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Synthesis and thermal polymerization of a novel stilbene-maleimide AB-monomer

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Summary

A novel AB-monomer, 3-maleimidostilbene (ST-MAI), was synthesized. DSC investigation indicated that the ST-MAI monomer melted at 127°C and thermally polymerized in the temperature range of 180 ~ 300°C. IR investigation on the thermal polymerization processes proved that the thermal polymerization included not only copolymerizaiton between stilbene and maleimide, but also homopolymerization of maleimide. The largest reaction conversion of maleimide and stilbene unit in a ST-MAI monomer was about 82% and 50% respectively. The glass transition temperature of cured ST-MAI resin was 234°C, determined by DSC. The decomposition temperatures for 10% weight loss was above 430°C in both air and nitrogen atmospheres.

Introduction

Network copolymers can be formed through the alternating copolymerization of bismaleimides and divinyl ethers (1, 2). These network copolymers are similar in their thermal and mechanical properties to other high performance resins, such as epoxy, bismaleimide and polyimide materials. In addition, these network copolymers have good solubility in ordinary solvent and low processing temperature; they are good candidates to replace other resins in some aerospace applications. Considering characterization of this kind of network copolymers, it is promising to use stilbene for this purpose. Stilbene is electron rich monomer that does not undergo free radical initiated homopolymerization. In contrast to the reluctance of this monomer to homopolymerize is the great facility with which maleimide and stilbene copolymerize to give copolymer(3). The present work is attempted to prepare a new AB-monomer containing both maleiimde and stilbene on the same molecule and possessing the perfect stoichiometry for network alternating copolymerization. The results of our investigation on the preparation and thermal polymerization of this new monomer were reported.

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Experimental

Materials and measurement

Maleic anhydride was recrystallized from toluene/acetic anhydride (2: 1). Aniline was distilled over KOH under vacuum. The preparation of 3-aminostilbene was according to the procedures described in the literature (4), with some modification. All other solvents were analytical grade.

Perkin-Elmer DSC 7e was used to measure the reaction heats of thermal polymerization of ST-MAI. The experiments were performed under different conditions, which included constant temperatures at 180, 190, 220, 240, 250°C and heating at the rate of 5, 10°C/min from ambient to 300°C. The heat and baseline calibrations were performed before the measuring experiments. The weights of sample were in the range of 5 ~ 10 mg and the flow rate of nitrogen gas was 20 ml/min. NMR spectra were recorded on a Varian Unity-400 Spectrometer with $CDCl_3$ as solvent and TMS as internal standard. IR spectra were recorded on BIO-RID FTS 15 spectrometer in KBr pellet.

Synthesis

To a solution of maleic anhydride (1.96g, 0.02mol) in 10ml of dry CH_2Cl_2 was added a solution of 3-aminostilbene(3.90g, 0.02mol) in 20ml of dry CH_2Cl_2 over a period of 2h at ice bath temperature under a nitrogen atmosphere, and then stirred overnight at room temperature. The insoluble maleiamic-acid was separated by filtration, washed with hot acetone and water, and dried under vacuum. Yield 5.63g (ca. 96%). The maleiamic-acid thus obtained was added to 40ml of solutions of 0.024M sodium acetate in acetic anhydride. The mixture was placed in a bath at 80°C for 0.5h under a nitrogen atmosphere, and following poured into saturated aqueous sodium bicarbonate solution. The precipitate was collected, washed with water (4 X 400mL) and dried at 50°C under vacuum overnight. The crude products were purified on chromatography column containing silica gel eluted with CH_2Cl_2 and subjected to rotary evaporation. Pure ST-MAI was obtained as a bright yellow crystalline solid. Yield 5.34g (ca. 95% recovery), mp. 126-127°C.

Anal. Calcd for $C_{14}H_{13}N$: C, 86.11; H, 6.71; N, 7.78. Found: C, 86.02; H, 6.85; N, 7.14. IR (KBr pellet): 1778, 1730, 1380, and 710cm^{-1} vs (imide ring); 1148cm^{-1} (C-N-C maleimide); 3010, 823cm^{-1} (olefin hydrogen of maleimde); 3060, 962cm^{-1}(olefin hydrogen of stilbene). ^{1}H-NMR(in ppm, TMS as internal standard): 6.92(S, 2H); 7.2-7.6 (m, 11H).

Results and discussion

DSC characterization of thermal polymerization

DSC curves of ST-MAI monomer are shown in Figure 1. On the initial DSC scan to 350 °C (Figure 1A), a endothermic peak at 127°C and a exothermic peak in the 180-300°C range were observed, which were respectively associated with the melting and polymerizing of ST-MAI monomer. After the initial run, the temperature was held at 300 °C for 30min, following the second run was carried out. As shown in Figure 1B, both

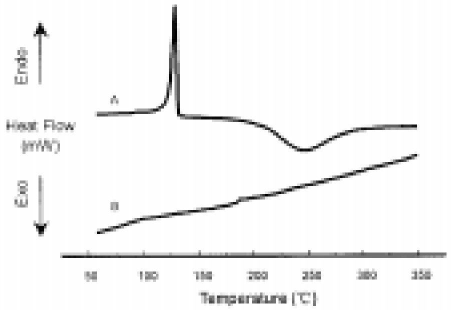


Figure 1. DSC curves of ST-MAI monomer, A: first run; B: second run.

