The Study on Synthesis of Asymmetric Diamine Containing Carbonyl and Ether Groups in Backbone and Its Polyimide

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Abstract

The asymmetric aromatic diamine 4,4'-(3,4'-diaminobenzoyl) diphenyl ether (simplified as 3,4-DAKE) was prepared from the reaction of diphenyl ether with equimolar 3-and 4-nitrobenzoyl chloride in the presence of lewis acid such as $AlCl_3$, and then reduction with usual procedure.

Glass transition temperature (Tg) of 3,4-DAKE /pyromellitic dianhydride (PMDA) polyimide (PI) was 283℃, more 12℃ than the Tg of 4,4'-bis(3-aminobenzoyl)diphenyl ether (simplified as DAKE)/PMDA PI. DSC showed that 3,4-DAKE/PMDA PI had melting temperature (Tm) at 343.6 and 363.9℃. DSC of DAKE/PMDA PI and 3,4'-diaminophenyl ether (3,4'-ODA)/PMDA PI did not show their Tm below 400℃.The thermogravimetric analysis (TGA) showed that 3,4-DAKE/PMDA PI exhibited 5 % weight loss at 488.9℃, similar to 3,4'-ODA/PMDA PI (490.1℃).

Key Words:

Asymmetric diamine containing carbonyl and ether groups.

Introduction

Polyimides (PIs) which have many excellent Performances have extensive use in high science and technology. Its use, however, is limited by its difficult processing. Great efforts have been made to improve the processing property of polyimides, however, very little effect was produced. A successful result was the polyimides terminated with the reactive group, PMR-15, for example. The synthesis of 3,4'-diaminophenyl oxide (3,4'-ODA) was an attempt to improve the processing property of polyimide, but the effect was also limited. We imagined that polyimides prepared with asymmetric monomer containing long chain may possessed some special properties in comparison with that of those polyimides

produced by symmetric monomer. Our first effort was to synthesis 4,4'-(3,4'-diaminobenzoyl) diphenyl ether and to check the properties of its polyimides.

Experimental

A. The Synthesis of Monomers

1. 4-(3-Nitrobenzoyl) Diphenyl Ether

4-(3-Nitrobenzoyl) diphenyl ether was synthesized by the Friedel-Crafts acylation of diphenyl ether with equimolar 3-nitrobenzoyl chloride using anhydrous aluminum chloride. The crude product was recrystallized from a suitable solvent ; 57% yield; mp 80-87℃; the purity was checked by TLC; ^{1}H NMR and ^{13}C NMR established the identity of this compound.

2. 4-(4-Nitrobenzoyl) Diphenyl Ether

4-(4-Nitrobenzoyl) diphenyl ether was similarly prepared from the reaction of diphenyl ether with equimolar 4-nitrobenzoyl chloride; 98.4% yield, mp 118-119℃; the purity was checked by TLC. IR. ^{1}H NMR and ^{13}C NMR established the identity of this compound.

3. 4,4'-(3,4'-Dinitrobenzoyl) Diphenyl Ether

4,4'-(3,4'-Dinitrobenzoyl) diphenyl ether was synthesized by the Friedel-Crafts acylation of diphenyl ether with equimolar 3- and 4-nitrobenzoyl chloride in the presence of anhydrous aluminum chloride. The crude product was recrystallized from a suitable solvent; 73.3% yield. The purity was checked by TLC. IR. ^{1}H NMR and ^{13}C NMR established the identity of this compound.

4. 4,4'-(3,4'-Diaminobenzoyl) Diphenyl Ether (3,4-DAKE)

3,4-DAKE was prepared by the reduction of dinitrocompound prepared above. This compound can be unlimitedly dissolved in many solvents; 75% yield; mp 150-153℃. IR, ^{1}H NMR and ^{13}C NMR established the identity of this compound.

