Compatibility of Nylon 6 and PMMA–Oligoamide Graft Copolymer

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Synopsis

PMMA–oligoamide graft copolymers, which were prepared by reacting poly(methyl methacrylate-co-methacryloyl chloride) with oligoamide, were blended with nylon 6. The compatibility was examined by measuring thermal properties such as melting point and crystallization temperature. It was observed that the melting point was significantly depressed as the grafted PMMA was added to nylon 6, suggesting that the blend is a miscible system. It was concluded that hydrogen bonding between amide groups of the two polymers enhanced the miscibility.

INTRODUCTION

Solubilities of multicomponent systems have been extensively investigated from theoretical and practical standpoints. Every polymer has some solubility in every other polymer, but the magnitude, in most cases, is extremely low. Polymer incompatibility arises from the very small entropy gains when the different kinds of long chains are mixed. Hence the blend components are readily separated into the phases containing predominantly their own kinds. In fact, in the limit of high molecular weight, only polymer pairs with zero or negative heat of mixing form one phase.

By rough count, over 50 miscible polymer binary blends are known to exist.[1,2] These miscible blends have chemical structures capable of interacting by variety of specific mechanisms including hydrogen bonding, such as between α-hydrogen of PVC and carbonyl oxygen of poly(ϵ-caprolactone),[3] phenyl group coupling, such as between the aromatic rings of poly(phenylene oxide) and polystyrene,[4] and dipolar interaction, such as in the blend of poly(vinylidene fluoride) and poly(methyl methacrylate) (PMMA).[5]

Although, in most cases, two polymers form an immiscible system, it has been known that the chemical modification of either one component or both components of bicomponent polymer blend improves the miscibility. One of the direct methods is to introduce specific interactions between constituents of the individual chains, and the other is to make graft and block copolymers. Via the latter, for example,[6] it is reported that a compatibilized PVC–acrylic polymer can be obtained by blending the mixture of poly(ethylhexyl acrylate)-*g*-PMMA copolymer and homopolymers with PVC. Compatibilization of the polymer

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blend of isotactic polypropylene and nylon 6 can be also achieved in the presence of maleic anhydride-grafted polypropylene.[7]

In the present study, it is tried to enhance the miscibility of PMMA and polycaprolactam, which form an immiscible system,[8] by grafting oligoamide onto PMMA. The miscibility is examined and discussed in terms of molecular interactions.

EXPERIMENTAL

Materials. Methyl methacrylate (MMA), methacrylic acid (MAA), azobisisobutyronitrile (AIBN), *n*-hexane, dioxane, and benzyl alcohol were purified by the standard methods. Others were reagent grade and used without further purification.

Copolymerization of MMA and MAA.[9] Two kinds of poly(methyl methacrylate-co-methacrylic acid) [P (MMA/MAA)-A and P (MMA/MAA)-B] were prepared, having different contents of carboxylic acid, by heating MMA and MAA in benzene solution in the presence of AIBN as catalyst for 6.5 h at 65°C with continuous stirring. The amounts of monomers, catalyst, and solvent fed in the copolymerization are listed in Table I. The polymer solution was diluted with methyl ethyl ketone (MEK) and precipitated into a sevenfold excess of *n*-hexane. The polymer was purified by reprecipitating it from a 3% MEK solution into a tenfold excess of *n*-hexane, then filtered and dried *in vacuo* at 60°C.

Chlorination of P(MMA/MAA). Thionyl chloride was added drop by drop over 1 h to the dioxane solution of P(MMA/MAA)-A and further reacted for 23 h at 60°C.[10] After the reaction had been completed, excess of thionyl chloride and gaseous products (hydrochloric acid and sulfur dioxide) were distilled off *in vacuo.* Then dry dioxane was added to prepare a 3% solution of poly(methyl methacrylate-co-methacryloyl chloride)-A [P(MMA/MAC)-A], which was ready for further modification.

P(MMA/MAA)-B was also chlorinated under the same conditions as above and 3% solution of P(MMA/MAC)-B in dioxane was prepared.

