

Steam and Heat Setting of Nylon 6 Fiber.

VII. Infrared Spectra of Nylon 6 Prepared from N-Deuterated ϵ -Caprolactam and the Water Accessibility of Nylon 6 in Steam Setting*

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Synopsis

The infrared spectrum of deuterated ϵ -caprolactam was examined. It was confirmed spectroscopically that the hydrogen of the N—H group in ϵ -caprolactam is exchanged for deuterium after repeated exchange reactions. The deuterated ϵ -caprolactam was polymerized, and the infrared spectrum of the polymer (called as N—D polymer) is compared with that of the normal nylon 6 polymer (called N—H polymer) which was steam-set in D₂O vapor at 135°C. Characteristic absorption bands of N—D polymer are observed at 967, 896, 888, 876, and 719 cm.⁻¹. The water accessibility of both N—H and N—D polymer was estimated from the spectra of both samples subjected to the repeated steam setting in D₂O and H₂O alternately at 130°C. The results show that at the initial stage of the repeated steam setting, H₂O and D₂O molecules may penetrate into the ordered regions in the polymers and partially break down intermolecular hydrogen bonds; such phenomenon may be followed by an exchange reaction and recrystallization. Subsequent stages of steam setting, however, no longer bring about such an effect.

1. INTRODUCTION

The question of whether or not water molecules enter into crystalline regions in high polymers has often been discussed. Sakurada¹ and Nitta² have reported on these problems for PVA from the viewpoint of x-ray diffraction and infrared spectral data; however, no report has been published concerning these problems in polyamides. Many investigations³⁻⁷ have been carried out on deuteration of high polymers, but only a few reports, such as those of Sobue⁸ and Kessler and Sutherland⁹ have been published on polyamides.

It is known from x-ray investigations that dye molecules do not enter into the crystals in dyeing. Water molecules are, however, so small that their presence in crystals might not be detected. The present investigation was carried out to obtain information on the role of water molecules and structural changes in nylon 6 on steam-setting. When ordinary nylon 6 (hereafter called N—H polymer) in the solid state, comes in contact with

* This material appeared in part in *Kobunshi Kagaku*, **17**, 545 (1960).

deuterium oxide the active hydrogen atom of the acid amide group which exists in the amorphous region exchanges easily with a deuterium atom. However it is well known that the active hydrogen occluded in crystalline regions exchanges only with great difficulty.

The water accessibility of nylon 6 was estimated from the degree of the exchange reaction at high temperature and the extent to which water molecules enter into crystal was investigated. A deuterated polymer (hereafter called N—D polymer) was prepared from deuterated ϵ -caprolactam. This polymer was treated with H_2O , and the accessibilities compared with those of the N—H polymer described above. Also, the infrared spectra of deuterated ϵ -caprolactam and N—D polymer, not hitherto reported, are described.

2. EXPERIMENTAL

N—H Polymer Sample

A thin film was prepared by casting and drying a formic acid solution of poly- ϵ -caprolactam on a glass plate. The film was melted and quenched in film form to decrease crystallinity. The thickness of the films obtained was 5–40 μ .

N—D Polymer Sample

Deuteration of ϵ -Caprolactam. An equimolar quantity of deuterium oxide (purity >99.6%) was added to 1/20 mole of purified ϵ -caprolactam, and reaction of the mixture was carried out at 70°C. for 2.5 hr. After reaction, the water produced by the exchange reaction and excess deuterium oxide were separated by distillation. Deuterated lactam was poured into a glass vessel in the molten state and cooled and dried in vacuum. The reaction was repeated out by placing the obtained lactam in contact with an equimolar quantity of fresh D_2O in the same method described above.

Their reaction cycle was repeated several times until almost all hydrogen atoms had been exchanged with deuterium.

The deuterium atom of deuterated lactam and polyamide is easily exchanged with hydrogen, even in presence of a small amount of water in the atmosphere; thus the handling of the deuterated material was carried out in a glove box in which the air is replaced by completely dry N_2 gas.

