

Polymer Communication

A new simple procedure to calculate monomer reactivity ratios by using on-line ^1H NMR kinetic experiments: Copolymerization system with greater difference between the monomer reactivity ratios

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Abstract

Free radical copolymerization reaction of vinyl acetate (VA) and methyl acrylate (MA) in solution of benzene- d_6 using benzoyl peroxide (BPO) as the initiator was studied with on-line ^1H NMR kinetic experiments at 60 °C. It was observed that composition drifts in the comonomer mixture with reaction progress is significant. Hence, the monomer reactivity ratios of VA/MA system could be calculated by the data collected only from one sample via on-line following the comonomer mixture and copolymer compositions at different reaction time intervals up to medium overall monomer conversions. The results were in good agreement with the literature data reported for this system. The good fitting between theoretical and experimental changes in the comonomer mixture compositions as a function of reaction progress was observed, indicating the accuracy of the monomer reactivity ratios calculated by the new procedure presented here.

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1. Introduction

On-line ^1H NMR kinetic experiments allow us to calculate simultaneously individual and overall monomer conversions as well as the comonomer mixture and copolymer chain compositions as a function of reaction progress. This is one of the advantages of this on-line technique relative to the off-line techniques and some of the on-line techniques. ^1H NMR spectroscopy has been proven to be one of the most important and reliable techniques for studying the polymer structure and the copolymer composition [1–4]. On-line ^1H NMR kinetic experiments have been successfully used for the kinetic study of free radical homo- and copolymerization [5–10].

Earlier, our group reported the monomer reactivity ratios and polymerization rate coefficient of the vinyl acetate/methyl acrylate (VA/MA) system by using on-line ^1H NMR kinetic experiments [11]. There is greater difference between the reactivity ratios of VA (r_{VA}) and MA (r_{MA}). In general, for systems with greater differences between the monomer reactivity ratios such as VA/MA [11–18], VA/ethyl acrylate [19], VA/butyl acrylate [19] and VA/butyl methacrylate [20] the significant composition drifts in the comonomer mixture and copolymer are expected. For this reason, the comonomer mixture and instantaneous copolymer compositions change significantly by progress of the reaction and thus it is possible to calculate the monomer reactivity ratios by on-line following these changes during the copolymerization reaction only for one initial comonomer mixture composition. It should be noted that viscosity of the reaction medium increases with the polymerization progress and thereby reactivities of macroradicals may be affected. To avoid this, it is necessary to prepare solutions with

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higher amounts of solvent or allow reaction to proceed up to low and medium overall monomer conversions.

In this work, it is shown for first time (to our knowledge) that monomer reactivity ratios can be calculated by data collected only from one initial comonomer mixture composition via on-line monitoring progress of the copolymerization reaction.

2. Experimental section

2.1. Materials

The monomers, VA and MA (from Aldrich chemical Co.), were washed three times with a 5% sodium hydroxide solution followed by three times washing with distilled water to remove their inhibitors and then dried over calcium chloride. Benzene- d_6 as the solvent was purchased from ARMAR chemicals (Dottingen, Switzerland). BPO (from Fluka chemical Co.) was used as the initiator without further purification.

2.2. Sample preparation

Solution samples were prepared with different monomer mixture compositions at constant initiator and overall monomer concentrations. First, initiator solution in benzene- d_6 was prepared. The defined amount of this solution was then added to the monomer mixture so that initiator and overall monomer concentrations were adjusted to be close to 2×10^{-2} M and 1 M, respectively. Two samples VM40.0 and VM51.1 were prepared with mole fractions 0.4003 and 0.5114 of MA in the initial comonomer mixture, respectively. Total volume of each sample was 1.00 ml. The final reaction mixture was then conducted to the NMR tube (5 mm in diameter). The solutions in the NMR tubes were degassed with nitrogen gas (99.9% purity) to exclude oxygen from the reaction mixtures, which acts as a retardant in the free radical polymerization reactions.

