Determination of microstructure of hydrophobically modified water-soluble polymers by ^{13}C n.m.r.

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Determination of the microstructure of *N*-octylacrylamide/sodium acrylate copolymers has been performed by ^{13}C n.m.r. The ^{13}C n.m.r. spectra were obtained in a CD_3OD/D_2O mixture in order to minimize the hydrophobic aggregation. These hydrophobically modified water-soluble polymers exhibit a random distribution of the hydrophobic groups along the polymer chain.

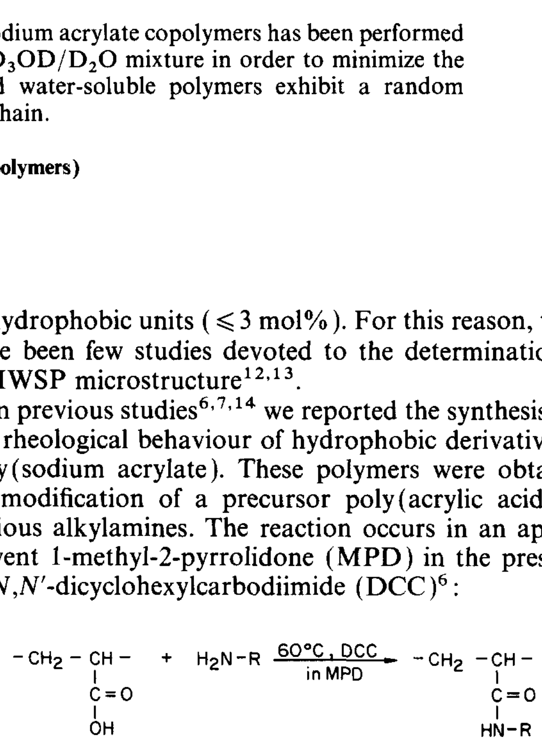
(Keywords: ^{13}C n.m.r.; microstructure; hydrophobic; water-soluble polymers)

INTRODUCTION

Hydrophobically modified (otherwise referred to as hydrophobically associating) water-soluble polymers have recently received increasing attention[1–7]. Typically these materials are water soluble ionic or neutral polymers containing a small amount of very hydrophobic groups (up to 5 mol%). They are mainly synthesized by micellar copolymerization[1,2,8] or by modification of a precursor polymer[3,6]. In semi-dilute aqueous solution the association of the hydrophobic groups may lead to an increase in the apparent molecular weight resulting in viscosity enhancement. Consequently, such materials can efficiently control the flow properties of aqueous fluids in many industrial applications.

The rheological behaviour of hydrophobically modified water-soluble polymers (HMWSP) depends on both the size and the content of hydrophobic groups[3,4,7]. In general, the association tendency increases with these parameters. Another factor governing the association behaviour of HMWSP is the distribution of the hydrophobic groups along the polymer chain, which is controlled by the method of synthesis used. For instance, Valint and Bock[9] have shown that HMWSP with block-type or random distribution of hydrophobic groups show large differences in their rheological behaviour. For HMWSP prepared by a micellar process, Hill *et al.* proposed a block-type distribution of the hydrophobic moieties[8]. The size of the hydrophobic blocks, and hence the aggregation efficiency, was controlled by the surfactant concentration in the polymerization mixture. Obviously, it is of great importance to determine the copolymer microstructure and relate it to the rheological properties of the system. Unfortunately, ^{13}C n.m.r. spectroscopy, which is usually used for microstructure determination[10,11], is not sensitive enough to be used for samples with a low content of hydrophobic units ($\leqslant 3$ mol%). For this reason, there have been few studies devoted to the determination of HMWSP microstructure[12,13].

In previous studies[6,7,14] we reported the synthesis and the rheological behaviour of hydrophobic derivatives of poly(sodium acrylate). These polymers were obtained by modification of a precursor poly(acrylic acid) by various alkylamines. The reaction occurs in an aprotic solvent 1-methyl-2-pyrrolidone (MPD) in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC)[6]:



$$-CH_2-\underset{\underset{\underset{OH}{|}}{C=O}}{\underset{|}{CH}}- \; + \; H_2N-R \xrightarrow[\text{in MPD}]{60^\circ C,\ DCC} -CH_2-\underset{\underset{\underset{HN-R}{|}}{C=O}}{\underset{|}{CH}}-$$

In this way it is easy to control both the alkyl group length and the extent of modification. In semi-dilute solution the hydrophobically modified samples exhibit pronounced thickening efficiency which is further strengthened upon addition of salts[6,7,14].

