Preparation and Characterization of Soluble Polyimides

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SYNOPSIS

Two kinds of soluble polyimides from pyromellitic dianhydride with Congo red and 4-sulfanilamide were prepared, respectively. Their structures were characterized by IR and ^{1}H-NMR, and the thermal properties were investigated by DSC and TG–DTA. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

As polyimides from aromatic diamines have high thermal stability, toughness, mechanical, and electrical characters, they have been widely used.[1] However, the traditional polyimides have poor solubility in organic solvent and poor processability, which restrict their uses considerably.[2–4] To extend the utility of these high-performance materials, it has been long desired to synthesize soluble or thermoplastic polymers. Earlier efforts to increase tractability were made by placing alkyl groups on the aromatic ring of diamines[5–7] or incorporating other flexible groups into the main chain of polyimides.[1,8–12] We report here on the syntheses and characterization of polyimides from Congo red and 4-sulfanilamide, which were found to be soluble in common solvents.

EXPERIMENTAL

Materials and Instrumentation

Pyromellitic dianhydride was produced by Shanghai Coal Chemicals, Congo red was a product of the Shanghai Reagent Factory, and 4-sulfanilamide and DMF were of analytical grade. The supplies were used without further purification.

Infrared spectra were recorded with a 7400 IR spectrometer. ^{1}H-NMR spectra were measured by an FT-80A spectrometer in DMSO-d_6. DSC was carried out with a Perkin-Elmer 7 series thermal analysis system at a heating rate of 20°C/min in N_2. TG–DTA were determined by a PCT-1 balance at a heating rate of 10°C/min in air.

Syntheses of Polyimides

The polyimides were prepared by a polycondensation reaction. In the reaction, the pyromellitic dianhydride and the diamines were in the molar ratio of 1.02 : 1 with a solid concentration of 20%.

Syntheses of Polyimide from 4-Sulfanilamide

Into a flask equipped with a mechanical stirrer, thermometer, and addition funnel were placed 8.6 g (50 mmol) 4-sulfomilamide dissolved in 83 mL DMF, and 11.1 g (51 mmol) pyromellitic dianhydride powder was added gradually to the solution with stirring for 30 min. The solution was kept at ambient temperature for 1 h and then at 50°C for an additional 3 h. The polyamic acid solution was obtained. To the solution was added a large quantity of toluene to precipitate the polyamic acid. The precipitation was washed several times with toluene and dried *in vacuo* at 80°C and the polyamic acid powder was obtained. The polyamic acid (PAA) powder was heated *in vacuo* at 300°C for 2.5 h to dehydrate it and the polyimide powder was obtained.

Syntheses of Polyimide from Congo Red

Polyimide from Congo red was synthesized as described above with Congo red 13.9 g (20 mmol), pyromellitic dianhydride 4.5 g, (20.4 mmol), and DMF

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Journal of Applied Polymer Science, Vol. 56, 1295–1298 (1995)
 CCC 0021-8995/95/101295-04

78 mL and methylene dichloride was used as the precipitating agent.

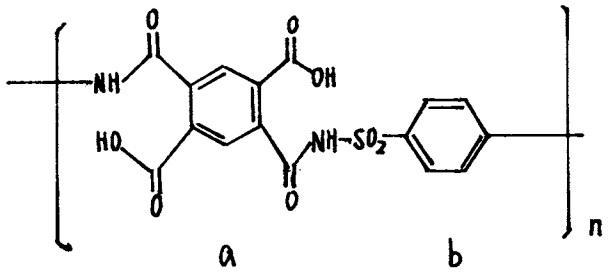
RESULTS AND DISCUSSION

Polyimide from 4-Sulfanilamide

From Figure 1 (a), it can be seen that the spectrum has absorption bands at 1590 and 1500 cm^{-1} (phenyl); 1320, 1129, and 580 cm^{-1} (—C—SO_2—); 1700 and 2880–2400 cm^{-1} (—COOH); and 3300–3000, 1670, 1525, and 1320 cm^{-1} (amide).

