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Polymer 44 (2003) 3837–3846

polymer

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Synthesis and properties of star-like wholly aromatic polyester fibers

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Received 20 August 2002; received in revised form 4 March 2003; accepted 4 April 2003

Abstract

Novel star-like wholly aromatic copolyesters having four arms based on a tetraamine star core, *p*- and *m*- hydroxybenzoic acids and 6-hydroxy-2-naphthoic acid have been successfully synthesized and spun into fibers for the investigation of the effect of the star-like structure on improving compressive properties of the fiber. The reactivity of the star core was demonstrated using a model compound with FTIR, ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of the star-like terpolymer having a molar ratio of 10:1 of the monomers to star core showed a characteristic peak at around δ62 ppm which corresponds to a tetra-substituted carbon and thereby demonstrates that the star core was really incorporated into the polymer. The star-like copolyester exhibited a clear stir opalescence and liquid crystalline morphology in the temperature range of 150–280 °C. However, no transition was observed in the DSC thermogram except a clear T_g at 110 °C. The star-like terpolymer fiber, prepared from a polymer with a molar ratio of 500:1 for the monomers to imide core, was spun in the liquid crystalline state at 180 °C. Fiber structure and properties have been studied.

Keywords: Star-like aromatic copolyesters; Liquid crystal; Fibers

1. Introduction

The liquid crystalline polymers (LCP) have found applications as high modulus fibers and films with unique properties [1–3]. The thermotropic polymers have the advantage that they can be melt processed into fibers or molded parts [4–6]. The axial compressive strength of high performance polymeric fibers is much lower than their tensile strength. The poor axial compressive strength of these polymeric fibers is believed to be due to insufficient lateral interactions between the highly oriented molecules or supramolecular structures, causing them to buckle under an axial compressive load [7,8].

Various methods have been used to improve the compressive properties of high performance fibers by providing lateral interactions. Schematic diagrams of these methods are given in Fig. 1. The introduction of hydrogen bonds in high performance polymers has been attempted as a means to improve compressive strength [9]. The somewhat higher compressive strength of poly(*p*-phenylene terephthalamide) (PPTA), M5, and dihydroxy methyl pendant PBI compared with that of poly(*p*-phenylene benzobisoxazole) (PBO) and poly(*p*-phenylene benzobisthiazole) (PBZT) has been thought to be a result of hydrogen bonding [10–13]. Intermolecular crosslinking has also been considered an effective approach to improve compressive strength [8,9,14–18]. In another approach, a graft copolymer of polyamide and polypeptides has been synthesized by anionic polymerization [19]. It was hoped that the aromatic polyamide would provide the strength and polypeptides, chemical components of spider silk, would provide toughness to the copolymer fiber.

The use of star-like copolymers also has the potential to improve fiber compressive strength. Bhattacharya and coworker [20] synthesized rigid-rod star-block copolymers consisting of flexible poly(dimethylsiloxane) cores having two to six arms, at each end of which a (methoxybenzoyl) oxybenzoic acid mesogen was attached through an amide linkage. All the polymers of this series showed phase separation between the flexible segments and the rigid blocks and nematic liquid crystalline textures in a polarized optical microscope. Some tetrahedrally oriented four-armed star and branched aramids were synthesized by Reichert and Mathias [21]. It was reported that the star aramids exhibited

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doi:10.1016/S0032-3861(03)00323-9

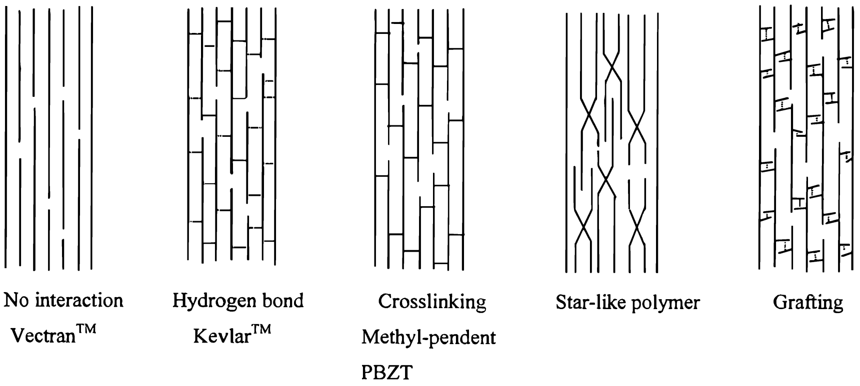

Fig. 1. Schematic morphology diagrams in various fibers for the improvement of compressive strength.

better solubility than branched aramids by disruption of chain packing.

In this paper, we report the synthesis, characterization, and fiber properties of star-like wholly aromatic copolyesters having four arms based on *p*- and *m*- hydroxybenzoic acids and 6-hydroxy-2-naphthoic acid for the investigation of the effect of star-like structure on improving compressive properties of the fiber.

2. Experimental

2.1. Materials

2,7-Dinitro-9-fluorene (97%), aniline hydrochloride (97%), aniline (99.5%), benzoyl chloride, hydrazine monohydrate (98%), palladium on activated carbon, trimellitic anhydride, 4-hydroxybenzoic acid (99%), 3-hydroxybenzoic acid (99%) and 2-hydroxy-6-naphthoic acid (99%) were commercially available from the Aldrich Chemical Co. Aniline was purified by distillation just prior to reaction.

