Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Kinetic Study of Radical Polymerization VIII. A Comprehensive Study of Solution Copolymerization of Vinyl Acetate and Methyl Acrylate by ^{1}H-NMR Spectroscopy

Mahdi Abdollahi[a]; Ali Reza Mahdavian[b]; Arezou Nouri[b]
[a] Faculty of Engineering, Department of Polymer Engineering, Tarbiat Modares University, Tehran, Iran [b] Polymer Science Department, Iran Polymer and Petrochemical Institute, Tehran, Iran

To cite this Article Abdollahi, Mahdi , Mahdavian, Ali Reza and Nouri, Arezou(2007) 'Kinetic Study of Radical Polymerization VIII. A Comprehensive Study of Solution Copolymerization of Vinyl Acetate and Methyl Acrylate by ^{1}H-NMR Spectroscopy', Journal of Macromolecular Science, Part A, 44: 8, 839 — 848

To link to this Article: DOI: 10.1080/10601320701407847

URL: http://dx.doi.org/10.1080/10601320701407847

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 839–848

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320701407847

Kinetic Study of Radical Polymerization VIII. A Comprehensive Study of Solution Copolymerization of Vinyl Acetate and Methyl Acrylate by ^{1}H-NMR Spectroscopy

MAHDI ABDOLLAHI,[1] ALI REZA MAHDAVIAN,[2] and AREZOU NOURI[2]

[1]*Faculty of Engineering, Department of Polymer Engineering, Tarbiat Modares University, Tehran, Iran*
[2]*Polymer Science Department, Iran Polymer and Petrochemical Institute, Tehran, Iran*

Received December, 2006, Accepted January, 2007

Radical copolymerization reaction of vinyl acetate (VA) and methyl acrylate (MA) was performed in a solution of benzene-d_6 using benzoyl peroxide (BPO) as the initiator at 60°C. Kinetic studies of this copolymerization reaction were investigated by on-line ^{1}H-NMR spectroscopy. Individual monomer conversions vs. reaction time, which was followed by this technique, were used to calculate the overall monomer conversion, as well as the monomer mixture and the copolymer compositions as a function of time. Monomer reactivity ratios were calculated by various linear and nonlinear terminal models and also by simplified penultimate model with $r_{2(VA)} = 0$ at low and medium/high conversions. Overall rate coefficient of copolymerization was calculated from the overall monomer conversion vs. time data and $k_p \, . \, k_t^{-0.5}$ was then estimated. It was observed that $k_p \, . \, k_t^{-0.5}$ increases with increasing the mole fraction of MA in the initial feed, indicating the increase in the polymerization rate with increasing MA concentration in the initial monomer mixture. The effect of mole fraction of MA in the initial monomer mixture on the drifts in the monomer mixture and copolymer compositions with reaction progress was also evaluated experimentally and theoretically.

Keywords: vinyl acetate; methyl acrylate; free radical copolymerization; kinetic study; on-line ^{1}H-NMR; monomer reactivity ratios; rate coefficient

1 Introduction

^{1}H-NMR spectroscopy has been proven to be one of the most important and reliable techniques for studying polymer structure and copolymer composition (1–4). On-line ^{1}H-NMR spectroscopy has been successfully used for the kinetic study of free radical homo- and copolymerization reactions (5–9).

Most of the studies on the copolymerization of vinyl acetate (VA) and methyl acrylate (MA) have been focused on the determination of copolymer composition and monomer reactivity ratios (10–17). To our knowledge, no report on the polymerization rate coefficient for this system has been reported yet. Brar et al. (17) have used 1D and 2D-NMR spectroscopic techniques to get an insight into the copolymer microstructure and monomer reactivity ratios. However, they used off-line NMR spectroscopy in their studies and hence, it was not possible to follow the reaction kinetics with respect to their individual and overall monomer conversions vs. time, as well as overall polymerization rate constant of various initial feed compositions.

To calculate the polymerization rate coefficient, it is necessary to measure the overall monomer conversion as a function of reaction time. Collecting these data by off-line techniques, such as gravimetry needs to prepare the same several samples, 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 monomer conversion with 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 overall monomer conversion data vs. time from one sample by detecting the polymerization progress by on-line techniques such as dilatometery and NMR.

The present research deals with the kinetics of the free radical copolymerization of VA and MA using on-line ^{1}H-NMR spectroscopy. Individual monomer conversions vs. time that were obtained from the spectra recorded as a

---

Address correspondence to: Ali Reza Mahdavian, Polymer Science Department, Iran Polymer and Petrochemical Institute, P. O. Box 14965/115, Tehran, Iran. Tel.: +9821 4458 0000; Fax: +9821 4458 0023; E-mail: a.mahdavian@ippi.ac.ir

function of reaction progress are used to calculate the overall monomer conversion as well as the monomer mixture and the copolymer compositions. Monomer reactivity ratios are calculated by both linear and nonlinear methods at low and medium/high conversions. Overall polymerization rate coefficients are estimated for various initial feed compositions too. Also, composition drifts in the monomer mixture and the copolymer are evaluated experimentally and theoretically.

2 Experimental

2.1 Materials

The monomers, VA and MA (from Aldrich Chemical Co.), were washed three times with a 5% sodium hydroxide solution followed by washing three times 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) and used as received. Benzoyl peroxide (BPO) (from Fluka Chemical Co.) was used as initiator without further purification.

2.2 Sample Preparation

Reaction mixtures were prepared with the concentrations mentioned in Table 1. Monomer mixture composition was varied in each sample and the other parameters were kept constant. At first, the initiator solution in benzene-d_6 was prepared. A measured amount of this solution was then added to the monomer mixture so that initiator and overall monomer concentrations were adjusted to be close to 4×10^{-2} M and 1 M, respectively. Total volume of each sample was 1.00 ml. 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, which acts as a retardant in the free radical polymerization reactions. Although the exact control of BPO concentration was difficult but it was determined exactly via the first spectrum recorded for each sample in spite of being aware that the overall monomer concentration was exactly 1 M.

