PII: S0032-3861(96)00808-7

Synthesis of thermoassociative copolymers

D. Hourdet*, F. L'Alloret and R. Audebert
*Université Pierre et Marie Curie, Laboratoire de Physico-Chimie Macromoléculaire,
CNRS URA 278, E.S.P.C.I., 10 rue Vauquelin, 75231 Paris Cedex 05, France*
(Received 14 June 1996; revised 12 August 1996)

The synthesis of thermoassociative water-soluble copolymers, with polyether as pendant chains, was developed by macromonomer copolymerization and grafting techniques. The discussion was specially focused on the coupling reactions, between ω-methyl α-aminopolyethers and carboxylic units borne on the backbone, which provide in quantitative yield well-defined grafted copolymer structures. According to the thermodynamical properties of poly(ethylene oxide) or poly(propylene oxide) side-chains (lower critical solution temperature), aqueous solutions of grafted copolymers exhibit a microphase separation of polyether grafts upon heating and generate, above C^*, thermothickening properties of the solutions. The general basis of this behaviour is discussed, and the roles played by structural and external parameters highlighted. © 1997 Elsevier Science Ltd.

(Keywords: polyethylene oxide; carbodiimide; grafting)

INTRODUCTION

Most of the aqueous polymer solutions used in industrial applications, as thickeners to control the rheology of aqueous based fluids, are characterized by a loss of viscosity under heating.

This usual feature turns out to be a major drawback in many applications carried out in a wide range of temperatures, such as aqueous suspensions, coatings, drilling fluids and general work in deep subterranean formations. In most cases, the decrease of viscosity with temperature leads to a loss of efficiency or a lack of control of the process.

From this technological point of view, it would indeed be more convenient to use hydraulic fluids which could keep their rheological properties constant in the whole range of temperatures investigated, or which could enhance reversibly their viscosity upon heating. We could expect in this case to obtain the required properties at the temperature of the application.

Until recently, literature dealing with such rheological properties was very scarce, contrary to the well-known opposite phenomenon of gelation upon cooling, observed with a large number of natural polymers. Some patents or academic studies have reported thickening or gelation behaviours of aqueous solutions upon heating with block copolymers poly(ethylene oxide) (PEO)–poly(propylene oxide) (PPO)–PEO[1], cellulose ether derivatives (-methyl, -hydroxypropyl and -ethyl(hydroxyethyl))[2–5], or more sophisticated systems involving nonionic cellulose ethers and ionic surfactants[6] or hydrophobically modified polymers and neutral surfactants[7]. Except for this last group, where the driving force is the phase transition of the surfactant, it appears that in most of the systems depicted, the gelation was controlled through hydrophobic interactions between the polymer chains.

On this basis, we have proposed a general concept for thermoassociative polymer solutions, which is based upon the switch properties of polymers characterized by a lower critical solution temperature (LCST). The concept and design of these so-called thermoassociative, thermothickening or thermostimulated copolymers have been described in previous papers[8,9] and can be pictured as a highly water-soluble macromolecular backbone containing some LCST blocks or side chains (*Figure 1*). These thermosensitive moieties can undergo reversible microphase segregation with increasing temperature (*Figure 1*). For polymer concentrations higher than C^* (the overlap concentration of the chains), this transition gives rise to a viscosity enhancement of the solution through interchain associations. Such expected features have been successfully confirmed with polyacrylate derivatives-*g*-PEO copolymers which have been developed in our department[8–11] and exemplified more recently by Möller and coworkers[12,13], with similar structures.

We can add that such an associative mechanism is not restricted to aqueous polymer solutions, but can be extended to a large number of systems (copolymers in organic fluids or melts) using LCST properties as the driving force.

In our previous studies[9,10], we have shown that such graft copolymers, in aqueous solutions, can provide a strong increase of viscosity with temperature, which can reach values of several orders of magnitude higher than those measured with equivalent unassociative polymers (unmodified backbone). The thermothickening behaviour of these systems can be easily controlled by external parameters such as polymer concentration, nature and concentration of added salt, pH and temperature. Nevertheless, the nature of both components (backbone and grafts) is assumed to play a prevalent role in the microscopic structure, and so on the macroscopic properties.

A better knowledge of the thermothickening behaviour proceeds through a broadening of the experimental

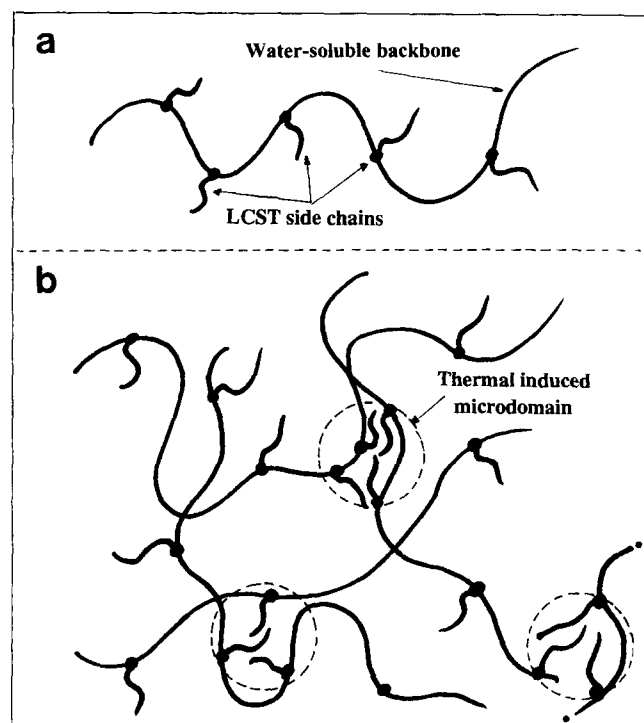* To whom correspondence should be addressed

Figure 1 Thermoassociative concept in aqueous solutions: (a) copolymer structure; (b) association mechanism ($T >$ LCST)

concerning the best method of synthesis and the choice of experimental conditions for the control of the copolymer architecture.

In the last part of this paper, the rheological behaviour of some typical systems with the temperature will be given to illustrate the close relation between molecular structure and macroscopic properties.

EXPERIMENTAL

Monomers, reagents and solvents

Acrylic acid (AA, Fluka), acrylamidomethyl-propane-sulfonic acid (AMPS, Fluka) and acrylamide (AM, Aldrich) monomers were used without further purification.

Dicyclohexylcarbodiimide (DCCI) and N'-(3-dimethyl-aminopropyl)-N-ethylcarbodiimide hydrochloride (EDC), purchased from Janssen, were of analytical grade, as were all other reagents.

Water was purified with a Milli-Q system from Millipore and all organic solvents ($\geq 99\%$ purity) were used as received.

Water-soluble backbones

Poly(AA) (PAA) in concentrated aqueous solution, 12.5% (w/w) for $\overline{M}_w = 500\,000\,\mathrm{g\,mol^{-1}}$ (PAA 500), 25% (w/w) for $\overline{M}_w = 150\,000\,\mathrm{g\,mol^{-1}}$ (PAA 150) and $\overline{M}_w = 90\,000\,\mathrm{g\,mol^{-1}}$ (PAA 90), were purchased from Polysciences. In order to obtain pure PAA in acidic form, commercial solutions were diluted at 1% with HCl $5 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$ and ultrafiltered with a large excess of deionized water through a pellicon cassette system (Millipore) with ultrafiltration membranes of 10 000 nominal molecular weight cut-off. The PAA solutions were then concentrated and freeze-dried.

PSVA is a terpolymer of acrylamidomethyl-propane sulfonic acid (AMPS), N-methyl vinyl acetamide (NMVA) and AA produced by Hoechst. The molar comonomer composition is respectively 65/20/15. Initially at 15% by weight in 8% sodium chloride aqueous solution, PSVA was purified in the same way as PAA.

PVEAM is an alternating copolymer of vinyl-methyl-ether and maleic anhydride, supplied by GAF. The given average molecular weight is $68\,000\,\mathrm{g\,mol^{-1}}$.

Carboxymethyl-cellulose (CMC, Drispac Regular from Aqualon), is characterized by a mean carboxymethyl content of $0.89\,\mathrm{unit^{-1}}$ and a weight-average molecular weight of $10^6\,\mathrm{g\,mol^{-1}}$. CMC was used as powder form without further purification.

PAS-AA copolymer was prepared at room temperature, in deoxygenated water (pH = 9) by radical copolymerization of AMPS and AA. The feed molar concentrations of monomers were respectively 0.44 and $0.11\,\mathrm{mol\,l^{-1}}$. The reaction was initiated at room temperature with a redox system: ammonium persulfate (APS)/N,N,N',N'-tetramethylethylenediamine (TEMED). Reaction was allowed to proceed until total conversion (4 h), and copolymer was purified under $\mathrm{Na^+}$ form by ultrafiltration using a 40 000 nominal molecular weight cut-off membrane. A weight-average molecular weight of $700\,000\,\mathrm{g\,mol^{-1}}$ was roughly estimated from viscosity measurements using the Mark–Houwink relation given by Fischer *et al.*[14] for AMPS homopolymer. The chemical composition of PAS-AA copolymer, determined by ^{1}H nuclear magnetic resonance (n.m.r.) and titration,

data with a special focus on the chemical structure of the antagonistic components of these comb-like copolymers, i.e.

