Br Copy

AFWAL-TR-87-4072

ADA 191666

HIGH STRENGTH/HIGH MODULUS AROMATIC HETEROCYCLIC ABA BLOCK COPOLYMERS

T.T. Tsai
F.E. Arnold
Polymer Branch
Nonmetallic Materials Division

W.F. Hwang
University of Dayton Research Institute
Dayton, Ohio 45469-0001

May 1987

Final Report for period March 1984 to March 1985

Approved for Public Release; Distribution Unlimited

MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433-6533

20040224186

NOTICE

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is released to the National Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

Ivan J. Goldfarb, Work Unit Scientist
Polymer Branch
Nonmetallic Materials Division

RICHARD L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

FOR THE COMMANDER

GAIL E. EICHELMAN, Assistant Director
Nonmetallic Materials Division

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for public release; distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
AFWAL-TR-87-4072

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
AFWAL/MLBP
Polymer Branch

6b. OFFICE SYMBOL *(If applicable)*
AFWAL/MLBP

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS *(City, State, and ZIP Code)*
AFWAL/MLBP
Wright-Patterson AFB, OH 45433

7b. ADDRESS *(City, State, and ZIP Code)*

8a. NAME OF FUNDING / SPONSORING ORGANIZATION

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
61102F	2303	Q3	07

11. TITLE *(Include Security Classification)*
High Strength/High Modulus Aromatic Heterocyclic ABA Block Copolymers

12. PERSONAL AUTHOR(S)
T.T. Tsai, W.F. Hwang and F.E. Arnold

13a. TYPE OF REPORT
Final

13b. TIME COVERED
FROM 3/1/84 TO 3/30/85

14. DATE OF REPORT *(Year, Month, Day)*
1987 May

15. PAGE COUNT
24

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Ordered Polymers Benzimidazole Benzobisthiazole

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

A series of novel ABA block copolymers were synthesized containing a rigid-rod (B) block for reinforcement and a flexible coil (A) block as the matrix. Poly [(benzo [1, 2d: 4, 5d'] bisthiazole-2, 6-diyl)-1, 4-phenylene] (PBT) was the rigid-rod (B) block utilized in this study and was polymerized in such a way as to provide carboxylic acid end-groups. The carboxy-terminated PBT was copolymerized with the AB monomers, 3, 4-diaminobenzoic acid and 4-amino-3-mercaptobenzoic acid, which generates a benzimidazole or benzthiazole (A) block, as well as grafts the blocks together. Composition of the blocks could be varied by the weight of AB monomer used in the copolymerizations. Solution behavior of the copolymers in methanesulfonic acid was determined, and fibers were obtained by wet spinning techniques. The block copolymers exhibited typical tenacities of 200 ksi, 16 msi modulus and an elongation to break of 1.4 percent. Critical concentration values for fabrication increased approximately 3 percent over mechanical mixtures of the same heterocyclic components.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
T.E. Helminiak

22b. TELEPHONE *(Include Area Code)*
(513) 255-9155

22c. OFFICE SYMBOL
AFWAL/MLBP

DD Form 1473, JUN 86 *Previous editions are obsolete.*

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Task No. 2303Q307, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. T.E. Helminiak as the ML Project Scientist. Co-authors were Dr. F.E. Arnold, Materials Laboratory, (AFWAL/MLBP), Dr. T.T. Tsai and Dr. W.F. Hwang, University of Dayton Research Institute. This report covers research conducted from March 1984 to March 1985.

TABLE OF CONTENTS

LIST OF TABLES

SECTION I
INTRODUCTION

Over the past decades nonmetallic materials have continued to penetrate the structure materials market. They have been adaptable to the increasing demands on materials with regard to mechanical properties (tensile, shear, and compressive properties), toughness, reliability to fatigue, thermal stability, processability, low moisture absorption, hydrolytic stability and low cost. Improvements in this area have been through specific molecular design and architecture, i.e., polymer synthesis, and the concept of using two or more existing polymers to obtain new improved products.

