Hydrophilic graft polyacrylonitrile copolymers: 1. Synthesis and characterization in dilute solution

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Radical copolymerization of methoxy-poly(ethylene glycol) monomethacrylate (A(8); $\bar{M}_n \sim 470$), a water-soluble macromonomer, with acrylonitrile (B) was studied in homogeneous dimethylsulphoxide solution at 60°C in the following conditions: $[A(8)]^0 + [B]^0 = 0.5$–1.5 mol l^{-1}; molar fraction of A(8) in the monomer feed, $f^0_{A(8)} \leqslant 0.75$. The process obeys the terminal unit model ($r_{A(8)} = 1.35$, $r_B = 0.38$), and readily yields graft copolymers over a broad range of composition and molecular weight ($\bar{M}_w \sim (0.5$–$9.0) \times 10^5$). The reactivity ratio of a macromonomer of higher molecular weight (A(21); $\bar{M}_n \sim 10^3$) may be estimated to be about 0.66, a significantly larger value than those of the shorter-chain (A(8)) and ordinary alkyl methacrylates. Light scattering measurements in dimethylformamide (DMF) solution at room temperature only lead to apparent values of the second virial coefficient A_2 and of the radius of gyration $(\bar{s}_z^2)^{0.5}$ for these heterogeneous copolymers. Although DMF is a poorer solvent for the polyether than for polyacrylonitrile and in spite of the branched structure, the apparent dimensions of the copolymers seem only slightly lower than those of polyacrylonitrile of the same molecular weight.

(Keywords: radical copolymerization; acrylonitrile; methoxy-poly(ethylene glycol) monomethacrylate; macromonomer; reactivity ratios; compositional polydispersity; dilute solution in dimethylformamide)

INTRODUCTION

Because of the highly dipolar character of the cyano group[1], acrylonitrile (AN) appears as an important or a major component in a wide variety of polymeric materials that have been technologically important for a long time in a number of fields, such as synthetic fibres[2], thermoplastic elastomers[3], or barrier polymers[4] for instance. In some cases, and for specific purposes, the hydrophilicity of AN-based materials has to be improved, and block or graft copolymers of polyacrylonitrile (PAN) and poly(ethylene oxide) (PEO) appear of special interest for two complementary reasons. (a) Incompatibility of the chemically different blocks may induce self-organization of the copolymer chains into a biphasic structure with discrete hydrophilic PEO microdomains. (b) PEO blocks display a rather unique series of specific properties[5] such as high solubility in both water and organic solvents, high crystallinity but rather low melting temperature ($T_m \leqslant 66$°C) and very low glass transition temperature ($T_g = -65$°C). Previous work in this laboratory[6] has clearly shown that anionic and radical, as well as polycondensation, methods were actually unreliable and inefficient for the preparation of linear homogeneous block copolymers of high molecular weight, for a number of reasons, such as extensive branching in anionic PAN[7] and in the related block copolymers[8], to important transfer of PAN macroradicals to the internal units of the PEO chain[6,9] in radical processes, or imperfect difunctionality of radical telechelic PAN[6] in polycondensation processes. The already well known strategy of synthesis of graft copolymers through the use of macromonomers[10] and the availability of PEO macromonomers lead us to focus our attention on the radical copolymerization of AN and methoxy-poly(ethylene glycol) monomethacrylates ($\bar{M}_n \leqslant 10^3$) in homogeneous solution. Closely related work in the same field has essentially addressed (a) radical copolymerization of AN with *p*-vinylbenzyldiethylene glycol monomethyl ether[11], which may just be considered as a representative ethylene oxide macromonomer ($n = 2$ in the PEO lateral group); and (b) photo-induced grafting of PEO macromonomers on preformed brominated PAN chains[12–14], where copolymerization essentially results from a transfer process.

In the following text, A(n) refers to the PEO methacrylate with a lateral polyether chain of number-average degree of polymerization n, and B refers to acrylonitrile; F_i and W_i refer to the molar and weight fractions of monomer i (molar mass M_i) in the copolymer obtained from an initial monomer feed containing f_i^0 molar fraction of monomer i.

EXPERIMENTAL

Solvents, monomers and reagents

Dimethylformamide (DMF), dimethylsulphoxide (DMSO) and acrylonitrile (B) were twice distilled over CaH_2, under reduced pressure for the two first solvents. Azobisisobutyronitrile (AIBN) was recrystallized from methanol–toluene solution. The methoxy-poly(ethylene glycol) monomethacrylates A(5), A(8) and A(21) were used as received from Polysciences. Their structure and number-average molecular weights were checked by ^{1}H n.m.r. spectroscopy ($CDCl_3$ solution, chemical shifts δ (ppm) calculated with respect to the solvent signal

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at 7.25 ppm) and g.p.c. measurements (tetrahydrofuran solution, PL gel columns 100–500 Å, calibration with Toyo Soda poly(ethylene glycol) standards) as detailed further (see 'Results and discussion').

Polymerizations

The monomers, solvent and initiator were introduced in a Pyrex glass double-walled reactor fitted with a magnetic or mechanical stirrer and connected to an external Lauda 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.

