Soluble Polyimides with Polyalicyclic Structure. 4.[1] Colorless Polyimides from Bicyclo[2.2.1]heptane-2-*endo*,3-*endo*,5-*exo*,-6-*exo*-tetracarboxylic 2,3:5,6-Dianhydride

Toshihiko Matsumoto and Toshikazu Kurosaki*

Department of Industrial Chemistry, Faculty of Engineering, Tokyo Institute of Polytechnics, 1583 Iiyama, Atsugi, Kanagawa 243-02, Japan

Received February 21, 1995
Revised Manuscript Received May 23, 1995

Introduction

Wholly aromatic polyimides are an important class of materials exhibiting not only excellent high-temperature stability, which makes them suitable for continuous high-temperature use due to their practical insolubility in common organic solvents, but also mechanical and electrical properties. Most of these materials cannot be molded as polyimides but must first be prepared as a soluble precursor poly(amic acid) and then processed into final form by thermal or chemical means. Moreover, the aromatic polyimides have strong reddish–yellow color in almost all cases, which is caused by the inter- and/or intramolecular charge-transfer (CT) complex formation.[2–4] These facts considerably restrict their practical application. Therefore, much effort has been concentrated on synthesizing soluble and colorless polyimides without sacrificing their desired properties.[5–14]

We have already reported the synthesis and properties of soluble polyimides from bialicyclic or tetraalicyclic dianhydrides and aromatic diamines.[15–17] Although the polyimides that have been prepared so far have been almost colorless to pale yellow, most recently we found that entirely colorless polyimides could be prepared from a bialicyclic dianhydride, bicyclo[2.2.1]heptane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride and aromatic diamines in the presence of a tervalent phosphorus compound on the polymerization. The present report relates the syntheses and characterization of the soluble and colorless polyimides.

Results and Discussion

Bicyclo[2.2.1]heptane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (**3**) was prepared according to a procedure which was a modification of a previously reported one.[18] The synthetic route is illustrated in Scheme 1 together with melting points and yields. Bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboxylic anhydride (**1**) was treated with carbon monoxide in methanol in the presence of a catalytic amount of 5% Pd/C and a stoichiometric amount of $CuCl_2$ to afford the tetramethyl 2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarboxylate (**2**). The tetracarboxylate was hydrolyzed with hydrochloric acid followed by dehydration with acetic anhydride to give the dianhydride **3**.

Scheme 1

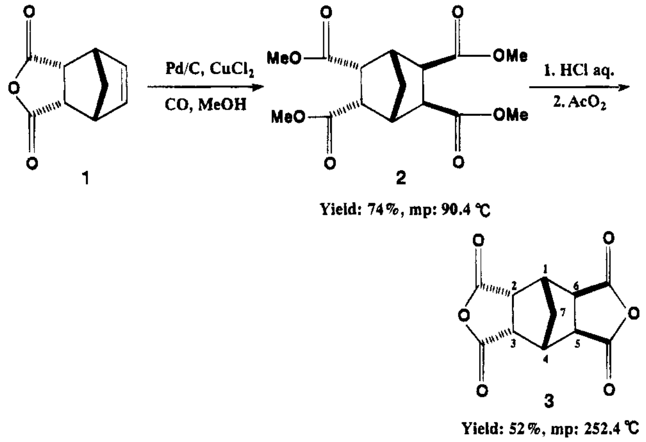

Table 1. Polymers from 3 and Aromatic Diamines[a]

polymer	diamine	η_{inh} (dL/g)[b]	T_5 (°C) in N_2[c]	film[d]
4a	DDE	0.80	470	flexible
4b	DDM	1.16	484	flexible
4c	1,3-BAB	0.77	445	flexible
4d	BAPS	0.70	456	flexible
4e	BAPF	0.70	496	brittle

[a] Polymerization: diamine, 2.0 mmol; **3**, 2.0 mmol; NMP, 5 mL; room temperature; 2 days; additional 2 days after adding a mixture of triphenyl phosphite (0.5 mL) and pyridine (0.2 mL). Imidization: 80 °C, 2 h; 250 °C, 2 h. [b] Precipitated poly(amic acid). Measured in NMP at 30 °C at a concentration of 0.5 g/dL. [c] Sample form, film; 5% weight loss temperature measured by TGA with a heating rate of 10 °C/min. [d] Polyimide film.

