Toughening and Phase Separation Behavior of Nylon 6–PEG Block Copolymers and *In Situ* Nylon 6–PEG Blend Via *In Situ* Anionic Polymerization

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ABSTRACT: We have prepared *in situ* molded products of morphologically different nylon 6/polyethylene glycol (PEG) copolymers and their blends via anionic polymerization of ε-caprolactam in the presence of several kinds of PEG derivatives using sodium caprolactamate as a catalyst and carbamoyl caprolactam derivative as an initiator. Three carbamoyl caprolactams, such as tolylene dicarbamoyl dicaprolactam (TDC), hexamethylene dicarbamoyl dicaprolactam (HDC), and cyclohexyl carbamoyl caprolactam (CCC), with different functionalities and activities were used. Phase separation behavior was investigated by dynamic mechanical thermal analysis (DMTA) and DSC during *in situ* polymerization and melt crystallization. The mechanical properties of these molded products were evaluated. PEG segments in the block copolymers showed amorphous characteristics, whereas a large fraction of unreacted PEG segments was crystallized in as-polymerized samples, except for the products obtained using the CCC activator. The presence of PEG derivatives retarded the crystallization of nylon 6 part during *in situ* polymerization as well as melt crystallization. However, PEG segments did not alter the crystalline structure of nylon 6, showing α-crystalline modification. The nylon 6–PEG–nylon 6 triblock copolymers showed the highest impact strength, whereas the nylon 6–PEG diblock copolymers and *in situ* nylon 6–PEG blends showed no improved toughness. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1285–1303, 1999

Key words: ε-caprolactam; *in situ* anionic polymerization; nylon 6–PEG block copolymer; enhanced toughness and impact strength; phase separation

INTRODUCTION

Nylon 6 RIM (reaction injection molding) product, which is obtained via anionic ring opening polymerization of ε-caprolactam using an activator such as *N*-acyl caprolactam or carbamoyl caprolactam, is well known as an engineering plastic, because of its high strength, good fatigue resistance, and wearing durability. However, its applications have been restricted particularly to aerospace and auto industries because of poor impact toughness at low temperature. To improve toughening properties of nylon 6, it is a common practice to either blend rubbery soft segments into nylon 6 matrix or introduce rubbery soft segments into the nylon 6 main chains through the activated anionic copolymeriza-

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tion of ε-caprolactam (CL) with reactive rubbery compounds such as derivatives of polyethylene glycol (PEG), polypropylene glycol (PPG), polytetramethylene oxide (PTMG), hydroxy-terminated butyronitrile rubber (HTBN), or amine-terminated butyronitrile rubber (ATBN).[1–7] Using amine- or hydroxy-terminated rubber modifiers, the block copolymer of nylon 6 and rubbery component can be produced with very high yield copolymers. The *in situ* anionic copolymerization of CL by using dicarbamoyl dicaprolactam as an activator requires no prior synthesis of macroactivator of rubbery component.[8]

Although the ultimate properties of the final product are known to depend highly on the phase-separated morphology of rubbery domains, there are only a few articles systematically studying the effect of modifier and activator types on the development of the phase-separated morphology and their mechanical properties.[9–11] The mechanism by which toughness is improved in the block copolymers or *in situ* blend systems is intimately related to macrophase separation and microphase segregation. By introducing soft segments of different functionalities with different reactivities to nylon 6 main chain or nylon 6 matrix, one can anticipate a variety of phase separation behavior leading to varying impact toughness values. This study was conducted by selecting three different derivatives of PEG as a rubbery soft segment such as PEG, PEG-diamine, and monomethyl ether of PEG (MPEG), and three different types of carbamoyl activators, such as tolylene dicarbamoyl dicaprolactam (TDC), hexamethylene dicarbamoyl dicaprolactam (HDC), and cyclohexyl carbamoyl caprolactam (CCC). Nylon 6–PEG-type diblock copolymer can be produced out of CL and MPEG by choosing a proper activator system. PEG–nylon 6–PEG-type triblock copolymer may be produced from CL and PEG-diamine (or PEG), by selecting a dicarbamoyl dicaprolactam system such as TDC or HDC. On the other hand, *in situ* nylon 6–PEG blend can be obtained from CL and PEG (or PEG-diamine) by using monofunctional carbamoyl caprolactam such as CCC.

In this article, our study is focused on the investigation of the crystallization and phase separation behavior of *in situ* polymerized products and its effect on the toughness.

EXPERIMENTAL

Materials

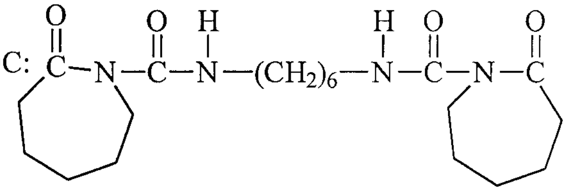
CL was supplied kindly by Kohap, Korea, and sodium caprolactamate (NaCL) was obtained through the courtesy of DSM, the Netherlands. Tolylene diisocyanate (TDI) was purchased from Kokusan, Japan. MPEG ($\bar{M}_n$ = 2000), PEG ($\bar{M}_n$ = 2000), and hexamethylene diisocyanate (HDI) were bought from Aldrich Chemical Co., and PEG-diamine (Jeffamine ED2001; $\bar{M}_n$ = 2000) was obtained from Huntsman Co. Cyclohexyl isocyanate (CHI) was purchased from TCI, Japan. All the above chemicals were used as received without further purification.

Synthesis

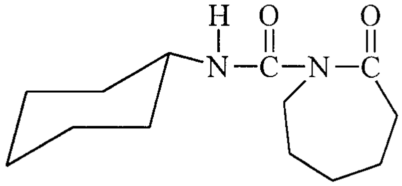
Synthesis of Activators

Three types of activators, TDC, HDC, and CCC, were chosen because of their diverse functionalities and different activity. TDC, HDC, and CCC are the adducts of TDI, HDI, and CHI with CL, respectively. TDC and HDC are bifunctional activators having two carbamoyl residues at both ends, whereas CCC is monofunctional. HDC and CCC were fast activators, whereas TDC was a slow activator. The synthesis and purification procedures were already described in our recent articles.[8,12–14] The chemical structures of these three activators are summarized as follows:

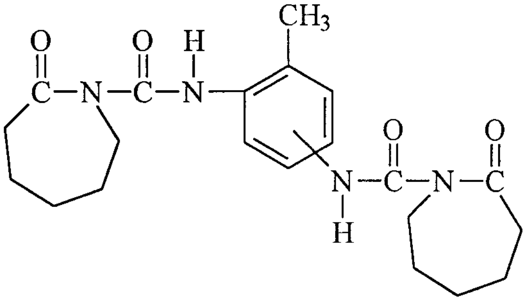
HDC:



CCC:



TDC:



Synthesis of Nylon 6–PEG Triblock Copolymers and In Situ *Blends*

PEG, PEG-diamine, and MPEG were used as modifiers. CL, PEG-diamine (or PEG), and activator were mixed in a 500-mL quasi-adiabatic reactor maintained at about 100°C for 0.5–1 h under a dry nitrogen atmosphere. A homogeneous molten mixture was formed in the reactor, in which through the aminolysis of activator by PEG-diamine [or alcoholysis of activator by PEG (i.e., PEG macroactivator)] can be formed. Subsequently, the mixture of NaCL catalyst and the required CL amount, which was melted separately in an oven at 100°C, was charged into the reactor while vigorously stirring. This homogeneous molten mixture was quickly transferred from the reactor into two different stainless steel molds maintained under vacuum at 160°C in a silicone oil bath, and then *in situ* polymerization was carried out for 0.5 h. One mold is designed for the preparation of sample for tensile test according to ASTM D638 and the other is for Izod impact strength test according to ASTM D256. More details are explained in a previous report.[13] The modifier feed varied from 5 to 20 wt % of the total product. The molar amount of activator added was twice the molar feed of PEG-diamine (or PEG) in the case of HDC and TDC activator systems. However, in the case of CCC activator, the molar feed of CCC was four times that of PEG-diamine (or PEG). The feed composition of NaCL was set to 1 mol % of the CL feed in every case.

During *in situ* polymerization, a considerable proportion of PEG and PEG-diamine added initially forms A–B–A-type triblock copolymer because of TDC and HDC activators. However, the CCC activator yielded nylon 6–PEG *in situ* blend. Polymers made in this way were designated as $AJxx$ (A stands for the initial of the type of activator, J for PEG-diamine modifier, and xx represents the weight percentage of modifier initially fed) or $APxx$ (P stands for PEG modifier). For example, $TJ10$ indicates that TDC was used as an activator and PEG-diamine (the commercial name is Jeffamine) as a modifier was used at 10 wt % of the total product. In the case of homopolymerization, we have used the same amount of catalyst and just half of the total amount of activator utilized in copolymerization as mentioned above. The sample code was defined as $AHxx$, where A stands for the initial of activator type used, H stands for homopolymer, and the amount of A used is one half of the sample code of $AJxx$. For example, $HH10$ indicates that HDC was used as an activator and the amount of activator HDC used in this sample is half of the amount of activator used in the $HJ10$ sample.

The as-polymerized samples were purified by removing unreacted monomer and water-soluble oligomers for 24 h using soxhlet extraction with water for further analytical experiments to evaluate polymerization yield of CL and the yield of copolymerization of PEG segment. The as-polymerized samples contain nylon homopolymer, nylon–PEG block copolymer, and unreacted monomer and modifier. The as-polymerized samples, however, were used without purification for the other experiments.

