7248 *Macromolecules* **1999,** *32,* 7248−7250

# Synthesis and Properties of New Polyamides Based on Bis[4-(4-aminophenoxy)phenyl]diphenylmethane

**Der-Jang Liaw,* Been-Yang Liaw, and Chao-Min Yang**

*Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan 106, Republic of China*

*Received April 9, 1999; Revised Manuscript Received July 2, 1999*

ABSTRACT: A new diamine, bis[4-(4-aminophenoxy)phenyl]diphenylmethane (**BAPDM**), bearing diphenylmethylene linkage was prepared starting from bis(4-hydroxyphenyl)diphenylmethane. The diamine was reacted with various aromatic dicarboxylic acids to obtain a series of new polyamides with moderate to high inherent viscosities of 0.65−0.97 dL $g^{-1}$. Almost all of the polymers could be readily dissolved in NMP, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, dimethyl sulfoxide, *m*-cresol, pyridine, tetrahydrofuran, and cyclohexanone. All of the polymers were amorphous, and the polyamide films had a tensile strength range of 85−108 MPa. These polyamides had glass transition temperatures between 237 and 272 °C and 10% weight loss temperatures in the range 500−524 °C in nitrogen.

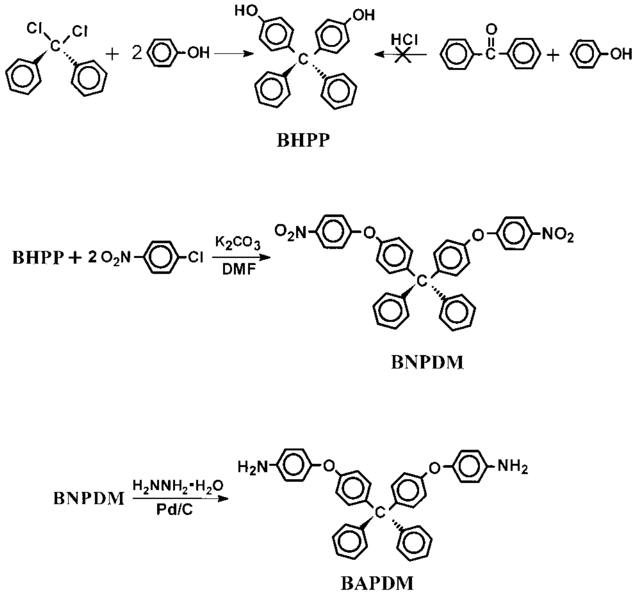
## Introduction

Aromatic polyamides exhibit a number of useful properties such as thermal stability, chemical resistance, and low flammability coupled with excellent mechanical properties in the form of fibers. However, their processability is difficult owing to the poor solubility and high softening and/or melting temperature.[1] The need for engineering plastics overcoming these problems recently increased. Therefore, several approaches such as incorporation of bulky substituent[2−6] or bulky pendant groups[7−11] into rigid polymer backbones have improved their processability.

Another successful approach that has improved the solubility of polyamides is the introduction of flexible linkages such as isopropylidene[12−15] or hexafluoroisopropylidene[15,16] groups between the rigid phenyl rings in the polymer backbone. However, chain flexibility of the propylidene groups can be attributed to decreasing thermal stability, although it may contribute to solubility increase.[17] To achieve a combination of desired properties such as solubility, thermal stability, and mechanical properties, it is of interest to develop new soluble polyamides which are more thermally stable than that bearing propylidene groups.

It has been recognized that the phenyl substituent of diphenylmethylene was bulkier than methyl substituent for isopropylidene. Because of the higher local conformational rigidity of diphenylmethylene, a polymer with a diphenylmethylene linkage exhibits higher thermal stability than that with an isopropylidene linkage.[18] Several literature sources reported that incorporation of diphenylmethylene into polymers such as poly(arylene ether nitrile),[19] poly(arylene ether phenyl-s-triazine),[20] poly(arylene ether benzoxazole),[21,22] epoxy,[23] and polyester[24] leads to the polymers with excellent solubility, mechanical properties and thermal stability. It was indicated that some of the diphenylmethylene-containing polymers showed relatively higher thermal stability than those with hexafluoroisopropylidene or isopropylidene units while the former had as good a solubility as the latter. The results demonstrated that the introduction of a diphenylmethylene unit into the polymer backbone would be expected to be a potential structural modification to the rigid polymers. However, there is little literature on the characteristic obtained by introducing a diphenylmethylene unit into polyamides.

**Scheme 1. Synthesis of BAPDM**



In the present article, we will report the synthesis of a series of new polyamides bearing a diphenylmethylene unit based on a new diamine, bis[4-(4-aminophenoxy)phenyl]diphenylmethane (Scheme 1).

