Compositional heterogeneity effects in hydrophobically associating water-soluble polymers prepared by micellar copolymerization

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An aqueous micellar radical copolymerization technique has been used to prepare water-soluble copolymers of acrylic acid/styrene, acrylamide/styrene and acrylic acid/ethylphenylacrylamide. In this process, the hydrophobic monomer (1–2 mol% based on the monomer feed) is dispersed within surfactant micelles while the water-soluble monomer is dissolved in the aqueous medium. This synthesis leads to block copolymers in which the number and length of the hydrophobic blocks vary with the degree of conversion. Kinetic studies have shown that the compositional heterogeneity results from the balance between the values of the reactivity ratios of the monomer pairs and the micellar effect inherent to the technique. The latter always leads to an enhanced apparent reactivity for the hydrophobic monomer. It is shown that an optimization of the process can be achieved which eventually corrects for the drift in the average copolymer composition with conversion. The thickening ability of the hydrophobically modified water-soluble copolymers is directly affected by the extent of their compositional heterogeneity. Analysis of the data provides some criteria for selecting appropriate systems with good controllable rheological properties.

(Keywords: water-soluble polymers; amphiphilic polymers; hydrophobic polyelectrolytes)

INTRODUCTION

Over the past few years, extensive studies have been focused on water-soluble polymers modified with low amounts of a hydrophobic monomer (1–3 mol%)[1-3] for their use as rheology modifiers in a number of applications including enhanced oil recovery and latex paints[1-6]. In aqueous solution above a critical polymer concentration, the hydrophobic groups associate intermolecularly and thereby produce a greater viscosity than for the analogue without the hydrophobe. Depending on the method of synthesis, the hydrophobes can be distributed anywhere in the copolymer, for example at each end of the backbone or within the chain as pendent groups in a random or blocky fashion.

Copolymers based on acrylamide have certainly been among those most investigated[7-31]. Their preparation may be difficult because of the insolubility of the hydrophobic monomer in water, and a few methods have been devised to overcome this problem. An ingenious approach was that developed by Evani[7], Turner et al.[8-10] and Valint et al.[11]. In this process the hydrophobic monomer is solubilized within surfactant micelles, whereas the hydrophilic monomer is dissolved in the aqueous continuous medium. This one-step micellar copolymerization route was found to give hydrophobically modified water-soluble polymers (HMWSPs) which could be adequately used as aqueous

viscosifiers. The intriguing question which was addressed by several groups[12-21], and partly solved, asks how the initial monomer segregation in the reaction mixture affects the copolymer microstructure. The high local concentration of the hydrophobes in the micelles should favour their incorporation in the copolymer as blocks rather than isolated units. Information on the copolymer microstructure is not straightforward here since analytical techniques such as n.m.r. cannot be used because of the extremely low amount of hydrophobe in the copolymer. However, direct evidence of a blocky structure was provided by Dowling and Thomas[13] and McCormick and coworkers[14-18] from photophysical studies on polyacrylamides containing styryl, naphthyl or pyrenyl groups as hydrophobes. In our laboratory, we clearly established that the thickening properties of hydrophobically modified polyacrylamides were directly related to the molecular structure[19,20]: the longer the hydrophobic blocks, the greater the thickening efficiency at a constant hydrophobe level. The length of the blocks could be monitored by adjusting the hydrophobe to surfactant ratio in the synthesis[13,18-21].

Another problem to face in this micellar polymerization process is the compositional heterogeneity of the high conversion samples. Kinetic studies on polyacrylamides modified with alkylphenylacrylamides indicated a greater incorporation of the hydrophobe at the beginning of the polymerization[21,22]. In the course of the reaction, the average hydrophobe incorporation was found to decrease towards the initial feed composition,

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and the higher the hydrophobe to surfactant ratio, the larger the decrease. These results imply that the propagating radicals are sampling the micellar phase, where the hydrophobes are in high concentration, for a time sufficient to give a polymer richer in hydrophobe than would be calculated from the volume-average concentration, assuming equal reactivity ratios. Additionally, there is the faster exchange time of one hydrophobe between two micelles ($\sim 10^{-7}$ s) compared to that of the addition of the hydrophobe onto a growing radical ($\sim 10^{-4}$ s)[21]. This induces a net flow of hydrophobes from inactive micelles towards micelles where there is a growing radical head-group[21,32]. For this particular class of HMWSPs, the reactivity ratios of the monomers are similar[20,21] and the micellar effects (concentration, residence time of the active end of the propagating radical and exchange dynamics) are solely responsible for the compositional sample heterogeneity.

The above results stress the major effects of the homogeneity and microstructure of the copolymers on their ability to be effective thickeners. The few investigations to date on the variation of sample heterogeneity with conversion have been primarily conducted on polyacrylamides modified with alkylphenylacrylamides[20-22]. For a better understanding of the parameters which control the rheological behaviour of HMWSPs prepared by micellar polymerization, it was imperative to extend these studies to other monomer pairs.

The choice of the monomers was guided by the following requirements.

1. The hydrophobes should have a small size (short length) like, for example, styrene. In this case, the thickening ability of the HMWSP is only expected to be given by the blocky structure of the copolymer. Previous studies dealing with the acrylamide/ethylphenylacrylamide pair (AM/eΦAM) have shown that no enhancement of viscosity with respect to that of the homopolymer analogue is realized when the short hydrophobes are randomly and singly distributed in the copolymer[19,20].

2. The reactivity of the hydrophobic comonomer should be varied with respect to that of the hydrophilic monomer. This should allow discrimination between the concurrent effects of the reactivity parameter values, which depend on a given monomer pair in any copolymerization reaction, and the micellar effects inherent to this particular process.

3. The hydrophilic monomer should be either neutral, as is acrylamide, or partially charged, as may be the case for acrylic acid. This should provide some insight into the combined effects of attractive hydrophobic interactions and repulsive electrostatic forces on the rheological behaviour of HMWSPs[26-31,33-38].

These criteria led us to select the acrylic acid/styrene (AA/S) monomer pair. Note that this pair has been widely used in emulsion polymerization[39-42] to prepare either polystyrene latexes functionalized by carboxylic groups or the so-called alkali-soluble/alkali-swellable emulsion polymers (ASEs)[36] used as thickeners. As discussed elsewhere[20], micellar and emulsion processes are quite different. In this paper we present a detailed study on the synthesis and characterization of acrylic acid/styrene copolymers prepared by micellar copolymeriza-

tion. The samples were carefully characterized by means of several techniques including light scattering, viscometry, ^{1}H n.m.r., and u.v. and fluorescence spectroscopy. For a meaningful comparison with the previous studies on the AM/eΦAM copolymers, we also studied, although in less detail, the micellar copolymerization of the crossed monomer pairs acrylic acid/ethylphenylacrylamide (AA/eΦAM) and acrylamide/styrene (AM/S). Analysis of the data enabled us to propose a general picture of the mechanistic processes occurring in these micellar polymerization systems.

EXPERIMENTAL

Reagents

Acrylic acid (Aldrich, 99%) was used as received. Stock solutions of partially neutralized acrylic acid (i.e. a mixture of AA and sodium acrylate (NaA)) were prepared by neutralization of acrylic acid with sodium hydroxide (1.5 M) under continuous stirring and cooling of the system ($T < 20°$C). The degree of neutralization α, defined by the molar ratio [NaA]/([AA] + [NaA]), was varied between 0 and 1. Styrene (Aldrich) was distilled under reduced pressure and stored at 4°C. Acrylamide (Merck) was twice recrystallized from chloroform, dried under vacuum and stored at 4°C. N-(4-Ethylphenyl)-acrylamide (eΦAM) was synthesized according to the method of Valint *et al.*[11]. Cetyltrimethylammonium bromide (CTAB) (Fluka) was twice recrystallized from an acetone/ethanol mixture (3/1 v/v). Sodium dodecyl sulfate (SDS) (Touzart & Matignon) was used without purification. The initiators potassium persulfate (KPS) (Aldrich) and 4,4'-azobis(4-cyanovaleric acid) (ACVA) (Aldrich) were used without further purification. Because of the poor solubility of ACVA in water at room temperature, a stoichiometric amount of NaOH was added to dissolve ACVA completely as its salt form in water prior to its addition into the reaction mixture.

Nomenclature

The sample names refer to the composition of the initial monomer feed: for example, AA$_{100}$/NaA$_0$/S$_2$ represents an acrylic acid/styrene copolymer prepared from non-neutralized acrylic acid and a styrene content of 2 mol% based on the total monomer feed; and AA$_{90}$/NaA$_{10}$/eΦAM$_1$ was prepared from 10%-neutralized acrylic acid ($\alpha = 0.1$) and ethylphenylacrylamide at a level of 1 mol% relative to the total monomer feed.

Synthesis of copolymers

The acrylic acid/styrene (AA/S), acrylic acid/ethylphenylacrylamide (AA/eΦAM) and acrylamide/styrene (AM/S) copolymers were prepared by an aqueous micellar copolymerization technique which has been detailed elsewhere[11,20,21].

In general, for all polymerizations, the initial concentrations of acrylic acid and acrylamide in water were kept constant at 10 wt% and 3 wt%, respectively. The concentrations of KPS and ACVA were 0.3 wt% and 0.6 wt% relative to the monomer feed, respectively. The initial amount of hydrophobic monomer was varied between 0 and 3 mol% based on the total monomer feed. The surfactant content was kept at 2 wt%.

