

Crystallization of Cyclic Oligomers on the Surface of Nylon 6 Fibers

YASUHARU FUJIWARA* and S. HAIG ZERONIAN, *Division of Textiles and Clothing, University of California, Davis, California 95616*

Synopsis

When scoured nylon 6 filament was exposed to either water vapor or *n*-alcohol vapor, a portion of the cyclic $[\text{NH}(\text{CH}_2)_5\text{CO}]_x$, with $x = 2$ through 7, and the ϵ -caprolactam present migrated to the filament surface and crystallized. A variety of crystal forms were observed. The variations depended partly on the vapor to which the sample had been exposed. During water vapor exposures, the cyclic dimer migrated more easily to the filament surface than the cyclic monomer and the cyclic tetramer migrated more easily than the cyclic trimer. It is postulated that the secondary valence forces acting between the dimer and the nylon 6 polymer are weaker than that between the ϵ -caprolactam and the polymer since the dimer forms intramolecular hydrogen bonds. Consequently, the dimer migrates more easily than the monomer, which can form hydrogen bonds with the polymer. Also the cyclic trimer can form hydrogen bonds with the nylon 6 polymer and thus migrates less easily than the cyclic tetramer, which can form intramolecular hydrogen bonds. In alcohol vapor exposures, the *n*-alcohol used influenced the concentration of cyclic monomer and oligomer, which migrated to the surface of the nylon 6 filament. The variation of the monomer and oligomer concentration on the fiber surface with the alcohol used in the exposure is discussed.

INTRODUCTION

Polymerization of ϵ -caprolactam to form nylon 6 results in a product containing about 10% of low molecular weight materials which consist of both monomer and oligomers.^{1,2} Much of these low molecular weight compounds are extracted from the polymer by either washing with hot water or heating under reduced pressure since they can affect the properties of the filaments spun from the polymer. However, small amounts of monomer and oligomers remain. Also, reformation of oligomers may occur from the thermal treatment during melt spinning of the polymer.^{3,4} Hence nylon 6 fibers normally contain small quantities of both monomer and oligomers.

When nylon 6 fibers are immersed in polar liquids, dissolution of the low molecular weight compounds may occur. Exposure to the vapors of such liquids normally would not cause extraction of these compounds. However, it can be speculated by analogy with research on other polymers⁵ that the monomer and oligomers migrate to the surface, provided the vapor concentration is high enough. If suitable surface conditions exist, crystallization might occur.

The objective of the present work was to study by scanning electron microscope (SEM) changes in surface morphology of nylon 6 filaments caused by exposure to the vapors of water and alcohols at room temperature. In addition, when crystals formed on the fiber surfaces, the composition of the oligomers in the crystals was analyzed by gel permeation chromatography (GPC) and infrared

* Present address: Department of Home Economics, Mukogawa Women's University, Nishinomiya, 663, Japan.

(IR) analysis and compared to the composition of the oligomers remaining within the fibers.

EXPERIMENTAL

Materials

Nylon 6 filament yarn (9 denier per filament), prepared by a continuous polymerization–spinning process, was supplied by Toyobo Company, Japan. The filaments were drawn to four times their original length and did not contain any additives. *n*-Alcohols (methyl, ethyl, propyl, butyl, pentyl, and heptyl) were reagent grade.

Spin finish was removed by washing the filaments for 2 min in an 0.2% aqueous solution of sodium dodecyl sulfate. Then, the sample was rinsed several times with distilled water, and most of the water was extracted by centrifugation at 3000 rpm for 5 min before the sample was dried at room temperature in a vacuum desiccator over phosphorus pentoxide. The sample was stored in the desiccator until used. Scouring decreased the weight of the sample by 0.7%.

Extraction of Low Molecular Weight Species in Scoured Filaments

The scoured filaments were extracted with methanol in a Soxhlet for about 40 hr. Extraction decreased the weight of the filaments by roughly 3.3%. A pale-yellow solid residue (residue I) was left when the methanol solution was allowed to evaporate at room temperature.

Exposure of Nylon 6 Filaments to Water and *n*-Alcohol Vapors

Scoured nylon 6 filament was exposed to water and *n*-alcohol vapors in a desiccator at 21°C for up to 15 days. Filaments were also exposed to different humidities at 21°C in a desiccator for 15 days. The relative humidities were controlled by saturated salt solutions.⁶

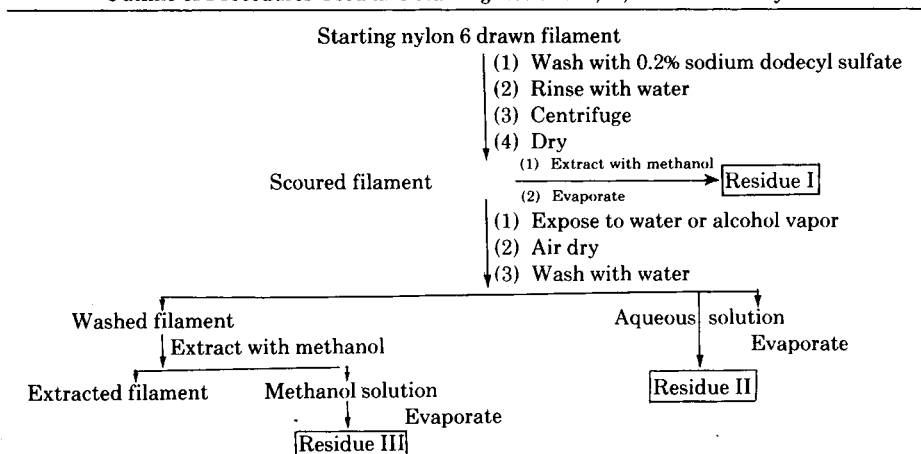
Extraction of Low Molecular Weight Species from Scoured Filaments Exposed to Vapors

Extraction with Distilled Water. The sample was washed with distilled water. The solution was allowed to evaporate at 50°C under reduced pressure (approximately 20 Torr), and the solid residue (residue II) was collected. The washed filament was dried.

Extraction with Methanol. The water-washed filament after drying was Soxhleted with methanol. The methanol solution was then evaporated yielding a solid residue (residue III).

The procedures used for scouring, the exposure to water or alcohol vapor, the washing of exposed filaments, and the extraction of the washed filaments are summarized in Table I.

