248 *Chem. Mater.* **1993,** *5,* 248–250

Cross-Linkable Copolymers of Poly(*p*-phenyleneterephthalamide)

Larry J. Markoski,[‡] Kenneth A. Walker,[‡]
Gary A. Deeter,[‡] Gary E. Spilman,[†]
David C. Martin,[*,§,†] and Jeffrey S. Moore[*,‡,†]

The H. H. Dow Building and W. H. Dow Laboratory
Departments of Chemistry and
Materials Science and Engineering and
The Macromolecular Science and Engineering Center
The University of Michigan
Ann Arbor, Michigan 48109-1055

Received October 22, 1992
Revised Manuscript Received December 22, 1992

Current high-performance extended-chain and rigid-rod polymers such as poly(*p*-phenyleneterephthalamide) (PPTA or Kevlar), poly{(benzo[1,2-d;4,5-d′]bisthiazole-2,6-diyl)-1,4-phenylene} (PBZT), and poly{(benzo-[1,2-d;4,5-d′]-bisoxazole-2,6-diyl)-1,4-phenylene} (PBZO) form fibers that are extremely stiff (modulus $\sim$ 100–350 GPa) and strong in tension (tensile strength $\sim$ 2.0–3.5 GPa) but are relatively weak in compression (tensile strength: compressive strength $\sim$ 10:1).[1] These relatively poor compressive characteristics now limit the use of these materials in structural applications. The weakness in compression is presumably due at least in part to the ease of buckling of individual molecules or microfibrils, resulting from the lack of strong lateral interchain interactions.[1b] The addition of transverse covalent bonding might improve compressive strengths of these fibers. However, to maintain excellent tensile properties, we believe that it will be necessary to preserve high chain orientation. These ideas suggest the concept of an ordered, 3D polymer network. Such a model might represent an intermediate structure between carbon fiber (strong in compression and brittle) and current high-strength aromatic polymer fibers (weak in compression and tough). Figure 1 schematically represents the structures of these limiting cases and that of a cross-linked, extended-chain polymer fiber. By controlling the extent of lateral covalent bonding, it may be possible to tune mechanical properties between these two extremes.

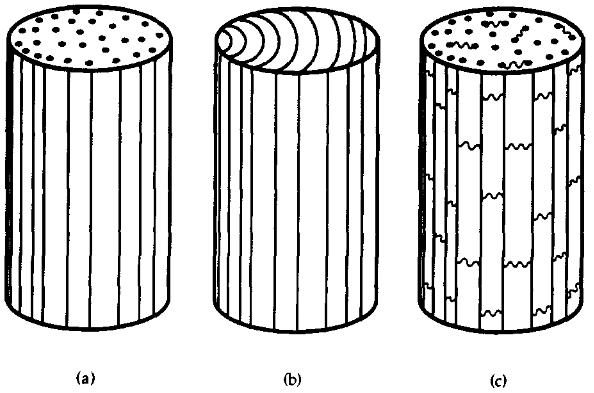
(a) (b) (c)

Figure 1. Schematic representations of the morphology of (a) an extended-chain polymer fiber, (b) a carbon fiber, and (c) a cross-linked, extended-chain polymer fiber. The extended-chain polymer fiber (a) consists of highly oriented linear chains. These fibers are strong and stiff in tension, but are weak in compression. The carbon fiber (b) consists of highly oriented planes. These fibers are strong and stiff in both tension and compression, but they exhibit limited plastic deformation. A cross-linked, extended-chain polymer fiber (c), in which the degree of cross-linking can be varied, may provide a means to fibers that are strong and stiff in tension and compression, yet also tough.

To achieve a high level of chain orientation, fiber processing schemes such as dry-jet wet-spinning of lyotropic liquid-crystal solutions are often employed.[2] To use these processing methods and also to introduce interchain covalent bonding into such oriented fibers, a chemical reaction must occur in the solid state following fiber spinning. Polymer chains thus need to be equipped with a reactive group that lies dormant throughout the initial stages of fiber processing but which can be triggered into a reactive state at some later time. In terms of the established fiber processing schemes, it might be desirable to design cross-link chemistry that could take place during postspinning heat treatment. For such a system, processing and chemical reactivity would be intimately coupled; thus, attainment of optimal mechanical properties might be strongly dependent on the timing of the chemical event relative to the physical changes that accompany postspinning heat treatment.

