A Study on Fine Structure of Nylon 4
by Deuteration Method

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Abstract

For the examination of the amorphous structure of solid linear polymer by chemical technique, experiments by deuteration and others were made on variously annealed nylon 4 membranes. The membranes, wet annealed by steam and dry annealed in N_2 atmosphere, were deuterated with D_2O vapor at various temperatures of $25\sim135°C$, respectively, and the amount of the cohesive structure which was relaxed and deuterated at the deuteration temperature was measured by IR spectrophotometry on ν_{NH} band, and the cohesive energy(ΔF_i) of the deuterated structure was calculated from deuteration temperature (T_i) by $\Delta F_i = 2.92\,T_i + 625$ which was introduced on the base of Flory's theory of melting point depression under the existence of diluent, and (1) the lateral order distributions of these samples were estimated more quantitatively than ever. (2) The cohesive energy of nylon 4 showed the values of about $1.5\sim1.8$ Kcal/mol and they were between those of nylon 3 and nylon 6 in order of C-numbers of their structural units. (3) By the examination of the deuteration curves and by some supplementary experiments, the mechanism of annealing effect on the amorphous structure of the nylon 4 membranes was clarified by the analysis of the rearrangement of the molecular segments in the amorphous region. (4) The fine structure of the membranes was supposed to be constructed with two types of domains, in one of which molecular segments were rich and had some order and the change of lateral order occurred, in the other, segments were poor and had no order and so they were insensitive to the annealing.

1. Introduction

The fine structure of coagulated molecular chaines in the linear polymer solid such as fiber and film has an important influence on the physical properties and chemical reactivities of them, and it has been investigated on many polymers.

On the crystalline parts of polymers, their fine structures have been elucidated

on many polymers by X-ray diffraction and other physical techniques. On the other hand, the study on the structure of the amorphous part was not active because of the irregularity and the complexity of the arrangement of molecular segments and also the dificiency of analytical techniques.

Recently, investigators who are interested in the amorhous structure of linear polymer increased more and more, so that various informations of it have come to be presented to us.

For instance, the random coiled chain structure model which was presented by Flory on the base of his thermodynamic theory and has been assented generally was denyed by some investigators, and some heterogeneous structure models, e. g. the two phase model of grains and random coils, collapsed ball model, meandered chain-bundle model, etc., were presented hypothetically. [1]

Annealing is an important technique in the manufacturing process of fibers and films with synthetic polymers, and many studies have been carried out standing on both points of science and technology.

Annealing effect, i. e. the relaxation of coagulated chain segments followed by reorientation and stronger coagulation, is one of the important phenomena which is brought about in the amorphous region. So that the examination of the annealing mechanism of amorphous chain segments by carefull experiments should lead us to the explanation of the structure of the amorphous region of a polymer.

2, Experimental

Sample membranes were prepared with nylon 4 by the method described in the previous paper [2], and annealed without tension. Wet annealing was carried out in steam in a closed glass tube and dry annealing was carried out with electric

Table 1.　Nylon 4 membranes of sample use

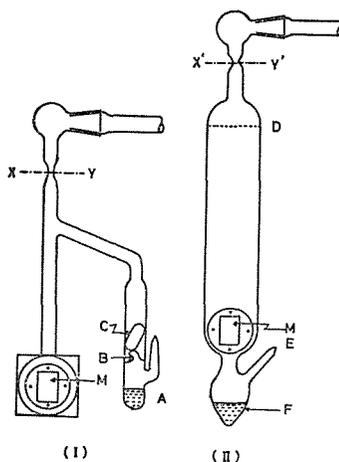| cord	Annealing condition			Density (g/cm^3)	Degree of Crystallinity
	Temp, (°C)	Period (min)	Atmosphere		
A	Original Membrane			1.257	0.22_2
B	40			1,258	$0 \cdot 23_0$
C	80			1,261	0.25_2
D	100	10	H_2O	1,263	0.28_4
E	125			1,264	0.27_6
F	120			1,258	0.23_1
G	180	10	N_2	1,261	0.25_2
H	240			1,266	0.27_5

Fig. 1   Deuteration apparatuses used at high temperature.
A, F : D_2O pool, B : partition, C : glass ball, D : part
for oppening, E : entrance of D_2O, M : sample membrane.

oven in N_2 atmosphere. The properties of these sample membranes were shown in Table 1, in which their densities were measured by the density gradient tube method with the medium of $C_6H_6-CCl_4$ mixtures. The degree of crystallinity was calculated by the density–crystallinity equation with the density values of 1.338 and 1.228 for the crystalline and amorphous region, respectively.

Deuterations of these sample membranes were carried out with D_2O vapor (99. 7% D content) by using the apparatus shown in Figure 1 in the temperature range of 25~135°C for various reaction periods until the reactions were equilibrated, and procedures with these apparatuses were as follows.

Apparatus (I) was used at the deuteration temperatures lower than about 100°C. D_2O pool(A) partitioned by a glass wall(B) holding a glass ball(C) is branched off from deuteration cell containing sample membrane(M). The apparatus was cut off from vacuum line by melting at x-y part after exhaustion. When deuteration started, (B) was broken by beating with (C) and D_2O vapor was introduced into the deuteration cell. The structure of the cell is similler to that described in the previous paper [2]. In order to interrupt deuteration and to measure the IR absorbance of (M) directly, (A) was dipped into liquid N_2 to remove D_2O moisture from the membrane, and the cell was put into the IR spectrophotometer. After the measurement, the reaction was continued again by melting the ice in the pool and holding the apparatus in a bath thermostated.