Polymerization and Preparation of Film. About 5 g. of deuterated lactam was well dried and polymerized for 14 hr. at 250°C. in a sealed glass tube after the air in the tube had been replaced by dry nitrogen gas. The piece of N—D polymer obtained above was melted and cast to a thin film on a heated stainless plate and quenched by immersing it with the plate in cold mercury. A thin film of N—D polymer could be stripped with care from the plate. Drawing was carried out after the film had been steeped in deuterium oxide.

Deuteration of N—H Polymer by D₂O Vapor and Steam Setting of N—H or N—D Polymer

N—H polymer was deuterated by D₂O vapor according to the method described by Tadokoro et al.¹⁰

N—H or N—D polymer was sealed into a glass tube with a small amount of D₂O or H₂O and heat-set at various temperatures and times as described below.

Alternate steam setting with D₂O and H₂O was carried out as follows. N—H or N—D polymer film was affixed to a stainless steel frame and was steam-set with D₂O or H₂O in the order: D₂O → H₂O → D₂O → H₂O → D₂O or H₂O → D₂O → H₂O → D₂O → H₂O continuously, and the infrared spectrum was scanned after each steam setting.

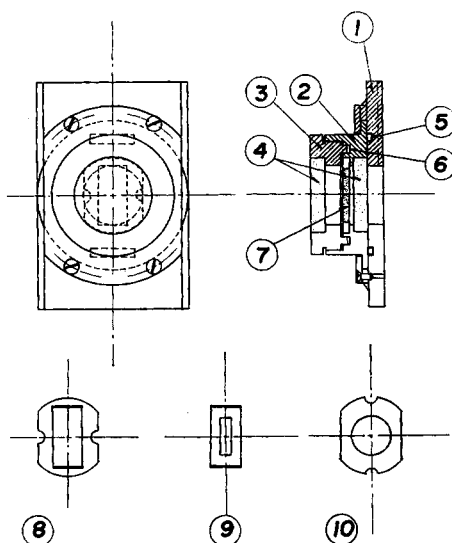


Fig. 1. Cell for deuterated sample: (1) cell holder; (2) cell (rotator); (3) cell cover; (4) NaCl plates; (5) spring; (6) packing; (7) specimen; (8) sample holder; (9) sample holder for micro specimen; (10) sample holder for dichroism measurement.

Scanning of Infrared Spectra

A Perkin-Elmer model 13 infrared spectrophotometer with a NaCl prism was used. The spectrum of the monomer was measured in CCl₄ solution, and absorption of solvent was compensated for by inserting solvent in the reference beam. The film was affixed to a sample frame as shown in Figure 1 and dried over P₂O₅ in vacuum for 2.5 hr. at 60–65°C. and then sealed into a NaCl cell for infrared measurement.

3. RESULTS AND DISCUSSION

Deuteration of ϵ -Caprolactam

Infrared spectra of deuterated and undeuterated ϵ -caprolactam are shown in Figure 2. Ogata¹¹ previously examined the deuteration of ϵ -

