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Kinetic Study of Atom Transfer Radical Copolymerization of Methyl Acrylate and Methyl Methacrylate Initiated with Poly(vinyl acetate) Macroinitiator

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Atom transfer radical bulk copolymerization of MA and MMA was performed in the presence of CuCl/PMDETA as catalyst system and trichloromethyl-terminated poly(vinyl acetate) macroinitiator at 80°C. The overall monomer conversion was followed gravimetrically and chemical composition of the copolymer was determined by ^{1}H-NMR spectrometry. The results have been used to calculate monomer reactivity ratios by linear and nonlinear methods. Reactivity ratios calculated were in the range of 0.3766–0.4988 and 1.8832–2.0963 for MA and MMA, respectively. These values were in good agreement with the values reported for a similar system in the free radical copolymerization. It was observed that the copolymerization system tends to produce a random copolymer with longer sequences of MMA than MA in the initial stage of polymerization before any significant decrease of the concentration of MMA in the monomer mixture. Copolymer microstructures in this study indicated that radical stabilization capability of MMA compared to MA is higher. The accuracy of the reactivity ratios were confirmed by 95% joint confidence limits. It was found that considering the effect of conversion in these methods makes the calculation result more accurate. The theoretical composition drifts in the comonomer mixture and copolymer as a function of the overall monomer conversion are also reported.

Keywords: atom transfer radical polymerization (ATRP); methyl acrylate; methyl methacrylate; poly(vinyl acetate) macroinitiator; monomer reactivity ratios

1 Introduction

The development of controlled living radical polymerization (CLRP) for the synthesis of polymers with controlled architecture, molecular weight, and narrow polydispersity is among the most significant accomplishments in polymer chemistry (1). Among three kinds of CLRP methods, the atom transfer radical polymerization (ATRP) is one of the most successful methods to polymerize styrens, (meth) acrylates and a variety of other monomers in a controlled fashion (2, 3).

The recent development of ATRP has opened a new route for the controlled synthesis of several block copolymers (4, 5). A wide variety of block copolymers can be derived from the same family of vinyl monomers (6, 7) or different families of vinyl monomers via ATRP (8).

Atom transfer radical copolymerization of various monomers has been performed in order to comparing monomer reactivity ratios of this system with free radical copolymerization and to evaluating mechanism of atom transfer radical polymerization. Monomer reactivity ratios in free radical and atom transfer radical copolymerization of methyl methacrylate/butyl acrylate (9), alkyl 4-vinylbenzoate/butyl acrylate (10), styrene/n-octyl methacrylate (11), benzyl methacrylat/ethyl methacrylate (12), allyl methacrylate/butyl acrylate (13) phenyl methacrylate/methyl methacrylate (14) styrene/methyl methacrylate (15) and phenoxycarbonylmethyl methacrylate/ethyl methacrylate (16) have been studied and the results does not show any significant difference in monomer reactivity ratios. In the present study, we explore the reactivity ratios of methyl acrylate and methyl methacrylate monomers in ATRP with the assumption that there are some similarities between the mechanism of ATRP and free radical polymerization. Secondly, we like to explore further the effect of the macroinitiators in this reaction.

The three-component ATRP initiating system contains an organo-halide-type initiator, catalyst in the form of a salt of transition metal in the lower oxidation state, and a complexing ligand based mostly on amine-type. The combination of a catalyst and an appropriate ligand affects the redox potential of the system, leading to the equilibrium between dormant

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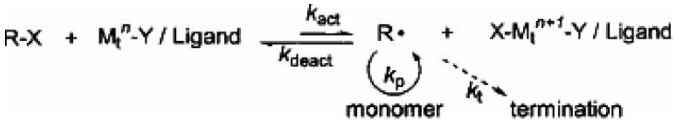

Sch. 1. Schematic illustration of ATRP mechanism (2).

and active forms of growing chains, which minimizes an extent of termination reactions. Thus, the equilibrium between halogenated polymer chain (dormant form) and growing free macroradical (active form), is the key step of ATRP, as simply described in the commonly accepted Scheme 1 (2).

Halogen-terminated poly(vinyl acetate) telomer with low molecular weight has been used as the macroinitiator (R-X) in atom transfer radical homopolymerization of various monomers (17–21). It has been found that poly(vinyl acetate) telomer can be used as an effective macroinitiator in ATRP. In the present study, atom transfer radical copolymerization of methyl methacrylate (MMA)/methyl acrylate (MA) was performed at first time by using trichloromethyl-terminated poly(vinyl acetate) telomer as the macroinitiator. Monomer conversion and copolymer composition were obtained by gravimetry and ^{1}H-NMR spectroscopy, respectively. Then monomer reactivity ratios were calculated by various methods mentioned in literature and composition drifts in the comonomer mixture and copolymer were investigated. These results have been used in this paper to explore the reactivity ratios of the monomers and the accuracy of various methods with their effects on the compositional drift of the ATRP.

