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

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Synopsis

Chemical reactions on polymers in homogeneous medium were used to characterize the structure of the macromolecules. The polymer was in the form of polyamide fibers dissolved in *m*-cresol to give a fairly highly concentrated solution (approximately 6%). Kinetic studies of hydrolysis, acetylation, and deamination reactions on the polyamide fibers were carried out in homogeneous medium at different temperatures. All the three reactions studied followed first-order kinetics. Rate constants and apparent activation energies were determined for these reactions, which show two rates—an initial fast rate followed by a slow one. A new microfibrillar model of the polymer dissolved in *m*-cresol is proposed, and the existence of two rates is explained on the basis of the two-phase structure of the proposed microfibril. The fast rate is attributed to the free chain segments, and the slow rate is shown to correspond to the regions which are strongly hydrogen bonded and which hold the various chains together to give the microfibrillar structure of the polymer in the homogeneous phase. The apparent activation energy for hydrolysis was 3.20 and 0.18 kcal/mole for the fast and slow rates, respectively. The apparent activation energy values for acetylation were 1.50 and 0.80 kcal/mole, while those for the apparent deamination reaction were 6.90 and 4.60 kcal/mole, respectively. Lower values of apparent activation energies are attributed to the ease of reaction in the difficult-to-penetrate regions of the microfibril due to the role played by the solvent of the homogeneous phase in carrying the reacting species inside these regions while simultaneously breaking the hydrogen bonds between the polypeptide chains. The apparent deamination reaction is shown to be a resultant reaction of simultaneous deamination and "amination" through hydrolytic breakdown of the polypeptide chain.

INTRODUCTION

In an earlier communication[1] results of kinetic studies of hydrolysis, acetylation, and deamination reactions on polyamide fibers in heterogeneous medium were reported. The study was extended to investigate these reactions on polyamide fibers in homogeneous medium. Such a study offers a unique availability of the molecular chain for reaction uniformly along the length of the polymer molecule. The solvent used for dissolving the polymer may also have its own influence on the chemical modification reactions.

Hydrolysis of the polypeptide linkage of the polyamide fibers in homogeneous medium has been studied by several workers.[2–8] The literature survey, however, indicates that there is hardly any work reported describing acetylation and deamination reactions on polyamide fibers in homogeneous medium. Similarly, no attempt has been made so far in the literature to study the internal structure of the polyamide fibers using chemical reactions in the homogeneous medium.

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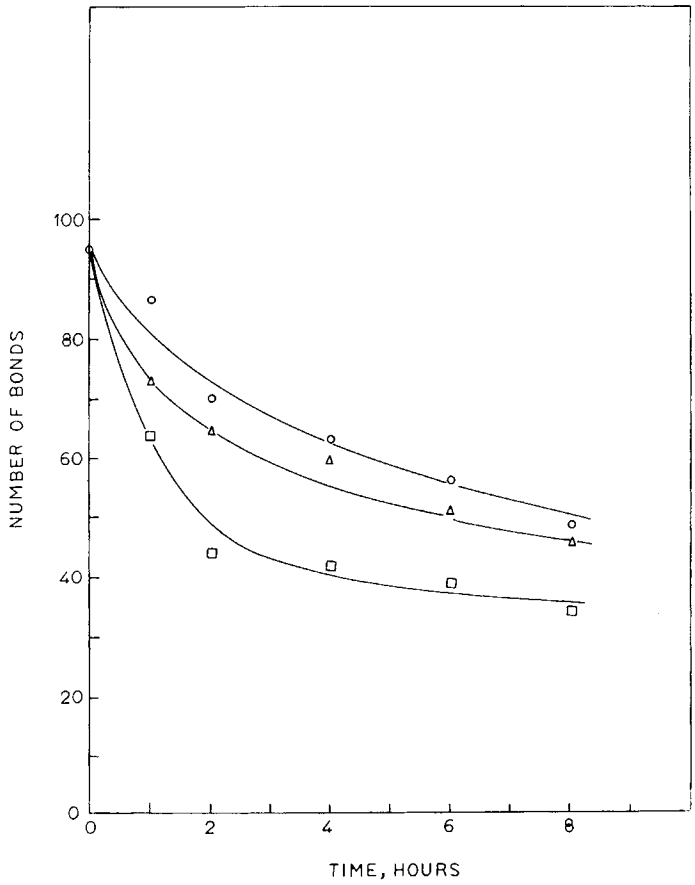

Fig. 1. Relation between number of bonds retained in the polymer and time of hydrolysis at 40°C (○), 50°C (△), and 60°C (□).

The present paper reports the results and interpretation of the kinetic studies of hydrolysis, acetylation, and deamination reactions of polyamide fibers dissolved in *m*-cresol.

EXPERIMENTAL

Materials

Nylon 6 fibers in the form of yarn (denier 12/1, type semidull) kindly supplied by 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 nitrate, and phenol, were of Analar (pure) grade. Acetone, ethyl alcohol, benzene, phenol, *m*-cresol, and methanol were of c.p. grade and were carefully distilled before use.

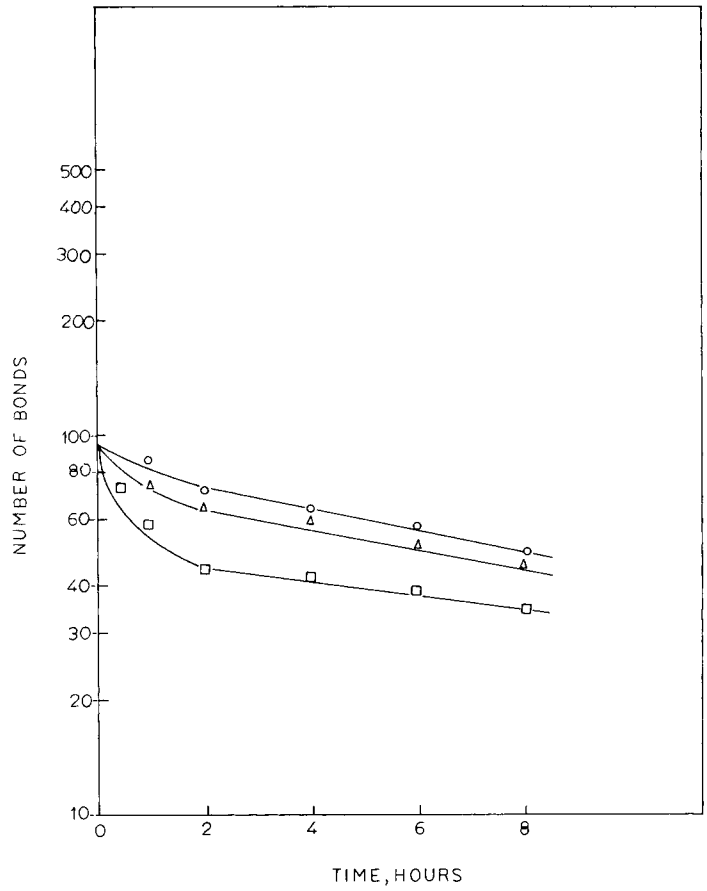

Fig. 2. Logarithmic plot of number of bonds retained in the polymer vs time of hydrolysis at 40°C (○), 50°C (△), and 60°C (□).