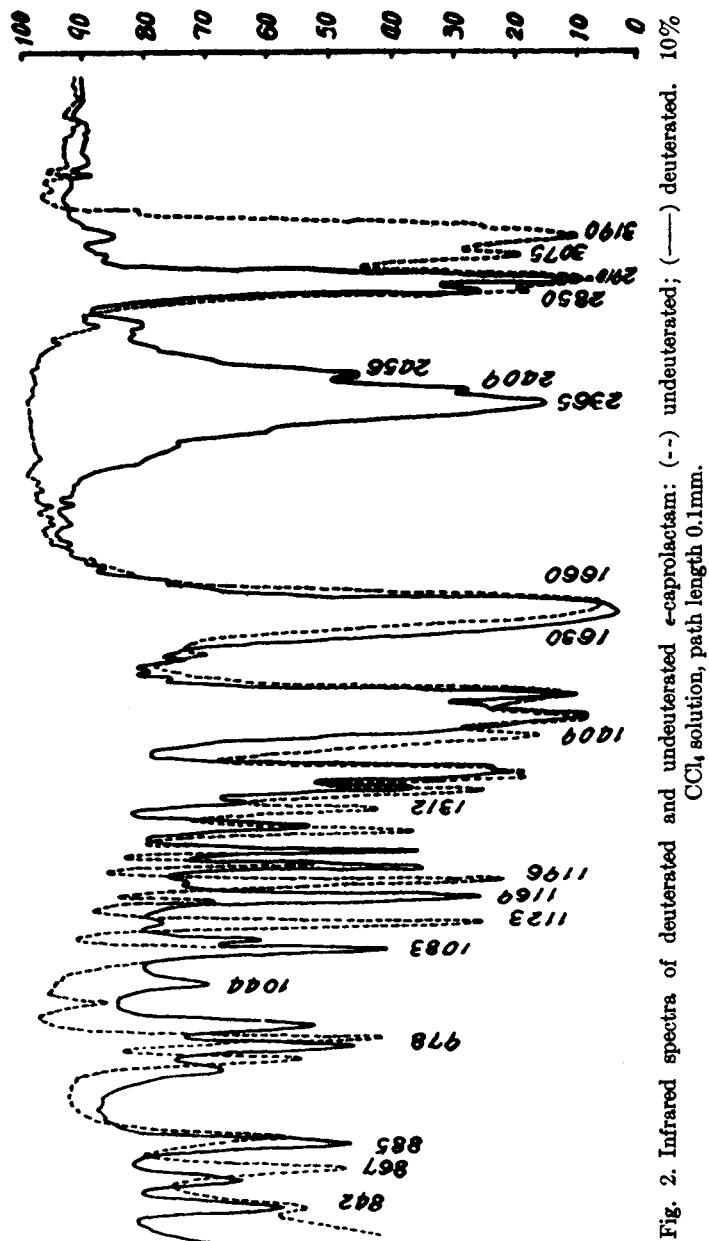
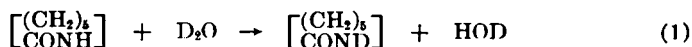


Fig. 2. Infrared spectra of deuterated and undeuterated ϵ -caprolactam: (—) undeuterated; (---) deuterated. 10% CCl_4 solution, path length 0.1mm.

caprolactam and reported that ϵ -caprolactam could not be deuterated by contact with D_2O . Therefore, it is necessary to prepare the deuterated lactam by deuteration of Na lactam which is a reaction product of sodium and ϵ -caprolactam.

However, it is found that an exchange reaction between ϵ -caprolactam and deuterium oxide as shown in eqs. (1) and (2) proceeds easily at even low temperatures such as $30^\circ C$.



or

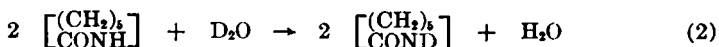


Figure 2 shows that when ϵ -caprolactam is deuterated, the N—H stretching vibration bands at 3190 and 3075 cm^{-1} decreases markedly in intensity and shift to several N—D vibration bands having a maximum intensity at 2365 cm^{-1} . The stretching vibration of the CO group at near 1560 cm^{-1} also shifts to a somewhat lower frequency. The vibration bands in the region from 1500 to 850 cm^{-1} seem to be assigned to complex overlapping of C—H bending, N—D bending, and C—C stretching

