POLYIMIDES DEVELOPED IN CIAC

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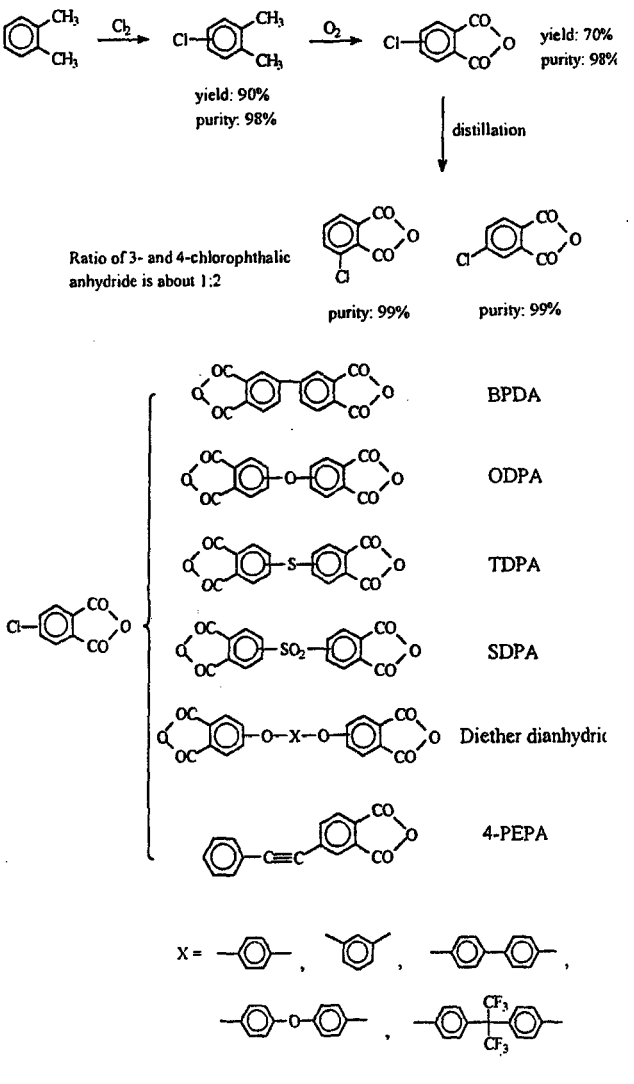
1. Chlorophthalic anhydride as starting material for polyimides

Polyimides are most comprehensive in properties and have most wide-spread applications.

The crucial barrier for polyimides to be more widely used as polymer materials is the cost, especially for those based on bridged biphthalic dianhydride, because these polyimides usually are thermoplastic or with some properties superior to that based on pyromellitic anhydride or trimellitic anhydride.

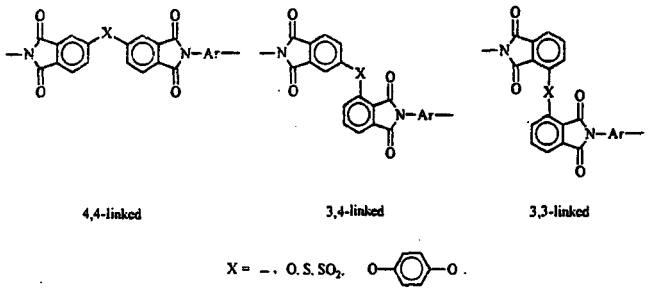
Since early 70's, Changchun Institute of Applied Chemistry (CIAC) focused its attention on the exploring the synthesis of dianhydride and polyimides from chlorophthalic anhydride. Our consideration for using chlorophthalic anhydride as the starting material is:



- Chlorophthalic anhydride could be produced in low cost comparable with phthalic anhydride;
- Chlorine in this compound has activity high enough in the nucleophilic reaction to have products with high yield;
- The isomers, 3- and 4-chlorophthalic anhydride are important stating materials not only for polyimides but also for other chemicals, such as dye

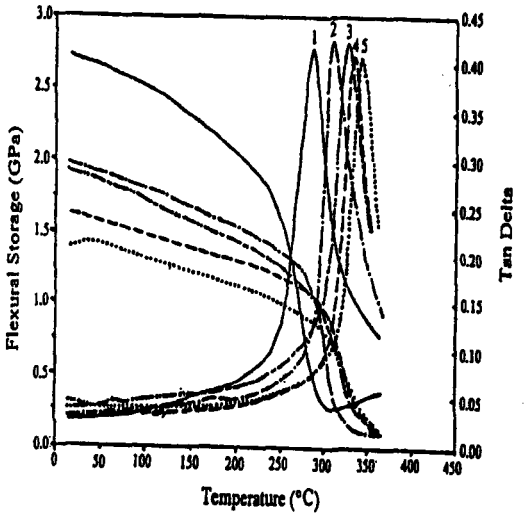
intermediates, pharmucuticals, agrochemicals, etc.

