

Free-Radical Homo- and Copolymerization of Vinyl Acetate and *n*-Butyl Acrylate: Kinetic Studies by Online ¹H NMR Kinetic Experiments

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ABSTRACT: Free-radical homo- and copolymerization of vinyl acetate (VAc) and *n*-butyl acrylate (BA) in benzene-*d*₆ were performed by using benzoyl peroxide as an initiator at 70°C. Polymerization kinetic was followed by online ¹H NMR kinetic experiments. Significant drift in the comonomer mixture composition with reaction progress was observed. Reactivity ratios of VAc and BA were calculated by terminal unit model (TUM) as well as by simplified penultimate unit model (PUM) with $r_{VAc} = 0$. It was found that copolymer composition can be described well by the TUM. "Lumped" kinetic param-

eter ($k_p, k_t^{-0.5}$) was estimated from experimental data. A good fitting between the theoretical and experimental drifts in the comonomer mixture and copolymer compositions with reaction progress was observed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 543–553, 2012

Key words: vinyl acetate/butyl acrylate; free-radical copolymerization; online ¹H NMR kinetic experiments; comonomer reactivity ratios; rate coefficient

INTRODUCTION

¹H NMR spectroscopy has been proven to be one of the most important and reliable techniques for studying polymer structure and copolymer composition.^{1–4} Following the reaction conversion by online ¹H NMR spectroscopy so called online ¹H NMR kinetic experiment has been successfully used to study kinetics of the free-radical homo- and copolymerization reactions.^{5–9} Online ¹H NMR kinetic experiments allow us to simultaneously calculate individual and overall comonomer conversions as well as the comonomer mixture and copolymer compositions as a function of reaction progress. This is one of the advantages of this online technique in comparison with the offline techniques and some of the online techniques.

One of the most important industrial lattices, widely used in architectural coatings and paints market, is the vinyl acetate (VAc)/*n*-butyl acrylate (BA) emulsion copolymer. Most of studies on the copoly-

merization kinetics of VAc and BA in bulk, emulsion, or solution have been focused on the determination of copolymer composition and microstructure as well as the comonomer reactivity ratios.^{10–17} Results showed that VAc (macro)radicals are extremely reactive toward other vinyl comonomers compared with its own less reactive comonomer. In other words, VAc is one of the least reactive of any common monomers toward free-radical attack.^{18–20}

To calculate copolymerization rate coefficient, it is necessary to measure the overall comonomer conversion as a function of reaction time. Collecting these data by offline techniques such as gravimetric method needs to prepare the several samples with same initial comonomer mixture composition, carrying out the (co)polymerization reaction at the same conditions, stopping the reaction at various time intervals, separating the produced (co)polymer via precipitation and finally determining the overall comonomer conversion via gravimetric method. These several steps are tedious and may result in incorrect data due to polymer loss in the precipitation and purification stages. In contrary, it is possible to collect data of overall comonomer conversion versus time from one sample by following the copolymerization progress by online techniques such as dilatometry and NMR.

In this research, kinetics of the free-radical copolymerization of VAc and BA are studied by performing

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online ^1H NMR kinetic experiments. Conversion of individual comonomers calculated from spectra recorded at the various reaction time intervals is used to calculate the overall comonomer conversion as well as the comonomer mixture and copolymer compositions. Accurate comonomer reactivity ratios are then calculated by terminal unit model (TUM) and simplified penultimate unit model (PUM) at low and medium/high conversions. The results obtained from simplified PUM are then used to evaluate effect of the penultimate units in the growing chains on the reactivity ratios of VAc and BA. To our knowledge, there is no report on the copolymerization rate coefficient for BA/VAc system. Overall polymerization rate coefficient and "lumped" kinetic parameter ($k_p.k_t^{-0.5}$) are estimated in this study for various initial feed compositions. Finally, composition drifts in the comonomer mixture and copolymer are evaluated experimentally and theoretically, from which accuracy of the estimated comonomer reactivity ratios is also evaluated.

EXPERIMENTAL

Materials

The monomers, VAc and BA (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 (Bz- d_6) as the solvent was purchased from ARMAR chemicals (Dottingen, Switzerland) and used as received. Benzoyl peroxide (BPO) (from Fluka Chemical Co.) was used as initiator without further purification.

Sample preparation

Solution samples were prepared with different comonomer mixture compositions at constant overall monomer concentration (Table I). At first, given concentration of initiator (BPO) in the benzene- d_6 was prepared. Given amount of initiator solution was then added to the given molar ratio of comonomer mixture so that initiator and overall comonomer concentrations were adjusted to be approximately $4 \times 10^{-2} M$ and exactly $1M$, respectively, (Table I). Total volume of each sample was chosen to be 1.00 mL. Exact adjusting of BPO concentration at $4 \times 10^{-2} M$ for all samples was not possible because total volume of the final solution of each sample was adjusted to be exactly 1.00 mL while BA and VAc liquid comonomers have different densities. Therefore, different volume of initiator solution in the benzene- d_6 is required to prepare samples containing different mole fraction of the comonomers in the initial reaction mixture at the constant total volume

TABLE I
Concentration of the Comonomers and Initiator (in Benzene- d_6 Solution) in the Initial Reaction Mixture^{a, b}

Sample	f_{BA}^c	$[\text{BPO}] \times 10^2 \text{ (mol L}^{-1}\text{)}^d$
VB0 ^e	0	4.239
VB6	0.0563	4.227
VB13	0.129	4.215
VB24	0.236	4.191
VB38	0.381	4.155
VB39	0.390	4.155
VB55	0.553	4.119
VB100	1.000	4.000

^a All reactions were performed at 70°C.

^b Overall comonomer concentration for all samples was exactly $1M$.

^c Mole fraction of BA in the initial feed.

^d Concentration of BPO in all solutions was adjusted to be close to $4 \times 10^{-2}M$ (see the experimental section for more details).