TABLE I
Outline of Procedures Used in Obtaining Residues I, II, and III from Nylon 6



Analysis by GPC

The GPC technique reported by Mori et al.⁷ was employed in this study. The gel used was crosslinked polyacrylamide, Bio-Gel P-4 (Bio-Rad Laboratories). Samples were analyzed using 0.1*N* hydrochloric acid as an eluant. Samples were dissolved in 0.1*N* hydrochloric acid at 80°C to make solutions with a concentration of 3.5 mg/ml; 0.2 ml of the solutions was injected in the column. The flow rate was 16 ml/hr. The effluent was passed through a microflowcell placed in a Beckman DB-G grating spectrophotometer, and the absorbance of the solutions at 210 nm was measured continuously.

In the nylon 6 sample used in our experiments there was approximately 3.3% by weight of low molecular weight compounds. Most of low molecular weight species in nylon 6 are ϵ -caprolactam and cyclic oligomers.⁸ The weight percent of the total linear oligomers is only 0.17% by weight of the polymer,⁹ and the absorption coefficients of linear monomer and the oligomers are low.⁷ Thus, the presence of a small amount of the linear compounds does not effect the results to be presented in the discussion section.

The elution volume of the cyclic monomer and cyclic oligomer was ascertained by comparing the chromatogram of the residue with those of residues from which the cyclic monomer and/or dimer had been removed by fractional sublimation.¹⁰ The absorption peaks in the chromatogram were corrected using the molar absorption coefficient of cyclic monomer and oligomer.⁷

Determination of Monomer Content by IR Spectroscopy

IR spectra were taken with a Perkin-Elmer Model 281 IR spectrophotometer using a potassium bromide pellet technique. The calibration curve for determination of ϵ -caprolactam in low molecular weight compound mixtures was obtained by measuring the absorbance of samples containing known weights of the cyclic monomer and oligomers. Pure cyclic monomer was obtained by crystallization of ϵ -caprolactam from a petroleum ether solution. The cyclic oligomeric mixtures were obtained by eliminating the monomer from residue

I by washing with carbon tetrachloride and then heating the product at 0.1 Torr pressure and 100°C for 30 min. The absorbances at 1480 and at 2855 cm^{-1} were employed as peaks characteristic of the monomer and of sample size, respectively. The absorption band at 2855 cm^{-1} has been assigned to CH_2 symmetrical stretching vibration.¹¹

A plot of the ratio of the absorbances at 1480 and 2855 cm^{-1} against ϵ -caprolactam content in mixtures of cyclic monomer and oligomer was found to be linear at monomer concentrations from 30% to 100%.

SEM Observations

The fibers were coated with gold. For coating, the samples were placed in an evacuated chamber at 0.02 Torr pressure and approximately 55°C for 3 min. Under such conditions the monomer can sublime. However, the cyclic oligomers will not sublime, and the SEM photographs show the crystals formed by these oligomers.

Specimens were observed with a Cambridge Stereoscan Mark IIA microscope operating in the secondary mode at 10 kV acceleration voltage.

Dimensional Changes

Width. Single filaments were immersed in liquid water or in an *n*-alcohol for about 50 hr at room temperature before measuring their widths with a light microscope. The width of filaments dried over phosphorus pentoxide in a desiccator was also measured, and the percent increase of the width of the filaments on exposure to water or *n*-alcohol was calculated. The data presented is the average of 50 determinations.

Length. Single filaments were suspended in a closed chamber with a 1.5-mg weight hung at the lower end and exposed to water or *n*-alcohol vapor for 15 days at 21°C. The length of the filaments was determined with a cathetometer. The filaments were then dried over phosphorus pentoxide and their lengths re-measured to calculate the percent increase in length of the filaments on swelling in water or *n*-alcohol vapor. The data presented is the average of three determinations.

RESULTS AND DISCUSSION

Fiber Characterization

The total amount of low molecular weight species in the scoured nylon 6 filament was approximately 3.3%. This determination was made from the weight loss of the filaments after extraction with methanol. A comparison of the IR spectrum of residue I (Fig. 1) with those of Zahn et al.¹² and Mori et al.¹³ confirmed that the low molecular weight species consisted primarily of cyclic monomer and cyclic oligomers.

The surface of scoured filaments was smooth (Fig. 2), and deposits of low molecular weight material were not observed.

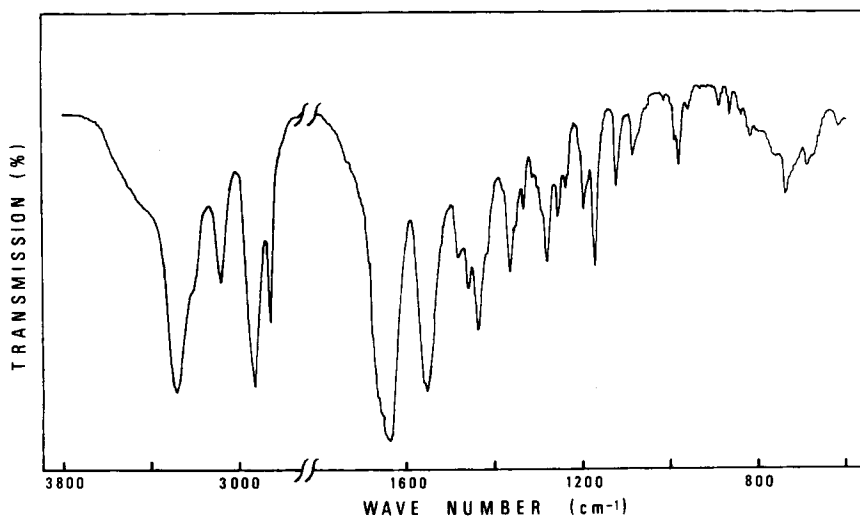


Fig. 1. Infrared spectrum of low molecular weight compounds in nylon 6.

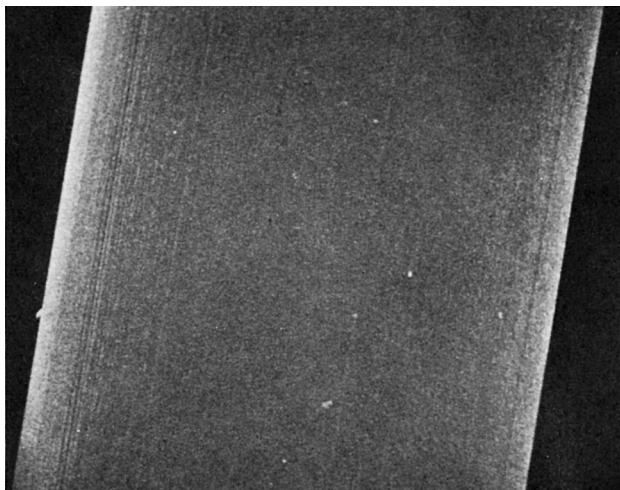


Fig. 2. Scanning electron micrograph of scoured nylon 6 filament ($\times 1200$).