Synthesis of Nylon 6–PEG Diblock Copolymer

For the synthesis of nylon 6–PEG diblock copolymer, the macroactivator was prepared first by reacting 0.1 mol of MPEG (ca. 27.4 g) and TDI 0.1 mol of TDI (ca. 27.4 g) in a three-necked flask maintained under nitrogen atmosphere at 60°C through vigorous stirring. When a homogeneous mixture was formed, the reaction temperature was raised to 70°C and kept at the same temperature for 24 h to assure the complete reaction. After 24 h, 0.1 mol of CL (ca. 11.3 g) was introduced into the molten product to block the terminal isocyanate group. The reaction was continued for another 24 h to achieve a final product. After cooling, the melt turns into a yellowish white condensate that consists mainly of MPEG-TDI-CL adduct, which is the macroactivator (hereafter called MPEG-TDC). However, the possibility of the formation of MPEG-TDI-MPEG condensate and TDI-CL adduct (i.e., TDC activator) cannot be excluded. The feed of macroactivator was also varied so that the PEG content varies from 5 to 20 wt % of the total product. This polymerization procedure does not need any other activator. The rest of the polymerization procedures was the same as above. In this *in situ* polymerization, A–B-type diblock copolymer can be anticipated with a small amount of nylon 6 homopolymer. Synthesized copolymers were designated as $MPxx$, where MP stands for MPEG macroactivator and xx stands for the weight percentage of PEG.

^{1}H-NMR Measurement

The sample was dissolved in phenol/$CDCl_3$ (7/3 v/v). ^{1}H-NMR spectra were obtained by using a Brüker FT-NMR AC200F spectrometer (200 MHz) by averaging 64 scans at room temperature.

GPC Measurement

GPC measurements were conducted on a Waters model 150-CV GPC equipped with a differential refractive index detector. The unit, consisting of 10^3, 10^4, and 10^5 Å μ-styragel HT-6E columns, was operated at 100°C temperature, using *o*-chlorophenol as an eluent as well as a solvent. The injection volume was 200 μL and the flow rate chosen was 1.0 mL/min. The system was calibrated with polystyrene standards, the molecular weights of which were 985,000, 475,000, 165,000, 68,000, 34,500, 22,000, 9200, 3600, and 1250, respectively.

Differential Scanning Calorimetry

The melting and crystallization behavior of the as-polymerized samples were studied using a Perkin–Elmer DSC-4 in the range of −50–230°C. Each sample was heated from 20 to 230°C in the first scan. After cooling down to −50°C, the sample was reheated (second heating) up to 230°C. To understand the crystallization behavior of the modifier in the course of copolymerization, comparatively low temperature DSC studies were performed by heating the samples initially from −20 to 80°C, then cooling down to −50°C, and finally reheating to 230°C at a rate of 10°C/min under nitrogen atmosphere.

X-ray Diffraction

X-ray measurements were performed on a Mac Science 18 kV rotating anode-type X-ray diffractometer with Ni-filtered Cu K_α radiation in the transmission mode at room temperature using the sampling interval of 0.02° at a scanning speed of 2.5°/min. The voltage and tube current were 35 kV and 150 mA, respectively.

Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal measurements were performed in the bending mode on a DMTA (Model: MK-II, Polymer Lab.) by using a flat sample at a heating rate of 2°C/min from −150 to 150°C and at a frequency of 1 Hz under nitrogen atmosphere.

Mechanical Testing

Tensile tests were performed on an Instron machine (load cell: 1000 kgf) with a crosshead speed of 10 mm/min and a chart speed of 200 mm/min at room temperature. Initial modulus was calculated at 2% elongation. The impact strength was measured using Izod tester (Toyoseiki Co.) by pendulum method at room temperature. All mechanical tests were conducted after conditioning the as-molded samples at 20°C and 65% relative humidity (RH) for 1 day.

RESULTS AND DISCUSSION

Synthesis of Block Copolymer

In Figure 1 is shown the NMR spectra of TJ20 (nylon 6–PEG–nylon 6 triblock copolymer) before and after purification. Each NMR peak is assigned to the corresponding hydrogen in the nylon 6–PEG block copolymer and unreacted residual CL monomer. The formation of nylon 6–PEG block copolymer can be identified from the characteristic ethylene unit of PEG appearing at 3.3 ppm in the proton NMR spectrum of the purified TJ20 sample. Based on the NMR peak assignments, the polymerization yield of CL, the PEG content, and the copolymerization yield of PEG for all samples could be calculated from the area of each characteristic peak using the following equations:

$$\text{Polymerization yield of CL} = \frac{A_{2.0\text{ ppm}}}{A_{2.0\text{ ppm}} + A_{2.23\text{ ppm}}}$$

$$\text{PEG content (wt \%)} = \frac{A_{3.3\text{ ppm}} \times (44/4)}{[A_{3.3\text{ ppm}} \times (44/4)] + [A_{3.3\text{ ppm}} \times (113/2)]} \times 100$$

$$\text{Copolymerization yield \% of PEG} = \frac{\text{PEG content after purification}}{\text{PEG content before purification}} \times 100$$

All calculated results are listed in Table I. Even though polymerization yield of CL decreased slightly with increasing modifier feed ratio, it showed >94% for all samples. When PEG-diamine was used as a modifier, the highest copolymerization yield (>85%) was obtained for the TDC activator system. The HDC activator system showed little lower copolymerization yield. We consider two types of reaction of bifunctional carbamoyl activator during *in situ* polymerization. One is the formation of nylon 6 homopolymer through the initiation reaction of activator and the other is the formation of PEG macroactivator

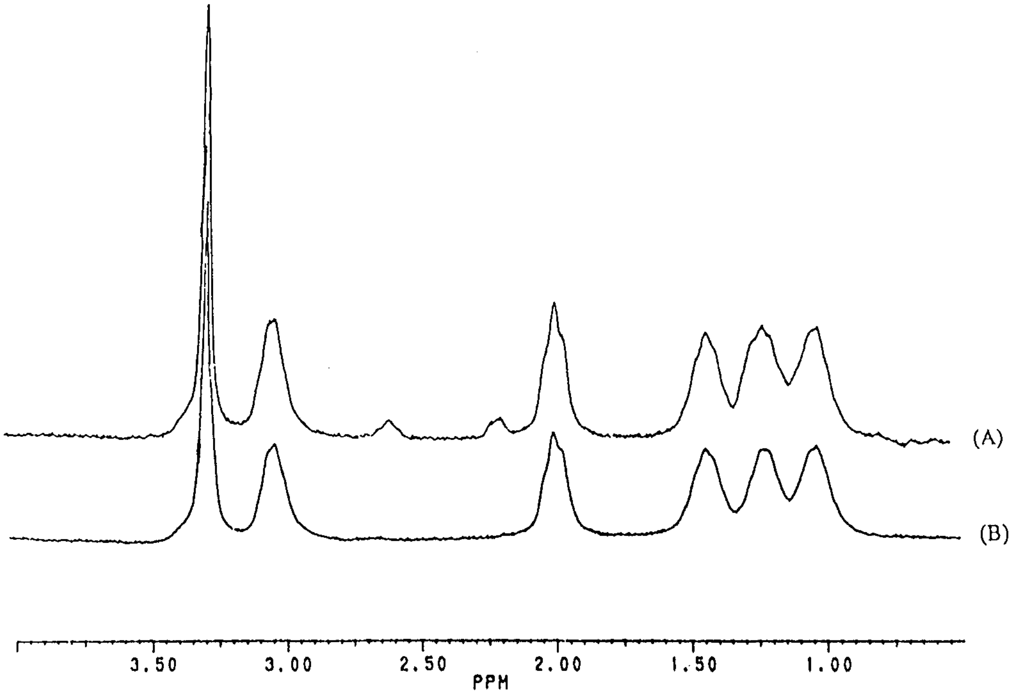


Figure 1 Proton NMR spectra of *TJ*20 (A) before and (B) after purification.

through the aminolysis of activator by PEG-diamine, followed by the initiation of macroactivator. Since the latter is more probable in the case of a slow activator TDC relative to that of a fast activator HDC, the TDC activator would show higher copolymerization yield than HDC activator. When PEG was used as a modifier, the yield of copolymerization was appreciably lower than in the case of PEG-diamine modifier. This observation may be attributed to the fact that the alcoholysis of activator by PEG is much slower than the aminolysis by PEG-diamine; therefore, the formation of homopolymer is more probable in the PEG case during *in situ* polymerization. Thus, when PEG-diamine was used as a modifier and TDC as an activator, nylon 6–PEG triblock copolymer having relatively high yield of copolymerization may be obtained through a simple one shot RIM process without requiring PEG macroactivator. However, based on polymerization kinetic results in previous articles, the molding cycle should be considered a little

Table I Yield of Copolymerization of PEG Segment

Sample Code	Yield (%)	Sample Code	Yield (%)	Sample Code	Yield (%)
*HJ*05	82	*TJ*05	87	*CJ*05	3
*HJ*10	78	*TJ*10	92	*CJ*10	17
*HJ*15	88	*TJ*15	94	*CJ*15	15
*HJ*20	62	*TJ*20	98	*CJ*20	9
*HP*05	37	*TP*05	35	*CP*05	6
*HP*10	45	*TP*10	56	*CP*10	12
*HP*15	67	*TP*15	52	*CP*15	15
*HP*20	55	*TP*20	88	*CP*20	15
*MP*05	30				
*MP*10	25				
*MP*15	46				
*MP*20	45				

Table II Molecular Weight Data of Nylon 6 and Copolymers by GPC

Sample Code	$\bar{M}_n$	$\bar{M}_w$	Polydispersity
*HH*10	21,996	121,943	5.54
*HJ*10	28,439	176,672	6.21
*HJ*20	36,663	105,690	2.88
*HP*10	18,132	122,948	6.78
*HP*20	11,496	58,109	5.05
*CH*10	21,104	35,477	1.68
*CJ*10	11,153	20,084	1.80
*CJ*20	7346	11,132	1.51
*CP*10	14,500	22,665	1.56
*CP*20	5794	7618	1.31
*TH*10	20,313	187,550	9.23
*TJ*10	47,371	344,759	7.28
*TJ*20	29,357	270,279	9.21
*TP*10	18,492	164,107	8.87
*TP*20	9758	60,611	6.21
*MP*05	48,157	148,735	3.09
*MP*10	47,604	216,870	4.56
*MP*15	37,152	195,316	5.26
*MP*20[a]	—	—	—

[a] *MP*20 was not soluble.

longer than in the case of HDC activator system.[12–14]

When a macroactivator is used, the yield of copolymerization is much lower than what has been expected from other PEG-diamine cases. This indicates that a considerable amount of MPEG-TDI-MPEG compound, which has no functional active group at both ends, can be formed by leaving some unreacted TDI during the synthesis of the macroactivator. Thus, the unreacted TDI in a macroactivator produced TDC activator, resulting in nylon 6 homopolymer during *in situ* polymerization.

