Polyoxyethylenic macromers from polyoxyethylene monomethyl ethers and isocyanatoethyl methacrylate. Synthesis and characterization of copolymers with styrene and methyl methacrylate, obtained through bulk, solution and soap-free emulsion polymerizations

Guy Levesque*, Véronique Moitié. Benoit Bacle and Pierre Depraétère†
Laboratoire de Chimie des Composés Thioorganiques (associé au CNRS), Institut des Sciences de la Matière et du Rayonnement, Université de Caen, 5 rue d'Edimbourg, F-14032 Caen, France
†Laboratoire de Pharmacie Galénique, Université de Caen, 5 rue Vaubénard, F-14032 Caen, France

(Received 22 April 1988; revised 1 June 1988; accepted 6 June 1988)

Polyoxyethylenic (POE) macromers were prepared from polyoxyethylene methyl ethers and isocyanatoethyl methacrylate and characterized by ^{13}C and ^{1}H nuclear magnetic resonance spectroscopy. Copolymers with styrene and methyl methacrylate (MMA) were obtained from these macromers upon free-radical initiation under various conditions (solution, bulk, soap-free emulsion) and some physical properties were studied (e.g. glass transition temperatures, stability of latex). Phase separation was observed in some copolymers with MMA as determined through dilatometry. Polystyrene latices, prepared without any emulsifying agent other than POE macromers themselves, were stable in the presence of high electrolyte concentrations.

(Keywords: polyoxyethylene monomethyl ether; isocyanotoethyl methacrylate; macromer copolymerization graft copolymers)

INTRODUCTION

The synthesis of graft and block copolymers of ethylene oxide represents an interesting problem[1] and some important solutions have arisen from the use of polyoxyethylene (POE) macromers—i.e. polymers end-capped by a polymerizable group[2]. Previously described POE macromers have been obtained either through alkylation of polyoxyethylene with a mixture of chloromethylstyrenes[3], or through esterification by acryloyl and methacryloyl chlorides[4–7].

We report here the synthesis and some applications of POE macromers readily available from commercial isocyanatoethyl methacrylate (IEM, Dow) and polyoxyethylene monomethyl ether (POEME).

EXPERIMENTAL

Polyoxymethylene methyl ethers (commercial samples, Aldrich) were dried over silica gel for at least 48 h. IEM was kindly supplied by Dow Chemicals and used without purification.

Transmission electron micrographs were obtained on a Jeol 120 CX, fitted with a side-entry goniometer and operating at 120 kV.

Density measurements were done according to known procedures in a mercury-filled dilatometer[8,9].

Macromer synthesis

Method A (POEME 1900 and 5000). In a 250 ml reactor protected against moisture and equipped with nitrogen inlet, mechanical stirrer, introduction funnel and reflux condenser were placed 30 g POEME. Under heating (oil bath), the POEME was melted and allowed to begin stirring; then, 10 mg dibutyltin dilaurate (Tinstab SA) and 1.3 molar equivalents IEM were added over ~1 h. The reaction mixture was stirred at 60°C for 15 h, cooled and poured into a large volume of hexane/diethyl ether for macromer precipitation. Purification was obtained by dissolution in dichloromethane and precipitation as above. The macromer yield after drying was nearly quantitative.

Method B (POEME 350, 550, 750). As the molecular weights of macromers is lowered, their polymerizability increases so it was advisable to prepare them in solution, with addition of a free-radical scavenger. The following procedure was adopted. POEME (30 g) was dissolved at 30°C in 100 ml dichloromethane containing 0.1 g hydroquinone; addition of IEM was followed by warming at 41°C for 15 h and finally the solvent evaporated before washing the macromer with warm heptane to remove excess IEM. A model compound was prepared in a similar manner.

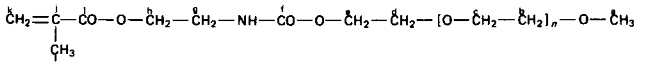
All these macromers look like the starting POEME and were characterized through ^{13}C n.m.r. (*Table 1*) and size exclusion chromatography.

