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## ALTERNATING COPOLYMERIZATION OF MALEIMIDE AND ETHYL ATROPATE WITHOUT INITIATOR

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**Key Words:** Maleimide, Ethyl Atropate, Alternating Copolymer, Contact-Charge Transfer Complex

### ABSTRACT

The copolymerization of maleimide(MI)( $M_1$ ) and ethyl atropate (EAP)( $M_2$ ) was carried out by self-initiation at 60°C, in which  $M_2$  ( $Q=0.43$ ,  $e=0.92$ ) and  $M_1$  ( $Q=0.44$ ,  $e=1.35$ ) constituted a pair of electron donor and acceptor monomers on Price-Alfrey equation. A high alternating tendency was observed, the monomer reactivity ratios  $r_1=0.048\pm 0.016$  and  $r_2=0.12\pm 0.012$  were calculated by a nonlinear least-squares procedure. The spontaneous alternative copolymerization is considered to be carried out by the induced radicals produced via a contact-type charge transfer complex between  $M_1$  and  $M_2$ , which was confirmed by UV spectra. Thermogravimetric analysis (TGA) shows that the resulting copolymers have high thermal stability.

### INTRODUCTION

Polymerizations involving electron donor-acceptor interaction or charge-transfer interaction have been a topic of interest in recent years [1]. Three classes of

polymerization are the subject of major concern in this area. The first is in polymerization, the monomer was initiated by charge-transfer complex composed of monomers as electron-donor (or acceptor) and the other component as electron-acceptor (or donor) [2]. The second class in which the polymerization of the monomers is carried out by an additional initiator system termed "exciplex" formed by bi-components [3]. The third is an alternating radical copolymerization in which it is thought that a charge-transfer complex formed by monomer pairs participates as the species in the propagation process of polymerization [4], the mechanism of which has long been a subject of controversy, mainly including two theories, radical and complex mechanism [5].

Sadhir [6] reported that a CTC pair of N-vinylpyrrolidone with maleic anhydride can be formed via a partial electron transfer from the former to the latter, and the initiating species were radicals formed under laser-irradiation, and the alternating copolymer was formed by radical mechanism.

Rivas *et al.* [7] studied the copolymerization system consisting of 2-bromoacrylic acid as electrophilic monomer and 2-oxazoline as a nucleophilic one. It was found that the Zwitterion polymerization occurs spontaneously between them, and the complex mechanism was considered to play the main role.

Otsu *et al.* [8] found that N-alkylcitraconimides and styrene were a kind of very interesting monomer pairs, they could constitute the CTC and be polymerized into alternating copolymer with high molecular weight by radical mechanism whether the initiator AIBN was present or not, but the CTC was very difficult to observe from the UV spectrum.

2-Substituted acrylate and acrylic acid are very important and interesting monomers. They are not only widely used in the industry, but also can exert biological influence on the human bodies [9]. However, it was found that 2-alkylacrylic esters and acids, except methacrylic ester and acid, were reluctant to polymerize extensively because of the steric hindrance of 2-substituent [10].

Recently, we prepared a series of 2-substituted acrylates and acrylic acids. We found that some of them can spontaneously copolymerize with MI. This contribution is focused on the pair of MI and EAP.

## EXPERIMENTAL

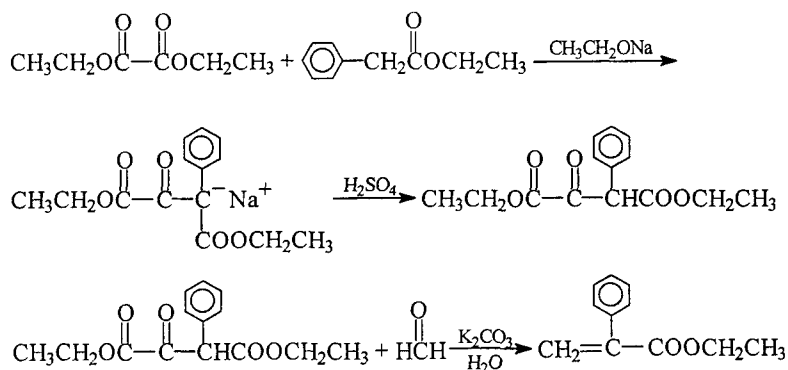
### Materials

Ethyl phenylacetate (EA) (Shanghai First Reagent Factory) and diethyl oxalate (DEO) (Jiangsu Jincheng Reagent Factory, China) were purified by distilla-

tion at reduced pressure, the fraction of 78°C/10 mmHg for EA and 98-101°C/21 mmHg for DEO was collected respectively. All other chemicals were purified by ordinary procedure.