2.2. Measurements

All of the FTIR spectra were obtained by using the Perkin Elmer 1600 series Fourier transform infrared spectrophotometer (FTIR). Solid state FTIR (KBr pellets) was performed on all products. Nuclear magnetic resonance (NMR) spectra were obtained by using the Varian XL-400 unit. ^{13}C NMR analysis on 2,7-diamino-9,9-bis(4-aminophenyl)fluorene and the imide monomer were performed on samples dissolved in DMSO-d_6 while the analyses on star-like terpolyesters were performed on samples dissolved in pentafluorophenol-d or D_2SO_4.

TA instrument DSC (Model Q100) and TGA (Model 2950) units were used to carry out thermal analysis. Fiber diameters were measured using laser diffraction. The tensile properties of the fibers were measured on an Instron tensile tester at a gauge length of 2.54 cm at a crosshead speed of 1.27 mm/min. The torsional modulus measurements were carried out using a free torsional pendulum apparatus placed in a vacuum oven [22]. Scanning electron microscopy was carried out on as-spun and heat-treated fibers using a Hitachi S-800 microscope operated at 15 kV. A Rigaku-Geigerflex unit with Cu Kα radiation was used to record the flat plate wide angle X-ray scattering patterns using a Statton–Warhus camera with a rotating anode generator operated at 45 kV and 25 mA.

2.3. Fiber spinning

The star-like polymer prepared with a 500:1 molar ratio of the monomers to star core was dried in vacuum at 105 °C for 12 h before spinning. Fibers were melt spun at 180 °C using a 500 μm diameter spinneret. The extruded monofilament was solidified in room temperature air and then collected at a take-up speed of 60 m/min.

2.4. Synthesis of 2,7-dinitro-9,9-bis(4-aminophenyl) fluorene dihydrochloride

In a nitrogen atmosphere, a mixture of 54.0 g (0.2 mol) of 2,7-dinitrofluorenone, 80.0 g (0.6 mol) of aniline hydrochloride, and 600 ml (6.6 mol) of aniline was refluxed in a 500 ml three-necked flask for about 24 h. The dihydrochloride salt, which precipitated on cooling to room temperature, was collected by filtration. After drying in a vacuum oven at 120 °C for 24 h, the yield was 57.2 g (56%).

2.5. Synthesis of 2,7-dinitro-9,9-bis(4-aminophenyl) fluorene

2,7-Dinitro-9,9-bis(4-aminophenyl)fluorene dihydrochloride (6.0 g) was dissolved in 300 ml water followed by mixing with a solution which contained 40 g sodium hydroxide and 600 ml water. The precipitate was collected by filtration and washed with water and then was dried in a vacuum oven at 120 °C for 24 h. It can also be purified by recrystallization in a mixture of water and ethanol. Yield: 4.7 g (92%).

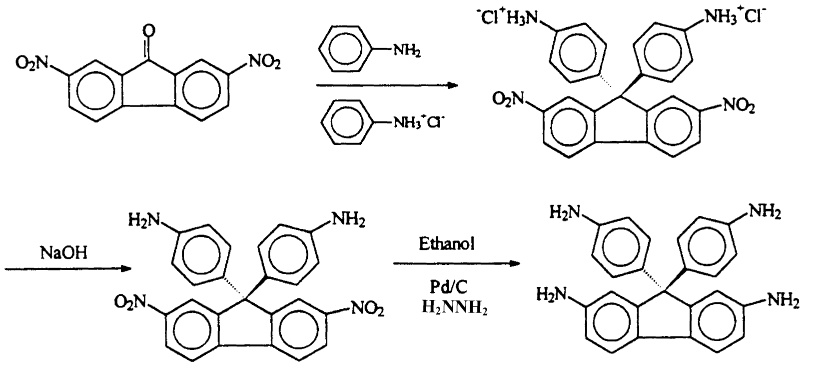

Fig. 2. Synthesis of 2,7-diamino-9,9-bis(4-aminophenyl)fluorine.

2.6. Synthesis of 2,7-diamino-9,9-bis(4-aminophenyl) fluorene

2,7-Dinitro-9,9-bis(4-aminophenyl)fluorene (9.2 g), 230 ml ethanol and 1.12 g Pd/C were heated to reflux. Hydrazine monohydrate (105 ml) was added dropwise to the refluxing mixture which was then heated under reflux for 24 h. The precipitate, after removing ethanol, was collected by filtration and washed with water followed by drying in the vacuum oven at 100 °C for 24 h. Yield: 5.4 g (68%).

2.7. Synthesis of imide monomer (star core)

2,7-Diamino-9,9-bis(4-aminophenyl)fluorene (8.0 mmol 3.024 g) and 32 mmol (6.144 g) of trimellitic anhydride were placed into a 50 ml round bottom flask and subsequently dissolved in 15 ml anhydrous DMAc. After heating the reaction mixture for 1 h at 60 °C (no refluxing at this time), 25 ml anhydrous toluene was added and the reaction system was refluxed until 0.6 ml water distilled azeotropically into a Dean-Stark trap. Rotary evaporation was used to remove the residual toluene and the rest of the mixture was slowly poured into 100 ml of stirred methanol to give a pale green precipitate. This precipitate was slightly viscous and it was stirred for at least 4 h. Then it was recrystallized from aqueous DMAc after treatment with activated carbon. Yield was 84%.

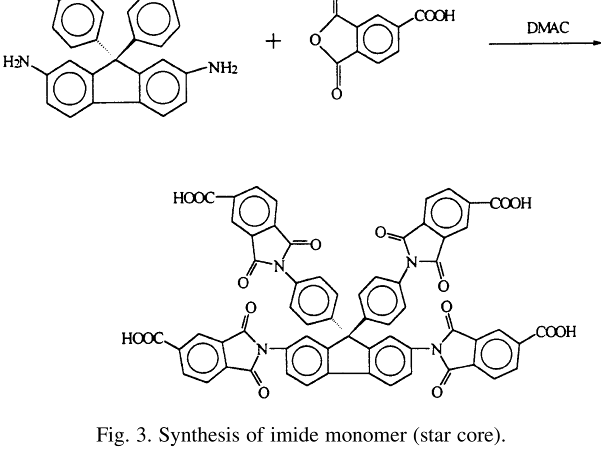

Fig. 3. Synthesis of imide monomer (star core).

