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Acidic Hydrolysis of Polyacrylonitrile: Effect of Neighboring Groups

Liya B. Krentsel, Yaroslav V. Kudryavtsev, Alexandr I. Rebrov, Arkady D. Litmanovich,* and Nicolai A. Platé

A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky prosp. 29, 117912 Moscow B-71, Russia

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ABSTRACT: Hydrolysis of polyacrylonitrile (PAN) was carried out in 65% HNO_3 at 21 °C. The composition and structure of hydrolyzed samples (HPAN) were determined using ^{13}C NMR spectrometry. The HPAN are multiblock copolymers containing acrylonitrile (A) and acrylamide (B) units. A set of individual rate constants for the reaction of central A units in AAA, AAB + BAA, and BAB triads, k_0, k_1, and k_2, respectively, describes fairly well both the reaction kinetics and the HPAN distribution of units. Thus, the accelerating effect of neighboring groups (k_0:k_1:k_2 = 1:18:36) is the principal, if not exclusive, factor determining the peculiarities of the acidic PAN hydrolysis. Less than 3% of acrylamide groups are involved in cyclization (formation of glutarimide cycles) under the hydrolysis conditions used, so that cyclization may be neglected in the analysis of the hydrolysis kinetics and the HPAN structure within the framework of the neighbor effect.

Introduction

The acidic hydrolysis of polyacrylonitrile (PAN) differs from the alkaline process both in the product structure and in the reaction mechanism.

The alkaline PAN hydrolysis proceeds with retardation caused by the electrostatic repulsion between carboxylate and hydroxyl ions. According to recent studies,[1−5] the main route of the hydrolysis involves formation of $(-C{=}N-)_n$ conjugated sequences as intermediates. Conjugated sequences hydrolyze into sodium acrylates (ANa) and amidines, and the latter hydrolyze into amides (AAm). Simultaneously, simple consecutive transformations of nitrile (AN) groups into AAm and then into ANa groups proceed. This complicated mechanism manifests itself over a broad temperature range (25−85 °C). After complete hydrolysis of the amidines, the reaction product is a ANa−AAm copolymer with a Bernoullian distribution of units.[2]

On the contrary, PAN hydrolysis by concentrated acids at 15−50 °C leads to the formation of a AN−AAm copolymer, sometimes containing also small amounts of acrylic acid groups.[6−11] At elevated temperature (110 °C), AAm groups cyclization occurs with formation of glutarimide (GI) cycles.[10,11] (GI cycles were never observed in the products of alkaline PAN hydrolysis because of their extreme instability in an alkaline medium as shown by Sawant and Morawetz.[12])

It should be especially emphasized that not random but multiblock copolymers are formed in the course of the acidic PAN hydrolysis. To explain this result, Lovy et al.[6] and Stoy et al.[7] proposed a certain zip mechanism, bearing in mind evidently the accelerating effect of neighboring AAm groups. Stoy et al.[7] pointed out that hydrolysis proceeds with acceleration. However, the authors[6,7] did not present any quantitative interpretation of their results relating to the multiblock structure of the reaction products.

The goal of the present study is to ascertain whether it is possible to describe quantitatively changes in the product structure during the acidic PAN hydrolysis in terms of the accelerating neighboring group effect. For that, it is necessary to test whether the same set of individual rate constants describes both the reaction kinetics and the distribution of units in the product chain.[13]

PAN hydrolysis has been carried out in 65% HNO_3 because according to Lovy et al.[6] and Stoy et al.[7] in such system at 15−50 °C, binary copolymers are formed containing only AN and AAm groups.

The composition and structure of hydrolyzed samples were determined using ^{13}C NMR spectrometry.

