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Steam and Heat Setting of Nylon 6 Fiber. IX. Changes in Infrared Spectra with Deuteration of Heat-Set Nylon 6*

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Synopsis

The degree of crystallinity of nylon 6 is increased by both steam and dry heat setting, while the diffusion rate of dyes is increased by steam setting and decreased by dry heat setting. These phenomena have been explained in connection with the state of the amorphous regions. This explanation are confirmed from a quantitative analysis of infrared spectra. Heat-set nylon 6 films were deuterated with D_2O at 60°C., for 100 hr. in the vapor phase. Integral intensities of N—D stretching vibration band on the spectra are calculated from the equation:

$$[1/(1-\alpha)l]\int \log (I_0/I)d\nu = K'C$$

where I_0 and I are the intensity of the incident and the transmitted light respectively, l the thickness, and α the degree of crystallinity. Here $K'C$ represents the number of free N—H groups in the amorphous fraction. The value $K'C$ is increased by steam setting and decreased by dry heat setting.

1. INTRODUCTION

In the previous reports it was confirmed that various properties of nylon 6 such as density, crystallinity,[1] dyeability, diffusion coefficient of dye,[2] swelling property,[3] stress relaxation,[4] thermal stress[4] and moisture regain[5] are markedly affected by heat setting. In these investigations the unexpected experimental results were found that the diffusion rate of dye is increased by steam setting but decreased by dry heat setting, in spite of a similar increase of crystallinity in both types of heat setting. After a systematic investigation of differences between steam setting and dry heat setting, it was concluded that these findings would be explained by the fact that the number of intermolecular bonds is decreased by steam setting but increased by dry heat setting. In this paper, to verify this, an experiment was carried out by means of infrared spectroscopy.

The spectra of polyamides have been investigated by many authors; for instance, nylon 66 has been studied by Elliott et al.[6] and Thompson and

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* This material appeared in part in *Kobunshi Kagaku*, **17**, 679 (1960).

Torkington[7] nylon 11 by Tobin and Carrano[8] and nylon 610 by Sandeman and Keller.[9] Tobin and Torkington[8] have reported on the infrared dichroism of comparatively thin nylon 6 films and the infrared spectra in the molten state. Mizushima et al.[10] decided the assignment of the absorption bands of nylon 6 in the region from 3500 to 1000 cm.$^{-1}$ in comparison with the bands of nylon 6 and the bands of many polypeptide compounds. Sandeman and Keller[9] also described the absorption bands of nylon 6 from 1200 to 800 cm.$^{-1}$ using fairly thick films, and Kessler and Sutherland[11] investigated the region from 800 to 650 cm.$^{-1}$

It is known from these works that nylon 6 shows N—H stretching vibration bands at 3500–3000 cm.$^{-1}$ and the absorption frequency shifts to somewhat lower frequency side in the presence of hydrogen bonding.[8] Therefore if these absorption intensities can be evaluated quantitatively, the number of free amide groups in the polymer might be estimated from these values.

Also, the N—H group in the amino endgroup and amide group are easily replaced by N—D by treatment with D_2O, and the absorption frequency of the infrared spectrum varies greatly according to the difference in transition moment. As the D_2O molecule does not penetrate into crystalline regions, the exchangeable N—H groups would exist in amorphous region accessible to D_2O and these groups would not be in a state favorable for formation of hydrogen bond between neighboring molecules. In the present study, the N—H in the amorphous region was exchanged with D_2O and the content of free N—H group per unit volume of amorphous region was calculated for nylon 6 films subjected to various heat setting treatments.

2. EXPERIMENTAL

Materials

Nylon 6 film was prepared from a formic acid solution of the polymer (degree of polymerization $\bar{P} = 470$) which contained no impurities such as catalyst, plasticizer, and titanium dioxide. As the degree of crystallinity of the resulting film was too high, it was melted and then quenched with the use of the apparatus shown in Figure 1, and the degree of crystallinity was thus reduced. The melting procedure is as follows. The nylon 6 film above obtained affixed to a thin glass tube *B*, of which the surface was coated by silicon oil, and this tube was hung in the thick glass tube A. After the air in the space between tubes *A* and *B* was replaced completely by nitrogen gas, the apparatus was put into an oil bath to heat. Several minutes after the temperature in the tube *B* exceeded the melting point of the polymer, the apparatus was removed from the bath, and cold carbon tetrachloride (−5 to −10°C.) was poured into tube *B* through the opening, where a thermometer had been inserted, to quench the tube *B* from inside. By this method the materials could be melted in film form without being subjected to oxidation. The resulting films were extracted by benzene–ethanol (50:50) mixture for 6 hr. and with ether for 4 hr. in a Soxhlet

