

Preparation of Polyimides from Substituted Bisphthalimides

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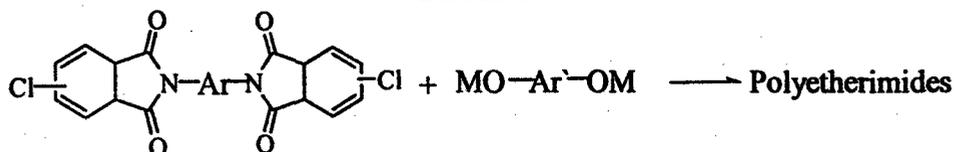
Introduction Polyimides are most useful high performance polymers which exhibit excellent thermal, electrical, and mechanical properties, and have been used widely in aerospace, electronics, and other industries over the past several decades. Aromatic polyimides are generally prepared through a two-step procedure by the reaction of aromatic diamines with aromatic dianhydrides in NMP (or DMAc) giving soluble polyamic acids, followed by thermal cyclodehydration^[1]. In recent years, there has been an increasing interest in the preparation of polyetherimides, a subgenus of polyimides, by the reaction of chlorine substituted bis-phthalimides with salts of dihydroxyaromatic compounds since the chlorophthalic anhydrides are more accessible^[2]. US Pat [3] disclosed the process for polyetherimides (PEIs) with bis(chlorophthalimide)s and bisphenol A, but the molecular weights of polymers were too low to be applied. Herein, we describe the preparation of PIs by the condensation of bis-chlorophthalimides with sodium bisphenols and self-condensation of 4-chloro -N-4-hydroxyphenylphthalimide. The successful synthesis of polyimides by the polymerization of aromatic dichloride containing phthalimide moiety in the presence of a catalytic mixture of nickel salt, Ph₃P, and Zn dust is also reported.

Experimental N, N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP) were stirred over phosphorous pentoxide 5hrs, and dimethylsulfoxide (DMSO) stirred over powdered calcium hydride overnight, then distilled under reduced pressure, stored over 4-Å molecular sieves. Water content of solvents was measured by WS-5 Model Mini-Amount Water Detective Instrument (Zibo Tongye Instrument Factory, China). Inherent viscosities were determined at 0.5% concentration in DMAc, concentrated sulfuric acid or mixed cresol with an Ubbelohde capillary viscometer at 30 ± 0.1 °C.

Results and Discussion

1 PEIs from Bis(chlorophthalimide)s

Scheme 1



The bis-chlorophthalimides were prepared by the reaction of 4-chlorophthalic anhydride with corresponding aromatic amines following the literature procedure^[4]. Sodium bisphenol A was prepared by the reaction with sodium hydroxide, K₂CO₃, Na₂CO₃, or their mixture in the mixture of DMAc and toluene. The toluene was removed by distillation in a nitrogen atmosphere, with stirring, to effect azeotropic drying of the reactants. The content of water in toluene was periodically determined

by WS-5 Model Mini-Amount Water Detective Instrument. After removal of most amount of water, bis-chlorophthalimide was added to the solution, then the mixture was heated to 160°C for 4 hours, with stirring. The resulting polymer was obtained by pouring the solution to methanol. The content of water in reaction solution is principal factor to affect polymerization as shown in Table 1. When water in distilled toluene is above 70ppm, the inherent viscosities of polymers 1-4 are below 0.35 dL·g⁻¹. The Moisture might be control in below 50ppm by adding drying agent such as anhydrous magnesium sulphate in azeotropic trap. The inherent viscosities of polymer 5,6,8-10 are above 0.4 dL·g⁻¹.