---

* To whom correspondence should be addressed

0032-3861/88/122271-06$03.00

Table 1 ^{13}C n.m.r. characterization of macromers (TMS, CDCl$_3$)



$$\overset{k}{C}H_2{=}\underset{\overset{|}{\overset{l}{C}H_3}}{\overset{j}{C}}{-}\overset{i}{C}O{-}O{-}\overset{h}{C}H_2{-}\overset{g}{C}H_2{-}NH{-}\overset{f}{C}O{-}O{-}\overset{e}{C}H_2{-}\overset{d}{C}H_2{-}[O{-}\overset{c}{C}H_2{-}\overset{b}{C}H_2]_n{-}O{-}\overset{a}{C}H_3$$

	δ (ppm)					
M_n of POEME = Carbon atoms	120[a] ($n=1$) model	350	550	750	1500	5000
a	58.8	58.9	58.8	58.9	58.9	58.9
b, c	70.6	70.6	70.6	70.7	70.7	70.7
d	63.8	63.7	63.6	63.7	63.7	63.7
e	64.1	64.2	64.3	64.1	64.2	64.2
f	157.0	156.5	156.5	156.6	156.6	156.4
g	40.3	40.2	40.2	40.3	40.3	40.2
h	69.7	69.6	69.5	69.6	69.6	69.6
i	167.3	167.2	167.1	167.2	167.2	167.1
j	136.6	136.1	136.4	136.6	136.2	136.1
k	125.7	125.8	125.7	125.7	125.8	125.8
l	18.2	18.2	18.1	18.2	18.3	18.3

[a] Prepared from 2-(2-methoxyethoxy)ethanol

Macromer–MMA copolymers

Purified methyl methacrylate (MMA), POE macromer, toluene and azobisisobutyronitrile (AIBN) were introduced under nitrogen into a polymerization apparatus; solvent volume was about the same as the monomer volume and AIBN was used at concentration 1% mol/mol of monomer. Polymerization took place under heating at 70°C for 24 h. The polymer solution was concentrated and poured into a large volume of hexane. Polymers were dissolved in dichloromethane and precipitated again, washed with hexane and dried *in vacuo*. The copolymer compositions were deduced from ^{1}H n.m.r. spectra: integration area in the range $\delta = 3$–4 ppm is proportional to side-chain proton concentrations whereas resonances at $\delta < 3$ ppm result from main-chain protons only.

Bulk copolymerization with styrene

POE macromers were dissolved in purified styrene together with a small amount of 2-hydroxy-2-methyl-1-phenylpropanone (Darocur^R 1173, Merck) and the degassed solution placed in a Pyrex tube which was sealed under vacuum. The tube was rotated at room temperature while irradiated with a 6 W u.v. lamp for 48 h. The opened tubes were broken to give transparent blocks of copolymers in nearly quantitative yield. Purification before analysis was realized through dissolution in chloroform followed by precipitation in diethyl ether and drying. The main characteristics of these copolymers are reported later in *Table 4*.

Solution copolymerization with styrene

POE macromer, styrene and a fivefold volume of toluene were mixed with 1% mol AIBN/mol monomers, heated at 80°C for 36 h and precipitated as above.

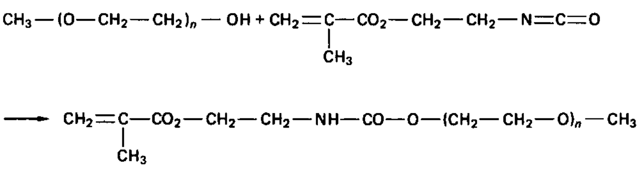
Soap-free emulsion copolymerization of POE macromers and styrene

In a cylindrical reactor modified with vertical humps in order to avoid laminar flow were placed the following under nitrogen: 40 g styrene; 200 ml degassed water; then, under stirring, a solution of 4 g macromer 550 in 200 ml water; finally, 0.64 g potassium persulphate and 0.40 g sodium metabisulphite, each in 50 ml water. Polymerization was completed upon heating at 40°C for 48 h and vigorous stirring: only a faint styrene odour could be detected. Emulsions were obtained from all macromers through such a procedure.

