

The study of acetylene-terminated polyimide oligomer derived from BPADA

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Abstract

The acetylene-terminated polyimide oligomer derived from 2, 2-bis [4-(3,4dicarboxyphenoxy) phenyl] propane dianhydride(BPADA) and 3-Ethynylaniline (APA) was synthesized. The crosslinking behavior of oligomer was studied by differential scanning calorimetry and infrared measurements. The dynamic mechanical properties of the cured polyimide film at 250°C had a glass transition temperature (T_g) at 330°C with a considerable drop in the storage modulus at this temperature. The tensile and thermal properties of the cured films were also evaluated. TGA curves show that the temperatures of 5% weight loss (Td₅) are 491 °C in nitrogen and 489°C in air respectively.

Introduction

Aromatic polyimides have been used in a wide range of applications in electronic and aerospace industries because of their very high thermal stability and mechanical durability. However, the insoluble and infusible nature of polyimides sometimes results in defects in the manufacturing processes. The development of soluble or thermoplastic polyimides has been attracting major research interests, although such polyimides would have drawbacks such as lower thermal stability and lower solvent resistance. There has been a strong demand for polyimides having good processing ability, high thermal stability, and high solvent resistance. One promising approach is to use crosslink sites that react by thermal curing during processing or after processing. The precursors are soluble in polar organic solvents but the cured products are insoluble and exhibit high thermally stability. The crosslink sites have to be carefully chosen not to deteriorate the inherent high-temperature performance of polyimides. Acetylene was chosen as the reactive end group because among the compounds commonly used, it offers a major advantage in terms of stability, curing temperature and thermal resistance of the final crosslinked material.

Thermosetting acetylene-terminated polyimide precursors were developed in the 1970s. These polyimides are noted for their excellent thermo-oxidative stabilities and good mechanical properties, but their utilization was severely limited due to a short gel time and low solubility in common organic solvents that resulted in processing difficulties.¹ To overcome these significant drawbacks, one of the main approaches developed was to use more soluble polyisoimide oligomers, which could be thermally isomerized into polyimides and subsequently crosslinked through acetylene end groups to yield polyimide networks. Another method was the introduction of flexible segments such as methylene, isopropylidene, or hexafluoroisopropylidene groups into polyimides.^{2,3} These approaches provided higher solubility and longer gel times so that processing characteristics were markedly improved.

The work reported herein that a new acetylene-terminated polyimide oligomer based on 2, 2-bis [4-(3,4dicarboxyphenoxy) phenyl] propane dianhydride (BPADA) and 3-Ethynylaniline (APA) was prepared and characterized. The processibility of polyimides may be improved by terminating reactive end groups, controlling molecular weight and introducing some flexible molecules in the rigid polymer chain.

Experiment

The synthesis of acetylene-terminated oligomers

The acetylene-terminated oligomers from BPADA were synthesized. APA (6.43g , 0.55mol) and 50ml DMAc were placed in a flame-dried 250 ml three necked round-bottom flask which was equipped with nitrogen inlet, mechanical stirrer and drying tube. After the diamine was dissolved completely, BPADA (14.28 g, 0.275 mol) was added and the reaction mixture was stirred at room temperature for 4 h under a nitrogen atmosphere. The oligoamide acid solution was put into culture dish and dried in an air oven at 80°C for 4 h, then the material was dried at 150°C for 4 h in a vacuum oven, finally ground to obtain oligomer powder.

The preparation of films

The obtained imide oligomers were molded by using $6 \times 6 \times 0.005$ cm³ polyimide film frame on a 15×15 cm² stainless steel plate with UPILEX-S separator films under 1.4 MPa by heating initially to 180°C for 10 min and subsequently to 250 °C for 1 h. The dark red film-like specimens of $6 \times 6 \times 0.005$ cm³ were obtained.

Result and discussion

The thermal properties of uncured oligomer powder were measured by DSC. Fig. 1 shows the DSC curves of oligomer powder in the first and second scan. There is no glass transition observed in the first scan due to the low molecular weight of oligomer powder. The exothermic peak due to the crosslinking reaction appeared at 200-330°C in the first heating run of DSC. A higher glass transition temperature was observed in the second heating run as a result of ethynyl crosslinking. Glass transition temperature of the oligomers is 330°C.

