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Melting and recrystallization in modified porous nylon-6 membranes

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Abstract

For the porous membranes prepared from a calcium chloride–methanol solution of nylon-6, the behaviors of melting and recrystallization were investigated by DSC measurements. For thin samples annealed at 200 °C, a double peak was observed on the DSC curve. Further immersing them in an aqueous solution of calcium chloride or magnesium chloride and then drying, the higher side peak intensity decreased with the immersion time and disappeared finally. The residual single peak temperature for samples with magnesium ions was 7 °C higher than those with calcium ions, reflecting the increase of three structural units of crystal length during the heating process. The structural models adsorbed calcium and magnesium ions are proposed.
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Keywords: Nylon-6; Porous membrane; Melting; Recrystallization; Ion adsorption

1. Introduction

For the annealed nylon membranes, a complex peak of melting is generally observed on the DSC curves [1–5]. The successive endothermic peaks are due to the meltings of original crystals reorganized in the heating process and recrystallized parts after melting of original crystals, respectively [1–5]. Therefore the melting behaviors reflecting cohesive states before DSC measurements should be obtained under the depression of both reorganization in the heating process and recrystallization after melting, called the zero entropy production path method [6]. DSC measurements for nylon-6 crosslinked by adequate acetylation [5] or grafted by methoxymethylation [2,7] demonstrated the presence of the zero entropy production path. This general idea could be also understood from the fact that the difference between the heat changes of crystallization in the cooling process and fusion in the following heating process, which corresponds to the quantity recrystallized in the heating process, is extrapolated to zero with increasing the heating rate [4]. Further, we found from DSC measurements for porous nylon membranes that the adsorbed calcium ions also suppressed the growth of crystals and the recrystallization after melting [1–4,8]. The porous membranes investigated here are prepared from a nylon-6 solution of calcium chloride–methanol mixture [9]. Therefore the calcium ions should be familiar with amide groups in nylon-6 membranes and advantageous in approaching to the surface of crystals, comparing with other ions [10].

In this study, the difference in the adsorption effects of magnesium and calcium ions on a double

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peak of melting obtained for above membranes is discussed structurally by exchanging the melting behaviors of samples with calcium and magnesium ions into the crystal length distributions, respectively [11].

2. Experimental

2.1. Preparation of nylon-6 porous membranes

Porous membranes were prepared from a nylon-6 solution of calcium chloride–methanol mixture (nylon-6: 6.67 g, $CaCl_2$: 20 g, and CH_3OH: 100 ml). The solution flowed out on the glass plate was kept in the desiccator of 100% RH at the room temperature (24 °C) and after casting, the thin membranes with the thickness of about 5 μm (porosity ∼60.4%) were prepared. The membranes for DSC measurements were dried in the desiccator with phosphorus pentoxide after washing enough in water.

2.2. Annealing

Annealing for the porous nylon-6 membranes was performed for 30 min at 200 °C using DSC. The adsorption treatment of calcium or magnesium ions was done for samples after annealing (control samples). The crystallinity from DSC for control samples was 42.9%.

2.3. Adsorption procedure

Annealed samples were immersed in an aqueous solution (15 wt.%) of calcium chloride, magnesium chloride, potassium chloride, or sodium chloride at 40 °C for several minutes under stirring. Then the samples without washing were dried enough in the desiccator with phosphorus pentoxide and used as samples for DSC measurements.

2.4. Thermal analysis

The behaviors of melting and recrystallization for samples were measured using DSC (MAC Science 3200S) at the heating rate 10 °C/min under N_2 flow of 100 ml/min.