The critical flocculation concentrations were determined by nephelometry after dilution with a 500-fold excess of the used NaCl solution. Results are reported later for some latices in *Figure 3*.

MACROMER SYNTHESIS AND CHARACTERIZATION

Reactions between IEM and POEMEs of various molecular weights in the range 350–5000 g mol^{-1} (Aldrich) were conducted without solvent or in toluene solution at 30–60°C in the presence of a catalytic amount of dibutyltin dilaurate according to the general procedure used to condense IEM with alcohols. The addition of a free-radical inhibitor proved to be essential.



$$CH_3{-}(O{-}CH_2{-}CH_2)_n{-}OH + CH_2{=}\underset{\overset{|}{CH_3}}{C}{-}CO_2{-}CH_2{-}CH_2{-}N{=}C{=}O$$

$$\longrightarrow CH_2{=}\underset{\overset{|}{CH_3}}{C}{-}CO_2{-}CH_2{-}CH_2{-}NH{-}CO{-}O{-}(CH_2{-}CH_2{-}O)_n{-}CH_3$$

Identification of POE macromers was achieved mainly by using ^{13}C n.m.r. spectroscopy and comparison with starting POEMEs and a model compound obtained from the reaction between IEM and 2-(2-methoxyethoxy)-ethanol (*Table 1*). The POE macromers used in the subsequent work were free of any residual hydroxyethyl group detectable in the ^{13}C n.m.r. spectra by a signal at $\delta = 61.5$ ppm.

The macromer molecular weights, as determined by g.p.c. (size exclusion chromatography), were very similar to those of the initial POEMEs. However, when the macromer synthesis was conducted in the absence of a free-radical scavenger, gelled insoluble polymers were obtained, as in the previously described homopolymerization of some POE macromers[7].

DeVos and Goethals[10] have reported the determination of the concentration of hydroxyl groups in commercial samples of POEME from various origins, including those we have used for this work (Aldrich, $M_n = 1900$ and 5000 g mol^{-1}). They found respectively 1.26 and 1.20 hydroxyl groups per molecule in these polymers. As we have used IEM in a molar ratio of ~1.30 to POEME, we may expect to have completely transformed the terminal hydroxyl groups into polymerizable methacrylate groups. This expectation might explain the observed insolubility of macromer homopolymers. However, crosslinking was observed only in a few cases when a high proportion (weight/weight) of macromers ($M_n = 1900$ or 5000 g mol^{-1}) was bulk copolymerized with styrene under photoinitiation. (The molar ratio of macromer to styrene was then just more than 1%).

Although these observations are in accordance with the results of DeVos and Goethals, the question of an artefact in their estimation of POEME functionality through ^{13}C n.m.r. spectral integration cannot be ruled out.

Copolymerization with methyl methacrylate (in toluene solution) never gave rise to crosslinking and this may be assigned to the limitation of molecular weight as the probability of chain transfer or disproportionation reactions of the growing end is higher in this case.

COPOLYMERS OF POE MACROMERS AND METHYL METHACRYLATE

Preparation

POE macromers are soluble in warm MMA: some of them were copolymerized with MMA under free-radical initiation, either in toluene solution or without solvent. High yields were achieved and the copolymers may be considered as graft copolymers, readily accessible from commercial reagents.

In recent years, several papers (refs. 11–13 and references therein) have been devoted to the estimation of copolymerization parameters of various macromers (generally the smallest oligomers) according to the classical ultimate scheme. Copolymerization parameters were also reported for the acrylonitrile–POE acrylate system using numerical analysis[14]. However, only the macromer reactivity parameter could be appreciated with some accuracy with respect to the disparity of molar masses of the two monomers.