2.3. ^1H NMR kinetic experiments

All NMR experiments reported in this study were carried out on a Bruker Avance 400 MHz NMR spectrometer. The sample cavity was equilibrated at 60 °C (i.e., the temperature at which all the kinetic NMR experiments were carried out) by a BVT 3000 (± 0.1 °C) temperature control unit. A typical ^1H NMR kinetic experiment consists of the following sequence of steps.

First, the cavity was set to the desired reaction temperature (i.e., 60 °C), and a sample containing only benzene- d_6 (the solvent) was introduced into the sample cavity and allowed to equilibrate for approximately 10 min. The magnet was then thoroughly shimmed using the benzene- d_6 sample. Second, the sample tube containing the reaction mixture was inserted into the sample chamber, and the start time was recorded. The sample containing the reaction mixture was allowed to equilibrate for 10 min. The first recorded spectrum (after the sample tube containing the reaction mixture was inserted into the cavity) was regarded as the spectrum representing zero overall monomer conversion. Although approximately

10 min have passed from insertion of the sample into the cavity to the first scan, negligible conversion has occurred because of the low overall rate of reaction. It should be noted that all kinetic samples contained high amounts of benzene- d_6 . This high amount of benzene- d_6 had to be used because of better thermal conductivity of benzene relative to the comonomer mixture, maintaining the system isothermal due to the decreased concentration of comonomers and thereby decreased polymerization rate and to avoid an excessive viscosity increase at higher conversions.

3. Results and discussion

On-line ^1H NMR technique has been used for copolymerization reaction of VA and MA in order to determine the monomer reactivity ratios and overall polymerization rate coefficient [11]. In this work, possibility of the calculation of reactivity ratios of VA and MA with a new simple procedure will be discussed by using data obtained from on-line ^1H NMR kinetic experiments for VA/MA system. In this procedure, monomer reactivity ratios will be calculated by data collected only from one sample with proper initial comonomer mixture composition.

A typical ^1H NMR spectrum of an initial reaction mixture containing 0.4003 mole fraction of MA (sample VM40.0) at the overall monomer conversion of 40.34 mol% with the signal assignments has been shown in Fig. 1. Signal assignments for copolymerization systems were carried out with regard to the spectra recorded for homopolymerization of both VA and MA and comparing them with spectra related to the copolymerization systems [11]. From Fig. 1 it is clear that signals related to the $-\text{CH}$ protons of both VA ($-\text{CH}^p$) and MA ($-\text{CH}^m$) incorporated into the copolymer chain can be used to follow the reaction progress. In all the spectra of each sample, the overall integral for $-\text{CH}_3$ proton signals of MA (about 3.7–4.0 ppm in Fig. 1) existing in the monomer mixture ($-\text{CH}_3^d$) and in the produced copolymer ($-\text{CH}_3^n$) was adjusted to an arbitrary value of 3. The integral for the signals of each other protons in the same spectrum is automatically scaled according to this value. All other spectra recorded at various time intervals are then scaled similar to the first spectrum so that the overall integrals of all proton signals in the all other spectra for each sample were equal to the first spectrum of each sample. Thus, the individual conversions of both VA and MA can be monitored as a function of reaction time.

Individual monomer conversions of both VA and MA at the any reaction time were calculated via Eqs. (1) and (2), respectively.

$$x_{\text{VA}}(t) = \frac{I(-\text{CH}^p)_{\text{VA}}^{\text{copolymer}}(t)}{I(-\text{CH}^p)_{\text{VA}}^{\text{copolymer}}(t) + I(=\text{CH}^e)_{\text{VA}}^{\text{monomer}}(t)} \quad (1)$$

$$x_{\text{MA}}(t) = \frac{I(-\text{CH}^m)_{\text{MA}}^{\text{copolymer}}(t)}{I(-\text{CH}^m)_{\text{MA}}^{\text{copolymer}}(t) + I(=\text{CH}^a)_{\text{MA}}^{\text{monomer}}(t)} \quad (2)$$

where $x_i(t)$ is the individual conversion of monomer i at time t . $I(-\text{CH})_i^{\text{copolymer}}(t)$ and $I(=\text{CH})_i^{\text{monomer}}(t)$ indicate the