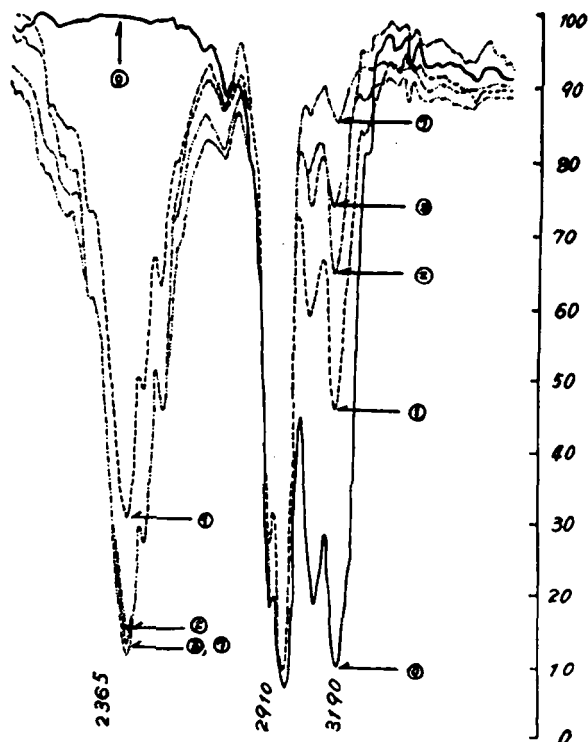


Fig. 3. Change of infrared spectrum by repeated deuteration. Numbers in circles shows number of times reaction repeated.

TABLE I
Absorption Bands of Deuterated and Undeuterated ϵ -Caprolactam

Undeuterated ϵ -caprolactam		Deuterated ϵ -caprolactam		Assignment
Wave number, cm. ⁻¹	Intensity	Wave number, cm. ⁻¹	Intensity	
3190	vs			N—H stretching vibration
3075	s			
2910	vs	2910	vs	CH ₂ stretching vibration
2850	s	2850	s	
2670	w	2670	w	
		2456	m	N—D stretching vibration
		2409	s	
		2365	vs	
		2281	m	
1660	vs	1630	vs	C=O stretching vibration
1481	s			
		1475	s	
		1455	s	
		1439	s	
1434	s			
1409	s			
		1362	s	
1357	s			
		1354	s	
1350	s			
		1337	m	
1333	s			
		1320	w	
1312	m			
		1292	m	
1285	m			
1266	m	1266	m	
1230	m	1230	m	
1196	s	1196	vw	
		1169	s	
1160	w			
1123	s	1123	vw	
		1099	w	
1083	m	1083	m	
		1044	m	
1018	w			
		993	m	
978	m			
		970	m	
959	m			
		949	w	
893	m			
		885	m	
867	m			
		859	m	
842	w	842	m	

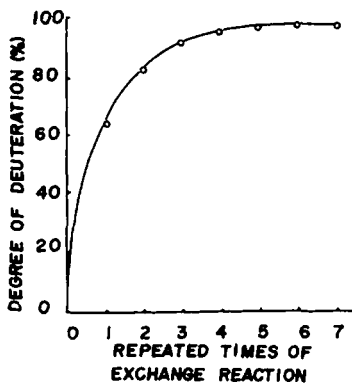


Fig. 4. Relation between degree of deuteration and number of times exchange reaction repeated.

vibration, so the change in the spectra at this region is quite remarkable, as shown in Table I.

In order to prepare N—D polymer, the degree of deuteration must be 100% in monomer, so that the exchange reaction was repeated seven times, fresh deuterium oxide being used each time. The infrared spectra obtained after each deuteration are shown in Figure 3. The degree of deuteration was calculated each time from the decrease in the ratio of optical density D_{N-H}/D_{C-H} as calculated from the intensities of the N—H stretching vibration band at 3190 cm.^{-1} and the C—H antisymmetric vibration band at 2910 cm.^{-1} by the base-line method. Figure 4 shows the relation between degree of deuteration and the number of times deuteration was carried out. The degree of deuteration reaches 95% after the fifth time, and this seems to be an equilibrium value. These evaluations were carried out by using peak heights of infrared spectra, so that some error may be included.

