

Preparation and Properties of Graft and Block Copolymers of Poly(*p*-phenylene Terephthalamide) with Polybutadiene

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Synopsis

Graft copolymers of polybutadiene (PBD) onto poly(*p*-phenylene terephthalamide) (PPTA) were prepared by the nucleophilic substitution of *N*-metalated PPTA with telechelic PBD having bromide end groups. Block copolymers were synthesized by the condensation reaction of telechelic PBD having acid chloride end groups with amino-group-terminated PPTA. The structure of these copolymers was identified by IR spectra. Graft and block copolymers contained PBD segments up to 85 wt % and 45 wt %, respectively. Thermomechanical analyses (TMA) proved the existence of distinctive primary absorption peak corresponding with T_g of PBD for both graft and block copolymers. The T_g 's of both types of the copolymers were further ascertained by the DSC curves. TMA curves suggested that the microphase separation occurred between PPTA and PBD. The incorporation of PPTA segments into PBD increased the decomposition temperature compared with the blend polymer composed of PPTA and PBD with the same composition.

INTRODUCTION

Graft and block copolymerizations are generally useful to improve mechanical, chemical, and thermal properties of the original homopolymers. If the individual polymer segments in copolymers have opposite properties such as polar and nonpolar and/or flexible and rigid natures, many interesting properties are conceivable.

Poly(*p*-phenylene terephthalamide) (PPTA) provides fibers with ultrahigh modulus/high tensile strength and good thermal stability owing to its molecular rigidity.^{1,2} Therefore, PPTA copolymer with flexible molecules is interesting in its forming a new type of composite, which corresponds to the extension of the chopped-fiber-reinforced composite to the molecular level.³

Graft copolymerization onto aliphatic polyamide has been widely investigated by using anionic or radical initiated reaction.⁴⁻⁹ Kashani et al.¹⁰ reported graft copolymerization of acrylonitrile onto poly(*m*-phenylene isophthalamide) by anionic initiation. This is the first successful example of graft copolymerization onto aramid. On the other hand, chemical modification of *p*-oriented aramid was limited owing to its difficulty in dissolution. Recently, Takayanagi and Katayose¹¹ succeeded in synthesis of *N*-substituted PPTAs via metalation of PPTA with sodium hydride in dimethylsulfoxide (DMSO), being followed by reaction with alkyl or aralkyl halides.

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TABLE I
 The Preparation Conditions and Composition of PPTA-*g*-PBD

Code	M_w of PPTA	NaH ^a (mmol)	Br (PBD) ^a (g)	Grafting (%)	PBD conv. (%)	Elemental analysis found (%)		
						C	H	N
G-1	4900	30.0	23.65	567	67	81.59	9.68	1.77
G-2	4900	30.0	15.92	335	61	80.35	9.15	2.66
G-3	4900	30.0	3.61	104	78	73.35	7.43	6.08
G-4	4900	30.0	0.60	15	72	68.65	5.32	10.06
G-5	4900	24.5	15.92	233	44	76.17	8.24	3.49
G-6	4900	15.0	15.92	110	21	79.81	7.49	3.04
G-7	21900	30.0	23.65	283	36	85.27	9.93	5.62
G-8	36400	30.0	23.65	194	26	74.24	7.88	4.02

^a 2.98 g of PPTA was employed.

Block copolymerization of polyamide has been studied by condensation reaction of component prepolymers having reactive functional groups at their chain ends. This technique was applied to prepare PPTA-*b*-nylon 6 and 66.³

In this paper, polybutadiene (PBD) is selected as polymer chain to graft- and block-copolymerization with PPTA. The synthesis, characterization, and physical properties of the graft and block copolymers of PPTA and PBD are reported.

EXPERIMENTAL

Materials. The PPTA samples were prepared by low temperature polycondensation of terephthaloyl chloride and *p*-phenylenediamine in a mixed solvent of hexamethylphosphoramide (HMPA) and *N*-methylpyrrolidone (NMP).¹² The amino-group-terminated PPTA was prepared by polycondensation of terephthaloyl chloride with excess molar amount of *p*-phenylenediamine. Molecular weights of PPTA samples were determined by measuring intrinsic viscosity at 303 K in 97% sulfuric acid,¹³ which were 1300, 4900, 21,900, and 36,400.