## Results and Discussion

In general, bisphenols could be prepared by the acid-catalyzed condensation of ketone compounds with excess phenol in the presence of hydrogen chloride.[15−28] However, the reaction of benzophenone and phenol under the same conditions did not afford the desired bisphenol **BHPP** (Scheme 1). It could be explained by the steric hindrance of the bulky phenyl substituents. The **BHPP**

---

* Corresponding author: Telephone: 886-2-27376638. Fax: 886-2-23781441 or 886-2-27376644. E-mail: liaw@ch.ntust.edu.tw.

10.1021/ma990545h CCC: $18.00

**Scheme 2. Preparation of Polyamides**

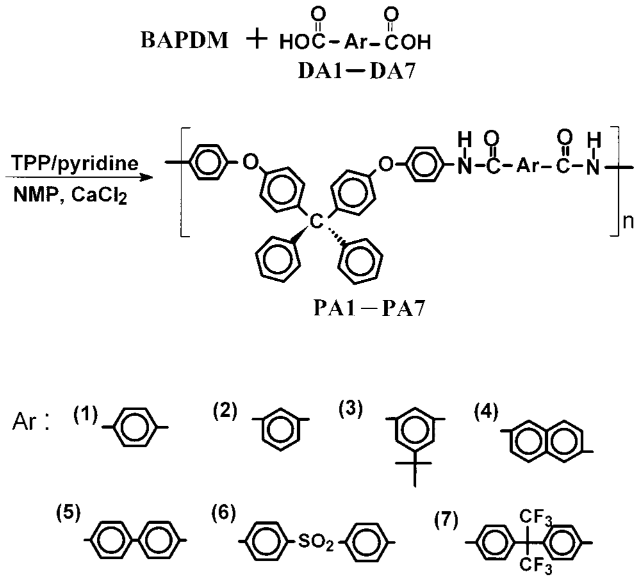


**Table 1. Inherent Viscosity and Thermal and Mechanical Properties of Polyamides**

| polymer code | $\eta_{inh}$[a] (dL g$^{-1}$) | $T_g$[c] (°C) | $T_{d_{10}}$[e] (°C) | tensile strength (MPa) | elongation at break (%) | tensile modulus (GPa) |
|---|---|---|---|---|---|---|
| **PA1** | 0.79 | -[d] | 524 | 85 | 11 | 3.2 |
| **PA2** | 0.72 | 237 | 518 | 106 | 10 | 2.7 |
| **PA3** | 0.83 | 242 | 515 | 100 | 8 | 2.8 |
| **PA4** | 0.97 | 253 | 519 | 89 | 8 | 2.7 |
| **PA5** | 0.89[b] | 272 | 500 | 100 | 7 | 3.0 |
| **PA6** | 0.65 | 257 | 505 | 90 | 6 | 2.3 |
| **PA7** | 0.70 | 256 | 522 | 108 | 8 | 2.7 |

[a] Measured in DMAc at a concentration of 0.5 g dL$^{-1}$at 30 °C. [b] Measured in DMAc containing 1 wt % LiCl at a concentration of 0.5 g dL$^{-1}$ at 30 °C. [c] Glass transition temperature ($T_g$) measured by DSC at a heating rate of 20 °C min$^{-1}$. [d] Glass transition temperature ($T_g$) is not detectable by DSC. [e] Temperature at which 10% weight loss ($T_{d_{10}}$) was recorded on TGA at a heating rate of 20 °C min$^{-1}$.

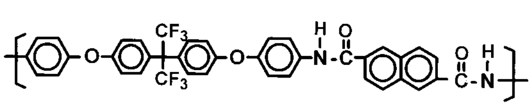
was successful prepared by refluxing dichlorodiphenylmethane and phenol (molar ratio 1:2) in xylene. The dinitro compound **BNPDM** was prepared by aromatic nucleophilic substitution reaction from **BHPP** with *p*-chloronitrobenzene in the presence of potassium carbonate. The catalytic hydrogenation of **BNPDM** to the diamine **BAPDM** was accomplished by means of hydrazine monohydrate as well as a catalytic amount of Pd/C. The chemical structure of the synthesized compounds was checked by elemental analyses and by IR and NMR spectroscopy. The NMR data of **BAPDM** is listed as follows. $^1$H NMR (DMSO-$d_6$, ppm): $\delta$ = 7.25–7.21 (t, 4H), 7.17 (d, 2H), 7.12 (d, 4H), 7.01 (d, 4H), 6.76–6.70 (dd, 8H), 6.58 (d, 4H), 4.97 (s, 4H). $^{13}$C NMR (DMSO-$d_6$, ppm): $\delta$ = 158.39, 148.11, 146.89, 146.48, 140.97, 132.82, 131.51, 128.74, 126.94, 122.13, 116.15, 115.80, 63.49.