B. Polymer Synthesis

The polyamic acids (PAAs) were prepared at a concentration of 15% solids(w/w) by slow addition of a stoichiometric amount of the dianhydride to a mechanically stirred solution of the diamine in DMAc at temperature below 10℃. Polymerizational solutions were stirred for about 2 hours.

Inherent viscosity of 3,4-DAKE/PMDA PAA was 76.2ml/g. Inherent viscosity of 4,4'-Bis(3-aminobenzoyl) diphenyl ether(DAKE)/PMDA PAA was 140ml/g.

C. Films

The PAA solutions (15% solids concentration) were decanted onto a horizontal plate

glass and were thermally converted to polyimides by heating in air at 100℃,200℃ and 300℃ for 1 hour at each temperature.

Film of 3,4-DAKE/PMDA PI was brittle.

D. Characterization

Nuclear Magnetic Resonance (NMR) spectra were taken on Bruker DPX-300, 300MHz NMR Spectrometer and Jeol FX-90Q, 90MHz Spectrometer.

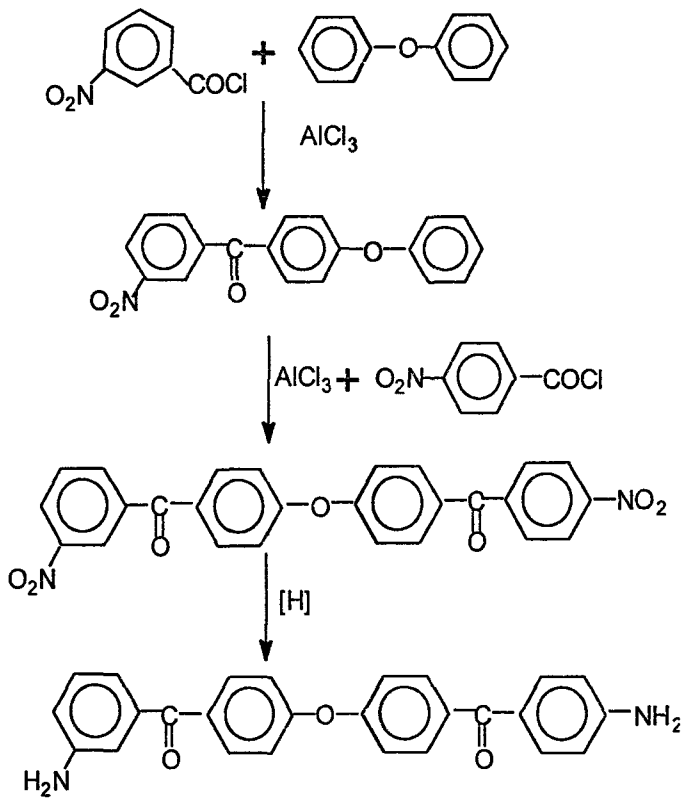
Inherent Viscosities were obtained from 0.5% PAA solutions in DMAc at 35℃.

Differential Scanning Calorimetry (DSC) was performed on a perkin-Elmer DSC 7 at a heating rate of 20℃/min.

Thermogravimetric Analysis (TGA) was conducted on a Perkin-Elmer TGA 7 at a heating rate of 2.5℃/min in flowing air on thin film samples.

Results and Discussion

Diamine was readily synthesized by the Frieclel-Crafts acylation of diphenyl ether with equimolar 3- and 4-nitrobenzoyl chloride in the presence of anhydrous $AlCl_3$ and then reduction in general procedure.



The yield of 3,4-DAKE was 75%,without recrystallization; while the yield of DAKE

was 73 % after recrystallization.3,4-DAKE can not be purified by recrystallization, because it easily dissolved in many solvents.

The experiment showed that the reaction of diphenyl ether with equimolar 3-or 4-nitrobenzoyl chloride produced only one compound, 3-or 4-nitrobenzoyldiphenly ether, if the conditions of the reaction were correctly controlled. The ^{13}C NMR spectrum of 4-nitrobenzoyldiphenyl ether and ^{1}H NMR, ^{13}C NMR spectra of 3,4-DAKE are shown in Figure 1, 2 and 3.