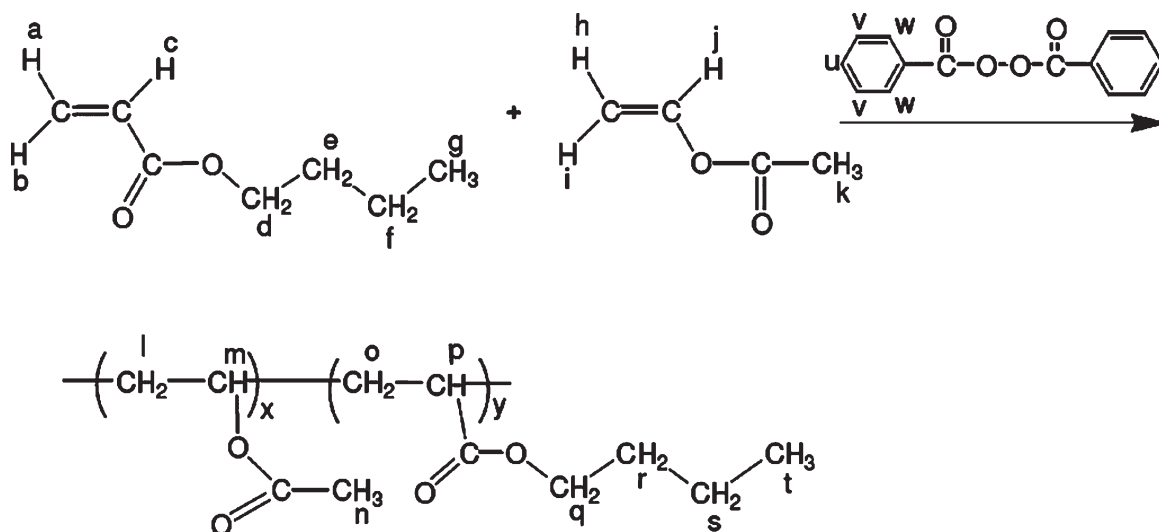
^e Numbers in the front of sample codes indicate the approximate mole percentage of BA in the initial comonomer mixture.

and overall comonomer concentration of the final solution. The final reaction mixture was then conducted to a NMR tube (5 mm in diameter). The solution in the NMR tube was degassed with nitrogen gas (99.9% purity) to exclude oxygen from the reaction mixtures.

^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 70°C by a BVT 3000 ($\pm 0.1^\circ\text{C}$) temperature control unit. A typical ^1H NMR kinetic experiment consists of the following sequence of steps.^{19,20}

First, the cavity was set to the desired reaction temperature (i.e., 70°C), and a sample containing only benzene- d_6 (as 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 reaction mixture (Table I) 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 and first spectrum was then recorded. The first recorded spectrum was regarded as a spectrum representing zero overall comonomer conversion with zero reaction time. Although approximately 10 min has passed from insertion of sample into the cavity relative to the first scan, negligible conversion has occurred due to 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



Scheme 1 Schematic presentation of the free-radical copolymerization of VAc and BA initiated by benzoyl peroxide (BPO) in the benzene- d_6 solution.

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. However, concentration of overall comonomers has been adjusted to be 1M which seems to be high enough.

In the online ^1H NMR kinetic experiments, there may be a limitation in terms of the solvent type (chemical nature) selection because signals of solvent protons in the ^1H NMR spectrum may overlap with signals of reference protons of comonomers or copolymers. However, overlapping of above-mentioned signals may occur rarely. Moreover, this limitation can be avoided by using 100% deuterated solvent.

RESULTS AND DISCUSSION

In continuum to previous works on the kinetic study of free-radical homo- and copolymerization of VAc and methyl acrylate (MA),^{19,20} we used online ^1H NMR kinetic experiments for the free-radical copolymerization of VAc and BA to determine the comonomer reactivity ratios, overall polymerization rate coefficient and composition drifts in the comonomer mixture and copolymer.

A typical ^1H NMR spectrum of the initial reaction mixture containing 0.381 mol fraction of BA (sample VB38 in Table I) at the overall comonomer conversion of 42.16 mol % with the signal assignments (see Scheme 1) has been shown in Figure 1. Signal assignments for copolymerization systems were carried out with regard to the spectra recorded for

homopolymerization of both VAc and BA and comparison them with spectra recorded for the copolymerization systems. The last spectra recorded for each sample with corresponding final reaction time are shown in Figure 2. It is clear from Figures 1 and 2 that the signals concerned to the $-\text{CH}$ protons of both VAc ($-\text{CH}^m$) and BA ($-\text{CH}^p$) incorporated into the copolymer chain could be used to follow the reaction progress. However, slightly overlapping of $-\text{CH}$ proton of BA ($-\text{CH}^p$) incorporated into the copolymer chain with $-\text{CH}_2$ protons of VAc ($-\text{CH}_2^l$) and BA ($-\text{CH}_2^o$) incorporated into the copolymer chain may be occurred in the medium/high conversion (see Figs. 1 and 2). Therefore, another signal from BA should be chosen to precisely follow the conversion of BA. It is clear from Figures 1 and 2 that overall intensity for $-\text{CH}_3$ protons signals of both monomeric and polymeric BA (i.e., $-\text{CH}_3^k$ and $-\text{CH}_3^t$, respectively) can be used to follow

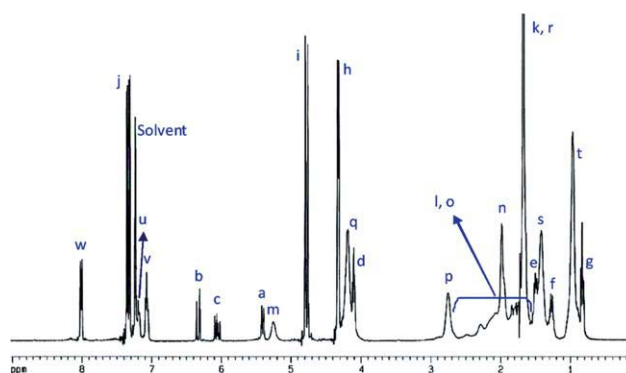


Figure 1 A typical ^1H NMR spectrum of the comonomer mixture and the produced copolymer after the overall comonomer conversion of 42.16 mol % for sample VB38 [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

