The synthesis and characterization of semicrystalline homopolyimides and copolyimides

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Introduction

Aromatic polyimides are high-performance polymeric materials possessing an exceptional array of properties. Thermal stability, chemical resistance, and excellent mechanical properties have enabled this class of polymer to be used in a variety of applications such as electronic packaging, films, adhesives, and matrix materials for composites. Semicrystalline polyimides offer the further advantages of increased solvent resistance and retention of mechanical properties above the glass transition temperature. These features have made semicrystalline polyimides the focus of considerable research over the recent years. For the thermoplastic polymers, different structures and different lengths of main chains will have a directly impact on the crystal properties of polymers. Therefore, the change of repeating units would have an impact on crystallization, the crystal structure and melting behaviors, thermal properties accordingly at last. Based on the idea above, in this study we synthesized an array of semicrystalline homopolyimides and copolyimides based on 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) /4,4'-oxydianiline (4,4'-ODA) /1,3-bis-(4-aminophenoxy)benzene (TPER) by changing the percent of 4,4' -ODA /TPER. The goal of this research work is to focus on the development of polyimide having good thermal stability and fast crystallization kinetics.

Experimental

Polymer Synthesis

The TPER and 4,4'-ODA were always dissolved together first (except two homopolyimides) in the DMAc and to this was added the s-BPDA. These solutions were stirred and allowed to react under a nitrogen atmosphere for 24 h, to afford the poly(amic acid)s. All poly(amic acid)s were made to achieve a 10% solids concentration.

The poly(amic acid)s were converted to the respective polyimides using method of thermal imidization, films of the poly(amic acid)s were solvent cast onto glass plates and placed in a dry box in the presence of a nitrogen flow until smooth nontacky films were obtained. The plates were then placed in a oven, and the temperature raised to 60 °C and held for 2h,then 2h each at 100°C,150°C,180°C;then the plates were moved to a vacuum oven,1h each at 250°C,300°C,350°C.The oven was allowed to cool to below 200 °C before removing the films.

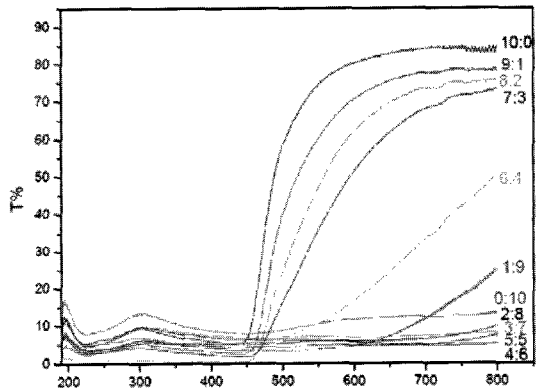

Fig1. transmittance of the elven polyimide films

Results and Discussion

Eleven polyimides films have been successfully synthesized including two homopolyimides and nine copolyimides. By UV, we can see that the transmittance(T%) changed regularly according to the increase of 4,4'-ODA contents. when the molar ratio of 4,4'-ODA /TPER was 4:6, the T% was the lowest, then it

turned to be more and more higher either as the increase of 4,4'-ODA contents or as the decrease of 4,4'-ODA contents(Fig 1).

TGA was utilized to determine the material's thermal stability as indicated by weight loss at high temperatures. Dynamic experiments were at a slow heating rate of 10 °C/min were conducted from room temperature to 850 °C in nitrogen environments. The results of the TGA experiments are shown in Table 1.By this test, we could see that all the samples exhibited excellent thermal stability in nitrogen, as evidence -d by the temperatures for 5% weight loss were higher than 540 °C.

To understand the melting behavior and crystalline condition, DSC measurement were conducted.

Table 1. Temperatures (°C) for 5% Weight Loss at a Heating Rate of 10 °C /min in Nitrogen

ODA:TPER	Temp(°C)	ODA:TPER	Temp(°C)
0:10	546	6:4	543
1:9	542	7:3	569
2:8	540	8:2	575
3:7	541	9:1	562
4:6	556	10:0	573
5:5	546		

Fig.2 showed the first heating scans of eleven initial films, both the Tgs and the final peak temperatures of melting endotherms turned to be increasingly higher as the increase of the 4,4'-ODA contents. The Tgs changed from 210 to 260℃.All the polymers have crystalline ability proved by the existence of the melting endotherms. More interesting, multiple melting endotherms were observed in most of the curves in Fig 2. They were strongly depended on the percent of 4,4'-ODA /TPER as well.

Mechanical properties were also investigated by tensile properties testing. It was observed that with an increase in 4,4'-ODA contents there was an increase in elongation of the films at break but with the similar tensile modulus, about 3.2-3.6GPa. It suggested that the mechanical properties of copolyimides were as good as homopolyimides.

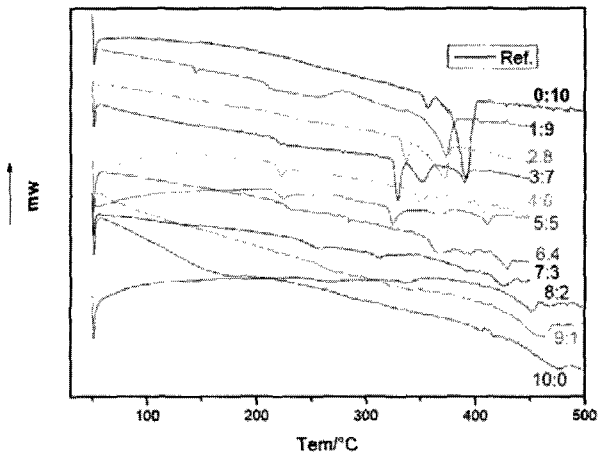

Figure 2. First heatDSC scans for homopolyimides and copolyimides

From the results above we can find that almost all the properties of the eleven films changed regularly according to the percent of 4,4'-OD A /TPER ,like transmittance(T%)、Tgs、elongation. The reason has already mentioned above, as the different reactivities between two diamines, copolymers obtained will have different lengths of repeat units. Then the change of repeating units would have a directly impact on crystallization rate and the crystalline structure. Then polymers we polymerized have got different properties accordingly. In this research work, crystallization kinetics and morphology of semicrystalline polyimides were also investigated, these polyimides were ascertained to be high thermally stable semicrystalline polymers and estimated to be used as a new kind of engineering material.

References (omitted)