

# Catalytic Polymerization of Maleic Anhydride

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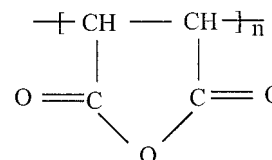
**ABSTRACT:** This study examined the polymerizations of maleic anhydride in solution and in the bulk phase catalyzed by nanocrystalline titania or sodium acetate. Through IR and  $^1\text{H-NMR}$ , the monomer and polymer were characterized, and the structure of the polymer was confirmed.

Moreover, the polymer molecular weight was measured to be 400–800 in solution and 2000–3000 in the bulk phase. The mechanism of the catalytic polymerization was also investigated. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2868–2874, 2003

## INTRODUCTION

In a molecule of maleic anhydride (MA), there is a conjugated-bond and electron-withdrawing carboxyl group. Therefore, it is difficult to polymerize, even with heating. However, MA can be copolymerized relatively easily with other monomers such as styrene and propenoic acid. Because the homopolymer has more carboxyl groups, it can act as a good surfactant and can also be used as a detergent, a softener, a water-treatment reagent, and so forth. Its incredible utility makes the study of the homopolymerization of MA worthwhile.

As previously reported, MA can be polymerized in several ways. In 1963, Lang and Pavelich<sup>1</sup> discovered that  $\gamma$ -rays and free radicals could initiate MA and, therefore, make it polymerize. Subsequently, Braun<sup>2</sup> and others made MA polymerize with  $\text{Bz}_2\text{O}_2$  as an initiator, and they believed that the product took cyclohexanone as a unit. Regel and Schneider<sup>3</sup> and others obtained a compound with the structure of 2,5-dioxotetrahydrofuran-3,4-diyl with  $\text{Bz}_2\text{O}_2$  and  $\gamma$ -ray as initiators. Schopov<sup>4</sup> thought that a triethylamine or pyridine base-catalyzed polymerization might take place and that the polymer had a structure with repeating units consisting of cyclopentanone connecting with the monomer. Bacskai<sup>5</sup> repeated the experiment performed by Braun and confirmed with methods such as NMR and from the amount of generated gas that the structure should be the following chain compound:



This agrees with the conclusion of this article.