One of the conventional approaches to the design of improved structural materials is the reinforced polymer composite technology. The transfer of stresses from a matrix polymer to the reinforcing entities such as rigid particles, chopped fibers, or continuous filaments, has been a very effective technique for improving mechanical properties of polymeric materials. The ultimate properties of these materials, however, are limited by the interfacial adhesion problem existing between the reinforcing elements and the matrix and by the difference in thermal expansion coefficient between these two components. These limitations have created serious drawbacks of these materials in impact resistance, fracture toughness, and damage tolerence. This necessitated the consideration of an improved material concept. This consideration, coupled with the development in the synthesis of aromatic heterocyclic rigid-rod polymers, had originated the concept of molecular composite.

The concept of reinforcement [1,2] on the molecular level using intrinsic rigid rod-polymers represents one of the most exciting emerging technologies in the field of structural materials. The fundamental interest in this area is based on the improvements in fracture and impact toughness, as well as dimensional stability over those of conventional reinforced composites. The feasibility of fabricating "real" molecular composites, in which rigid-rod polymers are molecularly (50°A) dispersed in a flexible coil matrix, has recently been realized in our laboratory. [3]For its weight, the strength and modulus properties of the molecular composites obtained exceed structural materials used in aircraft such as the metals aluminum, titanium and steel, and nonmetallic composites such as graphite/epoxy.

The success of obtaining molecular composites is based on guidelines established through observed solution behavior of physical blends of rigid-rod/flexible coil polymers in a common acidic solvent. To insure the molecular dispersity of the rigid-rod polymers in the blends, one can only process from solutions at lower than its corresponding critical concentration, (Ccr) [4,5] to prevent the segregation of the rigid-rod reinforcement. This has restricted the processing of molecular composites from solutions with rather low concentration (2-4 wt. percent).

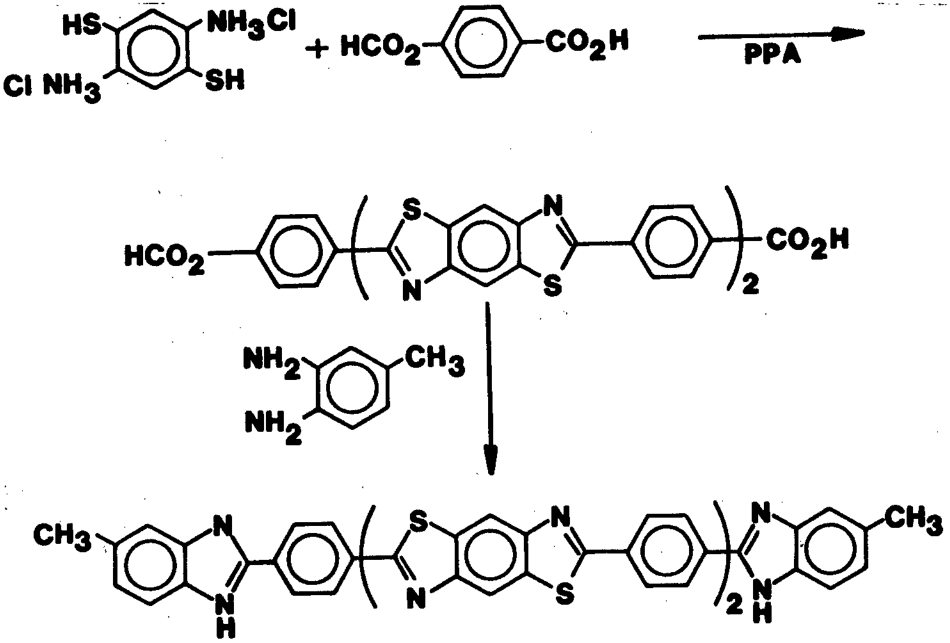
This paper describes our research on the synthesis and properties of ABA block copolymers composed of a rigid-rod (B) block for reinforcement and a flexible coil (A) block as the matrix. In addition to better processability (Ccr), it was anticipated that the block copolymer would have better mechanical strength than those from physical blends of the same rigid-rod/flexible coil composition. In the block copolymer, the rigid-rod constituent would be chemically bonded to the flexible coil matrix, while in the physically blended molecular composite the reinforcing rigid-rod polymer is only physically entangled in the matrix. Hence, the translation of stress or strain from the reinforcing rigid-rod molecule in the matrix would be more efficient in the block copolymer than in the physical blend. This would not only provide higher tensile strength, but also fracture toughness and dimensional stability.

