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Kinetics of Hydrolysis, Acetylation, and Deamination Reactions on Polyamide Fibers in Heterogeneous Medium

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Synopsis

The kinetics of reactions, namely, hydrolysis, acetylation, and deamination, on polyamide fibers has been studied at different temperatures. Rate constants and apparent activation energies of these reactions were determined. All the three reactions studied show two rates, the initial fast rate, followed by the slow one. The existence of two rates has been explained on the basis of two-phase structure of the polyamide fibers, the fast rate corresponding to the weakly hydrogen-bonded regions and the slow rate corresponding to the regions which are strongly hydrogen bonded in the regular fashion. For hydrolysis, the fast rate was 38 times faster than the slow one, while the fast rate of acetylation reaction was about 162 times that of the slow rate. The ratio between the fast and slow rates was constant at all the temperatures studied in case of the hydrolysis and acetylation reactions. This ratio, however, was found to be extremely temperature sensitive for the deamination reaction. The hydrolysis and acetylation reactions were found to be strongly temperature dependent leading to the increase in the extent of modification with increase in temperature. Deamination, on the other hand, showed negative temperature dependence giving progressive decrease in the modification with increase in temperature. All the three modifications studied observed first-order kinetics. The apparent activation energy for hydrolysis was 1.38 and 1.05 kcal/mole corresponding to the fast and slow rates, respectively. The apparent activation energy values for acetylation were 2.53 and 3.29 kcal/mole, while those for deamination reaction were −8.28 and −46.0 kcal/mole, respectively. The apparent activation energy values for the deamination reaction bore negative signs possibly because of the negative temperature dependence of this reaction. The apparent activation energy for slow reactions in case of acetylation and deamination was found to be higher than that of the fast rate, while the reverse was true in case of hydrolysis, showing that the acetylation and deamination reactions, being the chemical modification of polyamide fibers at the —NH_2 groups, proceed by altogether different mechanisms than the hydrolytic breakdown of the polyamide linkage.

INTRODUCTION

A variety of problems are associated with synthetic polymeric textile fibers owing to the hydrophobic character of the polymer surfaces. Desired properties could be, however, imparted to these fibers through chemical modification of the polymer. Among the synthetic fibers, the polyamide fibers give perhaps a unique opportunity for such modifications through their polar groups, namely, —NH_2, —NHCO—, and —COOH. Surface static electricity can be reduced while hydrophilicity can be increased to impart many desired properties to the polyamide fibers. It is, therefore, of importance to study

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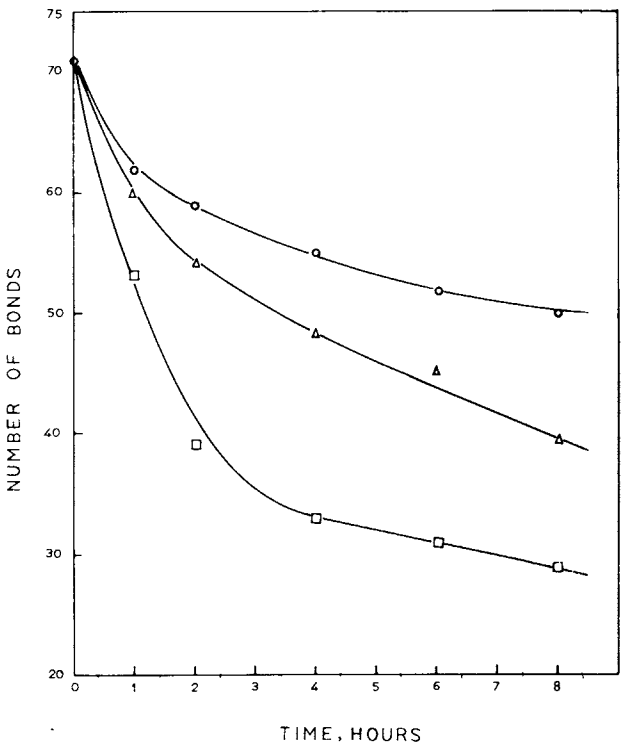

Fig. 1. Relation between number of bonds retained in fibers and time of hydrolysis at 40°C (○), 50°C (△), and 60° (□).

the course and reaction kinetics of important chemical modifications of the polyamide fibers.

Moncrieff[1,2] studied crosslinking reactions of cyanuric chloride and semicarbazide with polyamide fibers and observed that the crosslinked fibers possessed greater thermal stability. McCreath[3] also observed similar behavior of formaldelyde-treated polyamide fibers. Heat bending, wrinkle resistance, and pleat retention properties were imparted to polyamide fiber fabrics by crosslinking reaction with N-methylolacrylamide–hypophosphorus acid solution.[4] Hornuff and Jaensch[5] observed that benzoylation brought about remarkable changes in the fiber properties such as better dimensional stability and improved dyeability and resistivity. Hashimoto[6,7] reported that acetylation of end-amino groups of polyamide fibers increased the light stability and that the rate of acetylation was proportional to the amount of residual end-amino groups.

Lokhande, Androsov, and Golovanov[8] studied the changes in zeta potential and isoelectric point of partially acetylated polyamide fibers and observed that the isoelectric point of the polyamide fibers was shifted to the lower pH values. Hydrolyzed and deaminated polyamide fibers were also investigated with respect to the influence of structural changes on zeta potential, isoelectric point, and dyeability of the polyamide fibers. Hydrolytic degradation of polyamide fibers in mineral acids was studied by Bossert et al.[9] and Kyuchi and Tamotsu.[10] Pakshver and Mankash[11] reported that the rate of hydroly-

