Relation between the Behavior of Water and Hydrogen Bonding in Poly(hexamethylene adipamide) Films with Different End Group Balance

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(Received January 4, 1996)

ABSTRACT: As an extension of the previous studies [M. Tomokiyo *et al.*, submitted to *Sen-i Gakkaishi*], an attempt was made to elucidate the intrinsic role of terminal groups in the hydrogen bonding formation and the existing state of water in poly(hexamethylene adipamide) (nylon 66) with different molar fraction of amino end group f_N . ($f_N = [\text{NH}_2]/([\text{NH}_2] + [\text{COOH}])$) For this purpose, the heat-pressed nylon 66 films were subject to infrared (IR) and $\tan \delta$ - t analyses and at the same time the films which absorbed 10 wt% of water were subject to ^1H NMR measurements to determine relaxation time T_1 of water. Analyses on the change in the wave numbers of NH and CO stretching vibrations (κ_{vNH} , κ_{vCO}), the activation energy evaluated from the temperature dependence of κ_{vNH} and κ_{vCO} and the activation enthalpy and entropy for α_a and α_b relaxations indicated that the stronger hydrogen bond is formed for nylon 66 with larger f_N , which corresponds to the higher molecular packing density and higher activation energy for flow of the melt for these polymers. ^1H NMR revealed that water which penetrated into nylon 66 is composed of two electro-magnetically different species, one of which might be the ionized water by end groups, and those species are also composed of at least two components with shorter $T_1(T_{1,B})$ and with longer $T_1(T_{1,A})$. The existence of ionized water was supported by the pH measurement of water containing nylon 66. The both T_1 were shorter for nylon 66 with lower f_N , denoting that the nylon interacts more strongly with water, which is quite comparative to the facts that nylon 66 with low f_N exhibits the lower resistance to the penetration of water for this polymer. These facts led to an idea that water in polyamide is ionized by the polar terminal end groups and based on this idea a tentative hydrogen bonding for nylon 66 with high and low f_N (amino end rich and carboxyl end rich, respectively) is proposed.

KEY WORDS Poly(hexamethylene adipamide) / End Group Balance / Amino End Group / Carboxyl End Group / Relaxation / Ionization / Hydrogen Bonding /

Authors have already pointed out the importance of the balance of terminal groups of poly(hexamethylene adipamide) (nylon 66) in the water adsorption behavior, the rheological and thermal properties and the crystallization kinetics of the polymers¹ and the fiber structure formation during its melt-spinning process.² All these data have revealed that 1) nylon 66 with higher molar fraction of amino end group f_N is more resistant to the water adsorption, lowers the crystallization rate but exhibits the lower molecular mobility brought about by an increase in the activation energy for flow of the polymer melt and 2) the nylon 66 with larger f_N is fabricated into the fiber having amorphous region characterized by stronger cohesive nature of molecular chains. All result seems to support the idea that nylon 66 with high f_N has inherently stronger molecular interaction in the amorphous region to hinder the structural change induced by heat and humidity to some extent. However, the essential reason for the above phenomena has not been fully understood yet. Since polyamide has a potential ability to form hydrogen bond between amide groups (amino hydrogen and carboxyl groups) and it has unavoidably some water in any shape, the hydrogen bond might play an important role in any instance and is naturally influenced by the existence of water in polymer. The importance of water on structure changes and some properties for polyamide has been insisted by many authors.^{3–7} Wasias found so-called water-induced

crystallization for nylon 6.³ By dilatometric technique Kettle noted the glass-transition temperature T_g of nylon 6 as a function of water content decreased first sharply, then slowly with an increase in water content with plateau region (water content region 3–5 wt%).⁴ The transition of α_2 to α_1 crystal for nylon 66 by water has been reported by Vergelati *et al.*⁵ and the relaxation times (T_2) of water which penetrated into nylon 66 has been found to be shorter by three order of magnitude than that of bulk water by Fyfe *et al.*⁶

However, all the literature has ignored the effect of the balance of terminal groups which might facilitate the ionization of water penetrated in polyamide. Thus, in order to explain the phenomenological facts described above the hydrogen bonding in polyamide should be discussed in view of f_N and the existing state of water in the polymer with different f_N .