## EXPERIMENTAL

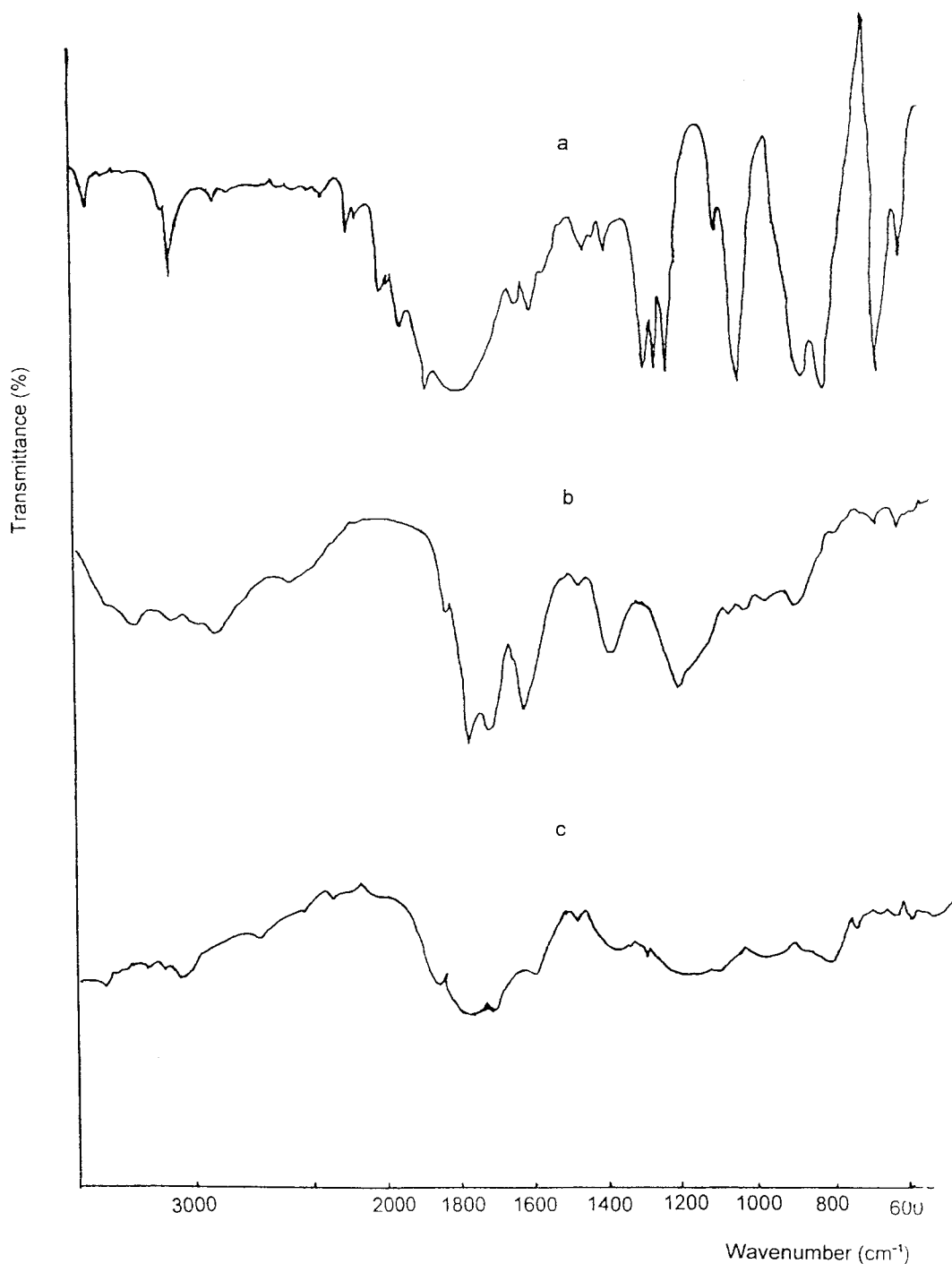
### Materials and instruments

MA was obtained from the Chinese Medical and Pharmaceutical Co. (Beijing, China); nanocrystalline titania was prepared as described. All other chemicals used in this study were analytical reagents. IR spectra were performed on a model 7400 instrument from the Shanghai Analytical Instrument Factory with KBr pellets;  $^1\text{H-NMR}$  spectra were measured with a Varian FT-80A spectrometer in dimethyl sulfoxide- $d_6$ . The ultraviolet (UV) spectra of the polymerizing solutions were recorded with a UV/7530-G spectrometer. The viscosity data were determined with a JD-79 rotary viscosimetry and an Ubbelohde viscometer.

### Preparation of nanocrystalline titania

Ammonium water was added dropwise to titanium sulfonate or titanyl sulfate with an appropriate concentration until the pH reached 7–9. The obtained white flocculate deposit was washed with deionized water and separated with centrifugation seven or eight times. Then, concentrated nitric acid was added to the deposit until the pH was 1–2 and the deposit dissolved. At this time, glycol (2–3 times as much as  $\text{TiO}_2$ ) was weighed into the solution, and when it dissolved, the system was evaporated at 90–100°C until the solution gelatinized. Thereafter, the gel was dried for 3 h at the same temperature in a drying stove

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**Figure 1** IR spectra of (a) the monomer, (b) the polymer in solution, and (c) the polymer in the bulk phase.

and then was transferred into a muffle furnace and calcined at 520°C for 3 h. Finally, white nanocrystalline titania was obtained.

#### Polymerization in solution

A solution of 27 g of MA dissolved in 63 g of dimethylformamide (DMF) and 0.54 g of nanocrystalline titania/sodium acetate (NaAc) were mixed in a flask equipped with a reflux condenser, a ther-

mometer, and a mechanical stirrer. The mixture was then heated to the boiling point of the solvent. After 15 min, the system using titania as a catalyst changed from white (because of titania powder suspended in the solution) to yellow and then to dark brown. The system using NaAc changed from white to red and then darkened. Six hours later, the mixture was poured into another container, and the solvent in the system was removed. Finally, a dark brown/red powder was obtained.