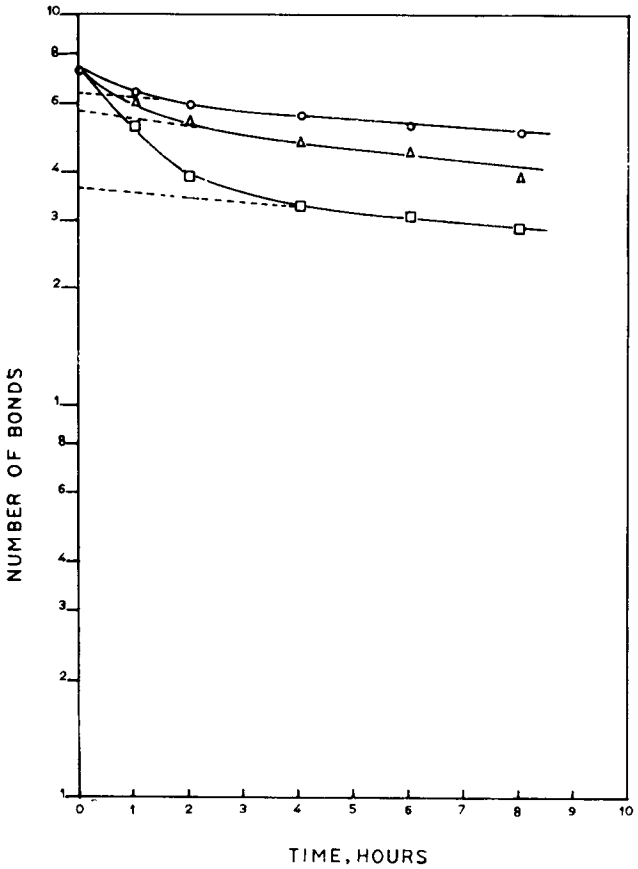

Fig. 2. Logarithmic plot of number of bonds retained in fibers vs. time of hydrolysis at 40°C (○), 50°C (△), and 60°C (□).

sis was determined by diffusion and concluded that the polyamide fibers did not possess a polyphase structure. Liquori and Mele[12] studied the kinetics of hydrolytic rupture of the amide linkage and observed that the fission takes place independently of the location of the bonds in the chain and follows first-order kinetics. Thus, the authors observed only one rate throughout the progress of hydrolysis. Rusznak and Lepenye[13] in their kinetic study of hydrolysis of linear polyamides suggested that the process may be described by a kinetic equation valid for gaseous reaction on solid surface. Recently, Zosin, Savitskii, and Utevskii[14] determined the activation energy of chain scission in various aromatic polyamide fibers before and after annealing treatment and observed that such a treatment increased the level of activation energy in case of individual type of fibers.

Literature survey with respect to the chemical modification of the fibers shows that, although various types of chemical modification reactions have been effected in the heterogeneous medium[1–14] with a view to impart particular desired properties to the polyamide fibers, very little work seems to have been carried out on the reaction kinetics of important chemical reactions and practically no work is reported in the homogeneous medium. This paper re-

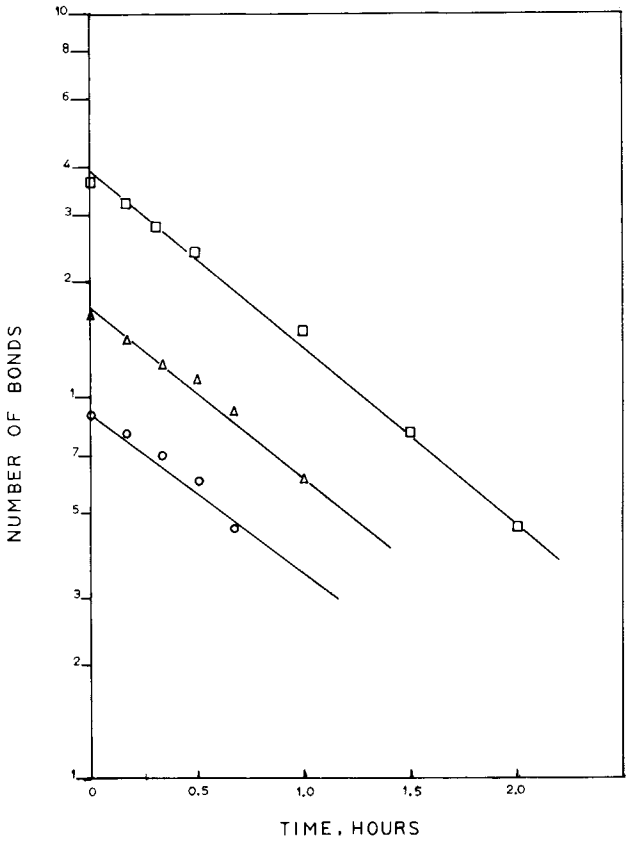

Fig. 3. Rate curves for fast hydrolytic reaction at 40°C (○), 50°C (△), and 60°C (□).

ports a systematic study of reaction kinetics of hydrolysis, acetylation, and deamination reactions on polyamide fibers in the heterogeneous medium.

EXPERIMENTAL

Materials. Nylon 6 fibers in the form of yarn (denier 12/1, type semidull) kindly supplied by The Century Enka (India) Ltd. were used in the present investigation after refluxing in carbon tetrachloride for 6 hr. All the chemicals used in the present work, viz., hydrochloric acid, glacial acetic acid, acetic anhydride, sodium acetate, sodium nitrite, and phenol, were of Analar (pure) grade. Benzene, benzyl alcohol, and methanol, also used in the present investigation, were of c.p. grade. These were distilled carefully before use.

Hydrolysis. About 2 g polyamide fibers was taken in a quick-fit flask mounted in a thermostatically controlled bath to which 100 ml of 5% hydrochloric acid solution was added. The reaction was carried out at different temperatures (40°, 50°, and 60°C) for varying periods of time (0–4 hr). The flask was shaken intermittently. For each sample the total end-amino groups[15] and the total carboxyl content[16] were estimated. Molecular weights of the samples taken out at different times were calculated from the end-group data.

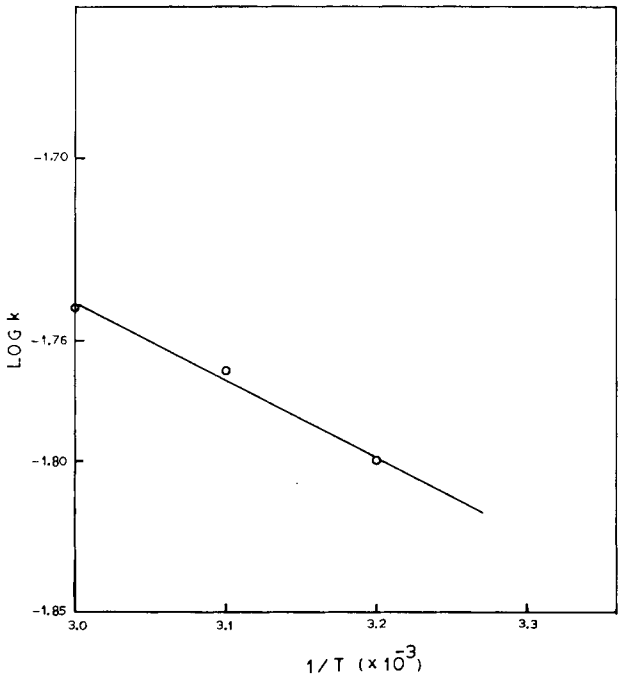

Fig. 4. Apparent activation energy E of fast hydrolytic reaction.