In view of the polymerization mechanism, nylon 6–PEG block copolymer cannot form in the ideal situation where CCC activator is used as an activator. A small amount of PEG, however, still remained even after purification, which may be due to incomplete purification and/or unidentified side reaction.

Molecular Weight and Polydispersity

Molecular weight data of the as-polymerized samples are summarized in Table II. When the addition of modifier is increased, the average molecular weight is decreased. This is attributed to the increasing concentration of carbamoyl units initiating polymerization in the system with an increasing amount of modifier as mentioned in the Experimental section. For a given concentration of modifier, the *C*-series sample shows much lower molecular weight in comparison with *T*- and *H*-series samples, which is attributed to the difference in functionality of activator (i.e., the functionality of CCC activator is 1), whereas that of TDC and HDC activators is 2. Thus, based on the assumption of a complete polymerization, the *C*-series sample must show half the molecular weight of *T*- or *H*-series sample for the same content of modifier. *TJ*- or *HJ*-series samples show higher molecular weight than *TP*- or *HP*-series samples. This is why, since the amount of macroactivator formed through the aminolysis of activator by PEG-diamine is more than that through the alcoholysis of activator by PEG, the concentration of carbamoyl units in the mixture is lower at the initial polymerization stage in the PEG-diamine case than in the PEG case.

As nearly full conversion is reached, the branching or crosslinking in the activated anionic polymerization of CL has been suggested as being an important reaction. Petit et al.[15] observed a rapid change in the imide and lactam ion concentrations at the initial stages of polymerization and attributed this phenomenon to a Claisen-type condensation between low molecular weight growing chains and/or initiating species, which results in branching and/or crosslinking. There is also a possibility of limited thermally initiated polymerization as reaction approaches 200°C, which can contribute to the branching reaction. Generally speaking, the effect of branching reaction during polymerization has been reflected on the molecular weights and the polydispersity of the polymers. Polydispersity becomes narrower in the sequence of TDC, HDC, and CCC. The broader polydispersity for the HDC-activated polymers as compared to the CCC-activated polymers can be interpreted as a result of the occurrence of more branching and crosslinking reactions associated with the Claisen-type condensation in the course of polymerization.[12,14] When TDC is used as an activator, the TDC moiety can convert into the TDI residue and CL via thermal dissociation above 150°C.[16] Once the TDI residue is formed, the reaction between free isocyanate group and the terminal amine group of PEG-diamine (in the case of copolymerization) can easily produce polyurea. As a result, polyureas can further be branched and/or crosslinked through the thermally dissociated isocyanate group of the TDC residue. However, even though the forma-

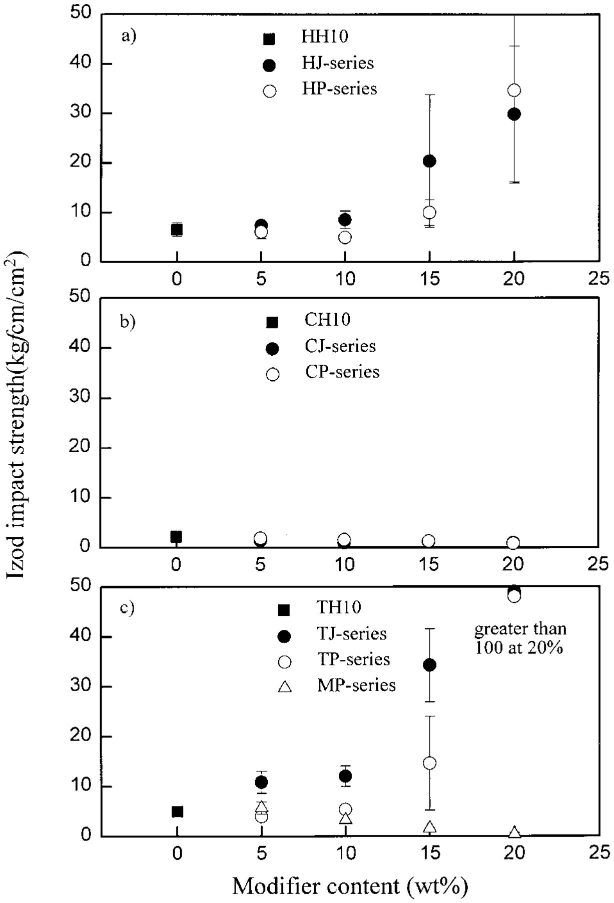


Figure 2 Influence of modifier contents on the impact strength of the as-molded nylon 6–PEG block copolymer samples prepared using various activators. (a) HDC activator; (b) CCC activator; (c) TDC and MPEG–TDC activators.

tion of urea bonds by the dissociated isocyanate group is not available in the TDC-activated homopolymerization, the TDC-activated homopolymer still shows higher molecular weight and broader polydispersity relative to the HDC- and CCC-activated homopolymers. The reason is yet unresolved to the best of our knowledge.

Mechanical Properties

Figure 2 depicts changes in impact strength as a function of modifier content. When PEG or PEG-diamine was used as a modifier along with HDC or TDC activator, a considerable amount of nylon 6–PEG–nylon 6 triblock copolymer could be formed as discussed. Impact strength in HDC-activated copolymer is observed to increase slightly with the modifier percentage both in PEG and PEG-diamine systems. As the modifier concentration increases in the TDC activated copolymer, the Izod impact strength is greatly improved over the entire modifier range studied for both PEG and PEG-diamine systems. The PEG-diamine system showed much greater impact strength than the PEG system. For the *MP*-series sample which consisted mainly of nylon 6–PEG diblock copolymer, the increase of impact strength was no longer discernible with increasing modifier content. Instead, it showed a decreasing tendency above 10% modifier content. The CCC-activated system showed lower impact strength as compared with those activated by other initiators. When the CCC activator was used, nylon 6 and PEG form an *in situ* blend rather than nylon–PEG block copolymer. The extent of soft segment introduced in the form of copolymer in the nylon 6 matrix is practically nil. Therefore, the modifier could be segregated from the nylon 6 matrix, forming large separated domain during polymerization.

The increase in impact strength caused by the addition of rubbery component to the hard domain or the incorporation of soft segment into hard domain chain originates from the inhibition of craze propagation by the rubbery domains dispersed in the hard matrix. Strong adhesion between the hard matrix and the dispersed phase is essential to obtain sizable increase in impact strength. Thus, impact modifiers or coupling agents containing functional groups such as anhydride or carboxylic acid are mostly used to enhance interfacial adhesion in nylon 6/modifier–melt blend systems.[10,11,17] In principle, these modifiers or coupling agents can react with nylon 6 during molding.

It has been demonstrated that the ultimate physical properties of nylon 6 copolymers showed strong dependence on the types of copolymers formed during *in situ* polymerization depending on the activator type used. Even if the same type and the same feed composition of modifier are used, the properties can be different because of the differences in the interfacial adhesion. In the case of nylon 6–PEG–nylon 6 triblock copolymer system, the improved impact strength has been observed in spite of decreasing molecular weight with increasing modifier content. In this triblock copolymer system, the interface of microphase domains is expected to be strong as the interface regions consisting of covalent linkages between nylon 6 and modifier. Another reason the TDC activator/PEG-diamine modifier system showed better impact strength and toughness relative to the HDC activator/PEG modifier system can be correlated with the fact that the former system had more content of the PEG segment in the copolymer than the latter system. Since the HDC activator/PEG modifier system contains more unreacted modifier and homopolymer than the TDC activated or PEG-diamine modifier system as discussed earlier (see Table I), impact strength is believed to be inferior because of macrophase separation between the copolymer and the unreacted modifier.

Since, in the case of CCC-activated system, any strong covalent bonds at the interface of separated region are not possible and macrophase separation is expected, the improvement of impact strength was not shown with the increasing modifier content. Diblock copolymer system such as *MP*-series sample shows some improved impact strength relative to the CCC-activated system, but the improvement is not significant. This is attributed to the low copolymerization yield in conjunction with the polymerization-induced phase separation, resulting in macroscopic domains. The phase morphology of as-polymerized sample will be discussed in detail later.

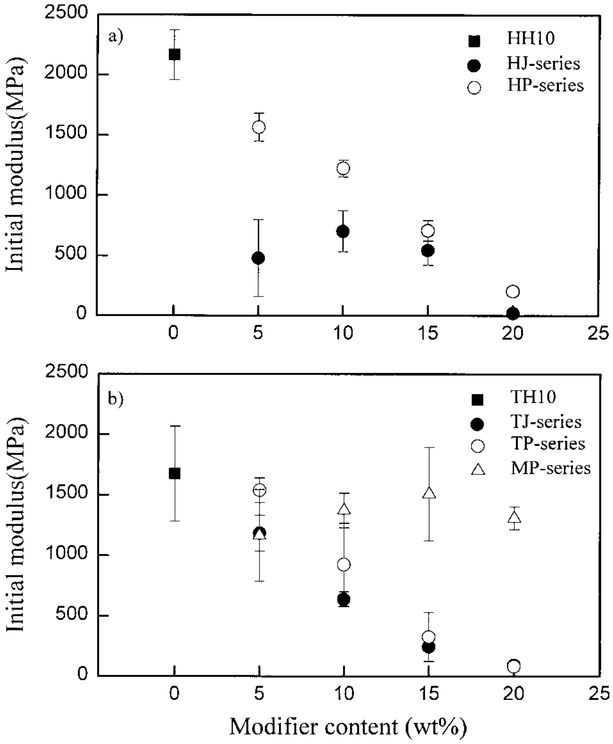


Figure 3 Influence of modifier contents on the initial modulus of the as-molded nylon 6–PEG block copolymer samples prepared using various activators. (a) HDC activator; (b) TDC and MPEG–TDC activators.

