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### Saponification Kinetics of Acrylonitrile Terpolymer and Polyacrylonitrile

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## Saponification Kinetics of Acrylonitrile Terpolymer and Polyacrylonitrile

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### ABSTRACT

Saponification kinetics of acrylic terpolymer and polyacrylonitrile were studied. The influence of alkali concentration and the time of hydrolysis on the degree of saponification were determined by the residual nitrogen content. The order of reaction was graphically determined and the rate of saponification was found to be faster in the terpolymer than in the homopolymer. Chemical and infrared spectroscopy methods reveal that the reaction is initiated through cyclization of nitrile groups, followed by hydrolysis to amide and carboxylic groups of the  $-(C=N)_n-$  segments produced.

The saponification of nitrile groups in the terpolymer initially yields amide groups, then slows down to yield carboxylic groups.

### INTRODUCTION

Water-soluble acrylic polymers are widely used in various branches of industry, and the hydrolysis products of polyacrylonitrile have an important place among them, which can be obtained by saponification with alkali [1-3] or acid [4]. The special features of the course of saponification of polyacrylonitrile and copolymers of acrylonitrile

are due to the high chemical stability of the carbon chain of macromolecules and the reactivity of nitrile groups.

Mikhailova and co-workers [5] have studied the saponification kinetics of an acrylonitrile terpolymer containing methyl acrylate and sodium itaconate. The effect of the reaction medium on the extent of acrylic fiber saponification in alkali has also been studied [6, 7].

This paper presents some studies on the kinetics of the saponification of terpolymer of acrylonitrile/methyl acrylate/sodium methallyl sulfonate compared to acrylonitrile homopolymer in which saponification is carried out under alkaline conditions.

## EXPERIMENTAL

### Synthesis of Polyacrylonitrile

Acrylonitrile (Ranbaxy Laboratories, Ltd.) was polymerized using potassium persulfate (4.0 mol% with respect to monomer) and sodium metabisulfite (0.4 mol% with respect to monomer) redox initiators at 55°C under constant stirring in an inert atmosphere according to the method reported by Betchtold [8].

The intrinsic viscosity was determined in *N,N*-dimethylformamide (DMF) as a 0.2% solution at 25°C. The Mark-Houwink relationship was employed in the form

$$[\eta] = 2.525 \times 10^{-4} \bar{M}_v [9]$$

$$1.06 = 2.525 \times 10^{-4} \bar{M}_v^{0.75}$$

$\bar{M}_v$  was found to be 69,000. Nitrogen analysis by Kjeldahl's method indicated a value of 25.7% compared to 26.4% (theoretical value).

The acrylonitrile terpolymer was supplied by Indian Petrochemicals Ltd., Baroda, India. The terpolymer having a composition of acrylonitrile 91.5-92%, methyl acrylate 7-7.5%, and sodium methallyl sulfonate 1% had a nitrogen content of 24.1%. The intrinsic viscosity in DMF as a 0.2% solution at 25°C was 1.104 dL/g.

### Saponification Kinetics

The polymer (150 g) and the saponifying agent (aqueous sodium hydroxide) were heated to 85°C with continuous stirring. The amount of sodium hydroxide used was determined by using the saponification index (S.I.) defined as

$$\text{S.I.} = \frac{\text{weight of the saponifying agent}}{\text{weight of the polymer}}$$

The concentration of the polymer in the mixture was maintained at 10% throughout the course of the reaction. The saponifications were carried out with compositions via S.I. of 0.25, 0.5, 1.0, and 1.25. The polymer fractions were taken out at intervals of 5, 10, 15, 20, 25, 30, 60, 90, 120, 180, and 240 min.

The polymer was cooled and precipitated with 2 N hydrochloric acid at pH 3.0. The precipitate was washed with water, followed by thorough washing with methanol. It was dried in vacuum at 50°C. The same experiments were conducted with the terpolymer.

### Analysis and Structural Changes of Products

The nitrogen content of the various fractions was determined using Kjeldahl's method (Tables 1 and 2 and Figs. 1 and 2). This value was used for determining the degree of saponification (p) from the relation

$$p = \frac{\% \text{ N at instant } t}{\text{initial } \% \text{ N of the polymer}}$$

where  $t$  denotes time.

The reaction order was calculated using Wilkinson's method [10], where  $t/p$  vs  $t$  was plotted, and the order is half the value of the slope (Figs. 3 and 4). The rate constants for the saponification reaction were calculated from initial sections of the kinetic curve (Figs. 1 and 2) from a second-order rate equation:

$$k = \frac{[\bar{N}]_0 - [\bar{N}]_t}{[\bar{N}]_0 [\bar{N}]_t t}$$

where  $[\bar{N}]_0$  is the initial nitrogen content (mol) and  $[\bar{N}]_t$  is the nitrogen content at instant  $t$ . The values of  $k$  for various sets of saponification conditions are tabulated in Table 3.

To trace the gradual chemical changes occurring during the saponification of the homo- and terpolymer, the IR spectra of the solid fractions obtained at a S.I. of 0.5 were taken by using a FTIR Nicolet 5 MX spectrophotometer. The nitrile group in polyacrylonitrile exhibits

TABLE 1. Nitrogen Content of the Saponified Polyacrylonitrile with Saponification Time at an S.I. of 0.25, 0.5, 1.0, and 1.25

Saponification time, min	S.I.			
	0.25	0.5	1.0	1.25
5	24.5	21.0	13.0	12.0
10	13.5	12.5	11.4	11.0
15	12.7	12.0	11.0	10.5
20	12.5	11.7	10.7	10.0
25	12.2	11.5	10.5	9.4
30	12.5	11.3	10.5	9.2
60	11.7	10.2	9.5	8.7
90	11.5	9.7	9.2	8.3
120	11.5	9.5	8.9	8.0
180	11.3	9.3	8.5	7.8
240	11.2	9.0	8.5	7.6