The polymerization reactions were carried out in 250–800 ml reactors (depending on the required amount of

polymer) with double walls to contain the hot water required to heat the reaction mixture. Each reactor was fitted with a condenser, mechanical stirrer, rubber septum cap, thermometer, nitrogen inlet/outlet and an outlet at the bottom for sampling during the polymerization. The surfactant was introduced after the reactor had been purged with nitrogen for at least 0.5 h. Nitrogen was simultaneously bubbled through the aqueous solution of monomers in a separate flask connected to the reactor, after which the monomer solution was transferred to the reactor. This procedure of de-aeration prevents the extensive formation of foam, which occurs when the surfactant-containing reaction mixture is directly de-aerated. Afterwards, the mixture was heated to the required temperature (60°C for ACVA initiation, 70°C for KPS initiation). When the surfactant had dissolved, the hydrophobic monomer (styrene or ethylphenylacrylamide) was added. After complete solubilization of the hydrophobic monomer and when the temperature had equilibrated, the aqueous solution of initiator was injected with a syringe. Styrene and the initiator solution were de-aerated with nitrogen separately for 15 min prior to their addition to the reactor. The polymerization time was 4–7 h. Partially neutralized polymers were precipitated in acetone and repeatedly washed in a mixture of acetone and methanol (9/1 v/v) to remove surfactant, residual initiator and monomers; finally, the polymers recovered by filtration were dried under reduced pressure at 50°C for three days. In some experiments, samples were withdrawn at different reaction times, i.e. at different degrees of conversion. Each polymer fraction was accurately weighed to give the percentage conversion *versus* time. For poly(acrylic acid) in the pure acidic form, we did not find a suitable precipitant. In this case, the conversion–time data were obtained as follows. Each weighed fraction of the reaction mixture was freeze dried to remove water and unreacted AA; the resulting raw polymer still contained surfactant, the amount of which was known from the initial surfactant concentration; therefore, the weight of the polymer formed could be calculated.

For all experiments, the polymer concentrations were corrected for water content (~3–5 wt%) determined by the Karl Fischer method.

Static light scattering

The weight-average molecular weights of homo-poly(acrylic acid) samples were determined in 0.2 N HCl aqueous solution[43] (under such experimental conditions, all monomer units were converted into the acidic form whatever the initial degree of neutralization of the PAA sample) from static light scattering using a multiangle spectrometer (Amtec model MM1) at 632.8 nm. The value of the refractive index increment dn/dc measured at 632.8 nm using a Brice–Phoenix differential refractometer was 0.133 ± 0.006 (dn/dc = 0.146 at 546 nm elsewhere[43]). The molecular weights of AM/S copolymers were determined by static light scattering in formamide according to the method of Biggs *et al.*[21]. As detailed later, this technique could not be used for AA/NaA/S and AA/NaA/eΦAM copolymers.

Viscometric studies in dilute solution

The intrinsic viscosities [η] of homopoly(acrylic acid) and acrylic acid copolymers were determined in 0.05 M

LiCl solution in dimethylformamide (DMF) at 25°C. In order to ensure their solubility in dimethylformamide, the partially neutralized polymers were acidified with hydrochloric acid, dialysed against water to eliminate the salt and freeze dried. Measurements were carried out using a Contraves Low Shear 30 instrument (measuring system 2T-2T) interfaced with a personal computer and driven by a software package supplied by the manufacturer.

U.v. spectral analysis

For the determination of styrene content in the copolymers by u.v. spectroscopy, ethylbenzene was chosen as the saturated analogue to establish a calibration curve for the absorbance. As this compound is insoluble in water, an organic cosolvent, which was also a solvent for the polymers, had to be used. DMF and dioxane, which are good solvents for poly(acrylic acid), cannot be used alone because of their high absorbances in the wavelength range corresponding to the ethylbenzene absorption ($\lambda_{max} = 250$ nm). As the absorbance of dioxane is lower than that of DMF, the composition of the mixture selected was 1/4 dioxane/water (v/v), which corresponds to the smallest amount of dioxane required to dissolve ethylbenzene.

A spectrum with four absorption bands between 255 and 268 nm was recorded for ethylbenzene and similarly, with a slight shift towards higher λ in the absorption maxima, for the styrene copolymer. Two bands, at 257 and 266 nm, were selected for the measurement of the extinction coefficient of ethylbenzene (171 ± 8 and 133 ± 6 dm^3 mol^{-1} cm^{-1}, respectively). The weight and molar fractions of styrene in acrylic acid copolymers can be calculated from the absorbance maxima D_0 using

$$\text{wt\%} = \frac{D_0}{\epsilon_\lambda l} \frac{104}{y} 100 \tag{1}$$

and

$$\text{mol\%} = \frac{\text{wt\%}/104}{(\text{wt\%}/104) + (100 - \text{wt\%})/[72\alpha + 94(1 - \alpha)]} \tag{2}$$

where y is the weight of polymer in grams per litre, ϵ_λ is the molar absorption coefficient measured for ethylbenzene in cubic decimetres per mole per centimetre, l is the path length of the cell in centimetres and α is the degree of neutralization of acrylic acid. The values 104, 94 and 72 are the molecular weights of the styrene, sodium acrylate and acrylic acid units, respectively.

The ethylphenylacrylamide contents in AA/eΦAM copolymers were determined by u.v. spectroscopy as previously described[21].

^{1}H n.m.r.

Because of the difficulties encountered in the use of u.v. spectroscopy for the determination of the styrene content (see later), we turned to ^{1}H n.m.r. spectroscopy. Copolymer solutions of 0.5–1 wt% in D$_2$O were studied at room temperature using a 200 MHz Bruker AC200 instrument.

Rheological measurements in semi-dilute solution

Viscosity–shear rate measurements were performed at 25°C on the aqueous polymer solutions with a Carri-Med CLS 100 and a Contraves Low Shear 30 instrument

(measuring system 1-1). The preparation of the solutions has been described in a previous paper[20].

RESULTS AND DISCUSSION

Choice of experimental conditions

The characteristics of HMWSPs depend critically on the different parameters involved in the polymerization reaction. We discuss below the criteria which led us to select the most appropriate conditions for the synthesis of AA/S copolymers.

Initiator. In our previous work on associating polymers based on hydrophobically modified poly-acrylamide, potassium persulfate (KPS) was used as the water-soluble initiator[19-21]. In the present study, the polymerization reactions were carried out at different pH values in order to neutralize to various extents the acrylic acid. Since the rate of KPS decomposition depends on the pH[44], we used 4,4'-azobis(4-cyanovaleric acid) (ACVA) for most of our experiments. It has been reported[45] that the rate of 2,2'-azobis(isobutyronitrile) decomposition does not depend on pH, and we assumed that this is valid for ACVA as well.

Surfactant. Owing to the anionic character of partially neutralized acrylic acid or poly(acrylic acid), it can be expected that the choice of the surfactant (anionic or cationic) plays an important role in the copolymerization mechanism of acrylic acid and styrene, the latter being located within the micelles. In particular, both electrostatic and hydrophobic interactions between monomer(s) and surfactant might affect the copolymer characteristics. In recent work, Corona-Galvan et al.[40] performed emulsion copolymerization of acrylic acid with styrene (volume ratio AA/S of 15/85) using either an anionic surfactant (sodium dodecyl sulfate (SDS)) or a cationic surfactant (cetyltrimethylammonium bromide (CTAB)). They found that in the case of CTAB, a rather random copolymer was created, whereas in the case of SDS, a more blocky structure was formed. The above observation was discussed in terms of the interaction of acrylic acid with the charged surfaces of the micelles (attraction in the case of CTAB and repulsion in the case of SDS). Similar findings were previously reported on the related styrene/methacrylic acid system[46].

A first series of tests was carried out with CTAB as the cationic surfactant in order to facilitate styrene incorporation into the copolymer by increasing the local acrylic acid concentration in the vicinity of the micelles through the opposite charge of the monomer/surfactant pair. However, we observed that the system, once polymerized, phase separated on dilution with water. Also, the polymers after precipitation and recovery were often insoluble (or formed a gel-like system) in water. On the other hand, these samples were soluble in dimethylformamide. This behaviour can be accounted for by the attractive interactions between poly(acrylic acid) and CTAB. Note that even a repeated precipitation and washing procedure could not totally remove CTAB from the sample. This phenomenon of highly cooperative binding in an oppositely charged polyelectrolyte/ionic surfactant mixture has been extensively reviewed[47-49].

Given these circumstances, all the experiments described below refer to samples prepared by micellar copolymerization in the presence of SDS.

Effect of pH. In free radical polymerization, the molecular weight of a poly(carboxylic acid) decreases strongly upon increasing the pH (from 2 to 7)[50,51]. We carried out a series of polymerizations of acrylic acid in aqueous solution at various pH values. SDS was added to the reaction medium in order to mimic the experimental conditions to be used in the syntheses of HMWSPs by micellar polymerization. The results showing the effect of pH on the molecular weight of homopoly(acrylic acid) are given in *Table 1*. The molecular weight decreases drastically from 1.9×10^6 to 7×10^4 upon increasing the pH from 2.4 to 4.9.

