(9) Lubowitz, H. R. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1971**, *12* (1), 329.
(10) St Clair, T. L.; Jewell, R. A. "LARC-160: A New 550 °F Polyimide Laminating Resin", Proceedings of the 8th National SAMPE Symposium, Oct 1976.
(11) St. Clair, T. L.; Jewell, R. A. "Solventless LARC-160 Polyimide Matrix Resin", Proceedings of the 23rd National SAMPE Symposium, May 1978.
(12) Gibbs, H. H. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1979**, *35*, 207.
(13) Gibbs, H. H.; Breder, C. V. "Copolymers, Polyblends, and Composites"; American Chemical Society: Washington, D.C., 1975; Adv. Chem. Ser. No. 142, p 442.
(14) Lindow, D. F.; Friedman, L. *J. Am. Chem. Soc.* **1967**, *89*, 1271.
(15) Friedman, L.; Rabideau, P. W. *J. Org. Chem.* **1968**, *33*, 451.
(16) Friedman, L.; Lindow, D. F. *J. Am. Chem. Soc.* **1968**, *90*, 2324.
(17) Garapon, J.; Stille, J. K. *Macromolecules* **1977**, *10*, 627.
(18) Recca, A.; Garapon, J.; Stille, J. K. *Macromolecules* **1977**, *10*, 1344.
(19) Recca, A.; Stille, J. K. *Macromolecules* **1978**, *11*, 479.
(20) Vancraeynest, W.; Stille, J. K. *Macromolecules* **1980**, *13*, 1361.
(21) Stille, J. K. *Macromolecules* **1981**, *14*, 870.
(22) Norris, S. O.; Stille, J. K. *Macromolecules* **1976**, *9*, 496.
(23) Wolfe, J. F.; Stille, J. K. *Macromolecules* **1976**, *9*, 489.
(24) Beever, W. H.; Stille, J. K. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 65*, 41.
(25) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(26) Fox, T. G., Jr.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.
(27) Swedo, R. J.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2815.
(28) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515.
(29) Jones, M. E. B.; Thornton, D. A.; Webb, R. F. *Makromol. Chem.* **1961**, *49*, 62.
(30) Shamis, E. M.; Dashevskii, M. M. *J. Org. Chem. USSR (Engl. Transl.)* **1967**, *3*, 1044.
(31) Logullo, F. M.; Seitz, A. H.; Friedman, L. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 54.
(32) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(33) Imai, Y.; Johnson, E. F.; Katto, T.; Kurihara, M.; Stille, J. K. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2233.
(34) Baker, W.; Boarland, M. P. V.; McOmie, J. F. W. *J. Chem. Soc.* **1954**, 1476.
(35) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: Philadelphia, 1978.
(36) Breitmaier, E. "^{13}C NMR Spectroscopy", 2nd ed.; Verlag Chemie: New York, 1978.
(37) Jones, A. J.; Garratt, P. J.; Vollhardt, K. P. C. *Angew. Chem.* **1973**, *85*, 260.
(38) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: New York, 1966; p 238.
(39) "Eight Peak Index of Mass Spectra", 2nd ed.; Mass Spectrometry Data Center: Aldermaston, Reading, UK, 1974.
(40) Heller, S. R.; Milne, G. W. A. "EPA/NIH Mass Spectral Data Base"; U.S. Government Printing Office: Washington, D.C., 1978.

Biphenylene End-Capped Aromatic Prepolymers: Polyimides, Poly(ether–keto–sulfones), and Polyquinoxalines

John P. Droske, Urszula M. Gaik, and John K. Stille*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.
Received March 8, 1983

ABSTRACT: Biphenylene end-capped polyimide, poly(ether–keto–sulfone), and poly(phenylquinoxaline) prepolymers were synthesized. The polyimide prepolymer of $\overline{DP}$ = 3 obtained from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride, 4,4′-diaminodiphenyl ether, and 2-aminobiphenylene was melt processed at 325 °C under 500 psi in the presence of a Ni(0) catalyst for 15 min to give films that showed good mechanical properties and a T_g of 261 °C. The polymerization to give a biphenylene end-capped poly(ether–keto–sulfone) could not be controlled under conventional conditions (aluminum chloride in methylene chloride) by utilizing a monomer imbalance to yield the desired molecular weight prepolymer. Poly(phenylquinoxaline) prepolymers prepared by the reaction of 4,4′-oxydibenzil, 3,3′-diaminobenzidine, and 2-(phenylglyoxalyl)biphenylene were melt processed at 340 °C under 500 psi in the presence of a Ni(0) catalyst for 15 min to give an insoluble film with a T_g of 291 °C and improved mechanical properties above T_g.

