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Synthesis of Heteroarm Star-Shaped Block Copolymers with Cyclotriphosphazene Core and Their Compatibilizing Effects on PPO/Nylon 6 Blends

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ABSTRACT: The preparation and compatibilizing ability of heteroarm star-shaped block copolymers (**6** and **8**) composed of polystyrene and nylon 6 units diverged from the phosphazene core were investigated. The heteroarm star-shaped copolymers were prepared by a partial coupling reaction of the acid chloride of hexakis(4-carboxyphenoxy)cyclotriphosphazene [**4**, $(4\text{-}ClCOC_6H_4O)_6N_3P_3$] with polystyrene having a terminal amino group ($PSt-NH_2$) or poly(styryllithium), followed by the ring-opening polymerization of ϵ-caprolactam (ϵ-CL) with the residual carboxyl group in the phosphazene core. The coupling reaction of telechelic $PSt-NH_2$ and poly(styrylllthium) with **4** occurs smoothly to give carboxyphenoxycyclotriphosphazenes carrying 2.2−4.7 polystyrene chains, **5** and **7**, respectively. The polymerization of ϵ-CL with hexakis(4-carboxyphenoxy)cyclotriphosphazene [**2**, $(4\text{-}HOOCC_6H_4O)_6N_3P_3$] showed that all carboxyl groups participate in the initiation of polymerization to give hexaarmed star-shaped polymers. This implies that the residual carboxyl groups in **5** and **7** could also initiate the polymerization of ϵ-CL. The molecular weights of copolymers obtained from the polymerization of ϵ-CL with **5** and **7** are in agreement with those of calculated values, suggesting the formation of heteroarm star-shaped block copolymers with phosphazene core (**6** and **8**). When these copolymers were used as a compatibilizer of an immiscible blend, poly(2,6-dimethylphenylene oxide) (PPO) and nylon 6, DSC profiles showed a single transition temperature that shifted to lower temperature from the T_g of PPO. The SEM photograph indicates that PPO disperses regularly and finely with 0.3 μm size in the nylon domain. Furthermore, the tensile strength and elongation at break of ternary blends increased with increasing the copolymer content. These results indicate that the effective penetration of each block sequence of the heteroarm star-shaped copolymers into the blend components is operative, that is, these copolymers act as an excellent compatibilizer for PPO/nylon 6 blends.

Introduction

Interest in hyperbranched polymers has increased tremendously since they have the possibility of imparting properties and functionalities that are not obtained from conventional linear polymers.[1−6] Hexachlorocyclotriphosphazene is one the familiar monomer for the preparation of organic−inorganic hybrid polymers. A number of poly(organophosphazenes) have been synthesized via the ring-opening polymerization of the cyclotriphosphazene followed by displacement of a P−Cl group with nucleophiles by Allcock et al.[7−9] On the other hand, we have reported the preparation of vinyl polymers containing cyclotriphosphazenes as the pendant group, which are characterized by five functional arms on the phosphazene ring.[10,11] One of the attractive fields of the cyclophosphazene chemistry might be the preparation of star-shaped polymers with a phosphazene core, since the functional groups having the ability to initiate the polymerization could be easily introduced into the phosphazene ring. Recently, we reported a new type of star-shaped poly(amino acid) that take the α-helical structure, utilizing hexakis(4-aminophenoxy)-cyclotriphosphazene as an initiator for the ring-opening polymerization of *N*-carboxyanhydride of β-benzyl-L-aspartate.[12] The preparation of such a star-shaped polymer diverged from the phosphazene core has also been reported.[13] The ring-opening polymerization of ϵ-caprolactam (ϵ-CL) with poly(carboxylic acids) and poly(ethyleneimines) is known to give star-shaped polyamides.[14,15] So, the polymerization of ϵ-CL with cyclophosphazene carrying carboxyl groups is also expected to form hexaarmed polymers.

Block and graft copolymers have been of interest as compatibilizing agents for immiscible blends. For the compatibilizing process, the interpenetration of segments of copolymers and blend components is necessary to achieve a strong mechanical adhesion caused by the reduction of the surface tension due to the presence of the copolymers. This indicates that the molecular architecture is an important parameter for achieving efficient compatibilities. Recent reports have demonstrated that block copolymers rather than graft copolymers are effective to obtain compatible blend systems.[16] For immiscible blends of poly(2,6-dimethylphenylene oxide) (PPO) and nylon 6, e.g., compatibilizers such as copolymers of styrene and maleic anhydride or PPO and nylon 6 have been reported.[17−19] It is of interest how heteroarm star-shaped block copolymers diverged from a core act as a compatibilizer. However, there have been few reports on compatibilizing effects of such star-shaped copolymers on the immiscible blends.[20−25]

In this paper, we report the preparation of (i) hexaarmed star-shaped nylon 6 with cyclophosphazene core and (ii) heteroarm star-shaped block copolymers via a partial coupling reaction of terminal activated polystyrenes with the acid chloride of hexakis(4-carboxyphenoxy)cyclotriphosphazene, followed by the polymerization of ϵ-CL with a residual carboxyl group on the phosphazene ring, and (iii) compatibilizing abilities of these block copolymers on a typical immiscible blend, PPO and nylon 6.