Dissolution of Polyamide Fibers

The polyamide fibers cut to an average length of about 2 cm were thoroughly dried over P_2O_5. About 2 g fiber was put in a conical flask containing 50 ml *m*-cresol at about 30°C. It was thoroughly mixed, and the flask was stoppered and kept overnight in order to give sufficient time for complete dissolution of the fibers. The polyamide solution in *m*-cresol was then used for the various chemical modification reactions.

Hydrolysis

The homogeneous mixture of the polyamide fiber was placed in a quick-fit flask and the reaction was carried out at different temperatures (40°, 50°, and 60°C) for varying periods of time (0–8 hr) in 5% HCl solution. The flask was shaken intermittently. The reaction mixture was withdrawn at different in-

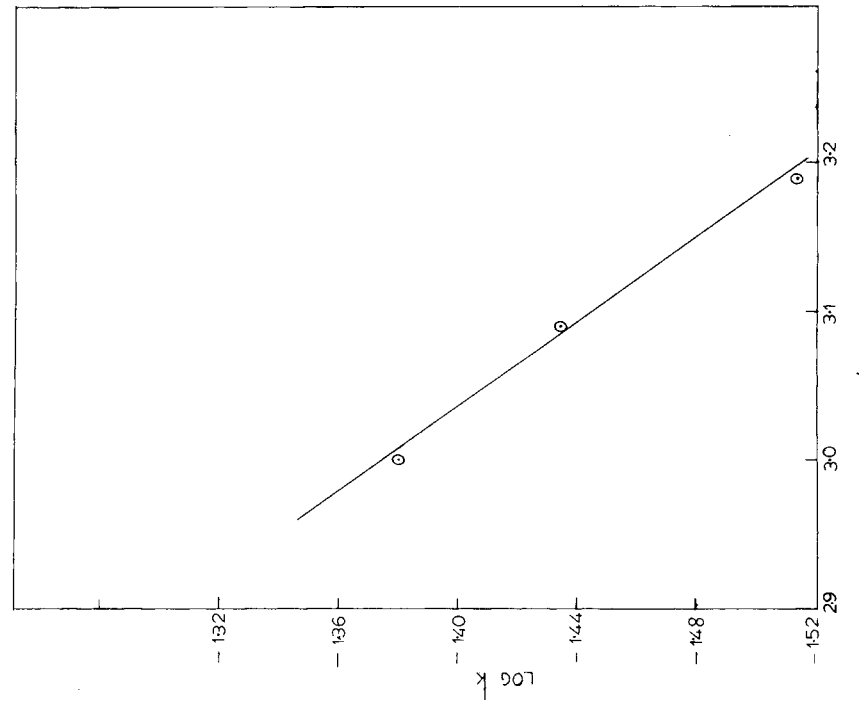

Fig. 4. Apparent activation energy E_{fast} of fast hydrolytic reaction.

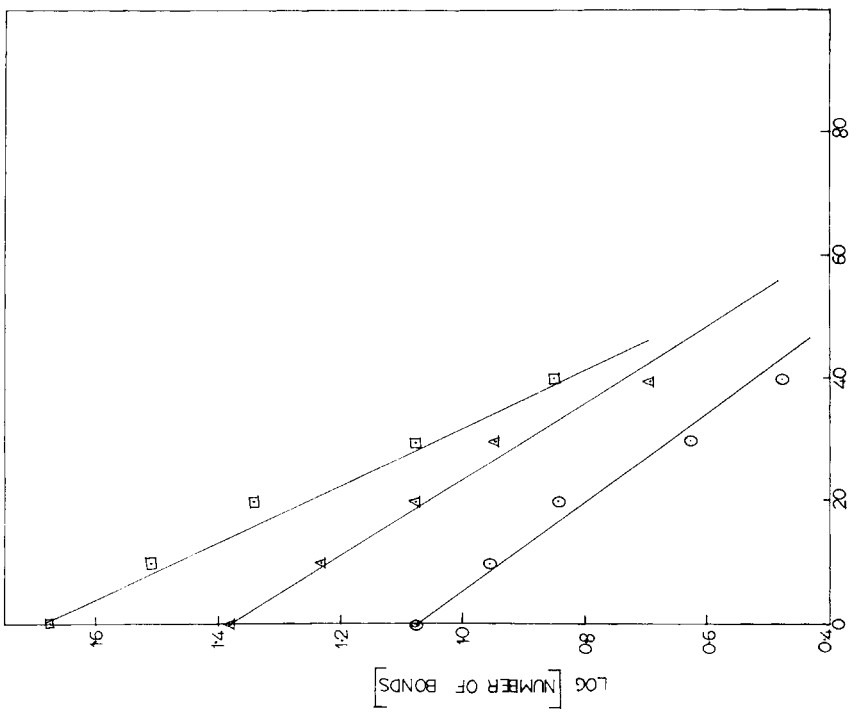

Fig. 3. Rate curves for fast hydrolytic reaction at 40°C (○), 50°C (△), and 60°C (□).

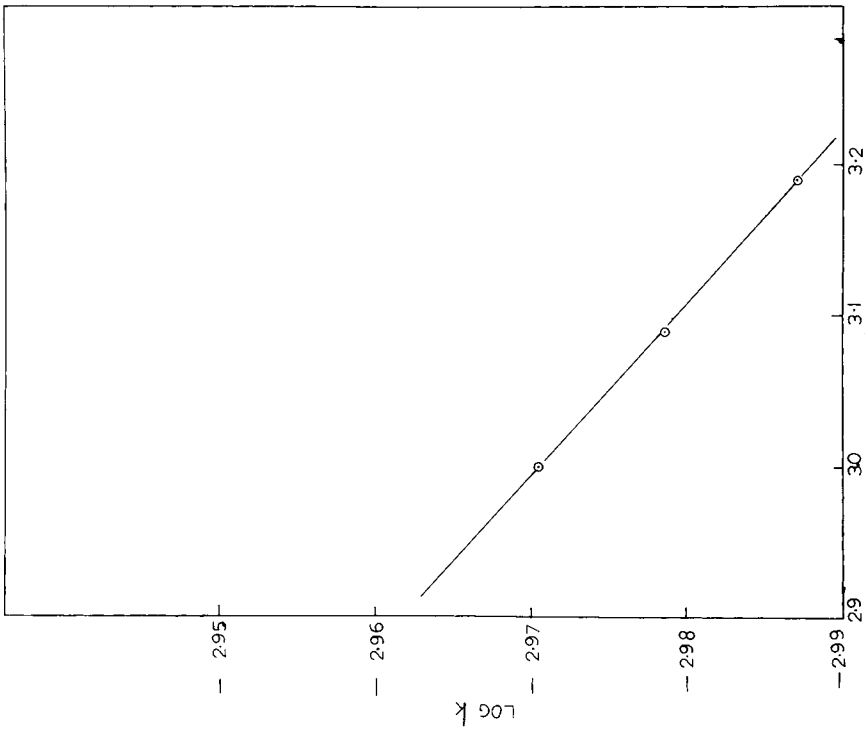

Fig. 6. Apparent activation energy E_{slow} of slow hydrolytic reaction.

