

# Radical Polymerization of *N*-[(1-*n*-butoxycarbonyl)ethyl]maleimide

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**ABSTRACT:** Poly(*N*-[(1-*n*-butoxycarbonyl)ethyl]maleimide) (PBAM) was synthesized by solution polymerization with 2,2'-Azobis(isobutyronitrile) (AIBN) as radical initiator. The resulting polymer (PBAM) was characterized by infrared spectroscopy (IR), thermogravimetry (TG), and differential thermal analysis (DTA). The initial decomposition temperature of PBAM is 321.6°C; the glass transition temperature of PBAM was 240.5°C. The effects of solvent, temperature, initiator concentration ([I]), and monomer concentration ([BAM]) on polymerization were also discussed. The overall activation energy ( $E_a$ ) of homopolymerization was determined ( $E_a = 93.5$  kJ/mol). It was revealed that the rate of polymerization ( $R_p$ ) can be expressed as  $R_p \propto [I]^{0.58}[\text{BAM}]$ . © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 424–427, 2001

**Key words:** *N*-substituted maleimide; solution polymerization; *N*-[(1-*n*-butoxycarbonyl)ethyl]maleimide; homopolymerization; heat-resistant polymer

## INTRODUCTION

*N*-Substituted maleimides have become interesting monomers, which can be either radically copolymerized with other vinyl monomers<sup>1,2</sup> or homopolymerized<sup>3</sup> despite their 1,2-disubstituted ethylene structure. Because of the five-membered ring structure hindered from the free rotation of poly(*N*-Substituted maleimide), they have excellent thermal stability.<sup>4</sup> They are excellent heat-resistant modifier polymers that can be commercially produced.<sup>5</sup>

The poly(*N*-[(1-*n*-butoxycarbonyl)ethyl]maleimide) synthesized in this paper bears a ester polar group in the side chain. Therefore, the solubility and toughness are improved and thermal stability is superior to *N*-alkyl-maleimides.<sup>6</sup> This

polymer will open a new path for blend, modifier, and functional polymer material.

## EXPERIMENTAL

### Materials

BAM was synthesized and purified according to ref. 7; 2,2-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol; other materials were analytically pure.

### Homopolymerization

Radical homopolymerization was performed with AIBN as a radical initiator in a sealed glass tube at 60°C. The sample was timing taken out and cooled with ice to stop reaction. After polymerization, the polymer solution was poured into excess ethanol to precipitate the polymer. The polymer was filtered by reprecipitation twice from chloroform solution to excess ethanol, and dried *in*

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**Table I** The Effects of Solvent  $[I] = 2.0 \times 10^{-2}$  mol/L,  $[BAM] = 1.0$  mol/L,  $T = 60^\circ\text{C}$ 

Solvent	$\epsilon$	$Y * 100$	$[\eta]$ (dL/g)
DMF	36.71	0	
THF	7.6	0	
Acetone	20.7	3.2	
Chloroform	4.9	58.2	0.596
Benzene	2.3	53.3	0.536
Toluene	2.4	49.6	0.347
Dioxane	2.09	0	
Decalin	0	2.6	

*vacuo* until the weight was stable. The polymer was isolated as white powder.

### Characterization

Infrared spectrum of PBAM was recorded on a Perkin-Elmer 1710 Fourier Transform spectrometer.

The TG and DTA curves were recorded on a Shimadzu DT-40 analyzer.

The intrinsic viscosity  $[\eta]$  was measured by Ubbelohde viscometer with benzene as solvent at  $30^\circ\text{C}$ .

## RESULTS AND DISCUSSION

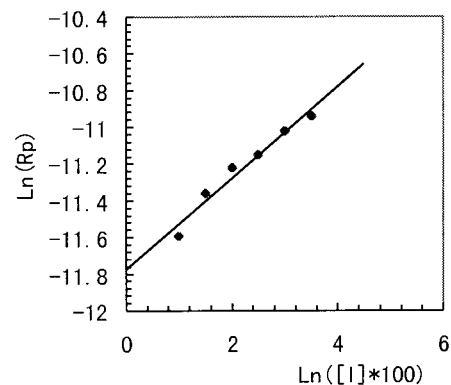
### The Effects of Solvent on Yield and Intrinsic Viscosity $[\eta]$

The polymerization was carried out with AIBN ( $2.0 \times 10^{-2}$  mol/L) as an initiator in different solvent at a constant monomer concentration ( $[BAM] 1.0$  mol/L) at  $60^\circ\text{C}$  for 16 h. The results are summarized in Table I.