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Experimental Section

Materials. Hexachlorocyclotriphosphazene was kindly supplied from Nihon Seika Co. Ltd. and purified by recrystallization from *n*-hexane. Aminoethane thiol, 4-hydroxybenzoic acid ethyl ester, and ϵ-CL were used as received. Poly(2,6-dimethylphenylene oxide) ($M_n = 26\,000$) and nylon 6 ($M_n = 15\,000$) were used as received. *sec*-BuLi as a 1.05 M solution in cyclohexane was purchaed from Kanto Chemical Co. Ltd. Styrene was distilled from CaH_2 before use. For the ionic polymerization, styrene was vacuum distilled immediately prior to polymerization and THF was refluxed on sodium and distilled finally through a vacuum line from sodium benzophenone.

Preparation of 2. To a stirred solution of hexachlorocyclotriphosphazene (20 g, 0.058 mol) in dry benzene was added a solution of 4-hydroxybenzoic acid ethyl ester (66.9 g, 0.4 mol) and triethylamine (58 g, 0.58 mol) in dry benzene at room temperature. After being stirred for 25 h, the resulting amine hydrochloride was filtered off, and then the solvent was removed under reduced pressure. Hexakis(4-ethoxycarbonylphenoxy)cyclotriphosphazene (**1**) was purified by recrystallization from methanol and then hydrolyzed with NaOH in aqueous methanol. The reaction mixture was poured into a large excess of water. After filtration, the mixture was acidified with 2 N HCl. The precipitated white solid was collected and washed with water.

1: yield, 86%, mp 91 °C. IR (KBr) 1720, 1600, 1490, 1450, 1200−1150 cm^{-1}. ^1H NMR ($CDCl_3$, TMS) δ 6.7−7.9 (m, 24H, arom H), 4.3 (q, 12H, $-CH_2-$), 1.3 (t, 18H, $-CH_3$). ^{31}P NMR (DMSO-d_6, H_3PO_4) δ 7.7. Anal. Calcd for $C_{54}H_{54}N_3O_{18}P_3$: C, 57.60, H, 4.83; N, 3.73%. Found: C, 57.86; H, 4.88; N, 3.73%.

2: yield, 83%. mp > 280 °C. IR (KBr) 1690, 1600, 1450, 1240−1150 cm^{-1}. ^1H NMR (DMSO-d_6, TMS) δ 9.8−10.8 (brs, 6H, −OH), 6.9−7.8 (m, 24H, arom H). ^{13}C NMR (DMSO-d_6, TMS) δ 165.5, 152.5, 130.5, 128.0, 119.8. ^{31}P NMR (DMSO-d_6, H_3PO_4) δ 8.7. Anal. Calcd for $C_{42}H_{30}N_3O_{18}P_3$: C, 52.66; H, 3.13; N, 4.39. Found: C, 52.64; H, 3.11; N, 4.51.

Preparation of Acid Chloride (4). Thionyl chloride (30 mL) was added to **2** (1.17 g, 1.22 mmol), the mixture was refluxed for 1.5 h, and then excess thionyl chloride was removed by distillation. The residue was washed with dry *n*-hexane, and the organic layer was removed under dry nitrogen. The acid chloride dissolved in dry THF was filtered under nitrogen and then recrystallized from THF. **4**: yield, 80%, mp 193 °C. IR ($CHCl_3$) 1780, 1750, 1600, 1250−1120 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.1−8.0 (m, arom H). ^{13}C NMR ($CDCl_3$) δ 166.9, 155.1, 133.3, 130.8, 121.0. ^{31}P NMR ($CDCl_3$, H_3PO_4) δ 6.7.

Preparation of Polystyrene with Cyclophosphazene Core. The polystyrene with phosphazene core was prepared by a coupling reaction of terminally activated polystyrenes, which were prepared by radical and anion polymerizations, with acid chloride **4**.

A typical procedure of coupling reaction of polystyrene with terminal amino group (PSt−NH_2) with **4** is as follows: In a three-necked flask, styrene (20 g, 0.19 mol), aminoethanethiol (1.5 g, 0.19 mmol), and AIBN (0.16 g, 0.97 mmol) in THF (100 mL) were placed. The mixture was stirred at 60 °C for 24 h under a nitrogen atmosphere and then poured into large amounts of methanol. The polymers with relatively low molecular weights were removed by fractional reprecipitation from THF to methanol. The number average molecular weight of the polymer obtained was M_n 10 700 ($M_w/M_n = 1.9$). The number (n) of the terminal amino group per polystyrene chain, determined by potentiometric titration of polymer solution with a 0.02 N perchloric acid−DMF solution, was $n = 0.7$. Similarly, the following polystyrenes with terminal NH_2 group were prepared by changing the concentration of aminoethanethiol: $M_n = 22\,600$ ($M_w/M_n = 2.0$; $n = 0.6$) and $M_n = 8400$ ($M_w/M_n = 2.2$; $n = 0.7$).

A solution of polystyrene with $M_n = 10\,700$ (PSt−NH_2 content, 70%; 24 g, 1.66 mol) and triethylamine (0.72 g, 7.1 mmol) in dry THF (100 mL) was added to a stirred solution of **4** (0.76 g, 0.71 mmol) in dry THF (100 mL) at room temperature and refluxed for 5 h. After hydrolysis, the reaction mixture was poured into large amounts of methanol to precipitate polystyrene with carboxyphenoxycyclotriphosphazene (**5b**). The polymer was purified by reprecipitation from THF to methanol.

