

Polyimides derived from 1, 4-bis [3-oxy- (*N*-aminophthalimide)] benzene

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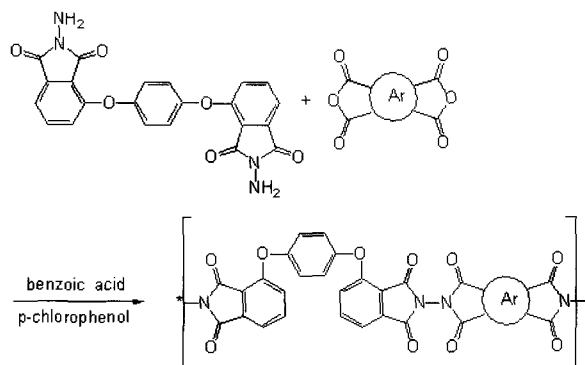
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Dine-Hart prepared successfully *N, N'*-diaminonaphthalene -1,4,5,8-tetracarboxydi-imide and *N, N'*-diamino pyromellitimide, but high-molecular-weight polyimides could not be obtained due to the lower reactivity of monomers and poor solubility of the resulted polymers¹. 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_g s, excellent thermal stability, and good solubility.²⁻⁸

A series of homo- and co-polyimides derived from 3, 3'-bis (*N*-aminophthalimide) (BAPI) were reported by Yan in our laboratory in 2006⁹. The obtained polymers have high solubility, thermal stability and T_g s, some of them also showed high optically transparent properties. As the continuing work of our research on hydrazine-based polyimides, we herein report the synthesis and properties of a series of polyimides derived from 1, 4-bis [3-oxy- (*N*-aminophthalimide)] benzene, which was prepared from 1, 4-bis [3-oxy- (*N*-phenylphthalimide)] benzene and hydrazine.

1, 4-bis [3-oxy- (*N*-aminophthalimide)] benzene (BOAPIB) was prepared from 1, 4-bis [3-oxy- (*N*-phenylphthalimide)] benzene and hydrazine. A series of five-member-ring, hydrazine-based polyimides were prepared from this diamine and various aromatic dianhydrides via one-step polycondensation in *p*-chlorophenol. The inherent viscosities of these polyimides were in the range of 0.17-0.61 dL/g in DMAc or in *m*-cresol at 30 °C. The films were cast from their corresponding NMP solution, except the polymer 4, 4'-BTDA/BOAPIB from its sulflane solution.



Scheme 1. Synthesis of polymers from BOAPIB

The solubility of the polymers derived from 1, 4-bis [3-oxy- (*N*-aminophthalimide)] benzene (BOAPIB) was summarized in Table 1. All polymers showed good solubility in polar aprotic solvents and phenols at room temperature. The enhanced solubility was contributed to the introduction of ether linkage and the bent chain structure. The solubility of polyimides from 4, 4'-aromatic dianhydrides was somewhat better than that from 3, 3'-aromatic dianhydrides, especially for the polymers based on HQDPAs. This result is on the contrary with that previously reported about the isomer effect on the

polyimides.

Table 1. Solubility of polyimides in different solvents

Polymer	CHCl ₃	TCE ^a	THF	DMAc	DMF	DMSO	NMP	<i>m</i> -cresol
4,4'-BPDA/BOAPIB	-	+	-	++	++	++	++	++
3,3'-BPDA/BOAPIB	-	-	-	++	+	++	++	++
4,4'-ODPA/BOAPIB	-	++	-	++	++	++	++	++
3,3'-ODPA/BOAPIB	-	++	-	++	++	++	++	++
4,4'-BTDA/BOAPIB	-	+-	-	*	*	++	*	+
3,3'-BTDA/BOAPIB	-	++	-	++	++	++	++	++
4,4'-HQDPA/BOAPIB	+-	++	-	++	++	+	++	++
3,3'-HQDPA/BOAPIB	+-	+	-	+	+	+	+	+
BPADA/BOAPIB	++	++	+-	++	++	+	++	++

Key: ++ soluble at room temperature; + soluble on heating.

+- partially soluble on heating; - insoluble on heating.

^a TCE, 1,1,2,2-tetrachloroethane.

* gelation.