2 Experimental

2.1 Materials

Methyl acrylate (MA) (Merck, 99.9%) and methyl methacrylate (MMA) (Merck, 99.9%) were passed from the basic alumina column over calcium hydride (CaH_2). CuCl was washed by glacial acetic acid (three times), absolute ethanol and diethyl ether in turn and then dried under vacuum. N,N,N′, N″,N″-pentamethyldiethylenetriamine (PMDETA, Merck, 99.8%) as ligand and tetrahydofuran (THF) as the solvent were used as received. Trichloromethyl-terminated poly(vinyl acetate) telomer was prepared by telomerization of VAc monomer in the presence of chloroform (18, 20) with 81% end functionality, molecular weight of 2432 g mol^{-1} and molecular weight distribution of 1.77 and used as macroinitiator in atom transfer radical copolymerization of MA and MMA. After the telomerization reaction, unreacted monomer and chloroform were evaporated at room temperature. THF was then added to product and refluxed for 5 h at 50°C to decompose traces of unreacted AIBN initiator (20). Finally, THF was evaporated at room temperature and the polymer was dried under vacuum at 50°C up to a constant weight.

2.2 Atom Transfer Radical Copolymerization of MA and MMA with Macroinitiator

A required amount of CuCl was introduced to a glass tube equipped with a magnetic stirrer. The glass tube was sealed with a rubber septum and was cycled between vacuum and nitrogen three times. The mixtures containing MA and MMA, macroinitiator (PVAc-CCl_3 telomer) and ligand (PMDETA) were degassed by nitrogen purging for 20 min before adding to the glass tube. The ratio of reaction ingredients $[MA + MMA]_0/[PMDETA]_0/[CuCl]_0/[PVAc\text{-}CCl_3]_0$ was 100/2/1/1. The "freeze–pump–thaw" cycle was carried out three times to remove oxygen from the glass tube and sealed under vacuum. The sealed tube was immersed in a preheated oil bath at a desired temperature. The tube was then removed from the oil bath and reaction mixture was dissolved in THF, filtered and dried under vacuum to a constant weight and conversion was determined gravimetrically. The dried copolymer was redissolved in THF and passed through a neutral alumina column to remove the remaining copper catalyst. The sample was then dried again under vacuum at 50°C up to a constant weight and used in ^{1}H-NMR spectroscopy.

2.3 Characterization

Weight based-overall monomer conversion (W) was calculated by the polymer weight in the sample drawn out. Poly(vinyl acetate)-block-poly(MA-co-MMA) terpolymers were first dried, then dissolved in THF, passed from a neutral alumina column to remove the catalyst (CuCl) and finally dried at 60°C under vacuum oven to a constant weight. Terpolymers were dissolved in $CDCl_3$ and characterized by using 400 MHz ^{1}H-NMR spectroscopy (DRX 400 Bruker Avance) at ambient temperature.

3 Results and Discussion

3.1 Calculation of Copolymer Composition (F) by ^{1}H-NMR

Terpolymers with various mole fractions of MA and MMA were prepared via vinyl acetate telomer initiated-atom transfer radical bulk copolymerization of MA and MMA with different initial mole fractions of comonomer mixture (Table 1) at 80°C. ^{1}H-NMR spectroscopy was used to

Table 1. Data obtained for atom transfer radical copolymerization of MA and MMA initiated with vinyl acetate telomer

Sample	f	F	W (%)	x (%)	x_{MA} (%)	x_{MMA} (%)
1	0.779	0.3638	19.0	18.53	11.25	24.21
2	1.2727	0.6155	16.0	15.58	10.60	21.92
3	2.4965	1.2371	12.4	12.10	9.37	18.91
4	4.7143	1.7933	11.6	11.27	8.77	23.06
5	8.5238	3.9020	10.15	9.99	8.88	19.41

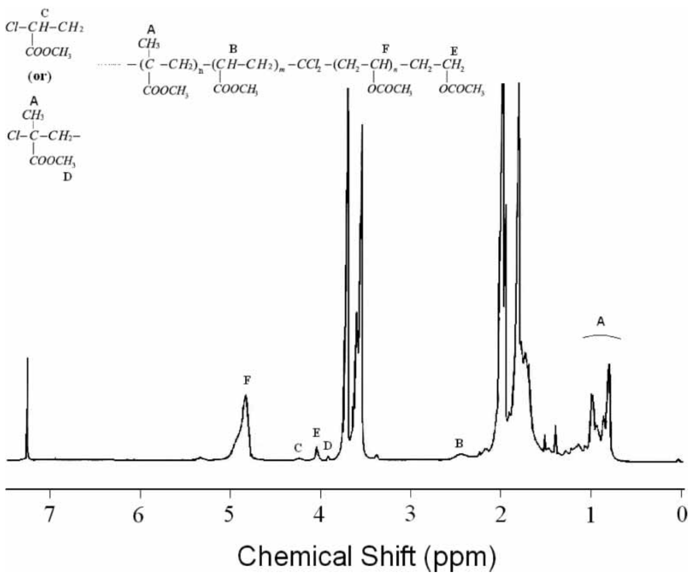

Fig. 1. ^{1}H-NMR spectrum of terpolymer prepared by vinyl acetate telomer initiated-atom transfer radical copolymerization of MA and MMA for sample 1.

