^{13}C NMR STUDY OF HYDROLYZED POLY(ACRYLONITRILE)

Jan LÖVY, Václav JANOUT and Hana HRUDKOVÁ

Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6

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Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

A method for the determination of chain microstructure of hydrolyzed poly(acrylonitrile) (PAN) and of copolymers of acrylonitrile with acrylamide by means of ^{13}C NMR spectroscopy is described. Besides the overall composition of poly(acrylonitrile-co-acrylamide), this method permits the population of all acrylamide-centered compositional triads to be determined; it is then possible to follow the values of the rate constants of nitrile group hydrolysis in dependence on its neighbours. Under certain circumstances the knowledge of the mentioned triads permits also the copolymerization parameters for copolymerization of acrylonitrile with acrylamide to be determined. It was confirmed that acid-catalyzed hydrolysis of PAN in concentrated nitric acid yields acrylonitrile–acrylamide block copolymers.

Acid-catalyzed hydrolysis of poly(acrylonitrile) (PAN) performed below 293 K follows an autoaccelerated zip mechanism. It yields acrylonitrile–acrylamide multiblock copolymers[1]. These have the form of strongly hydrated gels with important mechanical properties suggesting their potential practical application[2]. So far, the structure of hydrolyzed PAN and the course of the acid catalyzed hydrolysis were followed only by indirect methods (elemental analysis[1], infrared spectroscopy[1], and both wide-angle and small-angle X-ray scattering[3]). By means of ^{13}C NMR spectroscopy it is possible to obtain more precise and unequivocal information both about the course of acid hydrolysis, about the composition of the product and about the microstructure of the obtained copolymer.

Hydrolysis was studied both with atactic and with isotactic PAN. Copolymers of acrylonitrile with acrylamide prepared from reaction mixtures with varying composition were also studied for comparison. PAN was hydrolyzed in concentrated nitric acid which has, with respect to PAN, the properties of a solvent–precipitant mixture. For this system, a model was proposed consisting of highly ordered structures of PAN chains[1,4–7]. This model is used to explain the autoaccelerated zip mechanism of hydrolysis leading to the formation of multiblock copolymers.

EXPERIMENTAL

Atactic PAN (containing 23% mm, 47% mr and 30% rr triads by ^{13}C NMR analysis[9]) and all the studied copolymers were prepared by precipitation polymerization of acrylonitrile or by copolymerization of acrylonitrile with acrylamide in aqueous medium with potassium persulphate as iniciator[1]. Isotactic PAN was prepared by radiation-iniciated polymerization of acrylonitrile (in the form of urea complex)[8] at 195 K (53% mm, 32% mr and 15% rr triads by ^{13}C NMR analysis). Molecular weights determined by light scattering were as follows: atactic PAN, $\overline{M}_w$ 100 000, isotactic PAN, $\overline{M}_w$ 140 000.

Polymer Hydrolysis

Acid catalyzed hydrolysis of nitrile groups in the polymers was performed at 288 K and 293 K in 65% nitric acid. Dissolution of the polymers in the acid proceeded for 25 h. at 277 K (where hydrolysis is not perceptible). Concentration of the polymer in the acid was 4%. At suitable intervals, the hydrolyzed polymer was precipitated in water in the form of thin fibres, and was subsequently washed and dried to constant mass.

Measurement of ^{13}C NMR Spectra

The spectra of the studied polymers were measured in the form of 10% solutions (*w*/*v*) in hexadeuterio dimethyl sulphoxide, in a mixture of water with hexadeuteriodimethyl sulphoxide, or in a 60% (w/v) solution of NaSCN in ^2H_2O. The solutions were sealed in the measuring cells under nitrogen. ^{13}C NMR spectra were measured using the spectrometer Varian XL-200 (50 MHz) at 357 K (pulse width 7 μs corresponding to a flip angle of 70°, pulse interval 2 s, spectral width 10 kHz, 32 K data points). The optimum measuring conditions for quantitative analysis were based on T_1 measurements, yielding 0·2 s for CH_2, 0·4 s for CH—CN and less than 0·5 s for $CH-CONH_2$.