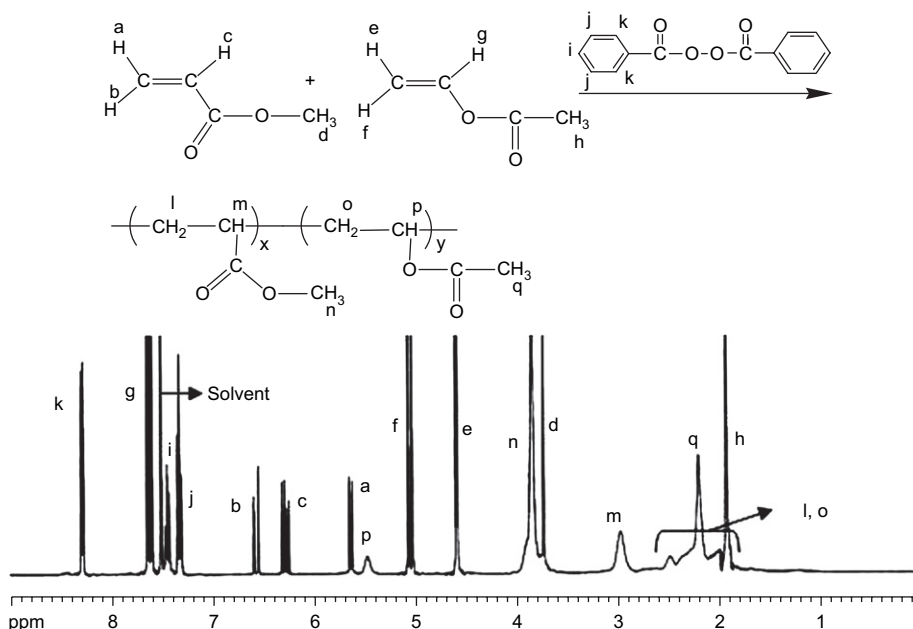


Fig. 1. A typical ^1H NMR spectrum of the monomer mixture and produced copolymer after the overall monomer conversion of 40.34 mol% for sample VM40.0 together with the copolymerization reaction scheme.

intensities of methine proton resonance signal of monomer i incorporated into the copolymer chain and one of the two methylene proton resonance signals of unreacted monomer i at time t , respectively. Overall monomer conversion ($x(t)$), mole fraction of monomer i in the monomer mixture ($f_i(t)$) and that in the produced copolymer chains ($F_i(t)$) at any time t after reaction progress are related to the individual monomer conversions by the following equations:

$$x(t) = f_i^0 x_i(t) + f_j^0 x_j(t) \quad (3)$$

$$f_i(t) = \frac{\frac{n_i^0}{n_j^0} [1 - x_i(t)]}{\frac{n_i^0}{n_j^0} [1 - x_i(t)] + [1 - x_j(t)]} \quad (4)$$

$$F_i(t) = \frac{\frac{n_i^0}{n_j^0} x_i(t)}{\frac{n_i^0}{n_j^0} x_i(t) + x_j(t)} \quad (5)$$

where f_i^0 is the mole fraction of monomer i in the initial reaction mixture and n_i^0 is the molar amount of monomer i in the initial feed. $F_i(t)$ is indeed the cumulative mole fraction of monomer i in the copolymer chains produced up to the reaction time t . Subscripts i and j indicate monomers MA and VA, respectively. From individual monomer conversion data obtained by on-line ^1H NMR kinetic experiments, it is possible to calculate $x(t)$, $f_i(t)$ and $F_i(t)$ as a function of time via Eqs. (3)–(5).