Introduction

In the preceding paper, the preparation and processing of biphenylene end-capped polyquinoline prepolymers were described. These prepolymers underwent chain extension and cross-linking in the melt to yield high-quality cross-linked films. Thus, the extension of this approach to other types of thermally stable polymers was undertaken in an effort to determine the scope of this prepolymer curing reaction. Polyimides are one of the most industrially important thermally stable polymers[1] while certain poly(ether–sulfones) and poly(phenylquinoxalines) have potential for commercial application. Consequently, the preparation and cross-linking/chain extension reactions of biphenylene end-capped prepolymers of these types were carried out.

Results and Discussion

Polyimides. The poor melt flow of high molecular weight polyimides necessitated the determination of a $\overline{DP}$ suitable for melt processability. Thus, phenyl end-capped polyimide prepolymers[1] of calculated $\overline{DP}$ of 3 and 11 were prepared from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (in the appropriate excess) and 4,4′-diaminodiphenyl ether with aniline as the end cap (Scheme I).

Scheme I

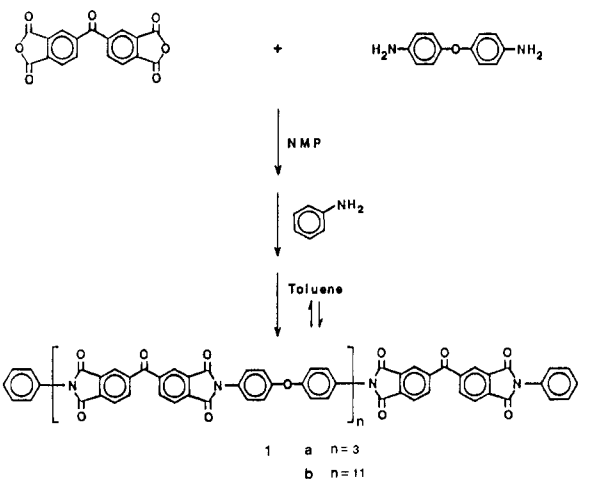


Table I
Properties of Poly(ether-keto-sulfone) Prepolymers Melt Processed at 300 °C under 1000 psi

polymer	T_g, °C (DSC) after processing	solubility[a]	$E'_{25°C}$, dyn/cm²	$E'_{\text{above } T_g}/T$,[b] (dyn/cm²)/°C
3a	170	>90		
3b	172	>90	2.2×10^{10}	c
4a	173		2.3×10^{10}	$1.9 \times 10^7/328$
4b	178	49	1.0×10^{10}	$1.4 \times 10^7/(280\text{-}364)$

[a] Percent soluble after 24 h in methylene chloride. [b] $E'_{\text{above } T_g}$ is the lowest value of the storage modulus obtained above T_g. The temperature at which the modulus was observed is given. [c] Not measurable even at the highest sensitivity of the instrument.

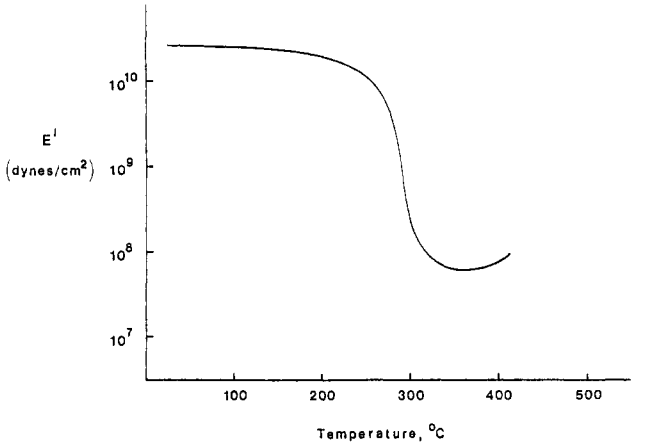
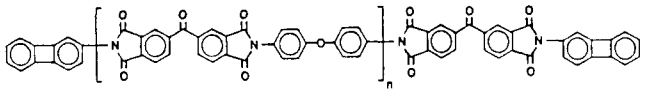


Figure 1. Young's modulus as a function of temperature for **2** melt processed in the presence of bis(triphenylphosphine)dicarbonylnickel(0) at 325 °C under 500 psi for 15 min.