### Preparation of EAP and MI

EAP was prepared according to the procedure in Reference [11], but we improved the procedure as follows:



Scheme I

To 500 mL of absolute ethanol, 23 g (1 mol) sodium with fresh surface was added under refluxing, to which 136 mL (1 mol) diethyl oxalate was introduced as fast as possible at 60°C with strong stirring, then 175 mL (1 mol) ethyl phenylacetate was added. The reaction solution was poured immediately into a 1,000 mL beaker when the crystalline was just formed, the crystallization would be finished instantly. After cooling, the solution was filtered and the solid was washed several times with ether until the yellow color disappeared, and then dried under vacuum. The oxalo-ester was obtained by acidification of the sodium salt, then the EAP could be obtained by the reaction of oxalo-ester with formaldehyde in the presence of potassium carbonate with a yield of 64.8%. The crude product could be purified by redistillation under reduced pressure to constant refractive index.  $^1\text{H}$  NMR ( $\delta$  ppm): 7.32 (m, 5H, phenyl), 6.34 (s, 1H, trans-H of  $\text{CH}_2=$ ), 5.88 (s, 1H, cis-H of  $\text{CH}_2=$ ), 4.25 (q, 2H,  $-\text{CH}_2-$ ) and 1.24 (t, 3H,  $-\text{CH}_3$ ); IR: ( $\text{cm}^{-1}$ ): 1723 (C=O), 1615 (C=C);  $n_{\text{D}}^{20}$ : 1.5240.

MI was synthesized by the method of Tawney [12], and was recrystallized from a chloroform-hexane solvent mixture, m.p. 93-94°C (yield 46%).  $^1\text{H}$  NMR ( $\delta$  ppm): 10.9 (s, 1H,  $-\text{NH}-$ ), 6.9 (s, 2H,  $-\text{CH}=\text{CH}-$ ).

### Polymerization Procedure

Copolymerization of  $M_1$  and  $M_2$  was performed in ampoule using dioxane as solvent. A typical procedure is as follows: an ampoule was charged with MI, EAP and solvent with definite ratio and degassed three times by freeze-thaw cycles at 77 K, then sealed. The copolymerization was carried out for 72 hours in different conditions, and the powder-like product with white color was precipitated by ether and purified by dissolution/precipitation with dioxane/ether. The homopolymers of  $M_1$  and  $M_2$  were obtained by radical and anionic methods reported by Tawney [12] and Tsuruta [13], respectively, and purified with acetone and methanol in Soxhlet extractor separately.

### Measurements

IR spectra were obtained on a Magna-550 FTIR spectrometer;  $^1\text{H}$  NMR spectra were registered on Bruker MSL-300 spectrometer using  $\text{DMSO-d}_6$  as solvent and TMS as internal standard. UV spectra were recorded on Shimadzu UV-240 spectrometer. Molecular weight and molecular weight distribution were measured with Waters 180°C gel permeation chromatography (GPC) with the columns of Bondgel E-500, 125 and 1,000, column length: 90 cm, injection volume: 0.3 mL (concentration: 0.1 g/mL), solvent and eluent: THF, flow rate: 1 mL/min, pump pressure: 20 Kg/cm<sup>2</sup> (1.99x10<sup>6</sup> Pa), refractive index detector, polystyrene standards were used for calibration. TGA was recorded with General V4.1C Dupont 2000 thermogravimetric analyzer at heating rate of 20°C/min in a nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Spontaneous Copolymerization of $M_1$ with $M_2$