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 388 to 497 °C in air. The $T_{5\%}$ of the polymer from 3, 3'-BTDA is obviously lower than the other polymers, which is due to its lower molecular weight. The T_g value of polymers from 4, 4'-dianhydrides were higher than that from 3, 3'-dianhydrides, except for the polyimides from isomeric BPDAs. This conclusion agreed with our previously reported polyimides derived from and 3, 3'-BAPI, but did not agree with most studies about isomeric polyimides¹⁰. It can be assumed that T_g s are contributed by molecular structure, interaction between chains and molecular weight, etc. Usually, the T_g s of polyimide derived from 3, 3'-dianhydride are higher than that from 4, 4'-dianhydride, owing to the higher rotation barrier of the bond. On the other hand, the interaction between molecular chains also played important role in the contribution to T_g s. Polyimides based on 3, 3'-dianhydride has more bent chain than that from 4, 4'-dianhydride, therefore, the packing between the molecular chains of the latter may be tighter than that of the former. The balance of two factors determined the T_g values of the polyimides. Furthermore, the lower molecular weight of polyimides based on 3, 3'-dianhydrides, especially for polyimides from isomeric BTDA and ODPA, may also affect the T_g s. In addition, we assumed that the contrary result with previously reported on isomeric polyimides²⁰ should be a complement to the isomeric effect of polyimides based on isomeric dianhydride. The representative DMTA curves of 4, 4'-HQDPA/BOAIB and 3, 3'-HQDPA/BOAPIB was shown in Figure 1.

Table 2: Thermal and mechanical properties of isomeric polyimides

Polymer	T_g (°C)		$T_{5\%}$ (°C) ^c	Tensile strength (MPa)	Modulus (GPa)	Elongation (%)
	DMTA ^a	DSC ^b				
4,4'-BPDA/BOAPIB	359	318	462	92	1.64	9.1
3,3'-BPDA/BOAPIB	375	345	497	94	2.77	5.0
4,4'-ODPA/BOAPIB	326	317	468	85	1.33	8.3
3,3'-ODPA/BOAPIB		293	463			
4,4'-BTDA/BOAPIB	330	315	442	75	1.30	9.8
3,3'-BTDA/BOAPIB		290	388			
4,4'-HQDPA/BOAPIB	300	291	456	103	1.33	13.1
3,3'-HQDPA/BOAPIB	271	271	454	84	1.13	11.0
BPADA/BOAPIB	267	269	449	91	1.41	11.8

a Obtained from DMTA at a heating rate of 3 °C /min at 1Hz.

b Obtained from DSC at a heating rate of 10 °C /min in air.

c 5% weight loss in air obtained from TGA at a heating rate of 10 °C /min in air.

d Films were both brittle.

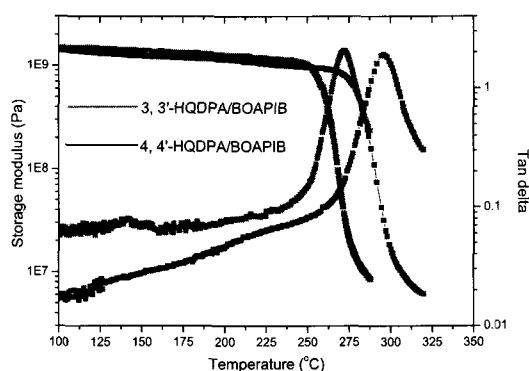


Figure 1. DMTA curves of polyimides 4,4'-HQDPA/BOAPIB and 3,3'-HQDPA/BOAPIB

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References

1. Dinehart RA. *J Polym Sci, Part A-1*, 1968, 6, 2755
2. Ghassemi H, Hay AS. *Macromolecules*, 1993, 26, 5824
3. Ghassemi H, Hay AS. *Macromolecules*, 1994, 27, 3116
4. Ghassemi H, Hay AS. *Macromolecules*, 1994, 27, 4410
5. Sugioka T, Hay AS. *J Polym Sci, Part A: Polym Chem*, 2001, 39, 1040
6. Hay AS, Ghassemi H. U.S. Patent, 5,459,227
7. Hay AS, Ghassemi H. U.S. Patent, 5,420,234
8. Hay AS, Ghassemi H. U.S. Patent, 5,359,092
9. Yan, J.L.; Wang, Z.; Gao, L. X.; Ding, M.X. *Macromolecules*, 2006, 39, 7555
10. Mengxian Ding, *Isomeric polyimides*, *Prog. Polym. Sci.*, 2007, 32, 623