Preparation of Oligoamides. Commercial nylon 6 chip (100 g, Tong Yang Nylon Co., Korea) was hydrolyzed in a sealed flask with 300 mL of 6*N* HCl at 100°C for 2 h. Most of the HCl was then removed under vacuum at 100°C for 2 h. The residues were cooled to room temperature and 100 mL of methanol was added. Then 200 g of triethylamine as an acid acceptor was added dropwise for 2 h to remove residual HCl and to isolate the acidic component in the amine group and further reacted for 3 h. The reactants were precipitated into a large excess of cold water, kept overnight in a refrigerator, filtered, and purified by washing with cold distilled water. After drying *in vacuo* at 60°C, the hydrolyzed nylon

TABLE I
The Amounts of Monomers, Catalyst, and Solvent Fed in the Copolymerization

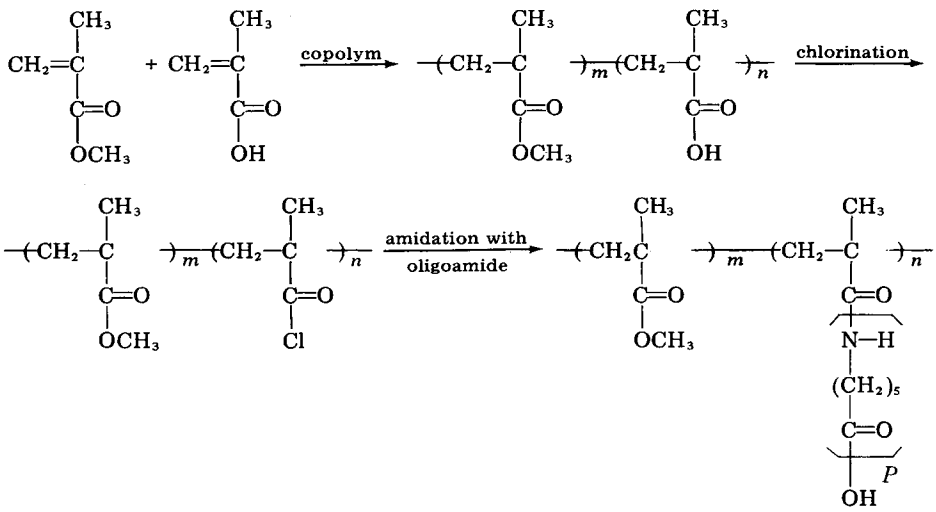
	MMA (g)	MAA (g)	AIBN (g)	Benzene (g)	MAA wt % in the feed
Copolymer A	361	20	0.722	361	5.2
Copolymer B	90	10	0.180	105	10

6 was extracted with hot methanol. Both the extractant (oligoamide A) and the residue (oligoamide B) were used in amidation reaction.

Amidation of Poly(MMA-co-MAC). 5 g of oligoamide A was dissolved in 200 mL of phenol containing 20 mL of triethylamine in excess. Then 200 mL of 3% dioxane solution of P(MMA/MAC)-A was added dropwise at 80°C for 3 h with continuous stirring, and further reacted for 5 h. After the reaction had been completed, the solution was precipitated into a tenfold excess of ethyl ether and filtered. After drying *in vacuo* at 40°C for 24 h, they were extracted with hot methanol for 24 h and the residue was collected as PMMA-*g*-oligoamide-A.

Oligoamide B was reacted with P(MMA/MAC)-B under the same conditions as above. The product was extracted with hot methanol and the residue was found to be oligoamide B. On cooling the extracted solution to room temperature, PMMA-*g*-oligoamide-B was precipitated, then filtered and washed with distilled water.

The reaction procedure is described by the following scheme.



Titrating Analysis. The content of acid groups of P(MMA/MAA), from which the composition of copolymers could be calculated, was determined by titrating a 0.5% solution of the copolymer in acetone with an ethanolic solution of potassium hydroxide.[11] Amine end groups of the oligoamides were measured by the direct titration in phenol–methanol solution with 0.1*N* HCl in the presence of Thymol Blue as an indicator. Carboxylic groups were titrated in benzyl alcohol at 60°C with 0.2*N* aqueous potassium hydroxide and phenolphthalein as an indicator.[12]

Elementary Analysis. The elementary constitution of PMMA-*g*-oligoamide was obtained from a MT-2 CHN Coder (Yanagimoto Co., Japan).

Infrared Spectroscopy. Infrared (IR) spectra were obtained by using a Jasco IR-A2 Infrared Spectrophotometer (Jasco, Japan). The samples were prepared by film casting.