Bromine-terminated PBD sample was DBBD manufactured by the Polymer Corp. The number-average molecular weight was 2900, determined by vapor pressure osmometry. The microstructure of DBBD was composed of 20% of *cis*-1,4, 60% of *trans*-1,4, and 20% of 1,2-vinyl groups.

Acid chloride terminated PBD was prepared by chlorination reaction of carboxylic-acid-terminated PBD (JSR CTPB, Japan Synthetic Rubber Co., Ltd.) with thionyl chloride.¹⁴ The number-average molecular weight of this sample was 4600, determined by vapor pressure osmometry. The microstructure of CTPB was composed of 18% of *cis*-1,4, 30% of *trans*-1,4, and 52% of vinyl groups.

HMPA, NMP, and DMSO were fractionally distilled at reduced pressure after drying over calcium hydride. Benzene was purified by distillation over calcium hydride. All the purified solvents were stored over molecular sieves under nitrogen atmosphere. Sodium hydride as a metalation agent was commercially obtained.

Graft Copolymerization. The following procedure is a typical one for preparation of *N*-grafted copolymers of PPTA, which was denoted by G-1-8 in Table I.

TABLE II
The Preparation Conditions and Composition of PPTA-*b*-PBD

Code	M_w of PPTA	PBD ^a (g)	PPTA- <i>b</i> -PBD PPTA/PBD (wt ratio)	Elemental analysis found (%)		
				C	H	N
B-1	4900	20.7	55/45	63.59	6.40	5.66
B-2	4900	2.3	69/31	69.11	6.15	8.11
B-3	4900	0.9	81/19	67.77	5.65	9.82
B-4	4900	0.3	96/4	65.53	4.67	10.85
B-5	1300	20.7	38/62	70.32	7.95	3.63

^a 2.30 g of PPTA was employed.

In a 500-mL three-necked separable flask, equipped with a nitrogen gas inlet, dropping funnel, and mechanical stirrer, were placed 1.44 g (30 mmol) of sodium hydride (50 wt % in mineral oil), 2.98 g (25 m equivalent of amide unit) of PPTA, and 100 mL of DMSO under nitrogen atmosphere. The reaction mixture was heated to 323 K and kept for 2 h, with which a red homogeneous solution of *N*-metalated PPTA was obtained. To the well-stirred solution of metalated PPTA in DMSO, a solution 15.92 g of bromine-terminated PBD dissolved in 200 mL benzene was added dropwise for 30 min at 300 K. The system became turbid and the stirring was continued further for 4 h. The reaction product was recovered by pouring it in a large amount of methanol. The reaction mixture was extracted by benzene to remove unreacted PBD until the extracts did not show any turbidity with excess of methanol. After the isolated polymer was dried at 323 K for 48 h *in vacuo*, a brown rubbery solid product was obtained in a yield of 9.98 g (percentage of grafting is 335%).

Block Copolymerization. The following procedure is typical for preparation of block copolymer denoted by B-1–5 in Table II.

In a 300-mL three-necked separable flask equipped with mechanical stirrer and nitrogen gas inlet, 11.90 g (110 mmol) of *p*-phenylenediamine was dissolved in a mixed solvent of 140 mL of HMPA and 60 mL of NMP and stirred while being cooled in an ice bath. To the well-stirred cooled solution, 20.30 g (100 mmol) of powdered terephthaloyl chloride was added. After 4 h, 0.1 of polymer solution which contained 2.30 g of amino-terminated PPTA (97% yield, $[\eta] = 0.85$, $M_w = 4900$) was transferred to another 200 mL of three-necked separable flask equipped with dropping funnel, mechanical stirrer, and nitrogen gas inlet. Then 12.5 g of acid-chloride-terminated PBD dissolved in 50 mL of benzene was added to the amino-terminated PPTA solution with vigorous stirring at 300 K under nitrogen atmosphere. The stirring was further continued for 4 h. The procedures for isolation and extraction were similar to those described in graft copolymerization. The isolated product was dried, which was 4.28 g of block copolymer.

