as an adjustable parameter. Computer calculations through a least-squares minimizing method lead to an optimized value of $K = 0.487$. As shown in *Figure 2b*, the agreement of the experimental points with the composition curve recalculated using this value is very good for $f_B^0 \leqslant 0.50$ and still fairly good up to $f_B^0 \sim 0.65$. Such behaviour may be considered as highly satisfactory, since the experimental data may be interpreted in a self-consistent and quantitative way with only one adjustable parameter ($K < 1$, as expected since B–B interactions are definitely stronger than A–A ones) in spite of the relative crudeness of the model. It may oversimplify the analysis of the preferential sorption process[37] and does not take into account the composition drifts for x^* and y^*, which may be significant even for low conversion. An independent and reliable check of the physical value of the copolymerization model would be the analysis of copolymer microstructure. However, because of the structural similarity of the poly(acrylic) backbone for the two different

Table 4 ^{13}C n.m.r. characteristic chemical shifts of the acrylate backbone carbon atoms (C^1H_2–C^2H–C^3O–) for a typical copolymer ($F_B = 0.478$) and its parent homopolymers (DMSO, 120°C)

	δ (ppm)		
Sample	C1[a]	C2[b]	C3[b]
A_n	32.7–36.0	41.04	173.62
A_xB_y	32.7–36.0	40.99	172.95
			173.43
B_n	32.5–35.0	40.67	172.90

[a] Sensitive to configurational effects (I = 0.19, H = 0.49, S = 0.37 for A_n obtained at 30°C[39]); broad and very poorly resolved resonance for A_xB_y and B_n

[b] Insensitive to configurational effects

Table 5 Molecular weights and normalized average degrees of polymerization DP_w^* of some representative copolymers

Solvent	W_B	$M_w \times 10^{-5}$	$(S_z^2)^{0.5}$ (nm)	$A_2 \times 10^4$ (ml g^{-2} mol)	DP_w^*
EtOH–H_2O	0.047	3.73[a]	62	0.90	1830
		4.10[b]	90	4.2	2010
EtOH–H_2O	0.791	3.60[b]	170	18	2070
DMF	0.246	1.16[a]		4.8	780
DMF	0.766	0.751[a]		1.6	440

Light scattering measurements in [a]DMF, [b]TFE

monomers, ^{13}C n.m.r. spectroscopy (see 'Experimental' part) proved to be inefficient for the determination of unit distribution in the chain. The carbonyl pattern (see *Table 4* for typical chemical shifts) of a representative sample essentially shows two overlapping broad peaks, which correspond precisely to the carbonyl peak of the respective parent homopolymers (the C=O pattern does not show any well defined splitting according to tacticity effects in A_n, as already observed[38,39]). Deconvolution only leads to the estimation of the overall copolymer composition, $F_B = 0.47$, in excellent agreement with the value derived from the other analytical methods, $F_B = 0.48$. However, structural studies relying on d.s.c., SAXS and solid-state n.m.r. spectroscopy, and reported in the following publications, will emphasize significant differences between samples of identical composition but prepared in homogeneous or heterogeneous phase. Thus the proposed copolymerization model cannot be definitely ascertained on unambiguous physical grounds. Preferential monomer sorption phenomena by the growing chains in the heterogeneous phase are probably an important factor in the propagation process, but weak and non-negligible modification of the intrinsic reactivities of the species through solvent polarity effects, already advocated in the literature[40], cannot be completely ruled out (see also previous discussion on the approach of monomer reactivity through ^{13}C n.m.r. spectroscopy). Finally, molecular dispersion of the monomers in the reaction medium at 60°C has not been checked, and their possible self-association, especially for monomer B, may be tentatively considered as a potential factor of the copolymerization process. Vapour-phase osmometry measurements, as will be reported elsewhere, have shown that, at 60°C and for concentration lower than 0.1 mol l^{-1}, 38% of the monomer B is aggregated in dimers in pure water while it is entirely monomeric in DMF solution.

Molecular weights

Only some molecular-weight measurements were performed by light scattering in DMF or TFE solution, DMF and TFE being the only common good solvents of the parent homopolymers A_n and B_n. The experimental weight-average degrees of polymerization DP_w were normalized to standard copolymerization conditions [A+B]* = 1 mol l^{-1} and [ACVA]* = 5×10^{-3} mol l^{-1} according to:

$$DP_w^* = \frac{\overline{M_w}[A+B]^*}{M[A+B]}\left[\frac{[ACVA]}{[ACVA]^*}\right]^{0.5}$$

with

$$M = M_A F_A + M_B F_B \qquad (4)$$

Three main features may be derived from the experimental results given in *Table 5*:

(i) The good agreement between the M_w values of a given sample studied in two solvents of strongly different refractive index ($n_D = 1.2907$ and 1.4305 for TFE and DMF, respectively) is in favour of the lack of any aggregation phenomena in the solutions, as expected. These apparent M_w values may be considered as quite reliable for samples of weak chemical heterogeneity[41].