For the coupling reaction of poly(styryllithium) with **4**, all operations were carried out under a high-vacuum system and all reagents were added via breakseals. The poly(styryllithium) formed by living polymerization of styrene (6.9 mL, 60 mmol) with *sec*-BuLi in THF at −78 °C was added to a vigorously stirred solution of **4** (0.075 g, 0.07 mol) in THF. The polymer (**7**) precipitated by pouring into large amounts of aqueous methanol containing 1 wt % of NaOH was washed with 1 N HCl, water, and MeOH and purified by reprecipitation from THF to methanol. Details of the preparation of **7** will be reported elsewhere.[26] The contents of carboxyphenoxycyclotriphosphazene units in polystyrenes were determined by the titration with potassium methoxide using thymol blue as indicator in dry pyridine.

Polymerization of ϵ-CL with 2. A typical procedure for the polymerization of ϵ-CL with **2** is as follows: **2** (0.12 g, 0.13 mmol) and ϵ-CL (4.8 g, 42 mmol) were placed into a glass ampule. The ampule was evacuated at 2.6 Pa and then flame sealed. The ampule was placed in an oven maintained at 250 °C for a definite time. After cooling, the ampule was opened, and then the polymer was cracked and ground. The ground polymer was extracted by a Soxhlet extractor with water and then dried in a vacuum at 80 °C.

Polymerization of ϵ-CL with 5 and 7. **5** (0.1 g, 0.11 mmol) and ϵ-CL (4.8 g, 42 mmol) were placed in ampules. The ampules were degassed under vacuum and sealed off. Then the polymerization was carried out in an oven maintained at 230 and 250 °C. The copolymer obtained was poured into water. Similarly, the polymerization of ϵ-CL with **7** was carried out.

Blend. Blend polymers were prepared by coprecipitation of the mixture of the components from dilute solution. For the SEM measurement, these blends were compressed into a pellet at 250 °C. The pellet was fractured at liquid nitrogen temperature, and the fracture was treated with chloroform at room temperature. The surface was coated with gold and observed with a Hitachi S-510 scanning electron microscope.

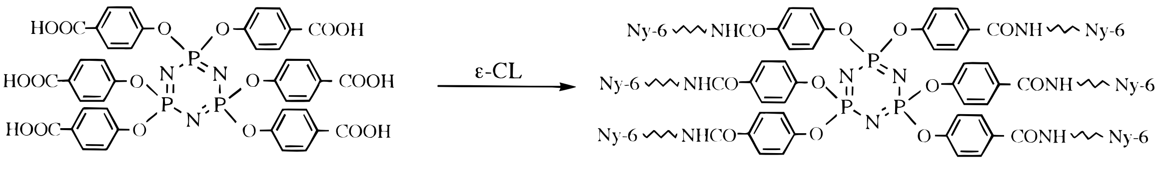
Mechanical Properties. Dumbbells (gage length, 10 mm; width, 4 mm; thickness, 2 mm; radius of curvature, 60 mm) composed of PPO, nylon 6, and star-shaped copolymer **8a** were molded at 270 °C by a handmade instrument. The specimens were immersed in water for 24 h so as to attain a constant content of water. The tensile tests were performed with a Shimadzu AG-2000E at the extension rate of 5 mm/min at room temperature. Particular care was paid to the alignment of grips and specimen to achieve uniaxial elongation. The tests were run in duplicate. If the difference of the values was over 10%, a reexamination was carried out.

Measurement. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL GSX 270 NMR spectrometer. FT-IR spectra were recorded with a Nihon Bunko spectrometer. Gel permeation chromatography (GPC) was performed on a Nihon Bunko PU-880 instrument equipped with Tosoh TSKgel G3000H and G4000H columns, using THF or toluene/hexafluoroisopropyl alcohol as the eluent. The columns were calibrated with polystyrene standards. Glass transition temperatures were recorded with a Shimadzu DSC-50 differential scanning calorimeter. Samples were first heated to 230 °C, cooled to room temperature, and then reheated at a heating rate of 10 °C/min. The second run was accepted. The T_g value was taken as the midpoint temperature of the baseline shift during the transition. Inherent viscosity was measured in an Ubbelohde type viscosimeter at 30 °C at a concentration of 0.25 g of polymer in 100 mL of 60/40 phenol−tetrachloroethane mixture.

Results and Discussion

Preparation of Hexaarmed Nylon 6. The reaction of hexachlorocyclotriphosphazene with 4-hydroxybenzoic acid ethyl ester afforded totally substituted cyclophosphazene (**1**) which was then hydrolyzed with NaOH to the corresponding carboxylic acid (**2**). Allcock et al.[27]

Scheme 1. Polymerization of ϵ-CL with 2



2 **3**

Table 1. Preparation of Star-Shaped Nylon-6 with Phosphazene Core (3)

					$10^{-3}M_n$					
[**2**] (mmol)	ϵ-CL (mmol)	temp (°C)	time (h)	conversion (%)	NMR	GPC	M_w/M_n	T_m (°C)	T_g (°C)	η^a (dL/g)
0.11	18.5	230	88	55.4	12.1	10.3 (11.7)^b	2.0	215	39	0.41
0.11	42.4	230	96	28.3	13.6	11.2 (13.7)	1.9	213	42	0.48
0.10	17.7	250	23	45.0	11.2	8.3 (9.3)	1.7	212	37	0.37
0.31	47.2	250	15	31.3	6.3	5.5 (6.3)	1.5	205	30	0.20

[a] Measured with $C = 0.25$ g/dL at 30 °C in 60/40 phenol−tetrachloroethane. [b] The values in parentheses are calculated from the ratio of [ϵ-CL]/[**2**] and conversion.

have shown that the hydrolysis of ester with NaOH was accompanied by unfavorable decomposition of the phosphazene ring. However, our results showed that no significant decomposition was observed under the conditions we describe.