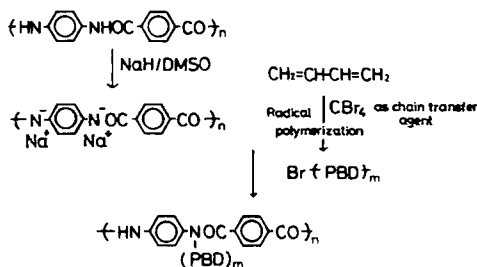
Characterization and Physical Properties. Infrared spectra of the copolymers were obtained with the KBr disk method by Perkin-Elmer Model 567.

Thermogravimetric (TGA) and differential thermal analyses (DTA) were performed by Shimadzu Model DT-30 at a heating rate of 10 K/min under air atmosphere. Differential scanning calorimetry (DSC) curves were obtained by using UNIX (Rigaku Denki Co.) at a heating rate of 10 K/min under nitrogen atmosphere.

Measurements of dynamic storage tensile modulus E' and $\tan \delta$ as a function of temperature were conducted by Rheovibron DDV-IIB (Toyo Baldwin Co., Ltd.) at 11 Hz under nitrogen atmosphere.

RESULTS AND DISCUSSION

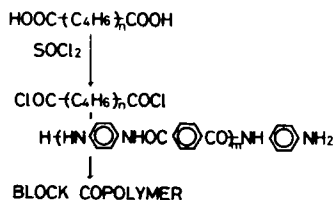
Copolymer Synthesis. The graft copolymers of PBD onto PPTA backbone were obtained by the nucleophilic substitution reaction of *N*-metalated PPTA with bromine-terminated PBD. The reaction scheme is shown in the following.



Scheme 1

Table I shows the effect of the reaction conditions on the percentage of grafting (PG) determined by nitrogen content in the copolymer and the increase in weight of the PPTA. With increasing the molar ratio of PBD to PPTA in the reaction system, PG increased. PG could be controlled by changing the degree of metalation of PPTA. Table I also shows the effect of molecular weight of PPTA on PG. Grafting reaction proceeded more easily when lower molecular weight of PPTA was reacted owing to an increase of its solubility in the reaction medium. Graft copolymerization was completed after 4-h lapse after addition of PBD. Figure 1 shows the relation between the weight fractions of PBD in the copolymer and the reaction system. The content of PBD in the graft copolymer increased linearly with the amount of PBD in the reaction system. *N*-sodium PPTA could not be substituted completely, owing to the steric hindrance with the bulky PBD segment at the grafting point. The conversion of PBD was 50–80%. Unreacted *N*-sodium PPTA with PBD was easily regenerated to its original PPTA by proton-donor solvent as the coagulant, such as alcohol or carboxylic acid.

The block copolymer of PPTA with PBD was synthesized by Shotten-Baumann reaction of amino-group-terminated PPTA with acid-chloride-group-terminated PBD prepolymers as shown in the following reaction scheme:



Scheme 2

Amino-group-terminated PPTA was prepared by using an excess molar ratio of *p*-phenylenediamine to terephthaloyl chloride. Therefore, the molecular weight of amino-group-terminated PPTA was not too high. The solution as the

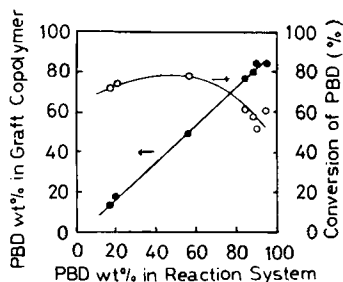


Fig. 1. Relation of the composition between graft copolymer and reaction system and relation between PBD conversion and the composition in reaction system (PPTA $M_w = 4900$).

polymerization was conducted was directly employed, since PPTA has poor solubility in organic solvents. Acid-chloride-terminated PBD was prepared by chlorination of carboxylic-acid-terminated PBD with thionyl chloride. This reaction was confirmed by IR spectra of the reacted polymers.¹⁴ C=O stretching vibration of carboxylic acid at 1712 cm^{-1} disappeared and that of acid chloride at 1800 cm^{-1} appeared after chlorination.

