

High Strength and High Toughness Aromatic Polyamide Fiber. I. Preparation and Properties of Block Poly(*p*-phenylene and 4,4'-Diphenyl Ether Terephthalamide) Fiber

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Synopsis

High strength and high toughness organic fibers can be prepared by molecular design of a suitable block copolymer with mixed segment of rigid and flexible molecular chains. In this paper, the synthesis of fiber forming high molecular weight block copolymer of poly(*p*-phenylene terephthalamide) (PPTA) and poly(4,4'-diphenyl ether terephthalamide) (DPETA) was studied by the low temperature solution polycondensation method. The high molecular weight block copolymer could be obtained in the mixed solution of 1,3-dimethyl-2-imidazolidone (DMI) and *N,N'*-dimethyl acetamide (DMAc) in the presence of triethylamine. The copolymer structures were characterized by elemental analysis and IR spectra. The thermal stability of the block copolymer was better than that of PPTA homopolymer and the ordered copolymer. The wet spinning of the block copolymer was performed using the reaction solution as the spinning dope. The maximum tensile strength and elongation were observed for the filament containing 50% PPTA. The block copolymer had high strength and high Young's modulus but had a low elongation compared with the ordered copolymer.

INTRODUCTION

The demand for rigid reinforcing agents is growing steadily as a result of their increasing use in composite materials. Although glass fibers, carbon fibers, and silicon carbide whiskers have high strength and high stiffness, they are seldom ductile. This lack of ductility leads to problems of low fracture toughness and difficulty in the design of structures. High strength and high toughness filaments can be used for making high toughness composites and are important for reliability of structural strength. We have studied the preparation of high strength and high toughness metallic filaments using the method of glass-coated melt spinning to obtain filaments with a tensile strength of 2.1 GPa and elongation of 23.6%.^{1,2} The filament was micropoly-crystalline with a grain size of 50 nm and had a mixed structure of body-centered cubic (bcc) and face-centered cubic (fcc) phases. The high toughness of the filament is related to its micropoly-crystalline structure and the uniformly mixed structure of bcc and fcc phases, the high strength stemming mainly from the bcc phase and the ductility enhanced by the fcc phase. However, the metallic filament has high density which limits its application in composites.

It is possible to obtain high strength and high toughness organic polymer filament by molecular design of a suitable copolymer with uniformly mixed segments of rigid and flexible molecular chains. Graft and block copolymerizations are generally useful to improve mechanical, chemical, and thermal properties of the original homopolymers. If the individual polymer segments have opposite polarity and/or flexibility, many interesting properties are conceivable.^{3,4} Poly(*p*-phenylene terephthalamide) (PPTA) provides fibers with ultrahigh modulus, high tensile strength, and good thermal stability, owing to its molecular rigidity.^{3,5} PPTA block copolymers with flexible comonomer segments would be interesting for forming high toughness filaments. In the present work, poly(4,4'-diphenyl ether terephthalamide) (DPETA) was selected as a flexible segment for block copolymers of PPTA and DPETA prepared by low temperature solution polycondensation. This paper describes the synthesis of fiber-forming high molecular block copolymers, characterization and thermal stability of the copolymers obtained, spinning of the copolymer, and mechanical properties of the as-spun filaments.

EXPERIMENTAL

Materials

4,4'-Diamino-diphenyl ether (**1**) (mp 462 K) and terephthaloyl chloride (**2**) (mp 356 K) were purified by multiple recrystallization from tetrahydrofuran (THF) and hexane, respectively. The commercially available 1,4-phenylenediamine (**3**) (mp 415 K) was purified by vacuum distillation.

Hexamethylphosphoric triamide (HMTA), *N*-methyl-2-pyrrolidone (NMP), *N,N'*-dimethyl acetamide (DMAc), 1,3-dimethyl-2-imidazolidone (DMI), and THF were each purified by vacuum distillation after drying over calcium hydride. All the purified solvents were stored over molecular sieves under nitrogen atmosphere.

Triethylamine was purified by distillation from phthalic anhydride. Other chemicals such as α -picoline, lithium chloride, lithium carbonate, calcium carbonate, and calcium chloride were used without additional purification.

Polymer Synthesis

Block copolyamide from **1** and **3** with **2** was prepared according to following route in Figure 1. **1** was initially dissolved in solvent and cooled to 269 K. **2** in powder form was added to the solution in the presence of triethylamine with vigorous stirring for 1 h under nitrogen atmosphere. Then **3** together with lithium chloride was added to the solution. **2** and triethylamine were then added to the solution. The reaction was continued with vigorous stirring for 4 h at 269 K under nitrogen atmosphere. The whole solution was added to excess acetone, followed by filtering and washing the precipitated copolyamide with methanol and water.