The backbone:	chemical nature (charged or neutral, level of hydrophily), molecular weight and intrinsic stiffness;
The grafts:	chemical nature (which governed the association process), molecular weight, degree of grafting, distribution along the backbone.

The present paper is devoted to the synthesis of a wide family of water soluble copolymers, which will be used later on to exemplify the general concept of thermo-thickening, and to give an accurate picture of this switch mechanism induced by heating.

The syntheses are more specifically devoted to grafted structures with polyether side chains. The choice of polyether (PEO, PPO or copolymers (PEPO)) results at first from the knowledge of their thermodynamic properties in water (LCST behaviour). Another interesting point is the fact that they are easily available, under monofunctional form, in a wide range of molecular weights of low polydispersity. Starting with two kinds of functionalized polyether (vinyl and amine), both copolymerization with hydrophilic comonomers and chemical modification of water-soluble backbones have been investigated with a larger development towards grafting. The latter was carried out in water and in organic solvent, using carbodiimide as coupling reagent between the amine end groups of the polyether chains and the carboxylic groups of the hydrophilic backbone.

A set of 30 samples, differing either by the nature of the main chain or the nature, size and number of the polyether side chains, is presented in this study. This set of data is used to support a comprehensive discussion

agree with the feed molar ratio AMPS/AA, respectively 80/20.

Polyacrylamide (PAM) was obtained by radical polymerization in deoxygenated water using redox initiation: APS and sodium metabisulfite. The reaction was initiated at room temperature and then brought to 90°C during 3 h until full conversion. Purification was carried out by ultrafiltration (40 000 molecular weight cut-off) and freeze-drying. A viscosity-average molecular weight of $650 000 \, g \, mol^{-1}$ was calculated from viscosity measurements[15]. Partial hydrolysis of PAM was performed in basic medium according to the method described by Halverson *et al.*[16]. This reaction, which is stoichiometrically controlled, was carried out in order to obtain partly hydrolysed polyacrylamide (PHAMx) with $x = 10, 30$ and 50% (in acrylic acid units content).

Polyethers

ω-Methyl, α-aminopolyethers were selected for their LCST properties and their ability to be incorporated onto hydrophilic backbones containing carboxylic units. Five amino functionalized polyethers were used:

- Three PEO derivatives of general formula CH_3O $(C_2H_4O)_nC_2H_4NH_2$ with molecular weights, given by the supplier, of $5000 \, g \, mol^{-1}$ (PEO5: Fluka), 10 000 and $25 000 \, g \, mol^{-1}$ (PEO10 and PEO25: Shearwater Polymers),
- Two (propylene oxide–ethylene oxide) random copolymers (Jeffamine from Texaco) of general formula CH_3O $(C_2H_4O)_n(CH_2CH(CH_3)O)_mCH_2CH(CH_3)NH_2$. The parameters given by Texaco were: $n = 1/m = 8$ for the Jeffamine® M-600 (PPO) and $n = 18.6/$ $m = 1.6$ for the Jeffamine® M-1000 (PEPO).

These polyether derivatives, which are water soluble at room temperature under their acidic form, were used without further purification. Two PEO macromonomers (ω-methyl, α-vinylpolyethylene oxide) were also used for copolymerization studies. The first one was an ω-methyl, α-methacrylate derivative with a molecular weight of $1000 \, g \, mol^{-1}$ (MAPEO1 from Polysciences). The second one was an ω-methyl, α-acrylate PEO obtained by amidification, activated by carbodiimide (DCCI), between acrylic acid and PEO5. This reaction, which is a standard method of peptide synthesis, has been performed at room temperature in methylene chloride. The PEO macromonomer (APEO5) was separated from insoluble dicyclohexylurea by-product by filtration, and from the residual AA by precipitation in diethylether. APEO5 was finally washed several times with diethylether, and dried under vacuum overnight at $T = 30°C$.

Analytical methods

^1H n.m.r. Characterization of precursors and modified samples was carried out by ^1H n.m.r. in D_2O using a Brucker WP 250 spectrometer (250 Mhz).

Size exclusion chromatography. Size exclusion chromatography (s.e.c.) analyses were performed with a Waters 6000 A chromatographic system equipped with four SHODEX OH-pak columns equilibrated at $T = 35°C$ in aqueous solution ($LiNO_3$ $0.5 \, mol \, l^{-1}/$ NaN_3 $6.2 \times 10^{-3} \, mol \, l^{-1}$). The flow rate was 1 ml min^{-1} and the eluate was monitored at the column output using

a differential refractometer (Waters R401). Samples were injected into the column at a concentration of $(2-3) \times 10^{-3} \, g \, ml^{-1}$, after filtration through $0.22 \, \mu m$ Millex filters (Millipore).

S.e.c. was generally used to follow with time the reaction between PEO derivatives and water soluble backbones or comonomers. The incorporation extent was obtained by measuring the chromatographic areas of each component during copolymer synthesis. S.e.c. was also performed to check the average molecular weights of the copolymers, on the basis of Pullulan standards used for the calibration of the columns.

Viscometry. Intrinsic viscosities of precursors and grafted derivatives were determined at given temperatures and salt concentrations with an automatic Ubbelohde viscometer (SEMATech. Ti1).

Rheological measurements. Viscosity analyses of precursors and grafted derivatives were carried out on a Carri-Med controlled stress rheometer (Rheo) with a cone/plate geometry (cone diameter = 2.0 cm, angle = 2° and truncation = 55 μm) using a vapour lock to prevent aqueous solutions from evaporation at high temperature.

Temperature was controlled by a high power Peltier system. The rheological analyses were performed between 20 and 75°C with a heating rate of 2°C min^{-1}. Viscosity (η in Pa s) was recorded either at constant shear stress ($\sigma = 5, 10$ or $50 \, N \, m^{-2}$) or constant shear rate ($\gamma = 10$ or $100 \, s^{-1}$).

Complementary experiments were performed at higher temperatures with a Couette rheometer (Fann 50). Studies were carried out between 20 and 200°C, at constant shear rate (104 s^{-1}) and under a nitrogen pressure of 25 atm.

Potentiometric titration. Functionality of PEO precursors was determined by titration of amine functions. Initially put under H^+ form with an excess of HCl, amines were back titrated with KOH 0.1 N in a water/ ethanol mixture (30/70 in bulk) using a Tacussel titrator (TT-Processeur 2) with a glass electrode.

RESULTS AND DISCUSSION

Characterization of polyether precursors

Polyether precursors were characterized either by viscometry, s.e.c., potentiometric titration or ^1H n.m.r. (see *Figure 2*), in order to check the monomer ratio in PEO–PPO copolymers and to determinate the key parameters for the copolymer syntheses: the molecular weight and the amine content (*Table 1*).

PEO samples, studied by viscometry[17] and s.e.c., are characterized by a small polydispersity index ($I \approx 1.2$) and molecular weights which are not very different from those given by the suppliers. Nevertheless, the most important feature concerns the calculated average number of amines per polyether chain. In fact, if one could expect to have one amine per chain for a pure ω-methyl, α-aminopolyether, the experimental values, ranging between 0.5 and 1.5, are charged with consequence on the copolymer synthesis. For PEO5 and PEPO, which have less than 1 amine per chain, the yield of incorporation cannot exceed 46 and 74%, respectively. For other polyethers, characterized by a functionality higher than 1, crosslinking of the
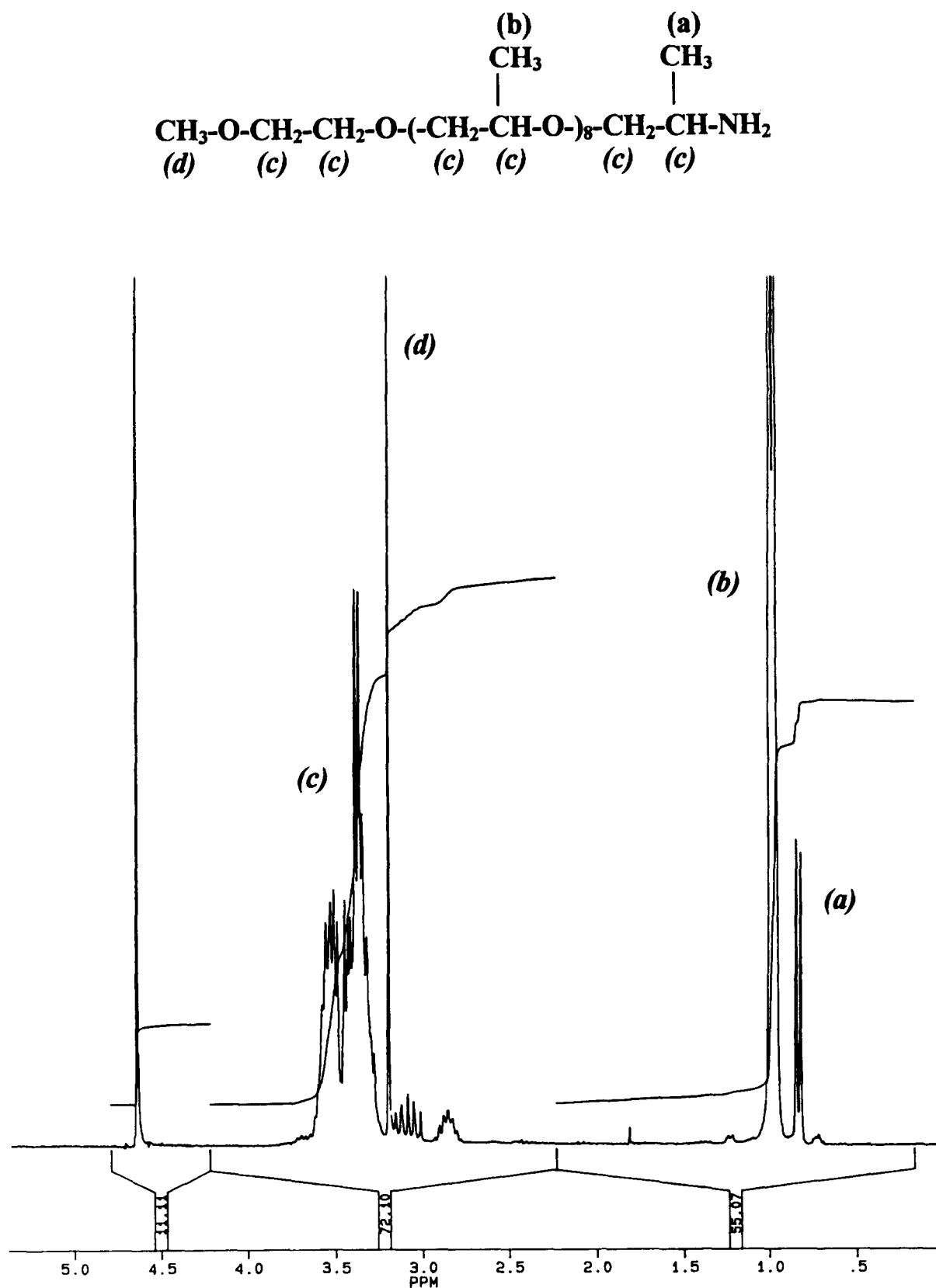
Figure 2 ^{1}H n.m.r. spectrum of PPO in D_2O (250 MHz)