Infrared Spectra of N—D Polymer

Infrared spectra of N—H polymer, deuterated N—H polymer, and N—D polymer are shown in Figure 5. Deuterated N—H polymer was prepared by subjecting N—H polymer to steam setting at 150°C. for 300 min. in order to permit D_2O to penetrate the crystalline region sufficiently. To make the samples equal in crystallinity, both N—D and N—H polymer were also steam-set at 150°C. for 45 min. in D_2O and H_2O , respectively. The degree of deuteration as estimated by a method described below, was 97% and 95% in N—D polymer and deuterated N—H polymer, respectively. In the infrared spectra of these two polymers, the intensities of N—H band at 3290 cm.^{-1} decrease markedly, and the band shifts to strong N—D bands at 2485 and 2425 cm.^{-1} . The bending vibration of the N—H group at 1548 cm.^{-1} (Amide II) also shifts to the N—D bending band at 1460 cm.^{-1} (Amide II'), and the C=O stretching band at

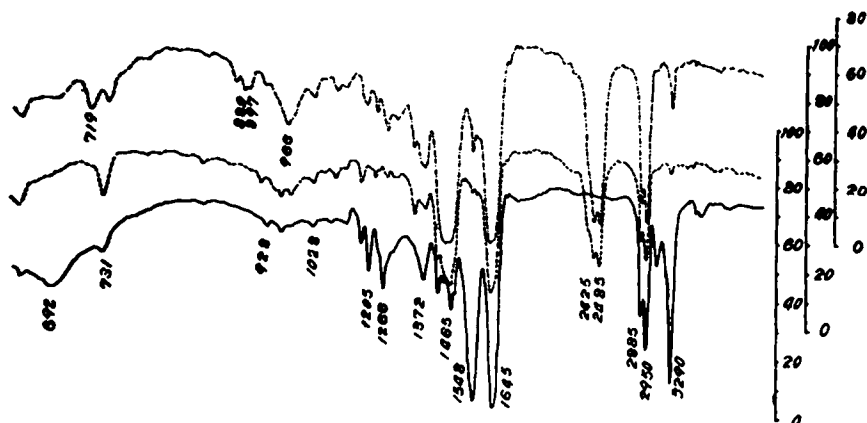


Fig. 5. Infrared spectra of N—H, deuterated N—H, and N—D polymers: (· · · ·) N—D polymer (degree of deuteration 97%); (— —) deuterated N—H polymer (degree of deuteration 95%); (—) N—H polymer.

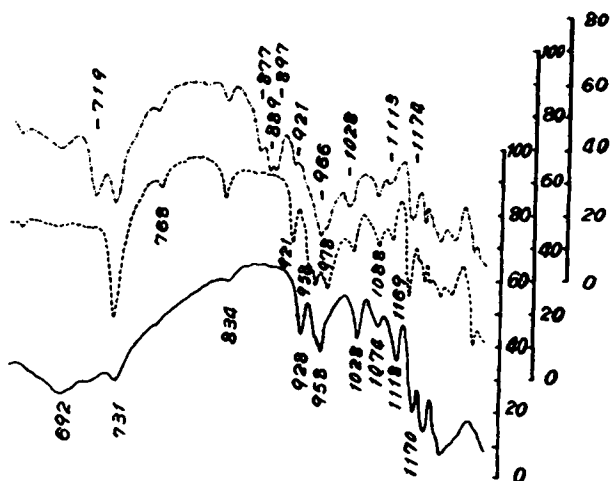


Fig. 6. Infrared spectra of N—H, deuterated N—H, and N—D polymers: (· · · ·) N—D polymer (N—D 97%); (— —) deuterated N—H polymer; (—) N—H polymer.

1650 cm.^{-1} (Amide I) has a tendency to shift towards a somewhat lower frequency.

Many crystalline-sensitive and amorphous-sensitive bands which relate to fine structure of the polymer appear in the region from 1300 to 600 cm.^{-1} . The spectra of this region, scanned with the use of thick film, are shown in Figure 6. This figure indicates many differences between N—D polymer and deuterated N—H polymer. When N—H polymer is deuterated, the Amide III bands at 1266 and 1205 cm.^{-1} shift to the Amide III' band at near 1000 cm.^{-1} and the Amide V bands at 719 and 695 cm.^{-1} disappear with shifting to a lower frequency region. These absorption

