

Preparation and properties of Novel Polyimide with Side-chain Containing Fully Aromatic Ester*

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ABSTRACT: A novel side-chain polyimide (SLCPI) was prepared by polycondensation of 4-(3'',5''-diaminobenzoy)benzoic-4'-biphenyl.ester(DABBBE) and 4-aminophenyl ether(ODA) with 4,4'-oxydiphthalic anhydride (ODPA) in N-Methyl-2-Pyrrolidone(NMP) It was characterized by inherent viscosity, mechanical properties, and solubility and by Fourier transform infrared, ¹H-nuclear magnetic resonance,differential scanning calorimetry,and thermogravimetric analysis. The resulting polyimide with side group showed good solubility in polar aprotic solvents, and formed tough film, which maintained the same high modulus and strength of classical polyimides,and even improved. But its thermal stability and glass transition temperature were decreased in a certain extent.

Key words: polyimide; film materials; side-chain; synthesis

INTRODUCTION

It is known that the aromatic polyimides have a excellent thermal stabilities and mechanical properties, however, suffer from insolubility and infusibility, making their processing difficult and expensive. In order to attain processable polyimides, Studies on the structure-property relationship of polyimides indicated that introducing alkyl groups and bulky substitute¹⁻⁴ such as pendent aryl or heterocyclic rings could reduce unfavorable factors, for example, the molecular chain stiffniss, high polarity, and high intermolecular association force, to enhance processibility.

In this study, a novel diamine with fully aromatic ester involving biphenyl unit was synthesized (see Fig.1). Based on it, a novel soluble polyimide was prepared by chemical imidization in acetic anhydride and pyridine at room temperature⁵. In contrast, m-phenylenediamine(m-PDA) was introduced in the same way. Systematic studies were carried out to investigate the effects of incorporating rodlike side group into polyimide backbone on its physical properties.The results showed that the high modulus¹ and strength of polyimides films were maintained and even improved, because the poyimide main chains structure was not changed by introducing this class of side group without flexible spacer. However, its thermal stability and glass transition temperature was decreased in a certain extent comparing that of no side chain.

EXPERIMENTAL

Materials

3,5-dinitrobenzoic acid was obtained from the Shanghai Wulian Chemical Corp. (Shanghai, China), 4-hydroxybiphenyl was purchased from Fluka (Switzerland), 5% palladium on activated carbon (from Acros Organics, New Jersey) was used as received. Reagent-grade 4,4'-oxydiphthalic anhydride (ODPA), From the Shanghai Institute of Synthetic Resins (Shanghai, China), was used after recrystallization from actic anhydride and actic acid and then drying at 180 °C under a vacuum for 5h. ODA and m-PDA (from the Shanghai Institute of Synthetic Resins)

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were used after recrystallization from ethanol. N-Methyl-2-Pyrrolidone(NMP, Qunli Chemical Reagents Corp., Shanghai, China) was purified by vacuum-distillation over phosphorus pentoxide and stored over 4-A molecular sieves. Tetrahydrofuran (THF) and Pyridine from the Chengdu Kelong Chemical Reagents Corp. (Chengdu, China) were dried by 4-A molecular sieves before use.

Measurements

The tensile strength and modulus were characterized by an Instron Model 4505 universal tester with a crosshead speed of 5mm/min; Thermogravimetry (TGA) was measured on a TA Instruments TGA2950 at a heating rate of 10°C/min under N₂; DSC was studied using a TA Instruments DSC2910 at rate 10°C/min, N₂.

