Kinetic study of atom transfer radical homo- and copolymerization of styrene and methyl methacrylate initiated with trichloromethyl-terminated poly(vinyl acetate) macroinitiator

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Atom transfer radical bulk copolymerization of styrene (St) and methyl methacrylate (MMA) was performed in the presence of CuCl/PMDETA as a catalyst system and trichloromethyl-terminated poly(vinyl acetate) telomer as a macroinitiator at 90 °C. The overall monomer conversion was followed gravimetrically and the cumulative average copolymer composition at moderate to high conversion was determined by ^{1}H NMR spectroscopy. Reactivity ratios of St and MMA were calculated by the extended Kelen–Tudos (KT) and Mao–Huglin (MH) methods to be $r_{St} = 0.605 \pm 0.058$, $r_{MMA} = 0.429 \pm 0.042$ and $r_{St} = 0.602 \pm 0.043$, $r_{MMA} = 0.430 \pm 0.032$, respectively, which are in good agreement with those reported for the conventional free-radical copolymerization of St and MMA. The 95% joint confidence limit was used to evaluate accuracy of the estimated reactivity ratios. Results showed that in the controlled/living radical polymerization systems such as ATRP, more reliable reactivity ratios are obtained when copolymer composition at moderate to high conversion is used. Good agreement between the theoretical and experimental composition drifts in the comonomer mixture and copolymer as a function of the overall monomer conversion was observed, indicating the accuracy of reactivity ratios calculated by copolymer composition at the moderate to high conversion. Instantaneous copolymer composition curve and number-average sequence length of comonomers in the copolymer indicated that the copolymerization system tends to produce a random copolymer.

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1. Introduction

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

Advantages of the ATRP technique are numerous [3]: catalytic amounts of transition metal complexes are used; many (macro)-initiators are commercially available, including multifunctional and hybrid systems; a large range of monomers can be polymerized (with the exception of unprotected acids); end-functionalization is very simple; there is no Trommsdorf effect; a large range of temperature can be used. One of the advantages of ATRP over the other

CLRP techniques (mainly nitroxide-mediated polymerization (NMP) and reversible addition–fragmentation chain transfer (RAFT)) is that in ATRP, block copolymerization can be achieved in any order (with halogen exchange), which is not possible for other CLRP methods. Difficulties in polymerization of di-substituted alkenes such as methacrylates by NMP method [4] as well as difficulties in the introduction of end functionality to the polymer by NMP and RAFT methods [3] are likely good reasons to justify the use of ATRP in the present study.

The three-component ATRP initiating system contains an organo-halide-type initiator, catalyst in the form of a salt of transition metal in the lower oxidation state, and a complexing ligand based mostly on amine-type. The combination of a catalyst and an appropriate ligand affects the redox potential of the system, leading to the equilibrium between dormant and active forms of growing chains, which minimizes the extent of termination reactions. Thus, the equilibrium between halogenated polymer chain (dormant form) and growing free macroradical (active form) is the key step of ATRP, as simply described in Scheme 1 [2].

The recent development of ATRP has opened a new route for the controlled synthesis of several block copolymers [5,6]. A wide variety of block copolymers can be derived from the same family of

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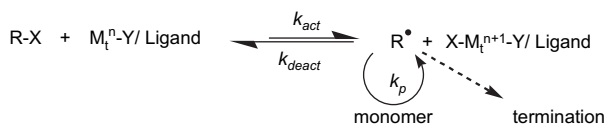
Scheme 1. Schematic illustration of ATRP mechanism [2].

vinyl monomers [7] or different families of vinyl monomers via ATRP [8].

