

# Kinetics Study of An Acrylic Tetrapolymer: Poly(IBMA–MMA–MAA–TBMA)

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**ABSTRACT:** In this study, the polymerization kinetics and the molecular structure of the tetrapolymer poly[isobornyl methacrylate (IBMA)–methyl methacrylate (MMA)–methacrylic acid (MAA)–*tert*-butyl methacrylate (TBMA)] were investigated. The relationships among the tetrapolymer composition, monomer conversion, and reaction time were studied. Kinetic equations of the four-component copolymerization related to the mean sequence length, the run number, the reactivity ratio, and the monomer concentration were derived. The mean sequence length of the monomer IBMA increases with the reaction time and monomer conversion. However, those of the other three monomers remain an insignificant variation. Furthermore, the run number decreases rapidly at the end of polymerization. These results suggest that the slow polymerization rate of IBMA is due to its bulky side group. The mean sequence lengths of IBMA, MMA, MAA, and TBMA at the end of polymerization are 1.772, 1.304, 1.169, and 1.229, respectively. On the other hand, the run number of the prepared tetrapolymer is 70.25. The results of the mean sequence length, run number, and the single glass transition temperature suggest that the prepared tetrapolymer is a random copolymer. The molecular weight distribution of the prepared tetrapolymer is significantly affected by polymerization conditions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 853–863, 2001

**Key words:** photoresist; kinetics; acrylic tetrapolymer; IBMA–MMA–MAA–TBMA

## INTRODUCTION

Photoresists (PRs) are the key chemicals for microlithographic technology in the semiconductor processes.<sup>1–3</sup> The various patterns on silicon wafers are formed from the exposure and developing steps of PRs. The line widths of the patterns significantly affect the memory size of an integrated circuit (IC). Thus, PRs play a very important role

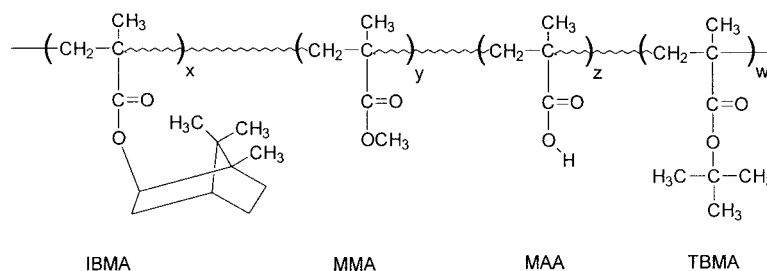
in the semiconductor industry. PRs of 193 nm have been extensively studied because of their importance in 0.15- and 0.13- $\mu\text{m}$  IC processes.<sup>4,5</sup>

One of the most promising 193-nm PRs is based on an acrylic tetrapolymer, isobornyl methacrylate (IBMA)–methyl methacrylate (MMA)–methacrylic acid (MAA)–*tert*-butyl methacrylate (TBMA), as shown in Figure 1. Each component of the acrylic tetrapolymer plays an important role in the lithographic properties: IBMA provides the etching resistance. MMA is responsible for the mechanical properties, optical properties, and positive development characteristics. On the other hand, MAA and TBMA control the aqueous base development characteristics and the acid-cleavage reaction of the side group, respectively. The effects

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**Figure 1** Molecular structure of the acrylic tetrapolymer poly(IBMA-MMA-MAA-TBMA).

of the molecular structure on PR performance were demonstrated on the *i*-line<sup>6</sup> and 248-nm (ref. 7) lithographic processes. For the IBMA-MMA-MAA-TBMA tetrapolymer, the segmental distribution of the each component in the tetrapolymer as well as other molecular parameters should have significant effects on the lithographic properties. However, the details on the synthesis and characterization of the molecular structure of the tetrapolymer have not been fully explored yet.

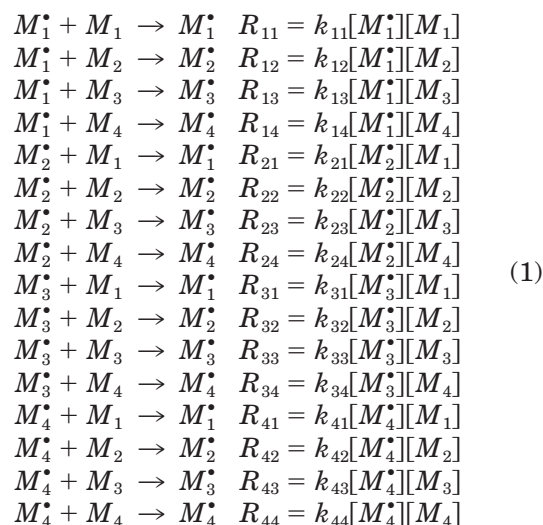
In this study, the polymerization kinetics and the molecular structure of the IBMA-MMA-MAA-TBMA tetrapolymer were investigated. The tetrapolymer was prepared from a solution polymerization of four monomer components by using 2,2'-azobisisobutyronitrile (AIBN) as the polymerization initiator. Both the macroscopic and microscopic structures of the studied tetrapolymer were studied experimentally and theoretically. The relationships among the tetrapolymer composition, monomer conversion, and reaction time were investigated. Kinetic equations of the four-component copolymerization related to the mean sequence length, the reactivity ratio, and the monomer concentration were derived. The reaction rate constants, the mean sequence length, and the run number of the tetrapolymer were obtained from the NMR results and theoretical calculation. The experimental results can be used as a basis for relating the molecular structure of the tetrapolymer to the 193-nm lithographic performance.