The initiation and propagation of ϵ-CL with carboxylic acids have been demonstrated to occur via a monomer-activated mechanism due to the interaction between carboxylic acid and amide.[28] We first examined whether **2** acts as initiator for the ring-opening polymerization of ϵ-CL (Scheme 1). The polymerization was carried out using various ratios of [ϵ-CL]/[**2**] at 230 and 250 °C. The polymerization results and characteristics of nylon **6** with phosphazene core (**3**) are summarized in Table 1. The molecular weights of **3** measured by ^{1}H NMR spectra and GPC are essentially consistent with the values calculated from initial ratios and conversions. This implies that only the carboxyl group in **2** participates in the initiation process. As expected, the phosphazene ring remained intact without suffering ring rupture during the polymerization, as evidenced by FT-IR spectra of polymers that exhibited a characteristic $-P{=}N-$ stretching absorption between 1250 and 1160 cm^{-1}.

^{13}C NMR spectra of **3** are very useful for the confirmation of the formation of hexaarmed polymers. As shown in Figure 1, **3** with $M_n = 1750$ obtained at [ϵ-CL]/[**2**] = 60 and 13% conversion exhibited a peak at 130.5 ppm which is assignable to the ortho carbon of an unreacted carboxyl group in **2**, but the peak was not observed for the **3** with $M_n = 3800$ that was obtained at the same ratio and 42% conversion. These spectroscopic data indicate that all carboxylic acid in **2** could initiate the polymerization of ϵ-CL, although some of carboxyl groups initiate the polymerization with delay.

One of characteristic features of star-shaped polymers is that intrinsic viscosities are considerably lower than those of linear polymers since the former take a spherical structure. In fact, the intrinsic viscosity of **3** with $M_n = 11\,200$ in 60/40 phenol−tetrachloroethane at 30 °C with 0.48 dL/g, which was roughly one-half the value of the linear nylon 6 with almost the same molecular weight ([η] = 1.1 dL/g, $M_n = 13\,000$). Such a decrease in viscosity has also been reported for hexaarmed and octaarmed nylon 6.[15]

Preparation of Heteroarm Star-Shaped Block Copolymers. The heteroarm star-shaped block copolymers composed of polystyrene and nylon 6 chains diverged from the phosphazene core were prepared as shown in Scheme 2. The processes consist of the reaction of **4** with polystyrene having a reactive group at the polymer end, hydrolysis of residual acid chloride, and the ring-opening polymerization of ϵ-CL by carboxylic acids on the phosphazene ring. Polystyrenes were prepared by radical and living anion polymerizations. For the radical polymerization, polystyrenes were synthesized in the presence of aminoethanethiol. This procedure is known to give a telechelic polystyrene with terminal NH_2 group (PSt−NH_2).[29]

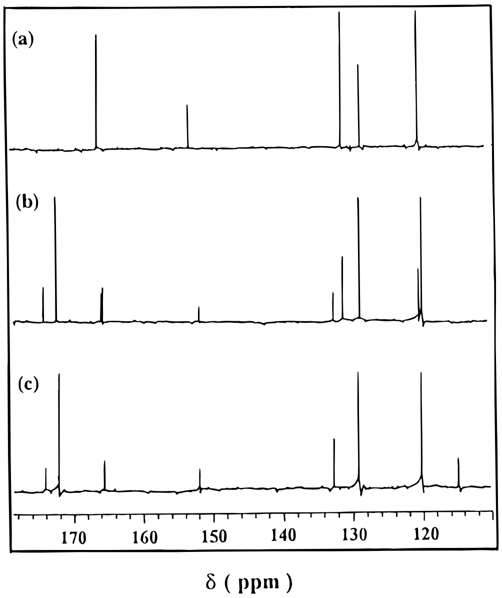
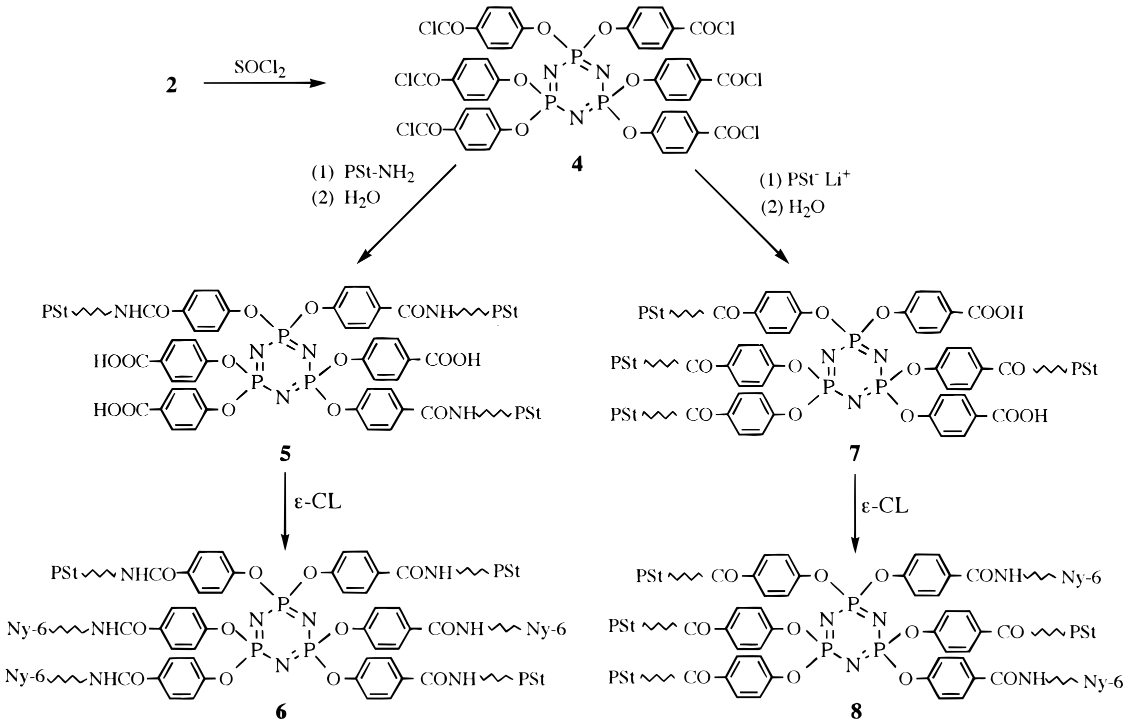