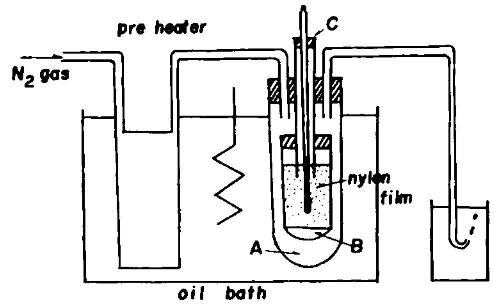

Fig. 1. Apparatus for melting nylon film.

apparatus to remove carbon tetrachloride and silicon oil. The infrared spectra indicate that the materials were purified sufficiently in this way.

Heat Setting

The materials were heat-set in a sealed tube to prevent oxidation. After drying, the film was put in a bag of clean gauze, and suspended in the sealed tube by steel wire. The tube was then flushed with nitrogen and sealed. For steam-setting, distilled water was added in the sealed tube. These sealed tubes were heated in an oil bath at various temperatures for 30 min. and then the seal was broken. The treated films were dried sufficiently before use.

Deuteration

Compounds having N—H or O—H groups can be deuterated by contact with D_2O vapor, but the deuterated compound also easily undergoes the reverse exchange reaction if it comes in contacts with only a slight amount of moisture in the atmosphere. Therefore, the deuterated compounds were handled in a perfect atmosphere.

The apparatus for vapor-phase deuteration which was used by Tadokoro et al.[12] is shown in Figure 2. As in the previous paper,[13] the nylon 6 film was affixed to a stainless steel frame and deuterated in a reaction tube. After the exchange reaction reached equilibrium, the reaction tube was

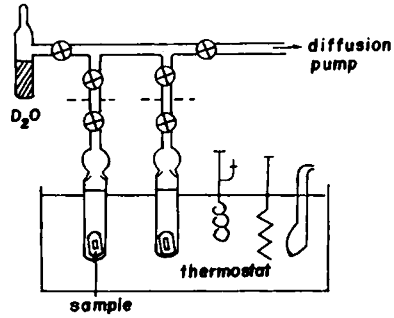

Fig. 2. Apparatus for deuteration in vapor phase.

sealed off and brought into the completely dry atmosphere in a glove box to be opened. After drying, the film was sealed into a rock salt cell and then absorption spectrum was scanned.

Measurement of Infrared Spectra

Perkin-Elmer model 21 and 13 spectrophotometers were used for this measurement. In both cases a NaCl prism was used, and spectra were scanned by the double-beam method.

3. RESULTS AND DISCUSSION

Infrared Spectrum of Heat Set Nylon 6

Infrared spectra of two kind of films, of thickness 10 and 40 μ, which were steam-set at 110, 130, or 140°C. or dry-heat-set at 160, 180, or 190°C. for 30 min. were compared with that of unset film. Typical results are shown in Figure 3.

The spectra of the thin films show no change produced by heat setting in the region from 2 to 13 μ. However those of thick films change greatly in the region of 8–13 μ. This change is attributed to the fact that the absorption bands of this region are those of C—C stacking and CONH in-plane vibration, which change sensitively in their intensity according to the variation of crystallinity with heat setting. The absorption intensities are comparatively weak at the longer wavelengths (more than 8 μ); therefore the thin films transmit most of the light and there is no appreciable change in the spectra. The bands in the region of 1100–800 cm.$^{-1}$ are crystalline- or amorphous-sensitive bands of the polymer, but changes in