Copolymerization of  $M_1$  with  $M_2$  in different feed ratio was found to occur in absence of initiator at 60°C to give the polymer powder with white color, as indicated in Table 1. The copolymer composition, either the conversion of the monomers is low (A:<10%) or high (B:>10%), is about 50:50. Obviously, this is a typical alternating copolymerization system. We also found that in all cases in this system, the molecular weight distribution of the copolymers are much narrower, but its molecular weight is independent on the polymerization time, that is, it is not a "living radical" polymerization system. The further investigations are being conducted. Based on the data in the Table 1, the relationship of the initial rate of copolymerization and  $M_n$  of the copolymers with monomer feed molar ratio are

TABLE 1. Effect of Monomers Feed Ratio on Copolymerization of MI and EAP

Sample No.	Feed Ratio (M <sub>1</sub> /M <sub>2</sub> , mol/mol)	M <sub>n</sub> (×10 <sup>-4</sup> )	M <sub>w</sub> /M <sub>n</sub>	Yield (%)	Composition** (M <sub>1</sub> %)
1	1 : 9	Oligomer	/	/	/
2	2 : 8	Oligomer	/	/	/
3	3 : 7	1.05	1.12	0.9	45
4	5 : 5	1.07	1.14	8.1	48
5	7 : 3	1.41	1.27	9.4	51
6	9 : 1	1.04	1.37	3.8	58

\* Polymerization conditions: solvent, dioxane; temperature, 65°C; polymerization time, 72h; conversion, <10%.

\*\* the values derived from the NMR data

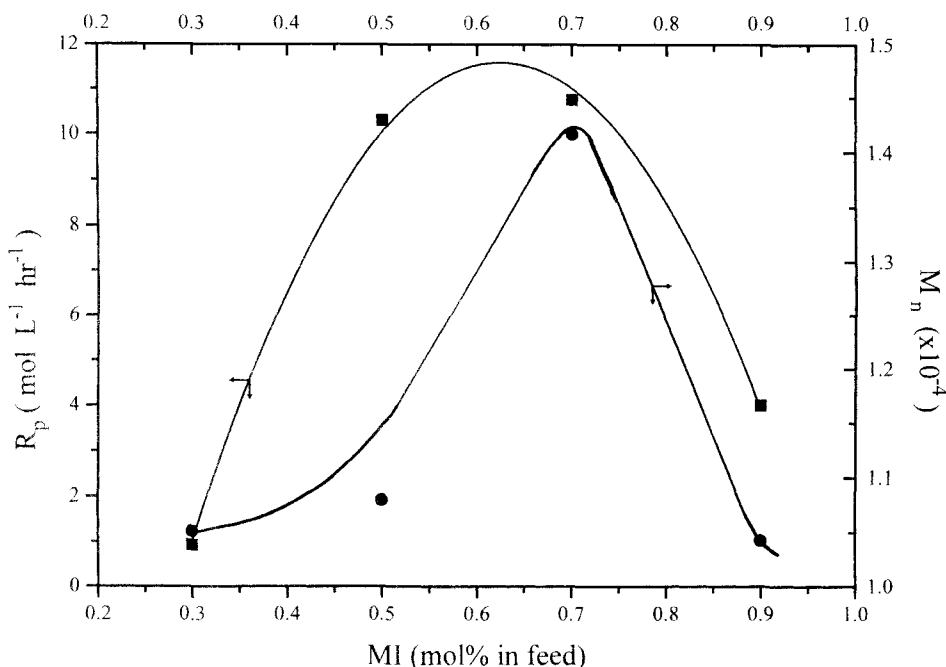
derived, which is shown in Figure 1. A maximum initial rate of copolymerization occurs at about 3:2 of monomer feed ratio (M<sub>1</sub>/M<sub>2</sub>) and a maximum M<sub>n</sub> at about 7:3, which is different from many other alternating copolymerization system in which a maximum only appeared at about 1:1 monomer feed composition [14].

### Measurement of Monomers Activity Ratios and Q, e Values

Monomers activity ratios of M<sub>1</sub> and M<sub>2</sub> were measured by Fineman-Ross method (intercept-slope method) [15] and Kelen-Tudos method [16], respectively at low conversion of the monomers (<10%), both of them are coincident, which is shown in Table 2. The  $r_1=0.048\pm0.016$  and  $r_2=0.12\pm0.012$ . In order to ascertain which one is donor, and which one is acceptor, the Q, e values of the monomers were calculated, which represent the stabilization and polarity of the monomers respectively [17]. Q<sub>2</sub> found to be 0.43 and e<sub>2</sub> -0.92. For maleimide, the literature values of Q and e, 0.44 and 1.35, respectively, are used [18]. A negative value of e indicates that monomer M<sub>2</sub> is a donor. Therefore, in this system M<sub>2</sub> is electron-donor and M<sub>1</sub> is electron-acceptor.