RESULTS AND DISCUSSION

^{13}C NMR spectra of the studied polymers are shown in Fig. 1. The spectrum 1*a* corresponds to atactic PAN. The triplet structure of the signals CH—CN and CH—CN (about 27 and 120 ppm) reflects the stereoregularity of the polymer; various signals in both triplets are proportional to the concentration of the triads mm, mr and rr (ref.[9]). The signal at 32·8 ppm corresponds to the carbon of the CH_2 group. In Fig. 1*h* the spectrum of poly(acrylamide) is shown exhibiting a singlet signal of the amide group carbon (177·7 ppm) and a broad signal of the CH_2 group (34–36 ppm); the triplet character of this signal reflects the stereoregularity of poly(acrylamide)[10]. The signal of the $CH-CONH_2$ carbon (41·5 ppm) is partly overlapped by the solvent signal of hexadeuteriodimethyl sulphoxide.

The spectra of acrylonitrile–acrylamide copolymers (Fig. 1*b*–1*g*) obtained partly by hydrolysis of atactic PAN (Fig. 1*b*–1*d*), partly by copolymerization of acrylonitrile with acrylamide at various composition of the original monomer mixture (Fig. 1*e*–1*g*) are further shown. The assignment of chemical shifts to various carbons in the polymers is summarized in Table I. A qualitative difference in the two series of copolymers is evident from a comparison of the spectra. In the first approximation

it can be stated that the spectra of hydrolyzed PAN (Fig. 1*b*–1*d*) approximately correspond to a superposition of the spectra of acrylonitrile and acrylamide homopolymers, indicating block structure of the copolymers. Also the triplet structure of the CH—CN signals is preserved, reflecting the tacticity of PAN blocks. Both with atactic and with isotactic PAN it was observed that the relative intensities of the triplet components of the CH—CN signal do not change in the course of hydrolysis. To the contrary, the spectra of polymers prepared by copolymerization (Fig. 1*e*–1*g*)

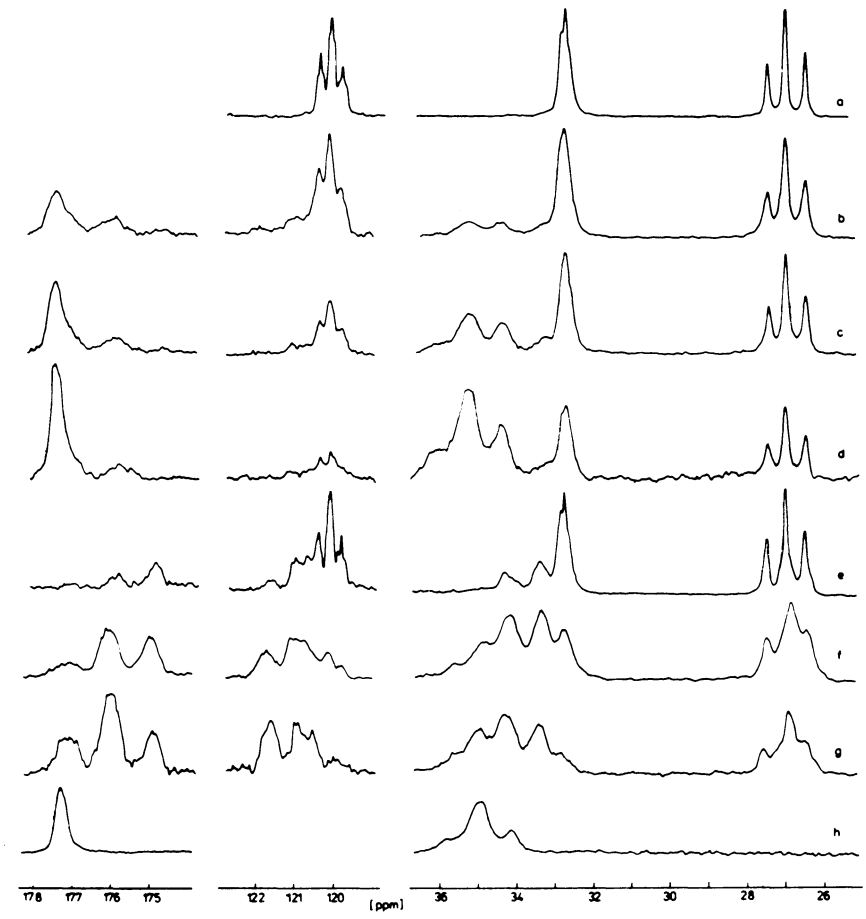
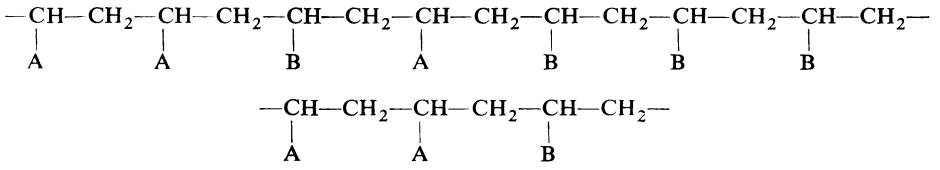