## THEORETICAL BACKGROUND

### Tetrapolymer Composition Equation and Reactivity Ratio

The theoretical analysis of the two-component and three-component copolymerization was described in the literature.<sup>8-11</sup> The kinetic equations related to

the four-component copolymerization were derived in this study. Suppose that the four studied monomers, IBMA, MMA, MAA, and TBMA, are represented by  $M_1$ ,  $M_2$ ,  $M_3$ , and  $M_4$ , respectively. Then, 16 types of the propagation reaction are shown as eq. (1). Furthermore, the following assumptions are made for the propagation reactions: (i) the reactivity of a particular radical is independent of its size; (ii) the reactivity is also independent of the nature of the polymeric chain bound to the radical sites; (iii) monomer molecules are consumed solely by the propagation reactions; and (iv) the steady-state approximation for radicals:



are given by eqs. (2a)–(2d)

$$-\frac{d[M_1]}{dt} = R_{11} + R_{21} + R_{31} + R_{41} \tag{2a}$$

$$-\frac{d[M_2]}{dt} = R_{12} + R_{22} + R_{32} + R_{42} \tag{2b}$$

$$-\frac{d[M_3]}{dt} = R_{13} + R_{23} + R_{33} + R_{43} \tag{2c}$$

$$-\frac{d[M_4]}{dt} = R_{14} + R_{24} + R_{34} + R_{44} \quad (2d)$$

From the steady-state assumption for radicals  $[M_1] \sim [M_4]$ , eqs. (3a)–(3d) can be derived:

$$R_{12} + R_{13} + R_{14} = R_{21} + R_{31} + R_{41} \quad (3a)$$

$$R_{21} + R_{23} + R_{24} = R_{12} + R_{32} + R_{42} \quad (3b)$$

$$R_{31} + R_{32} + R_{34} = R_{13} + R_{23} + R_{43} \quad (3c)$$

$$R_{41} + R_{42} + R_{43} = R_{14} + R_{24} + R_{34} \quad (3d)$$

Combination of eqs. (1), (2), and (3) yields the tetrapolymer composition as eqs. (4a)–(4c):

$$\begin{aligned} d[M_1] : d[M_2] : d[M_3] : d[M_4] \\ = \{[M_1](\alpha k_{11} + \beta k_{21} + \delta k_{31} + k_{41})\} \\ : \{[M_2](\alpha k_{12} + \beta k_{22} + \delta k_{32} + k_{42})\} \\ : \{[M_3](\alpha k_{13} + \beta k_{23} + \delta k_{33} + k_{43})\} \\ : \{[M_4](\alpha k_{14} + \beta k_{24} + \delta k_{34} + k_{44})\} \quad (4a) \end{aligned}$$

in which  $\alpha, \beta, \delta$  and  $A, B, C$  are defined as eqs. (4b) and (4c):

$$\begin{aligned} \alpha &= \frac{k_{44}}{k_{11}} \left( \frac{-1}{r_{21}r_{43}r_{32}} + \frac{1}{r_{23}r_{41}r_{32}} - \frac{1}{r_{42}r_{23}r_{31}} - \frac{B}{r_{43}r_{31}} - \frac{C}{r_{21}r_{42}} - \frac{BC}{r_{41}} \right) = \frac{k_{44}}{k_{11}} \alpha^* \\ \beta &= \frac{k_{44}}{k_{22}} \left( \frac{1}{r_{13}r_{31}r_{42}} - \frac{1}{r_{13}r_{41}r_{32}} - \frac{1}{r_{12}r_{31}r_{43}} - \frac{A}{r_{32}r_{43}} - \frac{C}{r_{12}r_{41}} - \frac{AC}{r_{42}} \right) = \frac{k_{44}}{k_{22}} \beta^* \\ \delta &= \frac{k_{44}}{k_{33}} \left( \frac{-1}{r_{13}r_{21}r_{42}} - \frac{1}{r_{12}r_{41}r_{23}} + \frac{1}{r_{12}r_{21}r_{43}} - \frac{A}{r_{23}r_{42}} - \frac{B}{r_{13}r_{41}} - \frac{BC}{r_{43}} \right) = \frac{k_{44}}{k_{33}} \delta^* \quad (4b) \end{aligned}$$

$$\begin{aligned} A &= \frac{1}{[M_1]} \left( \frac{1}{r_{12}}[M_2] + \frac{1}{r_{13}}[M_3] + \frac{1}{r_{14}}[M_4] \right) \\ B &= \frac{1}{[M_2]} \left( \frac{1}{r_{21}}[M_1] + \frac{1}{r_{23}}[M_3] + \frac{1}{r_{24}}[M_4] \right) \\ C &= \frac{1}{[M_3]} \left( \frac{1}{r_{31}}[M_1] + \frac{1}{r_{32}}[M_2] + \frac{1}{r_{34}}[M_4] \right) \quad (4c) \end{aligned}$$

The reactivity ratio of a monomer pair can be obtained as below: First, the copolymer composition equation, eq. (5a), can be rearranged as eq. (5b). Therefore, the relationship between  $(1 - \gamma)[M_j]/[M_i]$  and  $\gamma([M_j]/[M_i])^2$  is a straight line with the slope  $r_{ji}$  and the intercept  $(-r_{ij})$ . Therefore,  $r_{ij}$  and  $r_{ji}$  can be obtained for different monomer pairs:

$$\theta = \frac{d[M_i]}{d[M_j]} = \frac{\left(1 + r_{ij} \frac{[M_i]}{[M_j]}\right)}{\left(1 + r_{ji} \frac{[M_j]}{[M_i]}\right)} \quad r_{ij} = \frac{k_{ii}}{k_{ij}} \quad (5a)$$

$$(1 - \theta) \frac{[M_j]}{[M_i]} = \theta \left( \frac{[M_j]}{[M_i]} \right)^2 r_{ji} - r_{ij} \quad (5b)$$

#### Distribution of the Monomers in a Tetrapolymer: Mean Sequence Length and Run Number ( $R$ )

Let  $P_{11}$  be the probability that a growing radical chain  $[M_1^*]$  adds to the monomer  $M_1$ . Hence, it is possible to express  $P_{11}$  as eq. (6):

$$P_{11} = \frac{R_{11}}{R_{11} + R_{12} + R_{13} + R_{14}} \quad (6)$$

The probability of forming a sequence of exactly  $x$  units of monomer  $M_1$  is  $P_{M1}(x)$ , as shown in eq. (7):

$$\begin{aligned} P_{M1}(x) &= P_{11}^{x-1}(P_{12} + P_{13} + P_{14}) \\ &= P_{11}^{x-1}(1 - P_{11}) \quad (7) \end{aligned}$$

Therefore, the instantaneous mean sequence length of  $m_{M_i}$  can be expressed as eq. (8):

$$m_{M_i} = 1 + \frac{[M_i]}{\sum_{j \neq i} \frac{[M_j]}{r_{ij}}} \quad i, j = 1, 2, 3, 4 \quad (8)$$