Table 1. Concentration of the components (in benzene-d_6 solution) in the initial reaction mixture[a,b]

Sample	f_{MA}^{o}[c]	[BPO] × 10^2 (mol L^{-1})[d]
VM0.0[e]	0	4.0004
VM05.0	0.0502 (0.0503[f])	4.3342
VM06.2	0.0594 (0.0608[f])	4.0056
VM13.5	0.1338 (0.1346[f])	4.4580
VM13.6[g]	0.1373 (0.1356[f])	4.1790
VM20.5	0.2061 (0.2050[f])	5.6514
VM40.0	0.3989 (0.4003[f])	5.2866
VM51.1	0.5108 (0.5114[f])	5.7139
VM100.0	1	5.9861

[a] The reaction temperature was set at 60°C.

[b] Overall monomer concentration for all samples was exactly 1 M.

[c] Mole fraction of MA in the initial feed.

[d] Concentration of BPO in all solutions was set to be close to 4×10^{-2} M and was determined exactly from the first spectrum recorded for each sample in spite of being aware that overall monomer concentration is exactly 1 M (see Experimental section).

[e] Numbers in the front of sample codes indicate the mole fraction of MA in the initial monomer mixture.

[f] These quantities were obtained from the first spectrum recorded for each sample and used in the calculations.

[g] This sample was used only in determining the monomer reactivity ratios. For this reason, only two spectra were recorded at the two different times (or conversions).

2.3 ^{1}H-NMR Experiments

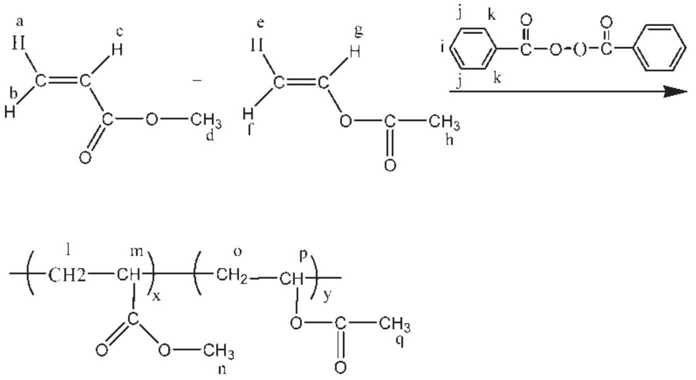
All NMR experiments reported in this study were carried out on a Bruker Avance 400 MHz NMR spectrometer. The sample cavity was equilibrated at 60°C (i.e., the temperature at which all of the experiments were carried out) by a BVT 3000 (± 0.1°C) temperature control unit. A typical ^{1}H-NMR kinetic experiment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

First, the cavity was set at 60°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 reactions mixture (Table 1) was inserted into the sample chamber and considered as the starting time. 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. 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 of the samples contained high amount of benzene-d_6. This was preferred because of better thermal conductivity (isothermal condition) and also avoiding an excessive viscosity increase at higher conversions.

3 Results and Discussion

In continuum to our previous research on the kinetic study of free radical homo- and copolymerization (7–9, 18, 19), we used the on-line ^{1}H-NMR technique in copolymerization reaction of VA and MA in order to determine the monomer reactivity ratios, overall polymerization rate coefficient as well as composition drifts in the monomer mixture and in the copolymer with time. Advantages and disadvantages of applying this on-line technique to follow polymerization reaction have been discussed before in detail (7).

A typical ^{1}H-NMR spectrum of the initial reaction mixture containing 0.4003 mole fraction of MA (sample VM40.0 in



Sch. 1. Schematic diagram for free radical copolymerization of VA and MA initiated by benzoyl peroxide (BPO) in benzene-d$_6$ solution.

Table 1) at the overall conversion of 40.34 mol% with the signal assignments (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 VA and MA and compared them with spectra related to the copolymerization systems. The last spectra recorded for each sample are shown in Figure 2. It is clear that the signals related to the -*CH* protons of both VA (-CH^p) and MA (-CH^m) incorporated into the copolymer chain could be used to follow the reaction progress. In all spectra of each sample, the overall integral for -CH$_3$ proton signals of MA (3.7–3.9 ppm in Figure 1) existing in the monomer mixture (-CH_3^d) and in the produced copolymer (-CH_3^n) was adjusted to an arbitrary value of 3. The integral 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 similarly so that the overall integrals of all proton signals in the other spectra for that 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.

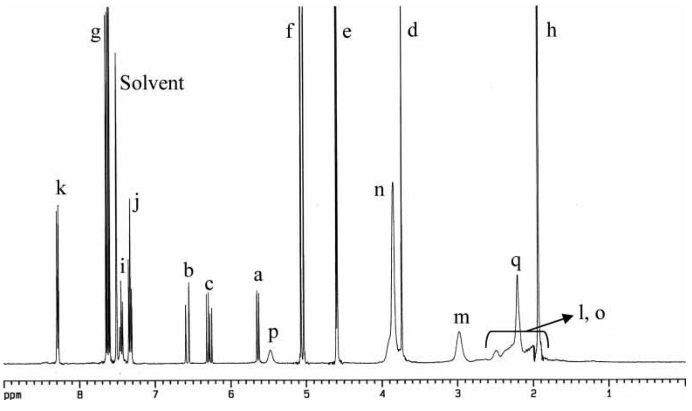


Fig. 1. A typical ^{1}H-NMR spectrum of the monomer mixture and the produced copolymer after the overall monomer conversion of 40.34 mol% for the sample VM40.0.

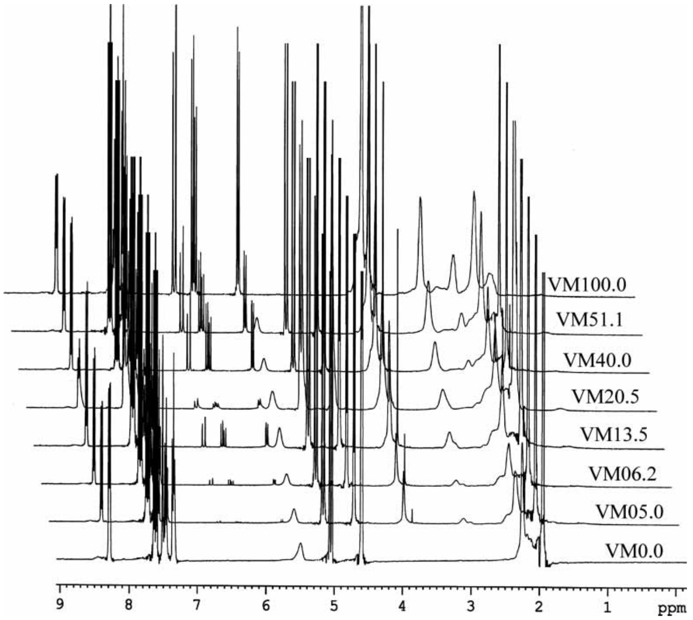


Fig. 2. The final ^{1}H-NMR spectra recorded for VA/MA copolymerization systems with various monomer mixture compositions (see Table 1).