Figure 1 shows the conversion–time plots for the homopolymerization of AA at various pH values in the presence of 2 wt% SDS. We observe a strong dependence of the rate of polymerization on the pH, in agreement with the previous results of Kabanov et al.[51]. Indeed, the system should be regarded as a mixture in variable proportions of two monomers, acrylic acid and sodium acrylate, the latter being much less reactive than the

Table 1 Effect of pH and degree of neutralization α on the molecular weight M_w of homopoly(acrylic acid) synthesized in water at 60°C in the presence of 2 wt% of SDS ([monomer] = 10 wt%, [initiator (ACVA)] = 0.06 wt%)

Run	α	pH[a]	$10^{-6} M_w$[c]
IL38	0.00	2.4	1.90
IL27	0.10	3.5	1.80
IL29	0.25	3.8	1.90
IL30	0.50	4.3	0.80
IL37	0.75	4.9	0.07
IL09[b]	1.00	9.1	0.11

[a] The pH values were directly measured at 60°C inside the reactor after addition of all the components
[b] Polymerized without SDS
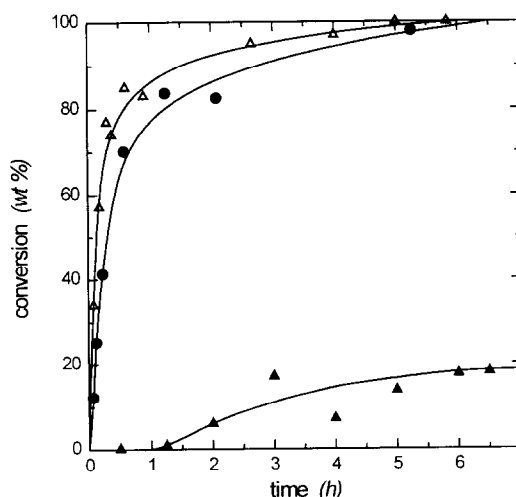[c] From light scattering in aqueous 0.2 N HCl solution

Figure 1 Conversion as a function of time for the homopolymerization of acrylic acid at three different degrees of neutralization (experimental conditions for the polymerizations are given in *Table 3*): (△) AA$_{100}$/NaA$_0$ (IL38); (●) AA$_{90}$/NaA$_{10}$ (IL50); (▲) AA$_{25}$/NaA$_{75}$ (IL37)

former. This causes the strong decrease in the rate of polymerization and subsequently in M_w observed upon increasing the pH of the solution. As the main goal of this study was to obtain copolymers with sufficiently high molecular weights to be effective thickeners, it was necessary to carry out the experiments in the low pH range. On the other hand, we encountered in the course of this study some solubility problems for the HMWSPs prepared at too low a neutralization degree. These problems were due to the somewhat hydrophobic character of the acidic form of the polymer. Therefore, we selected for most of our experiments a pH of 3.5 corresponding to a degree of neutralization $\alpha = 0.1$ for acrylic acid.

Characterization of AA/S copolymers

Molecular weight determination. The molecular weight of the AA/S copolymer is a parameter of paramount importance since it controls the viscosity of the polymer solutions. As previously shown for another type of hydrophobically modified water-soluble polymer[20], water cannot be used as a solvent for static light-scattering experiments because the hydrophobic interactions give rise to aggregation phenomena even in very dilute solutions. The use of an organic solvent which is a good solvent for both moieties of the copolymer avoids this drawback.

Dimethylformamide (DMF) is a good candidate, but its dielectric constant is large enough so that the electrolyte character of the polymer still prevails. In this case, the scattered intensity is dominated by the osmotic pressure of the counterions and does not give any information on the molecular weight[52]. This is illustrated in *Table 2*, which shows the ratio between the scattering intensities of the polymer solution and solvent for pure DMF. This ratio is close to 1, and this result cannot be accounted for solely by the low value of the refractive index increment ($dn/dc = 0.067\,\mathrm{cm^3\,g^{-1}}$). We then tried to use as a solvent for the copolymers a 0.05 M LiCl solution in DMF in order to screen the electrostatic interactions. It can be seen in *Table 2* that the intensity of the scattered light has strongly increased even though dn/dc is about the same as in pure DMF ($dn/dc = 0.070\,\mathrm{cm^3\,g^{-1}}$). However, the Zimm plot shows an upward curvature and the increase in scattered intensity does not vary in proportion to the polymer concentration. This could be explained by a saturation of the scattered intensity due to the high polymer concentration, but the low dn/dc value did not allow us to work at a lower concentration.

Table 2 also shows the molecular weight results for a homopolymer sample, measured by static light scattering in aqueous 0.2 N HCl solution. In contrast with the data from DMF, one recovers the classical concentration dependence of the scattered intensity leading to a reliable value of the molecular weight.

As it is not possible to use the above water-based solvent for the characterization of HMWSPs and because of the problems mentioned above, we abandoned the direct measurement of the molecular weights of AA/S copolymers by static light scattering in organic solution. The procedure we used to determine the molecular weights of AA/S and AA/eΦAM copolymers included the following steps:

1. determination of the weight-average molecular weights M_w of homopolymers of acrylic acid over a wide range using static light scattering in a suitable solvent (as described above, in aqueous 0.2 N HCl solution);
2. determination of the intrinsic viscosities $[\eta]$ of the above homopolymers of acrylic acid in dimethylformamide in the presence of LiCl;
3. from the data obtained in steps 1 and 2, establishment of a Mark–Houwink-type equation ($[\eta] = KM^a$) for homopoly(acrylic acid) in DMF solution (0.05 M LiCl);
4. determination of the intrinsic viscosities of the hydrophobically modified copolymers in LiCl solution in dimethylformamide; and
5. determination of the copolymer molecular weights from the intrinsic viscosity–molecular weight relationship established for the homopolymers.

A similar approach was previously used for the molecular weight determination of hydrophobically modified (hydroxyethyl) cellulose[53]. The use of this procedure rests on the assumption that the low styrene content does not significantly modify the conformation of the poly(acrylic acid) chain in order to apply the intrinsic viscosity–molecular weight relationship established for homopoly(acrylic acid) to AA/S copolymers. As for any molecular weight determination from viscometric measurements, we must assume that all the samples investigated have similar molecular weight distributions. We are well aware of the limitations of the method used, but we face here a difficulty commonly encountered for this type of copolymer.

The weight-average molecular weights of various homopoly(acrylic acid)s prepared under different initial conditions are given in *Table 3* (including the data from *Table 1*). The experimental conditions differ in the degree of neutralization of acrylic acid and in the choice of initiator and surfactant. A broad range of molecular weights was obtained, which enabled us to establish the Mark–Houwink relationship after the measurement of the intrinsic viscosities of these homopolymers.

The next step in the characterization of AA/S copolymers was to perform intrinsic viscosity measurements on homopoly(acrylic acid)s of known molecular weight. *Figures 2* and *3* show examples of the variations in the reduced viscosity for a homo(polyacrylic acid) and a copolymer, respectively, in DMF and in DMF with LiCl. Again, a classical polyelectrolyte behaviour is observed in pure DMF, i.e. an increase in the reduced

Table 2 Light-scattering data for poly(acrylic acid) solutions in various solvents: relative scattered intensities $I/I_0{}^a$ and molecular weights M_w determined from Zimm plots (run IL02)

Solvent	$10^3 C_p{}^b$ (g ml^{-1})	$\left(\dfrac{I}{I_0}\right)_{\theta=90°}$	$10^{-6} M_w$
DMF	0.90	1.1	
0.05 M LiCl in DMF	3.60	5.5	13
	1.40	5.5	3.2
0.2 N HCl in water	0.77	70	1.4
	0.18	20	1.4

^{a} I_0 and I are the intensities scattered by the solvent and the solution at polymer concentration C_p
^{b} The highest concentration used for the Zimm plot

Table 3 Polymerization conditions, molecular weights and intrinsic viscosities for homopoly(acrylic acid) samples (several values for the same sample are the results of repeated measurements)

| Run	Sample[a]	Surfactant[b]	Initiator	$10^{-6}M_{LS}$[c]	$[\eta]$[d] (ml g^{-1})	$10^{-6}M_V$[f]
IL02	AA_{100}/NaA_0		KPS	1.4 ± 0.2	735, 707	1.4, 1.3
IL03	$AA_{100}NaA_0$	CTAB	KPS	1.2 ± 0.2	562, 540	0.9, 0.8
IL05	AA_0/NaA_{100}		KPS	0.05 ± 0.009	43	0.01
IL09	AA_0/NaA_{100}		ACVA	0.11 ± 0.02	118	0.06
IL13	AA_{100}/NaA_0	CTAB	ACVA	1.9 ± 0.3	894	2.0
IL14	AA_{100}/NaA_0		ACVA	2.4 ± 0.4	963^e, 1084, 913	2.3, 2.8, 2.1
IL15	AA_{100}/NaA_0	SDS	ACVA	0.8 ± 0.1	448	0.6
IL20	AA_{90}/NaA_{10}		ACVA	0.47 ± 0.08	386	0.5
IL21	AA_{95}/NaA_5		ACVA	0.40 ± 0.06	414	0.5
IL27	AA_{90}/NaA_{10}	SDS	ACVA	1.8 ± 0.3	866	1.9
IL29	AA_{75}/NaA_{25}	SDS	ACVA	1.9 ± 0.3	936	2.1
IL30	AA_{50}/NaA_{50}	SDS	ACVA	0.8 ± 0.1	653	1.1
IL37	AA_{25}/NaA_{75}	SDS	ACVA	0.07 ± 0.01		
IL38	AA_{100}/NA_0	SDS	ACVA	1.9 ± 0.3		
IL50	AA_{90}/NaA_{10}	SDS	ACVA			