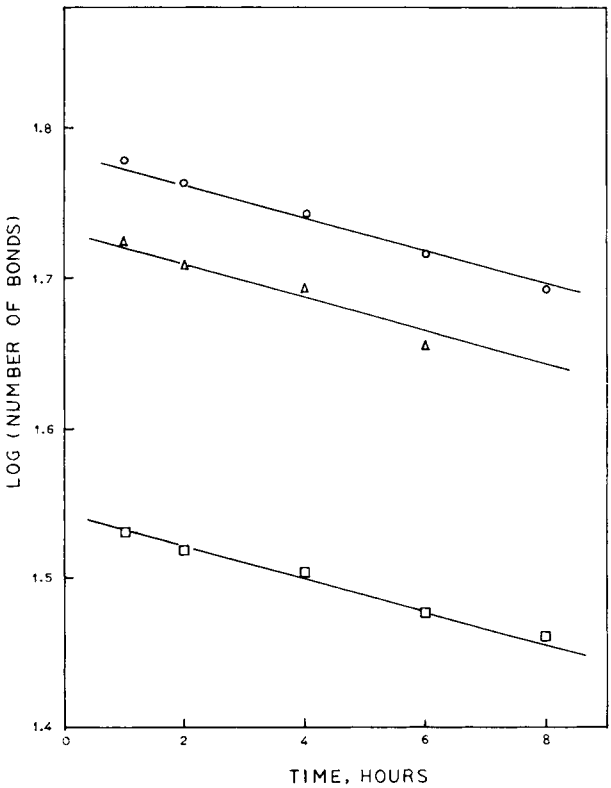

Fig. 5. Rate curves for slow hydrolytic reaction at 40°C (○), 50°C (△), and 60°C (□).

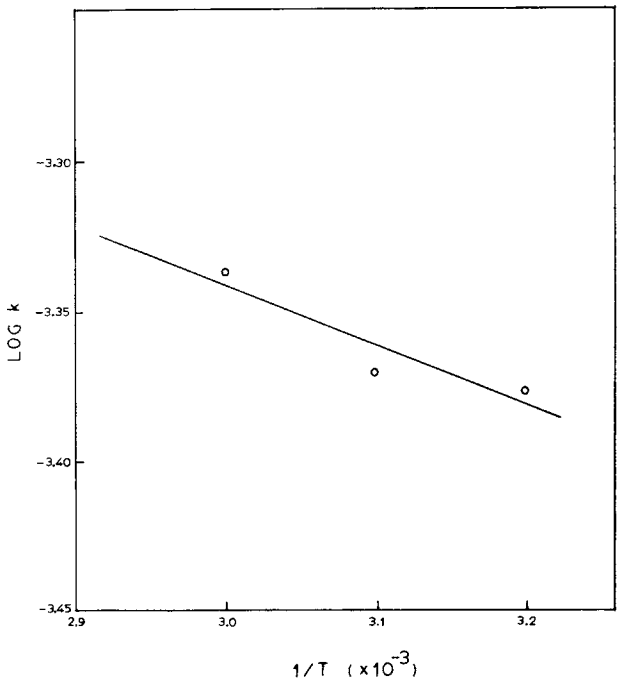

Fig. 6. Apparent activation energy E of slow hydrolytic reaction.

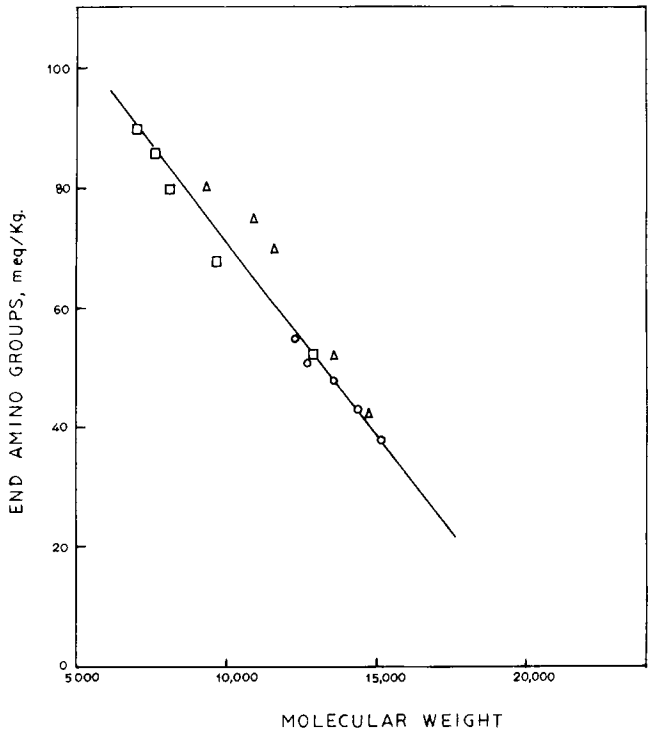

Fig. 7. Correlation between molecular weight and end-amino groups of polyamide fibers hydrolyzed at 40°C (○), 50°C (△), and 60°C (□).