### Copolymerization Mechanism and Characterization of Copolymer

In the copolymerization of M<sub>1</sub> and M<sub>2</sub>, no initiator was used. When the two monomers were just mixed, it was colorless, then it turned slowly to deep yellow in

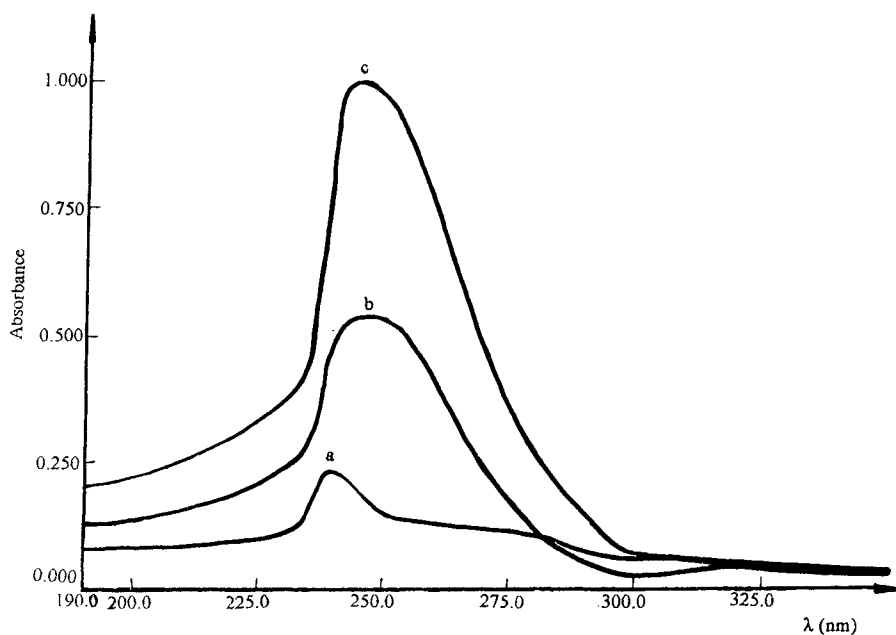


**Figure 1.** Relationship of Initial Polymerization Rate ( $R_p$ ) and Molecular Weight ( $M_n$ ) with Monomers Feed Ratio.

TABLE 2. 2 Measurements of Monomers Activity Ratios of MI ( $r_1$ ) and EAP ( $r_2$ )

	$r_1$	$r_2$
Fineman-Ross Method	$0.051 \pm 0.001$	$0.14 \pm 0.022$
Kelen-Tudos Method	$0.048 \pm 0.016$	$0.12 \pm 0.012$

one day. It has been well known that electron donor-acceptor complexes exist in many copolymerization systems, such as maleic anhydride/styrene, maleic anhydride/vinyl ethers and maleic anhydride/vinyl sulfides [19]. In some of these systems, radical alternating copolymerization has been known to be induced spontaneously. In order to determine the mechanism of the initiation reaction the interaction between  $M_1$  and  $M_2$  was investigated by UV. Figure 2 shows the UV spectra of the  $M_1$ ,  $M_2$  and the mixture of  $M_1$  and  $M_2$  in dioxane, in which no new peaks for the mixture were detected in long wavelength direction, although the existence of the



**Figure 2.** UV Spectra of  $M_1$  (a),  $M_2$  (b), and Mixture of  $M_1$  and  $M_2$  (c) (solvent: dioxane; concentration:  $5 \times 10^{-5}$  mol/L).

new peaks is always taken as a evidence for the formation of a charge transfer complex. Yamada *et al.* [20] also found that no charge transfer complex was found in the case of N-alkylmaleimides and styrene, and the alternating copolymer was formed by a contact-type CTC between them. Otsu *et al.* reported [21] a system of isobutyl vinyl sulfide, a strong electron-donating monomer, and methyl acrylate or acrylonitrile, a weak electron-accepting monomer, which did not show any evidence for the CTC formation spectroscopically either, however, the spontaneous copolymerization can proceed.