Individual monomer conversions of both VA and MA at each reaction time were calculated via Equations (1) and (2).

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

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

where x_i is the individual conversion of monomer i. $I(\text{-}CH)_i^{\text{copolymer}}$ and $I(\text{-}CH)_i^{\text{monomer}}$ indicate the intensities of methine and one of the two methylene proton resonance signals of the monomer i incorporated into the copolymer chain and in the feed respectively. Overall monomer conversion (x) and mole fraction of the monomer i in the monomer mixture (f_i) and in the produced copolymer chain (F_i) are related to the individual monomer conversions by the following equations:

$$x = f_i^o x_i + f_j^o x_j \tag{3}$$

$$f_i = \frac{n_i^o/n_j^o(1 - x_i)}{n_i^o/n_j^o(1 - x_i) + (1 - x_j)} \tag{4}$$

$$F_i = \frac{n_i^o/n_j^o x_i}{n_i^o/n_j^o x_i + x_j} \tag{5}$$

where f_i^o is the mole fraction of monomer i in the initial reaction mixture and n_i^o is the molar amount of monomer i in the initial feed. From individual monomer conversions (subscript i for MA and subscript j for VA) determined by on-line ^{1}H-NMR, it is possible to calculate x, f_i and F_i through Equations 3–5.

The on-line ^{1}H-NMR spectra recorded for sample VM40.0 (see Table 1) as a function of the reaction time have been

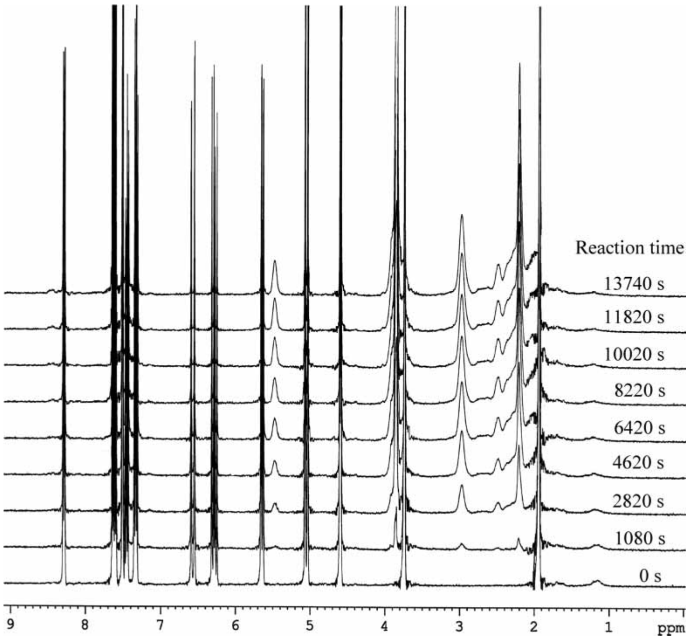


Fig. 3. Progress of the copolymerization reaction as a function of time for the sample VM40.0.

shown in Figure 3. 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 were 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. 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.

3.1 Determination of the Monomer Reactivity Ratios

The monomer reactivity ratios are important factors for predicting copolymer composition for each initial mixture of the monomers and to understanding the kinetic and mechanism of copolymerization reaction. In general, the reactivity ratios of monomers are determined at low conversion. In classic terminal model of copolymerization it has been suggested that for a given pair of monomers, the composition of copolymer is just a function of instantaneous composition of feed (20, 21).

Among several methods for determination of monomer reactivity ratios, the following terminal methods are extensively used for obtaining monomer reactivity ratios at low conversions: Mayo-Lewis (ML) (20), Finemann-Ross (FR) (22), inverted Finemann-Ross (inverted FR) (23), Kelen-Tudos (KT) (24), extended Kelen-Tudos (extended KT) (25–27), Joshi-Joshi (JJ) (28), Mao-Huglin (MH) (29), Tidwell-Mortimer (TM) (30) and error in variable (EV) (31, 32) methods. Mayo-Lewis, extended Kelen-Tudos and Mao-Huglin methods are also applicable for high conversions.

When $r_2 = 0$, the simplified penultimate model with $r_2 = 0$ could be used for calculation of monomer reactivity ratios. Kelen, Tudos and coworkers (33) proposed a linear method to calculate monomer reactivity ratios with simplified penultimate model, i. e. $r_2 = 0$, which was intended to be applicable for the systems not limited to low conversion data. In the present study, this model was used to calculate r_1 (ultimate reactivity ratio of monomer 1) and r'_1 (penultimate reactivity ratio of monomer 1), which are defined as k_{111}/k_{112} and k_{211}/k_{212} respectively. k_{ijm} is the rate constant for the reaction of radical—$M_i\ M_j^*$ with monomer M_m (i, j, m = 1 or 2).

On-line ^{1}H-NMR spectroscopy has been successfully applied for kinetic study of free radical homo- and copolymerization before (5–9). The monomer reactivity ratios and overall polymerization rate coefficients are kinetic parameters that can be derived by this on- line method. Davis et al. (5, 6) applied this technique for copolymerization of styrene with other comonomers and estimated the overall polymerization rate coefficient. We reported the determination of copolymer composition and then the monomer reactivity ratios by on-line ^{1}H-NMR method for conventional free radical copolymerization of various systems (8, 9). The monomer reactivity ratios together with the overall rate coefficient of copolymerization are necessary to complete investigation on the kinetic and mechanism of the copolymerization reaction. In this study, both mentioned kinetic parameters were determined.

The monomer mole fractions in the initial feed and in the produced copolymer chain, as well as the corresponding individual and overall monomer conversions have been given in Table 2.