3. Results and discussion

3.1. Adsorption effects of calcium ions

Fig. 1 shows DSC curves for porous nylon-6 membranes annealed at 200 °C and then immersed in an aqueous solution of calcium chloride (15 wt.%) at 40 °C for various times. Fig. 2 shows plots of the onset temperature, the lower side peak temperature, the higher side peak temperature, and the end temperature of melting against the immersion time for same porous nylon-6 membranes as Fig. 1. The intensity of the higher side peak at 219 °C in a double peak of melting observed for the control sample decreased gradually with increasing the immersion time, because of the suppression effects of calcium ions on the recrystallization after melting. Over 4 min, the higher side peak was disappeared at all and the lower side peak at 209 °C was remained as a single peak, and that, the recrysrallization after melting was depressed

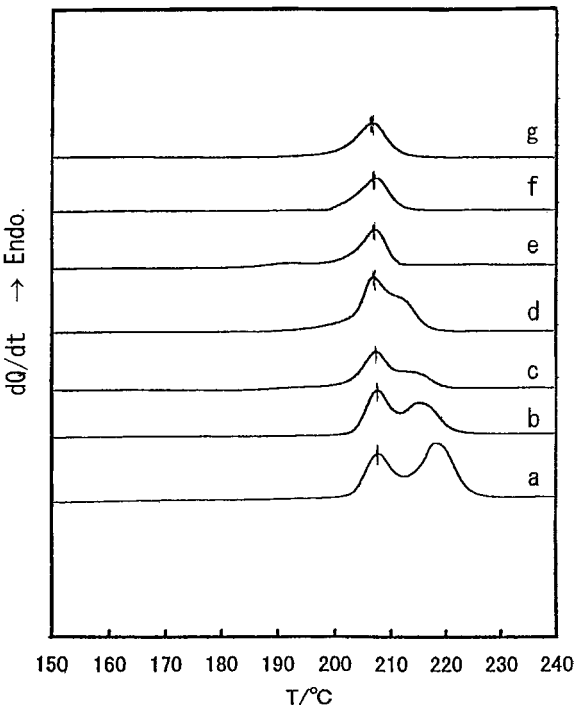

Fig. 1. DSC curves for porous nylon-6 membranes annealed at 200 °C and then immersed in an aqueous solution of calcium chloride (15 wt.%) at 40 °C for various times. (a) 0 min, (b) 1 min, (c) 2 min, (d) 3 min, (e) 4 min, (f) 5 min, and (g) 6 min.

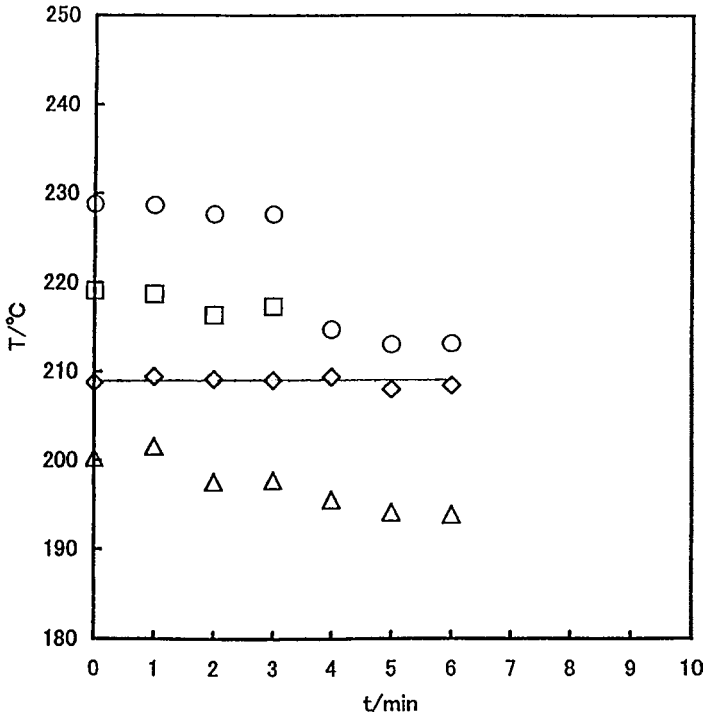

Fig. 2. Plots of the onset temperature (△), the lower side peak temperature (◇), the higher side peak temperature (□), and the end temperature (○) of melting for porous nylon-6 membranes annealed at 200 °C and then immersed in an aqueous solution of calcium chloride (15 wt.%) at 40 °C; *t*: the immersion time.

perfectly by the adsorption of calcium ions. The onset temperature of melting peak for samples immersed over 2 min was below 200 °C, e.g. 193 °C for the sample immersed for 6 min. This result suggests the minor destruction of crystals by immersing.