Experimental Section

PAN ($M_\eta = 1.2 \times 10^5$) prepared by the redox technique was kindly provided by Dr. L. M. Zemtsov (Topchiev Institute of Petrochemical Synthesis, Moscow). PAN was dissolved in 65% HNO_3 (4 wt %) for 48 h at ≤4 °C; the hydrolysis does not proceed during the dissolution. The hydrolysis was carried out at 21 °C. The reaction products were precipitated into cold water, water−ethanol mixture, or methanol (depending on the degree of conversion), washed with the precipitant, reprecipitated from DMSO into methanol, and dried in a vacuum at 40 °C.

^{13}C NMR spectra were recorded on a Bruker MSL-300 spectrometer, equipped with a 10 mm probe, operating at 75.45 MHz in the inverse gated decoupled mode using DMSO-d_6 8% (w/v) solutions of polymers at 25 °C. About 15 000 scans were accumulated for each spectrum with a preacquisition delay of 5 s, carbon $\pi/2$ pulse lengths of 7.6 μs, an acquisition time of 0.442 s, and a spectral width of 18518 Hz. Chemical shifts were indirectly referenced to TMS via the solvent signal at 39.43 ppm. Besides, to estimate possible glutarimide content in the hydrolyzed samples, NMR spectra were also recorded in NaSCN/D_2O (55%) solution. In this case, chemical shifts were referenced via the NaSCN signal at 132 ppm; the other conditions of the measurements were the same as those mentioned above. The NMR spectra were deconvoluted by a standard computer procedure using a Gaussian/Lorentzian model to fit shapes of NMR peaks.

Results and Discussion

^{13}C NMR spectra of hydrolyzed PAN (HPAN) of different composition are shown in Figure 1. The signals were assigned according to Lovy et al.[6] recommendations. Let A stand for AN and B for AAm units. The nitrile C atom signal (near ∼120 ppm) is not used for the estimation of A-centered triads fractions, because

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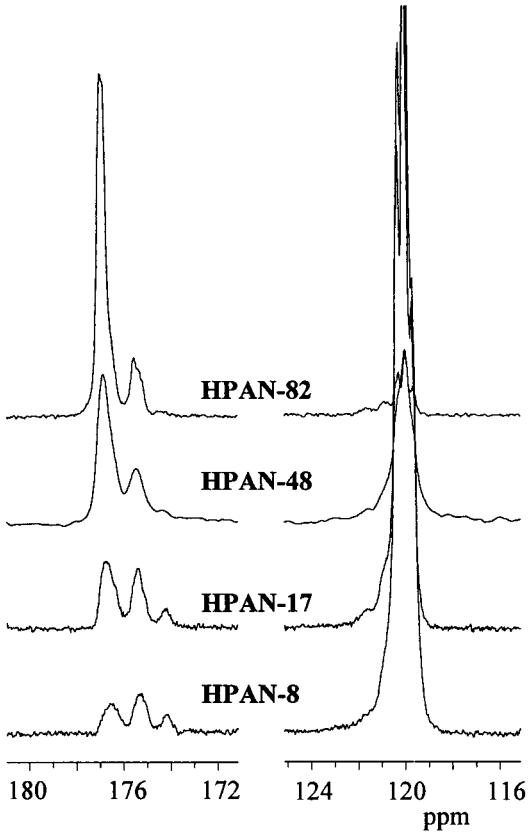


Figure 1. ^{13}C NMR spectra of HPAN samples, carbonyl, and nitrile regions.

both the nature of neighboring groups and the microtacticity of the chain lead to signal splitting; even in pure PAN this signal constitutes a triplet.[6] On the contrary, the carbonyl signals are insensitive to the chain microtacticity and may be used for the estimation of B-centered triads. Signals near 174.3, 175.4, and 176.8 ppm are assigned to ABA, ABB* (ABB* = ABB + BBA), and BBB triads, respectively. The sample composition (the mole fraction of B) was determined from the ratio of integrals of the total carbonyl signal to the sum of carbonyl and nitrile signals; probabilities of B-centered triads *P*(ABA), *P*(ABB*), and *P*(BBB) were estimated from the ratio of the integrals of the corresponding signals to the sum mentioned. The other parameters of the HPAN structure: the mean length of A and B blocks l_A and l_B, the probability of a boundary between A and B blocks, *R*, and the same parameter for a Bernoulli copolymer, R_{Ber}, were calculated using the following relations:

$$l_A = P(A)/P(AB), \quad l_B = P(B)/P(BA), \quad R = 2P(AB), \quad R_{Ber} = 2P(A)\,P(B)$$

where $P(B) = 1 - P(A)$ and $P(AB) = P(BA) = P(ABA) + P(ABB^*)/2$.