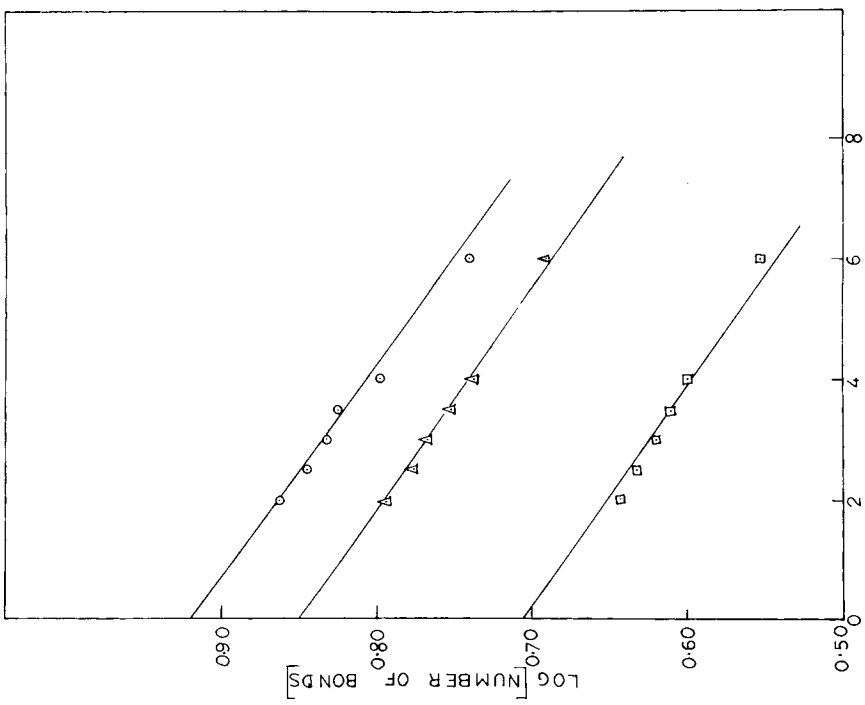

Fig. 5. Rate curves for slow hydrolytic reaction at 40°C (O), 50°C (Δ), and 60°C (□).

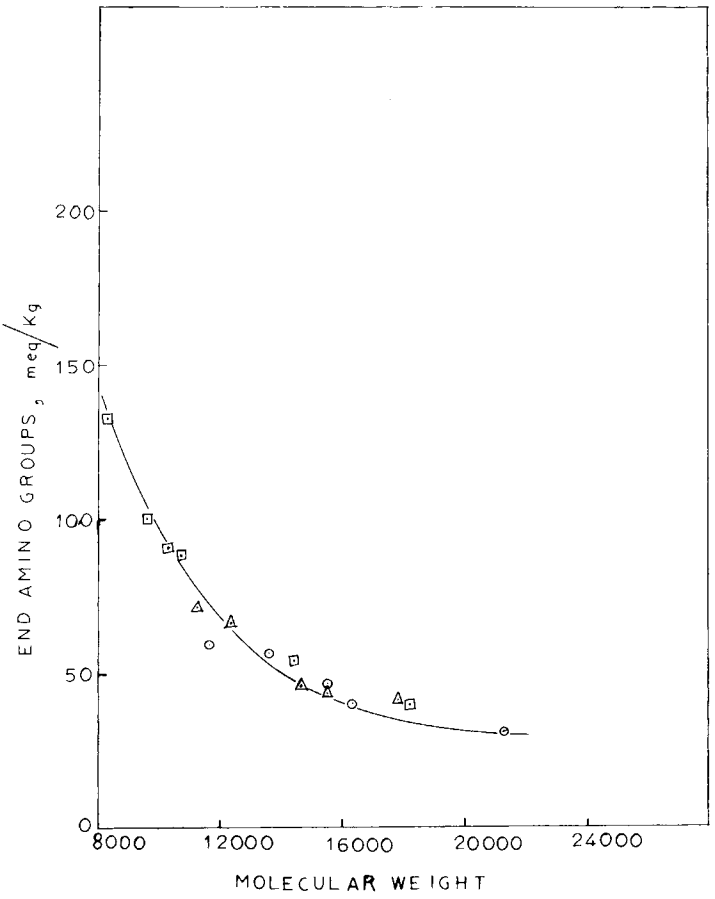

Fig. 7. Correlation between molecular weight and end amino groups of polymer hydrolyzed at 40°C (○), 50°C (△), and 60°C (□).

tervals and mixed with excess acetone. The polyamide fibers were precipitated as soon as the mixture was cooled to room temperature. The precipitate was filtered and washed thoroughly with 0.2 g/l. sodium carbonate solution and finally with distilled water until free from acid. The modified polyamide powder was dried at 105°–110°C for 2–3 hr and cooled in a P_2O_5 desiccator. Molecular weights of the samples were calculated from the end group data.

Acetylation

The reaction was carried out at different temperatures (40°, 60°, and 70°C) for varying periods of times (0–8 hr). The flask was shaken occasionally. After the completion of the reaction the fibers were precipitated by adding an excess of pure distilled ethyl alcohol. The polymer was filtered and washed thoroughly with benzene and then with distilled water, dried at 105°–110°C, and cooled in a P_2O_5 desiccator. The end amino groups were determined by Moore's method.[9]

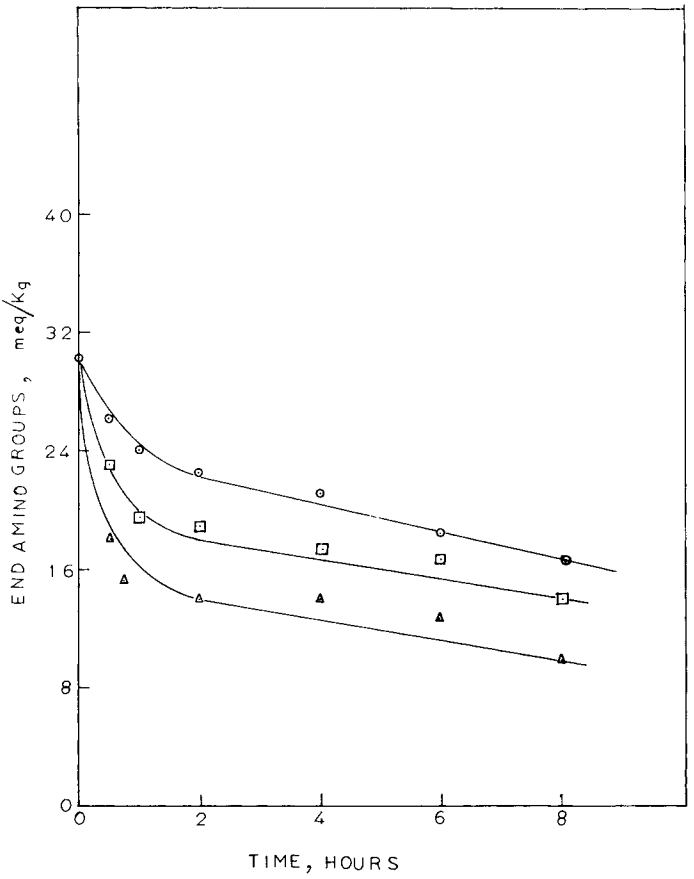

Fig. 8. Relation between number of end amino groups retained in polymer and time of acetylation at 40°C (○), 60°C (□), and 70°C (△).