Attempts to cross-link aromatic polymer fibers are known.[3] Sweeny[3a] has recently reported interesting work on the cross-linking of PBZT and PPTA copolymers that incorporate aryl halide comonomers. The thermal elimination of halogen in these materials is apparently accompanied by interchain coupling, and improvements in compressive properties based on shear modulus and recoil stress-to-failure tests were demonstrated as the level of cross-linking increased. While this work convincingly established the importance of lateral bonding to compressive strength, the chemical nature of this system has several drawbacks. First, the cross-linking reaction is relatively slow, requiring several minutes to hours for significant extents of reaction to occur even at elevated temperatures (e.g., for iodo-containing PBZT copolymers, 50% of total halogen loss required ca. 5 min at 500 °C). Second, bromo- and iodo- were the most favorable halides, meaning that the cross-linking reaction is accompanied by a large loss of mass. This may lead to voids, perhaps explaining the drop in tensile properties at high cross-link levels. Third, at high halo-comonomer compositions, lyotropic liquid-crystal ordering is not observed, and the corresponding fibers show significantly reduced tensile properties (fibers air-gap spun from isotropic solutions).

We previously described the synthesis of a new monomer, XTA, designed specifically as a reactive derivative of terephthalic acid that could be incorporated into many types of currently-interesting rigid-rod or extended-chain polymers.[4] This monomer contains the benzocyclobutene

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[‡] Department of Chemistry.

[†] The Macromolecular Science and Engineering Center.

[§] Department of Materials Science and Engineering.

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(4) Walker, K. A.; Markoski, L. J.; Moore, J. S. *Synthesis* **1992**, 1265–8.

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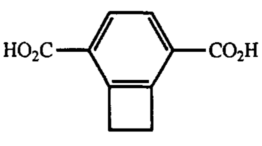

XTA

(BCB) moiety which has been shown to be a thermally cross-linkable group.[5] At elevated temperatures, the cyclobutene ring opens to generate the reactive *o*-quinodimethane intermediate, which is capable of heterocycloaddition chemistry if suitable dienophiles are available.[6] In the absence of dienophiles, *o*-quinodimethanes will undergo cyclodimerization[7] followed by a cascade of reactions that ultimately lead to poly(*o*-xylenes) or dibenzocycloocta-1,5-dienes.[8] Thus, the anticipated cross-linking reactions should not result in a change in mass.

The difference between XTA and other known BCB monomers is that the cyclobutaarene ring of XTA is incorporated directly into the polymer backbone instead of being used as an end group or as a pendant group. Consequently, we envisioned that XTA could be substituted for terephthalic acid in rigid-rod polymers without disrupting the liquid-crystalline ordering characteristic of many of these macromolecules. Besides the preservation of liquid-crystalline order, several other points needed to be demonstrated to show the potential of XTA as a useful cross-linkable substitute for terephthalic acid. These include the ability to synthesize high molecular weight aromatic polymers and copolymers of XTA that maintain adequate chemical and thermal stability in extreme solvents such as 100% H_2SO_4. Moreover, the feasibility of performing the cross-linking reaction in the solid state and at low XTA compositions was unknown at the start of this work. Finally, we hoped to confirm that the cross-linking reaction could be executed with little change in polymer mass. This preliminary report addresses these issues using copolymers of phenylenediamine, terephthalic acid, and XTA (see Scheme I).

Scheme I. Synthesis of PPTA-*co*-XTA Copolymers

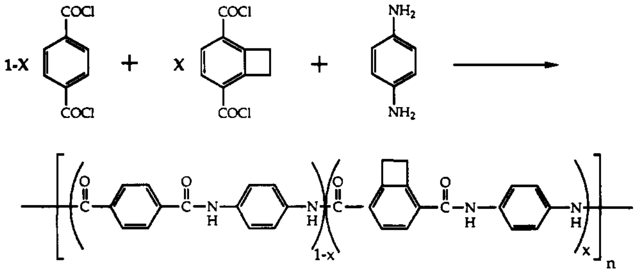

Table I. Viscosity, Solubility, and DSC Data of PPTA-*co*-XTA Polymers

mol % XTA[a]	inherent viscosity[b] (dL g^{-1})	T_r[c] (°C)	heat of rxn (kcal mol^{-1})[d]	solubility[e] of copolymers in 98% H_2SO_4	
				pristine	heat-treated[f]
0	5.0	ND	ND	s	s
1	4.9	ND	ND	s	i
5	4.8	373	0.41	s	i
10	5.5	392	1.0	s	i
25	4.8	379	2.3	s	i
50	5.5	380	4.5	s	i
100	4.5	375	8.1	s	i

[a] Mole percent of total diacid that is XTA. [b] Inherent viscosity at 30 °C in 98% H_2SO_4 at a concentration of 0.5 g dL^{-1}. [c] Temperature at which the maximum of the reaction exotherm was observed (heating rate 15 °C min^{-1}). [d] Enthalpy per mole of copolymer repeat unit. [e] s = soluble; i = insoluble. [f] Samples heated rapidly (ca. 100 °C min^{-1}) to 400 °C and held at this temperature for 30 s. ND = no exotherm detected by DSC.