The main goal of the present work is to elucidate the microstructure of these hydrophobically modified poly(sodium acrylate)s. We used the ^{13}C n.m.r. technique applied to copolymers with a relatively high content of hydrophobic units (up to 30 mol%). Despite the high content of hydrophobic groups, the copolymers used are soluble in water mainly because of their ionic nature (pH ≈ 8) and the rather small size of the alkyl group (octyl).

EXPERIMENTAL

Preparation of samples

Poly(acrylic acid) was purchased from Polysciences Inc. and the average molecular weight, given by the supplier, was 150000. Its hydrophobically modified derivatives were prepared as described previously[6] and

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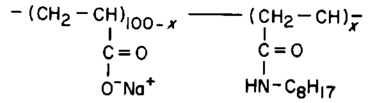
used in the sodium salt form:



$$\begin{array}{ccc} -(CH_2-\underset{|}{C}H)_{100-x} & \text{———} & (\underset{|}{C}H_2-CH)_x- \\ C=O & & C=O \\ | & & | \\ O^-Na^+ & & HN-C_8H_{17} \end{array}$$

where x is the modification ratio in mol%. An example of the sample designation is as follows: 10C8 contains 10 mol% *N*-octylacrylamide units. Details about their rheological behaviour in aqueous solution have been given elsewhere[7,14]. The modification ratio has been determined by elemental analysis (nitrogen to carbon ratio), ^1H n.m.r. and ^{13}C n.m.r. spectroscopy (see *Table 1*). There is a very good correlation between the values of the ratio as determined by each of the three techniques and the calculated values (i.e. according to a reaction yield of 100%).

N.m.r. experiments

Proton decoupled ^{13}C n.m.r. spectra were recorded on a Bruker WP 250 Spectrometer operating at 62.5 MHz. The sample temperatures were generally in the range 45–60°C because of variation in the heating effects of the decoupling irradiation. Polymer concentrations were about 8–12 wt% in D_2O or in D_2O/CD_3OD mixture. A spectral width of 12 500 Hz and a flip angle of 30° were used; the acquisition time was 0.65 s and the delay time between pulses was 0.5 s. Approximately 50 000 transients were necessary to obtain a signal-to-noise ratio sufficiently good for further analysis. Chemical shifts from tetramethylsilane were established by referencing to internal methanol d_4 at 49 ppm.

Deconvolution of overlapped peak components was achieved on a HP 9836 computer with the aid of a home-made program using generated peaks of Lorentzian shape.

RESULTS AND DISCUSSION

High resolution ^{13}C n.m.r. spectroscopy is a powerful tool to investigate the triad structure in homopolymers (tacticity)[15] or in copolymers (microstructure)[16,17]. In order to have a good signal-to-noise ratio, polymer concentration must be sufficiently high. But, for hydrophobically modified polymers, the viscosity drastically increases with polymer concentration and gel formation may even be observed due to the aggregation of hydrophobic groups[1–3,8,18]. In such aggregated systems the spectral resolution is very poor. The viscosity of the semi-dilute aqueous solutions of our associating copolymers depends largely on the alkyl chain length: the longer the alkyl chain, the higher the viscosity[14]. For this reason, it is important to optimize the alkyl group length in order to obtain copolymers exhibiting low aggregation tendency. The octyl group seems to be a valuable choice for this purpose. Furthermore, we will assume that the modification reaction leads to the same distribution, whatever the alkyl chain length. This is certainly verified because the reaction occurs in homogeneous solution. Whatever the modification ratio and the alkylamine used, no aggregation appears in the reaction mixture: its viscosity remains practically unchanged during the reaction time.

To determine the distribution of alkylacrylamide and acrylate groups, we have to focus on the spacing of carboxyl groups along the polymer chain, and thus sequences of three monomer units (triad structure) are considered. If the alkylacrylamide segment is termed M and the acrylate group A, the triads which are centred on an acrylate segment are: AAA, AAM = MAA and MAM.