The values of  $m_{M_i}$  during the polymerization are calculated by eq. (8), in which the reactivity ratio is obtained from the previous section. Furthermore, the accumulated mean sequence length  $\bar{m}_{M_i}$  during the polymerization can be calculated by using eq. (9) or eq. (10), where  $W$  is the weight of the reaction mixture. In this study,  $\bar{m}_{M_i}$  is determined from eq. (10):

$$\bar{m}_{M_i} = \frac{\int_{[M_i]_0}^{[M_i]_t} m_{M_i} d(V[M_i])}{\int_{[M_i]_0}^{[M_i]_t} d(V[M_i])} \quad (9)$$

$$\bar{m}_{M_i} = \frac{\frac{1}{W} \int_{[M_i]_0}^{[M_i]_t} m_{M_i} d(V[M_i])}{\frac{1}{W} \int_{[M_i]_0}^{[M_i]_t} d(V[M_i])} = \frac{\int_{[M_i]_0}^{[M_i]_t} m_{M_i} d\left(\frac{[M_i]}{d}\right)}{\int_{[M_i]_0}^{[M_i]_t} d\left(\frac{[M_i]}{d}\right)} \quad (10)$$

The run number,  $R$ , of the tetrapolymer is the average number of sequences of either monomer per 100 monomer units. The rate of sequence formation,  $ds/dt$ , regardless of length, is simply the rate at which the sequence is ended. Neglecting chain termination, the instantaneous values of  $R$  and  $ds/dt$  are given by eqs. (11) and (12):

$$\frac{ds}{dt} = \sum_{i=1}^4 \sum_{\substack{j=1 \\ i \neq j}}^4 R_{ij} \quad (11)$$

$$\begin{aligned} R &= 100 \frac{ds}{-d[M]} \\ &= 100 \left( \frac{\frac{k_{44}}{k_{11}} \alpha^* \times \sum_{i=2,3,4} k_{1i} [M_i] + \frac{k_{44}}{k_{22}} \beta^* \times \sum_{i=1,3,4} k_{2i} [M_i] + \frac{k_{44}}{k_{33}} \delta^* \times \sum_{i=1,2,4} k_{3i} [M_i] + \sum_{i=1,2,3} k_{4i} [M_i]}{\sum_{i=1}^4 \left\{ [M_i] \left( \frac{k_{44}}{k_{11}} \alpha^* \times k_{1i} + \frac{k_{44}}{k_{22}} \beta^* \times k_{2i} + \frac{k_{44}}{k_{33}} \delta^* \times k_{3i} + k_{4i} \right) \right\}} \right) \\ &= 100 \left( \frac{\alpha^* \sum_{i=2,3,4} \frac{1}{r_{1i}} [M_i] + \beta^* \times \sum_{i=1,3,4} \frac{1}{r_{2i}} [M_i] + \delta^* \times \sum_{i=1,2,4} \frac{1}{r_{3i}} [M_i] + \sum_{i=1,2,3} \frac{1}{r_{4i}} [M_i]}{\sum_{i=1}^4 \left\{ [M_i] \left( \alpha^* \times \frac{1}{r_{1i}} + \beta^* \times \frac{1}{r_{2i}} + \delta^* \times \frac{1}{r_{3i}} + \frac{1}{r_{4i}} \right) \right\}} \right) \quad (12) \end{aligned}$$

Then, the accumulated run number of the tetrapolymer during the polymerization,  $\bar{R}$ , can be determined in a similar way as that of the accumulated mean sequence length and expressed as eqs. (13a) and (13b):

$$\bar{R} = \frac{\int_{[M]_0}^{[M]_t} R d\left(\frac{[M]}{d}\right)}{\int_{[M]_0}^{[M]_t} d\left(\frac{[M]}{d}\right)} \quad (13a)$$

$$[M] = \sum_{i=1}^4 [M_i] \quad (13b)$$

## EXPERIMENTAL

### Materials

MMA (99%, Lancaster), IBMA (Aldrich), and TBMA (>98%, TCI) were purified by vacuum distillation. MAA (99%), 1-4 dioxane (99+%, Acros), AIBN (99%, TCI), THF (99.9%, Acros), chloroform-D (CDCl<sub>3</sub>, 99.8%, CIL), and deuterium oxide (D<sub>2</sub>O, 100%D, Acros) were used without further purification.

### Polymer Synthesis

Table I shows the reaction conditions for preparing the tetrapolymer, poly(IBMA-MMA-MAA-TBMA). Here, the details of polymerization are

**Table I** Reaction Conditions for Preparing the Studied Polymers

Reaction Condition	Reaction Temperature (°C)	AIBN Concentration (mol % Monomer)	Initial Monomer Concentration (mol/L Solvent)
(i)	70	1	4
(ii)	80	1	4
(iii)	90	1	4
(iv)	80	0.5	4
(v)	80	2	4
(vi)	80	1	3
(vii)	80	1	5

described as below by using the reaction condition (i) as an example. The reaction mixture consisted of 0.4 mol IBMA, 0.25 mol MMA, 0.15 mol MAA, 0.2 mol TBMA, 0.1 mol AIBN, and 250-mL *p*-dioxane. It was stirred and maintained at 80°C for 11 h. Then, it was poured into a 2000-mL stirring hexane, precipitated, dissolved in THF, precipitated in hexane again, and dried in a vacuum oven at 150°C for 5 h. A white powder was obtained with a yield of 95%.

<sup>1</sup>H-NMR ( $\delta$ , ppm, reference to TMS, in CDCl<sub>3</sub>): 0.8–1.1 (CH<sub>3</sub> on the isobornyl group and CH<sub>3</sub> side group on the vinyl linkage), 1.1–2.0 (*tert*-butyl group, CH<sub>2</sub> on the vinyl linkage, and CH, CH<sub>2</sub> group on the isobornyl group), 3.56 (CH<sub>3</sub> group attached to the COO side group of MMA), 4.33 (CH on the isobornyl group attached to the COO side group).

## Kinetics Study

### Monomer Conversion with Reaction Time

The monomer concentration during the copolymerization was evaluated as below: First, the polymerization reaction was stopped at each measured time and the polymer purified as described in the polymer synthesis section. Then, the composition of each monomer in the prepared tetrapolymer was determined from the <sup>1</sup>H-NMR spectra and then compared with the starting monomer concentration to obtain monomer conversion. Hence, the monomer conversion with the reaction time was obtained.