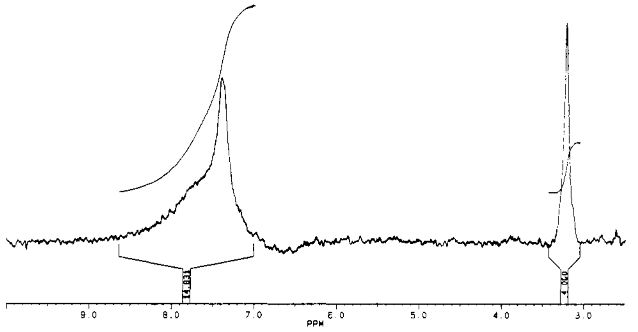

Figure 2. Representative ^1H NMR spectrum of the copolymer containing 50 mol % XTA recorded in 98% D_2SO_4 (room temperature, 360 MHz).

Copolymers were prepared by an adaptation of the low-temperature solution method typically used[9] for the synthesis of PPTA (supplementary material; see paragraph at end of paper). The mole fraction of diacid that was XTA ranged from 1 to 100% (see Table I). Dilute solutions of the copolymers for characterization purposes were readily prepared by heating the polymers in 98% sulfuric acid at 60 °C. Using deuterated sulfuric acid, ^1H NMR spectra of the copolymers were obtained. A representative spectrum, that for the copolymer incorporating 50% XTA, is given in Figure 2. The singlet at $\delta = 3.2$ corresponds to aliphatic protons on the cyclobutaarene ring and is evidence of the stability of this repeat unit in sulfuric acid. The relative ratio of aliphatic to aromatic protons confirms the chemical composition, and the absence of observable end groups suggests high molecular weight polymer. These spectra have not provided any information about the copolymer microstructure (assumed to be nearly random). The ^1H NMR spectra also confirm the absence of trapped polymerization solvent which is prevalent if adequate measures are not taken during polymer workup. Finally, as judged by NMR, solutions of the XTA copolymers are stable for extended time at room temperature in concentrated sulfuric acid. Viscosity data on the copolymers are provided in Table I. The inherent viscosities in 98% sulfuric acid at 30 °C and concentrations of 0.5 g dL^{-1} were found to be in the range 4.5–5.5 dL g^{-1}. These values are comparable to those of commercially available PPTA homopolymer and suggestive of high molecular weight (>20 000).[10]

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(6) For a recent example of a monofunctional BCB monomer that undergoes thermal Diels–Alder polymerization see: Hahn, S. F.; Martin, S. J.; McKelvy, M. L. *Macromolecules* **1992**, *25*, 1539–45.

(7) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949–54.

(8) For a recent review on the chemistry of *o*-quinodimethanes see: Martin, N.; Seoane, C.; Hanack, M. *Org. Prep. Proc. Int.* **1991**, *23*, 237–72.

(9) (a) Kwolek, S. U.S. Patent 3,671,542, 1972. (b) Kwolek, S. U.S. Patent 3,819,587, 1974. (c) Bair, T. I.; Morgan, P. W. U.S. Patent 3,673,143, 1972. (d) Bair, T. I.; Morgan, P. W. U.S. Patent 3,817,941, 1974. (e) Bair, T. I.; Morgan, P. W.; Killian, F. L. *Macromolecules* **1977**, *10*, 1396–1400.

Concentrated solutions (20 wt %) of these copolymers have been prepared in 100% sulfuric acid at 80 °C. As determined by polarized light microscopy, polymers incorporating 100% XTA are lyotropic at this concentration. At temperatures below ca. 100 °C, a birefringent fluid is observed with a texture reminiscent of other lyotropic aramid solutions.[11] From preliminary fiber spinning studies, these solutions appear to be suitable for use in the dry-jet wet process. Optimization of fiber spinning for the various copolymers is currently in progress.