2.8. Synthesis of model compound

Toluenesulfonyl chloride (TsCl) (2.06 g, 13.0 mmol) was dissolved in pyridine (10 ml) and the solution was maintained at room temperature for 30 min. To the reaction mixture was added DMF (1.5 ml) for 30 min at room temperature, and then the reaction mixture was added all at once at 120 °C to a warmed solution of *p*-hydroxybenzoic acid (0.552 g, 4.00 mmol) and imide core (1.07 g, 1.00 mmol) in a mixed solvent of pyridine (11 ml) and an amide solvent such as DMF (9 ml) preheated at 120 °C for 5 min. The whole solution was maintained at 120 °C for 4 h. The model compound was separated by pouring the solution into methanol. After extraction by methanol, acetone and water for 96 h, the precipitate was collected by filtration and vacuum dried at 80 °C. Yield: 1.2 g (88%).

2.9. Synthesis of star-like poly[(p-hydroxybenzoic acid)-co-(m- hydroxybenzoic acid))-co-(2-hydroxy-6-naphthoic acid)].

TsCl (2.06 g, 13.0 mmol) was dissolved in pyridine (10 ml) and the solution was maintained at room temperature for 30 min. The reaction mixture was treated with DMF (1.5 ml) for 30 min at room temperature, and then added all at once at 120 °C to a warmed solution of *p*-hydroxybenzoic acid (0.552 g, 4.00 mmol), *m*- hydroxybenzoic acid (0.414 g, 3.00 mmol), 2-hydroxy-6-naphthoic acid (0.564 g, 3.00 mmol) and star core (different molar ratio to the acids) in a mixed solvent of pyridine and DMF preheated at 120 °C for 5 min. The whole solution was maintained at 120 °C for 4 h. Polymers were separated by pouring the solutions into methanol. After extraction by methanol, acetone and water for 96 h, the precipitate was filtered and vacuum dried at 80 °C. Yield is approximately 86% based on the different molar ratios of monomer to star core. In the polymerization of star-like terpolyester, two different molar ratios, 10:1 and 500:1, of the monomers to star core were used.

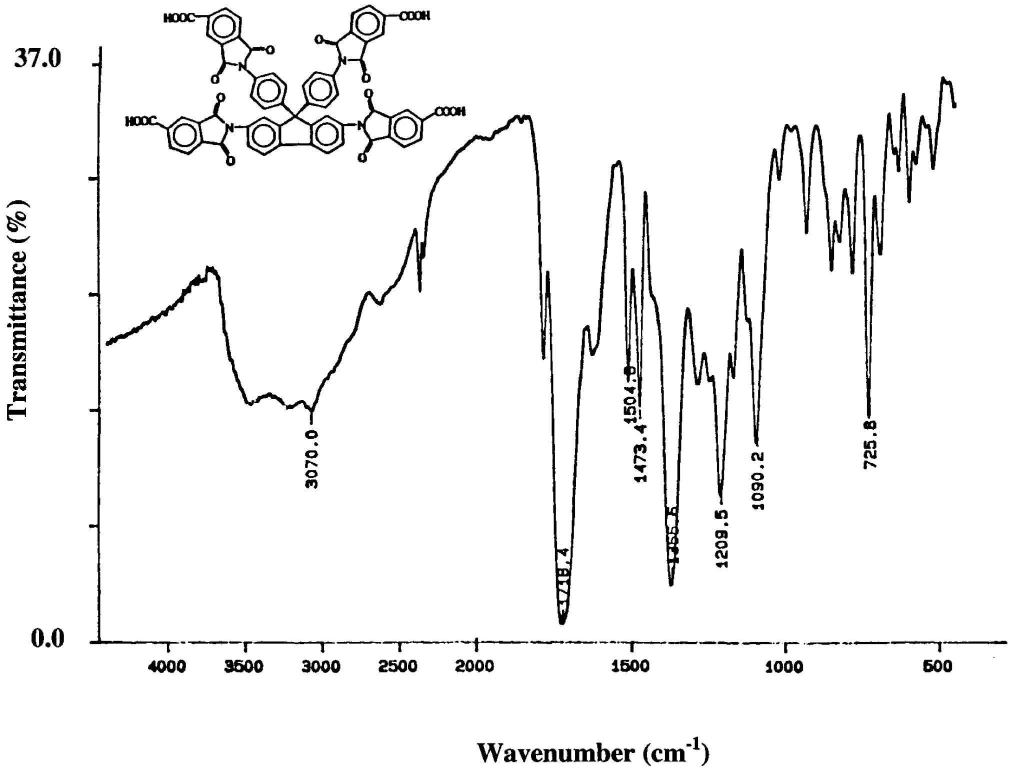

Fig. 4. FTIR spectrum of the imide monomer (star core).

3. Results and discussion

3.1. Synthesis and characterization

There are several steps involved in the synthesis of star-like copolyesters and terpolymers. First, 2,7-diamino-9,9-bis(4-aminophenyl)fluorene was obtained. Since this product has four amino groups extending along four different directions, it was conjectured that it might be a useful core for the preparation of polyesters, polyamides, polyimides, and polyurethanes with interesting properties. The reactions employed in synthesizing the tetramine core are shown in Fig. 2. The successful synthesis of the compound was confirmed using spectroscopy and elemental analysis.

