Precursor polymers: 1. Synthesis and characterization of processable precursors to aramids

Issifu I. Harruna*
Chemistry Department, Morris Brown College, Atlanta, GA 30314, USA, and High Performance Polymers and Ceramics Center, Clark Atlanta University, Atlanta, GA 30314, USA

and Kofi B. Bota and Sherita D. McLamore
Chemistry Department and High Performance Polymers and Ceramics Center, Clark Atlanta University, Atlanta, GA 30314, USA
(Received 9 October 1992; revised 8 March 1993)

Processable precursor polymers to aramids, poly(imino-1,4-phenyleneiminocarbonyl-1,4-phenylenecarbonyl) and poly(imino-1,3-phenyleneiminocarbonyl-1,4-phenylenecarbonyl), were prepared and studied. The precursor polymers were made from the reaction of 2,5-dichlorobicyclo[2.2.2]octane-1,4-dicarbonyl chloride with 1,4-phenylenediamine or 1,3-phenylenediamine. The polymeric precursors were subsequently converted in approximately 97% yields, via dehydrohalogenation and retro Diels–Adler reactions, to the corresponding aramids by refluxing in 1 M solution of potassium hydroxide or sodium hydroxide. Only the *p*-phenylene precursor polymer exhibited liquid crystal characteristics in solution. The solubility and thermal properties were examined.

(Keywords: precursor polymers; aramids; dehydrohalogenation)

Introduction

Desirable properties of main chain liquid crystalline aramids, such as poly(imino-1,4-phenyleneiminocarbonyl-1,4-phenylenecarbonyl), include high crystallinity, a high degree of orientation, high modulus and tensile properties, low solubilities in common organic and inorganic solvents, high glass transition temperatures and relatively high melting points.

These properties are considered valuable for many applications, but impose serious limitations in processing and fabrication techniques. The high melting temperatures of aramids often exceed the decomposition temperatures, thereby eliminating melt processing as an option. Low solubilities in organic and inorganic solvents reduce solvent options to 98% sulfuric acid, *N*-methyl-2-pyrrolidone/$CaCl_2$, hexamethylphosphoramide/*N*-methyl-2-pyrrolidone/LiCl, dimethylsulfoxide/$KOBu^t$/methanol, and nitromethane/Al_2Cl_6.

In order to allow easier processing and fabrication, the melting transitions of these rigid chain polymers must be substantially depressed and their solubility in common organic and inorganic solvents increased.

Recently, intense synthetic efforts have been devoted to achieving easier processability while retaining the remarkable properties associated with these polymers[1–7]. These approaches are to some extent self-defeating, since two of the advantages of liquid crystalline polymers are the high heat performance and the solvent resistance. One approach that has not been tried is to prepare liquid crystalline precursor polymers which are more processable, and which can can be chemically transformed to the desired high temperature liquid crystalline polymer after it has been processed into the desired shape. This concept has gained wide acceptance in the preparation of preceramic polymers[8], but is just beginning to be explored for the preparation of intractable organic polymers. Preparations of prepolyphenylene polymers[9–11] are some of the few examples in the literature.

We present herein the preparation of a polymeric precursor to poly(imino-1,4-phenyleneiminocarbonyl-1,4-phenylenecarbonyl) and its subsequent chemical transformation into the aramid. The *m*-phenylene precursor polymer was also prepared and transformed into the corresponding aramid.

Experimental

Solvent purification. All organic solvents were purified by fractional distillation and dried over molecular sieves.

Physiochemical characterizations. Infra-red spectra were obtained on KBr discs with a Nicolet 5DX *FT*i.r. spectrophotometer. Elemental analysis data were provided by Atlantic Microlabs, Inc. Photospectrometry elemental analysis was performed on the polymers utilizing the ETEC Autoscan scanning electron microscope with a Kevex Delta Plus X-ray microanalysis system. X-ray diffractions were performed with a Rigaku Ru-200 generator with D/Max B goniometer operating at 45 kV and 100 mA. Transmission patterns were collected. Gas chromatograph data were obtained with a Varian 3400 gas chromatograph. Proton-decoupled ^{13}C n.m.r. spectra were determined on deuterated *N*,*N*-dimethylformamide (DMF) solutions with a Bruker AC-80 spectrometer equipped with an Aspect 3000 computer. ^1H n.m.r. spectra were determined in deuterated DMF with a Bruker WM-250 spectrometer equipped with an Aspect 3000 computer. Melting, decomposition and glass transitions of the polymers were determined on the Perkin–Elmer DSC 7 differential scanning calorimeter under nitrogen atmosphere and in air. The thermo-

*To whom correspondence should be addressed

0032-3861/93/153328-04

gravimetric analyses were done in nitrogen atmosphere with the Du Pont 990 thermal analyser. All thermograms were obtained at a heating rate of 10°C min^{-1} in sealed aluminium pans. Transition temperatures were taken as the peak minimum (endotherm) and maximum (exotherm).

