

Synthesis of New Highly Organosoluble Polyimides Bearing a Noncoplanar Twisted Biphenyl Unit Containing *t*-Butyl Phenyl Group

Yun-Hi Kim, Hyung-Sun Kim, Seong-Kuk Ahn, Sung Ouk Jung, and Soon-Ki Kwon*

Dept. of Polymer Science & Engineering and Research Institute of Industrial Technology,
Gyeongsang National University, Chinju 660-701, Korea

Received April 18, 2002

Keywords : Polyimide, Organosoluble, 3,3',4,4'-Biphenyltetracarboxylic dianhydride (s-BPDA).

Aromatic polyimides are widely used in the semiconductor and electronic packaging industry because of their outstanding thermal stability, good insulation properties with low dielectric constant, good adhesion properties with common substrates, and superior chemical stability.^{1,2} However, their applications were limited in many fields because the early polyimides were insoluble and intractable. Therefore, considerable research has been undertaken to identify new ways to circumvent these restrictions.

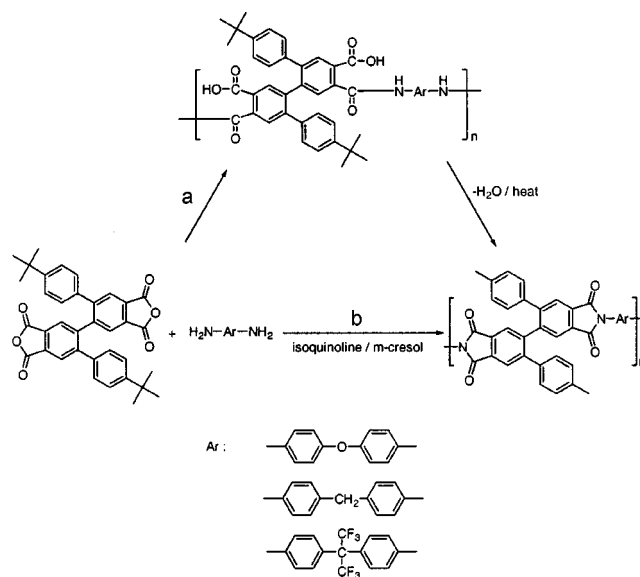
To circumvent these problems, solutions of polyimides would be desirable, instead of precursors. Flexible links (e.g. O-, -SO₂-, -CH₂-) or bulky groups (fluorenylidene, hexafluoropropylidene, etc.) are commonly employed as solubilizing moieties, but it often costs a desirable in thermal stability and chain stiffness of polyimides. Alternatively, the solubilizing units may be derived from substituted biphenyls, increasing entropy factors due to rotational isomerism of benzene rings relative to aryl-aryl bond.^{3,4} The relevant compounds of this class are biphenyltetracarboxylic dianhydrides. Among them, 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) was commercialized in the early 1980s and is widely used at present.⁵

It has been known that polymers containing *t*-butyl group have excellent gas permeability.⁶⁻¹⁴ Soluble polyimides containing bulky *t*-butylphenyl group offer particular promise in gas separation membrane application due to their superior mechanical property, high permeability and permselectivity. Thus, we tried to synthesize new s-BPDA-based polyimides containing bulky *p*-*t*-butylphenyl group, which is expected to give good solubility and high permeability and permselectivity with good thermal stability and mechanical property. In this communication, we report the synthesis and characterization of new soluble polyimides derived from s-BPDA containing bulky *p*-*t*-butylphenyl group, and conventional aromatic diamines.

Monomer Synthesis. The monomer was obtained by various organic reaction. 3,3',4,4'-Tetramethylbiphenyl was obtained by Ni-coupling of 4-bromo-*o*-xylene. The bromination of 3,3',4,4'-tetramethylbiphenyl gave 2,2'-dibromo-4,4',5,5'-tetramethylbiphenyl, which was reacted with *p*-*t*-butylbenzene boronic acid to generate 2,2'-bis(4''-*t*-butylphenyl)-4,4',5,5'-tetramethylbiphenyl. 2,2'-Bis(4''-*t*-butylphenyl)biphenyltetracarboxylic dianhydride (BBBPAn) was obtained by oxidation and dehydration of 2,2'-bis(4''-*t*-butylphenyl)-4,4',5,5'-tetramethylbiphenyl. The yields in each

steps were very high and the obtained products in each steps were confirmed by various spectroscopies.