### Reaction Rate Constant

The consumption of the monomer  $M_1$  can be described by eq. (14) from the combination of eqs. (1) and (2). Based on the assumption of the steady-state approximation during the polymerization

for radicals, the radical concentration can be related to each other by eq. (15). Hence, the monomer concentration during polymerization can be described by eqs. (16) and (17). By plotting  $\ln([M_1])$  versus the polymerization time, the reaction rate constant  $k$  defined in eq. (18) is obtained. Similarly, the reaction rate constants for the other three monomers can be determined in the same way:

$$\begin{aligned}
 -\frac{d[M_1]}{dt} &= R_{11} + R_{21} + R_{31} + R_{41} \\
 &= (k_{11}[M_1^\bullet] + k_{21}[M_2^\bullet] + k_{31}[M_3^\bullet] \\
 &\quad + k_{41}[M_4^\bullet])[M_1] \quad (14)
 \end{aligned}$$

$$[M_1^\bullet] = \alpha[M_4^\bullet], [M_2^\bullet] = \beta[M_4^\bullet], [M_3^\bullet] = \delta[M_4^\bullet] \quad (15)$$

$$-\frac{d[M_1]}{dt} = k[M_1] \quad (16)$$

$$\ln[M_1] = -kt + \ln([M_1]_0) \quad (17)$$

and

$$k = (\alpha k_{11} + \beta k_{21} + \delta k_{31} + k_{41})[M_4^\bullet] \quad (18)$$

### Reactivity Ratio

In this study, the reactivity ratio of IBMA to the other three monomers or vice versa was obtained by using eq. (5b). Four initial monomer ratios were used in this study, which were 80/20, 65/35, 50/50, and 35/65. At the initial period of the polymerization reaction,  $\theta$  can be approximately calculated by the composition of the copolymer and  $[M_j]/[M_1]$  was close to the feed monomer ratio. On

**Table II** Reactivity Ratios of the Studied Monomers

Monomer ( <i>j</i> )	<i>r<sub>ij</sub></i>			
	Radical ( <i>i</i> )			
	IBMA	MMA	TBMA	MAA
IBMA	—	1.075 <sup>a</sup>	0.893 <sup>a</sup>	1.185 <sup>a</sup>
MMA	0.892 <sup>a</sup>	—	1.01 <sup>b</sup>	1.1 <sup>b</sup>
TBMA	1.157 <sup>a</sup>	0.96 <sup>b</sup>	—	1.02 <sup>b</sup>
MAA	0.757 <sup>a</sup>	0.87 <sup>b</sup>	0.85 <sup>b</sup>	—

<sup>a</sup> Experimental results.<sup>b</sup> *Q-e* method.

the other hand, the reactivity ratios of MMA, MAA, and TBMA to each other were calculated from the *Q-e* values reported in the literature.<sup>12</sup> Table II shows the reactivity ratios of the studied monomers.

### Mean Sequence Length

The instantaneous mean sequence length of each component during the polymerization was calculated by eq. (8) combined with the <sup>1</sup>H-NMR spectra of the polymers. In this calculation, the reactivity ratio was obtained from the previous section. Furthermore, the accumulated mean sequence length during the polymerization can be calculated by using eq. (10).

### Run Number

The instantaneous run number (*R*) of the prepared tetrapolymer during the polymerization was calculated according to eq. (12) along with the <sup>1</sup>H-NMR spectra of the polymers. In addition, the accumulated run number,  $\bar{R}$ , during the polymerization reaction was calculated by eq. (13a).

### Characterization

Infrared spectra of polymer thin films prepared from KBr pellets were recorded at room temperature using a Bio-Rad Digilab Division FTS-40 FTIR spectrophotometer. <sup>1</sup>H-NMR spectra of the prepared polymers were determined by a solution using a nuclear magnetic resonance spectrometer (Custom Scientific Instrument, Inc. EX-400) at 400 MHz. The molecular weight distribution of the prepared polymers was determined by a gel permeation chromatographer (GPC) with a solvent delivery system (Spectro-

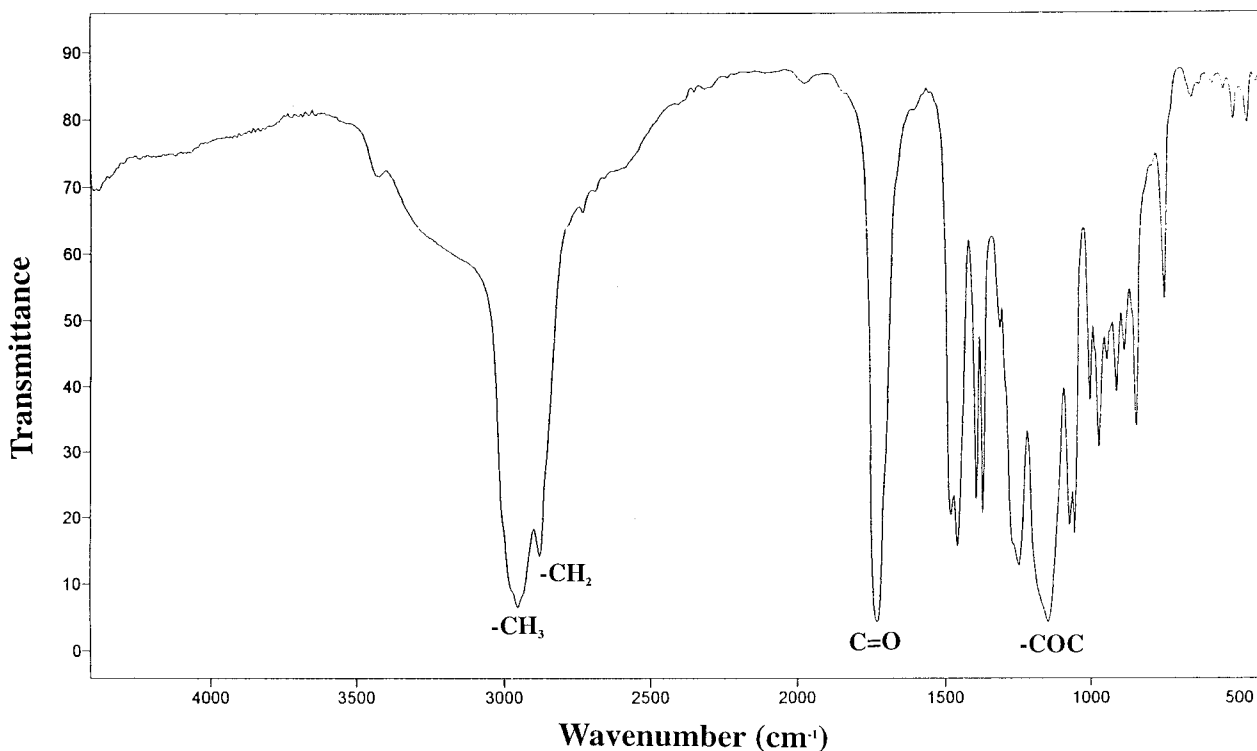
flow 400, ABI), a refractive index detector (RI-71, Shodex), and a GPC column (PLgel 5- $\mu$ m MIXED-C, Polymer Laboratories). Thermal analysis by differential scanning calorimetry (DSC) was done using a Perkin-Elmer DSC-7 with a heating rate of 10°C/min under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Synthesis of Polymers