Preliminary spectra were recorded in D_2O, as shown in *Figure 1a* for sample 20C8. Linewidth is very large and no triad peaks are observed. The polymer solution has a high viscosity and looks like a physical gel: the molecular motions inside the solution are supposed to be slowed down. In fact, it was shown that the aggregation tendency increases with the modification ratio[3,14]. This tendency is practically absent for sample 3C8 but it obviously becomes very effective for

Table 1 Determination of modification ratio for various copolymers

Sample	Calculated	Elemental analysis (%)	^1H n.m.r. (%)	^{13}C n.m.r. (%)
3C8	3	3	2.9	–
10C8	10	10.4	10.2	10
20C8	20	21.1	20	19.7
28C8	30	28.7	28.7	28.4

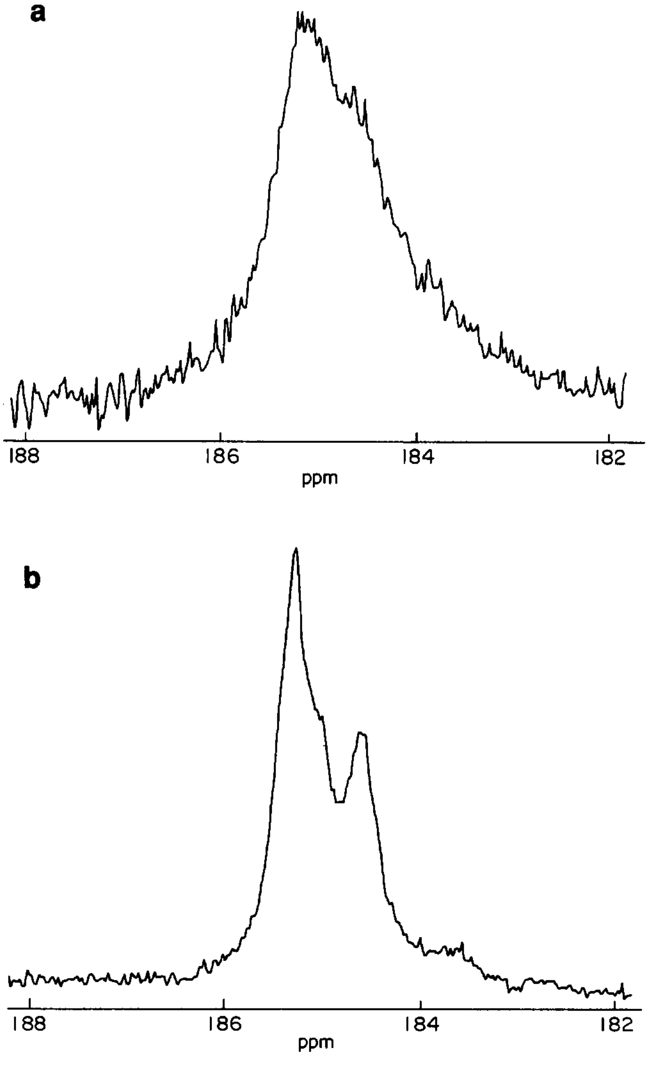


Figure 1 ^{13}C n.m.r. spectra of acrylate group for copolymer sample 20C8. Solvent: (a) D_2O; (b) 30% CD_3OD/70% D_2O

modification ratios higher than 10%, even for such a short alkyl chain. In order to improve spectral resolution, hydrophobic aggregation must be reduced. This can be achieved by addition of small amounts of a solvent which can disrupt hydrophobic associations. Gelman *et al.* have shown that methanol can suppress hydrophobic aggregation in aqueous solutions of hydrophobically modified hydroxyethylcellulose[19]. Effectively, by addition of methanol, the gelled aqueous solution of sample 20C8 becomes fluid, but its viscosity remains higher than that of the precursor (hydrophobic aggregation is not completely suppressed). It must be noted that methanol is a non-solvent for poly(sodium acrylate) and phase separation may occur if it is added in large amounts. As a consequence, n.m.r. spectra were run in a mixture of D_2O/CD_3OD. The solvent composition (typically 20–30% CD_3OD) depends on the copolymer studied and it is optimized to give the smallest viscosity without phase separation. *Figure 1b* shows the resolved carboxylate peaks of sample 20C8 in the mixture D_2O/CD_3OD. Three triad peaks (AAA, MAA = AAM and MAM) are observed at chemical shift 185.5 ppm, 184.8 ppm and 183.9 ppm, respectively. When the modification extent is raised, the peak position is unchanged while a general increase in linewidths is observed on each spectrum. Since the relative broadening is the same for all peaks, including the solvent, this phenomenon results from the rise in macroscopic viscosity due to residual hydrophobic aggregation (see above).