By using these data at low and medium/high conversions, the monomer reactivity ratios were calculated by different

Table 2. Data obtained from ^{1}H-NMR spectra at low and medium/high conversions for free radical copolymerization of VA/MA system[a]

Sample	f^o_{MA}	F_{MA}	x_{VA}	x_{MA}	x
VM05.0	0.0503	0.5778 (0.3450)	0.0174 (0.0997)	0.4491 (0.9925)	0.0391 (0.1446)
VM06.2	0.0608	0.5838 (0.4277)	0.0272 (0.0849)	0.5884 (0.9795)	0.0613 (0.1393)
VM13.5	0.1346	0.6571 (0.5998)	0.0251 (0.0936)	0.3090 (0.9015)	0.0633 (0.2024)
VM13.6	0.1356	0.6602 (0.6375)	0.0153 (0.0530)	0.1895 (0.5938)	0.0390 (0.1264)
VM20.5	0.2050	0.7236 (0.6540)	0.0196 (0.1048)	0.1996 (0.7685)	0.0565 (0.2408)
VM40.0	0.4003	0.8357 (0.7813)	0.0327 (0.1471)	0.2495 (0.7873)	0.1195 (0.4034)
VM51.1	0.5114	0.8767 (0.8333)	0.0232 (0.1714)	0.1580 (0.8182)	0.0921 (0.5021)

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

Table 3. Reactivity ratios of VA and MA reported in the literature together with the results obtained in this work

R_{VA}	r_{MA}	Temp. in °C	Technique	Conversion in %	Reference
0.405^{a}	2.580^{a}	60	emulsion	<6	(11)
0.030^{a}	6.380^{a}	60	bulk	high	(12)
0.030^{a}	6.700^{a}	50	bulk	<3	(13)
0.030^{a}	6.300^{a}	60	bulk	<1	(14)
0.020	6.750	30	aqueous dispersion	high	(16)
0.04	7.28	60	Solution (benzene)	<5	(17)
Terminal model					
-0.0013	5.9825	60	Solution (benzene-d$_6$)	<12	Our data (KT method)^{b}
-0.0034	6.5609	60	solution (benzene-d$_6$)	<12	Our data (extended KT method)^{b}
-0.0045	5.8765	60	solution (benzene-d$_6$)	<12	Our data (JJ method)
-0.00401	6.0036	60	solution (benzene-d$_6$)	<12	Our data (ML method)
-0.0016	5.9532	60	solution (benzene-d$_6$)	<12	Our data (TM method)^{c}
0.0087	7.5912	60	solution (benzene-d$_6$)	medium/high	Our data (extended KT method)^{b}
Simplified penultimate model					
0	5.7684 (6.7032)^{d}	60	solution (benzene-d$_6$)	<12	Our data (KT method)^{b}
0	5.8195 (9.7499)^{d}	60	solution (benzene-d$_6$)	<12	Our data (extended KT method)^{b}

[a] Reactivity ratios recalculated by Greenly (15, 34).
[b] The correlation coefficients for linear methods at low (<12) and medium/high conversions were higher than 0.990 and 0.970, respectively.
[c] With initial guesses of $r_{MA} = 1$ and $r_{VA} = 0$. Iteration number was 5 and the final s was 5.2738×10^{5}.
[d] Reactivity ratio presented inside the parenthesis is r'_{MA} (penultimate reactivity ratio of MA).

methods (the results are given in Table 3). The reactivity ratios estimated in this work are in good agreement with the values of reactivity ratios reported in the literature (Table 3). The VA and MA reactivity ratios 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.

The 95% joint confidence limits for the reactivity ratios of VA/MA could not be obtained due to the negative values of r_{VA}. Only for medium/high conversion data, r_{VA} obtained by extended Kelen- Tudos method had positive value. The 95% joint confidence limit for these positive values of reactivity ratios has been shown in Figure 4. The joint confidence limit is relatively narrow, justifying the high degree of certainty in the numerical values of the monomer reactivity ratios. Where the reactivity ratio of VA was negative, only the confidence limit for the reactivity ratio of MA (r_{MA}) could be calculated. This confidence limit for reactivity ratio of MA obtained by KT, extended KT, JJ, ML and TM methods (terminal models in Table 3) at low conversion (<12%) was 5.6419–6.3446, 5.1190–8.4088, 5.0977–6.7742, 5.2324–6.8885 and 5.6089–6.3187 respectively. Obviously, the confidence limits for r_{MA} from all methods were narrow, indicating the high degree of certainty in the numerical values of r_{MA}. However, it is believed that the monomer reactivity ratios obtained by nonlinear Tidwell-Mortimer method are more accurate than those of linear

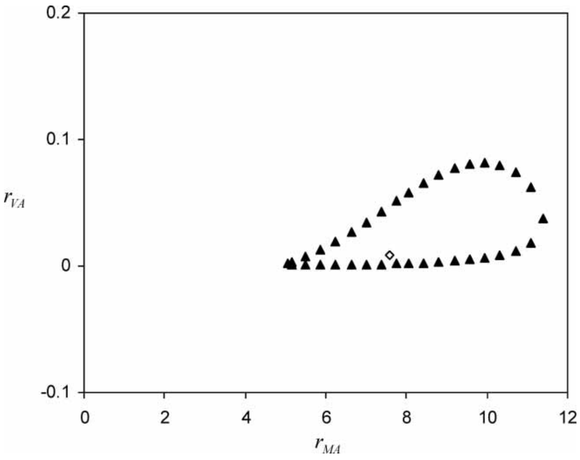


Fig. 4. The 95% joint confidence limits (▲) for reactivity ratios of VA and MA obtained by extended Kelen- Tudos method (◇) at medium/high conversion.

methods. For this reason, the reactivity ratios obtained by nonlinear method will be preferentially used later to evaluating the composition drifts in the monomer mixture and in the produced copolymer.

3.2 Estimation of the Overall Polymerization Rate Coefficient

Individual monomer conversions of VA and MA as a function of reaction time for the reaction system containing 0.4003 mole fraction of MA in the initial monomer mixture (sample VM40.0) have been shown in Figure 5. The reaction temperature in all of the experiments was set at 60°C. Figure 5 reveals that both monomers polymerize (and are very likely to copolymerize) and that MA is incorporated into the copolymer at a very higher rate than VA. The same trend was observed for all other initial feed compositions, that is, MA is always preferentially incorporated into the copolymer. As mentioned before, individual monomer conversions vs. time data may be used to deduce the changes in the monomer mixture and copolymer compositions as a function of overall monomer conversion and to calculate the overall monomer conversion vs. time. Calculating the drifts in the monomer mixture and the copolymer compositions with the overall monomer conversion will be discussed later.