Inherent viscosities were measured at 30°C with a Cannon-Fenske viscometer at concentrations of 0.5 g/100 ml in DMF and 98% sulfuric acid for the precursor polymers and aramids, respectively.

Synthesis: preparation of 2,5-dichlorobicyclo[2.2.2]-octane-1,4-dicarbonyl chloride (IV). Diethyl-1,4-bicyclo-[2.2.2]octanedione-2,5-dicarboxylate (*I*) was obtained by the method reported by Humber *et al.*[12] with minor modifications. The hydrolysis of *I* with 48% hydrobromic acid in glacial acetic acid produced 1,4-bicyclo[2.2.2]-octanedione-2,5-dicarboxylic acid (*II*) in excellent yield. The reduction of *II* in dry methanol with sodium borohydride at 0°C gave the crude 1,4-bicyclo[2.2.2]-octanediol-2,5-dicarboxylic acid (*III*). Crude *III* was purified by removing the methanol and excess HBr under vacuum[12]. The residue was washed with acetone and filtered. Acetone was removed from the product under vacuum and the white crystals dried.

Dichloro-2,5-bicyclo[2.2.2]octane-1,4-dicarbonyl chloride (*IV*) was prepared by refluxing *III* in thionyl chloride with a catalytic amount of DMF for 4 h. The excess thionyl chloride was vacuum-distilled off and the viscous residue dissolved in tetrahydrofuran and precipitated with dry hexane and dried. The monomer (*IV*) was obtained in good yield, with 99.8% purity.

The phenylenediamine monomers were obtained from Aldrich Chemical Company. 1,4-Phenylenediamine (*V*) was sublimed and 1,3-phenylenediamine (*VI*) was recrystallized from ether. The monomers were 99.9% and 99.5% pure, respectively.

Preparation of polymers. Typically, precursor polymers were prepared in the following manner. A 100 ml three-necked round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet tube, a condenser with a calcium chloride drying tube and 1.5 g of lithium chloride was flame dried and simultaneously flushed with nitrogen. After the flask had cooled to room temperature, 1,4-phenylenediamine (0.0066 mol, 0.68 g) was added while maintaining a positive nitrogen pressure. A thermometer and rubber septum were put in place and 10 ml of anhydrous *N*-methylpyrrolidone (NMP) and 10 ml of anhydrous tetramethylurea (TMU) were carefully added to the flask by means of syringes. The mixture was stirred and warmed to 40°C until all the solids dissolved. The solution was cooled to room temperature; 0.0066 mol (1.98 g) dissolved in 20 ml of NMP was added by means of a syringe through the septum. An additional 10 ml of NMP was added and the septum was replaced by a glass stopper. The reaction mixture was stirred under reflux for 4 h.

The reaction mixture was cooled to room temperature and poured into 200 ml of ice/water. The mixture was filtered and the solids washed twice each with water, methanol and acetone. It was dried for 24 h in a vacuum oven to give the product in 98.8% yield.

Conversion to aramid. Typically, 0.5 g of the polymer was refluxed in a 1 M solution of potassium hydroxide or sodium hydroxide for 4 h. The mixture was acidified, and the solid polymer was collected and washed several times with water. The analysis and spectroscopic data were in agreement with the proposed structures.

Results and discussion

The synthetic route to the precursor polymers is shown in *Figure 1*. Polymer *I* was converted to poly(imino-1,4-phenyleneiminocarbonyl-1,4-phenylenecarbonyl) (*III*) and polymer *II* was converted to poly(imino-1,3-phenyleneiminocarbonyl-1,4-phenylenecarbonyl) (*IV*) via dehydrohalogenation and retro Diels–Alder reactions. *Figure 2* illustrates the conversion of the precursor polymers to aramids. Typically, conversions of the precursor polymers gave approximately 97% yields to aramids. Bulk pyrolysis of the polymer precursors did not yield aramids because the chloride subsitutients are not good thermal leaving groups.

The ^{13}C n.m.r. spectra show the carbonyl carbon (C=O) chemical shifts at $\delta = 162.5$ ppm. The methylene ($-CH_2$), methine (–CH) and quaternary carbon chemical shifts appear between $\delta = 15.2$ and 66.5 ppm. The aromatic carbons appear between $\delta = 128.0$ and 132.0 ppm. ^1H n.m.r. studies show the methylene ($-CH_2$) and methine (–CH) chemical shifts in the $\delta = 2.5$ and 4.0 ppm region. The aromatic protons and the amine (–NH) protons appear at about $\delta = 8.0$ and 8.2 ppm, respectively.