Exposure to Water Vapor

When scoured nylon 6 filaments were exposed to water vapor, the low molecular weight species present in the sample migrated to the filament surfaces, and formed crystals. Both needle-type (Fig. 3) and plate-like crystals (Fig. 4) were observed after the filaments had been exposed to water vapor for 12 hr. As the samples were exposed to water vapor for extended periods of time, the crystals increased in size. Samples exposed for 24 hr showed further development of plate crystals (Fig. 5). Trapezoidal-shaped crystals (Fig. 6) were also observed as the exposure to water vapor was increased. The trapezoid-shaped crystals were composed of thin platelet crystals stacked on top of each other (Fig. 7).

Some crystals developed in close contact with the surface of the filaments (Fig. 6), while in other cases a space could be observed between the crystals and the filament surfaces (Fig. 7). Even for the crystals contacting the surface, the di-

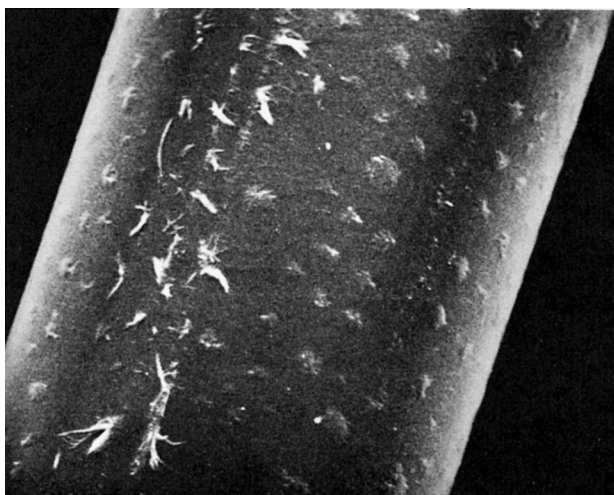


Fig. 3. Needle-type crystals on surface of nylon 6 filament after exposure to water vapor for 12 hr ($\times 1100$).

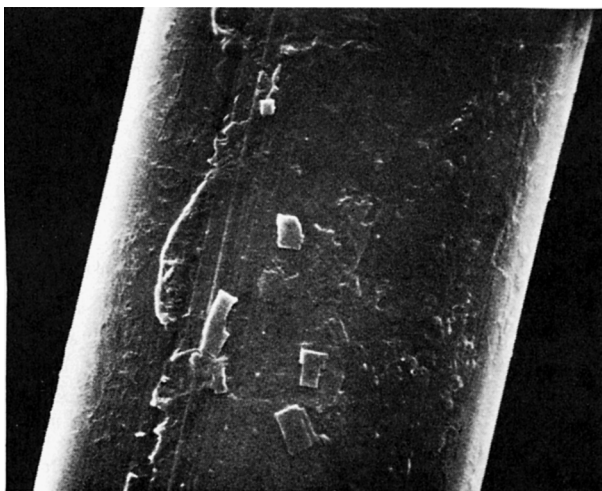


Fig. 4. Plate-like crystals on surface of nylon 6 filament after exposure to water vapor for 12 hr ($\times 1100$).

rection of the sides of the square or rectangular crystals with respect to the fiber axis was not regular as for epitaxial crystallization of polymers^{14,15} or epitaxially grown nonpolymeric crystals.^{16,17} After extensive exposure to water vapor, networks of fibril-type crystals were observed (Fig. 8). When observed under crossed nicols, plate crystals were isotropic in the plane direction but showed strong birefringence in the direction perpendicular to the crystal planes. Similar observations have been made on nylon 6 cyclic dimer crystals crystallized from aqueous solutions.^{18,19}

Nylon 6 filaments were exposed also in atmospheres of different relative humidities for 15 days. Crystals were not observed on filament surfaces until the relative humidity was increased to 93%. In comparison to the crystals formed at 100% R.H. (Figs. 6 and 7), the crystals developed at 93% R.H. were relatively thin (Fig. 9) and fibril-type crystals were not observed.

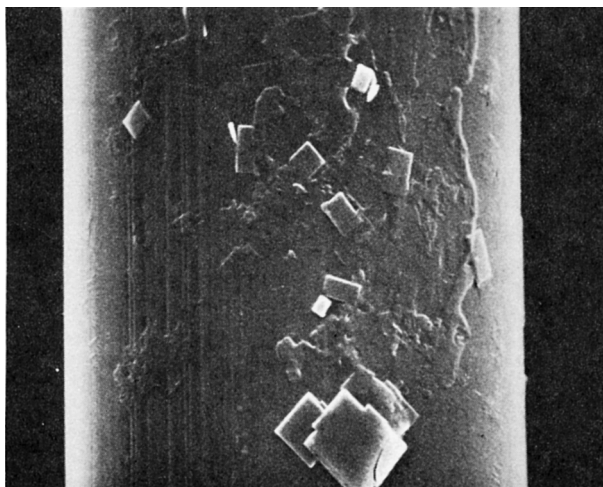


Fig. 5. Development of plate-like crystals on surface of nylon 6 filament after exposure to water vapor for 24 hr ($\times 1100$).

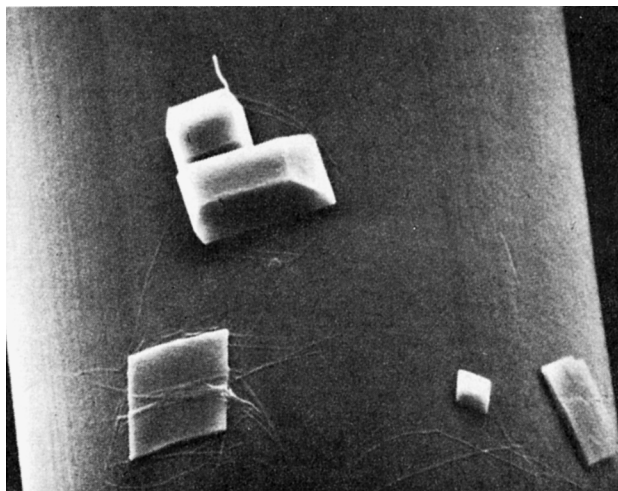


Fig. 6. Trapezoid-shaped crystals on surface of nylon 6 filament after exposure to water vapor for 7 days ($\times 1500$).