Figure 6 indicates the overall monomer conversion as a function of reaction time for various mole fractions of MA in the initial reaction mixture. This figure shows obviously that with increasing MA amount in the initial feed, the overall rate of polymerization increases remarkably. This observation is consistent with previous data reported on the propagation- and termination- rate coefficients of MA (35, 36) and VA (34, 35, 37, 38) homopolymerizations. The propagation rate coefficients (k_p) for bulk homopolymerization of pure MA and pure VA at 60°C have been reported to be close to 27850 (35) and 7860 $\text{Lmol}^{-1}\text{s}^{-1}$ (36), respectively. Thus, on the basis of preceding data, k_p of MA is greater than that of VA by a factor of 3.5 approximately.

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

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

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

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

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

where x is the overall monomer conversion and k_{over} is the overall polymerization rate coefficient. k_{over} is equal to the

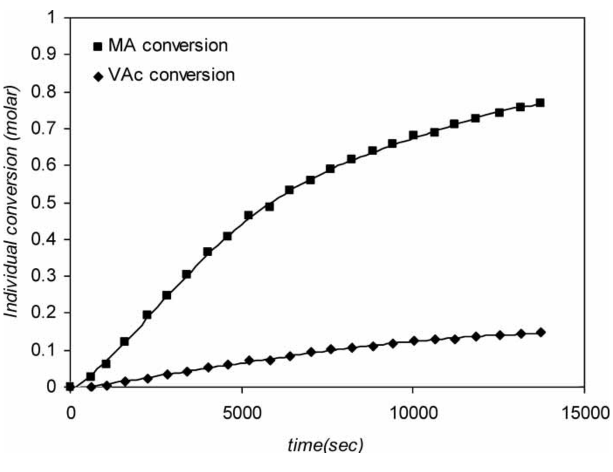


Fig. 5. Individual monomer conversions of VA and MA vs. reaction time calculated from ^{1}H-NMR spectra for the free radical copolymerization of the sample VM40.0.

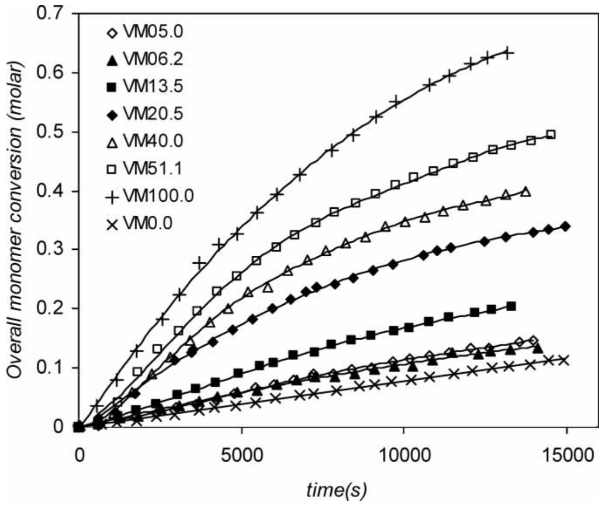


Fig. 6. Overall monomer conversion as a function of reaction time curves for various mole fractions of MA in the initial reaction mixture.

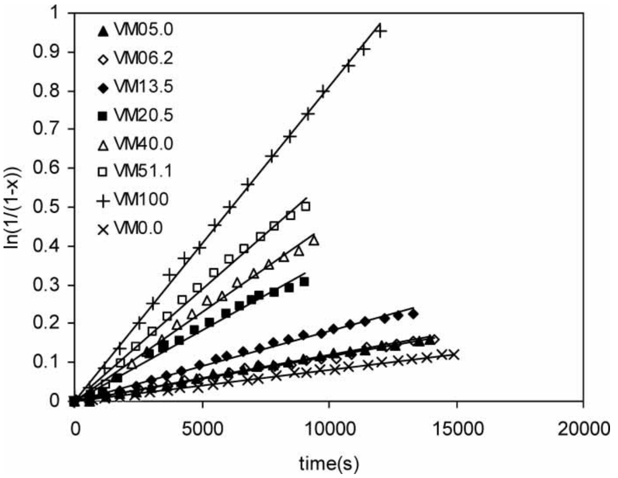


Fig. 7. Dependency of ln(1/(1-x)) vs. time plots on the mole fraction of MA (or VA) in the initial reaction mixture.

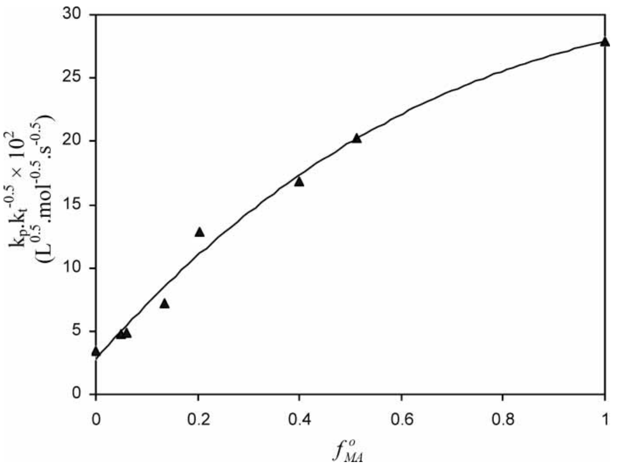


Fig. 8. Variation of $k_p\ k_t^{-0.5}$ as a function of MA mole fractions in the initial feed.

slope of $\ln(1/(1 - x))$ vs. time curve. The corresponding curves have been shown in Figure 7.

The straight lines in Figure 7 were obtained by fitting Equation (7) to the data sets. According to this figure, increasing the mole fraction of MA in the initial monomer mixture has a significant effect on the slope, i.e., on the overall rate coefficient of polymerization (k_{over}). Since the efficiency of initiator, the decomposition rate constant of BPO and its concentration are known; Equation (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 0.7 (39) and k_d for BPO in benzene solution at 60°C has been reported to be close to $2.0 \times 10^{-6}\ s^{-1}$ (34). Using these values, together with the BPO concentration given in Table 1, yields the $k_p \cdot k_t^{-0.5}$ values listed in Table 4 and plotted as a function of MA mole fraction in the initial feed in Figure 8. $k_p \cdot k_t^{-0.5}$ increases with increasing amount of MA in the initial reaction mixture (Figure 8). The same trend is observed for the known values of k_p and k_t for the respective homopolymerizations and could confirm above variation in Figure 8. Furthermore, Figure 8 shows that the increase in the rate of polymerization is more pronounced when going from 0 to 0.2 mole fraction of MA in the initial reaction mixture than from 0.2 to 1.0 mole fraction of MA.