characterize terpolymer composition. Figure 1 shows the assignments of ^{1}H-NMR signals to the corresponding protons for sample 1 containing 0.267 mole fraction of MA in the initial feed (21). As shown in Figure 1, it is clear that signals with chemical shifts of 0.7–1.2 ppm are related to the methyl protons of MMA and signals appeared in 2.4 and 4.2 ppm are related to the methine proton of MA. Thus, it is possible to calculate the mole ratio of MA to MMA (F_{MA}/F_{MMA}) incorporated into the copolymer via Equation (1)

$$F = \frac{F_{MA}}{F_{MMA}} = \frac{I_{CH(2.4)} + I_{CH(4.2)}}{I_{CH_3(0.7-1.2)}/3} \qquad (1)$$

In which F is the mole ratio of MA to MMA in the produced copolymer and I_{CH} and I_{CH_3} indicate the intensities of MA methine and MMA methyl proton resonance signals, respectively. For example, F value for sample 1 (Figure 1) was calculated to be 0.3642 $((2.372 + 0.271)/[(11.437 + 9.498 + 0.858)/3] = 0.3638)$. Results of copolymer composition calculations are given in Table 1.

Now, overall molar conversion (x), as well as individual molar conversions of MA (x_{MA}) and MMA (x_{MMA}), can be calculated by given values of overall weight conversion (W) and initial feed (f, mole ratio of MA to MMA in the initial comonomer mixture) and copolymer compositions (F) (Table 1) via the following equations (22):

$$x_{MMA} = \frac{W(\mu + f)}{(\mu + F)} \qquad (2)$$

$$x_{MA} = x_{MMA}(F/f) \qquad (3)$$

$$x = f_{MA} \times x_{MA} + f_{MMA} \times x_{MMA} \qquad (4)$$

in which μ is the molecular ratios of MMA (100.12 gmol^{-1}) to MA (86.09 gmol^{-1}). Results of calculations are given in Table 1.

3.2 Determination of the Reactivity Ratios of MA and MMA

Monomer reactivity ratios are generally determined at low conversion. In terminal model of copolymerization, a given pair of monomers, the instantaneous copolymer composition is a function of instantaneous feed only (23, 24).

Among several procedures available to determine monomer reactivity ratio, the methods of Mayo-Lewis (ML) (23), Finemann-Ross (FR) (25), inverted Finemann-Ross (26), Kelen-Tudos (KT) (27), extended Kelen-Tudos (22), Joshi- Joshi (JJ) (28) Tidwell-Mortimer (TM) (29), Mao-Huglin (MH) (30) have been extensively used. The extended Kelen-Tudos and Mao-Huglin methods are also used at high conversion.

3.3 Finemann-Ross (FR) Method (25)

The values of f (from polymerization recipe) and F (from ^{1}H-NMR spectra) (Table 1) were used to calculate G and H according to the following Equations (5) and (6):

$$G = \frac{f}{F}(F - 1) \qquad (5)$$

$$H = \frac{f^2}{F} \qquad (6)$$

The linear relationship between G and H (Eq. (7)) could be given as follows:

$$G = r_{MA} \times H - r_{MMA} \qquad (7)$$

Substituting G and H will result in a plot, in which its slope is r_{MA} and the intercept will give r_{MMA} (Figure 2). The obtained values of r_{MA} and r_{MMA} by this method were 0.4170 and 2.0160, respectively.

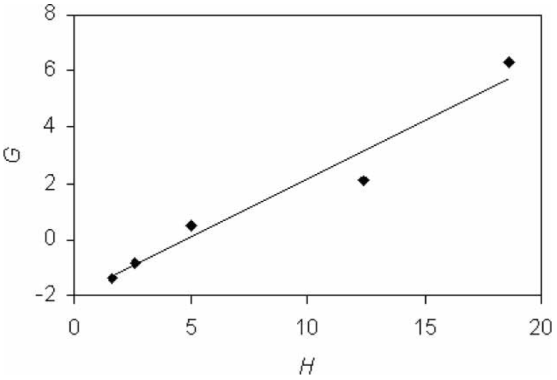

Fig. 2. G vs. H in the FR plot.

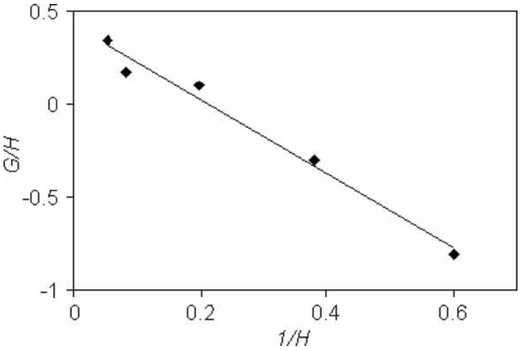

Fig. 3. G/H as a function of 1/H in the inverted FR method.