Apparatus (II) of an ampoule type was used mainly for the reaction at the temperature higher than 100°C. Procedure of the reaction was similar to that described in our previous paper [3].

Since the deuteration cell had glass windows, the IR absorbance of the sample membranes was directly determined on ν_{NH} band at 3300 cm^{-1} by applying base line method without correction on the assumption that the Lambert-Beer's law might be applicable to the nylon 4 membrane. The degree of deuteration, R_D, was calculated by $R_D = (1 - D_{NH}^a/D_{NH}^b) \times 100(\%)$, where D_{NH}^a and D_{NH}^b are the absorbance of ν_{NH} bands after and before deuteration, respectively.

On other experiments, their exposition will be offered later in the chapter of discussion.

3. Results and Discussion

3.1 Examination of Deuteration of Nylon 4 by IR Absorbance

Degree of deuteration of nylon 4 membrane by D_2O could be measured conveniently by IR method at ordinary temperature. But at higher temperature it was necessary to care for the fact that the accuracy of data should be decreased by the increase of thickness and the deformation of membranes caused by swelling and also the fact that the absorbance of NH band should be decreased with the progress of deuteration.
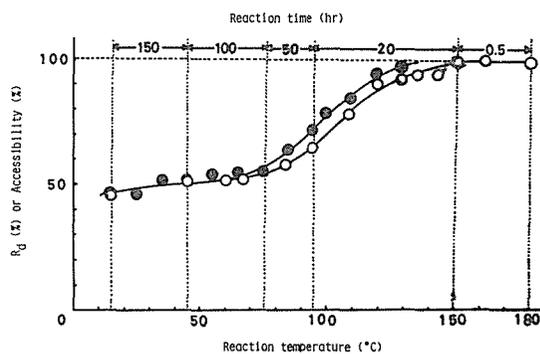

Fig. 2　Deuteration curves of nylon 4 membrane with D_2O vapor and D_2O aqueous solution.
(●) : deuteration with D_2O vapor,
(○) : with D_2O aqueous solution.

Values of the degree of deuteration which were measured by the IR method were compared in Figure 2 with these measured previously [3] on similar sample membranes from the depression of D content of D_2O-H_2O mixture in which the sample was immersed. It is obvious in the figure that both plots coincide satisfactorily in a low temperature range, but differ to some extent each other at high temperature range. However this result shows that R_D plot indicates the feature

of fine structure of the sample membrane as well as the accessibility plot, and so
following experiments were carried out by the IR method.

Prior to the deuteration experiments, it was necessary to dispel the doubts
that the deuteration of amide groups which were coherent by hydrogen bonding
might proceed by proton- transfer mechanism instead of relaxation by swelling
as same as the case of polyvinyl alcohol[4]. ND groups might be revealed by
hydrolysis of polymer chains with hot D_2O, and these phenomena should introduce
some error into the values of the degree of deuteration.

Recently examinations on the diffusion of water into nylon 4 membrane[2]
and hydrolysis[9] of its molecular chains followed by deuteration were carried
out. They confirmed that as soon as the membrane contacts to D_2O, its molecules
diffuse into the center of the membrane. The quantity of sorbed water and the
degree of deuteration increase uniformly in all parts of the membrane with
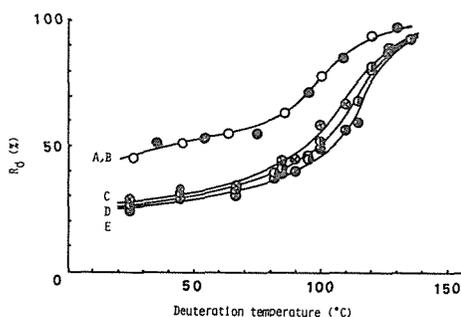

Fig. 3   Degrees of deuteration of wet annealed membranes of
nylon 4 at various temperatures.
A : non ann., B : 40°C ann., C : 80°C ann.,
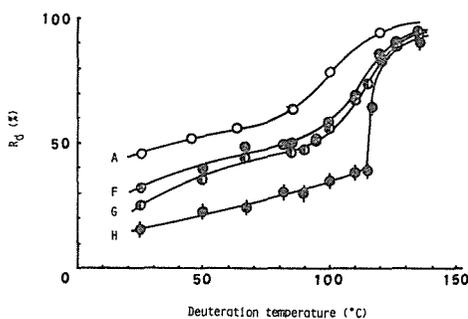D : 120°C ann., E : 125°C ann.

Fig. 4   Degrees of deuteration of dry annealed membranes of
nylon 4 at various temperatures.
A : 50°C ann., F : 120°C ann., G : 180°C ann., H : 240°C ann.

gradual relaxation of hydrogen bonding caused by D_2O sorbed in earlier contact period. The proton transfer does not occur in the fine structure of nylon 4 at both intermolecular and intramolecular reactions, and that although the hydrolysis of nylon 4 was more dependent to the temperature of water than nylon 6, but the influence of the hydrolysis to the degree of deuteration of NH groups was negligible.