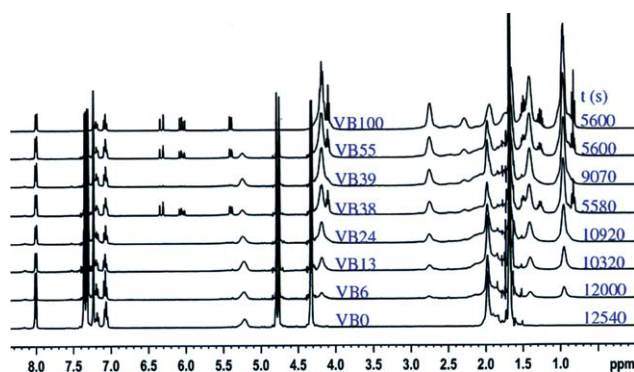


Figure 2 The final ^1H NMR spectra recorded for BA/VAc copolymerization system with various comonomer mixture compositions (see Table I) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

conversion of the BA comonomer because precise intensity for one proton of monomeric BA can be obtained from other proton signals of monomeric

$$x_{\text{BA}}(t) = \frac{[I(-\text{CH}_3^g)_{\text{BA}}^{\text{monomer}}(t) + I(-\text{CH}_3^t)_{\text{BA}}^{\text{copolymer}}(t)] - [3 \times I(=\text{CH}^b)_{\text{BA}}^{\text{monomer}}(t)]}{[I(-\text{CH}_3^g)_{\text{BA}}^{\text{monomer}}(t) + I(-\text{CH}_3^t)_{\text{BA}}^{\text{copolymer}}(t)]} \quad (2)$$

where $x_i(t)$ is the individual conversion of comonomer i at time t . $I(-\text{CH}^m)_{\text{VAc}}^{\text{copolymer}}(t)$ and $I(=\text{CH}^i)_{\text{VAc}}^{\text{monomer}}(t)$ indicate intensities of methine proton resonance signal of VAc incorporated into the copolymer chain and one of the two methylene protons resonance signal of unreacted VAc at time t , respectively (Scheme 1 and Fig. 1). $I(-\text{CH}_3^t)_{\text{BA}}^{\text{copolymer}}$ and $I(-\text{CH}_3^g)_{\text{BA}}^{\text{monomer}}$ indicate intensities of methyl protons resonance signal of BA incorporated into the copolymer chain and that in the unreacted BA, respectively (Scheme 1 and Fig. 1). $I(=\text{CH}^b)_{\text{BA}}^{\text{monomer}}(t)$ indicates intensity of one of the two methylene protons resonance signal of unreacted BA at time t (Scheme 1 and Fig. 1).

Overall comonomer conversion $[x(t)]$ and mole fraction of the comonomer i in the comonomer mixture at time t $[f_i(t)]$ and in the copolymer chain produced during time t $(x(t))$ are related to the individual conversion of comonomers i $[x_i(t)]$ and j $[x_j(t)]$ by the following equations:

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

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

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

where f_i^0 is the mole fraction of comonomer i in the initial reaction mixture and n_i^0 is the molar amount

BA (i.e., $=\text{CH}^a$, $=\text{CH}^b$, or $=\text{CH}^c$). In all spectra of each sample, the overall intensity for $-\text{CH}_3$ protons signals of both monomeric and polymeric BA ($-\text{CH}_3^g$ and $-\text{CH}_3^t$ protons appeared in the chemical shift range of about 0.7–1.1 ppm in Fig. 1) was adjusted to an arbitrary value of 3. The intensity for signals of each other proton 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 intensities 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 VAc and BA can be monitored as a function of reaction time.

Individual conversions of VAc and BA at any reaction time were calculated via eqs. (1) and (2).

$$x_{\text{VAc}}(t) = \frac{I(-\text{CH}^m)_{\text{VAc}}^{\text{copolymer}}(t)}{I(=\text{CH}^i)_{\text{VAc}}^{\text{monomer}}(t) + I(-\text{CH}^m)_{\text{VAc}}^{\text{copolymer}}(t)} \quad (1)$$

of comonomer i in the initial feed. $\bar{F}_i(t)$ is indeed the cumulative mole fraction of monomer i in the copolymer chains produced during the reaction time t . Subscripts i and j indicate comonomers BA and VAc, respectively. It is clear from eqs. (3)–(5) that $x(t)$, $f_i(t)$, and $\bar{F}_i(t)$ as a function of time can be calculated from individual comonomers conversion data obtained by online ^1H NMR kinetic experiments.

Online ^1H NMR spectra recorded at the various time intervals for sample VB38 (see Table I) as a function of the reaction time have been shown in Figure 3. It is clear from this figure that by progress of the copolymerization reaction, intensities of the signals 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 BA/VAc copolymerization reaction. Furthermore, the isothermal conditions were established during the course of reaction due to low rate of the copolymerization reaction and high amount of the solvent.

Determination of the reactivity ratios of BA and VAc

The comonomer reactivity ratios are important factors to predict copolymer composition for any initial comonomer mixture and to understand the kinetics and mechanism of copolymerization reaction. In general, reactivity ratios of the comonomers are

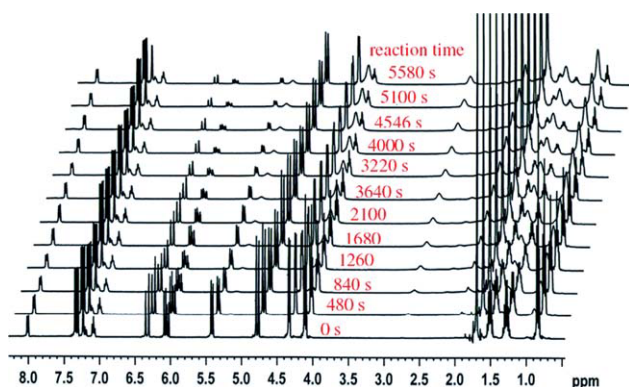


Figure 3 Progress of the copolymerization reaction as a function of time for sample VB38 [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

determined at low conversion. In classic TUM of copolymerization it has been suggested that for a given pair of comonomers, the copolymer composition is just a function of instantaneous composition of feed and comonomer reactivity ratios.^{21,22}

In conventional free-radical copolymerization, comonomer reactivity ratios are generally determined by performing experiments with various initial comonomer compositions at low conversion where composition drift in the comonomer mixture can be considered to be negligible. The average chemical composition of the resulting copolymer is analyzed by various methods such as ¹H NMR. Then, copolymer composition versus initial comonomer composition is fitted with the differential copolymer composition (Mayo-Lewis) equation.²¹ To obtain statistically correct estimates of the comonomer reactivity ratios, nonlinear least square methods should be applied.²³ However, it will be shown in the next section that in the case of BA/VAc copolymerization system, composition drift in the comonomer mixture is significant even at low conversion. Hence, one has to use integrated form of the copolymerization equation (i.e., Meyer-Lowery equation),²⁴ (for corresponding equation, see the next section) or methods in which effect of the conversion is also considered in calculation of the comonomer reactiv-

ity ratios. Consequently, extended Kelen-Tudos (KT)²⁵ and Mao-Huglin (MH)²⁶ methods were chosen in this study to calculate the comonomer reactivity ratios in such situation. Then, Meyer-Lowery equation was used to evaluate accuracy of the calculated reactivity ratios.

