Alkaline Hydrolysis of Styrene-Acrylonitrile Copolymers

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ABSTRACT

Styrene-acrylonitrile copolymers of different compositions have been hydrolyzed by concentrated potassium hydroxide in dioxane solutions as well as in ethanol and aqueous suspensions. The reaction rate was followed by the amount of liberated ammonia which was absorbed in $0.1\ N\ H_2SO_4$, thus resulting in pH changes. With a tenfold excess of KOH, first-order hydrolysis rate constants were obtained. A plot of the conversion of nitrile groups versus time plot follows the familiar pattern. The hydrolysis rate decreased greatly as the acrylonitrile content in the copolymer decreased. The reaction rates decreased in the order dioxane > ethanol > water. Compared to the statistical samples, the alternating SAN copolymer showed the highest resistance toward hydrolysis. The relation between the distribution of triads of the repeating units in the copolymer and the hydrolysis rate constants demonstrated the dominant influence of the structure of the copolymer on the hydrolysis rate.

INTRODUCTION

The hydrolysis reaction of acrylonitrile-based polymers has been studied by a number of authors both in solution and in suspension. Most of these investigations have been concerned with the alkaline degradation [1, 2] or acidic hydrolysis [3, 4] of polyacrylonitrile, but rarely with acrylonitrile co-

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polymers [5]. These studies indicate that the several possible structural changes result from degradation and that the main reaction results of complete hydrolysis are conversion of nitrile to the amide as an intermediate and then to the acid groups. The hydrolysis reaction rate in solution are proportional to both hydroxyl and acrylonitrile group concentrations, and the reaction in suspension occurs on the surface and, therefore, depends on the rate of hydroxyl ion penetration into statistical coils of the polymer [6].

Recently, some work dealing with alkaline degradation of styrene-acrylonitrile (SAN) copolymers in dilute solution was reported [7, 8].

This paper deals with alkaline hydrolysis of SAN copolymers of different compositions with concentrated potassium hydroxide in dioxane solution as well as in ethanol and aqueous suspensions. The relationship between the microstructure of the copolymers and the hydrolysis rate constants was established.

EXPERIMENTAL

Materials

Styrene was washed with 5% aqueous sodium hydroxide solution, dried over calcium chloride, and distilled under nitrogen at 10 torr immediately before use. Acrylonitrile was dried over calcium chloride and distilled at atmospheric pressure under nitrogen at 77°C.

Styrene-acrylonitrile (SAN) random copolymer samples of different composition were obtained by the usual free-radical copolymerization in dimethylformamide solution at 65°C in the presence of azobisisobutyronitrile at low conversions. An alternating SAN copolymer sample was prepared in the presence of dry zinc chloride at 40°C in bulk at low conversion [9]. The copolymers were purified by repeated precipitation from acetone solution into methanol.

Measurements

Infrared spectra were recorded on a Perkin-Elmer spectrophotometer Model 147 from film cast from acetone solutions onto sodium chloride plates. ^{1}H NMR spectra were obtained on a 90-MHz Varian EM-90 spectrometer and ^{13}C NMR spectra on a Jeol FX 90 QFT spectrometer with complete proton decoupling. The measurements were carried out on deuterated chloroform solutions with TMS as internal standard. The glass-transition temperature
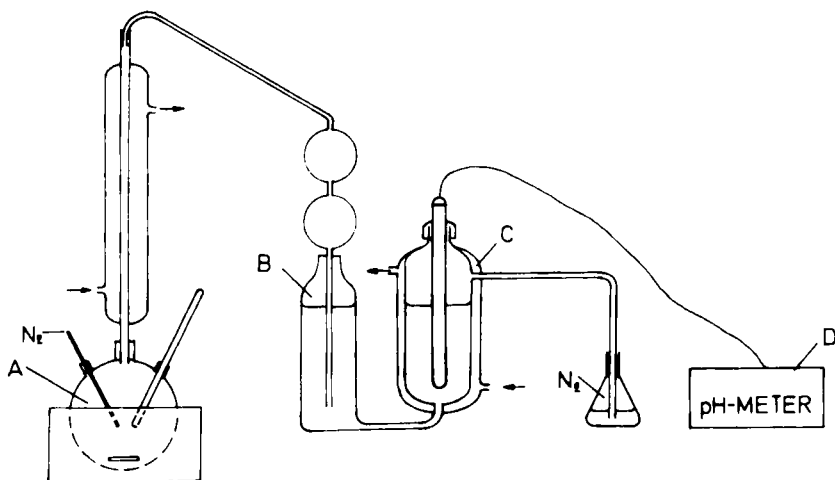
FIG. 1. Apparatus for the alkaline hydrolysis of SAN copolymers. (A) Reaction vessel with thermostatted bath, (B) ammonia trap with o.1 N H$_2$SO$_4$, (C) thermostatted measuring vessel with glass electrode, (D) pH meter.