Wet Spinning

The reaction solution was also used as a spinning dope. The dope was filtered through a glass filter and deaerated under reduced pressure. The dope

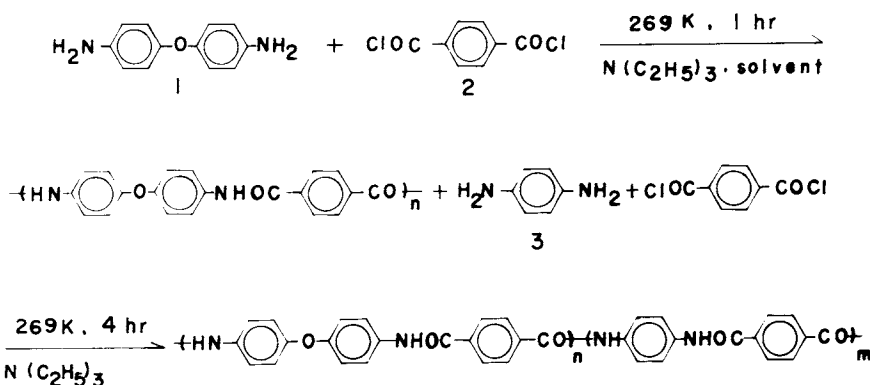


Fig. 1. Block copolymerization of 4,4'-diamino-diphenyl ether (1) and 1,4-phenylenediamine (3) with terephthaloyl chloride (2).

was extruded from a injector into a coagulating bath of saturated aqueous calcium chloride solution, and the thread was coiled on a winding drum. The drum was placed in a flowing water to leach out dissolved salts, and the fiber was then dried.

Characterization and Physical Properties

The intrinsic viscosity $[\eta]$ of the copolymer obtained was determined in concentrated sulfuric acid at 303 K with an Ostwald viscometer. Elementary analyses of carbon, hydrogen, and nitrogen was carried out with a Yanaco MT-3 microanalyzer. Infrared spectra were obtained with the KBr disk method on a grating infrared spectrophotometer (Hitachi 285). Thermogravimetric (TG) and differential thermal analysis (DTA) were performed by using a thermal analyzer (Rigaku Denki Co.) at a heating rate of 20 k/min in air.

Tensile tests of the as-spun filaments were conducted using an Instron type machine (Toyo Baldwin Co.) at room temperature. All tests were performed with a crosshead movement of 2 mm/min and a gauge length of 10 mm. The fracture morphology of the fiber was observed by scanning electron microscope (Hitachi Scanscope SSM-2).

RESULTS AND DISCUSSION

Preparation of Block Copolymer

The preparation of the block copolymer shown in Figure 1 was examined to obtain the high molecular weight polymer and high tenacity fibers. The effect of solvent on the polycondensations of 1 and 3 (molecular ratio 1:1) with 2 was studied by the low temperature solution technique in a series of polar aprotic solvents such as HMTA, NMP, DMAc, and THF. Obtaining high molecular weight required the use of two or more solvents as reaction medium.⁵ It is well known that binary mixtures of HMTA with NMP or DMAc in certain ratios are the most effective solvents for PPTA.^{5,6} The preparation of the block copolymer was carried out in various HMTA solutions, and the viscosities of the polymers obtained were measured to evaluate the molecular

TABLE I
Polycondensation of 1 and 3 with 2 in Various Solvents^a

Solvent	Yield (%)	$[\eta]^b$
HMTA : NMP 7 : 3	100	1.44
HMTA : NMP in Li ₂ CO ₃ 7 : 3	> 95	0.77
NMP in LiCl	> 95	0.70
HMTA : DMAc 8 : 2	97	1.56
HMTA : THF 9 : 1	90	1.02
DMI in CaCl ₂	> 95	0.82
DMI : DMF 1 : 1	> 95	0.15
DMI : NMP 1 : 1	> 95	1.34
DMI : DMAc 1 : 1	> 95	3.52
DMI : DMAc 6 : 4	> 95	2.30
DMI : DMAc 7 : 3	> 95	1.70
DMI : DMAc 4 : 6	> 95	1.20
DMI : DMAc in α -picoline 1 : 1	> 95	1.39

^a Polymerization was carried out with 17.5 mmol of monomer in 50 mL of solvent.