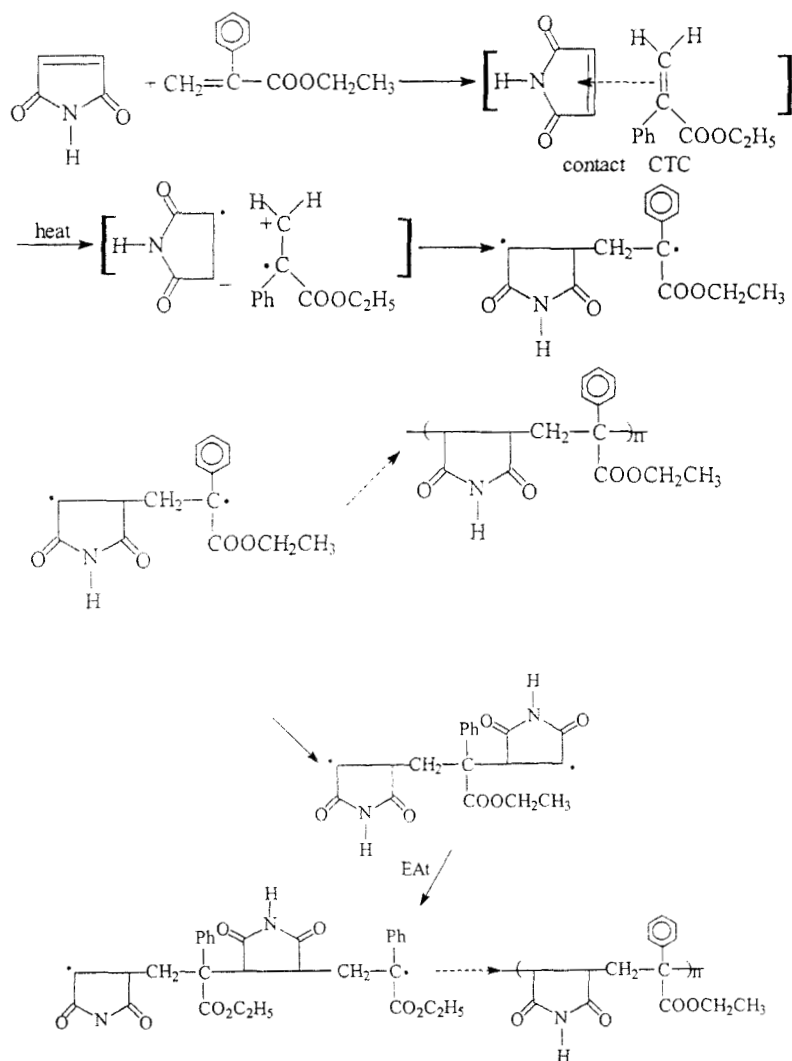
In our system, however, the weak contact-type CTC could be confirmed spectroscopically, the absorbance of mixture of  $M_1$  and  $M_2$  as Figure 2 shows is much higher than that of the corresponding  $M_1$  and  $M_2$ , the molar extinction coefficient for the former is  $1.84 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ , and for  $M_1$  and  $M_2$  is  $1.0 \times 10^4$ ,  $0.34 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ , respectively. It means that a specific interaction exists when the  $M_1$  and  $M_2$  are mixed, which induced the increase of the absorbance.

As we described in the above-mentioned section, the maximum initial copolymerization rate and maximum copolymer molecular weight appeared at 3:2



and 7:3 ( $M_1/M_2$ ) of monomer feed ratio separately, and if the chain propagation in alternating copolymerization system is conducted strictly on the CTC, then these maximum values should occur at 1:1 of monomers feed ratio. It means that there may exist another addition mode besides CTC mechanism in our system, the monomers may be propagated in alternative addition. In another systems such as maleic anhydride-vinyl acetate [22], maleic anhydride-divinyl ether [23], and maleic anhydride-styrene [24], the same phenomenon were observed.