When reactivity ratio of the second comonomer is zero ($r_2 = 0$), the simplified PUM with $r_2 = 0$ can be used to calculate ultimate (or equivalently terminal) (r_1) and penultimate (r_1') reactivity ratios of the first comonomer. A linear method has been proposed to calculate comonomer reactivity ratios with simplified PUM, i.e., $r_2 = 0$, which was intended to be applicable for the systems not limited to low conversion data.^{27,28} This model was used in the present copolymerization system with $r_{VAc} = 0$ (see the following section) to calculate r_{BA} and r_{BA}' , which are defined as k_{111}/k_{112} and k_{111}/k_{112} , respectively. K_{ijm} is the rate constant for the reaction of radical $-M_iM_j^*$ with monomer M_m ($i, j, m = 1$ or 2).

Online ¹H NMR kinetic experiments have already been used successfully for kinetic study of the free-radical homo- and copolymerization of various comonomer pairs.^{5-9,19,20} Kinetic parameters of the comonomer reactivity ratios and overall polymerization rate coefficients can be derived by this online technique. Davis et al.^{5,6} applied this technique for copolymerization of styrene with other comonomers and estimated the overall polymerization rate coefficient. Our group determined copolymer composition and then the comonomer reactivity ratios for conventional free-radical copolymerization of various comonomer pairs by online ¹H NMR kinetic experiments.^{7-9,19,20} In this study, comonomer reactivity ratios and overall rate coefficient of the copolymerization were determined.

Mole fraction of the comonomers in the initial feed and in the produced copolymer chain as well as the corresponding individual and overall comonomer conversions have been given in Table II.

By using low (<13%) and medium/high (14–41%) conversion data collected in Table II, reactivity ratios of VAc and BA were calculated by extended KT (see Figs. S1 and S2 in the supporting Information) and

TABLE II
Experimental Data Obtained from ¹H NMR Spectra at Low and Medium/High Conversions for Free-Radical Copolymerization of BA/VAc System^a

Sample	f_{BA}^0	F_{BA}	x_{VAc}	x_{BA}	x
VB6	0.0563	0.4562 (0.3777)	0.0542 (0.0922)	0.6485 (0.8194)	0.0931 (0.1388)
VB13	0.129	0.6059 (0.4826)	0.0523 (0.1467)	0.5872 (0.9041)	0.1168 (0.2462)
VB24	0.236	0.7305 (0.6809)	0.0438 (0.1284)	0.3805 (0.8591)	0.1239 (0.3051)
VB38	0.381	0.8240 (0.7700)	0.0369 (0.1383)	0.2805 (0.7468)	0.1299 (0.3712)
VB39	0.390	0.8137 (0.7752)	0.0214 (0.1444)	0.1462 (0.7784)	0.0701 (0.3918)
VB55	0.553	0.9001 (0.8740)	0.0119 (0.1179)	0.0845 (0.6287)	0.0524 (0.4066)

^a Data presented inside the parenthesis are related to the medium/ high conversion data.

TABLE III
Reactivity Ratios of VAc and BA Reported in the Literature Together with the Results Obtained in This Work

r_{VAc}	r_{BA}	Temperature (°C)	Technique	x (%)	Reference
0.06	3.07	–	–	–	10
0.018	3.485	–	–	–	11
0	8	–	Emulsion	–	12
0.04	5.53	–	Emulsion	–	13
0.024	10.67	–	Emulsion	–	14
0.026	5.9	–	Bulk	–	15
0.03 ± 0.01	6.67 ± 2.17	60	Solution (bz)	<5	16 (KT method)
0.03 ± 0.01	7.43 ± 0.71	60	Solution (bz)	<5	16 (EV method)
TUM (our data)					
0.0141 ± 0.0245	6.631 ± 1.053	70	Solution (bz- d_6)	<13	extended KT method ^a
0.0130 ± 0.0171	6.666 ± 0.870	70	Solution (bz- d_6)	<13	MH method ^b
0.0296 ± 0.0246	7.468 ± 1.604	70	Solution (bz- d_6)	>14	extended KT method ^a
0.0277 ± 0.0122	7.406 ± 1.041	70	Solution (bz- d_6)	>14	MH method ^b
Simplified PUM (our data)					
0	6.917 ± 2.492 (4.811 ± 3.752) ^c	70	Solution (bz- d_6)	<13	MH method ^b

^a The correlation coefficients for linear methods at both low (<13%) and medium/high (>14%) conversions were higher than 0.96.

^b Reactivity ratios of MH method were calculated with initial guesses of $r_{BA} = r_{VAc} = 1$ (in TUM) $r_{BA} = r'_{BA} = 1$ (in simplified PUM).

^c Reactivity ratio presented inside the parenthesis is r'_{BA} (penultimate reactivity ratio of BA).

MH (see Tables S1–S3 in the supporting Information) methods. Summary of the calculation results has been given in Table III. The reactivity ratios estimated in this work are in good agreement with some of reactivity ratios of BA and VAc reported in the literature specially with the reactivity ratios values reported by Brar et al.¹⁶ (Table III). Brar et al. have estimated reactivity ratios of VAc and BA by methods in which effect of the conversion is not considered in the calculation of comonomer reactivity ratios [i.e., KT and error in variables (EV) methods]. Hence, estimated reactivity ratios are significantly dependent on a method used for calculation of reactivity ratios, indicating that effect of conversion must also be considered to calculate more accurate reactivity ratios in the case of copolymerization systems such as BA/VAc. Moreover, reactivity ratios of VAc and BA have been found to be dependent on the polymerization technique; significantly different values of the reactivity ratios were obtained for emulsion polymerization in comparison with bulk, solution and aqueous dispersion polymerizations (see Table III). It is clear from Table III that there is no significant difference between the ultimate (r_{BA}) and penultimate (r'_{BA}) reactivity ratios of BA, suggesting that BA/VAc copolymerization system can be described well by the TUM.

