Investigation of the Fine Structure of High Polymers by the Method of Deuterium Exchange.   I.   Changes in Lateral-Order Distribution of Nylon 6 by Heat Setting*

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Synopsis

The lateral-order distribution of nylon 6 was evaluated by deuteration and infrared spectroscopic measurement. Unset, dry-heat-set, and steam-set samples are placed in contact with D_2O vapor at various temperatures from 25 to 150°C. After equilibrium of the reaction is attained, they are dried and sealed in a NaCl cell. The ratio of the intensity of N—D to C—H vibration bands in the 3-4 μ region is calculated from the infrared spectra and plotted against temperature of deuteration. The curves obtained show the accessibility of the sample to D_2O vapor at various temperatures, and the differential of the curve gives the lateral-order distributions of nylon 6. The lateral-order distribution shows that regions of amorphous and of intermediate order decrease, and regions of higher and crystalline increase on dry heat setting, while regions of intermediate order markedly decrease and amorphous and crystalline regions increase on steam setting. These phenomena suggest that loosening of polymer molecules in the amorphous regions and crystallization are caused by the steam setting.

1. INTRODUCTION

In order to investigate the fine structure of crystalline high polymers, especially of cellulose fibers, various methods have been devised on the base of Howsmon's lateral-order concept; for example, Marchessault and Howsmon[1,2] estimated lateral-order distribution from moisture regain of materials fractionally dissolved in various concentrations of aqueous NaOH. In addition, the hydrolysis method of Maeda,[3] the formic acid esterification of Nickerson,[4] the NO_2 oxidation of Roseveare[5] and so on are well known methods.   In these methods, however, large amounts of material and elaborate techniques and work-ups are required to obtain exact distribution curves, and in addition, undesired changes in fine structure occur in the process of these treatments which cannot be avoided.

The concept of lateral-order distribution in the fine structure of cellulosic materials, in which one considers a continuous distribution of lateral order from completely amorphous to completely crystalline, would be reasonably

* This material appeared in part in *Kobunshi Kagaku*, **18**, 198 (1961).

applicable to the fine structure of synthetic crystalline polymers, but little systematic study has been carried out on this problem, the sole exception being Kanatsuna's reports[6,7] of the measurement of the lateral-order distribution of nylon 6 by phenol adsorption.

When nylon 6 comes in contact with D_2O vapor, the hydrogen atom of amide group is easily exchanged for a deuterium atom, and the number of exchanged amide groups involved can be estimated from infrared spectroscopic measurements. On the basis of these facts the evaluation of molecular packing in amorphous regions in variously heat-set nylon 6 materials has been carried out by the comparison of the accessibility to deuterium oxide.[8,9] An evaluation of accessibility by the deuterium exchange method was previously reported on cellulosic materials by Frilette et al.[10] and Marrinan and Mann.[11] In these studies, the extent of the exchange reaction was calculated indirectly from the change of density or reflectance of D_2O, but no estimation of the lateral-order distribution was carried out.

In the present investigation, the lateral-order distribution of variously heat-set nylon 6 films was evaluated by a new method which was devised by the authors. Samples having different physical structure were prepared by heat-setting and placed in contact with D_2O vapor at various temperatures from 25 to 150°C. After reaction equilibrium had been attained, the samples were dried and the accessibilities were calculated from the intensities of infrared N—D vibration band. The lateral-order distribution was calculated by differentiation of the accessibility–temperature curve. In this new method, neither undesired recrystallization nor swelling effect interferes with evaluation of the lateral-order distribution, and only a small amount of material is necessary to carry out the measurement.

2. EXPERIMENTAL

Materials

Nylon 6 films (thickness 5–10 μ) were prepared by a method previously described.[9] To decrease the crystallinity of the films, the films were melted and quenched and then were heat-set as follows: (a) unset; (b) steam-set at 130°C. for 60 min. in an autoclave; (c) dry-heat-set at 170°C. for 60 min. in a Wood's metal bath.

