Polyimides using hydrazine as the diamine

Zhen Wang[1], Jingling Yan[1, 2], Lianxun Gao[1], and Mengxian Ding[1]

1. State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China

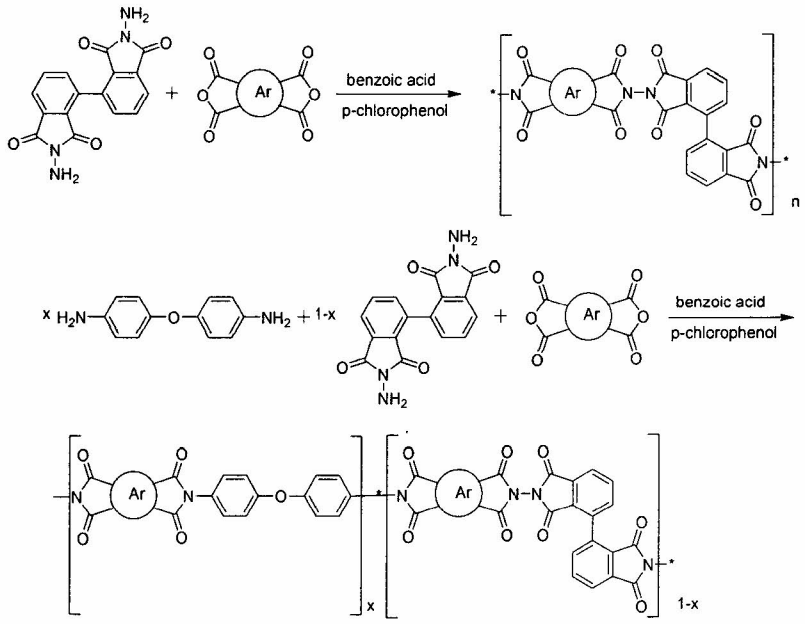
2. Graduate School of Chinese Academy of Science

Hydrazine is the simplest diamine and its reactions with phthalic anhydride and its derivatives have been reported for many years.[1-2]However, only a few reports on polyimides based on hydrazine have been seen in the literatures. In 1960's, Dine-Hart prepared successfully N, N'-diaminonaphthalene -1,4,5,8-tetracarboxydi-imide and N,N'-diamino pyromellitimide, but high-molecular-weight polyimides could not be obtained due to the lower reactivity of monomers and poor solubility of the resulted polymers.[3] In 1990's, Hay and coworkers obtained high-molecular-weight polyimide from monomers with six-membered ring N-amino imide by the introduction of flexible moieties or copolymerization with other diamine monomers. These polyimides showed very high T_gs, excellent thermal stability, and good solubility.[4-10]

The introductions of alicyclic monomers or rigid but non-planar structures are effective methods to improve the solubility and optical properties of polyimides.[11-12] The basic of hydrazine (pKb_1=5.88) is in the middle of alkyl amines and aromatic amines, but hydrazine-based polyimides can be regarded as wholly aromatic. What's more, N, N'-biphthalimide adopted twisted conformation because of the steric repulsion of the four C=O groups.[13]This promotes us to investigate five-membered ring polyimides using hydrazine as the diamine. To our best knowledge, no all five-membered ring, hydrazined-based polyimides was studied in detail in the literature. In this paper, we present the synthesis and properties of a series of novel hydrazine-based polyimides with five-membered ring imide.

1. Synthesis of monomer and polymers

3,3'-Bis(N-aminophthalimide) (BAPI) was prepared from 3,3'-bis(N-phenylphthalimide) and hydrazine in moderate yield (70%). A series of homo- and co-polyimides were synthesized via conventional method in p-chlorophenol. Inherent viscosities of the polymers were in the range of 0.18-0.50 dl/g in DMAc at 30°C. Homo-polyimide films based on BPDA, BTDA, and ODPA were brittle, while homo-polyimide films based on 6FDA, 3,3'-HQPDA, and 4,4'-HQPDA were transparent and flexible. Using 4,4'-diaminodiphenylether as the copolymerization monomer, transparent and flexible films were cast from the DMAc solutions of co-polyimides based on BPDA, BTDA, and ODPA.