Deamination

The reaction was carried out at different temperatures (0°, 10°, and 15°C) for varying periods of time (0–2 hr). The samples removed at different periods of time were mixed with excess acetone when the polymer was precipitated. The precipitate was thoroughly washed with acetone and water and then dried in the same way as in case of hydrolysis and acetylation. The molecular weights of the samples were determined by viscosity measurement in *m*-cresol,[10] and the end amino group estimation was done by conductometric titration using Waltz and Taylor's method.[11]

RESULTS AND DISCUSSION

In the present investigation activation energies of hydrolysis, acetylation, and deamination of polyamide fibers dissolved in *m*-cresol were determined. The complex nature of the reactions as evident from the dependence of the rate on

TABLE I
Various Characteristics of Modified Polyamide Fibers

Temperature, °C	Time, hr	Molecular weight	End amino groups, meq/kg
		Hydrolysis	
	0	23200	30.00
	1	21270	31.00
	2	16310	40.00
40	4	15530	46.00
	6	13600	56.00
	8	11690	59.00
	0	23200	30.00
	1	17857	42.00
	2	15503	45.00
50	4	14600	46.00
	6	12422	66.00
	8	11236	71.00
	0	23200	30.00
	1	14492	54.00
	2	10752	88.00
60	4	10260	90.00
	6	9615	100.00
	8	8264	133.00
		Acetylation	
	0		30.00
	0.5		26.50
	1		24.00
40	2		22.40
	4		21.00
	6		19.00
	8		18.00
0	0		30.00
	0.5		23.00
	1		19.60

temperature is further complicated by the solvent used to make the medium homogeneous. In view of this, the activation energy of the reactions was termed the "apparent" activation energy.

It was found that the deamination reaction of the polyamide fibers in homogeneous medium is accompanied by mild hydrolysis of the polypeptide chain by nitrous acid. The rate constants of the deamination reactions were therefore described as the "apparent" rate constants.

The results of the present investigation on hydrolytic degradation of polyamide fibers in hydrochloric acid are plotted in Figures 1 to 7. Increase in the amount of end amino group content of the polyamide fibers hydrolysed at different temperatures can be seen from Table I. Figures 1 and 2 indicate that the hydrolytic attack is very fast up to 2 hr of reaction time, which however slows down to a considerable extent as the reaction proceeds. The results also indicate that the hydrolytic reaction on polyamide fibers is strongly temperature dependent and that higher temperatures bring about enhanced hydrolytic breakdown of the polypeptide chains. This is also evident from the data on molecular weight and end amino groups given in Table I, showing that the molecular weight de-

TABLE I (*Continued*)

Temperature, °C	Time, hr	Molecular weight	End amino groups, meq/kg
60	2		18.80
	4		17.20
	6		16.40
	8		14.00
	0		30.00
	0.5		18.00
	1		15.40
70	2		14.00
	4		13.80
	6		12.60
	8		9.80
		Deamination	
	0		30.00
	0.16		20.00
	0.33		26.00
0	0.50		32.00
	1		34.00
	2		36.00
	0		30.00
	0.16		26.00
	0.33		33.00
10	0.50		40.00
	1		42.00
	2		45.00
	0		30.00
	0.16		20.00
15	0.33		36.00
	0.50		43.00
	1		45.00
	2		48.00

creases coupled with the simultaneous increase in the amount of the end amino groups during the course of the hydrolytic reaction on polyamide fibers. Figure 2 gives the plot of log number of bonds versus time of hydrolysis. The existence of two distinct rates of hydrolysis can be seen from this figure.

Logarithmic plots of the two rates versus time are given in Figures 3 and 5. A linear relationship is observed in both cases, showing that the hydrolysis of the polyamide fibers in the presence of hydrochloric acid follows first-order kinetics.

Rate constants for fast (k_{fast}) and slow (k_{slow}) reactions as well as the ratio k_{fast}/k_{slow} were determined and are shown in Table II. It can be seen that k_{fast} is temperature sensitive and that its value of 3.06×10^{-2} min^{-1} goes on increasing with increase in the temperature of hydrolysis and assumes a value of 4.60×10^{-2} min^{-1} at 60°C. However, k_{slow} increases only marginally (0.103×10^{-2} min^{-1} at 40°C increased to 0.107×10^{-2} min^{-1} at 60°C). The ratio k_{fast}/k_{slow} therefore becomes temperature sensitive, contrary to the observations made in the identical studies but in the heterogeneous medium, where the ratio k_{fast}/k_{slow} remained independent of the temperature of the hydrolytic reactions.[1]

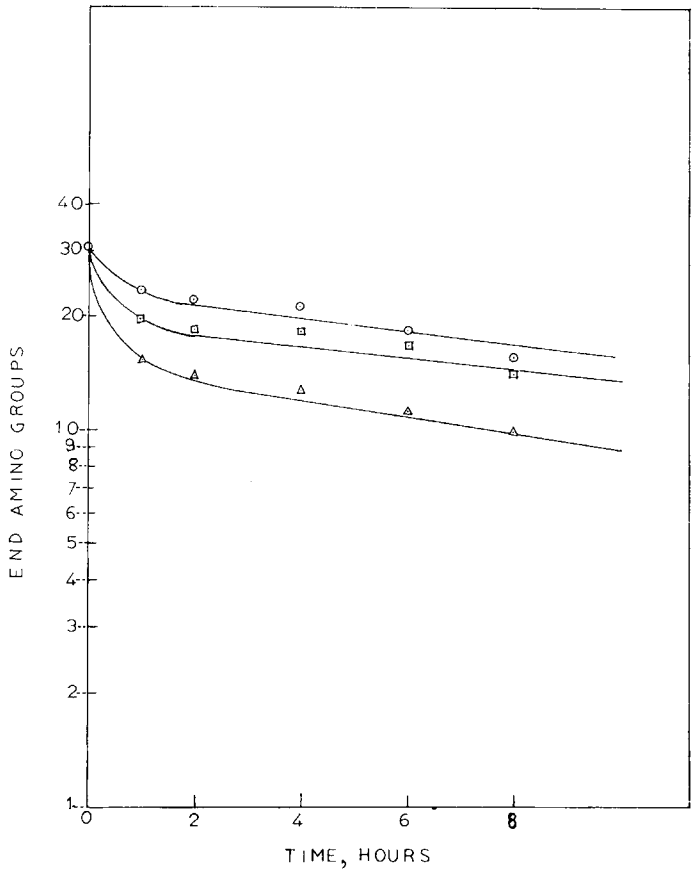

Fig. 9. Logarithmic plot of number of end amino groups retained in polymer vs time of acetylation at 40°C (○), 60°C (□), and 70°C (△).

In the homogeneous medium the hydrolytic reaction occurs in the presence of the solvent *m*-cresol, which seems to play an important role. At higher temperatures the entropy of the system increases and the solvent molecules acquire higher kinetic energy. Thus, the solvent accelerates the hydrolytic reaction as the temperature of the system is increased, and hence the higher values of k_{fast}.