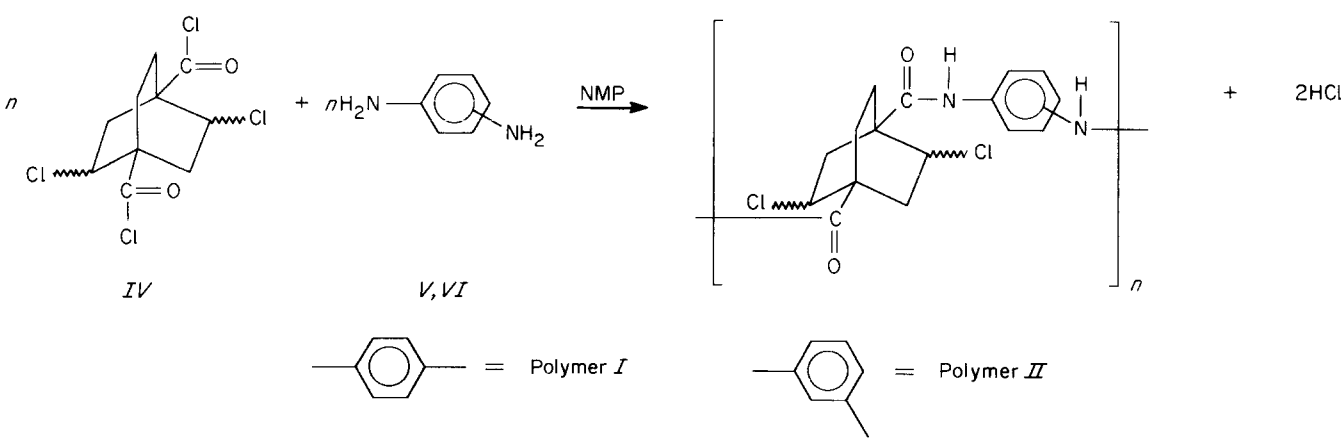

Figure 1 Preparation of precursor polymers

The infra-red absorption assignments and elemental analysis data are presented in *Tables 1* and *2*, respectively. *Table 3* shows the solubility properties. The inherent viscosities of precursor polymers *I* and *II* were 0.79 and 0.69 dl g^{-1}, respectively. The inherent viscosities of the aramids *III* and *IV* were 0.92 and 0.81 dl g^{-1}, respectively.

Solutions of polymer *I* (25% w/w in NMP or DMF) under cross-polarized light caused depolarization of plane-polarized light when thin layers were viewed at 32× magnification. The photomicrographs of the birefringent phase appears as a threaded schlieren texture, characteristic of the nematic mesophase which is typical of rigid-rod polymers.

X-ray diffraction shows that polymer *I* is partially crystalline and polymer *II* is non-crystalline. X-ray microanalysis shows the presence of silicon, probably from the silicon grease used on glass joints during polymerization.

Thermogravimetric analysis (t.g.a.) of polymer *I* under nitrogen shows that the polymer is thermally stable up to 310°C. The d.s.c. thermogram under nitrogen shows a glass transition temperature at 140°C and a decomposition endotherm at 334°C. In air, a glass transition temperature is observed at 130°C. Polymer *II* shows a glass transition temperature at 99°C and decomposes at 347°C under nitrogen. The t.g.a. of polymer *II* in air shows the offset of decomposition at about 280°C, with approximately 21% weight loss at 500°C. This corresponds to a loss of 98% of the hydrogen chloride (HCl).

Films of the precursor polymer to poly(imino-1,4-phenyleneiminocarbonyl-1,4-phenylenecarbonyl) made from lyotropic solutions will be prepared and their