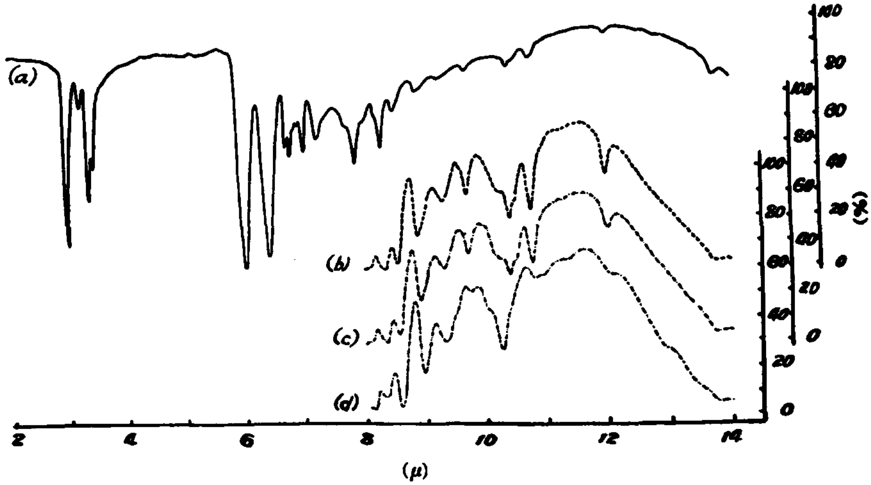

Fig. 3. Infrared spectra of heat set nylon 6 films: (*a*) unset nylon 6, film thickness 10 μ; (*b*) nylon 6 films, steam-set at 140°C., film thickness 40 μ; (*c*) nylon 6 film, dry-heat-set at 180°C., film thickness 40 μ; (*d*) unset nylon 6 film, film thickness 40 μ.

the intensity of these bands cannot be related to the structural change in amorphous region produced by heat setting. Tobin and Torkington[8] reported that nylon 6 has a weak shoulder in the neighborhood of 3420 cm.$^{-1}$ which shows the existence of a free N—H group which does not form a hydrogen bond. In fact, Mizushima et al.[10] and Kessler and Sutherland[11] reported that N—H groups which formed hydrogen bonds showed an absorption band in the neighborhood of 3300 cm.$^{-1}$, but when the hydrogen bonds were broken the band shifted to 3400–3450 cm.$^{-1}$. While Trifan and Terenji[15] reported that the free N—H band in polyamide was seen only in the molten state and not at room temperature. Tsuboi[16] described an absorption band of water bound to peptide groups in Amilan film (nylon 6) appearing at 3497 cm.$^{-1}$

Therefore, we investigated the spectrum of this region which is a weak shoulder at the neighborhood of 3420 cm.$^{-1}$ with the thick nylon 6 film (thickness 40 μ). However, the shoulder was affected by the moisture absorption of the film and it was difficult to separate the shoulder from the neighboring absorption band. It is therefore not possible to discuss the structural changes of the amorphous region on the basis of findings regarding this shoulder.

Infrared Spectrum of Deuterated Nylon 6

The infrared spectra of deuterated polymer have been studied by many investigators, for instance, Marrinan and Mann,[17] and Yoshino[18] for cellulose; Krimm et al.[19] and Tadokoro et al.[20] for poly(vinyl alcohol); Tadokoro et al.,[12] Kessler and Sutherland,[11] and Sobue and Fukuhara[21] for polyamide. In a previous paper in this series,[13] we described the spectra of nylon 6 films steam-set by deuterium oxide vapor and those of polymers which are prepared from the previously deuterated caprolactam.

In this paper, deuteration was carried out by treating nylon 6 with D_2O vapor at 60°C. to investigate the state of the amorphous regions of the polymer at room temperature. An example of the resulting spectra is shown in Figure 4. The relation between deuteration period and the optical densities of C—H and N—D stretching vibration bands at 2950 and 2485 cm.$^{-1}$, respectively, are shown in Figure 5. In this experiment, a thin film was deuterated in D_2O vapor for 81 hr. at 60°C. and then immersed in heavy water for 109 hr. at the same temperature. This figure indicates that the equilibrium in vapor-phase deuteration is surely attained after 30–40 hr.

Nylon 6 deuterated in the vapor phase shifts its N—H stretching vibration band at 3290 cm.$^{-1}$ to that of the N—D bands at 2425 and 2485 cm.$^{-1}$. In this case, the varied intensity would relate to the number of free N—H groups in the amorphous region, where D_2O vapor is accessible at the deuteration temperature. Therefore, the intensity variation of the variously heat-set nylon sample was then estimated.

Films, 10–20 μ in thickness, were steam-set at 110, 120, or 134°C. and dry-heat-set at 160, 170, or 180°C. for 30 min. and then were deuterated

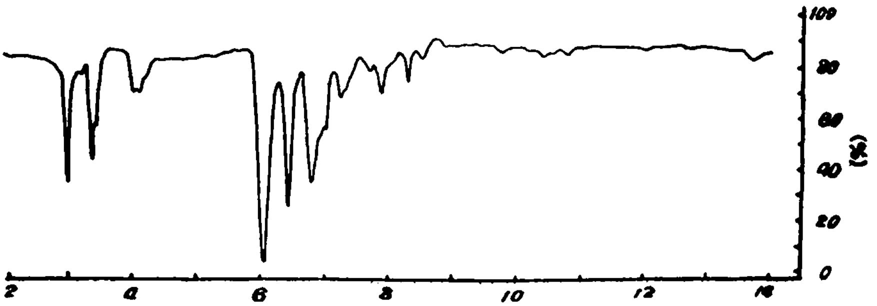

Fig. 4. Infrared spectrum of deuterated nylon 6 film.