measurements were carried out on Perkin-Elmer DSC-2 instruments under a stream of nitrogen and a heating rate of 20°C/min. For the pH measurements, a Radiometer pH meter Model pHM 64 with a combined glass electrode was used.

Alkaline Hydrolysis Procedure

The hydrolysis reactions were performed on dioxane solutions and on fine-powdered SAN copolymer samples in ethanol (96 at.%) or aqueous suspensions with potassium hydroxide solutions. The apparatus for the measurements is shown in Fig. 1. The reaction was performed in a 100-mL thermostatted round-bottomed vessel (A) equipped with magnetic stirrer, condenser, and nitrogen inlet. The liberated ammonia was carried out by a constant stream of nitrogen and absorbed in 50 mL 0.1 N H$_2$SO$_4$ (B) followed by measurement of pH changes in an thermostatted (20°C) cell equipped with a glass electrode (C). The nitrogen outlet passed through an phenolphthaleine indicator solution in order to check for completion of ammonia absorption. In all experiments an amount of SAN copolymer containing 5 mmol acrylonitrile was used in 50 mL of 1N potassium hydroxide solution. For the dioxane experiments, the above

amount of the SAN copolymer was dissolved in 35 mL dioxane and a solution of 2.8 g KOH in 3 mL water and 7 mL ethanol was added and made up to 50 mL with dioxane. Homogeneous solutions were obtained. For each series, blank experiments were carried out in order to evaluate the pH before hydrolysis.

RESULTS AND DISCUSSION

A series of statistical copolymers of styrene and acrylonitrile with various compositions was obtained by radical copolymerization in DMF solution at low conversion to ensure compositional homogeneity. In addition, an alternating SAN copolymer was prepared in the presence of zinc chloride [9]. The copolymer composition and triad sequence distribution of the monomer units are summarized in Table 1. The compositions of the samples were estimated from the nitrogen contents, and the triad sequence distribution were calculated according to Harwood [10] on the base of comonomer feed composition and reactivity ratios, using the values $r_{ST} = 0.30$ and $r_{AN} = 0.16$ for DMF solution polymerization [11]. The structure of the alternating SAN sample was confirmed by ^{13}C NMR spectroscopy [9] and by the estimated T_g value [12] which is, as can be seen, about 10°C higher than that for statistical copolymer of the same composition.

The alkaline hydrolysis was carried out with potassium hydroxide in dioxane solutions for copolymer samples with up to 55 mol% AN. Because of the low solubility of copolymers with higher AN content, these reactions were performed in ethanol or aqueous suspensions only. The hydrolysis rate of acrylonitrile moieties in the SAN copolymer is presumably proportional to both the AN and the hydroxyl ion concentrations. In order to determine the influence of the structure on the hydrolysis reaction rate, the experiments were carried out with tenfold excess of potassium hydroxide. In this way the apparent first-order rate constants, k, were obtained from the linear plot according to the familiar equation

$$k = \frac{1}{t} \ln \frac{a}{a-x},$$

where a is the initial AN concentration and x is the concentration of AN hydrolyzed at time t.