TABLE II. Adsorption Bands of N—H, Deuterated N—H, and N—D Polymer

N—H polymer, unset		Deuterated N—H polymer, steam-set in D ₂ O ^a		N—D polymer, steam-set in D ₂ O ^b		Assignment
Wave number, cm. ⁻¹	Dichroism	Wave number, cm. ⁻¹	Wave number, cm. ⁻¹	Dichroism		
3290	⊥	3290	3290	⊥	}	N—H stretching
3070						
2950	⊥	2950	2950	⊥	}	C—H stretching
2885	⊥	2885	2885	⊥		
		2485	2485	⊥	}	N—D stretching
		2425	2425	⊥		
1645		1628	1640			C=O stretching, Amide I
		1561				
1548		1543	1548			N—H bending, Amide II
1480						
1465						
		1460			}	N—D bending, Amide II'
		1448				
1438						
1420		1418				
1372		1378	1375			
		1350	1344			
1296		1300	1300			
		1290				
		1277	1274			
1266						N—H bending, Amide III
		1239	1258			
		1223	1224			
1205						N—H bending, Amide III
			1182			
1170		1169	1174			
1118		1116	1113			
1074		1088	1086			
1028	⊥	1028	1028	⊥		
977	⊥	978	978		}	N—D bending, Amide III'
958	⊥	958	966	⊥		
		946				
928						
		921	924			
			897		}	Crystalline-sensitive band
			889			
			877			
834	⊥	832	837	⊥		
		768	769	⊥		
731		732	734	⊥		
			719	⊥	}	Amide V
692		695	696			

^a Degree of deuteration was 95%.

^b Degree of deuteration was 97%.

bands at near 1000 cm.^{-1} are also found in N—D polymer; however, comparatively strong bands at 896 , 888 , and 876 cm.^{-1} and a broad band at near 967 cm.^{-1} are characteristic only of N—D polymer. Moreover, the Amide V band at 719 cm.^{-1} is found to be strong and resistant to deuteration in N—D polymer. To investigate these differences more precisely, N—D polymer was steam-set with H_2O as shown in Figure 7. The spectrum in this figure closely resembles that of N—H polymer, but the bands at 896 , 888 , 876 , and 967 cm.^{-1} do not decrease in intensity but rather increase, so they seem not to be related to deuteration but to fine structure of the polymer. As a matter of fact, the x-ray interference spots

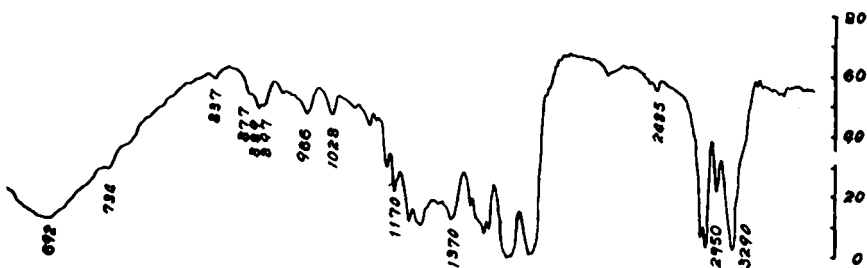


Fig. 7. Infrared spectrum of N—D polymer steam-set at 135°C. for 30 min.

from the (020) plane were fairly strong in drawn N—D polymer as compared to that of N—H polymer. This agrees with the report of Miyake¹² on the special crystalline structure with an Amide V band at 720 cm.^{-1} and suggests that the N—D polymer is different from the N—H polymer in fine structure.

The absorption bands in the infrared spectra of N—H, deuterated N—H, and N—D polymer are listed in Table II.

Change of Accessibility by Alternate Steam Setting with H_2O and D_2O

It has been shown in previous reports¹³⁻¹⁵ that many properties of nylon 6 such as diffusion velocity of dyestuffs, swelling properties, and moisture regain are markedly affected by steam setting, and the presence of water is very important on heat setting. In this experiment, to what extent water molecules penetrate the crystalline region and how they contribute to crystallization are investigated.