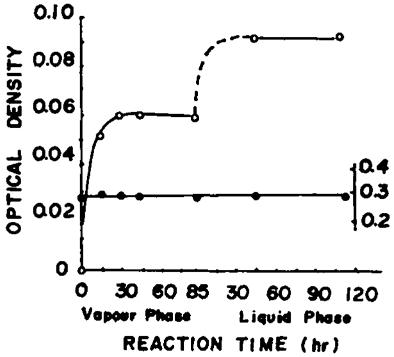

Fig. 5. Relation between intensity of N—D band and deuteration time: (-○-) N—D stretching vibration band at 2485 cm.$^{-1}$; (-●-) C—H stretching vibration band at 2950 cm.$^{-1}$

by the vapor-phase method at 60°C. for 100–120 hr. Infrared spectra of these materials were recorded, and the absorption intensities were calculated.

Generally, for quantitative intensity evaluation of a certain band in the infrared spectrum, it must be ascertained that the band is attributable safely to the vibration of the group in question and that Lambert-Beer's law can be applied in the measurement. For an ideal dilute solution following equation is well known:

$$I/I_0 = e^{-kcl} \qquad (1)$$

where I_0, I are intensities of incident and transmitted light, respectively, C is the concentration of the solution, l is the thickness of the solution, and k is the molar absorption coefficient.

Compared to the ultraviolet spectrum, the infrared spectrum has a wider distribution of vibration energy, so calculations from integral intensity are more accurate than from peak height. The equation can then be represented as follows

$$(1/l) \int \ln (I_0/I)d\nu = KC \qquad (2)$$

Equation (2) is satisfied for an ideal dilute solution. If it is possible to apply eq. (2) to a homogeneously dissolved material or chemically combined group in a polymer, for instance the exchanged deuterium atom which exists homogeneously in nylon 6, KC may be calculated from measured values of I_0, I, and l. In fact, however, the polymer is heterogeneous and the crystalline part cannot be deuterated, so that eq. (2) should be amended to exclude the effect of crystalline part as shown in eq. (3):

$$[1/(1 - \alpha)l] \int \log (I_0/I)d\nu = K'C \qquad (3)$$

where α is the degree of crystallinity of the polymer.

In eq. (3) K' should be constant for the same polyamide sample. Thus, the integral intensities of the N—D band for variously heat-set samples were evaluated from infrared spectra and values of $K'C$ were calculated by using eq. (3). Here, K' is equal to $K/2.3$.

I_0 and I were determined for the doublet at 2425 and 2485 cm.$^{-1}$ by the base-line method, and log I_0/I was calculated for individual frequency and plotted against the frequency. Then log $(I_0/I)d\nu$ was calculated from the area on the graph. The film thicknesses were measured by the Elcometer (British East Lancashire Chemical Co., Ltd.), which has a measuring range of 0–50 μ.

The crystallinity of the polymer was calculated from density, which was measured by a density gradient column composed of carbon tetrachloride and ligroin. In the evaluation of density, correction was made to avoid the diffusion of liquid into the polymer.[23]

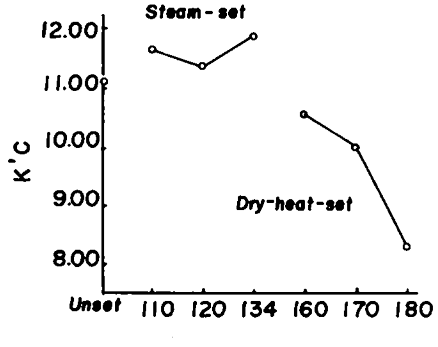

Fig. 6. Relation between $K'C$, and various heat-setting treatments.

To get information on the effect of amino and carboxyl endgroups on deuteration, the sample film was acetylated with acetic acid anhydride and pyridine, and the spectrum before and after acetylation and after deuteration was examined. The degree of acetylation of the polymer was 96.5%, but the intensities of N—H and N—D band showed no change. This indicates that the estimation is not affected by these endgroups.