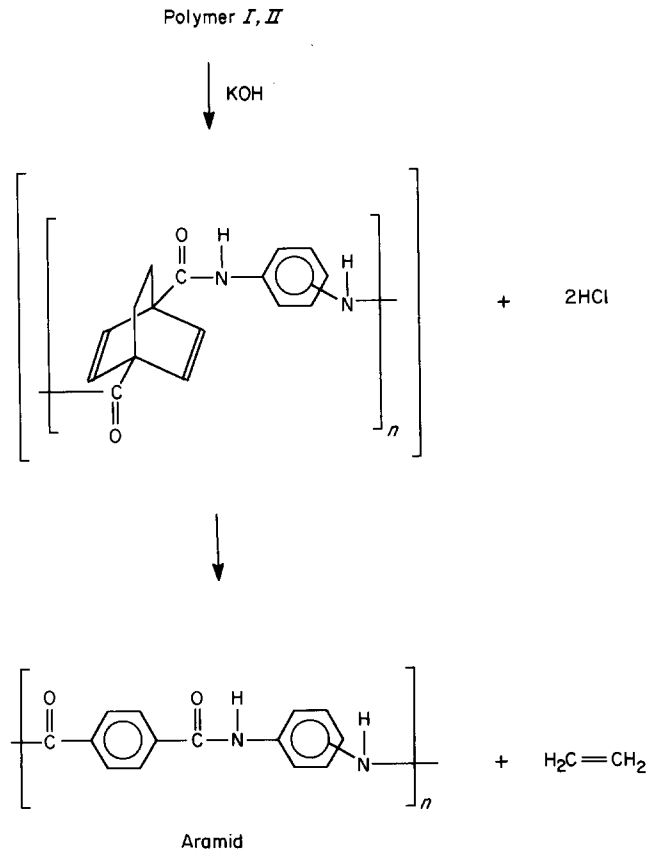

Figure 2 Conversion of precursor polymers to aramids

Table 1 Infra-red absorption assignments

Polymer	Functionalities (cm^{-1})				
	NH	$-CH_2$	C=O	C–O	Aromatic
I	3321	2860	1657	1242	834
II	3324	2860	1653	1242	860
III[a]	3459	–	1694	1237	829
IV[b]	3460	–	1692	1340	835

[a] Poly(imino-1,4-phenyleneiminocarbonyl-1,4-phenylenecarbonyl) obtained by aromatization of *I*
[b] Poly(imino-1,3-phenyleneiminocarbonyl-1,4-phenylenecarbonyl) obtained by aromatization of *II*

Table 2 Elemental analysis data

Polymer	Found (%)				Calculated (%)			
	C	H	Cl	N	C	H	Cl	N
I	56.73	4.73	20.07	8.24	56.65	4.76	20.64	8.25
II	56.23	4.78	19.88	8.14	56.65	4.76	20.64	8.25
III	70.23	4.11	0.42	10.99	70.58	4.24	–	11.75
IV	70.98	4.10	0.39	11.45	70.58	4.24	–	11.75

Table 3 Solubility properties (at room temperature)

Polymer	DMF[a]	NMP[b]	DMAC[c]	TMU[d]	DMSO[e]	H_2SO_4
I	Soluble	Soluble	Partially soluble	Partially soluble	Soluble	–
II	Soluble	Soluble	Soluble	Partially soluble	Soluble	–
III	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Soluble
IV	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Soluble

[a] Dimethylformamide
[b] *N*-methylpyrrolidone
[c] Dimethylacetamide
[d] Tetramethylurea
[e] Dimethylsulfoxide

mechanical properties studied. In addition, 2,5-diacetate analogues of polymers *I* and *II* will be prepared, studied and converted to aramids.

Acknowledgements

This work was supported in part by the US Army Research Office, under grant no. DAAL03-90-G-0190. Preliminary work for this project was supported by the Office of Naval Research under grant no. NOOO14-88-J-1170.

References

1 Matsuda, K. *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.* 1979, **20**, 122
2 Flory, P. J. *Macromolecules* 1978, **11**, 141
3 Flory, P. J. and Ronca, G. *Mol. Cryst. Liq. Cryst.* 1979, **54**, 289
4 Rogers, H. G., Gaudiana, R. A., Minns, R. A. and Spero, D. M. *J. Macromol. Sci.-Chem.* 1986, **A23**, 905
5 Harruna, I. I. and Polk, M. B. *J. Polym. Sci., Polym. Chem. Edn* 1990, **28**, 285
6 Harruna, I. I. and Polk, M. B. *Polym. Commun.* 1991, **32**, 39
7 Takayanagi, M. and Katayose. J. *J. Polym. Sci., Polym. Chem. Edn* 1981, **19**, 1133
8 Zeldin, M., Wynne, J. and Allcock, H. R. (Eds) 'Inorganic and Organometallic Polymers' ACS Symp. Series no. 32, American Chemical Society, Washington, DC, 1988
9 Stille, J. K. and McKean, D. R. *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.* 1987, **28**, 65
10 Rehahn, M., Schluter, A., Wegner, G. and Feast, W. J. *Polymer* 1989, **30**, 1060
11 Ballard, D. G. H., Courtis, A., Shirley, I. M. and Taylor, S. C. *Macromolecules* 1988, **21**, 294
12 Humber, L. C., Myers, G., Hawkins, L., Schmidt, G. and Boulerice, M. *Can. J. Chem.* 1964, **42**, 2852
13 House, H. O., Babad, H., Toothill, R. B. and Noltes, A. W. *J. Am. Chem. Soc.* 1962, **84**, 4141