(ii) TFE, where the second virial coefficient A_2 and the radius of gyration reach much higher values, is a thermodynamically better solvent than DMF for the copolymer chain. This feature arises from strong hydrogen-bond interactions between the weakly self-associated alcohol and the ester carbonyl bonds of the acrylate backbone[42] and the anionic sites of the zwitterionic units[43].

(iii) For heterogeneous copolymerization, the DP_w^* values appear insensitive to the monomer feed composition and systematically much higher than the corresponding ones observed for homogeneous copolymerization. This typical difference cannot be ascribed to the transfer constant to the solvent being stronger for DMF. Compare, for instance, C_T(EtOH) of about $(4.2–4.4) \times 10^{-4}$ at 80°C for various alkyl acrylates, including monomer A[44], with $C_T(DMF) \sim 10^{-5}$ for ethyl acrylate at 50°C[45] (C_T(DMF) for monomer A is not given in the literature, to the best of our knowledge). The higher DP_w^* values observed in aqueous ethanol arise more likely from increased kinetic chain length (higher values of the characteristic $k_p/k_t^{0.5}$ ratio) associated with polymerization at the interface between monomer solution and insoluble macroradicals, as already observed for an analogous n-butyl acrylate–zwitterionic comonomer system[1]. Moreover, broadening of the molecular-weight distribution in heterogeneous copolymerization can also contribute to the observed behaviour.

Thermal stability

The comparison of the thermal stabilities of a representative homogeneous copolymer ($F_B \sim 0.40$, DMF as copolymerization solvent), of the parent homopolymers (A_n, B_n), of a low-molecular-weight model compound of the zwitterionic unit (model M, see 'Experimental' part) and of analogous ammoniopropanesulfonate polyzwitterions (B'_n[1], poly[3-(methacrylamidopropyl)dimethylammoniopropane-1-sulfonate], and B''_n[46], poly[3-(methacryloyloxyethyl)dimethylammoniopropane-1-sulfonate]) was performed by thermogravimetric analysis (t.g.a.) carried out under a nitrogen atmosphere. Some typical t.g.a. curves, giving the variations of the ratio of the sample weight w at temperature T to its initial value w_0 ($T^0 = 100$°C) *versus* temperature and the first derivative $d(w/w_0)/dt$ vs. T are shown in *Figure 3*. According to the derivative traces, the degradation involves a multi-step process in the case of the zwitterionic chains. Assuming first-order kinetics, an apparent overall activation energy E_a may be estimated with a given temperature range where experimental results can be linearized according to the following equation[47]:

$$\ln\left(-\frac{\ln(1-\alpha)}{T^2}\right) = \ln\left[\frac{AR}{\theta E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \qquad (5)$$

where α is the polymer fraction volatilized at temperature T ($\alpha = (w_0 - w)/w_0$), θ is the heating rate, A is the Arrhenius