TABLE 2. Nitrogen Content of the Acrylonitrile Terpolymer with Saponification Time at an S.I. of 0.25, 0.5, 1.0, and 1.25

Saponification time, min	S.I.			
	0.25	0.5	1.0	1.25
5	20.2	18.5	10.2	7.8
10	11.5	10.5	7.7	6.2
15	10.7	9.5	7.0	5.5
20	10.5	9.0	6.5	5.24
25	10.3	8.2	6.0	5.0
30	10.0	7.4	5.7	4.5
60	9.2	6.5	5.0	4.0
90	9.1	5.9	4.6	3.8
120	8.0	5.5	4.5	3.6
180	8.0	5.2	4.3	3.5
240	7.8	5.2	4.0	3.5

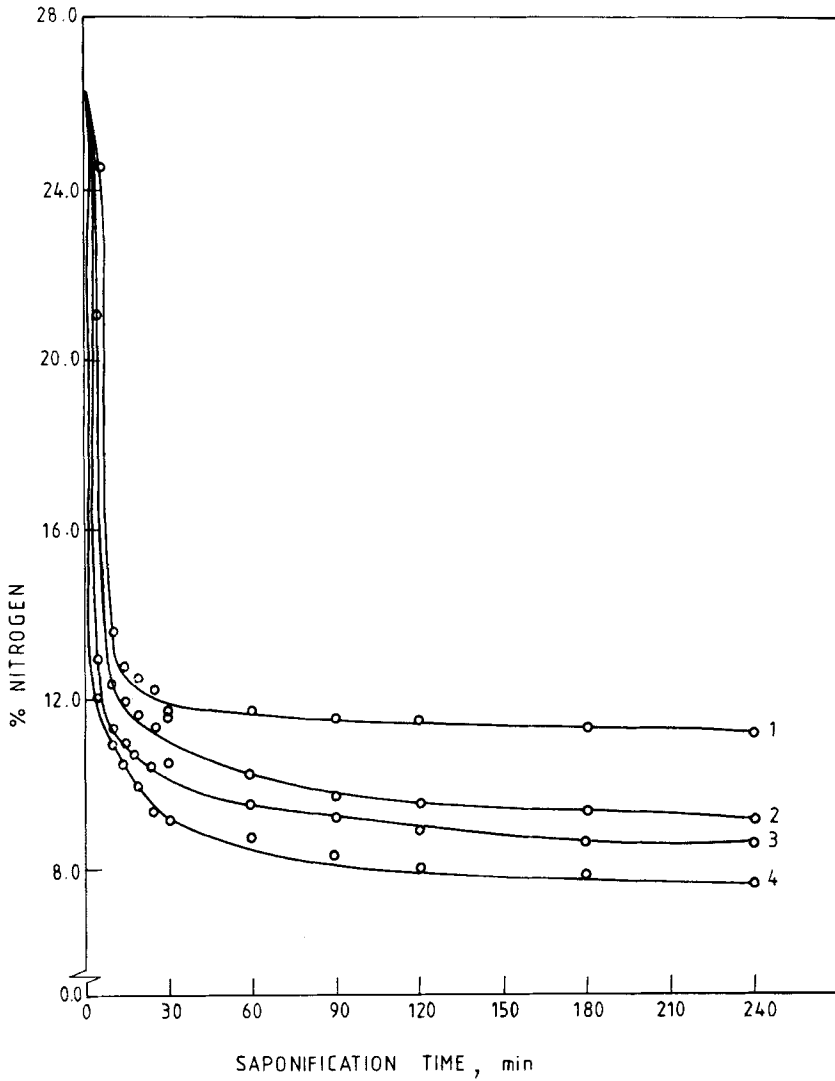


FIG. 1. The nitrogen content of saponified polyacrylonitrile as a function of saponification time at 85°C in relation to S.I. of (1) 0.25, (2) 0.5, (3) 1.0, and (4) 1.25.