Polymerizations of **3** with various aromatic diamines referred to below were carried out in *N*-methyl-2-pyrrolidone (NMP) at room temperature in a nitrogen stream for 2 days and then for an additional 2 days with the addition of more of NMP and a mixture of triphenyl phosphite and pyridine (TPP/Py). The polymerization proceeded homogeneously to a viscous solution without gelation in each case. An aliquot of the poly(amic acid) solution was cast on a glass plate using a doctor blade and then heated under vacuum at 80 °C for 2 h and 250 °C for 2 h to effect cyclization to the soluble polyimide. The remainder of the polymer solution was poured into methanol. The precipitated polymer was dried under reduced pressure at room temperature for 1 day. The soluble polyimides were also obtained as a solid from the precipitated polymers by heating at 250 °C for 2 h under reduced pressure. Five types of the aromatic diamines were used here: 4,4′-diaminodiphenyl ether (DDE), 4,4′-diaminodiphenylmethane (DDM), 1,3-bis(4-aminophenoxy)benzene (1,3-BAB), bis[4-(4-aminophenoxy)phenyl]sulfone (BAPS), and 9,9-bis(4-aminophenyl)fluorene (BAPF).

The poly(amic acid)s as precipitated possessed inherent viscosities (η_{inh}) in the range from 1.16 to 0.7 dL/g. These results along with the film quality and the 5% weight loss temperature (T_5) of the corresponding polyimides are listed in Table 1. The polymer solutions, which were cast on glass plates immediately after the polymerization, formed flexible and tough polyimide films on heating under vacuum, except for that prepared from **3** and BAPF (polymer **4e**). Thus, the presence of TPP/Py in these polymerizations usually enhanced the film formability in a series of our polyimide syntheses, compared with ones prepared without it. TPP/Py works as a condensing reagent for the amide-linkage formation between the terminal amino and the terminal dicarboxylic acid groups of the polymer. The latter would be formed by reacting the dianhydride with a trace amount of contaminating water in the polymerization medium. Consequently, this might make the molecular weight of the poly(amic acid) increase and contribute to the enhancement of the film formability. Elemental analysis of the polyimide films and the precipitated poly(amic acid)s revealed that the phosphorus content was below 0.1% and that these polymers did not contain a unit derived from triphenyl phosphite. Interestingly, the IR spectra of the precipitated polymers showed that

0024-9297/95/2228-5684$09.00/0

Table 2. Solubility of Polyimide Films Prepared from 3 and Aromatic Diamines

	solubility[a]				
solvent	4a	4b	4c	4d	4e
concentrated H_2SO_4	++	++	++	++	++
m-cresol	++	−	++	+	++
sulfolane	++	+	++	+	++
N-methyl-2-pyrrolidone	++	++	−	+	−
N,*N*-dimethylformamide	++	++	−	+	−
N,*N*-dimethylacetamide	++	++	−	+	−
1,3-dimethyl-2-imidazolinone	−	−	++	+	+
dimethyl sulfoxide	−	−	−	−	−

[a] ++, soluble at room temperature; +, soluble on heating; −, insoluble even on heating.

the poly(amic acid)s partly contained the imide moiety; that is, the absorptions at 1765−1775 and 1710−1720 cm^{-1} due to the imide carbonyl appeared weakly in addition to those of the carboxylic and amide−carbonyl groups of poly(amic acid)s at *ca.* 3300 and 1550−1650 cm^{-1}. The TPP/Py system has been well-known as one of the condensing reagents for amide-linkage formation from carboxylic and amino groups;[19,20] therefore, the use of the TPP/Py reagent system in the condensation for imide synthesis would seem to accelerate imide formation over amide formation. The thermal properties of the polyimide films were estimated by T_5's measured using thermogravimetric analysis that was carried out at a heating rate of 10 °C/min in a nitrogen atmosphere. All of the polyimides exhibit good thermal stability with the T_5's over *ca.* 450 °C, although the T_5's measured in air were somewhat lower (20−30 °C) than those obtained in a nitrogen atmosphere. The solubility of the polyimide films was investigated qualitatively, and the results are summarized in Table 2.

The transmission UV−vis spectrum of about a 20-μm-thick polyimide film obtained from **3** and DDM was determined. The polyimide film showed a cutoff at around 280 nm and was entirely transparent and colorless, whereas those prepared without TPP/Py when polymerized were slightly reddish−yellow. The transmittances were 85−95% in the range from 350 to 700 nm. The film can compete in transparency and colorlessness with poly(ethylene terephthalate) that is known to be a colorless polymer film. This optical transparency and colorlessness over a broad range was also attained for the polyimides from **3** and the other diamines. Their nature is considered to contribute to inhibition of intra- and/or intermolecular CT complex formation by incorporation of a polyalicyclic unit in the polymer chain. Furthermore, because it has been reported that tervalent phosphorus compounds such as TPP served as an antioxidizing agent or as a reductant for *N*-oxides and peroxides,[21−23] TPP/Py is thought to inhibit trace amounts of readily oxidizable compounds which are contained in the reactants and the solvent from being oxidized to colored substances during the polymerization or heat imidization. The colorlessness of the polyimide films was maintained up to 300 °C even when heated in air and 400 °C in a N_2 atmosphere.