As shown in *Table 2* (for copolymers from POEME with $M_n = 5000$ g mol^{-1}) the copolymer compositions, determined from ^{1}H n.m.r. spectra, are very similar to the initial monomer ratio. Similar results were obtained starting from a macromer of $M_n = 1900$ g mol^{-1} as well at low or moderate polymerization yield. The deviation between monomer feed composition and the observed copolymer composition becomes greater when the macromer chain length is smaller (macromers from POEME 550 and mainly POEME 350).

Table 2 Copolymers obtained from macromer 5000 and MMA in toluene

No.	Macromer in (%) monomer feed	Copolymer yield (%)	Macromer (% w/w) in copolymers[a]
1	5	90	5
2	10	91	18
3	15	60	21
4	25	72	20
5	30	90	30
6	42	89	35
7	50	86	46

[a] From ^{1}H n.m.r.

Physical behaviour

According to Anderson and Rodriguez[15], POE–PMMA blends remain homogeneous over a large composition range (0–35%) with the formation of plasticized alloys which have low glass transition temperatures. We have studied the graft copolymers obtained from macromers of $M_n = 1900$ and 5000 g mol^{-1}. Differential scanning calorimetry measurements were made after annealing the copolymers overnight at 55°C. The macroscopic appearance agreed with the d.s.c. results, homogeneous transparent samples showing only one glass transition temperature while apparently heterogeneous ones presented at least a melting temperature (*Table 3*).

The copolymers of POEME macromers and MMA seemed to be homogeneous below ~45% POE (w/w) if the starting POEME has an $M_n = 1900$ g mol^{-1}, and below 40% if $M_n = 5000$ g mol^{-1}. Similar observations were made on blends prepared from the starting POEME and PMMA (Diakon^R, grade 8 from ICI) as reported in *Table 3*.

However, copolymers of macromers 1900 and MMA were examined in more detail and their specific volumes measured from 30 to 120°C (*Figure 1*). From these results, it appears that one or two glass transitions occur for each sample studied; the first transition takes place in the range 65–85°C and the second is close to the PMMA glass transition temperature (100–105°C). In the glassy state it appears that the expansion coefficient is greater for the lowest concentrations of POE macromer whereas the expansion coefficient above the first T_g increases as the POE macromer concentration increases.

Thus the d.s.c. study was unable to detect for these copolymers what specific volume variation indicated: namely the presence of two amorphous phases for a large range of compositions ($\leqslant$40% POE macromer). Their heterogeneous character was emphasized when they were submerged in water for several hours, where they became cloudy.

COPOLYMERS OF POE MACROMERS AND STYRENE

The behaviour of styrene in copolymerization with POEME macromers is quite different from that of MMA. POEME macromers are soluble in styrene at room temperature. Attempts were made to copolymerize them without solvent in the presence of a photochemical

Table 3 Thermal properties of POE–PMMA graft copolymers and blends

	Copolymers			Blends		
POEME (wt%)	Aspect[a]	T_g (°C)	T_m (°C)	Aspect	T_g (°C)	T_m (°C)
0 (PMMA)[b]	H	105	–			
5	A	80	–			
15	H	45–50	–			
20				H	40	–
25	H	50	–			
30	H	–	–	H	45	–
42	A	–	60	A	–	57
50	A	–	57	A	–	65
100	A	(Macromer)	60	A	(POEME)	66

[a] H = apparently homogeneous; A = anisotropic
[b] PMMA = Diakon^R, grade 8 from ICI

free-radical initiator. Careful exclusion of moisture in the macromer was needed as we observed demixing in bulk copolymerization of water-containing macromers. Most of the macromers were bulk copolymerized with styrene under photochemical initiation; using low to moderate concentration of macromers in styrene, transparent blocks of copolymers could be prepared, containing only traces of residual monomer. Compositions of purified samples were often identical—in the limit of ^1H n.m.r. sensitivity—to the initial styrene-to-macromer ratio.