The imide monomer (star core) was synthesized by reacting 2,7-diamino-9,9-bis(4-aminophenyl)fluorene with

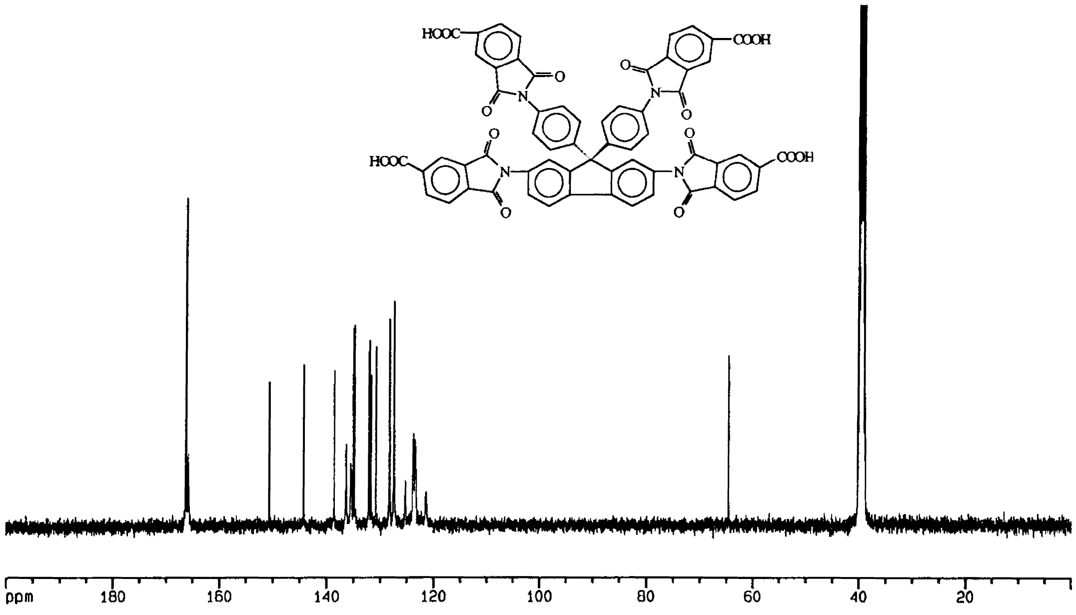

Fig. 5. ^{1}H NMR spectra of the imide monomer (star core).

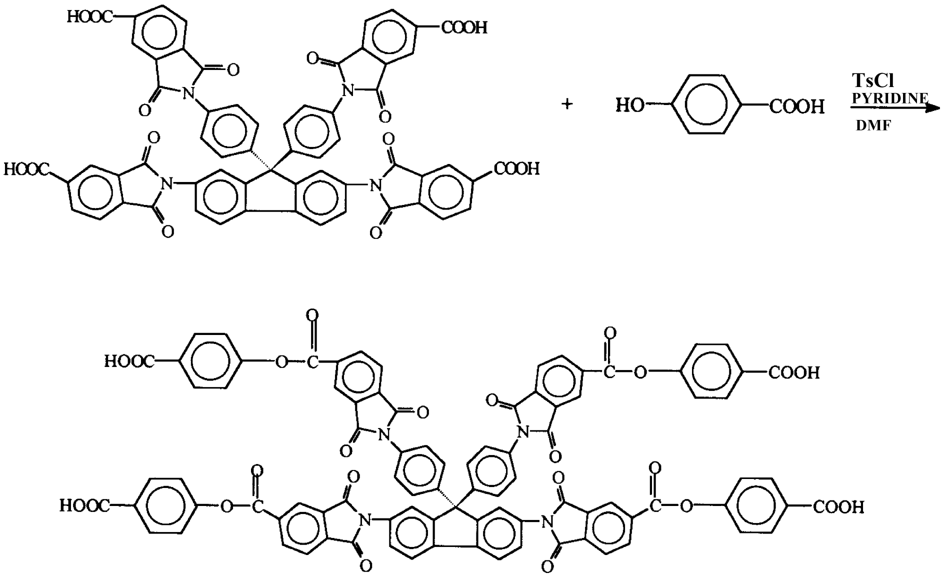

Fig. 6. Synthesis of model compound.

trimellitic anhydride as shown in Fig. 3. As amino groups were replaced by imide groups, an imide C=O stretching peak appears at 1718.4 cm^{-1} as shown in the FTIR spectrum of Fig. 4. If the amino groups had not reacted with the anhydride group, there would be strong peaks at 1865 and 1782 cm^{-1}, which are characteristic of the C=O stretch in the anhydride structure. However, those peaks were absent. Moreover, the disappearance of two peaks at 1299 and 1281 cm^{-1}, which are characteristic of the C–N stretch in the aromatic amine group demonstrates that all four amine groups were successfully replaced by imide groups.

The ^{13}C NMR spectrum of the star core comonomer is shown in Fig. 5. There are two important peaks in this spectrum. One which appears at δ166 ppm corresponds to the carbon of the imide group. The other which appears at ca. 65 ppm is characteristic of the quaternary carbon of the anthrone ring system.

A model compound was prepared under polymerization conditions involving reaction of the star core with hydroxybenzoic acid to confirm the reactivity of the star core with hydroxyl comonomers (Fig. 6). The infrared spectrum of the model compound is shown in Fig. 7. The most important difference between the infrared spectra of the star core and model compound is the decrease in intensity of the –OH (–COOH group) stretch peak above 3000 cm^{-1} after reaction.