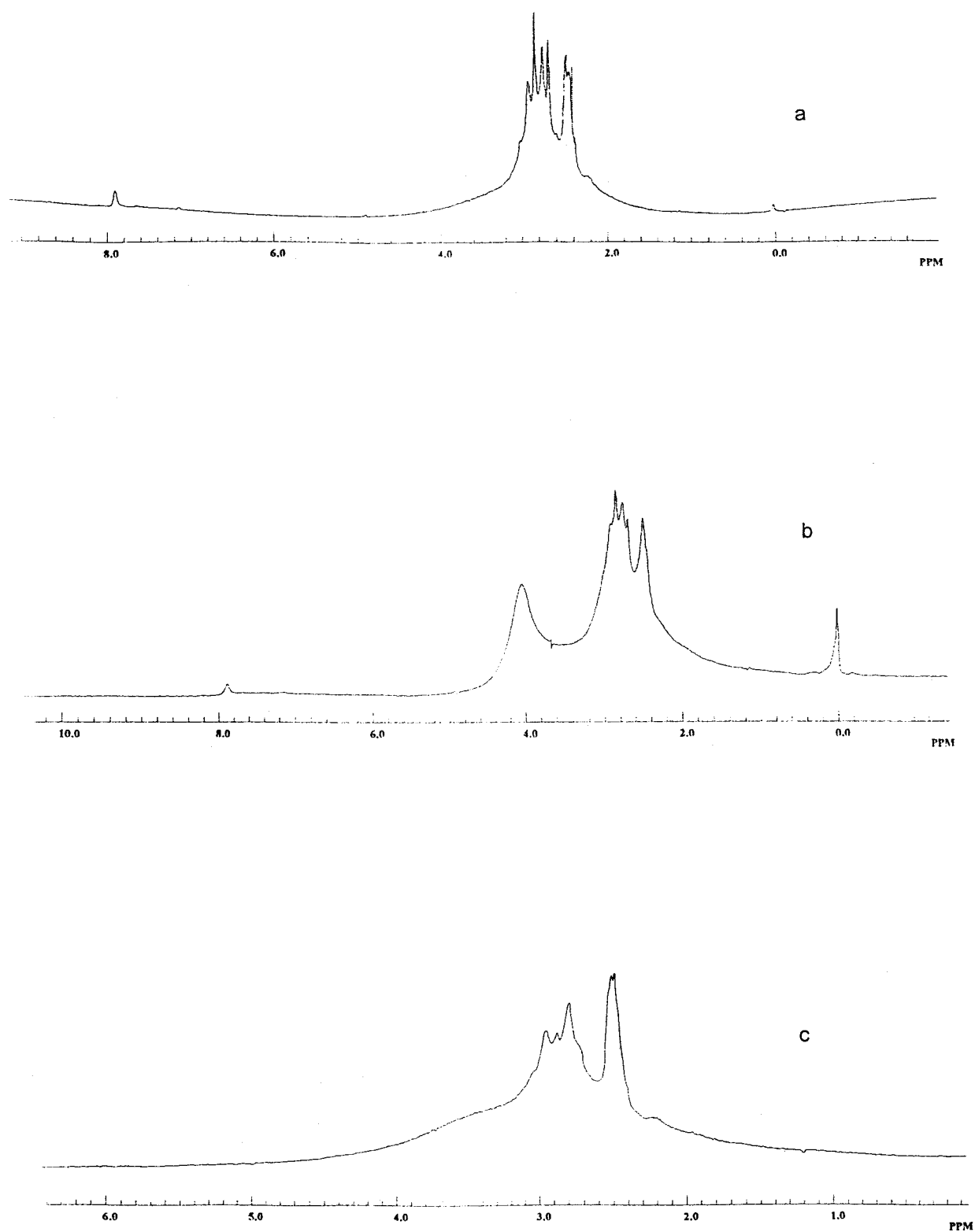


Figure 2  $^1\text{H-NMR}$  spectra of the polymer: (a) untreated, (b) changed by  $\text{D}_2\text{O}$ , and (c) further treated.

### Bulk polymerization

MA (10 g) was mixed with nanocrystalline titania/NaAc in an appropriate proportion. Afterward, the mixture was placed in a tube located in a oil bath and heated to  $165^\circ\text{C}$  or so; as it melted, it became

white because of the suspended catalyst. With the time increasing, the color became brown or red and then darkened. About 0.5 h later, gas bubbles appeared in the tube until the system gelled at last. A brittle and dark brown foamy solid was obtained.