The B consumption was monitored by gas–liquid chromatography, using a Perkin–Elmer 900 gas chromatograph fitted with a dual flame ionization detector and connected with a Hewlett–Packard 3370 B integrator. Separation was performed at 120°C on a column of poly(ethylene oxide) (0.23 g) deposited on Chromosorb W ($l=1.50$ m, $\phi=1/8$ inch). B consumption was calculated using dioxane as internal reference (2% in volume in the reaction medium).

The recovery and purification of the copolymers were performed according to the following two procedures, depending on the sample composition.

(a) The A-poor copolymers ($F_{Ai}<0.18$, $W_A<0.66$) were precipitated from the reaction medium into a 10-fold excess of distilled water, and they were further purified by precipitation of their DMF solution into water followed by a thorough washing with methanol in a Waring blender.

(b) The A-rich copolymers ($F_A>0.18$, $W_A>0.66$) were precipitated from the reaction medium into a 10-fold excess of diethyl ether; they were then dissolved in distilled water, and the solutions were exhaustively dialysed for at least 48 h using cellulosic Spectrapor membranes of molecular weight cut-off 3000 and finally freeze-dried.

The lack of any trace of the macromonomer A in the g.p.c. diagram of the copolymer (see later) clearly shows the good efficiency of the purification process. In all cases the copolymers were dried at 50°C under 10^{-2} torr. Their composition was derived from N and O (Unterzaucher–Monar) elemental analysis, which systematically lead to very self-consistent results as shown below:

F_A from	N analysis:	0.178	0.557	0.761
	O analysis:	0.171	0.547	0.755

Molecular-weight measurements

Refractive index increments in DMF solution, dn/dc, were measured at room temperature on a Brice–Phoenix BP 10004 differential refractometer: dn/dc (ml g^{-1}) at $\lambda=546$ and 632 nm are 0.038 and 0.042 for $A(8)_n$, and 0.082 and 0.087 for B_n. In all cases the dn/dc values measured on the copolymers were in good agreement with the calculated ones according to the additivity rule:

$$dn/dc=\sum_i w_i(dn/dc)_i$$

Light scattering measurements were performed at room temperature on Fica apparatus for the same wavelengths.

For copolymers, gel permeation chromatography (g.p.c.) experiments were carried out on dimethylacetamide (DMAC)/10^{-2} N LiBr solutions at 80°C using a GPC-150 Waters chromatograph fitted with PL gel columns (10^3, 10^4, 10^5, 10^6 Å). Apparent molecular weights and polydispersity indices were calculated using standard polystyrene calibration.

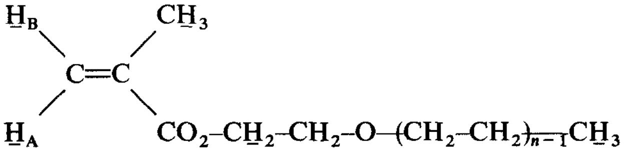
Fractionation of copolymer 3 ($W_A=0.477$, $\bar{M}_w=7.75\times10^4$)

Copolymer fractionation was performed by precipitation starting from a 2% (wt/vol) DMF solution and using toluene–diethyl ether (1/2 vol) as non-solvent. The successive fractions were obtained by simultaneous addition of non-solvent and temperature lowering: non-solvent volume fraction $\gamma=0.647$, $t=45$°C for the first fraction; $\gamma=0.748$, $t=18$°C for the last one. Some important fractions were refractionated using the same system and starting from a more dilute 1% (wt/vol) DMF solution. The excellent agreement between the average composition of the original copolymer, $W_A=0.477$, and that of the cumulated recovered fractions, $W_A=0.474$, shows that, in spite of a relative low yield of 80%, no selective loss occurred during the separation process.

RESULTS AND DISCUSSION

The macromonomer structure

Monofunctionality of the macromonomer is a necessary prerequisite to obtain soluble copolymers. Goethals *et al.*[15] have recently questioned the validity of such an assumption for a series of commercial monomethoxy-poly(ethylene glycols) (including Polysciences samples), which are the precursors of the corresponding methacrylate macromonomers. The three Polysciences samples were characterized by g.p.c. and ^{1}H n.m.r. spectroscopy: see typical g.p.c. elution curves and ^{1}H n.m.r. spectrum in *Figures 1* and *2*. At 200 MHz the ^{1}H n.m.r. spectra are well enough resolved to allow quantitative analysis of the hydrogen resonance patterns of the methacryloyloxyethyl and methoxy end-groups:



H_A, m, $\delta=6.13$ ppm

H_B, m, $\delta=5.58$ ppm

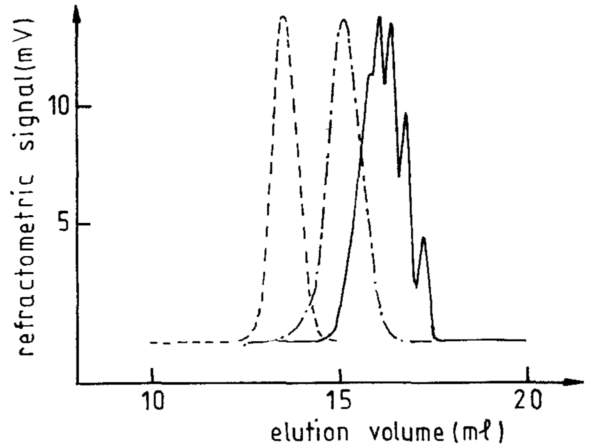


Figure 1 G.p.c. diagram (THF solution) of Polysciences PEO macromonomers: (——) A(5); (— · — · —) A(8); (– – – –) A(21)