The results in Table I show that BAM cannot be polymerized in a solvent with high dielectric constant ( $\epsilon$ ) such as *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), and acetone. Dioxane is a low dielectric constant but has a lone

**Table II** The Effects of  $[I]$  on  $R_p$  and  $[\eta]$  in Benzene at  $60^\circ\text{C}$ 

	1.0	1.5	2.0	2.5	3.0	3.5
$R_p \times 10^5$ (mol/L · s)	0.925	1.162	1.338	1.440	1.633	1.773
$[\eta]$ (dL/g)	0.729	0.636	0.536	0.482	0.438	0.392

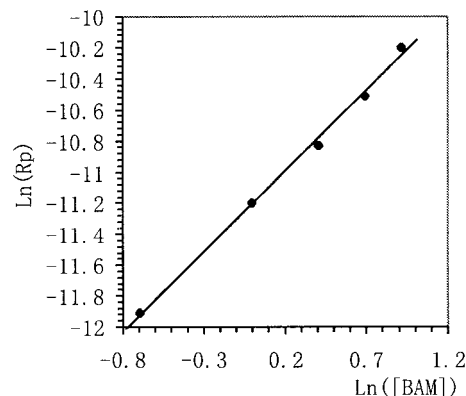

**Figure 1** The plot of  $\ln(R_p)$  against  $\ln([I] \times 100)$  in benzene at  $60^\circ\text{C}$ ,  $[BAM] = 1.0$  mol/L.

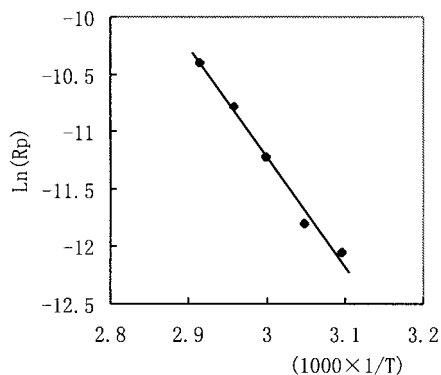
electron pair; however, the degradative chain transfer may result in no polymer formation. The reason that the polymerization yield was higher in chloroform than in benzene and toluene lies in the fact that chloroform was an electron-acceptor solution but benzene and toluene are electron-donor solutions. The polymerization yield should have been high in decalin, which is a low dielectric constant and which has no lone electron pair. However, BAM was not soluble in decalin, so the yield was too low.

### The Effects of Initiator and Monomer Concentration on Polymerization

The initial polymerization rate ( $R_p$ ) increased with the increasing of initiator concentration ( $[I]$ ) but  $[\eta]$  decreased. The results of  $R_p$  in different initiator concentrations were shown in Table II ( $T = 60^\circ\text{C}$ ,  $[BAM] = 1.0$  mol/L).

From the plot (Fig. 1) of  $\ln(R_p)$  against  $\ln([I]$


**Figure 2** The plot of  $\ln(R_p)$  against  $\ln([BAM])$  in benzene at  $60^\circ\text{C}$ ,  $[I] = 2.0 \times 10^{-2}$  mol/L.



**Figure 3** The plot of  $\ln(R_p)$  against  $(1000 \times 1/T)$ .

$\times 100$ ), a straight line was obtained and the slope is 0.58, i.e.,  $R_p \propto [I]^{0.58}$ . This means that the main way of termination of the polymerization process is bimolecular termination.

From the plot (Fig. 2) of  $\ln(R_p)$  against  $\ln[BAM]$ , a straight line was obtained, whose slope was 1.0. This means  $R_p \propto [BAM]$ .

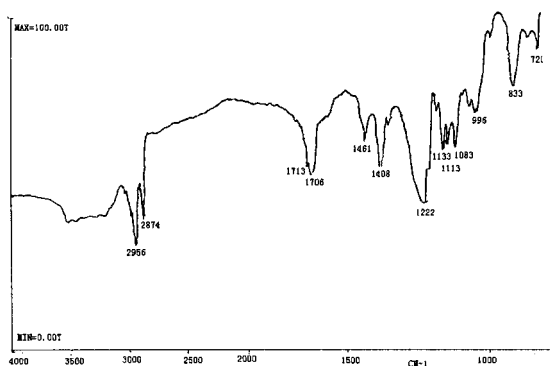
### The Effects of Temperature

To obtain the overall activation energy of polymerization,  $R_p$  was investigated in benzene at 45–70°C with  $[I] = 2.0$  mol/L and  $[BAM] = 1.0$  mol/L.