On-line ^1H NMR spectra recorded for sample VM40.0 as a function of the reaction time have been shown in Fig. 2. It could be found that by progress of the polymerization reaction, intensities of the peaks related to the protons of monomers incorporated into the copolymer chains are increasing. So, the

progress of reaction can be followed with time. As a consequence, it is possible to investigate the kinetics of VA/MA copolymerization reaction. It should be noted that the isothermal conditions were established during the course of reaction due to low rate of the copolymerization reaction and high amount of the solvent.

4. Determination of the monomer reactivity ratios

Individual and overall conversions of MA and VA as a function of time for the reaction system containing 0.5114 mole

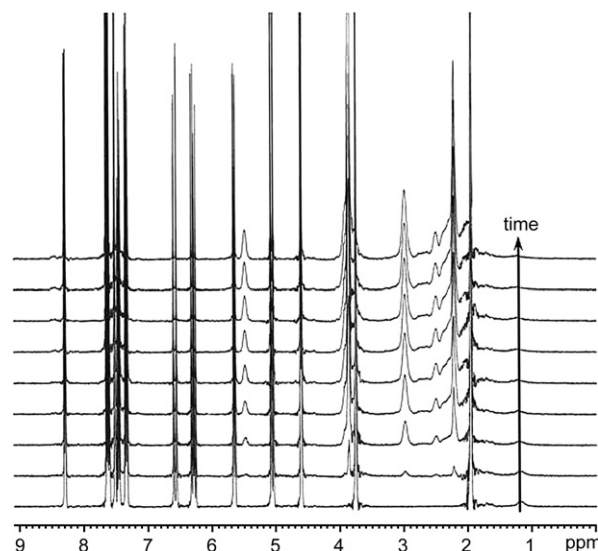


Fig. 2. Progress of the copolymerization reaction as a function of time for sample VM40.0 containing 0.4003 mole fraction of methyl acrylate in the initial feed.

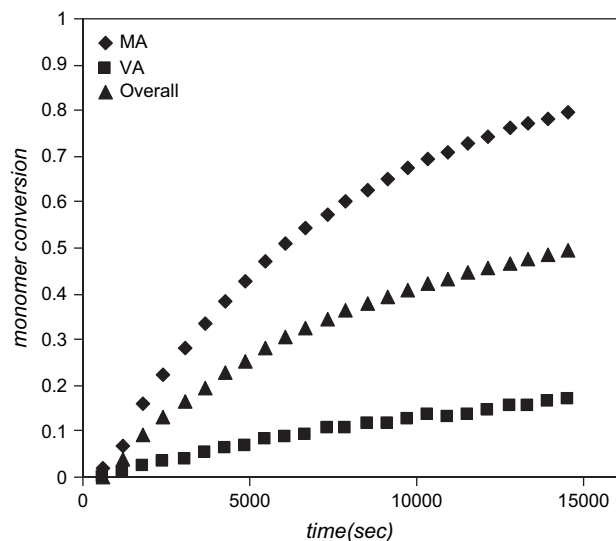


Fig. 3. Individual and overall conversions of VA and MA as a function of reaction time for the free radical copolymerization of sample VM51.1 containing 0.5114 mole fraction of methyl acrylate in the initial monomer mixture.

fraction of MA in the initial comonomer mixture (sample VM51.1) have been shown in Fig. 3. The reaction temperature in the experiments was set at 60 °C. Fig. 3 reveals that both monomers copolymerize and that MA is incorporated into the copolymer at a very high rate than VA. The same trends were observed for other initial feed composition, that is, MA is always preferentially incorporated into the copolymer chain. As mentioned before, individual monomer conversions versus time data may be used to deduce changes in the comonomer mixture composition as a function of the overall monomer conversion.