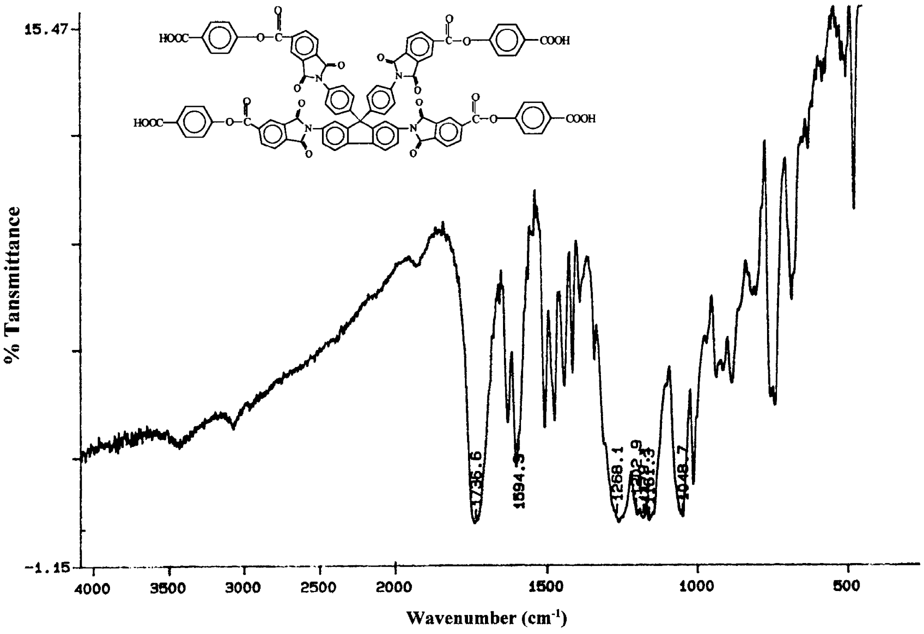

Fig. 7. FTIR spectrum of the model compound.

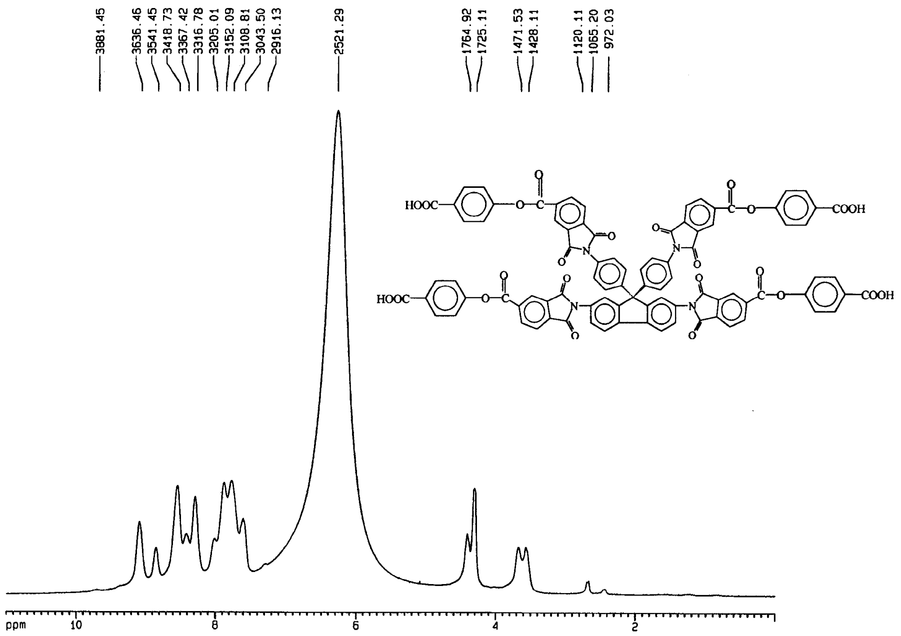

Fig. 8. ^{1}H NMR spectra of the model compound.

This is because the four –COOH groups reacted with –OH groups in hydroxybenzoic acid and formed the ester bond. Strong peaks at around 1736.6 cm^{-1} in Fig. 7 are C=O stretching peaks. Figs. 8 and 9 exhibit ^{1}H and ^{13}C NMR spectra of the model compound, respectively. In the ^{1}H NMR spectrum, the large peak at δ6.3 ppm corresponds to the protons on the benzene rings of the carboxybenzeneoxycarbonyl benzene structure. Based on the spectrum of the star core, the peaks above 7.7 ppm correspond to the star core. Moreover, the peaks at δ167 and 68 ppm in the ^{13}C NMR spectrum of the model compound demonstrate that the star core reacted with hydroxybenzoic acid. From these spectroscopic results, it is concluded that the star core reacted with hydroxybenzoic acid and formed a four-arm star structure.