[a] The nomenclature refers to the composition of the monomer feed (see Experimental)
[b] [Surfactant] = 2 wt% of the total recipe
[c] Molecular weight determined by light scattering in aqueous 0.2 N HCl solution
[d] Intrinsic viscosity measured in DMF/0.05 M LiCl
[e] Measured in DMF/0.01 M LiCl
[f] Molecular weight calculated from the Mark–Houwink equation $[\eta] = 0.199M^{0.58}$
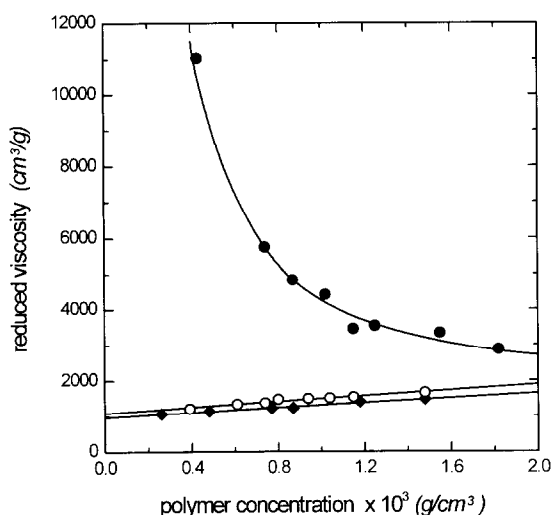
Figure 2 Reduced viscosity as a function of polymer concentration for a homopoly(acrylic acid) sample (run IL14) in DMF (●), DMF/0.01 M LiCl (◆) and DMF/0.05 M LiCl (○) ($T = 25°C$)
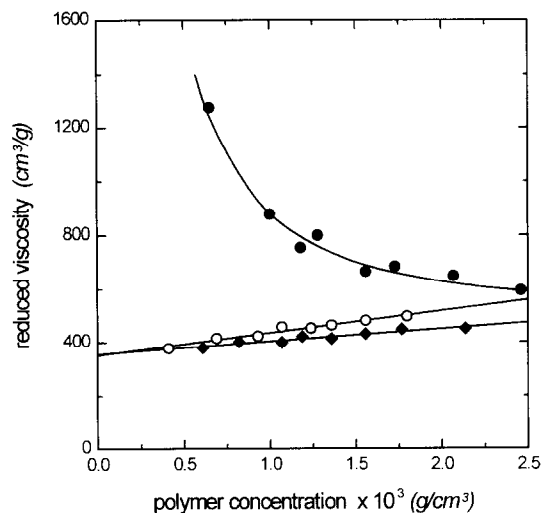
Figure 3 Reduced viscosity as a function of polymer concentration for an AA/S copolymer (run IL04) in DMF (●), DMF/0.01 M LiCl (◆) and DMF/0.05 M LiCl (○) ($T = 25°C$)

viscosity at low polymer concentration. In both cases, the intrinsic viscosity is independent of the amount of LiCl.

The results for the homopoly(acrylic acid) solutions in DMF/0.05 M LiCl at 25°C are given in *Figure 4*. They provide the following Mark–Houwink relationship for this polymer/solvent pair

$$[\eta] = 0.199M_w^{0.58} \tag{3}$$

The experimental value of the exponent ($a = 0.58$) confirms that DMF is a good solvent for poly(acrylic acid). It is known that DMF is also a good solvent for polystyrene.

The measured intrinsic viscosities and the molecular

weights calculated from equation (3) are given in *Tables 3* and *4* for the homopolymers and copolymers, respectively.

A comparison of the data obtained under different conditions indicates that the presence of styrene and/or surfactant tends to decrease the molecular weight of the polymer. Concerning the effect of the surfactant, one can invoke some chain transfer reactions which may be attributed to the presence of impurities in SDS, particularly alcohols[20]. As for the effect of styrene on molecular weight, it has been shown for styrene copolymerization with various alkyl methacrylates[54] that the rate of polymerization is reduced through the styrene penultimate effect. A similar effect can take place

Table 4 Polymerization conditions[a], molecular weights and intrinsic viscosities of the acrylic acid/styrene copolymers

Run	Sample[b]	Surfactant[c]	$[\eta]^d$ (ml g^{-1})	$10^{-6} M_V$[f]
IL04	$AA_{100}/NaA_0/S_3$	CTAB	312, 356[e], 351	0.3, 0.4, 0.4
IL12	$AA_{100}/NaA_0/S_3$	CTAB	818	1.7
IL16	$AA_{100}/NaA_0/S_3$	SDS	Insoluble in DMF	
IL17	$AA_{90}/NaA_{10}/S_3$	SDS	638	1.1
IL18	$AA_{90}/NaA_{10}/S_2$	SDS	456	0.6
IL19	$AA_{90}/NaA_{10}/S_1$	SDS	381, 338	0.5, 0.4
IL23	$AA_{90}/NaA_{10}/S_3$	SDS	400	0.5
IL24	$AA_{90}/NaA_{10}/S_2$	SDS	725	1.4
IL26	$AA_{90}/NaA_{10}/S_1$	SDS	658	1.2
IL32	$AA_{50}/NaA_{50}/S_1$	SDS	369	0.4
IL39 (1–5)	$AA_{90}/NaA_{10}/S_2$	SDS	[g]	[g]
IL40 (1–5)	$AA_{100}/NaA_0/S_2$	SDS	[g]	[g]
IL42 (1–5)	$AA_{50}/NaA_{50}/S_2$	SDS	[g]	[g]

[a] The initiator was KPS for run IL04, ACVA for all other runs
[b] The nomenclature refers to the composition of the monomer feed (see Experimental)
[c] [Surfactant] = 2 wt% of the total recipe
[d] See *Table 3*
[e] See *Table 3*
[f] See *Table 3*
[g] Several samples taken at various degrees of conversion (see the molecular weight data in *Figure 5*)
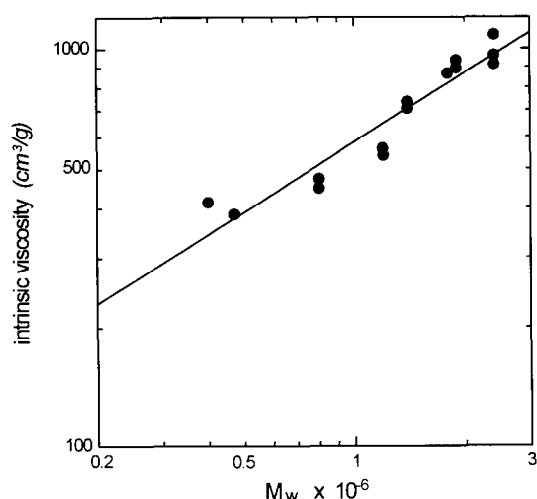
Figure 4 Log–log dependence of the intrinsic viscosity on the weight-average molecular weight of homopoly(acrylic acid). Determination of the parameters K and a for the Mark–Houwink relationship in DMF/0.05 M LiCl ($K = 0.199$, $a = 0.58$)
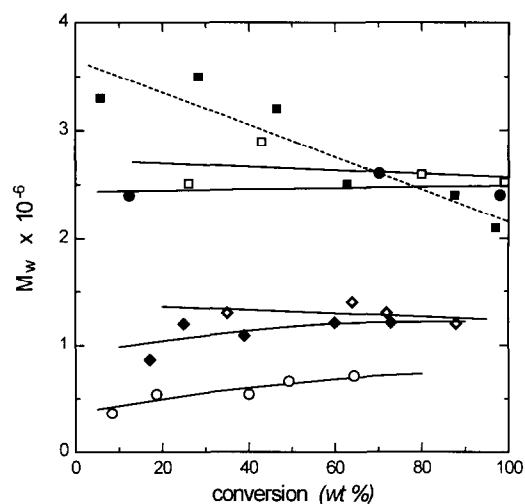
Figure 5 Variation in the weight-average molecular weight as a function of conversion for various copolymers: (●) AA_{90}/NaA_{10} (IL50); (□) $AA_{100}/NaA_0/S_2$ (IL40); (◆) $AA_{90}/NaA_{10}/S_2$ (IL39); (○) $AA_{50}/NaA_{50}/S_2$ (IL42); (--■--) $AA_{90}/NaA_{10}/e\Phi AM_1$ (IL46); (◇) AM/S_2 (IL45)

in the AA/S copolymerization, which could lead to lowering of the molecular weight.

In *Figure 5* are reported the variations in the weight-average molecular weight as a function of conversion for various monomer pairs: acrylic acid/styrene, acrylamide/styrene and acrylic acid/ethylphenylacrylamide. The experimental conditions as well as the calculated numbers of hydrophobe molecules per micelle are given in *Table 5*. Inspection of *Figure 5* shows that the molecular weights of AA/S and AM/S copolymers do not vary significantly with conversion as in the case of the homopolymerization of acrylic acid. On the other hand, the evolution of molecular weight for the AA/eΦAM pair follows the same trend as that observed for AM/eΦAM copolymerization[21], i.e. a significant decrease in molecular weight during the course of the

polymerization. From these data, it can be inferred that the nature of the hydrophobe affects the molecular weight of the copolymer formed in the course of the polymerization. The lowering of the molecular weight of AM/eΦAM copolymers with conversion shown in the work of Biggs *et al.*[21] was interpreted in terms of a degradative chain transfer reaction to the pendent ethylphenyl group. This effect does not come into play when styrene is used instead of eΦAM, since no hydrogen abstraction can occur. However, as shown later, a different rate of hydrophobe incorporation into the copolymer can also play an important role in the molecular weight evolution.

The experimental conversion–time curves determined for the various monomer pairs are given in *Figures 6–8*.