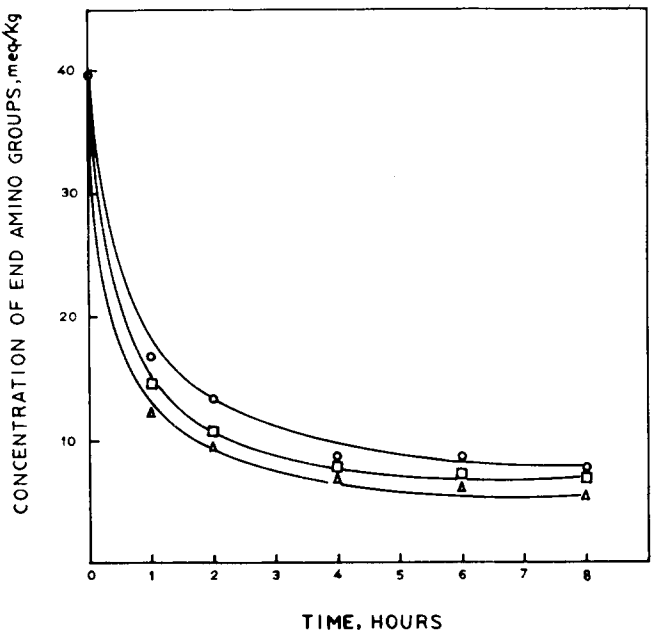

Fig. 8. Relation between number of end-amino groups retained in fiber and time of acetylation at 40°C (○), 60°C (□), and 70°C (△).

Acetylation. About 2 g nylon fibers was acetylated by the method of Peters.[17] The reaction was carried out at different temperatures (40°, 60°, and 70°C) for various time (0–8 hr). The flask was shaken occasionally. The residual end-amino groups were determined by Moore's method.[15]

Deamination. About 2 g polyamide fibers was taken in a conical flask and 100 ml glacial acetic acid and 16 g sodium acetate were mixed thoroughly with the fibers. Then 100 ml precooled 2% sodium nitrite solution was added to the flask. The flask was kept in an ice bath and was shaken frequently. The reaction was carried out at different temperatures (viz., −5°, 0°, +10°, and +20°C) for varying periods of time (0–2 hr). The samples taken out at different periods of time were washed thoroughly with distilled water till free from acid. The residual end-amino groups of the samples were estimated by Moor's method.[15]

RESULTS AND DISCUSSION

The polyamide chains are built up by the polypeptide linkages; and when two such chains run parallel to each other, they are in a position to have hydrogen bond formation between >NH of one chain and the >CO of the adjacent chain. It is possible, therefore, that the concentration of such hydrogen bonds may be very high at some places while such regular type of hydrogen bonds may be almost absent in some other regions in the fiber structure. This gives rise to at least a two-phase structure of the polyamide fibers. In fact, like any other textile fiber containing polar groups, the polyamide fibers may have a polyphase structure. Results in the literature, so far, seem to be contrary to this concept.[11,12]

In the present investigation, activation energies of hydrolysis, acetylation, and deamination of polyamide fibers in heterogeneous medium have been determined. In view of the complex nature of these reactions and also the complexity involved in the dependence of rates from temperature, the activation energy of a reaction has been termed the apparent activation energy.

Results of the present investigation on hydrolytic degradation of polyamide fibers have been plotted in Figures 1–7. Figures 1 and 2 indicate that the hydrolytic attack at a given temperature is very fast in the beginning which

TABLE I
Various Characteristics of Modified Polyamide Fibers

Temperature, °C	Time, hr	Molecular Weight	End-amino groups, meq/kg
	Hydrolysis		
	0	17,390	32.00
	1	15,200	38.00
	2	14,420	43.00
40	4	13,530	48.00
	6	12,730	51.00
	8	12,260	55.00
	0	17,390	32.00
	1	14,690	42.00
	2	13,360	52.00
50	4	11,627	70.00
	6	10,920	75.00
	8	9,385	80.00
	0	17,390	32.00
	1	12,820	52.00
60	2	9,731	68.00
	4	8,117	80.00
	6	7,668	86.00
	8	7,004	90.00
	Acetylation		
	0		32.00
	1		16.72
40	2	—	13.20
	4		8.80
	6		8.80
	8		7.92
	0		32.00
	1		14.52
	2		10.56
60	4	—	7.92
	6		7.04
	8		7.04
	0		32.00
	1		12.32
	2		9.68
70	4	—	7.04
	6		6.16
	8		5.28

(*continued*)

TABLE I (*continued*)

Temperature, °C	Time, hr	Molecular Weight	End-amino groups, meq/kg
	Deamination		
	0		32.00
	0.16		22.00
	0.5	—	13.20
—5	1		12.10
	2		8.80
	4		6.60
	0		32.00
	0.16		28.16
	0.5		22.00
0	1	—	13.64
	2		11.44
	4		10.56
	0		32.00
	0.16		29.92
	0.5		26.40
+10	1	—	22.00
	2		18.48
	4		17.60
	0		32.00
	0.16		31.68
	0.5		30.80
+20	1	—	29.92
	2		26.40
	4		22.00

TABLE II
Rate Constants and Apparent Activation Energy Values for Various Modifications of Polyamide Fibers

Reaction	Temperature °C	Rate constants k, $min^{-1} \times 10^{-2}$			Apparent activation energy E, kcal/mole	
		k(fast)	k(slow)	k(fast)/k(slow)	E(fast)	E(slow)
	40	1.6	0.0420	38		
Hydrolysis	50	1.7	0.0426	39	1.38	1.05
	60	1.8	0.0460	37		
	40	1.38	0.0085	162		
Acetylation	60	1.73	0.0107	162	2.53	3.29
	70	2.0	0.0120	160		
	−5	4.060	0.1400	29		
	0	3.422	0.0300	114		
Deamination	+10	2.33	0.0019	1160	−8.28	−46.0
	+20	1.26	—	∞		

slows down to a considerable extent as the reaction proceeds. It can also be seen that the hydrolytic reaction on polyamide fibers is strongly temperature dependent. This is also evident from the data on molecular weight and end-amino groups tabulated in Table I, in which the molecular weight decreased