Polyamides were prepared by the direct polycondensation of **BAPDM** with various of aromatic dicarboxylic acids (**DA1**–**DA7**) in NMP using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2).

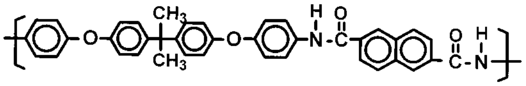
As listed in Table 1, the polyamides had inherent viscosities between 0.65 and 0.97 dL g$^{-1}$. The polymer films, except **PA5**, were obtained by casting from their DMAc solutions. All of the polymer films showed a transparent, flexible, and tough nature. The formation of a polyamide was confirmed by IR and NMR spectroscopy, and elemental analyses. Specifically, polymer **PA7** showed resonance at 10.49 ppm in $^1$H NMR spectrum due to the amide proton.

For comparison, the analogous polyamides **PA4′** and **PA4″**, having hexafluoroisopropylidene and isopropylidene unit, respectively, in the main chain were prepared by condensation of 2,6-naphthalenedicarboxylic acid (**DA4**) with corresponding diamine, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and 2,2-bis-[4-(4-aminophenoxy)phenyl]propane.

PA4′:



PA4″:



They were taken as references to examine the influence of different substitutions in the diphenylmethylene unit on polymer properties such as solubility and thermal stability.

The solubility of these polyamides was tested in various solvents. Most of the polyamides exhibited good solubility in a variety of solvents such as NMP, *N*,*N*-dimethylacetamide, DMF, dimethyl sulfoxide, *m*-cresol, pyridine, tetrahydrofuran, and cyclohexanone at room temperature or upon heating at 70 °C. Polymers **PA1** and **PA5** containing rigid and symmetric *p*-phenylene units showed less solubility than the others. It was observed that the polymer **PA4** showed a slightly higher solubility than **PA4′** and **PA4″**. The higher rigidity of pendent diphenyl substituent compared with hexafluoroisopropylidene (**PA4′**) and isopropylidene (**PA4″**) units may be responsible for this result. This fact demonstrates that the rigidity of the pendent group has a distinct influence on the solubility of polymer.

The crystallinity of the polymers was estimated by means of wide-angle X-ray diffractograms. All of the polymers showed amorphous patterns. The amorphous behavior of the polyamides is due to the bulky pendent phenyl group which increased significantly the disorder in chains and therefore caused less chain packing.[29] In addition, the pendent phenyl group also decreases the intermolecular force between the polymer chains, subsequently causing a decrease in crystallinity.[30] After annealing at 300 °C for 3 h, polymer **PA5** bearing biphenylene group displayed a little reflection peak around $2\theta = 24°$. The semicrystalline behavior of **PA5** should be associated with the fact that the symmetric and rigid biphenylene group has larger intermolecular force between polymer chains which led to a higher crystallinity. The other polymers exhibited amorphous diffraction patterns after annealing.

The thermal properties of the polyamides are also tabulated in Table 1. Glass transition temperatures ($T_g$'s) of the polymers, determined by means of differential scanning calorimeter (DSC), were found to be in the range of 237–272 °C. The highest $T_g$ value was observed for the biphenylene-containing polymer **PA5**. The thermogravimetric analysis (TGA) curve showed that all polymers begin to degrade around or below 450 °C. The decomposition temperatures at 10% weight loss ($T_{d_{10}}$) reach to 500–524 °C in nitrogen. The comparative TGA curves of polyamides **PA4**, **PA4′**, and **PA4″** are indicated in Figure 1. As expected, polymer **PA4″** with

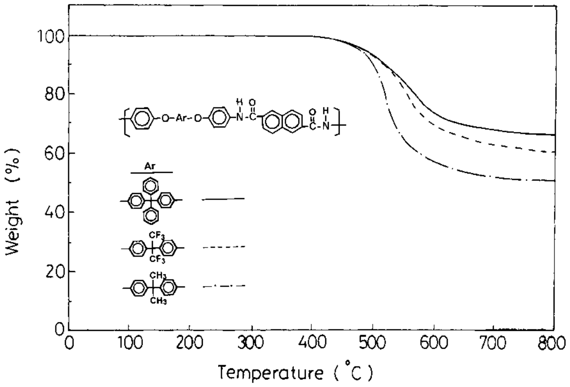


**Figure 1.** TGA curves of **PA4**, **PA4′** and **PA4″** in nitrogen: (—) **PA4**; (- - ) **PA4′**; (− · −) **PA4″**.

an isopropylidene unit began to decompose at lower temperatures and showed less char yield than the others. Polymer **PA4** bearing diphenylmethylene exhibited less weight loss compared with polymer **PA4′** having a hexafluoroisopropylidene group.