3.4 Inverted Finemann-Ross Method (26)

The linear relationship in the FR method between r_{MA} and r_{MMA} could be shown as Equation (8) for the inverted FR method.

$$G/H = -r_{MMA}(1/H) + r_{MA} \tag{8}$$

According to the data available in Table 1, G/H vs. 1/H has been plotted in Figure 3. The reactivity ratios could be obtained from the slope ($r_{MMA} = 2.0087$) and intercept ($r_{MA} = 0.4245$) of the best fitted line (Figure 3).

3.5 Mayo-Lewis (ML) Method (23)

This method uses the calculated values of G and H in FR method. The difference is that, for each G and H value, the corresponding line should be plotted using Equation (9) by substituting an arbitrary value for r_{MA}. Then the position of the crossing point of all lines will show a real amount of reactivity ratios (Figure 4).

$$r_{MMA} = H \times r_{MA} - G \tag{9}$$

where $r_{MMA} = 2.0963$ and $r_{MA} = 0.4988$.

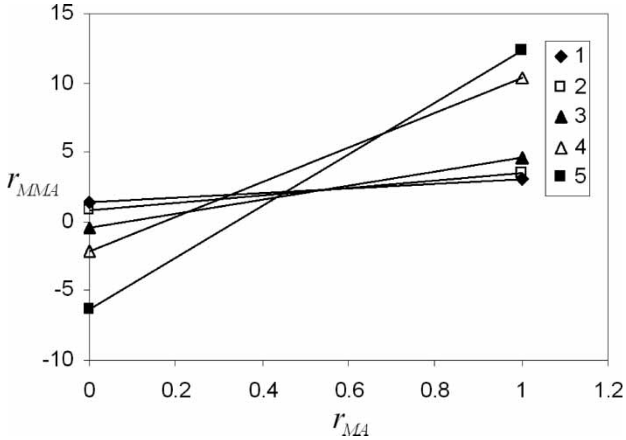

Fig. 4. r_{MMA} vs. r_{MA} for various samples in the ML method.

3.6 Kelen- Tudos (KT) Method (27)

Kelen-Tudos has been used in copolymerization reactions. The major criticisms that can be expressed against such linearization methods is that r_{MMA} and r_{MA} do not play symmetrical roles, for instance, Equation (9) The KT method aims at preventing the nonsymmetrical characteristic of the composition equation from affecting the reactivity ratio values determined experimentally. In this method, the reactivity ratios are related to each other due to the following equation (Equation (10)):

$$\eta = \left[r_{MA} + \frac{r_{MMA}}{\alpha}\right]\xi - \frac{r_{MMA}}{\alpha} \tag{10}$$

Where

$$\alpha = (H_{\max} \cdot H_{\min})^{0.5}, \quad \xi = \frac{H}{\alpha + H} \text{ and } \eta = \frac{G}{\alpha + H} \tag{11}$$

$H_{\max}$ and $H_{\min}$ are the maximum and minimum values of H, respectively. The domain for variation of ξ is between 0 and 1, meanwhile, this domain for H is 0 and ∞. The amount of G and H could be extracted from Table 1, and the result of calculations has been plotted in Figure 5. According to this plot, r_{MMA} and r_{MA} were obtained to be 1.9146 and 0.4034, respectively.

3.7 Extended Kelen-Tudos (KT) Method (22)

It is accepted that linear least-squares (LLS) methods, such as FR and KT, can only be applied to experimental data at sufficiently low conversion, because the calculation is based on the differential copolymerization equation. The only exception is the extended KT method, which involves a rather more complex calculation, but is still a LLS method. It can be applied from low (<15%) to medium-high (<40%) conversions without significant systematic error.

Hence, the individual molar conversion of monomers (x_{MMA} and x_{MA}) could be obtained from Equations (2) and (3) (Table 1).

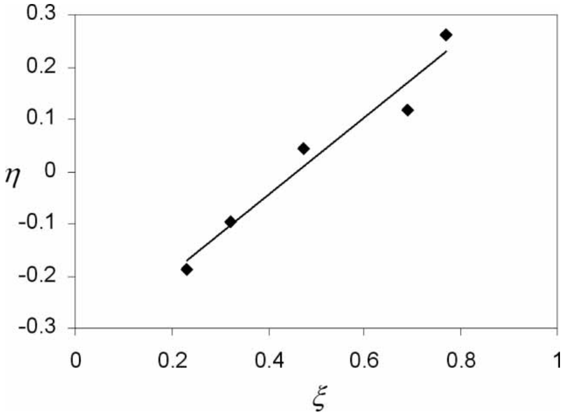

Fig. 5. η vs. ξ in the KT method.

The parameter Z could be calculated as below (Equation (12):

$$Z = \frac{\log(1 - x_{MA})}{\log(1 - x_{MMA})} \tag{12}$$

Then:

$$G = \frac{(F-1)}{Z} \quad and \quad H = \frac{F}{Z^2} \tag{13}$$

By substituting the new G and H values in Equation (10), the corresponding reactivity ratios, at low conversion, would be obtained from the consequent plot of η vs. ξ (Table 1 and Figure 6).

The obtained reactivity ratio is 2.0524 for MMA and 0.3766 for MA.