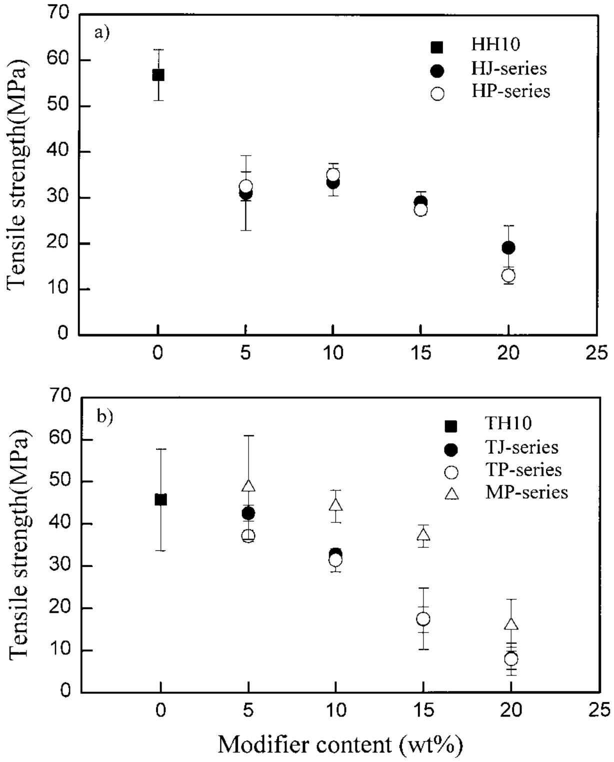


Figure 4 Influence of modifier contents on the tensile strength of the as-molded nylon 6–PEG block copolymer samples prepared using various activators. (a) HDC activator; (b) TDC and MPEG–TDC activators.

As the modifier percentage increases in the copolymer, the initial modulus (Fig. 3) and tensile strength (Fig. 4) decrease regardless of modifier type. This is attributed to the soft domain where an external stress is concentrated, forcing the copolymer to yield at lower applied stress. The PEG-diamine-containing copolymers show lower modulus and tensile strength relative to the PEG-containing copolymers. Similarly, higher modulus values are obtained for the HDC-activated polymers with lower copolymerization yield than the TDC-activated polymers with higher copolymerization yield in the same modifier system. The trend of ultimate elongation (Fig. 5) with the modifier–feed ratio parallels that of the Izod impact properties (Fig. 2) regardless of the type of activators, because as the extensibility increases, so does the impact strength. For the same modifier, the extensibility of TDC-activated copolymer is better than that of the HDC-activated copolymer. For the same activator, the extensibility decreases on the order of PEG-diamine, PEG, and MPEG modifier.

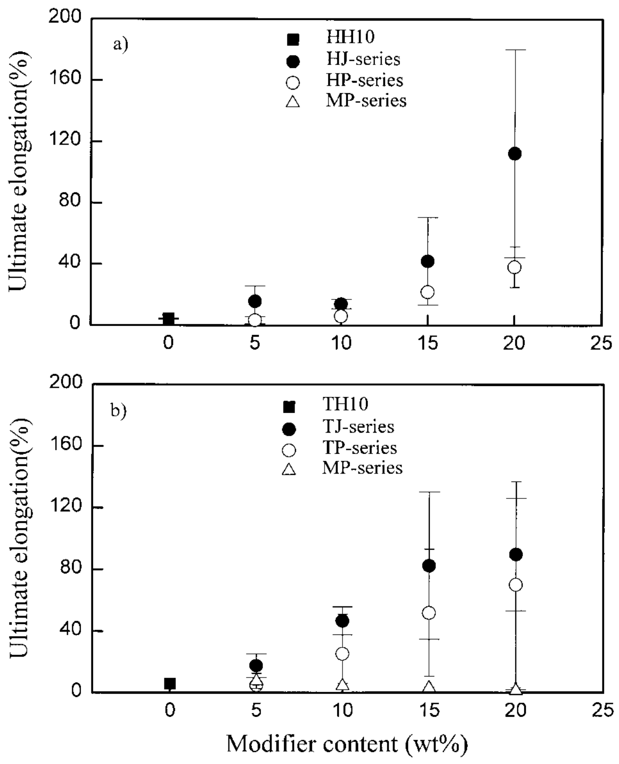


Figure 5 Influence of modifier contents on the ultimate elongation of the as-molded nylon 6–PEG block copolymer samples prepared using various activators. (a) HDC activator; (b) TDC and MPEG–TDC activators.

Crystal Structure

Figure 6 shows the X-ray diffractograms of *TJ*-series samples. It is well known that nylon 6 generally shows α- or γ-crystal structures depending on the thermal and processing conditions.[18,19] All *TJ*-series samples are shown to have the α-crystal structure, which is evidenced by the (200) diffraction peak at $2\theta = 20°$ and the combined (002)/(202) diffraction peak at $2\theta = 23.5°$.[18] There is no values identifiable with the γ-phase characteristic diffraction peak. The intensity of the diffraction curve drastically decreases, whereas its width increases starting from 15% PEG-diamine feed ratio. This implies that the degree of crystallization and the crystallite size of nylon 6 block are considerably reduced above the 15% PEG-diamine content. This observation is attributed to the fact that PEG-diamine probably inhibits crystallization of nylon 6 block. The reduction of crystallite size of nylon 6 block is also caused by the decreased molecular weight of nylon 6 with increasing PEG-diamine feed ratio. All samples other than *TJ*-series samples showed nearly identical X-ray diffraction results, which indicates that the types of modifiers and activators do not affect the resultant crystalline structure.

DMTA Study

Dynamic mechanical methods have been extensively used for the elucidation of microphase separation and the domain structure of the block copolymers. Figure 7(a) presents the storage and loss modulus as a function of temperature at 1 Hz for the *TJ*-series samples. As the PEG-diamine content in the copolymer increases, the onset temperature of glass transition is shifted to a lower temperature. This phenomenon clearly indicates the gradual increasing trend of elastic nature of *TJ*-series samples. From the loss tangent curve [Fig. 7(b)], the dynamic thermal transition can be estimated. The peak of loss tangent curve of nylon 6 homopolymer at −65°C may be attributed to a crank shaft and microbrown motion of free amide groups and several ethylene carbon groups, whereas the relaxation peak at 30°C may be assigned to glass transition of the main chains.[20] The transition at 30°C of nylon 6 homopolymer is known to be very sensitive to the moisture content.[21] The main transition at 30°C is somewhat lower than those reported by others.[20,21] This may be due to different moisture contents of our nylon 6 samples. At a first glance, the main tan δ

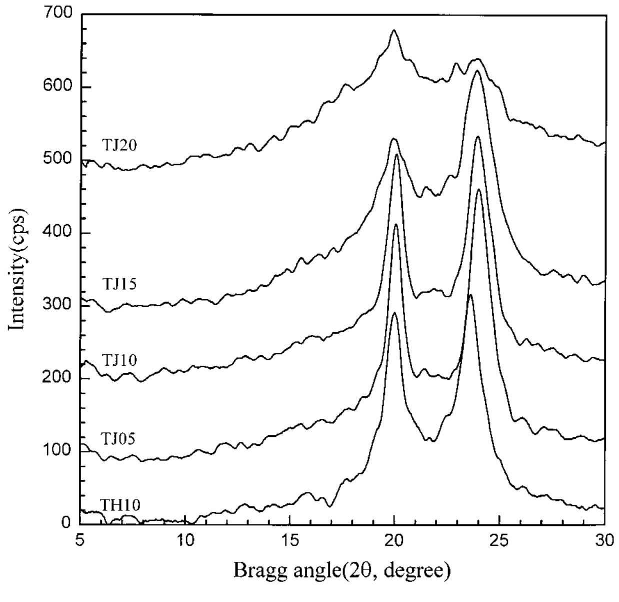


Figure 6 X-ray diffractograms of the as-molded nylon 6 homopolymer (*TH*10) and *TJ*-series samples.

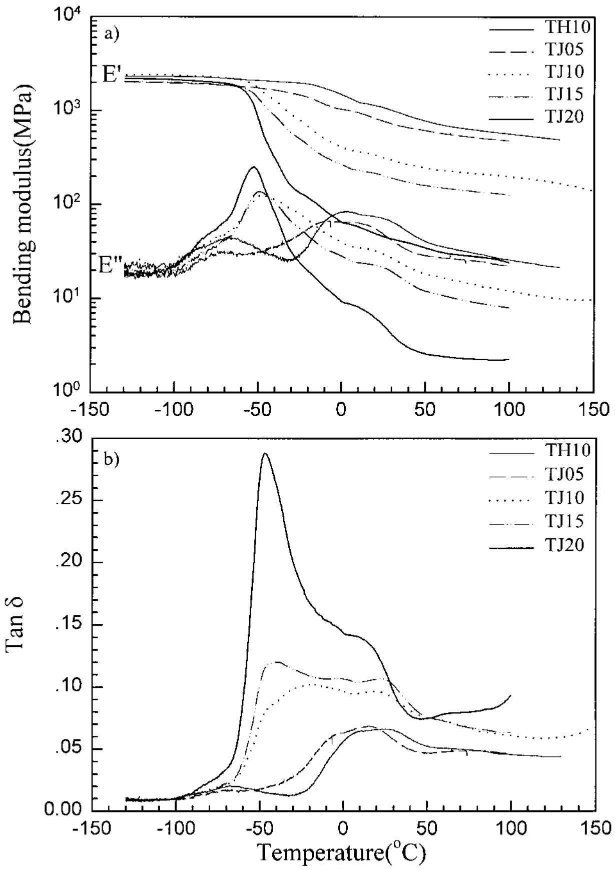


Figure 7 Dynamic mechanical properties of the as-molded nylon 6 homopolymer (*TH*10) and *TJ* series. (a) Storage and loss modulus; (b) loss tan δ.

peak at 30°C gradually increases in magnitude without significant shift with increasing content of modifier. Meanwhile, a new transition that corresponds to the main glass transition of PEG-diamine blocks in the copolymer comes into notice around −50°C. Tan δ suddenly shoots up to a higher value in the *TJ*20 sample. These two distinct transition peaks and the increasing values of lower transition peak with the PEG-diamine amount shown in *TJ*-series samples indicate that, in spite of the formation of triblock copolymer through covalent linkages, amorphous nylon 6 chains and the blocked PEG segments are not molecularly miscible, and a considerable amount of the blocked PEG segments remain amorphous without undergoing crystallization.