Table II shows the effect of the reaction conditions on the composition of the block copolymers. The content of PBD in the copolymer was determined by nitrogen content and the increase in weight of the starting PPTA. Figure 2 shows the relationship of the PBD compositions in the copolymer and in the reaction system. With increasing PBD content in the reaction system, the PBD content in the copolymer was also increased. When more than 70 wt % of PBD in the reactant was reacted, the content of PBD in the copolymer almost levels off to constant value.

Infrared Spectra. Figure 3 shows IR spectra of PPTA-*g*-PBD with the variation of PBD content. With increasing the content of PBD, characteristic absorptions of PBD segments were clearly observed at 2860 cm^{-1} and 2920 cm^{-1} (C—H stretch vibration), 1440 cm^{-1} (C—H scissoring vibration), 970 cm^{-1} (C—H *trans*-olefinic bending vibration), and 915 cm^{-1} (C—H vinyl olefinic bending vibration). These spectra support that PBD segments were grafted onto PPTA segment.

Figure 4 shows IR spectra of PPTA-*b*-PBD, in which the almost same characteristic absorptions as found in the graft copolymer were observed.

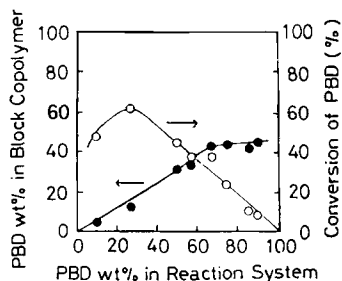


Fig. 2. Relation of the composition between block copolymer and reaction system and relation between PBD conversion and the composition in reaction system (PPTA $M_w = 4900$).

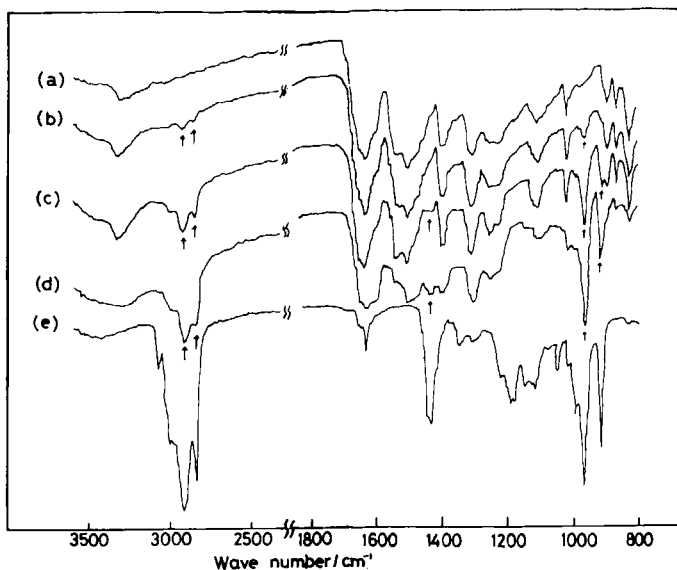


Figure 3. Infrared spectra of: (a) PPTA; (b) PPTA-*g*-PBD (PPTA/PBD = 87/13 by weight); (c) PPTA-*g*-PBD (PPTA/PBD = 55/45 by weight); (d) PPTA-*g*-PBD (PPTA/PBD = 23/77 by weight); (e) bromine-terminated PBD.

However, the absorption of C—H *cis*-olefinic bending vibration at 730–665 cm^{-1} was not clearly observed. The reason is attributed to its weak absorbance coefficient.¹⁵