The plots of the degree of deuteration of the sample membranes at various temperatures are shown in Figure 3 and 4, and the effects of annealing were observed distinctly in these plots.

3.2 Calculation of Intermolecular Cohesive Energy at Various Temperature

As proved in previous papers [2,3], the deuteration reaction in nylon 4 membrane is caused not by proton-transfer mechanism but by diffusion of D_2O into the membrane, in which cutting off of hydrogen bonds between segments occurs. So that these experimental results can be analysed by thermodynamics. Referring to the studies of Kanetsuna [5,6] et al., the cohesive energy distribution of nylon 4 chains in these samples was calculated under the conception that the free energy of cohered chain was regarded as the cohesive energy of the chain.

When nylon 4 membrane is deuterated by D_2O under various temperatures, it is possible to convert the deuteration temperature to cohesive energy by applying the Flory's theory. The chemical potential of a structural unit of nylon 4 in solutions which is equal to that of solid phase at equilibrium state exists for every deuteration temperature. The magnitude of chemical potential varies successively from a perfect amorphous structure to a perfect crystalline one. Then they can be written with Flory's symbols as follows.

deuteration temp. (steam contact temp.)	chemical potential in coherent structure	chemical potential in solution
t_1 ············	$\mu_u^1 - \mu_{u1}^0$	$= \mu_{u1} - \mu_{u1}^0$
t_2 ············	$\mu_u^2 - \mu_{u2}^0$	$= \mu_{u2} - \mu_{u2}^0$
······	···············	···············
t_i ············	$\mu_u^i - \mu_{u i}^0$	$= \mu_{u i} - \mu_{u i}^0$
······	···············	···············
t_c ············	$\mu_u^c - \mu_{u c}^0$	$= \mu_{u c} - \mu_{u c}^0$

wher μ_u^0 is the chemical potential of structural unit in a complete amorphous state, μ_u^c is that in complete crystalline state, μ_u^1, μ_u^2, ·····, μ_u^i, ····· are those in some inteamediate structure and μ_{u1}, μ_{u2}, ·····, $\mu_{u i}$, ·····, $\mu_{u c}$ are those in

solutions at respective temperatures.

Phase equilibrium equation is shown as follows by Flory,

$$-\Delta F_u^i = (\mu_u^i - \mu_{ui}^0) = -RT_i \left(\frac{V_{ui}}{V_{1i}}\right) \ (V_{1i} - \chi_{1i} \cdot V_{1i}^2) \tag{1}$$

where ΔF_u^i is a cohesive energy of inter structural unit, V_{ui} is specific volume
of structural unit in liquid phase, V_{1i} is a specific volume of D_2O(diluent), v_{1i} is
a volume fraction of D_2O in the membrane, and χ_{1i} is interaction parameter
between nylon 4 and D_2O that changes its value as the temperature varies, and
is shown as

$$\chi_{1i} = BV_{1i} / RT_i \tag{2}$$

where B is van Laar's constant.

When (1) is applied to the theory of melting point depression of polymer in
the existence of diluent, following equation (3) will be obtained,

$$\frac{\frac{1}{T_m} - \frac{1}{T_m^0}}{v_{1i}} = \left(\frac{R}{\Delta H_u}\right) \left(\frac{V_{ui}}{V_{1i}}\right) \left\{ 1 - \left(\frac{BV_{1i}}{R}\right) \left(\frac{v_{1i}}{T_m}\right) \right\} \tag{3}$$

where T_m^0 is melting point of dry nylon 4 , T_m is that of wet polymer and ΔH_u
is the heat of fusion of the polymer lsolid.

Melting points of the wet polymer samples and volume fractions of sorbed water
were measured at various temperatures. From these the values of v_{1i} in amorphous
regions were calculated.

Data were introduced into (3) and a linear plot of
$$(1/T_m - 1/T_m^0)/v_{1i} \ \ vs. \ \ v_{1i}/T_m$$
is obtained as shown in Figure 5. And so (2) was determined from the ratio
of the slope and the intercept of the straight line, and was put into (1) as
shown in (4),

$$- \Delta F_u^i = -RT_i \left(\frac{V_{ui}}{V_{1i}}\right) \left\{ v_{1i} - \left(\frac{-560}{T_i}\right) v_{1i}^2 \right\} \tag{4}$$
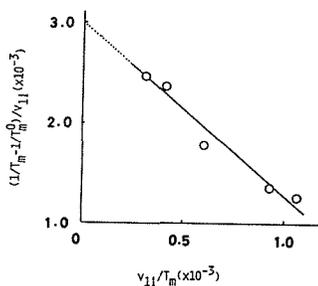

Fig. 5   Plots of $(1/T_m - 1/T_m^0)/v_{1i}$ vs.v_{1i}/T_m

To V_{ui}/V_{1i}, the value of 3.85 at 25°C was applied regardless of deuteration temperature. The reason is that V_{ui} and V_{1i} may be variable according to the temperature change, but temperature dependence of the ratios of volume expansion coefficients of both materials is supposed to be very small. Therefore the influence of temperature to the ratio was neglected.