FIG. 1

^{13}C NMR spectra of poly(acrylonitrile) (*a*) and of hydrolyzed PAN: degree of hydrolysis 24% (*b*), 51% (*c*), 72% (*d*); copolymer of acrylonitrile with acrylamide with 17 mol% of amide groups in the chain (*e*), 45 mol% of amide groups in the chain (*f*), 55 mol% of amide groups in the chain (*g*), polyacrylamide (*h*)

exhibit a broadening of the CH—CN signals with increasing content of amide groups in the chain (the pronounced triplet character disappears). Remarkable changes are also observed in the range of CH_2 carbons.

The differences between the copolymers prepared by PAN hydrolysis and by copolymerization of acrylonitrile with acrylamide can be characterized in detail by means of the amide carbonyl band. With hydrolyzed PAN, the dominating signal lies at 177·4 ppm, at a chemical shift value near to that of amide carbonyl in pure acrylamide homopolymer (177·7 ppm). In the range of amide carbonyl the copolymers prepared by copolymerization exhibit three signals of comparable intensity (Figs 1*e*–1*g*). In the acrylamide homopolymer, the carbonyl signal shows very small sensitivity to polymer stereoregularity[10]. The triplet structure of this signal in copolymers indicates that the chemical shift of the carbonyl carbon signal is sensitive to the neighbouring functional groups. Based on the above analysis, the triplet components are assigned to the triads ABA, ABB and BBB in the polymer chain



A = CN, B = $CONH_2$

TABLE I

^{13}C NMR chemical shifts of poly(acrylonitrile) (PAN), poly(acrylamide) (PAA), hydrolyzed PAN (H) and acrylonitrile–acrylamide copolymers (C) (in ppm from tetramethylsilane, solutions in hexadeuteriodimethyl sulphoxide)

Polymer	CH—CN	CH—$CONH_2$	—CH_2—[a]			—CN[a]			—$CONH_2$		
	A	B	AA	AB	BB	AAA	AAB	BAB	BBB	ABB	ABA
PAN	26·7–27·6	—	32·8	—	—	120·0	—	—	—	—	—
PAA	—	41·4–41·8	—	—	34·5–36·2	—	—	—	177·7	—	—
H	26·6–27·6	41·4–41·8	32·8	33·4	34·4–35·2	120·0	121·1	121·8	177·4	176·0	174·7
C	26·6–27·6	41·3–41·8	32·8	33·5	34·3–35·8	120·0	120·8	121·7	177·0	175·9	174·4

[a] Chemical shifts of the diads AA, AB and BB, and of the triads AAA, AAB and BAB are only approximate; strong overlap of band components; unsuitable for quantitative determination of sequence populations.

The sensitivity of the chemical shift to neighbouring groups can be also observed in the range of nitrile group carbons (about 120 ppm); however, stronger band overlap makes this range less suitable for quantitative determination of the content of the triads AAA, AAB and BAB.

The degree of hydrolysis, or overall composition of the copolymers, was determined from the integrated intensities of the CH_2 and CH—CN carbon signals. The intensity of the CH_2 band corresponds to the number of all monomer units in the copolymer, the intensity of the CH—CN carbon signal to the number of nitrile groups in the copolymer. The CH—$CONH_2$ band is partly overlapped by the solvent band of hexadeuteriodimethyl sulphoxide and is therefore not suitable for the determination of polymer composition. When ^2H_2O with NaSCN was used as solvent, overall composition could also be determined from the relative integrated intensities of the CH—CN and CN—$CONH_2$ bands. For a given copolymer the values of degree of conversion as determined in the two solvents were equal, and it is therefore not probable that they could be affected by possible aggregation leading to a partial disappearance of the spectrum[11,12]. Most measurements were made in hexadeuteriodimethyl sulphoxide; in ^2H_2O with NaSCN, strong dielectric heating takes place during measurement due to ^1H decoupling, and the temperature of the sample is hard to define.