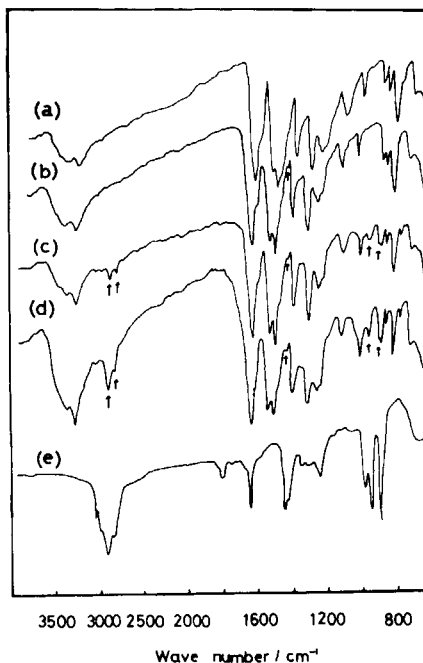


Fig. 4. Infrared spectra of: (a) PPTA; (b) PPTA-*b*-PBD (PPTA/PBD = 96/4 by weight); (c) PPTA-*b*-PBD (PPTA/PBD = 69/31 by weight); (d) PPTA-*b*-PBD (PPTA/PBD = 55/45 by weight); (e) acid-chloride-terminated PBD.

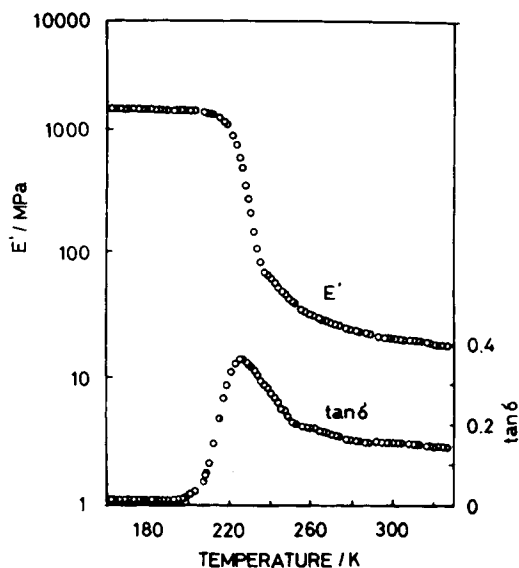


Fig. 5. Dynamic mechanical properties E' and $\tan \delta$ as a function of temperature for PPTA-*g*-PBD (PPTA $M_w = 4900$; PPTA/PBD = 15/85).

Solubility. The solubilities of both types of copolymers were surveyed. In the case of graft copolymers, only the samples of higher PBD content were soluble in NMP or HMPA. However, the degree of substitution at $-\text{NH}$ bond and the formation of intermolecular hydrogen bond of the PPTA backbone were depressed by the bulky substituent of PBD segments. The graft copolymer was decomposed in concentrated sulfuric acid and was insoluble in tetrahydrofuran as a good solvent for PBD. Samples of not highly grafted copolymer were partially soluble in NMP containing 5 wt % of lithium chloride, and their solubility was increased with increasing PG.

The solubility of the block copolymer indicated the same tendency as that of the graft copolymer. The block copolymer was not soluble in NMP or HMPA, but partially soluble in NMP containing 5 wt % of lithium chloride. The solubility of both copolymers in NMP containing 5 wt % lithium chloride was more increased than that of PPTA homopolymer.

Dynamic Mechanical Properties. Figure 5 shows that the dynamic mechanical properties of the storage modulus E' and $\tan \delta$ as a function of temperature for the graft copolymer contained 85 wt % of PBD. The specimen was prepared by casting from NMP. The $\tan \delta$ peak at 233 K is the primary absorption corresponding to T_g of PBD segments. T_g 's of this copolymer and PBD homopolymer as found by DSC curves were located at the same temperature, 186 K. Since the primary absorption temperature of PBD segment in graft copolymer did not vary, PBD segments were separated in microdomain phase due to their incompatibility with PPTA main chains. The T_g of the PBD segment in this copolymer was not observed in the copolymer with less than 30 wt % of PBD.