Interestingly, the storage modulus [Fig. 8(a)] in a diblock (*MP* series) system reveals the delayed onset of relaxation as the MPEG content is increased, as compared with the *TJ* series. On the other hand, the loss modulus curves show no significant transition corresponding to the MPEG segment. Here again, two transition peaks are observed in the loss tangent curves [Fig. 8(b)]. The crank shaft transition of nylon homoblock at −65°C persists in all cases of the *MP* series. Like *TJ*-series samples, there is no new peak at −50°C for the amorphous MPEG segment in the *MP* series. This result suggests that most of MPEG block and unreacted MPEG in *MP* series are not present in the amorphous state (i.e., they can be crystallized during cooling to room temperature after polymerization). This possibility of the crystallization of MPEG segments may be attributed to the formation of large MPEG domains through the macrophase separation during *in situ* polymerization. The great difference in impact strength and tensile properties of *TJ*- and *MP*-series samples is thought to be caused by their great difference in morphologies as reflected in the DMTA behavior.

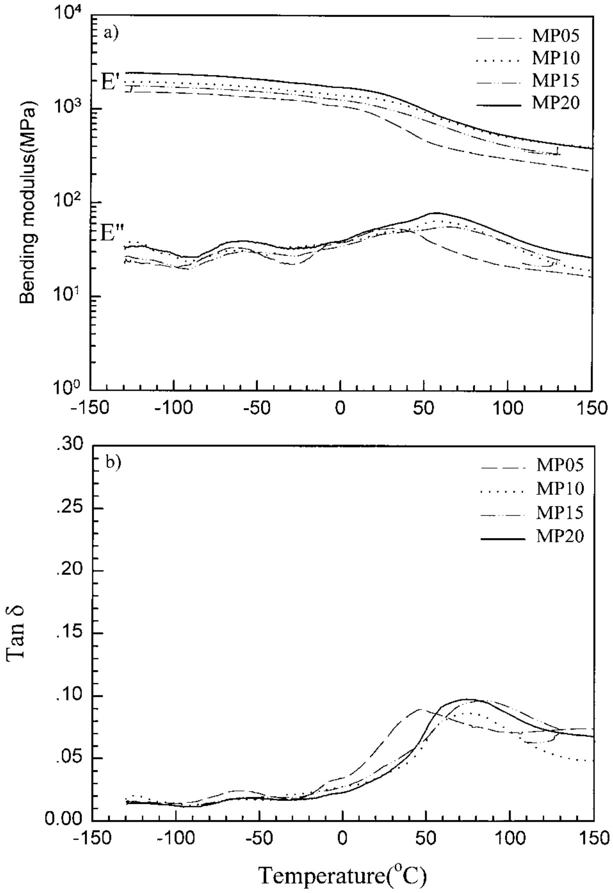


Figure 8 Dynamic mechanical properties of the as-molded *MP*-series samples. (a) Storage and loss modulus; (b) loss tan δ.

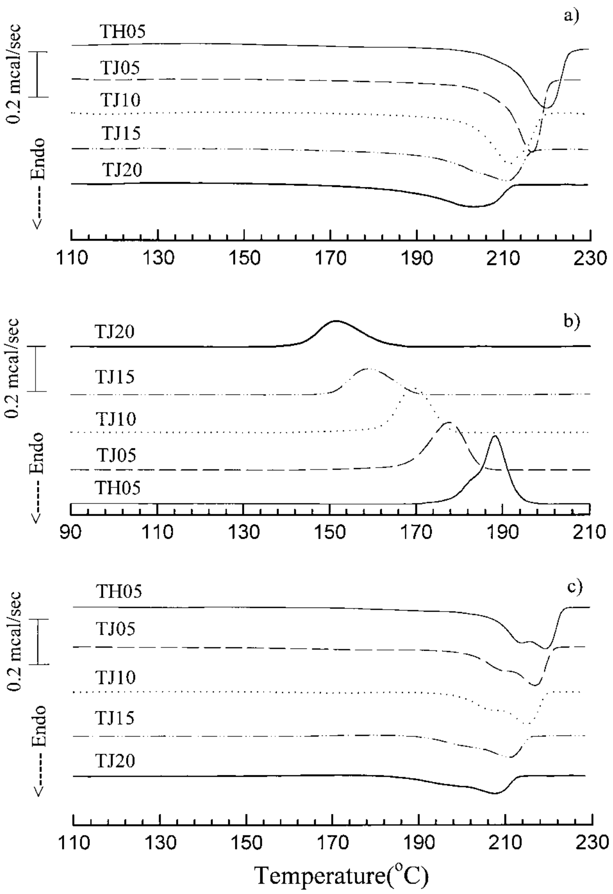


Figure 9 DSC thermograms of nylon part for nylon 6 homopolymer (*TH*05) and *TJ*-series samples. (a) Melting curves for the as-polymerized samples; (b) nonisothermal crystallization curves upon cooling from 230°C at a rate of 10°C/min; (c) melting curves for nonisothermal crystallized samples.

The Effects of PEG Segments on the Crystallization and Melting Behaviors of Nylon Matrix

The polymerization-induced phase separation and subsequent crystallization were shown to be possible in previous reports.[8,12–14] The information about the crystal formed during *in situ* polymerization can be demonstrated from the melting thermogram through the first scan on DSC. Figure 9(a) shows the melting thermograms of the as-polymerized *TJ*-series samples obtained during the first heating scan from −20 to 230°C. As the content of PEG-diamine is increased, the melting point is depressed. Concurrently, the melting curve gets broader. The depression of melting temperature is caused by the attractive interactions of the constituents in conjunction with the size and perfection of the nylon 6 crystallite. Since the interaction parameter cannot show a great negative value because of very poor miscibility between nylon 6 and PEG segments in the melt state, the contribution from the crystalline morphology and the reduced molecular weight to the melting point depression of nylon 6 block of *TJ*-series samples is more dominant than from the small negative interaction parameter. This explanation is also supported by the GPC and X-ray diffraction results. As the content of PEG-diamine incorporated into the nylon 6 main chain is increased, the intermolecular hydrogen-bonding density and molecular weight of nylon 6 segment is reduced. Thus, the crystal formed during *in situ* polymerization is thermodynamically unstable due to the formation of intermolecular defects and the reduction of crystal size, which makes the contribution of the high free energy of the end surfaces of crystal lamella greater. Therefore, the melting point depression occurs in the *TJ* series.

In many cases, the behavior of the melting point depression parallels the reduction of melting transitional enthalpy. The total amount of nylon 6 crystalline region formed during *in situ* polymerization can be evaluated by the normalized heat of fusion, which is obtained by dividing the measured heat of fusion per unit gram of sample with the weight fraction of nylon 6 in the sample. The normalized heat of fusion decreases with increasing PEG-diamine feed ratio. The normalized heat of fusion was observed to decrease dramatically, especially in the *TJ*20 sample. From this result, it is noted that the block-copolymerized PEG segment does not favor undergoing polymerization-induced crystallization.

Figure 9(b) shows the exothermic curves associated with the nonisothermal melt crystallization during cooling from melt of the *TJ*-series samples. Considering that the peak temperature of nonisothermal crystallization shifts to a lower temperature and the normalized heat of crystallization reduces with increasing PEG content, it is noted that the block-copolymerized PEG segment also retards the rate of crystallization in the melt crystallization. Figure 9(c) shows the melting transition curves of the melt crystallized *TJ*-series samples, exhibiting double melting endotherms. Since the origin of the double melting transition is well discussed in many articles,[22–24] further discussion is not made in this study. The melting point depression in the second scan is similar to in the first run, but the heat of fusion is much smaller relative to that in the first scan.

This indicates that the crystallinity of the as-polymerized sample is higher than that of the melt-crystallized one. The *MP*- and *CJ*-series samples also show similar crystallization behavior. This indicates that the crystallization behavior of nylon 6 matrix is not influenced by the types of PEG segments in the sample after polymerization.

Morphology of PEG Segment in As-Polymerized Sample

Samples prepared in this study can be classified into three groups depending on the existence types of PEG segments in the sample. One group consists mainly of nylon 6–PEG–nylon 6 triblock copolymer (the *TJ*- and *TP*-series samples); another group comprises mainly of nylon 6–PEG diblock copolymer (the *MP*-series samples), and the other is the sample where PEG is simply mixed with nylon 6 matrix such as *CJ*- or *CP*-series samples. As discussed above, the mechanical properties were highly dependent on the chemical bonding and micro/macro-type phase separation of PEG segments and nylon 6.

Nylon 6–PEG–Nylon 6 Triblock Copolymers (TJ and TP Series)

The triblock copolymers (*TJ*-series samples) showed the drastic increase in impact strength with the PEG feed ratio, whereas the diblock copolymers (*MP* series) and the PEG/nylon 6 blends (*CJ* or *CP* series) showed no improvement in toughness. This result seems to have a very close relation to the size or crystallinity of the dispersed phase and interfacial adhesion, that is, the morphological structure of PEG segments.

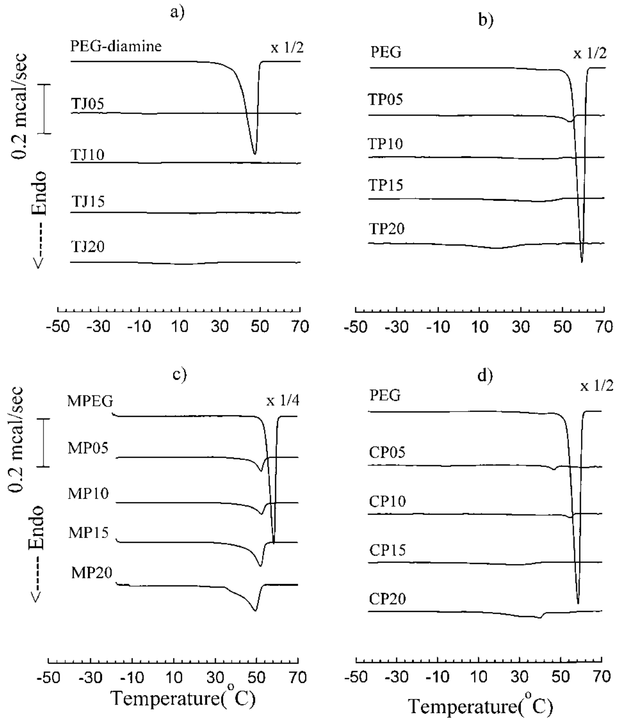


Figure 10 Melting transition curves of PEG part for the as-polymerized samples. (a) As-polymerized *TJ*-series samples; (b) as-polymerized *TP*-series samples; (c) as-polymerized *MP*-series samples; (d) as-polymerized *CP*-series samples.