SECTION II
RESULTS AND DISCUSSION

Poly[(benzo[1,2d:4,5d'] bisthiazole-2, 6-diyl)-1, 4-phenylene (PBT)[6] was the rigid-rod (B) block utilized in this study and was polymerized in such a way as to provide carboxylic end-groups. The carboxy terminated PBT was copolymerized with two AB monomers, 3, 4-diaminobenzoic acid, and 4-amino-3-mercaptobenzoic acid hydrochlorides. The AB monomers generate a benzimidazole or benzthiazole (A) block and grafts the blocks together during the copolymerization. The benzobisthiazole and benzimidazole heterocyclic's are the same polymers used in the previously reported[3] mechanical blend work.

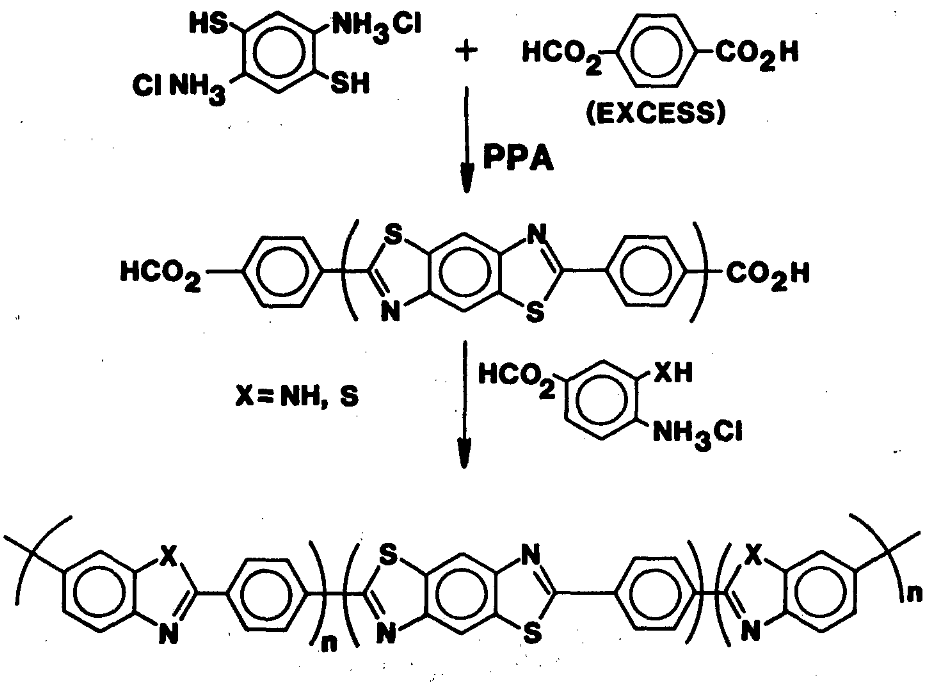
Model Compound Studies

Prior to the polymerizations, model compound studies were initiated in an effort to assess the approach. A two-mole excess of terephthalic acid (TA) was reacted with 2,5-diamino-1, 4-benzenedithiol dihydrochloride in polyphosphoric acid (PPA) to yield a low molecular weight PBT which analyzed as a dimer. The material was purified, redissolved in PPA and heated to 190°C to determine the stability of the terminal carboxy groups. No carbon dioxide, a possible decarboxylation product, was found in the outlet gas stream and when condensed with 3,4-diaminotoluene, a quantitative yield of the model imidazole oligomer was obtained.