TABLE 1 SAN Copolymer Compositions and Calculated Triad Distributions

Samples no.	Monomer feed, AN, mol%	Polymer composition, AN, mol%		T_g, °C	Sequence distributions[a,b]					
		Calculated	From N content		SSS	SSA AAS	ASA	SAS	AAS SSA	AAA
1	45.5	38	37.8	105	19.0	49.2	31.7	85.9	13.5	0.5
2	57.8	50	49.5	111	3.2	29.5	67.3	67.3	29.5	3.2
3[c]	50.0 (Alt)	50 (Alt)	50.0 (Alt)	119	0	0	100	100	0	0
4	70.2	55	54.2	112	1.3	20.1	78.7	52.7	39.8	7.5
5	80.9	60	59.0	111	0.81	16.4	82.0	36.8	47.7	15.0
6	89.8	70	68.8	104	0.1	6.3	93.5	17.2	48.5	34.3
7	92.8	75	74.6	-	0.09	4.7	95.0	10.6	43.9	45.5
8	95.0	80	80.9	103	0.03	3.4	96.0	6.0	37.0	56.9
9	96.7	85	84.8	94	0.01	1.9	98.0	2.3	28.8	68.0
10	99.1	95	94.6	-	0	0.2	99.8	0.2	9.6	89.7
11	100.0	100	100.0	97	-	-	-	-	-	100

[a]Triad distributions based on r_{ST} and r_{AN} and monomer feed ratios (r_{ST} = 0.30, r_{AN} = 0.16) [11].
[b]S = styrene, A = acrylonitrile.
[c]Alternating SAN composition and triads sequence distribution obtained by ^{13}C NMR measurements.
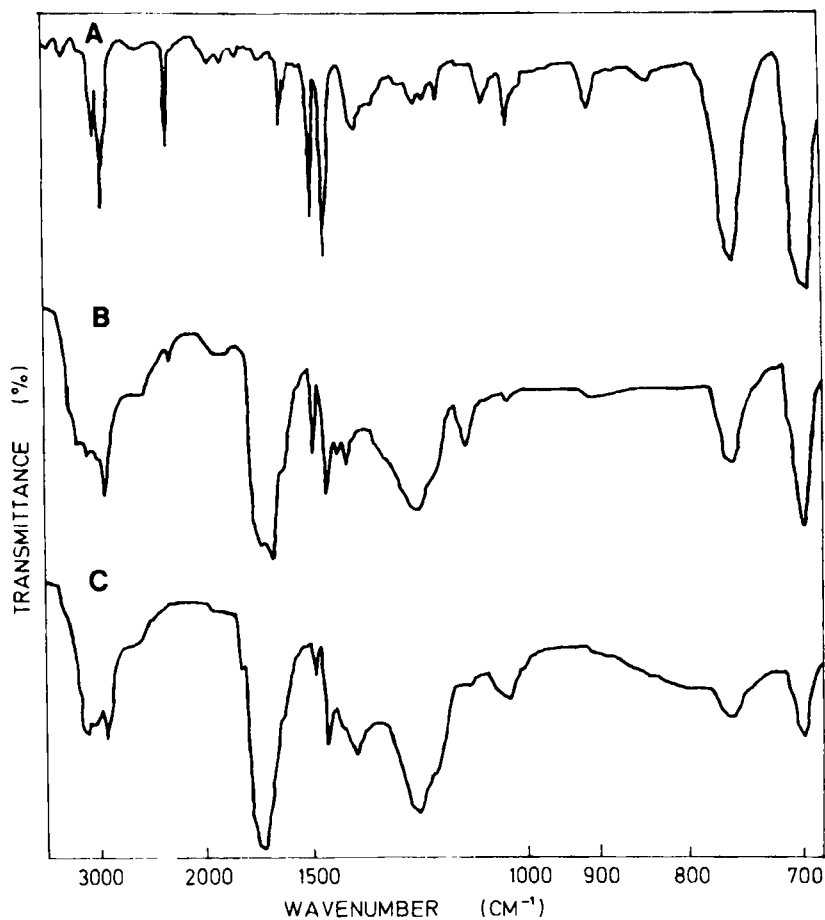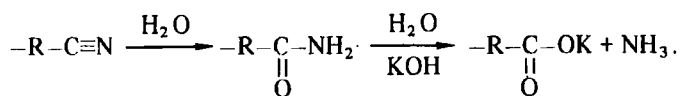
FIG. 2. IR spectra of the initial SAN copolymer (A) and the partially (B) and completely hydrolyzed product (C).