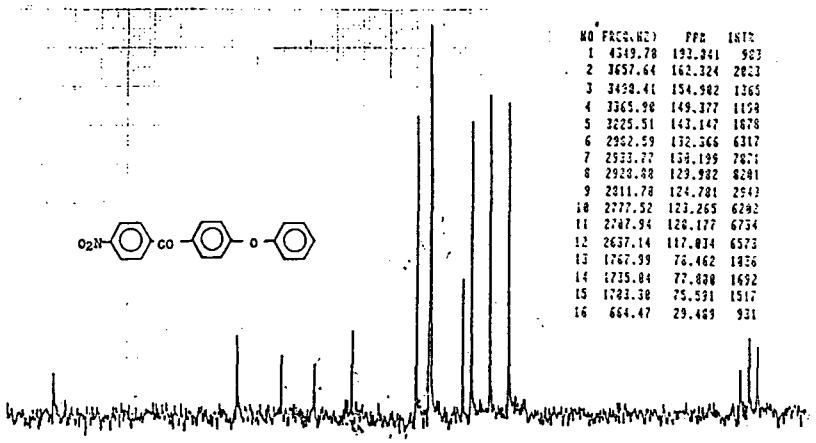


Fig.1 The ^{13}C NMR Spectra of 4-Nitrobenzoyldiphenyl Ether

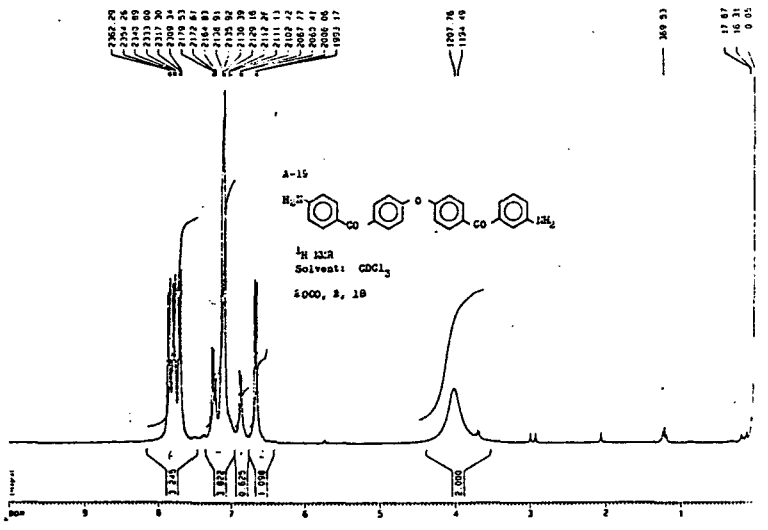


Fig.2 The ^{1}H NMR Spectra of 3,4-DAKE

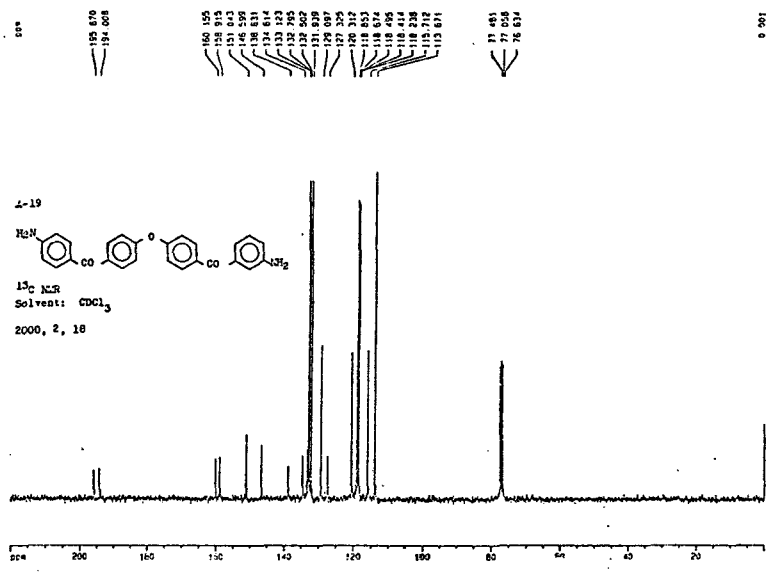
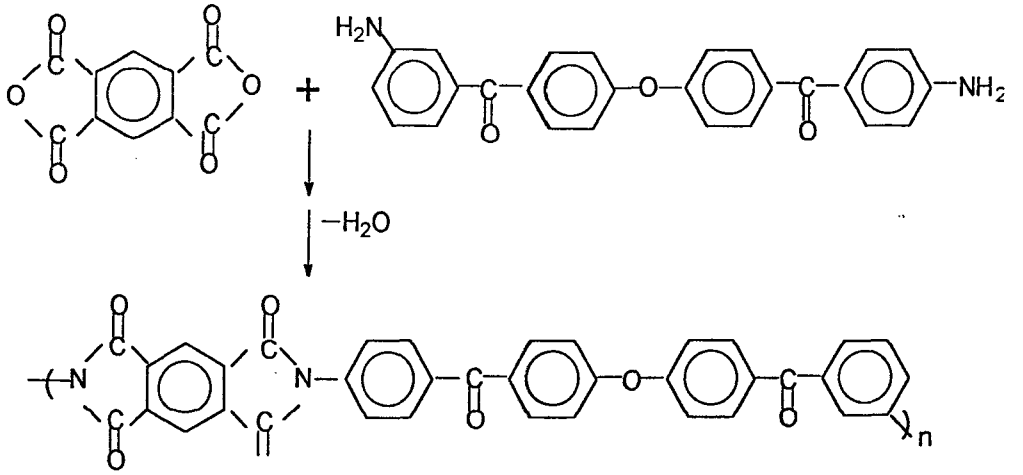


Fig.3 The ^{13}C NMR Spectra of 3,4-DAKE

3,4-DAKE/PMDA PAA was prepared by addition of the PMDA to the solution of 3,4-DAKE in DMAc which resulted in substantial viscosity increase shortly after addition. PAA solution of DMAc (or DMF) decanted onto a horizontal plate glass was thermally cyclodehydrated to from the polyimide by stage heating to 300℃.



We reported[1] that the films of DAKE/Aromatic Dianhydride PI were tough, flexible and transparent. The film of 3,4-DAKE/PMDA PI was transparent, however, was brittle. Inherent viscosity 72.6 ml/g of 3,4-DAKE/PMDA.PAA was not the reason for the film to be brittle, because the film of 3.4'-ODA(3,4'-dianiline oxide)/PMDA PI was also brittle, while the inherent viscosity of 3.4'-ODA/PMDA PAA was 180ml/g, enough large[2].

Tg as determined by differential scanning calorimetry(DSC) on the cured films was 283 ℃, more 12℃than DAKE/PMDA PI.

It is significant that the melting temperature(Tm) of 3,4-DAKE/PMDA PI was 343.6 and 363.9℃, very remarkable. The DSC of 3,4'-ODA/PMDA and DAKE/PMDA did not show Tm below 400℃. DSC curves of the polyimides 3,4'-DAKE/PMDA, 3,4'-ODA/DAKE and DAKE/PMDA are shown in figure 4.

