# Reactivity Ratios of N-cyclohexylmaleimide and Methylmethacrylate by Infrared Spectroscopy

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ABSTRACT: The copolymerization of N-cyclohexylmaleimide (CHMI) and methylmethacrylate (MMA) with azobisisobutyronitrile as the initiator was investigated. Infrared spectroscope was applied to determine the copolymer compositions of the copolymers synthesized at 60, 70, 80, and 90°C while the conversions of the copolymerizations were controlled to be below 10%. According to the Mayo-Lewis equation, the reactivity ratios of N-cyclohexylmaleimide and methylmethacrylate were calculated. It was proved that N-cyclohexylmaleimide was less reactive, and the optimum temperature of the copolymerization was 80°C. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 516-522, 1999

**Key words:** reactivity ratio; infrared spectroscopy; *N*-cyclohexylmaleimide; methylmethacrylate

# **INTRODUCTION**

Poly(methylmethacrylate) (PMMA) has many excellent properties, such as colorlessness, high light transmittancy, chemical resistance, weathering corrosion resistance, and dimensional stability; therefore, it is used for various applications in glazing and optical uses.<sup>1</sup> However, PMMA has low heat resistance, and its heat deflection temperature is as low as 96°C. Recently, further improvement in the heat-resistant property has been strongly desired.<sup>2,3</sup> The copolymerization of N-cyclohexylmaleimide (CHMI) and methylmethacrylate (MMA) has been known as one of the best ways to enhance the heat resistance of PMMA. The incorporation of rigid polar maleimide units in the backbones increases the backbone rigidity and molecular interactions, so the glass transition temperature of the copolymer is increased greatly. Moreover, the copolymer exhibits a higher thermal degradation temperature than

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Journal of Applied Polymer Science, Vol. 74, 516-522 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/030516-07 PMMA. However, the coloration of the copolymer at high temperature (230°C) has been pointed out as an undesirable characteristic, because monomeric CHMI tends to cause coloration. Owing to steric hindrance and polar effect, it is difficult for CHMI to copolymerize with MMA, and residual CHMI has a high concentration in the copolymer. Therefore, the reaction compositions and conditions were crucial to the copolymerization of MMA and CHMI. When the reactivity ratios of CHMI and MMA were calculated, we designed the copolymerization by varying the reaction compositions and temperatures accordingly and reduced the concentration of residual CHMI in the copolymer to be below 0.5%. Thus, colorless copolymers were synthesized successfully. In this article, the reactivity ratios of CHMI and MMA were determined by infrared spectroscopy, because infrared spectroscopy has the advantages of sensitivity, rapidity and less complication.

#### **EXPERIMENTAL**

#### Materials

CHMI was prepared by a procedure described by Kita<sup>5</sup> and recrystallized from chloroform, then

Lable I Cop	olymeri	zation c	DI CHIMI	and MIN	IA at Ull	Terent	empera	rures								
Number	60.1	60.2	60.3	60.4	70.1	70.2	70.3	70.4	80.1	80.2	80.3	80.4	90.1	90.2	90.3	90.4
Reaction temperature																
(0°C)	60	60	60	00	70	70	70	70	80	80	80	80	90	06	06	00
Weight ratio CHMI (g):																
MMA (g)	10:40	15:35	20:30	25:25	10:40	15:35	20:30	25:25	10:40	15:35	20:30	25:25	10:40	15:35	20:30	25:25
Reaction																
time (min)	06	06	06	06	17	17	17	17	9	9	9	9	2	2	2	7
Conversion																
(wt %)	7.4	7.0	6.8	6.3	7.8	7.6	7.3	6.9	6.9	6.7	6.4	6.1	7.6	7.3	7.1	7.0
AIBN (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

dried under reduced pressure in a vacuum oven at room temperature for 4 hours. MMA was purified by washing successively with 5% NaOH and distilled water, dried with anhydrous  $Na_2SO_4$  and finally distilled at reduced pressure at 60°C. Azobisisobutyronitrile (AIBN) was recrystallized from chloroform. Solvent methanol was refluxed along with CaO for 5 hours and distilled.