To the value of v_{1i} at 25°C, 0.382 was applied for the reason that when the values of v_{1i} were calculated from the experimental results of accessibility and the hygroscopic degree at various temperatures, the values were almost similar to that at 25°C in the reaction temperature range.

Thus, to calculate the cohesive energy from deuteration temperature, a practical equation was obtained as follows,

$$\Delta F_u^i (\Delta F_i) = 2.92 \ T_i + 625 \tag{5}$$

As a matter of course, this equation is a temporal one, because some assumptions are used for the introduction of it.

3.3 Cohesive energy of nylon 4 and lateral order distribution by annealing

Figure 6 shows plots of cohesive energy distribution, which were made by differentiation of the curves of Figures 3 and 4 and by application of equation (5).

To this day, many informations on the arrangement of molecular chains in amorphous region have been rather qualitative differing from quantitative one for the crystalline part. But studies on the structure of amorphous region are in progress recently. Measurement on the lateral order distribution of linear polymer solid is useful on this point of view. If lateral order[7] is represented with cohesive energy of chain segment, it may be capable to express the amount of fine structure of linear polymer solid more numerically not only in crystalline region but in amorphous one. It is worthy to note that Kanetsuna et al.[5,6] investigated formerly phenol adsorption studies on nylon 6 and polyester fibers. They showed the lateral order distribution semiquantitatively, in which cohesive energy of repeating unit expressed with chemical potential was used as the degree of order and the amount of adsorbed phenol was used as the amount of accessible unit. Another studies of this kind, for example, can be shown as follows. Kitamura, Kobayashi and Yoshida[8] also studied lateral order distribution of PET fiber by phenol adsorption method. In their study, the amount of phenol adsorbed on carbonyl groups by hydrogen bonding and phenol concentration were adopted as the measures of the distribution. On the other hand, Koshimo and Tagawa[9] studied by the deuteration of nylon 6 with D_2O vapor. In their study, deuteration reactions were carried out at various temperatures, and the amount of accessible region was obtained from the degree of deuteration by plotting against the deuteration temperature.
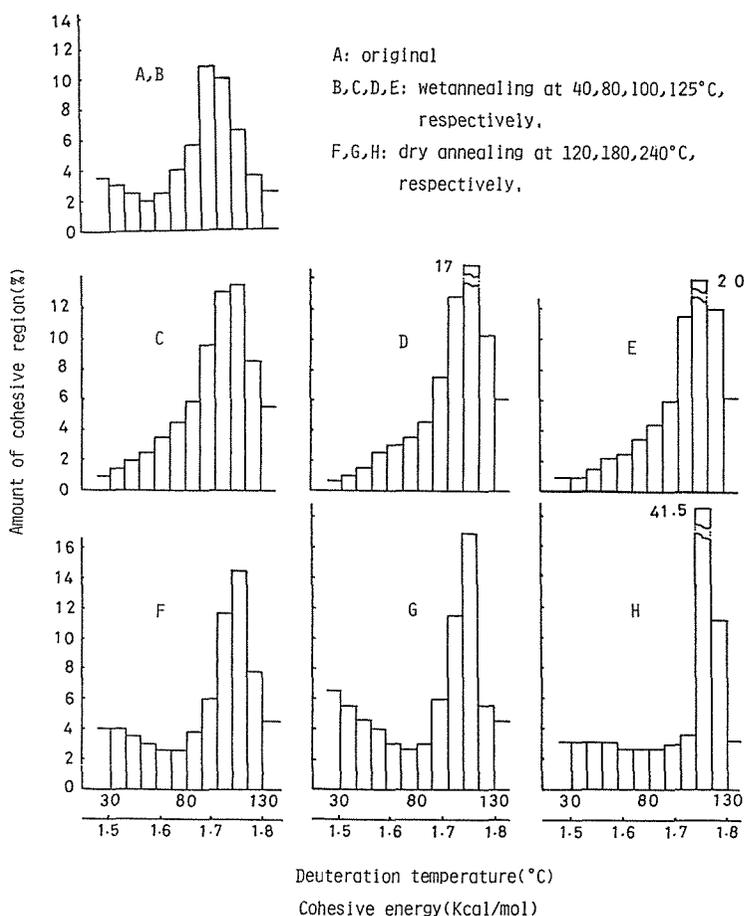
Fig. 6 Inter-molecular cohesive energy distributions of nylon 4 membranes.

As a physical method, Manabe[10] et al. presented a method to determine the structure of amorphous region quantitatively in accordance with a plot of dynamic loss tangent vs. reaction temperature of polymer. These results are very worthy but are not always fully satisfactory, because only one axis of the co-ordinate of lateral order distribution curve was represented quantitatively. In this respect the

Table 2. Properties of aliphatic polyamides (Nylon X) fibers.

Number of X in Nylon X	Amide Groups per 100 Chain Atoms.	Crystalline mp (°C)	Tg (°C)	Moisture Sorption (%) at 21°C, 65% RH
3	23	330	108	10
4	20	265	75	7.3
5	16.7	258	77	5.2
6	14.3	228	50	4.4

results shown in Figure 6 will be more quantitative than those reported formerly.