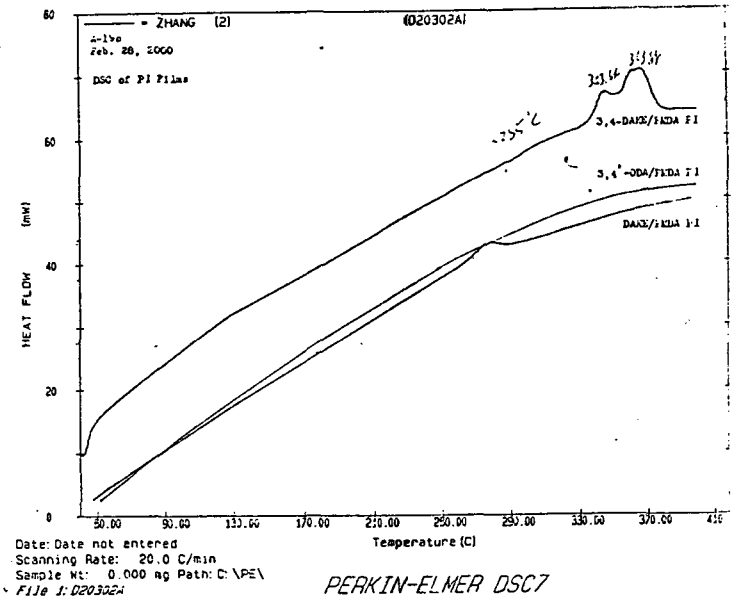


Figure.4 Differential scanning calorimetric curves

By thermogravimetric analysis (TGA) 3,4-DAKE/PMDA PI exhibited 5% weight loss at 488.9℃ in air. 3,4'-ODA/PMDA PI exhibited 5% weight loss at 490.1℃ in air. Thin film thermogravimetric analysis (TGA) of polyimides 3,4-DAKE/PMDA and 3,4'-ODA/PMDA are reported in Table I, and the TGA curves of polyimides 3,4'-DAKE/PMDA, and 3,4'-ODA/PMDA are shown in figure 5.

Table I Thermogravimetric Analysis (TGA) of polyimides 3,4'-DAKE/PMDA and 3,4'-ODA/PMDA

weight loss / polyimide	2%	5%	10%	15%	50%
3,4-DAKE/PMDA	429.5	488.9	519.8	537.6	629.0
3,4'-ODA/PMDA	467.5	490.1	506.7	524.5	610.0

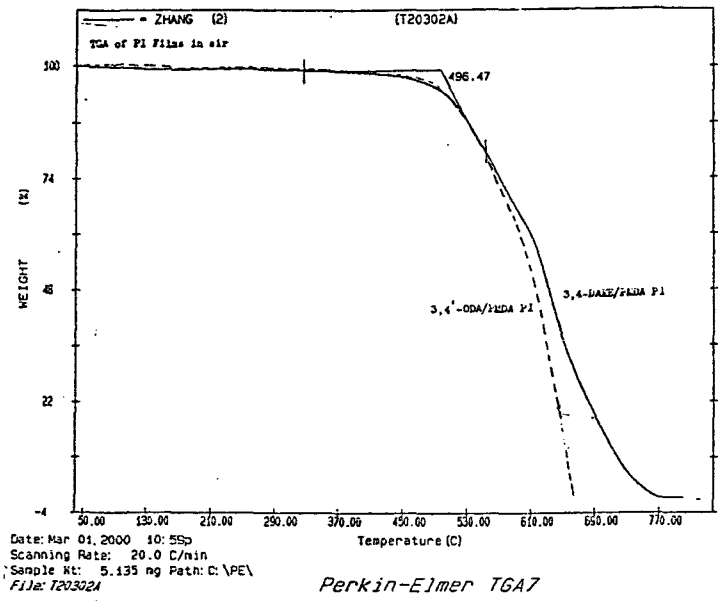


Figure.5 Thermogravimetric Analysis (TGA) curves of 3,4-DAKE/PMDA PI and 3,4'-ODA/PMDA PI.

Conclusions

Asymmetric polyimide was prepared by the reaction of PMDA and long chain asymmetric diamine 3,4-DAKE. DSC showed that this polyimide possessed two melting temperature at 343.6 and 363.9℃, very remarkable . Tg and thermo-oxidative of asymmetric polyimide was similar to that of symmetric polyimide.

References

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2. The experiment result of Long-qing zhang's laboratory