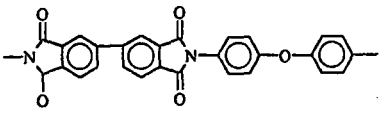
2. Polyimides based on 3,3'-linked biphthalic dianhydride possess interesting properties, comparing with that of 4,4'-linked polymers:

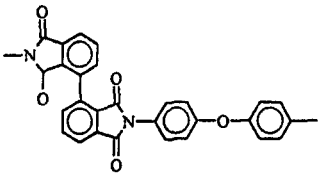


The advantages for 3,3'-linked polyimides are:

- About 20 ℃ higher Tg;
- Improved solubility;
- Larger permeability.



1 = 

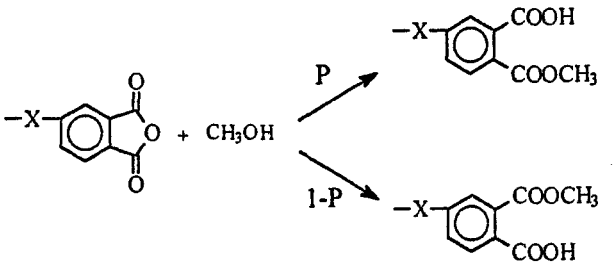
5 = 

DMA for 3,3-and 4,4-linked polyimides based on BPDA/ODA

3. Polyamic acids prepared from aprotic solvents containing large amount of water

Aprotic solvent such as DMF, DMAC, NMP, et al. containing water up to 20-25% can be used for the preparation of polyamic acis from dianhydride and diamine. The inherent viscosity of polyamic acid decreases with the increasing of amount of water, but that of the polyimides imidized thermally was not affected with the water apparently, hence the mechnical properties. Water-containing solvent can be used to control the viscosity of the polyamic acid for applications where high viscosity is not needed for certain processing.

4. Isomerism of dianhydride in acylation

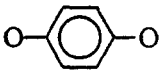


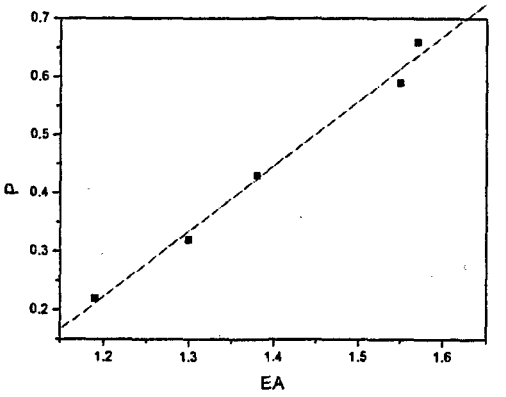
p,p-异构体 = P^2

m,m-异构体 = $(1-P)^2$

m,p-以构体 = $2P(1-P)$

Composition of diester-diacid isomers

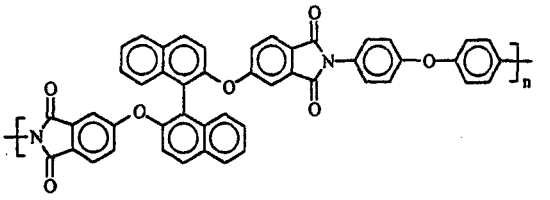
X	EA	P	p,p-	m,p-	m,m-
O=S=O	1.57	0.66	0.43(0.44)	0.45(0.44)	0.12(0.12)
C=O	1.55	0.59	0.35(0.34)	0.48(0.50)	0.17(0.16)
C(CF3)2	(1.48)[a]	0.53	0.20(0.27)	0.50(0.52)	0.22(0.21)
-	1.38	0.43	0.19(0.21)	0.48(0.44)	0.33(0.35)
O	1.30	0.32	0.10(0.11)	0.44(0.43)	0.46(0.46)
	1.19	0.22	0.61(0.62)	0.34(0.32)	0.05(0.06)



Dependence of selectivity of esterification of dianhydride on its EA value

5. Optically active polyimides:

Chirality is not only interesting for biology but also for functional materials, such as NLO, conducting polymers, chiral stationaly phase for HPLC, waveguide material, optical switch material, etc. Polyimides with axially dissymmetry, e.g. 1,1'-binaphthyl-2,2'-diyl units have been synthesized. The optical rotation was remained unchanged at 250 ℃ for 96 hours.



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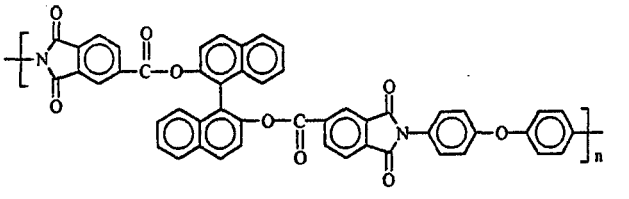

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