Figure 2 shows spectra of the precursor and four modified polymers under conditions of optimum resolution. The spectrum for the precursor polymer (*Figure 2a*) is sufficiently well resolved to be sensitive to the polymer chain tacticity, i.e. syndiotactic, isotactic and atactic triads. The tacticity effects are also perceptible for sample 3C8 (*Figure 2b*) but disappear for the samples with higher modification ratio ($x \geqslant 10\%$, *Figures 2c–2e*) mainly because of the residual hydrophobic aggregation occurring even after addition of methanol. So tacticity will not be considered for deconvolution calculations. However, resolution remains sufficiently good for determination of the copolymer microstructure. The spectrum of sample 28C8 (*Figure 2e*) exhibits a poorer signal-to-noise ratio and anyway it seems difficult to explore spectra of copolymers containing more than

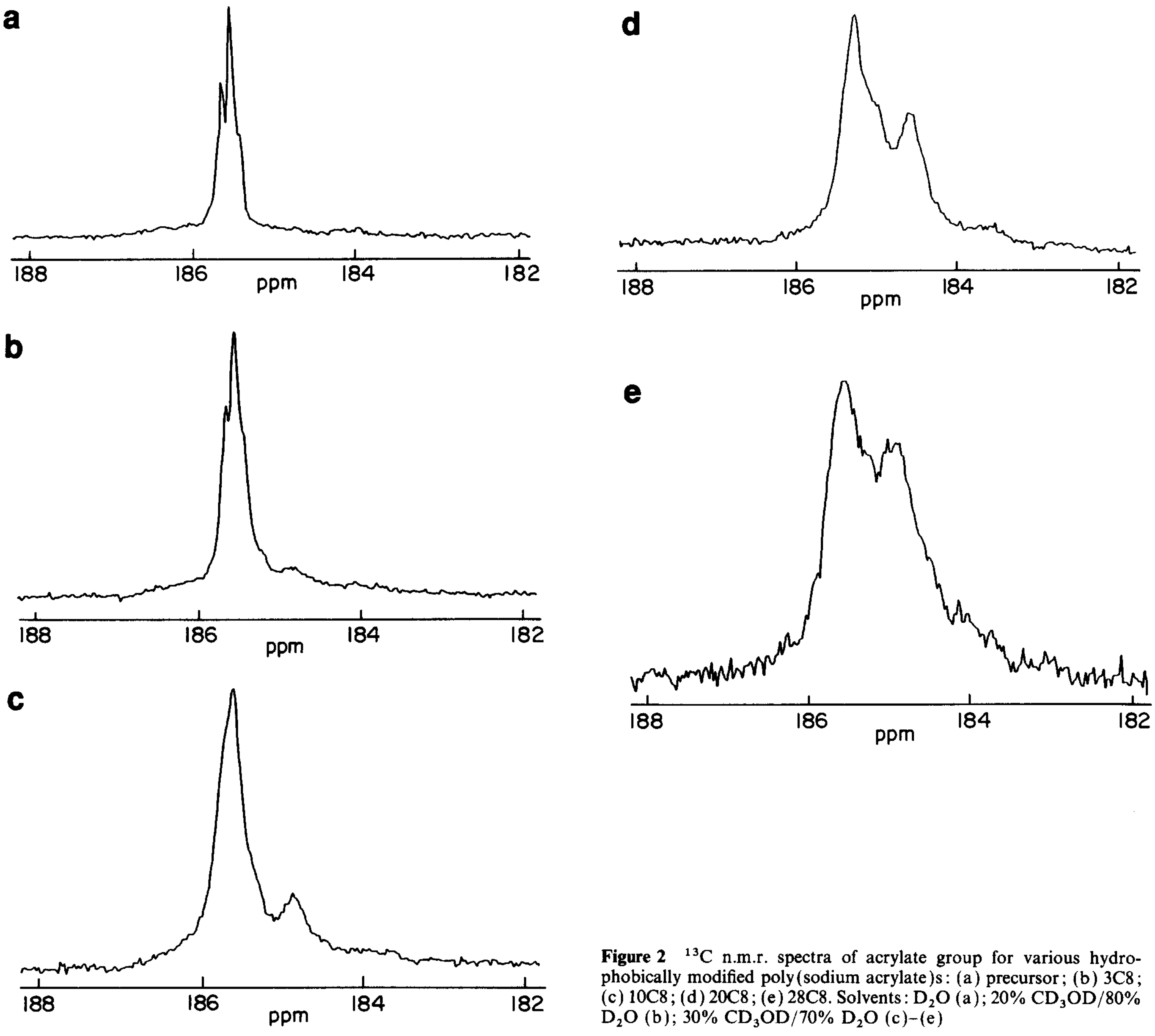


Figure 2 ^{13}C n.m.r. spectra of acrylate group for various hydrophobically modified poly(sodium acrylate)s: (a) precursor; (b) 3C8; (c) 10C8; (d) 20C8; (e) 28C8. Solvents: D_2O (a); 20% CD_3OD/80% D_2O (b); 30% CD_3OD/70% D_2O (c)–(e)

30 mol% octyl groups because of their poor solubility in water and in water/methanol mixtures.