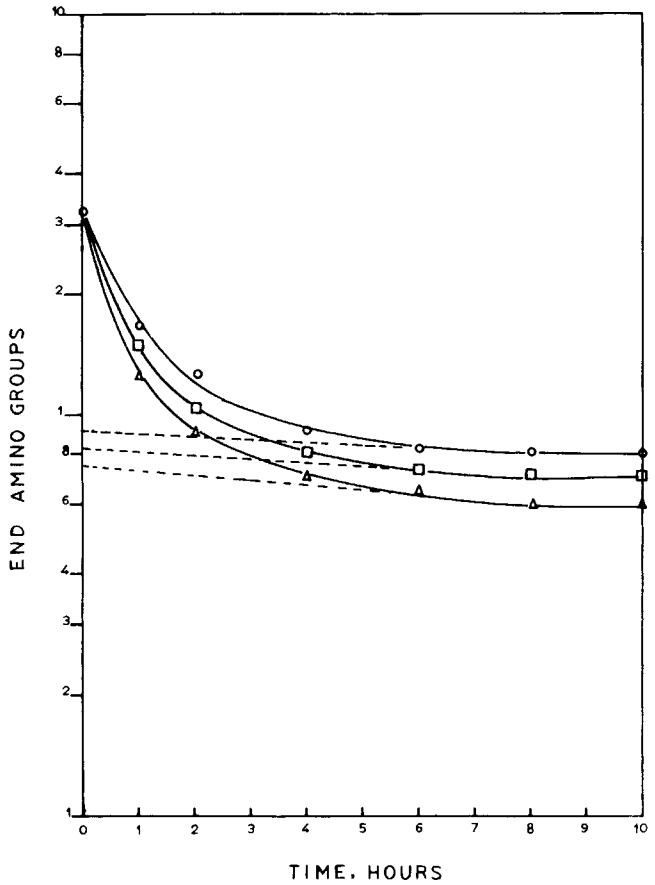

Fig. 9. Logarithmic plot of number of end-amino groups retained in fibers vs. time of acetylation at 40°C (○), 60°C (□), and 70°C (△).

while the amount of end-amino groups increased with progress of the hydrolytic action on the polyamide fibers. Figure 2 gives the plot of log (number of bonds) versus time of hydrolysis. It can be seen from this figure that two distinct rates exist. Figures 3 and 5 give the logarithmic plots of the two rates, and in both the cases a linear relationship is obtained, showing that the hydrolysis of the polyamide fibers in the presence of hydrochloric acid observes first-order kinetics. Rate constants in both the cases have been determined and are shown in Table II. It seems that the initial fast attack is almost 38 times faster than the slow rate. It is interesting to note that the ratio between the fast and the slow rates is independent of the temperature of hydrolytic reaction.

The apparent activation energy of hydrolytic reaction is 1.55 kcal/mole when the attack is governed by the fast rate, while its value is 1.05 kcal/mole in case of the slow attack. Although the rate constant values of the fast and slow attacks differ to a very great extent, the corresponding values for the apparent activation energy representing these two rates are quite comparable, which goes to show that the mechanism of chain scission during hydrolysis is one and the same throughout the reaction, while, on the other hand, the ease

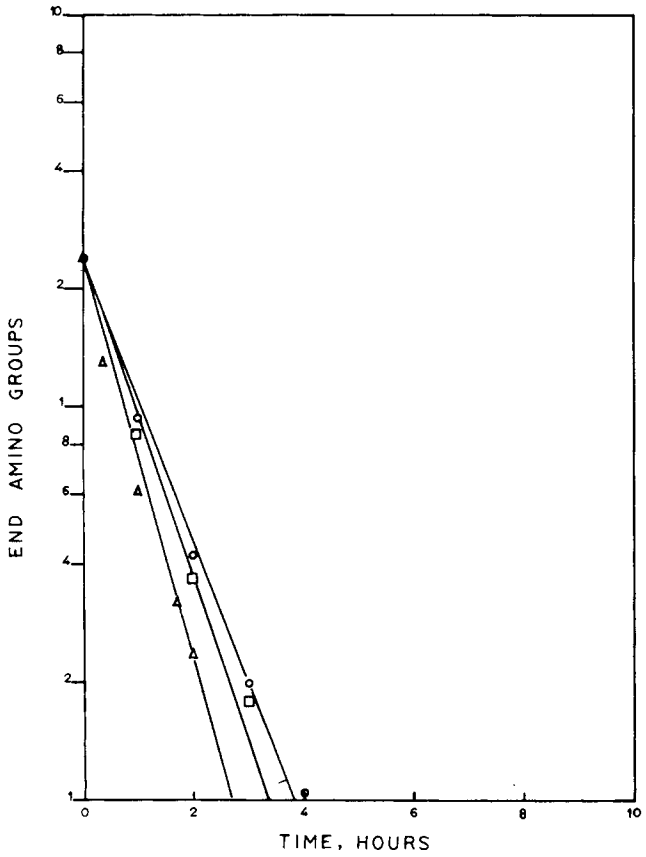

Fig. 10. Rate curves for fast acetylation reaction at 40°C (○), 60°C (□), and 70°C (△).

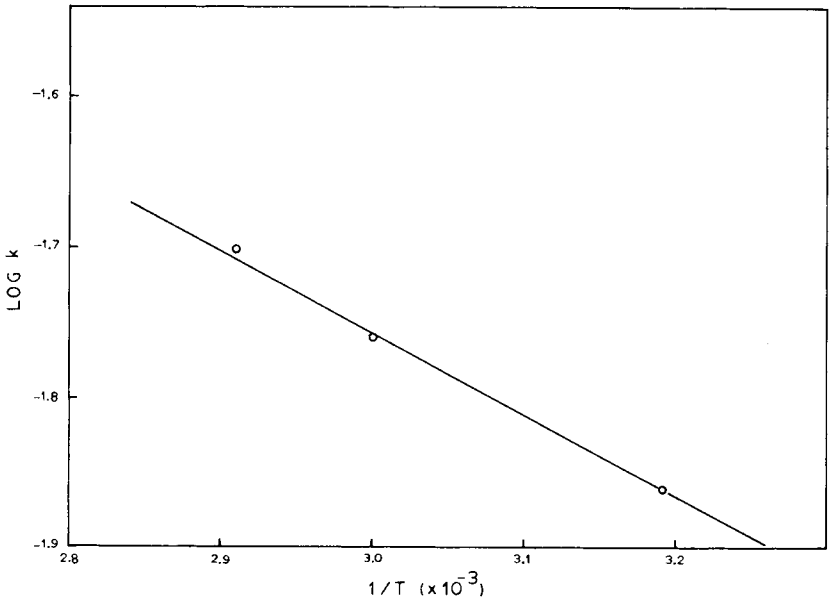

Fig. 11. Apparent activation energy E of fast acetylation reaction.