Polymers

The carboxy-terminated PBT polymers were prepared using PPA as the polymerization solvent. Polymerizations were carried out in both the isotropic and anisotropic phase. Using various excess amounts of terephthalic acid (Table 1), we obtained polymers with intrinsic viscosities of 10-24 dL/g as measured in methanesulfonic acid. Polymerizations carried out in the anisotropic or liquid crystalline phase required polymer concentrations above 5 wt. percent. Dehydrochlorination of the aminomercapto monomer at concentrations that would give a polymer concentration above 5 wt. percent was extremely difficult due to the high viscosity of the PPA (84 percent P_2O_5); whereby, the gaseous hydrogen chloride caused excessive foaming problems. The foaming problem was alleviated by using a recently new synthetic method called the P_2O_5 adjustment method.[7] In the early stages of the polycondensation, a low viscosity PPA (77 percent P_2O_5) was used that allowed a facile dissipation of the thermally generated hydrogen chloride gas. The removal of the gas was also aided by carrying out the initial phase of the polymerization under reduced pressure (710 mm) with a positive nitrogen flow. After dehydrochlorination was complete, powdered P_2O_5 was added to the polymerization mixture to bring the final P_2O_5 content to 82-84 percent.

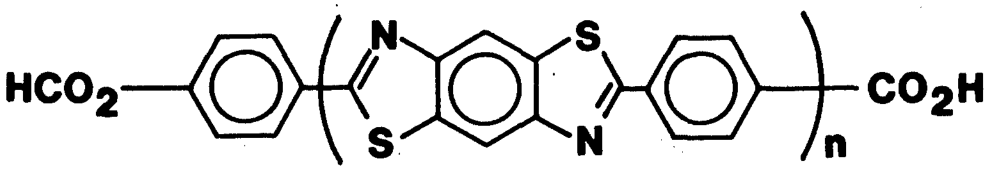


Carboxy-terminated PBT polymer prepared in the liquid crystalline phase had to be purified to remove excess TA prior to copolymerization. High viscosity polymer was always obtained even though a large excess of TA was employed. (Table 1). Although large amounts of TA were present during the polymerization, to become effective, TA had to penetrate the liquid crystalline phase for reaction. Carboxy-termination had to occur in the oligomeric stage prior to generation of the liquid crystalline phase. No driving force exists for TA molecules to enter the liquid crystalline phase. Polymers prepared at concentrations below 5 wt. percent could be used directly without isolation or purification.

The copolymerizations were normally carried out at 1 percent or less to facilitate the dispersion of AB-monomer throughout the viscous media. Dehydrochlorination of the AB-monomer was also extremely difficult due to the highly viscous PPA polymer solutions. After dehydrochlorination, the mixture of the AB-monomer and carboxy-terminate PBT was slowly heated to 190-200°C and maintained at that temperature for 24 hours. The polymers were isolated by precipitation into water. Composition of the (B) blocks could be varied by the weight of AB-monomer used in the copolymerizations. Intrinsic viscosities of the block copolymers are shown in (Table 2) along with the viscosities of the carboxy-terminated PBT's used in the copolymerization. At very high PBT viscosities (24 dL/g), the resulting blocks copolymer viscosities became erratic. We believe that this is due to the inability of the AB-monomer to penetrate and copolymerize in the highly viscous media.

Three block copolymers, A,B, and D (Table 2), were investigated for the feasibility of forming molecular composite fibers. As pointed out previously, the success of obtaining molecular composites depends greatly on the determination of the critical concentration point of the material in solution. The observed solution behavior of the block copolymers was similar to that of the physical blends (1-3). There still existed a critical concentration point at which the solution phase separated into optically anistropic liquid crystalline domains dispersed in an optically isotropic solution when observed under the cross Nicol of a polarized optical microscope. In general, these liquid crystalline domains are much smaller in size in the

TABLE I
SYNTHESIS OF CARBOXY-TERMINATED PBT



POLYMER CONCN. (WEIGHT) %	EXCESS TA %	$[\eta]^a$ dL/g
15.0	2	24.0
14.0	3	17.7
10.0	3	6.6
10.4	2	11.0
4.4	0.9	12.9
3.2	0.8	10.7