Fig. 4 shows experimental changes in the comonomer mixture compositions versus overall monomer conversion up to 50 mol% for various amounts of MA in the initial reaction mixture. Again, this figure reveals that in various mole fractions of MA in the initial feed, incorporation of MA into the copolymer chains is more favored than VA. The overall

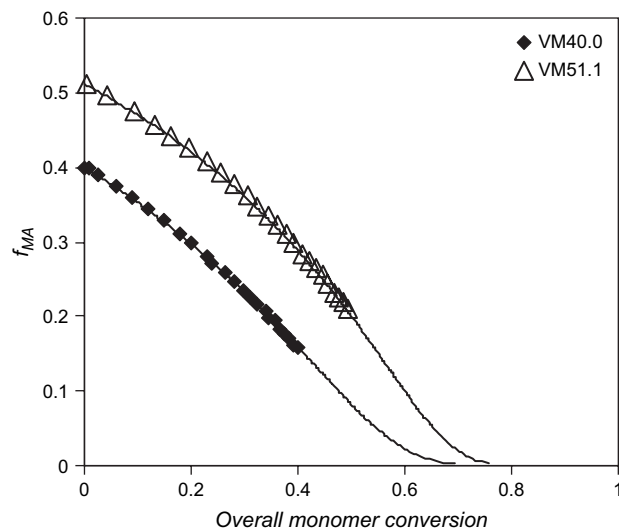


Fig. 4. Comonomer mixture composition as a function of overall monomer conversion for various mole fractions of MA in the initial feed (symbols show the experimental data and continuous lines indicate the theoretical data calculated by Meyer–Lowry equation using reactivity ratios of Mao–Huglin method).

$$f(t) = \frac{f_{MA}(t)}{f_{VA}(t)} = \frac{I(-CH^a)_{MA}^{\text{monomer}}(t)}{I(=CH^e)_{VA}^{\text{monomer}}(t)} \quad (6)$$

$$F(\Delta t') = \frac{F_{MA}(\Delta t')}{F_{VA}(\Delta t')} = \frac{I(-CH^m)_{MA}^{\text{copolymer}}(t') - I(-CH^m)_{MA}^{\text{copolymer}}(t)}{I(-CH^p)_{VA}^{\text{copolymer}}(t') - I(-CH^p)_{VA}^{\text{copolymer}}(t)} \quad (7)$$

$$x_{MA}(\Delta t') = \frac{I(-CH^m)_{MA}^{\text{copolymer}}(t') - I(-CH^m)_{MA}^{\text{copolymer}}(t)}{I(-CH^a)_{MA}^{\text{monomer}}(t)} \quad (8)$$

$$x_{VA}(\Delta t') = \frac{I(-CH^p)_{VA}^{\text{copolymer}}(t') - I(-CH^p)_{VA}^{\text{copolymer}}(t)}{I(=CH^e)_{VA}^{\text{monomer}}(t)} \quad (9)$$

$$x(\Delta t') = \frac{[I(-CH^m)_{MA}^{\text{copolymer}}(t') - I(-CH^m)_{MA}^{\text{copolymer}}(t)] + [I(-CH^p)_{VA}^{\text{copolymer}}(t') - I(-CH^p)_{VA}^{\text{copolymer}}(t)]}{I(-CH^a)_{MA}^{\text{monomer}}(t) + I(=CH^e)_{VA}^{\text{monomer}}(t)} \quad (10)$$

changes in the comonomer mixture compositions with increasing conversion are very high; indication that the reactivity ratio of MA should be much greater than that of VA, as obtained in the previous work [11].

According to the above observations, following the reaction progress and comonomer mixture compositions as a function of reaction time by on-line ^1H NMR kinetic experiments only for one sample with proper initial comonomer mixture composition allow us to collect the sufficient data for calculation of the monomer reactivity ratios. These data can be obtained via the following equations:

in which t is any time during the polymerization reaction and t' is also any time after time t . The mole ratio of monomers in the comonomer mixture at time t (i.e. $f(t)$) and that in the copolymer chains produced during the time interval $\Delta t'$ between t' and t (i.e. $F(\Delta t')$) as well as the corresponding individual and overall monomer conversions during this time interval have been given in Table 1 for both samples VM40.0 and VM51.1. It should be noted that data obtained for each sample are enough to calculate the monomer reactivity ratios. However, it is preferable to combine data of two samples and then calculate the more reliable reactivity ratios of VA and

