

**$^{13}\text{C}$  NMR spectroscopy of cationic copolymers of acrylamide**

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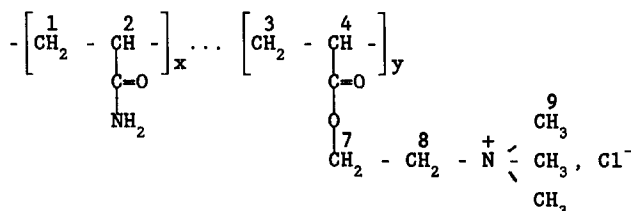
Random copolymers of acrylamide and a quaternary ammonium acrylate monomer have been investigated by  $^{13}\text{C}$  NMR spectroscopy in aqueous solution. Cleavage of the ester function has been shown to occur in mild alkaline media with a simultaneous intrachain reaction giving imide group formation. Sequential length distribution of the comonomers has been analyzed from triads composition and the experimental results lead to a nearly Bernouillian statistics although a more alternating distribution would be predicted from the reactivity ratios. This fact has been attributed to the compositional heterogeneity of our copolymers which have been prepared at high degree of conversion.

Introduction

In the the last years, cationic polyelectrolytes have found growing fields of application, especially in waster-water treatment. However, because of the high price of the available cationic monomers, their copolymers with acrylamide are generally used in practical applications. In previous publications (1-3), we investigated the adsorption and flocculation mechanisms of such copolymers towards negatively charged particles as a function of their molecular weight and ionic degree. Knowledge about their intramolecular structure is also of importance for a complete description of our systems since the sequential length distribution of comonomers is one of the important factors that affects bulk as well as solution properties of copolymers. Therefore, the present paper deals with the determination of the intra-chain structure of our copolymers by means of  $^{13}\text{C}$  NMR which is one of the most advanced methods for this purpose.

Experimental partMaterials

Random copolymers of acrylamide (A) and acryloyloxytrimethylammonium chloride (C) were prepared by conventional radical copolymerization. Their general formula is :



Details of this preparation and of the physico-chemical characterizations have been given elsewhere (3,4). The cationic unit content, expressed as  $\tau\% = (y/x+y) \cdot 100$ , was carefully determined from elemental nitrogen analysis, titration of the chloride counterion and  $^1\text{H}$  NMR at 250 MHz. At

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our high conversion levels (generally > 90%), the final composition of the copolymers was always found to be very close to that of the initial monomer feed. Series of copolymers of various molecular weights were obtained on the whole composition range ( $\tau = 0$  to 100%) (3).

### <sup>13</sup>C NMR spectra

Proton-decoupled <sup>13</sup>C NMR spectra were run at 60°C in 5 to 10% aqueous. D<sub>2</sub>O solutions with a Bruker WP 250 spectrometer operating at 62.5 MHz. The spectral width was 12500 Hz and a flip angle of 30° was used with intervals of 0.65 s, between the RF pulses. In such conditions, about 50.000 scans were necessary to get a good enough signal to noise ratio for further analysis of the spectra. Chemical shifts from T.M.S. were established by referencing to internal dioxane at 67.4 ppm. The 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. Using a twice higher magnetic field did not improve the resolution because of the intrinsic broadening of the polymer signals.

## Results and discussion

### Assignment of spectra

On figure 1 are reported the spectra of both homopolymers and of a medium-charged copolymer ( $\tau = 30\%$ ). Spectra were easily assigned from the variation of peak intensities with composition. The values of the different <sup>13</sup>C chemical shifts are given in Table 1. Carbon atoms of the acrylic chain backbone always display a rather broad overlapping pattern while the <sup>13</sup>C resonance peaks of the amide (C<sub>5</sub>) and ester (C<sub>6</sub>) functions remain well-separated on the whole composition range. Moreover, they appear as singlets in both homopolymers spectra and are thus insensitive to tacticity effects in agreement with literature data concerning polyacrylamide (5).

Table 1

	C <sub>1</sub> , C <sub>3</sub>	C <sub>2</sub> , C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>
$\delta$ ppm	$\approx 36$	$\approx 43$	180.1	175.9	65.5	59.4	54.9

Chemical ageing of the samples appeared to be very slow in pure water solutions (about a few months) and was not observed on spectra at the timescale of the NMR experiments. On the contrary, salt and above all alkaline solutions (pH  $\geq 8$ ) of copolymers occurred to display a faster degradation which never took place for homopolymers in the same experimental conditions.

The effect of ageing resulted in the presence of five more peaks on the spectra : three broad ones around 33.5, 40.5 and 178.1 ppm and two narrow ones at 56.6 and 68.5 ppm. After sufficient standing ageing could lead either to the complete vanishing of the cationic unit <sup>13</sup>C signal (except for C<sub>9</sub>) when  $\tau \leq 15\%$ , or to a whole precipitation of the polymeric species for higher  $\tau$  values. In this last case, the spectrum of the supernatant only consisted in the two narrow peaks quoted above and a third one at 54.9 ppm which was previously cancelled by the C<sub>9</sub> signal of the copolymer. From <sup>13</sup>C and <sup>1</sup>H NMR this spectrum could be assigned to N,N',N'' trimethylaminoethanol chloride. Such a compound resulted from a cleavage of the ester function induced by its reaction with a neighbouring amide group in alkaline medium. It gives rise to imide substituents on the chains, which strongly decrease their solubility. The position of the