Figure 1. ^{13}C NMR spectra of hexaarmed nylon 6 with phosphazene core (a) **2**, (b) **3** with $M_n = 1750$, and (c) **3** with $M_n = 3800$.

Although the molecular weights of PSt−NH_2 were controlled by varying the amount of aminoethanethiol, the polydispersity of molecular weights was considerably large ($M_w/M_n = 2.5{-}3.0$). Since the polystyrenes with low molecular weights are unsuitable for the preparation of star-shaped polymers, they were removed by fractional precipitations, and the polymers with $M_w/M_n < 2.2$ were used for the coupling reaction. Figure 2A showed typical GPC curves for the coupling reaction of **4** with PSt−NH_2 ($M_n = 107\,000$). The molecular weights shifted to a high molecular weight region with reaction time, together with a broad distribution of molecular weights.

Scheme 2. Preparation of Heteroarm Star-Shaped Block Copolymers



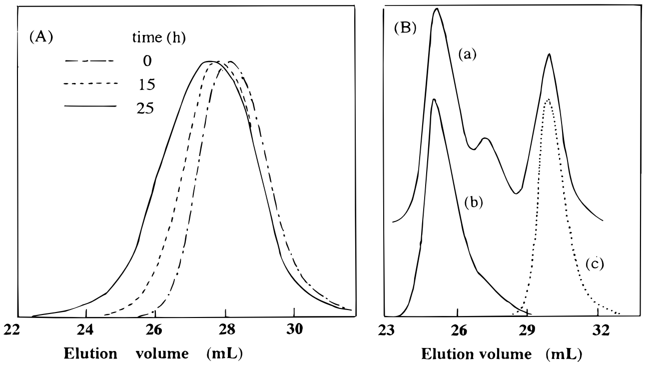


Figure 2. Change of molecular weight distribution for the coupling reaction of **4** with PSt−NH$_2$ (A) and poly(styryllithium) (B): (a) polystyrene terminated with **4**; (b) polystyrene obtained from fractional precipitation of the polymer (a); (c) polystyrene terminated with methanol.

It seems that the ratio of the molecular weight of the polymer formed (**5b**, M_n = 18 600) to the original one is a rough measure of the displacement of acid chloride with PSt−NH$_2$, i.e., ca. two acid chlorides in **4** were displaced by PSt−NH$_2$. However, the titration of the carboxyl group in the polymer **5b** showed a different result; that is, the displacement occurs much better than the values estimated from the shift of molecular weights (Table 2). This discrepancy might be due to the predominant attachment of a relatively low molecular weight PSt−NH$_2$, which could not contribute to the apparent increase in the molecular weights. Similarly, polystyrenes with carboxyphenoxycyclotriphosphazene, **5a** (M_n = 11 700 and number of carboxyl group (x) x = 1.3), **5c** (M_n = 29 000 and x = 3.8) and **5d** (M_n = 29 400 and x = 3.6) were prepared from the coupling reaction of **4** and PSt−NH$_2$ with M_n = 8400 and M_n = 22 600, respectively. It seems that the degree of displacement of acid chloride with PSt−NH$_2$ has a tendency to decrease with increasing the molecular weights of PSt−NH$_2$.

The polymer with carboxyphenoxycyclotriphosphazene was also prepared by the end-capping of living polystyrene anion by **4**. For the living polymerization of styrene (55 mmol) with *sec*-BuLi (0.1 mmol) and [*sec*-BuLi]/[**4**] = 0.67, GPC curves of the resulting polymer showed four peaks as shown in Figure 2B. From the comparison of the molecular weights of these polymers with that of polystyrene terminated by degassed methanol (M_n = 54 800), it seems that the first elution peak having the largest peak area corresponds to the polymer with four or more polystyrene chains on the cyclophosphazene core (**7a**, M_n = 268 200). In fact, the titration of carboxyl group of the polymer with high molecular weight (Figure 2B.b) separated by fractional precipitation from THF to methanol showed that the 1.7 carboxyl groups were present in the polymer **7a**, i.e., ca. 70% of acid chloride on the phosphazene ring was replaced with living polystyrenes. Similarly, the polymer **7b** with M_n = 154 500 and 1.9 carboxyl groups on the phosphazene ring was prepared.