Therefore, in our copolymerization system, the mechanism of CTC and alternative addition of the monomers might be co-existed. It can be described as follows:



Scheme II

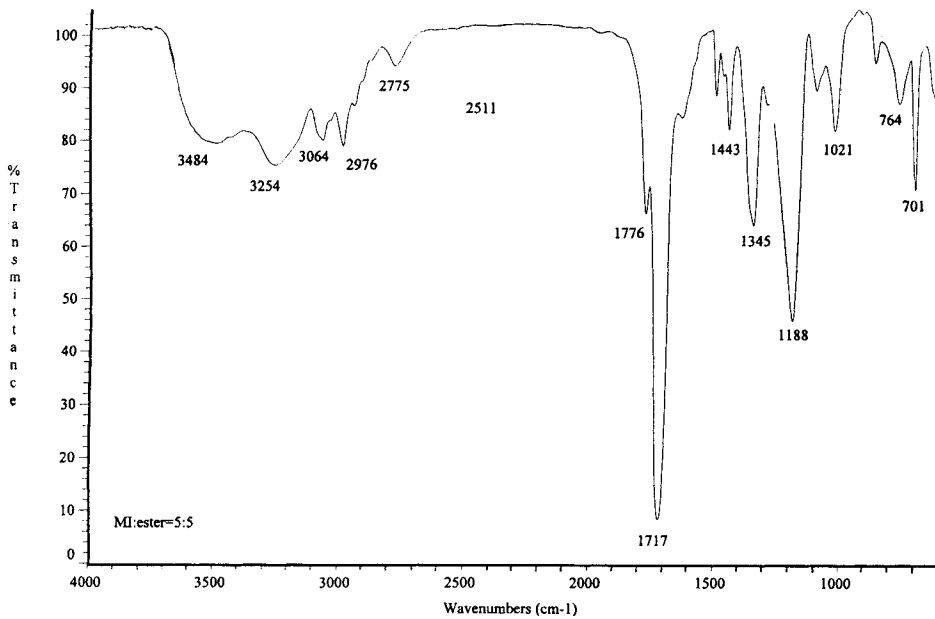


Figure 3. IR Spectrum of Copolymer.

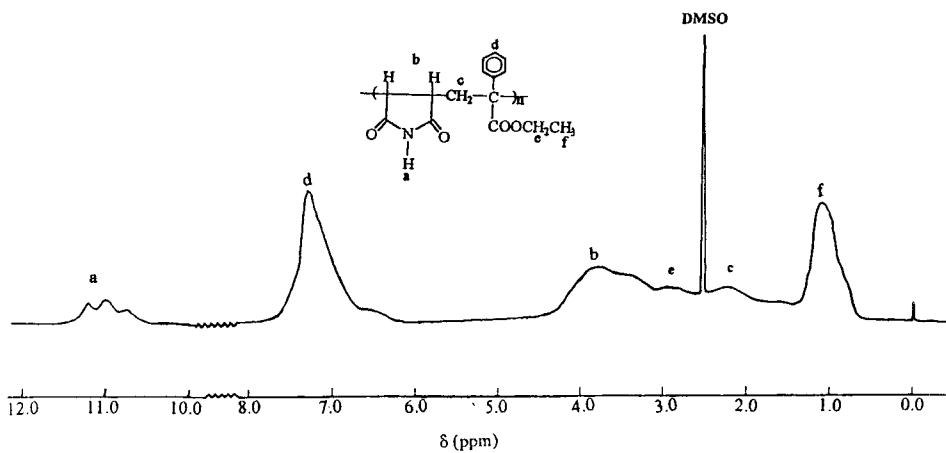
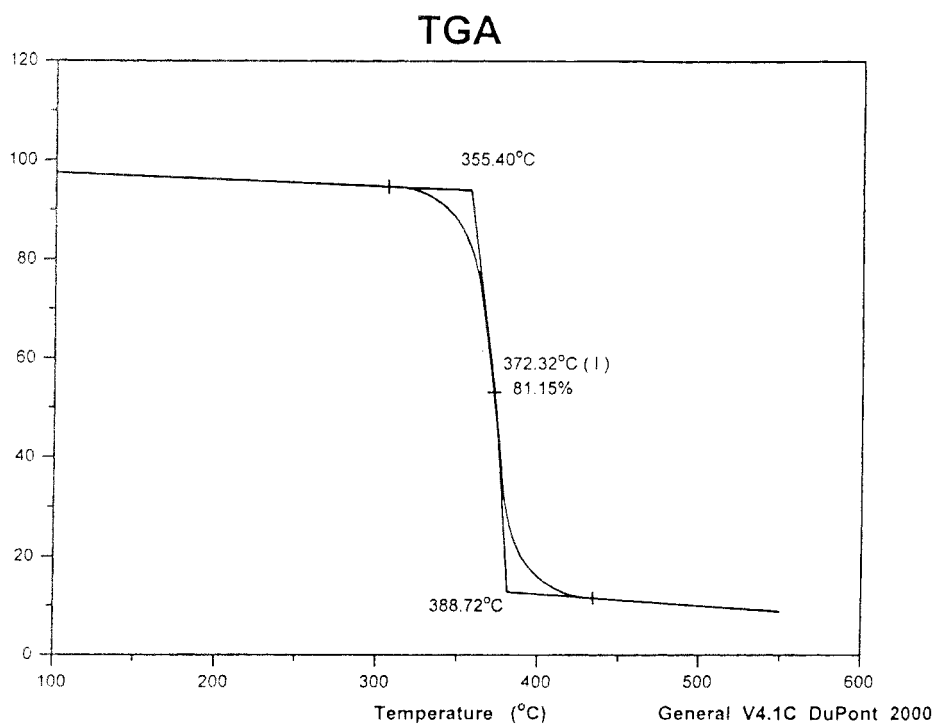