Films of N—H and N—D polymer, $5\text{--}10\ \mu$ in thickness, were affixed on the frames as described before and then deuterated in D_2O vapor for 40 hr. at 60°C. or steam-set continuously for 30 min. at 130°C. using D_2O and H_2O alternately. The degree of deuteration was calculated as in the case of monomer at each step by:

Degree of deuteration (%) =

$$\left(1 - \frac{D_{\text{N-H}}/D_{\text{C-H}} \text{ in deuterated sample}}{D_{\text{N-H}}/D_{\text{C-H}} \text{ in N-H polymer}} \right) \times 100$$

where D_{N-H} represents the optical density of the N—H band at 3290 cm.^{-1} , and D_{C-H} represents the optical density of the C—H band at 2950 cm.^{-1} . Results are shown in Table III.

TABLE III
Changes in Accessibility in Alternate Steam Setting in D_2O and H_2O

Sample no.	Reaction	Reagent	Degree of deuteration, %	Exchangeable region, % ^a	
N—H Polymer					
I ^b	Deuteration in vapor	D_2O	34	34	
	1st steam setting	D_2O	49	15	
	2nd " "	H_2O	13	36	
	3rd " "	D_2O	44	31	
	4th " "	H_2O	9	40	
II ^c	Deuteration in vapor	—	—	—	
	1st steam setting	H_2O	0	—	
	2nd " "	H_2O	41	49	
	3rd " "	H_2O	7	26	
	4th " "	D_2O	36	29	
		H_2O	9	27	
	N—D Polymer				
	III ^d	1st steam setting	D_2O	90	—
		2nd " "	H_2O	41	49
		3rd " "	D_2O	79	38
4th " "		H_2O	43	36	
5th " "		D_2O	79	36	
IV ^e	1st steam setting	H_2O	17	73	
	2nd " "	D_2O	40	23	
	3rd " "	H_2O	17	23	
	4th " "	D_2O	45	28	
	5th " "	H_2O	19	26	

^a Per cent of exchangeable region after polymer stabilized by preceding heat setting.

^b Density and crystallinity of N—H polymer after fifth steam setting: 1.1721, 56%.

^c Density and crystallinity of N—H polymer after fifth steam setting: 1.1783, 61%.

^d Density and crystallinity at N—D polymer after fifth steam setting: 1.1675, 52%.

^e Density and crystallinity of N—D polymer after fifth steam setting: 1.1761, 59%.

Figure 8 shows the relation between heat-setting time and degree of crystallinity of the samples which were steam-set continuously or intermittently at 130°C. It is found from the figure that the crystallinity of the samples subjected to heat setting for above 30 min. is almost constant. This suggests that D_2O or H_2O molecules enter into a region of fairly high order and accelerate the growth of crystals as a lubricant at the first steam setting as shown in Table III, and N—D or N—H groups produced by the exchange reaction in this process would be occluded in the crystalline region. After the second steam setting, the reaction seems to occur in the

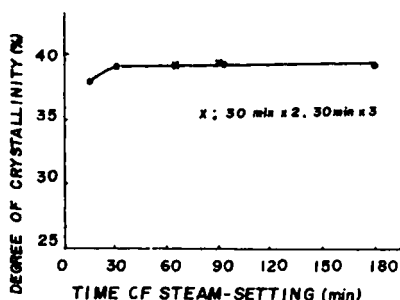


Fig. 8. Relation between degree of crystallinity and time of steam setting.

amorphous region and the surface of the crystalline region and not to occur in inner parts of the crystal. Such speculation is reasonable because the degree of deuteration is also nearly a constant value for each step of the steam setting.

The pattern of the alternate exchange reaction is also shown in Table III. It is considered for the N—H polymer in Table III that the region of 34% which was deuterated by D_2O vapor at low temperature would be the most loosely packed (lowest order) part in the amorphous portion. The succeeding 15% region deuterated in steam setting with D_2O , which was a pseudocrystalline region in the previous vapor-phase deuteration, would be crystallized by the steam setting, crystallinity thus going from 51% to 64%. Therefore, after the second steam setting, the exchange reaction would occur in the amorphous region except for this crystalline region of 64%. In the case of N—D polymer, 60–70% of crystalline region seems to be generated in the first or the second steam setting. An error of several per cent may be involved in the above evaluation.