**TABLE I**  
Change in Weight Loss and Gelation Time with the Amount of Catalyst

Amount of catalyst (%)	Weight loss (%)	Gelation time (h)
1.0	22.0	26.0
1.5	17.8	20.5
2.0	15.0	16.0

When the solid was dissolved in water, plenty of foaming occurred.

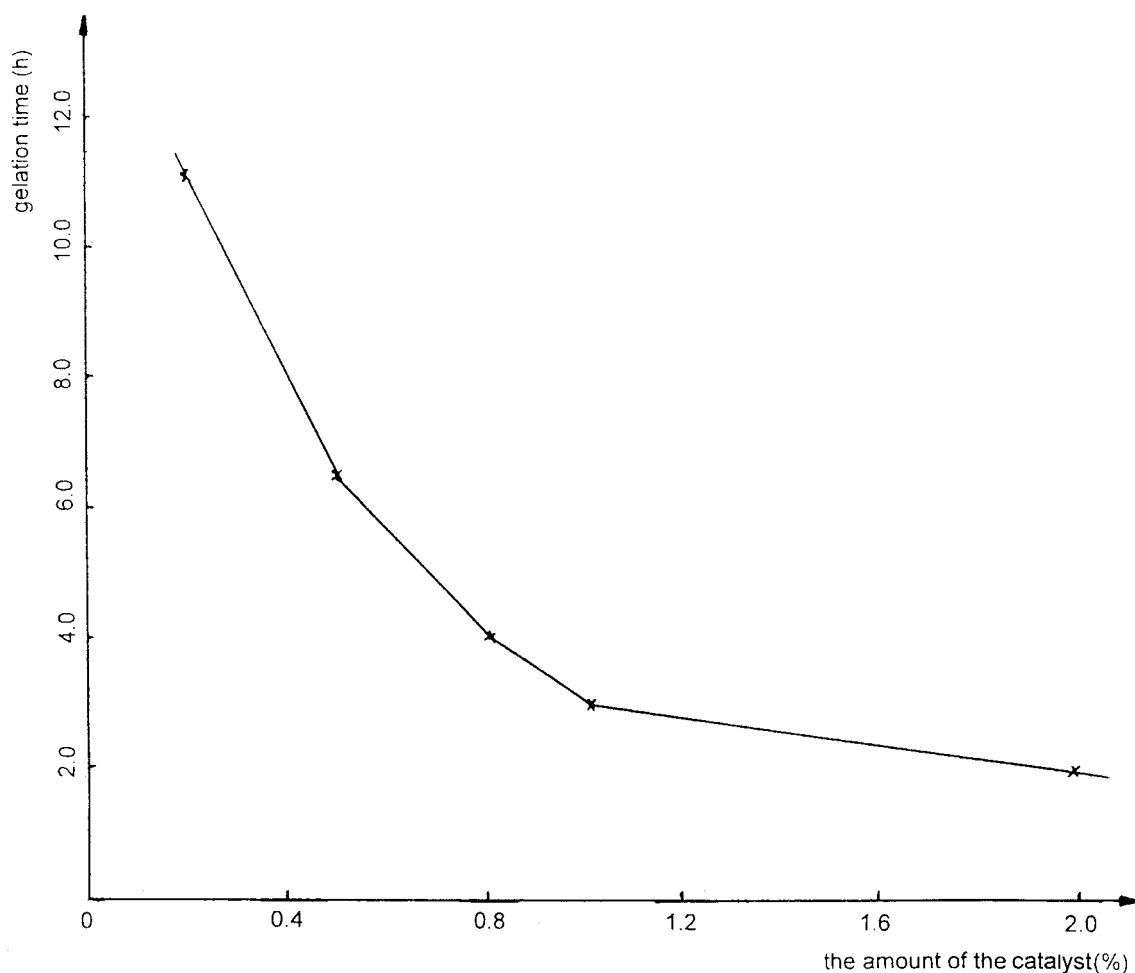
## RESULTS AND DISCUSSION

### Characterization by IR and $^1\text{H-NMR}$

Figure 1(a-c) presents the IR spectra of the MA monomer and the polymer catalyzed by nanocrystalline titania in solution and in the bulk phase, respectively. The characteristic absorption bands of the carboxyl are at 1850, 1760, and 1780  $\text{cm}^{-1}$ . The C—H characteristic absorption band in spectrum a is at 3100  $\text{cm}^{-1}$ , but it disappears in spectra b and c. The characteristic absorption bands at 1242 and 900  $\text{cm}^{-1}$  are of the C—O—C group. The C=C absorption bands are at