Table 1

Copolymerization data obtained from on-line ^1H NMR kinetic experiments spectra at different reaction time intervals up to medium overall monomer conversion for free radical copolymerization of vinyl acetate/methyl acrylate system at 60 °C

$f(t)$	$F(\Delta t)$	$x(\Delta t)$	$f(t)$	$F(\Delta t)$	$x(\Delta t)$
VM51.1			0.3029	2.3510	0.0492
0.9843	7.1000	0.1277	VM40.0		
0.9045	6.6453	0.1145	0.6610	4.7441	0.1137
0.8435	6.1273	0.1123	0.6380	4.5870	0.1272
0.7909	5.7791	0.1075	0.5575	3.8942	0.1202
0.6489	4.6907	0.0950	0.5234	3.7212	0.1241
0.6086	4.4744	0.0913	0.4248	3.0099	0.1020
0.4747	3.6522	0.0743	0.3914	2.8324	0.0895
0.3417	2.6817	0.0572	0.2474	1.9968	0.0573

MA. The results of calculation of the monomer reactivity ratios by different methods including Finemann and Ross (FR) [21], Kelen and Tudos (KT) [22], Mao and Huglin (MH) [23], Joshi and Joshi (JJ) [24] and Tidwell and Mortimer (TM) [25] methods have been given in Table 2.

The monomer reactivity ratios estimated by this new simple technique are in good agreement with those reported in the literature (Table 2). The slightly greater reactivity ratios in this work than those obtained in the previous works for this system at low conversions (below 6%) [11,12,14] may be attributed to the effect of conversion and thereby viscosity on the reactivities of macroradicals. This is supported by greater reactivity ratios obtained for this system at medium/high conversions ($r_{\text{MA}} = 7.5912$ and $r_{\text{VA}} = 0.0087$) relative to those at low conversion ($r_{\text{MA}} = 5.9532$ and $r_{\text{VA}} = -0.0016$) [11]. Basically in copolymerization systems the monomer reactivity ratios vary with increasing percentage of conversion [15,26]. The reasons can be explained as follows.

Progress of the polymerization reaction causes an enhancement of viscosity of the reaction medium, while the latter changes the monomer diffusion to macroradicals. In other words, at high conversions both the propagation rate constant and the monomer collision to macroradicals are lowered. At

Table 2

Reactivity ratios of vinyl acetate and methyl acrylate reported in the literature together with the results obtained in this work

r_{VA}	r_{MA}	Temp. in °C	Medium	Reference
0.030 ^a	6.380 ^a	60	Bulk	Mayo et al. [12]
0.030 ^a	6.700 ^a	50	Bulk	Garret and Park [13]
0.030 ^a	6.300 ^a	60	Bulk	Kulkarni et al. [14]
0.020	6.750	30	Aqueous dispersion	Casinos [17]
0.04	7.28	60	Solution/benzene	Brar and Charen [18]
-0.0016	5.9532	60	Solution/benzene- d_6	Abdollahi et al. [11]
0.1077	6.9484	60	Solution/benzene- d_6	This work (FR method)
0.0962	6.7985	60	Solution/benzene- d_6	This work (KT method)
0.1076	6.9469	60	Solution/benzene- d_6	This work (JJ method)
0.0957	7.7036	60	Solution/benzene- d_6	This work (MH method ^b)
0.0863	6.6257	60	Solution/benzene- d_6	This work (TM method ^c)

^a Reactivity ratios recalculated by Greenley [15,16].

^b With initial guesses of $r_{\text{MA}} = r_{\text{VA}} = 1$.

^c With initial guesses of $r_{\text{MA}} = 1$ and $r_{\text{VA}} = 0$.

this situation, the effect of penultimate group is considerable and the system tends to adopt second-order Markov statistics (penultimate model) [27,28], thus affecting the monomer reactivity ratios.