Table 4. Dependency of the overall rate coefficient and $k_p\ k_t^{-0.5}$ for VA/MA copolymerization system on the mole fraction of MA in the initial feed

Sample	f^o_{MA}	$k_{over} \times 10^5$ (s^{-1})	$k_p \cdot k_t^{-0.5} \times 10^2$ $(L^{0.5}mol^{-0.5}s^{-0.5})^a$
VM0.0	0	0.8171	3.4531
VM05.0	0.0503	1.1840	4.8066
VM06.2	0.0608	1.1510	4.8605
VM13.5	0.1346	1.8072	7.2340
VM20.5	0.2050	3.6273	12.896
VM40.0	0.4003	4.5840	16.850
VM51.1	0.5114	5.7319	20.266
VM100.0	1	8.0763	27.898

[a] These values were calculated according to the Equation 7 with assuming that f' (for BPO) and k_d (for BPO in benzene solution at 60°C) are close to 0.7 (39) and $2.0 \times 10^{-6}\ s^{-1}$ (34), respectively.

With the experimental data at hand it is possible to calculate an estimate for average k_t in MA and VA homopolymerizations at 60°C and low conversions (in benzene-d_6 solution) as well as to compare these value with previously reported k_t data in bulk homopolymerizations of MA (35, 36) and VA (34, 37, 38). Using k_p values of 27850 and $7860\ L \cdot mol^{-1}s^{-1}$ (35) for MA and VA, respectively, k_t values are calculated to be 9.9656×10^9 and $5.1812 \times 10^{10}\ L \cdot mol^{-1}s^{-1}$. These values of k_t are in good agreement with the bulk values for MA and VA that have been reported to be about 1.31×10^8 (35, 36) and $10^7 - 10^9\ L \cdot mol^{-1}s^{-1}$ (34, 37, 38) respectively. It should be noted that the value of k_t is dependent on the 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. We believe that our approach to the determination of $k_p \cdot k_t^{-0.5}$ is a sufficiently reliable procedure.

3.3 Composition Drifts in the Monomer Mixture and the Copolymer

Other important information about VA/MA copolymerization system can be obtained via plots of the monomer mixture and copolymer compositions vs. the overall monomer conversions. These data could be calculated from the individual monomer conversions of MA and VA according to Equations 3–5.

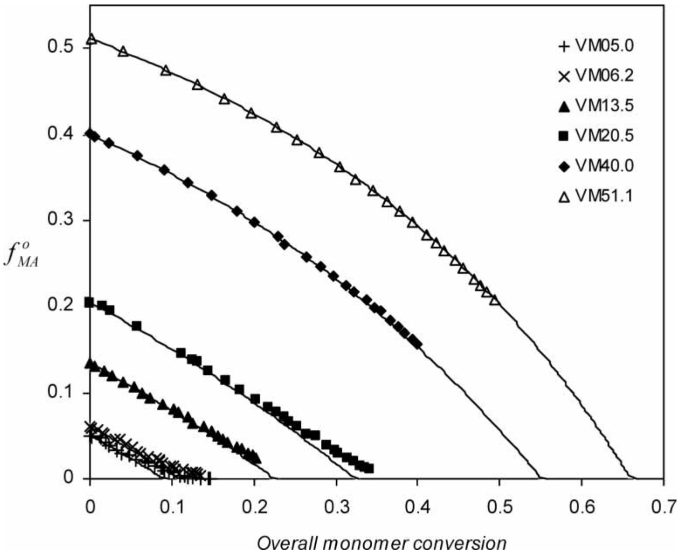


Fig. 9. Monomer mixture composition as a function of the overall monomer conversion for various mole fractions of MA in the initial feed (symbols show the experimental data and continuous lines indicate the theoretical data calculated by Meyer-Lowry equation using reactivity ratios of Tidwell-Mortimer method).

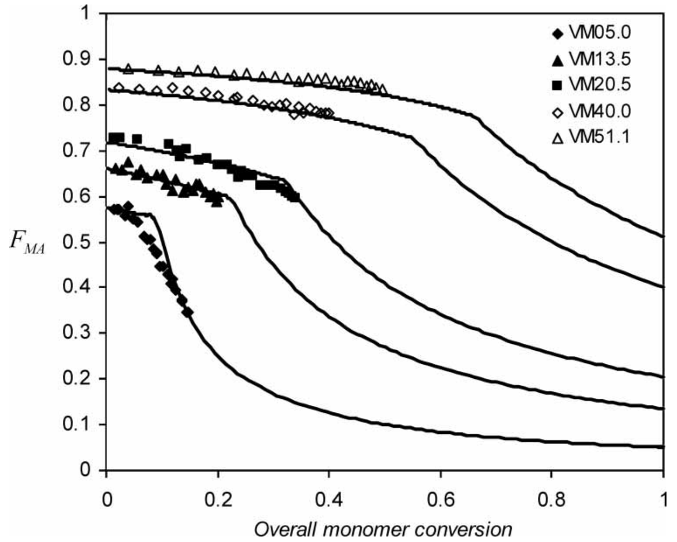


Fig. 10. Dependency of the copolymer composition drifts versus overall monomer conversion plots on the mole fraction of MA in the initial reaction mixture (symbols show the experimental data and continuous lines indicate the theoretical data calculated by Meyer-Lowry Equation 9 in conjunction with material balance Equation 10 using reactivity ratios of Tidwell-Mortimer method).

