

Synthesis and Characterization of Novel Soluble Aromatic Polyimides from 1,4-Bis-(4'-*t*-butylphenyl)pyromellitic Dianhydrides and Aromatic Diamines

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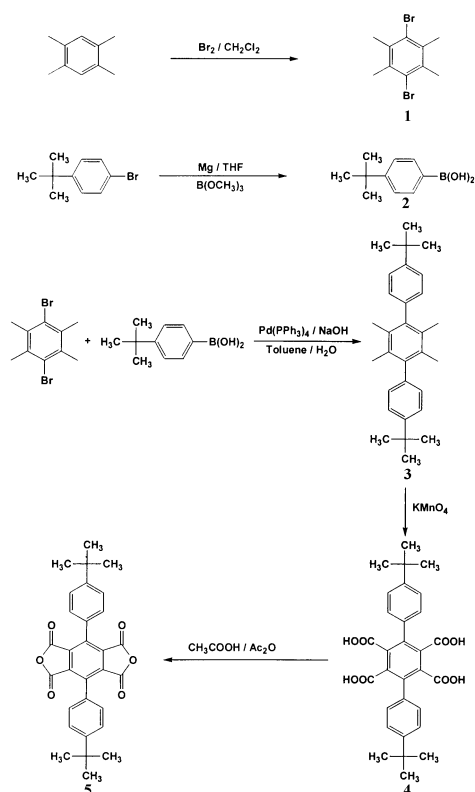
Aromatic polyimides are known for their excellent thermal stability and balanced mechanical and electric properties.¹ Polyimides are mainly used in the aerospace and electronic industries in the forms of films and moldings. Other uses for these polymers such as adhesives, composite matrices, coatings, foams, and gas separation membranes are rapidly increasing.²⁻⁹ However, aromatic polyimides are difficult to process because of high softening temperatures and limited solubility in commercially available solvents. To overcome these difficulties, structural modifications of the polymer backbone, such as the addition of bulky lateral substituents, flexible alkyl side chains, noncoplanar biphenylene moieties and kinked comonomer have been utilized either by lowering the interchain interactions or by reducing the stiffness of the polymer backbone.¹⁰⁻²¹

It had been known that polymers containing trimethylsilyl or *t*-butyl group have excellent gas permeability.²²⁻²⁴ Soluble polyimides containing bulky and rigid *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 of

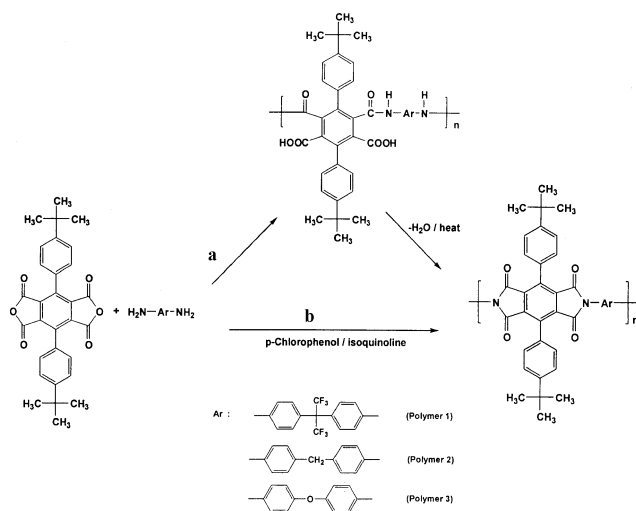
new polyimides containing bulky *t*-butylphenyl group, which is expected to give good solubility and high gas permeability as well as permselectivity. In this communication, we report the synthesis and characterization of new soluble polyimides derived from new pyromellitic dianhydride containing bulky *t*-butylphenyl group and conventional aromatic diamines.