The polymer films had tensile strength of 85−108 MPa, elongation at break of 6−11%, and tensile modulus of 2.3−3.2 GPa (Table 1), indicating that they exhibited good mechanical properties.

**Acknowledgment.** The authors thank the National Science Council of the Republic of China for support of this work under Grant NSC 89-2216-E011-008.

## References and Notes

(1) Cassidy, P. E. *Thermally Stable Polymers*; Dekker: New York, 1980.
(2) Liaw, D. J.; Liaw, B. Y. *Macromol. Symp.* **1997**, *122*, 343.
(3) Jeong, H. J.; Oishi, Y.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3193.
(4) Liaw, D. J.; Liaw, B. Y. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1069.
(5) Yagci, H.; Mathias, L. J. *Polym. Prepr. (Am. Chem. Sci., Div. Polym. Chem.)* **1998**, *39* (1), 262.
(6) Spiliopoulos, I. K.; Mikroyannidis, J. A.; Tsivgoulis, G. M. *Macromolecules* **1998**, *31*, 522.
(7) Spiliopoulos, I. K.; Mikroyannidis, J. A. *Macromolecules* **1998**, *31*, 1236.
(8) Akutsu, F.; Inoki, M.; Araki, K.; Kasashima, Y.; Naruchi, K.; Miura, M. *Polym. J.* **1997**, *29*, 529.
(9) Lozano, A. E.; Abajo, J. de; Campa, J. G. de la; Preston, J. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1987.
(10) Liaw, D. J.; Liaw, B. Y. *Macromol. Chem. Phys.* **1999**, *200*, 1326.
(11) Liaw, D. J.; Liaw, B. Y.; Chung, C. Y. *Acta Polym.* **1999**, *50*, 135.
(12) Liaw, D. J.; Liaw, B. Y.; Tsai, M. Y. *Polym. J.* **1997**, *29*, 474.
(13) Liaw, D. J.; Liaw, B. Y. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1075.
(14) Liaw, D. J.; Liaw, B. Y.; Su, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1997.
(15) Negi, Y. S.; Suzuki, Y. I.; Kawamur, I.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Sci.* **1996**, *34*, 1663.
(16) Liaw, D. J.; Wang, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 1209.
(17) Park, J. W.; Lee, M.; Lee, M. H.; Liu, J. W.; Kim, S. D.; Chang, J. Y.; Rhee, S. B. *Macromolecules* **1994**, *27*, 3459.
(18) Sundararajan, P. R. *Macromolecules* **1990**, *23*, 2600.
(19) Matsuo, S.; Murakami, T.; Takasawa, R. *J. Polym. Sci., Part A: Polym. Sci.* **1993**, *31*, 3439.
(20) Matsuo, S. *J. Polym. Sci., Part A: Polym. Sci.* **1994**, *32*, 2093.
(21) Matsuo, S.; Mitsuhashi, K. I. *J. Polym. Sci., Part A: Polym. Sci.* **1994**, *32*, 2199.
(22) Hilborn, J. G.; Labadie, J. W.; Hedrick, J. L. *Macromolecules* **1990**, *23*, 2854.
(23) Masato, F.; Shoji, O.; JP 05,295,089; *Chem. Abstr.* **1993**, *123*, P324978.
(24) Morgan, P. M. *Macromolecules* **1970**, *3*, 536.
(25) Freitag, D.; Westeppe, U.; Wulff, C. H.; Fritsch, K. H.; Casser, C.; Weymans, G.; Schrader, L.; Waldenrath, W. Eur. Pat. 359,953; *Chem. Abstr.* **1990**, *113*, P133101.
(26) Freitag; D.; Westeppe, U. *Macromol. Chem., Rapid Commun.* **1991**, *12*, 95.
(27) Geiger, C. C.; Davies, J. D.; Daly, W. H. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 2317.
(28) Liaw, D. J.; Liaw, B. Y. *Polymer* **1999**, *40*, 3183.
(29) Liaw, D. J.; Liaw, B. Y.; Li, L. J. Sillion, B.; Mercier, R.; Thiria, R.; Sekiguchi, H. *Chem. Mater.* **1998**, *10*, 734.
(30) Liaw, D. J.; Liaw, B. Y.; Chen, J. R.; Yang, C. M. *Macromolecules,* in press.

MA990545H