The ring-opening polymerization of ε-CL with **5** and **7** was carried out at 250 °C (Table 2). It should be noted that these polymers are stable at 250 °C under a nitrogen atmosphere. The heteroarm star-shaped block copolymers with low molecular weights of nylon 6 units are partially soluble in THF, but most of copolymers prepared are still insoluble in benzene, dioxane, and THF. The GPC traces of the copolymers exhibited a relatively broad peak at the high molecular weight region, compared to those of the original polymers. The increases in molecular weights and the ratios of polystyrene to nylon 6 units attached to the phosphazene ring, determined by GPC and ^{1}H NMR spectra, respectively, are essentially consistent with the values calculated from the molecular weights of PSt−NH$_2$, initial ratio of [ε-CL]/[polymer], and conversion. IR spectra of copolymers **6** and **8** obtained showed peaks at 1640, 1600, and 1250 cm^{-1}. These results suggest that ε-CL is polymerized by the residual carboxyl group on the phosphazene ring giving rise to heteroarm star-shaped copolymers.

Table 2. Polymerization of ϵ-CL with 5 and 7[a]

polymer (**5** and **7**)[b]							heteroarmed star-shaped block copolymer (**6** and **8**)				
							PSt/Ny-6		10^{-4} Mn		
	10^{-4} M_n	no. of −COOH[c]	ϵ-CL [mol]	[ϵ-CL] [polymer][b]	time (h)	convn (%)	obs[d]	calc	obs[e]	calc	
5a	1.17	1.3	0.028	135	30	45.0	1.4	1.7	3.6	1.9	**6a**
			0.045	273	30	21.2	1.5	1.8	2.9	1.8	**6b**
5b	1.86	2.1	0.062	590	30	25.6	1.0	1.1	3.1	3.6	**6c**
5c	2.90	3.8	0.127	1200	36	34.4	0.4	0.6	6.6	7.6	**6d**
5d	2.94	3.6	0.172	705	31	35.9	1.3	1.0	4.7	5.8	**6e**
7a	26.82	1.7	0.018	3000	70	30.3	1.9	2.6		32.1	**8a**
7b	15.45	1.9	0.027	4500	45	10.4	3.4	3.7		20.7	**8b**

[a] At 250 °C. [b] Polystyrene with carboxyphenoxycyclotriphosphazene. [c] Number of COOH group in the phosphazene ring. [d] Determined by ^{1}H NMR spectra. [e] Determined by GPC measurement.

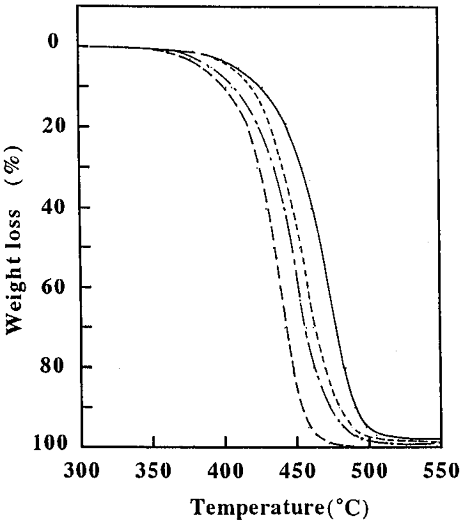


Figure 3. Thermogravimetric analysis of heteroarm star-shaped block copolymer (—) nylon 6, (- - -) **6d**, (- · -) **6e**, and (— —) polystyrene.

Effects of 6 and 8 on the Blend of PPO/Nylon 6.

The thermal properties of synthesized polymers were first investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis. The glass transition temperatures of **3** were in the temperature range 42−30 °C, which were somewhat lower than that of linear nylon 6 (T_g = 40−52 °C).[30] For the heteroatom star-shaped block copolymer **6e**, two glass transition temperatures of nylon 6 and PSt units were observed at 43 and 100 °C, respectively. Thermogravimetric analysis showed that the onset temperatures of decomposition of **6d** and **6e** were 380 and 362 °C, respectively, indicating that the thermal stability decreased with increasing the content of polystyrene (Figure 3).

It is well recognized that the copolymers with long blocks act as effective compatibilizers to the immiscible blend. However, the copolymers with more than suitable molecular weights have a tendency to associate into micelles in the bulk of the blend. It is of high interest to determine how star-shaped block copolymers act as a compatibilizer of immiscible blends, PPO and nylon 6. The heteroarm star-shaped block copolymer **6e**, prepared by the combination of radical and ring-opening polymerization, and **8a**, prepared via ionic polymerization of styrene and ring-opening polymerization, was used as compatibilizers.