In this paper, we attempt to discuss the above problems in view of the hydrogen bonding and the existing state of water as a function of f_N with aid of infrared (IR) spectroscopy, $\tan \delta$ - T and ^1H NMR analyses.

EXPERIMENTAL

Nylon 66 Films with Different f_N

Three kinds of nylon 66 chips differing in f_N (manufactured by Asahi Chemicals Co., Ltd., Japan) were separately extruded into water bath to form chips again

using a twin screw-extruder (Laboplasto mill, Toyo Seiki Co., Ltd., Japan) under the following conditions to elase the thermal history imposed on each chip: cylinder temperature, 283°C; die temperature, 290°C; screw revolution, 70 rpm; feeding rate, 30 rpm; extruding volume, 50 g min⁻¹.

The chips thus obtained were subject to heat-pressing (50 kg cm⁻² at 290°C for 3 min) to give films with thickness of 0.08 mm, using a press-forming apparatus (Model AYSR-5, Kanefuji Kinzoku Co., Ltd., Japan). The concentration of terminal groups were determined by the procedure described previously¹ and the f_N (= number of amino end group/total numbers of amino and carboxyl end groups) were calculated and listed in Table I. The films were conditioned at 20°C and RH = 65% for 7 days before using in any experiments. The water content of the films was all 1.52 (±0.02) wt% as determined by Carl-Fisher method. (KF-06, VA-06, Mitsubishi Kasei Co., Ltd.).

FT-IR Measurements

The films were cut into the size with 10 × 100 × 0.08 mm and subject to IR measurements (Model FTS-60A/896, BIO-RAD Co., Ltd., U.S.A.) by ATR method at below glass transition temperature (35–65°C) with interval of 5°C under following operating conditions: crystal plate for ATR, zinc-selen; scanning speed, 80 kHz; low pass filter, 30 kHz; accumulation, 400 times; resolution, 8.0 cm⁻¹.

The apparent activation energy relating to the strength of hydrogen bond was estimated by the plot of $\ln \kappa_{\text{vNH}}$ and $\ln \kappa_{\text{vCO}}$ vs. $1/T$. Here, κ_{vNH} and κ_{vCO} are wave number for NH and CO stretching vibrations, respectively, and T is the measuring temperature in K.

Tan δ - T Analysis

The tan δ - T curves for the films with size of 3 × 40 × 0.08 mm were recorded on Vibron DDV01FP (Orientec Inc., Japan) under the following conditions: frequency, 1–110 Hz; heating rate, 2°C min⁻¹; measuring interval, 1°C min⁻¹; sample length, 20 mm; adding amplitude, 16 μ m; initial charge to film, 115 g mm⁻²; scanning of temperature, -100–180°C.

The activation enthalpy ΔH^* , entropy ΔS^* , and free energy ΔF^* for α_a and α_b relaxations were estimated from the relation between T_{max} and the corresponding measuring frequency f_{max} by using Eyring's procedure as follows^{8,9}:

$$k_a \propto \frac{1}{\tau} = \frac{kT}{h} \exp\left(\frac{-\Delta F^*}{RT}\right) = \frac{kT}{h} \exp\left(\frac{-\Delta H^*}{RT}\right) \exp\left(\frac{\Delta S^*}{R}\right) \quad (1)$$

$$\omega_{\text{max}} \tau = 2\pi f_{\text{max}} \tau = 1 \quad (2)$$

$$\ln\left(\frac{1}{2\pi f_{\text{max}}}\right) + \ln\left(\frac{kT_{\text{max}}}{h}\right) = \frac{\Delta H^*}{RT_{\text{max}}} - \frac{\Delta S^*}{R} \quad (3)$$

where, k_a is Eyring's rate constant; k , Boltzmann's constant (1.38066×10^{-23} J K⁻¹); h , the Planck's constant (6.62618×10^{-34} Js); R , the Gas constant (1.987 cal mol⁻¹ K⁻¹); τ , the relaxation time; ΔH^* , the activa-

tion enthalpy (cal mol⁻¹); ΔS^* , the activation entropy (cal mol⁻¹ K⁻¹). In addition, activation energy ΔE^* was evaluated by the frequency dependence of $1/T_{\text{max}}$ as

$$\Delta E^* = -R \frac{d \ln f}{d\left(\frac{1}{T_{\text{max}}}\right)} \quad (4)$$

T_1 Measurement of Water in Polymer

The longitudinal relaxation time T_1 of the water absorbed in nylon 66 films with highest f_N and lowest f_N was measured by the inversion recovery method on a NMR spectrometer (Model GSX-400, JEOL, Japan) under the following operating conditions: central observation frequency, 399.78 MHz; observation width, 128000 kHz; data point, 16 k; delay time, 4 s; pulse width, 27 μ s for 180° pulse.