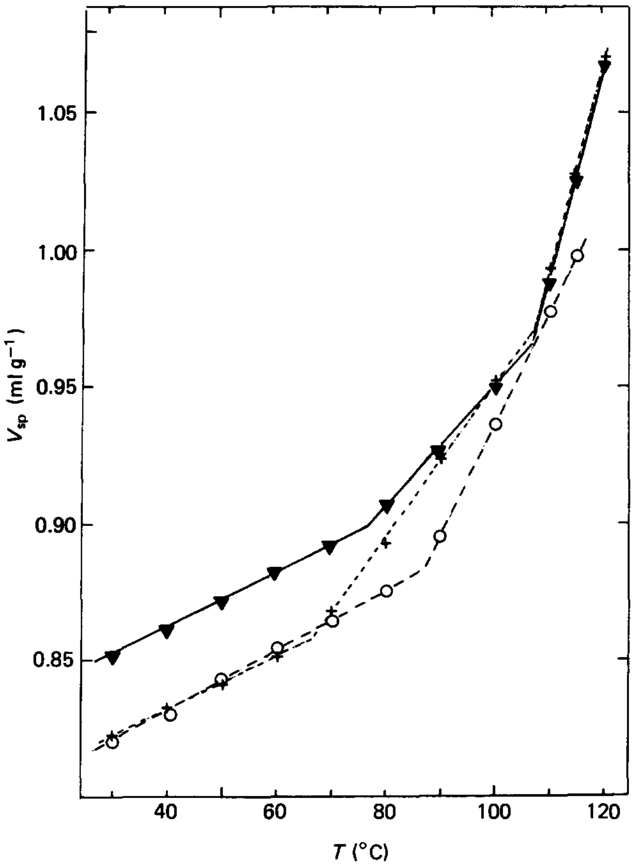


Figure 1 Specific volume of some POE–PMMA copolymers vs. temperature: (▼) 15% w/w POE macromer from POEME 1900; (+) 30% w/w POE macromer from POEME 1900; (●) 50% w/w POE macromer from POEME 1900

The copolymers obtained from POEME 1900 were high-swelling insoluble gels when the macromer concentration was more than 15% w/w. All other samples were soluble but presented rather large molecular-weight distributions (*Table 4*), thus indicating both complex polymerization kinetics and heterogeneity of composition. (Remember that a 15% w/w macromer-to-styrene ratio corresponds to less than 1% mol/mol.)

This was confirmed when solution copolymerization experiments were stopped at low or moderate yields. Results collected in *Table 5* show significant deviations of the initially formed copolymers in comparison to the starting styrene–macromer composition. Methacrylate esters present as end-groups in the macromers are much more rapidly incorporated in the copolymer than styrene.

So, bulk copolymers must be very heterogeneous, containing copolymers formed of more than 50% (w/w) POEME and nearly pure polystyrene. This is visualized by immersing small fragments of these materials in water: copolymers containing more than 15% POEME become cloudy in relation with water diffusion.

Emulsion copolymerization

As emulsion polymerization under redox initiation takes place more rapidly than solution polymerization, we tried to prepare copolymers of POEME macromers and styrene under these conditions. It seemed interesting to us to copolymerize styrene in soap-free emulsion as

Table 5 Solution copolymerization of styrene and POE macromers

M_n of macromer	Macromer (%) in monomer feed (w/w)	Copolymer yield (%)	Copolymer composition (w/w %)	(mol/mol × 10^3)
5000	20	25	64	36.4
5000	5	5	69	43.8
1900	10	10	46	44.3