[a] IN METHANESULFONIC ACID AT 30°C

solution of ABA block copolymer than in the corresponding physical blends of the same PBT/ABPBI compositions and same PBT chain length. In contrast to previous results[1] on the scanning electron microscopy study of the cast films of physical blends of PBT/ABPBI, the cast films of the corresponding block copolymers did not show any discernible aggregates of PBT. Furthermore, the experimentally determined Ccr, as shown in Table 3 of the block copolymer in methanesulfonic acid, is much higher than that of the corresponding physical blend.

The spinning and heat treatment conditions for the three block copolymers are listed in Table 4. Mechanical properties of both the as-spun and heat treated fibers are summarized in Table 5. The best properties of these fibers were 14.9 Msi/246 Ksi/2.3% (M/T/E) for heat treated fiber A, 13.6 Msi/227 Ksi/2.5% fiber B and 16.8 Msi/234 Ksi/1.35% for fiber D.

Young's Modulus of the block copolymers fibers compared favorably with that of the physical blends, as shown in Table 6, and they in general follow the linear rule or mixtures as discussed extensively elsewhere[2]. The two systems, block copolymer A and B, with lower modulus are probably less than uniaxially oriented than the other systems for they have higher breaking strain. The modulus data suggested that one does not need very large PBT molecules to have the reinforcing efficiency. From the tensile data one clear trend is the tensile strength of the block copolymer systems which is much better (up to 33 percent) than that of the physical blend. This enhancement in tensile strength is most illuminating when one considers the fact that the molecular weight of both the flexible coil (A) block and the central rigid rod block (B) is much lower than that in the physical blend.

From the above observations e.g., increase in the critical concentration point and enhancement in tensile properties, the ABA block copolymer systems clearly show their advantages in preventing the segregation of PBT molecules, and in the efficiency of translation of strength.

TABLE 2
INTRINSIC VISCOSITIES AND COMPOSITION OF BLOCK COPOLYMERS

BLOCK COPOLYMER	$[\eta]$ PBT	COMPOSITION PBT/ABPBI	$[\eta]$[a] BLOCK COPOLYMER
A	10.7	30/70	8.5
B	12.9	25/70	10.7
C	12.9	50/50	7.0
D	17.7	30/70	7.3
E	24.0	30/70	5.0
		PBT/ABPBT	
F	17.7	30/70	6.5
G	11.0	50/50	5.8

[a] IN METHANE SULFONIC ACID AT 30°C.

TABLE 3
CRITICAL CONCENTRATIONS OF BLOCK COPOLYMERS IN METHANE SULFONIC ACID

BLOCK COPOLYMER	$[\eta]$ dL/g	COMPOSITION PBT/ABPBI	C_{CR}^{a}
A	8.5	30/70	5.45
B	10.7	25/75	5.20
D	7.3	30/70	5.80
PHYSICAL BLEND	PBT/18 ABPBI/16	30/70	4.00

[a] DETERMINATION AT ROOM TEMPERATURE.

TABLE 4

SPINNING AND HEAT TREATMENT DATA OF BLOCK COPOLYMER

BLOCK COPOLYMER	AIR GAP (IN)	WET-DRAW RATIO	HT[a] TEMP(C°)	HT DRAW RATIO
A	1.2	2.74	455	3.84
B	2.2	2.00	471	2.56
D	2.2	2.50	455	3.20

[a] HEAT TREATMENT WAS CARRIED OUT UNDER N_2.