The composition of the low molecular weight materials, i.e., residues I, II, and III (see Table I) were analyzed by GPC (Fig. 10). By weight there was 3.3% residue I in the nylon 6 filaments, and it consisted of a mixture of cyclic monomer and of all cyclic oligomers up to and including the heptamer (Fig. 10). The amount of residue II present in the filaments was 0.9% of the filament weight, and it was 30% of the weight of extractable low molecular weight compounds present in the scoured filaments. Residue II consisted of cyclic monomer and all cyclic oligomers up to and including the pentamer (Fig. 10). It appears therefore that in the presence of water vapor the cyclic hexamer and heptamer cannot migrate to the filament surface. These cyclic oligomers were present in residue I but not in residue II.

Residue I consists of residues II and III. Comparison of the GPC chromatograms in Figure 10 shows that the chromatogram of residue III complements that

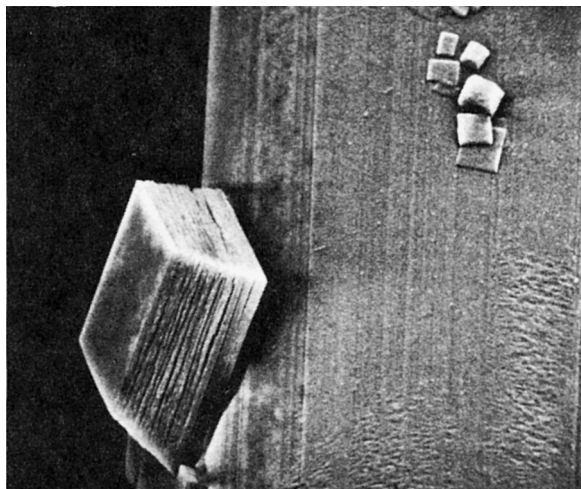


Fig. 7. Lamellar structure of trapezoidal crystal grown on nylon 6 filament; sample exposed to water vapor for 15 days ($\times 1300$).

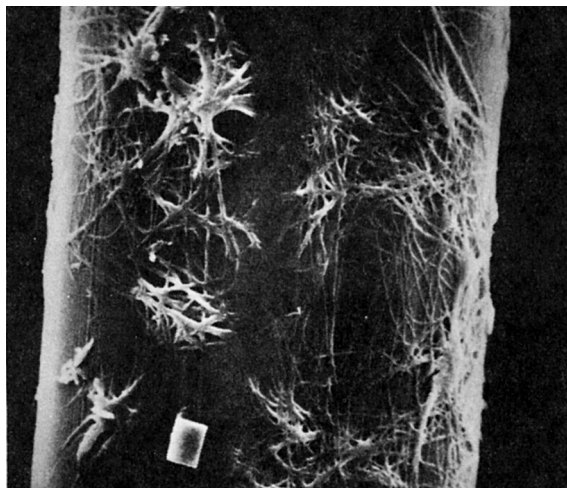


Fig. 8. Networks of fibril-type crystals on surface of nylon 6 filament exposed to water vapor for 15 days ($\times 1100$).

of residue II. Residue III contains relatively large amounts of the cyclic trimer and pentamer and a relatively small amount of the cyclic dimer. Cyclic hexamer and heptamer are also present. In contrast, residue II contains a relatively large amount of cyclic dimer, a relatively small amount of cyclic trimer, and still less of cyclic pentamer. Cyclic hexamer or heptamer is not present in this residue. Thus, the different types of crystals found on the surface of filaments exposed to water vapor consist mainly of cyclic dimer, trimer, and tetramer. As noted previously, any deposited monomer crystals would have evaporated during the preparation of specimens for the SEM.

Seventy-three percent of cyclic dimer in the filament migrated to the surface on exposure to water. In contrast, the amount of cyclic monomer, trimer, and tetramer migrating to the surface was 27%, 17%, and 26%, respectively. The amount of cyclic monomer migrating to the filament surface was calculated from

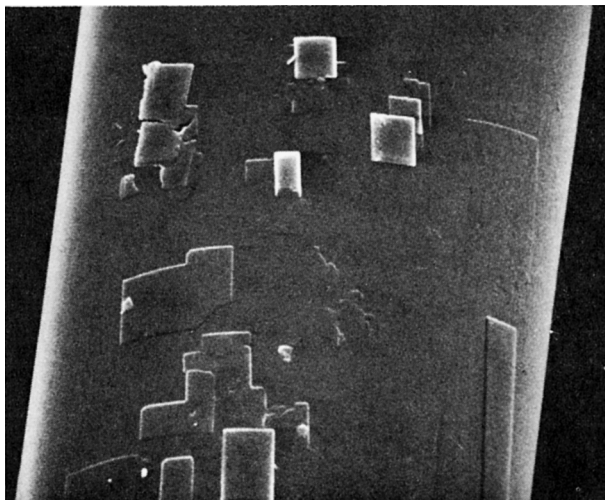


Fig. 9. Crystals developed on surface of nylon 6 filament exposed in atmosphere of 93% R.H. for 15 days ($\times 1300$).

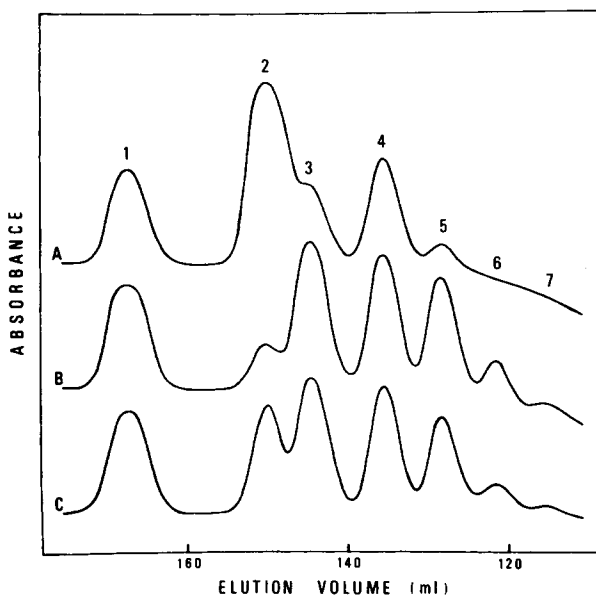


Fig. 10. Gel permeation chromatograms of residues from nylon 6 filament: A, residue II from nylon 6 exposed to water vapor; B, residue III from nylon 6 exposed to water vapor; C, residue I; 1 = monomer; 2 = dimer; 3 = trimer; 4 = tetramer; 5 = pentamer; 6 = hexamer; 7 = heptamer.

the monomer content in residues II and III (Table II). These were estimated from IR spectra. Since the weights of residues II and III were known, the percent monomer that migrated to the surface could be calculated. The estimate of cyclic dimer, trimer, and tetramer migrating to the filament surfaces was calculated from the area of the peaks in the chromatograms of residues II and III and knowing the weights of residues II and III (Table II). It should be noted however that the peaks of the dimer and trimer in the chromatograms overlapped. Thus, the estimate of the amount of cyclic dimer and trimer migrating to the filament surface is approximate.