Deuterium Exchange Reaction

The various heat-set materials described above were cut into 10 pieces, each 2 × 3 cm. in size, and affixed to stainless steel frames. In the case of deuteration at the temperatures below 100°C., a vapor-phase deuteration apparatus was used,[9] and for exchange at temperature of 100–150°C., the materials were sealed into glass tubes with a small amount of D_2O and deuterated under the experimental conditions listed in Table I. After the reaction, these materials were dried at 60°C. for 2.5 hr. in vacuum without contact with the atmosphere and then sealed into a special NaCl cell[8] for

TABLE I
Experimental Conditions for Deuterium Exchange of Nylon 6 Films

Reaction temperature, °C.	Reaction time, hr.
25	112.5
40	61.5
60	112.5
80	61.5
100	1.0
110	1.0
120	1.0
130	1.0
140	1.0
150	1.0

infrared spectroscopic measurements in a glove box in a completely dry atmosphere.

Infrared Spectroscopic Measurement

Absorption intensities of the N—H, C—H, and N—D bands in 3–4 μ region of the deuterated samples were quantitatively measured with a Perkin-Elmer model 13 infrared spectrophotometer equipped with a NaCl prism in double-beam system.

Measurement of Density

After spectroscopic measurement, densities of the various heat-set nylon 6 samples, the undeuterated film, and the unset films deuterated at various temperatures were measured by use of a benzene–carbon tetrachloride density gradient column and the degrees of crystallinity calculated.

3. RESULTS AND DISCUSSION

Infrared Spectra of Nylon 6 Deuterated at Various Temperatures

Infrared spectra of the unset nylon 6 deuterated at various temperatures are shown in Figure 1. That reaction equilibrium is attained under these experimental conditions was ascertained in a previous study.[9] It is found from Figure 1 that intensities of the N—H band at 3290 cm.$^{-1}$ decrease markedly with reaction temperature and the intensities of the N—D bands at 2485 and 2425 cm.$^{-1}$ increase, though there is no change in C—H bands at 2950 and 2885 cm.$^{-1}$

Figures 2 and 3 show the spectra of unset, steam-set, and dry-heat-set nylon 6 films which were deuterated at 80 and 120°C., respectively. These spectra show that the deuteration is more extensive for the unset sample in comparison with the other films.

When the degree of deuteration is calculated from the intensities of the absorption bands, the method involving the use of the integral value of
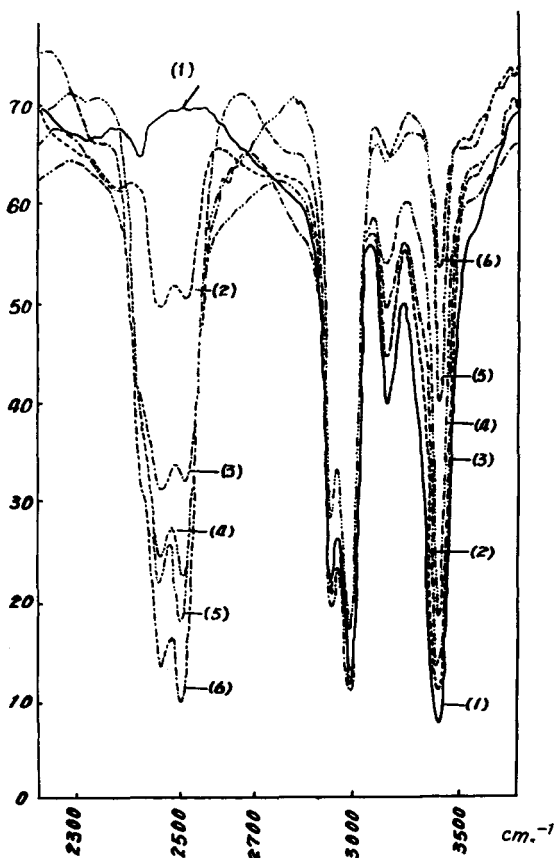
Fig. 1. Infrared spectra of nylon 6 deuterated at various temperatures: (1) unset, undeuterated; (2) 40°C., 61.5 hr.; (3) 80°C., 61.5 hr.; (4) 110°C., 60 min.; (5) 130°C., 60 min.; (6) 150°C., 60 min.

the N—D bands is more exact than the value obtained from the decrease of N—H peak intensity as described before.[8,9] However the integration method requires much effort, and therefore, the peak height intensity ratios D_{N-D}/D_{C-H} and D_{N-D}/D_{C-H} were calculated from the optical densities of the N—H, C—H, and N—D absorption bands at 3290, 2950, and 2485 cm.$^{-1}$ for the unset samples deuterated at various temperatures. The cross plot of these values was then made as shown in Figure 4; good linearity was found.

