

# Kinetics for Copolymerization of Methyl Methacrylate with *N*-Cyclohexylmaleimide

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**ABSTRACT:** The kinetics for the radical copolymerization of methyl methacrylate (MMA) with *N*-cyclohexylmaleimide (NCMI) was investigated. The initial copolymerization rate  $R_p$  is proportional to the initiator concentration to the power of 0.54. The apparent activation energy of the overall copolymerization was measured to be 69.0 kJ/mol. The monomer reactivity ratios were determined to be  $r_{\text{NCMI}} = 0.42$  and  $r_{\text{MMA}} = 1.63$ .  $R_p$  reduces slightly, and the molecular weight of the resultant copolymer decreases with increasing the concentration of the chain transfer agent *N*-dodecane-thiol (RSH). The more the transfer agent, the narrower the molecular weight distribution of the resulting copolymer. The following chain-transfer constant of RSH for the copolymerization of MMA with NCMI in benzene at 50°C was obtained:  $C_s = 0.23$ . The glass transition temperature ( $T_g$ ) of the copolymer increases with increasing  $f_{\text{NCMI}}$ , which indicates that adding NCMI can improve the heat resistance of Plexiglas. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1293–1297, 1999

**Key words:** methyl methacrylate; *N*-cyclohexylmaleimide; copolymerization; kinetics

## 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>3–8</sup> by way of radical or anionic polymerization in spite of their 1,2-disubstituted ethylene structure. Many works on their radical polymerization and copolymerization have been performed so far because of the superiority of their polymers or copolymers in thermal stability.<sup>9,10</sup> However, the coloration of these copoly-

mers has been pointed out as an undesirable characteristic because the monomeric maleimide used tends to cause this disadvantage. *N*-Substituted maleimide having aliphatic or alicyclic groups such as *N*-butylmaleimide or *N*-cyclohexylmaleimide (NCMI) are colorless materials, and their copolymerization with MMA provides a resin without coloration.<sup>11</sup> The present studies were undertaken to investigate the copolymerization kinetics of MMA with NCMI, including the apparent activation energy of the overall copolymerization, the monomer reactivity ratios, and the influence of the chain transfer agent RSH on the copolymerization.

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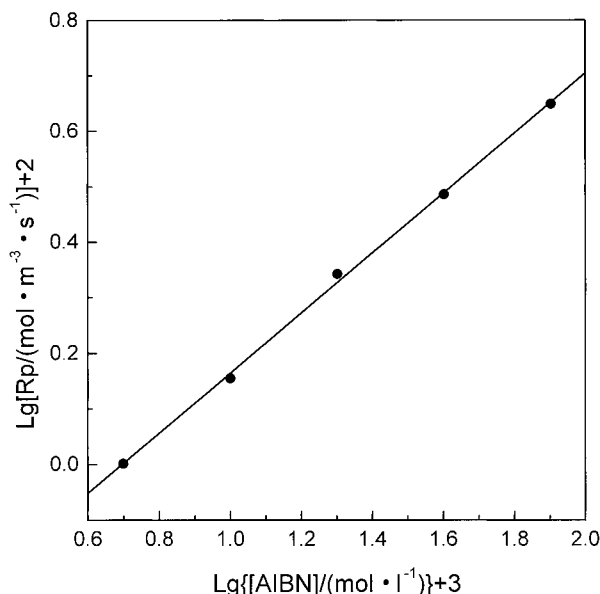
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## EXPERIMENTAL

### Materials

Raw materials were purified by standard procedures. MMA was distilled under reduced pressure



**Figure 1** Relationship between initial copolymerization rate  $R_p$  and  $[AIBN]$ ;  $[MMA] = [NCMI] = 0.50M$ ; solvent, MEK; temperature,  $50^\circ C$ .

immediately before use. NCMI, a commercial product, recrystallized twice from dry acetone, was dried in vacuum before use. *N*-dodecanethiol (RSH), A.R. grade, was used without further purification.

### Polymerization

Copolymerization was carried out in dilatometers as described<sup>12</sup> previously. The monomer conversion was controlled to be less than 10% by mole. The initial polymerization rate (in  $\text{mol m}^{-3} \text{s}^{-1}$ ) is given by eq. (1).

$$R_p = \Delta V / [\bar{M}_0 \cdot V_0 (1/d_0 - 1/d_p)] \quad (1)$$

where  $\bar{M}_0$  is the average molecular weight of the monomer units in copolymer;  $1/d_p$  is the specific volume of copolymer;  $1/d_0$  is the specific volume of the monomer mixture, of which the composition is the same as that of the respective copolymer (where  $d_0$  and  $d_p$  were rectified; see Jiang et al.<sup>13</sup>);  $\Delta V$  (in  $\text{m}^3 \cdot \text{s}^{-1}$ ) is the contraction of the reactant volume;  $V_0$  is the initial reactant volume.