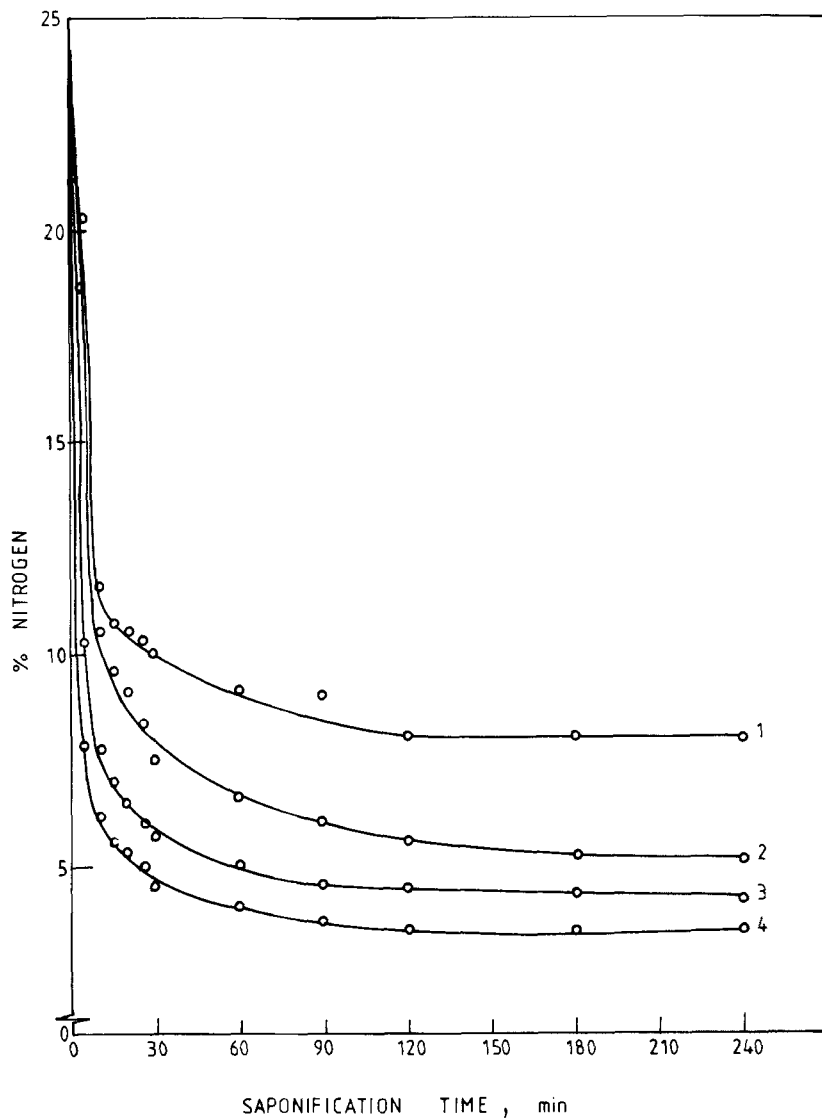


FIG. 2. The nitrogen content of acrylonitrile terpolymer as a function of saponification time at 85°C in relation to S.I. of (1) 0.25, (2) 0.5, (3) 1.0, and (4) 1.25.

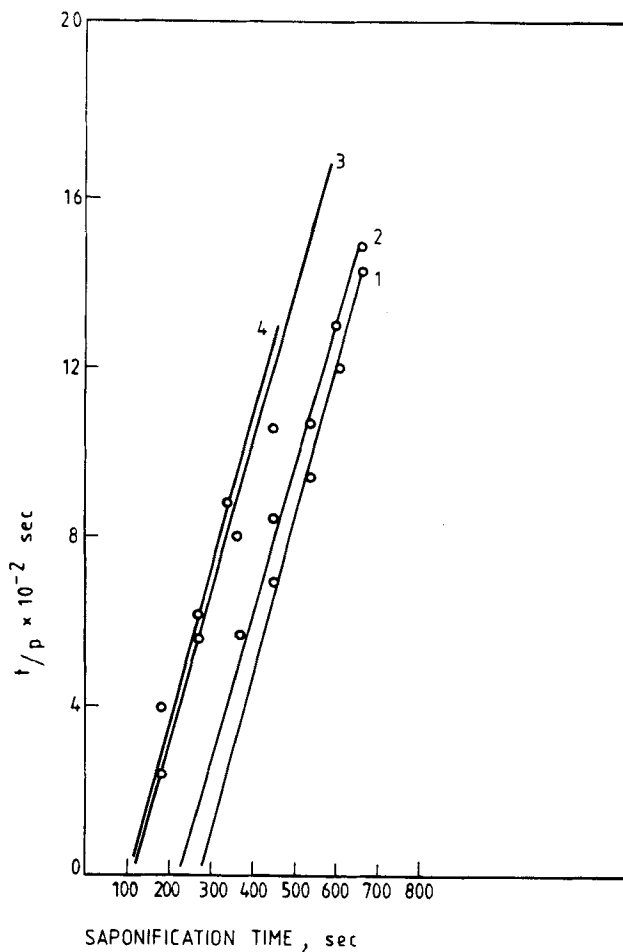


FIG. 3. The conversion time of nitrile groups ( $t/p$ ) as a function of saponification time at S.I. of (1) 0.25, (2) 0.5, (3) 1.0, and (4) 1.25 for the homopolymer.



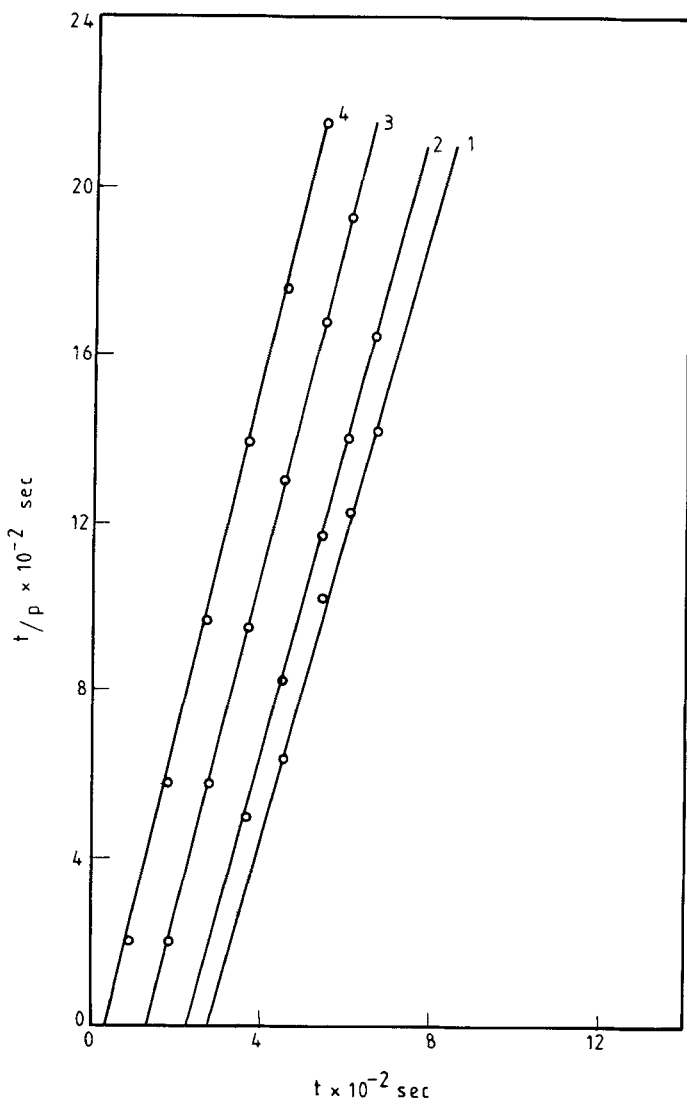


FIG. 4. The conversion time of nitrile groups ( $t/p$ ) as a function of saponification time at S.I. of (1) 0.25, (2) 0.5, (3) 1.0, and (4) 1.25 for the terpolymer.