Table 5 Experimental conditions used in the copolymerization experiments carried out as a function of conversion[a]

Run	Sample	[SDS][b] (wt%)	N_H[c]	N'_H[d]
IL40	$AA_{100}/NaA_0/S_2$	2	28	28
IL39	$AA_{90}/NaA_{10}/S_2$	2	26	39
IL42	$AA_{50}/NaA_{50}/S_2$	2	23	43
IL45	AM/S_2	0.6	39	
IL51	$AA_{90}/NaA_{10}/e\Phi AM_1$	1	8	12
IL46	$AA_{90}/NaA_{10}/e\Phi AM_1$	2	13	19
IL48	$AA_{90}/NaA_{10}/e\Phi AM_1$	3	29	39

[a] $T = 60°C$; [initiator (ACVA)] $= 0.6$ wt% of the monomers, except for the AM/S sample (run IL45, 0.36 wt%); [monomer] $= 10$ wt%, except for the AM/S sample (run IL45, 3 wt%)
[b] Weight percentage of the total recipe
[c] Number of hydrophobes per micelle calculated from $N_{agg} = 60$ and a critical micelle concentration (c.m.c.) of 9×10^{-3} M for SDS[55]
[d] Number of hydrophobes per micelle calculated by taking into account the change in the c.m.c. and N_{agg} caused by the ionic strength of the medium[56] in the presence of NaA. For $\alpha = 0.1$, [NaA] $= 0.13$ M, $N_{agg} \approx 100$, c.m.c. $\approx 1.6 \times 10^{-3}$ M; for $\alpha = 0.5$, [NaA] $= 0.6$ M, $N_{agg} \approx 126$, c.m.c. $\approx 0.5 \times 10^{-3}$ M
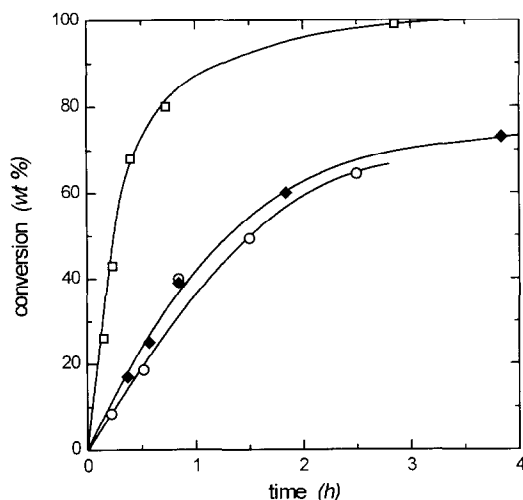
Figure 6 Conversion as a function of time for various copolymers prepared at a constant styrene content in the monomer feed (2 mol%) and different neutralization degrees of acrylic acid: (□) $AA_{100}/NaA_0/S_2$ (IL40); (♦) $AA_{90}/NaA_{10}/S_2$ (IL39); (○) $AA_{50}/NaA_{50}/S_2$ (IL42)

Figure 7 Conversion as a function of time for various $AA_{90}/NaA_{10}/e\Phi AM_1$ copolymers prepared at a constant monomer feed composition (1 mol% $e\Phi AM$, $\alpha = 0.1$) and various SDS levels: (▼) IL51 ([SDS] $= 1$ wt%); (■) IL46 ([SDS] $= 2$ wt%); (+) IL48 ([SDS] $= 3$ wt%)
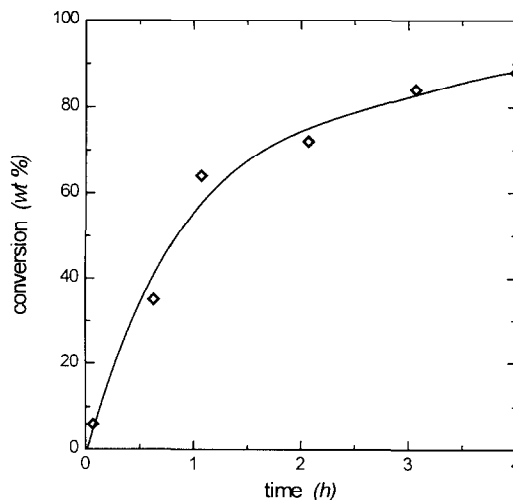
Figure 8 Conversion as a function of time for an AM/S_2 copolymer (run IL45)

Two factors affect considerably the rate of polymerization: (1) the degree of neutralization of acrylic acid (as previously shown in *Figure 1* relative to the homopolymer) and (2) the nature of the hydrophobic comonomer. In this respect, it is interesting to note that $e\Phi AM$ (1 mol%) has only a little effect on the rate of polymerization at a degree of neutralization $\alpha = 1$ (compare run IL50 in *Figure 1* with runs IL46 and IL48 in *Figure 7*), unless the hydrophobe/surfactant ratio is greatly augmented (run IL51, *Figure 7*). This result supports some similar findings of Biggs *et al.*[21] for the micellar copolymerization of AM and $e\Phi AM$. In contrast, styrene does exert a significant influence on the rate of polymerization of partially neutralized acrylic acid (compare run IL50 in *Figure 1* with run IL39 in *Figure 6*). This observation points out the role played by the choice of the hydrophobe in the synthesis of associating copolymers by micellar copolymerization. As shown below, the nature of the hydrophobe also influences the ratio of hydrophobe incorporation into the copolymer.

Hydrophobe incorporation. A variation in the rate of hydrophobe incorporation into the copolymer as a function of conversion can significantly affect the rheological properties of the sample obtained at full conversion. In the case of $AM/e\Phi AM$ copolymers, a rate of hydrophobe incorporation faster than that obtained for the homogeneous solution was found, thus favouring the formation of a hydrophobe-rich copolymer at the beginning of the copolymerization[20,21]. Consequently, the thickening ability of the copolymer will decrease with increased conversion degree since a more hydrophile-rich copolymer or even a homopolymer can be obtained at higher conversions. In order to characterize the extent of heterogeneity in the copolymer composition, we determined the variation in the rate of hydrophobe incorporation during the course of the polymerization. The techniques used were u.v. spectroscopy and [1]H n.m.r. (see earlier).

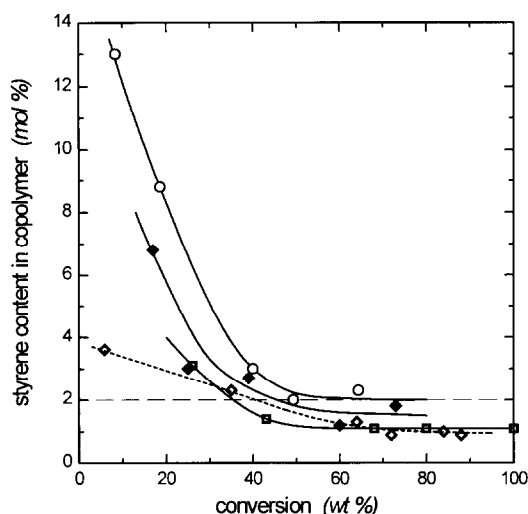U.v. spectroscopy is convenient for the determination of u.v. active compounds and has been used by several

Figure 9 Average styrene content as a function of conversion for various copolymers prepared at a constant styrene content in the initial feed (2 mol%): (□) $AA_{100}/NaA_0/S_2$ (IL40); (◆) $AA_{90}/NaA_{10}/S_2$ (IL39); (○) $AA_{50}/NaA_{50}/S_2$ (IL42); (--◇--) AM/S_2 (IL45)
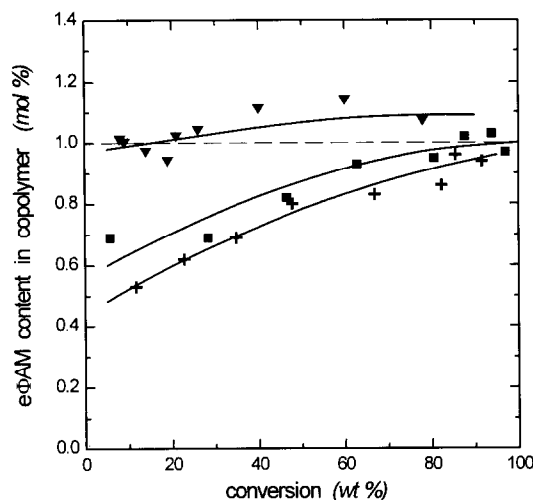
Figure 10 Average eΦAM content as a function of conversion for $AA_{90}/NaA_{10}/e\Phi AM_1$ copolymers prepared at a constant eΦAM content in the monomer feed (1 mol%) and various SDS levels: (▼) IL51 ([SDS] = 1 wt%); (■) IL46 ([SDS] = 2 wt%); (+) IL48 ([SDS] = 3 wt%)

authors for polyacrylamide derivatives containing aromatic groups as hydrophobes[11,13–22]. This is the method we previously used for the determination of the molar content of eΦAM in AM/eΦAM copolymers[20–22]. However, two problems arise when using styrene as the hydrophobe. First, the values of the extinction coefficients of styrene units in the copolymer (see earlier) are two orders of magnitude lower than that for eΦAM (12 400 dm^3 mol^{-1} cm^{-1} at 245 nm)[21], making the experiments less accurate and more difficult to perform. Second, the determination of the styrene content in a copolymer by u.v. spectroscopy is questionable since it was shown by Switala and Wojtczak[57] and Switala-Zeliazkow[58] that the extinction coefficient of styrene in a copolymer depends on several parameters such as the styrene content in the copolymer, the monomer sequence distribution (blocky or random) and the selected absorption band. This is the result of a hypochromic

effect which is related to the extent of isolation of styrene units in the copolymer. Indeed, our u.v. data obtained for samples based on styrene and taken at final conversion do confirm that the measured percentage of styrene depends significantly on the absorption band. This led us to the conclusion that u.v. spectroscopy is not adequate for the determination of the styrene content in associating copolymers.