CO_2–$C\underline{H}_2$–CH_2, t, $\delta = 4.30$ ppm, $J = 2.4$ Hz

O–$C\underline{H}_3$, s, $\delta = 3.38$ ppm

$C\underline{H}_3$–C=CH_2, s, $\delta = 1.95$ ppm

Significant shifts of the ratios [CO_2–CH_2]/[O–CH_3] and [α-CH_3]/[O–CH_3] from their theoretical values of 2/3 and 1, respectively, are a measure of corresponding shifts from pure monofunctionality. Moreover, quantitative comparison of the chain-end hydrogen atoms (CH_2= and O–CH_3) with the methylenic ones or with the total spectrum leads directly to the average chain length $\bar{n}$ of the macromonomer. The experimental results given in *Table 1* show that the two macromonomers of higher molecular weights, A(8) and A(21), are monodisperse and that their various molecular-weight data are in fairly good agreement (unknown method for Polysciences values). The determination of functionality is more difficult. The introduction of 0.01, 0.02 and 0.03 molar fraction of difunctional chains leads respectively to an increase of only 2, 4 and 6% of the ratios [CO_2–CH_2]/[O–CH_3] and [α-CH_2]/[O–CH_3] with respect to their calculated values for monofunctional species. Taking into account that the experimental accuracy is not better than about 3%, strict monofunctionality cannot be definitely ascertained, but the amount of possible difunctional chains in the three macromonomer samples is very probably lower than 2%.

Copolymerization kinetics of the A(8)–B system

Among the solvents that allow the A–B copolymerization to occur in homogeneous phase, DMSO shows the lowest transfer constant with respect to B radicals[16] ($C_T \simeq 1.1 \times 10^{-5}$ at 60°C) and moreover currently yields the less discoloured B polymers. B homopolymerization is best carried out within a monomer concentration range of about 2.5–6 mol l^{-1}, where no kinetic deviation with respect to the classical scheme may be observed[17]. However, in our case, for a total initial monomer concentration $[M]^0 > 3$ mol l^{-1} and for $f^0_{A(8)} > 0.1$, copolymerizations systematically result in gelled reaction medium, which can be redissolved by further dilution only with great difficulty. Irreversible gelation has already been observed in the homopolymerization of similar PEO macromonomers in water or toluene solution[18]. Thus copolymerization of the A(8)–B pair was best performed in relatively dilute DMSO solution at 60°C in the presence of AIBN as radical initiator in the following conditions:

$$0.5 < [M]^0\ (\text{mol}\,l^{-1}) < 1.5 \qquad [\text{AIBN}]^0/[M]^0 = 10^{-2}$$

The B consumption does not show any inhibition period (the eventually stabilized macromonomer has not been purified) and obeys first-order kinetics up to conversion of about 45% only for B-rich monomer feeds ($f_B > 0.75$); see *Figure 3*. This allows the derivation of an apparent pseudo-first-order rate constant K_B:

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

which may be compared with the corresponding literature value for B homopolymerization in identical conditions (DMSO, 60°C)[16]:

$$K_B = (k_p/k_t)^{0.5}(2fk_d)^{0.5} = 5.89 \times 10^{-4}\,l\,\text{mol}^{-1/2}\,s^{-1}$$

where the kinetic constants k_d, k_p, k_t and the initiator efficiency f have their usual meaning. As shown in *Figure*