To ascertain whether polystyrene chains on the phosphazene ring are located at the interface, the differential scanning calorimetry of PPO/**8a** binary blend was measured. It is well-known that over a considerable range of molecular weights polystyrene and PPO are miscible in all proportions.[31−33] As shown in Figure 4, **8a** exhibits a glass transition temperature of polystyrene units at 95 °C and a melting temperature of nylon 6 units at 220 °C. Since the T_g of PPO is very close to the T_m of nylon 6, it is difficult to distinctly observe two endothermic transitions at less than 5 wt % of **8a**. However, for the blends with more than 10 wt % of **8a**, apparent shifts of T_g of PPO to lower temperatures were observed, and the T_g values decreased with increasing the amount of **8a**. For all the blends only a single T_g was observed, indicating that **8a** is miscible with PPO in the entire composition range. It can be seen from Figure 5 that the degree of lowering of T_g was affected by the polystyrene units in **6** and **8**. The T_g values of PPO/**6e** are lower than those of PPO/**6d**, suggesting that the effective penetration of polystyrene chains into the PPO domain is operative for the former blend. For these copolymers the number and chain length of polystyrene attached to the phosphazene ring are almost the same as each other, but the ratio of PSt to nylon 6 in **6e** is higher than that of **6d**. In addition, the most effective lowering in T_g was observed for PPO/**8a**. These results suggest that the relatively high PSt/nylon 6 ratio and long polystyrene units is a requisite for the achievement of sufficient miscibility.

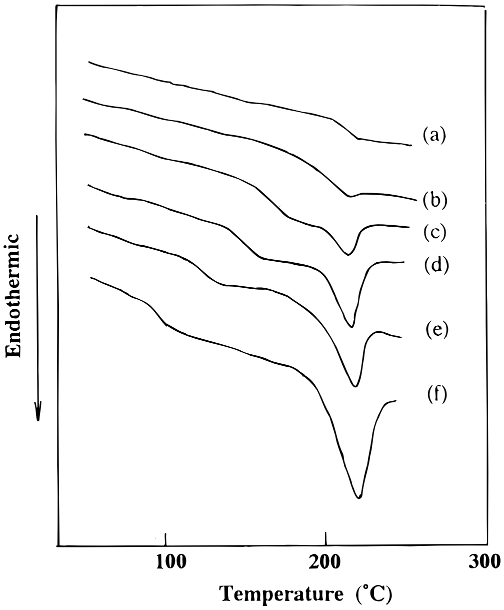


Figure 4. DSC profiles of PPO/**8a** blend: (a) 100/0; (b) 90/10; (c) 70/30; (d) 50/50; (e) 30/70; (f) 0/100.

For the ternary blend, 45/45/10 PPO/nylon 6/**8a**, DSC thermograms showed a single glass transition temperature at 195 °C, which corresponds to the phase composed of PPO and polystyrene units in **8a**. As shown in Figure 7, the scanning electron microscopy of a fractured surface of the binary blend of polymer

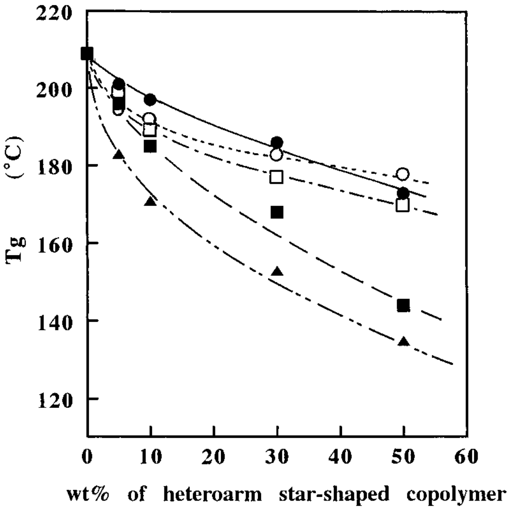


Figure 5. Composition dependence of T_g: (○) **6a**; (●) **6c**; (□) **6d**; (■) **6e**; (▲) **8a**.

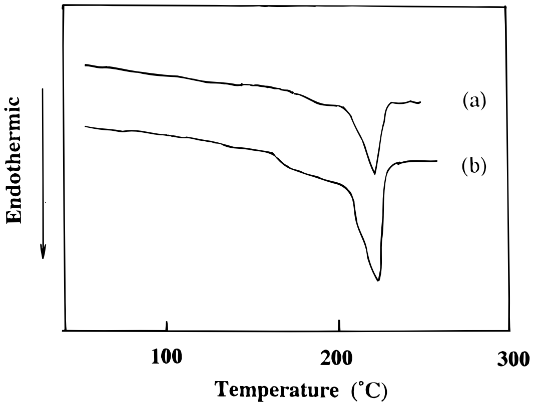


Figure 6. DSC profiles of ternary blend. PPO/nylon 6/**8a**: (a) 45/45/10; (b) 40/40/20.