Prepolymer **1a** ($\overline{DP}$ = 3) showed far superior flow properties compared to **1b** ($\overline{DP}$ = 11) when melt processed at 325 °C and 500 psi. (Neither prepolymer afforded a good film under the melt-processing conditions due to the low molecular weight of the prepolymers.) Thus, biphenylene end-capped polyimide prepolymer (**2**), with a calculated



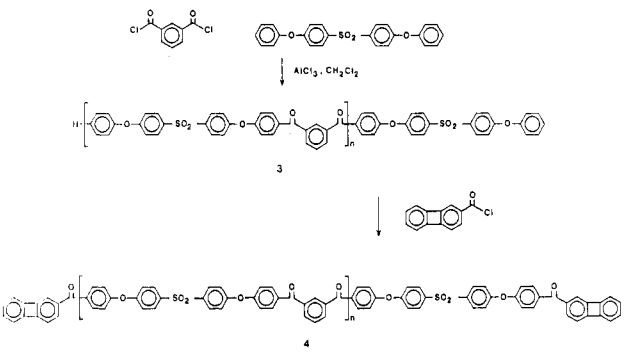
2

$\overline{DP}$ = 3, was prepared similarly, using 2-aminobiphenylene[2] as the end cap. The infrared spectra of both **1a** and **2** indicated complete imidization, as evidenced by the absence of an OH absorption after refluxing the intermediate amide–acid in toluene. The characteristic imide C=O stretch (1770, 1710 cm^{-1}) also was observed. The poor solubility of **2** in common organic solvents hindered a molecular weight approximation by GPC.

Differential scanning calorimetry (DSC) of uncured phenyl end-capped **1a** showed a glass transition at 175 °C. Biphenylene end-capped **2**, melt processed at 325 °C under 500 psi for 15 min in the presence of 10 mol % (based on biphenylene) bis(triphenylphosphine)dicarbonylnickel(0), gave a film that showed a clearly resolved T_g at 261 °C (ΔT_g = +86 °C, DSC). Young's modulus measured as a function of temperature showed that the cured film maintained mechanical properties above the T_g (Figure 1).

While the resultant film from **2** ($\overline{DP}$ = 3) was suitable for the determination of its mechanical properties, the film quality indicated that there was some restricted flow during the melt processing of **2** in the presence of the Ni(0) catalyst. Restricted flow also was observed in the melt processing of biphenylene end-capped polyquinoline ($\overline{DP}$ = 3) and was attributed to the short cure time in the presence of the Ni(0) catalyst. In general, the properties

Scheme II



3

4

Table II
Molecular Weight of Poly(ether-keto-sulfones) and Polyquinoxalines

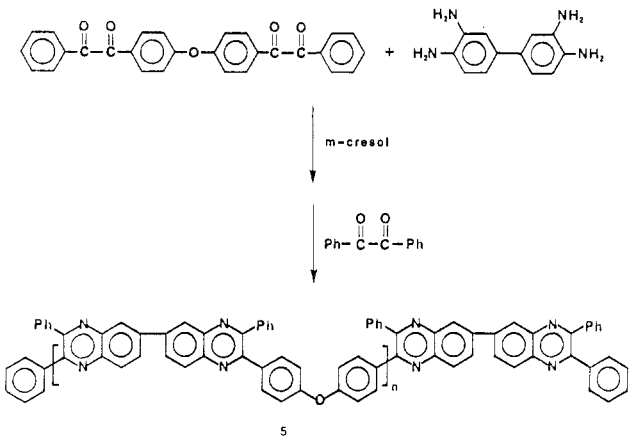
polymer	GPC[a] $\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$
3a	69 000	180 000	630 000
3b	75 000	230 000	970 000
4a	18 000	52 000	88 000
4b	13 000	35 000	57 000

[a] Relative to polystyrene standards.

of films obtained by melt processing **2** in the presence of the Ni(0) catalyst were analogous to the properties of the films obtained by melt processing biphenylene end-capped polyquinoline prepolymers in the presence of the Ni(0) catalyst.

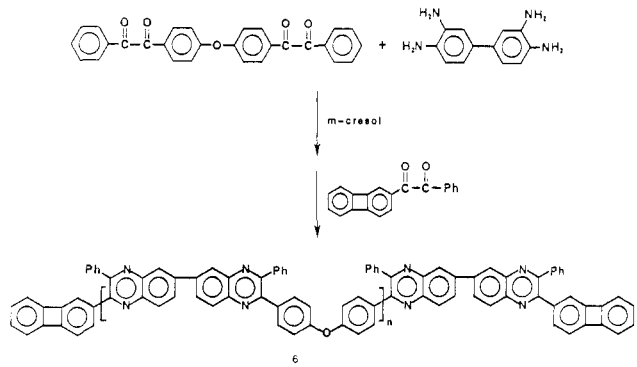
Poly(ether–keto–sulfones). Poly(ether–keto–sulfones) were prepared from isophthaloyl dichloride and 4,4′-diphenoxyphenyl sulfone by using calculated stoichiometric imbalances of the monomers (sulfone in excess) in an attempt to give $\overline{DP}$'s of 11 and 22 (**3**, Scheme II). The polymerizations were performed under Friedel–Crafts conditions (aluminum chloride in methylene chloride),[3] and in both polymerizations, polymer precipitated early in the reaction due to aluminum chloride complexation. This complicated end capping of the prepolymers via the addition of a monofunctionalized monomer late in the polymerization reaction. To circumvent this difficulty, a solution of the isolated prepolymer and biphenylene-2-carboxylic acid chloride[2] in methylene chloride was added to a mixture of aluminum chloride in methylene chloride with the expectation that the end-capping reaction would occur prior to polymer precipitation. The resulting prepolymers, **4a,b** (calculated $\overline{DP}$ = 11, 22), were melt processed in the presence of the Ni(0) catalyst at 300 °C under 1000 psi. In both cases, the resulting films showed little improvement in properties compared to **3** melt processed in the absence of catalyst (Table I). Subsequent gel permeation chromatography showed that **3** (calculated $\overline{DP}$ = 11, 22) were actually high polymers of approximately the same molecular weight rather than prepolymers with