Atom transfer radical copolymerization of various monomers has been performed in order to compare the monomer reactivity ratios of this system with those reported for the conventional free-radical copolymerization and to evaluate the mechanism of atom transfer radical polymerization. Monomer reactivity ratios in conventional free-radical and atom transfer radical co-polymerizations of methyl methacrylate/butyl acrylate [9], methyl methacrylate/2-hydroxyethyl methacrylate [10], styrene/n-octyl methacrylate [11], benzyl methacrylate/ethyl methacrylate [12], phenyl methacrylate/methyl methacrylate [13] and methyl acry-late/methyl methacrylate [14] have been studied and the results did not show any significant difference in the monomer reactivity ratios, indicating that there are similarities between the mecha-nism of ATRP and conventional free-radical polymerization (Scheme 1).

Copolymer compositions measured at low conversion are usually used to determine the monomer reactivity ratio. Among other methods, only the Mayo–Lewis (ML) [15], extended Kelen–Tudos (KT) [16] and Mao–Huglin (MH) [17] methods consider the drift in the comonomer and copolymer compositions with con-version. In other words, the above mentioned methods can be used at moderate to high conversion to calculate accurate re-activity ratios. Usually, in the conventional free-radical co-polymerization, monomer reactivity ratios are obtained by fitting the copolymer composition at low conversion versus the initial comonomer feed composition. However, in the controlled/living radical polymerization, the copolymer chain forms slowly throughout the reaction time and thereby measurement of the copolymer composition at low conversion can be affected by the structure of initiator, which may preferentially react with one of the comonomers [18,19]. Therefore, to obtain reliable results, it is necessary to measure the cumulative copolymer composition at conversion higher than about 10–15%. As a result, ML, extended KT and MH methods are the right choices to measure the monomer reactivity ratios in such situation where the effect of conversion on the calculation of monomer reactivity ratios should also be considered.

Monomer reactivity ratios of styrene (St) and methyl metha-crylate (MMA) in the atom transfer radical copolymerization have been reported in the literature [20,21]. However, copolymer com-positions measured at low conversion have been used to calculate monomer reactivity ratios, which can result in less reliable re-activity ratios of St and MMA. Sawamoto et al. [20] reported the atom transfer radical copolymerization of St and MMA and also applied Fineman–Ross method [22] to evaluate their data obtained at low conversion. Brar and Puneeta [21] synthesized copolymers of St and MMA by the atom transfer radical copolymerization and used KT [23] and error-in-variables model (EVM) [24] methods to calculate monomer reactivity ratios from copolymer composition measured at low conversion (<15%). Results of both studies in-dicated that the reactivity ratios of St and MMA for atom transfer radical copolymerization are different from those reported in lit-erature for the conventional free-radical polymerization of St and MMA. Although this difference has been attributed to the different polymerization conditions, however, it is believed that using co-polymer composition at low conversion for the atom transfer

radical copolymerization of St and MMA may be the main reason for observed differences in the reactivity ratios [18,19].

A wide variety of monomers have been polymerized by ATRP reaction. However, ATRP of vinyl acetate (VAc) has been reported to be difficult and impossible due to the low equilibrium constant ($K_{eq} = K_{act}/K_{deact}$, see Scheme 1) and possible side reactions such as the decomposition of the dormant species [25]. Recently, cobalt-mediated radical polymerization of VAc has been reported for the controlled synthesis of poly(vinyl acetate) (PVAc) with respect to the molecular weight and its distribution as well as the chain end functionality [26]. Nowadays, PVAc-based block copolymers are readily obtained by combination of cobalt-mediated radical poly-merization with a second type of controlled/living radical poly-merization (for example, ATRP) [27,28]. On the other hand, conventional free-radical polymerization techniques producing mono- or di-functional polymers can also be suitably associated with some CLRP systems to give novel block copolymers. For ex-ample, PVAc-based block copolymers have been synthesized by consecutive radical telomerization of VAc with chloroform or car-bon tetrachloride and ATRP of various monomers in the presence of trichloromethyl (CCl_3)-terminated PVAc telomer [29–36]. It has been found that PVAc telomer can be used as an effective macro-initiator in the ATRP.