Thin Layer Chromatography (TLC). The TLC plate coated with Kieselgel 60 (Merck) was activated by heating at 110°C for 30 min. Stock solutions of the samples for TLC were prepared by dissolving 20 mg of each sample in 10 mL of

formic acid. Each solution containing about 20 μg of sample was spotted on the starting line of the plate with a microsyringe. The spotted plate was dried for about 10 min, and then the spots were developed in a closed chamber at room temperature by the usual method.[13] The eluent was mixture of phenol 30/chloroform 70 by volume. When the solvent front reached 10 cm from the starting line, the development was stopped by drying the plate in a vacuum oven at 80°C for 1 h. The position of the polymer samples were visualized by heating the plate in an oven after it was sprayed with 1% iodine solution of methanol.

Thermal Analysis. Films of PMMA-*g*-oligoamide, nylon 6, and their mixtures were cast from formic acid solution with the concentration of 1 g/10 mL onto a glass plate under vacuum at 70°C for 24 h and used for the thermal analysis. A differential scanning calorimeter (Perkin Elmer Model DSC-II) was used for the thermal analysis. The heating and cooling programs used for differential scanning calorimetry (DSC) are as follows: (a) the melt sample, which was kept at 250°C for 15 min, was quenched in situ by liquid nitrogen; it was then reheated with a heating rate of 20°C/min; (b) the sample was heated to 250°C with a heating rate of 40°C/min in a nitrogen atmosphere; the melt sample was kept for 15 min; it was then cooled with a cooling rate of 10°C/min.

Program (a) was used to examine the change of the cold crystallization and melting temperatures of the melt-blended samples with the blend compositions. Program (b) was employed to investigate the effect of the blend composition on the melting and premelt crystallization temperatures of as-cast samples.

RESULTS AND DISCUSSION

Copolymerization. To synthesize PMMA-*g*-oligoamide, first MMA and MAA were copolymerized and the resultant P(MMA/MAA) was identified by IR spectroscopy.

Figure 1 (dotted line) shows the presence of O—H stretching band of carboxyl group at 3200–3400 cm^{-1}, indicating that the copolymer contains MAA units. MMA and MAA have the almost same reactivity in benzene, so that copolymerization of them could be achieved to fairly high conversion without danger of an appreciable drift in the composition of the copolymer.[9] From the titration results, the compositions of copolymer A and B were found to be 4.85 wt % and

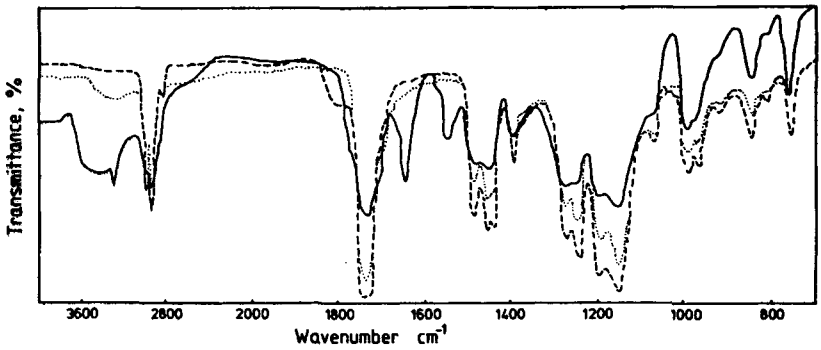


Fig. 1. IR spectra of P(MMA/MAA) (. . .), P(MMA/MAC) (- - -), and PMMA-*g*-oligoamide (—).

TABLE II
Analyzed Data of Oligoamides

	NH_2	COOH	Average MW	Average DP	Melting[a] point
	(meq/g)				
Oligoamide A	1.48	1.52	660	6	198
Oligoamide B	0.78	0.83	1274	11	201

[a] Obtained from DSC at the heating rate of 40°C/min.

9.61 wt % of MAA, respectively, and these were thought to be comparable with the compositions in the feed, A (5.6 wt %) and B (11.0 wt %).

The intrinsic viscosities of copolymer A and B in tetrahydrofuran (THF) at 20°C were found to be 0.55 and 0.53 dL/g, respectively, and had a good film-forming property.

Chlorination. Conversion of acid groups to chloroformyl groups in the copolymer was effected with thionyl chloride,[14] and the conversion of acid groups to chloroformyl groups was identified by comparing its IR spectrum with that of P(MMA/MAA). Figure 1 shows that O—H stretching band at 3200–3400 cm^{-1} disappears, while C=O stretching band of acid chloride at 1800 cm^{-1} appears. The conversion of acid groups to chloroformyl groups was also identified[15] by dropping a 2% ethanolic solution of $AgNO_3$ to P(MMA/MAC), leading to precipitation of AgCl.