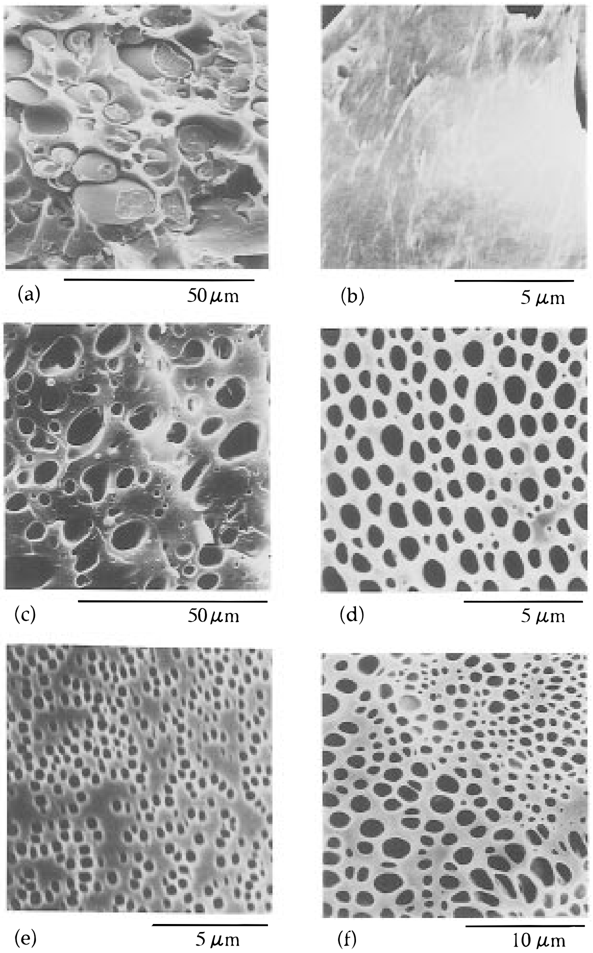


Figure 7. SEM photographs of PPO/nylon 6/heteroarm star-shaped copolymer blends: (a) 50/50 PPO/nylon 6; (b) 45/45/10 PPO/nylon 6/**8a**. For (c) and (d), the surface was etched with chloroform. (c) 50/50 PPO/nylon 6; (d) 48/48/4 PPO/nylon 6/**8a**; (e) 45/45/10 PPO/nylon 6/**8a**; (f) 45/45/10 PPO/nylon 6/**6e**.

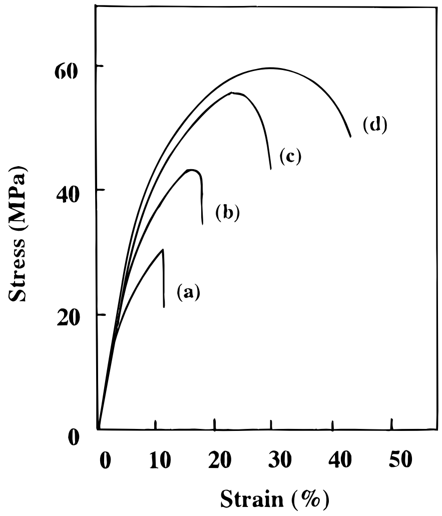


Figure 8. Stress–strain curves of 50/50 PPO/nylon 6. **8a**: (a) 0; (b) 1; (c) 5; (d) 10 wt %.

prepared at liquid nitrogen temperature indicates a lack of interfacial adhesion. For the ternary blend, PPO/nylon 6/**8a**, the fracture is smooth, indicating that a specimen containing 10 wt % of **8a** exhibits a tough fracture. Figure 7d showed the surface of 48/48/4 nylon 6/PPO/**8a** blend etched with chloroform to facilitate observation of the PPO size. The domains are clearly smaller than in the blend without heteroarm star-shaped copolymers, having an average size near 0.8 μm. Further addition of **8a** exhibited a more regular and finer dispersion of PPO with an average size of 0.3 μm (Figure 7e). When 10 wt % of **6e** carrying polystyrene prepared by radical polymerization was used, the average size of PPO is considerably large (average size 1.5 μm) as compared with that of **8a**, indicating that **6e** acts as compatibilizer but its compatibilizing ability is somewhat lower than that of **8a**, probably due to the short polystyrene chains. These results are in agreement with the general observation, i.e., the longer the blocks are, the better the compatibilizing effects. Thus, star-shaped copolymers composed of polystyrene with high molecular weights and nylon 6 with relatively low molecular weights acts as an effective compatibilizer for immiscible blend of PPO and nylon 6.

Even though block copolymers are an efficient dispersing agent for polymer blends, it is often observed that the mechanical phase adhesion is slightly improved, probably due to the lack of sufficient interpenetration of segments of the block of the copolymers and blend components.[34,35] Comparative experiments on mechanical properties were carried out between a simple binary blend and ternary blends containing 1, 5, and 10 wt % of **8a**. As shown in Figure 8, the addition of **8a** gives higher modulus, strength, and elongation, as well as showing yield behavior. These improvements are due to the increase of adhesion at the PPO/nylon 6 interface by the copolymer. That is, the star-shaped copolymer properly locates at the interface, and the effective penetration of each block sequence of the copolymer into the blend components is operative; in other words, polystyrene chains diverged from the phosphazene core penetrate and spread into PPO domains. A similar situation might be operative between nylon 6 attached to the phosphazene core and nylon 6 of blend components. The heteroarm star-shaped copolymers prepared in this study have not been optimized as the compatibilizer of PPO and nylon 6 blends, but their beneficial effects on PPO/nylon 6 blends are obvious.

In summary, the carboxyl group in the **2** initiates the ring-opening polymerization of ϵ-CL to give hexaarmed nylon 6 with phosphazene core. When polystyrenes with carboxyphenoxycyclotriphosphazene was used as an initiator, the polymerization of ϵ-CL also proceeded to give heteroarm star-shaped copolymers. These copolymers act as the compatibilizer of immiscible blend PPO/nylon 6, especially copolymers with high molecular weight polystyrene units (**8a**), where PPO disperses regularly and finely with 0.3 μm size in the nylon domain. Reflecting this, the modulus, tensile strength, and elongation at the break were improved. These results indicate that each block sequence of **8a** penetrates efficiently into the blend components. Thus, new design of heteroarm star-shaped block copolymers functions efficiently as a compatibilizer of immiscible blends. Further studies of new star-shaped compatibilizers are now in progress.

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