1605, 848, and 649  $\text{cm}^{-1}$ . The peak at 649  $\text{cm}^{-1}$  in spectrum a disappears in spectra b and c. At 2900  $\text{cm}^{-1}$ , the peak existing in spectra b and c but not in spectrum a is attributable the vibration absorption peak of the C—H bond in the methine. Also, the peaks in spectra b and c are almost all broader than those in spectrum a. However, the absorption peaks at 1200–1300 and 1780  $\text{cm}^{-1}$  in spectra b and c are still the same as those in spectrum a.

Figure 2 presents the spectra of the polymer catalyzed for 6 h by nanocrystalline titania in solution. In spectrum a, the peaks at 7.88, 2.94, and 2.83 ppm can be attributed to the protons in the structure of DMF remaining in the polymer. The peak at 2.90 ppm is related to the protons of  $-\text{C}=\text{CH}_2$  in the end group of the polymer molecule. At 2.0–4.0 ppm is the multiplet of the proton of the methine in the structure of  $-\text{CH}-\text{CH}-$ . The peaks at 7.10 ppm of the proton in the ethylenic link ( $\text{HC}=\text{CH}$ ) structure in the MA monomer completely disappear (partly because of the high temperature during the treatment of the product). The peak at 2.59 ppm is due to the proton in DMF, and there exists a peak at 2.79 ppm that is associated with the protons in a small amount of poly-