Figure 2 shows the FTIR spectrum of the prepared tetrapolymer IBMA-MMA-MAA-TBMA. The characteristic absorption bands of —COC, C=O, and —CH<sub>2</sub> and —CH<sub>3</sub> are shown at 1170, 1720, and 2850–3000 cm<sup>-1</sup>, respectively. These peaks indicate the existence of the specific functional groups of the four components. However, they cannot elucidate the composition of the tetrapolymer. <sup>1</sup>H-NMR provides a powerful tool for characterizing the composition of the tetrapolymer. Figure 3 exhibits the <sup>1</sup>H-NMR spectrum of the tetrapolymer IBMA-MMA-MAA-TBMA in CDCl<sub>3</sub>. The compositions of the four monomers in the tetrapolymer were determined by comparing with the <sup>1</sup>H-NMR spectra of their homopolymers, poly(isobornyl methacrylate) (PIBMA), poly(methyl methacrylate) (PMMA), poly(methacrylic acid) (PMAA), and poly(*tert*-butyl methacrylate) (PTBMA), respectively. The compositions of IBMA, MMA, and TBMA in the tetrapolymer were obtained by comparing the peak areas of the resonance peaks at 4.33, 3.56, and 1.39 ppm, respectively. On the other hand, the composition of MAA in the tetrapolymer was evaluated by the total proton number balance and the resonance peaks in the range of 0.8–2.0 ppm. The mol ratios of the four monomers determined from Figure 3 are 0.391:0.255:0.152:0.202 for IBMA, MMA, MAA, and TBMA, respectively. The ratio is almost identical to the feeding mol ratio of 0.4:0.25:0.15:0.2. Furthermore, the yield of the polymerization of the tetrapolymer is as high as 95%. These results suggest the successful preparation of the designed tetrapolymer.

The polymerization of the four monomers can be further investigated from the relationships of the monomer conversion and the tetrapolymer composition with respect to the reaction time as shown in Figure 4. This figure shows that the IBMA fraction in the tetrapolymer gradually increases with increasing reaction time. However,



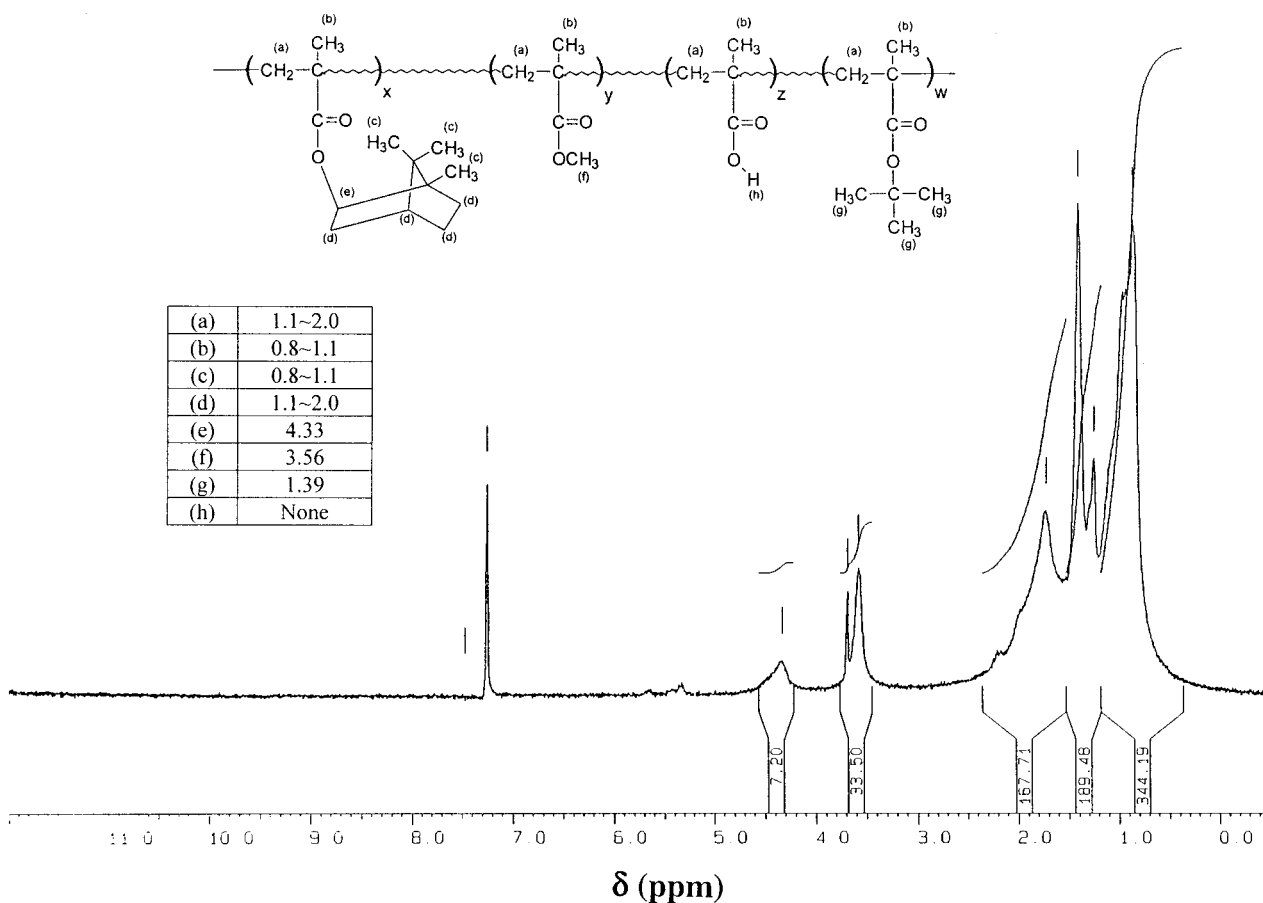
**Figure 2** FTIR transmission spectrum of the acrylic tetrapolymer poly(IBMA-MMA-MAA-TBMA).