The fundamental Bloch equation¹⁰ for this relaxation of the magnetization (initial, M_0 ; after a time t , M_t) is given by eq 5 and 6.

$$M_t = M_0 \left[1 - 2 \exp\left(-\frac{t}{T_1}\right) \right] \quad (5)$$

$$\ln\left[\left(1 - \frac{M_t}{M_0}\right)/2\right] = -\frac{t}{T_1} \quad (6)$$

If the relaxation is composed of two components differing in T_1 ($T_{1,A}$, $T_{1,B}$) and the fraction of the latter is given as χ_B (that is, $\chi_A = 1 - \chi_B$), then the following equations might hold by assumption of the additivity rule.

$$M_{t,A} = (1 - \chi_B) M_0 \left[1 - 2 \exp\left(-\frac{t}{T_{1,A}}\right) \right] \quad (7)$$

$$M_{t,B} = \chi_B M_0 \left[1 - 2 \exp\left(-\frac{t}{T_{1,B}}\right) \right] \quad (8)$$

$$M_{t,\text{total}} = M_{t,A} + M_{t,B}$$

$$\ln\left[\left(1 - \frac{M_{t,\text{total}}}{M_0}\right)/2\right] = \ln\left[(1 - \chi_B) \exp\left(-\frac{t}{T_{1,A}}\right) - \chi_B \exp\left(-\frac{t}{T_{1,B}}\right)\right] + C \quad (9)$$

Constant term C is introduced to delete the contribution brought about by inhomogeneity of magnetic field. As a reference, T_1 's of the deionized water and the cellulose/water system were also measured.

pH Change of Water Containing Nylon 66 Chips

Nylon 66 chips described above were stood in deionized water for one day and the separated chips were dried in air and finally vacuum-dried at 50°C. A thirty g of each resultant chip was immersed in 100 ml of deionized water at 25°C and the pH of the surrounding water was measured as a function of time by a pH meter (Model F-21, Horiba Co., Ltd., Japan). The pH of deionized water containing no polymer was also measured as control.

Figure 1. The f_N dependence of wave numbers for NH and CO stretching vibrations ($\kappa_{\nu_{\text{NH}}}$ and $\kappa_{\nu_{\text{CO}}}$, respectively) at various measuring temperatures.

RESULTS AND DISCUSSION

Nature of Hydrogen Bonding of Nylon 66 Films by IR and $\tan \delta$ - T Analysis

Figure 1 shows the f_N dependence of the wave numbers for NH and CO stretching ($\kappa_{\nu_{\text{NH}}}$ and $\kappa_{\nu_{\text{CO}}}$, respectively) at given temperatures.

Both $\kappa_{\nu_{\text{NH}}}$ and $\kappa_{\nu_{\text{CO}}}$ are decreasing functions of f_N , indicating that nylon 66 with larger f_N forms stronger hydrogen bond in polymer. Especially, $\kappa_{\nu_{\text{NH}}}$ drastically shifted towards shorter wave number side when f_N goes from 0.48 to 0.62. Note that if water in polymer is ionized by end groups, the f_N value of 0.48 is just the turning point from acid to alkali. The ionization of water contacted with nylon 66 chips with different f_N are shown in Figure 2, clearly indicating that the water contacting with carboxyl end rich nylon 66 becomes promptly acidic and the water contacting with amino end rich nylon 66 keeps neutral, offsetting the acidity of water probably by dissolution of carbon dioxide in air. Therefore, the penetrated water is also anticipated to be ionized by the balance of terminal end groups.