### Isolation and Purification of Copolymer

After polymerization for a given time, the contents of the dilatometer were poured into a large

amount of methanol with rapid stirring to precipitate the products. The precipitated polymer was filtered and washed thoroughly with methanol and purified by reprecipitation from the tetrahydrofuran (THF) solution into excess methanol. Dried at room temperature for several hours first, the samples were heated in a vacuum oven at  $60^\circ C$  for at least 24 h.

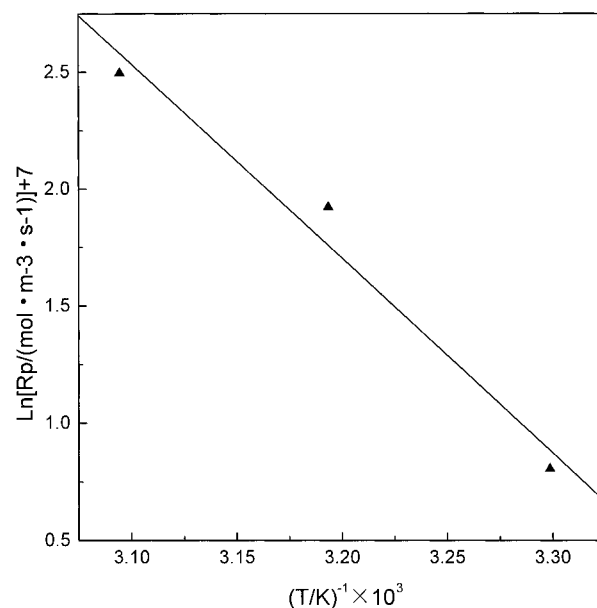
### Analysis and Characterization

The density was measured by a pycnometer; the copolymer composition was calculated from nitrogen elemental analysis; molecular weight was determined by means of gel permeation chromatography (GPC) [poly(methyl methacrylate) (PMMA) standards was used for calibration]. The glass transition temperature ( $T_g$ ) of copolymer was measured by differential scanning calorimetry (DSC; PE Pyris-1 Series) in a flowing nitrogen atmosphere (the heating rate was  $10^\circ C/\text{min}$ ). The ultraviolet spectra of methyl methacrylate (MMA), NCMI, and their mixtures were determined by UV-VIS-730 spectrometer.

## RESULTS AND DISCUSSION

### Copolymerization Behavior of MMA and NCMI

The kinetic study was implemented at  $50^\circ C$  using methyl ethyl keton (MEK) as the solvent. The



**Figure 2** Arrhenius plot for the variation of  $R_p$  with temperature;  $[MMA] = [NCMI] = 1.0M$ ;  $[AIBN] = 0.01M$ ; solvent, MEK.

**Table I** Effects of the Chain Transfer Agent, RSH, at Different Concentration on the Initial Copolymerization Rate  $R_p$  and the Molecular Weight of the Resultant Copolymer

[RSH] ( $10^{-3}$ mol/L)	2	5	10	20	50
$R_p$ , $10^{-2}$ mol m $^{-1}$ s $^{-1}$	5.81	5.59	5.47	5.23	4.54
$\bar{M}_n$ , $10^4$ g/mol	9.10	6.42	4.77	3.57	1.93
$\bar{M}_w$ , $10^4$ g/mol	14.09	9.58	6.59	4.65	2.41
$\bar{M}_w/\bar{M}_n$	1.55	1.49	1.38	1.30	1.25

[AIBN] = 0.025M; [MMA] = 2.0M; [NCMI] = 0.5M; solvent, benzene; temperature 50°C.

influence of the initiator concentration [AIBN] on the initial copolymerization rate  $R_p$  was examined over a wide range. The slope of the line in Figure 1, 0.54, means that the rate is proportional to the initiator concentration to the power of 0.54, thus indicating that termination of copolymerization is predominantly a bimolecular process.

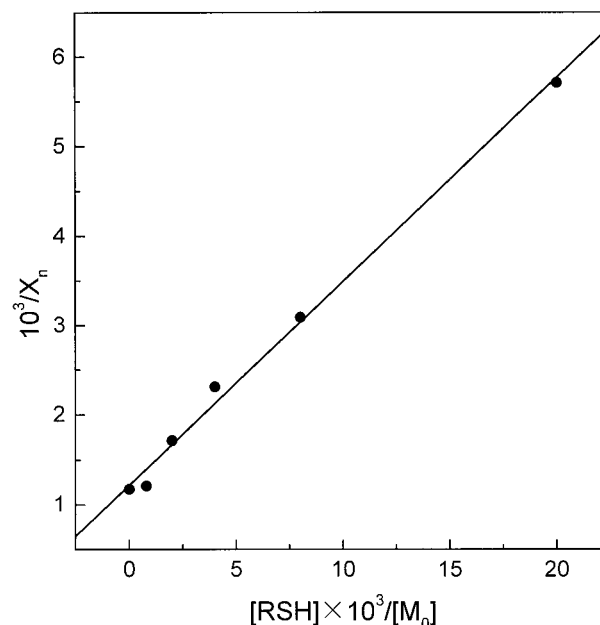
The relationship between  $R_p$  and the reaction temperature was studied in the range of 30–50°C. The plot of  $\ln R_p$  versus  $1/T$  is given in Figure 2. From the slope of the straight line, the apparent activation energy of the overall copolymerization  $E_{app}$  is calculated to be 69.0 kJ/mol. The value is in agreement with those of usual free-radical copolymerization initiated by thermal initiator decomposition.<sup>14</sup>