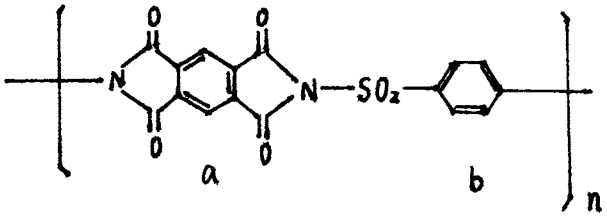
In Figure 2 (a), the chemical shifts can be assigned as follows: 10.82 ppm (—COOH), 7.25 ppm (—SO_2NHC—) (the peaks above can all be exchanged by D_2O), 8.00 ppm (phenyl ring a), and 7.82 ppm (phenyl ring b). Obviously, PAA has the structure of amide acid.

From Figures 1(a) and 2(a), together with the inherent viscosity of 0.46 dL/g, it can be concluded that the product is a PAA with the following structure:



Compared with Figure 1(a), Figure 1(b) shows that the absorption bands at 2880–2400 and 1700 cm^{-1} have disappeared, while the bands at 1780, 1720, and 720 cm^{-1} can be seen, which are the absorption bands of the imide structure. In Figure 2(b), the peaks at 10.82 and 7.25 ppm have entirely disappeared, while the peaks at 7.81–7.42 ppm become double doublets (phenyl ring b) and 8.28 ppm is the peak of phenyl ring a.

The IR and ^{1}H-NMR results imply that the PAA dehydrated completely and the final product is a polyimide (PI), which has the following structure:



The Polyimide from Congo Red

Similar characterization has been made for PI from Congo red. In the IR spectrum of PAA, the bands at 3000–2600 and 1700 cm^{-1} may be assigned to the structure of —COOH, and four bands are expected at 3360, 1635, 1450, and 1360 cm^{-1} for —CONH—. This suggests that the product (PAA) has the structure of amide acid. The ^{1}H-NMR spectrum of PAA may be assigned as 10.75 ppm (—COOH), which can be exchanged by D_2O, and the multiplet at 8.72–

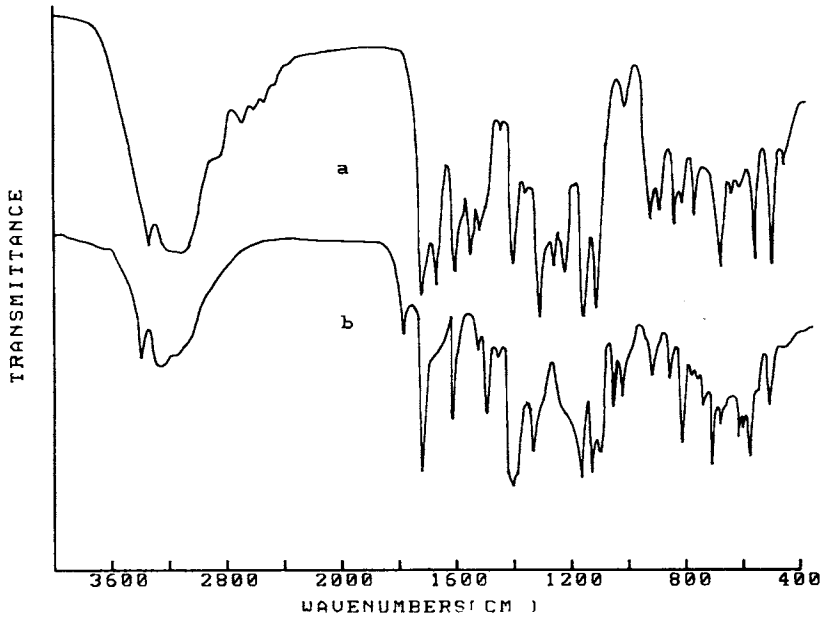


Figure 1 IR spectra of (a) PAA and (b) PI from 4-sulfanilamide.

