A Study on the Synthesis and Properties of Co-condensation Type Soluble Polyimides

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Abstract

In this study, the co-condensation type polyimides were prepared by the condensation between diamine monomers (4,4'-di(4-aminophenoxy)diphenylsulfone and 4,4'-diamino diphenylether or 4,4'-diamino diphenylmethane) and diphenylether 3,3',4,4'-tetracarboxylic acid dianhydride followed by a chemical imidization. The polyimides were found to be soluble in strong polar solvents when 4,4'-di(4-aminophenoxy)diphenylsulfone/4,4'-diamino diphenylether and 4,4'-di(4-aminophenoxy)diphenylsulfone/4,4'-diamino diphenylmethane molar ratios are 10:0 ~ 3:7 and 10:0 ~ 5:5, respectively. The glass transition temperatures of polyimides were observed to be 255 ~ 265 ℃ and decreased with the increase of the molar ratio of 4,4'-di(4-aminophenoxy)diphenylsulfone. The initial decomposition temperatures in N_2 were observed to be 555 ~ 590 ℃ and almost independent of the structure and the molar ratio of the diamine monomers.

Key Words: Polyimide, Soluble, Co-condensation

The commonly used aromatic polyimides are not soluble in organic solvents after the imidization process because of the high rigidity and strong intermolecular interaction. However, the solubility of polyimides could be much improved if their structure and preparation are modified. The solubility could be improved by:

(1) increasing of the flexibility of the molecular chain: "Flexible" groups such as -O-, $-CH_2-$ are introduced to increase the flexibility of the molecular chain[1];

(2). decreasing the intermolecular interaction: The regularity and symmetry could be decreased by the means of co-condensation polymerization, the introduction of bulky side group and the replacement of aromatic group with alicyclic group to reduce the tendency of crystallization and the intermolecular interaction[2-6]; and

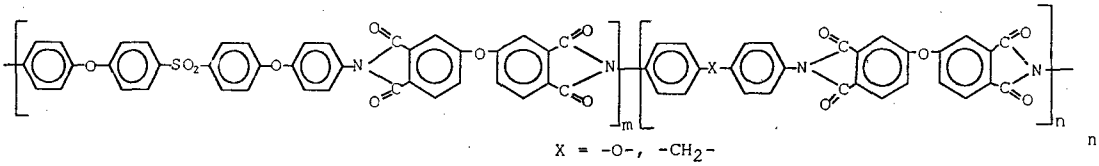
(3). the usage of thermal solution imidization.

In this paper, co-condensation type polyimides were prepared using 4,4'-di(4-aminophenoxy)diphenylsulfone and 4,4'-diamino diphenylether or 4,4'-diamino diphenylmethane as the diamine co-monomers to condense with diphenylether 3,3',4,4'-tetracarboxylic acid dianhydride. The solubility and thermal property of the resultant polyimides were characterized and the relationships between the property and structure were discussed.

1. Experimentation

Co-condensation type polyimides with following structure were prepared using 4,4'-di(4-aminophenoxy)diphenylsulfone, 4,4'-diaminodiphenylether (Chemical Grade, Shanghai No.3 Reagent Company) or 4,4'-diaminodiphenylmethane (Chemical Grade, Shanghai No.3 Reagent Company) as diamine monomers to react with an equivalent amount of diphenylether 3,3',4,4'-tetracarboxylic acid dianhydride (Industrial Product, Shanghai Resin Research Institute) in NMP (Analytical Grade, Shanghai No.1 Reagent Company) at room temperature for 4 hours followed by

an imidization reaction with acetic anhydride (Analytical Grade, Shanghai General Reagent Company) and triethyl amine (Analytical Grade, Shanghai No.3 Reagent Company) at room temperature for 16 hours.



4,4'-di(4-aminophenoxy)diphenylsulfone was prepared from the reaction between dichlorodiphenylsulfone (industrial product, Shanghai No.9 Dye Company) and *p*-amino phenol (Chemical Grade, Shanghai Xu Hang Chemical Company) followed by recrystallization. 4,4'-diamino diphenylether and 4,4'-diamino diphenylmethane were recrystallized with ethanol before use.

The intrinsic viscosities of the resultant polyimides were measured using an Ubbelodhe Viscometer at 30 ℃ using NMP as the solvent.

The DSC and TGA curves of polyimides were recorded on Perkin Elmer DSC7 and TGA7, respectively, under the protection of N_2 with a scan rate of 20 ℃/min.

2. Results and Discussions

2.1.Synthesis and the Solubility of Polyimides

The molar ratio of the co-amine monomers and the solubility of the resultant polyimides in NMP are listed in Table 1.