Table 4 Bulk photocopolymerization of styrene and POEME macromers

POE macromer molecular weight (g mol^{-1})	Macromer/styrene ratio (w/w %)	Copolymer composition (w/w %)	(mol/mol × 10^3)	$\bar{M}_n$ (g mol^{-1} × 10^{-3})	$\bar{M}_w$ (g mol^{-1} × 10^{-3})
350	4.80	1.90	5.9	27.4	122
	9.00	3.30	10.1	18.4	78
550	4.70	3.31	6.5	37.0	168
	9.00[a]	5.35	10.4	30.2	240
750	0.97	0.83	1.15	31.1	148
	2.90	2.66	3.8	32.4	155
	4.50	3.20	4.6	30.1	175
	6.40	5.06	7.3	33.1	195
1900	0.98	1.60	0.9	27.8	128
	2.88	2.80	1.6	25.4	126
	4.55	4.90	2.8	21.2	109
	6.38	6.62	3.9	23.7	102
	8.90	9.02	5.4	25.4	117
	12.8	12.7	7.9	22.3	83
	16.4		insoluble		
	22.6		insoluble		

[a] This sample was studied by dilatometry and exhibited a glass transition near 62°C

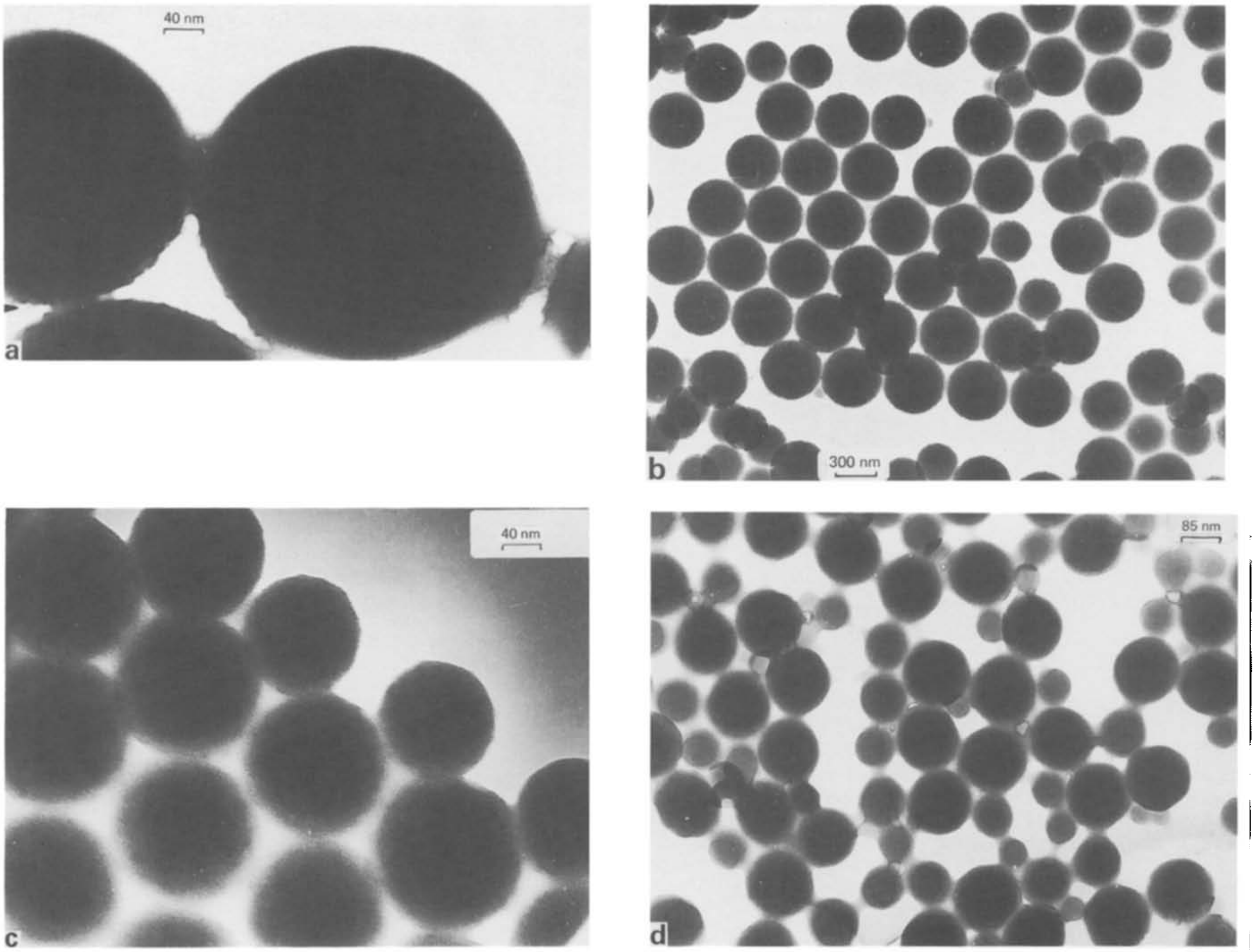


Figure 2 Transmission electron micrographs of POEME–styrene copolymer latex from POEME 350 as a function of POEME/styrene ratio: (a) POEME/styrene = 1% w/w; (b) POEME/styrene = 3% w/w; (c) POEME/styrene = 5% w/w; (d) POEME/styrene = 10% w/w

POE macromers could be surface-active agents because of their good solubility in water as well as in styrene.

Some preliminary tests have indicated that the best results are obtained when using more water than is usual for emulsion polymerization. Thus stable polystyrene emulsions were obtained from all macromers and styrene when water was present in ~10 times the monomer volume.

The emulsions so obtained were studied by transmission electron microscopy and tested for stability in the presence of an electrolyte at various temperatures. A similar study was recently published by Kawaguchi *et al.*[16] concerning copolymers of styrene with various amounts of *N*-acryloylpyrrolidine (NAP) prepared in soap-free emulsion polymerization.