From these considerations, it is possible to explain that in the case of N—D polymer, which originally has a rather lower crystallinity, the H_2O molecule penetrated fairly far within the crystal, leaving 27% of crystalline region in the first steam setting. On the other hand, D_2O did not penetrate so far into the crystalline region, leaving 51% in the case of N—H polymer which had originally a rather high crystallinity.

Table III shows the region exchanged in each steam-setting, and the value denoted by "exchangeable region" represents the fraction of exchangeable region after the polymer has been stabilized by a previous steam setting. This value is nearly constant after the first or the second steam setting, as shown by values of 31–40% and 26–33% in N—H polymer and 36–49% and 23–28% in N—D polymer. It is impossible to explain why this value is larger in both N—H and N—D polymer when D_2O is used in the first steam-setting as shown in samples I and III. This tendency is not only experimentally reproducible but also reasonable by virtue of the fact that the densities of these samples measured after the fifth steam setting are somewhat smaller than those steam-set first with H_2O .

The results obtained above support the view that the effect of heat setting depends on the hysteresis of heat to which the polymer has been subjected, and the facts that higher resistance to swelling and easier crystalline transition¹⁶ from β to α in Bunn's model at lower temperatures, compared with dry heat setting, are caused by the lubricating action of water in steam setting.

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Résumé

On a examiné le spectre infrarouge de l' ϵ -caprolactame. On a obtenu la confirmation par spectroscopie de l'échange de l'hydrogène du groupe N—H de l' ϵ -caprolactame par le deutérium après répétition de la réaction d'échange. On polymérise la ϵ -caprolactame deutérée et on compare le spectre infrarouge du polymère (appelé polymère N—D) qui est fixé dans un jet de vapeur d'eau lourde à 135°C. On observe les bandes d'absorption caractéristiques du polymère N—D à 967, 896, 888, 876 et 719 cm^{-1} . On estime l'accessibilité de l'eau pour les deux polymères (N—H et N—D) à partir des spectres d'échantillons fixés alternativement par la vapeur d'eau lourde et d'eau légère à 130°C. A partir des résultats, on peut conclure qu'au stade initial du traitement par la vapeur, les molécules de H₂O et D₂O peuvent pénétrer dans les régions ordonnées du polymère en rompant partiellement les liaisons hydrogènes intermoléculaires. Cette réaction peut être suivie de la réaction d'échange et d'une recristallisation. Les étapes suivantes de la fixation par la vapeur n'apportent cependant plus de changement.

Zusammenfassung

Das Infrarotspektrum von deuteriertem ϵ -Caprolactan wird gemessen. Spektroskopisch wird für den Wasserstoff der N—H-Gruppe in ϵ -Caprolactan ein Austausch mit Deuterium nach Wiederholung der Austauschreaktion bestätigt. Das deuterierte ϵ -Caprolactan wird polymerisiert und das Infrarotspektrum des Polymeren (N—D-Polymeres genannt) mit demjenigen von normalem, mit D₂O-Dampf bei 135°C behan-

deltem Nylon-6-Polymeren (N—H-Polymeres genannt) verglichen. Charakteristische Absorptionsbanden des N—D-Polymeren werden bei 967, 896, 888, 876 und 719 cm^{-1} beobachtet. Die Angreifbarkeit von N—H- und N—D-Polymerem durch Wasser wird aus den Spektren von Proben bestimmt, die der wiederholten Dampfbehandlung abwechselnd in D_2O und H_2O bei 130°C unterworfen wurden. Die Ergebnisse zeigen, dass im Anfangsstadium der wiederholten Dampfbehandlung H_2O - und D_2O -Moleküle in die geordneten Bereiche der Polymeren eindringen und intermolekulare Wasserstoffbindungen zum Teil zerstören können; darauf kann die Austauschreaktion und Rekristallisation folgen. Das darauf folgende Stadium der Dampfbehandlung bewirkt jedoch keine weiteren derartigen Effekte.

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