^b Measured in concentrated sulfuric acid at 303 K.

weight of the copolymer. The results are listed in Table I. The high intrinsic viscosities were obtained in mixtures of HMTA:DMAc with a volume ratio of 4 : 1.

Because HMTA is carcinogenic, the use of DMI mixed solvent was examined instead of HMTA; the results are summarized in Table I. Although the polycondensation proceeded in the gell state, the higher molecular weight copolyamide (e.g., $[\eta] = 3.52$) was obtained in the mixed solution of DMI : DMAc (1 : 1 ratio) than in HMTA : DMAc. Yields of copolymers were more than 95%. On the basis of these results, the copolyamide with different

TABLE II
Polycondensation of 1 and 3 with 2 from Various Feeding Molecular Ratios^a

Mole ratio 1 : 2	$[\eta]^b$
1 : 1.1	0.57
1 : 1.01	3.52
1 : 1	1.12

^a Polymerization was carried out with 17.5 mmol of monomer in 50 mL of solvent.

^b Measured in concentrated sulfuric acid at 303 K.

TABLE III
Polycondensation of 1 and 3 with 2 from Various Feed Ratios^a and Elemental Analysis of the Copolymers Obtained

Mole ratio 1 : 3	η_{rel}^b	$[\eta]^c$	Elemental Analysis ^d (%)		
			C	H	N
9 : 1	4.51	2.85	71.64 (70.58)	4.52 (4.30)	8.70 (8.49)
7 : 3	4.42	2.83	70.84 (70.13)	4.42 (4.14)	8.73 (8.99)
1 : 1	3.74	3.52	69.64 (69.62)	4.66 (4.47)	9.61 (9.55)
3 : 7	3.07	2.13	68.80 (69.04)	4.09 (4.11)	10.14 (10.19)

^a Polymerization was carried out with 17.5 mmol of monomer in 50 mL of solvent.

^b Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 303 K.

^c Measured in concentrated sulfuric acid at 303 K.

^d Paratheses enclose calculated values including 1/2 H₂O.

sequence length was prepared in a 1 : 1 mixture of DMI : DMAc from various initial feed ratios of 1 and 2, and the results are listed in Table II. The results indicated that the highest molecular weight copolymer was obtained at a monomer feed ratio of 1 : 2 of 1 : 1.01.

Table III shows results of the copolycondensation at various monomer feed ratios of 1 for 3 in 1 : 1 DMI : DMAc mixed solution. The relative viscosities η_{rel} of the polymer obtained increase with increasing 1, while the maximum $[\eta]$ was observed at 1 : 3 of 1 : 1. The solubility of the copolymers in concentrated sulfuric acid increases with increasing 1. The low viscosity of the polymer containing the high ratios of PPTA is considered to be due to the solubility of the polymer in the mixed solution being poor and copolycondensation being hindered by the gel state of the reactive mixture. Table III also

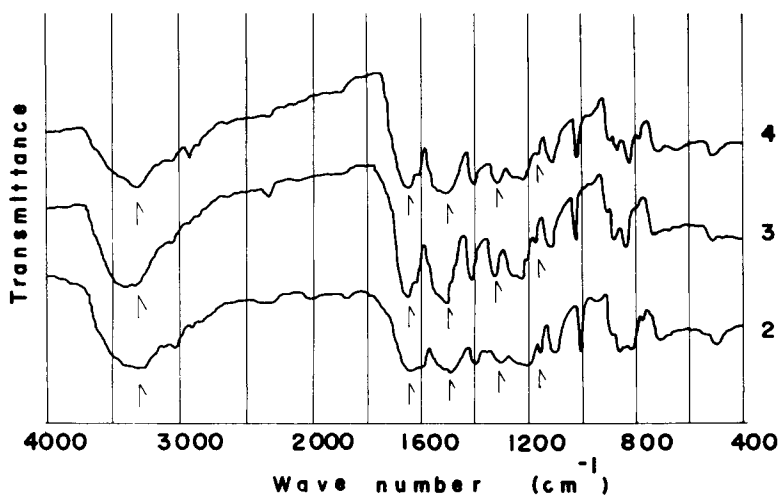


Fig. 2. IR spectra of the copolymer: (2) 30% PPTA; (3) 50% PPTA; (4) 70% PPTA.