Figure 6 shows the dynamic viscoelastic functions of E' and $\tan \delta$ as a function of temperature for the block copolymers: (a) PPTA/PBD = 38/62 and (b)

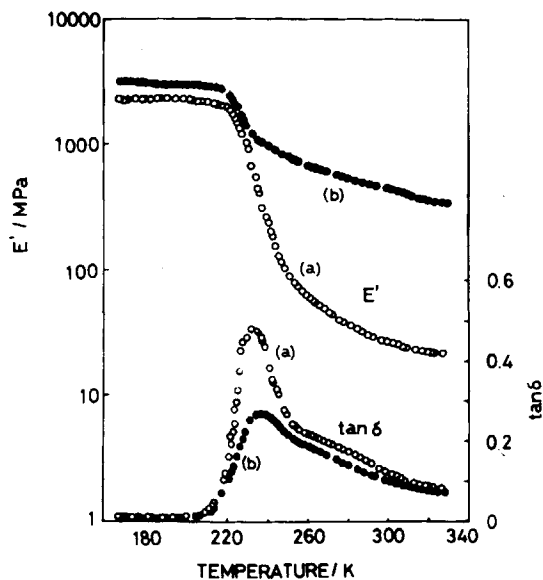


Fig. 6. Dynamic mechanical properties E' and $\tan \delta$ as a function of temperature for PPTA-*b*-PBD: (a) PPTA $M_w = 1300$, PPTA/PBD = 38/62; (b) PPTA $M_w = 4900$, PPTA/PBD = 55/45.

PPTA/PBD = 55/45. The sample was moulded by heat compression at 423 K. The similar curves of $\tan \delta$ were obtained for the graft copolymers. The $\tan \delta$ peak at 235 K indicates the primary absorption temperature of PBD segments. The T_g of PBD in the block copolymer and PBD homopolymer was observed at 191 K by DSC. The difference of T_g in the graft and block copolymers are due to the difference of microstructure of employed PBD. Behavior of the block copolymer is understood by the microphase-separated structure. The T_g of the block copolymer containing less than 35 wt % of PBD could not be observed by DSC. This fact suggests that the PPTA formed a continuous phase when the PPTA content in the block copolymer was more than 65 wt %. The E' of the block copolymer containing 55 wt % of PPTA ($M_w = 4900$) maintained the modulus value over 100 MPa in the rubbery region, whereas that of the copolymer containing 38 wt % of PPTA ($M_w = 1300$) was slightly above 10 MPa. The

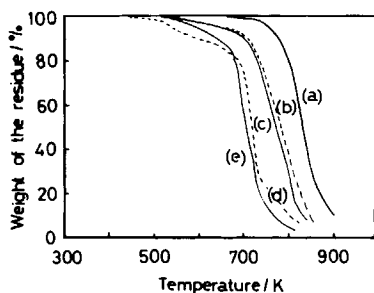


Fig. 7. TGA curves of: (a) PPTA ($M_w = 4900$); (b) PPTA-*g*-PBD (PPTA/PBD = 87/13); (c) PPTA-*g*-PBD (PPTA/PBD = 49/51); (d) PPTA-*g*-PBD (PPTA/PBD = 15/85); (e) bromine-terminated PBD.

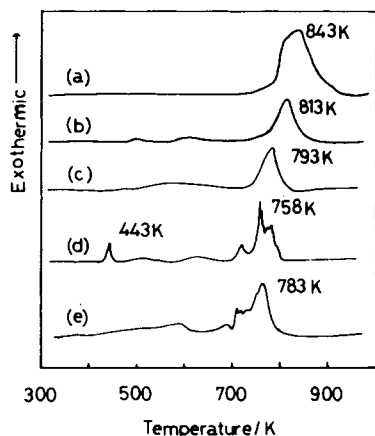


Fig. 8. DTA curves of: (a) PPTA ($M_w = 4900$); (b) PPTA-*g*-PBD (PPTA/PBD = 87/13); (c) PPTA-*g*-PBD (PPTA/PBD = 49/51); (d) PPTA-*g*-PBD (PPTA/PBD = 15/85); (e) bromine-terminated PBD.

molecular weight of PPTA in copolymer is also considered to contribute to the increase in the storage modulus. The PPTA in copolymers might play a role of the hard domain as found in the hard segment of segmented polyurethane. PPTA segments have a strong intermolecular interaction, and they form a hard domain, which was surrounded by soft segment phase.