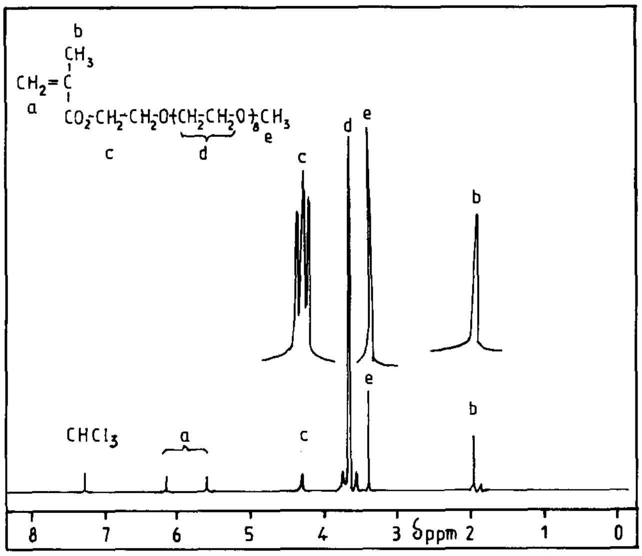


Figure 2 ^1H n.m.r. spectrum (200 MHz) of macromonomer A(8) in $CDCl_3$ solution

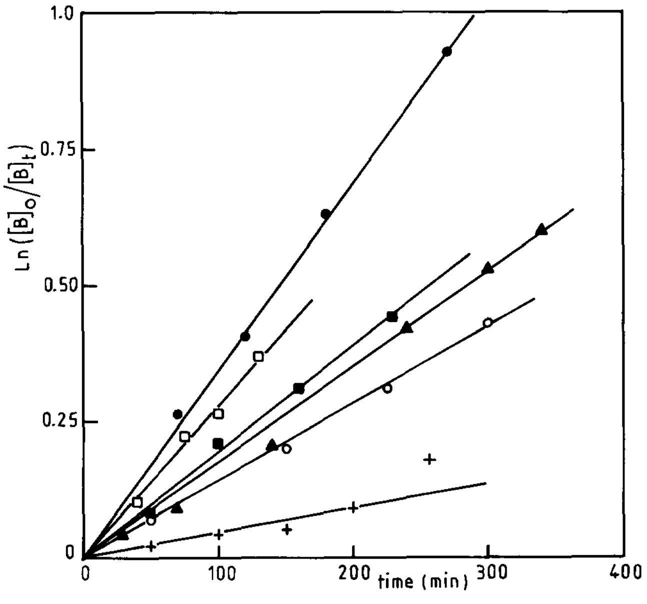


Figure 3 First-order kinetics of B consumption for copolymerization of various A(8)–B systems: $f^0_A = 0.011$ (●), 0.031 (○), 0.06 (+), 0.113 (▲), 0.168 (■), 0.249 (□)

Table 1 Structural characterization of the Polysciences polyoxyethylene (POE) macromonomers A(5), A(8) and A(21)

		G.p.c.		^1H n.m.r.			
Monomers	$\bar{M}_n$ (Polysciences)	$\bar{M}_w$	$\bar{M}_n$	CO_2CH_2/OCH_3	CH_3/OCH_3	$\bar{n}$	$\bar{M}_n$
A(5)	336	260	200	0.656	1.00	4.8	310
A(8)	468	485	450	0.690	1.02	8.4	470
A(21)	1070	1220	1180	0.668	1.06	20.5	1000

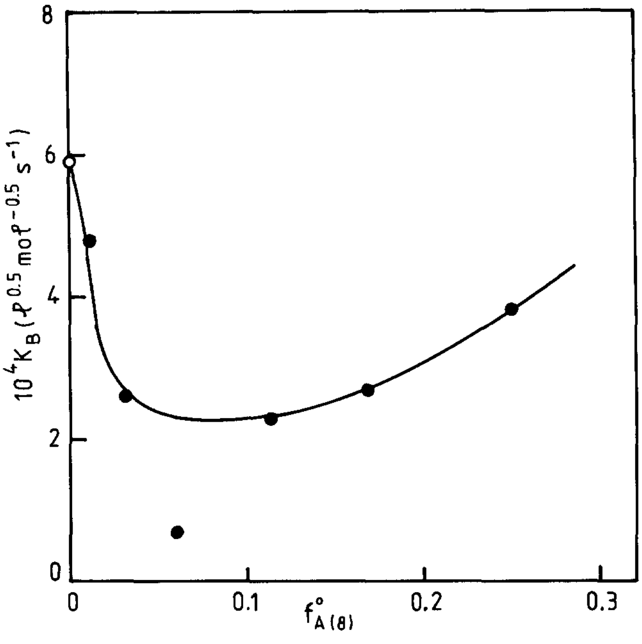


Figure 4 Variations of the apparent first-order rate constant K_B of B consumption with monomer feed composition for A(8)–B copolymerization (○, literature data[16])

4, K_B in the A(8)–B system is always lower than for B homopolymerization and goes through a minimum at about $f_B \sim 0.08$: the interpretation of these non-monotonic variations with monomer feed composition is beyond the scope of the present work.

Transfer to the polyether chain

Previous work in this laboratory[6] has shown that the transfer constant of a polyacrylonitrile radical $B_n^\bullet$ to an oxyethylene unit is about 4.7×10^{-4} at 50°C. Assuming simple additivity, as observed for polyoxyethylene (POE) chains, dioxane or crown ethers[6], the transfer constants to the macromonomers should be about 3.9×10^{-3} and 9.6×10^{-3} for A(8) and A(21), respectively. Transfer to the polyether chain either in the macromonomer or in the copolymer in the case of high conversion may probably occur, resulting in grafting on the macromonomer lateral group and in highly branched structures.

Monomer reactivity ratios

The experimental results of a representative series of copolymerizations A(8)–B are given in *Table 2*. The reactivity ratios were calculated according to the Kelen–Tüdös[19] method adjusted to high conversion degrees τ ($0.19 \leqslant \tau \leqslant 0.57$ for our systems). All the data may be reasonably linearized (regression coefficient $R(9) = 0.972$) and lead to the following reactivity ratios: $r_A = 1.35$, $r_B = 0.38$.

Comparison of the calculated instantaneous copolymerization diagram with the experimental data is shown in *Figure 5*. The differences observed, especially for low f^0_B values, merely arise from the composition drift that necessarily occurs for increasing conversion (see later). Moreover the r_A and r_B values are derived essentially from copolymerization of A-poor monomer feeds ($f^0_A \leqslant 0.25$), and a more systematic study over the whole composition range should yield more reliable and accurate reactivity ratios.