In Figure 3 $\ln \kappa_{\nu_{\text{NH}}}$ and $\ln \kappa_{\nu_{\text{CO}}}$ are plotted against $1/T$. The activation energies (ΔE) estimated from Figure 3 for ν_{NH} and ν_{CO} are also higher for the sample with larger f_N , although the absolute value for ν_{NH} is larger than that for ν_{CO} , as shown in Figure 4. Far lower ΔE values evaluated here than that reported for hydrogen bond ($3\text{--}8 \text{ kcal mol}^{-1}$) might be explained by the fact that the present experiment was carried out below T_g . This in turn means that we just evaluate the vibrational movement of the hydrogen bonding in a kind of molecularly frozen state. Then, if the hydrogen bond is formed by purely NH and CO from polymer alone, one can expect the same ΔE value, irrespective of estimating procedure. The different results from the analysis on ν_{NH} and ν_{CO} might be influenced by the existing state of water in polymer as pointed out above.

Figure 2. The change in pH of the water surrounding nylon 66 chips as a function of contacting time: ●, deionized water; ○, nylon 66 with $f_N=0.36$; △, $f_N=0.48$; □, $f_N=0.62$.

Figure 5 shows the $\tan \delta$ - T curves for nylon 66 films. Two α (referred as to α_a and α_b for convenience) and β dispersions are seen around 80°C , 30°C , and -70°C , respectively. α dispersion has been known to shift toward around $ca. 0^\circ\text{C}$ with an increase in water content in nylon 66 and is attributed to micro Brownian motion of segment related to hydrogen bonding.¹¹ Prevorsek¹² found two α dispersion peaks in the mechanical relaxation measurements on nylon 6 with water content of more than 2.0 wt%, concluded that higher dispersion (corresponding to α_a in the present case) comes from nylon 6 with no water and the lower temperature dispersion (corresponding to α_b in the present case) is from nylon 6 with some water. β dispersion has been attributed to

Figure 3. Arrhenius plot of NH and CO stretching vibrations ($\kappa_{\nu \text{ NH}}$ and $\kappa_{\nu \text{ CO}}$, respectively): $\circ$, nylon 66 with $f_N = 0.36$; $\triangle$, $f_N = 0.48$; $\square$, $f_N = 0.62$.

Figure 4. The f_N dependence of activation energy for NH and CO stretching vibrations ($\kappa_{\nu \text{ NH}}$ and $\kappa_{\nu \text{ CO}}$, respectively): $\circ$, $\kappa_{\nu \text{ CO}}$; $\bullet$, $\kappa_{\nu \text{ NH}}$.

segmental motion of the water bonded amide group and the peak temperature has been known to shift towards higher side with a decrease in water content, finally disappearing upon complete drying of nylons.¹²⁻¹⁵ α_b becomes more distinct for nylon 66 with lower f_N . If we take the assignment for α_b described above, the present observation is well correlated with the fact that nylon 66 with lower f_N relatively easily absorbs water.¹ In turn, the amorphous region characterized by α_b dispersion is hard to be formed for nylon 66 with larger f_N .

Thermo-kinetic results are summarized in Table I. For both α_a , α_b relaxations ΔS^* vs. ΔH^* plot gives each master line, irrespective of f_N , as shown in Figure 6. The linearity of both dispersions is expressed as follows:

Figure 5. The $\tan \delta$ - T curves for nylon 66 with different f_N : Real line, nylon 66 with $f_N = 0.36$; dotted line, $f_N = 0.48$; chained line, $f_N = 0.62$.

$$\Delta S^* = 2.66 \times 10^{-3} \Delta H^* - 36.6 \quad \text{for } \alpha_a \quad (10)$$

$$\Delta S^* = 3.16 \times 10^{-3} \Delta H^* - 32.3 \quad \text{for } \alpha_b \quad (11)$$

This means that the two dispersions have obviously different relaxation mechanism, but relaxation mechanism for each one of dispersion is inherently the same, irrespective of f_N . ΔH^* and ΔS^* for α_a and α_b relaxations are plotted as a function of f_N in Figure 7. Both ΔH^* and ΔS^* for α_a and α_b relaxations increase with an increase in f_N . ΔH^* for α_a is higher than that of α_b but the reverse is observed for ΔS^* . Generally, the movement or rearrangement of the moving unit takes place at molecular level when α relaxation proceeds in polymer system and the order of molecular displacement changes

at the instance when the moving unit moves by acquiring ΔH^* and overcoming some potential barrier. ΔS^* is a measure for the above order of displacement. Then, the larger ΔH^* for α_a than that for α_b can be understood by