Fairly good linearity between the two sets of values shows that the intensities of those absorption bands are not affected by neighboring bands, and the D_{N-D}/D_{C-H} intensity ratio may correspond to the accessibility to D_2O in the polymer.

Densities of Deuterated Materials

To measure the density of high polymers, the density gradient column method or the flotation method, which consists of dropping a sample into a
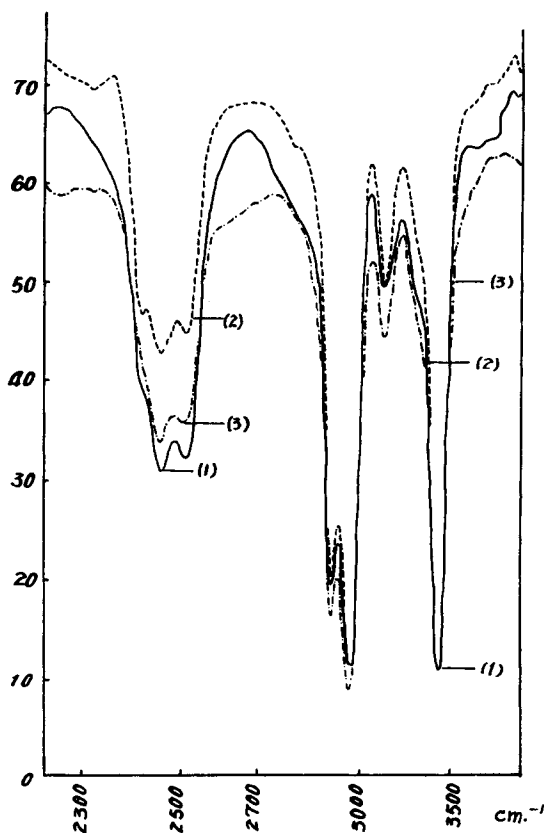
Fig. 2. Infrared spectra of various heat-set nylon 6 reacted in D_2O vapor at 80°C. for 61.5 hr.: (*1*) unset; (*2*) steam-set, 130°C., 60 min.; (*3*) dry-heat-set, 170°C., 60 min.

mixture of solvents such as benzene and carbon tetrachloride is well known. In such a method, it is assumed that the solvent molecules do not penetrate into the amorphous portion of the sample. In practice, however, the solvent molecule would penetrate fairly far into the sample, depending on the kind of solvent or on the amorphous structure of the polymer. For this reason it is necessary to state the time elapsed between immersion of the sample and measurement of the density.

In this experiment, the density of a bone-dry sample was measured at various times after the sample was placed into a column, and the densities were plotted against square root of time. As shown in Figure 5, the plotted points are on a straight line after 49 min. When a sample is dropped into a density column, the sinking of the sample may involve two separate processes. The one is settling as a result of the weight of the sample and the other is that dependent on solvent intrusion into the polymer.