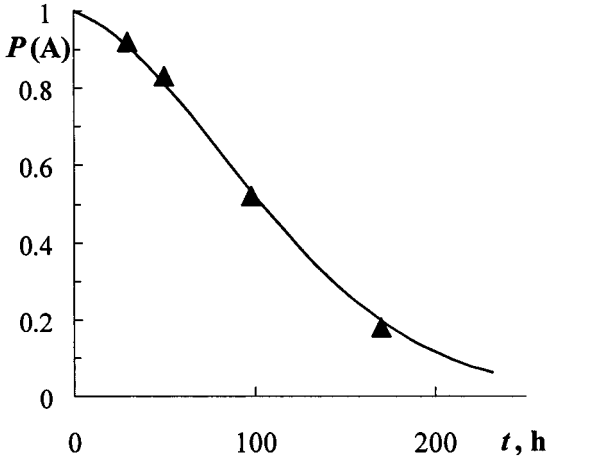


Figure 2. Kinetics of PAN hydrolysis: points, experimental data; curve, calculation for $k_0 \approx 1.7 \times 10^{-3}$ h^{-1} and $k_0{:}k_1{:}k_2$ = 1:18:36.

The data collected in Table 1 indicate the multiblock structure of HPAN samples. Indeed, *R* values found are significantly less than the corresponding R_{Ber} values. In turn, the mean block lengths are significantly greater than those for Bernoullian copolymers. For example, for HPAN-48 $l_A = 6.5$ and $l_B = 6.0$ were found, whereas for a Bernoullian copolymer of the same composition l_A = 2.1 and $l_B = 1.9$.

The hydrolysis kinetics was described within the framework of the neighboring group effect using the Keller equations[14] (the first-order kinetics is adopted because the hydrolysis was carried out in a large excess of HNO_3):

$$\begin{aligned} dP(AAA)/dt &= -(k_0 + 2\bar{k})P(AAA) \\ dP(AAB^*)/dt &= -(k_1 + \bar{k})P(AAB^*) + 2\bar{k}P(AAA) \\ dP(BAB)/dt &= -k_2P(BAB) + \bar{k}P(AAB^*) \end{aligned} \qquad (1)$$

where k_0, k_1, and k_2 are individual rate constants for the reaction of central A units in AAA, AAB*, and BAB triads, respectively, $P(AAB^*) = P(AAB) + P(BAA)$, and $\bar{k} = (2k_0P(AAA) + k_1P(AAB^*))/(2P(AAA) + P(AAB^*))$.

This set of equations was solved numerically under the initial conditions $P(AAA)_{t=0} = 1$, $P(AAB^*)_{t=0} = P(BAB)_{t=0} = 0$ corresponding to the homopolymer PAN. The kinetic curve $P(A) = P(AAA) + P(AAB^*) + P(BAB)$ vs time calculated for $k_0 \approx 1.7 \times 10^{-3}$ h^{-1} = 4.7×10^{-7} s^{-1} and $k_0{:}k_1{:}k_2$ = 1:18:36 fits the experimental data fairly well (see Figure 2).

P(AB) values necessary for subsequent calculations were obtained from $P(AB) = P(AAA) + P(AAB^*)/2$. Then, *R*, l_A, and l_B values were calculated as mentioned above. Their dependencies on the HPAN composition are plotted in Figure 3. It is seen that the calculated curves fit the experimental data.