The melt viscosity measurement of the oligomers was carried out, and the melt viscosity as a function of curing temperature was displayed in Fig. 2. The oligomer exhibited minimum melt viscosity as low as 180Pa·s. The lower minimum melt viscosities of the oligomers were the contribution of methylene group in the dianhydride monomer (BPADA) and low molecular weight.

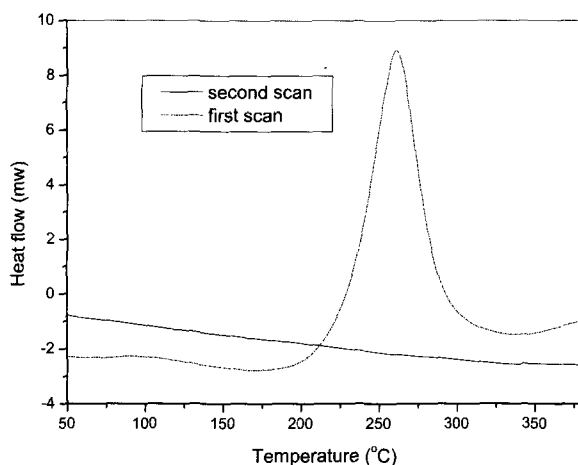


Figure 1 the DSC scan of acetylene-terminated polyimide oligomer

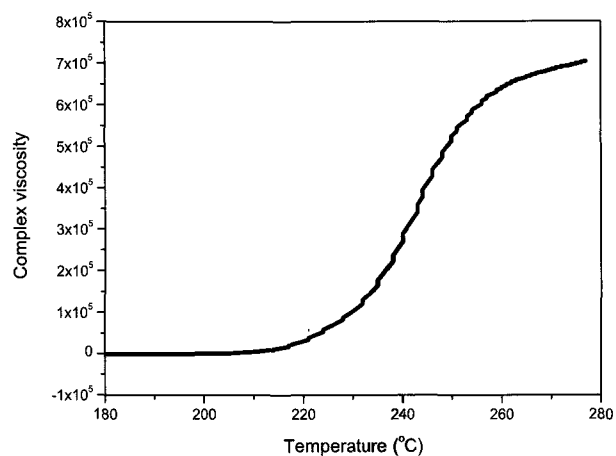


Figure 2 The rheology curve of acetylene-terminated polyimide oligomer at different temperatures

The T_g values of cured imide oligomer films were determined by DMA. The peak on the $\tan\delta$ as a function of temperature curves was considered as the T_g of the cured film. Fig. 4 shows that the cured polyimide film at 250°C had a glass transition temperature (T_g) at 330°C with a considerable drop in the storage modulus at this temperature.

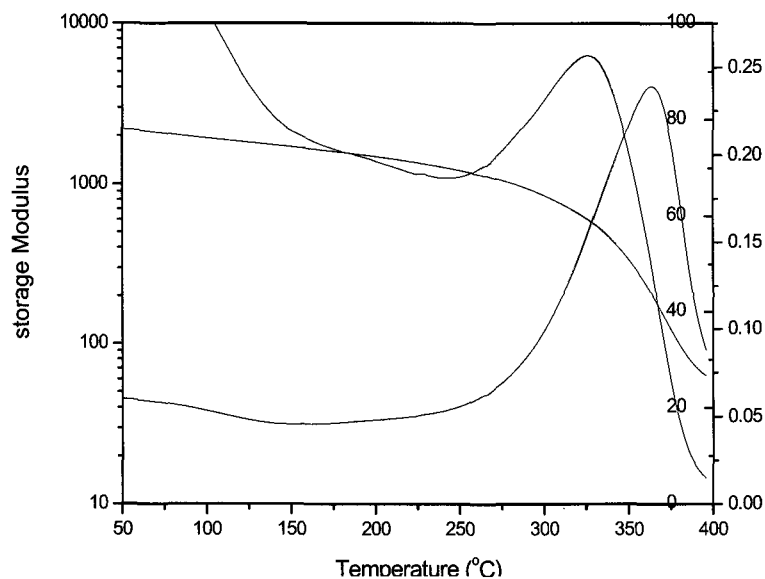


Figure 5 The DMA curves of cured polyimide film

Reference

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