Two of the Refs. [12] and [13] do not utilize NMR technique for monitoring monomer conversion, like other references stated in this study. In the mentioned references, monomer conversion and copolymer composition for various VA/vinyl monomer systems have been obtained by various methods such as gravimetry, titration, etc. Therefore, different values of reactivity ratios may be due to different analyses methods used in the previous works relative to the NMR method.

Using the Meyer–Lowry equation [29], theoretical mole fraction of MA in the comonomer mixture ($f_{\text{MA}}(t)$) was obtained as a function of the overall monomer conversion and compared with the corresponding experimental data in Fig. 4. The monomer reactivity ratios obtained by all methods were checked in the Meyer–Lowry equation. The best fitting of theoretical and experimental was obtained for reactivity ratio values of MH method. Thus, the monomer reactivity ratios obtained by MH method were preferentially used in the Meyer–Lowry equation (see also Section 5). Fitting of the theoretical values of comonomer mixture composition drifts versus overall monomer conversion with the corresponding experimental data was good, indicating the accuracy of the monomer reactivity ratios obtained by new procedure presented here.

5. Joint confidence limits

Simple intervals do not clearly convey the message of which pair of parameters is 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 better the experimental design, the smaller the area of uncertainty.

The 95% joint confidence limits for the reactivity ratios of VA/MA system have been shown in Fig. 5. MH method gives the most precise estimate, although this estimate is only slightly better than that obtained by the TM method. 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 method considers the effect of conversion in calculating monomer reactivity ratios, resulting in more reliable reactivity ratios but greater than those obtained by other methods. Greater reactivity ratios can be due to considering the effect of conversion in calculating monomer reactivity ratios by MH method.

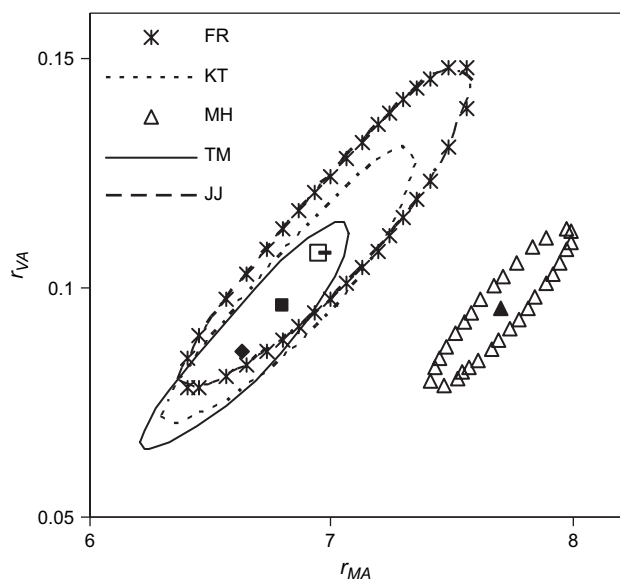


Fig. 5. Monomer reactivity ratios and 95% joint confidence limits for the reactivity ratios of VA and MA obtained in this work by Mao–Huglin (\blacktriangle), Tidwell–Mortimer (\blacklozenge), Kelen–Tudos (\blacksquare), Joshi–Joshi (\square) and Finemann–Ross (\blacksquare) methods.

6. Conclusions

Progress of the free radical copolymerization reaction of VA and MA in solution of benzene- d_6 using BPO as the initiator was followed via on-line ^1H NMR kinetic experiments at 60°C . Significant composition drifts in the comonomer mixture with reaction progress allowed us to calculate monomer reactivity ratios by data collected only from one sample via on-line following the reaction progress up to the medium overall monomer conversions. The results were in good agreement with the literature data reported for this system. The 95% joint confidence limits confirmed that MH and TM estimates are more reliable and precise than those given by other methods. The good fitting between the theoretical and experimental changes in the comonomer mixture compositions with

reaction progress was observed; indicating the accuracy of the monomer reactivity ratios calculated by the new simple procedure presented here.

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