TABLE II
Amount of Low Molecular Weight Material Migrating to Nylon 6 Filament Surface (Residue II)
or Remaining in Filament (Residue III) After Exposure to Water or *n*-Alcohol Vapor

Vapor	Residue II ^a , %	Residue III ^a , %	Total residue, %	Monomer content in residue, % ^{b,c}	
				Residue II	Residue III
Water	0.9	2.3	3.2	31	33
Methanol	2.1	1.3	3.4	27	49
Ethanol	1.9	1.5	3.4	31	47
Propanol	0.6	2.5	3.1	42	27
Butanol	0.8	2.7	3.5	72	28
Pentanol	0.4	3.0	3.4	80	30

^a Procedures for obtaining residues I, II, and III are given in Table I.

^b Monomer contents in residue were obtained by IR method.

^c Monomer content in residue I = 35%.

The ability of the cyclic monomer or oligomers to migrate to the filament surface will be affected by such factors as the size of the migrating molecules and the attraction between the low molecular weight compounds and the polymer molecules due to secondary valence forces. Hermans²⁰ has discussed the feasibility of intramolecular hydrogen bonds in caprolactam cyclic oligomers. He suggested that in the cyclic dimer the two CONH groups assume positions opposite each other favorable for the formation of two intramolecular hydrogen bonds. In the cyclic tetramer also pairwise engagement of all the CONH groups was shown to be geometrically possible. However, with the cyclic trimer only two out of the three CONH groups could possibly form intramolecular hydrogen bonds. In terms of this hypothesis, then the cyclic dimer and cyclic tetramer should be able to migrate more easily to the surface of nylon 6 filaments than the caprolactam or the cyclic trimer since the cyclic dimer or tetramer is less likely to form hydrogen bonds with the polymer chains than either the ϵ -caprolactam or the cyclic trimer. Thus, the cyclic dimer migrates more easily than the cyclic monomer and the cyclic tetramer more easily than the cyclic trimer. The amount of cyclic monomer diffusing to the filament surface approximately equals the amount of cyclic tetramer even though the latter has less attraction to the polymer chains. Diffusion is affected by the size of the molecules, and the cyclic tetramer is larger than the cyclic monomer.

To attempt to understand the mechanism of crystallization of the migrating low molecular weight species, endeavors were made, without success, to induce crystallization of isolated cyclic monomer or dimer on filament surfaces. Pure cyclic monomer and dimer were isolated by sublimation from residue I. Finely powdered cyclic monomer or dimer was then separately placed on the surface of nylon 6 filaments which had been extracted with methanol. The filaments were exposed to water vapor for 15 days. Formation of crystals from the powder however were not observed by polarizing light microscope.

Exposure to *n*-Alcohol Vapors

All exposures reported in this section were made for 15 days. When nylon 6 filament was exposed to methanol vapor, a large number of crystals were formed on the surface (Fig. 11). Most of the crystals were square or rectangular platelets

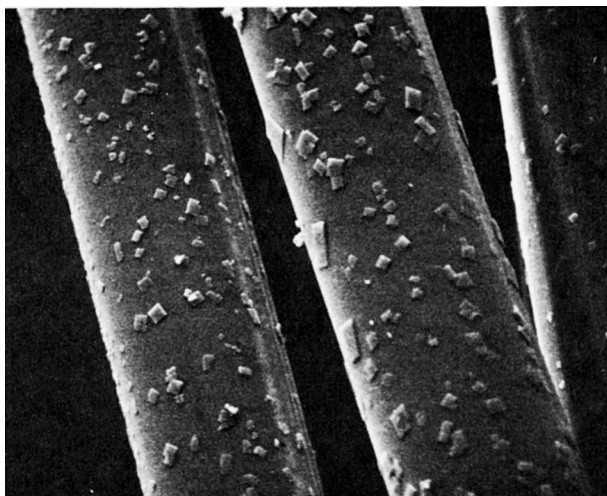


Fig. 11. Surface of nylon 6 filament exposed to methanol vapor for 15 days ($\times 400$).

and were unequal in size. In addition, irregular-shaped crystals were observed especially in regions where filaments were in contact with each other during exposure to methanol vapor. When exposed to ethanol vapor, a large number of square or rectangular platelets and pieces of broken platelets as well as irregular shape masses (Fig. 12) were observed on filament surfaces. One form of oligomer aggregation which was observed rarely is shown in Figure 13. This type of aggregation was also observed on filaments exposed to water vapor. It is interesting to note that when observations were made with a light microscope, crystals with dimensions of the same order of magnitude as the filament diameter were observed. These large crystals may have been formed from cyclic monomer molecules since such crystals were not observed by SEM. Monomer crystals would have sublimed during sample preparation for the SEM.

With *n*-propanol vapor exposures, the resulting square or rectangular crystals

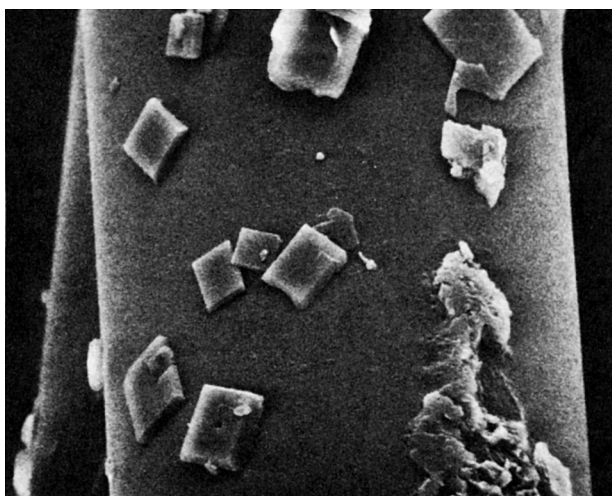


Fig. 12. Surface of nylon 6 filament exposed to ethanol vapor for 15 days ($\times 1200$).