**Figure 3** Plot of the gelation time versus the amount of the catalyst.

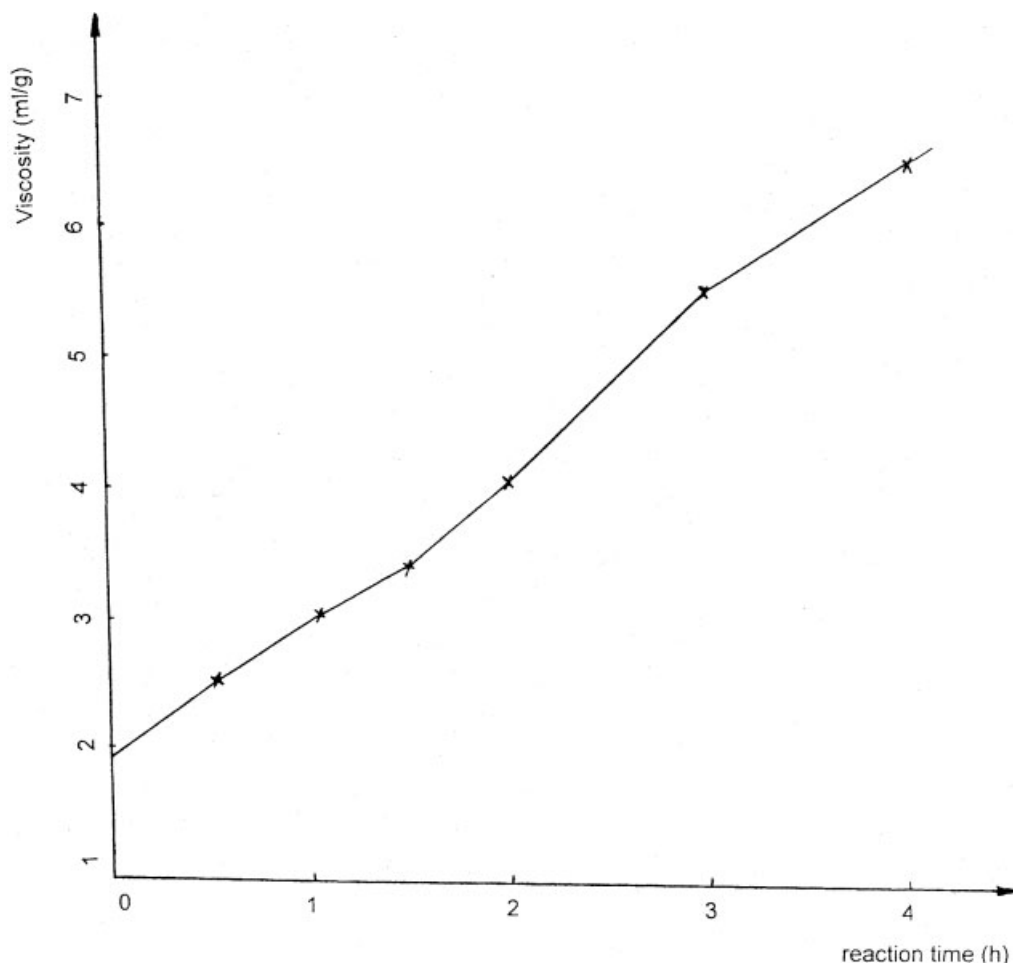


Figure 4 Plot of the viscosity versus the reaction time.

(maleic acid). When there is an exchange by  $D_2O$  (see spectrum b), the broad multiplet does not disappear. On the basis of spectrum b, DMF was still mixed in the polymer. Therefore, the polymer was further treated. As can be seen in spectrum c, after the treatment, the peaks of DMF weaken greatly and even disappear. The multiplet at 2.50–4.0 ppm, however, remains the same. According to these data, the peak at 7.10 ppm associated with the MA monomer disappears and changes into the peak of the proton in the methine and in the end group of the polymer.

#### Decarboxylation and polymerization during the reactions<sup>6</sup>

During the experiment in the bulk phase, when the reaction proceeded to some extent, gas bubbles were blown off from the mixture. If the gas entered into the clear and calcareous water, the water became white and turbid immediately. For this reason, the gas blown off can be judged to be  $CO_2$ . This means that during the reaction, decarboxylation took place.

As was reported, not only for the radical polymerization with  $Bz_2O_2$  as an initiator but also for the anionic catalytic polymerization initiated by pyridine

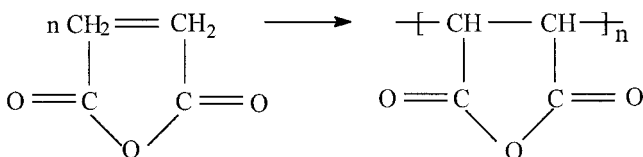
or sodium hydrate, carbon dioxide evolved during the reaction. The position at which decarboxylation occurred directly influenced the confirmation of the polymer structure. In the study of the radical polymerization, there are two ideas. One is that of Braun,<sup>2</sup> that the main structure of the polymer is cyclopentanone and that the structure is complicated. The second is that of Bacskai,<sup>5</sup> that the structure of the polymer is  $[-HC-CH-]_n$ , and that  $CO_2$  comes from the decarboxylation of the MA monomer. The difference between the two ideas is that Braun's conception holds that the polymerization results in the evolution of  $CO_2$ , that there is  $CO_2$  in the polymerization equation, and that a great difference exists between the structures of the polymer and monomer; Bacskai's theory states that decarboxylation and polymerization are independent of each other and that the structure units of the polymer and monomer are the same. Moreover, the idea of anionic catalytic polymerization has often been entertained, and it has been thought the generation of  $CO_2$  is due to the polymerization and that the structure is made up of different units.

The results of the IR and  $^1H$ -NMR spectra in this study lead to agreement with Braun.<sup>2</sup> That is, the

**TABLE II**  
Molecular Weight of the Polymer Catalyzed by Nanocrystalline Titania

Method used	Diagram-plotted method	One-point method
In solution	460	720
In bulk phase	2650	2780

decarboxylation and polymerization are two independent reactions. The polymerization equation is as follows:



The effect of the amount of the catalyst on the gelation time and the amount of gas generated in the bulk phase can be seen in Table I. When the reaction temperature was fixed, the gelation time decreased with an increasing amount of the catalyst, and the amount of CO<sub>2</sub> released was directly proportional to the reaction time. When the amount of the catalyst was increased, the reaction time decreased. Moreover, several experiments were conducted as previously described. Under the same conditions, MA was heated at 165°C for a long time (e.g., 3, 10, or 20 h). No gas was released from the tube at all. Therefore, we judged that the catalyst could work for decarboxylation, too.

In addition, Figure 3 presents the relationship of the gelation time and the amount of the catalyst at 180°C. When the amount of catalyst was lower than about 0.8%, the gelation time decreased greatly with an increasing amount of the catalyst. When it was higher than about 0.8%, the change in the gelation time was not obvious. When the ratio of the MA monomer to titania reached 500:1 or even higher, the catalysis was not obvious. Also, the reaction did not occur without the catalyst.