Table 1 Preparation of PEIs from 4, 4'-Bis (4-chlorophthalimido) diphenyl ether

Polymer	Bisphenols	Base	Solvent	Time (h)	Content of H ₂ O (ppm)	η_{inh} , dL·g ⁻¹
1	BPA	NaOH	DMSO	10	~150	0.20
2	BPA	NaOH	DMSO	10	~70	0.30
3	BPA	NaOH	DMSO	10	~70	0.31 ^a
4	BPA	NaOH	DMAc	10	~70	0.35
5	BPA	NaOH	DMAc	10	~40	0.49
6	BPA	NaOH	DMAc	10	20~30	0.7-0.82
7	BPA	K ₂ CO ₃	DMAc	24	~70	0.34
8	BPA	Na ₂ CO ₃	DMAc	24	~50	0.40
9	BPA	K ₂ CO ₃ /Na ₂ CO ₃	DMAc	24	~50	0.52
10	BPA	K ₂ CO ₃ /Na ₂ CO ₃	DMAc	24	20~30	0.84

^a Excess of 3% Sodium hydroxide.

2 PEIs from AB-type Monomer

Scheme 2

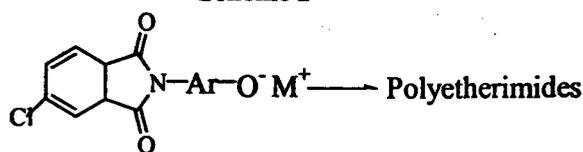


Table 2 PEIs from AB-type Monomer

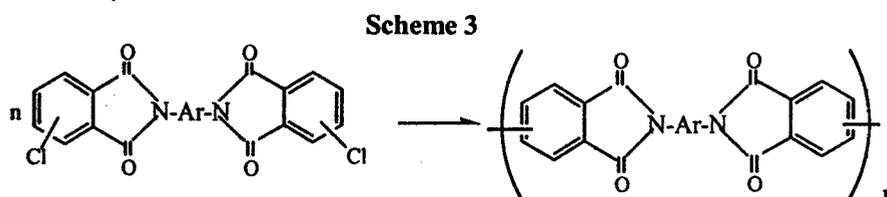
Polymer	Aminophenols	Base	Solvent	η_{inh} , dL·g ⁻¹
1	4-aminophenol	NaH	DMSO	0.24 ^a
2	4-aminophenol	NaH	NMP	0.20 ^a
3	4-amino-m-cresol	NaH	DMAc	0.27 ^b

^a Inherent viscosities determined in concentrated sulfuric acid; ^b in mixed cresol.

Many synthetic polyimides studies have been focused on the AB-type monomer systems. From a practical point of view, using AB-type monomers can avoid the strict stoichiometric control, which is required in AA-BB polycondensation systems, thereby offering advantages in the preparation and processing of this kind of material. So far, there is no report on the preparation of AB-type PI via

chlorophthalimidophenols. The monomer for PIs was conveniently prepared by the reaction of chlorophthalic anhydride with hydroxy substituted aniline. The polymerization was taken place in the aprotic solvent which containing NaH. The particpate of polymer was obtained after 2 Hours reaction at 160°C, probably because the backbone of polymer is too rigid to be soluble in reaction solvent.

3 Biphenyl Type PIs from Bis(chlorophthalimide)s



The reactions of 4-chlorophthalic anhydride with aromatic diamines afford bis(phthalimide) **1a-e** (diamines: 4, 4'-diaminodiphenyl ether, **1a**; 4, 4'-diaminodiphenyl methane, **1b**; 4, 4'-diaminodiphenyl sulfone, **1c**; 4,4-diamino-3, 3'-dimethyldiphenyl methane, **1d**). High molecular weight polyimides have been prepared by nickel-catalyzed polymerization of **1d** in dipolar aprotic solvents. The polymerization of **1a-c** proceeded rapidly with polymer precipitate, the molecular weights were low to medium. On the other hand, monomer **1d** proceeded homogeneously. Polymer were isolated in excellent yields. The inherent viscosities of polymer 0.8 dL·g⁻¹ at 0.5% concentration in the m-cresol at 30°C. We proposed that the structure of diamines have crucial effect on the effective polymerization. The amount of catalyst on the polycondensation to be appropriate a 5% of monomer was established. The effect of the reaction temperature on the inherent viscosities of the resulting polymer was investigated. The polycondensation 100°C gave polymer the highest value. Raising the temperature gave inferior results. The properties of some polyimides were tested.

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