First, we obtained the melting thermogram of PEG portion in the sample from the first heating scan from −50 to 70°C at the rate of 10°C/min to investigate the initial state of PEG segments in the sample prepared by *in situ* polymerization and subsequent cooling to the ambient temperature. The melting transition corresponding to the PEG portion is not observed for the *TJ*-series [Fig. 10(a)] samples irrespective of the PEG feed composition. This indicates that most of PEG segments incorporated in the nylon 6 main chains are in amorphous state even after the sample is cooled to room temperature, which is 25°C below the melting temperature of the pure PEG-diamine. Next, we obtained the nonisothermal crystallization curve by cooling from 70 to −50°C. [Since this temperature range is far below the melting points of nylon 6, it should not affect nylon phase (i.e., the initial morphology of nylon 6 phase formed during polymerization can be kept unchanged during this experiment) at a scan rate of −10°C/min.] The triblock copolymerized PEG segment shows no clear crystallization exotherms [Fig. 11(a)]. Also, in the second heating cycle from −50 to 230°C, no significant melting transitions of the PEG segments were noticed except for the *TJ*20 sample [see Fig. 11(b)]. These observations suggest that the PEG phase in the *TJ*-series samples are microphase separated. In view of the very small microdomains, crystallization is prohibited. The formation of microdomains of PEG segments incorporated in triblock copolymer is caused by the fact that, since *in situ* copolymerization is carried out via accelerated anionic ring opening polymerization mechanism in the presence of carbamoyl activator, the nylon 6 phase is solidified so fast through the polymerization-induced crystallization of nylon block that PEG segments cannot have enough time to segregate and form a separated macrophase. Both the melting point depression and the lower fusion enthalpy of unreacted PEG segments are attributed to the formation of much less perfect crystalline structure also caused by the microphase-separated PEG domain due to a very rapid *in situ* polymerization. The morphological state of PEG segment in the *TJ* series as revealed by the DSC observation is consistent with the DMTA result. This kind of morphology of PEG segments in the *in situ* polymerization of CL and PEG is thought to be the main factor to enhance the impact strength.

When PEG is used as a modifier instead of PEG-diamine for the *TP*-series samples, there is a considerable amount of unreacted PEG due to slower alcoholysis of the TDC activator by PEG compared to the aminolysis by PEG-diamine as discussed in the previous article.[8] To investigate the difference in the morphology between two types of PEG segments (i.e., PEG incorporated in triblock copolymerization and unreacted PEG existing in as-polymerized *TP*-series samples), a similar DSC experiment was carried out. Figure 10(b) shows the melting thermograms of *TP*-series samples measured during the first heating scan from −50 to 70°C. The melting transition peak is clearly observed even in the *TP*05 sample containing only 5% PEG feed ratio and the fusion enthalpy is much larger than that in the *TJ* series. This suggests that unreacted PEG phase can form a separated domain, the size of which is much larger than the average size of microdomains formed in the PEG block during *in situ* polymerization. This fact may be attributed to greater mobility and diffusion of the unreacted PEG compared to the reacted PEG, and thus, the crystallization can take place more easily even at the small undercooling on the basis of heterogeneous nucleation mechanism rather than homogeneous nucleation one.

*PEG–Nylon 6 Diblock Copolymers (*MP *Series)*

Figure 10(c) shows the melting endotherm corresponding to the PEG segment in the *MP*-series samples obtained during the first heating scan from −20 to 70°C at the rate of 10°C/min. Unlike triblock copolymer (*TJ* and *TP* series) samples, the melting transition peak of the PEG is clearly discerned at nearly the same temperature of 51°C. This temperature is only 7°C lower that the melting temperature of MPEG and the fusion enthalpy is also much larger than in *TJ* and *TP* series. This indicates that a considerable portion of PEG segments is crystalline in the *MP*-series samples. Since MPEG macroactivator is used as a modifier and an activator for the *MP*-series samples, only the nylon 6–PEG diblock copolymer can form basically. A considerable amount of unreacted PEG, however, was found to exist in the sample as shown in Table I. Thus, it is unclear whether the melting transition is caused by block copolymerized PEG segment or unreacted PEG. To confirm this, the first scan DSC thermograms were obtained for the purified *MP*-series samples, in which no significant melting transition peaks were observed. This indicates that, for the nylon 6–PEG diblock copolymer system, the blocked PEG segments chemically linked to the nylon 6 are also finely dispersed into microdomain and cannot crystallize through the heterogeneous nucleation mechanism as in the case of *TJ*-series samples. Instead, unreacted PEG can form a large segregated domain due to macroscopic phase separation. Therefore, the residual PEG can be crystallized during *in situ* polymerization.

The crystalline fraction of PEG segments in the *MP* series, calculated from the enthalpy of fusion, was shown to be about 0.5–0.6. When the correction for the copolymerization yield of PEG is undertaken (Table I), the degree of crystallinity of the unreacted PEG is nearly the same as that of the MPEG bulk. This suggests that macrophase domains permit crystallization in the unreacted PEG segments as in the MPEG bulk, whereas crystallization appears to be prevented in the blocked PEG segments. However, the reason the melting temperature of the unreacted PEG is still lower than that of the pure PEG may be attributed to the fact that the macrophase-separated domains of the unreacted PEG contain sizable defects because of the confined geometry imposed by the rapid solidification of nylon 6 matrix through activated anionic polymerization. Thus, the mechanical, thermal, and dynamic properties shown earlier are well supported by this difference in morphology of PEG between the diblock copolymers (*MP* series) and the triblock copolymers (*TJ* series).

*PEG–Nylon 6 Blends (*CP *Series)*

In principle, PEG modifier cannot react chemically with nylon 6 chains in the *CP* series. Hence, PEG homopolymer and/or PEG derivatives produced via alcoholysis of CCC can exist only as the *in situ* blends in the *CP* series, undergoing phase separation. The phase-separated domain in the

CP series appear much larger than those of other series samples. Figure 10(d) shows the melting thermogram corresponding to the PEG portion of the *CP* series obtained during the first heating scan from −50 to 70°C at the rate of 10°C/min. The melting transition peaks are not pronounced. The fusion enthalpy of the *CP* series is nearly the same as that of the *TP* series, but much smaller than that of the *MP* series. This indicates that the domain size of the most of the separated PEG phases in the *CP* series is small enough to prevent crystallization, that is, unreacted PEG is microphase separated, unlike the case of the *MP* series. This is explained as follows. Since CCC is the fastest activator, ending polymerization in 30 s at 160°C compared with the slowest TDC activator, the nylon 6 phase is solidified so fast through the polymerization-induced crystallization that even unreacted PEG chain having much higher mobility than the blocked PEG segment cannot have enough time to form a thermally equilibrated separated macrophase. Therefore, the separated phase of PEG is entrapped in the nylon 6 matrix before it reaches a thermodynamic equilibrium. *CP*-series sample, however, showed very poor impact strength even though microphase separation took place (see Fig. 4). This is attributed to the very poor interfacial adhesion caused by no chemical reaction between PEG and nylon 6.

Morphology of PEG Segment in Melt Crystallized Sample

To investigate the differences in the phase separation behavior of the as-polymerized sample and the sample crystallized from the melt state of both nylon 6 and PEG, the nonisothermal crystallization thermogram of PEG portion in the sample was obtained upon cooling from the melt ($>T_m$ of nylon 6) to −50°C. Then the melting transition thermogram was obtained upon heating at the rate of 10°C/min.

Nylon 6–PEG–Nylon 6 Triblock Copolymers (TJ and TP Series)

Figure 11(a) shows the crystallization exotherm of PEG units of the *TJ* series during cooling from 230 to −50°C at the rate of 10°C/min. Starting at 10% PEG feed ratio, unlike in the as-polymerized sample, the sample shows the crystallization. This indicates that, as the liquid–liquid phase separation proceeded because of the immiscibility between nylon 6 and PEG, by keeping the sample at 230°C for 10 min and/or the rate of solidification much slower than in the *in situ* polymerization, PEG segment can have enough time to form thermodynamically equilibrated phase separation upon cooling, and thus, a considerable amount of PEG segments forms a relatively large domain, which can be crystallized on the basis of heterogeneous or homogeneous nucleation mechanism.

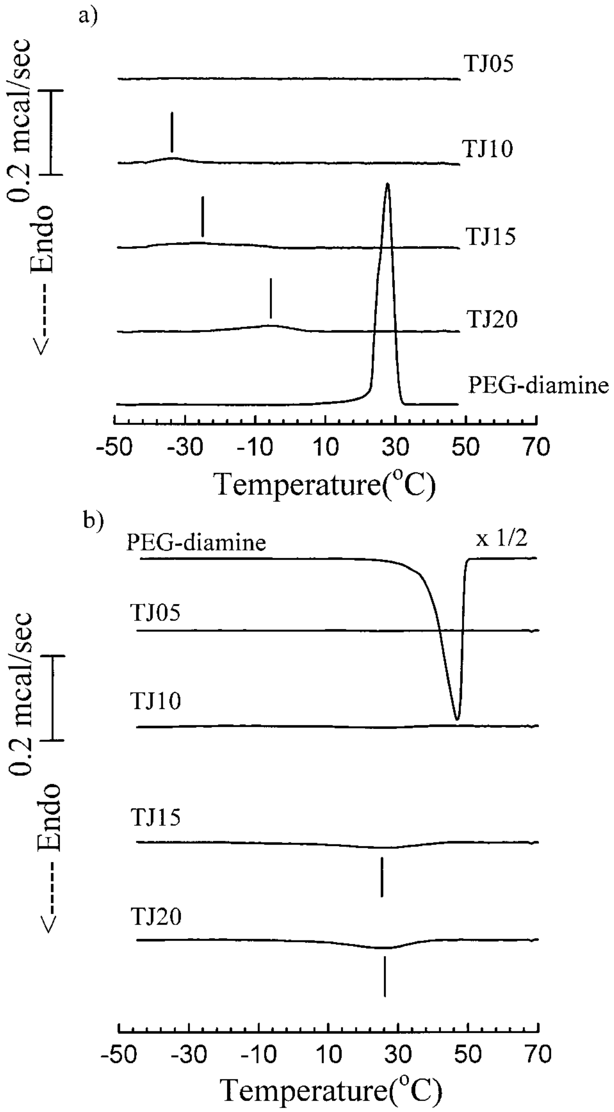


Figure 11 Nonisothermal crystallization DSC curves of PEG part for the as-polymerized *TJ*-series samples (a) when they are cooled from 230°C at a rate of 10°C/min, and (b) at their melting curves.