It is recognized on these nylon 4 sample membranes, as well as other linear polymers, that as the annealing temperature rises, the distribution of cohesive energy of molecular chains shifts to that of higher grade resulting from the increase of crystalinity. These phenomena will be analyzed later.

Some properties of aliphatic polyamids (nylon x) are shown in Table 2. It is obvious in this table that the properties of these nylons tend to change in relation to the number of carbon atoms in structural unit. It is supposed that if values of ΔF_i are measured under similar experimental condition on nylon 3, nylon 4 and nylon 5 or 6, the value of nylon 4 may exist between those of nylon 3 and nylon 5 or 6. In fact, ΔF_i of nylon 6 fiber, which was found by Kanetsuna [5,6] with phenol adsorption method, became about 0.7~1.3 Kcal/mol. That of nylon 3 membrane, which was found by the authors [11] with a polymer synthesized from acryl amide became about 1.7~2.1 Kcal/mol. While ΔF_i of nylon 4 found in this study became about 1.5~1.8 Kcal/mol which were sited between those of nylon 3 and nylon 6. It will be reasonable to express from these results that ΔF_i values of nylon 3, 4 and 6 are in relation to the number of carbon atoms of structural unit.

3.4 An examination by the division of cohesive region

From the results of Figures 3 and 4, an observation was made on the transition of chain arrangement by annealing. Whole ranges of cohesive regions of the samples were tentatively divided into four regions at the temperatures of 30, 85 and 130°C which were characteristic. The degree of moisture sorption of original membrane was 22% by our experiment, and so T_g of 65°C at dry state was inferred to fall down to 30°C by referring to the study of Takizawa [12] et al. From this reason, 30°C is noticed as a characteristic temperature of wet nylon 4, although an obvious curvature could not be observed at this temperature in the deuteration curve and dilatometry curve shown in Figure 7. The dilatometry curve for dry nylon 4 indicated a curvature at 120°C which was supposed as a transition point of crystalline region. But for the humid nylon 4 sample, the temperature would shift to 85°C as referred to the study of Haga [13] et al. on nylon 6. Remarkable advance of deuteration occurred at about the temperature in every sample on account of remarkable increase of swollen region caused by the transition of cohesive structure.

The sample membranes dispersed in water almost completely at 130°C, and so this temperature was regarded as the dispersion point of these nylon 4 membranes.

Divided regions are classified in Figure 8. "Region I": the structure whose cohesive energy, ΔF_i, is lower than 1.505 Kcal/mol may be amorphous in the existence of water at the temperature lower than 30°C. "Region II": ΔF_i of the
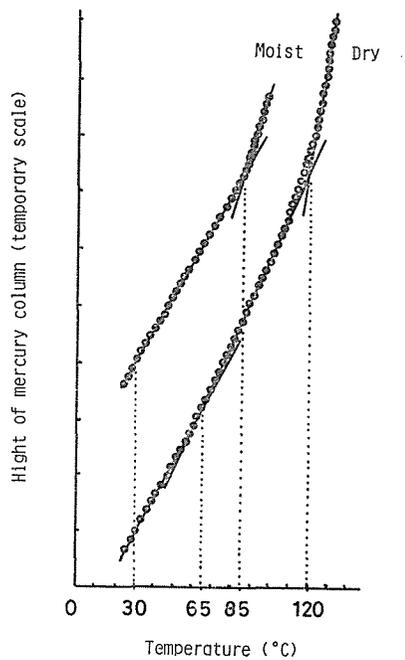
Fig. 7   Dilatometry curves of dry and moist
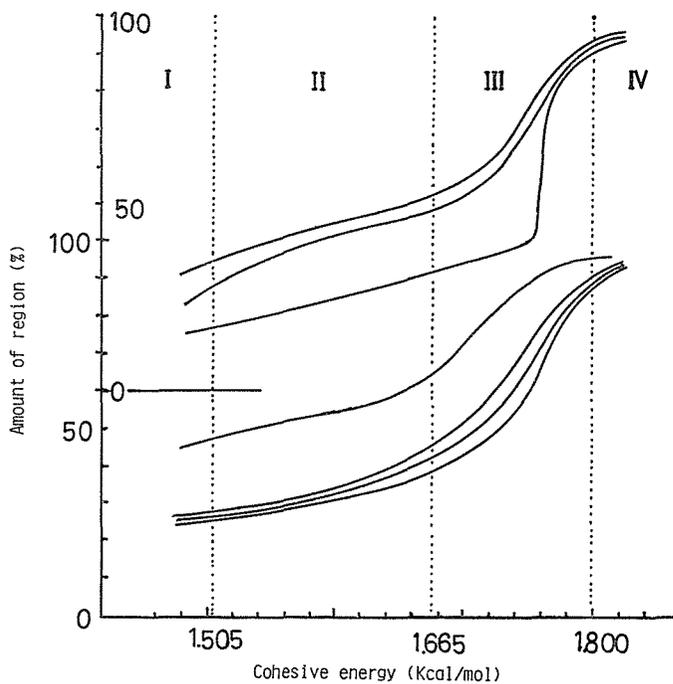(moisture content 22%) nylon 4.