^{1}H n.m.r. can also be used for the determination of the styrene content in copolymers[59,60]. The calculation of the styrene content in the copolymer is based on the measurement of the relative intensity of the styrene proton resonance at 7–7.5 ppm with respect to the intensity of the CH proton resonance (2.5 ppm) or the CH_2 proton resonance (1.5–2.2 ppm). Note that the accuracy is rather poor ($\pm$10%) owing to the low styrene content, but there is no systematic error as in the case of u.v. determination. Therefore, all the measurements of the styrene content reported below were obtained by means of ^{1}H n.m.r.

Figure 9 shows the variation in the molar percentage of styrene in the copolymer as a function of monomer conversion. Let us recall that in the case of the AM/eΦAM copolymerization in a micellar medium[21], the highest extent in the heterogeneity of hydrophobe incorporation was about two to two and a half times that of the final hydrophobe content. In our case, styrene tends to incorporate much faster and the amount of styrene in the low conversion copolymers can be up to eight to 10 times higher than that in the final polymer product. This amount depends on the degree of neutralization of acrylic acid; the incorporation of styrene in the uncharged AA/S and AM/S copolymers follows the same trend, while the extent of AA/S heterogeneity increases drastically upon increasing the degree of neutralization. The rate of styrene consumption is therefore much faster than in the case of AM/eΦAM copolymerization. We calculated that for partially neutralized AA/S copolymers, practically all of the hydrophobe is already consumed at 25–30% conversion of the total monomer feed. Thus, copolymer samples taken at high conversion levels consist of a mixture of homopoly(acrylic acid) chains and copolymer chains the hydrophobe numbers and sequences of which are variable. As shown in the next section, this heterogeneity in copolymer composition affects quite considerably the thickening ability of the high conversion samples. It should also be noted that the sample heterogeneity increases upon increasing the initial number of hydrophobes per micelle[21]. This number is higher for the AA/S copolymers studied here ($N_H \approx 30$, see *Table 5*) than in the earlier study on AM/eΦAM copolymers ($N_H < 10$). This, of course, enhances the extent of heterogeneity in the AA/S copolymer composition. This initially higher number of styrene hydrophobes per micelle was deliberately chosen in order to compensate for the lower hydrophobicity of styrene compared to that of eΦAM. It must be remarked that the overall amount of styrene incorporated in samples obtained at full conversion is systematically lower than that in the initial monomer feed. We did not succeed in finding out which step in the process was responsible for the loss of styrene. We discard the possibility of styrene content underestimation by ^{1}H n.m.r.

Figure 10 shows the variations in ethylphenylacrylamide incorporation into $AA_{90}/NaA_{10}/e\Phi AM$

copolymers prepared at different SDS concentrations (see *Table 5*). A striking feature is that the eΦAM hydrophobe incorporates into the copolymer at a slower rate than acrylic acid (runs IL46 and IL48). This behaviour, not observed so far in micellar copolymerization, is opposite to that observed for AM/eΦAM and AA/S copolymerizations and clearly shows that the drift in copolymer composition observed in a micellar copolymerization is not necessarily in favour of a faster incorporation of the hydrophobe located within the micelles. It is worth noting that by adjusting the eΦAM/surfactant ratio in this system, it is even possible to reverse the sign of the variation in the eΦAM incorporation *versus* conversion plot (run IL51). Thus, increasing the eΦAM/surfactant ratio in the formulation amounts to reducing the heterogeneity in the copolymer.

General mechanism involved in a micellar copolymerization

From the results depicted in *Figures 9* and *10* and those previously obtained for AM/eΦAM micellar copolymerizations, we are able to provide a more comprehensive explanation of the heterogeneity in copolymer composition which occurs in micellar copolymerization. Two main parameters control the compositional sample heterogeneity in the process:

1. the reactivity ratios of the monomer pairs; in a classical homogeneous solution polymerization the consumption of monomers is solely governed by the reactivity parameter values and the local monomer concentration at the locus of growing radicals; and
2. the micellar effect, which promotes a faster consumption of the hydrophobic monomer solubilized within the micelles.

The reactivity ratios of monomers can be determined experimentally and many of them can be found in the literature[61,62], whereas the effect of the monomer segregation in a micellar copolymerization remains an unknown parameter. In a first approach, we attempted to determine the effect of the reactivity ratios on the kinetics of the reaction by calculating for the three monomer pairs investigated the theoretical composition–conversion curves from the well known Mayo–Lewis and Skeist equations[63]. However, for the systems investigated, it is not necessary to know precisely the actual values of the reactivity parameters: (1) the reactivity parameters for the hydrophilic/hydrophobic monomer pairs in aqueous solution are not available, obviously because of the insolubility of the hydrophobes in water; and (2) the data obtained in other solvents must be used with caution because acrylic acid and acrylamide are monomers for which the reactivity strongly depends on the nature of the solvent[64] (electrostatic forces, hydrogen bonding and dipolar interactions are the most important factors responsible for the variations in the monomer reactivity). Thus, for the three monomer pairs considered, depending on the experimental conditions, the literature data show that either one or the other monomer can be the more reactive[61,62,64]. The situation is still more complicated in the present case because the physical properties of the medium differ for the two types of monomers: the water-soluble monomer is within a polar and hydrogen-bonding solvent, while the hydrophobic monomer inside the micelles is within a non-polar

environment. For the systems considered here, it has been shown that the copolymerization behaviour is mainly controlled by the modification of the reactivity of AM or AA according to the nature of the solvent, while the reactivity of S remains essentially unaffected[64]. Therefore, as a basis for discussion, we consider that the data previously reported for highly polar and/or hydrogen-bonding solvents (like alcohols, dimethyl sulfoxide and DMF) provide representative values of the reactivity parameters.

For the AA/S pair, the reactivity ratios indicate a higher reactivity for styrene compared to acrylic acid[64]. We chose for our calculation $r_{AA} = 0.15$ and $r_S = 1.03$ as measured in DMF at 50°C[65] (acrylic acid was in the acidic form). We have, however, checked that the use of different values of the reactivity ratios as reported by other authors does not strongly modify the calculated curves.

Data reported for the AM/S system in various polar and hydrogen-bonding solvents show that styrene is always more reactive than acrylamide[61,62,64,66,67]. The values $r_{AM} = 0.33$ and $r_S = 1.49$ obtained in ethanol[61,62] have been used.

As the reactivity parameters for the AA/eΦAM pair were not available in the literature, we took for this calculation the known reactivity parameters for the AA/AM pair. This is justified since it was previously found that the homogeneous copolymerization of acrylamide and eΦAM yields a copolymer with a constant composition as a function of conversion, which implies that the monomers have similar reactivities[20,21]. The reactivity ratios for the AA/AM pair have been determined in aqueous solution as a function of pH by different authors[64,66]. At low pH $r_{AA} > r_{AM}$, but when the pH increases the values of the copolymerization parameters tend to become closer and eventually acrylamide becomes more reactive than acrylic acid. We took the values $r_{AA} = 1.19$ and $r_{AM} = 0.59$ ($\approx r_{eΦAM}$) determined at a pH of ~3.7, with NaOH as the neutralizing agent, at 60°C[68], which is close to our experimental conditions.

The trends shown in *Figure 11* must be considered as indicative but they reproduce qualitatively the experimental behaviour. This led us to consider the three following cases based on the relative values of the reactivity ratios involved in the monomer pair.

Case 1: the hydrophobic monomer is more reactive than the hydrophilic monomer. The copolymerization of acrylic acid with styrene is a good example of this case. In solution polymerization, the drift in copolymer composition with time is due to the higher reactivity of styrene (*Figure 11*). This drift is enhanced when the copolymerization reaction is carried out in a micellar medium (*Figure 9*). In this process, the hydrophobic monomer is overconcentrated within the micelles. In fact, as mentioned above, the hydrophobe/surfactant ratio and the dynamics of micellar systems were found to be the driving forces for the rate of hydrophobe incorporation and the formation of a blocky-structured copolymer[20,21]. In the present study it was found experimentally (*Figure 9*) that the rate of styrene incorporation increases with increased degree of neutralization. This observation can be connected with (1) the lower reactivity of partially neutralized acrylic acid compared to
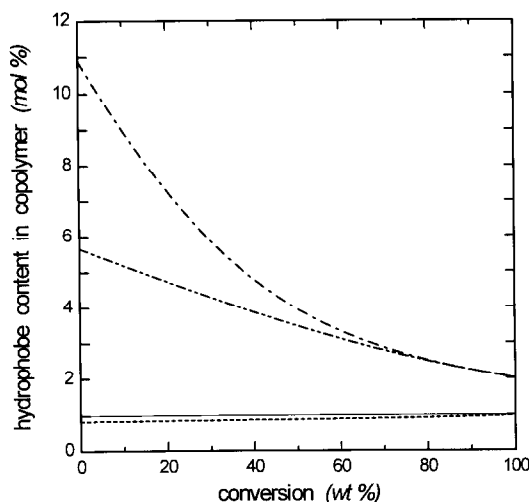
Figure 11 Theoretical hydrophobe content (styrene or eΦAM) as a function of conversion for the homogeneous solution polymerizations of various monomer pairs: (−·−·−) AA/S; (−··−··−) AM/S; (———) AM/eΦAM; (− − −) AA/eΦAM. Hydrophobe contents in the monomer feed: [S] = 2%, [eΦAM] = 1%. See text for copolymerization parameters

acrylic acid and (2) the smaller number of micelles in the initial solution since the aggregation number of SDS is increased in the presence of acrylic acid in its salt form (see *Table 5*). Therefore, the number of hydrophobes per micelle is higher, and it was previously found that this results in an enhanced incorporation rate of the hydrophobe[21].