Scheme 1. Synthesis of homo- and co- polyimides from BAPI (Aromatic dianhydrides used: BPDA, BTDA, ODPA, 6FDA, 4,4'-HQPDA, and 3,3'-HQPDA)

2. Properties of polymers

2.1 Solubility

The solubility of the homo- and co-polyimide powders derived from 3,3'-bis(N-aminophthalimide) (BAPI) was summarized in Table 1. All polymers showed good solubility in polar aprotic solvents and phenols at room temperature, what's more, polyimides based on 6FDA and 4,4'-HQPDA were soluble in chloroform, TCE and THF. Copolymers showed similar solubility compared with the corresponding homo-polymers. We think that the enhanced solubility was contributed to the unique twisted, non-coplanar structure. It has been reported that N, N'-biphthalimide adopted twisted conformation because of the steric repulsion of the four C=O groups.[13] Furthermore, 3,3'-biphenyl unit also showed non-coplanar conformation because of the steric hindrance.[14-15] Both of them inhabited chains packing and hindered the formation of intermolecular changed-transfer complexes. These facts caused the enhanced solubility of these polyimides.

Table 1. Solubility of polyimides in different solvents

Polymer	$CHCl_3$	TCE[b]	THF	DMF	DMAc	DMSO	NMP	m-cresol	p-chlorophenol
BPDA/BAPI	–	–	–	±	+	+	+	+	+
BTDA/BAPI	–	–	–	+	+	+	+	+	+
ODPA/BAPI	–	–	–	+	+	+	+	+	+
6FDA/BAPI	+	+	±	+	+	+	+	+	+
4,4'-HQPDA/BAPI	±	+	–	+	+	+	+	+	+
3,3'-HQPDA/BAPI	–	–	–	±	+	+	+	+	+
BPDA/BAPI/ODA	–	–	–	±	+	+	+	+	+
BTDA/BAPI/ODA	–	–	–	+	+	+	+	+	+
ODPA/BAPI/ODA	–	–	–	+	+	+	+	+	+

2.2 Thermal and mechanical properties

The thermal and mechanical properties of isomeric polyimides were summarized in Table 2. The temperatures of 5% weight loss ($T_{5\%}$) of all polyimides ranged from 495 to 530 ℃ in air. It also can be concluded that the thermoxidative stability of copolymers were slightly higher than those of homo- polymers.

The tensile strengths of homo- and co- polyimides at break, the modulus, and the elongations at break are in the range of 85-132 MPa, 1.77-2.77 GPa, and 5.0-10.3%, respectively. The films of homo-polyimides from BPDA, BTDA, and ODPA were highly brittle, however their co-polyimides showed excellent mechanical properties because of higher molecular weights and lower chain stiffness.

The representative DMTA curves of homo- and co-polyimides were displayed in Figure 1. All polymers possessed very high T_gs, which is due to their rigid and rotation-restricted structures.

2.3 Optical properties

Transmission UV-visible spectra of polyimide films was shown in Figure 2. The cutoff wave length of the absorption and transmittance of 6FDA/BAPI was lower than that the other obtained polyimide films. It should be pointed out that polyimide film based on 4,4'-HQPDA/BAPI, which is non-fluorinated and wholly aromatic, also possessed excellent optical properties, with a cutoff at 368 nm and high transmittance in visible area. The polyimide films of 6FDA/BAPI and 4,4'-HQPDA/BAPI were colorless, other films were pale yellow or yellow.

Table 2: Thermal and mechanical properties of isomeric polyimides

Polymer	T_g(℃)[a]	$T_{5\%}$(℃)[b]	Tensile strength(MPa)	Modulus (MPa)	Elongation (%)
BPDA/BAPI	-[c]	523	-	-	-
BTDA/BAPI	-	514	-	-	-
ODPA/BAPI	-	505	-	-	-
6FDA/BAPI	431	495	88	1780	9.5
4,4'-HQPDA/BAPI	378	516	106	1950	6.5
3,3'-HQPDA/BAPI	375	497	94	2772	5.0
BPDA/BAPI/ODA	432	530	117	1770	10.3
BTDA/BAPI/ODA	400	515	132	2470	7.2
ODPA/BAPI/ODA	391	519	85	2390	7.0

[a] Obtained from DMTA at heating rate of 3℃/min at 1 Hz.

[b] Five percent weight loss obtained from TGA at a heating rate of 20℃/min in air.

[c] Not measured because their films were brittle.