Fig. 8   Division of the cohesive region of nylon 4 into Ⅰ～Ⅳ

structure is 1.505~1.665 Kcal/mol. It may be high density amorphous region which swells by water at the temperatures lower than 85℃. "Region III": ΔF_i of the structure is 1.665~1.800 Kcal/mol. It may be low grade crystalline or high grade para crystalline state which transforms its coherent system and swells at 85~130 ℃. "Region IV": ΔF_i of the structure is higher than 1.800 Kcal/mol. High grade crystalline structure which is hard to swell in water at the temperature lower than 130℃. These four regions were shown in Figure 8 together with the deuteration curves which were drawn carefully by the results shown in Figures 3 and 4.
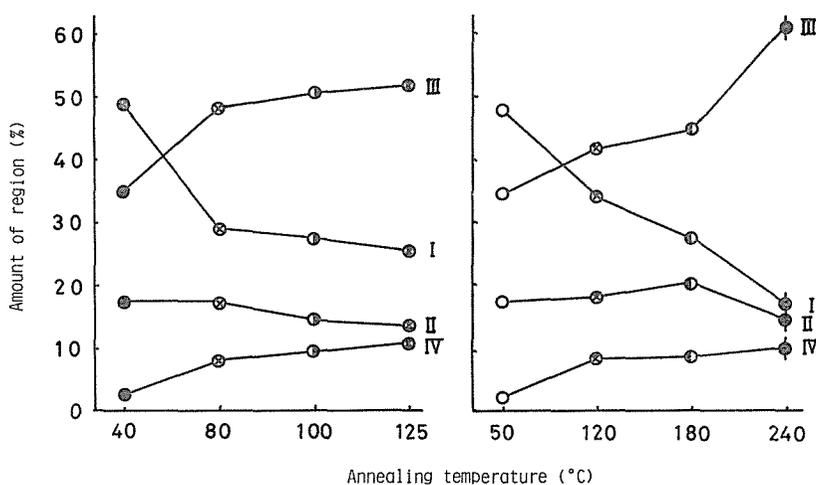

Fig. 9　Changes of region I ~ IV by annealing

Table 3.　Increase of the amounts of regions III and IV, and that of crystalline region obtained from the X-ray peak area.

	Ann. Condition (°C)	Wet annealing				Dry annealing			
	Region	40	80	100	125	50	120	180	240
Rate of increase	III	1	1.50	1.50	1.53	1	1.20	1.30	1.76
	IV	1	3.00	3.30	4.00	1	2.70	3.00	3.30
	Peak area	1	1.03	1.16	1.19	1	1.04	1.23	1.52

Figure 9 shows the change of amounts of region I and II against the advance of annealing temperature. The ratios of the change of amounts of III and IV are shown in Table 3 with the ratios of crystalline region which were measured by the peak area of wide angle X-ray diffraction patterns of sample membranes. These data showed that the crystalline region of these membranes consisted

chiefly of III structure rather than IV structure, despite the rate of increase of IV
was larger than that of III.

The increment of every region at every annealing temperature was calculated
by subtracting the amount of the region of wet annealing sample at 40℃ or dry
annealing one at 50℃ from the amount of the region of the wet annealing
sample or dry annealing one, respectively. They were collected in Table 4. These
increments were integral types, and differential one, i. e. the inherent increments
were introduced from the table and shown in Figure 10. It shows clearly the
mechanism of mutual transition of structure as follows. In the case of wet
annealing, the greater part of the molecular segments of I rearranged to the
crystalline structure of III or IV without staying at the structure of II in spite of
weak annealing at 80℃. Furthermore, the II structure which was proper to the

Table 4. Increments of the amounts of region I ～ Ⅳ

at every annealing temperature

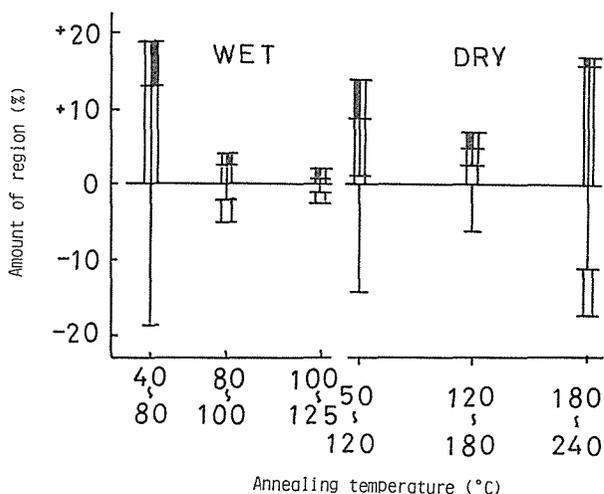| Ann. Condition (℃) Region		Wet annealing				Dry annealing			
		40	80	100	125	50	120	180	240
Increment of region(%)	I	0	−19	−21	−22	0	−14	−20	−31
	Ⅱ	0	0	− 3	− 4	0	+ 1	+ 4	− 2
	Ⅲ	0	+13	+16	+17	0	+ 8	+10	+26
	Ⅳ	0	+ 6	+ 7	+ 8	0	+ 5	+ 7	+ 8

Fig. 10 Inherent increments of I ～ Ⅳ regions at

various annealing temperature ranges.