According to the known mechanism of the alkaline hydrolysis of polyacrylonitrile [13], 1 mol of AN liberates 1 mol of ammonia:

$$-R-C{\equiv}N \xrightarrow{\text{H}_2\text{O}} -R-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[\text{KOH}]{\text{H}_2\text{O}} -R-\underset{\underset{O}{\|}}{C}-OK + NH_3.$$

The same mechanism has been confirmed for concentrated alkaline hydrolysis of the SAN copolymers by their IR spectra (Fig. 2). The characteristic changes involve disappearance of the nitrile group absorption peak at $2\ 250\ cm^{-1}$ (A) and formation of a new peak at $1\ 650\ cm^{-1}$ due to amide carbonyl absorption and NH stretching at $3\ 200\text{-}3\ 500\ cm^{-1}$ and bending vibrations at $1\ 560\ cm^{-1}$ (B). With the progress of the reaction these peaks gradually disappear with the simultaneous appearance of the carboxyl carbonyl peak at $1\ 710\ cm^{-1}$ (C). The absorption of ammonia in 0.1 N $H_2 SO_4$ results in pH changes from which the concentration of hydrolyzed AN was calculated.

The first-order plots and the initial rate constants in dioxane solutions are shown in Fig. 3. It is evident that, in spite of equal AN concentration, the initial hydrolysis rates are strongly dependent on the composition of the copolymer, being higher as the content of AN in the copolymer is increased. Moreover, the alternating copolymer showed the highest resistance toward hydrolysis, with the rate constants of the order of six times lower than for the random copolymer of the same composition (Table 2).

The alkaline hydrolysis of SAN copolymers in ethanol suspension is shown in Figs. 4 and 5. During hydrolysis in suspension, an induction period of up to an hour was observed. It increased as the AN content in copolymer was lowered. The induction periods have been omitted from the graphs for better comparison of results. The conversion versus time plots follow the familiar pattern and show the retarding effect of lower AN content in the copolymer. Again, the lowest reaction rate are observed for the alternating copolymer.

Table 2 shows that the reaction rate is about three times faster in solutions than in suspension, probably because the reaction rate in ethanol suspension is affected not only by time and alkali concentration, but also by diffusion of the reactants into the copolymer particles. The same rules apply to hydrolysis in aqueous suspension, as illustrated in Figs. 6 and 7. The hydrolysis curves show two distinct steps. At first the reaction follows first-order kinetics; then the rate slows down in spite of the large excess of alkali. This effect is probably due to the formation of the new hydrophilic moieties resulting in an increasing charge along the polymeric chain as the reaction proceeds. The same behavior has also been reported for the alkaline hydrolysis of poly(vinyl amides) [14]. The initial reaction rates, under the experimental conditions used, for AN content up to 70 mol% are much higher in aqueous alkaline suspension while, for higher AN content, the rates are higher in ethanol solutions. This is probably due to solubility effects since the reaction products are completely soluble in aqueous alkaline solution but insoluble in alcoholic alkaline solutions.
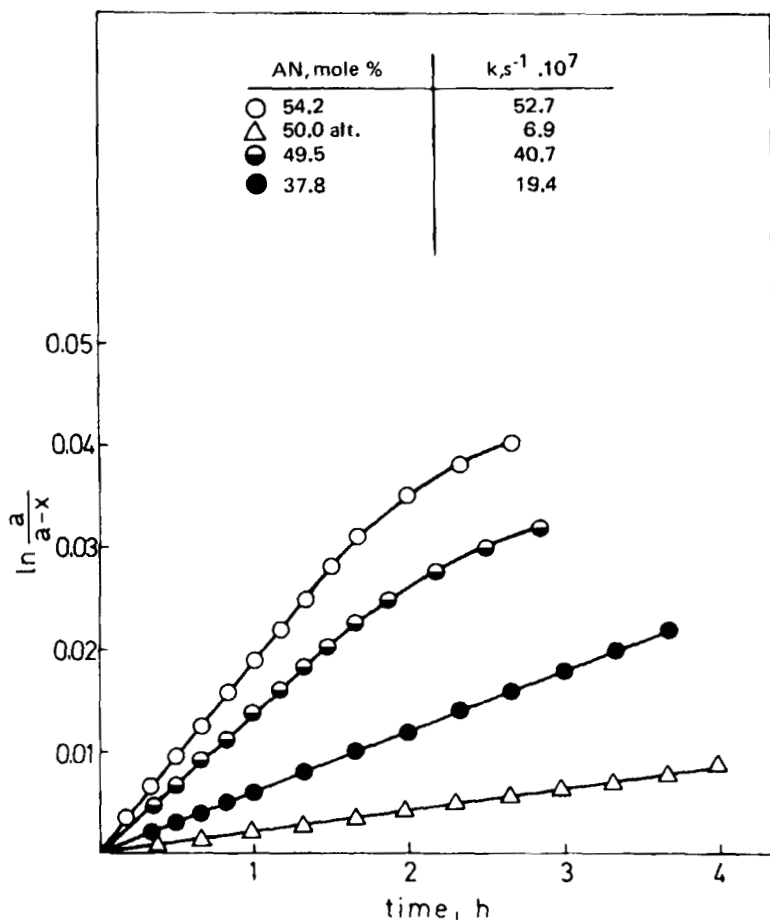
FIG. 3. The degree of alkaline hydrolysis of the SAN copolymers versus time in dioxane solutions: [AN] = 0.1 mol/L, [KOH] = 1.0 mol/L at 70°C.