In the former process, the sample will reach to an equilibrium position because of increase of flow resistance and increase of density of the gradient column liquid as the sample sinks deeper. While in the latter, intrusion of
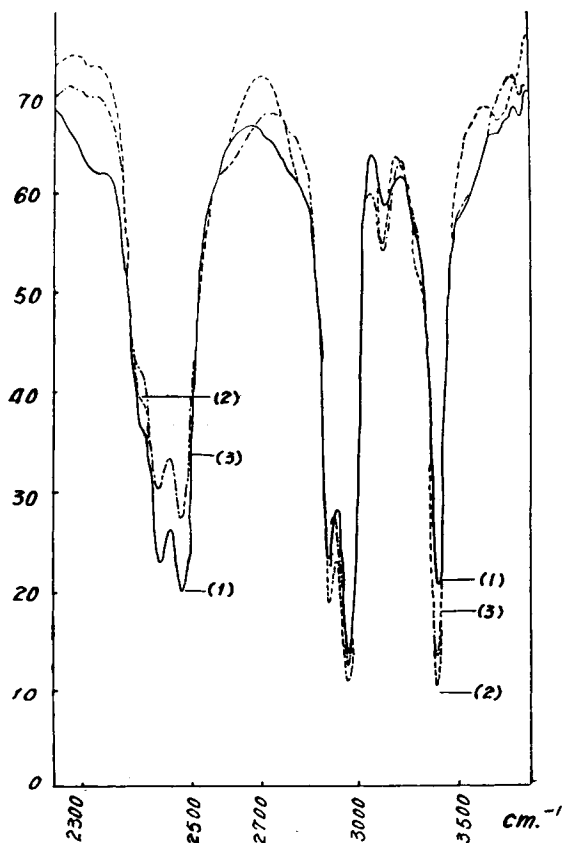
Fig. 3. Infrared spectra of various heat-set nylon 6 reacted in D_2O vapor at 120°C. for 60 min.: (1) unset; (2) steam-set, 130°C., 60 min.; (3) dry-heat-set, 170°C., 60 min.

liquid will begin at the moment the sample is immersed in solvent and continues until the inner part of the sample is filled with the liquid.

Therefore, in the early part of the time–density curve in Figure 5 (up to about 49 min.) these two processes will overlap. The straight line portion of the curves (after 49 min.) shows the increase in measured density attributable to penetration of solvent. The true density of the sample, in which no liquid intrudes into the amorphous portion, will be obtained by extrapolating the straight line to zero time.

The hypothesis that the straight line represents intrusion of liquid into sample is derived by the following reasoning. On the problem of penetration of liquid into fibrous materials, Crank represented the amount of penetrating liquid by the following equation:[12]

$$C_t/C_\infty = 2(Dt/\pi)^{1/2}$$

where, C_t, C_∞ represent the amount of intruded liquid at time t and infinite time, respectively, and D represents the diffusion coefficient.

If the density values measured at time zero, t, and infinity are ρ_0, ρ_t, and ρ_∞, respectively, and no volume change as a result of swelling occurs in the measuring process, then

$$C_t/C_\infty = (\rho_t - \rho_0)/(\rho_\infty - \rho_0) = 2(Dt/\pi)^{1/2}$$

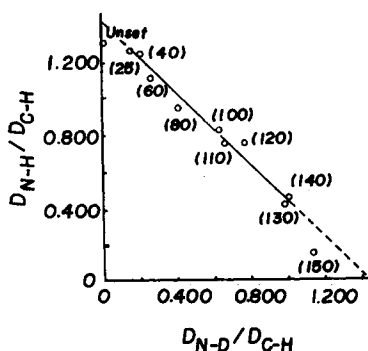$$\rho_t = 2(\rho_\infty - \rho_0)(Dt/\pi)^{1/2} + \rho_0$$

Fig. 4. Relationship between D_{N-D} 2485 cm.$^{-1}/D_{C-H}$ 2950 cm.$^{-1}$ and D_{N-H} 3290 cm.$^{-1}/D_{C-H}$ 2950 cm.$^{-1}$ in infrared spectra of nylon 6 deuterated at various temperatures.   Numbers in parentheses show temperature of deuteration (°C.).
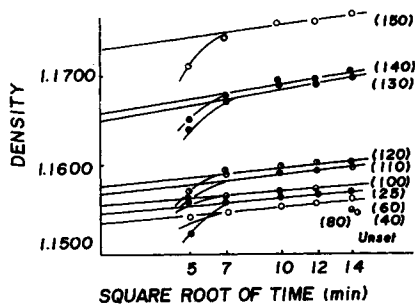
Fig. 5. Relation between density and measuring time by density gradient method. Numbers in parentheses show temperature of deuteration (°C.).
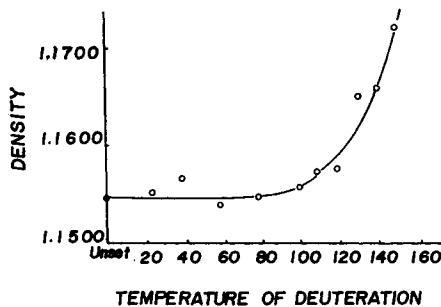
Fig. 6. Relation between density and temperature of deuteration.