⊢━┥: I, ⊟: IL, ⊟: III, ▰: IV

sample was transitional to III and IV by stronger wet annealing at 80～125℃. The mobility of segments on dry annealing were not quick in spite of higher annealing temperature, and the transition from the structure I to II was observed on the dry annealing samples at 120～180℃.

Under more severe annealing at 240℃, the greater part of II which was proper to the sample, was supposed to be rearranged to III structure, and a small part of it to IV structure as well as the case of wet annealing. Referring to the results of dry annealing at 120 and 180℃, it was supposed too that a part of I which was expected to rearrange to II if the temperature was lower, came back again to I structure and the other part skipped to III structure over II structure.

The rearrangement of the segments from the structure I to II and III was traced by another experiment. The original membranes which were deuterated at 30℃, i.e. NH groups of I structure were translated to ND groups, were annealed by dry method at 180 and 240℃, respectively. Then they were hydrogenated with H_2O vapor at various temperatures by the procedure similar to that of deuteration. And the amounts of residual ND groups in the structures of I, II and III were measured. The results which were shown in Figure 11 proved that the structure of I changed to that of II or III in relation to the temperature of annealing. It makes us expect too the possibility of transition of II to III or IV.

Data in Table 5 show that the amount of the structure I increased by annealing despite the increase of the long period of crystalline part which was measured by the small angle X-ray diffraction method. This results mean that intermediate
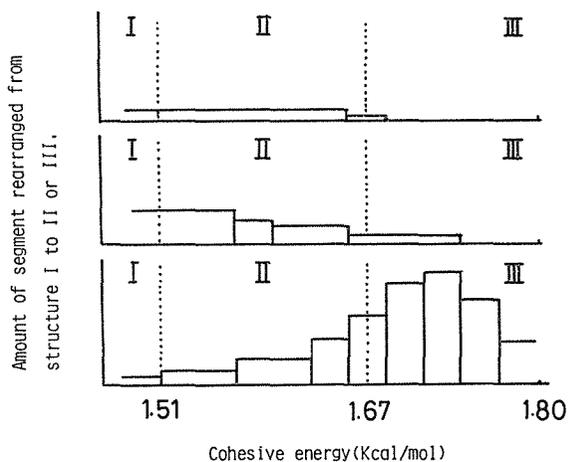

Fig. 11　Trasition of coherent structure of segments from I to II or III by dry annealing.
Top figure : original, middle f. : 180℃ ann., bottom f. : 240℃ ann.

Table 5. Advance of the thickness of crystalline lamella
and increase of the amount of region I with the
rise in annealing temperature.

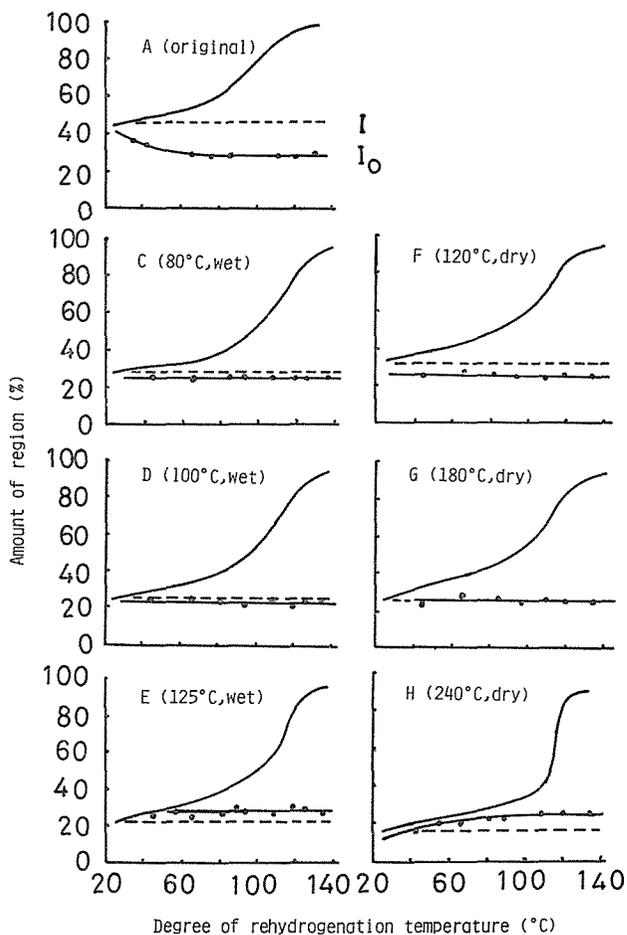| Annealing temperature (°C)	Amount of region I			Long period
	before ann. (%)	after ann. (%)	Increment (%)	
120		33.0	—6.7	78.9
180	39.7	40.3	0.6	90.2
240		50.2	10.5	94.0

Fig. 12 Rehydrogenation of region I of membranes which were
variously annealed and swollen.

structure is "evolved" by annealing to crystalline structure of lamella, but a part of it is "degenerated" to amorphous structure by annealing.