In order to explain the fact that the initial hydrolysis rate constants are strongly dependent on the composition of the SAN copolymers in spite of constant nitrile concentration, the relationship between the rates and the microstructure of the copolymer [15] has been considered. The plot of the rate constants obtained versus the amount of the AAA (A = acrylonitrile) and SAS (S = styrene) sequence triads as well as the composition of the co-

TABLE 2 Initial Rate Constants of Alkaline Hydrolysis of SAN Copolymers in Dioxane Solutions and Ethanol and Aqueous Suspensions[a]

Sample no.	AN, mol%	Initial rate constant, $k \times 10^7$, s^{-1}			k_D/k_E	k_E/k_A
		Dioxane (k_D)	Ethanol (k_E)	Aqueous (k_A)		
1	37.8	19.4	6.1	0.6	3.2	10.1
2	49.5	40.7	13.2	1.6	3.1	8.3
3	50.0 (Alt)	6.9	3.6	0.3	1.9	1.2
4	54.2	52.7	22.9	-	2.3	-
5	59.0	-	42.0	12	-	3.5
6	68.8	-	111	45	-	2.5
7	76.6	-	161	-	-	-
8	80.9	-	-	192	-	-
9	84.8	-	305	501	-	0.6
10	94.6	-	681	1050	-	0.6
11	100.0	-	1047	1995	-	0.5

[a]The hydrolysis reaction was carried out in dioxane solutions at 70°C, ethanol suspension at 70°C, and aqueous suspension of 100°C. [AN] = 0.1 mol/L, [KOH] = 1.0 mol/L.