Star-like poly[(*p*-hydroxybenzoic acid)-co-(*m*-hydroxy-

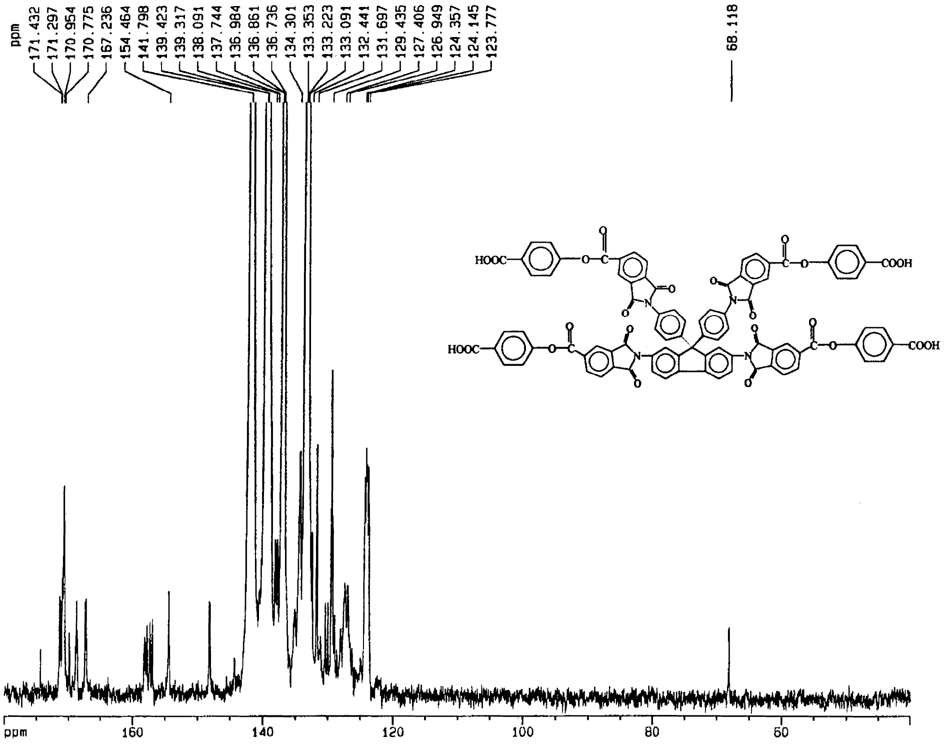

Fig. 9. ^{13}C NMR spectrum of the model compound.

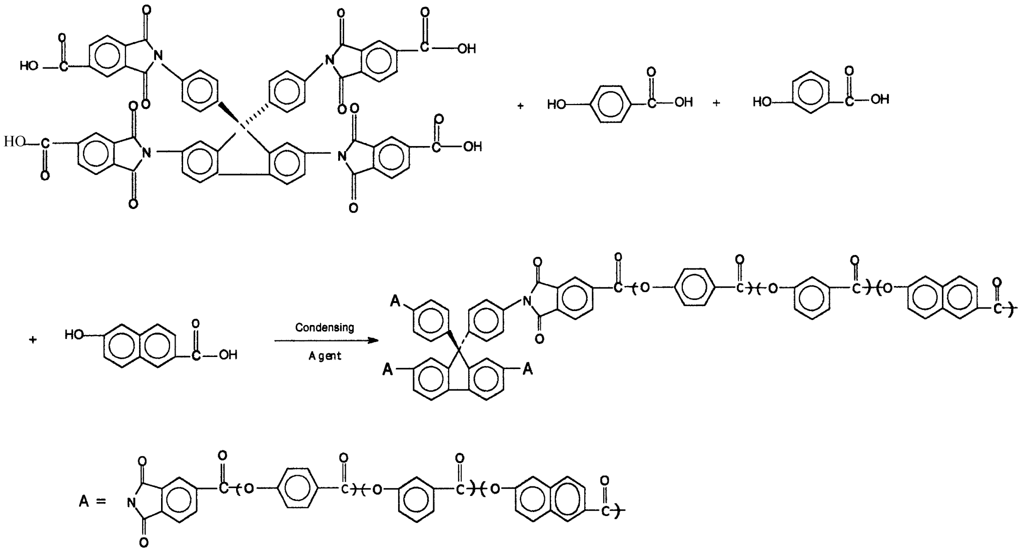

Fig. 10. Synthesis of star-like polymers.

Table 1
Elemental analysis data

Materials	C		H		N	
	Calc.	Found	Calc.	Found	Calc.	Found
2,7-diamino-9,9-bis(4-aminophenyl)fluorene	79.4	79.23	5.85	5.93	14.80	14.77
Star core monomer	68.16	68.33	2.81	2.88	5.21	5.30
Star-like terpolymer(500:1)	70.91	72.03	2.98	3.68	2.31	3.52

benzoic acid)-co-(2-hydroxy-6-naphthoic acid)]s were synthesized by the solution polymerization method. The initial molar ratio of acids used to form the three units in the arms (*p*-hydroxybenzoic: *m*-hydroxybenzoic: hydroxynaphthoic) is 4:3:3. Copolymerization was carried out by varying the aging time of the initial reaction of TsCl and pyridine. Formation of the sulfonium salt of TsCl and pyridine before addition of DMF seemed to be essential to obtain reproducible results, and is completed after 10 min at room temperature. The replacement of DMF by *N*,*N*-dimethylacetamide (DMAc) or N-methylpyrrolidone (NMP) largely retarded the reaction. These results cannot be explained by the polymer solubility. It is assumed that these amides are involved in the reaction itself. Two kinds of star-like polymer were synthesized with molar ratios of monomer to star core of 10:1 and 500:1, respectively. The synthesis reaction is shown in Fig. 10.