Synthesis of monomers

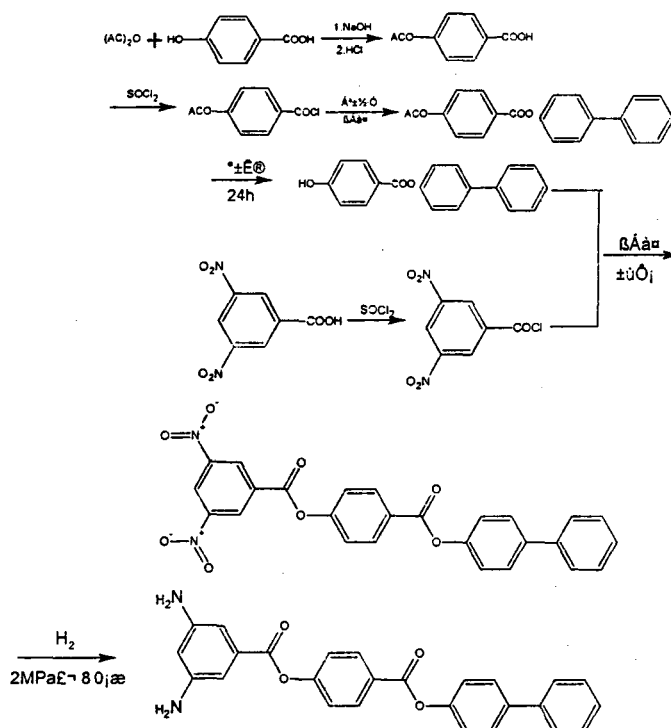


Figure.1 Synthesis route of diamine DABBE

4-acetoxybenzoic acid

Into a 250-ml three-necked round-bottomed flask with a mechanical stirrer was placed 17.2g (mol) of 4-hydroxy benzoic acid, 50ml (6.25M) of NaOH aqueous solution and 100ml of water. And 21.3ml of acetic anhydride was drop into it, and the mixture was stirred for 30min with an ice-bath.,then 50ml (6.25M) of HCl aqueous solution was added with stirring for another 30min. The white precipitate was filtered and washed with water. A purified sample of 4-acetoxybenzoic acid with a mp of 188~189°C was obtained by recrystallization from ethyl acetate (19.5g;yield 84%).

4-acetoxybenzoic -4'-diphenyl ester

4-acetoxy benzoic acid 16g (0.1mol) and approximately 6 mol equiv of thionyl chloride were stirred at reflux temperature for 5h, and then the excess thionyl chloride was removed by distillation under reduced pressure. The acid chloride product was isolated as a light yellow

crystal.

A flask equipped with a mechanical stirrer was charged with a solution of 4-phenylphenol 17g (0.1mol) and pyridine 10ml in 100ml of dry THF. The prepared acid chloride dissolved in 40ml dry THF was added dropwise to the stirred solution at 0°C. The mixture was stirred at ambient temperature for 12h and was subsequently poured into a large amount of water. The white solid precipitate was filtered off, washed with water, and a purified sample was obtained by recrystallization from ethanol (mp 126~127°C; yield 87%).

FTIR (KBr), cm^{-1} : 2922, 2850 (CH_3); 1754, 1734 ($\text{C}=\text{O}$); 1281, 1235 ($\text{C}-\text{O}-\text{C}$). $^1\text{H-NMR}$ (CDCl_3), δ (ppm): 2.35 (s, 3H, $\text{CH}_3\text{COO}-$); 7.23~7.66 (m, 11H, aromatic of biphenyl and aromatic ortho to acetoxy); 8.25 (m, 2H, aromatic meta to acetoxy).

4-hydroxybenzoic -4' -diphenyl ester

25g (0.075mol) of prepared 4-acetoxybenzoic -4' -diphenyl ester and 200ml of ammonia (25%~28%) were placed into a 500ml flask equipped with a magnetic stirrer. After stirring for 24h at room temperature, the dilute HCl aqueous solution was added to acidify the ammonium salt, and the precipitate was subsequently filtered and washed repeatedly with water. A purified sample of 4-hydroxybenzoic -4' -diphenyl ester was obtained by recrystallization from ethanol (mp 245~246°C; yield 90%).

FTIR (KBr), cm^{-1} : 3395 ($-\text{OH}$); 1703 ($\text{C}=\text{O}$); 1282, 1217 ($\text{C}-\text{O}-\text{C}$). $^1\text{H-NMR}$ ($\text{C}_3\text{D}_6\text{O}$), δ (ppm): 7.02 (m, 2H, aromatic ortho to hydroxy); 7.33~7.76 (s, 9H, aromatic of biphenyl); 8.08 (m, 2H, aromatic meta to hydroxy); 9.38 (m, 1H, hydroxy).

4-(3'' ,5'' -dinitrobenzoxy)benzoic-4' - diphenyl ester

The product was obtained by 3,5-dinitrobenzoic acid and 4-hydroxybenzoic -4' -diphenyl ester as a light yellow solid according to the procedure described for 4-acetoxybenzoic -4' -diphenyl ester. It was recrystallized from 1,2-dichloroethane (mp 218~219°C; yield 92%).

FTIR (KBr), cm^{-1} : 1743, 1726 ($\text{C}=\text{O}$); 1547, 1344 (NO_2); 1258, 1205 ($\text{C}-\text{O}-\text{C}$). $^1\text{H-NMR}$ (CDCl_3), δ (ppm): 7.25~7.68 (s, 11H, aromatic of biphenyl and aromatic ortho to 3,5-dinitrobenzoxy); 8.36 (s, 2H, aromatic meta to 3,5-dinitrobenzoxy); 9.35 (s, 3H, aromatic ortho to NO_2).

4-(3'' ,5'' -diaminobenzoxy)benzoic-4' - diphenyl ester

A hydrogenation pressure kettle was charged with 4-(3'' ,5'' -dinitrobenzoxy)benzoic-4' -diphenyl ester (7g, 0.014mol) and a catalytic amount of 10% palladium on activated carbon in 100ml of THF. The hydrogen was introduced continually for 4~5h at about 80°C under 2MPa pressure. The catalyst was then filtered off and the solution was poured into a large amount of water to yield white diamine DABBBE. A purified sample was obtained by recrystallization from ethanol (mp 195~196°C; yield 65%).