Preparation of Oligoamides. Oligoamides were obtained by the hydrolysis of nylon 6 chips rather than the stepwise reaction of ϵ-aminocaproic acid.[16,17] Thus, our oligoamides were polydisperse.

Two kinds of oligoamides, i.e., oligoamide A and oligoamide B were prepared. The analytical data for oligoamide A and B are listed in Table II. The value of equivalent of carboxylic acid groups was slightly higher than that of amine end groups, probably due to a trace of residual hydrochloric acid. The melting points of oligoamides were 3–4°C lower than the literature values.[16]

Amidation. The amidation reaction can be achieved in water by the Schotten–Baumann technique[18] or in solvents under anhydrous conditions,[14] either with or without an acceptor for the liberated hydrochloric acid. In the present study, the second method was chosen, because of the insolubility of the oligoamide in water.

The IR spectrum of PMMA-g-oligoamide(amidation product) indicates amide I, amide II, and NH stretching bands at 1640, 1530, and 3300 cm^{-1}, respectively (solid line in Fig. 1).

The elementary analysis data are listed in Table III, which indicates that N % of PMMA-g-oligoamide-B is 2.7 times larger than that of PMMA-g-oligoamide-A. The values deviate somewhat from calculated values since the

TABLE III
Elementary Analysis of PMMA-g-Oligoamides

	C (%)		H (%)		N (%)	
	Calcd	Found	Calcd	Found	Calcd	Found
PMMA-g-oligoamide A	62.3	60.5	8.45	9.79	3.42	3.30
PMMA-g-oligoamide B	62.1	59.9	8.93	9.98	7.21	9.01

TABLE IV
Solubility Characteristics of P(MMA/MAA) and PMMA-*g*-Oligoamides[a]

	MEK	Dioxane	THF	Phenol	Formic acid	Acetic acid
P(MMA/MAA)	O	O	O	O	O	O
PMMA-*g*-oligoamides	X	X	X	O	O	O

[a] O, soluble; X, insoluble.

calculated values are based on the average molecular weight of oligoamides. PMMA-*g*-oligoamides were not soluble in solvents for P(MMA/MAA), but they were soluble in formic acid, phenol, and acetic acid (Table IV).

From the solubility characteristics, it can be seen that intermolecular cross-linking did not occur. But it was not clear whether intramolecular reaction occur by the formation of anhydride and imide bonds, because the bands in the IR spectrum overlap with others. Since secondary amines in the amide groups are assumed to be stable due to the partial double bond characteristics and excess moles of oligoamides were fed in the amidation reaction, it is thought to be difficult to form anhydride and imide bonds. At any rate, even if these bonds were formed, they did not affect our experimental purpose.

Graft copolymers were also identified by TLC according to the polarity controlled adsorption process.[19] This process permits separation of polymers by difference in the chemical composition without interference of the molecular weight, thus making it possible to determine the compositional heterogeneity. PMMA-*g*-oligoamides are more polar than P(MMA/MAA), and they have strong affinity to the adsorbent. Therefore, the interaction between PMMA-*g*-oligoamides and adsorbent is stronger than that between P(MMA/MAA) and adsorbent, so that migration is retarded.

Figure 2 shows the thin layer chromatogram of copolymer A, copolymer B, PMMA-*g*-oligoamide-A, and PMMA-*g*-oligoamide-B obtained with phenol–chloroform (30:70 by volume). Copolymer A migrated up to the solvent front, while the migration of copolymer B was retarded due to its high polarity. Likewise the migrations of PMMA-*g*-oligoamide-A and -B were retarded as compared with copolymer A and B. However, PMMA-*g*-oligoamide-A was separated into two components in the chromatogram and this was explained that PMMA-*g*-oligoamide-A contained some unreacted copolymer A.

Solubility Characteristics of Two Polymer Mixtures in Formic Acid as

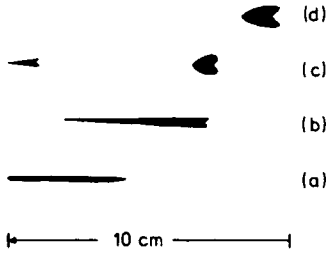


Fig. 2. Thin layer chromatogram of copolymer A (a), copolymer B (b), PMMA-*g*-oligoamide-A (c), and PMMA-*g*-oligoamide-B (d) obtained with phenol–chloroform (30:70 by vol).

the Cosolvent. Formic acid as a mutual solvent of PMMA and nylon 6, i.e., each polymer is soluble in formic acid. But solutions containing mixtures of PMMA and nylon 6 were opaque, or translucent, and phase separation was observed after a few hours. The same behavior was also observed in the system of P(MMA/MAA) and nylon 6. On the other hand, mixtures of PMMA-*g*-oligoamides and nylon 6 formed a clear solution in formic acid and no phase separation was observed. From this it may be assumed that PMMA-*g*-oligoamides and nylon 6 may form a miscible system.