The ^{13}C NMR spectrum of the star-like terpolymer (10:1)

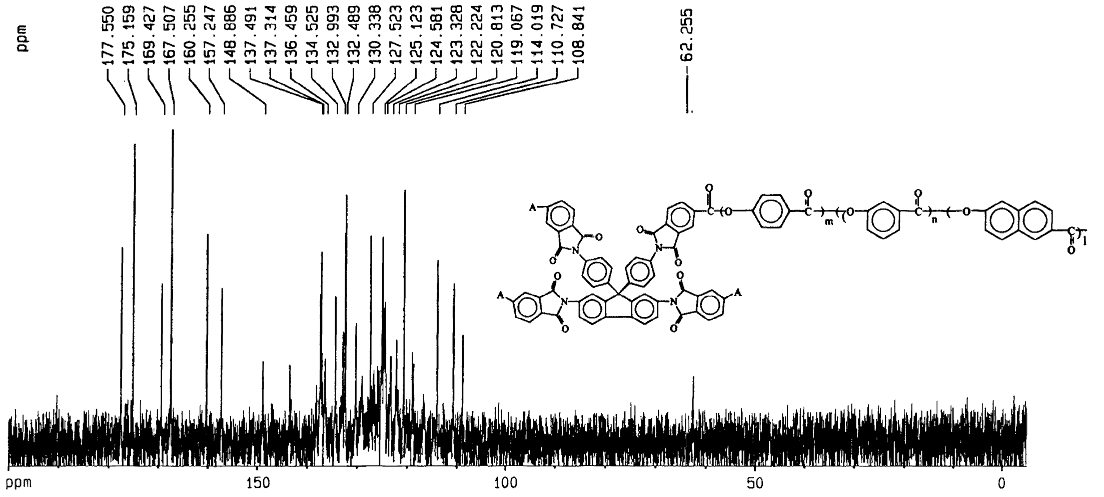

Fig. 11. ^{13}C NMR spectrum of the star-like polymer (500:1).

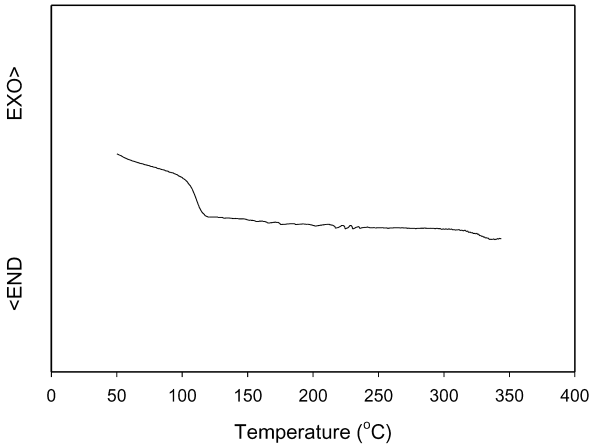

Fig. 12. DSC thermogram of the star-like copolyester with a heating rate of 20 °C/min.

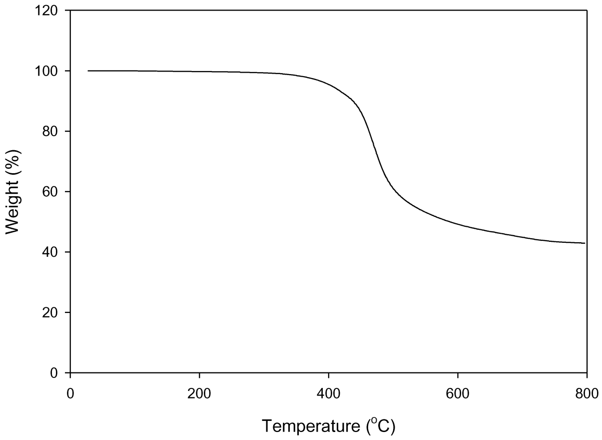

Fig. 14. TGA thermogram of the star-like copolyester (500:1) with a heating rate of 10 °C/min.

Table 2
Mechanical properties of as-spun and annealed fibers

	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Torsional modulus (GPa)
As-spun fiber	10.4 ± 1.5	163 ± 38	1.69 ± 0.4	0.90 ± 0.1
Heat treated fiber	8.4 ± 1.2	143 ± 34	1.60 ± 0.5	1.01 ± 0.1

is given in Fig. 11. The characteristic peak at approximately δ 62 ppm which is seen in the star core and model compound spectra is also present in the spectrum. This demonstrates that the star core was incorporated into the polymer.

The elemental analysis data for 2,7-diamino-9,9-bis(4-aminophenyl)fluorene, star-core comonomer and star-like terpolymer (500:1) are shown in Table 1. The results for 2,7-diamino-9,9-bis(4-aminophenyl)fluorine and star core monomer were within acceptable limits. However, that of star-like terpolymer exhibited a larger deviation from the theoretical values particularly in nitrogen and hydrogen. As a great deal of pyridine was used as a condensing agent, it is proposed that pyridine remains in the system as a component of pyridinium salts formed at chain ends.

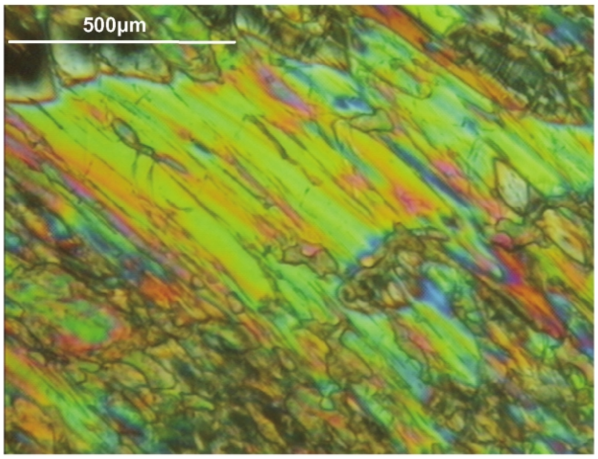

Fig. 13. Polarized light micrograph of the star-like copolyester at 180 °C.

The DSC profile of the star-like polymer (500:1) is shown in Fig. 12. While it exhibited a clear T_g at around 110 °C, no notable melting transition was seen. However optical microscopy exhibited liquid crystalline behavior at ca. 150 °C (Fig. 13). The liquid crystalline state was maintained up to ca. 280 °C, and above this temperature an isotropic region developed. Polymer degradation also begins to occur at ~280 °C (Fig. 14). It is interesting that the star-like terpolyester exhibits a wide anisotropic melting temperature range. Clear stir-opalescence was also observed in the liquid crystalline region.