Scheme III



5

Scheme IV



6

different $\overline{DP}$'s (Table II). As a result, a low incorporation of biphenylene end groups was realized due to the limited number of chain ends, and this explained the poor cross-linking results. Apparently, under the polymerization conditions, the reaction was relatively insensitive to monomer stoichiometry.

Poly(phenylquinoxalines). The effect of a stoichiometric imbalance of the monomers on the viscosity of resultant poly(phenylquinoxalines) has been reported.[4] An imbalance shown to give $[\eta]_{inh}$ = 0.5 dL/g (0.5% solution (w/w), sulfuric acid) was selected for the preparation of poly(phenylquinoxaline) prepolymers since the biphenylene end-capped polyquinoline with $[\eta]_{inh}$ = 0.47 dL/g, gave an optimum combination of processability and cured polymer properties with a minimum biphenylene incorporation. The polymerization of 4,4′-oxydibenzil and 3,3′-diaminobenzidine, with the tetraamine in excess, gave a prepolymer, which was phenyl end-capped by the addition of benzil to the polymerization mixture late in the reaction (Scheme III). The resulting polymer (**5**) had $[\eta]_{inh}$ = 0.52 dL/g (0.5% solution (w/w), sulfuric acid), in agreement with the reported values.[4] Melt processing of phenyl end-capped **5** at 325 °C under 500 psi for 15 min gave a high-quality, transparent film, which confirmed that the prepolymer had a suitable $\overline{DP}$ for melt processing.

A biphenylene end-capped poly(phenylquinoxaline) prepolymer (**6**) was prepared similarly except 2-(phenylglyoxalyl)biphenylene was used as the end cap (Scheme IV). Prepolymer **6** had an inherent viscosity of 0.44 dL/g (0.5% solution (w/w), sulfuric acid). Differential scanning calorimetry of **6** showed T_g = 267 °C and an uncatalyzed ring-opening exothermic maximum for the biphenylene end group at 480 °C. Gel permeation chromatography relative to polystyrene standards showed that **6** had a molecular weight distribution similar to that of phenyl end-capped polyquinoxaline **5** (Table II).

Melt processing **6** in the presence of bis(triphenylphosphine)dicarbonylnickel(0) at 340 °C under 500 psi for 15 min gave an insoluble film that showed an increased T_g relative to uncured **6** (T_g = 299 and 267 °C, respectively, DSC). However, the film quality clearly demonstrated that restricted flow was present during processing. A higher quality film was obtained by employing a stepwise processing approach. Prepolymer **6** containing the Ni(0) catalyst was introduced into a 225 °C press, 500 psi was applied, and the temperature was increased over 15 min to 370 °C and maintained at 370 °C for 15 min. The resulting film was suitable for dynamic mechanical testing (Rheovibron) and demonstrated a light-to-moderate cross-link density [$E_{25°C} = 2.5 \times 10^{10}$ dyn/cm^2, $E'_{\text{above } T_g} = 7.2 \times 10^7$ dyn/cm^2 (measured at 365 °C), $E''_{max}(T_g)$ = 268 °C]. The degree of cross-linking was about the same as that observed in cured polymers prepared from the biphenylene end-capped polyquinoline and polyimide prepolymers.

Experimental Section

All melting points are uncorrected. Proton NMR spectra were measured with a Varian EM-360 spectrometer and a JEOL FX-100 Fourier transform spectrometer. All chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Infrared spectra were determined with a Beckman AccuLab 3 spectrometer. Elemental analyses were performed by Micro-Tech Laboratories.

Dilute solution viscosity measurements of polymer solutions were obtained with a Cannon-Ubbelohde microdilution viscometer no. 200 (sulfuric acid). Gel permeation chromatography was done in chloroform at a flow rate of 2.5 mL/min with a Waters GPC equipped with a 6000 A pump, U6K injector, R401 RI detector, 730 data module, and 500-, 10^3-, 10^4-, and 10^5-Å μ-Styragel columns.