In calculation of simple intervals, reactivity ratios are considered to be statistically independent. On the other hand, reactivity ratios are simultaneously calculated and therefore cannot be considered statistically independent. Therefore, simple intervals do not clearly convey the message of which pair of parameters is consistent with the data. The specifica-

tion 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 TUM reactivity ratios of VAc and BA estimated by various methods have been shown in Figure 4 (for 95% joint confidence limits of the simplified PUM reactivity ratios, see Figure S3 in the supporting Information). It is clear from Figure 4 that the area of uncertainty

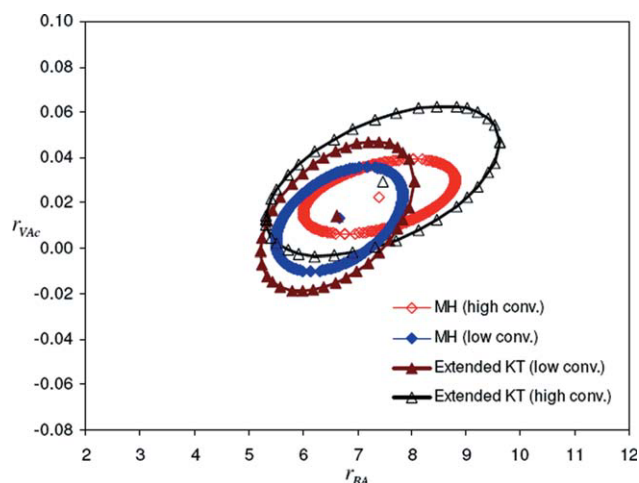


Figure 4 The 95% joint confidence limits for TUM reactivity ratios of VAc and BA estimated at low and medium/high conversions by extended KT (\blacktriangle and \triangle) and MH (\blacklozenge and \diamond) methods [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

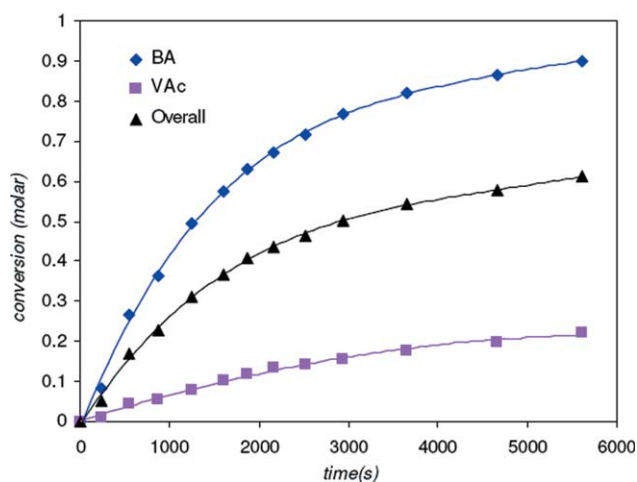


Figure 5 Individual and overall conversions of VAc and BA versus reaction time calculated from ^1H NMR spectra recorded for the free-radical copolymerization of sample VB55 containing 0.553 mol fraction of BA in the initial reaction mixture [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

is small enough for both methods. Therefore, as expected, both MH and extended KT methods result in more reliable reactivity ratios. However, MH method gives the most precise estimate. It should be noted that in all calculations where reactivity ratios of VAc and BA are required, reactivity ratios obtained by MH method will be used preferentially.

Estimation of the overall polymerization rate coefficient

Individual conversion of VAc and BA as a function of reaction time for the copolymerization system containing 0.553 mol fraction of BA in the initial comonomer mixture (sample VB55) has been shown in Figure 5. It is clear from Figure 5 that both comonomers polymerize (and are likely to copolymerize) and that BA is incorporated into the copolymer at a very higher rate than VAc. The same trend was also observed for all other initial feed compositions, that is, BA is always preferentially incorporated into the copolymer chain. In other words, VAc (macro)radicals are extremely reactive toward other vinyl comonomers compared with the own less reactive comonomer^{18–20} (see the next section as well as supporting Information for more details). As mentioned before, individual comonomers conversion versus time data may be used to deduce the changes in the comonomer mixture and copolymer compositions as a function of overall comonomer conversion and to calculate the overall comonomer conversion versus time.

Figure 6 indicates overall comonomer conversion as a function of reaction time for various mole fractions of BA in the initial reaction mixture. This figure shows obviously that with increasing BA amount in

the initial feed, the overall rate of (co)polymerization increases remarkably. This observation is consistent with previous data reported on the propagation- and termination-rate coefficients of BA^{29–34} and VAc^{34–38} homopolymerizations. The propagation rate coefficients (k_p) for bulk homopolymerization of pure BA and pure VAc at 70°C have been reported to be close to 41,700^{29,30} and 11,700^{36,37} L mol⁻¹ s⁻¹, respectively. Thus, on the basis of preceding data, k_p of BA is greater than that of VAc by a factor of about 3.5 approximately.

The rate of polymerization (R_p) under steady state conditions (i.e., steady free-radical concentration) is expressed as following equation:

$$R_p = k_p \cdot [M] \cdot \left(\frac{f' \cdot k_d \cdot [I]}{k_t} \right)^{0.5} \quad (6)$$

in which k_p and k_t are average propagation- and termination-rate coefficients, respectively, f' is efficiency of the initiator, k_d is rate constant of the initiator decomposition and $[I]$ and $[M]$ are concentrations of the initiator and overall comonomers, respectively.