3.2. Structure and properties of the star-like polymer fiber

The tensile properties of the fiber are listed in Table 2. The modulus and strength of star-like polymeric fibers are not on the high performance level even though the fiber was prepared in the liquid crystalline state at 180 °C. The main reason for the inferior mechanical properties is considered to be the low molecular weight of the star-like polymer used in the fiber due to difficulties in polymerization. The intrinsic viscosity of the star-like polymer (500:1) in *p*-chlorophenol at 50 °C was 0.38 g/dl.

In the X-ray photograph of Fig. 15, it is noted that the star-like polymeric fiber is well oriented without further drawing but exhibits very low crystallinity even after heat-treatment. The lack of lateral packing due to steric hinderance by the star-core results in inherently amorphous structure in the fiber. In addition, the meta-ester units also prevent ordered chain packing in the solid fiber.

A linear correlation has been observed between the

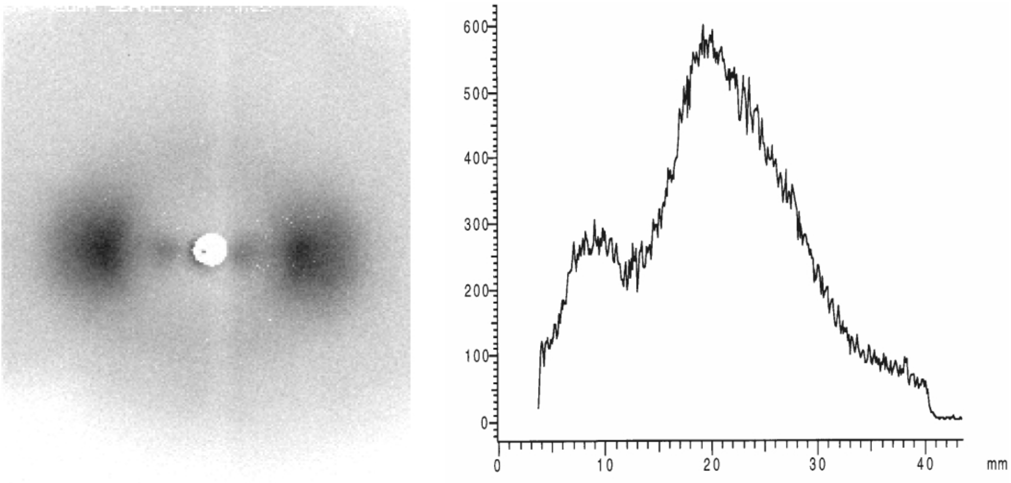

Fig. 15. X-ray photograph of the annealed fiber from the star-like polymer (500:1).

compressive strength and torsional modulus for a number of liquid crystalline fibers [23,24]. The torsional modulus of the star-like polymeric fiber is 0.9–1.0 GPa at room temperature which is much higher than that of VectranTM fiber (0.6 GPa). VectranTM fiber has an extended and well-oriented rigid-chain structure and does not have any intermolecular cross-linking.

The improvement in the torsional modulus for the star-like polymer can be attributed to the presence of the star core. Each core of the star-like polymer acts as an entanglement point connecting four linear arms together. This improved torsional modulus implies higher compressive strength, but the compressive properties of star-like polymeric fiber could not be measured by the recoil compression test due to the low tensile strength of the fiber (Fig. 16).

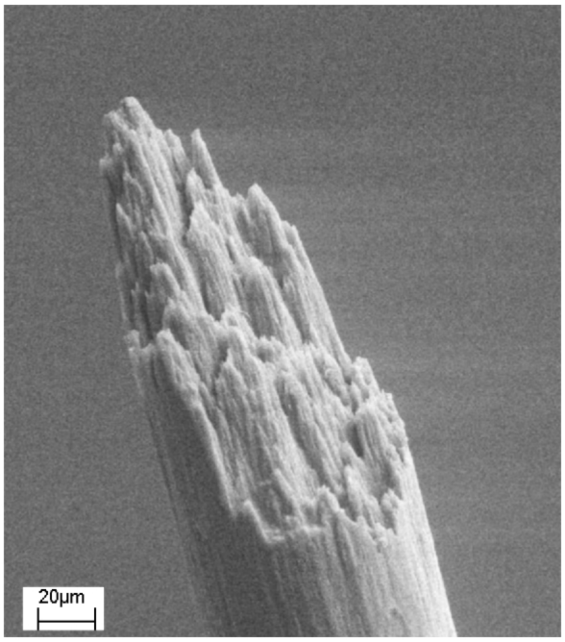

Fig. 16. Scanning electron micrograph of a fractured fiber of the star-like polymer (500:1).

4. Conclusion

Novel star-like wholly aromatic copolyesters having four arms based on *p*- and *m*- hydroxybenzoic acids and 6-hydroxy-2-naphthoic acid have been successfully synthesized and spun into fibers. The star-like copolyester exhibited clear stir opalescence and liquid crystalline morphology in the temperature range of 150–280 °C. The star-like polymer fiber spun in the liquid crystalline state at 180 °C had inferior tensile properties due to low crystallinity because of steric hinderance preventing the packing of the molecules. However, its torsional modulus was 50% higher than that of theVectran$^{\text{TM}}$fiber.

Acknowledgements

The financial support from the Office of Naval Research and the National Textile Center is highly appreciated. We are grateful to Dr L. Gelbaum for NMR assistance.

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