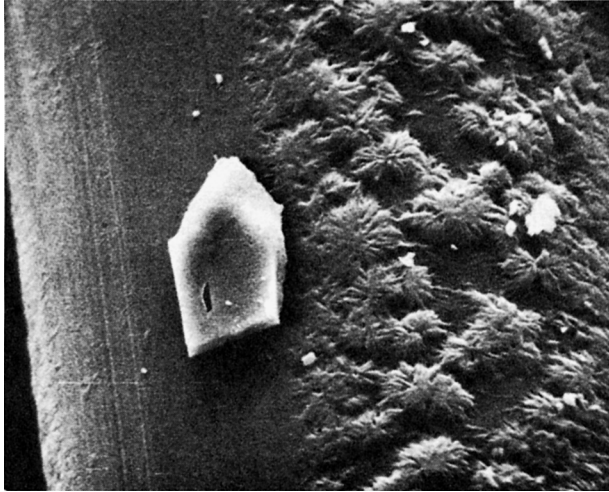


Fig. 13. Rarely observed aggregation on surface of nylon 6 filament exposed to ethanol vapor for 15 days ($\times 1800$).

were both smaller and fewer than those grown by methanol or ethanol exposures (Fig. 14). This observation agrees with our findings, to be discussed in detail below, that the amount of low molecular weight material which migrated to the filament surface by exposure to propanol vapor was less than 20%, while in the case of methanol or ethanol vapor exposures more than 50% of the low molecular weight material migrated to the surface. Needle-type crystals were also observed growing with the square platelet crystals with *n*-propanol vapor exposures (Fig. 14).

When exposed to butanol vapor, many crystal forms together with very small square platelets (Fig. 15) were found on the filament surfaces. Rod-like crystals consisting of smaller rods twisting round each other were observed (Fig. 16). The end of the rods contacted the filament surfaces through fine fibrils which could

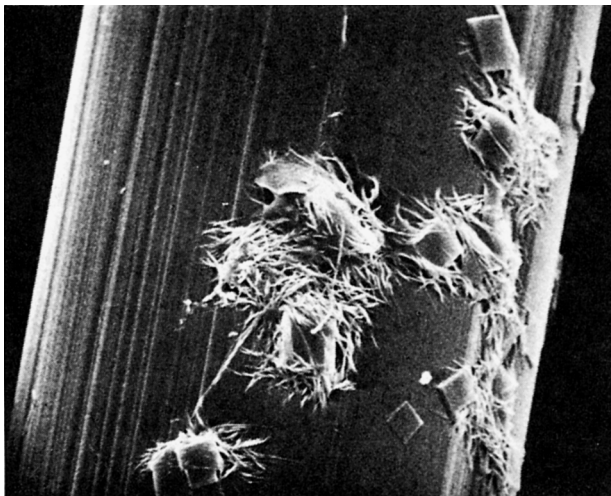


Fig. 14. Surface of nylon 6 filament exposed to propanol vapor for 15 days ($\times 1300$).

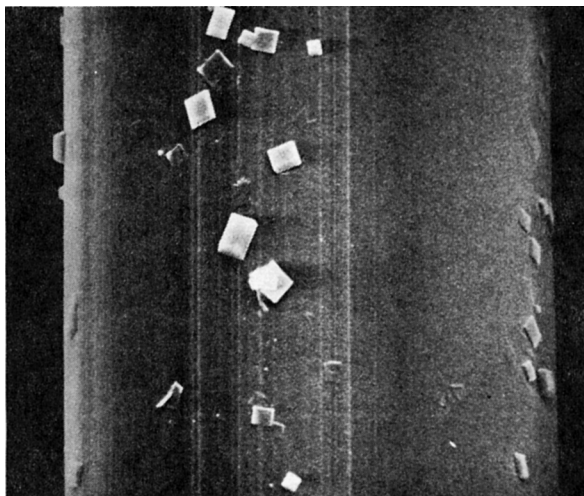


Fig. 15. Surface of nylon 6 filament exposed to butanol vapor for 15 days ($\times 1200$).

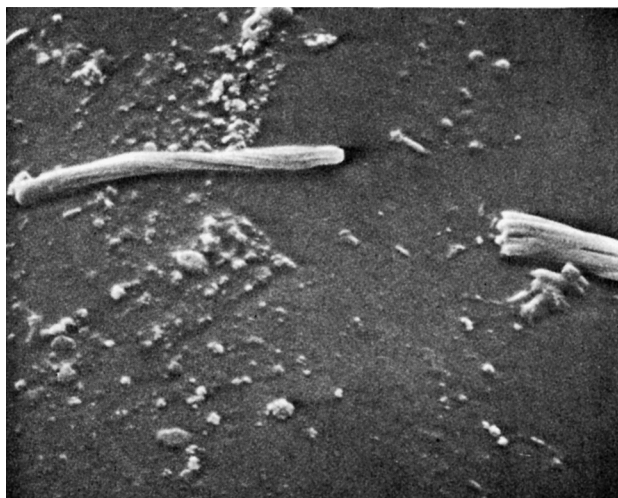


Fig. 16. Rod-like crystals observed on surface of nylon 6 filament exposed to butanol vapor for 15 days ($\times 3900$).

have been the growth points (Fig. 17). Needle-type crystals were also observed (Fig. 18) as well as aggregates of fibril-type crystals growing over square platelet crystals (Fig. 19). Square platelets growing on top of fibril-type crystals were noted in other areas.

When the nylon 6 filaments were exposed to pentanol vapor, crystals also formed on their surfaces. The crystals were small in size, and no crystals were observed on the surface of about half the filaments. In areas where crystals occurred, the square or rectangular platelet crystals predominated (Fig. 20). Some crystals were not developed well. Rod-like crystals and aggregated fibril-type crystals were observed as well (Fig. 21).

Crystal formation on the surface of nylon 6 filaments was not observed on exposure of the samples to higher alcohols such as *n*-hexanol or *n*-heptanol, although the time of exposure was extended to 90 days.