3.2. Adsorption effects of magnesium ions

Fig. 3 shows DSC curves for porous nylon-6 membranes annealed at 200 °C and then immersed in an aqueous solution of magnesium chloride (15 wt.%) at 40 °C for various times. Fig. 4 shows plots of the onset temperature, the lower side peak temperature, the higher side peak temperature, and the end temperature of melting against the immersion time for same porous nylon-6 membranes as Fig. 3. The intensity of the higher side peak for the control sample decreased with the immersion time as well as the case of calcium chloride. However the lower side peak temperature increased gradually with increasing the immersion time up to 5 min. Over 5 min, the higher side peak was disappeared at all and only the lower side peak with the peak temperature 216 °C was remained. This temperature is only 3 °C lower than the higher side peak temperature 219 °C for the control sample. The onset temperature of melting peak was almost equal to the annealing temperature 200 °C.

3.3. Adsorption effects of other ions

For samples immersed in an aqueous solution of potassium chloride or sodium chloride, any adsorption effect was not observed on DSC curves.

3.4. Adsorption number of ions per amide group

For each sample, the adsorption number of calcium or magnesium ions per amide group, *n*, was calculated by:

$$n = \frac{\Delta W/M_{\mathrm{i}}}{W/M_{\mathrm{ny}}} \quad (1)$$

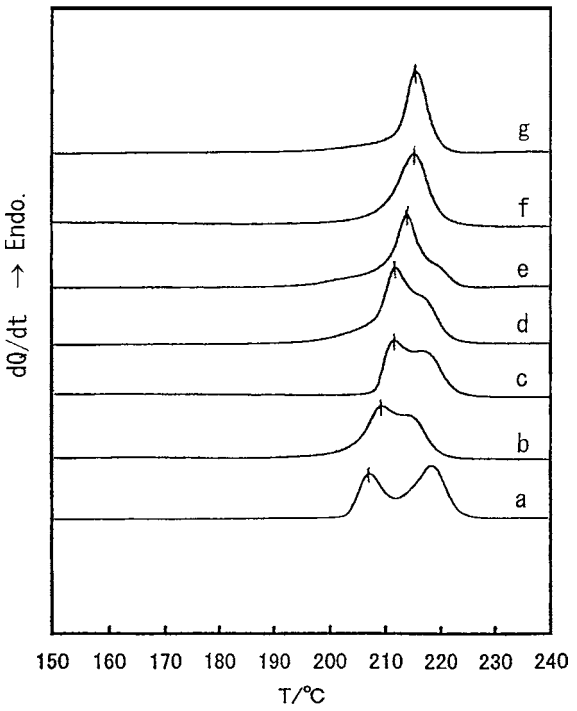

Fig. 3. DSC curves for porous nylon-6 membranes annealed at 200 °C and then immersed in an aqueous solution of magnesium chloride (15 wt.%) at 40 °C for various times. (a) 0 min, (b) 1 min, (c) 2 min, (d) 3 min, (e) 4 min, (f) 5 min, and (g) 6 min.

where ΔW is the weight of calcium or magnesium ions adsorbed in a sample, M_i is the molar weight of calcium or magnesium ion, W is the weight of a sample without calcium or magnesium ions, and M_{ny} is the molar weight of nylon-6 structural unit. Table 1 shows the values of n against the adsorption time, t, of calcium and magnesium ions for the total weight (n shown out parentheses) and for the weight of only amorphous parts (n shown in parentheses) of a nylon-6 porous membrane. For samples with calcium ions, $n_{sat} \cong 0.61$, and for samples with magnesium ions, $n_{sat} \cong 0.55$ were obtained, respectively, where n_{sat} is the value of n at the saturation point of 4 min for calcium ions and 5 min for magnesium ions. At these immersion times, the higher side peak of melting is disappeared. Further, considering the crystallinity of 42.9% for the control sample, the adsorption should be done only in the amorphous regions. For only the weight of amorphous parts, n_{sat} showed 1.07 for calcium ions and 0.96 for magnesium ions. $n_{sat}(= 1.07) > 1$ for calcium ions means the erosion of the end surface of crystals, thereby increasing only a little amorphous parts. $n_{sat}(= 0.96) < 1$ means that the migration of magnesium ions to the end surface of crystals is not a little better than calcium ions. These results suggest that one calcium or magnesium ion per amide group is adsorbed coordinately in the amorphous regions.