Case 2: the hydrophobic and hydrophilic monomers have similar reactivities. This is the situation encountered in the copolymerization of acrylamide with ethylphenyl-acrylamide. A constancy in copolymer composition was found both theoretically and experimentally for samples prepared by homogeneous copolymerization[20,21]. Therefore, the faster consumption of the eΦAM which takes place in the early stages of the micellar copolymerization can be solely attributed to the micellar effects discussed above. The compositional heterogeneity of the resulting copolymers depends on the initial hydrophobe/surfactant ratio. A random copolymer structure might even be obtained by using a low hydrophobe/surfactant ratio in such a way that each micelle is occupied by one hydrophobe molecule. This latter case amounts roughly to that of homogeneous polymerization, in spite of the presence of surfactant.

Case 3: the hydrophobic monomer is less reactive than the hydrophilic monomer. This situation corresponds to the copolymerization of acrylic acid with eΦAM. In a solution copolymerization, the hydrophobe content of the polymer in the early stages of the polymerization is lower than that in the feed and that at higher conversions owing to the lower value of $r_{e\Phi AM}$ with respect to r_{AA} (*Figure 11*). This case is most interesting since the resulting drift in the copolymer composition can be reduced or even annealed in the micellar process by optimizing the hydrophobe/surfactant ratio as discussed above (see *Figure 10*, run IL51).

Rheological properties of the AA/S copolymers in the semi-dilute regime

We have seen in the previous section that the AA/S copolymers exhibit a strong heterogeneity in composition as a function of conversion. We investigate here how this compositional heterogeneity can affect the rheological behaviour in the semi-dilute regime for samples obtained at various conversion degrees.

Copolymers obtained at full conversion. *Figure 12* shows the viscosity–shear rate data measured in the semi-dilute regime ($C_p = 2$ wt%) for three samples prepared by copolymerization of 10%-neutralized acrylic acid with different amounts of styrene (0, 1 and 2 mol% in the monomer feed, respectively). The overall rheological behaviour is that classically observed for semi-dilute polymer solutions: a Newtonian plateau at low shear rates and a shear-thinning effect at higher shear caused by the orientation and disentanglement of the polymer chains. No specific effect inherent to associating polymers is observed: the viscosity values for the copolymer samples are lower than that for the unmodified poly(acrylic acid). The differences in the viscosities of the aqueous copolymer solutions can be mainly accounted for by the differences in molecular weight. The zero shear viscosities η_0 (100, 200 and 450 cP for samples IL26, IL24 and IL27, respectively) vary as a function of the molecular weight M (1.2×10^6, 1.4×10^6 and 1.8×10^6, respectively) as $\eta \approx M^{3.6}$, in good agreement with the theoretical prediction[69] ($\eta \approx M^{3.4}$ in semi-dilute solution). This result shows that intermolecular hydrophobic interactions do not seem to occur in aqueous solutions of AA/S copolymers obtained at full conversion.

The important conclusion which can be drawn from these rheological measurements on full conversion samples is that the copolymer heterogeneity is certainly at the origin of the poor thickening ability. A polymer solution contains around 25% of hydrophobically
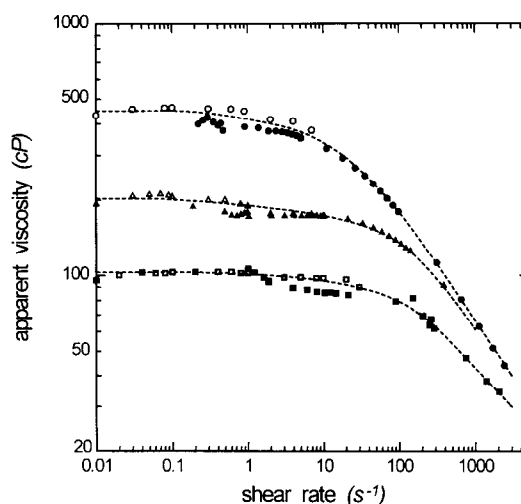

Figure 12 Viscosity–shear rate behaviour in aqueous solutions of various AA$_{90}$/NaA$_{10}$/S polymers obtained at full conversion and with different styrene contents in the monomer feed (polymer concentration $C_p = 2$ wt%): (○, ●) IL27, [S] = 0 mol%, $M_w = 1.8 \times 10^6$; (□, ■) IL26, [S] = 1 mol%, $M_w = 1.2 \times 10^6$; (△, ▲) IL24, [S] = 2 mol%, $M_w = 1.4 \times 10^6$. Experimental data obtained using Low Shear 30 (open symbols) and Carri-Med (filled symbols) rheometers
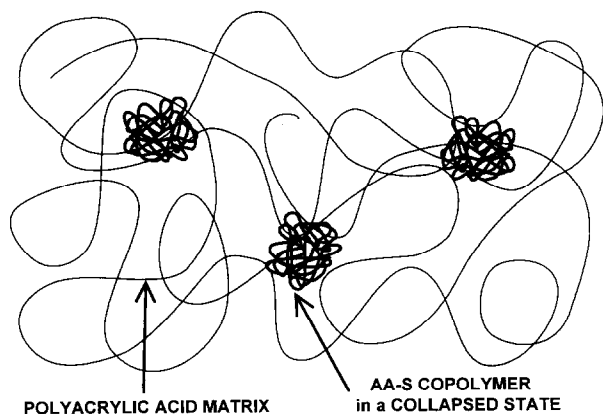
Figure 13 Schematic picture of an aqueous solution of a sample taken at high conversion, showing collapsed AA/S copolymer coils isolated within a matrix of the homopolymer semi-dilute solution
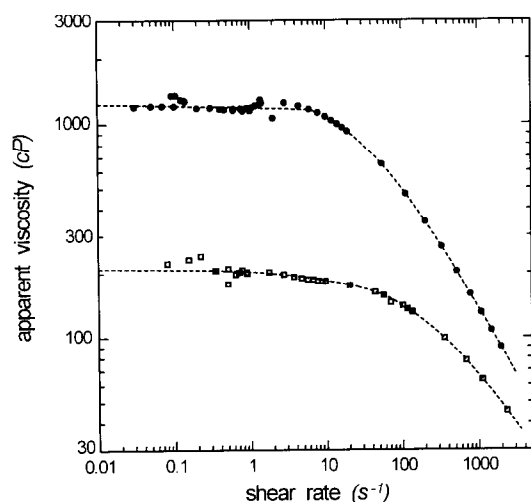

Figure 15 Viscosity–shear rate behaviour for an $AA_{90}/NaA_{10}/S_2$ copolymer (IL24, recovered at full conversion) in aqueous solution at various NaCl contents (polymer concentration $C_p = 2\,wt\%$; open symbols, Low Shear 30 data; filled symbols, Carri-Med data): (O, ●) without salt; (◆) 0.01 M NaCl; (☆) 0.05 M NaCl; (⊓, ■) 0.1 M NaCl; (▲) 0.25 M NaCl; (▼) 0.5 M NaCl

Figure 14 Viscosity–shear rate behaviour for $AA_{90}/NaA_{10}/S_2$ copolymers (run IL39) obtained at two different conversions (polymer concentration $C_p = 2\,wt\%$): (●) IL39-1, 17% conversion, $M_w = 0.9 \times 10^6$, [S] = 6.8 mol%, (□) IL39-5, 73% conversion, $M_w = 1.2 \times 10^6$, [S] = 1.8 mol%

Figure 16 Viscosity–shear rate behaviour for an $AA_{90}/NaA_{10}/S_2$ copolymer (IL39-1, recovered at 17% conversion) in aqueous solution at various NaCl contents (polymer concentration $C_p = 2\,wt\%$; open symbols, Low Shear 30 data; filled symbols, Carri-Med data): (O, ●) without salt; (△) 0.05 M NaCl; (□, ■) 0.1 M NaCl

modified poly(acrylic acid) chains with variable amounts of styrene and 75% of pure homopoly(acrylic acid). Therefore, one would not expect the copolymer chains to associate via hydrophobic interactions throughout the whole sample volume but rather to form isolated clusters in a matrix of homopolymer chains, as schematically depicted in *Figure 13*.