Figure 6. The relation between activation entropy ΔS^* and activation enthalpy ΔH^* for α_a and α_b relaxations of nylon 66 samples with various f_N : $\circ$ (real line), α_a relaxation; $\bullet$ (dotted line), α_b relaxation.

taking the strength of hydrogen bond in both regions into consideration. That is, the molecular packing density in the amorphous region characterized by α_a dispersion is higher due to relatively strong hydrogen bonding than that characterized by α_b dispersion.

On the other hand, the reverse tendency for ΔS^* might be explained by an idea that molecular region giving α_b relaxation is considerably influenced by water and the existence of water makes the molecular displacement more orderly. This tendency proved to be much more stronger for nylon 66 with higher f_N .

In the case of molecular motion in polymeric solid, a modified theory of self-diffusion of chain led to the following ΔS^* - ΔH^* linear relationship.¹⁶

$$\Delta H^* = \frac{1}{9\Delta\alpha} \Delta S^* + \Delta H_{\text{tor}}^* \quad (12)$$

where α is the isobaric coefficient of thermal expansion; $\Delta\alpha$ represents the difference in α between the rubbery and glassy states for the α relaxation and ΔH_{tor}^* corresponds to the internal torsional energy of a polymer chain.

Some authors have related this linear relationship to the thermal expansion coefficient on the basis of the above theory^{17,18}. According to the theory, the isobaric coefficient of thermal expansion $\Delta\alpha$ for α_a and α_b

Table I. Thermokinetic parameter for α -relaxation

End-group fraction f_N (-)	α_b -Relaxation [low-temperature side of α -relaxation]			α_a -Relaxation [high-temperature side of α -relaxation]		
	ΔE^*	ΔH^*	ΔS^*	ΔE^*	ΔH^*	ΔS^*
	kcal mol ⁻¹	kcal mol ⁻¹	cal mol ⁻¹ K ⁻¹	kcal mol ⁻¹	kcal mol ⁻¹	cal mol ⁻¹ K ⁻¹
0.36	85.8	85.2	229.5	96.7	96.0	217.2
0.48	93.8	93.2	259.2	111.0	110.3	259.5
0.62	114.5	113.9	319.8	121.3	120.6	282.0
$\Delta\alpha^a$		3.44×10^{-4} (K ⁻¹)			2.95×10^{-4} (K ⁻¹)	

^a Evaluated from eq 12.

Figure 7. The f_N dependence of the activation enthalpy ΔH^* (a) and activation entropy ΔS^* (b): Symbols are the same as in Figure 6.

relaxations were evaluated from Figure 6, to be $2.95 \times 10^{-4} \text{ (K}^{-1}\text{)}$ and $3.44 \times 10^{-4} \text{ (K}^{-1}\text{)}$, respectively. Thermal parameters are collected in Table I. Since $\Delta\alpha$ is the difference between rubbery and glassy states, the above results again confirms that the molecular packing density in the amorphous region related to α_a dispersion is relatively higher than that for α_b .

The Existing State of Water in Nylon 66

Figure 8 shows ^1H NMR spectra measured at 60°C for water absorbed in nylon 66 films with $f_N=0.32$ and 0.62 , and as references the spectra of cellulose/water system are also shown. Obviously, the cellulose/water system gives a broad singlet. In contrast to this, nylon 66/water systems exhibit characteristically two separate peaks. This means that the water in nylon 66 is composed of two electro-magnetically different components and this does not mean that the water has two components differing in relaxation time, because we can estimate two components with two different relaxation time for a singlet peak for cellulose/water system.

The existence of the ionized water in the vicinity of end groups of polymer might be only possible explanation for the existence of two electro-magnetically different components, attributing a larger peak to ionized one, as proved in Figure 2.

Figure 9 shows the plot of $\ln((1-M_t/M_0)/2)$ vs. t of nylon 66/water systems, including cellulose/water system.