3.5. Crystal length distribution

The endothermic peak of melting for each sample with n_{sat} was exchanged into the distribution of the crystal length, l, using the following equation [11]:

$$l = \frac{2\sigma_e T_m^0}{h_u(T_m^0 - T_m)} \quad (2)$$

where T_m^0 is the equilibrium melting temperature, h_u is the heat of fusion per m^3, σ_e is the surface free energy per m^2, and T_m is the corrected melting temperature [11]. In the calculation, $T_m^0 = 501.1$ K, $\sigma_e = 65 \times 10^{-3}$ J/m^2 [12], and $h_u = 2.33 \times 10^8$ J/m^3 were used. Here, T_m^0 is the intersection temperature of $T_m = T_a$ and the extrapolation line of the end temperature of melting against T_a, where T_a is the annealing temperature. Fig. 5 shows l distribution curves of $l_p = 106.1$ A (about six structural units) in the range from 79.0 to 127.7 A for the sample with calcium ions and $l_p = 162.7$ A (about nine structural units) in the range from 105.6 to 221.8 A for the

Table 1
The values of n against the adsorption time, t, of calcium and magnesium ions for the total weight (n shown out parentheses) and for the weight of only amorphous parts (n shown in parentheses) of a nylon-6 porous membrane

	t (min)						
	0	1	2	3	4	5	6
Ca^{2+}	0 (0)	0.31 (0.54)	0.43 (0.75)	0.51 (0.89)	0.62 (1.09)	0.60 (1.05)	0.61 (1.07)
Mg^{2+}	0 (0)	0.12 (0.21)	0.22 (0.39)	0.34 (0.60)	0.45 (0.79)	0.55 (0.96)	0.54 (0.95)

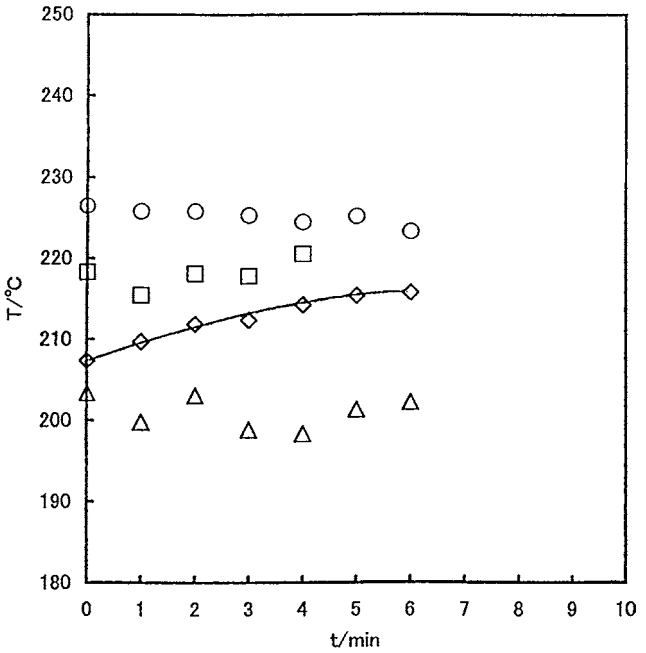

Fig. 4. Plots of the onset temperature (△), the lower side peak temperature (◇), the higher side peak temperature (□), and the end temperature (○) of melting for porous nylon-6 membranes annealed at 200 °C and then immersed in an aqueous solution of magnesium chloride (15 wt.%) at 40 °C; *t*: the immersion time.

