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Miscibility of polyamide-6,6 with aromatic polyamides

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Summary

The polyamides with aromatic rings in the main chain were synthesized by the solution polymerization of 4,4′-diphenylmethane diisocyanate and aliphatic dicarboxylic acid in the presence of catalyst. The thermal properties and the miscibility behaviours with polyamide-6,6 of these aromatic polyamides were studied. The aromatic polyamides synthesized with one kind of dicarboxylic acid had typical thermal properties of crystalline polymers, whereas those synthesized with the mixtures of dicarboxylic acids were not easily crystallized. The observed miscibility behaviours showed some differences from those predicted by binary interaction model.

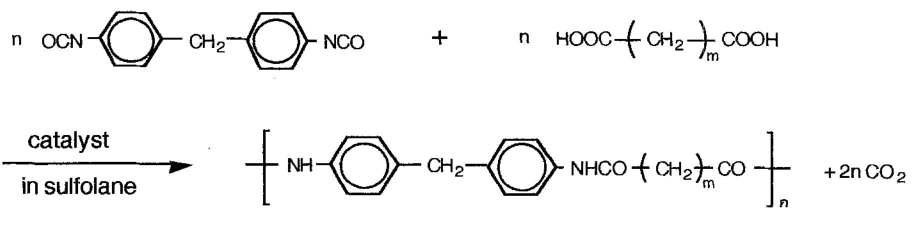
Introduction

In order to predict the miscibility of hydrogen-bonding polymers, complicated experimental procedures for the characterization of intermolecular interactions are required(1).

The work of Ellis showed that the miscibility of polyamide blends can be described by relatively simple binary interaction model(2,3). This method does not take directly into account the interactions between the amide groups in blends on the assumption that the net exchange of hydrogen bonding interactions is close to zero. However, Côté, *et al.*, observed the discrepancies between predicted and observed behaviours, and suggested such parameters as rigidity of chain or average interamide distance to be the causes(4).

In this paper, we report the results on the miscibility of polyamide-6,6 with series of aromatic polyamides synthesized specially by the following reaction between 4,4′-diphenylmethane diisocyanate(MDI) and aliphatic dicarboxylic acid (*Scheme 1*)(5).

Scheme 1:



Experimental

MDI(Tokyo Kasei) was melted at 50°C and white precipitate of dimer in the melt was removed before use. Adipic acid(Showa), pimeric acid(Janssen), suberic acid(Janssen), azelaic acid(Aldrich), sebacic acid(Junsei), 1,10-decanedicarboxylic acid(Aldrich), tridecanedioic acid(Tokyo Kasei), and 1,14-tetradecanedioic acid(Tokyo Kasei) were used as received. Sulfolane(Aldrich) was dried over 4Å molecular sieve before use. Polyamide-6,6($\overline{M}_n$=20,000) was supplied by Tongyang Nylon Co.(Korea). 3-Methyl-1-phenyl-2-phospholene-1-oxide used as catalyst was synthesized by the known procedure(6).

Dicarboxylic acid and small amount(about 0.125 mol% of monomers) of 3-methyl-1-phenyl-2-phospholene-1-oxide were dissolved in sulfolane. The stoichiometric amount of MDI solution was dropwisely added at 200°C, and the mixture was stirred for 4 hours. The viscosity rise accompanied with polymerization was controlled by adding additional sulfolane, and the solid content of final solution was adjusted to about 15%(w/v). During the reaction, dry N_2 gas was constantly purged. After the reaction, the reaction mixture was poured into 10-fold excess of methanol and the precipitate was dried under vacuum at 80°C. Yields were about 70 - 80%.

Details of synthesized aromatic polyamides are given in Table 1. Series 1 polyamides synthesized with one kind of dicarboxylic acid differ from series 2 polyamides synthesized with mixtures of dicarboxylic acids. In sample designation code, the number following H is the series number and the number in the parenthesis is the (average) methylene number(m) of aliphatic dicarboxylic acid used in the synthesis by *scheme 1*. For example, H1(6) indicates polyamide synthesized with suberic acid(m=6), while H2(6) indicates polyamide synthesized with the mixtures of dicarboxylic acids whose average number of methylene in dicarboxylic acids is six as shown in Table 1.

The blends were prepared by a dissolution-precipitation method. The polymers were dissolved in *m*-cresol at 60°C to give a concentration of 2%(w/v). This solution was added to 10-fold excess of methanol to cause a rapid coprecipitation. The precipitate was filtered off and dried under vacuum at 80°C.