The cross-linking reaction has been investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and solubility experiments. Table I shows that the temperature characterizing the maximum of the reaction exotherm is about 380 °C regardless of copolymer composition. The enthalpy of this reaction varies approximately linearly with mole percent XTA ($\Delta H \sim 8.0$ kcal/mol of XTA). Following brief (30 s) exposure at 400 °C in nitrogen, all of the copolymers shown in Table I are no longer soluble in concentrated sulfuric acid. As a control experiment, PPTA homopolymer (i.e., 0% XTA) was found to fully redissolve after being subjected to identical heating conditions. These results indicate that XTA is directly responsible for the cross-linking reaction and that this reaction can operate in the solid state. Interestingly, the heat-treated copolymer that contained only 1% XTA swelled considerably in 98% H_2SO_4 to an optically clear yellow gel that reversibly shrunk upon coagulation in water.[12] The ability to cross-link copolymers having such low XTA compositions suggests that the cross-link reaction need not require close proximity of two BCB groups on neighboring chains. The chemical nature of the cross-link juncture and the extent of cross-linking for various XTA compositions are currently under study in our laboratory.

TGA confirms that the XTA copolymers undergo cross-linking without significant mass loss. Figure 3 shows typical TGA curves for pristine copolymers in a nitrogen atmosphere. In all of the samples, little mass loss occurs before 500 °C, which is well above the cross-linking temperature.

In summary, high molecular weight copolymers incorporating various contents of the thermally-reactive XTA comonomer have been synthesized. These copolymers are stable in sulfuric acid and at high concentrations these solutions form birefringent fluids. The XTA copolymers can be cross-linked without significant mass loss in the solid state by brief exposure at 400 °C in nitrogen. Cross-linking occurs even for copolymers that contain only 1 mol % XTA. Fiber spinning of these reactive copolymers is in progress.

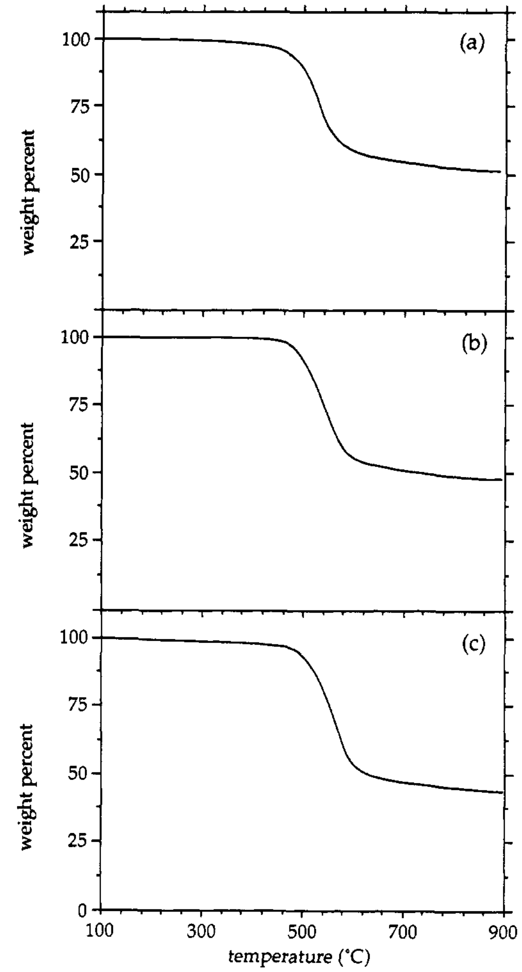

Figure 3. Thermogravimetric analysis traces recorded on pristine copolymers at a heating rate of 15 °C min^{-1} in a nitrogen atmosphere: (a) 100 mol % XTA: (b) 50 mol % XTA; (c) 25 mol % XTA.

Acknowledgment. This research is funded by the U.S. Army (DAAK60-92-K-0005). D.C.M. acknowledges support from the NSF Young Investigator Program (1992–1997). J.S.M. acknowledges the 3M Co. for support through their awards program for untenured faculty and the NSF Young Investigator Program (1992-1997). We thank James Markoski for help in the design and construction of the polymerization apparatus.

Supplementary Material Available: Experimental details of copolymer preparation (3 pages). Ordering information is given on any current masthead page.

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(10) Yang, H. H. *Aromatic High-Strength Fibers*; Wiley: New York, 1989; p 227.

(11) Panar, M.; Beste, L. F. *Macromolecules* 1977, *10*, 1401–06.

(12) The cross-linking of copolymers having small XTA compositions will of course be very sensitive to molecular weight. The fact that we were able to cross-link the copolymer having only 1% XTA to a completely insoluble material is further support of the high molecular weight nature of these macromolecules.