As appears from *Figure 2*, the POE–styrene latices consist mainly of spherical particles of ~0.2–0.4 μm diameter. Some of them however show an irregular surface but they are joined through the hydrophilic external structure formed from POE macromers as soon as water is drained off. Copolymer beads seemed to be covered in with a layer of soft matter whose extent increases with the POEME-to-styrene ratio. Collapsing of these external layers is evident for higher macromer concentrations, thus reinforcing the idea that POEME is grafted mainly at the particle surface.

The latex stability in the presence of an electrolyte was measured through nephelometry and appears promising, as is observed from *Figure 3*, in which we have reported both our results for some POEME macromer/styrene latices and the values of Kawaguchi *et al.*[16] on NAP/styrene statistical copolymer latices.

Although these NAP/styrene copolymers contained an important weight fraction of hydrophilic monomer units they exhibited only poor stability against electrolytes as compared with emulsions formed from POEME macromers and styrene; this result undoubtedly arises from the graft character of these copolymers.

As was observed on micrographs, latex particles probably present an externally hydrophilic surface, covered by POEME sequences, whereas such a structure is quite improbable with statistical copolymers. However, the presence of some microgels consisting of highly swelled crosslinked macromer-rich polymer cannot be excluded. More investigation is needed in order to separate and characterize such a polymer from latex beads.

ACKNOWLEDGEMENTS

Thanks are due to Professor Maryvonne Hervieu for her kind assistance in electron microscopy.