TABLE 5

TENSILE PROPERTIES OF BLOCK COPOLOYMER FIBERS

FIBER[a]	DIAMETER ($x10^{-3}$ IN) σ[b]	YOUNG'S MODULUS (10^6 psi)	TENSILE[c] STRENGTH (10^5 psi)	BREAKING STRAIN (%)
A-AS	2.16 (σ=0.15)	6.8 (σ=1.4)	1.3 (σ=0.18)	7.1 (σ=3.4)
A-HT	1.71 (σ=0.093)	13.1 (σ=1.2)	2.0 (σ=0.28)	1.8 (σ=0.2)
B-AS	1.78 (σ=0.074)	6.47 (σ=0.77)	1.1 (σ=0.11)	8.7 (σ=2.6)
B-HT	1.61 (σ=0.052)	13.11 (σ=0.51)	2.1 (σ=0.11)	2.3 (σ=0.3)
D-AS	1.99 (σ=0.044)	7.44 (σ=0.72)	1.26 (σ=0.07)	6.7 (σ=0.64)
D-HT	1.70 (σ=0.10)	15.9 (σ=0.69)	2.03 (σ=0.07)	1.41 (σ=0.11)

a. HT-HEAT TREATED FIBER, AS SPUN FIBER.
b. σ = STANDARD DEVIATION
c. AVERAGE PROP. OF AT LEAST TEN TESTS.

TABLE 6
COMPARATIVE TENSILE PROPERTIES OF BLOCK COPOLYMER AND PHYSICALLY BLENDED MOLECULAR COMPOSITE FIBERS

FIBERS	YOUNG'S MODULUS (MSI)	TENSILE STRENGTH (KSI)	ELONGATION AT BREAK (%)
PHYSICAL BLEND[a]	16.9	184	1.4
BLOCK COPOLY. A	14.9	246	2.3
BLOCK COPOLY. B	13.7	227	2.5
BLOCK COPOLY. D	16.8	232	1.4

[a] PHYSICAL BLEND OF 30 wt% PBT($[\eta]$=31dL/g) AND 70 wt% ABPBI ($[\eta]$=16.7)

SECTION III
EXPERIMENTAL

Model Chemistry

Synthesis of Carboxy-terminated PBT Oligomer

To a flask containing 103g of PPA (84 percent P_2O_5) were placed (2.91g, 11.9 mmol) of 4,6-diamino-1, 3-benzenedithiol dihydrochloride and (5.12g, 3.09 mmol) of terephthalic acid. The mixture was heated under a nitrogen atmosphere to 50°C overnight to effect dehydrochlorination and then heated as follows: 170°C for 16h and 190°C for 17h. During the entire reaction no carbon dioxide was detected by passing the outlet N_2 stream through a barium hydroxide solution. The dark solution was poured into water to give a colorless precipitate. With the aid of a blender, the model compound washed with conc. ammonium hydroxide, 10-percent sulfuric acid and finally with water. There was obtained 3.4g (89 percent) of oligmeric PBT product which analyzed as a dimeric benzthiazole structure showing carboxy groups in the IR.

Analysis Calcd. for $C_{36}H_{18}S_4N_4O_4$:C,61.87; H,2.59;N, 8.02
Found: C, 61.56; H, 2.91; N, 8.41

Model Synthesis of Imidazole/Thiazole Oligomer

The PBT Oligomer (3.1g, 4.43 mmol) and 3, 4-diaminotoluene (3.1g, 25.3 mmol) were added to 100g PPA (84 percent P_2O_5) at room temperature. The mixture was gradually heated, under a nitrogen atmosphere to 180°C and maintained at that temperature for 24 hours. After the solution cooled, the product was obtained by precipitation into water. The filtered product was thoroughly washed with ammonium hydroxide, 10 percent sulfuric acid, water and dried at 80°C, to give 3.8g (99 percent) of oligomer showing no carboxyl absorption in the IR.