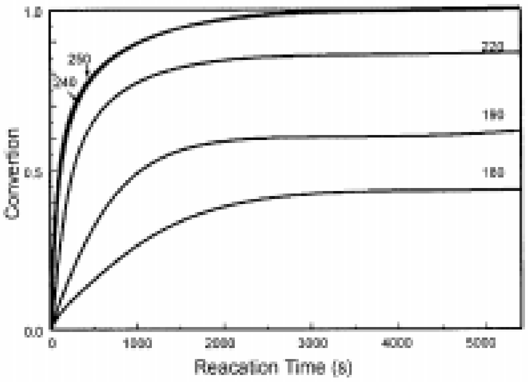


Figure 2. The conversion (α) as function of cure time at the temperature.

endothermic and exothermic peaks of ST-MAI monomer were vanished, and replaced by a small endothermic transition near 190°C. According to the temperature difference between melting endotherm and onset of exotherm in Figure 1A, the processing window of ST-MAI resin was estimated to be about 53°C. The thermal polymerization of ST-MAI monomer was further characterized in detail by isothermal DSC analysis. In typical experimental, isothermal scans were run in the 180-250 °C range up to two hours whenever there was no significant change in heat flow at each temperature within the limit of' equipment resolution. The conversion (α) of thermal polymerization was determined from the following equation:

$$\alpha = \frac{\Delta H_t}{\Delta H_\infty} \qquad (1)$$

where ΔH_t is the partial heat of reaction at time *t* and ΔH_∞ is the total heat of reaction that was determined from a dynamic DSC scan at the heating rate of 5°C/min. The conversion (α) as a function of time at different temperatures, from 180 to 250°C, was shown in Figure 2. It shows that as the reaction temperature elevated both the rate of polymerization and conversion of the monomer increase. But, it should be point out that the conversions given in Figure2 is apparent value, that is, the value is relative to the conversion of the 5°C/min dynamic experiments. For a thermal polymerization the viscosity in the system takes a dominant effect on the final conversion of monomers. As the polymerization proceeds, the viscosity increases, which will significantly reduce mobile of reactive groups or monomers, when the viscosity in the system exceeds the certain critical value, the polymer molecules encapsulated the function groups and polymerization will also be terminated. In fact, as IR investigation (see below), the thermal polymerization is difficult to reach 100% conversion even though the reaction time was long enough or the temperature was high enough.

IR characterization of thermal polymerization

The IR spectra obtained using the same samples on which DSC experiments had been performed were shown in Figure 3.

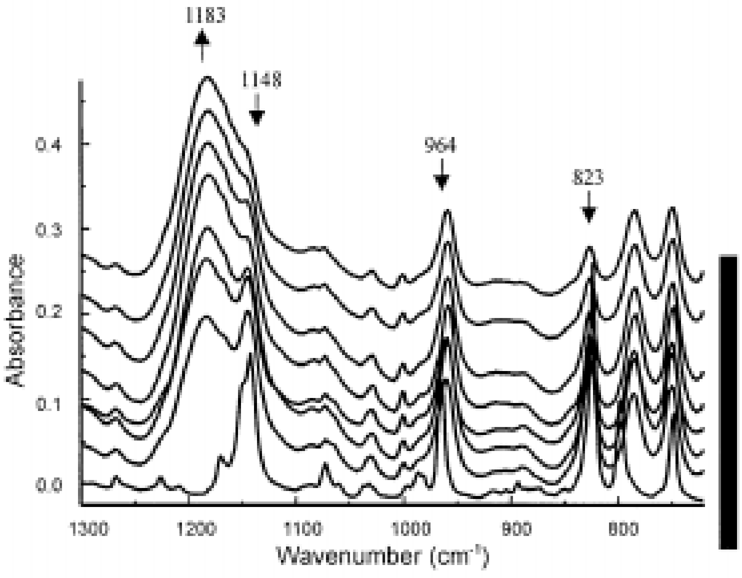


Figure 3. *FT* IR spectra of ST-MAI as a function of sequential cure conditions. Cured for 2h at: 1) 300℃; 2) 250℃; 3) 240℃; 4) 230℃; 5) 220℃; 6) 200℃; 7) 190℃; 8) uncured.