Chemical reactions of polymers have played an important role in the modification of natural and synthetic macromolecules, resulting in new types of derivatives. These reactions have also helped in the characterization of the polymer chains either in the solid polymer or in the homogeneous system. The use of polymer reactions, especially in homogeneous media, for characterization of macromolecular substances and for the understanding of the shape and state of the individual chain molecules is one of the most interesting aspects in such studies. Solvents break the hydrogen bonds or the other cohesive forces existing between chain molecules of a fiber and bring about complete separation of the individual chains. It is believed that the polymer chains exist in the form of coils in such solutions [Fig. 18(A)]. The behavior of polymer coils in solutions assumes

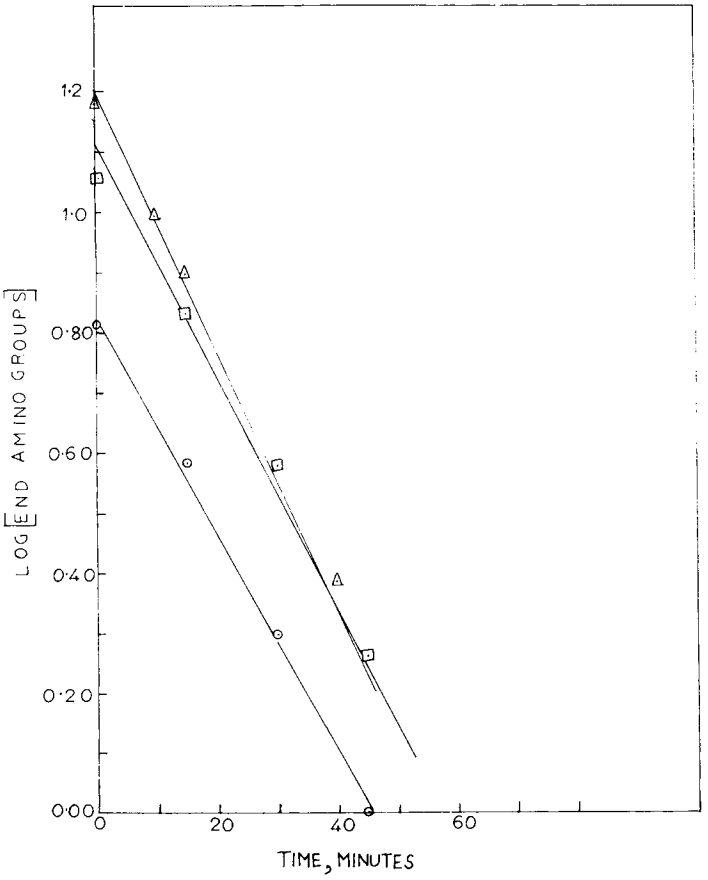

Fig. 10. Rate curves for fast acetylation reaction at 40°C (○), 60°C (□), and 70°C (△).

TABLE II
Rate Constants and Activation Energy Values of Various Modification Reactions of Polyamide Fibers in Homogeneous Medium

Reaction	Temperature, °C	Rate constants k, $min^{-1} \times 10^{-2}$		k_{fast}/k_{slow}	Apparent activation energy E, kcal/mole	
		k_{fast}	k_{slow}		E_{fast}	E_{slow}
Hydrolysis	40	3.06	0.103	29	3.20	0.18
	50	3.68	0.105	35		
	60	4.60	0.107	43		
Acetylation	40	4.00	0.066	60	1.50	0.80
	60	4.20	0.076	55		
	70	5.06	0.087	58		
		k_{fast} (apparent)	k_{slow} (apparent)			
Deamination	0	2.30	0.092	25	6.90	4.60
	10	2.53	0.133	20		
	15	4.60	0.151	30		

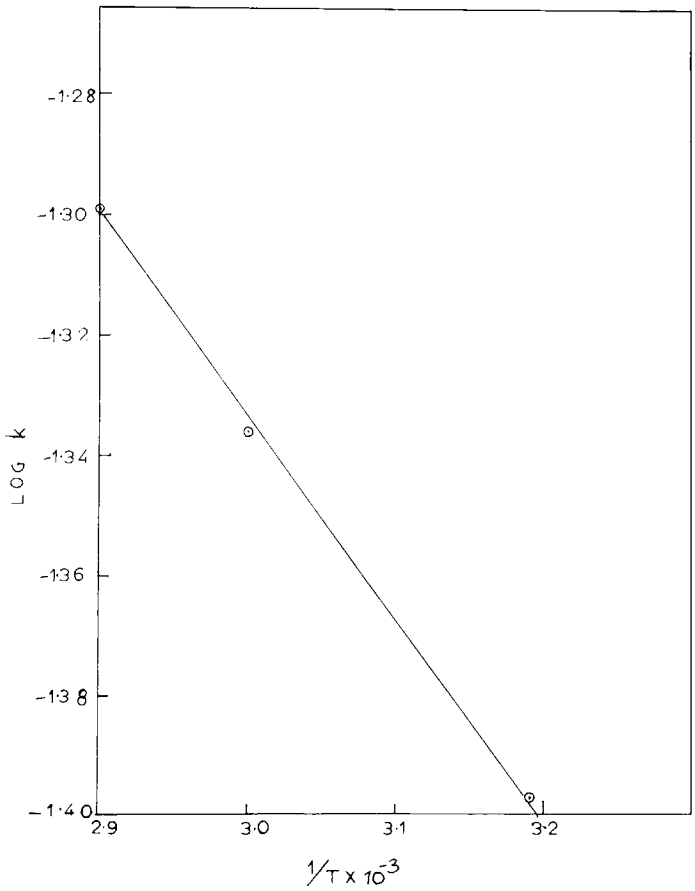

Fig. 11. Apparent activation energy E_{fast} of fast acetylation reaction.

considerable importance theoretically as well as from a practical point of view. It is obvious that in very dilute solutions molecular separation of the polymer chains occurs. The famous Flory-Huggins theory of polymer solutions is based on these ideas. It deals mainly with very dilute solutions and predicts that the polymer coils exist under ideal conditions with free interpenetrations [Fig. 18(B)]. A number of workers, however, felt that results with more concentrated solutions of polymer could not be explained on the basis of the Flory-Huggins theory.[12–14]

Braun[15] in his investigation of the structural properties of macromolecules in homogeneous solutions of fairly high concentrations has concluded that in such solutions the polymer coils are arranged in a close packing of individual particles penetrating each other to a very limited extent only in the small border zones. He proposed that concentrated polymer solutions (2.5%) have a morphological structure of cellular tissues and that the thickness of the "cell walls" increases with the polymer concentration [Fig. 18(C)].

The concentration of polyamide fibers in *m*-cresol used in the present investigation (mainly 5%–6%) falls in the category of "highly concentrated solutions" and is beyond the range of the concentrations used by Flory as well as Braun.