main chains can be expected during modification or copolymerization with derivatives of the same precursors. However such crosslinking side reactions, which can be clearly suspected for polyethers of average functionality higher than 1, cannot be fully excluded for the others (PEO5 and PEPO).

Consequently, most of the copolymerization and grafting reactions between amino-polyethers and carboxylic units of water soluble backbones have been conducted in rather dilute solutions (around C^* for modification of polymers), in order to prevent possible crosslinking or gelation of the reactive medium.

Table 1 Physicochemical parameters of polyether precursors

Polyether	M (g mol^{-1})	Total amine (meq g^{-1})	Amine groups per chain	$C_2H_4/CH_2-CH(CH_3)^a$
PEO5	6800^b	0.068^c	0.46	154/–
PEO10	$11\,600^b$	0.103^c	1.20	263/–
PEO25	$28\,500^b$	0.053^c	1.50	647/–
PEPO	1120^d	0.68^d	0.76^d	$21/2.8^d$
PPO	$600^{d,e}$	$\approx 1.66^{d,e}$	$\approx 1^{d,e}$	$1/9^{d,e}$

^{a} Average molar content per chain of PEO and PPO units
^{b} Molecular weight obtained by intrinsic viscosity using the following Mark–Houwink relation: $[\eta] = 2 + 2.4 \times 10^{-2} M^{0.73}$ (ml g^{-1})[17]
^{c} Total amine content from potentiometric titration
^{d} From ^{1}H n.m.r.

Table 2 Copolymerization of PEO macromonomers with watersoluble monomers

Comonomers	Reaction	WSM^a (% w/v)	PEO^a (% w/v)	Initiator (% w/v)	Time (h)	Temperature (°C)	τ^b	W^1_{PEO} (%)^c	Conversion (% B/PEO)^d	Nomenclature
AMPS + MAPEO1	1	–	10	$1.3 \times 10^{-2\,e}$	5	60	Gel		>90	PMAPEO1
	2	3.87	1.5	$2.3 \times 10^{-2\,e}$	5	60	9	30	75/>90	PAS/9/PEO1
	3	5	0.5	$2.8 \times 10^{-2\,e}$	5	60	2.7	11	75/>90	PAS/3/PEO1
AMPS + APEO5	4	2.13	1.92	$0.19/0.24^f$	4	20			Gel	
	5	1.59	0.96	$0.12/0.12^f$	4	20	1.60	33	83/59	PAS/1.7/PEO5
	6	1.86	0.72	$0.14/0.14^f$	4	20	0.95	22	93/65	PAS/1/PEO5
	7	2	0.6	$0.06/0.06^f$	4	20	0.85	20	93/70	PAS/0.8/PEO5
AM + APEO5	8	1.32	0.72	$1.3 \times 10^{-3}/8 \times 10^{-4\,g}$	12	20	0.35	25	–	PAM/0.4/PEO5

^{a} Concentrations of water-soluble monomer (WSM) and polyethylene oxide macromonomer (PEO)
^{b} Average number of polyether side chains per 100 comonomer B in the backbone. (Calculated from ^{1}H n.m.r.)
^{c} Weight fraction of PEO deduced from τ
^{d} Conversion of each comonomer obtained from s.e.c.
^{e} 4,4'-Azobis, 4-cyanovaleric acid (AVA)
^{f} K$_2$S$_2$O$_8$/TEMED
^{g} (NH$_4$)$_2$ S$_2$O$_8$/Na$_2$S$_2$O$_5$

Copolymerization of polyether macromonomers

Copolymerization of PEO macromonomers, with AMPS or acrylamide comonomers, were carried out in deoxygenated water using azo or redox initiators (see the experimental conditions listed in *Table 2*). Reactions were checked by s.e.c., and grafted copolymers were isolated from unreacted species by precipitation in acetone, followed by several washes, and finally dried under vacuum at room temperature.

For reactions 1–3 (*Table 2*) performed with MAPEO1, no gelation occurred during copolymerization except for the PMAPEO1 homopolymer (reaction 1) which was carried out at a higher macromonomer concentration (10% w/v, but 0.1 mol l^{-1}). The experimental data are, however, too scarce to comment on the insolubility of this comb-shaped polymer and to favour the presence of bifunctional PEO, a stereocomplex formation or a chain transfer to the comb polymer as was reported in the literature[18–20].

For these three reactions, the incorporation of the macromonomer is quantitative and higher than that of the comonomer AMPS. This result is opposite to those reported for the copolymerization of PEO-methacrylate in organic solvent, where the reactivity of the macromonomer decreases with increasing chain length[21,22], and can be ascribed to the micellization of macromonomers in water. Such behaviour has been described by Ito and coworkers[22,23], who studied the polymerization of ω-alkyl,α-methacrylate-PEO in benzene and water.

For ω-methyl,α-isobutyrate-PEO ($M \approx 1000$ g mol^{-1}) in water, which is the macromonomer model of MAPEO1, they found a critical micellar concentration of 7.1×10^{-5} mol l^{-1} and an average aggregation number of 19.

In our copolymerization, where the two monomers have very different reactivities, a rather block distribution of the PEO side chains can be reasonably expected. In the same way, and as was reported with micellar copolymerization between hydrophilic and hydrophobic monomers[24], we can assume that the copolymer chains have a broad spectrum of composition. This lack of homogeneity of the copolymer chains is moreover especially enhanced at high conversion[24].

The behaviour of APEO5 in water is quite different. For this monomer, a micellization cannot be expected because the α-acrylate function is less hydrophobic than the α-methacrylate, and the PEO chain length is five times larger than that of the previous one. Except for reaction 4, carried out at a higher comonomer concentration, no gelation occurred during the copolymerization. Nevertheless substantial chain branching and crosslinking are assumed. This is first supported by the s.e.c. data of reaction 7 (*Figure 3*), which clearly evidences the development of a double molecular weight distribution after less than 1 h of copolymerization. This heterogeneous distribution is always observed after purification (*Figure 3E*) but a breakdown of the 'superstructures', corresponding to the higher molecular weight species, occurred after heating the copolymer solution to 160°C during 1 h under high shear rate
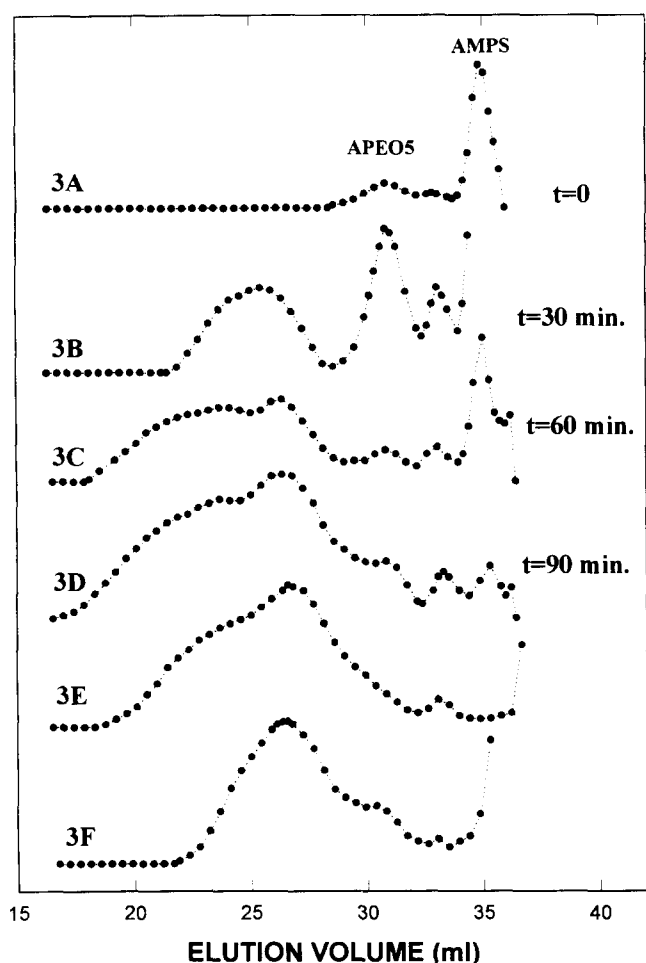
Figure 3 S.e.c. of PAS/0.8/PEO5: A–D, During radical copolymerization; E, After purification; F, After thermomechanical degradation ($t = 1$ h; $T = 160°C$; $\dot{\gamma} = 170\,s^{-1}$)