Thermal Behavior of As-Cast PMMA-*g*-Oligoamides. Figure 3 shows the thermograms of PMMA-*g*-oligoamide-A and PMMA-*g*-oligoamide-B. PMMA-*g*-oligoamide-B exhibited an endotherm peak at 181°C, which was its melting temperature and lower than that of oligoamide B, while PMMA-*g*-oligoamide-A did not exhibit melting peak. Since PMMA-*g*-oligoamide-B was grafted with oligoamide of long chain, it is predicted that this polymer could easily crystallize. It was known that polyolefin polymers,[20] which have 12 or more carbon atoms in the side chain, lead to chain crystallization. Matzner et al.[21] also reported that polyethylene–nylon 6 graft copolymer prepared via cationic process had reduced the melting peak due to the grafts.

Thermal Behavior of As-Cast Blend Samples. The mutual solvent approach is an ambiguous method for estimating miscibility. One of the most generalized methods is to analyze the thermal properties such as glass transition, melting, and crystallization behavior.

Blends of PMMA-*g*-oligoamides and nylon 6 were prepared to estimate the miscibility. As-cast samples for thermal analysis are listed in Table V. The blends were translucent and developed opacity in proportion to the nylon 6 content.

Practical difficulties were encountered in the measurement of glass transition temperature (T_g) because PMMA-*g*-oligoamides and nylon 6 were crystallizable polymers. Glass transition behavior ought to be indicative of the state of mixing in the remaining amorphous phases. However, the glass transition behavior may be subject to a variety of complications in crystallizable polymers. PMMA-*g*-oligoamides and nylon 6 seemed to form hydrogen bonds between amide groups, resulting in the suppression of segmental motion. Therefore, it was rather dif-

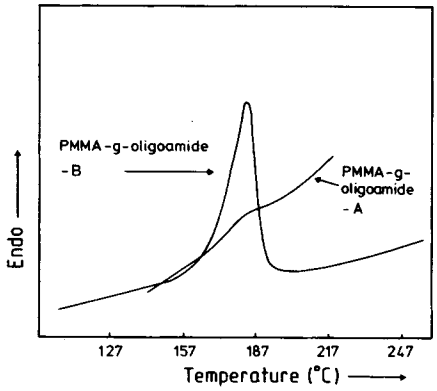


Fig. 3. DSC thermograms of solution cast PMMA-*g*-oligoamide-A and PMMA-*g*-oligoamide-B.

TABLE V
List of As-Cast Samples for Thermal Analysis

A series (PMMA-*g*-oligoamide A/nylon 6)		B series (PMMA-*g*-oligoamide B/nylon 6)	
Sample no.	Blend ratio	Sample no.	Blend ratio
A-1	100/0	B-1	100/0
A-2	80/20	B-2	80/20
A-3	60/40	B-3	60/40
A-4	40/60	B-4	40/60
A-5	20/80	B-5	20/80
A-6	0/100	B-6	0/100

ficult to use T_g measurement to prove the miscibility of the blends, and the degree of miscibility of the blends was determined by measurement of the melting temperature (T_m).

Figure 4 shows plots of the melting temperature versus the weight fraction of nylon 6 for solution cast A and B series. For A series, the melting temperatures of nylon 6 slightly decreased with increasing PMMA-*g*-oligoamide-A portions.

For B series, double melting peaks were observed. The lower ones were those of PMMA-*g*-oligoamide-B and higher ones were those of nylon 6. The lower melting temperatures decreased with increasing nylon 6 fractions, but the blend of 80% nylon 6 did not have a lower melting peak, indicating that a larger portion of nylon 6 prevents PMMA-*g*-oligoamide-B to crystallize.