TABLE 3. The Values of Rate Constant  $k$  at 85°C

Sample	Value of $k$ at S.I. of			
	0.25	0.5	1.0	1.25
Homo-PAN	0.07	0.08	0.09	1.104
Acrylonitrile terpolymer	0.08	0.107	0.113	0.146

symmetric valency vibrations of a characteristic frequency and appears in the spectrum as an absorption band at  $2245\text{ cm}^{-1}$ . Therefore, to quantify the nitrile nitrogen in the saponification products, a calibration curve was obtained by plotting the optical density of the band in relation to the nitrogen content in CN groups. Graduation was accomplished from mixtures of polyacrylonitrile and polyacrylic acid in proportions by weight of 10:0, 9:1, 8:2, 5:5, 3:7, 1:9, and 0:10. The samples for IR spectroscopy were prepared in the form of KBr pellets, i.e., 3 mg of the specimen and 197 mg KBr were thoroughly ground in a mortar and then compressed to obtain a transparent pellet. The nitrogen content and the optical density of the band at  $2245\text{ cm}^{-1}$  were calculated for each mixture specimen. Parallel determinations of the total nitrogen by Kjeldahl's method were also carried out to locate possible deviations from analytically predicted values (Table 4).

The nitrile nitrogen for the saponified products was determined from the calibration curve (Fig. 5) by calculating the optical density of the nitrile peak:

$$\text{optical density} = \log \frac{\% T \text{ at the base line}}{\% T \text{ at the band peak}}$$

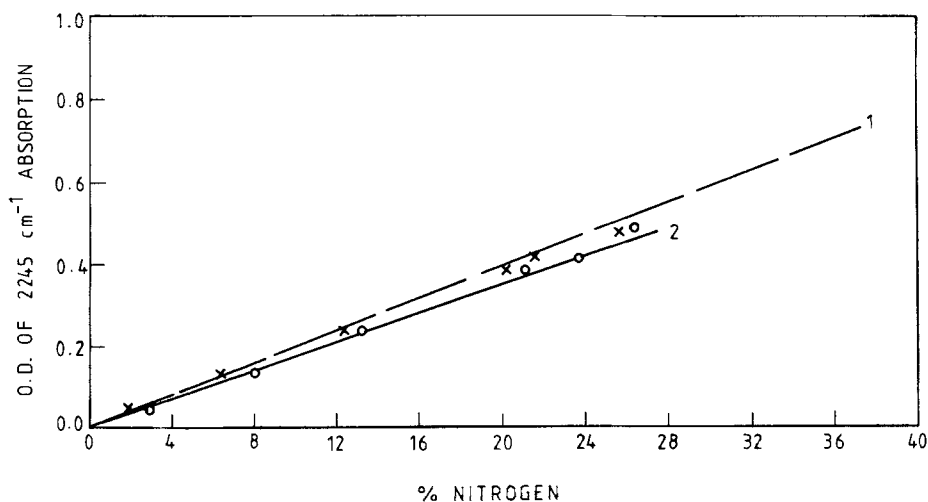
## RESULTS AND DISCUSSION

### Kinetic Studies

As saponification begins, the acrylonitrile homopolymer and the terpolymer change markedly in color from white to deep brown. The pronounced color change of the polymer accompanied by the evolution of ammonia is explained by changes in the chemical structure of the homo- and terpolymer as illustrated later from IR spectral studies. It was noted that for a S.I. of 0.5-1.25, the terpolymer turns light yellow to colorless within 60-70 min, whereas the homopolymer color persists even after 240 min of saponification.

TABLE 4. Relation between Optical Density and Nitrogen Content of Mixtures of Polyacrylonitrile:Polyacrylic Acid

PAN:PAA	$I_0$	I	A = log $I_0/I$	% N	
				Calculated theoretically	By analysis
10:0	44.72	14.556	0.4875	26.4	25.7
9:1	46.851	17.9258	0.4172	23.76	21.4
8:2	45.805	13.866	0.385	21.12	20.3
5:5	32.395	18.744	0.2376	13.2	12.4
3:7	32.395	23.4365	0.1405	7.92	6.5
1:9	40.725	37.1649	0.040	2.64	1.95

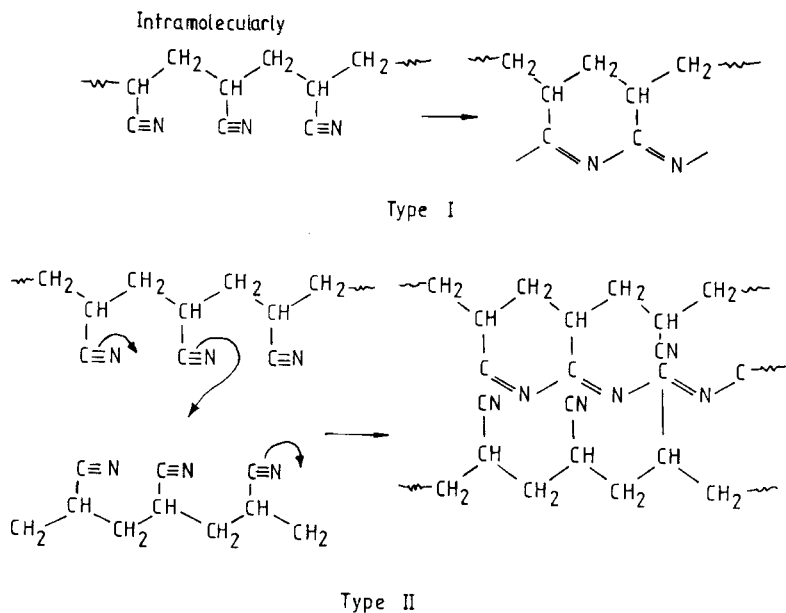
FIG. 5. The optical density of the 2245  $\text{cm}^{-1}$  band vs the nitrile nitrogen content: (1) determined by analysis, (2) calculated nitrogen.