The molecular weight of aromatic polyamide was measured with Waters LG-240 GPC at 100°C relative to polystyrene standards. *m*-Cresol was used as a solvent. Nuclear magnetic resonance(^{1}H-NMR) spectra were obtained in dimethyl sulfoxide-d_6 on a Varian VRX-200S-NMR. Elemental analysis was carried out with a Yanaco MT-2 CHN Corder.

Differential scanning calorimetry(DSC) was carried out with a Perkin-Elmer DSC-4 at a heating rate of 20°C/min. All runs were carried out with a sample of ca. 5 mg in N_2 atmosphere. Series 1 polyamides and their blends with polyamide-6,6 were quenched in liquid N_2 or cooled down at a rate of 150°C/min, after annealing at 280°C for 1 min and subsequent annealing for 10 sec at temperature 10°C above the melting temperature(T_m) of the aromatic polyamide. The glass transition temperature(T_g), crystallization on heating(T_c), T_m, the heat of fusion(ΔH_m) were measured on subsequent heating. Series 2 polyamides and their blends were scanned with the same method except that they were annealed only once at 280°C for 1 min.

Results and Discussion

Series 1 polyamides, quenched in liquid N_2 after annealing at temperatures above T_m, had typical DSC thermograms of crystalline polymers. They showed glass transition, crystallization, and melting behaviours on heating. This seems to be due to the regular structure of series 1 polyamides, and their transitions or peak temperatures are shown in Table 1. T_g, T_c, T_m, the overheating necessary for crystallization on heating(T_c-T_g) decreased, ΔH_m increased, and crystallization and melting peaks became sharper, as the methylene number in dicarboxylic acid

Table 1. Recipes for the synthesis and characteristics of aromatic polyamides

	Series 1			Series 2		
Designation	H1(6)	H1(8)	H1(10)	H2(6)	H2(8)	H2(10)
Feed(mole):						
MDI	1.00	1.00	1.00	1.00	1.00	1.00
adipic acid	-	-	-	0.20	-	-
pimeric acid	-	-	-	0.20	-	-
suberic acid	1.00	-	-	0.20	0.25	-
azelaic acid	-	-	-	0.20	0.20	0.10
sebacic acid	-	1.00	-	0.20	0.25	0.20
1,10-decanedicarboxylic acid	-	-	1.00	-	0.20	0.25
tridecanedioic acid	-	-	-	-	0.10	0.20
1,14-tetradecanedioic acid	-	-	-	-	-	0.25
m Value analyzed						
by ^{1}H-NMR	-	-	-	6.4	8.7	10.5
by elemental analysis	-	-	-	6.8	8.1	12.5
Molecular weight ^{a}($\times 10^{-3}$)						
number average	14	13	11	19	9	23
weight average	74	48	36	52	23	65
T_g(°C)	142	125	110	136	112	112
T_c(°C)	188	171	149	-	-	-
T_m(°C)	294	285	270	-	-	-
ΔH_m(J/g)	14.1	27.6	29.3	-	-	-

[a] relative to polystyrene standards

increased. All these results seem to be due to the increased chain flexibility. Whereas series 2 polyamides did not show distinct crystallization or melting behaviours. Irregular chain structure due to mixed dicarboxylic acids seems to be the cause.

DSC thermograms of H2(6)/polyamide-6,6 blends, obtained on heating after annealing at 280°C and subsequent quenching in liquid N_2 are shown in Fig.1. They show single T_g that varies smoothly with composition, suggesting miscibility between two polymers. Pure polyamide-6,6 does not show crystallization peak on heating, and this shows that its crystallization rate is fast enough to crystallize during quenching. However, the blends show crystallization peak at balanced compositions, and the overheating (T_c-T_g) necessary for crystallization on heating increases as the content of H2(6) in blends increases. This shows that the crystallization of polyamide-6,6 is retarded by the miscible H2(6) polymer(7,8).