Copolymers obtained at low conversion. In order to confirm the effect of the sample heterogeneity on the rheological behaviour, we measured the viscosity–shear rate dependence for two AA/S copolymer samples taken at different degrees of conversion: 17 and 73% (*Figure 14*). A direct comparison between the two samples is somewhat difficult since both molecular weights and hydrophobe contents are different. The low conversion sample of molecular weight 0.9×10^6 contains 6.8 mol% of styrene, while the high conversion sample of molecular weight 1.2×10^6 contains 1.8 mol% of styrene. In spite of its lower molecular weight, the low conversion sample exhibits a much larger viscosity (by a factor of five) than the high conversion sample. The
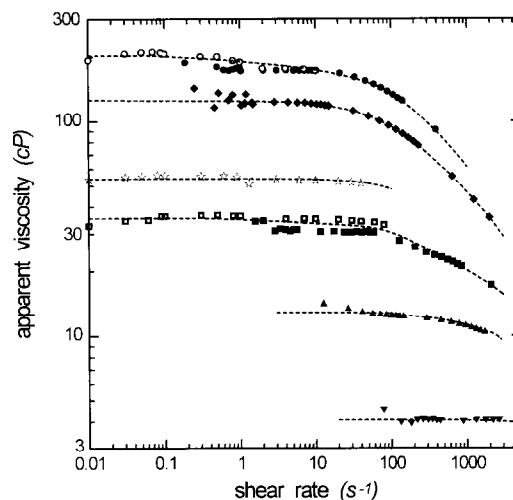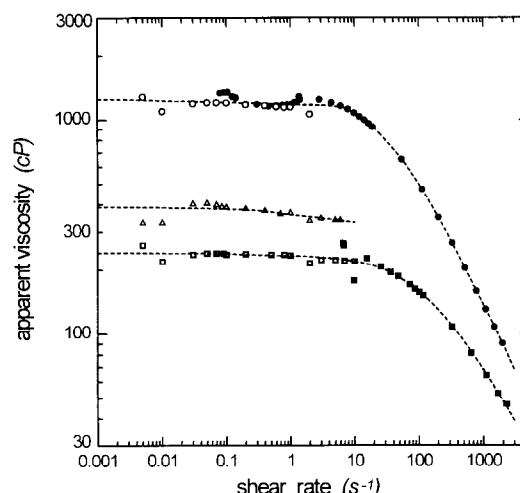
viscosity is also much higher than that of a homopolymer with double the molecular weight (run IL27, *Figure 12*). The improved thickening behaviour for the low conversion copolymer sample is probably due to the greater homogeneity in composition, which allows the formation of intermolecular hydrophobic associations.

Effect of salt. We carried out some rheological experiments in the presence of salt. For both high and low conversion samples, one observes a classical shear-thinning behaviour (*Figures 15* and *16*). The zero shear viscosity is a decreasing function of the salt content, as shown in *Figure 17*. In the same figure are also reported the data relative to an unmodified partially neutralized homopoly(acrylic acid) that shows the same trends. It should also be stressed that addition of salt induces in
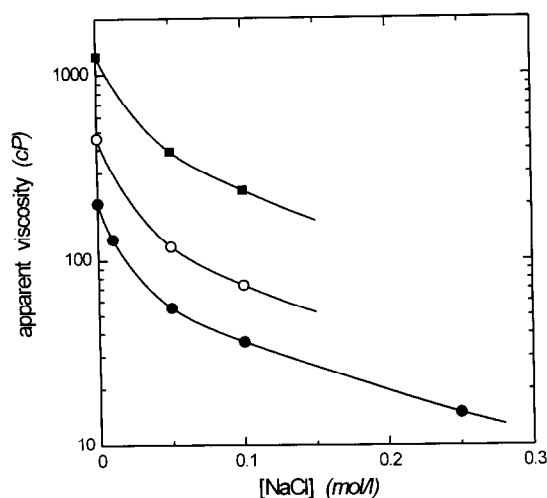
Figure 17 Influence of NaCl content on the zero shear viscosity of aqueous solutions of poly(acrylic acid) (O, run IL27) and AA$_{90}$/NaA$_{10}$/S$_2$ copolymers obtained at full conversion (●, run IL24) and 17% conversion (■, run IL39-1) (C_p = 2 wt%)
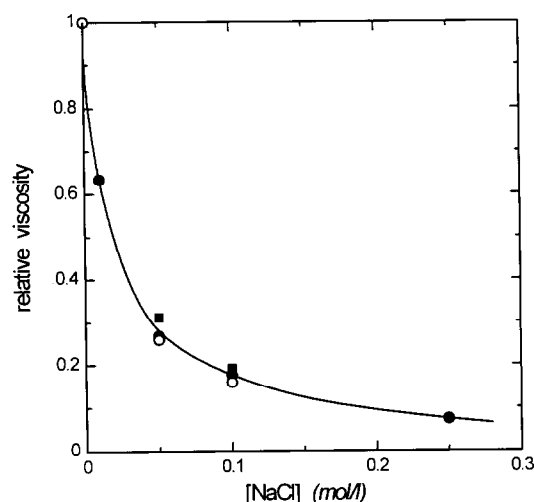

Figure 18 Viscosity ratio $\eta/\eta_{\text{no salt}}$ as a function of NaCl content for aqueous solutions of poly(acrylic acid) (O, run IL27) and AA$_{90}$/NaA$_{10}$/S$_2$ copolymers (●, run IL24; ■, run IL39-1) (C_p = 2 wt%)

all cases a progressive cloudiness of the solution which eventually phase separates for an NaCl concentration of ~0.7 M. Note, however, that the phase separation behaviour is different for the copolymer samples and the unmodified poly(acrylic acid). For the latter, there is a coacervation phenomenon (i.e. a liquid/liquid phase separation), while the copolymers flocculated in the form of a fine powder. This can be ascribed to the higher hydrophobicity of the copolymers. Similarly, Wang et al.[34] reported phase separation at very low NaCl concentrations (0.02 M) for semi-dilute solutions of random poly(sodium acrylate) hydrophobically modified with 10 mol% of octadecyl groups. This behaviour is quite different from that previously reported for AM/NaA/eΦAM terpolymers in salt solution[31]. An initial loss in viscosity was observed at low salt contents ([NaCl] ≤ 0.02 M), followed by a rapid increase in a way similar to that measured for the corresponding uncharged AM/eΦAM copolymer. The different nature of the backbone is probably at the origin of the above

results. It must be kept in mind that the thickening properties of neutral HMWSPs result from a subtle balance between the hydrophobicity of the associating sequences and the hydrophilic character of the backbone. In the case of charged systems, one must also add a further contribution arising from the electrostatic effect that amounts to increasing the aqueous solubility of the backbone. This contribution disappears under screening of the electrical charges by the salt. This screening effect accounts for the initial loss in viscosity observed for both types of copolymers at low salt contents. Once the interactions are screened out, the copolymers behave as if they are neutral and the backbone solubility plays a critical role. In the case of AM/eΦAM copolymers, water is a good solvent for the acrylamide backbone. The continuous increase in viscosity observed above a given threshold electrolyte concentration (> 0.02 M) reflects an increased number of hydrophobic liaisons which can be ascribed to the decreased solubility of the hydrophobic units (salting-out effect)[31,70]. The concentration fluctuations within the sample remain at the mesoscopic scale with no phase separation. On the other hand, water is a rather poor solvent for the poly(acrylic acid) backbone (θ temperature ~14°C). Its solubility is further decreased upon adding salt, leading eventually to phase separation[71]. For the partially neutralized homopoly(acrylic acid) under investigation (α = 0.1), we found that phase separation occurred at high ionic strength (~1 M NaCl), although no systematic study was performed to determine precisely the critical salt concentration. As the styrene solubility is also reduced in salted water, it is the whole copolymer (AA backbone plus S sequences) which becomes less soluble. Therefore, the competing hydrophobic/hydrophilic aspect of the copolymer is lost. As a consequence, the viscosity behaviour is solely dominated by that of the backbone. This is illustrated by *Figure 18* which shows the viscosity as a function of the electrolyte concentration, normalized to the viscosity of the corresponding sample in the absence of salt. The data relative to the copolymers and the unmodified homopolymer lie on a single curve.

CONCLUSION

Kinetic studies performed on the micellar copolymerization of various monomer pairs—acrylic acid/styrene, acrylic acid/ethylphenylacrylamide and acrylamide/styrene—have shown that the reaction mechanism of this particular process is essentially governed by two parameters: (1) the reactivity ratios of the monomers, as for any copolymerization reaction; and (2) the micellar effect which originates from the high monomer concentration within the micelles, the residence time of the active end of the growing radical in the micelle and the rate of hydrophobic monomer exchange between micelles. This effect will always lead to an enhanced apparent reactivity for the hydrophobic monomer solubilized within the micelles.

When the hydrophobic monomer is more reactive than the hydrophilic monomer (AA/S and AM/S cases), the two above effects reinforce each other to yield copolymers with a strong compositional heterogeneity. When both monomers have similar reactivities (AM/eΦAM case), the micellar effect is solely responsible for the

positive increase in the rate of hydrophobe incorporation into the copolymer. The copolymer heterogeneity is therefore reduced with respect to the former case. When the hydrophobic monomer is the less reactive (AA/eΦAM case), the two effects vary in the opposite direction. This case is most interesting since the lowered hydrophobe incorporation can be balanced by the micellar effect through optimization of the hydrophobe/surfactant ratio in the synthesis.

The rheological properties of HMWSPs prepared by micellar copolymerization are directly related to their structural compositional heterogeneity. AA/S copolymers obtained at full conversion do not exhibit associative properties: the hydrophobically modified copolymer chains are diluted within a continuous medium made of pure homopoly(acrylic acid). On the contrary, a good thickening ability is obtained with an AA/S sample obtained in the early stages of the reaction owing to a greater compositional homogeneity. AA/eΦAM copolymers characterized by a quasi-invariance of their average composition with conversion should also present some interesting rheological properties, and experiments are presently underway. We are also investigating the possibility of a semi-continuous process in order to correct for the drift in the average copolymer composition observed with the other monomer pairs.

Finally, it should be noted that the balance between the hydrophobicity of the associating sequences and the hydrophilic character of the backbone is critical. The appropriate conditions for the production of effective thickeners lie between the two limiting cases where the HMWSP exhibits no associative behaviour (hydrophobe content too low or hydrophobic groups too small, backbone too highly charged) or phase separates (hydrophobe content too high, backbone too hydrophobic, as is the case for acrylic acid). We hope that the conclusions reached in this study will help in defining the very narrow gap existing between these two limits.

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