Polymer Synthesis. It is known that there are two general methods for the preparation of polyimides. One procedure involves two steps and proceeds *via* poly(amic acid)s intermediate. The other is one-step solution polymerization. The one step method has some advantage over the two step method. Polyimides in bulk are more easily produced, and polyimides with higher crystallinity can be more readily obtained.¹⁵ The one step method is also useful for unreactive diamines and dianhydrides which can not form high molecular weight polyamic acids by the two step method.¹⁶⁻¹⁷ The disadvantage of the one step method is that insoluble polyimides can not form high molecular weight polyimides because of premature precipitation. We tried two general methods. When polyimides were synthesized by the conventional two step procedure involving a ring-opening polyaddition and subsequent thermal cyclodehydration, the polymer molecular weight was not enough for preparing of the free stand film. It may be suggested that dianhydride is deactivated by steric hindrance of *t*-butylphenyl substituents in 2,2' position of s-BPDA unit. Otherwise, the one-step polymerization at high temperature, as shown in synthetic route b, resulted in high viscosity. BBBPAn and diamines were reacted in *m*-cresol with 2% (w/w) isoquinoline as a



Scheme 1

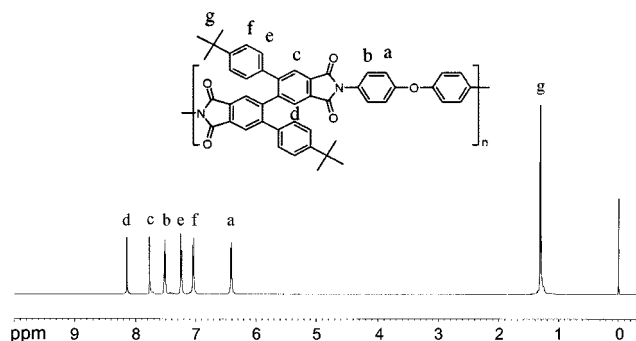
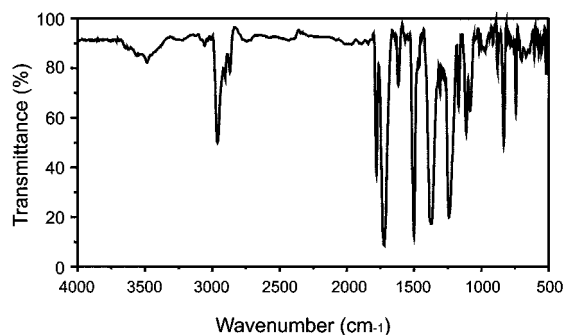
Table 1. The Results of Polymerization Yield, Elemental Analyses and Viscosities of Polyimides

Polyimide	Diamines	P.Y. (%)	Elemental Analyses			η_{inh}	
			C	H	N		
Polymer 1 C ₄₈ H ₃₈ N ₂ O ₅	ODA ^a	94	Cal.	79.78	79.78	3.88	1.43
			Found	80.80	5.30	3.83	
Polymer 2 C ₄₈ H ₄₀ N ₂ O ₄	MDA ^b	96	Cal.	81.67	5.56	3.89	0.56
			Found	82.19	6.23	3.96	
Polymer 3 C ₅₁ H ₃₈ N ₂ O ₄ F ₆	6FDA ^c	96	Cal.	71.50	4.44	3.27	0.41
			Found	70.86	4.57	3.42	

^a4,4'-oxydianiline, ^b4,4'-methylenedianiline, ^c4,4'-(hexafluoroisopropylidene)dianiline. ^d0.5 g/dL in CHCl₃ at 30 °C