FTIR (KBr), cm^{-1} : 3426, 3344 (NH_2); 1736 ($\text{C}=\text{O}$); 1269, 1204 ($\text{C}-\text{O}-\text{C}$). $^1\text{H-NMR}$ (CDCl_3), δ (ppm): 6.28 (s 1H, aromatic between NH_2); 6.94 (s, 2H, aromatic between NH_2 and $\text{C}=\text{O}$); 7.25~7.67 (s, 11H, aromatic of biphenyl and aromatic ortho to 3,5-diaminobenzoxy); 8.29 (s, 2H, aromatic meta to 3,5-diaminobenzoxy).

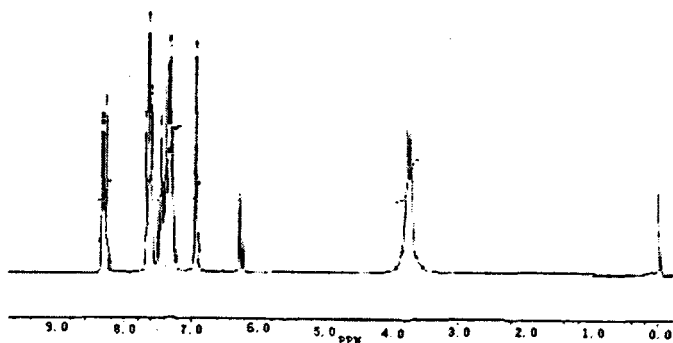


Figure.2 $^1\text{H-NMR}$ of diamine DABBBE

Preparation of polyimide films

Poly (amic acid)s were prepared by low-temperature solution polycondensation of diamine and dianhydride. The diamines [ODA and DABBBE (or m-PDA) in a 3/1 mol ratio] were dissolved in dry NMP and the solution was cooled to 0°C . After a stoichiometric amount of the solid dianhydride (ODPA) was added, the reaction flask was then sealed tightly, and stirring was continued for 12h at room temperature. The solid content of the precursor solution was about 15wt%.

The imidization mixture Ac_2O /Pyridine (1/1 by volume) was added to the reaction solutions of PAA: 5 mol of Ac_2O per repeating unit of the prepolymer. The mixture was stirred 12h after gelling, and then poured into a large amount of ethanol to attain light yellow PI solid (see Figure. 3).

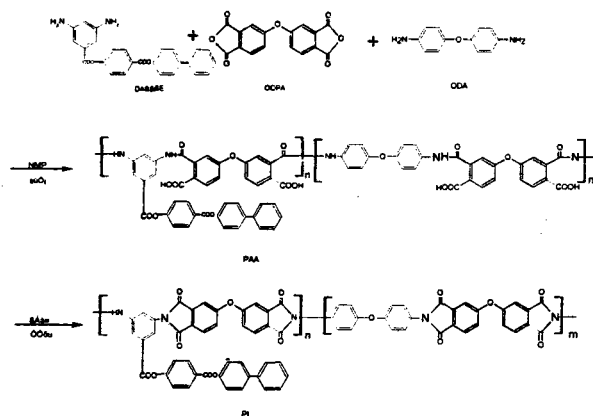


Figure.3 Preparation of polyimide with fully aromatic ester side group

After resulting PI solid was dissolved completely, the solution, having a concentration of 15wt%, then cast onto glass plate and dried respectively at 100, 200, 300°C under reduced pressure. The thickness of the resulting PI film was $10\sim 20\mu$.

RESULTS AND DISCUSSION

Synthesis of monomer

Diamine with directly linked pendent fully aromatic ester group containing biphenyl unit was prepared via 5 steps using 3,5-dinitrobenzoic acid as a starting material, illustrated in Figure. 1, and the key step in this route of synthesis was the selective hydrolyzation of acetoxy group. The structure of the resulting diamine compound with pendent group was confirmed by melting point,

FTIR, and $^1\text{H-NMR}$ spectroscopy. The results were in good agreement with the proposed structures.

Synthesis of polyimide

The preparation of aromatic polyimides by the conventional two-step polycondensation is known to be very sensitive to the stoichiometry of the reactants. So it required DABBBE, ODA, ODPA and NMP of high purity. A 2wt% excess of ODPA was used to increase the molecular weight of the PAA, on the first stage of this synthesis. The chemical structure of the obtained polyimide were characterized by FTIR spectroscopy, indicating that the polyimide was fully imidized, which was confirmed by the peaks of imidization [1778, 1713 (C=O) ; 1380 (C-N)] and no trace of amine or acid peak.

