POLYIMIDES FROM ISOMERIC DIANHYDRIDES

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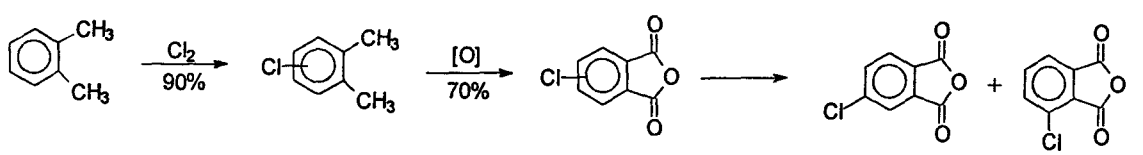
1. Introduction

"Isomerism" is important in polymer science for either theory or practice. The polyolefines and polyvinyls with different stereoregularity, which possess great different in properties compose various products in today's polymer market. However, the isomerism in polymers from polycondensation seems to be largely ingnored. Since the development of heterocyclic aromatic polymers in 1960s, the isomerism in these polymers has been conspicuous. The isomerism of polyolefines and polyvinyls appear in polymerization process, while the isomerism of polymers from polycondensation appear in the synthesis of monomers. As to be well-known that the existence of isomers is almost inevitable for the alkyl substituted benzene in petro-chemical processes and the nucleophilic or electrophilic substitution of aromatics. The application of these isomers is not only important for the understanding the relationship between the structure and properties of the polymers, but also dealing with the cost for the polymer production.

Polyimide has extended its application both in structural and functional materials. Isomeric polyimides may found special application, particularly in the latter area. In this paper, as a part of our series work, we would like to introduce some aspects in isomeric polyimides.

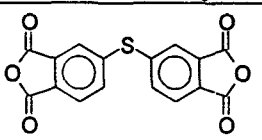
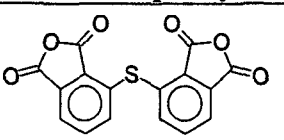
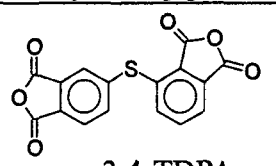
2. Isomerism polyimides from 3-chlorophthalic anhydride and 4-chlorophthalic anhydride

As in our previous work[1], we have reported the isomeric polyimides synthesized from 3-chlorophthalic anhydride and 4-chlorophthalic anhydride.

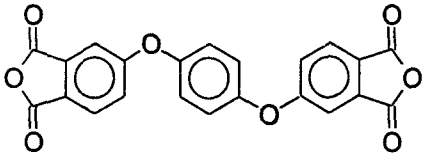
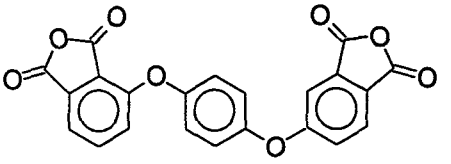


3-ClPA/4-ClPA=45/55 Purity: >99%

Polyimides from isomeric diphenyl sulfides dianhydride[1]

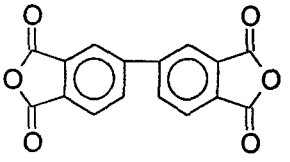
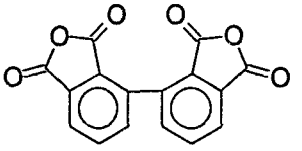
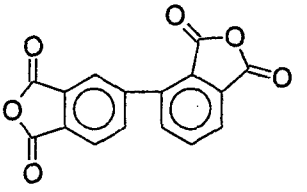
		
4,4-TDPA mp 218-220℃	3,3-TDPA mp 245-247℃	3,4-TDPA mp 207-207℃

Polyimides from isomeric diether dianhydride[1]

	
4,4-HQDPA mp 289-290℃	3,3-HQDPA mp 320℃

In this work, we found that the Tg of polyimide form 3,3-linked dianhydride was about 20-30℃ higher than that from 4,4-linked dianhydride. The solubility in some organic solvents and the gas permeability for former is better than that for the latter, whereas, the permselectivity is only slightly lower for the former.

3. Polyimides from isomeric biphenyl dianhydrides

		
4,4-BPDA	3,3-BPDA	3,4-BPDA

As a additional work to Ube's excellent work on s-BPDA and a-BPDA[2], 3,3-linked BPDA based polyimide has been synthesized in this laboratory, the results have been reported in literature [3].

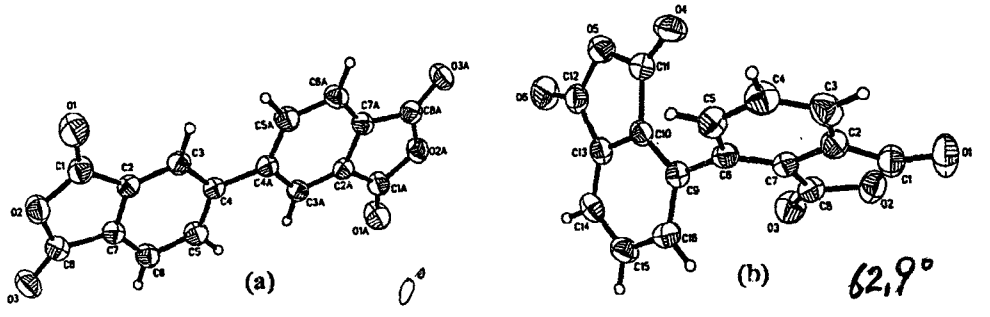


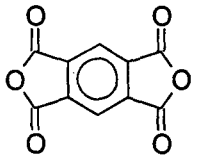
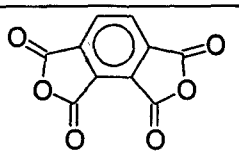
Figure 1. Molecular structures of (a) 4,4-BPDA and (b) 3,3-BPDA