A perusal of nitrogen-content data as a function of saponification time at a constant temperature of 85°C (Figs. 1 and 2) reveals that the ultimate nitrogen content of the copolymer is 3.5% at a S.I. of 1.25 and 7.8% at a S.I. of 0.25, whereas the decrease in the nitrogen content during saponification of homopolymer is less, viz., 7.6% at a S.I. of 1.25 and 11.2% at a S.I. of 0.25. It is evident from Figs. 1 and 2 that in both cases there is initially a rapid loss in nitrogen content but the rate slows down progressively with saponification time. It was further noted that even after a saponification time of 30 min at a S.I. of 0.25, there is a significant difference in the nitrogen content of homopolymer (12.5%) and terpolymer (10%), indicating a faster rate of saponification in the terpolymer than in the homopolymer under identical conditions.

The order of the reaction was determined from the slope of the plot of  $t/p$  vs  $t$ , and the hydrolysis reaction was found to be first order in polymer and first order in alkali.

The rate constants were determined from the second-order rate equation for the initial portions of the curve. It was noted (Table 3) that on increasing the S.I. from 0.25 to 1.25 for acrylic terpolymer, the value of  $k$  varies between 0.08 and 0.146, whereas under identical conditions the rate constant varies between 0.07 and 0.104 for homopolymer, indicating that the saponification rate is higher for the terpolymer. In both the homo- and the terpolymer the saponification rate increases with an increase in alkali concentration. The slower saponification rate of the homopolymer may be explained by the close packing of long chains, which hinders the attack of a nucleophile on the reactive nitrile groups. On the other hand, the terpolymer has much looser packing due to the presence of bulky ester groups and sodium methallyl sulfonate as side substituents which facilitate the attack of alkali. Subsequently, saponification begins with the formation of long carbon-nitrogen conjugated chains. In the acrylonitrile homopolymer the reaction can occur not only along the chain, resulting in a long, uninterrupted naphthyridine type of structure (Type 1), but also between chains, forming intermolecular crosslinkages. Such structures probably delay the attack of alkali in the subsequent step of saponification, leading to a slow rate and the development of a permanent color as compared to terpolymer, where the formation of such structures is probably hindered.

Morawetz [11] has explained the results of Moens and Smets [12] and proposed the explanation that the initial higher rate may be due to the catalysis by specific neighboring amide groups which are formed in the first step. However, with an increasing degree of saponification, the rate of the overall reaction decreases noticeably. This is perhaps due to the hindrance caused by the newly formed carboxylate groups through electrostatic repulsion toward the hydroxyl ion, which would attack the neighboring amide group. Nagese and Sakaguchi [13] report that this abnormality is caused by intramolecular interaction between two or more adjacent amide groups. These effects are stronger the closer the two amide groups are located, which is in agreement with our results.



### Infrared Spectral Studies

Figures 6 and 7 show the spectrum of polyacrylonitrile. In the region of  $\text{CH}_2$  group vibrations there appear two absorption bands corresponding to symmetrical vibrations ( $2840\text{ cm}^{-1}$ ) and antisymmetrical vibrations ( $2920\text{--}2960\text{ cm}^{-1}$ ). The spectrum also shows an intense distinct band at  $2245\text{ cm}^{-1}$  caused by the presence of nitrile groups (Table 5).

The deformation vibrations of the  $\text{CH}_2$  group give rise to  $1460$  and  $1360\text{ cm}^{-1}$  bands (bending vibrations) and also the  $1220\text{ cm}^{-1}$  band (torsional vibrations). The  $\text{CH}$  group does not have any characteristic band in the region of valency vibrations; however, deformation vibrations appear at  $1240\text{ cm}^{-1}$ . The second bending vibration is probably superimposed on  $\text{CH}_2$  group vibrations at  $1200\text{ cm}^{-1}$ . The rocking vibrations of the  $-\text{CH}$  group appear at  $1080\text{ cm}^{-1}$ .

The terpolymer is characterized by the occurrence of additional bands of the functional groups  $\text{CH}_3$  and  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$  and sulfonate groups. Covalent sulfonate groups appear in the  $1420\text{--}1330$  and  $1200\text{--}1145\text{ cm}^{-1}$  regions (Figs. 8 and 9).