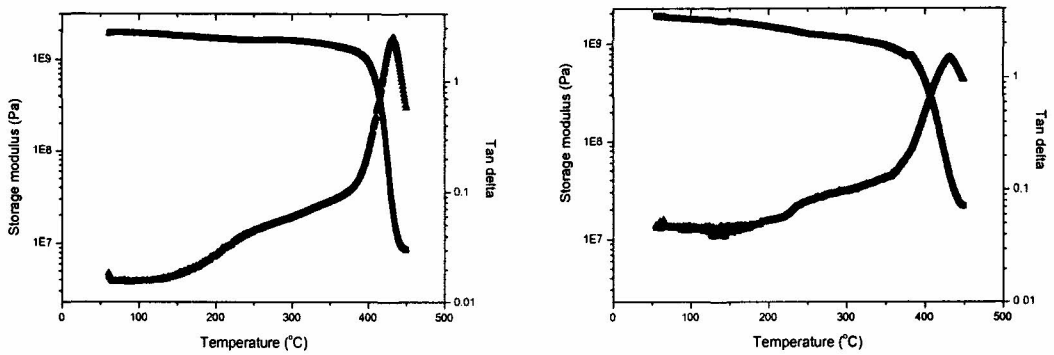


Figure 1. The representative DMTA curves of polyimides based on BAPI(the left: polyimide 6FDA/BAPI, the right: polyimide BPDA/BAPI/ODA)

3. Conclusion

A new diamine, 3,3'-bis(N-aminophthalimide), was prepared from inexpensive starting materials via simple procedure. A series of novel homo- or co-polyimides were synthesized via conventional one-step method in p-chlorophenol. These polymers possessed enhanced solubility, excellent thermooxdative stability, moderate mechanical properties, very high T_gs, and light coloration.

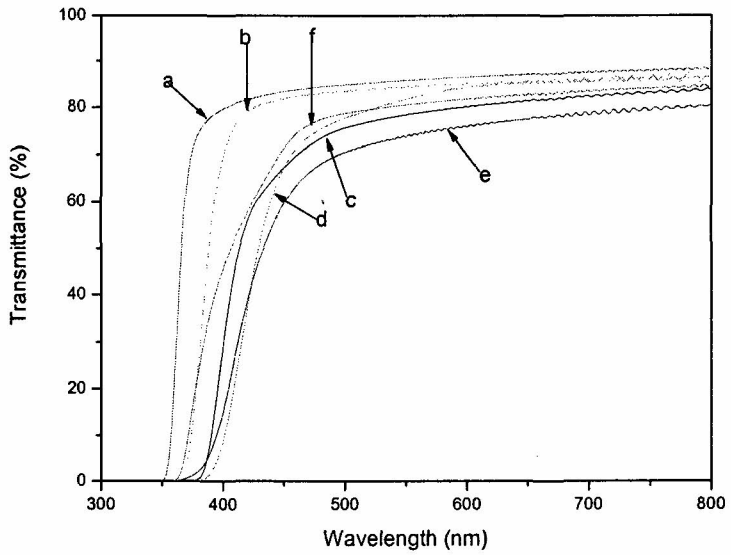


Figure 2. UV-visible spectra of polyimide films (about 15-20μm) (a: 6FDA/BAPI, b: 4,4'-HQPDA/BAPI, c: 3,3'-HQPDA/BAPI, d: BPDA/BAPI/ODA, e: BTDA/BAPI/ODA, f: ODPA/BAPI/ODA)

Acknowledgements The authors express their thanks to the National Science Foundation of China (NO. 50333030 and 10577018) and the National 973 Project of China (NO.G2003CB615604 and 2003CB615704)) for their financial supports.

References

1. Drew HDK, Hatt HH. J. Chem. Soc. 1937,16-26
2. Drew HDK, Hatt HH. J. Chem. Soc. 1937,26-33
3. Dine-hart RA. J Polym Sci, Part A-1 1968, 6, 2755-2764.
4. Ghassemi H, Hay AS. Macromolecules 1993, 26, 5824-5826.
5. Ghassemi H, Hay AS. Macromolecules 1994, 27, 3116-3118.
6. Ghassemi H, Hay AS. Macromolecules 1994, 27, 4410-4412.
7. Sugioka T, Hay AS. J Polym Sci, Part A: Polym Chem 2001, 39, 1040-1050.
8. Hay AS, Ghassemi H. U.S. Patent 5,459,227, October 17, 1995.
9. Hay AS, Ghassemi H. U.S. Patent 5,420,234, May 30, 1995.
10. Hay AS, Ghassemi H. U.S. Patent 5,359,092,October 25, 1994.
11. Martin ER, Timothy EL, editors. In Synthetic Methods in Step-Growth Polymers. John Wiley & Son, 2003; p265-333.
12. Abajo JH, Campa JG. Adv Polym Sci 1999, 140, 23-59.
13. Apreda MC, Foces-Foces C, Cano FH, and Garcia-Blanco S. Acta Cryst. 1978, B34, 3477-3479.
14. Tong YJ, Huang WX, Luo J, Ding MX. J Polym Sci, Part A: Polym Chem 1999, 37:,1425-1433.
15. Rozhanskii I, Okuyama K, Goto K. Polymer 2000, 41, 7057-7065.