Thermal Stability. Figures 7 and 8 show TGA and DTA curves of PPTA, PPTA-*g*-PBD, and PBD, respectively. With increasing percentage grafting of PBD (PG) the thermal stability of the graft copolymers was decreased compared with the original PPTA. Since the grafting reaction of PBD occurs at amide group of PPTA, the intermolecular force by the hydrogen bond in PPTA and the orderliness in crystallites are to be decreased. The rigidity of PPTA backbone is also decreased. These factors result in the decrease of thermal stability of the graft copolymer. DTA curves show that the main exothermic peak of decomposition shifted to the lower temperature side with increasing PG. Graft copolymer with 567% grafting degraded in several stages with rising temperature. PBD segments in the graft copolymer began to degrade near 440 K at the first stage and PPTA segments degraded near 760 K at the final stage.

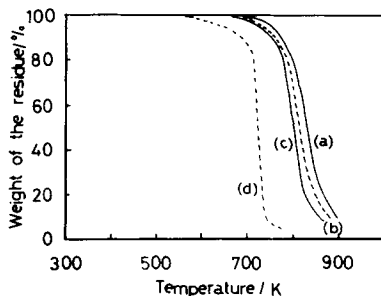


Fig. 9. TGA curves of: (a) PPTA ($M_w = 4900$); (b) PPTA-*b*-PBD (PPTA/PBD = 85/15); (c) PPTA-*b*-PBD (PPTA/PBD = 69/31); (d) carboxylic-acid-terminated PBD.

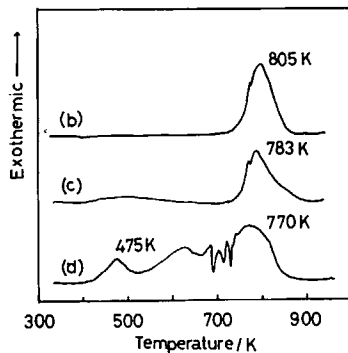


Fig. 10. DTA curves of: (a) PPTA ($M_w = 4900$); (b) PPTA-*b*-PBD (PPTA/PBD = 85/15); (c) PPTA-*b*-PBD (PPTA/PBD = 69/31); (d) carboxylic-acid-terminated PBD.

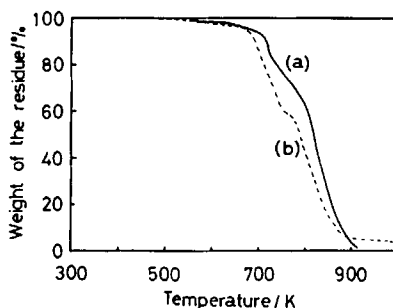


Fig. 11. TGA curves of the blend polymer composed of PPTA and PBD: (a) PPTA/bromine terminated PBD = 50/50 (PPTA $M_w = 4900$); (b) PPTA/carboxylic-acid-terminated PBD = 70/30 (PPTA $M_w = 4900$).

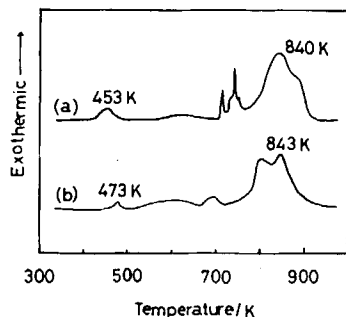


Fig. 12. DTA curves of the blend polymer composed of PPTA and PBD: (a) PPTA/bromine-terminated PBD = 50/50 (PPTA $M_w = 4900$); (b) PPTA/carboxylic-acid-terminated PBD = 70/30 (PPTA $M_w = 4900$).

Figures 9 and 10 show the TGA and DTA curves of PPTA-*b*-PBD. The thermal stability of the block copolymers exhibited a similar tendency as that of the graft copolymers. However, the thermal stability of the block copolymer is superior to that of the graft copolymer at the same PBD content. These facts suggest that the rigidity of PPTA segments in the copolymer are kept more effectively at the high temperature for the block copolymers in comparison with

the graft copolymers. The thermal stability of crystallite in the block copolymer is superior to that of graft copolymers.

Figures 11 and 12 show the TGA and DTA curves of the blends of PPTA and PBD. The blend polymer degraded in two stages, indicating the process of each polymer in the blends being degraded separately. On the other hand, both kinds of copolymers with the same content of PBD exhibited one-step degradation. Moreover, the blend polymer degraded more rapidly than those of both copolymers of the same PBD content.

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