Thermal analyses were performed with a DuPont 990 thermal analyzer equipped with a differential scanning calorimeter (DSC) cell base (heating rate 10 °C/min). Dynamic thermomechanical analyses were obtained on a Rheovibron DDV-II-C dynamic viscoelastometer (frequency 35 Hz).

3,3′,4,4′-Benzophenonetetracarboxylic Dianhydride. A sample of the dianhydride provided by Gulf Oil Chemicals Co. was recrystallized from acetone (charcoal) to give an off-white solid: mp 227.0–228.0 °C (lit.[5] mp 225.0–226.5 °C).

4,4′-Diaminodiphenyl Ether. Sublimation of 4,4′-diaminodiphenyl ether (Aldrich) at 155 °C (0.1 mmHg) gave off-white crystals: mp 190.0–192.0 °C (lit.[6] mp 187 °C).

2-Aminobiphenylene. To a solution of 4 g (21 mmol) of 2-acetylbiphenylene[7] in 72 g of trichloroacetic acid at 70 °C was added 2 g (31 mmol) of sodium azide in one portion. Nitrogen evolution from the solution began at once. After 1 h, the nitrogen evolution had ceased, and another 2 g of sodium azide was added. The solution was maintained at 70 °C under a static nitrogen atmosphere for 6 h, at which time it was poured into 100 g of ice and extracted with benzene. The benzene layer was washed with 100 mL of 10% hydrochloric acid, 2 × 100 mL of 10% sodium hydroxide, and 200 mL of water and dried over sodium sulfate. Removal of the benzene and washing of the residue with petroleum ether afforded 3.6 g of crude *N*-(2-biphenylene)acetamide. A solution of the crude amide in 200 mL of ethanol and 8 mL of concentrated hydrochloric acid was heated to the reflux temperature for 24 h. The ethanol was removed under reduced pressure and the resulting solid was washed with dry ether. The solid was dissolved in 300 mL of hot water, filtered, and basified with ammonium hydroxide to give a yellow precipitate. The precipitate was removed from the water by repeatedly extracting with ether. The solution was dried over magnesium sulfate. Removal of the solvent under reduced pressure and sublimation of the residue at 100 °C (0.05 mmHg) afforded 2.0 g (57%) of 2-aminobiphenylene as a bright yellow solid: mp 124.0–125.0 °C (lit.[7] mp 123–124 °C); ^{1}H NMR ($CDCl_3$) δ 3.3–3.8 (b, 2, NH_2), 5.8–7.0 (m, 7, aromatic).

4,4′-Diphenoxydiphenyl Sulfone. The monomer 4,4′-diphenoxydiphenyl sulfone was prepared by the reaction of sodium

phenolate and bis(4-chlorophenyl) sulfone in a mixture of chlorobenzene and dimethyl sulfoxide.[8] Recrystallization from 25% (v/v) chloroform in 2-propanol (charcoal) afforded shiny white crystals: mp 143.0–144.0 °C (lit.[8] mp 141–142 °C).

Isophthaloyl Dichloride. Isophthaloyl dichloride (Aldrich) was recrystallized twice from dry hexane to give white crystals: mp 43.5–44.5 °C (lit.[5] mp 42–43 °C).

Biphenylene-2-carboxylic Acid Chloride. A solution of 10.7 g (191 mmol) of potassium hydroxide and 6.1 g (38 mmol) of bromine in 160 mL of distilled water was added dropwise over 1 h to a stirred solution of 0.76 g (3.9 mmol) of 2-acetylbiphenylene[7] in 47 mL of *p*-dioxane cooled to 5 °C. After the addition, the solution was allowed to warm to room temperature and stirred for 6 h. An additional 50 mL of dioxane was added, and the yellow solution was stirred for 3 h. The solution was poured into 350 mL of saturated sodium bisulfite, acidified with hydrochloric acid to pH <6, and extracted with 2 × 300 mL portions of ether. The ether solution was washed twice with distilled water and once with saturated sodium chloride and dried over sodium sulfate. Removal of the solvent under reduced pressure afforded 0.7 g (90%) of biphenylene-2-carboxylic acid: mp 222.0–224.0 °C (lit.[7] mp 223–224 °C). A solution of the acid in 28 mL of thionyl chloride was heated to the reflux temperature for 17 h. Removal of excess thionyl chloride by distillation and sublimation of the residue at 80 °C (0.5 mmHg) afforded a yellow-orange solid: mp 95.5–97.0 °C. Recrystallization from dry benzene under an argon atmosphere gave bright yellow, air-sensitive biphenylene-2-carboxylic acid chloride: mp 95.5–96.5 °C.