If all of the PEG segments in the *TJ* series were macrophase separated, the normalized enthalpy of crystallization of PEG (in cal/1 g of PEG) must have nearly the same value as the pure PEG-diamine. However, the normalized value [shown in Fig. 11(a)] is at most one third of that of the pure PEG-diamine. Even though the crystallization temperature of PEG segment is increased with increasing PEG feed ratio, it is still much lower than that of the pure PEG-diamine. This suggests that, although PEG segments in *TJ*-series samples are phase separated during melt crystallization, the average size of PEG domain is not large enough to obtain the same degree of crystallinity or perfection as in the pure PEG-diamine.

Figure 11(b) shows the melting transition curve of PEG portion in the nonisothermal crystallized sample. Whereas the crystallization temperature of melt-crystallized PEG segments depends strongly on the PEG feed ratio, the melting peak appearing at 26°C shows no movement, irrespective of PEG content. The melting temperature of the melt-crystallized PEG segment is considerably high when compared with that of the as-polymerized sample (ca. 12°C). This sizable difference is caused by the fact that the dispersed phase of PEG segment formed in the sample during *in situ* polymerization is much different from that of the melt crystallized sample, that is, the domain size of dispersed PEG segment of the as-polymerized sample is considered much smaller than that of the melt-crystallized sample.

In fact, since some of the unreacted PEG is present in the *TJ*-series sample as shown in Table I, the crystallization behavior of the PEG portion discussed so far cannot be attributed wholly to the block copolymerized PEG segment. To investigate the contribution of the pure-blocked PEG segment to the melt-crystallization behavior, the DSC thermograms for the melt-crystallized blocked PEG segment in the purified *TJ*-series sample after removing the unreacted PEG segments are shown in Figure 12(a). The crystallization peak of the purified *TJ*-series appears at −33°C. However, the normalized enthalpy of crystallization of PEG segment is much less than one twelfth of that of pure PEG-diamine. This suggests that, whereas the melt-crystallization of blocked PEG segments can be induced by even the small amount of the unreacted PEG present in the sample, the blocked PEG segment itself cannot be easily crystallized in the absence of the unreacted PEG during crystallization from the melt.

Nucleation and growth are the prevalent mechanism of crystallization from the melt. There are two types of nucleation, namely, homogeneous nucleation and heterogeneous nucleation. Since, in general, homogeneous nucleation is possible only in the case of the complete exclusion of foreign nucleating matter, crystallization of most of practical polymers is initiated by the heterogeneous nucleation mechanism. One approach for crystallizing through the homogeneous nucleation is to reduce the size of the critical nucleus drastically via large undercooling during melt crystallization of the extremely pure sample. Therefore, the crystallization is performed mainly by the heterogeneous nucleation mechanism when the sample is crystallized under the small or medium undercoolings. The maximum temper-

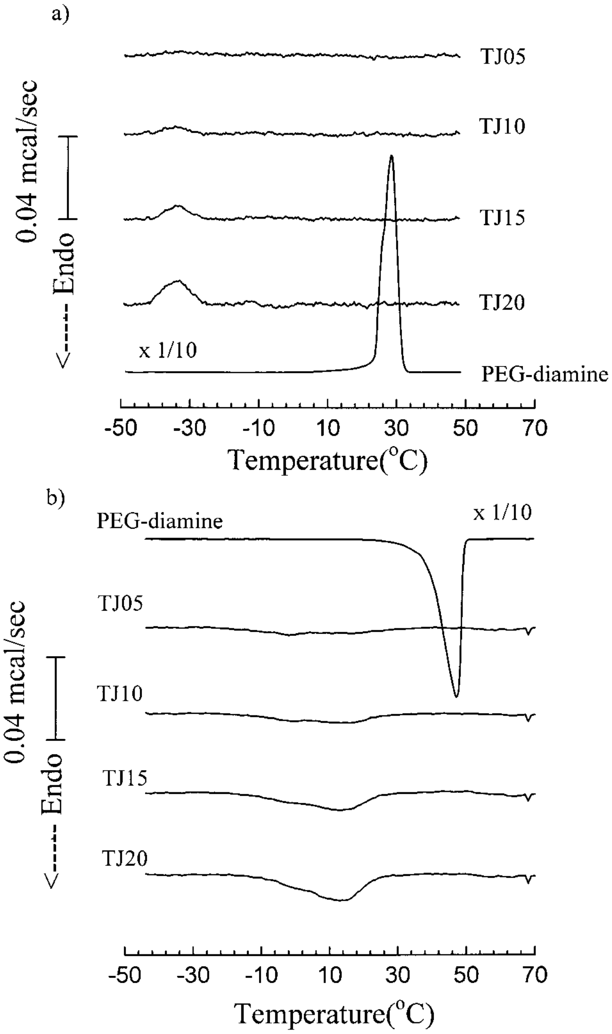


Figure 12 Nonisothermal crystallization DSC curves of PEG part for purified *TJ*-series samples when (a) they are cooled from 230°C at a rate of 10°C/min and (b) at their melting curves.

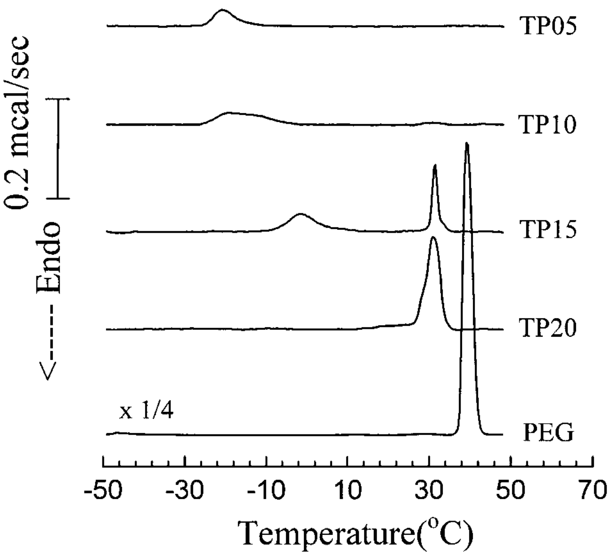


Figure 13 Nonisothermal crystallization DSC curves of PEG part for the as-polymerized *TP*-series samples when they are cooled from 230°C at a rate of 10°C/min.

ature (T_{homo}) for homogeneous nucleation is well known,[25] for instance,

$$T_{\text{homo}} = 0.8\ T_m^0$$

where T_m^0 is the equilibrium melting temperature of crystallizing material. If the equilibrium melting temperature of PEG-diamine used is assumed to be the same as that of PEG [M_w = 3000 (ca. 331 K)], the maximum crystallization temperature for homogeneous nucleation in PEG-diamine is around 256 K (−8°C). Therefore, the crystallization peak centered at −33°C for the blocked PEG segment of the purified *TJ*-series sample is interpreted to be caused by the homogeneous nucleation. This indicates that the domain size of dispersed PEG phase in the pure *TJ*-series is so tiny that there is little or no possibility of a certain foreign nucleating material to be included within the dispersed PEG domain. Such a dispersed PEG domain may be regarded as highly pure. The melting temperature of PEG segment of melt-crystallized purified *TJ* series is 13°C [see Fig. 12(b)], which is much lower than that of the impure ones. This can also be explained by the comparatively tiny domain size of the dispersed PEG phase in the pure *TJ*-series sample.

Figure 13 shows the nonisothermal crystallization curve of PEG units upon cooling *TP*-series samples. When compared with the behavior of the *TJ*-series sample [Fig. 11(a)], the PEG crystallization peak is seen more distinctly and the enthalpy of crystallization is much greater. This can be explained as follows. Since a considerable amount of unreacted PEG is present in *TP*-series sample, a large PEG phase can be completely separated from the nylon 6 matrix upon cooling from the melt. This unreacted PEG is readily crystallized, probably through the heterogeneous nucleation mechanism, and thus can also induce the crystallization of the blocked PEG segment. The melt-crystallized *TP*20 sample shows a single crystallization exotherm at 31°C, which may be attributed to the heterogeneous nucleation, whereas the *TP*15 sample shows dual crystallization peaks (ca. −2 and 31°C), called fractional crystallization peaks. In the fractional crystallization, the crystallization at a higher temperature is associated with heterogeneous nucleation, whereas that at the lower temperature may be attributed to homogeneous nucleation. This kind of fractional crystallization has been observed in polypropylene/thermoplastic rubber blends, polyvinylidene fluoride (PVDF)/nylon 6 blend,[26] PVDF/poly(butylene terephthalate) [PBT] blend,[26] nylon 6/polyolefin blend,[27] polyethylene oxide (PEO)–polyisoprene (PI) [or PEO-polystyrene (PS)] diblock copolymer,[28] PEO-PI-PEO (or PEO-PS-PEO) triblock copolymer,[29,30] and PEO-polyethylene methacrylate (PEMA) diblock copolymer.[31] The origin of fractional crystallization observed in many blend and block copolymer systems has been explained to be associated with the morphological effect (i.e., the size of crystallizable phase separated from major polymer matrix during melt crystallization).