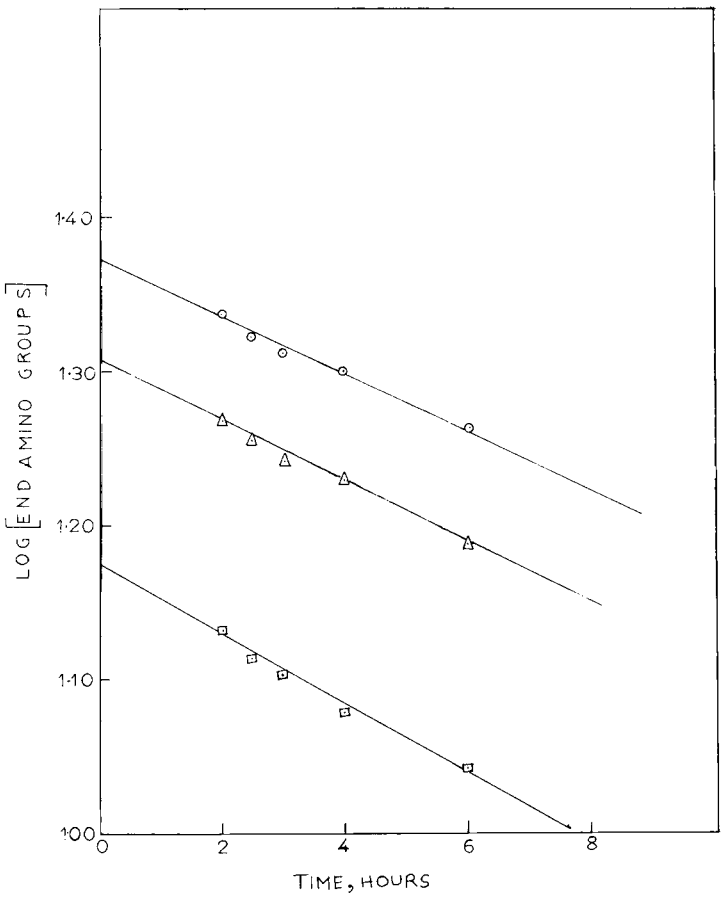

Fig. 12. Rate curves for slow acetylation reaction at 40°C (○), 60°C (□), and 70°C (△).

The results on hydrolytic reactions suggest that the solution of polyamide fibers in *m*-cresol does not contain the free coils of individual chains, a situation which would give only one rate of hydrolysis. These results also cannot be explained on the basis of the so-called "cell model" or "cellular model" of Braun.

The results of the present investigation lead us to propose a new microfibrillar-type model of polyamide chains in highly concentrated solutions in *m*-cresol [Fig. 18(D)]. In this model a few polypeptide chains are bonded by hydrogen bonding as in the case of parent polyamide fiber and therefore assume the nature of a "microfiber" except that the polymer chains in the parent fiber lie almost along the main axis while it may not be so in the microfiber. Of course, other forms of models including free polymer chain coils are not ruled out and may be present in small proportions. In fact, the solution is a continuous phase of various segments of the polymer present in the solution right from the individual chain up to the proposed microfibrillar level of polymer chain aggregation just sufficient to be dissolved in *m*-cresol. Since the concentration of the polyamide is very high, it is obvious that the aggregates of the microfibrillar type will be present in great abundance. The possibility of the microfibrillar level in the

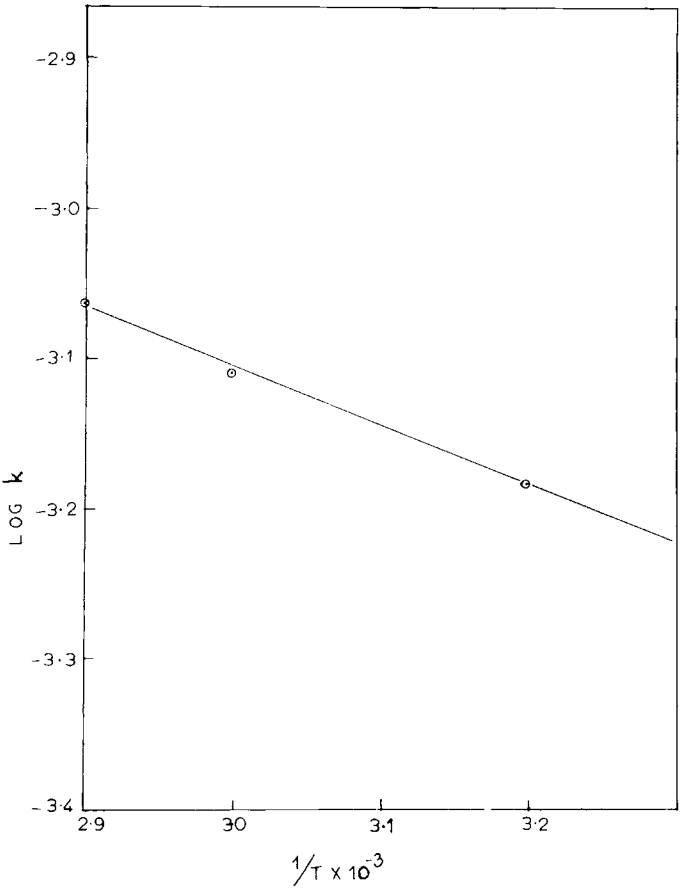

Fig. 13. Apparent activation energy E_{slow} of slow acetylation reaction.

homogeneous medium imparts "heterogeneity" to the system only to that extent to keep it in the apparent homogeneous form.

The two hydrolysis rates, fast and slow, are due to the nonbonded and some bonded microfibrillar regions. As the temperature of the hydrolytic reaction continues to increase, the rates also become faster because the microfibrillar aggregates split up and the accessible portion increases and consequently the fast rate increased, whereas there is not much change in the slow rate constant value.

Figure 7 is a plot of end amino groups versus molecular weight of the polyamide fibers hydrolyzed at different temperatures in the homogeneous medium. It is a nonlinear plot passing through the points representing various temperatures of the hydrolysis. Similar studies in the heterogeneous medium give a linear correlation between the two parameters, suggesting that the mechanism of hydrolysis in the heterogeneous medium is unaltered at various temperatures but that higher temperatures only increase the degree of the hydrolysis. The results of the present investigation, however, suggest that not only do higher temperatures increase the degree of hydrolysis but also bring about changes in the mode of hydrolysis. It seems that at elevated temperatures the solvent molecules are

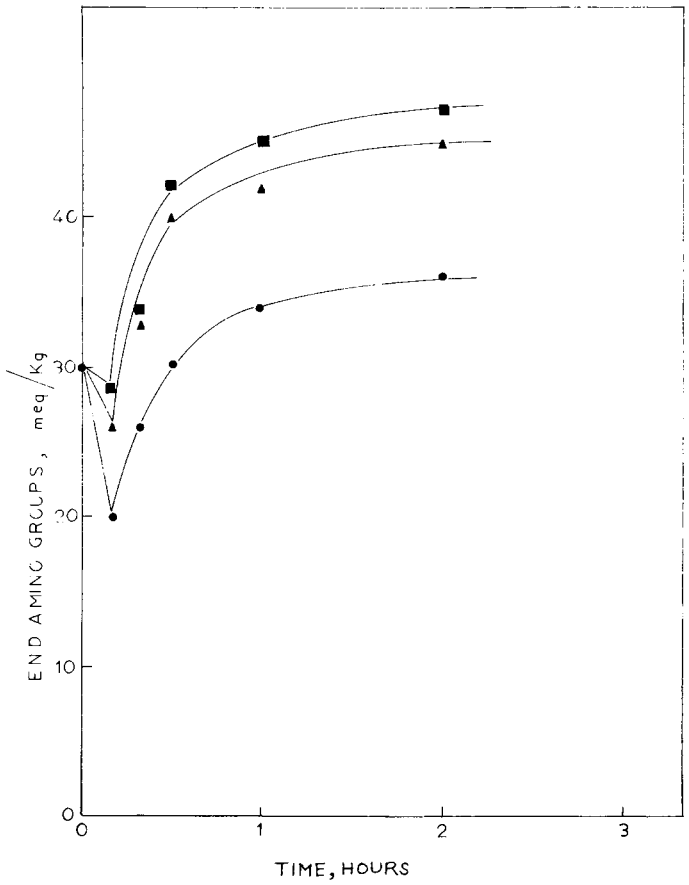

Fig. 14. Relation between number of residual end amino groups and time of deamination reaction at 0°C (●), 10°C (▲), and 15°C (■).

also energized and possess increased power of interaction with microfibrils of a given dimension obtained during the dissolution at lower temperatures. It is likely that the solvent molecules at higher temperatures bring about changes in the internal structure of the microfibril coupled with possible reduction in the size of the microfibril by the further disintegration. Thus, the state in which the polymer is present in the homogeneous medium at different temperatures differs and hence the mechanism of hydrolysis differs.