### Effects of the Chain Transfer Agent on Copolymerization

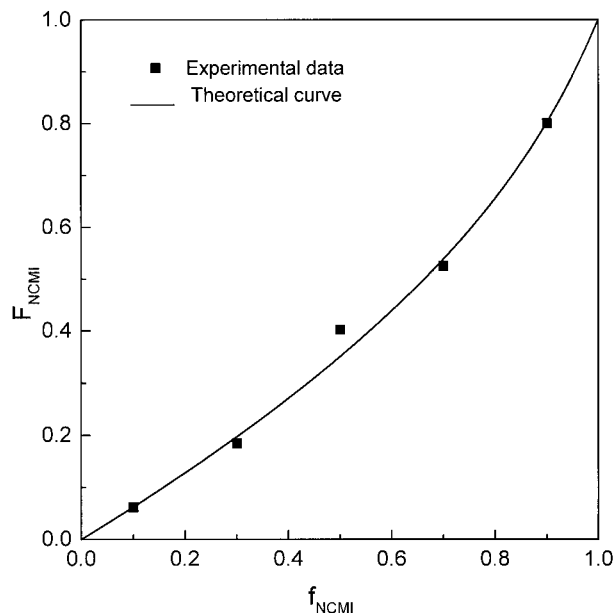
The influence of the chain transfer agent, RSH, at a different concentration on the initial copolymerization rate  $R_p$  and on the molecular weight of the resultant copolymer was also studied using benzene as solvent.  $R_p$  reduces slightly, and the molecular weight of the resultant copolymer decreases with the increasing of the chain transfer agent concentration, [RSH], as shown in Table I. The dispersity indices of resulting polymers mediate between 1.25 and 1.55, which are rather low for polymers made from conventional radical polymerization. It is known that for low conversion polymerization, where all of the kinetic parameters ( $[M]$ ,  $[I]$ ,  $[S]$ ,  $k_p$ ,  $k_t$ ) are approximately constant, the polymer molecular weight does not change with conversion.<sup>14</sup> This is why the molecular weight distributions measured in this work are rather narrow. We also know from Table I that the more the transfer agent, the narrower the molecular weight distribution of the resulting copolymer. Generally, radical chain polymerization involves several possible modes by which

propagation is terminated-disproportionation, recombination, and various transfer reactions. With increasing the chain transfer agent, the molecular weight of products was more and more predominated by chain transfer, and other terminated modes became negligible, so the molecular weight distribution of the resulting copolymer tended to be narrower.

The effect of chain transfer agent concentration on the number average degree of copolymerization,  $X_n$  (calculated according to eq. 2), is given in Figure 3, where the chain-transfer constant ( $C_s$ ) of RSH for the copolymerization of MMA and NCMI ([MMA] : [NCMI] = 4 : 1) in benzene at 50°C was obtained to be  $C_s = 0.23$ . The  $C_s$  value



**Figure 3** The effect of chain transfer agent concentration [RSH] on the reciprocal number-average degree of copolymerization of NCMI and MMA at 50°C; [NCMI] = 0.5M; [MMA] = 2.0M;  $[M_0] = [\text{NCMI}] + [\text{MMA}]$ ; [AIBN] = 0.025M; solvent, benzene.



**Figure 4** Copolymer composition diagram; [MMA] + [NCMI] = 1.0M; [AIBN] = 0.020M; solvent, MEK; temperature, 50°C.

is close to those reported previously<sup>15</sup> [The  $C_s$  value for 1-butanethiol in the polymerization of MMA at 60°C is 0.66, 2-propanethiol 0.38, 2-methyl-2-propanethiol 0.18].