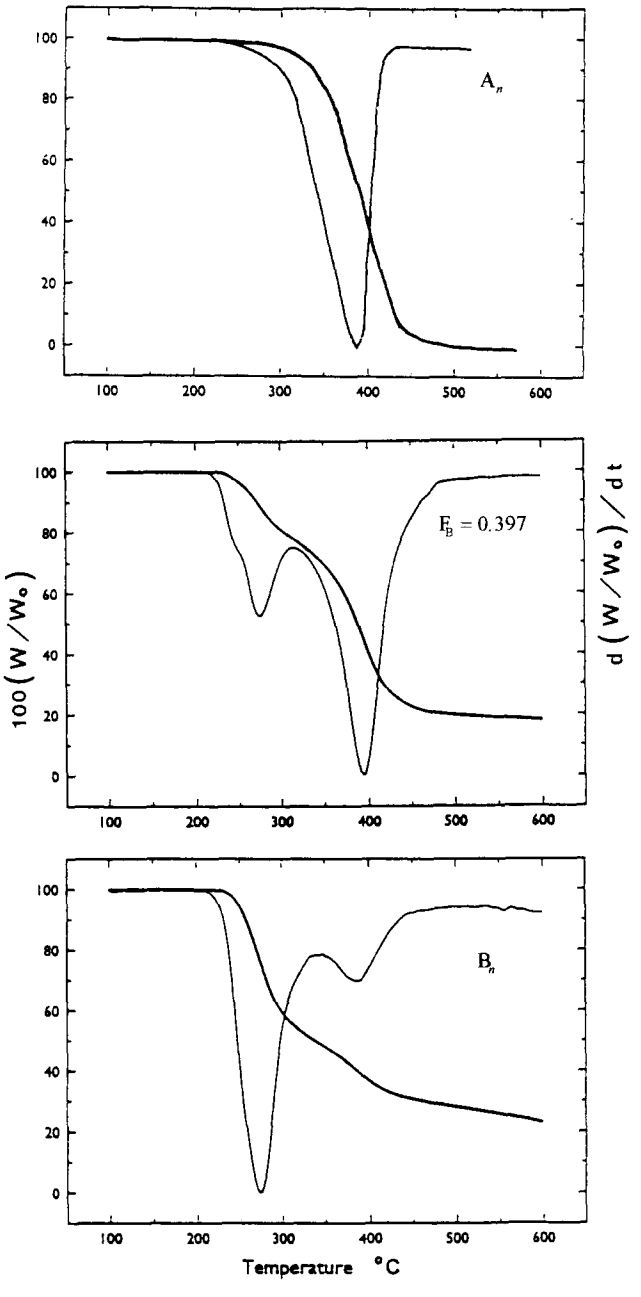


Figure 3 Thermogravimetric analysis of a representative copolymer ($F_B = 0.397$) and of the parent homopolymers A_n and B_n under nitrogen: residual weight $(w/w_0) \times 100$ and derivative trace *versus* temperature

frequency factor and R the gas constant. The E_a values given in *Table 6* have to be considered quite cautiously, since they depend strongly on the *a priori* assumed reaction order and are related to limited ranges of temperature and weight loss. However, comparison of these data and of the initial degradation temperatures T_i (arbitrarily measured at $\alpha = 0.05$) points out two main features. First, the introduction of the zwitterionic units strongly decreases the stability of the material: the copolymer stands as expected between its two parent homopolymers A_n and B_n, and the low-molecular-weight model compound appears as the least stable species. Secondly, the ammonioethoxydicyanoethenolate structure in the acrylate chain is less stable than the homologous ammoniopropanesulfonate structure in a methacrylamido[1] (B'_n) or a methacrylate[46] chain (B''_n, $T_i = 300°C$, $E_a = 103\,kJ\,mol^{-1}$ between 300 and 400°C, corresponding to $\alpha = 0.70$).

On the other hand, progressive and irreversible discoloration from pale yellow to brown was systematically observed at temperatures higher than 150°C for the zwitterionic chains in their viscoelastic state ($T_g(B_n) = 130°C$) and for the melted model compound ($T_m = 142°C$). This strongly suggests some degradation or rearrangement of the zwitterionic structure in a mobile phase, which necessarily limits the temperature range of safe use of the polymeric materials, even if this process occurs without any significant weight loss. Some i.r. measurements were performed at 160°C to monitor this reaction through the analysis of the variations of the two strong characteristic absorption bands of the zwitterionic structure, $\nu(C{\equiv}N)$ at 2170–2200 cm^{-1} (sharp doublet) and $\nu(C{=}C)$ at 1655 cm^{-1} using the vibration of the ester carbonyl $\nu(C{=}O)$ at 1740 cm^{-1} as internal reference. These variations are in very good agreement for the two bonds (differences lower than 3%) and the apparent decrease of the zwitterion concentration with time is compatible with a rather low first-order process characterized by a rate constant $k = 2.8 \times 10^{-6}\,s^{-1}$ for the homopolymer B_n and a copolymer ($F_B = 0.50$) (*Figure 4*). These preliminary results should obviously be checked over a broader conversion range. Moreover, when the thermal treatment is directly performed on the KBr–zwitterion pellets, where low amounts of salt may be dissolved in the liquid zwitterionic matrix, a new sharp absorption arises at 2364 cm^{-1} with a shoulder at 2338 cm^{-1} (frequency range of cumulated double bonds, but not adventitious CO_2), which still remains to be identified.