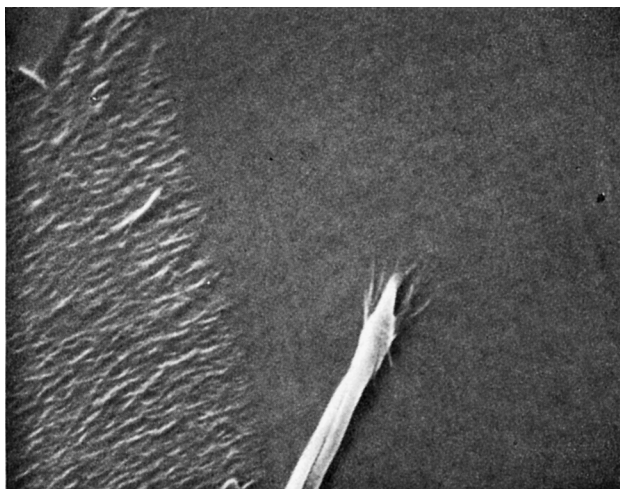


Fig. 17. Fibril growing out of end of rod-like crystals grown on surface of nylon 6 filament exposed to butanol vapor ($\times 3300$).

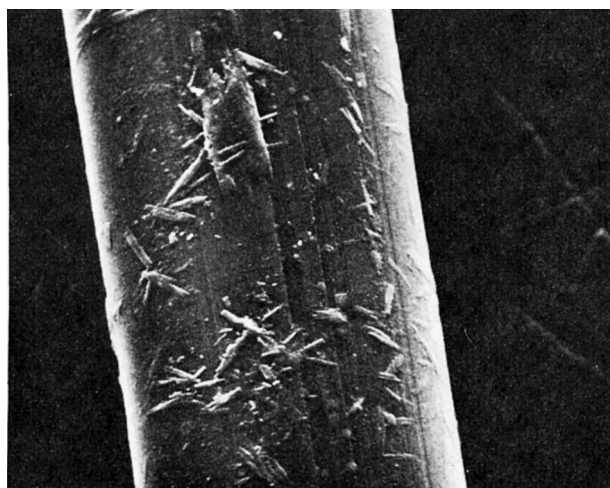


Fig. 18. Needle-type crystals grown on nylon 6 filament exposed to butanol vapor ($\times 960$).

It has been noted by other workers¹⁸ that needle-type crystals of cyclic dimer, which were crystallized by deposition of sublimated cyclic dimer, recrystallize to square or rectangular plate crystals from water. However, we have not yet been able to determine for our system whether each cyclic oligomer forms separate crystals or if different oligomers can crystallize together to form crystals. Attempts to establish this are being made.

As we have shown, cyclic oligomers can migrate and crystallize in various shapes when exposed to alcohol vapors. The form of the crystals may depend on the type and relative amount of the oligomers migrating to the surface of the filaments which would be affected by such factors as the alcohol used, the surface structure of the filament, temperature, and exposure period.

For nylon 6 samples exposed to the different alcohol vapors, it was found that

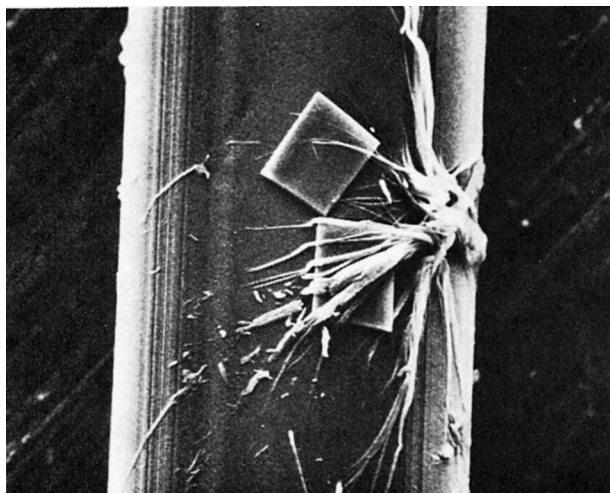


Fig. 19. Aggregates of crystals grown on nylon 6 filament exposed to butanol vapor ($\times 840$).

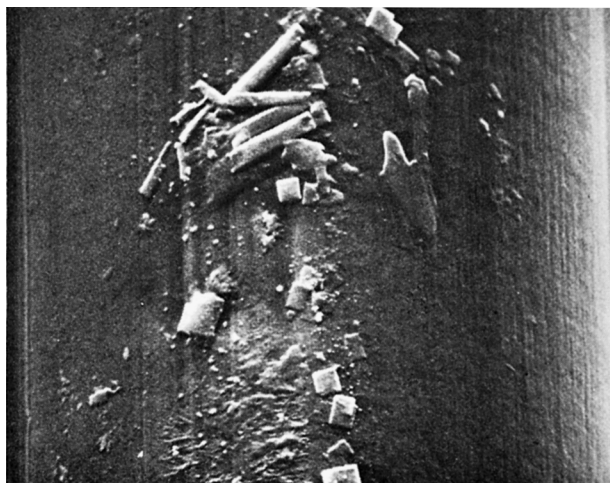


Fig. 20. Crystals grown on nylon 6 filament exposed to pentanol vapor ($\times 1600$).

as the size of the alcohol molecule increased, the smaller the amount of cyclic monomer and oligomer that migrated to the filament surfaces as indicated by measurements of residue II (Table II). On exposure to methanol vapor, 62% of total low molecular weight species migrated to the surface, whereas in the case of pentanol vapor, only 12% migrated. The composition of the total amount of migrated material, assumed to be residue II, was analyzed by GPC (Fig. 22). On methanol exposure, all low molecular weight species from cyclic monomer to cyclic hexamer migrated to the surface. The composition of the migrated species in the case of ethanol vapor exposure was almost the same as that of methanol vapor. The ratio of monomer to individual oligomer migrating was approximately the same as that obtained with methanol. When comparisons are made of the composition of residue II for samples exposed to water vapor with that of samples exposed to methanol vapor (cf. Figs. 10 and 22), it will be noted that for



Fig. 21. Additional crystal forms grown on nylon 6 filament exposed to pentanol vapor ($\times 1300$).