In Fig.2, DSC thermograms of H2(8)/polyamide-6,6 blends obtained on heating after quenching in liquid N_2 are shown. They show one glass transition, however, it does not change smoothly with composition. And the retardation of crystallization of polyamide-6,6 in blends is not so evident, and the change in crystallization peak is not so systematic as in Fig.1. These results suggest the possibility that two polymers are not fully miscible. In order to check the possibility that the crystallization peak might mask another T_g, we cooled down the annealed samples slowly enough to crystallize during cooling to have no

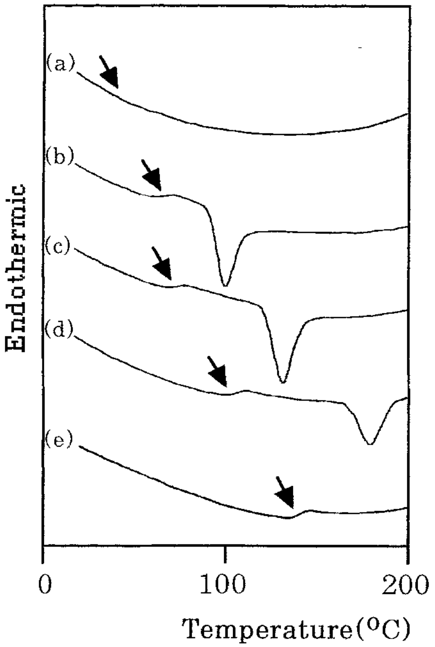


Fig.1. DSC thermogram obtained on heating of H2(6)/polyamide-6,6 blends quenched in liquid N_2: (a)0/100, (b) 30/70, (c)50/50, (d)70/30, (e)100/0 by weight.

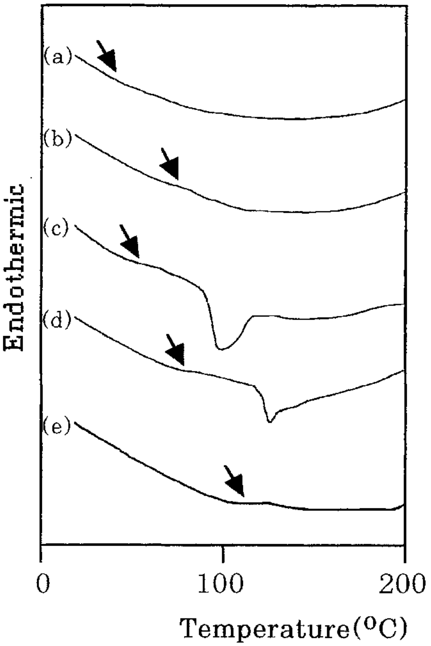


Fig.2. DSC thermograms obtained on heating of H2(8)/polyamide-6,6 blends quenched in liquid N_2: (a)0/100, (b) 30/70, (c)50/50, (d)70/30, (e)100/0 by weight.

crystallization peak on subsequent heating(8). The results for aromatic polyamide/polyamide-6,6 blends(50/50 by weight) cooled down with the cooling rate of 150°C/min in DSC are shown in Table 2. As estimated, polyamide-6,6 blend with H2(6) shows miscibility having single T_g, and blends with H2(8) shows phase separation behaviours having double T_g's.

Table 2. T_g of aromatic polyamide/polyamide-6,6(50/50 by weight) blends

Blends	T_g(°C)
polyamide-6,6 blends with:	
H1(6)	87
H1(8)	85
H1(10)	70, 131
H2(6)	84
H2(8)	70, 142
H2(10)	71, 133

Polyamide-6,6 blends with H1(6) or H1(8) had single T_g as shown in Table 2, and their DSC thermograms changed similarly with those of Fig.1. These results show that H1(6) and H1(8) are miscible with polyamide-6,6. Whereas polyamide-6,6 blends with H1(10) or H2(10) had double T_g's as shown in Table 2, and their DSC thermograms changed similarly with those of Fig.2. These results show that H1(10) and H2(10) are not miscible with polyamide-6,6.

In Fig.3 and Fig.4, the T_g data of Fig.1, Fig.2, and other blends are summarized. The miscible blends of H1(6), H1(8), or H2(6) have smoothly changing T_g-composition curves, whereas immiscible blends of H1(10), H2(8), or H2(10) show irregular changes of T_g.

In binary interaction model, the interaction energy parameter (χ_{blend}) of aromatic polyamide/polyamide-6,6 blends can be calculated using segmental interaction parameters. If we consider polyamide-6,6 and aromatic polyamides as the random copolymers composed of methylene(A), amide(B), and phenylene(C) units, they can be expressed as A_xB_{1-x}, $A_yB_zC_{1-y-z}$, respectively, where the subscripts x, y, and z are the segmental volume fractions in copolymers. The value of χ_{blend} can be calculated using segmental interaction parameters, χ_{ij}, by the following *equation 1*(9-11).

$$\chi_{blend} = [(1-x)(y-x) + z(x-y)]\chi_{AB} + (1-y-z)(1-x-z)\chi_{BC} + (1-y-z)(x-y)\chi_{AC} \qquad (1)$$

T. S. Ellis reported the values of χ_{AB}, χ_{BC}, χ_{AC} to be 7.984, 7.460, -0.288, respectively(3). The values of χ_{blend} calculated by *equation 1*, using segmental volume fractions from group contribution method, are shown in Fig. 5.