Figure 4.  $^1\text{H}$  NMR Spectrum of Copolymer.

Figure 3 showed the IR spectrum of copolymer, the typical absorption peaks such as 3488, 3258 (NH in MI), 1779, 1634 (C=O of MI), 1719 (C=O of EAP) and 764, 701  $\text{cm}^{-1}$  (monosubstituted benzene) appeared. We could also derive the structure information from the NMR spectrum of the copolymer, where all the resonance signals of protons corresponding with the alternating structure of the



**Figure 5.** TGA Measurement of Copolymer.

**TABLE 3.** Thermo-stability of Copolymers

Sample No.	Feed Ratio (M <sub>1</sub> /M <sub>2</sub> , mol/mol)	T <sub>i</sub> (°C)	T <sub>max</sub> (°C)	T <sub>f</sub> (°C)
3	3:7	349.5	372.1	383.2
4	5:5	355.4	372.3	388.7
5	7:3	362.8	383.3	395.4
6	9:1	362.1	375.1	385.9
PEAP*	---	289.0	305.0	322.0
PMI**	---	420.1	438.5	461.8

\* Polyethyl atropate

\*\* Polymaleimide

copolymer were found in Figure 4, such as 10.6-11.8(1H, NH in MI), 3.4-4.2 (2H, -CH- connected with C=O for MI), 6.2-8.0 (5H, benzene ring), 2.8-3.2 (2H, -OCH<sub>2</sub>-), 1.4-2.4 (2H, -CH<sub>2</sub>- for EAP) and 0.6-1.2 (3H, -CH<sub>3</sub>), the ratio of peak square is 1:2:5:2:2:3.

### Thermal Stability of the Copolymers

TGA analysis of the copolymers were performed to evaluate their thermal stability. Figure 5 shows the measurement results from which the initial decomposition temperature ( $T_i$ ), final decomposition temperature ( $T_f$ ) and the temperature of maximum rate of weight loss ( $T_{max}$ ) are summarized in Table 3. It can be observed that the thermal stability of the alternating copolymer of MI and EAP are quite high.

## CONCLUSION

The alternating copolymerization of maleimide ( $M_1$ ) and ethyl atropate ( $M_2$ ) was carried out without initiator at 60°C, the monomers activity ratio  $r_1 = 0.048 \pm 0.016$  and  $r_2 = 0.12 \pm 0.012$  are obtained. The formation of weak contact-type charge transfer complex between them was confirmed by UV spectra. A mixed mechanism involving the "CTC addition" and "cross propagation" of  $M_1$  and  $M_2$  for this system is suggested. The TGA measurements show the high thermal stability of the copolymers.

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