Table 6 Thermal degradation of poly(n-butyl acrylate) and of various zwitterionic species under nitrogen atmosphere

Sample	T_i[a] (°C)	Temperature range (°C)	Weight loss (%)	Activation energy (kJ mol^{-1})
A_n	325	340–385	9–46	126
(ref. 1)		385–410	46–85	166
AB	257	250–280	3–13	105
$F_B = 0.397$		290–360	16–34	24
		370–420	38–71	61
B_n	248	250–290	6–36	113
		300–410	40–65	10
Model M	227	220–260	3–44	168
B'_n	285	280–295	3–20	365
(ref. 1)		310–425	37–68	15
B''_n	300	300–400	5–70	103
(ref. 46)				

[a] Initial degradation temperature measured for a weight loss of 5%

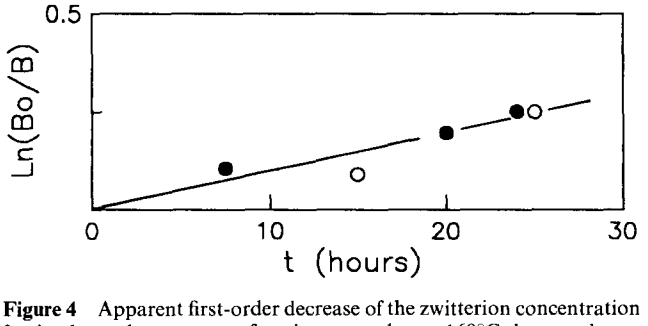
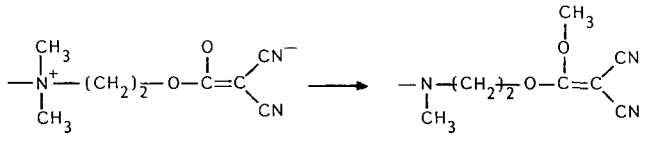


Figure 4 Apparent first-order decrease of the zwitterion concentration for isothermal treatment of various samples at 160°C: homopolymer B_n (●) and copolymer $F_B = 0.50$ (○)

The elucidation of the chemical process involved at 160°C is beyond the scope of the present work. Besides possible reaction analogous to the classical Hoffman degradation of quaternary ammonium salts, intramolecular alkylation of the cyanoethenolate anion may lead to the dicyanoenol methyl ether, which should display fairly similar characteristic i.r. absorptions[48].



CONCLUSIONS

Because of their identical acrylate structure, the free-radical copolymerization of n-butyl acrylate (A) and 2,2-dicyano-1-[2-(2-(acryloyloxy)ethyl)dimethylammonio-ethoxy] ethenolate (B) in homogeneous DMF solution obeys the terminal unit model with reactivity ratios characteristic of an ideal azeotropic comonomer pair, $r_A \sim r_B \sim 1$. However, in aqueous ethanol the copolymerization process is definitely more complex and is probably perturbed by a number of potential physical factors, such as preferential sorption of either monomer by the growing insoluble macroradicals. With respect to their ammoniopropanesulfonate homologues, the copolymers show enhanced sensitivity towards thermal degradation, which appears more particularly in the form of irreversible zwitterion rearrangement without weight loss for temperatures higher than 150°C. In spite of this drawback, these new amorphous and rather hydrophobic zwitterionomers meet most of the necessary requirements defined in the 'Introduction', and they may be considered as model polymers for further analysis of their expected heterogeneous structure and of their specific mechanical properties and for comparison with the homologous zwitterionic latexes obtained by emulsion copolymerization.