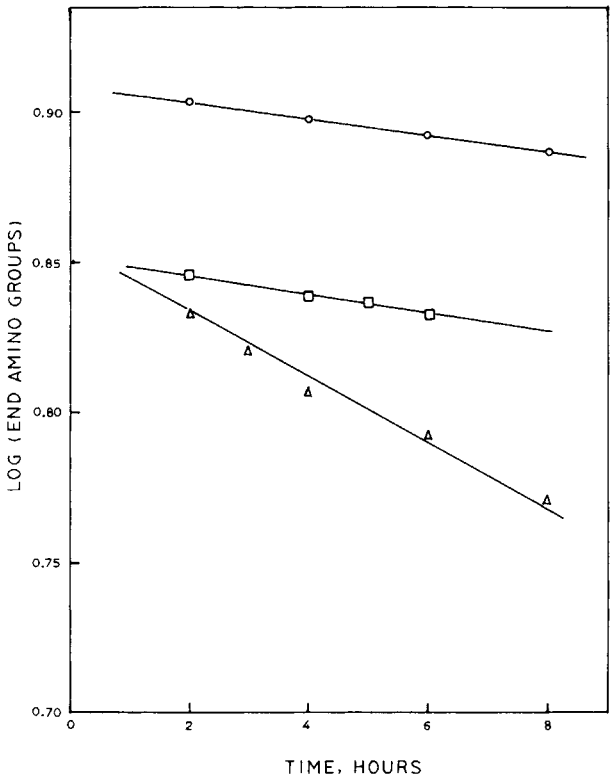

Fig. 12. Rate curves for slow acetylation reaction at 40°C (○), 60°C (□), and 70°C (△).

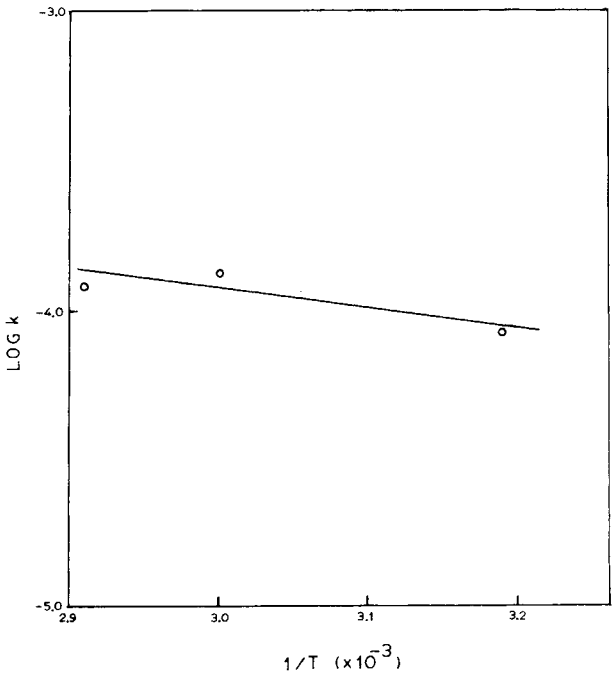

Fig. 13. Apparent activation energy E of slow acetylation reaction.

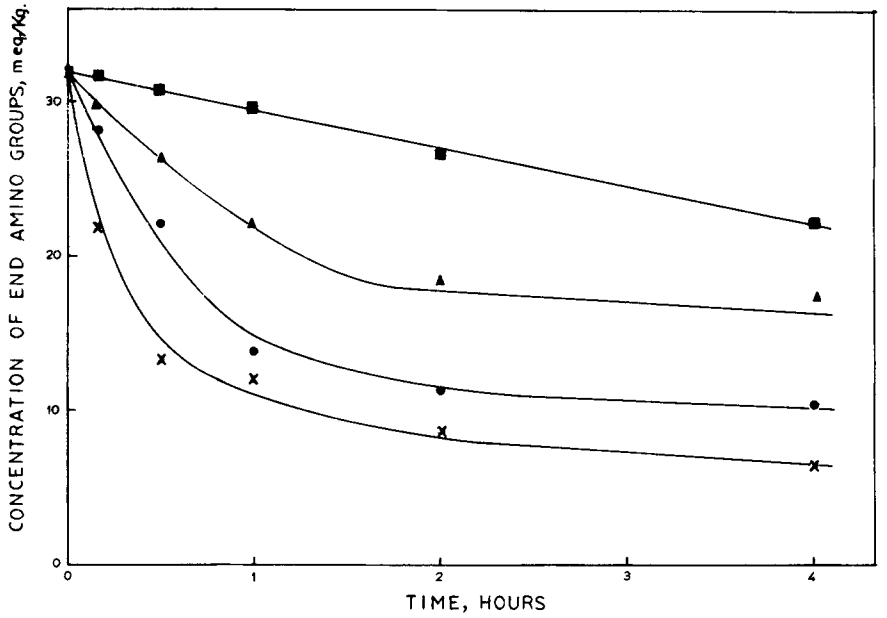

Fig. 14. Relation between number of residual end-amino groups and time of deamination reaction at −5°C (x), 0°C (●), +10°C (▲), and +20°C (■).

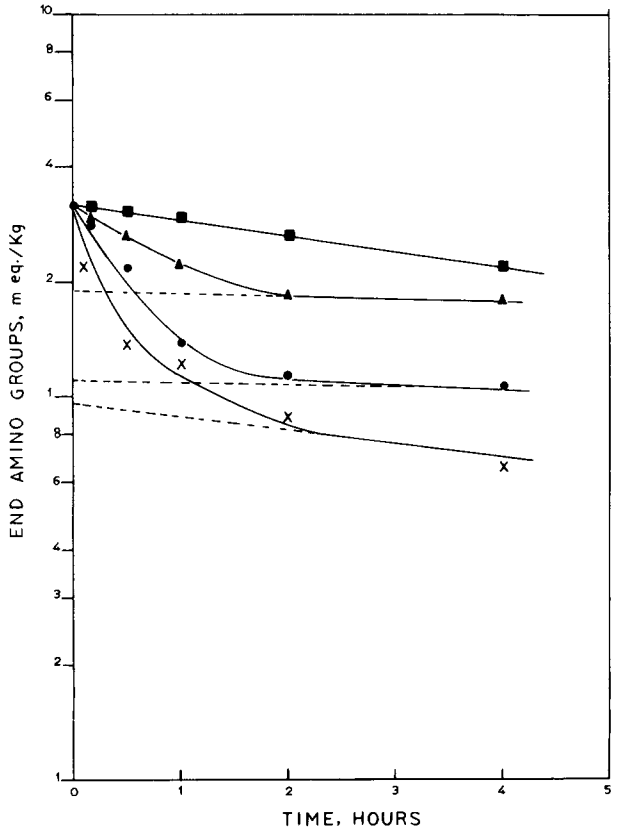

Fig. 15. Logarithmic plot of number of residual end-amino groups in fibers vs. time of deamination reaction at −5°C (x), 0°C (●), +10°C (▲), and +20°C (■).