Comparison of these primary r_A and r_B values with the corresponding ones for analogous alkyl methacrylates–acrylonitrile systems remains of interest, however.

(a) The reactivity ratio $r_{A(8)}$ is fairly similar to the reactivity ratios of low-molecular-weight alkyl methacrylates[20], $r \sim 1$–1.5; r(ethyl methacrylate) = 1.35 in DMSO solution at 54°C for instance[21].

(b) The only experiment carried out with the macromonomer A(21) (see run **12** in *Table 2*) involves a sufficiently low f^0_A fraction to allow a rough estimation of the corresponding r_B reactivity ratio, $r_B \sim \ln(1-\tau_B)/\ln(1-\tau_A)$ where τ_i is the molar conversion of monomer i[10]: $r_B \sim 0.66$. This value appears significantly higher than those observed with A(8), $r_B = 0.38$, or with various alkyl methacrylates[20], $r_B \sim 0.2$–0.3: $r_B = 0.28$ for acrylonitrile–ethyl methacrylate copolymerization in DMSO solution at 54°C[21]. The decrease of $r_B^{-1} = k_{BA}/k_{BB}$ values when increasing the chain length of the various methacrylates reflects a simultaneous decrease of their relative reactivities, with respect to acrylonitrile B as a reference, towards a common acrylonitrile-terminated macroradical B*. Such a trend, previously observed on analogous systems[22], may arise from increasing repulsive interactions between incompatible polymer chains when increasing the macromonomer chain length rather than from a pure 'kinetic

Table 2 Copolymerization of A(8) and B monomers in DMSO solution at 60°C ($[\mathrm{AIBN}]^0/[\mathrm{A+B}]^0 = 10^{-2}$)

	Monomer feed			Copolymer	
Run	$[\mathrm{A+B}]^0$ (mol l^{-1})	f^0_A	Time (min)	Yield (wt%)	F_A
0	1.50	0.00	260	54.6	0
1	1.50	0.011	270	45.0	0.023
2	1.50	0.031	280	40.4	0.057
3	1.50	0.052	160	54.1	0.090
4	1.52	0.060	280	18.6	0.120
5	1.53	0.113	340	54.7	0.177
6	0.873	0.137	450	41.6	0.213
7	1.54	0.168	250	38.0	0.258
8	1.49	0.249	130	22.7	0.378
9	0.512	0.513	340	57.3	0.632
10	0.520	0.760	465	32.0	0.779
11[a]	0.303	1.00	760	89.0	1.0
12[b]	1.50	0.016	160	55.8	0.029

[a] Homopolymerization in homogeneous benzene solution
[b] Copolymerization with PEO macromonomer A(21)

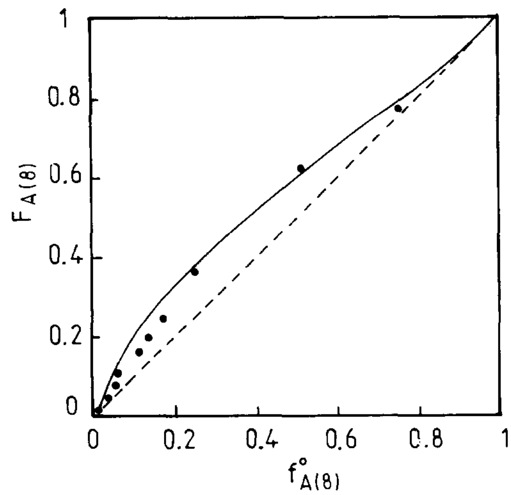


Figure 5 Composition diagram for A(8)–B copolymerization: (●) experimental data of *Table 2*; (– – – –) calculated curve ($r_{A(8)} = 1.35$, $r_B = 0.38$) for instantaneous copolymerization ($\tau \to 0$)

excluded volume' (steric effects)[22,23]. It obviously requires to be ascertained on a more systematic study beyond the scope of the present work.

(c) The knowledge of the reactivity ratios and of the Q and e parameters for acrylonitrile[24] ($Q_B = 0.48$, $e_B = 1.23$) allows the calculation of the corresponding Q and e values for the macromonomer: $Q_{A(8)} \sim 0.46$, $e_{A(8)} \sim 0.41$. These figures derived from a single copolymerization system have to be considered only as rough estimations, but they nevertheless appear fairly reasonable for a methacrylate monomer[24].

Compositional heterogeneity of the copolymer

Of the two independent contributions to the composition distribution of the copolymer, statistical or instantaneous heterogeneity[25,26] and conversion heterogeneity, we focused our attention on the latter, easily calculated from the integrated form of the Skeist equation, as proposed by Meyer and Lowry[27]. The variations of the instantaneous F_A and cumulative $\bar{F}_A$ compositions of the copolymers with total conversion $\tau = 1 - [M]/[M]_0$ are given in *Figure 6* for some representative monomer feed compositions. At a constant conversion $\tau = 0.5$, the width of the distribution measured by its mean-square standard deviation σ^2 shows a rather sharp maximum for a macromonomer fraction f_A^0 of about 0.06 (*Figure 7*).