the fraction of MAA in the copolymer exhibited a reverse trend, which decreases with increasing reaction time. However, the fractions of MMA and TBMA do not show a significant change with the reaction time, as shown in Figure 4. This result suggests that the reaction rate of the MAA monomer is the largest and that of IBMA is the slowest. A further study of the reaction rate was by studying the relationships between  $\ln([M_x])$  and the reaction time, as shown in Figure 5. The reaction rate constants of the four monomers calculated by eq. (17) and Figure 5 are in the following order:  $k_{\text{MAA}} > k_{\text{MMA}} > k_{\text{TBMA}} > k_{\text{IBMA}}$ . This result can be explained by the steric effect from the molecular structure since the size of the side group is IBMA > TBMA > MMA > MAA.

#### Reactivity Ratio of Monomers

Figure 6 shows the relationship between  $(1 - \theta)[M_j]/[M_1]$  and  $\theta([M_j]/[M_1])^2$ . Here,  $M_j$  ( $j = 2, 3, 4$ ) represents MMA, MAA, and TBMA, respectively. The reactivity ratios of IBMA to the other three monomers or vice versa are determined from Figure 6 and eq. (5b), which are listed in

Table II. A similar experiment as that of the IBMA system in Figure 6 was conducted for the monomer pair MMA-TBMA, which is shown in Figure 7. It is found that the reactivity ratios obtained from the above experiment are almost the same as those from the  $Q-e$  method. Hence, for the other three monomers, MMA, TBMA, and MAA, the reactivity ratios are calculated from the  $Q-e$  value. The reactivity ratios of the monomer pairs are listed in Table II. The reactivity ratios listed in Table II are all close to 1. This result indicates that the synthesized copolymer is probably a random copolymer as is the original design. Figure 8 exhibits the relationship between  $(1 - \theta)[M_2]/[M_1]$  and  $\theta([M_2]/[M_1])^2$  for the monomer pair of IBMA-MMA in the polymerization conditions ii, iii, v, and vi of Table I. An almost identical relationship was obtained for different polymerization conditions. Therefore, the reactivity ratios of the studied polymerization system are dependent on the monomer type but show an insignificant change for different polymerization temperatures, monomer concentrations, and initiator concentrations.

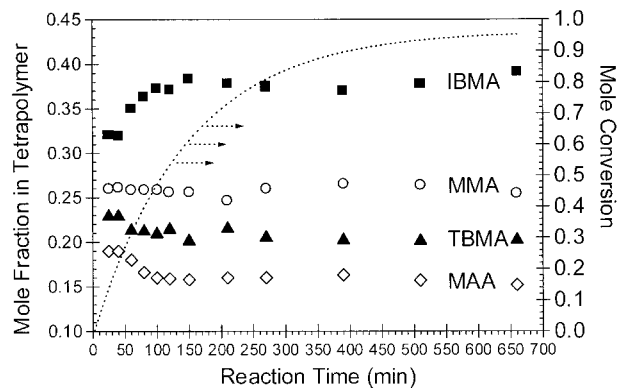


**Figure 3**  $^1\text{H-NMR}$  spectrum of the acrylic tetrapolymer in  $\text{CDCl}_3$ , poly(IBMA-MMA-MAA-TBMA).

### Mean Sequence Length

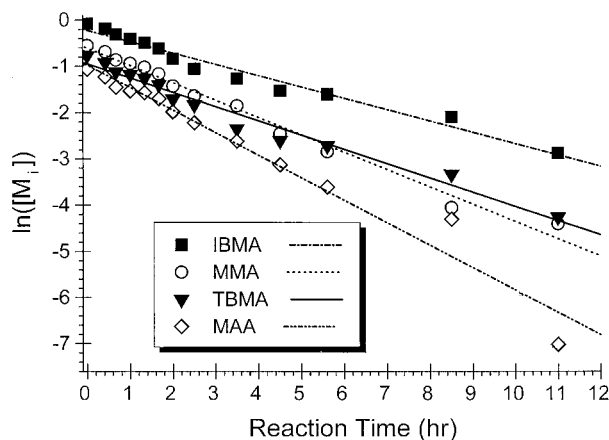
Figure 9 shows the relationship between the instantaneous mean sequence length ( $m_{Mi}$ ) and  $([M_i]d)$ . Figure 10 exhibits the relationships be-

tween the accumulated mean sequence length of the four monomer segments  $\bar{m}_{Mi}$  and the monomer conversion. The instantaneous mean sequence lengths of the monomer segment MMA, MAA, and TBMA are in the range of 1.1–1.3 and



**Figure 4** Relationships between the tetrapolymer composition and the monomer mole conversion with the reaction time by using reaction condition ii.



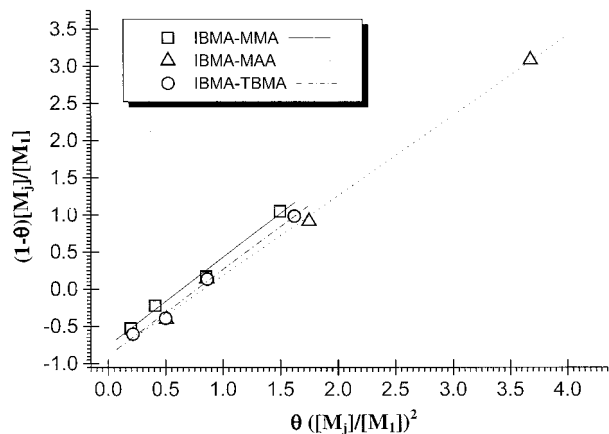


**Figure 5** Relationship between the monomer concentration ( $\ln[M_i]$ ) and the reaction time ( $t$ ) during the tetrapolymerization by using reaction condition ii.