polyether. Indeed, on the basic assumption that during the macromonomer synthesis all the α-amino functions have been transformed to α-acrylate ones, no more than 46% of APEO5 could be incorporated according to a standard propagation process. The higher conversion of the macromonomer APEO5, ranging between 60 and 70%, could be ascribed to an additional mechanism, such as chain transfer. This well-known reaction has been studied in the case of the polymerization of PEO, or PEO derivatives, with vinyl acetate[25], methacrylate derivatives[20,26] and acrylonitrile[27], and chain transfer constants to ethylene oxide units have been estimated in the range 10^{-4}–10^{-3}. Such a side-reaction has been, moreover, especially used to obtain polyacrylamide-g-PEO by Pantar and coworkers[28,29] poly(vinyl-2-pyridine)-g-PEO[30] or other PEO derivatives of hydrophobic polymers[31–33]. According to this chain transfer mechanism, the probability of branching is assumed to increase with the length of the PEO chains.

From this first set of experiments, we can conclude that macromonomer copolymerization is an interesting way to extend the family of water soluble backbone-grafted-PEOs, but several drawbacks hinder the achievement of well-known structures:

(1) The reactivity ratios of macromonomer and water-soluble comonomers can be quite different, even without micellization of the macromonomer. The resulting distribution of polyether grafts along the backbone is then dependent on the degree of conversion.

(2) Chain transfer reactions to ethylene oxide units can lead to ill-defined structures (branching or cross-linking).

(3) Even without these main drawbacks it seems unrealistic to synthesize by this method an homologous series of grafted copolymers with a well-controlled molecular weight.

Modification of water-soluble backbones

Coupling reaction between the terminal amine of the polyether chains (NH_2–Pether) and the carboxylic units of the backbones, was carried out, either in aprotic solvent or in water, using carbodiimide as activator to promote the amide formation according

($\gamma° = 170\,s^{-1}$). As observed in *Figure 3F*, thermomechanical degradation of the sample PAS/0.8/PEO5 again gives a single distribution, as observed during the first step of copolymerization (*Figure 3B*), and a low molecular weight peak corresponding to PEO5 grafts. On the other hand, an analysis of the conversion with time of the two comonomers indicates a surprisingly high conversion of

Table 3 Grafting reaction in NMP

	Reaction/Sample		
	1	2	3
PAA500 (% w/v)	2	3	1.25
PEO5 (% w/v)	0.7	1.57	1.74
Molar ratio[a] $\dfrac{(DCCI)}{[-NH_2]}$	3.5	9.3	4.3
Modification extent[b] τ (%)	0.13	0.24	0.54
W^c_{PEO} (%)	8.3	14.9	28.2
Grafting yield[d] (%)	76	94	80
Nomenclature[e]	PAA500/0.13/PEO5	PAA500/0.24/PEO5	PAA500/0.54/PEO5

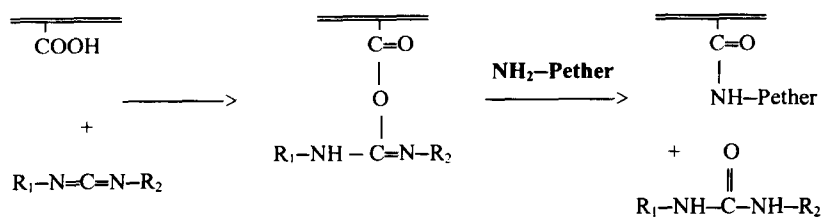[a] Molar ratio between carbodiimide and amino groups of PEO
[b] From ^{1}H n.m.r. using $M = 6800\,g\,mol^{-1}$ for PEO5 side chains
[c] Weight percentage of PEO calculated from τ, taking PAA backbones under ionized form (Na$^+$)
[d] Amidification yield taking into account only aminoterminated-PEO chains
[e] These three copolymers are the same as those reported in ref. 9. The change of τ values between these two papers, is due to the use of $M = 6800\,g\,mol^{-1}$ for PEO5 instead of $M = 5000\,g\,mol^{-1}$ given by the supplier

to the following scheme:

```
    ═╤═ ═               ═╤═ ═                         ═╤═ ═
     COOH               C=O           NH₂—Pether       C=O
                         |            ─────────>       |
      ────────>          O                            NH—Pether
                         |
       +                 |                             +    O
                   R₁—NH — C=N—R₂                            ‖
   R₁—N=C=N—R₂                                       R₁—NH—C—NH—R₂
```

Modification in organic medium. In *N*-methyl-2-pyrrolidone (NMP), the coupling between $-NH_2$ and $-COOH$ groups was activated by dicyclohexylcarbodiimide (DCCI) and maintained at 60°C during 24 h, according to the procedure described by Wang and coworkers[34,35]. For more details of the grafting reaction of amino-PEO with PAA, see ref. 9.

For reactions 1 and 3 (*Table 3*), the grafting yields, obtained from ^1H n.m.r. data, are around 70–80%, on the basis of the total number of amino groups found in the PEO5 chains. It is clear that if we take into account the whole number of polyether chains, the overall yield of the reaction drops to about 35% as mentioned previously[9]. Anyway, for the 3 purified PAA-*g*-PEO synthesized by this method, s.e.c. experiments show a total elimination of unreacted PEO chains. This grafting yield of 80% is fairly high if we consider:

(1) the long polyether chain linked to the amine which can hinder the reactivity of the latter;
(2) the low concentrations of precursor species, or rather the reactive groups which are amines $[(0.5–1.2) \times 10^{-3}\,mol\,l^{-1}]$ and carboxylic units activated by DCCI $((1.5–10) \times 10^{-3}\,mol\,l^{-1})$.

For reaction 2 (*Table 3*), where we have increased both the PAA backbone concentration and the molar ratio $[DCCI]/[-NH_2]$ (3–4 to 9) we obtained a near-quantitative grafting yield (94%). Nevertheless some crosslinking was assumed because the dissolution of this grafted PAA in water provides solutions of slightly higher viscosity compared with those of the other PEO-modified PAAs. Although such behaviour has been reported by Gramain and Frere[18,19] with PEO-grafted poly(acrylic chloride) and assigned to the formation of a stereocomplex enhanced by PEO grafts, we are more inclined here to favour the presence of bifunctional PEO, as previously discussed.

From these results it appears that the best way to achieve PAA-*g*-PEO with the highest grafting yield and without interchain crosslinking, is to compromise between a low PAA concentration and a fairly high molar ratio $[DCCI]/[PEO]$.

Judging by the good solubility of the two precursors in NMP, one can expect that the modification of poly(acrylic) acid with polyether chains would lead to a random distribution of the grafts along the PAA backbone, as has already been observed for similar conditions with alkylamines[36].

However, modification in NMP, or more generally in organic solvent, presents an important restriction due to the fact that most of the water-soluble backbones are not soluble in organic solvents.

Modification in aqueous medium. Modifications in water were carried out according to a similar reaction procedure, using a water soluble carbodiimide (EDC). The syntheses were performed in the following way.

The water soluble backbone (in Na^+ form) and the polyether were dissolved separately in water at room temperature during 24 h. The precursors were then mixed and the pH was adjusted to approximately 8 before heating at 60°C. The optimum pH range for EDC, corresponding to its lower rate of hydrolysis in water, was reported to be between 6 and 9[37,38].

The concentration of hydrophilic backbone was set at about C^*, typically between 0.5 and 1.5% (w/v) for the polymers of intermediate molecular weights (see *Table 4*), and the polyether content was adjusted according to the expected level of grafting.

The water soluble carbodiimide (EDC) was then added under vigorous stirring and the reaction, controlled by s.e.c., was maintained during a maximum of 24 h with occasionally additional feeds of EDC, which will be discussed later. For the PPO grafts, which $LCST \approx 40°C$, the reaction was performed at room temperature after a preheating step of 2 h at 60°C.

The crude medium was then purified either by one of the following.

- Concentration and precipitation in acetone followed by several washings and a final drying under vacuum at room temperature. The samples, redissolved in a minimum of water, were then purified in a similar way.
- Ultrafiltration, for PEO5 and PPO-derivatives, through membranes of 40 000 nominal molecular weight cut-off.