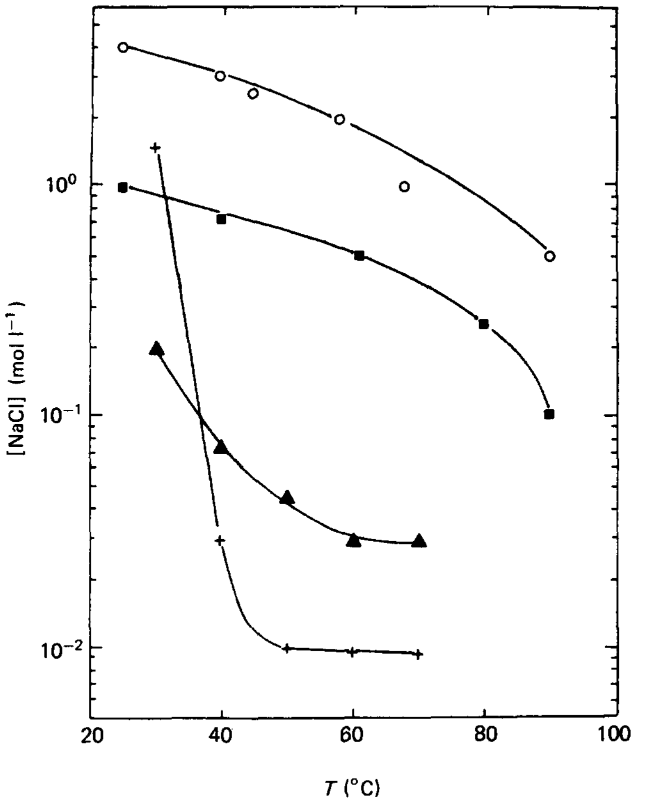


Figure 3 Influence of temperature and electrolyte concentration upon stability of POE macromer/styrene graft copolymer latex and *N*-acryloylpyrrolidine (NAP)/styrene statistical copolymer latex: (○) latex POE 550 macromer/styrene (10/90); (■) latex POE 350 macromer/styrene (3/97); and latex of statistical NAP/styrene copolymers, 20/80 (▲) and 10/90 (+) (data redrawn from ref. 16)

This work was supported by a grant from the Centre National d'Etudes Spatiales (Toulouse).

REFERENCES

1 Suzuki, T., Murakami, Y. and Takegami, Y. *Polym. J.* 1980, **12**, 183
2 Rempp, P. F. *Adv. Polym. Sci.* 1984, **58**, 1
3 Révillon, A. and Hamaide, T. *Polym. Bull.* 1982, **6**, 235
4 Sierra-Vargas, J., Franta, E. and Rempp, P. *Makromol. Chem.* 1981, **182**, 2603
5 Schneider, A., Dietzel, W. and Fritsche, P. *Acta Polym.* 1984, **35**, 186
6 Fish, D., Xia, D. W. and Smid, J. *Makromol. Chem., Rapid Commun.* 1985, **6**, 761
7 Germain, P. and Frère, Y. *Polym. Commun.* 1986, **27**, 16
8 Ramana Rao, G., Castiglioni, C., Gussoni, M., Zerbi, G. and Martuscelli, E. *Polymer* 1985, **26**, 811
9 Martuscelli, E., Silvestre, C., Addonizio, M. L. and Amelino, L. *Makromol. Chem.* 1986, **187**, 1557
10 DeVos, R. and Goethals, E. J. *Polym. Bull.* 1986, **15**, 547
11 Ito, K., Tsushida, H., Hayashi, A., Kitano, T., Yamada, E. and Matsumoto, T. *Polym. J.* 1985, **17**, 827
12 Ito, K., Tsuchida, H. and Kitano, T. *Polym. Bull.* 1986, **15**,425
13 Ito, K., Yokoyama, S., Arakawa, F., Yukawa, Y., Iwashita, Y. and Yamasahi, Y. *Polym. Bull.* 1986, **16**, 337
14 Schneider, A., Dietzel, W. and Fritsche, P. *Acta Polym.* 1984, **35**, 186
15 Anderson, C. A. and Rodriguez, F. 188th Amer. Chem. Soc. Meeting Preprints, Div. Mater. Sci. Eng. no. 123, 1984
16 Kawaguchi, H., Oshino, F. and Othsuka, Y. *Makromol. Chem., Rapid Commun.* 1986, **7**, 10