Table 1. Structure of Hydrolyzed PAN. Hydrolysis Conditions: 4 wt % PAN in 65% HNO_3; 21 °C[a]

sample	reaction time, h	content of B, mole fraction	*P*(ABA)	*P*(ABB*)	P(BBB)	l_A	l_B	*R*	R_{Ber}
HPAN-8	30	0.08	0.012	0.04	0.03	30	2.6	0.06	0.14
HPAN-17	50	0.17	0.017	0.065	0.09	16.6	3.4	0.10	0.28
HPAN-48	98	0.48	0.018	0.13	0.33	6.5	6.0	0.16	0.50
HPAN-82	170	0.82	0.003	0.12	0.69	2.8	13.0	0.13	0.30

[a] A = AN; B = AAm; $P(ABB^*) = P(ABB) + P(BBA)$; l_A (l_B) = the mean length of A (B) blocks; *R* and R_{Ber} = found and Bernoulli probabilities of a boundary between A and B blocks.

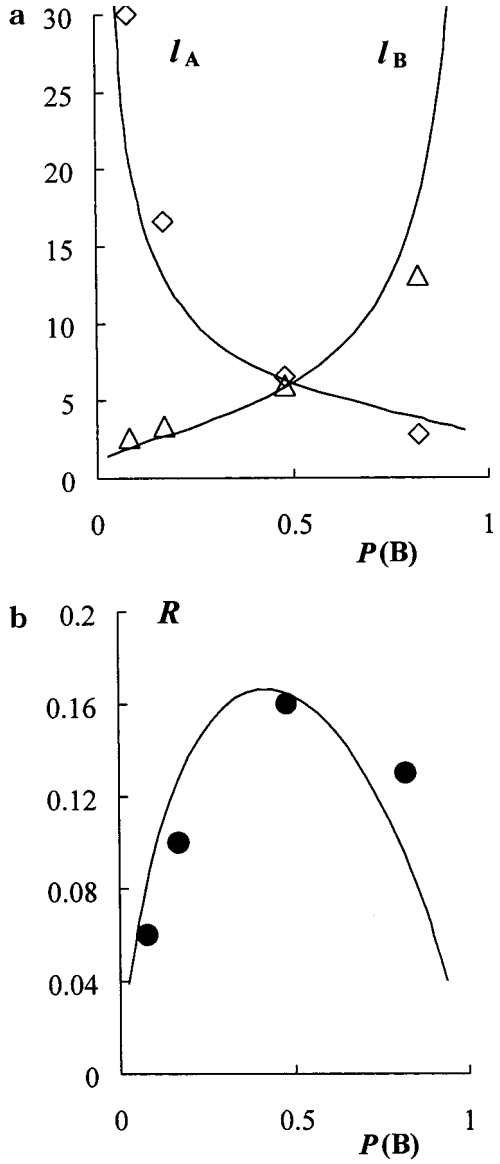


Figure 3. R, l_A, and l_B values of the HPAN: points, experimental data; curves, calculations for k_0:k_1:k_2 = 1:18:36.

Thus, the same set of rate constants k_0, k_1, and k_2 describes both the reaction kinetics and the distribution of units in the HPAN chain. This is a strong reason in favor of the accelerating effect of neighboring groups as the principal, if not exclusive, factor determining the peculiarities of the acidic PAN hydrolysis.

Note that Lovy et al.[6] studied hydrolysis of the PAN samples of different tacticity: one contained (%) 23 mm, 47 mr, and 30 rr triads and the other 53 mm, 32 mr, and 15 rr triads. The authors[6] did not mention any influence of the PAN tacticity on the HPAN multiblock structure. In particular, they found that "the relative intensities of the triplet components of the CH—CN signal do not change in the course of hydrolysis". Therefore, it may be assumed that the nature of the nearest neighbors (AN or AAm) determines the AN group reactivity, whereas the chain tacticity does not affect the acceleration noticeably.

