Polymerization of Bismaleimide and Maleimide Catalyzed by Nanocrystalline Titania

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ABSTRACT: Polymerization of 4,4′-bismaleimidediphenyl methane and *N*-phenylmaleimide was conducted in dimethyl formamide, catalyzed by nanocrystalline titania. The monomers and polymers involved were characterized with infrared spectroscopy, ^{1}H-NMR, and ^{13}C-NMR, respectively. The mechanism of the catalyzed polymerization was discussed as well. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 665–669, 1999

Key words: bismaleimide; maleimide; catalyst; nanocrystalline titania

INTRODUCTION

Both bismaleimide and maleimide are among the most important resins in the aerospace/aircraft and electrics/electronics industry because of their tractability, high thermal stability, high durability, good water resistance, fire resistance, radiation resistance, and relatively low cost.[1–5] However, their disadvantages—brittleness of cured resin, poor solubility in ordinary solvents, and high processing temperature—restrict its application considerably.[6]

From the 1970's on, many attempts (such as blending, copolymerization, and modification of bis or maleimide molecular structure) have been made to improve the polymer physical properties, and much research has been successful.[7–10] However, nearly all of the curing must be conducted at a high temperature and that high processing temperature is a problem that needs to be solved. Besides, due to the high processing temperature, it was usually difficult to polymerize the bismaleimide and maleimide in solution.

In this study, nanocrystalline titania was used as a heterogenerous catalyst for the polymerization of 4,4′-bismaleimidediphenyl methane (BMID) and *N*-phenylmaleimide (PMI) in dimethyl formamide (DMF). The success of this attempt, exhibiting a new access to the modification and a possible method for lowering the processing temperature, has been achieved. The method proposed herein can be also potentially used for the preparation of impregnent.

EXPERIMENTAL

Materials and Instruments

BMID was obtained from Hanyang Plastics Factory (Wu Han, China). PMI was synthesized as described. All the other reagents used in this study were of analytical grade and used without further purification. Infrared (IR) spectra were recorded with a 7400 instrument of Shanghai Analytical Instrument Factory with KBr pellets, ^{1}H-NMR spectra were obtained using a Varian FT-80A spectrometer in dimethylsulfoxide (DMSO)-d_6, ^{13}C-NMR spectra were determined by a Varian XL-200 spectrometer in DMSO-d_6, and viscosity of the polymerizing solution was measured by a rotary viscometry. The UV spectra of

Table I   Wavenumbers of IR Spectra of PMI and BMID Before and After Polymerization and Their Assignment (cm^{-1})

Sample	Imide Structure					Aromatic Ring		C=C	
PMI	1785	1700	1390	1150	750	1600	1500	1600	830
PPMI	1780	1710b	1390	1170b	730b	1600	1500		
BMID	1780	1720	1380	1110	720	1600	1510	1600	630
PBMID	1785b	1720b	1400	1130b	730b	1600	1510	1600s	830s

b = broad; s = shrink to small size; PPMI, PMI = after polymerization; PMID, BMID = after polymerization.

the polymerizing solution of BMID and PMI were recorded by an UV/7350-G spectrophotometer.

Synthesis of PMI

To 39.6 g of 0.4 mol maleic anhydride dissolved in acetone stirred with a mechanical stirrer, 37.2 g of 0.4 mol aniline was added dropwise. The mixture was stirred at ambient temperature for 4 h. The resulting precipitate was filtered and dried. It was then dissolved in DMF, and reacted with the mixture of sodium acetate and acetic anhydride at 60°C for 3 h. The reacted mixture was subsequently poured into water and a deposit appeared. The solid was filtered, washed with water, and dried. PMI was thus obtained with a yield over 78%.

Preparation of Nanocrystalline Titania

To titanium sulfate, an aqueous solution of appropriate concentration was added (sodium hydroxide aqueous solution) dropwise until the pH reached 7–9. The flocculate deposit was washed with deionied water and separated with centrifugation. Thereafter, concentrated nitric acid was added until the solution pH was 1–2 to dissolve the precipitate. To this solution, glycol (2–3 times as much as titanium dioxide) was added; the solution was evaporated at 90°–100°C until a flocculent deposit formed again. The precipitate was calcined at 500°C for 6 h and nanocrystalline titania (with an average particle size of 15 nm) was obtained.[11]

Catalytic Polymerization of BMID and PMI in DMF

Fifteen grams of BMID dissolved in 48 mL of DMF and 0.3 g of nanocrystalline titania were placed in a flask equipped with a mechanical stirer, a thermometer, and a reflux condenser connected with a drying column. All of the reagents and equipment for polymerization were carefully dried before use on the consideration that a little amount of water will destroy the catalytic activity of nanocrystalline titania by occupying the active points in its surface. The mixture was stirred vigorously and kept at the reflux temperature of DMF (155 ± 2°C). The color of the reaction mixture began to change from yellow to red. The polymerizing system gelled in 15 min. Completion of polymerization was indicated by the disappearance of the characteristic absorption band of the C=C linkage at 830 cm^{-1} in the IR spectrum. The BMID polymer was purified by reduced pressure distillation after polymerization was completed.

Catalytic polymerization of PMI in DMF was conducted under the same conditions as that of BMID. However, because the polymerization rate of PMI was much slower than that of BMID, the reaction took 6 h to complete. Thereafter, the reacted solution was poured into water, and the resulting precipitate was filtered, washed and dried. The polymer of PMI was thus prepared and purified.