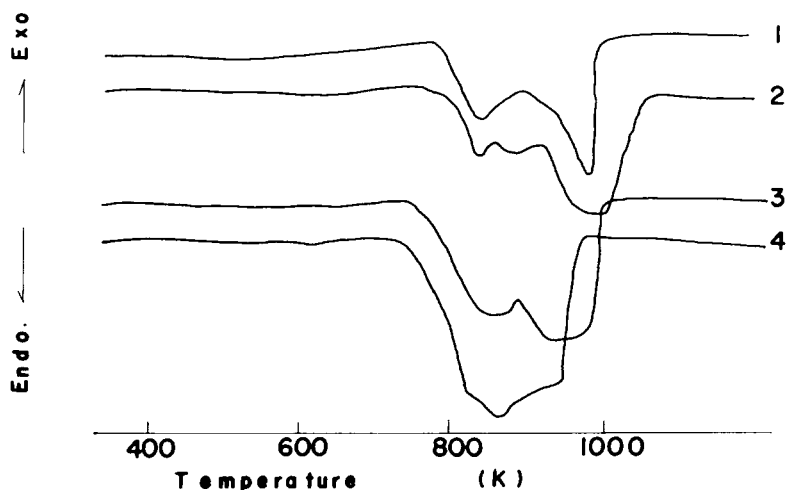


Fig. 3. DTA curve of the copolymer: (1) 10% PPTA; (2) 30% PPTA; (3) 50% PPTA; (4) 70% PPTA.

lists the elemental analyses of the copolyamides obtained, which were generally in good agreement with the calculated values.

Infrared spectra of these polymers were measured to prove copolyamide structure; IR spectra of the copolyamides containing 30, 50, and 70% PPTA are shown in Figure 2. Spectra of all copolyamides displayed a broad absorption peak centered at 3300 cm^{-1} due to hydrogen bonded NH groups and three peaks attributable to amide I, II, and III at 1640 , 1540 , and 1310 cm^{-1} , respectively.^{7,8} An absorption peak at 1160 cm^{-1} indicates the presence of the phenyl ether in the DPETA which increases with increasing ratio of DPETA.

Thermal Stability of Block Copolymers

The DTA and TG curves of the copolyamides were measured to determine thermal stabilities and are shown in Figures 3 and 4, respectively. Two endothermic peaks at 823 and 973 K are clearly observed for the copolymer of 10% PPTA. As the content of PPTA increases, the first peak increases, and both peaks shift and move together. Finally one broad peak centered at 848 K was found out for the copolymer of 70% PPTA. For the TG curves of the same copolymers of 10% PPTA, two steps of degradation are observed at 823 and 923–973 K, respectively. The DTA curve of PPTA homopolymer was reported to exhibit only one endothermic peak at about 800 K due to thermal decomposition.^{9,10} Although the DTA traces show multiple peaks, it is not clear whether these are due to physical changes associated with T_g 's or multiple T_m 's. We believe that the peak at 823 K in Figure 3 is mainly due to the decomposition of PPTA segments and the peak at 973 K to the degradation of DPETA segments. The important parameters characteristic of these degradation process are summarized in Table IV. The weight loss at 1073 K increases with increasing PPTA content. The order of thermal stability was 30% PPTA > 10 and 50% PPTA > 70% PPTA. One endothermic peak at about 783 K and degradation from 723 to 873 K were reported for the all-para linked

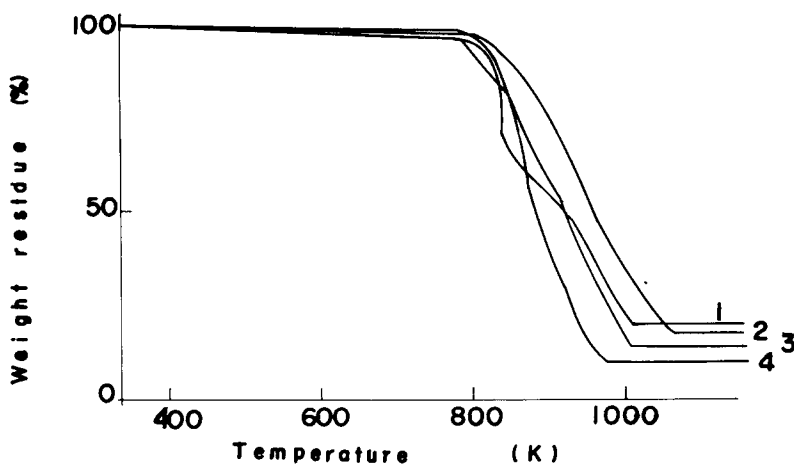


Fig. 4. TG curve of the copolymer: (1) 10% PPTA; (2) 30% PPTA; (3) 50% PPTA; (4) 70% PPTA.