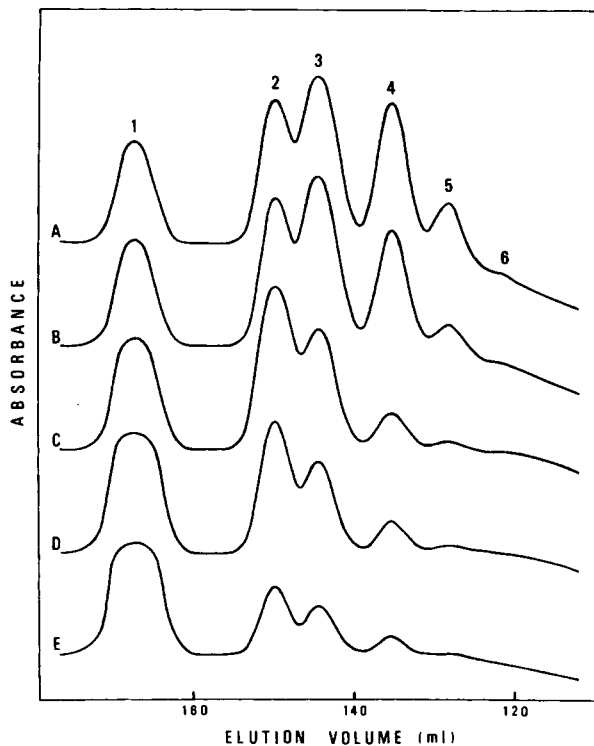


Fig. 22. Gel permeation chromatograms of residue II obtained from nylon 6 exposed to various *n*-alcohol vapors: A, methanol; B, ethanol; C, propanol; D, butanol; E, pentanol; 1 = monomer; 2 = dimer; 3 = trimer; 4 = tetramer; 5 = pentamer; 6 = hexamer.

the former exposure the migrated material contained a greater quantity of the cyclic dimer and smaller quantities of the cyclic trimer and pentamer than the migrated material of the methanol exposure.

When the nylon 6 filament was exposed to propanol vapor, the relative in-

tensities of the absorption peaks of cyclic dimer and trimer reversed when compared with those obtained with methanol or ethanol exposure (Fig. 22). Also, a greater quantity of cyclic monomer was present in the low molecular weight material which migrated to the surface on propanol vapor exposure than with either methanol or ethanol vapor exposures. The cyclic monomer content in residue II obtained from exposure of nylon 6 filaments to methanol vapor and propanol vapor was 27% and 42%, respectively. It should be noted that less low molecular weight material migrated to the fiber surface on exposure to propanol vapor than methanol exposure (Table II); thus, in absolute terms the amount of ϵ -caprolactam migrating to the filament surface was greater for methanol exposures than for propanol exposures (i.e., 0.57% and 0.25%, respectively, expressed on weight of filament).

The diffusion of the higher cyclic oligomers to the filament surface became progressively more difficult as the size of the n -alcohol molecule was increased. For example, about 10% of the low molecular weight species present in the filament migrated to the filament surface on exposure to pentanol vapor and 80% of the migrated species was cyclic monomer. In contrast, 62% of the low molecular weight species in the filament migrated to the filament surface on exposure to methanol vapor and only 27% of the migrated material was cyclic monomer. The swelling of nylon 6 exposed to alcohols decreased as the size of the n -alcohol molecule increased (Table III). It is possible that the amount of ϵ -caprolactam and oligomer diffusing to the fiber surface is affected by the amount of swelling of the fiber induced by the alcohol. However, other factors are also involved. Although water and n -butanol swell nylon 6 about the same amount (Table III) and the amount of residue II is roughly equal in these two cases (Table II), the composition of the residues differ greatly. The concentration of monomer in residue II is far higher for nylon 6 exposed to butanol vapor.

After the nylon 6 filaments exposed to alcohol vapors were washed with water, the filaments were extracted with methanol to remove low molecular weight species remaining in the filaments. GPC of residue III from this set of experiments is shown in Figure 23.

The chromatogram of residue III for samples previously exposed to methanol and then water washed showed that the absorption peaks of cyclic dimer, trimer, and tetramer were relatively small and that the peaks of cyclic monomer and pentamer were larger.

TABLE III
Dimensional Changes of Nylon 6 Filament on Exposure to Water or n -Alcohols

Medium (liquid or vapor)	Length change, % ^a	Width change, % ^b
Air (65% R.H.)	2.4	—
Water	5.3	4.4
Methanol	7.1	7.0
Ethanol	6.7	5.9
Propanol	6.6	5.6
Butanol	6.2	4.1
Pentanol	3.5	2.1

^a Lengths measured with filament exposed to vapor.

^b Widths measured with filament immersed in liquid.

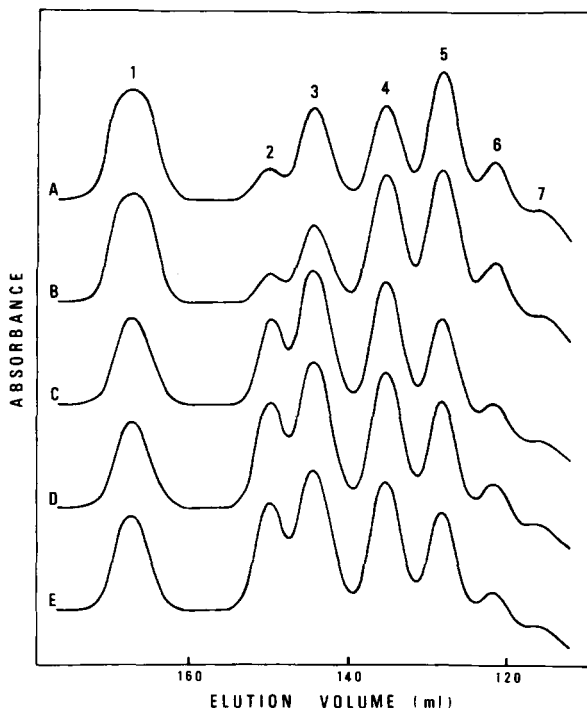


Fig. 23. Gel permeation chromatogram of residue III obtained from nylon 6 exposed to various *n*-alcohol vapors: A, methanol; B, ethanol; C, propanol; D, butanol; E, pentanol; 1 = monomer; 2 = dimer; 3 = trimer; 4 = tetramer; 5 = pentamer; 6 = hexamer; 7 = heptamer.

When filaments were exposed to methanol or ethanol vapors, more than half of the low molecular weight materials, especially the cyclic dimer, trimer, and tetramer, migrated to the filament surface. Thus, compositions of cyclic monomer and individual cyclic oligomers remaining in the filaments differ from those present in the starting filament (cf. Figs. 22 and 23). In the case of propanol-, butanol-, and pentanol-exposed fibers, the amount of material migrating is small, and the chromatograms of residue III for these samples does not differ greatly from that of residue I, i.e., the residue extracted from the starting fiber by methanol (cf. Figs. 23 and 10).

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