In this latter case, the ionic strength of the crude medium was adjusted to $0.1\,mol\,l^{-1}$ with NaCl in order to screen the electrostatic interactions between EDC-urea by-product and the carboxylate units of the backbone. EDC-urea was thence easily removed during the first step of ultrafiltration and the grafted copolymer was then washed with water, concentrated and then freeze-dried. An example of a ^1H n.m.r. spectrum of grafted copolymer is given in *Figure 4*. A large overview of the grafting reactions carried out in water, with various water soluble backbones and polyether chains, is given in *Table 4*.

We will consider first the analogous reaction to that performed in NMP (*Table 3*), which was the grafting of PEO5 onto a polyacrylate backbone (reactions 1–5, *Table 4*). Taking into account the main information obtained from synthesis in organic solvent, the reactions have been carried out at low polymer concentration using a high molar ratio $[EDC]/[NH_2]$ ranging between 9 and 12. We obtained in water very similar results, with most of the grafting yields ranging between 70 and 80%, on the basis of the amine content.
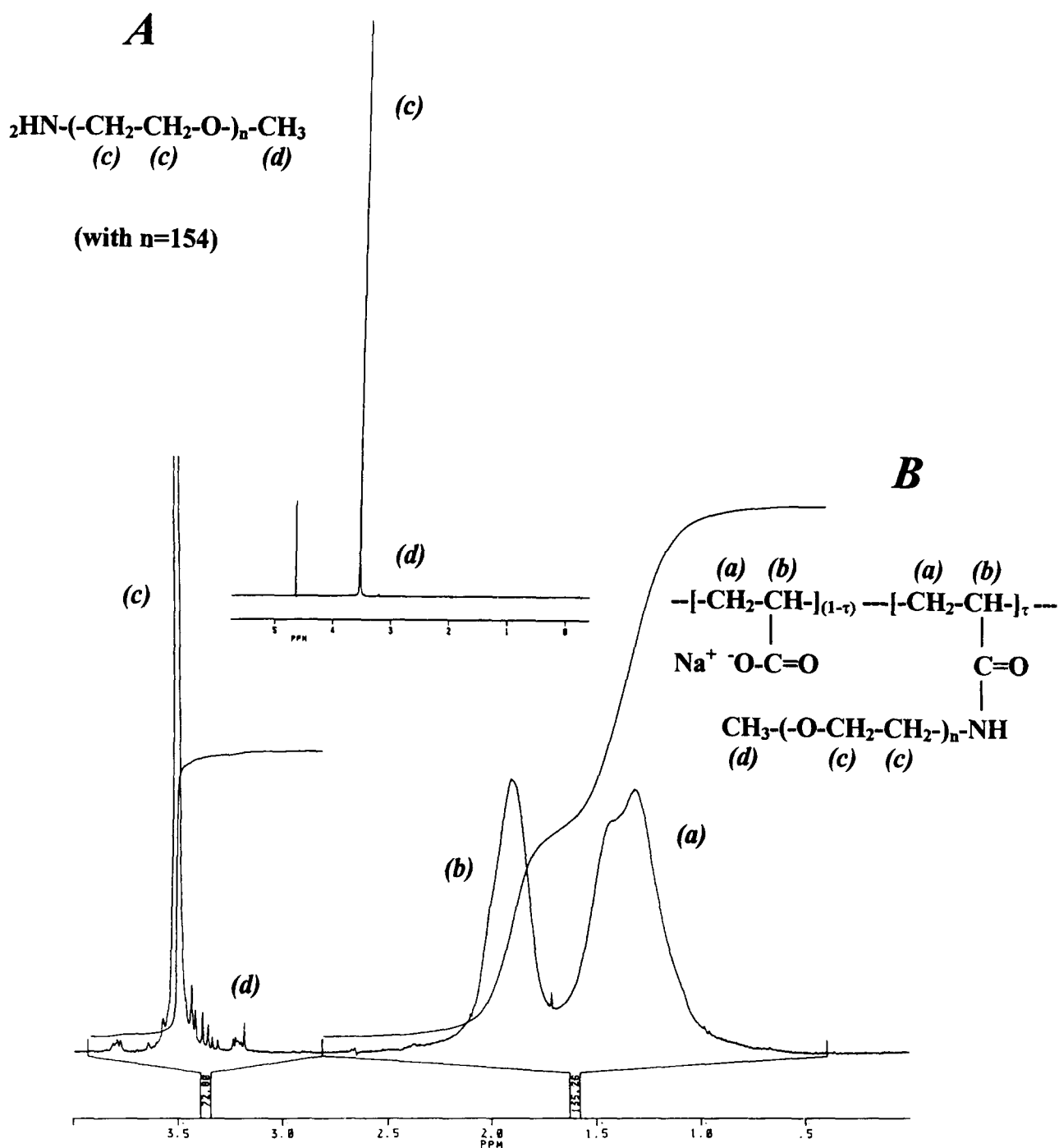
In these conditions, no crosslinking has been

Figure 4 ^{1}H n.m.r. spectra in D_2O (250 MHz): A, PEO5; B, PAA150/0.3/PEO5

observed except for syntheses 4 and 7 where the PEO5 concentrations were the highest. This can be clearly shown by s.e.c. during synthesis or by comparing the intrinsic viscosity of grafted copolymers and precursors. As expected without branching, the grafting gives rise only to a slight increase in the intrinsic viscosity, when the latter is measured in salt conditions which do not promote side chain associations. Nevertheless, the probability of crosslinking, which is related to the initial number of PEO chains and to the proportion of difunctional species, can be lowered by decreasing the precursor concentrations; see for comparison experiments 3 and 4, and 7 and 8.

The amide formation in water, promoted by EDC, was generally very fast for most of the reactions carried out

between PEO5 or PEPO (and probably PPO) and the carboxylate units of the polymer backbones. According to s.e.c. experiments, performed during the reactions, the aminopolyethers were grafted in less than 1 h. This has also been reported for several analogous couplings activated by water soluble carbodiimide[39,40].

Obviously the kinetics of the reaction are strongly dependent on amine, carboxylate and carbodiimide concentrations, and lower grafting rates are expected at low content of reagents[41]. This is, for example, the case for the reactions performed at low concentration with long polyether chains (reactions 9, 10 and 11 in *Table 4*), at low content of carboxylate units borne by the backbone (reaction 15) or at very low polymer concentrations, used to prevent the crosslinking of very long

Table 4 Grafting reactions in water

Reaction	Precursors	WSP^a (% w/v)	PE^b (% w/v)	$\dfrac{[\text{EDC}]^c}{[\text{NH}_2]}$	τ (%)^d	W_{PE} (% w/w)^{e,f}	Y (%)^g	$[\eta]$ ml g$^{-1\,h}$	Nomenclature
1	PAA90 + PEO5	0.42	0.5	9	0.55	26/29	73	175/175	PAA90/0.55/PEO5
2	PAA500 + PEO5	0.52	0.44	12	0.40	20/22	75	340/–	PAA500/0.4/PEO5
3	PAA150 + PEO5	0.31	0.42	16 (2)^i	0.55	28/29	72	–	PAA150/0.5/PEO5
4		0.85	0.88	9	0.6	29/30	90	≈ Gel	PAA150/0.6/PEO5
5		1.02	0.54	12	0.25	16/16	77	–	PAA150/0.3/PEO5
6	PAS-AA + PEO5	1.20	0.66	9	0.60	16/17	78	235/255	PAA-AA/0.6/PEO5
7		1.04	1.15	10	1.2	30/29	80	230/310	PAA-AA/1.2/PEO5
8		0.38	0.58	12	1.35	33/32	65	230/270	PAS-AA/1.4/PEO5
9	PAS-AA + PEO10	0.63	0.17	30 (3)^i	0.50	22/22	100	235/220	PAS-AA/0.5/PEO10
10	PAS-AA + PEO25	0.63	0.44	22 (3)^i	0.50	41/43	100	235/448	PAS-AA/0.5/PEO25
11		0.18	0.14	38 (3)^i	0.55	44/44	100	235/265	PAS-AA/0.6/PEO25
12	PAA150 + PEP0	0.98	1.03	2.6	6	–/42	90	–	PAA150/6/PEPO
13	PAA150 + PPO	1.38	0.83	1.5	6.7	–/30	71	–	PAA150/7/PPO
14		1.12	1.19	2	21	–/55	100	–	PAA150/21/PPO
15	PHAM10 + PEO5	0.12	0.12	72 (3)^i	0.22	18/17	45	–	PHAM10/0.2/PEO5
16	PHAM30 + PEO5	0.27	0.17	12	0.25	18/18	75	–	PHAM30/0.2/PEO5
17	PHAM50 + PEO5	0.27	0.15	16	0.25	17/17	80	–	PHAM50/0.2/PEO5
18	PSVA + PEO5	0.63	0.35	31 (4)^i	0.45	14/–	63	–	PSVA/0.4/PEO5
19	CMC + PEO5	0.05	0.06	43 (3)^i	1	23/–	52	3400–	CMC/1/PEO5
20	PVEAM + PEO5	0.31	0.32	19	0.60	27/–	76	–	PVEAM/0.6/PEO5