The apparent activation energy of the hydrolytic reaction in the homogeneous phase is 3.2 kcal/mole when the attack is governed by the fast rate, while its value is only 0.18 kcal/mole for the slow attack. It is surprising that the fast reaction rate is accompanied by the higher apparent activation energy value while the slow reaction taking place in the difficult-to-penetrate regions is having a much lower activation energy. In the homogeneous medium the chains in the microfibril assume random positions and the acid molecule has to overcome the barrier of the solvent before it travels up to the chain segment. In case of the slow hydrolytic reaction the solvent along with the acid molecules penetrates the ordered regions and sets the chains free which are simultaneously attacked by the acid

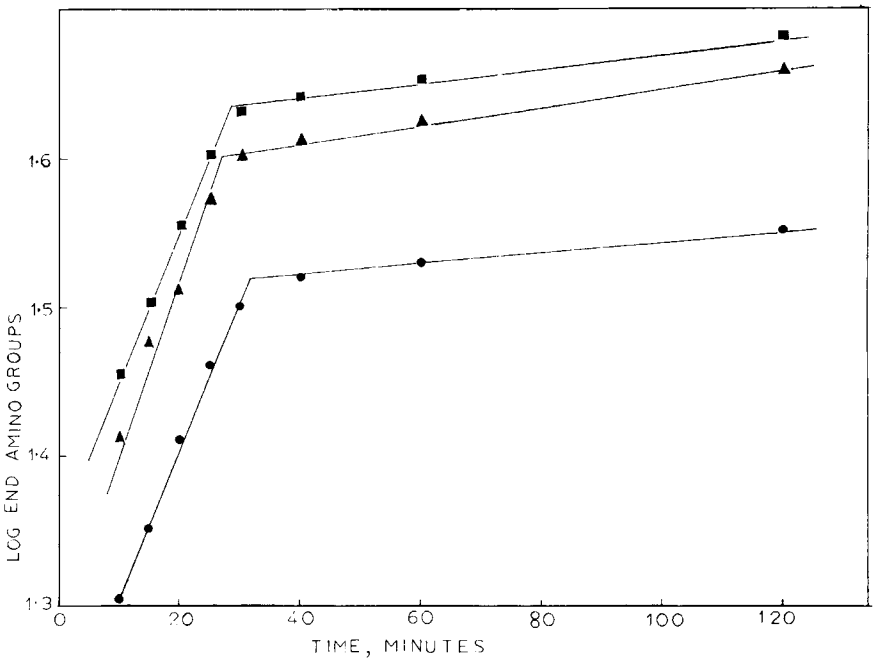

Fig. 15. Rate curves for fast and slow apparent deamination reactions at 0°C (●), 10°C (▲), and 15°C (■).

molecules brought into the open structure by the solvent. This means that the acid molecules do not require additional energy to open up the structures in the ordered regions but on the other hand, are helped by the solvent during the hydrolytic breakdown in the difficult-to-penetrate portions, and hence the apparent energy of activation is very low.

Table I and Figures 8 to 13 give the results of the kinetics of the acetylation reaction on the polyamide fibers in homogeneous medium. If the molecular separation occurs in the dissolution of polyamide fibers in *m*-cresol, then all the end amino groups should be available for acetylation reaction to an equal extent. Figures 8 and 9 give the plot of residual end amino group content of the acetylated fiber versus time. It can be seen that initially the rate of acetylation is fast up to about 1 hr of reaction time, followed by the slower rate. The extent of acetylation increases with increase in the temperature of the reaction. Figures 10 and 12 give the plot of log end amino groups versus time for both rates. A linear relationship exists for both rates, suggesting that the acetylation reaction on the polyamide fibers proceeds according to first-order kinetics. The rate constants and other characteristics of the polyamide fibers are given in Table II. The rate constants in case of both fast and slow reactions increase with increase in the temperature of acetylation reaction in the same proportion, thus giving almost constant ratio of k_{fast}/k_{slow} in the order of 58. The fact that two rate constants are obtained for acetylation reaction in homogeneous medium indicates that the acetylated end amino groups lie in regions of varying accessibilities. The values for the apparent activation energies corresponding to the fast and slow rates are 1.5 and 0.8 kcal/mole, respectively (Figs. 10 and 12). The observation that the slow reaction has a lower activation energy than the faster one indicates that the

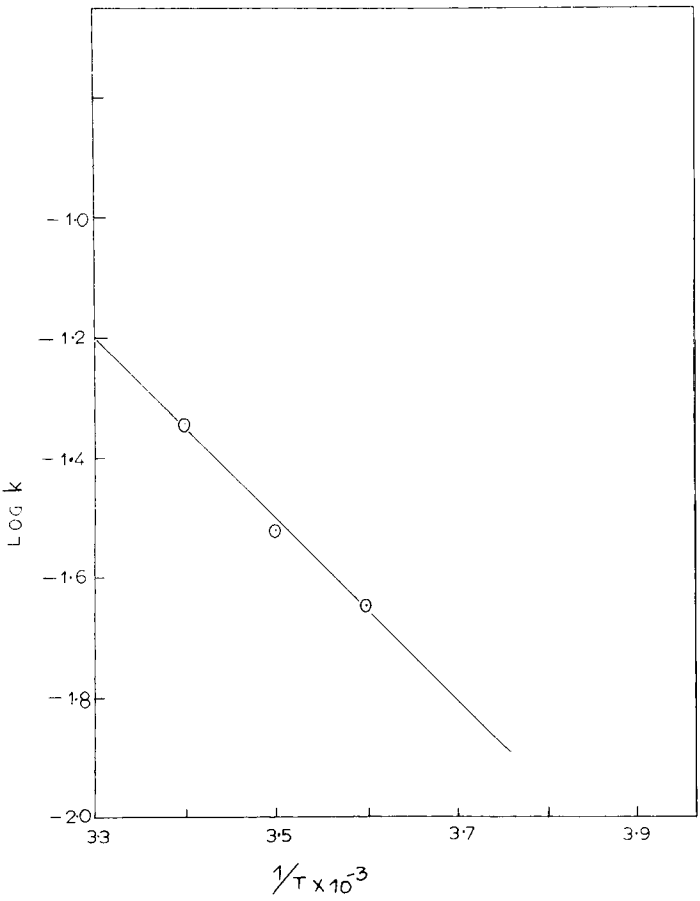

Fig. 16. Apparent activation energy E_{fast} of fast apparent deamination reaction.

solvent plays a role in opening the difficult-to-penetrate regions of the microfibril in solution and thus making the NH_2 groups available for the acetylation reaction in a comparatively easier manner.