Figure 9 shows the experimental changes in comonomer mixture composition versus overall monomer conversion up to 50 mol% for various amounts of MA (or VA) in the initial reaction mixture. This figure reveals that in the various mole fractions of MA in the initial feed, the incorporation of MA into the copolymer chain is more favored than VA. The overall changes in the comonomer mixture composition with increasing conversion is very high; indicating that the reactivity ratio of MA should be much greater than that of VA, as obtained before. In other words, the adduct radical of MA monomer is more likely to react with its own monomer relative to VA monomer while the adduct radical of VA monomer is more likely to react with MA monomer relative to its own monomer. This causes the higher rate of incorporation of MA into the copolymer chain than VA, resulting in the significant changes in the monomer mixture composition. It is observable from Figure 9 that the rate of incorporation of MA into the copolymer is very high so that the mole fraction of MA in the monomer mixture reduces rapidly to zero. After full consumption of the monomer MA, only VA will be present in the reaction mixture and the reaction will be thus progressed via homopolymerization of VA.

From the individual monomer conversion vs. time data at the same time for all samples it was observed that with increasing the amount of MA in the initial feed, individual conversion of MA decreases slightly while that of VA increases slightly (see individual monomer conversions at high conversion data in Table 2). In other words, the incorporation rate of MA into the copolymer chains increases slightly with increasing conversion due to decrease in MA amount in the monomer mixture (Figure 9). So, it is expected that the changes in copolymer composition will be less pronounced up to the overall monomer conversion at which all of the MA monomer in the monomer mixture has been consumed, as shown in Figure 10. The experimental data in Figure 10 reveal that until the MA monomer is present in the monomer mixture, the copolymer composition drift is not considerable. On the other hand, when there no MA exists in the monomer mixture (sample VM05.0 in Figure 10), the copolymer composition will be changed drastically with increasing overall monomer conversion due to the only homopolymerization of VA comonomer. From the monomer mixture and copolymer compositions versus overall monomer conversion curves (Figures 9 and 10) it is observed that the tendency of VA monomers to homopolymerize increases with increasing VA content in the initial feed even at low conversions. As a consequence, in order to obtain the relatively homogeneous copolymer composition, it is necessary to stop the reaction before full consumption of MA at low, medium or high conversions depending on the initial monomer mixture composition.

The instantaneous copolymer composition equation of Mayo-Lewis (20) is expresed as Equation (8):

$$F_i = \frac{r_i f_i^2 + f_i f_j}{r_i f_i^2 + 2 f_i f_j + r_j f_j^2} \tag{8}$$

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

Equation (5), it is cumulative average mole fraction of monomer i in the copolymer chain.

An integration of Equation (8) leads to the Meyer- Lowry (40) equation:

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

$$\text{where } \alpha = \frac{r_j}{1-r_j}; \quad \beta = \frac{r_i}{1-r_i}; \quad \gamma = \frac{1-r_ir_j}{(1-r_i)(1-r_j)}$$

$$\text{and} \quad \delta = \frac{1-r_j}{2-r_i-r_j}$$

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.

$$\bar{F}_i = \frac{f_i^o - f_i(1-x)}{x} \tag{10}$$

Using the Meyer- Lowry equation (40) in conjunction with the Equation (10), theoretical f_i and $\bar{F}_i$ were obtained as a function of overall monomer conversion for different feed compositions and compared with the corresponding experimental data in Figures 9 and 10. As mentioned before, the monomer reactivity ratios obtained by Tidwell-Mortimer method was preferentially used in the Meyer-Lowry equation. Fitting of the theoretical values of f_i and $\bar{F}_i$ vs. x with the corresponding experimental data was excellent, indicating the accuracy of the monomer reactivity ratios obtained here. The slight difference between the theoretical and experimental values of f_i vs. x for samples VM05.0, VM06.2 and VM20.5 at the higher experimental conversions may be attributed to the experimental error in the calculation of individual monomer conversions via Equations (1) and (2) and thereby f_i via Equation (4) due to the very low mole fraction (and thus very weak signal of protons) of MA in the monomer mixture as shown in Figure 2. The theoretical composition curve obtained from copolymer composition equation of Mayo-Lewis (20) (Equation (8)) using monomer reactivity ratios of Tidwell- Mortimer method and the experimental data of f_{MA}^o in Table 1 are shown in Figure 11. The experimental data are in good agreement with the theoretical curve.

Under conditions of $r_i \gg 1$ and $r_j \approx 0$ as be in the case of VA/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. Thus, homopolymerization of the more reactive monomer i is mostly carried out and then after complete consumption of monomer i, homopolymerization of the less reactive monomer j is started. It is clear that chains produced in the initial stages of reaction before finishing the monomer i (i.e. MA) in the monomer mixture will be copolymers with long blocks of MA units and very short (probably one monomer unit) of VA units. After this, homopolymer chains containing the VA units are formed. The final product after complete conversion will be almost the mixture of two corresponding homopolymer chains.

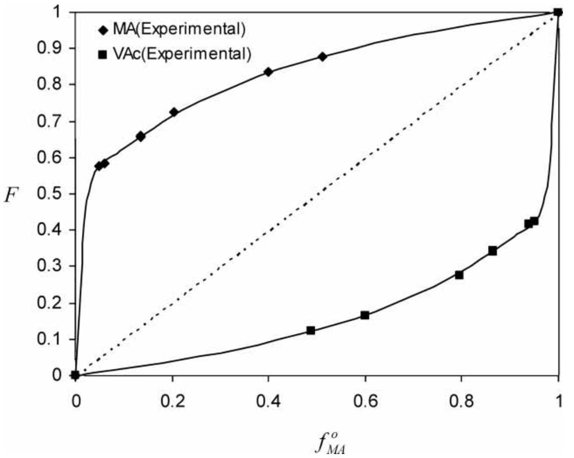


Fig. 11. Variation of copolymer composition (F_{VA} and F_{MA}) as a function of the mole fraction of MA in the initial feed (f_{MA}^o) for VA/MA copolymerization reaction (symbols show the experimental data and continuous lines indicate the theoretical curves obtained using reactivity ratios of Tidwell-Mortimer method in the copolymer composition Equation 8).