It should be mentioned that it is difficult to removal the nanocrystalline titania from the polymers we get, but it gives no effect to the analytic results below.

RESULTS AND DISCUSSION

PMI and its polymer were characterized by IR, ^{1}H-NMR, and ^{13}C-NMR. BMID and its polymeric products were characterized by IR only because of their poor solubility.

The characteristic absorption bands in the IR spectra and their assignments are listed in Table I. The typical IR spectra of PMI and its polymer are presented in Figure 1 as an example.

As can be seen in Figure 1, the IR spectrum of PMI polymer (spectrum b) shows some differences from that of PMI (spectrum a). The charac-

Figure 1 IR spectra of BMID before (spectrum a) and after (spectrum b) polymerization.

Scheme 1 Structure scheme for assignment of Ha, Hb, and Hc.

teristic absorption bands of imide structure at 1710 cm^{-1}, 1170 cm^{-1}, and 730 cm^{-1} in spectrum b are broader than corresponding bands in spectrum a. The characteristic absorption band of C=C linkage at 830 cm^{-1} nearly disappears in spectrum b, and that at 1600 cm^{-1} in spectrum a nearly disappear in spectrum b too. The small peak at 1600 cm^{-1} spectrum b is due to the characteristic absorption of aromatic ring. The IR spectra features of BMID monomer and polymer (see Table I) are nearly the same as that of PMI.

The ^{1}H-NMR spectra of PMI before (spectrum a) and after (spectrum b) polymerization are shown in Figure 2.

In spectrum a, the multiplet at 7.31–7.45 ppm is associated with the protons of aromatic ring, the singlet at 7.18 ppm is assigned to the protons in —CH=CH— structure of PMI, and a broad

singlet at 3.35 ppm is due to the existence of a certain amount of water. However, spectrum b, the ^{1}H-NMR of PMI polymer shows features different from spectrum a. The peaks at 3.90 ppm, 4.10–4.18 ppm, and 6.95–7.06 ppm are attributed to protons Ha, Hb, and Hc, respectively (see Scheme 1), in the structure of the polymer of PMI. The peaks due to the protons in the —CH=CH— structure of PMI at 7.18 ppm in spectrum a nearly disappear in spectrum b, and the protons in the aromatic ring in spectrum b give peaks broader than that in spectrum a.

^{13}C-NMR spectra of PMI before (spectrum a) and after (spectrum b) polymerization are shown in Figure 3. The peaks at 126.67, 127.68, and 128.84 ppm in spectrum a are assigned to *o-, m-,* and *p*-carbon atoms of the aromatic ring, and the peaks at 134.54 ppm and 131.5 ppm are due to C=C linkage and the quaternary carbon atom in an aromatic ring of PMI, respectively. The peak at 39.5 ppm is due to the DMSO solvent.

After polymerization, spectrum b, small broad multiple peaks appear at 171.0–181.5 ppm due to the polymer of PMI. The carbon–carbon double band peaks at 134.54 ppm almost disappeared. All of the peaks associated with the carbon atoms in aromatic ring become wider in spectrum b than

Figure 2 ^{1}H-NMR spectra of PMI before (spectrum a) and after (spectrum b) polymerization.

Figure 3 ^{13}C-NMR spectra of PMI before (spectrum a) and after (spectrum b) polymerization.

Figure 4 The dynamic curve of the polymerizing system of PMI in DMF catalyzed by nanocrystalline titanium dioxide.

in spectrum a. A peak relating to methine should appear at ∼ 40 ppm, which is covered by the DMSO peaks.

The inherent viscosities of the reaction mixture at different reaction times were measured. The inherent viscosity of PMI mixture increased steadily with the increasing reaction time. A plot of inherent viscosity *versus* reaction time is shown in Figure 4.

The UV spectra of PMI in DMF and the polymerizing solution of PMI are shown in Figures 5 and 6, respectively.

The UV spectrum of the polymerizing solution of PMI (Fig. 6) exhibit two peaks, of which one is

Figure 5 UV spectrum of PMI in DMF.

Figure 6 UV spectrum of a polymerizing solution of PMI in DMF.

at the wavelength of visible light corresponding to red color seen during the polymerization process. This color may be due to a carbanion, or result from the coordination between the surface of nanocrystalline titania and the PMI. The formation of both the carbanion and the coordination requires a clean catalyst surface.

Because the polymerizing system was not oxygen-free, as previously described, the free radical polymerization mechanism is neglected. An anionic mechanism or a coordination mechanism, resulting from the effect of crystalline titania, is proposed because all of the reagents and equipment for the polymerization were dried carefully before use and kept dry during polymerization. The red color shown during the procedure of polymerization supports the conclusion as well.

In addition, to make sure about the effect of nanocrystalline titania on polymerization, several comparison experiments were conducted as previously described.

BMID and PMI with no nanocrystalline titania were kept under the same reaction condition used for polymerization previously described. The viscosity, IR spectra, and nuclear magnetic resonance spectra of the solution were measured.

Through analyzing the data from the measurement, no change was found from either the spectra or viscosity data after treatment. Thus, polymerization with nanocrystalline titania could not proceed if there were some water or similar impurities in the solution, or the nanocrystalline titania had been exposed to air for long time.

In summary, it is concluded that the polymerization of BMID and PMI in solution can be conducted in DMF at 155 ± 2°C with the aid of

catalysis of nanocrystalline titania, proceeding with either anionic polymerization mechanism or coordination polymerization mechanism or both. Further attempts to get deep insight into this mechanism are currently in progress in our laboratory.

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