Since the rate of polymerization (or equivalently slopes of the curves in Fig. 6) is proportional to the $k_p \cdot k_t^{-0.5}$, it is seen from Figure 6 that by going from pure VAc to pure BA curve, an increase in the overall rate of polymerization and thereby an increase in the overall rate constant (or lumped rate constant, $k_p \cdot k_t^{-0.5}$) is expected. To investigate effect of the BA amounts in the initial reaction mixture on the overall rate of polymerization (and then on the lumped rate constant, $k_p \cdot k_t^{-0.5}$), the linear parts of the overall comonomer conversion versus time curves were plotted as first-order curves via eq. (7), which is derived by integration from eq. (6):

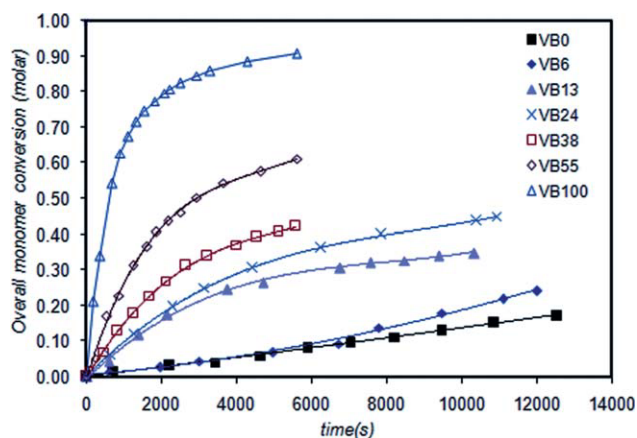


Figure 6 Overall comonomer conversion as a function of reaction time curves for various mole fractions of BA in the initial reaction mixture [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

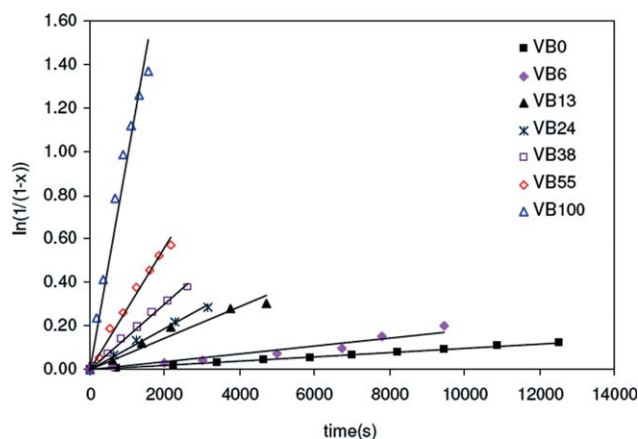


Figure 7 Dependency of $\ln[1/(1-x)]$ versus time plots on the mole fraction of BA (or VAc) in the initial reaction mixture [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

$$\ln\left(\frac{1}{1-x}\right) = k_{\text{over}} \times t \quad \text{where} \quad k_{\text{over}} = k_p \left(\frac{f' \cdot k_d \cdot [I]}{k_t} \right)^{0.5} \quad (7)$$

where x is the overall comonomer conversion and k_{over} is the overall polymerization rate coefficient. k_{over} is equal to the slope of $\ln[1/(1-x)]$ versus time curve. The corresponding curves have been shown in Figure 7. It is clear from Figure 7 that $\ln[1/(1-x)]$ is calculated from experimental data with maximum reaction time of 4500 s, except for experiments with very low conversion rate (i.e., VB0 and VB6). Slope of curves in the experiments VB0 and VB6 was evaluated in the reaction time range of 0–4500 s. For these experiments, however, there is no difference between slope of curve in the reaction time range of 0–12,000 s and that in the reaction time range of 0–4500 s. Correlation coefficient (R^2) of $\ln[1/(1-x)]$ versus time curves was at least 95%, indicating that corresponding curves can be considered to be linear. Therefore, we can neglect variation of BPO concentration with time and then integrate

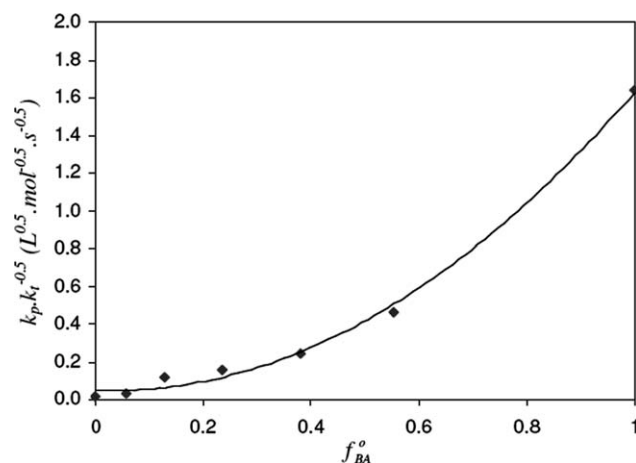


Figure 8 Variation of $k_p \cdot k_t^{-0.5}$ as a function of BA mole fractions in the initial reaction mixture.

eq. (6) to derive eq. (7) for estimation of the overall polymerization rate coefficient.

The straight lines in Figure 7 were obtained by fitting eq. (7) to data sets. According to this figure, increasing the mole fraction of BA in the initial comonomer mixture has a significant effect on the slope, i.e., on the overall rate coefficient of polymerization (k_{over}). Since efficiency of the initiator, the decomposition rate constant of BPO and its concentration are known; eq. (7) can be used to estimate $k_p \cdot k_t^{-0.5}$ from experimental data given in Figure 7. The value of f' (for BPO) is assumed to be about 0.7³⁹ and k_d for BPO in benzene solution at 70°C has been reported to be close to $1.27 \times 10^{-5} \text{ s}^{-1}$.³⁵ Using these values together with the BPO concentration given in Table I, lumped kinetic parameter ($k_p \cdot k_t^{-0.5}$) values were estimated (Table IV and Fig. 8). $k_p \cdot k_t^{-0.5}$ increases with increasing amount of BA in the initial reaction mixture (Fig. 8). The same trend of lumped kinetic parameter has been reported for the respective homopolymerization reactions and could confirm above variation in Figure 8. For example, $k_p \cdot k_t^{-0.5}$ values for homopolymerizations of BA and VAc in the benzene solution with monomer

TABLE IV
Dependency of the Overall Rate Coefficient and Lumped Rate Constant ($k_p \cdot k_t^{-0.5}$) on the Mole Fraction of BA in the Initial Reaction Mixture for BA/VAc Copolymerization System

Sample	f_{BA}^0	$k_{\text{over}} \times 10^5 \text{ (s}^{-1}\text{)}$	$k_p \cdot k_t^{-0.5} \times 10^2 \text{ (L}^{0.5} \text{ mol}^{-0.5} \text{ s}^{-0.5}\text{)}^a$
VB0	0	0.9576	1.623
VB6	0.0563	1.820	2.969
VB13	0.129	7.222	11.80
VB24	0.236	9.437	15.46
VB38	0.381	14.88	24.48
VB55	0.553	28.03	46.32
VB100	1.000	97.58	163.6

^a These values were calculated according to the eq. (7) with assuming that f' (for BPO) and k_d (for BPO in benzene solution at 70°C) are close to 0.7³⁹ and $1.27 \times 10^{-5} \text{ s}^{-1}$,³⁵ respectively.