3.8 Joshi-Joshi (JJ) Method (28)

The JJ method is an absolute analytical procedure for obtaining the monomer reactivity ratios, setting up least-squares condition that places equal weight on all experimental lines of the ML plot. In this method, monomer reactivity ratios could be calculated by Equations (14) and (15).

$$r_{MA} = \frac{\sum(1/1+H_i^2)\sum(H_iG_i/1+H_i^2) - \sum(H_i/1+H_i^2)\sum(G_i/1+H_i^2)}{(\sum H_i/1+H_i^2)^2 - \sum(1/1+H_i^2)\sum(H_i^2/1+H_i^2)} \tag{14}$$

$$r_{MMA} = \frac{\sum(H_i/1+H_i^2)\sum(H_iG_i/1+H_i^2) - \sum(H_i^2/1+H_i^2)\sum(G_i/1+H_i^2)}{(\sum H_i/1+H_i^2)^2 - \sum(1/1+H_i^2)\sum(H_i^2/1+H_i^2)} \tag{15}$$

in which H_i and G_i indicate the H and G values for sample i. Inspection of Equations (14) and (15) reveals that the JJ solution is almost identical to the one obtainable from the usual linearization procedure of FR (25):

$$r_{MA} = \frac{N\sum H_iG_i - \sum H_i \sum G_i}{(\sum H_i)^2 - N\sum H_i^2} \tag{16}$$

$$r_{MA} = \frac{\sum H_i \sum H_iG_i - \sum H_i^2 \sum G_i}{(\sum H_i)^2 - N\sum H_i^2} \tag{17}$$

N is the number of experiments. In the JJ procedure, only the weighting factor $1/(1+H_i^2)$ occurs with every summation term in H_i and G_i; $1/(1+H_i^2)$ corresponding to N in Equations (16) and (17). This factor seems to normalize the numerical extremities of the summation terms, imparting a uniform weight to every experimental line in the JJ procedure, and eliminating some of the well-known deficiencies of the simple least- square procedure. For instance, the simple least square procedure due to FR (25) fails to yield the same solution when the datum is merely inverted (inverted FR (26), i.e., the monomer formerly taken as M_1 is taken as M_2 and the former M_2 as M_1 (Equations (7) and (8)). In the JJ method, a unique solution is obtained from one and the same datum, whichever of the two monomers is taken first as M_1.

The monomer reactivity ratios of MMA and MA were calculated by the JJ method to be 1.9927 and 0.4212, respectively.

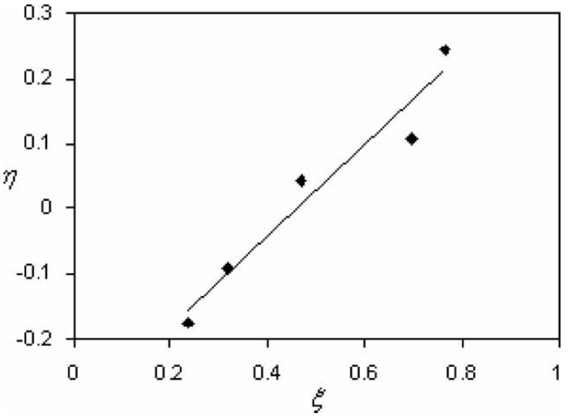

Fig. 6. η vs. ξ in the extended KT method at low conversion.

3.9 Mao-Huglin (MH) Method (30)

The Mao-Huglin method is a more recent method that was presented at 1993 (30). By considering the corresponding equations (30), computer simulation was used to a series of data at low conversions (Table 1). The results were obtained with initial assumption of $r_{MMA} = r_{MA} = 1$ and five iterations of calculations. The value of reactivity ratios by MH method for MMA was 2.0513 and for MA was 0.3769.

3.10 Tidwell-Mortimer (TM) Method (29)

The TM procedure is considered to be one of the most accurate procedures for determination of monomer reactivity ratio values (29). The method is a modification of the curve-fitting procedure. Therefore, the sum of squares of the difference between observed and computed polymer compositions are minimized. The computation procedure is basically a Gauss-Newton non-linear least-squares method, which was modified by Box (31) to assure rapid convergence to a pair of values. As a summary, the method consisting initial estimates of r_{MMA} and r_{MA} and a set of computations is performed to yield the sum of squares of the differences between the observed and computed polymer compositions. The summation is then minimized by iteration to yield monomer reactivity ratios. More detailed data about calculation method and the way to reach to real reactivity ratios have been discussed by Kress and coworkers (32). For our system, the initial estimate of reactivity ratios were $r_{MMA} = r_{MA} = 1$ and four

Table 2. The summary of the calculated monomer reactivity ratios by different methods for atom transfer radical copolymerization of MA and MMA together with reactivity ratios reported in the literature for conventional free-radical copolymerization

Method	r_{MMA}	r_{MA}
FR	2.0160	0.4170
Inverted FR	2.0087	0.4245
KT	1.9146	0.4034
Extended KT	2.0524	0.3766
JJ	1.9927	0.4212
ML	2.0963	0.4988
MH	2.0513	0.3769
TM	1.8832	0.4007
(38)[a]	2.1	0.4

[a] Data reported for conventional free- radical copolymerization of MMA and MA.

iterations were performed to obtain the minimum difference. The values of r_{MMA} and r_{MA} were found to be 0.4007 and 1.8832, respectively.