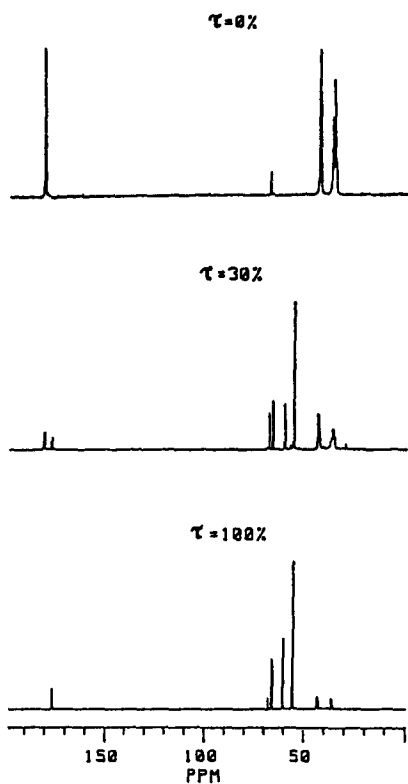


Figure 1: Comparison of  $^{13}\text{C}$  NMR spectra of homopolymers and copolymers (internal reference : dioxane,  $\delta = 67,4$  ppm)

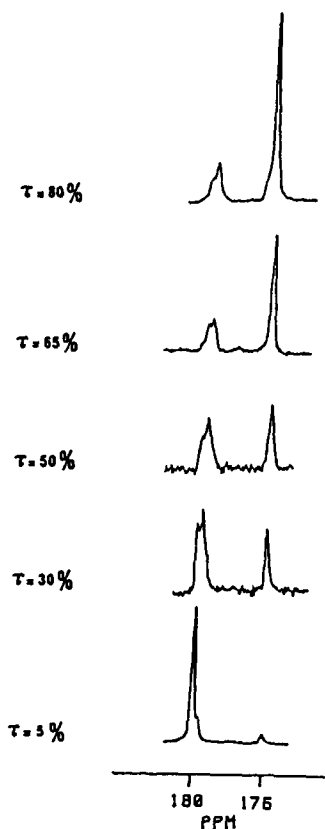


Figure 3: Effect of cationicity on the  $>^{13}\text{C}=\text{O}$  NMR pattern of copolymers

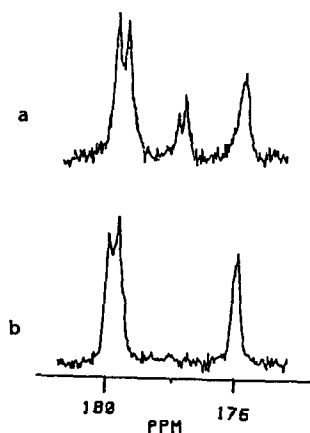


Figure 2:  $>^{13}\text{C}=\text{O}$  pattern for  $\tau = 30\%$  before (a) and after (b) partial degradation

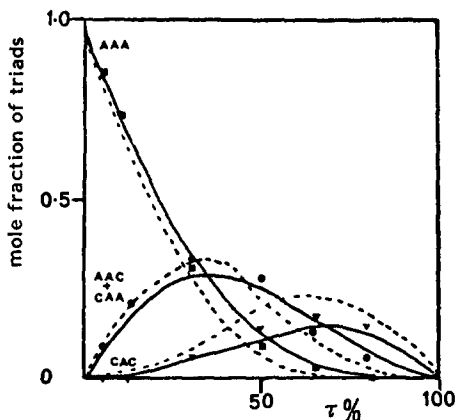


Figure 4: Comparison of experimental triads mole fractions ( $\blacksquare$ : AAA,  $\bullet$ : AAC and CAA,  $\blacktriangledown$ : CAC) with those calculated from Bernoullian (—) and first-order Markov (----) statistics

new  $^{13}\text{C}=\text{O}$  signal (178.1 ppm, see figure 2), observed at low degradation level, i.e. when the polymer is still soluble, is perfectly consistent with such an assumption (6).

Sequential length of copolymers.

The  $^{13}\text{C}$  NMR pattern of carbonyl resonances is given in figure 3 for a series of copolymers. A progressive broadening of  $\text{C}_5$ , with simultaneous splitting is observed when  $\tau$  increases. Such features can only arise from sequence distribution of comonomers since, as discussed above,  $^{13}\text{C}=\text{O}$  peaks of homopolymers are unaffected by tacticity. Unfortunately, the ester peak is not sensitive to these distribution effects: only some broadening and a small shift of 0.2 ppm can be observed when  $\tau$  decreases.

The three, bad-resolved components of the  $^{13}\text{C}=\text{O}$  amide signal ( $\text{C}_5$ ) correspond to the triads with a central acrylamide unit. The evolution of their relative intensities with  $\tau$  allows the following assignments:

AAA : 180.1 ppm  
 AAC and CAA : 179.75 ppm  
 CAC : 179.4 ppm

As expected, a cationic nearest neighbour causes an upfield shift of the acrylamide peak whereas the inverse effect is observed when the comonomer is an anionic one (7). Re-examining figure 2, we notice a relative diminution in intensity of AAC and CAC triads (i.e. those containing alternated diads) after ageing, which confirms the fact that the degradation reaction takes place between two neighbouring units.

Neglecting all aspects of next nearest neighbours, the mole fractions of the three above kinds of triads were estimated from their relative intensities after signal deconvolution. These results were compared in figure 4 to the distributions calculated from a Bernouilli model process and a first-order Markov one (8) taking into account the reactivity ratios ( $r_A = 0.64$  and  $r_C = 0.48$ ) determined by Tanaka (9). The experimental distribution appears intermediate between the two models and nearly Bernouillian, at least much less alternated than could be predicted from  $r_A$  and  $r_C$  values. In fact, this discrepancy is only an apparent one. At our high conversion level, the quasi-absence of drift observed for the final copolymer composition with respect to that of the initial monomer feed is also consistent with this deviation from the theoretical behaviour. It actually leads to an heterogeneity in the copolymer composition, responsible for an apparent distribution close to that of Bernouilli (7).

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