3,3′-Diaminobenzidine. The monomer 3,3′-diaminobenzidine was recrystallized from water with sodium dithionite and decolorizing charcoal under a nitrogen atmosphere (glovebag) to afford near-white crystals: mp 178–179 °C (lit.[9] mp 179–180 °C).

4,4′-Oxydibenzil. The monomer 4,4′-oxydibenzil was purified by recrystallization from ethanol to give bright yellow crystals: mp 110.5–111.5 °C (lit.[10] mp 106.4–107.4 °C).

2-Biphenylenyl Benzyl Ketone. To a solution of 1.52 g (0.01 mol) of biphenylene and 1.6 g (0.02 mol) of phenylacetyl chloride in 20 mL of carbon disulfide cooled to 10 °C was added 2 g of aluminum chloride. The reaction mixture was stirred at 10 °C for 2 h and then at 25 °C for 1 h. The mixture was poured onto 100 g of crushed ice and 10 mL of concentrated HCl, and 500 mL of 1:1 ether–carbon disulfide was added. The organic layer was washed twice with 200 mL water and dried ($CaCl_2$). The ether and carbon disulfide were removed under reduced pressure, and the product was purified by chromatography on silica gel (CH_2Cl_2) followed by recrystallization from ethanol to give 1.8 g (70%) of product: mp 131 °C; IR (KBr) 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.1 (s, 2), 6.55, 7.8 (m, 12); *m/e* 270. Anal. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.65; H, 5.34.

2-(Phenylglyoxalyl)biphenylene. A mixture of 0.54 g (2.0 mmol) of 2-biphenylenyl benzyl ketone and 0.27 g (2.4 mmol) of selenium dioxide in 6 mL of glacial acetic acid was heated to the reflux temperature for 6 h. The mixture was filtered hot, and the precipitated selenium was washed repeatedly with hot glacial acetic acid. The filtrates were combined, poured into 100 mL of distilled water, and extracted with methylene chloride. The methylene chloride layer was separated, washed twice with saturated sodium bicarbonate and once with water, and dried over sodium sulfate. Removal of the solvent under reduced pressure gave a solid that, after flash chromatography (230–400-mesh silica gel, 30% (v/v) hexane in methylene chloride), afforded 0.5 g (90%) of 2-(phenylglyoxalyl)biphenylene as a yellow solid: mp 112.0–113.0 °C; ^1H NMR ($CDCl_3$) δ 6.6–8.1 (m, aromatic). Anal. Calcd for $C_{20}H_{12}O_2$: C, 84.48; H, 4.26. Found: C, 84.55; H, 4.32.

Phenyl End-Capped Polyimide 1a. To 2 mL of distilled *N*-methylpyrrolidone was added 0.703 g (2.18 mmol) of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride. Solution of the dianhydride was effected by heating the mixture to 90 °C with mechanical stirring under a nitrogen atmosphere. The solution was cooled to 75 °C, and 0.218 g (1.09 mmol) of 4,4′-diaminodiphenyl ether in 0.6 mL of *N*-methylpyrrolidone was added dropwise over 30 min to the solution. An additional 0.4 mL of *N*-methylpyrrolidone was used to ensure complete transfer of the monomer. The solution was heated at 75 °C for 30 min, at which time 0.20 mL (0.20 g, 2.2 mmol) of distilled aniline was added dropwise over 30 min. Heating was continued for 1 h. The light brown solution was poured into 20 mL of vigorously stirred toluene, and the solution was heated to the reflux temperature in a Dean–Stark apparatus for 10 h (a precipitate appeared after ~2 h). The mixture was poured into 130 mL of ethanol, stirred for 1 h, and suction filtered to give a fine, yellow powder. The solid was dried at 75 °C (0.03 mmHg) for 40 h to afford 0.76 g (73%) of **1a**: IR (KBr) 3040 (aromatic C–H), 1770 and 1710 (C=O, imide) cm^{-1}. Anal. Calcd: C, 72.12; H, 3.03; N, 5.80. Found: C, 71.35; H, 3.34; N, 5.94.

Phenyl End-Capped Polyimide 1b. The above procedure was followed except 1.897 g (5.890 mmol) of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride, 1.000 g (5.000 mmol) of 4,4′-diaminodiphenyl ether, 0.20 mL (0.20 g, 2.2 mmol) of distilled aniline, and 6 mL of *N*-methylpyrrolidone were used. The yield of **1b** was 2.5 g (88%).