Properties of polyimide

In this study, one of the main objectives was the improvement of the solubility of polyimides through introducing bulky side chain. The results are summarized in Table 1.

Table 1 Solubilities of the polyimides in organic solvents

Sample code	NMP	DMF	Chloroform	THF	m-Cresol
ODPA/ODA+m-PDA	-	-	-	-	+
ODPA/ODA+ DABBBE	++	++	+	-	++

++, Soluble; +, swellable; -, insoluble in hot solvent

It is obvious that the polyimide with side chain was readily soluble in some polar aprotic solvents, whereas, the one without side chain was insoluble in any of these solvents except it did swell in m-cresol. This indicated that the introduction of this type of side chain could considerably enhance the solubility of polyimide.

The thermal stability of polyimide with side group was investigated by thermogravimetry under a nitrogen atmosphere (see Figure.4 and Table 2).

Table 2 Thermal properties of polyimides prepared

Sample code	η_{inh} (dL/g)	T_g ($^{\circ}\text{C}$)	T_d ($^{\circ}\text{C}$)	T_{d5} ($^{\circ}\text{C}$)	T_{d10} ($^{\circ}\text{C}$)
ODPA/ODA+m-PDA	1.18	275	517	541	562
ODPA/ODA+DABBBE	0.82	230	386	455	494

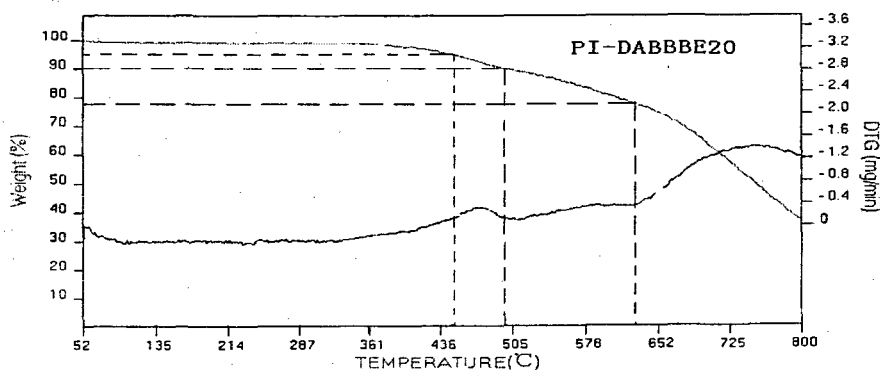


Figure.4 Thermalgravimetric diagram of polyimide with side group

It can be concluded that the polyimide with side group shows a relatively lower T_g and lower stability than that without side group, and the weight loss at the first step was almost equivalent

to the weight of the side group, which indicates that the pendent groups first degraded at about 400 °C. This was followed by a large weight loss at above 600 °C with an increasing temperature.

It was surprising that the film consisting of the polyimide with side chain showed higher tensile strength (see Table 3).

Table 3 Mechanical properties of polyimide films

Sample code	Strength at break (MPa)	Elongation at break (%)	Initial modulus (GPa)
PI-mPDA(25%)	133	12	2.8
PI-DABBBE(25%)	139	15	2.0

It is generally believed that the introduction of bulky side substitutes into polyimides main chains would deteriorate their mechanical properties. However, in this study, the prepared polyimide with side chain showed higher tensile strength than that of the one without side chain. These results may indicate that the rigid side group containing biphenyl unit in some way contributed to the improvements in the mechanical properties.

CONCLUSIONS

In this study, the diamine with fully aromatic ester side chain containing biphenyl unit was newly synthesized, and based on it, a novel polyimide was prepared. This side-chain polyimide maintained excellent mechanical properties and exhibited higher tensile strength than that without side chain. With the introduction of the side chain, the thermal stability of these polyimide decreased and displayed a two-step degradation behavior corresponding to the degradation of side chains and main chains, respectively. This polyimide displayed a lower glass transition temperature, whereas the solubility in aprotic solvents was enhanced.

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一种含全芳酯侧链的新型聚酰亚胺的合成和性质*

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摘要: 通过 4-(3',5'-二氨基苯甲酰氧基)苯甲酸-4'-联苯酚酯(DABBBE), 4-氨基苯醚(ODA) 和二苯醚二酐(ODPA) 在 N-甲基-吡咯烷酮(NMP) 中缩聚, 制备出一种新型侧链聚酰亚胺, 并测试其特性粘数, 机械性能和溶解性, 用 FTIR, ¹H-NMR, DSC 和 TGA 进行表征。该聚酰亚胺获得良好的溶解性, 可以溶解在许多非质子极性溶剂中, 并且所成的薄膜保持了传统聚酰亚胺的高模量和高强度, 甚至还有所上升。但是, 其热性能和玻璃化转变温度在一定程度上有所下降。