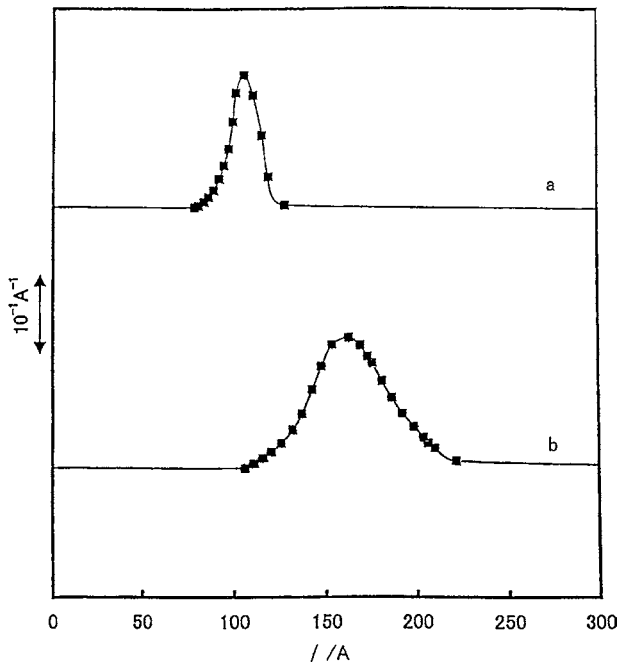

Fig. 5. The *l* distributions in porous nylon-6 membranes annealed at 200 °C and then immersed in an aqueous solution of calcium chloride (a) and magnesium chloride (b) at 40 °C for 4 and 5 min, respectively.