With heating temperature elevated, both IR bands at 1149 and at 823 cm^{-1} associated respectively with C-N-C and =C-H of maleimide decrease while a new band at 1180 cm^{-1} corresponding to C-N-C succinimde increases, which indicated that phenylmaleimide units were converted to phenylsuccinimide (5). In the same time, incorporation of stilbene groups into polymerization was indicated by the band at 964 cm^{-1} associated with =C-H of stilbene decrease. From the ratio of nominal absorbency of peak at 964 cm^{-1} and 823 cm^{-1} of curved and uncured ST-MAI monomer, the conversions of stilbene and maleimide groups were calculated and shown in Figure4. The largest conversions of stilbene and maleimide groups were 82% and 50%, respectively. As ST-MAI monomer possessing the perfect stoichiometry, the difference in conversion between stilbene and maleimide groups is due to that the two groups have different reaction abilities. It is well known that the polymerization of maleimide in heating curing can be proceeded not only by homopolymerization but also by alternating copolymerization. On the contrary, the stilbene cannot take place homopolymerization, it can only be copolymerized by the way of alternating. The difference of conversions of maleimide and stilbene indicated that in the thermal polymerization the homopolymerization of maleimide was simultaneously proceeding while the alternative copolymerization of stilbene and maleimide occurred. The results of TGA investigation on cued ST-MAI resin also indicated that the resin obtained was composed of two components to which we distributed as a homopolymer of maleimide and alternating network copolymer of stilbene and maleimide. The formed alternating network that decreased the freedom of band ration was also accounted for incomplete reaction. According to results above, the plausible pathways of thermal polymerization were proposed and illustrated in Scheme 1.

DSC and TGA characterization of cured ST-MAI resin

The glass transition temperature of ST-MAI resin cured for 1h at 160; 200; 250; 300°C was about 234°C, determined by DSC.

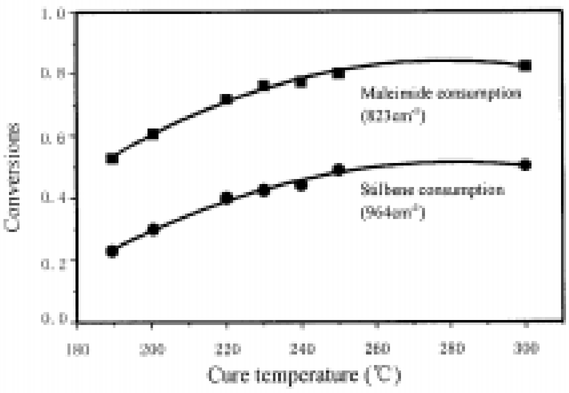


Figure 4. The consumputin of two groups as function of cure conditions.

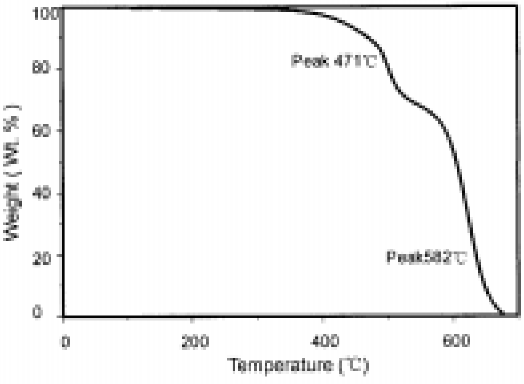
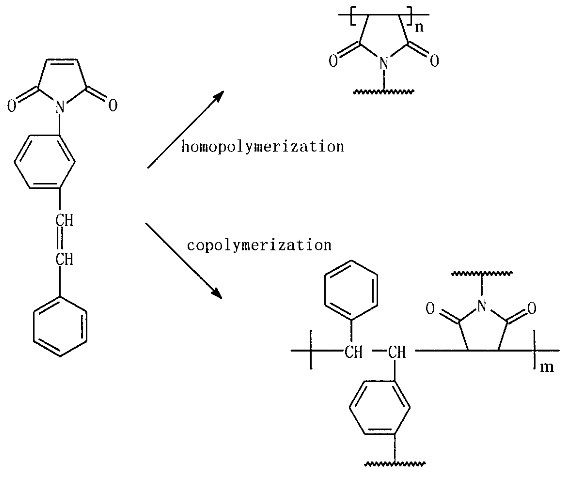


Figure 5. TGA thermogram of cured ST-MAI resin

TGA thermogram of cured ST-MAI resin thus obtained was shown in Figure 5. Two decomposition processes were observed, the largest rate of two mass loss were occurred at about 471 and 562°C respectively. The percentage of first mass loss was about 30%. Considering a typical decomposition temperature of maleimide resins, the two decomposition processes were assinged to homopolymeric components and alternating network polymeric components of ST-MAI resin. It is corresponded well with results of IR investigation.



Scheme 1. The plausible pathways of thermal polymerization.

Conclusions

A novel stilbene-maleimide AB-Monomer was synthesized and polymerized thermally, the resin thus obtained possessing widely processing window and moderate thermal stability. In addition, the monomer can be solved in ordinary solvent such as methylene chloride, acetone, etc.

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