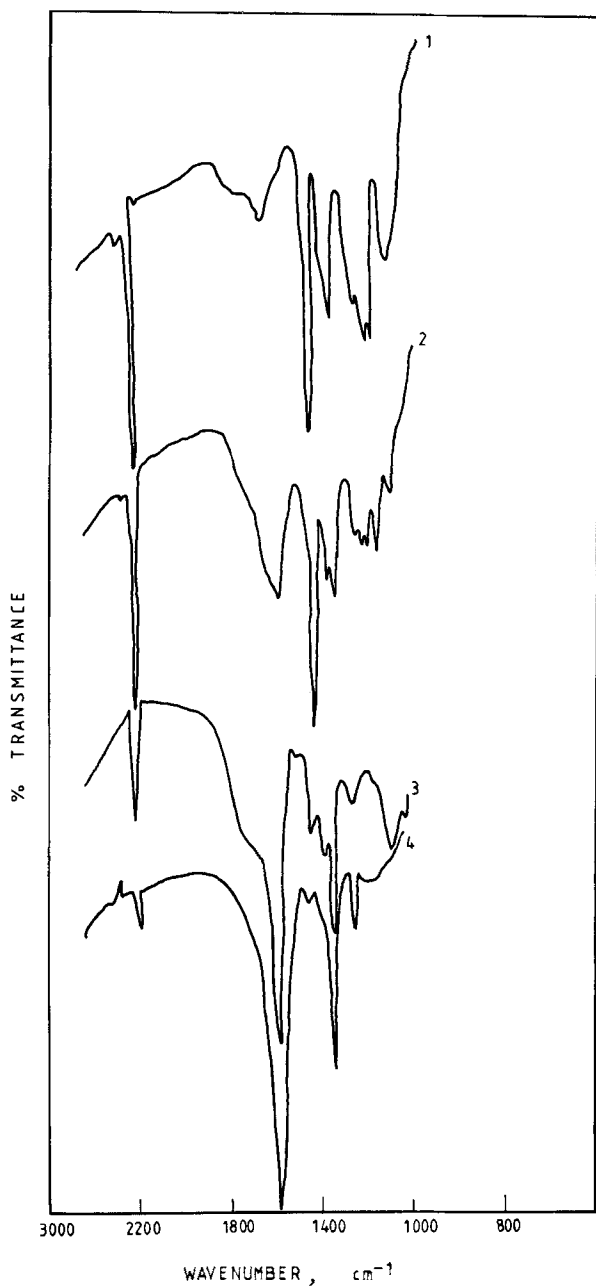


FIG. 6. Infrared absorption of by-products of alkaline saponification of polyacrylonitrile: (1) untreated, (2) 30, (3) 60, and (4) 180 min hydrolysis.

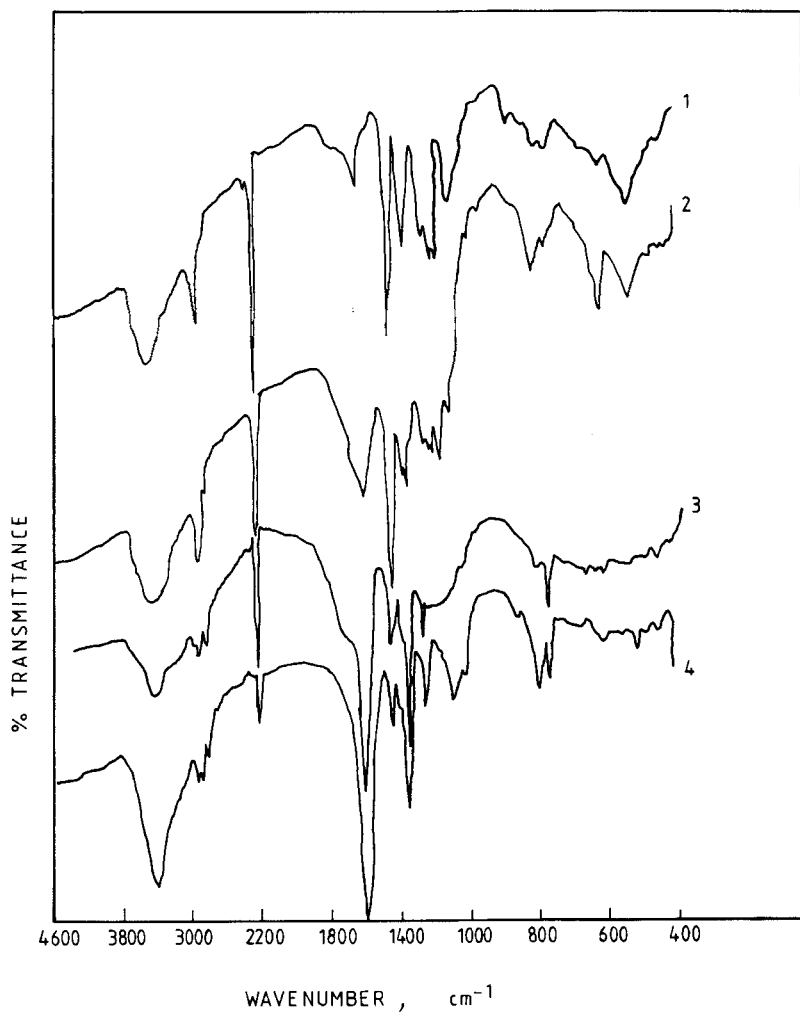


FIG. 7. Infrared absorption of by-products of alkaline saponification of polyacrylonitrile: (1) untreated, (2) 30, (3) 60, and (4) 180 min hydrolysis.

TABLE 5. Characteristic Frequencies of Polyacrylonitrile and Its Saponified Product

Polymer	Frequency	Assignment
PAN	660(s)	$\nu$ (C-S) vibrations
	1420-1330(s) and 1200-1145	Vibrations due to sulfonate end groups
	1440-1350(s) and 1230-1150(s)	Vibrations due to sulfate end groups
	1080(m)	Valency vibration of (C-C) bond
	1245(m)	Deformation vibrations of CH <sub>2</sub> groups
	1258(m)	Twisting and scissors vibration of CH <sub>2</sub> groups
	1365(m)	CH <sub>2</sub> vibrations of methyl groups
	1460(m)	Scissoring deformation vibrations of CH <sub>2</sub> groups
	2242(m)	Symmetrical valency vibrations of C=N group
	2840(w)	Symmetrical valency vibrations of CH <sub>2</sub> group
	2960, 2920(m)	Assymetrical valency vibrations of CH <sub>2</sub> group
Saponified product	1408-1416(m)	COOH valency vibration
	1590-1600(s)	Carboxylate ion absorption
	1680-1700(sh)	Amide groups absorption
	1740	Vibrations due to ester grouping
	1940(m)	Assymetrical valency vibrations of CH <sub>3</sub> groups
	3200, 3400, 3650	NH or OH stretching vibrations