4 Conclusions

Free radical copolymerization reaction of MA and VA was performed in benzene-d$_6$ using BPO as the initiator at 60°C. A complete kinetic study of this copolymerization system was investigated by on- line ^{1}H-NMR spectroscopy. First, individual monomer conversions were obtained by analysis of ^{1}H-NMR spectra and then overall monomer conversions, as well as the monomer mixture and the copolymer compositions, were calculated from individual monomer conversion data. Monomer reactivity ratios were obtained by various linear and nonlinear terminal methods at low and medium/high conversions. The simplified penultimate model with $r_j = 0$ were also used for estimation of the ultimate (r_i) and penultimate (r_i') reactivity ratios of monomer i. Overall polymerization rate coefficient was calculated from the overall monomer conversion versus time data and $k_p \cdot k_t^{-0.5}$ was then estimated. It was found that $k_p \cdot k_t^{-0.5}$ increases with increasing the mole fraction of MA in the initial feed, illustrating the increase in the polymerization rate with increasing the MA concentration in the initial reaction mixture. The effect of mole fraction of MA in the initial feed on the composition drifts in the monomer mixture and in the produced copolymer as a function of overall monomer conversion was also evaluated.

5 Acknowledgments

A.R.M. wishes to express his gratitude to TWAS (Third World Academy of Sciences) for some financial support of this work (RGA No. 01-094 RG/CHE/AS). Also supports of Iran Polymer and Petrochemical Institute (IPPI) are greatly acknowledged.

6 References

1. Brar, A.S. and Sunita (1993) *Makromol. Chem.*, **194**, 1707.
2. Brar, A.S. and Yadav, A. (2001) *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 4051.
3. Brar, A.S., Singh, G. and Shankar, R. (2005) *Polymer*, **46**, 7164.
4. Brar, A.S. and Kaur, M. (2002) *J. Molecular Structure*, **606**, 231.
5. Barner-Kowollik, C., Heuts, J.P.A. and Davis, T.P. (2001) *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 656.
6. Baener, L., Barner-Kowollik, C. and Davis, T.P. (2002) *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 1064.
7. Mahdavian, A.R., Abdollahi, M. and Bijanzadeh, H.R. (2004) *J. Appl. Polym. Sci.*, **93**, 2007.
8. Mahdavian, A.R., Abdollahi, M., Mokhtabad, L., Bijanzadeh, H.R. and Ziaee, F. (2006) *J. Appl. Polym. Sci.*, **101**, 2062.
9. Mahdavian, A.R. and Abdollahi, M. (2007) *J. Appl. Polym. Sci.*, **103**, 3253.
10. Chinai, S.N. and Campbell, R.H. (1961) *Anal. Chem.*, **33**, 577.
11. Avetisyan, I.S., Eliseeva, V.I. and Larinovo, O.G. (1967) *Vysokomol Soedin, Ser A*, **9**, 570, *Chem. Abst.* 1967, 67: 22290e.
12. Mayo, F.R., Walling, C., Lewis, F.M. and Hulse, W.F. (1948) *J. Amer. Chem. Soc.*, **70**, 1523.
13. Garret, T.A. and Park, G.S. (1966) *J. Polym. Sci., Polym. Chem. Ed.*, **4**, 2714.
14. Kulkarni, N.G., Krishnamurti, N., Chatterjee, P.C. and Sivasamban, M.A. (1970) *Makromol. Chem.*, **139**, 165.
15. Greenley, R.Z. (1980) *J. Macromol. Sci. Chem. A*, **14**, 445.
16. Casinos, I. (1991) *Makromol. Chem.*, **192**, 1091.
17. Brar, A.S. and Charen, S. (1994) *J. Appl. Polym. Sci.*, **53**, 1813.
18. Mahdavian, A.R., Abdollahi, M., Mokhtabad, L. and Ziaee, F. (2006) *J. Macromol. Sci., Part A: Pure Appl. Chem.*, **43**, 1583.
19. Abdollahi, M., Mahdavian, A.R. and Bijanzadeh, H.R. (2006) *J. Macromol. Sci., Part A: Pure Appl. Chem.*, **43**, 1597.
20. Mayo, F.P. and Lewis, F.M. (1944) *J. Amer. Chem. Soc.*, **66**, 1594.
21. Alfery, G. and Goldfinger, J. (1944) *J. Chem. Phys.*, **12**, 205.
22. Finemann, M. and Ross, S.D. (1950) *J. Polym. Sci.*, **5**, 259.
23. Finemann, M. and Ross, S.D. (1964) *J. Polym. Sci. Part A-1*, **2**, 1687.
24. Kelen, T. and Tudos, F. (1975) *J. Macromol. Sci.*, **A9**, 1.
25. Kelen, T., Tudos, F., Foldes-Berezsnich, T. and Turcsanyi, B. (1976) *J. Macromol. Sci.*, **A10**, 1513.
26. Kelen, T., Tudos, F., Turcsanyi, B. and Kennedy, J. (1977) *J. Polym. Sci. Polym. Chem. Ed.*, **5**, 3047.
27. Kelen, T. and Tudos, F. (1981) *J. Macromol. Sci.*, **A16**, 1238.
28. Joshi, R.M. and Joshi, S.G. (1971) *J. Macromol. Sci. Chem.*, **A5**(**8**), 1329.
29. Mao, R. and Huglin, M.B. (1993) *Polymer*, **34**, 1709.
30. Tidwell, P.W. and Mortimer, G.A. (1965) *J. Polym. Sci. A-1*, **3**, 369.
31. Box, M.J. (1970) *Technometrics*, **12**, 219.
32. Dube, M., Amin Sanyei, R., Penlidis, A., O'Driscoll, K.F. and Reilly, P.M. (1991) *J. Polym. Sci. Polym. Chem.*, **29**, 703.
33. Kelen, T., Tudos, F., Braun, D. and Czerwinski, W.F. (1990) *Makromol. Chem.*, **191**, 1853.
34. Brandrup, J., Immergut, E.H. and Grulke, E.A. *Polymer Handbook*, 4th Edn.; Wiley: New York, 1999.
35. Beuermann, S. and Buback, M. (2002) *Prog. Polym. Sci.*, **27**, 191.
36. Buback, M., Kuelpmann, A. and Kurz, C. (2002) *Macromol. Chem. Phys.*, **203**, 1065.
37. Hutchinson, R.A., Richards, J.R. and Aronson, M. (1994) *Macromolecules*, **27**, 4530.
38. Theis, A., Davis, T.P., Stenzel, M.H. and Barner-Kowollik, C. (2006) *Polymer*, **47**, 999.
39. Deb, P.C. and Kapoor, S.K. (1979) *Eur. Polym. J.*, **15**, 961.
40. Meyer, V.E. and Lowry, G.G. (1965) *J. Polym. Sci. Part A*, **3**, 2843.