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REFERENCES

1 Ehrmann, M. and Galin, J. C. *Polymer* 1992, **33**, 859
2 Ehrmann, M., Mathis, A., Meurer, B., Scheer, M. and Galin, J. C. *Macromolecules* 1992, **25**, 2253
3 Ehrmann, M., Galin, J. C. and Meurer, B. *Macromolecules* 1993, **26**, 988
4 Ehrmann, M., Muller, R., Galin, J. C. and Bazuin, C. G. *Macromolecules* 1993, **26**, 4910
5 Galin, M., Mathis, A. and Galin, J. C. *Macromolecules* 1993, **26**, 4919
6 Eisenberg, A. and King, M. 'Ion-Containing Polymers', Academic Press, New York, 1977
7 MacKnight, W. J. and Earnest, T. R. *J. Polym. Sci., Macromol. Rev.* 1981, **16**, 41
8 Bazuin, C. G. and Eisenberg, A. *Ind. Eng. Chem. Prod. Res. Dev.* 1981, **20**, 271
9 Mauritz, K. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* (C) 1988, **28**, 65
10 Fitzgerald, J. J. and Weiss, R. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* (C) 1988, **28**, 99
11 Eisenberg, A., Hird, B. and Moore, B. *Macromolecules* 1990, **23**, 4098
12 Bredas, J. C., Chance, R. R. and Silbey, R. *Macromolecules* 1988, **21**, 1633
13 Mathis, A., Zheng, Y. L. and Galin, J. C. *Polymer* 1991, **32**, 3080
14 Pujol-Fortin, M. L. and Galin, J. C. *Macromolecules* 1991, **24**, 4523
15 Galin, M., Chapoton, A. and Galin, J. C. *J. Chem. Soc., Perkin Trans. 2* 1993, 545
16 Galin, J. C. and Galin, M. *J. Polym. Sci. (B) Polym. Phys.* 1992, **30**, 1113
17 Pujol-Fortin, M. L., Thesis, Strasbourg, 1991
18 Bamford, C. H., Jenkins, A. D. and Wayne, R. P. *Trans. Faraday Soc.* 1960, **56**, 932
19 Overberger, C. G. and Labianca, A. D. *J. Org. Chem.* 1970, **35**, 1762
20 Monroy Soto, V. M. and Galin, J. C. *Polymer* 1984, **25**, 121
21 Reichardt, C. 'Solvents and Solvent Effects in Organic Chemistry', 2nd Edn, VCH, Weinheim, 1988
22 Dimroth, K. and Reichardt, C. *Z. Anal. Chem.* 1966, **215**, 344
23 Langhals, H. *Angew. Chem. Int. Edn* 1982, **21**, 724
24 Weast, R. (Ed.) 'CRC Handbook of Chemistry and Physics'. 64th Edn, CRC Press, Boca Raton, FL, 1983–84, D-232
25 Pradny, M. and Secvik, S. *Makromol. Chem.* 1985, **186**, 111
26 Tüdös, F., Kelen, T., Földes-Berezsnich, T. and Turcsanyi, B. *J. Macromol. Sci., Chem.* (A) 1976, **10**, 1513
27 Yezrielev, A. I., Brokhina, E. L. and Roskin, Y. S. *Polym. Sci. USSR* 1969, **11**, 1894
28 Greenley, R. Z. *J. Macromol. Sci., Chem.* (A) 1980, **14**, 427
29 Pujol-Fortin, M. L., Galin, M. and Galin, J. C. *Macromolecules* 1991, **24**, 443
30 Plochocka, K. *J. Macromol. Sci., Rev. Makromol. Chem.* (C) 1981, **20**, 67
31 Harwood, H. J. *Makromol. Chem., Macromol. Symp.* 1987, **10–11**, 331
32 Saini, G., Leoni, A. and Franco, S. *Makromol. Chem.* 1971, **144**, 235
33 Park, K. Y., Santee, E. R. and Harwood, H. J. *Am. Chem. Soc. Polym. Div. Polym. Prepr.* 1986, **27**(2), 81
34 Fukuda, T., Kubo, K. and Yung-Dae Ma *Prog. Polym. Sci.* 1992, **17**, 875
35 Slavnitskaya, N. N., Semchikov, Yu. D., Ryabov, A. V. and Bort, D. N. *Polym. Sci. USSR* 1970, **12**, 1993
36 Pichot, C., Guyot, A. and Strazielle, C. *J. Polym. Sci., Polym. Chem. Edn.* 1979, **17**, 2269
37 Myagchenkov, V. A., Kurenkov, V. J. and Frenkel, S. Ya. *Eur. Polym. J.* 1970, **6**, 1649
38 Llauro-Darricades, M. F., Pichot, C., Guillot, J., Rios, L. G., Cruz, M. A. E. and Guzman, C. C. *Polymer* 1986, **27**, 889
39 Goni, I., Gurruchaga, M., Valero, M. and Guzman, G. M. *Polymer* 1993, **34**, 1780
40 Kamachi, M. *Adv. Polym. Sci.* 1981, **38**, 56
41 Benoît, H. and Froelich, D. 'Light Scattering from Polymer Solutions' (Ed. M. G. Huglin), Academic Press, London, 1972, p. 467
42 Hamori, E., Prusinovski, L. R., Sparks. P. G. and Hughes, R. E. *J. Phys. Chem.* 1965, **69**, 1101
43 Pujol-Fortin, M. L. and Galin, J. C. *Polymer* 1994, **35**, 1462
44 Naudi, U. S., Singh, M. and Raghuram, P. V. T. *Makromol. Chem.* 1982, **183**, 1467
45 Fenervari, A., Boros Gyevi, E., Földes-Berezsnich, T. and Tüdös, T. *J. Macromol. Sci., Chem* (A) 1982, **18**, 431
46 Der-Jang Liaw and Wen-Fu Lee *J. Appl. Polym. Sci.* 1985, **30**, 4697
47 Coats, A. W. and Redfern, J. P. *Nature* 1964, **201**, 68
48 Libis, B. and Fleury, J. P. *Bull. Soc. Chim.* (Fr.) 1965, **6**, 3323