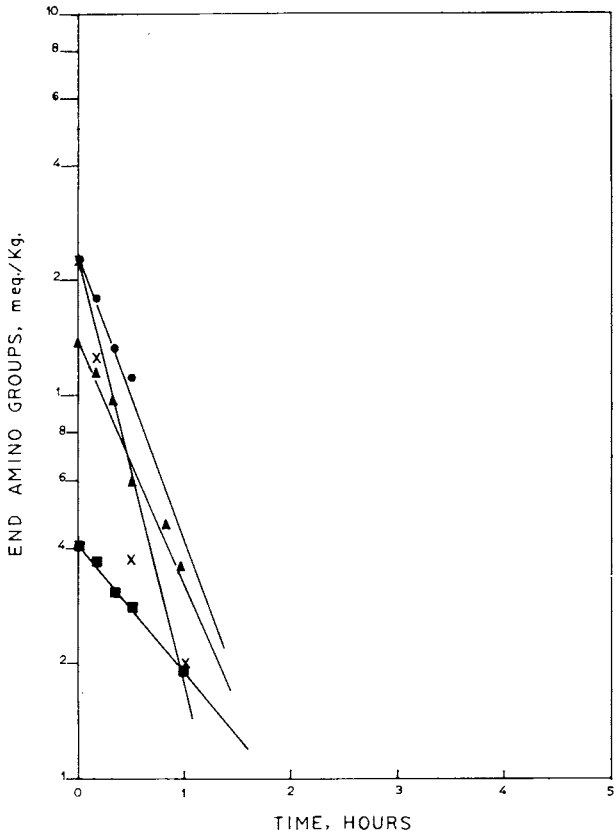

Fig. 16. Rate curves for fast deamination reaction at −5°C (x), 0°C (●), +10°C (▲), and +20°C (■).

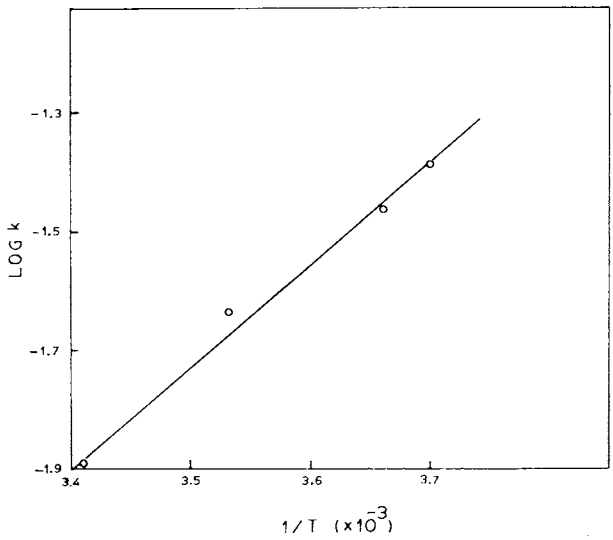

Fig. 17. Apparent activation energy E of fast deamination reaction.

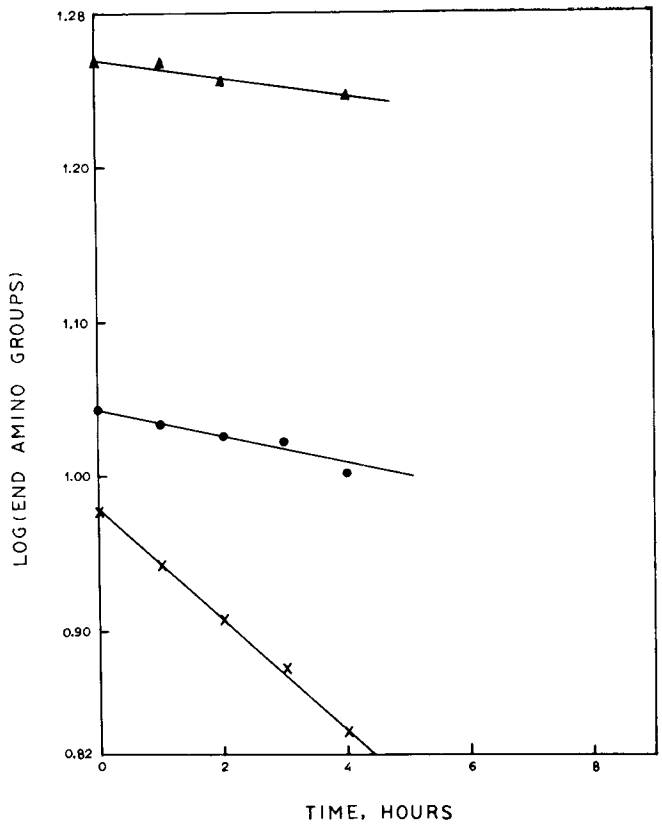

Fig. 18. Rate curves for slow deamination reaction at −5°C (x), 0°C (●), and +10°C (▲).

at which the acid molecules attack the polypeptide chain differs widely. This can be explained on the basis of the two-phase structure of polyamide fibers, and it is likely that initially the acid molecules bring about hydrolysis of the polyamide chains in the intercrystalline regions and also in the regions lying on the surface of crystallites. Since these regions happen to be less compact, the hydrolytic attack is fast in the beginning. Subsequently, it is slowed down as a result of an increased resistance to the entry of acid solution in the ordered regions. Consequently, the polyamide linkages contained in these regions are subjected to delayed attack, giving lower values of rate constants of hydrolysis.

Figure 7 gives the correlation between end-amino groups and molecular weight of the hydrolyzed polyamide fibers. These two parameters show a very good correlation giving a linear relationship. A common straight line is obtained passing through the points representing different temperatures of the hydrolytic reactions. This shows that the mechanism of hydrolysis is unaltered at the various temperatures studied, and the higher temperature has the influence of increasing the degree of hydrolysis.