## Copolymerization

The copolymerization of CHMI and MMA was carried out by bulk copolymerization method using AIBN as the free radical initiator in nitrogen atmosphere. A four-necked, round-bottom flask (250 mL) was equipped with a reflux condenser, a nitrogen gas inlet tube, and a thermometer. The assembly was placed in a thermostatted water bath and stirred by a mechanical stirrer. Nitrogen was passed through the reaction mixture continually. Different amounts of CHMI, MMA, and AIBN were fed according to Table I. The reaction temperatures were 60, 70, 80, and 90°C, and other reaction conditions were also summarized in Table I. After the copolymerization, the copolymers were washed with fresh methanol (50 mL) four times, and then the copolymers obtained were purified twice by dissolving in acetone (100 mL) and reprecipitating with methanol (100 mL). The purified copolymers were dried in vacuum at 60°C for 48 h.

### Characterization

Infrared analysis was performed by using Nicolet-5DXC Mattson 1000. Fourier transform infrared (FTIR) spectrometer (resolution:  $4 \text{ cm}^{-1}$ , scan: 10 times; Nicolet Corp., Japan). Thin transparent copolymer films were prepared by casting 5% tetrahydrofuran solutions of the copolymers on KBr plates, followed by solvent evaporation at room temperature for 4 hours.

# **RESULTS AND DISCUSSION**

According to the Lambert-Beer equation: A = KCL, where A = absorbance, K = absorptivity, C = concentration, and L = thickness;  $A_1$  (the absorbance of CHMI in the copolymer) and  $A_2$  (the absorbance of MMA in the copolymer) were linear to  $C_1$  (the concentration of CHMI in the copolymer) and  $C_2$  (the concentration of MMA in



Figure 1 Infrared spectra of PMMA and poly(CHMI-MMA) (18% wt, CHMI).

the copolymer), respectively, and the relations were depicted as follows.

$$A_1 = K_1 C_1 L_1 \tag{1}$$

$$A_2 = K_2 C_2 L_2 \tag{2}$$

Dividing eq. (1) into eq. (2), we got

$$\frac{A_1}{A_2} = \frac{K_1}{K_2} \times \frac{C_1 L_1}{C_2 L_2}$$
(3)

To the same sample,  $L_1 = L_2$  and  $C_1 + C_2 = 1$ .

Let  $K = (K_1/K_2)$ , thus eq. (4) would be described as follows:

$$\frac{A_1}{A_2} = K \times \frac{C_1}{C_2} \tag{4}$$

From the infrared spectra,  $A_1$  and  $A_2$  could be calculated. K was a constant determined by the wave frequency, material of the sample and the sample pattern.<sup>6</sup> So, after K was known,  $C_1/C_2$ would be determined easily according to eq. (4).

Figure 1 shows the infrared spectra of PMMA and poly(CHMI-MMA) (18% wt CHMI). In contrast with the infrared spectrum of PMMA, a characteristic peak appeared around 1710 cm<sup>-1</sup> in the infrared spectra of poly(CHMI-MMA). This characteristic peak was the peak of stretching vibration absorption of carboxyl groups of CHMI in the copolymer. By calculating the absorbance of this peak and the peak of carboxyl groups of

PMMA at 1730 cm<sup>-1</sup>, we could determine the concentrations of CHMI and MMA in the copolymers. That is to say:  $A_1$  = the absorbance of CHMI carboxyl groups and  $A_2$  = the absorbance of MMA carboxyl groups. Peak 1 and peak 2 were magnified and shown in Figure 2.

As is known, the infrared absorbance peak should be symmetrical. So the integrate curves of peak 1 and peak 2 were completed by adding the dotted curves (Fig. 3). We found that peak 1 had no effect on peak 2, but peak 2 affected peak 1 somewhat. According to the baseline method, by depicting the baseline 1', the absorbance of peak 2 were calculated easily from Figure 3.