Deconvolutions have been performed for the carbonyl peak of the acrylate group. The resolution of the carbonyl peak of the amide group is insufficient to allow further analysis. For deconvolution, peak positions are the same as those determined experimentally (i.e. 185.5 ppm for AAA triad, 184.8 ppm for MAA/AAM triad and 183.9 ppm for MAM triad). For each sample, the linewidth is determined on the AAA peak, which displays the best resolution, and we assume that all triads of a given sample have the same linewidth: a very classical assumption for such systems. Then we have to adjust coefficients of each triad to obtain the best fit with the experimental data. In this process, the initial value of the peak position appears critical (±0.05 ppm) and the linewidth has to be defined at ±2 Hz. This leads to an accuracy of about 5% of the value of each coefficient. Deconvolution of the acrylate group peak in three triads was performed and *Table 2* shows that deconvolution results are in good agreement with Bernoullian statistics.

A more complete analysis can be developed for sample 20C8 which presents the optimum resolution. The modification ratio is high enough and its aggregation tendency reduced by addition of methanol. In this case, the next nearest neighbours effect can be taken into account, i.e. sequences of five monomer units (pentads) are examined. However, only the triad AAA is divided into three pentads (AAAAA, MAAAA = AAAAM and MAAAM), because resolution of the other triads is not good enough to allow determination of the pentad positions. With this deconvolution, shown in *Figure 3*, the experimental spectrum is well simulated by the Bernoullian statistical model (*Table 3*). In this case, the deconvolution is much less accurate than for triad analysis.

CONCLUSION

The microstructure of hydrophobically modified water-soluble polymers can be determined by ^{13}C n.m.r. provided that the aggregation tendency of the hydrophobic groups is not very high (e.g. octyl groups). Usually, an organic solvent must be added to the solution in order to disrupt hydrophobic aggregation. The hydrophobically modified derivatives of poly(sodium acrylate), prepared by modification of a precursor polymer in homogeneous solution, present a random distribution of the hydrophobic groups along the polymer chain.

Table 2 Deconvolution data of acrylate peaks for modified copolymers: B, from Bernoullian statistical model; Exp, from experimental calculations

	Triad AAA		Triad MAA and AAM		Triad MAM	
Sample	B	Exp	B	Exp	B	Exp
3C8	94.1	94.5	5.8	5.4	0.09	0.1
10C8	81	81.5	18	17.5	1	1
20C8	64	63.5	32	32.5	4	4
28C8	51.8	53.5	40.3	39.5	7.8	7

Table 3 Pentad–triad deconvolution data of sample 20C8: Exp, from experimental calculations; B, from Bernoullian statistical model

Triad	Pentad	Exp	B
	AAAAA	42	41
AAA	AAAAM = MAAAA	19	20.5
	MAAAM	2.5	2.5
MAA = AAM		32.5	32
MAM		4	4

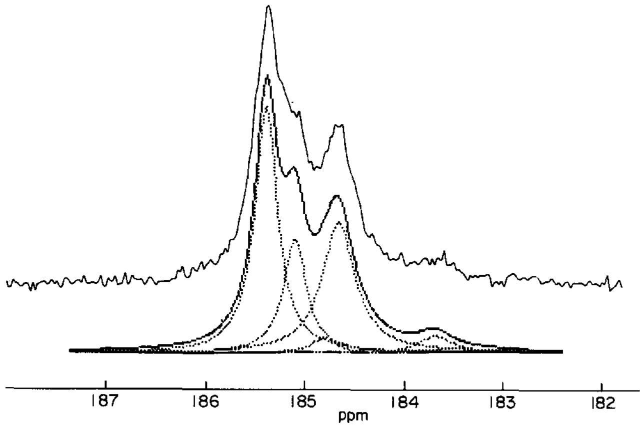


Figure 3 ^{13}C n.m.r. spectrum of acrylate group for copolymer sample 20C8 and its deconvolution. Numerical data are given in *Table 3*

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