Similar phenomenon was observed from the following experiments. Membranes which were used on the lateral order measurement were contacted to H_2O vapor at 30℃ and its I region was rehydrogenated. The amounts of the rehydrogenated region, I_0, were measured and they were shown in Figure 12 in contrast to the amounts of region I which were original in these membranes, respectively. The results showed that the severely annealed samples of E (125℃ wet annealing) and H (240℃ dry annealing) had larger amounts of region I_0 than those of region I, and they will give the conclusion similar to that above described.

By the general survey of these results shown in Figure 12, it is noted that the amounts of I_0 of every sample is almost constant. It suggests a conception as that the amorphous regions of these membranes which were annealed and swollen by water vapor at various temperatures, were commonly composed of two domains. One of which is composed of densely crowded molecular segments with some order between them. The other is a matrix in which segments are less dense and have no order. So that, the coagulation of segments with lateral order, formation of crystalline nuclei and "evolution" or "devolution" of lateral order by annealing should occur only in the former domain, and the latter one does not take part in these phenomena.

The basic system of fine structure of this membrane should be constructed fundamentally when the membranes were formed by the coagulation of dispersed nylon 4 molecules, and it should not easily be changed by thermal disturbance.

4. Summary

Nylon 4 membranes which are annealed in various conditions were deuterated at various temperatures of 25～135℃. The amount of cohesive structure which was swollen and deuterated at the deuteration temperature was measured by IR spectroscopy on ν_{NH} band.

The cohesive energy (ΔF_i) of the deuterated structure was calculated from the deuteration temperature (T_i) by the formula of $\Delta F_i = 2.92 T_i + 625$, which was introduced on the base of Flory's theory of melting point depression under the existence of diluent.

The cohesive energy of the nylon 4 membranes was found to be ranged within about 1.5～1.8 Kcal/mol, and these values existed between those of nylon 3 and nylon 6. Hence the cohesive energy was supposed to be a characteristic value which depends upon the number of carbon atoms of aliphatic polyamides.

For the purpose of the examination of annealing effect, all cohesive regions of these sample membranes were divided into four regions of I ($\Delta F_i < 1.505$ Kcal/

mol), II ($\Delta F_i = 1.505 \sim 1.665$ Kcal/mol), III ($\Delta F_i = 1.665 \sim 1.800$ Kcal/mol) and IV ($\Delta F_i > 1.800$ Kcal/mol) which were bounded by three characteristic temperatures of humid nylon 4. It was shown by the examination of these regions that the amounts of I and II decreases but these of III and IV increases, especially the changes of I and III are remarkable. The change of the amount of III was correspondent to that of the crystalline peak area of X-ray diffraction pattern. This result suggests that the crystalline regions of these membranes are composed of the structure whose ΔF_i is about $1.665 \sim 1.800$ Kcal/mol mainly, and of that of $\Delta F_i > 1.800$ Kcal/mol partially.

By further examination using other supplmentary examination, the reversible transition of cohesive structure by annealing was analysed. It was assured that, as annealing temperature rises, the segments of II rearranged to the structures of III and IV successibly in principle. But on account of the existence of water or the supply of larger thermal energy, the segments of I rearrange to the structure of III skipping over the structure of II. On the other hand, the segments of II, for the most part, are rearranged to that of I in some case. This makes us suppose the mechanism of annealing effect of linear polymer.

The examination performed by the hydrogene exchange tecknique on the sample membranes of nylon 4 suffered various thermal histories suggests a conception that these membranes have a basic system of fine structure composed of two types of domain. One of which contains molecular segments condensed and ordered in some degree, and the "evolution" or "devolution" of lateral order by annealing are occured amoung them. The other contains molecular segments rather diluted and disordered, so that they do not take part in these phenomena discribed here.

As a conclusion, most experimental results presented in this paper are reasonably explained by considering the theory of heterogeneous structure in the linear polymer.

Acknowledgement

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重水素化法によるナイロン4の微細構造の研究

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その非晶構造を化学的手段で調べるため，種々の条件で熱処理したナイロン4皮膜について重水素化法を主とした実験を行なった。水蒸気による湿熱処理，N_2 ガス中での乾熱処理をほどこした試料皮膜を 25～135℃ の種々の温度下で重水蒸気によって重水素化した。各重水素化温度で緩和され重水素化された凝集領域量をIR法によって ν_{NH} バンドの吸光度変化から測定した。重水素化された領域の凝集エネルギー（ΔF_i）を溶媒存在による融点降下の Flory の理論に基いて導かれた式，$\Delta F_i = 2.92\,T_i + 625$，を用いて重水素化温度（$T_i$）から計算した。その結果（1）これらナイロン4試料のラテラルオーダー（LO）分布を従来の例よりもより定量的に測定した。（2）ナイロン4の凝集エネルギーはほぼ 1.5～1.8 Kcal/mol で，ナイロン3とナイロン6の中間の値を示し，脂肪族ナイロンの炭素数に対応することを認めた。（3）各試料の重水素化曲線の解析および他の補助的実験によって非晶領域中の分子鎖セグメントの熱処理による動向を解析し，熱処理機構の解明に寄与した。（4）これら皮膜の微細構造は2種の構造の領域から成る。すなわち，セグメントが濃密でしかも若干のLOをもち，熱処理などによってLOの変化がそこで起る領域と，セグメントの存在はより希薄であり，しかもLOを持たず熱処理などに影響されない領域とである。