As to peak 1, the effect of peak 2 had to be taken in consideration, and the absorbance of Peak 1 was calculated as follows:  $A_1 = 0.8522 - 0.2925$ = 0.5597. Using eq. (4), where  $A_1 = 0.5597$ ;  $A_2$ = 1.0395,  $C_1 = 0.1006$ , and  $C_2 = 0.82$ ;

$$K = \frac{A_1}{A_2} \times \frac{C_2}{C_1} = \frac{0.5597 \times 0.82}{1.0395 \times 0.1006} = 4.3888.$$

Similarly, we calculated the absorptivity of Poly (CHMI-MMA) (25% wt CHMI), which was 4.4572.

Thus, the absorptivity of the experiment was determined by averaging both absorptivities as follows:

$$K = \frac{4.3888 + 4.4572}{2} = 4.423$$

Absorbance peaks of carboxyl groups of CHMI and MMA in the copolymers synthesized at 60°C, 70°C, 80°C, and 90°C are shown in Figure 4.

It was evident that with the increases of CHMI contents, peak 1 rose correspondingly. The other copolymers synthesized at 60, 70, and 90°C had similar tendencies. The absorbances of carboxyl groups of CHMI and MMA of all the copolymers are summarized in Table II. Using these data and letting K = 4.423, according to eq. (4), the concentrations of CHMI and MMA in the copolymers were obtained, and these results are also shown in Table II.

From Table II, it was seen that with the increases of CHMI contents in the feeds, the values of  $A_{\rm CHMI}/A_{\rm MMA}$  increased correspondingly, values of

$$\frac{d[M_1]}{d[M_2]}$$

showed evident increases. However, for sample 60.3 and sample 60.4, the difference of the

$$rac{d[M_1]}{d[M_2]}$$

values was little. That is to say, the increasing of CHMI contents from 40% wt to 50% wt had little effect on

$$rac{d[M_1]}{d[M_2]}$$

values.

Although the glass transition temperatures of the copolymers increased with the increases of



Figure 2 Magnified absorbance peaks of carboxyl groups of MMA and CHMI (18% wt CHMI).



**Figure 3** Effects of peak 1 and peak 2 on each other's absorbances by the baseline method (18% wt CHMI in the copolymer); 1'. the baseline;  $A_2 = 1.1987 - 0.1592 = 1.0395$ .

CHMI concentration in the copolymer,<sup>7</sup> it was meaningless to enhance CHMI contents in the feeds to produce PMMA with higher heat resistance when the reaction temperature was as low as  $60^{\circ}$ C, and the CHMI content in the feed was 40%. As to the samples synthesized at 70, 80, and  $90^{\circ}$ C, the maximum CHMI contents for the copolymerization was beyond 50% wt. So, the reaction temperature was an important factor for the copolymerization of CHMI and MMA. However, when a large amount of CHMI was incorporated in the copolymer, the impact strength would decrease greatly, and the cost would rise.

In Table II, we also found that the

$$rac{d[{M_1}]}{d[{M_2}]}$$

value of sample 60.1 was the largest among sample 60.1, sample 70.1, sample 80.1, and sample 90.1 in which the CHMI content in the feed was 20% wt. While the

$$\frac{d[M_1]}{d[M_2]}$$

value of sample 80.4 was larger than those of sample 60.4, sample 70.4, and sample 90.4. It



**Figure 4** Absorbance peaks of carboxyl groups of CHMI and MMA in the copolymers synthesized at 60, 70, 80, and 90°C (CHMI: peak 1; MMA: peak 2).