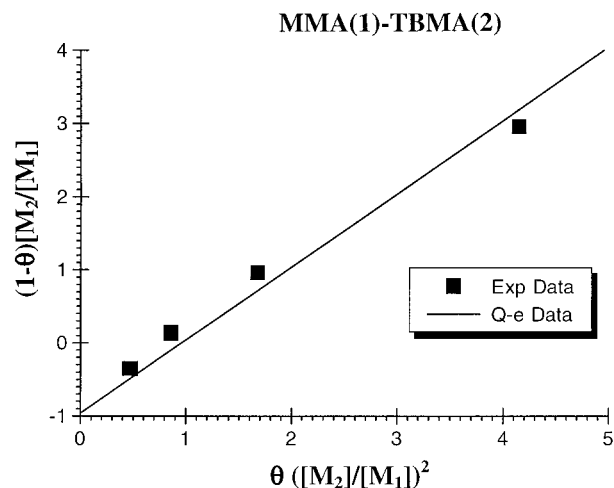
almost remain constant during the polymerization. However, the instantaneous mean sequence length of IBMA increases rapidly with the monomer consumption, as shown in Figure 9. This result provides further evidence of the slower polymerization rate of the monomer IBMA than that of the other three monomers. The accumulated mean sequence lengths of the four monomer segments at the end of polymerization are 1.772, 1.304, 1.169, and 1.229 for IBMA, MMA, MAA, and TBMA, respectively. This result suggests that a random tetrapolymer is produced in this study.

#### Run Number

Figure 11 shows the relationship between the instantaneous run number ( $\bar{R}$ ) and  $[M]/d$ . The

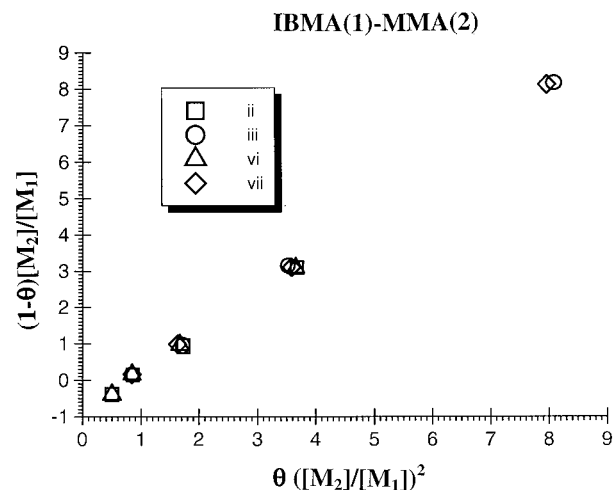


**Figure 6** Relationship between  $(1 - \theta)[M_j]/[M_1]$  and  $\theta([M_j]/[M_1])^2$  for obtaining the monomer reactivity ratios of IBMA-MMA, IBMA-MAA, and IBMA-TBMA.

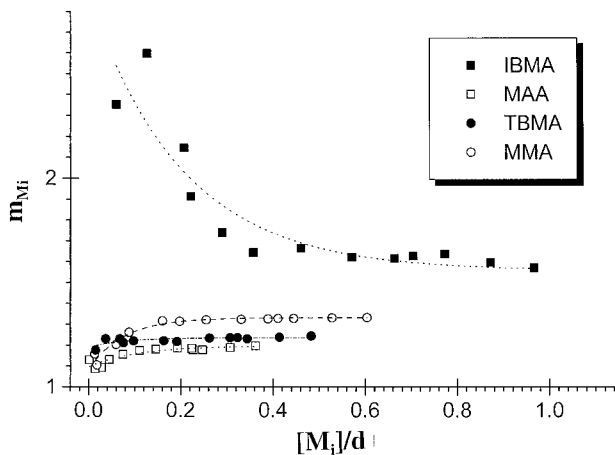


**Figure 7** Relationship between  $(1 - \theta)[M_2]/[M_1]$  and  $\theta([M_2]/[M_1])^2$  for the MMA(1)-TBMA(2) copolymerization from either the  $Q-e$  method or experiments.

run number shows an insignificant change at the initial stage of polymerization but decreases rapidly at the end of polymerization (i.e.,  $[M]/d \sim 0$ ). This probably resulted from the slow polymerization rate of the monomer IBMA. As shown in the study of the reaction rate constant and the mean sequence length, the sequence length of the monomer IBMA increases significantly during the final stage of polymerization and resulted in a large decrease of the run



**Figure 8** Relationship between  $(1 - \theta)[M_2]/[M_1]$  and  $\theta([M_2]/[M_1])^2$  for obtaining the monomer reactivity ratios of IBMA(1)-MMA(2) under different polymerization conditions (ii), (iii), (vi), and (vii) of Table I.

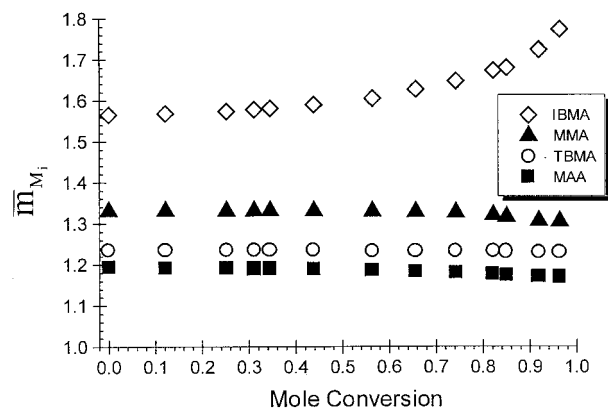


**Figure 9** Relationships between the instantaneous mean sequence length ( $\bar{m}_{Mi}$ ) and  $[M_i]/d$  during the polymerization by using reaction condition ii of Table I.

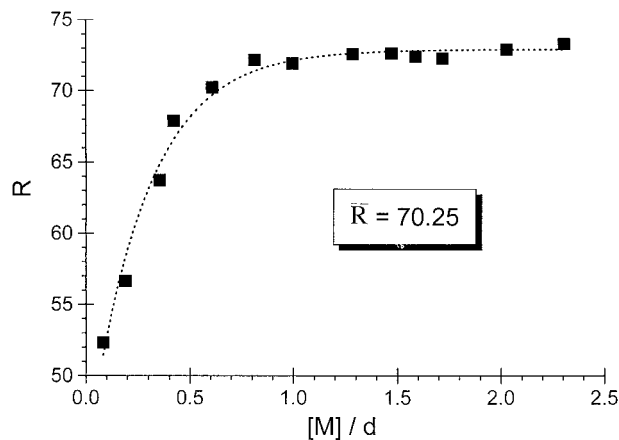
number. Figure 12 exhibits the relationship between the accumulated run number ( $\bar{R}$ ) and the monomer conversion. The run number decreases with increasing monomer conversion and is 70.25 at the end of polymerization, which suggests a random copolymer.