In the present study, CCl_3-terminated PVAc telomer was used as a macroinitiator for the first time in the atom transfer radical co-polymerization of St and MMA. To obtain more reliable reactivity ratios of St and MMA and compare them with those reported for the conventional free-radical copolymerization, atom transfer radical copolymerization of St and MMA initiated with CCl_3-terminated PVAc telomer was followed up to high conversion. Copolymer composition at moderate to high conversion was measured by ^{1}H NMR and then used to calculate monomer reactivity ratios. Theo-retical composition drifts in the comonomer mixture and co-polymer chains were also investigated by the monomer reactivity ratios calculated here. Results were compared with some experi-mental data to evaluate the accuracy of calculated reactivity ratios of St and MMA.

2. Experimental

2.1. Materials

Styrene (St) (Merck, >99%) and methyl methacrylate (MMA) (Merck, >99%) were distilled over calcium hydride under reduced pressure before use. CuCl (Merck, 97%) was washed by glacial acetic acid (three times), absolute ethanol and diethyl ether in turn and then dried under vacuum. N,N,N′,N″,N″-Pentamethyldiethylenetri-amine (PMDETA) (Merck, 99.8%) as a ligand and tetrahydrofuran (THF) as a solvent were used as-received. CCl_3-terminated poly-(vinyl acetate) telomer with 86.7% end functionality (i.e., telomer percentage), number-average molecular weight of 1330 g mol^{-1} (calculated from ^{1}H NMR) and polydispersity index of molecular weight distribution of 1.83 (measured by GPC) (see the next section for more details) was prepared by telomerization of VAc monomer in the presence of chloroform at 60 °C for 5 h [29–31] and used as a macroinitiator in the atom transfer radical homo- and co-polymerization of St and MMA (Table 1). Initial concentration of VAc in the reaction mixture was 2.42 M and the molar ratio of re-action ingredients [VAc]$_0$/[CHCl$_3$]$_0$/[AIBN]$_0$ was 1/4/0.01. Conver-sion of the reaction was 70.6% after 5 h. After performing the telomerization reaction, unreacted monomer and chloroform were evaporated at room temperature. THF was then added to product and refluxed for 5 h to decompose traces of the unreacted AIBN initiator [29–31]. Finally, THF was evaporated at room temperature and the polymer was dried under vacuum at 50 °C up to a constant weight.

Table 1
Atom transfer radical homo- and copolymerization recipes of St and MMA initiated with CCl₃-terminated PVAc macroinitiator[a]

Exp. No.	$[St]_0$ (mol l^{-1})	$f_{St}^0 = [St]_0/([St]_0 + [MMA]_0)$
MS1.0[b]	8.59	1.0
MS0.9	7.79	0.9
MS0.7	6.16	0.7
MS0.5	4.47	0.5
MS0.3	2.72	0.3
MS0.1	0.92	0.1
MS0.0	0 (9.30)[c]	0.0

[a] $[CCl_3\text{-PVAc}]_0:[CuCl]_0:[PMDETA]_0:([St]_0 + [MMA]_0) = 1:1:2:300$. Polymerization was carried out at 90($\pm$0.1) °C.
[b] Numbers given in the symbols indicate the mole fraction of styrene in the initial comonomer mixture (f_{St}^0).
[c] Value given inside the parenthesis shows the molar concentration of MMA.