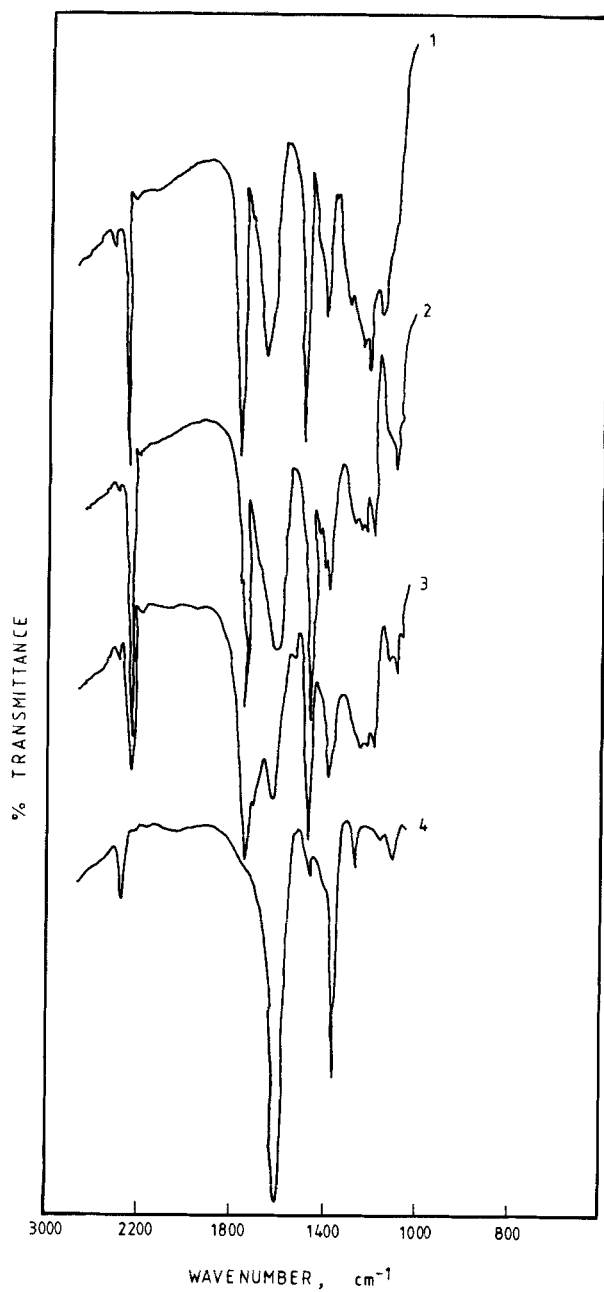


FIG. 8. Infrared absorption of by-products of alkaline saponification of acrylonitrile terpolymer: (1) untreated, (2) 30, (3) 60, and (4) 180 min hydrolysis.

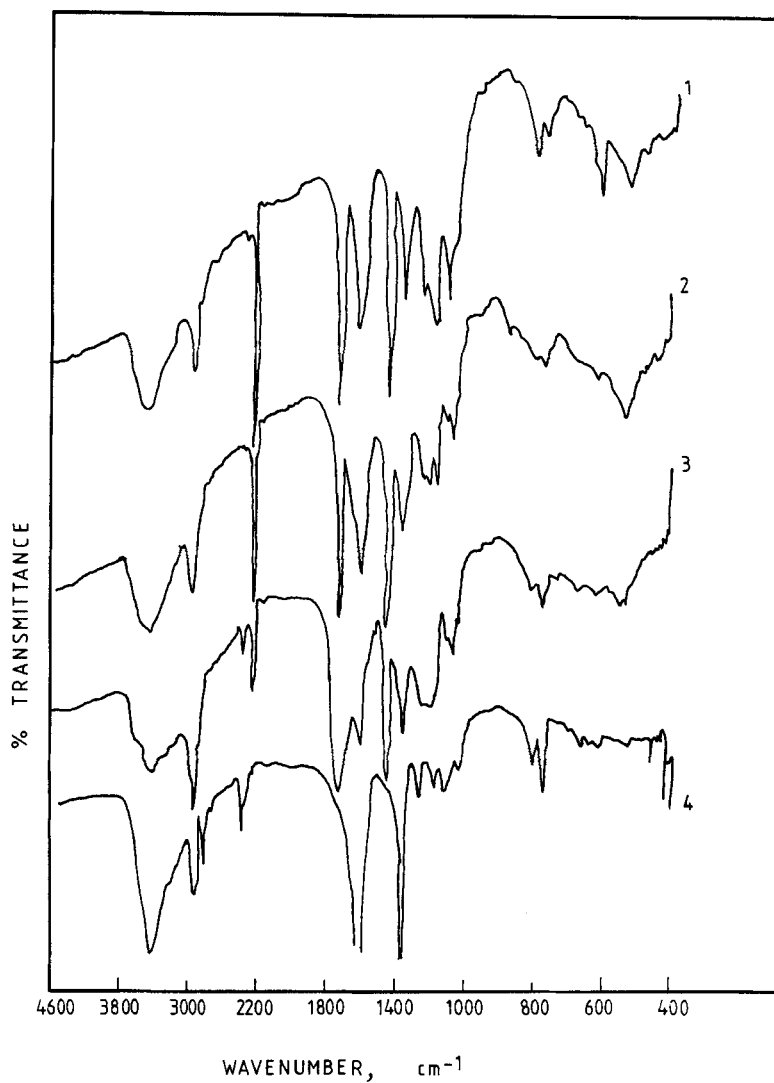


FIG. 9. Infrared absorption of by-products of alkaline saponification of acrylonitrile terpolymer: (1) untreated, (2) 30, (3) 60, and (4) 180 min hydrolysis.