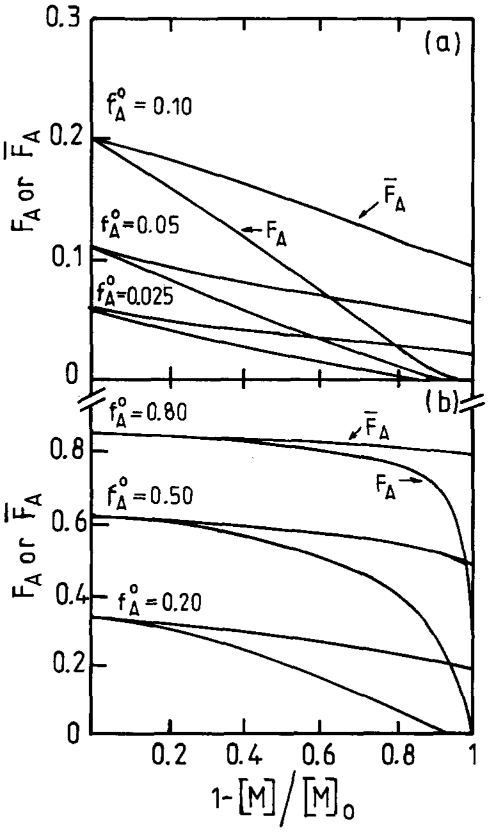


Figure 6 Variations of the instantaneous (F_A) and cumulative ($\bar{F}_A$) compositions of copolymers A(8)–B with conversion for some representative initial monomer feeds

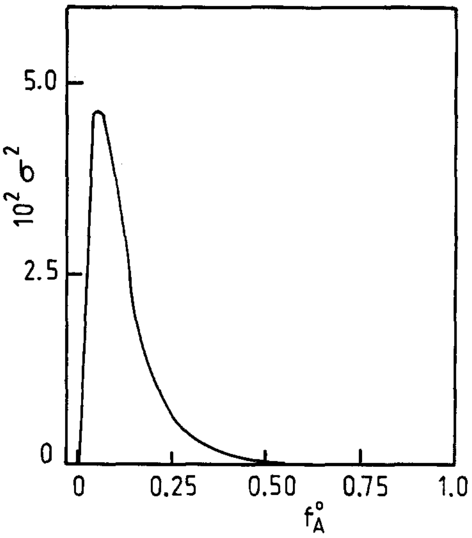


Figure 7 Variations of the mean-square standard deviation σ^2 of the compositional distributions of copolymer A(8)–B with initial monomer feed composition at a constant conversion $\tau = 0.5$

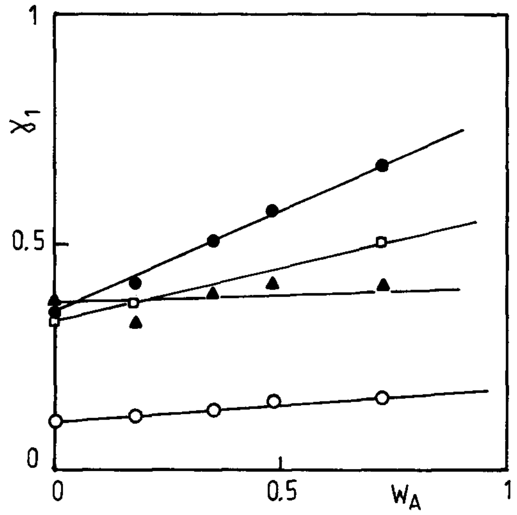


Figure 8 Variations of the γ_1 values with copolymer composition for copolymer A(8)–B solution in DMF precipitated with various non-solvent systems: (●) toluene–diethyl ether (1/2 vol); (□) n-hexane–diethyl ether (1/1 vol); (▲) diethyl ether; (○) water

Compositional distribution was tentatively analysed at an experimental level by fractionation choosing copolymer 3 ($W_A = 0.477$, $\bar{M}_w = 7.75 \times 10^4$) as a representative sample, which may be expected to be chemically heterogeneous enough according to the previous calculations ($f_A^0 = 0.052$, $\tau = 0.36$). *Figure 8* shows the nearly linear variations of the γ values (non-solvent volume fraction at the first cloud point, see 'Experimental' section) with composition for a series of copolymers of increasing A(8) content but of fairly similar molecular weights ($(5\text{–}8) \times 10^4$) and for various solvent–non-solvent systems. 'Cross-fractionation'[28], which has been shown to be the most reliable and efficient method for the analysis of compositional polydispersity, requires two systems characterized by the highest slopes of opposite signs in the γ_1–F_A diagram. Such solvent–non-solvent pairs cannot be found for copolymers A(8)–B, and sample 3 was fractionated only 'in one direction' using the most sensitive system: DMF as solvent and toluene–diethyl ether (1/2 vol) as non-solvent (see 'Experimental'). The cumulative distribution curve given in *Figure 9* is nearly symmetric and fairly narrow:

$$V = \frac{\sum_i w_i(w_A^i - \bar{w}_A)}{\sum_j w_j(\bar{w}_A - w_A^j)} = 0.85 \qquad (\text{with } w_A^i > \bar{w}_A \text{ and } w_A^j < \bar{w}_A)$$

$$\sigma^2 = 3.7 \times 10^{-4}$$

The apparent σ^2 value calculated for a hypothetical homogeneous copolymer of the same composition and fractionated in the same way may be estimated as about 0.9×10^{-4}, assuming that the accuracy on the composition of the various fractions is $\pm2\%$. The higher experimental σ^2 value reflects a true but very weak compositional heterogeneity, much weaker than that calculated on the basis of conversion heterogeneity alone, $\sigma^2=2.2\times10^{-3}$: compare also the experimental and calculated distribution curves in *Figure 9*. Such a discrepancy probably arises from the poor efficiency of the precipitation method, and the experimental heterogeneity is very probably strongly underestimated. Similar difficulties have already been observed for the fractionation of polyoxyethylene–polyacrylonitrile block copolymers[8].