^{a} Water-soluble polymer concentration (under Na$^+$ salt form)
^{b} Polyether concentration
^{c} Molar ratio between carbodiimide and amino groups of polyether chains
^{d} Average number of graft polyether per 100 monomer units calculated from ^{1}H n.m.r.
^{e} Estimated from chromatographic areas of precursors and grafted copolymers (see e.g. *Figure 2*)
^{f} Calculated from ^{1}H n.m.r. spectra considering polyelectrolyte, backbones under ionized form (Na$^+$)
^{g} Grafting yield obtained from ^{1}H n.m.r. or s.e.c. on the basis of amino-polyether content
^{h} x/y: intrinsic viscosity of precursor (x) and grafted copolymer (y) measured in 0.1 M NaCl at °C
^{i} (n), n-fold addition of EDC

chains (CMC, 19). For these reactions, and as a general rule, s.e.c. is very useful to control the grafting of aminopolyether chains onto the backbone. The knowledge of the grafting yield with time allows control of the conditions during the reaction, for instance changing the pH or adding new feeds of EDC (reactions 9, 10, 11, 15, 18 and 19 in *Table 4*). An example of a grafting reaction checked by s.e.c. (reaction 18) is depicted in *Figure 5*. Analysis of *Figures 5A–5C* shows that no grafting occurs during 18 h at pH = 10.5 even with a two-fold addition of EDC. Nevertheless, the grafting can be reactivated to a reasonable yield (63%) by decreasing the pH and adding further feeds of EDC and PEO5 (*Figures 5D* and *5E*). The s.e.c. of the ultrafiltered medium (*Figure 5F*) indicates a total removal of ungrafted PEO5 and EDC-urea by-product.

Despite the relative large size of our polyether grafts, the overall yields of coupling presented in this study are in good agreement with those reported in similar conditions between polyacrylic acid and low alkyl-amines ($Y = 80$–90%, ref. 36) or between aminated dextran and benzene carboxylate ($Y = 60$–70%, ref. 42). Prouchayret *et al.*[42] have shown that EDC can also promote coupling between hydroxyl groups (of dextran) and carboxylic derivatives at high content of EDC, but no evidence for such ester formation has been observed in our conditions. A closer comparison of our results can be done with an analogous synthesis which was reported recently by De Vos *et al.*[13]. These authors have prepared grafted copolymers by coupling in water (pH = 5.5 and

room temperature) poly(oxyalkene) monoamines [M-2070 (2000 g mol^{-1})] and M-600 (called PPO in our paper) onto a polyacrylamide backbone hydrolysed at 5%; using EDC and N-hydrosuccinimide (NHS) as the activator system. The PHAM concentration was around 2–3% (w/v) and the molar ratio EDC/NHS/COOH/NH$_2$ was set to 5/2/1/2.

From a careful examination of their ^{1}H n.m.r. spectra given for two copolymers, and using a suitable assignment of protonated groups, we have determined the number of polyether grafts per 100 monomer units (τ) and the overall grafting yield (Y). The calculated values are $\tau = 0.86$ ($Y = 9\%$) for PAM-g-M600 and $\tau = 0.52$ ($Y = 5\%$) for PAM-g-M2070. These grafting yields are obviously very low, specially if we take into account the fact that the succinimide derivatives are known to enhance the coupling reaction activated by water soluble carbodiimide[43]. These low values could be attributed to the very low content of carboxylic units borne by the backbone, and/or a high incompatibility between the precursors polyacrylamide and polyether.

In comparison, our worst yield of grafting ($Y = 45\%$) was also obtained with low-hydrolysed polyacrylamide (PHAM10: reaction 15 in *Table 4*).

Finally, according to the solubility in water of the whole set of precursors used, one can expect a random distribution of the grafts along the backbone except for PPO which gives a phase separation above 40°C. However, the possibility to promote a local aggregation of the polyether species by changing the temperature or
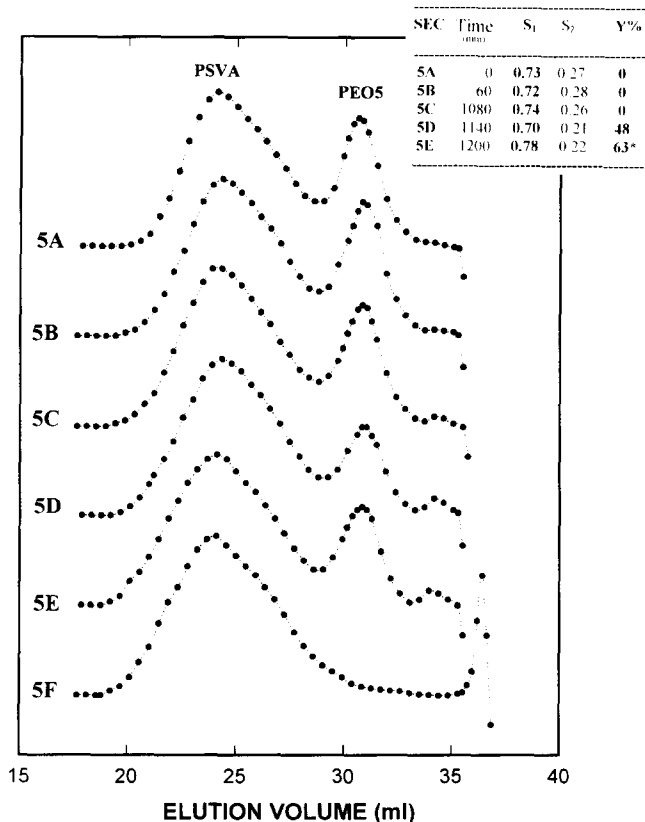
SEC	Time (min)	S_1	S_2	Y%
5A	0	0.73	0.27	0
5B	60	0.72	0.28	0
5C	1080	0.74	0.26	0
5D	1140	0.70	0.21	48
5E	1200	0.78	0.22	63*

Figure 5 Grafting reaction between PSVA and PEO5 followed by s.e.c.: $t = 0$ min, PSVA (20 g) + PEO5 (9.2 g) + H$_2$O (3200 ml), pH = 10.5, s.e.c. 5A; $t = 1$ min, +EDC (1 g); $t = 60$ min, s.e.c. 5B; $t = 61$ min, +EDC (1 g); $t = 1080$ min, s.e.c. 5C; $t = 1081$ min: pH = 10.5 → 8, +EDC (1 g); $t = 1140$ min, s.e.c. 5D; $t = 1141$ min, +PEO5 (2 g) + EDC (0.25 g); $t = 1200$ min, s.e.c. 5E; ultrafiltered PSVA-g-PEO5, s.e.c. 5F. In the table: S_1 and S_2 are the relative areas of PSVA or PSVA-g-PEO5 and PEO5, respectively; Y, grafting yield as previously defined, $Y = (S_2^1 - S_2^1)/S_2^1$ with $S_2^1 = 0.27$ and 0.31 before and after the second feed of PEO5, respectively

Figure 6 Variation of reduced viscosity with temperature for PAS/τ/PEO1 copolymers: — ● — , PAS/55/PEO1, $C_p = 10\%$ (w/w), [K$_2$CO$_3$] = 6.2% (w/w); — ■ — , PAS/30/PEO1, $C_p = 10\%$ (w/w), [K$_2$CO$_3$] = 6.2% (w/w); — ▲ — , PAS/9/PEO1, $C_p = 20\%$ (w/w), [K$_2$CO$_3$] = 1.4% (w/w); — ▼ — , PAS/3/PEO1, $C_p = 20\%$ (w/w), [K$_2$CO$_3$] = 1.4% (w/w); — ◆ — , PAS, $C_p = 10\%$ (w/w), [K$_2$CO$_3$] = 6.2% (w/w)

the nature of the solvent, could be an interesting way to synthesize polymers-g-polyether with a controlled distribution, as was done with alkylamines[36].

Rheological behaviour

As previously mentioned[9,10], two basic conditions are required to evidence the thermothickening ability of these systems.

First of all, if we exclude PPO, most of the polyether grafts used in this study are characterized by a high LCST (higher than 100°C depending on their molecular weight). Consequently, a coelectrolyte with a salting out effect has to be used to decrease the critical temperature in the range of observation screened with the classical rheometers, typically below 80°C. In most of the cases, potassium carbonate, which is known to decrease significantly the LCST of PEO, was used at concentrations ranging between 8 and 15% (w/w).

The second point is related to the ability of the side chains to interact intra- or intermolecularly. In dilute solutions the first mechanism prevails and gives rise to a decrease of the hydrodynamic radius of the coil. It is only above C^*, where the two mechanisms are expected, that interchain associations can provide a viscosity enhancement of the solution.