Table 1. Polyimides based on BPDA and ODA

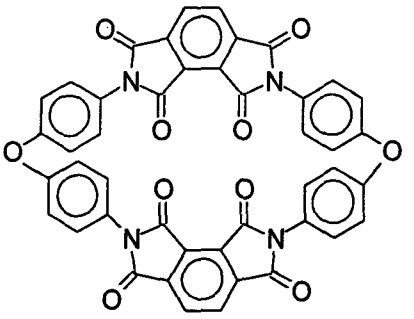
BPDA	Tg	$T_{5\%}$, air	Tg, N_2	Solubility				
	℃	℃	℃	m-Cresol	DMAC	TCE	$CHCl_3$	Acetone
3,3-BPDA	319	537	544	++	++	++	++	
4,4-BPDA	285	510	520	±	–	–	–	–

3. Polyimides from Pyromellitic dianhydride and Mellophanic dianhydride

Polyimide based on mellophanic dianhydride was firstly reported by Japanese scientists in the late 1960s[4], but in that work only copolyimides with PMDA was revealed.

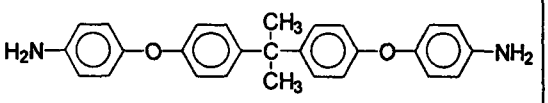
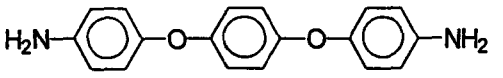
	
PMDA Mp 285-287℃	MPDA Mp 194-198℃

We recently reinvestigated the mellophanic dianhydride based polyimide. A cyclodimer from MPDA/ODA was found as a insoluble crystal in DMAC. Tough film can obtained from the polymer based on MPDA and several diamines.



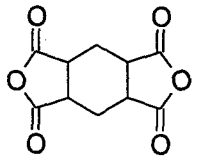
Cyclodimer from MPDA and ODA

Table 2. Tg of Polyimides from Mellophanic Dianhydride

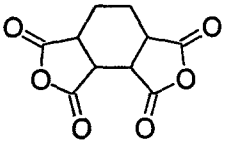
	
TPEQ	BAPP
Polyimide	Tg, ℃ (DSC)
PMDA/BAPP	216
MPDA/BAPP	251
PMDA/TPEQ	257
MPDA/TPEQ	267

4. Polyimides from 1,2,4,5-cyclohexane dianhydride and 1,2,3,4-cyclohexane dianhydride

The polyimides based on 1,2,3,4-cyclohexane dianhydride(1,2,3,4-CHDA) and 1,2,4,5-cyclohexane dianhydride(1,2,4,5-CHDA) were firstly reported by Russian scientists in middle 1970s and early 1980s[5,6]. 1,2,4,5-CHDA was prepared by hydrogenation of PMDA in the presence of Raney Ni under 10-12 Mpa at 200℃[6]. 1,2,3,4-CHDA was obtained by Diels-Alder addition of 1,3-hexadiene and maleic anhydride followed by oxidation and dehydration. According to the X-ray determination, thus prepared product was cis-1,cis-2,cis-3,cis-4-cyclohexane dianhydride[7]. Tough films have formed from this dianhydride and various diamine.



1,2,4,5-CHDA
mp 248-250℃



1,2,3,4-CHDA
mp 218-220℃

Table 3. Polyimides Based on Cyclohexane Dianhydride and ODA[6,8]

CHDA	Tg, ℃	Tensile Strength MPa	Tensile modulus GPa	Elogation, %
1,2,4,5-CHDA	315	140	-	38
Cis-1,2,3,4-CHDA	270	100	5.0	3.0
Trans-1,2,3,4-CHDA	295	100	3.8	7.5

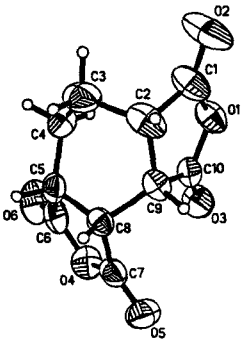
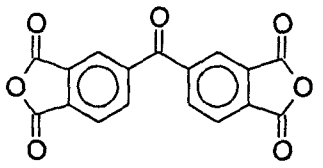
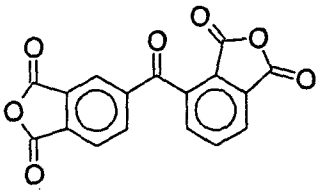


Figure 2. Molecular structure of cis-1,cis-2,cis-3,cis-4-cyclohexane dianhydride

5. Polyimides from isomeric benzophenone dianhydrides

3,4-BTDA is a by-product from the preparation of 4,4-BTDA by o-xylene and formaldehyde followed by oxidation and dehydration.

	
4,4-BTDA mp 224-226℃	3,4-BTDA mp 213-214℃

Flexible films have been cast from both dianhydride and various diamines.

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