**Thermal Properties**

The thermal properties of the five polymers, PMMA, PIBMA, PTBMA, and PMAA, and poly(MMA-IBMA-MAA-TBMA), were characterized by their DSC curves. The glass transition temperatures of MMA, PIBMA, PMAA, and PTBMA, and poly(MMA-IBMA-MAA-TBMA) are 108.2, 121.7, 227.3, 144, and 140.6°C, respectively.



**Figure 10** Relationships between the accumulated mean sequence length ( $\bar{m}_{Mi}$ ) and the monomer mol conversion by using reaction condition ii.

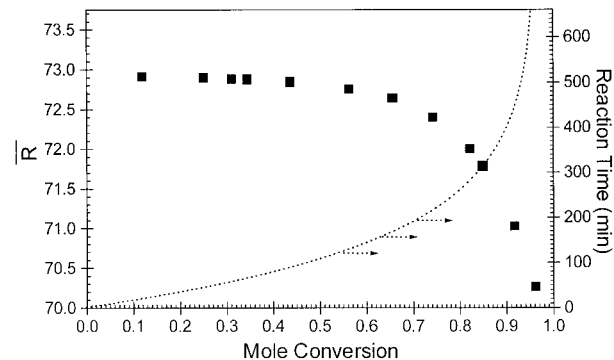


**Figure 11** Relationship between the instantaneous run number ( $\bar{R}$ ) of the tetrapolymer and  $[M]/d$ .

tively. The prepared tetrapolymer has a single glass transition temperature and was in a fair agreement with the  $T_g$  value calculated by the Fox equation. This result provides more evidence of the random copolymer.

**Molecular Weight Distribution**

Table III shows the effect of the polymerization conditions on the molecular weight of the prepared tetrapolymer. By increasing the reaction temperature (i-iii in Table I) and the initiator concentration (ii, iv, v in Table I), the molecular weight and its distribution of the prepared tetrapolymer decreased as expected. Furthermore, the molecular weight increased but its distribution decreased with increasing initial monomer concentration (ii, vi, vii in Table I).



**Figure 12** Relationships between the accumulated run number ( $\bar{R}$ ) of the tetrapolymer, the monomer mol conversion, and the reaction time.

**Table III** Molecular Weight ( $\bar{M}_n$ ,  $\bar{M}_w$ ) and Its Distribution (PDI) of the Tetrapolymer Under Different Polymerization Conditions

Reaction Condition	$\bar{M}_n$	$\bar{M}_w$	PDI
(i)	25,177	49,164	1.949
(ii)	22,147	39,687	1.792
(iii)	19,247	34,154	1.775
(iv)	52,148	93,919	1.801
(v)	18,488	31,915	1.730
(vi)	13,275	24,174	1.821
(vii)	27,574	43,419	1.575

## CONCLUSIONS

The tetrapolymer poly(IBMA–MMA–MAA–TBMA) was prepared and characterized in this study. The composition of the tetrapolymer is very close to the feed monomer fraction. The investigation of the tetrapolymer composition and reaction rate constant shows that the polymerization rate of the monomer is strongly affected by the size of the side group. Among the studied four monomers, MAA and IBMA have the fastest and slowest polymerization rates, respectively. The results of the mean sequence length, run number, and glass transition temperature suggests that the prepared tetrapolymer is a random copolymer. The molecular weight of the prepared tetrapolymer is significantly affected by the polymerization conditions. It increases with an increasing monomer concentration but decreases with an increasing reaction temperature and initiator concentration.

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## REFERENCES

- (a) Proceedings of Advances in Resist Technology and Processing XII, SPIE; Allen, R. D., Ed.; 1995; Vol. 2438; (b) Proceeding of Advances in Resist Technology and Processing XIII, SPIE; Kunz, R. R., Ed.; 1996; Vol. 2724; (c) Proceedings of Advances in Resist Technology and Proceedings XIV, SPIE; Tarascon-Auriol, R. G., Ed.; 1997; Vol. 3049; (d) Frechet, J. M. J.; Eichler, E.; Ito, H.; Wilson, C. G. *Polymer* 1983, 24: 995; (e) Ito, H.; Wilson, C. G.; Frechet, J. M. J.; Farral, M. J.; Eichler, E. *Macromolecules* 1983, 16, 510.
- Introduction to Microlithography, 2nd ed.; Thompson, L. F.; Wilson, C. G.; Bowden, M. J., Eds.; American Chemical Society: Washington, DC, 1994.
- Reichmanis, E. In *Polymers for Electronic and Photonic Applications*; Wang, C. P., Ed.; Academic: San Diego, 1993; Chapter 2.
- Allen, R. D.; Wallraff, G. M.; Hofer, D. C.; Kunz, R. R. *IBM J Res Dev* 1997, 41, 95.
- Allen, R. *Semicond Int* 1997, Sept., 72.
- Tsiartas, P. C.; Simpson, L. L.; Qin, A.; Wilson, C. G.; Allen, R. D.; Krukows, V. J.; Gallagher-Wetmore, P. M. In *Proceedings of Advances in Resist Technology and Processing XII, SPIE*; Allen, R. D., Ed.; 1995; Vol. 2438, p 261.
- Barclay, G. C.; Hawker, C. J.; Ito, H.; Orellana, A. In *Proceeding of Advances in Resist Technology and Processing XIII, SPIE*; Kunz, R. R., Ed.; 1996; Vol. 2724, p 249.
- Odien, G. *Principles of Polymerization*, 3rd ed.; Wiley: New York, 1991; Chapter 6.
- Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*, 2nd ed.; Prentice-Hall: Englewood Cliff, NJ, 1990; Chapter 12.
- Alfrey, T., Jr.; Goldfinger, G. *J Chem Phys* 1944, 12, 115.
- Walling, C.; Briggs, E. R. *J Am Chem Soc* 1945, 67, 1774.
- Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989.