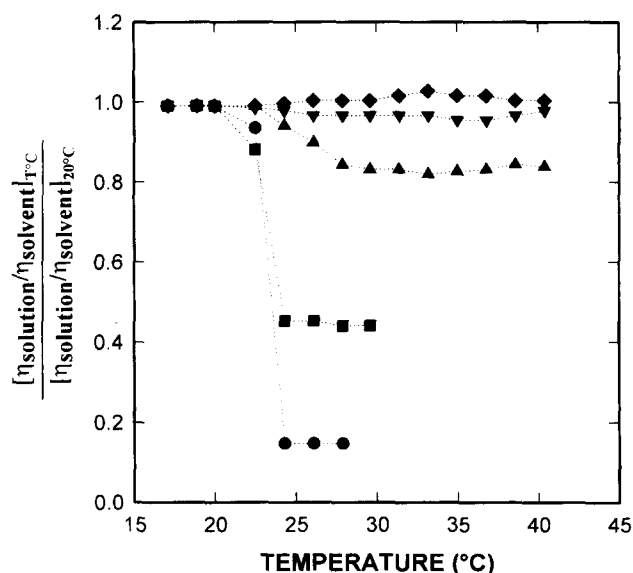From all the rheological experiments carried out to

test our samples, we can distinguish between two main kinds of thermoassociative behaviour.

The first kind of behaviour is related to the series PAS/τ/PEO1 where a sharp decrease in viscosity upon heating is observed with a clouding of the solution (*Figure 6*). The extent of this transition becomes smoother when the PEO content in the copolymer is decreased, but in any case the expected thermothickening behaviour can be observed. According to the strong heterogeneous compositions expected for these copolymers, we can assume that the main macroscopic behaviour observed (i.e. clouding and loss of viscosity with temperature) is related to a true phase separation of the copolymers which have a high PEO content. In a simplified way, the rheological behaviour of our PAS/τ/PEO1 copolymers seems very close to that expected for a mixture of homopolymers (PAS and PMAPEO1), by changing their relative weight fraction. A similar behaviour has been reported by Lacik *et al.*[24] for hydrophobic modified polyacrylic acid obtained at high conversion by micellar copolymerization. In the case of poly(acrylic acid-*co*-styrene), characterized by a molar styrene content of 1–2%, no specific effect inherent to associating systems has been observed. Such copolymer solutions are described by the authors as collapsed hydrophobic chains embedded in a semi dilute matrix of hydrophilic homopolyacrylic acid.

Obviously, such a heterogeneous architecture, characterized by long associative sequences (here pendant PEO), is unsuitable to provide a well-controlled 'microphase separation' involving the whole copolymer chain.

Excluding this specific case, all the copolymers previously synthesized display a thermothickening behaviour in aqueous solution. It can be depicted by a three-step mechanism using the typical curve obtained by plotting the viscosity, measured at a constant shear rate, against the temperature (*Figure 7*).

In the first domain, corresponding to the lower temperature range, the copolymer solution behaves as

a classical water-soluble system. A decrease of the viscosity upon heating is observed according to the Arrhenius law ($\eta = A\exp(E_\eta/RT)$).

When the critical association temperature is reached (T_{ass}, *Figure 7*), the polyether side chains self-assemble and give rise to a viscosity increase of the solution. At zero or at very low shear rates, the viscosity can reach values of several orders of magnitude higher than that of the precursor solution. In this second regime, the flow viscosity becomes very dependent on the shear rate and the extent of the Newtonian plateau decreases when the temperature is increased (*Figure 8*). This shear-thinning character results from a competition between the association of the grafts, promoted by heating, and the stretching of the supermolecular structures under shear. The latter favours intermolecular dissociations and intramolecular recombinations. For a fixed shear rate, this dynamic phenomenon gives rise to a reversible thickening curve with a maximum in viscosity as a function of temperature (T_{max}, *Figure 7*).

This behaviour is common for most of our grafted copolymers, whatever the nature of the precursors:

backbones (ionic or neutral) or grafts (PEO, PEPO or PPO). Nevertheless regarding the lipophilic/hydrophilic balance, the hydrophilic character of the main chain is a critical parameter. It must be high enough to maintain the water solubility of the whole copolymer at high temperatures or high salt concentrations. For instance, in the case of CMC/1/PEO (*Figure 9*), where the solubility of the backbone at high ionic strengths is poor, a macroscopic phase separation occurs when the temperature is high enough to induce a strong hydrophobicity of the PEO grafts (about 20° above T_{ass}). This white gel at rest, undergoes a sharp decrease of its viscosity under shear, with a very slow reversibility under cooling (*Figure 9*).

For all the systems, the key point of the thermothickening mechanism concerns the critical temperature of association (T_{ass}), which is governed by the LCST of the grafts. In semi-dilute solutions, and at copolymer concentrations that do not exceed 5%, the thermodynamic behaviour of the polyethers remains the same whether they are grafted or free in solution[9]. The critical T_{ass} can therefore be easily controlled through parameters which are directly connected to the phase diagram of the free grafts: the concentration of polyethers (grafting ratio and copolymer concentration); the nature and the size of the LCST grafts; added molecules such as salt which decrease or increase the solubility of polyethers in water. In more concentrated solutions the associative behaviour has to be depicted using a pseudo-ternary diagram (solvent, polyether, backbone). Generally the incompatibility between polyether and polyacrylic derivatives tends to lower the phase separation temperature and consequently the critical temperature of self-assembling.

The other important characteristics of these systems are the amplitude of the viscosification (the slope of the curve viscosity *versus* temperature) and the temperature range of the reversible thermothickening under shear. These two aspects are much more complex than the
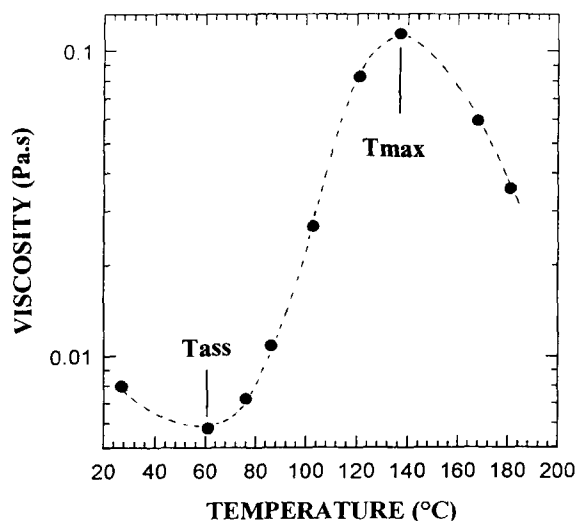

Figure 7 Typical variation of steady flow viscosity with temperature for thermothickening copolymers. Sample PAA90/0.55/PEO5, $C_p = 3\%$ (w/w), [K$_2$CO$_3$] = 8.3% (w/w), $\dot{\gamma} = 104\,\text{s}^{-1}$
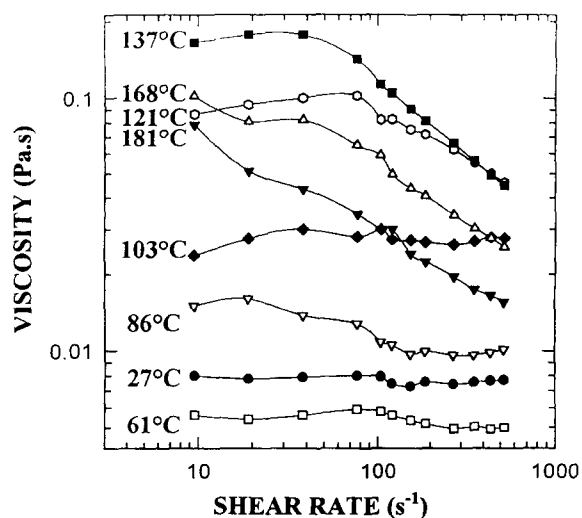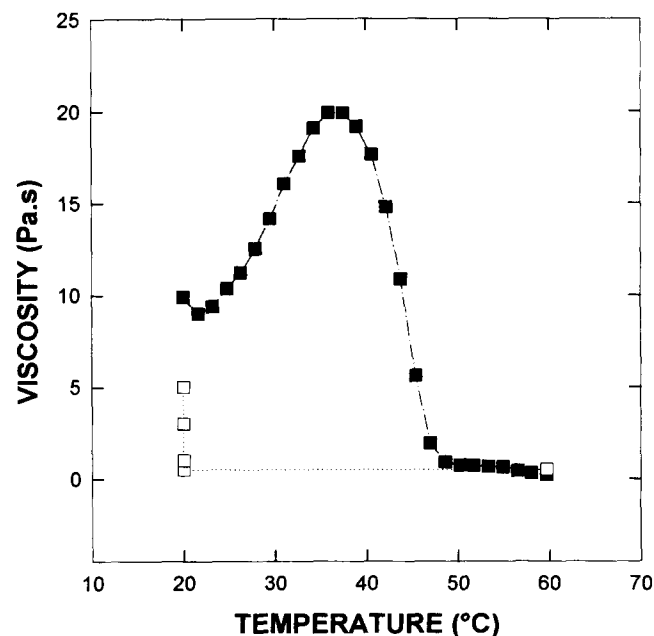

Figure 8 Variation of viscosity with shear rate for PAA90/0.55/PEO5 at different temperatures. $C_p = 3\%$ (w/w) and [K$_2$CO$_3$] = 8.3% (w/w)

Figure 9 Variation of viscosity with temperature of CMC/1/PEO5. $C_p = 1.9\%$ (w/w), [K$_2$CO$_3$] = 13.8% (w/w), shear stress $\sigma = 50\,\text{N m}^{-2}$, ■, heating; □, cooling

former because they are related both to the chemical architecture of the copolymer and to the experimental conditions of analysis (concentration, ionic strength, shear rate, ...). The effect of these parameters will be described in future reports, but as a general rule, we can say that at a given shear rate, the thermothickening of the copolymer solution increases when the following occur.