polymers are presented in Figs. 8 and 9. Almost identical curves for ethanol and aqueous suspension hydrolysis illustrate the dominant influence of the structure of SAN molecules on the hydrolysis reaction. The decrease in reaction rates with increasing styrene content can be explained by the steric hindrance arising from the increased number of single nitrile groups blocked by neighboring phenyl groups, which makes the approach of the hydrolytic agent difficult. Such an interpretation is supported by the fact that the alternating copolymer that has each nitrile group blocked by two phenyl rings, i.e., with no AAA triads present, exhibited the lowest hydrolysis rate in all media used.
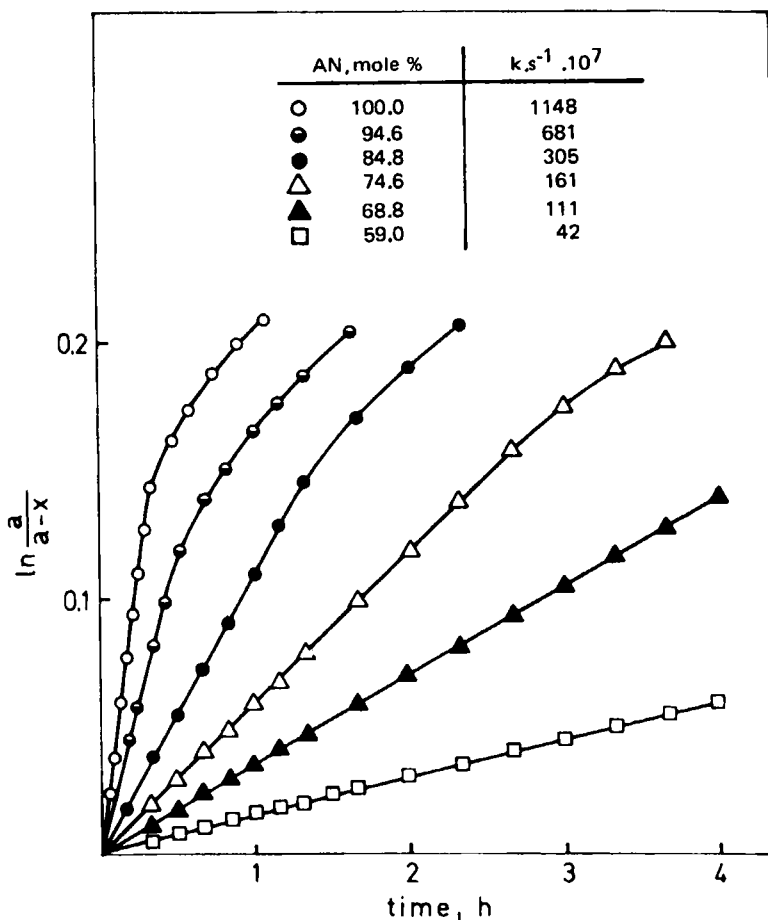
FIG. 4. The degree of alkaline hydrolysis of the SAN copolymers versus time in ethanol suspension: [AN] = 0.1 mol/L, [KOH] = 1.0 mol/L at 70°C.
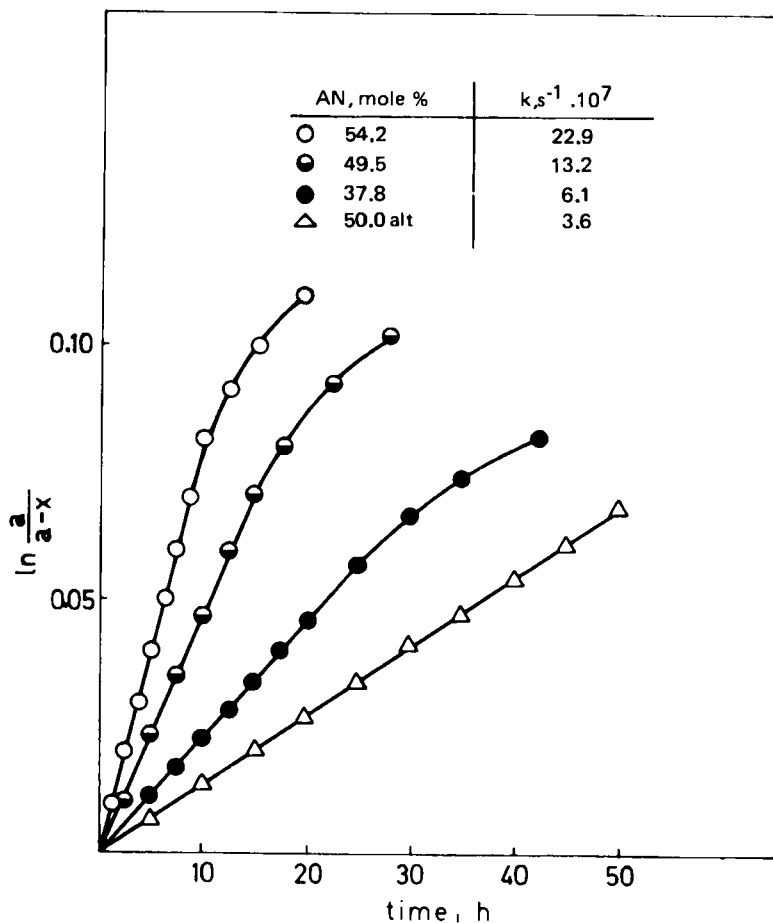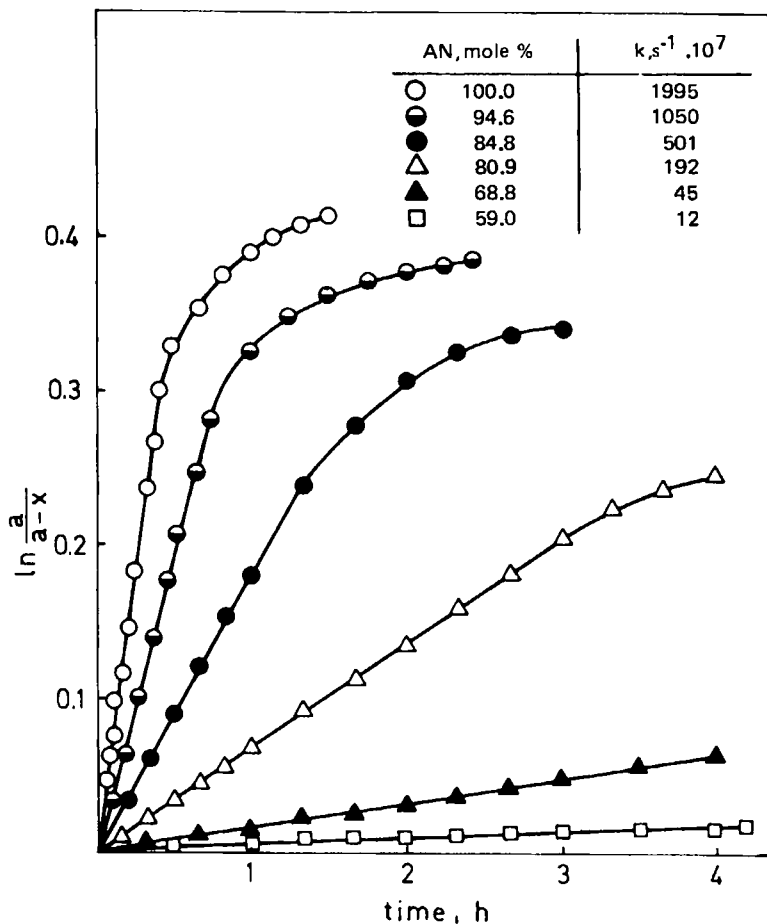
FIG. 5. The degree of alkaline hydrolysis of the alternating ($\triangle$) and random SAN copolymers versus time in ethanol suspension: [AN] = 0.1 mol/L, [KOH] = 1.0 mol/L at 70°C.