Anal. Calcd. for $C_{50}H_{30}N_8S_4$: C, 68.94; H, 3.47; N, 12.85
Found: C, 68.25; H, 3.21; N, 12.63

Synthesis of High Molecular Weight Carboxy Terminated PBT

Anisotropic Synthesis. A mixture of 2, 5-diamino-1, 4-benzenedithiol dihydrochloride (1.66g, 6.8 mmol) and 5.8g PPA (77 percent P_2O_5) was placed in a resin flask equipped with a high torque mechanical stirrer, nitrogen inlet/outlet tubes, and a pressure regulator. Under a nitrogen flow, the flask was evacuated by means of a water aspirator pump. The monomer was incorporated into the PPA solution by stirring, and the resulting mixture was then dehydrochlorinated by heating at 70°C under reduced pressure for 2 hours. To the clear-green solution, under reduced pressure, was added terephthalic acid (1.14 g 6.9 mmol, 20 percent weight excess) to form a paste-like mixture. To this mixture, after cooling to 50°C was added under reduced pressure 3.91g of P_2O_5. The P_2O_5 content of the PPA component of the product was approximately 83 percent, and the concentration of the polymer was 15 percent by weight based on the total weight of the resulting polymer. The reaction mixture was then heated as follows: 90°-100°C for 17 hours, 170°C for 8 hours and 190°C for 20 hours. The polymer was precipitated into water, washed with concentrated ammonium hydroxide to remove excess terephthalic acid, water dilute sulfuric acid, water, and methanol. On drying at 100°C under reduced pressure, the polymer had an intrinsic viscosity of 24 dL/g as determined in methanesulfonic acid at 30°C.

Isotropic Synthesis. The monomers 2, 5-diamino-1, 4-benzenedithiol dihydrochloride (3.039g, 12.4 mmol) and terephthalic acid (2.081g, 2.5 mmol, 1 wt. percent excess) were placed in a resin flask equipped with a high torque mechanical stirrer and nitrogen inlet/outlet. After the system was thoroughly flushed with nitrogen, PPA 76g (84 percent P_2O_5) was added which would make the resulting polymer concentration polymer concentration 4.3 percent. The reaction mixture was heated to 70°C and maintained at that pressure for 8 hours to complete dehydrochlorination. The yellow mixture was then heated as follows: 150°C for 16 hours and 190°C for 16 hours. Precipitation in water of a small amount of product provided polymer which possessed an intrinsic viscosity of 12.9 dL/g in methanesulfonic acid at 30°C. The remainder of the solution was used for subsequent synthesis of ABA block copolymers.

Synthesis of ABA Block Copolymer 25 Percent PBT/ 75 Percent ABPBI

An aliquot 14.8g of the above carboxy-terminated PBT solution (0.662g of PBT) and 3, 4-diaminobenzoic acid monohydrochloride (3.23g, 17.1 mmol) was placed in a resin flask equipped as above. After the system was thoroughly flushed with nitrogen, 103g PPA (84 percent P_2O_5) was added to dilute and reduce the viscosity of the PBT polymer. The mixture was stirred and slowly heated to 100°C to effect dehydrochlorination of the AB monomer. After completion of the dehydrochlorination, the mixture was heated to 180°C for 3 hours and 200°C for 16 hours. The viscous solution was cooled to 100°C, precipitated into water, washed with water, then dried at 140°C under reduced pressure to give 2.16g (82 percent) of polymer with an intrinsic viscosity of 10.7 dL/g as determined in methanesulfonic acid at 30°C.

Analysis Calcd for (25 percent, $C_{14}H_6N_2S_2)_n$ (75 percent $C_7H_4N_2 \cdot H_2O$)
C, 62.70; H, 3.93, N, 18.28.
Found: C 61.96; H, 3.94; N, 18.42.

Synthesis of ABA Block Copolymer 30 Percent PBT/ 70 Percent ABPBT

To (0.53g, 1.9 mmol) of carboxy-terminated PBT ([ ]=17.7 dL/g) was added 88g of PPA(84 percent P_2O_5). The mixture was heated under a nitrogen atmosphere at 160°C until a homogeneous solution was obtained. The solution was cooled to 50°C and 4-amino-3-mercaptobenzoic acid hydrochloride (1.92g, 9.3 mmol) was added under reduced pressure. The temperature was maintained at 50°C until dehydrochlorination was complete. The reaction mixture was slowly heated to 190°C and maintained at that temperature for 24 hours. On cooling to 80°C the polymer was precipitated into water, washed with water, methanol, and dried at 140°C under reduced pressure. The polymer exhibited an intrinsic viscosity of 6.5 dL/g as determined in methanesulfonic acid at 30°C.