Examination of the saponification products obtained after different time intervals show considerable changes in the IR spectra of the copolymer and homopolymer. The beginning of hydrolysis leads to color formation with a sharp increase in absorption in the region 1665-1700  $\text{cm}^{-1}$ .

The decrease of nitrogen content in the partially saponified terpolymer and homopolymer is related to a decrease in the number of nitrile groups during saponification, which is indicated by a decrease in intensity of the absorption band at 2245  $\text{cm}^{-1}$ . As indicated in Tables 6 and 7, the IR spectra of products isolated after saponification for 30-60 min (at S.I. = 0.5) of terpolymer still contain an intense 2245  $\text{cm}^{-1}$  absorption band, which disappears completely after 180 min. The saponification of polyacrylonitrile is slower and terminates in the equilibrium state with partial preservation of the CN groups.

The nitrogen fixed in the amide and imide groups was calculated from the difference between the Kjeldahl nitrogen and nitrile nitrogen (obtained from IR spectra). The results (Tables 6 and 7) show that in the first 30 min the nitrogen content of the saponification products almost coincides with nitrile nitrogen, thereby indicating the higher rate of saponification of nitrile groups to carboxyl groups without the formation of stable amide-imide groups. Stable imide-amide groups are formed in the second stage of the process, after which their propagation remains nearly constant.

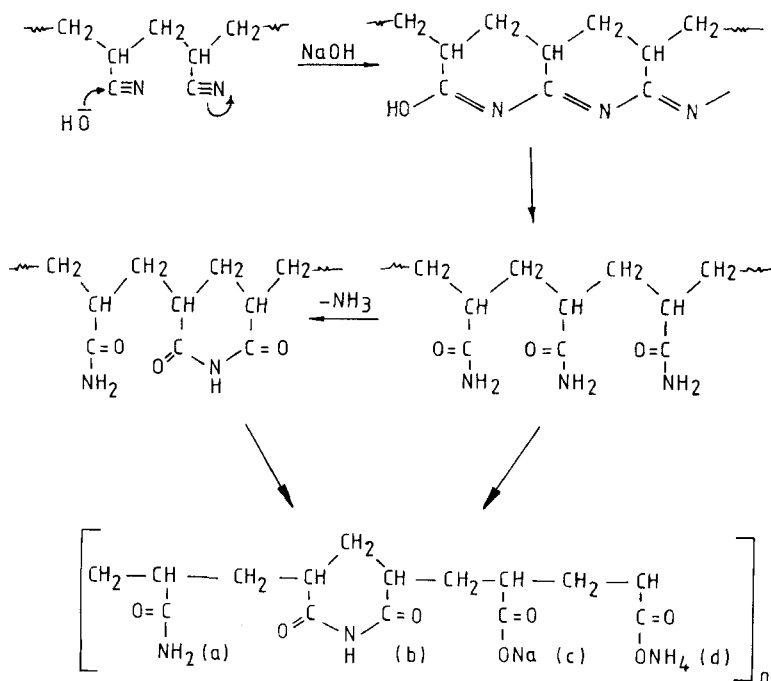


TABLE 6. Nitrogen Content of the Saponified Polyacrylonitrile with Saponification Time at S.I. = 0.5

Saponification time, min	Absorbance of CN band at 2245 $\text{cm}^{-1}$	% Nitrogen in products of saponification		
		Total nitrogen by Kjeldahls	Nitrile	Amide-imide
0	0.43	25.7	26.4	0
30	0.17	11.3	10.0	1.3
60	0.12	10.2	7.0	3.2
90	0.06	9.7	3.6	6.1
120	0.05	9.5	3.0	6.5
180	0.03	9.3	1.8	7.5
240	0.02	9.0	1.2	7.8

TABLE 7. Nitrogen Content of the Saponified Acrylic Terpolymer with Saponification Time at S.I. = 0.5

Saponification time, min	Absorbance of CN band at 2245 $\text{cm}^{-1}$	% Nitrogen in products of saponification		
		Total nitrogen by Kjeldahls	Nitrile	Amide-imide
0	0.40	24.1	23.0	0
30	0.12	7.4	7.0	0.4
60	0.11	6.5	6.4	0.1
90	0.02	5.9	1.2	5.0
120	0.01	5.5	0.6	4.0
180	0	5.2	0	5.2
240	0	5.2	0	5.2

A shoulder appears at  $1680\text{--}1700\text{ cm}^{-1}$  due to the amide group. It slowly disappears as the conversion from amide to carboxylic group proceeds. The increase in the carboxylate group content in the saponified samples is accompanied by a strong increase in the intensity of the  $1590\text{--}1000\text{ cm}^{-1}$  absorption band attributed to the formation of carboxylate groups ( $-\text{COONa}$ ). The N-H bending vibration is overlapped in the same region.

A shoulder at  $1416\text{ cm}^{-1}$  indicates the formation of a band which increases in intensity with the time of hydrolysis and after 90 min becomes a sharp band. This band is probably due to the valency vibra-

tions of the  $\overset{\text{O}}{\parallel}\text{C}-\text{O}^-$  group. The broad band appearing in the  $3200\text{--}3600\text{ cm}^{-1}$  region is due to the NH and OH groups stretching vibrations.

In conclusion, the accelerated rate of saponification of the terpolymer may be attributed to the presence of  $-\text{COOCH}_3$  and  $-\text{CH}_2\text{SO}_2^- \text{Na}^+$  side groups, which perhaps lower the packing density of the terpolymer, thereby facilitating the attack of a nucleophile.

#### ACKNOWLEDGMENT

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