Biphenylene End-Capped Polyimide 2. The procedure for the preparation of **1a** was followed except 0.365 g (2.18 mmol) of 2-aminobiphenylene was used as the end-capping agent instead of aniline. The yield of **2**, a fine, orange powder, was 1.03 g (85%): IR (KBr) 3040 (aromatic C–H), 1770 and 1710 (C=O, imide) cm^{-1}. Anal. Calcd: C, 73.91; H, 3.01; N, 5.39. Found: C, 73.21; H, 3.44; N, 4.93.

Poly(ether–keto–sulfone) 3a. This procedure is a modification of that described.[11] To 30 mL of dry methylene chloride was added 1.4224 g (3.534 mmol) of 4,4′-diphenoxydiphenyl sulfone and 0.6091 g (3.000 mmol) of isophthaloyl dichloride. To this solution, 4.0 g (30 mmol) of anhydrous aluminum chloride was added in one portion. The mixture was mechanically stirred at room temperature under a static nitrogen atmosphere for 16 h. The dark-colored precipitate that formed during the polymerization was collected by suction filtration and was washed with methanol by stirring vigorously in a blender. The washing was repeated three times with boiling methanol to give a beige polymer. (Reprecipitation from a methylene chloride solution afforded white polymer.) Drying at 75 °C (0.07 mmHg) for 32 h afforded 1.56 g (91%) of **3a**. The molecular weight of **3a** is reported in Table II.

Poly(ether–keto–sulfone) 3b. The above procedure was followed except 1.2972 g (3.223 mmol) of 4,4′-diphenoxydiphenyl sulfone was used. The yield of **3b** was 1.48 g (90%). Anal. Calcd: C, 72.18; H, 3.76; S, 6.02. Found: C, 70.53; H, 3.60; S, 6.48. The molecular weight of **3b** is reported in Table II.

Biphenylene End-Capped Poly(ether–keto–sulfone) 4a. To a slurry of 0.7 g of anhydrous aluminum chloride and 20 mL of dry methylene chloride was added dropwise over 4 h a solution of 300 mg of **3a** and 50 mg (0.234 mmol) of biphenylene-2-carboxylic acid chloride in 20 mL of dry methylene chloride. The mixture was stirred at room temperature under a static nitrogen atmosphere for 24 h. Suction filtration of the mixture afforded a dark precipitate. The precipitate was washed with boiling methanol as described above and dried to give 225 mg (67%) of **4a**.

Biphenylene End-Capped Poly(ether–keto–sulfone) 4b. The above procedure was followed except 21.4 mg (0.100 mmol) of biphenylene-2-carboxylic acid chloride and 300 mg of **3b** were used and the addition time was decreased to 1.5 h. The yield of **4b** was 240 mg (75%).

Phenyl End-Capped Poly(phenylquinoxaline) 5. To 20 mL of degassed, distilled *m*-cresol were added 0.6429 g (3.000 mmol) of 3,3′-diaminobenzidine and 1.2165 g (2.800 mmol) of 4,4′-oxydibenzil. The mixture was mechanically stirred at room temperature under a static nitrogen atmosphere for 5.5 h. To the red solution, 0.105 g (0.500 mmol, 25% excess) of recrystallized benzil was added, and the solution was heated for 1.5 h at 90 °C. The amber solution was poured into 300 mL of methanol, ground in a blender, and suction filtered. The resultant powder was washed twice with boiling methanol in a blender, suction filtered, and dried at 75 °C (0.1 mmHg) for 15 h to afford 1.7 g (98%) of **5** as a yellow powder: $[\eta]_{inh}$ = 0.52 dL/g (25.0 °C, 0.5% solution (w/w), sulfuric acid). Anal. Calcd: C, 83.37; H, 4.22; N. 9.73. Found: C, 83.73; H, 4.03; N, 9.62. The molecular weight of **5** is reported in Table II.

Biphenylene End-Capped Poly(phenylquinoxaline) 6. The above procedure was followed except 0.1420 g (0.5000 mmol, 25% excess) of 2-(phenylglyoxalyl)biphenylene was used as the end-capping agent instead of benzil. The yield of **6** was 1.7 g (98%):

$[\eta]_{inh}$ = 0.44 dL/g (25.0 °C, 0.5% solution (w/w), sulfuric acid). Anal. Calcd: C, 83.50; H, 4.21; N, 9.64. Found: C, 83.69; H, 4.26; N, 9.31. The molecular weight of 6 is reported in Table II.

Resin Melt Processing. Catalyst was added to the prepolymers as follows. The appropriate amount of bis(triphenylphosphine)dicarbonylnickel(0) (Aldrich) was added to the prepolymer swelled in benzene. The mixture was stirred for 1 h, the solvent was removed under reduced pressure, and the resulting powder was dried at 75 °C (0.05 mmHg) for 18 h.