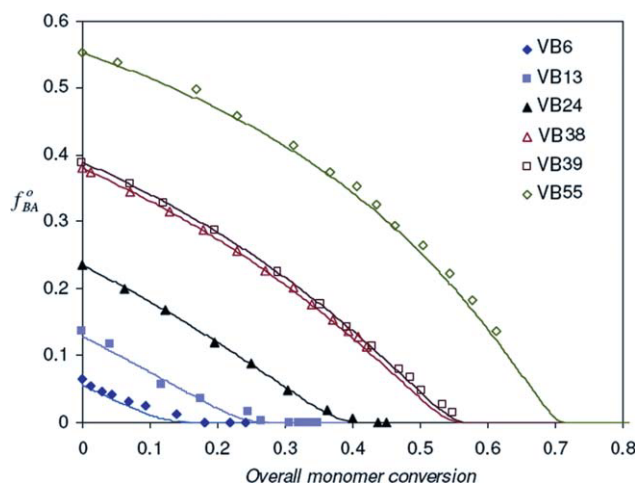


Figure 9 Comonomer mixture composition as a function of the overall comonomer conversion for various mole fractions of BA in the initial reaction mixture (symbols show the experimental data and continuous lines indicate the theoretical data calculated by Meyer-Lowry equation using TUM reactivity ratios of MH method at low conversion) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

concentration of 1M have been reported to be 94×10^{-2} (50°C)⁴⁰ and $0.7 \times 10^{-2} \text{ L}^{0.5} \text{ mol}^{-0.5} \text{ s}^{-0.5}$ (60°C).⁴¹ This trend, i.e., increasing $k_p \cdot k_t^{-0.5}$ by increasing amount of BA in the initial reaction mixture is in good agreement with $k_p \cdot k_t^{-0.5}$ values obtained in this work (Table IV). Furthermore, Figure 8 shows that the increase in the rate of polymerization is more pronounced when going from about 0.4 to 1.0 mol fraction of BA in the initial reaction mixture than from 0 to 0.4 mol fraction of BA. It is clear from trend of variations in the $k_p \cdot k_t^{-0.5}$ values versus f_{BA}^0 that rate constant of k_p and/or k_t may be described well by implicit PUM.

With the experimental data at hand it is possible to calculate an estimate for average k_t in BA and VAc homopolymerizations at 70°C and low conversions (in benzene-*d*₆ solution) as well as to compare these value with previously reported k_t data in the solution homopolymerizations of BA^{31–34} and VAc.^{34,35,38} Using k_p values of 41,700^{29,30} and 11,700^{36,37} $\text{L mol}^{-1} \text{ s}^{-1}$ for BA and VAc, respectively, k_t values are calculated to be 6.5×10^8 and $5.2 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$. These values of k_t are in good agreement with values of BA and VAc reported in the literature to be about 10^8 – $10^{931–34}$ and 10^7 – $10^{1034,35,38} \text{ L mol}^{-1} \text{ s}^{-1}$, respectively. It should be noted that the value of k_t is dependent on the type and concentration of solvent used in the reaction (i.e., the viscosity of the reaction mixture) and it is therefore not surprising to see slight deviations in k_t when varying the solvent.⁴² We believe that our approach is a sufficiently reliable procedure to estimate lumped kinetic parameter ($k_p \cdot k_t^{-0.5}$).

Composition drifts in the comonomer mixture and copolymer

Other important information about BA/VAc copolymerization system can be obtained via plots of the comonomer mixture and copolymer compositions as a function of the overall comonomer conversion. These data could be calculated from the individual conversions of BA and VAc according to eqs. (3)–(5).

Figure 9 shows experimental drifts in the comonomer mixture composition versus overall comonomer conversion up to about 65 mol % for various amounts of the BA (or VAc) in the initial reaction mixture. This figure reveals that in the various mole fractions of BA in the initial feed, the incorporation of BA into the copolymer chain is more favored than VAc. The overall changes in the comonomer mixture composition by increasing conversion is very high, indicating that the reactivity ratio of BA should be much greater than that of VAc, as obtained in the previous section (Table III). In other words, the adduct radical of BA comonomer is more likely to react with its own comonomer relative to VAc comonomer while the adduct radical of VAc comonomer is more likely to react with BA comonomer relative to its own comonomer. This causes the higher rate of incorporation of BA into the copolymer chain than VAc, resulting in the significant drifts in the comonomer mixture composition. It is clear from Figure 9 that the rate of incorporation of BA into the copolymer chain is very high so that the mole fraction of BA in the comonomer mixture reduces rapidly to zero. After full consumption of the

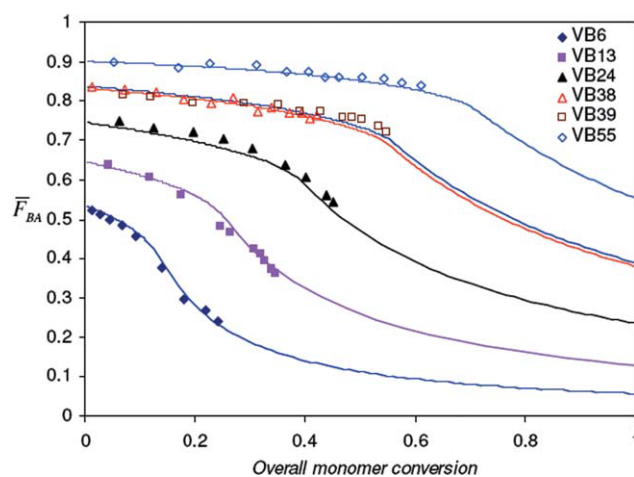


Figure 10 Dependency of cumulative copolymer composition versus overall comonomer conversion plots on the mole fraction of BA in the initial reaction mixture (symbols show the experimental data and continuous lines indicate the theoretical data calculated by Meyer-Lowry equation in conjunction with eq. (10) using TUM reactivity ratios of MH method at low conversion) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

comonomer BA, only VAc will be present in the reaction mixture and thus the reaction will be progressed via homopolymerization of VAc.