As a result, the amounts of reactivity ratios obtained by each method have been summarized in Table 2.

3.11 *Joint Confidence Limit Calculation for Different Methods (32, 33)*

Simple intervals do not clearly convey the message of which pair of parameters are consistent with the data since calculations of the reactivity ratios must be simultaneously determined and therefore, cannot be considered statistically independent. The specification of joint confidence limits, within which the correct values are believed to exist, properly conveys some idea of the goodness of the experiment and data. The smaller the experimental error and the better the experimental design, the smaller the area of uncertainty.

The 95% joint confidence limits for the reactivity ratios of MA/MMA system have been shown in Figure 7. The corresponding detail has been mentioned elsewhere (32, 33). It is clear that MH and extended KT methods gives the most precise estimate, although this estimate is only slightly better than that obtained by the KT and TM methods. For systems with greater difference between the monomer reactivity ratios such as the present case, more reliable and precise reactivity ratios will be obtained with considering monomer conversion in the calculations because of the significant changes in the monomer mixture compositions with reaction times. Among the models investigated in this study only MH and extended KT methods consider the effect of conversion in calculating monomer reactivity ratios, resulting in more reliable reactivity ratios.

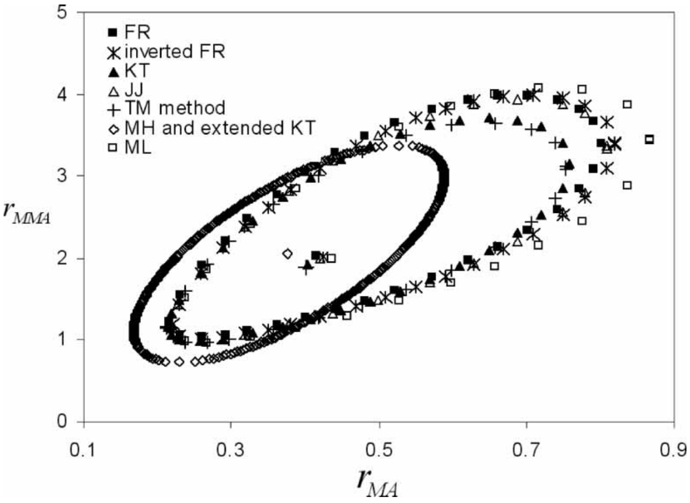

Fig. 7. Monomer reactivity ratios and 95% joint confidence limits for the reactivity ratios of MMA and MA obtained in this work by various methods.

Relative information about the radical reactivities can be obtained by copolymerization of monomers. Using the reactivity ratios for the MMA/MA system, the reactivities can directly be compared. Monomer reactivity ratios presented in Table 2 clearly indicate the better radical stabilization capability of MMA compared to MA. Thus, a moderately better stabilized radical is derived from a MMA macroradical. It is expected that tendency of incorporation of MMA into the copolymeric radical chains is higher than VAc. Higher radical stabilization of MMA can be confirmed by investigating kinetic of atom transfer radical homopolymerization of MA and MMA under the same conditions. Atom transfer radical bulk homopolymerization of MA and MMA at 80°C with trichloromethyl- terminated poly(vinyl acetate) telomer has been studied by Semsarzadeh and Rostami Daronkola (21). In that study, the apparent rate constant (k_p^{app}) at 80°C for homopolymerization of MA and MMA has been calculated by the slope of ln$[M]_0/[M]$ vs. time curve according to Equation (19) and therefore, the concentration of radicals, i.e. $[P^{\cdot}]$, could been obtained by Equation (20). Propagation rate constant (k_p) value for conventional free- radical homopolymerizations of MA and MMA at 80°C has been reported to be 47500 (34) and 1350 (35, 36) $\mathrm{Lmol^{-1}s^{-1}}$, respectively. By using this k_p values for ATRP of MA and MMA, together with obtained k_p^{app} values (8.64×10^{-6} and $1.20 \times 10^{-3}\ \mathrm{s^{-1}}$ for MA and MMA, respectively (21), the concentration of radicals for atom transfer radical homopolymerizations of MA and MMA has been calculated to be 1.82×10^{-10} and $8.89 \times 10^{-7}\ \mathrm{mol \cdot l^{-1}}$, respectively.

$$R_p = -\frac{d[M]}{dt} = k_p[p^{\cdot}][M] = k_p^{app}[M] \tag{18}$$

$$\ln\frac{[M]_0}{[M]} = k_p^{app} t \tag{19}$$

$$[p^{\cdot}] = \frac{k_p^{app}}{k_p} \tag{20}$$

From this data, it is clear that the concentration of radicals generated in atom transfer radical homopolymerization of MMA is much higher than those generated in atom transfer radical homopolymerization of MA at the same homopolymerization conditions, that is, according to Scheme 1 equilibrium constant ($K = k_{act}/k_{deact}$) in the case of MMA is greater than that in the case of MA. It is means that better stabilized radicals is derived from a MMA macroradical in comparison to the radicals obtained from a MA macroradical. As a result, in the copolymerization of MA/MMA system, MMA monomeric units are preferentially added to the macroradicals and thereby long sequences of MMA units can be formed in the initial stage of copolymerization as observed by investigating triads in the copolymer chain (21). This is expected also from the greater reactivity ratio of MMA than MA and will be discussed later.