A modified Wabash hydraulic press (Model 12 10) fitted with Carver heated platens (no. 2102) was used for the neat resin processing. A 170-mg sample of the prepolymer powder was placed in a small pile between 2–6 in. × 6 in. pieces of copper foil (0.005-in. thick, Baker no. 1-1714) with a 0.005-in. copper foil spacer. The assembly was placed in the hydraulic press and melt processed at 300–371 °C (572–700 °F) under 500–1000 psi for various times. plunging of the assembly into cold water immediately after processing facilitated removal of the film from the copper foil. Any residual copper that adhered to the surface of the film was removed by placing the film in concentrated ammonium hydroxide for ~30 min, followed by thorough rinsing with water.

Acknowledgment. This research was supported by a grant from the Army Research Office, Research Triangle, NC.

Registry No. 2, 87829-09-2; 4, 87830-94-2; 6, 87830-95-3; biphenylene-2-carbonyl chloride, 75292-39-6; 2-biphenylenyl benzyl ketone, 87830-92-0; 2-(phenylglyoxylyl)biphenylene, 87830-93-1; *N*-(2-biphenylene)acetamide, 86746-53-4; 2-biphenyleneamine, 55716-75-1; bis(triphenylphosphine)dicarbonylnickel, 13007-90-4.

References and Notes

(1) Hergenrother, P. M.; Johnston, N. J. "Resins for Aerospace"; American Chemical Society: Washington, D.C.; 1980; ACS Symp. Ser. No. 132.
(2) Vancraeynest, W.; Stille, J. K. *Macromolecules* **1980**, *13*, 1361.
(3) Somers, A.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1511.
(4) Hergenrother, P. M. *J. Macromol. Sci., Rev. Macromol. Chem.* **1971**, *C6*, 1.
(5) Stille, J. K., Campbell, T. W., Eds. "Condensation Monomers"; Wiley-Interscience: New York, 1972; p 695.
(6) Martin, K. V. *J. Am. Chem. Soc.* **1958**, *80*, 233.
(7) Baker, W.; Boarland, M. P. V.; McOmie, J. F. W. *J. Chem. Soc.* **1954**, 1476.
(8) Sivaramakrishnan, K. P.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1945.
(9) Vogel, H.; Marvel, C. S. *J. Polym. Sci.* **1961**, *50*, 511.
(10) Ogliaruso, M. A.; Shadoff, L. A.; Becker, E. I. *J. Org. Chem.* **1963**, *28*, 2725.
(11) Lin, S.-C.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2337.

Biphenylene End-Capped Polyquinoline and Polyimide Prepolymers as Matrix Resins for High-Use-Temperature Composites

John P. Droske and John K. Stille*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

William B. Alston

NASA—Lewis Research Center, Propulsion Laboratory, U.S. Army, AVRADCOM Research and Technology Laboratories, Cleveland, Ohio 44135. *Received March 8, 1983*

ABSTRACT: Graphite-reinforced composites were prepared from biphenylene end-capped polyquinoline and polyimide prepolymers. The composites demonstrated excellent initial properties and low weight loss after oxidative aging at 316 °C. However, the mechanical properties were severely diminished after aging for 50–100 h at 316 °C in air, and photomicrographs of the composites after aging showed the presence of voids.

Introduction

In the preceding two papers, the synthesis of certain biphenylene end-capped, low molecular weight polymers in which the oligomeric main chain consisted of polyaromatic units that are known to possess good thermal stability was described. The high molecular weight analogues of these polymers containing those polyaromatic recurring units, but without the biphenylene end caps, are some of the most resistant polymers to thermooxidative degradation known. Of those prepolymers synthesized, the biphenylene end-capped polyquinolines had the best processing characteristics, in that they were readily soluble in common organic solvents and could be melt pressed into films.

The ultimate utility of such prepolymers is in the preparation of high-strength fiber-reinforced composities. In order to evaluate the biphenylene approach to fiber-reinforced composites, the preparation of laminates of biphenylene end-capped polyquinolines and polyimides was undertaken.

Polyquinolines were selected because of their excellent processing characteristics, and polyimides were included since 2-aminobiphenylene was compatible with the polyimide processing technology exhibited by the state-of-the-art nadic end-capped polyimide, PMR-15.[1] The polyimide resin PMR-15 contains not only a benzylic carbon (diphenylmethane-type unit) in the main chain but aliphatic units resulting from the norbornene imide end groups. Thus, the thermooxidative stability and long-term high-temperature properties of PMR-15[1,2] would be expected to be less than those of high molecular weight polyimide resins void of aliphatic groups.[3,4] Modified PMR polyimide resins containing aromatic perfluoroisopropylidene units in the main chain and phenyl groups in place of diphenylmethane units have better thermooxidative stability and comparable high-temperature me-

0024-9297/84/2217-0014$01.50/0