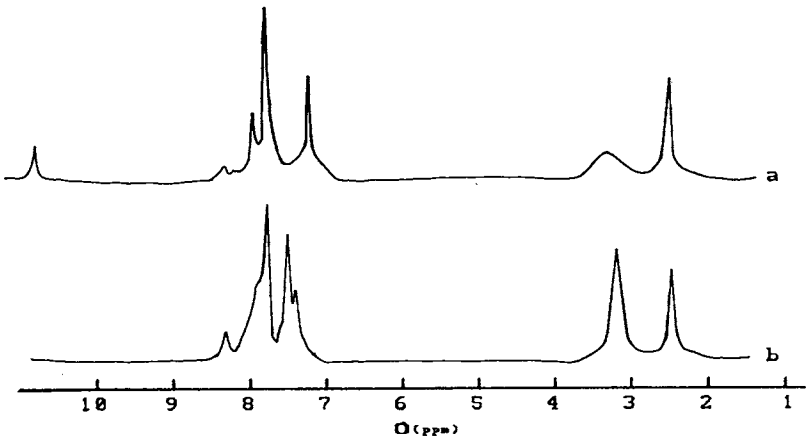
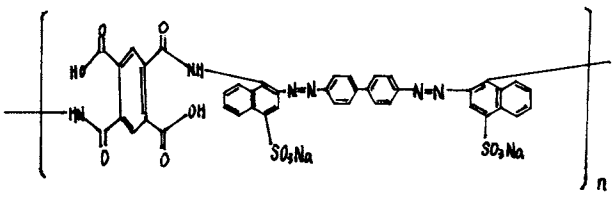
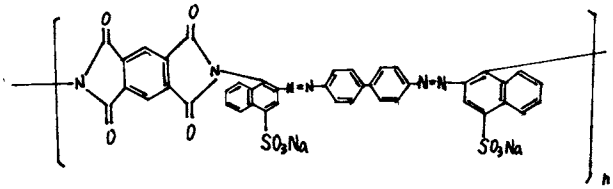


Figure 2 ^{1}H-NMR spectra of (a) PAA and (b) PI from 4-sulfanilamide.

7.57 ppm is due to the protons of aromatic rings. Compared with the ^{1}H-NMR spectrum of Congo red, it can be seen that the peaks get broader due to the polymerization. On the basis of the IR and ^{1}H-NMR results, together with its inherent viscosity 0.32 dL/g, we conclude that the product is PAA with the following structure:



After complete imidization, the bands at 3000–2600 cm^{-1} entirely disappeared while the bands at 1770, 1710, and 720 cm^{-1} appeared, which are the characteristic absorptions of the imide structure. In the ^{1}H-NMR spectrum of PI, the peak at 10.75 ppm disappeared and a great variation was observed in the peaks of protons of aromatic rings. Accordingly, the following PI is formed:



Solubility of Polyimides

The polyimide from 4-sulfanilamide has good solubility in *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), and chloroform and is slightly soluble in acetone or methanol. The polyimide from Congo red has good solubility in DMF, DMAc, DMSO and is soluble in chloroform and methanol and slightly soluble in acetone. With good solubilities, it is expected that the two kinds of PIs have good tractabilities.

Thermal Properties

The thermal properties of the two kinds of PIs were determined by TG–DTA and DSC. From the curves, it can be observed that PI from 4-sulfanilamide begins to decompose at ca. 420°C in the TG curve; meanwhile, the endotherm peak is at ca. 444°C in the DTA curve. From the DSC curve, it can be seen that the glass transition temperature (T_g) is ca. 330°C.

Similarly, the PI from Congo red begins to decompose at ca. 435°C, and the exotherm peak is at ca. 463°C. The T_g is ca. 285°C in the DSC curve.

This investigation was supported by the Fund for Excellent Young University Teachers of the State Education Commission of China and the Science Foundation of Nanjing University of Science and Technology.

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Received August 24, 1994
Accepted December 8, 1994