This equation shows linearity between density and square root of time, Such a relation was recently recognized by Stock,[13] and the necessity of extrapolating on time–density curve was reported by Juilfs.[14]

The relation between density and deuteration temperature is shown in Figure 6. Density does not change with deuterium exchange at below 80°C., but a rapid increase is found above 100°C.

Density and crystallinity of nylon 6 variously heat-set or deuterated at various temperatures are listed in Tables II and III, respectively.

TABLE II
Density and Crystallinity of Unset or Heat-Set Nylon 6

Sample	Density, g./cm.^{3}	Crystallinity, %
Unset	1.1553	41
Steam-set[a]	1.1608	46
Dry-heat-set[b]	1.1578	43

[a] Steam-set at 130°C. for 60 min.
[b] Dry-heat-set at 170°C. for 60 min.

TABLE III
Density and Crystallinity of Nylon 6 Deuterated at
Various Temperatures

Deuteration temperature, °C.	Density, g./cm.^{3}	Crystallinity, %
25	1.1558	41
40	1.1571	42
60	1.1542	40
80	1.1551	41
100	1.1562	42
110	1.1576	43
120	1.1580	43
130	1.1655	50
140	1.1660	51
150	1.1726	56

Accessibility and Lateral-Order Distribution of Variously Heat-Set Nylon 6

Figure 7 shows the relation among degree of deuteration, degree of crystallinity, and deuteration temperature for the unset nylon 6 sample treated with D_2O at temperatures from 25 to 150°C. Deuterium exchange reaction evidently occurs in the most loosely packed amorphous region at temperatures below 80°C. and proceeds to more closely packed regions on diffusion of D_2O vapor with increasing temperature. At higher temperatures (above 100°C.), rapid increase of crystallinity is observed as deuteration proceeds.

The increase of degree of crystallinity in the dry-heat-set film is not so large as in the deuterated unset sample at the same temperatures, so the
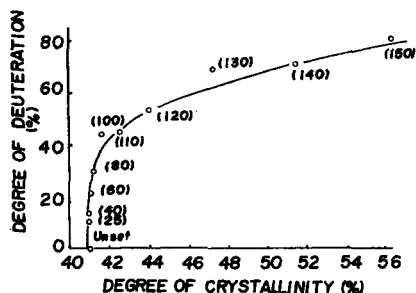
Fig. 7. Relation among degree of crystallinity, degree of deuteration, and tempera-ture of deuteration. Numbers in parentheses show temperature of deuteration (°C.).

penetration of D_2O vapor into the highly packed region seems to have a great effect on crystallization of the polymer.

Accessibilities to D_2O vapor in various heat-set samples are plotted against reaction temperatures in Figure 8, wherein accessibilities are represented by optical densities. It is shown in Figure 8 that accessibilities are the highest in the unset sample and the lowest in the steam-set sample at the same temperatures above 60°C. Curves are concave in shape for the heat-set samples because the regions deuterated decrease at the tem-peratures from 80 to 120°C.

Moreover, it is interesting to observe that the accessibility in the steam-set sample is higher than in other samples at temperatures below 60°C.