In the quenching experiment by program (a), melting and cold crystallization temperatures were observed, and these were plotted against the weight fraction of nylon 6 for A and B series (Fig. 5). In this experiment, only one depressed melting temperature was observed for the B series, suggesting good miscibility at the temperature above T_m. This result can be interpreted as extensive mixing of the segments of the blend due to the formation of hydrogen bonding between

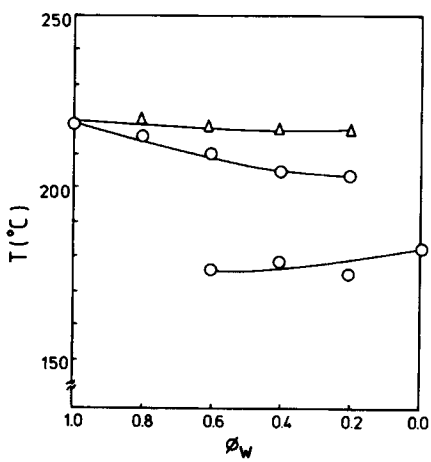


Fig. 4. Plots of melting temperature vs. the weight fraction (ϕ_ω) of nylon 6 for solution cast A and B series: (△) A series; (○) B series.

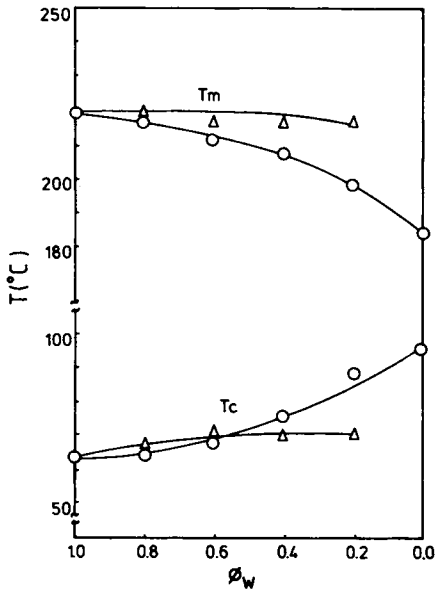


Fig. 5. Plots of melting (T_m) and cold crystallization temperature (T_c) vs. the weight fraction (ϕ_ω) of nylon 6 in quenched A and B series: (△) A series; (○) B series.

amide groups. On the other hand, for A series, a slight depression in T_m was observed, suggesting rather poor miscibility.

Cold crystallization temperature (T_c) was almost equal in the A series, whereas, for the B series, T_c increased with a decrease of nylon 6 fraction. From the facts of melting temperature depression and crystallization temperature increase, it is safe to say that PMMA-g-oligoamide-B restricts the molecular mobility of nylon 6 during the crystallization process, resulting in the suppression of crystal formation of nylon 6, and that this blend system is miscible. From the above

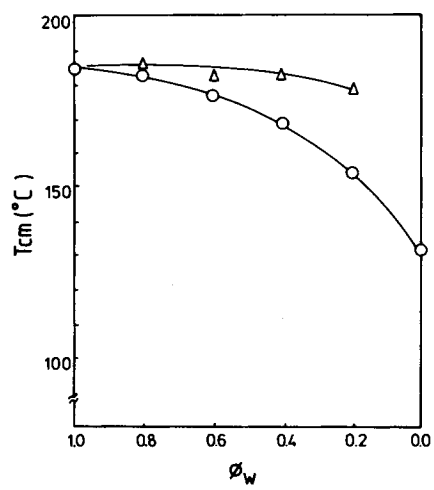


Fig. 6. Plots of premelt crystallization temperature (T_{cm}) vs. the weight fraction (ϕ_ω) of nylon 6 in A and B series: (△) A series; (○) B series.

results, it is concluded that hydrogen bonding between amide groups of the two polymers mainly contributes to the miscibility. Thus, we can state that in an immiscible system T_m and T_c remain constant for all blend portions,[5,22] but, in a miscible system, T_m depression and T_c increase are observed.[23]

In the premelt crystallization experiment by the program (b), nonisothermal crystallization temperature (T_{cm}) was observed, and this was also plotted against the weight fraction of nylon 6 for A and B series (Fig. 6). In this case T_{cm} is defined as the temperature at which the exothermic curve shows maximum peak under a given cooling rate (in the present experiment, cooling rate was 10°C/min). As can be seen in Figure 6, there was a large depression in T_{cm} for B series, depending strongly upon the nylon 6 concentration. As with the polymer diluent system, the depression in T_{cm} in the mixture may be explained as follows.[23] When crystallization developed, the transport process of nylon 6 segment to crystalline-melt interface became more protracted, as nylon 6 was diluted more with PMMA-*g*-oligoamide, causing retardation in the rate of nucleation and growth.

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