The first step of the acidic hydrolysis of nitriles is an electrophilic attack of hydroxonium ion on CN group and the proton addition to the N atom.[15] It may be assumed that the interaction of AN and AAm neighboring groups

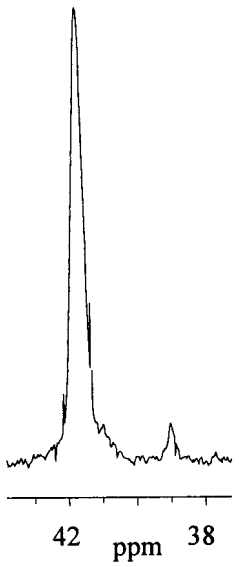
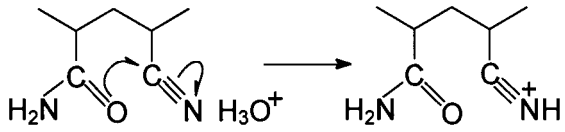


Figure 4. ^{13}C NMR spectrum of HPAN-62 in NaSCN/D_2O (55%) solution, amide, and glutarimide methine regions.

enhances the electron density on the N atom of AN group, thus facilitating that step



Assuming this mechanism, a synergetic action of two neighboring AAm groups is hardly possible. Most likely, a presence of the second AAm neighbor should enhance twice the probability of the AN−AAm interaction (and hence the accelerating effect) just in accordance with the observed ratio k_2:k_1 = 2.

Up to now no GI formation was mentioned for PAN hydrolysis by 65% HNO_3 at low temperatures. However, GI was found in the products of the PAN hydrolysis in 65% H_2SO_4.[16] Therefore, we tried to determine whether GI was formed under hydrolysis conditions used. According to Stoy et al.,[16] GI might be identified using C methine signals, ^{13}C NMR measurements being performed in NaSCN/D_2O (55%) solution. The ^{13}C NMR spectrum of HPAN-62 sample of composition P(B) = 0.62 in NaSCN/D_2O (55%) solution is shown in Figure 4.

Signals near 39 and 41.7 ppm correspond to the GI and AAm methine C resonances, respectively. From the integrals ratio it was estimated that, for this sample, less than 3% of AAm groups were involved in GI formation. This means that HPAN-48 and HPAN-82 contain about one GI cycle per 11 B-blocks of mean length l_B = 6 and per 5 B-blocks of l_B = 13, respectively. Therefore, GI formation was neglected when the rate constants and the parameters of HPAN structure were estimated.

Thus, the results obtained enabled us to conclude that the accelerating effect of neighboring groups is the principal, if not exclusive, factor determining the peculiarities of the acidic PAN hydrolysis. Beside its scientific interest, this conclusion appears to have some practical significance. Indeed, acidic PAN hydrolysis at low temperatures by action of HNO_3[6] or a H_2SO_4/H_3PO_4 mixture[16] is the only method to prepare

AN−AAm multiblock copolymers testified for various applications.[7−11,16] Note that ^{13}C NMR spectrometry gives the valuable but limited set of the HPAN structure parameters. Meanwhile, the theory of the neighboring group effect enables one to calculate any parameter of the reaction product structure as soon as the rate constants k_0, k_1, and k_2 are estimated.[13] The results obtained in the present work give an opportunity to apply the theory of the neighboring group effect to more detailed studies of the dependency of AN−AAm multiblock copolymers properties on their structure.

Conclusions

We established that both the kinetics of PAN hydrolysis in 65% HNO_3 at 21 °C and some parameters of the reaction product structure are described by the accelerating effect of neighboring units, the rate constants ratios found (k_0:k_1:k_2 = 1:18:36) being in accord with the mechanism of the acidic hydrolysis of nitriles. This shows that the theory of the neighboring group effect might contribute fruitfully to a study of the dependence of the properties of AN−AAm multiblock copolymers on their structure.

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