The lateral-order distribution curves in Figure 9 were obtained by plot-ting the fraction of the regions which become accessible with 10°C. incre-ments of temperature against deuteration temperatures, and the fraction
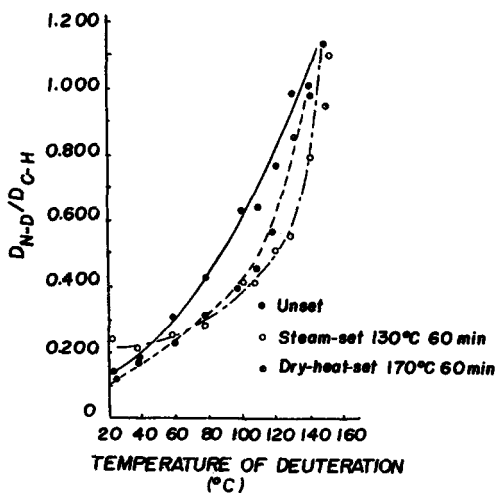

Fig. 8. Relation between the intensity of N—D absorption (2485 cm.$^{-1}$) in infrared spectra of various nylon 6 and temperature of deuteration.

is calculated from Figure 8.   A comparison of dry heat set and unset films (Fig. 9) shows that in the heat-set film, the fraction of the regions which become accessible to D_2O at temperatures below 115°C. are smaller and those accessible above 115°C. are higher.
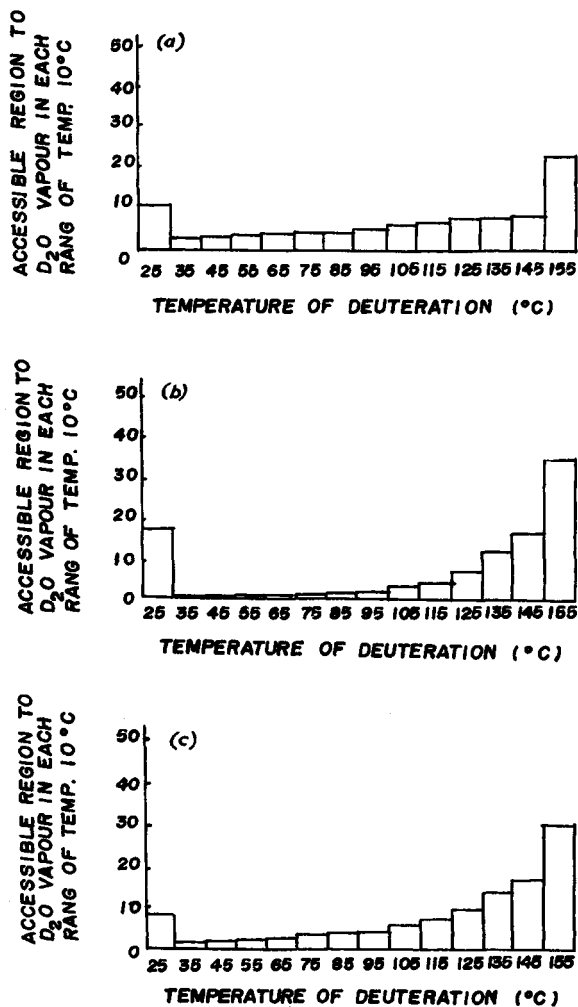

Fig. 9. Lateral-order distribution of variously heat-set nylon 6: (a) unset; (b) steam-set at 130°C. for 60 min.; (c) dry-heat-set at 170°C. for 60 min.

In the steam-set sample (Fig. 9b), this tendency is more apparent.   The fraction of the regions to be deuterated from 30 to 120°C. decreases markedly, and the fraction of the most accessible regions (deuterated below 30°C.) and of the most closely packed regions (deuterated at above 120°C.) increases remarkably.   These observations agree well with our previous results[15] in which the diffusion coefficient of dyestuffs in the dry-heat-set sample decreases with increasing degree of crystallinity and with formation

of close packing of molecules in amorphous region, while in case of steam-set samples, the diffusion coefficient increases markedly with loose packing of molecules in amorphous regions, in spite of much increase of crystallinity.

The lateral-order distributions shown in Figure 9 show good agreement with Kanatsuna's results,[6,7] obtained by a phenol adsorption technique. However the technique described here is characteristic in the following points.