The determination of polymer composition by the described procedure, together with the determination of the population of the triads ABA,ABB and BBB from the integrated intensities of the amide carbonyl band yield quantitative parameters characterizing the microstructure of the copolymers (Table II). Mean sequence lengths $\bar{N}_B$ and $\bar{N}_A$ were calculated from the relations[13]

$$\bar{N}_A = \frac{1 - n_B}{(n_{ABA} + n_{ABB}/2)\, n_B}, \quad \bar{N}_B = \frac{1}{(n_{ABA} + n_{ABB}/2)}. \tag{1}$$

Analysis of the data in Table II shows that the polymers prepared by copolymerization of acrylonitrile with acrylamide obey 1st order Markov statistics, characterized by two independent parameters P_{AB}, P_{BA}. These parameters are related to the mean sequence lengths: $\bar{N}_A = 1/P_{AB}$ and $\bar{N}_B = 1/_{PA}$. For these copolymers the copolymerization parameters could be calculated by means of the relations[13]

$$r_A = n_B^0/n_A^0(\bar{N}_A - 1), \quad r_B = n_A^0/n_B^0(\bar{N}_B - 1). \tag{2}$$

Greatly varying values of these parameters are found in the literature ($r_A = 0{\cdot}873$ and $r_B = 1{\cdot}357$, $r_A = 3{\cdot}5$ and $r_B = 0{\cdot}5$)[14,15]. Our values obtained for copolymers polymerized to 4% conversion ($r_A = 2{\cdot}1 \pm 0{\cdot}7$ and $r_B = 0{\cdot}4 \pm 0{\cdot}1$) are in relatively good agreement with ref.[15].

Hydrolyzed PAN, especially at lower degrees of hydrolysis, cannot be fully characterized by the two parameters P_{AB}, P_{BA} of 1st order Markov statistics. The structure of copolymers obeying 1st order Markov statistics can be quantitatively characterized by the so-called persistence ratio, ϱ, defined by the relation

$$\varrho = 1/(P_{AB} + P_{BA}) \tag{3}$$

($\varrho = 0{\cdot}5$ for alternating copolymers, 1·0 for statistical copolymers, and ∞ for purely block copolymers). The values of the parameter ϱ given in Table II for both kinds of copolymers are defined by the relation

$$\varrho = \bar{N}_A \,.\, \bar{N}_B/(\bar{N}_A + \bar{N}_B) \tag{4}$$

which is not limited to systems obeying 1st order Markov statistics.

From Table II it can be seen that for acrylonitrile–acrylamide copolymers the values ϱ correspond to a statistical distribution of A and B units, whereas hydrolyzed PAN exhibits block character which is most propounced at degrees of hydrolysis about 50%.

Besides the determination of copolymerization parameters and characterization of the microstructure of the copolymer chain, ^{13}C NMR spectroscopy can be also applied to the determination of the time dependence of the population of the triads ABA, ABB and BBB during hydrolysis. Such data make it possible to study the kinetics of the polymeranalogous reaction[16] by determining the rate constants of the reaction of the given group (in our case hydrolysis of the nitrile group) in dependence on the

TABLE II

Parameters characterizing the microstructure of acrylonitrile–acrylamide copolymers prepared by reaction of monomers (to 4% conversion) (C) and by hydrolysis of PAN (H)

Polymer[a]	n_B	n_B^0	n_{BBB}	n_{ABB}	n_{ABA}	$\bar{N}_B$	$\bar{N}_A$	ϱ
C	0·13	0·30	0·01	0·23	0·77	1·13	7·54	0·99
C	0·39	0·50	0·10	0·46	0·43	1·49	2·32	0·91
H	0·26	—	0·60	0·30	0·10	4·00	11·4	2·94
H	0·52	—	0·78	0·21	0·01	8·70	8·03	4·35
H	0·75	—	0·81	0·18	0·01	10·0	3·3	2·50

[a] n_B mole fraction of amide units in chain, n_B^0 mole fraction of acrylamide in original reaction mixture, n_{BBB}, n_{ABB} and n_{ABA} mole fractions of corresponding triads, $\bar{N}_B$ mean sequence length of acrylamide units, $\bar{N}_A$ mean sequence length of acrylonitrile units, ϱ persistence ratio.

neighbouring functional groups. Such study will be the subject of our subsequent work.

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