Table 1. Synthesis and Solubility of Polyimides

Structure	X = -CH_2- m : n (Molar Ratio)					X = -O- m : n (Molar Ratio)						
	10 : 0	8 : 2	6 : 4	5 : 5	4 : 6	10 : 0	8 : 2	6 : 4	5 : 5	4 : 6	3 : 7	2 : 8
Solubility[a]	+	+	+	+	−	+	+	+	+	+	+	−
Sample Number	1	2	3	4	/	1	5	6	7	8	9	/

Notes: a: refer to the solubility in NMP; +: soluble; -: insoluble.

It can be concluded that, in the system studied, as 4,4'-di(4-aminophenoxy)diphenylsulfone and 4,4'-diaminodiphenylmethane were selected to be diamine co-monomers, the resultant polyimides are soluble in NMP when the molar ratio of 4,4'-di(4-aminophenoxy)diphenylsulfone and 4,4'-diaminodiphenylmethane is between 10:0 and 5:5. As 4,4'-di(4-aminophenoxy)diphenylsulfone and 4,4'-diaminodiphenylether were selected to be diamine co-monomers, the resultant polyimides are soluble in NMP when the molar ratio of 4,4'-di(4-aminophenoxy)diphenylsulfone and 4,4'-diaminodiphenylether is between 10:0 and 3:7.

The solubility of polyimides in various solvents are listed in Table 2.

Table 2 Solubility of Polyimides in Various Solvents

Sample	chloroform	THF	dioxane	toluene	acetone	DMF	DMA	m-cresol	conc. H_2SO_4	methyl cellosolve
2	+	−	+−	−	−	+	+	+	+	−
5	+	−	+−	−	−	+	+	+	+	−

Notes: +: soluble; +−: partially soluble; −: insoluble

It can be observed that the resultant polyimides are soluble in strong polar solvents such as DMF, DMA, m-cresol, concentrated sulfuric acid and are not soluble in weak or non-polar solvents such as THF, dioxane, toluene and acetone. It is interesting to find that all these polyimides can be dissolved in chloroform.

2.2 Intrinsic Viscosities of Polyimides

The intrinsic viscosities of polyimides are listed in Table 3.

Table 3 Intrinsic Viscosities of Polyimides

Sample	1	2	3	4	5	6	7	8	9
$[\eta_r]$ (dl/g)	0.48	0.51	0.68	0.77	0.54	0.89	0.82	0.96	0.76

Note: Measured at 30 ℃ using NMP as the solvent.

2.3 Thermal Properties of Polyimides

The glass transition temperatures (T_g) and the initial decomposition temperatures (T_d) obtained from DSC and TGA curves, respectively are listed in Table 4.

It can be observed that T_gs of polyimides are between 255.4 and 265.3 ℃. The T_g exhibits slight increase as the content of the "flexible" diamine monomer — 4,4'-di(4-aminophenoxy)diphenylsulfone — increases. This indicates that the "flexible" diamine monomer does show higher flexibility and, as its content increases, the segment motion becomes easier. This result corresponds quite well to the results reported before[4].

The T_ds of polyimides are between 555 and 590 ℃ and seem to be independent of the structure and the molar ratio of diamine monomers.

Table 4 Glass Transition Temperatures and Initial Decomposition Temperatures of Polyimides

Sample	1	2	3	4	5	6	7	8	9
T_g(℃)[1]	255.4	261.8	265.3	264.9	258.5	265.2	265.0	264.2	260.6
T_d(℃)[1]	588.4	559.0	555.5	584.7	578.1	584.9	589.4	570.4	581.9

Notes: 1. Scan rate: 20 ℃/min., under the protection of N_2.

References:

1. A.Gungor, C.D.Smith, J.Wescott, S.Srinivasan and J.E.McGrath, ***Polym. Prepr.***, 32(1), 172. (1991)
2. C.V.Aradhani and S.P.Vernekar, ***Polymer Bulletin***, 24, 487. (1990)
3. Y.Yuki, U.Tunca and H.Kunisada, ***Polym. J.***, 22, 945. (1990)
4. Qing-hua Li, Jie Yin and Zi-kang Zhu, ***Gao Fen Zi Cai Liao Ke Xue Yu Gong Cheng (Polymeric Materials Science and Technology)***, 12(2), 38. (1996). (in Chinese)
5. Hong-yuan Wang, Jie Yin, Xiao-rui Wang, Li-min Sun, Jian-hua Fang, Hong-jie Xu and Zi-kang Zhu, to be published on ***Gao Fen Zi Cai Liao Ke Xue Yu Gong Cheng (Polymeric Materials Science and Technology).*** (in Chinese)
6. Jian-hua Fang, Jie Yin, Hong-jie Xu, Na Liu, Zhi-yun Cai and Zi-kang Zhu, to be published on ***Gao Fen Zi Cai Liao Ke Xue Yu Gong Cheng (Polymeric Materials Science and Technology).*** (in Chinese)