$$X_n = \bar{M}_n / [179F_{\text{NCMI}} + 100(1 - F_{\text{NCMI}})] \quad (2)$$

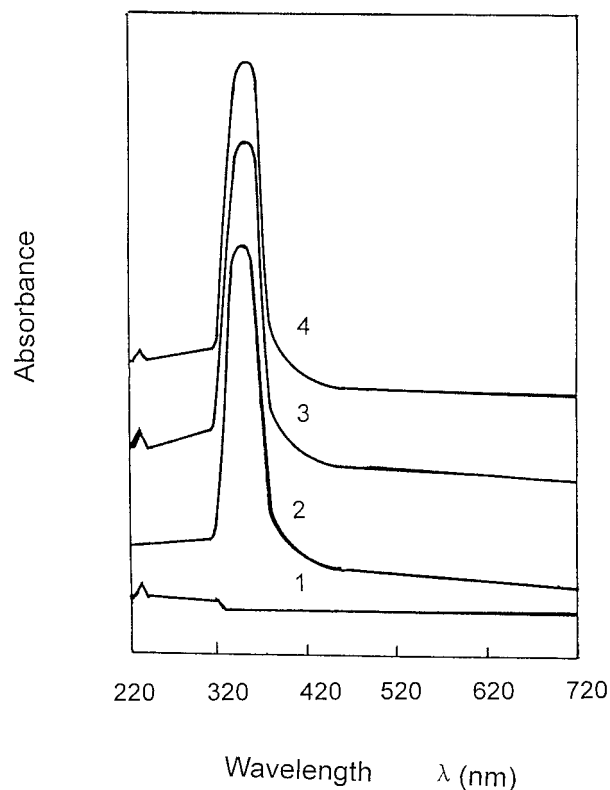
where  $F_{\text{NCMI}}$  is the mole fraction of NCMI in the copolymer composition, and 179 and 100 are the molecular weights of NCMI and MMA.

### Copolymer Composition

The monomer reactivity ratios were evaluated to be  $r_{\text{NCMI}} = 0.42$  and  $r_{\text{MMA}} = 1.63$  in terms of the Y-B-R method<sup>16</sup> using the copolymerization data in Table II, which are close to those reported for the copolymerization of MMA with NCMI<sup>17</sup> ( $r_{\text{NCMI}} = 0.37$ ;  $r_{\text{MMA}} = 1.08$ ). The fact of  $r_{\text{NCMI}} < 1$  and  $r_{\text{MMA}} > 1$  means that radicals preferentially add to MMA instead of NCMI; that is, the activity of MMA is greater than the activity of NCMI in this copolymerization system.  $r_{\text{NCMI}} \times r_{\text{MMA}} < 1$  means that the copolymerization of MMA and NCMI has a weak tendency toward alternative one. Figure 4 shows the diagram calculated from the Mayo–Lewis equation. Experimental results are illustrated in the same figure. The experimental points and the theoretical

curve are in good agreement. It seems unnecessary to introduce a penultimate effect for explaining the experimental results.

As we know that the copolymerization of the charge transfer complex (CTC) comonomer usually leads to an alternative copolymer.<sup>12,18</sup> Elsa-bee et al.<sup>19</sup> reported that MMA and *N*-phenylmaleimide could form a weak charge-transfer complex that had a contribution to the propagating process. For the same reason, we have applied the ultraviolet spectrometer to look over whether MMA and NCMI could produce a CTC. Experimental results given in Figure 5 indicate that the absorbance maximum at wavelength of 357 nm occurs in the UV spectrum of NCMI in MEK solution. No shift or intensification of this peak has been observed after MMA and AIBN were added orderly into the solution, which illustrates that it is not very possible to form a CTC between MMA and NCMI. At least, it is too weak to be determined, even though this kind of complex may exist. The diagram of the copolymer composition in Figure 4 ( $F_{\text{NCMI}} < f_{\text{NCMI}}$ ) indicates that the



**Figure 5** UV spectra for (1) MMA, (2) NCMI, (3) MMA + NCMI (molar ratio 1 : 1), and (4) MMA + NCMI + AIBN [MMA] = [NCMI] = 1.0M; [AIBN] = 0.01M; solvent, MEK.

**Table II Copolymerization Data for NCMI and MMA at 50°C**

$f_{\text{NCMI}}$	N Content in Copolymer (%)	$F_{\text{NCMI}}$	$T_g$ (K)
0.10	1.44	0.062	409.2
0.30	2.41	0.185	415.9
0.50	4.06	0.402	417.0
0.70	5.16	0.525	423.1
0.90	6.28	0.80	433.2

[MMA] + [NCMI] = 1.0M; [AIBN] = 0.020M; solvent, MEK.

resultant copolymer is not a strong alternative one. We may come to the conclusion that the copolymerization of MMA with NCMI does not essentially involve in CTC.

Table II also shows that the  $T_g$  of the copolymer obviously increases with increasing the content of feed NCMI in the copolymerization system. Similar tendencies were reported by Oishi et al.<sup>17</sup> and Halary et al.<sup>20</sup> The  $T_g$  of PMMA is 105°C,<sup>14</sup> so adding NCMI can improve greatly the thermal resistance of Plexiglas.

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