The synthetic route of the monomer is shown in Scheme 1. 1,4-dibromodurene (**1**)²⁵ was obtained by bromination of durene. *p*-*t*-Butylbromobenzene was reacted with trimethylborate by Grignard reaction to generate *p*-*t*-butylbenzeneboronic acid (**2**). 1,4-bis(4'-*t*-butylphenyl)durene (**3**) was obtained by Suzuki coupling reaction of *p*-*t*-butylbenzeneboronic acid (**2**) and 1,4-dibromo durene. 1,4-Bis(4'-*t*-butylphenyl)pyromellitic dianhydride (**5**) was obtained by oxidation of 1,4-bis(4'-*t*-butylphenyl)durene (**3**) following by dehydration of 1,4-bis(4'-*t*-butylphenyl)pyromellitic acid (**4**). The yields in each steps were very high. In the ¹H NMR spectra of 1,4-bis(4'-*t*-butylphenyl)pyromellitic dianhydride, the proton peaks of *t*-butyl group and aromatic ring appeared at 1.1 ppm and 7.2 ppm, respectively. In the FT-IR spectrum, instead of the broad acid peak disappeared, characteristic peaks of anhydride carbonyl group appeared at 1770 cm⁻¹ and 1870 cm⁻¹.

There are two general methods for the preparation of polyimides. (Scheme 2) One procedure involves two steps and proceeds via poly(amic acid)s intermediate. In this case, the polymer molecular weight is not high enough for preparing of the free standing film. However, the one-step polymerization at high temperature resulted in high viscosity as well as high molecular weight. It was known that the one step poly-



Scheme 1



Scheme 2

Table 1. Elemental Analysis and Viscosity of Polymers

Polymer	Diamine	Elemental Analysis (%)			η_{inh}^d	
		C	H	N		
Polymer 1 [C ₄₅ H ₃₄ O ₄ N ₂ F ₆] _n	6FDA ^a	Cal.	69.23	4.36	3.59	0.62
		Found	69.35	4.44	3.69	
Polymer 2 [C ₄₃ H ₃₆ N ₂ O ₄] _n	MDA ^b	Cal.	80.12	5.59	4.35	0.64
		Found	79.87	5.47	4.35	
Polymer 3 [C ₄₂ H ₃₄ N ₂ O ₅] _n	ODA ^c	Cal.	78.02	5.26	4.33	1.98
		Found	77.93	5.35	4.47	

^a4,4'-(hexafluoroisopropylidene)dianiline. ^b4,4'-methylenedianiline. ^c4,4'-oxydianiline. ^d0.05 g/dL in DMAc at 30 °C.

merization process is more favorable for unreactive dianhydrides.²⁶ The one step polymerization was carried out in *p*-chlorobenzene with 2% (w/w) isoquinoline as a catalysts and a polymer concentration around 5% (w/w). The first part of the reaction was proceeded at 60 °C for 2h and then the temperature was raised slowly up to 250 °C. Water formed during the imidization was continuously removed with a stream of argon. After 5 hrs, excess *p*-chlorophenol added and precipitated in methanol. The polymer was filtered and washed with methanol several times. The results of the polymerization are summarized in Table 1. The inherent viscosities of the obtained polyimides by one-step polymerization were in the range of 0.62-1.98 dL/g. The elemental analysis values agreed quite well with the calculated values for the proposed structure of polyimides. The IR spectra of the polymers also supported the formation of polyimides.

Table 2 shows the solubility behavior of prepared polyimides. The polyimides containing bulky *t*-butylphenyl group were soluble in organic solvents such as NMP, DMAc and *p*-chlorophenol.

The thermal stability of polymers was ascertained by TGA. The results of the TGA analyses showed the general excellent thermal stability of the polyimides. The 5% weight losses in nitrogen were at 500-510 °C, 20% at 550-570 °C, and 35% at 600-620 °C. The films of polyimide showed good mechanical property. Table 3 lists the tensile properties of the polyimide films. The films had tensile strength of 56-94 MPa, elongation at break of 6.7-34%, and tensile modulus range of 1.35-2.25 GPa.