Miscibility is predicted when

$$\chi_{blend} - \chi_c < 0 \qquad (2)$$

where the conformational entropy term, χ_c is given by

$$\chi_c = 0.5(n_1^{-1/2} + n_2^{1/2})^2 \qquad (3)$$

with n_1 and n_2 being the degrees of polymerization of component polymers. Fig.5 predicts the miscibility of polyamide-6,6 with all the aromatic polyamides in this study. The discrepancy between the experimental results and those predicted by binary interaction model can be explained as follows.

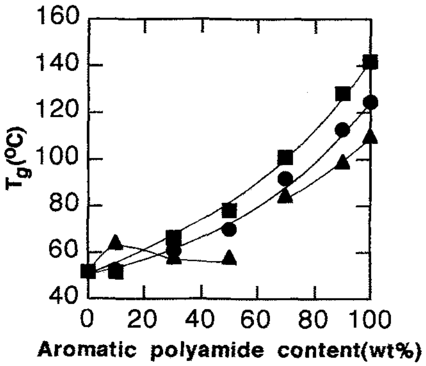


Fig.3. T_g of polyamide-6,6 blends with (■)H1(6), (●)H1(8), and (▲)H1(10).

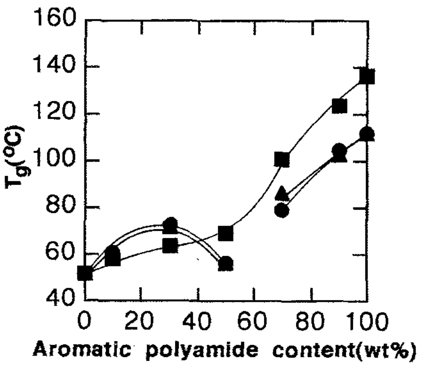


Fig.4. T_g of polyamide-6,6 blends with (■)H2(6), (●)H2(8), and (▲)H2(10).

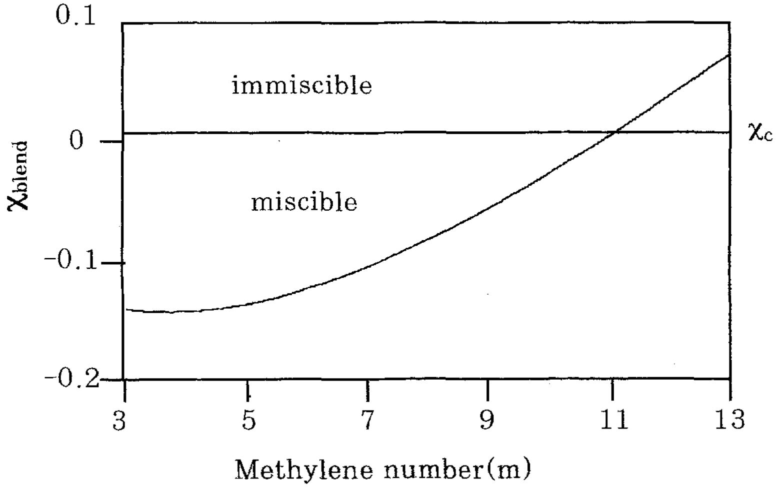


Fig.5. χ_{blend} of aromatic polyamide/polyamide-6,6 blends calculated by binary interaction model as a function of methylene number in dicarboxylic acid.

In binary interaction model, no provision was made to take into account the change, due to conformational restriction, in strength or amount of hydrogen bond of amide group in blending. This can be a cause of above discrepancy as in other report(4), and this suggests the decrease of intermolecular hydrogen bond through blending in our blends.

It has been shown that even in blends where the copolymers differ only in chain microstructure, the effect of sequence distribution may significantly affect miscibility(12). Strictly speaking, polyamide-6,6 and aromatic polyamides are not random copolymer of methylene, amide, and phenylene units. There exist some blockness of methylene group in a row. This can be another cause of the discrepancy.

H1(8) and H2(8) have similar m values. However, H2(8) shows suppressed miscibility compared with H1(8). Above two reasons can also be illustrated as the causes.

All these results show that binary interaction model can not predict exactly the miscibility behaviours of polyamide blends.

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