Analysis Calcd for (30 percent $C_{14}H_6N_2S_2$), (70 percent C_7H_3NS)

C; 63.13; H, 2.80; N, 10.51
Found: C, 62.31; H, 2.48; N, 10.20

Three ABA block copolymers (A,B,D Table 2) were used for solution morphology studies and were solution processed into fibers.

Determination of Critical Concentration, Ccr.

Solution of the block copolymers dissolved in 98 percent methanesulfonic acid (MSA) was prepared initially with the polymer concentration higher than the critical concentration point so that the solution was biphasic when examined under a cross-polarized optical microscope. The microscope used was a Lenitz optical microscope, model Ortholuy II Pol-BK. The solution was kept under a steady stream of dry nitrogen gas to ensure an inert atmosphere. After three days of stirring, and aliquot was removed, placed on a microscope slide, covered with a glass slide cover, and sealed with paraffin wax to prevent moisture contamination of the solution. The slide was examined on the microscope under crossed polars. If regions of higher birefringence were observed, and persisted after 48 hours, MSA was then added to the original solution to incrementally lower the polymer concentration. The newly diluted solution was allowed to stir for at least 48 hours before the next aliquot was repeated until the solution became optically transparent and isotropic i.e., the solution appeared homogeneously dark when examined under the microscope. The concentration of the polymer solution at this point was the Ccr at room temperature.

Wet Spinning of Block Copolymers

Solution of each of the three block copolymers was prepared with polymer concentration at lower than their Ccr. Each solution was transferred to a reservoir, and degassed in a vacuum oven at room temperature for 48 hours before fiber spinning. The fiber spinning apparatus essentially consisted of a solution delivery system, spinnerette coagulation bath, and take-up and drawing devices. The delivery system was a pressure-advanced piston which extrudes solution at constant pressure. A single-hole spinnerette was used with diameter of 0.025 cm. The air gap, the distance between spinnerette and the surface of the coagulant, was approximately 5 cm. The extruded wet and still swollen fibers were immersed in the coagulant water bath for 24 hours. The fibers were then wet-drawn in the water bath between a feed and a take-up drum rotating at different speeds. Fibers were then neutralized in 50-percent ammonium hydroxide for 24 hours and washed with distilled water. The fibers were air-dried followed by vacuum drying at 100°C.

Heat Treatment and Tensile Testing

Heat treatment of the dried fibers was carried out continuously using a cylinderical oven of 10 inches in length and under a constant stream of preheated nitrogen gas. The fibers were subjected to a constant strain through the difference in rotating speed between the feed and take-up drums. The residence time of fibers in heating zone was 30 seconds. Tensile properties of the fibers were measured by ASTM D3379 procedures. The gauge length was 1 inch and the strain rate 0.02 inch/minute. The diameters of the fibers were measured with a split-image microscope.

References

1. T.E. Helminiak, C.L. Benner and F.E. Arnold, Polymer Preprints, 16 (2), 659 (1975).

2. T.E. Helminiak, C.L. Benner, G.E. Husman and F.E. Arnold, U.S. Patent 4,207,407 (1980).

3. W.F. Hwang, D.R. Wiff, C.L. Benner, T.E. Helminiak, J. Macromol, Sci. Phys., B22 (2), 231 (1983).

4. W.F. Hwang, D.R. Wiff, C. Verschoore, G.E. Price, T.E. Helminiak and W.W. Adams, Polym.. Eng. and Sci., 23 (14), 784 (1983).

5. W.F. Hwang, D.R. Wiff, C. Verschoore, Polym. Eng. and Sci., 23 (14) 790 (1983).

6. J.F. Wolfe, B.H. Loo, and F.E. Arnold, Macromolecules, 4, 915 (1981).

7. J.F. Wolfe, P.D. Sybert,and J.R. Sybert, U.S. Patent 4, 533, 693 (1985).

☆U.S.Government Printing Office: 1988 — 548-054/80774