The calculated integral optical density, thickness, amorphous fraction, and $K'C$. for the variously heat-set nylon 6 films are listed in Table I. The relation between heat setting temperatures and $K'C$ are shown in Figure 6. From this figure it is seen that the N—D content per unit volume of amorphous region increases on steam setting and decreases on dry heat setting. This fact supports the concept discussed in previous reports that steam setting decreases the number of intermolecular bonds in the amorphous region and causes the network structure to become looser, while dry heat setting increases such bonds, and causes the structure to become more closely packed.

TABLE I
Characteristic Values for Heat-Set Nylon filaments in Water Adsorption

Treatment	Setting temperature, °C.	$\int \log (I_0/I) d\nu$	Film thickness l,μ	Amorphous fraction, $1 - \alpha$	$K'C$
Unset		154.25	18.3	0.756	11.1495
Steam-set	110	81.65	10.7	0.654	11.6679
"	120	99.95	14.7	0.626	11.3647
"	134	82.79	13.0	0.597	11.8876
Dry-heat-set	160	77.09	10.6	0.677	10.5706
"	170	105.55	16.1	0.654	10.0243
"	180	113.70	18.9	0.719	8.3670

This investigation was based on two hypotheses: first, that Lambert-Beer's law, is satisfied for an ideal dilute solution, is applicable to the polymer films, having heterogeneous fine structure, and secondly, when N—D content per unit volume of the amorphous part is calculated, the degree of crystallinity calculated from density can be used. As the colorimetry of polymer film is widely carried out as a general experimental method, for instance as in colored cellophane, the former hypothesis may be correct. However samples in which known amounts of N—H group have been deuterated are impossible to prepare for these samples, the applicability of the Beers-Lambert relation is not certain. For the latter hypothesis to be valid, the crystallinity as estimated from density must be equal to the fraction inaccessible to D_2O vapor, but this point is uncertain from this experiment. The measurement of thickness of the thin films (10–20 μ) is very difficult, and the calculation of integral optical density may be affected by the absorption band of CO_2 gas in the neighborhood of 2300 cm.$^{-1}$. On the whole, therefore, these results will be subject to some experimental error. However, considering the results of the previous reports, these results show the tendency of structural changes produced in amorphous regions by heat setting.

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Résumé

Le degré de cristallinité du nylon 6 augmente par chauffage, alors que la vitesse de diffusion des colorants augmente par chauffage à la vapeur et diminue lorsqu'on chauffe à sec. On a expliqué ces phénomènes comme étant en rapport avec l'état des régions amorphes. Cette explication a été confirmée par une analyse quantitative des spectres infra-rouges. Des films de nylon 6 chauffés ont été deutérés avec D_2O à 60°C en phase vapeur pendant 100 heures. Les intensités totales des bandes de vibration N—D ont été calculées sur les spectres de la façon suivante:

$$\frac{1}{(1-\alpha)l}\int \log (I_0/I)d\nu = K'C$$

où I_0 et I sont les intensités respectivement de la lumière incidente et transmise, l' l'épaisseur, et α, le degré de cristallinité. $K'C$ représente ici le nombre de groupes N—H libres dans la région amorphe. Alors que la valeur de $K'C$ croît par chauffage à la vapeur, elle décroît par chauffage à sec. On a remarqué des changements de structure dans la région amorphe.

Zusammenfassung

Der Kristallinitätsgrad von Nylon-6 wird durch Hitzebehandlung vergrössert, während die Diffusionsgeschwindigkeit von Farbstoffen durch Dampfbehandlung vergrössert und durch Trockenhitzebehandlung herabgesetzt wird. Diese Erscheinungen wurden in Verbindung mit dem Zustand der amorphen Anteile erklärt. Die Erklärung wird durch eine quantitative Analyse der Infrarotspektren bestätigt. Hitzebehandelter Nylon-6-Film wird mit D_2O bei 60°C während 100 Stunden in der Dampfphase deuteriert. Die integrale Intensität der N—D-Streckungsschwingungsbande im Spektrum wird in folgender Weise berechnet:

$$\frac{1}{(1-\alpha)l}\int \log\frac{I_0}{I}\,d\nu = K'C$$

wo I_0 und I die Intensität des einfallenden bzw. durchgehenden Lichtes, l die Dicke und α der Kristallinitätsgrad ist. $K'C$ stellt die Anzahl der freien N—H-Gruppen im amorphen Anteil dar. Der Wert von $K'C$ wird durch Dampfbehandlung vergrössert, durch Trockenhitzebehandlung herabgesetzt. Die Strukturänderungen im amorphen Anteil werden bestätigt.

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