FIG. 6. The degree of alkaline hydrolysis of the SAN copolymers versus
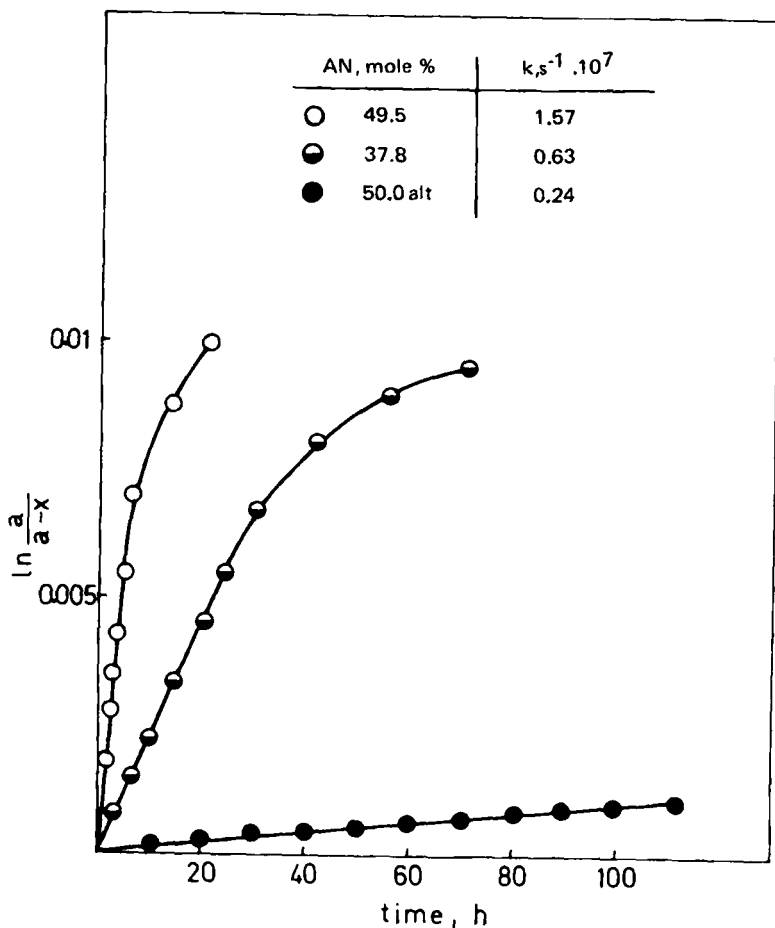time in aqueous suspension: [AN] = 0.1 mol/L, [KOH] = 1.0 mol/L at 100°C.