It may be possible to endow the polyimides constituted of polyalicyclic−aromatic structures with colorlessness by using triphenyl phosphite and pyridine as condensing reagents.

Experimental Section

Materials. Bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboxylic anhydride (**1**), carbon monoxide, 5% Pd/C, $CuCl_2$, and triphenyl phosphite were of commercial grade and were used as received. Solvents and the other reagents were purified as described in the previous papers.[17,18]

Measurements. IR spectra were measured using a Jasco VALOR-III Fourier transform spectrometer. UV−vis spectra were obtained on a Jasco Ubest-50 spectrometer. Melting points were measured using a Seiko Instruments SSC/5200 thermal analyzer. Inherent viscosities were measured in 0.5 g/dL NMP solutions of poly(amic acid)s at 30 °C using an Ostwald viscometer. Elemental analyses were performed at the Shonan Analysis Center Inc., using the molybdic acid−yellow method. Thermogravimetric analyses were performed using a Seiko Instruments SSC/5200 thermal analyzer at a heating rate of 10 °C/min in a N_2 atmosphere.

Polymerization. In a 30-mL three-necked flask were placed a diamine (2.00 mmol) and NMP (5 mL), and then **3** (0.472 g, 2.00 mmol) was added. The mixture was mechanically stirred for 2 days at room temperature under a nitrogen atmosphere. To the resultant solution were added NMP (5 mL) and a mixture of triphenyl phosphite (0.5 mL) and pyridine (0.2 mL), and then the mixture was stirred for 2 days. An aliquot of the solution was cast on a glass plate using a doctor blade, and the remainder was poured into methanol (300 mL). The precipitated polymer was filtered off and dried at room temperature for 1 day under reduced pressure. The polyimide film was prepared by heating the glass plate at 80 °C for 2 h under vacuum and then at 250 °C for 2 h.

Acknowledgment. The authors thank Miss Satoko Ikuma for her technical assistance. This work was partly supported by a research grant from the Iwatani Naoji Foundation.

References and Notes

(1) Part 3: Reference 17.
(2) Hasegawa, M.; Mita, I.; Kochi, M.; Yokota, R. *J. Polym. Sci., Part C: Polym. Lett.* **1989**, *27*, 263.
(3) Hasegawa, M.; Shindo, Y.; Sugimura, T.; Ohshima, S.; Horie, K.; Kochi, M.; Yokota, R.; Mita, I. *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 1617.
(4) Tokita, Y.; Ino, Y.; Okamoto, A.; Hasegawa, M.; Shindo, Y.; Sugimura, T. *Kobunshi Ronbunshu* **1994**, *51* (4), 245.
(5) Harris, F. W.; Feld, W. A.; Lanier, L. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1976**, *17* (2), 421.
(6) Oishi, Y.; Ishida, M.; Kakimoto, M.-A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1027.
(7) Wusk, M. J.; Jha, B.; King, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (3), 218.
(8) Gungor, A.; Smith, C. D.; Wescott, J.; Srinivasan, S.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (1), 172.
(9) Falcigno, P. A.; Jasne, S.; King, M. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1433.
(10) Kunimune, K.; Kobayashi, R.; Kawashima, M. Jpn. Kokai Tokkyo Koho 3-134125, 1991; 2-294220, 1990.
(11) Rogers, F. E. U.S. Patent 3356648, 1964.
(12) St. Clair, A. K.; St. Clair, T. L.; Shevket, K. I. *Proc. Div. Polym. Mater. Sci. Eng.* **1984**, *51*, 62.
(13) Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* **1991**, *24*, 5001.
(14) Jin, Q.; Yamashita, T.; Horie, K.; Yokota, R.; Mita, I. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2345.
(15) Itamura, S.; Yamada, M.; Tamura, S.; Matsumoto, T.; Kurosaki, T. *Macromolecules* **1993**, *26*, 3940.
(16) Yamada, M.; Kusama, M.; Matsumoto, T.; Kurosaki, T. *Macromolecules* **1993**, *26*, 4961.
(17) Kusama, M.; Matsumoto, T.; Kurosaki, T. *Macromolecules* **1994**, *27*, 1117.
(18) Yamada, M.; Kusama, M.; Matsumoto, T.; Kurosaki, T. *J. Org. Chem.* **1992**, *57*, 6075.
(19) Yamazaki, N.; Higashi, F. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 185.
(20) Yamazaki, N.; Higashi, F. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 2149.
(21) Sago, S.; Tomari, Y.; Kobayashi, T. Jpn. Kokai Tokkyo Koho 6-166808, 1994.
(22) Cadogan, J. I. G.; Machie, R. K. *Chem. Soc. Rev.* **1974**, *3*, 87.
(23) Cadogan, J. I. G., Ed. *Organophosphorus Reagents in Organic Synthesis*; Academic Press: London, 1979.

MA950207Q