Molecular weights and dilute solution properties of the copolymers A(8)–B

Because of the compositional heterogeneity, the branched structure of the copolymer and the misuse of linear polystyrene standards for calibration, light scattering (DMF solution at room temperature) and g.p.c. (DMAC, 10^{-2} M LiBr, 80°C) experiments lead only to apparent values of the molecular weights $\bar{M}_w$ and the polydispersity indices $\bar{M}_w/\bar{M}_n$, such as those given in *Table 3*. Critical analysis of these experimental results may suggest the following comments.

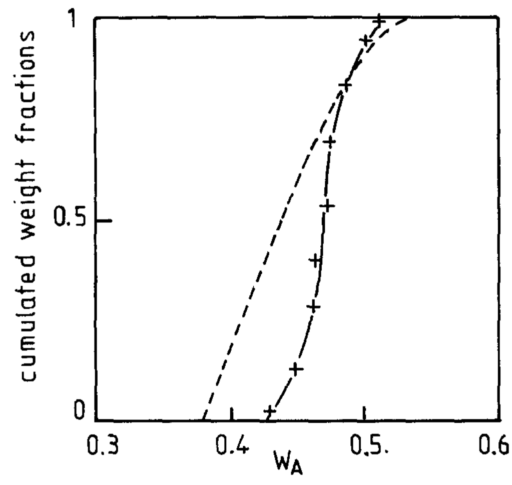


Figure 9 Integral composition distribution curve of copolymer 3 ($W_A=0.477$); (+) experimental data from fractionation; (----) calculated curve according to Meyer–Lowry equation

(a) The g.p.c. $\bar{M}_w$ data are fairly compatible with the corresponding light scattering ones for A-poor copolymers ($F_A<0.12$, $W_A<0.56$), being lower by only about 20%, while they are strongly underestimated for the A-rich copolymers ($F_A>0.25$, $W_A>0.76$). The increase of A content over a critical value yields simultaneously a drastic change in polymer structure (enhanced branching density) and in polymer–solvent interactions (chemical nature of the chain), which results in a strongly reduced hydrodynamic volume with respect to that of a linear polystyrene of identical molecular weight.

(b) The apparent polydispersity indices derived from g.p.c. data may appear reasonable for radical copolymerization in homogeneous solution at relatively high conversion: $\bar{M}_w/\bar{M}_n\sim1.6$–$3.6$. They are, however, probably biased by composition and branching effects, as are the molecular weights.

(c) The dependence of the copolymer chain length on monomer feed composition may be analysed using $\overline{DP}_w^*$ values normalized to standard monomer and initiator concentrations:

$$[\mathrm{M}]^*=1.5\,\mathrm{mol\,l^{-1}}$$

$$[\mathrm{AIBN}]^*=1.5\times10^{-2}\,\mathrm{mol\,l^{-1}}$$

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

with

$$\overline{DP}_w=\bar{M}_w/M \qquad \text{and} \qquad M=M_AF_A+M_BF_B$$

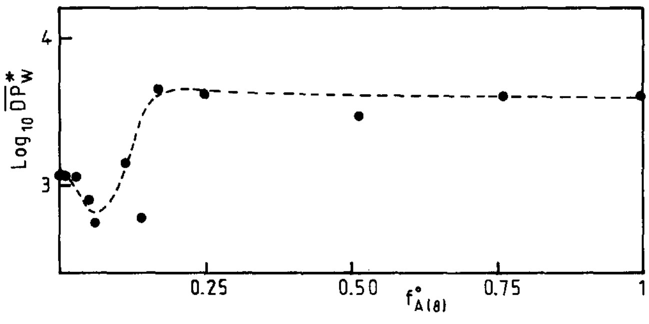


Figure 10 Variations of the normalized weight-average degree of polymerization $\overline{DP}_w^*$ of the A(8)–B copolymers with initial monomer feed composition

Table 3 Molecular weights, second viral coefficients A_2 and radius of gyration $(\bar{s}_z^2)^{0.5}$ of A(8)–B copolymers

Copolymer		Light scattering			G.p.c.	
Run	w_A	$\bar{M}_w\times10^{-5}$	$A_2\times10^3$ (ml g^{-2} mol)	$(\bar{s}_z^2)^{0.5}$ (Å)	$\bar{M}_w\times10^{-5}$	$\bar{M}_w/\bar{M}_n$
0	0	0.630	2.06	–[a]	0.490	1.71
1	0.178	0.723	1.59	–[a]	0.547	1.59
2	0.350	0.847	2.15	–[a]		
3	0.477	0.775	1.11	–[a]	0.710	1.60
4	0.557	0.603	0.773	–[a]	0.502	3.61
5	0.656	1.84	0.658	–[a]		
6	0.723	0.520	0.840	–[a]		
7	0.761	7.42	0.547	580		
8	0.835	8.89	0.205	500	1.01	3.00
9	0.951	5.10	0.180	390	0.970	2.21
10	0.982	8.81	0.048	350		
11	1.00	8.13	0.105	420		
12[b]	0.333	1.66	1.76	–[a]	1.01	2.24