3.11 Composition Drifts in the Monomer Mixture and Copolymer

Other important information about MMA/MA copolymerization system can be obtained via plots of the monomer mixture and copolymer compositions vs. the overall monomer conversions. The instantaneous copolymer composition equation of Mayo-Lewis (23) is express as Equation (21):

$$F_i = \frac{r_i f_i^2 + f_i f_j}{r_i f_i^2 + 2f_i f_j + r_i f_j^2} \tag{21}$$

F_i in this equation is the instantaneous mole fraction of monomer i (MA) in the produced copolymer.

An integration of Equation (21) leads to the Meyer-Lowry (37) equation as follows:

$$x = 1 - \left(\frac{f_i}{f_i^o}\right)^{\alpha} \left(\frac{1-f_i}{1-f_i^o}\right)^{\beta} \left(\frac{f_i^o - \delta}{f_i - \delta}\right)^{\gamma} \tag{22}$$

Where

$$\alpha = \frac{r_j}{1-r_j};\ \beta = \frac{r_i}{1-r_i};\ \gamma = \frac{1-r_i r_j}{(1-r_i)(1-r_j)} \text{ and } \delta = \frac{1-r_j}{2-r_i-r_j}$$

f_i is the instantaneous mole fraction of monomer i in the feed, f_i^o is f_i in the initial state. According to the Meyer- Lowry equation, the overall monomer conversion (x) is related to the monomer composition in the reaction mixture and reactivity ratios. Some of these parameters are related by a material balance in the following equation, where $\bar{F}_i$ is the cumulative average mole fraction of MA in the copolymer.

$$\bar{F}_i = \frac{f_i^o - f_i(1-x)}{x} \tag{23}$$

Using the Meyer-Lowry equation (37) in conjunction with Equation (23), theoretical f_i and $\bar{F}_i$ were obtained as a function of overall monomer conversion for different feed compositions, as shown in Figures 8 and 9, respectively. As mentioned before, the monomer reactivity ratios obtained by MH (or extended KT) method was preferentially used in the Meyer-Lowry equation.

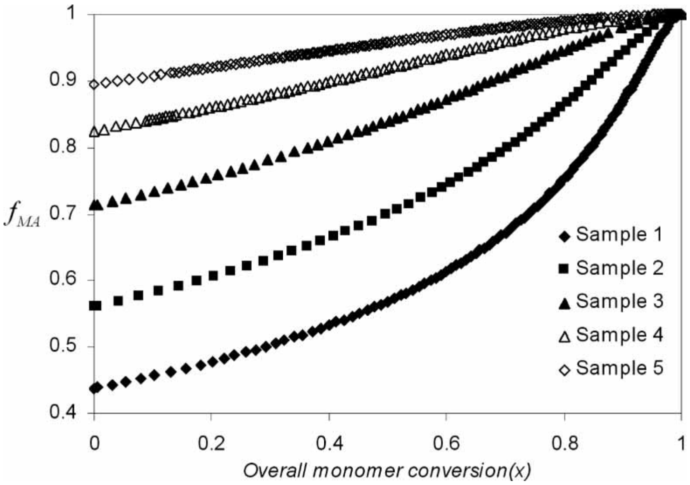

Fig. 8. Monomer mixture composition as a function of the overall monomer conversion for various mole fractions of MA in the initial feed calculated by Meyer- Lowry equation (Equation 22) using reactivity ratios of the MH method.

Figure 8 shows the theoretical changes in comonomer mixture composition vs. overall monomer conversion for various amounts of MA (or MMA) in the initial reaction mixture. This figure reveals that in the various mole fractions of MMA in the initial feed, the incorporation of MMA into the copolymer chain is more favored than MA. The overall changes in the comonomer mixture composition with increasing conversion is very high; indicating that the reactivity ratio of MMA should be much greater than that of MA, as obtained

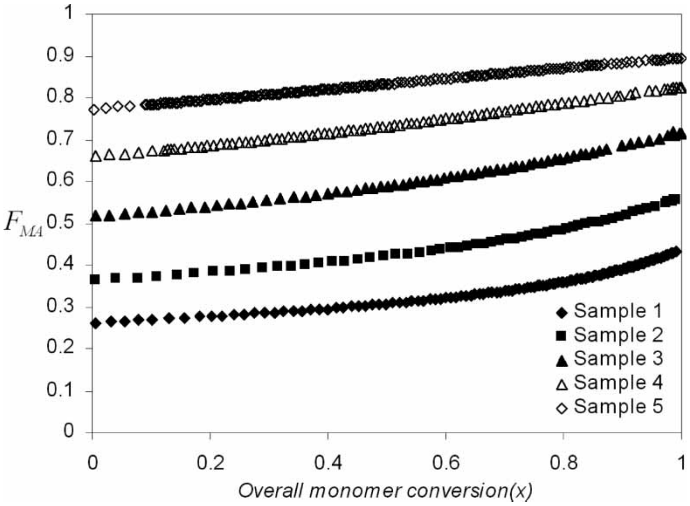

Fig. 9. Dependency of the copolymer composition drifts vs. overall monomer conversion plots on the mole fraction of MA in the initial reaction mixture calculated by the Meyer-Lowry equation (Eq. 22) in conjunction with the material balance equation (Eq. (23)) using reactivity ratios of the MH method.