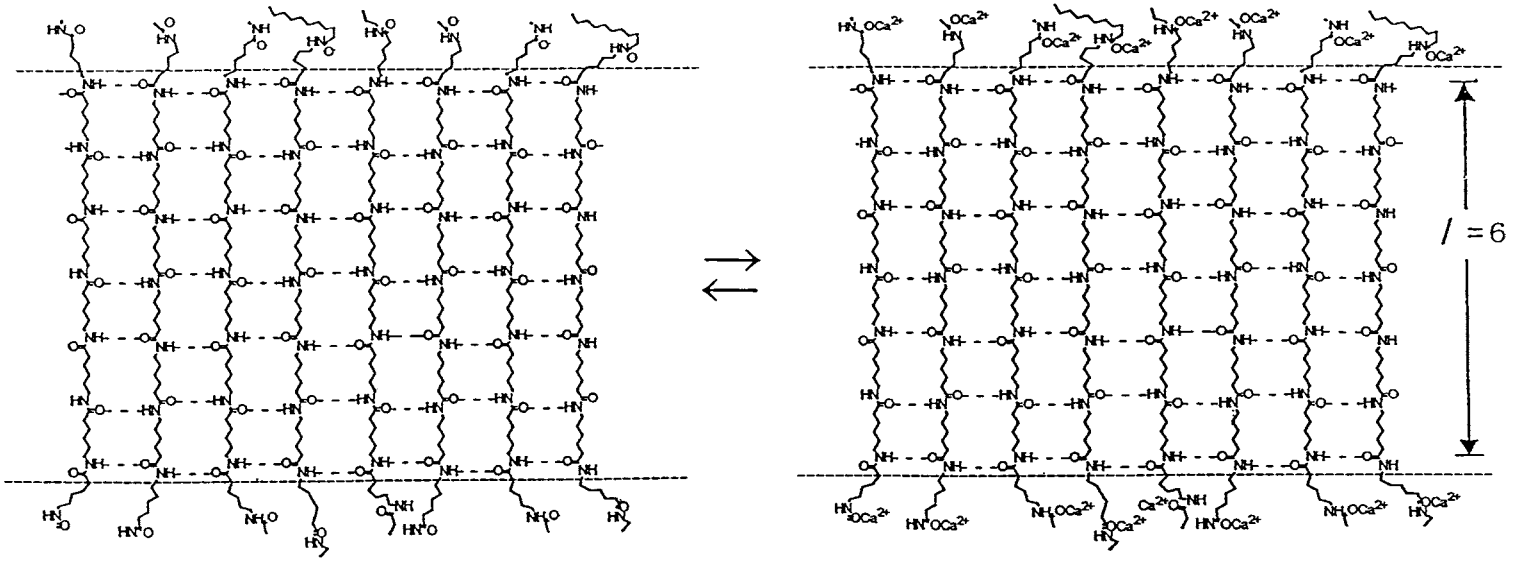

Fig. 6. The adsorption and desorption models of calcium ions around crystals with $l = 6$ in annealed porous nylon-6 membranes.

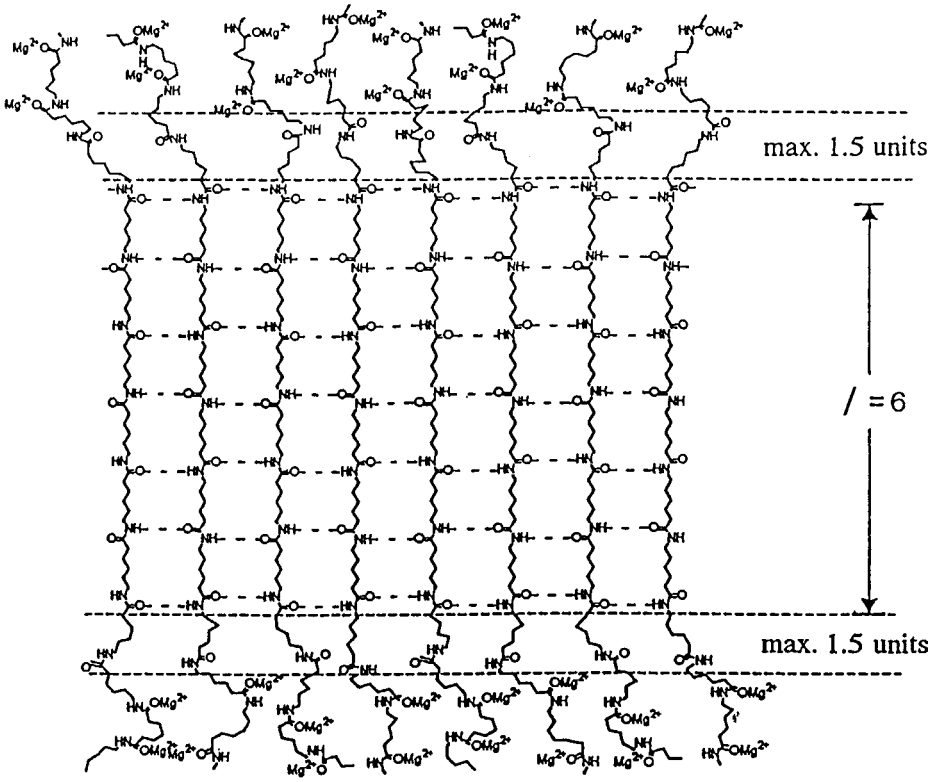

Fig. 7. The adsorption model of magnesium ions around crystals with $l = 6$ in annealed porous nylon-6 membranes.

sample with magnesium ions, where l_p is l at a peak. The l_p difference in both peaks, 56.6 A (about three structural units), is the increase of l in the heating process for samples with magnesium ions.

Fig. 6 shows the adsorption and desorption models of calcium ions around crystals with $l = 6$ in annealed porous nylon-6 membranes. Fig. 7 shows the adsorption model of magnesium ions around crystals with $l = 6$ in annealed porous nylon-6 membranes.

4. Conclusions

Calcium and magnesium ions are adsorbed coordinately at the rate of one ion per amide group in the amorphous regions, thereby calcium ions depressing the growth of crystals in the heating process and the recrystallization after melting. Whereas magnesium ions depressed the recrystallization after melting as well as calcium ions, the increase of three structural units in the crystal length occurred during the heating process. For potassium and sodium ions, any adsorption effect was not observed on DSC curves.

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