[a] $(\bar{s}_z^2)^{0.5}<300$ Å

[b] Copolymer with PEO macromonomer A(21)

The non-monotonic variation of $\overline{DP}_w^*$ with f_A^0 shown in *Figure 10* has to be considered cautiously since the experimental data may be partly biased by two factors: different conversion degrees and different polydispersities from sample to sample (the more interesting $\overline{DP}_n^*$ values cannot be safely estimated because the g.p.c. polydispersity indices are not reliable enough). However, the strong $\overline{DP}_w^*$ increase noticed for $f_A^0 > 0.15$ up to a nearly constant value may be considered as a well ascertained trend.

(d) The variations of the second virial coefficient A_2 and of the radius of gyration $(\bar{s}_z^2)^{0.5}$ cannot be discussed in a very quantitative way because of the interference of composition, molecular-weight and structure effects (unknown intramolecular interactions between the dissimilar A and B units along the graft copolymer chain). Some trends may, however, be tentatively outlined.

The A_2 values of the copolymers and of the homopoly(macromonomer) A(8) are systematically lower than those calculated for PAN B_n of identical molecular weights according to the literature[29], (A_2 (ml g^{-2} mol)$=2.43\times10^{-2}\bar{M}_w^{-0.22}$, DMF, 25°C): for $\bar{M}_w=8.13\times10^5$, $A_2(A_n)=0.10\times10^{-3}$ *versus* $A_2(B_n)=1.2\times10^{-3}$ for instance. They are moreover a nearly decreasing function of W_A over the whole composition range and independent of the molecular weights of the samples: $A_2=1.95\times10^{-3}-1.81\times10^{-3}W_A$ with $R(11)=-0.966$ (the apparently overestimated A_2 value for copolymer **2** is omitted). This linear decrease is probably fortuitous, but physically meaningful and representative of composition effects alone when considering only samples of $W_A \leqslant 0.72$, which show negligible fluctuations of molecular weight around an average value of about 6.5×10^4 (runs **0**, **1**, **3**, **4**, and **6** of *Table 3*). All these features strongly suggest that DMF at room temperature is a better solvent for the B than for the A units, and such an assumption is supported by the fact that PAN B_n displays higher intrinsic viscosity in DMF solution at 25°C than polyoxyethylene over the whole molecular-weight range: compare $[\eta]$ (dl g^{-1})$=2.37\times10^{-4}\bar{M}_w^{0.75}$ for B_n[29] with $[\eta]$ (dl g^{-1})$=4.41\times10^{-4}\bar{M}_w^{0.63}$ for POE[30].

The ratios of the radii of gyration of the copolymers and of linear B_n chains of either similar molecular weight $\bar{M}_w$ or similar degree of polymerization $\overline{DP}_w$ are on average about 0.85 and 2.2 respectively: $(\bar{s}_w^2)^{0.5}$ (Å)$=0.236\bar{M}_w^{0.57}$ for B_n in DMF solution at 25°C[29]. Comparison at the same backbone length seems more physically sound, and the corresponding experimental ratios between 1.9 and 2.6 may appear somewhat unrealistic for chains of high branching density (more than one A(8) graft for four B units in the backbone). Two factors may contribute to the increased $(\bar{s}_w^2)^{0.5}$ values for the copolymers: (i) polydispersity effects[31] (experimental $(\bar{s}_z^2)^{0.5}$ data for polydisperse copolymers *versus* $(\bar{s}_w^2)^{0.5}$ ones for B_n); (ii) intramolecular repulsion between incompatible A(8) and B_n blocks, and possible chain rigidity increase for very high A content (steric hindrance of the lateral grafts). Knowledge of the power law $(\bar{s}_w^2)^2=f(\bar{M}_w)$ for well defined A_n homopolymers would be of great interest, but its determination is beyond the scope of the present work.

CONCLUSIONS

The radical copolymerization of methoxy-poly(ethylene glycol) monomethacrylate of relatively low molecular weight (A(8); $\bar{M}_n \simeq 470$) with acrylonitrile (B) performed in homogeneous DMSO solution at 60°C obeys the terminal unit model ($r_{A(8)}=1.346$, $r_B=0.381$) and readily leads to graft copolymers of high molecular weight ($\bar{M}_w=(0.5\text{–}9.0)\times10^5$) over a broad composition range. In spite of some unavoidable drawbacks inherent in the radical process (random distribution of the polyether grafts and polydispersity in molecular weight and in composition), this copolymerization involving a water-soluble macromonomer definitely appears to be the most reliable and efficient route towards biphasic acrylonitrile-based materials showing discrete hydrophilic microdomains. The phase segregation and some bulk properties of these graft copolymers of potential technological interest will be analysed in a forthcoming communication.

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