Table II Ex	perimen	ital Resu	ults of th	e Copoly	ymers											
Number	60.1	60.2	60.3	60.4	70.1	70.2	70.3	70.4	80.1	80.2	80.3	80.4	90.1	90.2	90.3	90.4
Absorbance of $C_{\rm HMI}$ $C_{\rm HMI}$ $(A_{\rm CHMI})$ Absorbance of MMA	0.9622	0.7038	1.2135	0.8530	0.6080	0.8750	0.7914	1.1227	0.1556	1.1330	1.3325	1.5430	0.7635	0.8534	1.2909	0.7943
$(A_{ m MMA}) \ A_{ m CHMI} / A_{ m MMA}$	$1.1546 \\ 0.8334$	$0.7717 \\ 0.912$	1.1242 1.0794	0.7899 1.0798	$1.0179 \\ 0.5991$	$1.2652 \\ 0.7094$	0.6918 1.0399	0.8348 1.3449	$0.2380 \\ 0.6580$	$1.4071 \\ 0.8052$	1.2623 1.0556	$1.1345 \\ 1.3601$	$1.1756 \\ 0.6494$	$1.1095 \\ 0.7692$	$1.2446 \\ 1.0372$	$0.6110 \\ 1.3$
$[M_1]/[M_2]$	0.1400	0.2394	0.3724	0.5587	0.1400	0.2394	0.3724	0.5587	0.1400	0.2394	0.3724	0.5587	0.1400	0.2394	0.3724	0.5587
$d[M_1]/d[M_2]$	0.1884	0.2062	0.2440	0.2441	0.1355	0.1604	0.2351	0.3040	0.1488	0.1820	0.2387	0.3075	0.1468	0.1739	0.2345	0.2939
X	10.0	4.0	1.8	0.8	7.0	2.8	1.2	0.97	7.6	3.2	1.7	0.9	7.5	3.0	1.7	0.9
$Y_i$	2-	-4	-2.5	-1.5 -		-4.0 -	-2.5	-1.5	- 2-	-4	-2.4	-1.5		-4.0 -	-2.5	$^{-1.5}$
$d[M_1]$ : the c	oncentratic	on of CHM	II in the c	polymer.												

 $d[M_1]$ : the concentration of CHMI in the copolymer.  $d[M_2]$ : the concentration of MMA in the copolymer.  $[M_1]$ : the concentration of CHMI in the feed.  $[M_2]$ : the concentration of MMA in the feed. suggested that the reaction composition also had important effect on the copolymerization of CHMI and MMA, and the reaction conditions had to be determined according to the reaction composition.

According to the Mayo-Lewis equation

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}$$
(5)

eq. (6) was derived as follows:<sup>8</sup>

$$\frac{\rho - 1}{R} = r_1 - r_2 \frac{\rho}{R^2} \tag{6}$$

where

$$ho = rac{d[M_1]}{d[M_2]}, \ R = rac{[M_1]}{[M_2]},$$

 $r_{1}$  was reactivity ratio of CHMI, and  $r_{2}$  was reactivity ratio of MMA. Let

$$X=\frac{\rho}{R^2}, \ Y=\frac{\rho-1}{R},$$

the values of X and Y were calculated and are shown in Table II.

Thus, four plots were obtained and were depicted in Figure 5. The intercepts and the slopes of these four straight lines were  $r_1$  and  $-r_2$ , respectively, at different temperatures. We found  $r_1$  has the largest value of 0.23 at 80°C. In other words, the reaction temperature of 80°C was the optimum temperature for the copolymerization of CHMI and MMA. When the reaction compositions and other conditions were determined, this lead to the smallest residual concentration of CHMI in the copolymer, which will be studied in another paper.

# CONCLUSIONS

It was difficult for CHMI to copolymerize with MMA, and the largest value of  $r_1$  at 80°C was 0.23, and at 60°C,  $r_1$  had a value as small as 0.07. With the increases of the CHMI contents in the feeds, the concentrations of CHMI in the copolymers evidently rose at 70, 80, and 90°C. However, at 60°C, the concentration of CHMI in the copolymer showed little increase when the CHMI contents in the feeds rose from 40% wt to 50% wt. 40% wt was almost the



Figure 5 Plots on the reactivity ratios of MMA and CHMI at 60, 70, 80, and 90°C.

largest content of CHMI in the feed for the copolymerization at 60°C. The reaction composition also had important effect on the copolymerization of CHMI and MMA. To synthesize colorless heatresistant PMMA, both reaction temperature and reaction composition had to be taken into account.

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