(*1*) In the phenol adsorption method, the accessibility is calculated from the amount of adsorbed phenol which penetrates the more closely packed regions with increase of the concentration. As the phenol solution is involved in both swelling and recrystallization, the phenol which is first adsorbed into the highly packed region may be extruded out of the crystal when recrystallization occurs. So the amount of adsorbed phenol may not show the full extent of the region to which phenol initially penetrated. In the deuteration technique, recrystallization also occurs. However, polymer molecules deuterated before recrystallization becomes a part of the crystal, and the amount of N—D group both in amorphous and crystalline forms can be evaluated exactly from the infrared spectrum.

(*2*) Deuterium oxide molecule is sufficiently small to intrude into the closely packed fine structure, so one can estimate the ordering of molecules in the amorphous region more exactly than by the phenol adsorption method.

(*3*) Adsorption of phenol seems to consist of binding adsorption onto fiber molecules and condensed adsorption in intermolecular spaces, just as bound water and condensed water in moisture regain on nylon 6. As a result, among the samples of different crystallinity and different crystal size, the amount of condensed phenol in intermolecular spaces will vary, and the total adsorption of phenol will be not proportional to the ordering of molecules. The deuterium exchange method is more exact, as bound or condensed water in a sample can be dried and only acid amide groups with which D_2O vapor reacts are detected.

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Résumé

On a étudié la distribution de l'ordre latéral du nylon-6 à l'aide de deutérium et de mesures de spectroscopie infra-rouge. Des échantillons non-chauffés, traités à chaud et traités à la vapeur, sont mis en contact avec des vapeurs de D_2O à des températures situées entre 25 et 150°C. Lorsque l'équilibre de la réaction est atteint, on sèche les échantillons et on les scelle dans une cellule en NaCl. À partir des spectres infra-rouges on calcule le rapport d'intensité des bandes de vibration N—D et C—H entre 3 et 4 μ. Ce rapport est mis en graphique en fonction de la température de la réaction de deutéra-tion. Les courbes obtenues montrent l'accessibilité de l'échantillon aux vapeurs de D_2O pour les températures variant de 25 à 150°C et la diférentielle de la courbe donne les distributions de l'ordre latéral du nylon-6. La distribution de l'ordre latéral montre que les régions amorphes et d'ordre intermédiaire diminuent tandis que les régions d'ordre plus élevé et cristallin augmentent au cours du traitement à chaud. Dans le traitement à la vapeur les régions d'ordre intermédiaire diminuent d'une façon notable tandis que les régions amorphes et cristallines augmentent. Ces données laissent supposer que le relâchement des molécules polymériques dans la région amorphe ainsi que la cristallisa-tion sont dues au traitement à la vapeur.

Zusammenfassung

Die Verteilung der seitlichen Ordnung von Nylon 6 wird durch Deuterierung und infrarotspektroskopische Messung ermittelt. Hitze-, trockenhitze- und dampfbehan-delte Proben werden in Kontakt mit D_2O-Dampf bei verschiedenen Temperaturen von 25 bis 150°C hergestellt. Nach Erreichung des Reaktionsgleichgewichts werden sie getrocknet und in eine NaCl-Zelle eingeschmolzen. Das Intensitätsverhältnis der N—D- zur C—H-Schwingung im 3–4-μ-Bereich wird aus den Infrarotspektren berechnet und gegen die Deuterierungstemperatur aufgetragen. Die erhaltenen Kurven zeigen die Zugänglichkeit der Proben für D_2O-Dampf bei verschiedenen Temperaturen von 25 bis 150°C, und die Differentialkurve liefert die Verteilung der Seitenordnung von Nylon 6. Die Verteilung der seitlichen Ordnung zeigt, dass die Bereiche mit amorpher und mittlerer Ordnung bei der Trockenhitzebehandlung abnehmen und die Bereiche mit höherer und kristalliner Ordnung zunehmen. Hingegen nehmen bei der Dampfbe-handlung die Bereiche mit mittlerer Ordnung merklich ab und die Bereiche mit amorpher und kristalliner Ordnung zu. Diese Erscheinungen zeigen, dass durch die Dampfbe-handlung eine Lockerung der Polymermoleküle in den amorphen Bereichen und eine Kristallisation verursacht werden.