Figure 8. ^1H NMR spectra of cellulose (a), nylon 66 with $f_N=0.36$ (b), and nylon 66 with $f_N=0.62$ (c).

The completely linear plot is realized for water but for others considerable deviation from the linearity is found at shorter t region. Note that for nylon 66 systems the total peaks observed in Figure 8 were used in this analysis. Parameter fitting procedure according to eq 8 was made for polymer/water systems and the result is collected in Table II. Two components with different T_1 ($T_{1,A}$ and $T_{1,B}$) were proved to exist and both values are smaller for nylon 66 with low f_N , indicating that water generally more strongly interacts with nylon with low f_N and the fraction of the strongly interacting water is also larger for this polymer. This confirms the previous results obtained in water-absorption experiments.¹ $T_{1,B}$ of nylon 66/water systems is one-order longer than cellulose/water system. One of possibilities for this difference is that even the strongly interacted water in nylon 66 might be

Figure 9. The plot of $\ln((1-M_t/M_0)/2)$ vs. t of nylon 66/water and cellulose/water system: Long t region (a); short t region (b).

Table II. Longitudinal relaxation time T_1^a of proton in water and water absorbed in cellulose and nylon 66 with different f_N

Sample	Water content/%	T_1/s	$T_{1,A}^b/\text{s}$	$T_{1,B}^b/\text{s}$	$\chi_B^{b,c}$
Distilled water	100	2.85	—	—	—
Cellulose ^d	12.0	—	0.201	4.90×10^{-3}	0.250
Nylon 66 ($f_N=0.36$)	14.0	—	0.534	29.9×10^{-3}	0.492
Nylon 66 ($f_N=0.62$)	14.0	—	0.692	38.3×10^{-3}	0.336

^a Observed at 60°C using GSX-400 NMR spectrometer. ^b Using "two component model" described in the experimental term. ^c A fraction of water having $T_{1,B}$. ^d Membrane sample regenerated in 15 wt% H_2SO_4 solution using cupra ammonium dope at 25°C .

Figure 10. Tentative representation of hydrogen bonding of nylon 66 with $f_N = 0.62$ (a) and nylon 66 with $f_N = 0.36$ (b).

influenced by the existence of ionized water in polymers, as discussed before. The ionized water may relatively weaken the hydrogen bonding, compared with non-ionized water, if water is really incorporated in the hydrogen bonding formation in polar polymers. This tentative explanation can also give a reason for the fact that α_a relaxations for nylon 66, which are said to represent the molecular region dominated by hydrogen bonding, is observed at 80–130°C.¹ As is pointed out above, α_b relaxation is much influenced by water, now we can regard this water to be the water with $T_{1,b}$. The reason why the nylon with high f_N (rich in amino end group) is resistant to water and has stronger cohesive nature (for example, resistant to melt flow) and hydrogen bonding could be tentatively explained as shown in Figure 10.

Here, the hydroxyl ions generated for nylon 66 with high f_N may strengthen the original hydrogen bond between polymer by attacking amide carbon (or nitrogen), giving relatively stiff molecular chain assembly (strong cohesive nature). In contrast to this, the proton originated from nylon 66 with low f_N only works for destruction of the original hydrogen bond, loosening the molecular chain to make room accommodating other waters, and the higher molecular mobility for this polymer might result in higher isothermal crystallization as proved in the previous study.¹

CONCLUSIONS

Hydrogen bonding formation of nylon 66 films with different molar fraction of amino end group f_N in relation to the existing state of water penetrated in the polymers. Infrared (IR) and $\tan \delta$ - T analyses revealed that the stronger hydrogen bonding is formed for nylon 66 with higher f_N . The penetrated water was proved to be ionized

by the balance of end functional groups (carboxyl and amino end groups) of polymer. T_1 measurement on the water in polymers suggested that water exists as at least two components with shorter $T_1(T_{1,B})$ and larger $T_1(T_{1,A})$, both of which are longer for nylon 66 with higher f_N , denoting that the nylon interacts more weakly with water. Based on this idea a tentative hydrogen bonding for nylon 66 with high and low f_N (amino end rich and carboxyl end rich, respectively) is proposed.

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