Table 2. Solubility of Polymers^a

Solvents	Polymer 1	Polymer 2	Polymer 3
Ether	-	-	-
THF ^b	-	-	-
Acetone	-	-	-
Chloroform	++	-	-
DMF ^c	++	++	++
DMSO ^d	++	++	++
<i>m</i> -Cresol	++	++	++
NMP ^e	++	++	++
DMAc ^f	++	++	++
<i>p</i> -Chlorophenol	++	++	++

^a++: soluble, +: partially soluble, -: insoluble. ^bTHF: tetrahydrofuran. ^cDMF: dimethylformamide. ^dDMSO: dimethyl sulfoxide. ^eNMP: N-methylpyrrolidone. ^fDMAc: N,N-dimethylacetamide

Table 3. Mechanical Properties of Polyimides

Polymer	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (%)
Polymer 1	55.67	1.35	6.68
Polymer 2	88.03	1.25	8
Polymer 3	93.98	1.56	34

From the above results, the new synthesized polyimides containing bulky and rigid substituents by one-step method have good solubility in organic solvents and good thermal and mechanical property. Now we are progressing the study of gas separation properties of new polyimides.

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References

1. *Polyimides*; Wilson, D., Stenzenberger, H. D., Hergenrother, P. M., Eds.; Blackie & Son: Glasgow and London, 1990.
2. Rusanov, A. L.; Batirov, I. *Russ. Chem. Rev.* **1980**, *12*, 49.
3. Huang, S. J.; Hoyt, A. E. *Trends Polym. Sci.* **1995**, *3*(8), 262.
4. Sroog, C. E. *Prog. Polym. Sci.* **1991**, *16*, 561.
5. Cella, J. A. *Polym. Degrad. Stab.* **1992**, *36*, 99.
6. Volksen, W. *Adv. Polym. Sci.* **1994**, *117*, 111.
7. Takekoshi, T. *Adv. Polym. Sci.* **1990**, *94*, 1.
8. *Polyimides Fundamentals and Applications*; Gohsh, M. K., Mittal, K. L., Eds.; Marcel Dekker: New York, 1996.
9. Bessonov, M. I.; Zubkov, V. A. *Polyamic Acids and Polyimides, Synthesis, Transformation and Structure*; CRC Press: Boca Ratan, FL, 1993.
10. Review of rigid rod polymers; Ballauff, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 253.
11. Kim, W. G.; Hay A. S. *Macromolecules* **1993**, *26*, 5257.
12. Schmitz, L.; Rehahn, M.; Ballauff, M. *Polymer* **1993**, *26*, 4413.
13. Schmitz, L.; Rehahn, M. *Macromolecules* **1993**, *26*, 5257.
14. Giesa, R.; Keller, U.; Eiselt, P.; Schmidt, H. W. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 141.
15. Spiliopoulos, I. K.; Mikroyannidis, J. A. *Macromolecules* **1996**, *29*, 5313.
16. Itoh, M.; Mita, M. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1581.
17. Kaneda, T.; Katsura, T.; Nakagawa, K.; Makino, H.; Horio, M. *J. Appl. Polym. Sci.* **1986**, *32*, 3151.
18. Ghassemi, H.; Hay, A. S. *Macromolecules* **1994**, *27*, 4410.
19. Ghassemi, H.; Hay, A. S. *Macromolecules* **1994**, *27*, 3116.
20. Kim, S. I.; Shin, J.; Ree, M.; Hwang, G. T.; Kim, B. H.; Han, H. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2013.
21. Pyo, S. M.; Kim, S. I.; Shin, T. J.; Park, Y. H. Ree, M. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 937.
22. Takada, K.; Matsuya, H.; Masuda, T.; Higashimura, T. *J. Appl. Polym. Sci.* **1985**, *30*, 1605.
23. Kim, Y. H.; Shin, D. C.; Ha, C. S.; Cho, W. J.; Kwon, S. K. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4135.
24. Kim, Y. H.; Kwon, S. K.; Choi, S. K. *Macromolecules* **1997**, *30*, 6677.
25. Ludwig, S.; Matthias, R.; Matthias, B. *Polymer* **1993**, *34*, 646.
26. Masao, T.; Stephen, Z. D. C.; Frank, W. H. *Polymer Preprints* **1992**, *33*, 396.