FIG. 7. The degree of alkaline hydrolysis of the alternating (●) and random SAN copolymers versus time in aqueous suspension: [AN] = 0.1 mol/L, [KOH] = 1.0 mol/L at 100°C.

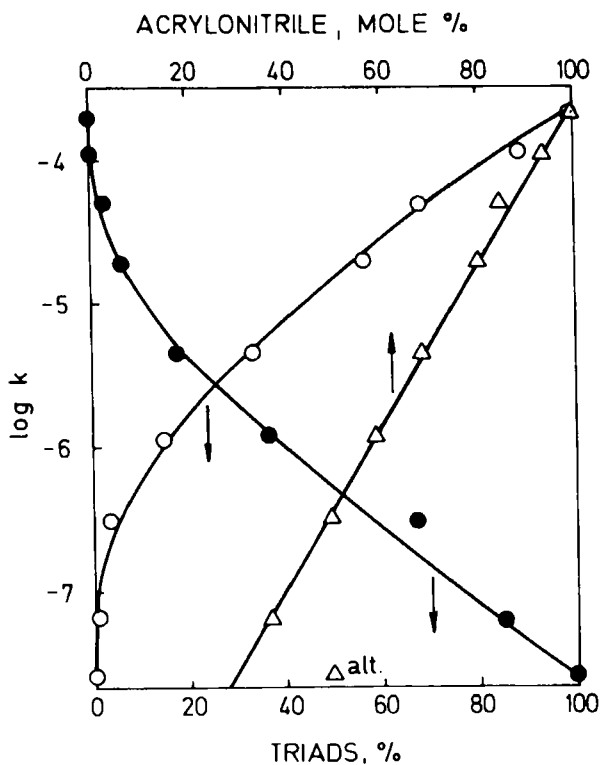FIG. 8. The influence of the composition (△) and triads SAS (●) and AAA (○) distributions of SAN copolymers on the initial rate constants of alkaline hydrolysis in ethanol suspension at 70°C.

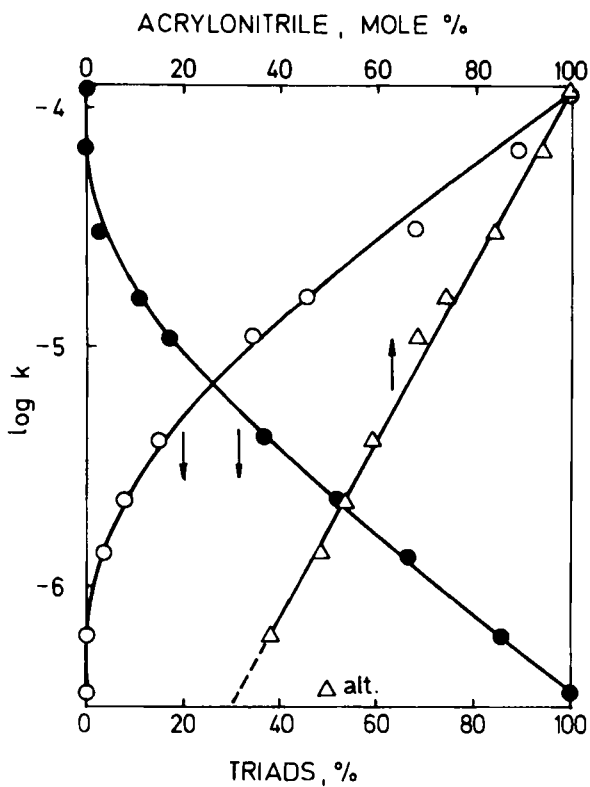FIG. 9. The influence of the composition ($\triangle$) and triads SAS ($\bullet$) and AAA ($\circ$) distributions of SAN copolymers on the initial rate constants of alkaline hydrolysis in aqueous suspension at 100°C.

ACKNOWLEDGMENT

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