before. In other words, the adduct radical of MMA monomer is more likely to react with its own monomer relative to MA monomer while the adduct radical of MA monomer is more likely to react with MMA monomer relative to its own monomer. This causes the higher rate of incorporation of MMA into the copolymer chain than MA, resulting in the significant changes in the monomer mixture composition. It is observable from Figure 8 that the rate of incorporation of MMA into the copolymer is high so that the mole fraction of MMA in the monomer mixture reduces to about zero at the last stage of copolymerization. It is clear that composition drifts in comonomer mixture increases with increasing mole fraction of MMA in the initial feed. It can be attributed to this fact that the higher the concentration of more reactive monomer, the higher the rate of incorporation of more reactive comonomer into the copolymeric radical chains.

It is expected that the changes in copolymer composition will be less pronounced up to the overall monomer conversion at which changes in the comonomer composition in the monomer mixture is considerable, as shown in Figure 9. The theoretical data in Figure 9 reveal that until changes in the comonomer composition is not significant, the copolymer composition drift is not considerable. In other words, when the amount of MA in the monomer mixture reduces drastically, the copolymer composition will be changed significantly with increasing overall monomer conversion.

The theoretical composition curve obtained from copolymer composition equation of Mayo-Lewis (23) (Eq. (21)) using monomer reactivity ratios of MH (or extended KT) method and the experimental data of f_{MA}^{o} obtainable from Table 1 are shown in Figure 10. The experimental data are in good agreement with the theoretical curve, suggesting the accuracy of calculated monomer reactivity ratios.

Under conditions of $r_i > 1$ and $r_j < 1$ as be in the case of MMA/MA pair monomers, both adduct radicals incline to react with the more reactive monomer i. Thus, if even the radical M_j^* is formed, it reacts immediately with M_i and generates the radical M_i^*. This later radical inclines to react with the own monomer. In other words, M_i tends to homopolymerize while M_j tends to copolymerize. It is clear that chains produced in the initial stages of reaction before significant decrease of the concentration of monomer i (i.e. MMA) in the monomer mixture will be random copolymers with long blocks of MMA units and short blocks of MA units. After this stage, random copolymer chains containing long blocks of MA units are formed.

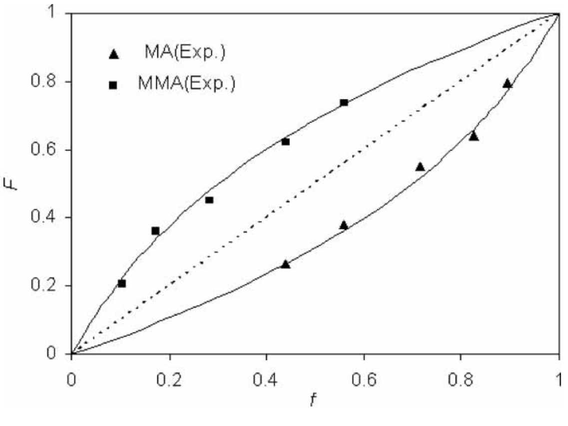

Fig. 10. The variation of copolymer composition (F_{MMA} and F_{MA} indicated on the corresponding curves) as a function of the mole fraction of MMA and MA in the initial feed (f_{MMA}^{o} and f_{MA}^{o}, respectively) for MMA/MA copolymerization (points are the experimental data and full lines are the theoretical curves obtained using reactivity ratios of MH method in the copolymer composition equation).

4 Conclusions

Atom transfer radical bulk copolymerization of MA and MMA was performed in the presence of CuCl/PMDETA as catalyst system and vinyl acetate telomer as macroinitiator at 80°C. Monomer reactivity ratios were calculated by various linear and nonlinear methods, which were in good agreement with the values reported for similar system in the free-radical copolymerization. It was observed that copolymerization system tends to produce a random copolymer with the longer sequences of MMA than MA in the initial stages of reaction before significant decrease in the concentration of MMA in the monomer mixture. This copolymer microstructure is the result of more radical stabilization capability of MMA compared to MA. The statistical methods of calculations of the certainty is based on a 95% joint confidence limits calculations of the reactivity ratios to investigate the accuracy of reactivity ratios obtained in ATRP. It was found that extended KT and MH methods are more accurate. The changes in comonomer mixture and copolymer compositions as a function of overall monomer conversion were also investigated theoretically and the effect of monomer reactivity ratios on composition drift was evaluated.

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