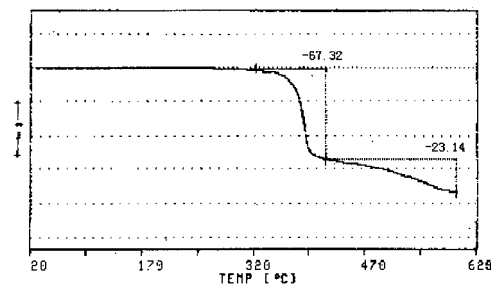
Figure 3 was the plot of  $\ln(R_p)$  against  $1000 \times 1/T$ . The overall activation energy ( $E_a$ ) was calculated from the slope of Figure 2 ( $E_a = 93.5$  kJ/mol). The energy of chain initiation of AIBN ( $E_d$ ) is 125.6 kJ/mol, so the energy of propagation reaction ( $E_p = E_a - E_d/2$ ) is 30.7 kJ/mol.

### The IR Spectrum of PBAM

Figure 4 is the IR spectrum of poly(*N*-[(1-*n*-butoxycarbonyl)ethyl]maleimide). IR ( $\text{cm}^{-1}$ ): 2956



**Figure 4** The IR spectrum of PBAM.



**Figure 5** The TG curve of PBAM.

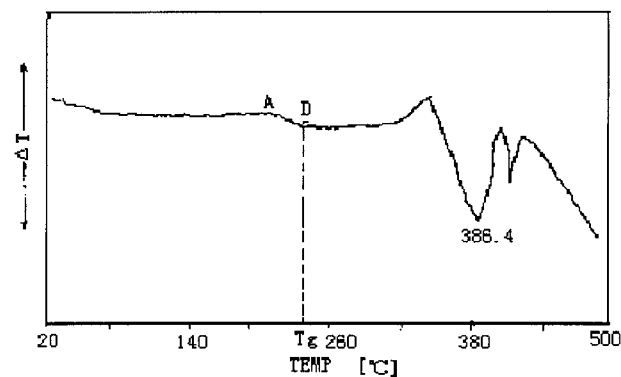
and 2874(H—C=C—H); 1713 and 1706 (C=O); 1408 and 1113(C—N), 1222(C—O); 1461(CH<sub>3</sub>); 720 ((CH<sub>2</sub>)<sub>n</sub>). Compared with the IR spectrum of monomer BAM,<sup>7</sup> other peaks appear at the appropriate position except that the characteristic peaks of the double bond (3102, 1593, 693) disappear.

### Thermal Analysis

Figure 5 is the TG curve of PBAM. There are two stages of weight loss. The initial decomposition temperature in the first stage was 321.6°C, the maximum decomposition temperature is 417.5°C. In the second stage, the minimum decomposition temperature is 417.5°C, the maximum decomposition temperature is 593.4°C. The TG curve shows that the PBAM has excellent thermal stability.

Figure 6 was the DTA curve of PBAM. It shows that PBAM has a high glass transition temperature ( $T_g = 240.5^\circ\text{C}$ ).

The special structure of PBAM with a five-member ring hindered from the internal rotation of polymer chain. Therefore, the decomposition temperature and glass transition temperature are very high.



**Figure 6** The DTA curve of PBAM.

## CONCLUSION

1. PBAM was successfully synthesized in benzene with AIBN as the radical initiator at 60°C.
2. The effects of solvent, initiator, and monomer concentration on the reaction were discussed. The initial polymerization rate ( $R_p$ ) can be expressed as  $R_p \propto [\text{AIBN}]^{0.59}[\text{BAM}]$ . The overall activation energy was determined ( $E_a = 93.5 \text{ kJ/mol}$ ).
3. PBAM was characterized by IR, TG, and DTA.

## REFERENCES

1. Iwatsuki, S.; Yamashita, Z., Prog Polym Sci Jpn 1977, 2, 1.
2. Oishi, T.; Fugimoto, M. J Polym Sci Part A Polym Chem 1992, 30, 1821.
3. Matsumoto, A.; Kubota, T.; Otsu, T. Macromolecules 1990, 23, 4508.
4. Otsu, T.; Matsumoto, A.; Kubota, T.; Mori, S. Polym Bull 1990, 23, 43.
5. Shan, G. R; Wang, Z. X.; Huang, Z. M.; Polym Mater (in Chinese) 1996, 2, 36.
6. Barrales-Rienda, J. M., et al. Br Polym J 1977, 9, 6.
7. Ai, J. Y.; Liu, P. S. Elastomerics (in Chinese) 2000, 1, 13.