Deamination of polyamide fibers was studied at 0, 10, and 15°C. The values of end amino group content of the fiber are given in Table I. The results are plotted in Figure 14–17. Figure 14 gives the plot of end amino group content versus time. An interesting observation of these plots is that at all the temperatures studied, viz., 0, 10, and 15°C, there is initially a decrease in the end amino group content followed by a sharp increase, thus giving a minimum at about 10 min. The minimum value is maximum at 0°C, decreasing with the increase in the temperature of deamination. It seems that up to 10 min of the apparent deamination reaction, the true deamination supersedes the amination reaction through the rupture of the polypeptide chains; after that, the situation is reversed resulting in the fast increase in the end amino groups in spite of the deamination reaction. In order to study the kinetics of the apparent deamination reaction, the observed curves from 10 to 120 min have been taken into consideration.

The so called "amination" reaction is faster initially but slows down after about half an hour of apparent deamination reaction. Figure 15 represents the rate

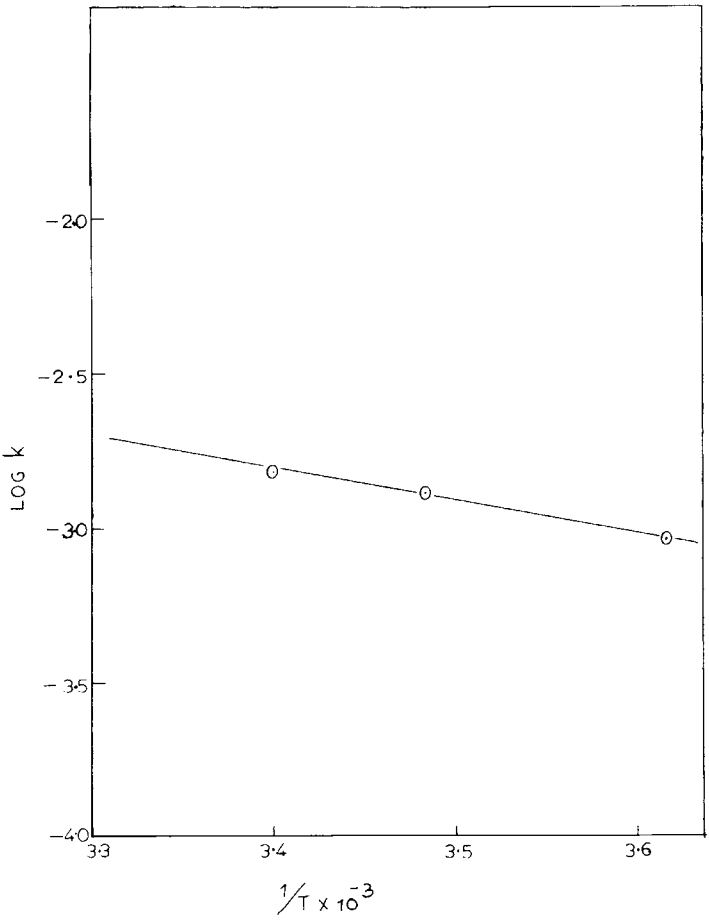

Fig. 17. Apparent activation energy E_{slow} of slow apparent deamination reaction.

curves for the fast and slow reactions. The linear relationship obtained in all cases indicates that the apparent deamination reaction on polyamide proceeds according to first-order kinetics. Rate constant values for both the fast and slow reactions are given in Table II. Both k_{fast} and k_{slow} go on increasing with increase in the temperature of the apparent deamination reaction. At all the temperatures studied, two rates have been observed because of the two-phase structure of the microfibrils present in the solution of *m*-cresol. No definite trend was observed for the ratio k_{fast}/k_{slow}, which shows the complexity of the apparent deamination reaction, although it appears to be favored at higher temperatures. The apparent deamination reaction in the homogeneous medium seems to be directly dependent on the rise in temperature, although a true deamination reaction is favored at lower temperatures in the heterogeneous medium.[1] In the present investigation the apparent deamination reaction is accompanied by an equally powerful amination or hydrolytic reaction which supersedes the true deamination reaction at the temperatures studied, with the result that the apparent deamination reaction becomes the sum total of the two simultaneous reactions giving a positive temperature dependence. Figures 16 and 17 give the

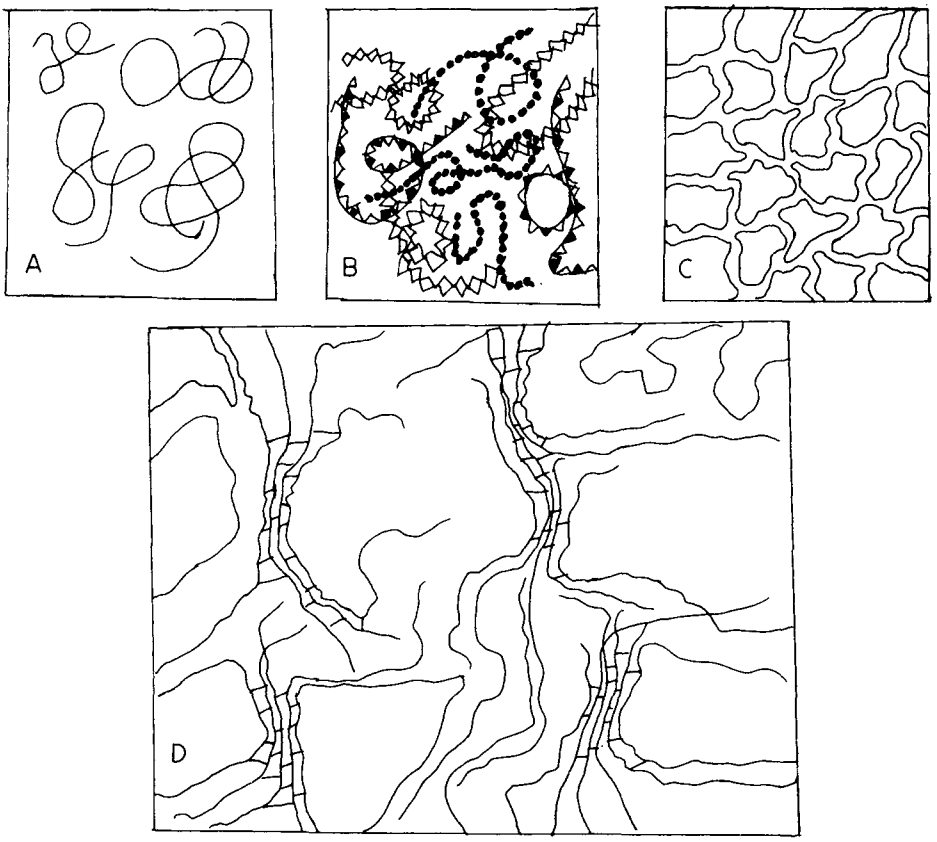

Fig. 18. Various models for polymer chain in solution: (A) isolated coils; (B) free interpenetration; (C) cell model; (D) proposed microfibrillar model.

values of apparent activation energy for the apparent deamination reaction for the fast and slow rates, the values being 6.90 and 4.60 kcal/mole, respectively. The activation energy data indicate that the apparent deamination studied in the present investigation of the end amino groups present in the difficult-to-permeate region is easier than that for the end amino groups present in the easily accessible portions of the microfibril in the *m*-cresol solution of the polyamide fibers. The results suggest that the solvent plays an important role; it penetrates inside the ordered regions, carries the deaminating and the hydrolysing species inside, breaks the hydrogen bonds, and brings about the apparent deamination reaction.

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