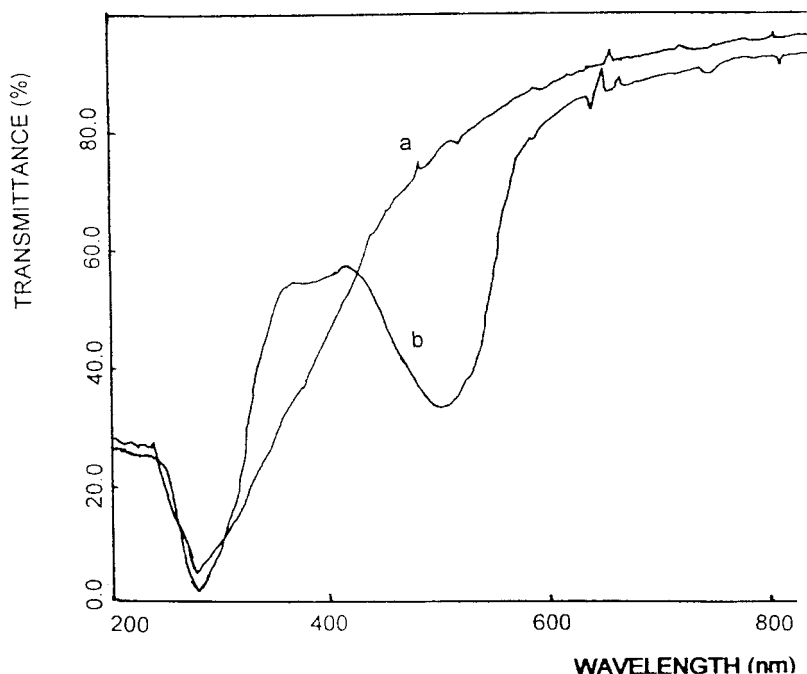
The inherent viscosities of the reaction mixtures at different reaction times were measured, as can be seen in Figure 4. The inherent viscosities of the MA mixtures in solution increased steadily with the reaction time.

Viscosimetry can be used to measure the molecular weight of a polymer. Of the many methods, using an Ubbelohde viscometer is the simplest. Because it was difficult to obtain the values of *k* and *α* of MA, the values of poly(sodium propenate)<sup>7</sup> were used for the calculation of the molecular weight. The solvent used was a water solution of NaOH at a concentration of 0.2 mol/L.

As shown in Table II, the molecular weight of the polymer obtained in solution was calculated to be 400–800. The molecular weight of the polymer in the bulk phase was 2000–3000, greater than that of the polymer in solution.

**Reaction mechanism**

The ultraviolet-visible (UV-vis) spectra of MA in DMF and a polymerization solution catalyzed by



**Figure 5** UV-vis spectra of the MA polymerizing system: (a) MA in DMF and (b) the polymerization solution catalyzed by NaAc in DMF.

NaAc are shown in Figure 5. In spectrum a, there exists one peak, the maximum wavelength of which is at 270 nm. Besides this peak, spectrum b of the polymerizing solution catalyzed by NaAc exhibits another peak that is at about 500 nm of visible light and corresponds to the red color seen in the reaction process. Spectrum c of the polymerizing solution catalyzed by nanocrystalline titania is the same as spectrum a. The red color may come from a carbanion. This is similar to the polymerizing solution of *N*-phenylmaleimide catalyzed by nanocrystalline titania.<sup>8</sup> NaAc is a kind of weak base, and increasing the chain is difficult; therefore, it leads to a low molecular weight. As for the catalysis of nanocrystalline titania, two mechanisms have been proposed. One is the coordination mechanism, which is based on the fact that a Ti atom is a transition-metal element that can coordinate with six ligands, but a Ti atom on the surface of TiO<sub>2</sub> only coordinates with four or five oxygen atoms;

therefore, the coordination is in an unsaturated state. As such, it can coordinate with the double bond of the monomer, and the reaction is activated. As far as the carbanion polymerization mechanism is concerned, it exists because many OH<sup>-</sup> ions adhere to the surface of TiO<sub>2</sub>, and then a weak base is formed. Concerning the catalysis of nanocrystalline titania, this study should be continued.

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