TABLE IV
Thermal Gravimetric Analysis of the Block Copolymer in Air

Content of PPTA (mol %)	Onset of degradation (K)	Temperature for overall 50% weight loss (K)	End of degradation (K)	Weight loss at 1073 K (%)
10	762	910	987	80
30	788	938	1033	82
50	763	905	987	86
70	758	867	956	90

ordered aramide containing an ether linkage.¹¹ It is interesting that the block copolyamide had better thermal stability than that for the PPTA homopolymer and the ordered copolymer. It was also reported for the aromatic polyamide containing ether linkage that the polymer having methylene or ether linkage between the *p*-phenylene was generally more thermally stable than that for *p*-phenylene links.¹²

Mechanical Properties of Block Copolymer Fibers

The block copolyamides were prepared in DMI:DMAc mixture solution containing lithium chloride and triethylamine. These solutions could be used directly for spinning fibers after filtrating and deaerating. Solutions of 50 g/L polymer content were readily spun into fibers. The tensile properties of the as-spun fiber were examined with an Instron type machine. Table V presents the average tensile strength, elongation, and Young's modulus for the copolyamide fibers containing various PPTA, along with data for the ordered copolyamide.¹¹ The Young's modulus increases with increasing content of PPTA. The maximum tensile strength and elongation were observed for the fiber containing 50% PPTA. The block copolymers have high strength and high stiffness but low elongation compared with the ordered copolymer.

TABLE V
Tensile Strength of the Block Copolymer Fiber

Fiber content of PPTA (mol %)	Tensile strength (MPa)	Elongation (%)	Young's modulus (GPa)
10 ^a	130 ± 20	8.5 ± 1.3	3
30 ^a	130 ± 10	13.4 ± 2	4
50 ^a	490 ± 30	26.5 ± 2.7	13
70 ^a	410 ± 60	13.9 ± 1.3	13
50 ^b	500	5.5	33
ordered copolymer ¹¹	392	55.0	6.7

^aAs-spun.

^bAfter hot drawing with a draw ratio of 1.5 at 573 K.

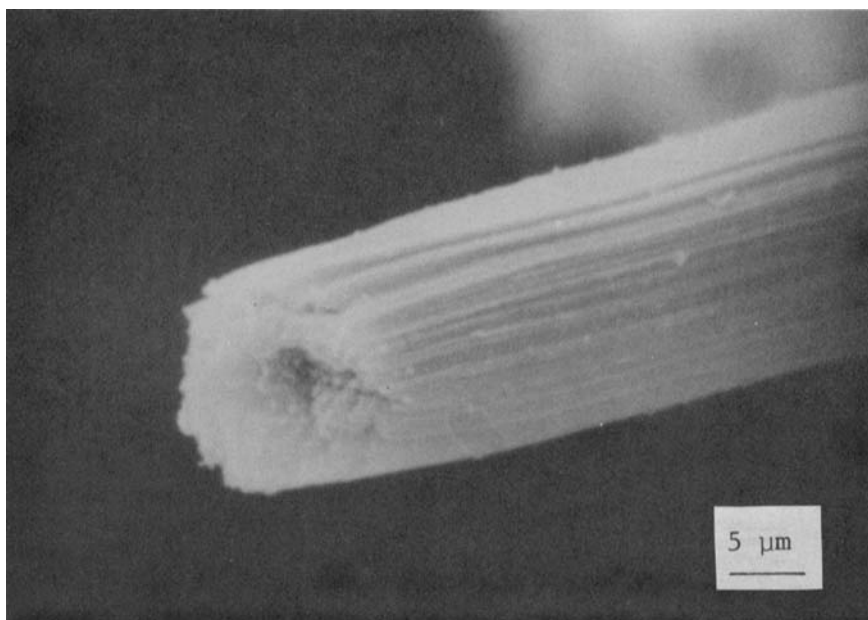


Fig. 5. Fracture morphology of the fiber containing 50% PPTA fractured at 470 MPa and elongation of 25%.

The fracture morphology of the fiber containing 50% PPTA is shown in Figure 5. The surface of the filament has many fibrous strips parallel to the fiber axis. Intergranular fracture was observed, but it is not clear whether the intergranulars are caused by phase separation in the block copolymer or are due to sample preparation history.¹³ More detail morphological studies are needed.

The elongation of the fiber is so low that hot-drawing did not proceed well.¹⁴ However, a strength of 500 MPa, Young's modulus of 33 GPa, and elongation of 5.5% were attained for the fiber containing 50% PPTA obtained by hot drawing with a draw ratio of 1.5 at 573 K.

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