Figures 8–13 give the results of kinetics of acetylation reaction of the polyamide fibers. Acetylation being chemical modification of the amino groups, their accessibility to the acetylating medium is of prime importance. The end-amino groups free from hydrogen bond formation and which are present

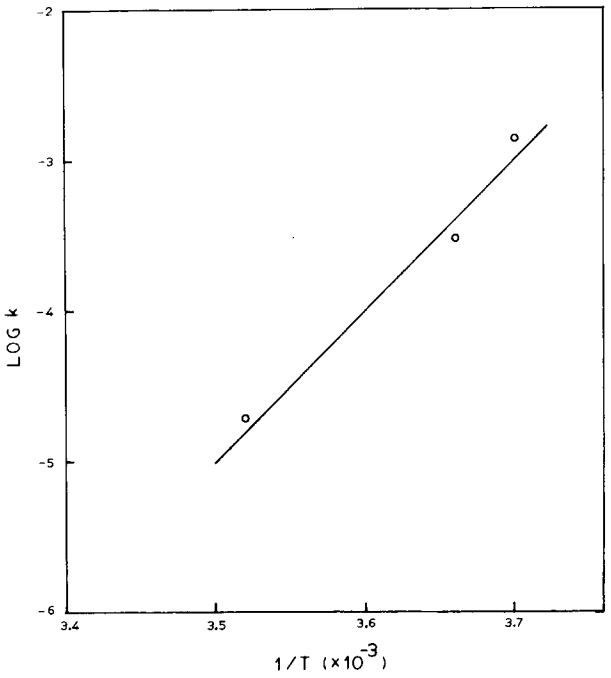

Fig. 19. Apparent activation energy E of slow deamination reaction.

in the amorphous regions may be acetylated readily. On the other hand, the amino groups which are strongly hydrogen bonded and are entrapped in the crystalline regions might remain unacetylated. Finally, the amino groups which may be present in the less ordered regions but may be hydrogen bonded in random fashion might be less readily acetylated requiring prolonged time of reaction. Figures 8 and 9 give the plots of end-amino group content of the unacetylated fibers versus time. It can be seen that initially the rate of acetylation is fast, followed by the slower rate. The extent of acetylation increases with the increase in temperature of the reaction. Figures 10 and 12 give the plots of log (end-amino groups) versus time for both the rates. In both cases, a linear relationship was obtained, showing that the acetylation reaction of polyamide fibers proceeds according to first-order kinetics.

Hashimoto[6,7] had also observed a similar trend, in which the rate of acetylation was proportional to the residual end-amino groups. The rate constants and other characteristics of the acetylated polyamide fibers are given in Table II. The ratio of the fast to slow rate constants is of the order of 162 which remains constant at all temperatures studied. The values for apparent activation energy corresponding to the fast and slow rates are 2.53 and 3.29 kcal/mole, respectively (Figs. 10 and 12). The higher activation energy for the slow rate seems to indicate that some of the crystalline portions are opened up during the acetylation reaction and the amino groups which are acetylated in this manner need additional energy to be supplied and hence a higher activation energy. Thus, the existence of two different rates of acetylation of the polyamide fibers shows that these fibers possess regions of vary-

ing accessibilities ranging from highly accessible regions to practically inaccessible ones.

Deamination of polyamide fibers is a highly exothermic and vigorous reaction, and therefore it was studied at much lower temperatures than the hydrolysis and acetylation reactions. Figures 14–19 give the various plots of deamination studies of the polyamide fibers at −5°, 0°, +10°, and +20°C. Figure 14 gives a plot of end-amino group content of the deaminated fibers versus time, while Figure 15 shows the same data on the logarithmic scale. These data indicate that initially deamination reaction proceeds rapidly, but slows down with further increase in the time of reaction at a given temperature, thus giving two rates at all temperatures of reaction studied except at a higher temperature of +20°C, at which the reaction proceeds throughout with one and the same rate. Figures 16 and 18 give the plots representing the rate curves for the fast and slow deamination reactions, respectively. The linear relationship obtained at both types of rate indicates that the deamination of polyamide fibers proceeds according to first-order kinetics.

As regards temperature dependence of the deamination reaction, it can be seen that there exists a negative temperature dependence, a fact which is opposite to that of the other two reactions studied, i.e., hydrolysis and acetylation. The deaminating species in the reaction mixture happen to be the nitrous acid formed *in situ* as a result of the reaction between sodium nitrite and acetic acid. Nitrous acid being unstable at higher temperatures, it decomposes at a very fast rate before it can be utilized for the deamination reaction of the polyamide fibers at such temperatures. This would result in lowering the efficiency of the deamination reaction as a whole and the slow reaction in particular. Lower temperatures, however, have exactly a reverse mechanism as a result of the stabilizing action on the deaminating species giving higher rates of deamination of the polyamide fibers. Rate constant values for both the fast and slow rates are given in Table II.

At lower temperatures, two rates are observed because of the two-phase structure of the polyamide fibers; while at the higher temperature, i.e., at 20°C, the two rates merge and give a single rate throughout the course of the reaction. It seems that due to the higher extent and rate of decomposition of nitrous acid, the concentration of deaminating species is lowered to such a level that it is able to deaminate only the easily accessible amino groups. Unlike the hydrolysis and the acetylation reactions, the strong dependence of the deamination reaction on the stability of nitrous acid can also be seen from the ratio of the rate constants of fast and slow reactions given in Table II. This ratio is extremely temperature sensitive and varies from about 30 at −5°C to 1160 at +10°C and reaches almost infinity at 20°C. Figures 17 and 19 give the values of apparent activation energy for the deamination reaction for the fast and slow rates, the values being −8.28 and −46.0 kcal/mole, respectively. The activation energy bears a negative sign possibly as a result of the negative temperature dependence of the deamination reaction. The activation energy data indicate that the deamination of the end-amino groups present in the accessible regions is comparatively easier than in cases of those present in the crystalline portions. It can also be concluded that considerable amount of decrystallization of the polyamide fibers is brought about during the reaction, followed by deamination of the amino groups thus set

free. This is evident from the amount of end-amino groups present in the deaminated samples given in Table I.

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