It is expected that the changes in the cumulative copolymer composition versus overall comonomer conversion will be pronounced, as shown in Figure 10. The experimental data in Figures 9 and 10 reveal that although until the BA monomer is present in the comonomer mixture, the cumulative copolymer composition changes gradually, however, when there exists no BA in the comonomer mixture (samples VB6, VB13, and VB24, for example), the copolymer composition will be changed drastically with increasing overall comonomer conversion due to the only homopolymerization of VAc comonomer. From the comonomer mixture and cumulative copolymer compositions versus overall comonomer conversion curves (Figs. 9 and 10) it is clear that the tendency of VAc comonomer to homopolymerization increases by increasing VAc content in the initial feed even at low conversions. As a consequence, to obtain the relatively homogeneous copolymer composition with high amount of BA, it is necessary to stop the batch reaction before full consumption of BA at low, medium or high conversions depending on the initial comonomer mixture composition or to choose a suitable strategy for comonomers feeding such as semi-batch process.

Moreover, it is clear from Figures 9 and 10 that cumulative mole fraction of BA in the produced copolymer (\bar{F}_{BA}) is very higher than the mole fraction of BA in the initial reaction mixture (f_{BA}^0). For example copolymer with \bar{F}_{BA} greater than 0.85 in the conversion range of 0–65% (Fig. 10) will be formed when the $f_{BA}^0 = 0.553$ (VB55) is used in the initial reaction mixture. In the other words, cumulative mole fraction of VAc in the produced copolymer (\bar{F}_{VAc}) is very low. Moreover, \bar{F}_{VAc} will further be decreased by further increasing the f_{BA}^0 . As a result, intensities of 1H NMR signals related to the protons of VAc incorporated into the copolymer chain will not be high enough to calculate accurate individual and overall comonomer conversions as well as the copolymer composition. Therefore, same as other works done on the copolymerization of VAc and BA,^{10–17} it is not possible to add more points in the f_{BA}^0 range of 0.56–0.99.

The instantaneous copolymer composition equation of Mayo-Lewis²¹ is expressed as eq. (8):

$$F_i = \frac{r_i f_i^2 + f_i f_j}{r_i f_i^2 + 2f_i f_j + r_j f_j^2} \quad (8)$$

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

An integration of eq. (8) leads to the Meyer-Lowry²⁴ equation as follows:

$$x(t) = 1 - \left(\frac{f_i(t)}{f_i^0} \right)^\alpha \left(\frac{1 - f_i(t)}{1 - f_i^0} \right)^\beta \left(\frac{f_i^0 - \delta}{f_i(t) - \delta} \right)^\gamma \quad (9)$$

where $\alpha = \frac{r_j}{1-r_j}$; $\beta = \frac{r_i}{1-r_i}$; $\gamma = \frac{1-r_j r_i}{(1-r_i)(1-r_j)}$; and $\delta = \frac{1-r_j}{2-r_i-r_j}$. $f_i(t)$ is the instantaneous mole fraction of comonomer i in the reaction mixture at time t , f_i^0 is mole fraction of comonomer i in the initial reaction mixture. According to the Meyer-Lowry equation, the overall comonomer conversion at any time [$x(t)$] is related to the comonomer composition in the reaction mixture at that time and comonomer reactivity ratios.

Some of these parameters are related by a material balance in the following equation, where $\bar{F}_i(t)$ is the cumulative average mole fraction of BA in the copolymer produced during time t .

$$\bar{F}_i(t) = \frac{f_i^0 - [f_i(t) \times (1 - x(t))]}{x(t)} \quad (10)$$

Using the Meyer-Lowry equation²⁴ in conjunction with the eq. (10), theoretical $f_i(t)$ and $\bar{F}_i(t)$ were calculated as a function of overall comonomer conversion for different feed compositions and compared with the corresponding experimental data in Figures 9 and 10. As mentioned before, the comonomer reactivity ratios obtained by MH method was preferentially used in the Meyer-Lowry equation. Fitting of the theoretical values of $f_i(t)$ and $\bar{F}_i(t)$ versus $x(t)$ with the corresponding experimental data was excellent, indicating the accuracy of the comonomer reactivity ratios obtained in this work (see Supporting Information for discussing on the composition curve and number average sequence lengths of comonomers).

As can be seen from Figures 9 and 10, kinetics of the reaction can be separated into two regions, i.e., first region with $f_{BA} \neq 0$ and second region with $f_{BA} = 0$. Experimental data obtained in this work correspond usually to the BA/VAc copolymerization section where both BA and VAc are present in the reaction mixture (i.e., first region with $f_{BA} \neq 0$). Hence, only the first region of the reaction is considered in the case of BA/VAc copolymerization (Fig. 7), meaning that $k_p/k_t^{0.5}$ parameter estimated from experimental data is related to the "lumped" kinetic parameter of BA/VAc copolymerization. It should be noted that in both regions, theoretical drifts in the comonomer mixture and copolymer compositions can be evaluated by eqs. (9) and (10).

CONCLUSIONS

Free-radical copolymerization of the BA and VAc was performed in benzene- d_6 by using BPO as the

initiator at 70°C. Kinetics of this copolymerization system were investigated completely by online ^1H NMR kinetic experiments. Comonomer reactivity ratios were obtained by the TUM at low and medium/high conversions as well as by the simplified PUM with $r_2 = 0$. Due to the significant drift in the comonomer mixture composition, extended KT and MH methods were used to calculate more accurate reactivity ratios of the BA and VAc. Results showed that both MH and extended KT methods result in more reliable reactivity ratios. However, MH method gives the most precise estimate. The simplified PUM with $r_j = 0$ (VAc in the present system) were also used to estimate ultimate (r_i) and penultimate (r_i') reactivity ratios of comonomer BA. Results showed that copolymer composition and microstructure as well as drifts in the comonomer mixture and copolymer compositions of BA/VAc copolymerization system can be described well by the TUM reactivity ratios. Overall polymerization rate coefficient was calculated from the overall comonomer conversion versus time data and lumped kinetic parameter ($k_p \cdot k_t^{-0.5}$) was then estimated. It was found that $k_p \cdot k_t^{-0.5}$ increases with increasing the mole fraction of BA in the initial feed. Effect of the mole fraction of BA in the initial feed on composition drifts in the comonomer mixture and copolymer as a function of overall comonomer conversion was also evaluated. It was observed that final product after complete conversion will be almost a mixture of two corresponding homopolymer chains.

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