catalysts and the concentration of materials was 8-10% (w/w). After the first part of the reaction was slowly heated to 110 °C for 1 h, the temperature was raised slowly up to 190 °C-200 °C and refluxed for 5h. The water formed during imidization was removed continuously with a stream of nitrogen. After reflux, the excess *m*-cresol was added to the reaction mixture and the reaction mixture precipitated into methanol. The polymer was filtered and washed with methanol several times. The yields of polymerization were 94-96%. The results of the polymerization are summarized in Table 1. The inherent viscosities of polyimides are 0.41-1.43. The inherent viscosity increased in the following order: polyimide 1 > polyimide 2 > polyimide 3. From the results, it is supposed that diamine with electron donating group is active for imidization because of its high nucleophilicity to dianhydride, and polyimide from diamine with electron donating group has higher molecular weight. The elemental analysis values agreed quite well with calculated values for the proposed structure of polyimides. The structures of obtained polyimides were also confirmed by IR and ¹H-NMR spectroscopies. Figure 1 showed IR and ¹H-NMR spectra of polymer 1. The IR spectrum of pellet of the polyimide 1 supported the formation of polyimide. The characteristic absorption bands of the polyimide ring appeared near 1778 (asym C=O str), 1722 (sym C=O str), 1371 (C-N str), 742 (imide ring deformation) cm⁻¹. In the ¹H-NMR, the protons of *t*-butyl group appeared at 1.3 ppm and 4,4'-oxyaniline protons appeared at 6.4 and 7.5 ppm, respectively.

The solubility of polyimides are studied in various solvents. Owing to the noncoplanar twisted biphenyl structure and bulky *t*-butyl phenyl group, the synthesized polyimides showed good solubility in common organic solvents such as chloroform, THF. The thermal properties of the polyimides were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA thermograms showed that the 5% weight losses in nitrogen were 540-550 °C. The glass transition temperature (T_g s) of polyimides observed at 348 °C-381 °C. The results of the TGA and DSC analyses showed the general excellent thermal stability of the polyimides. Now we are progressing the studies of mechanical properties and gas separation characteristics of the new polyimides.

**Figure 1.** The IR and ¹H-NMR spectra of polymer 1.

Acknowledgment. This work was supported by Korea Research Foundation Grant (KRF-2000-005-E00005).

References

- Ghosh, M. K.; Mittal, K. L. *Polyimides: Fundamentals and Applications*; Marcel Dekker: New York, 1996.
- de Alajo, J.; de la Campa, J. G. *Adv. Polym. Sci.* **1999**, *140*, 23.
- Li, F.; Fang, S.; Ge, J. J.; Honigfort, P. S.; Chen, J. C.; Harris, F. W.; Cheng, S. Z. D. *Polymer* **1999**, *40*, 4571.
- Li, F.; Ge, J. J.; Honigfort, P. S.; Chen, J. C.; Harris, F. W.; Cheng, S. Z. D. *Polymer* **1999**, *40*, 4571.
- Itaaki, H.; Yoshimoto, H. *J. Org. Chem.* **1973**, *38*, 76.
- Kim, Y. H.; Kim, H. S.; Ahn, S. K.; Kwon, S. K. *Macromolecules* submitted.
- Kim, Y. H.; Kwon, S. K.; Choi, S. K. *Macromolecules* **1997**, *30*, 6677.
- Ahn, S. K.; Kim, Y. H.; Shin, D. C.; Kwon, S. K. *Bull. Korean Chem. Soc.* **2000**, *21*, 377.
- Masuda, T.; Hamano, T.; Tsuchihara, K.; Higashimura, T. *Macromolecules* **1990**, *23*, 1374.
- Tsuchihara, T.; Masuda, T.; Higashimura, T. *J. Am. Chem. Soc.* **1991**, *113*, 8549.
- Seki, H.; Masuda, T.; Higashimura, T. *J. Polym. Sci. Polym. Chem. Ed.* **1995**, *33*, 117.
- Kim, Y. H.; Shin, D. C.; Ha, C. S.; Cho, W. J.; Kwon, S. K. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 937.
- Ahn, S. K.; Kim, Y. H.; Kwon, S. K. *Bull. Korean Chem. Soc.* **2000**, *21*, 377.
- Kim, Y. H.; Ahn, S. K.; Kwon, S. K. *Bull. Korean Chem. Soc.* **2001**, *22*, 451.
- Masao, T.; Stephen, Z. D. C.; Frank, W. H. *Polymer Preprints* **1992**, *33*, 396.
- Shu, T.; Allan, S. H. *Macromolecules* **1997**, *30*, 5979.
- Yi, M. H.; Huang, W.; Jin, M. Y.; Choi, K. Y. *Macromolecules* **1997**, *30*, 5606.