

Polyimides Derived from Isomeric BTDA and ODPa

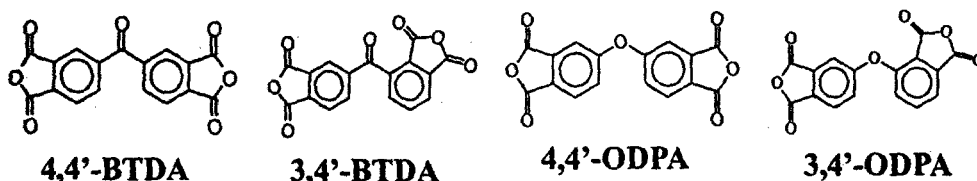
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3,4,3',4'-benzophenone dianhydride(4,4'-BTDA) and 3,4,3',4'-oxydiphthalic anhydride(4,4'-ODPA) have been widely used in the preparation of various polyimides, which were applied as advanced composites matrix, films, fibers, plastics etc. But the isomeric BTDA and ODPa have attracted few attention in the polyimide field. As a part of our effort to investigate the isomerism in polyimides[1-3], recently the isomeric BTDA and ODPa were synthesized and the study on the corresponding polyimides is carried out in our laboratory. In this report, we would like to reveal some primary results obtained very recently in this area.

1. Synthesis of the isomeric dianhydrides

- A. 2,3,3',4'-BTDA(3,4'-BTDA): as a by-product obtained in the production of 4,4-BTDA was purchased from Beijing Coking and Chemical Corporation.
- B. 2,3,3',4'-ODPA(3,4'-ODPA): was synthesized from 3-phthalic anhydride and 3,4-dimethyl phenol.



2. Properties of the polyimides derived from isomeric BTDA

As shown in Table 1 that the most apparent difference between the two isomeric polyimides is the T_g . The polyimide from 3,4'-BTDA/ODA has T_g more than 20 °C higher than that for 4,4'-BTDA/ODA. This phenomenon is contrary to that of polyimides from thiodiphthalic anhydrides and 1,4-bis(dicarboxyphenoxy)benzene dianhydrides, for these polyimides the T_g s of 4,4'-linked and 3,4'-linked isomers are almost the same[1].

The melt viscosity of PMR type resin from 3,4'-BTDA is lower than that from 4,4'-BTDA as shown in Figure 1. That may have potential application for composite preparation. This phenomenon may be attributed to the lower intermolecular interaction for 3,4'-BTDA based PMR resin. The gas separation property shows that the 3,4'-BTDA based polymer has higher permeability but only slightly lower permeaselectivity, especially for oxygen/nitrogen separation(see Table 2).

Table 1. Properties of polyimides derived from isomeric BTDA and ODA

Properties	3,4'-BTDA/ODA	4,4'-BTDA/ODA
T _g , °C (DSC)	292	269
T _{5%} , in N ₂	450	423
in Air	437	—
Tensile Strength, MPa	103	123
Elongation, %	7.0	11.4
Tensile Modulus, GPa	2.64	2.58

Table 2. Gas separation properties of polyimides derived from isomeric BTDA

Polyimides	Permeability(Barrer)			Permeaselectivity	
	H ₂	N ₂	O ₂	H ₂ /N ₂	O ₂ /N ₂
3,4-BTDA/MDA	5.25	0.0538	0.311	97.45	5.78
4,4-BTDA/MDA	4.66	0.0289	0.177	160.95	6.13
3,4-BTDA/DMMDA	6.29	0.0583	0.270	107.80	4.12
4,4-BTDA/DMMDA	8.64	0.0463	0.376	186.33	8.10

3. Properties of the polyimides derived from isomeric ODPA

Table 3. Properties of polyimides derived from isomeric BTDA and ODA

Properties	3,4'-ODPA/ODA	4,4'-ODPA/ODA
η_{inh}	0.42	0.45
T _g , °C (DSC)	274	262
T _{5%} , in N ₂	436	492
in Air	415	488
Tensile Strength, MPa	109	115
Elongation, %	15	49
Tensile Modulus, GPa	2.05	2.09

The T_g of 3,4'-ODPA based polyimide is also higher than that of 4,4'-linked polymer. The investigation of the contrary is now in progress in our laboratory.

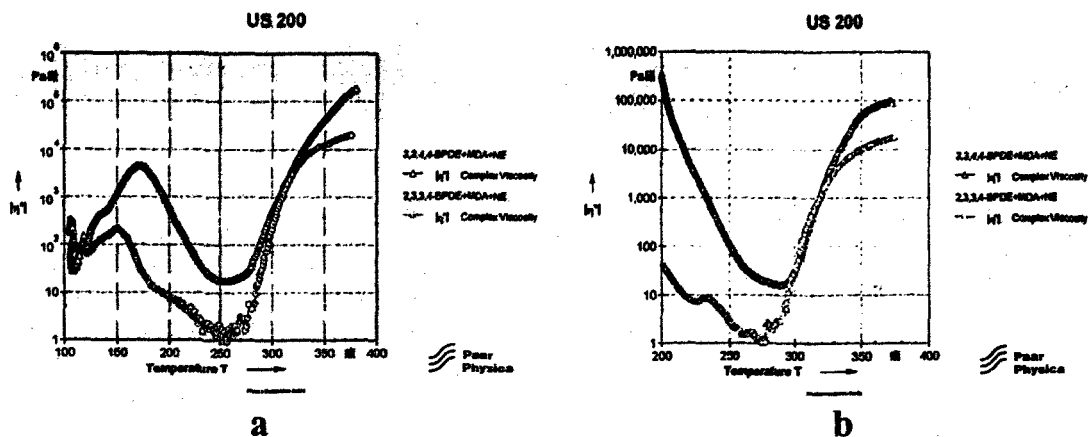


Figure 1. Rheologic behavior of PMR-15 prepared from 4,4'-BTDE and 3,4'-BTDE
 a. Resin dried at 40°C in Vacuum; b. Resin treated at 220°C for 2h

References

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