- The interchain associations are favoured. They can be controlled with the overlap concentration of the polymer chains, playing with the conformation (intrinsic stiffness, excluded volume effect) and the molecular weight of the backbone.
- The number of knots is large. The key parameters are related to the number and the size of the thermosensitive grafts (grafting ratio, copolymer concentration, molecular weight).
- The lifetime of the association and the fraction of active grafts are high. This is closely related to the phase diagram of the LCST grafts.

CONCLUSION

Thermothickening behaviour, based on the microphase separation of LCST moieties grafted on water soluble backbones, is a general concept which can be extended to a wide variety of copolymers. The synthesis of these copolymers has been developed in this study using two different strategies.

The copolymerization, which is basically the classical way, does not appear as the most suitable one if the control of the structural parameters is set as the main objective. Various reasons can be put forward.

(1) The polyether macromonomers are not totally monofunctional. The presence of divinylic species, even at a very low content, can promote consequently the formation of three-dimensional structures when the copolymerization is performed at high monomer concentrations.
(2) The transfer reactions to ethylene oxide units are also responsible for crosslinking or branching structures.
(3) The reactivities of the hydrophilic monomer and polyether macromonomer could be quite different.

For long polyether chains, well soluble in the solvent medium, one can expect that the macromonomer is less reactive than the hydrophilic monomer. In this case, the composition of the chains can be considered to be heterogeneous, especially when the copolymerization is carried out until high conversion.

On the other hand, for macromonomers with short tail and hydrophobic head (methacrylate for example), the micellization in water can reverse the reactivities of the two comonomers. Block structures are then expected, with once again a strong heterogeneous composition at high conversion. Moreover, we have shown that such structures are unsuitable to promote the physical gel formation by heating.
(4) Besides the aforementioned points, it seems difficult to set critical parameters, such as the molecular weight of the backbone, while changing the co-monomer ratio or the macromonomer size. This is an important drawback, from a fundamental point of view, if the final purpose is to underline the part of each structural parameter in the thermothickening process.

Nevertheless, the copolymerization method cannot be fully excluded from the preparation of polyether grafted copolymers. It is of course the basic way to obtain grafted copolymers with neutral backbones (polyacrylamide for example). Moreover transfer reactions to PEO chains could be an interesting way to produce thermothickening mixtures using classical precursors (PEO and hydrophilic monomer for instance).

On the other hand, the coupling reaction, activated by carbodiimide molecules between amino polyether chains and carboxylic groups of the backbone, has shown great potential for the preparation of well defined grafted structures.

First of all, the problems related to the gel formation, caused by difunctional polyether species, can be easily avoided by working at low polymer concentrations; typically around C^*. Even at these low concentrations, a quantitative yield can be obtained by increasing the feed of carbodiimide, at given conditions of pH and temperature.

These reactions can be carried out either in organic solvent or in water, but water appears to be more convenient for the following reasons.

- Most of the hydrophilic backbones are insoluble in organic solvent.
- The synthesis can be easily controlled by s.e.c., and the instantaneous composition of the grafted copolymers is directly obtained from the chromatographic area during the reaction.

Despite this preference for the water medium, modification in organic solvents remains an interesting way to prepare analogous copolymers differing by their structure (graft distribution). This could be the case for instance for similar reactions carried out both in organic medium and in water above the LCST of the grafts ($T = 60°C$ with PPO for example).

Another point for polymer modification is that this method allows an extension of the thermoassociative concept towards the natural polymers (polysaccharides for instance).

Finally, all the copolymers prepared by modification of water-soluble backbones have shown thermothickening properties, and for most of them the microphase separation remains stable in a wide range of temperatures and salt concentrations.

Advanced studies concerning the role of the structural parameters on the associative process, in relation to the external parameters that could be applied, will be reported later on.

ACKNOWLEDGEMENTS

REFERENCES.

1. Schmolka, I. R., *J. Am. Oil Chem. Soc.*, 1977, **54**, 110.
2. Suto, S., Nishibori, W. Kudo, K. and Karasawa, M., *J. Appl. Polym. Sci.* 1989, **37**, 737.
3. Klug, E. D., *J. Polym. Sci., Part C* 1971, **36**, 491.
4. Sarkar, N., *J. Appl. Polym. Sci.* 1979, **24**, 1073.
5. Werbowyj, R. S. and Gray, D. S., *Macromolecules* 1980, **13**, 69.
6. Carlsson, A., Karlström, G. and Lindman, B., *Colloids Surfaces* 1990, **47**, 147.

7. Loyen, K., Iliopoulos, I., Audebert, R. and Olsson, U., *Langmuir* 1995, **11**, 1053.
8. Hourdet, D., L'Alloret, F. and Audebert, R., *Polym. Prepr.* 1993, **34**, 972.
9. Hourdet, D., L'Alloret, F. and Audebert, R., *Polymer* 1994, **35**, 2624.
10. L'Alloret, F., Hourdet, D. and Audebert, R., *Colloid Polym. Sci.*, 1995, **273**, 1163.
11. Schlumberger Dowell, Eur. Patent 0 583 814 A1, 1993 and Eur. Patent 0 629 649, 1994.
12. De Vos, S. C. and Möller, M., *Makromol. Chem. Macromol. Symp.* 1993, **75**, 223.
13. De Vos, S., Möller, M., Vissher, K. and Mijnlieff, P. F., *Polymer*, 1994, **35**, 2644.
14. Fisher, L. W., Sochor, A. R. and Tan, J. S., *Macromolecules* 1977, **10**, 949.
15. Kuclicke, W. M., Knieuske, R. and Klein, J., *Prog. Polym. Sci., Jpn* 1985, **8**, 405.
16. Halverson, F., Lancaster, J. E. and O'Connor, M. N., *J. Am. Chem. Soc.* 1985, **18**, 1139.
17. Bailey, F. E. and Koleske, J. V., *Poly(ethylene oxide)* Academic Press, New York, 1976.
18. Gramain, P. and Frere, Y., *Polym. Commun.* 1986, **27**, 16.
19. Gramain, P. and Frere, Y., *Makromol. Chem.*, 1987, **188**, 593.
20. Bo, G., Wesslen, B. and Wesslen, K. B., *J. Polym. Sci., Part A* 1992, **30**, 1799.
21. Ito, K., Yokohama, S., Arakawa, F., Yukawa, Y., Iwashita, T. and Yamasaki, Y., *Polym. Bull.* 1986, **16**, 337.
22. Ito, K., Tanaka, K., Tanaka, H., Imai, G., Kawaguchi, S. and Itsuno, S., *Macromolecules* 1991, **24**, 2348.
23. Ito, K., Hashimura, K., Itsuno, S. and Yamada, E., *Macromolecules* 1991, **24**, 3977.
24. Lacik, I., Selb, J. and Candau, F., *Polymer* 1995, **36**, 3197.
25. Okamura, S., Katagiri, K. and Motoyama, T., *J. Polym. Sci.* 1960, **43**, 509.
26. Nandi, U. S., Kumar, G. S. and Bhaduri, G. C., *Ind. J. Chem.* 1981, **20A**, 759.
27. Fritzsche, P. and Schneider, A., *Acta Polym.* 1979, **30**, 270.
28. Pantar, A. V., *Eur. Polym. J.* 1986, **22**, 939.
29. Pantar, A. V., Atrey, M. and Rao, M. V. R., *Angew. Makromol. Chem.*, 1985, **129**, 163.
30. Ossenbach-Sauter, M., Thèse de Docteur d'Etat es Sciences Physiques, Université de Haute Alsace, 1981, Chap. 1, p. 22.
31. Kahrs, K. H. and Zimmermann, J. W., *Makromol. Chem.* 1962, **58**, 75.
32. Bartl, M. and Bonin, W. V., *Makromol. Chem.* 1963, **66**, 151.
33. Ceresa, R. J. US Patent No. 3110695, 1963 *Chem. Abstr.* 1964, **66**, 3169a.
34. Wang, T. K. Iliopoulos, I. and Audebert, R., *Polym. Bull.* 1988, **20**, 577.
35. Wang, T. K., Iliopoulos, I. and Audebert, R., *Polym. Prepr. ACS* 1989, **30**(2), 377.
36. Magny, B., PhD Dissertation, Thèse de l'Université Paris 6, 1992, Chap. 3, 52.
37. Williams, A. and Ibrahim, I. T., *J. Am. Chem. Soc.* 1978, **100**, 7420.
38. Williams, A. and Ibrahim, I. T., *J. Am. Chem. Soc.* 1981, **103**, 7090.
39. Lloyd, D. R. and Burns, C. M., *J. Polym. Sci., Polym. Chem. Edn* 1979, **17**, 3459.
40. Hoare, D. G. and Koshland, D. E., *J. Am. Chem. Soc.* 1966, **88**, 2057.
41. Lloyd, D. R. and Burns, C. M., *J. Polym. Sci., Polym. Chem. Edn* 1979, **17**, 3473.
42. Prouchayret, F., Sacco, D. and Dellacherie, E., *Polym. Bull.* 1989, **21**, 309.
43. Staros, J. V., Wright, R. W. and Swingle, D. M., *Anal. Biochem.* 1986, **156**, 220.