As discussed above, the crystallization peak at temperatures lower than −8°C is attributed to the crystallization of PEG by the homogeneous nucleation mechanism, whereas the crystallization taking place at temperatures higher than −8°C are attributed to the heterogeneous nucleation mechanism. *TP*05 and *TP*10 samples show only a single crystallization peak at the lower temperature of −20°C based on the homogeneous nucleation mechanism. Thus, the size of PEG domain crystallized at a higher temperature is much larger than that at lower temperature. The reason the crystallization temperature is shifted to a higher temperature with the increasing PEG feed ratio is that the large size of PEG phase separated from nylon 6 matrix is due to the increase of unreacted PEG content along with the PEG feed ratio. As observed in the melt-crystallization behavior of the purified *TJ*-series sample, the crystallization peak at the lower temperature of the *TP*-series sample is believed to be associated with the crystallization of the block copolymerized PEG segment highly limited in phase separation because of covalent bonding to nylon 6 chain. The reason the crystallization is not observable at the lower temperature, but observed only at the higher temperature, is because even the block-copolymerized PEG segments aggregate with the unreacted PEG phase and can form a large separated phase because of a considerable amount of unreacted PEG present in the sample. Thus, the blocked PEG segments seem to crystallize simultaneously with the unreacted PEG phase based on the heterogeneous nucleation mechanism. The PEG crystal melting temperature of the melt-crystallized *TP* series is shown to be 53°C, irrespective of the PEG feed composition. This melting temperature is only a little lower than that of the pure PEG bulk, and the melting enthalpy of PEG segment in the melt-crystallized *TP* series is much higher than in melt-crystallized *TJ* series. The normalized melting enthalpy of PEG segments in the melt-crystallized *TP* series is about 80% of that of the pure PEG.

*PEG–Nylon 6 Diblock Copolymers (*MP *Series)*

Figure 14(a,b) shows the nonisothermal crystallization curves of the PEG units on cooling the unpurified and purified *MP*-series samples from the melt, respectively. As seen in these figures, the PEG crystallization peak of PEG is observed at a lower temperature (ca. −20°C), as well as at a higher temperature in the unpurified samples, whereas a single crystallization curve is observed only at a lower temperature in the purified samples. This indicates that the exothermic curve at a lower temperature is attributed to the crystallization of diblock copolymerized PEG segment and the other curve is for unreacted PEG derivatives. The melting temperature of PEG segment of melt-crystallized *MP* series is shown to be 53°C, irrespective of the PEG feed. This melting temperature is only a little lower than that of the pure MPEG. The fusion enthalpy of melt-crystallized sample is much greater than that of as-polymerized *MP*-series sample shown in Figure 10(c). The normalized fusion enthalpy is about 94% of that of the melt-crystallized bulk PEG, irrespective of PEG feed. This indicates that more of diblocked PEG segments can be crystallized in the melt-crystallized samples than in the as-polymerized sample.

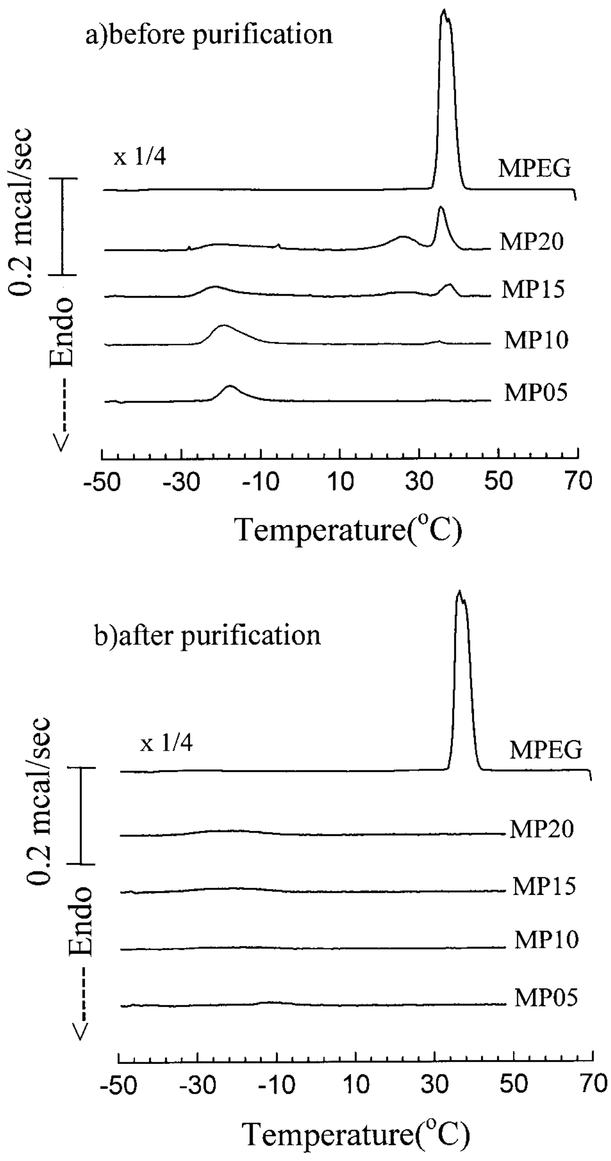


Figure 14 Nonisothermal crystallization DSC curves of PEG part for the as-polymerized *MP*-series samples when they are cooled from 230°C at a rate of 10°C/min. (a) Before purification; (b) after purification.

*PEG–Nylon 6 Blends (*CP *Series)*

Figure 15(a) shows the nonisothermal crystallization curves corresponding to the PEG units during cooling the *CP*-series samples from the melt. Figure 15(b) shows the melting transition curves of PEG portion of the melt-crystallized *CP*-series samples. The crystallization peak is observed only at a higher temperature for all *CP*-series samples, in which the melting enthalpy of PEG segment is more than 80% of that of the PEG homopolymer crystallized nonisothermally under the same conditions. These

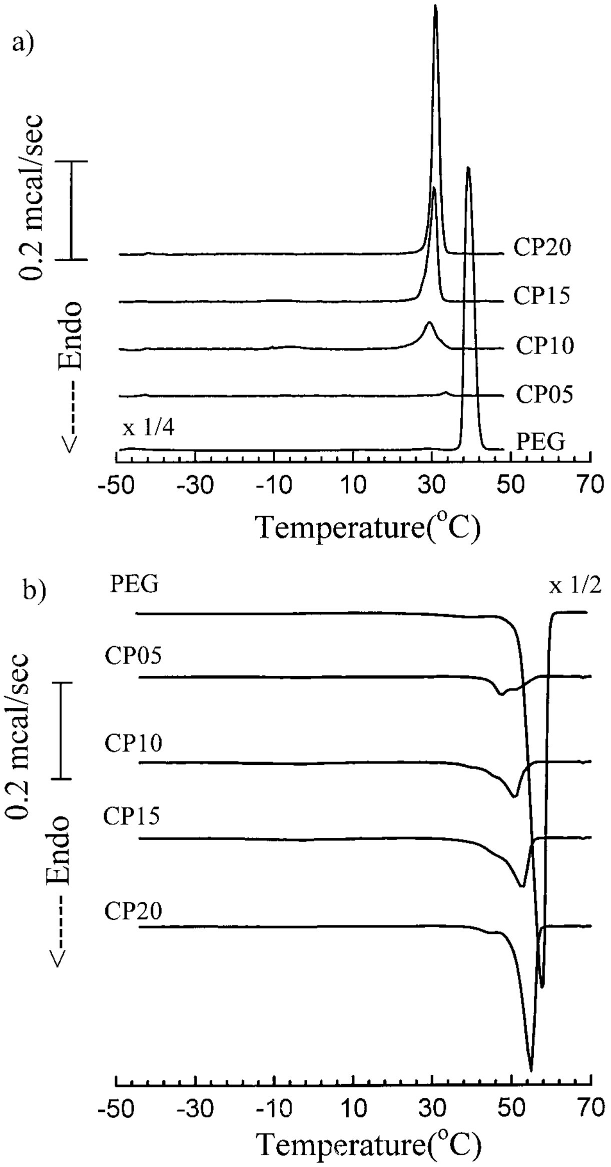


Figure 15 Nonisothermal crystallization DSC curves of PEG part for the as-polymerized *CP*-series samples (a) when they are cooled from 230°C at a rate of 10°C/min and (b) at their melting curves.

results also indicate that, whereas in as-polymerized *CP*-series sample the PEG segments are not well separated into macrophase due to extremely rapid polymerization followed by the fast solidification, the PEG segments can form a large PEG domain due to thermally induced phase separation during melting the sample.

CONCLUSION

We obtained the highest yield of nylon 6–PEG–nylon 6 triblock copolymers using TDC and HDC activators and PEG-diamine modifier. The CCC activator produces only *in situ* nylon 6–PEG blends. Nylon 6–PEG diblock copolymers were obtained when MPEG–TDC macroactivator was used. The as-polymerized samples contained a considerable amount of unreacted MPEG.

The nylon 6–PEG–nylon 6 triblock copolymers showed the highest impact strength. The nylon 6–PEG diblock copolymers and *in situ* nylon 6–PEG blends showed no improved toughness. Most block-copolymerized PEG segments showed amorphous characteristics. A large fraction of unreacted PEG segments was crystalline in the as-polymerized samples, except the products obtained using the CCC activator. The presence of PEG derivatives retarded the crystallization of nylon 6 part during both *in situ* polymerization and melt crystallization. However, the PEG segments did not alter the crystal modifications of nylon 6. All products showed the α-crystalline modification.

Toughness of nylon can also be improved by introducing a soft amorphous segment in the nylon main chain via *in situ*-activated anionic copolymerization rather than condensation copolymerization. The extent of improvement certainly depends on the types of activator and modifier as well as their functionality of the activator. When PEG-diamine is used as a modifier in the conjunction with various activators, the triblock copolymer shows the highest impact property. Among the three different types of activators used, TDC shows more enhanced toughness than HDC and CCC regardless of modifier types. The copolymers, produced via *in situ*-activated anionic copolymerization using TDC activator, were composed mostly of the nylon 6–PEG-diamine–nylon 6 triblock copolymers. These triblock copolymers showed the highest impact toughness. Impact toughness in such copolymers depends on the morphology of separated phase during the polymerization-induced crystallization. Separated PEG domain has the smallest size and is almost amorphous in the TDC-activated nylon 6–PEG-diamine triblock samples, whereas the separated PEG domain is very large and crystalline in the as-polymerized diblock copolymers. Although nylon 6–PEG *in situ* blend system can provide microphase separated domain (confirmed from DSC study) via CCC-activated polymerization, it does not show any improvement in toughness results because of the lack of chemical bonds in the interface.

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