2.2. Atom transfer radical homo- and copolymerization of St and MMA initiated with CCl₃-terminated PVAc macroinitiator

A required amount of CuCl was introduced to glass tubes equipped with a magnetic stirrer (Table 1). The glass tubes were sealed with a rubber septum and were cycled between vacuum and nitrogen three times. Mixtures containing required amounts of St, MMA, macroinitiator (CCl₃-terminated PVAc telomer) and ligand (PMDETA) (Table 1) were degassed by purging nitrogen for 20 min and then added to the glass tubes. The molar ratio of reaction ingredients $[St + MMA]_0/[PMDETA]_0/[CuCl]_0/[PVAc\text{-}CCl_3]_0$ was kept constant for all experiments (300/2/1/1) (Table 1). The molar ratio of comonomers was only variable in the experiments. The "freeze–pump–thaw" cycle was carried out three times to remove oxygen from the glass tubes and sealed under vacuum. The sealed tubes were then immersed in a preheated oil bath at a desired temperature (i.e., 90 $\pm$ 0.1 °C). The tubes were removed from the oil bath at the various time intervals and reaction mixture was dissolved in THF, filtered and dried under vacuum to a constant weight and conversion was then determined gravimetrically. The dried copolymer was redissolved in THF and passed through a short column of neutral alumina to remove the remaining copper catalyst. The sample was then dried again under vacuum at 50 °C up to a constant weight and used in ¹H NMR and GPC analyses. It should be mentioned that samples were taken from the glass tubes in the case of homopolymerization reactions and then analyzed directly by ¹H NMR to measure the unreacted monomers as well as the monomer conversion. Conversions obtained from gravimetric and ¹H NMR analyses were the same (see Table 2).

Table 2
Data obtained for the atom transfer radical homo- and copolymerization of St and MMA initiated with CCl₃-terminated PVAc macroinitiator at 90 °C (Table 1)

Exp. No.	X^a (%)	$\overline{M}_{n,theor}$[b] (g mol^{-1})	$\overline{M}_{n,GPC}$ (g mol^{-1})	PDI
MS1.0	42.28 (42.15)[c]	14 540	15 760	1.46
MS0.9	29.72	10 580	12 270	1.69
MS0.7	10.44	4554	6152	1.86
MS0.5	31.80	11 074	15 090	1.82
MS0.3	53.63	17 633	21 800	1.87
MS0.1	9.79	4282	7167	1.98
MS0.0	76.72 (76.52)[c]	23 863	28 570	1.97

[a] Overall mass conversion was obtained gravimetrically.
[b] $\overline{M}_{n,theor} = \sum[(([M_i]_0)/([CCl_3 - PVAc]_0)) \times x_i \times M_{n,M_i}] + \overline{M}_{n,macroinitiator}$ in which $\overline{M}_{n,macroinitiator}$ is the number-average molecular weight of CCl₃-terminated PVAc telomer ($M_{n,NMR}^{Telomer} = 1330$ g mol^{-1}) and $[M_i]_0$, x_i and M_{n,M_i} are the individual molar concentration, individual molar conversion (see data in Table 4) and molecular weight of comonomer i, respectively.
[c] Values given inside the parenthesis were obtained from ¹H NMR spectrum of the reaction mixture containing both unreacted monomer and produced polymer.

2.3. Characterization

Overall mass conversion (X) of comonomers was calculated gravimetrically. Poly(vinyl acetate)-*block*-poly(St-*co*-MMA) terpolymers were dissolved in CDCl₃ and characterized by using 400 MHz ¹H NMR spectroscopy (DRX 400 Bruker Avance) at ambient temperature. It is essential for quantitative NMR analyses to achieve complete relaxation of the nuclei between the individual pulses. The specific combination of the relaxation delay (D_1) (25 s) and pulse angle (30°) allows for a complete relaxation of the protons of both St and MMA, which has been verified by determination of the longitudinal relaxation time (T_1). Acquisition time (AQ) was about 2 s. Under these conditions, sum of AQ and D1 was at least five times greater than T_1, which is necessary for the best quantitative results. Polymer concentration in the CDCl₃ solution was about 2%.

Apparent (i.e., polystyrene-equivalent [37]) molecular weight and polydispersity of the terpolymers dissolved in THF were determined by a Waters 150C gel permeation chromatography (GPC) equipped with a 10^4, 10^3 and 500 Å set of Ultrastyragel columns and a refractive index (RI) detector. Polystyrene standards with the narrow molecular weight distributions and molecular weights in the range of analyzed molecular weights were used to calibrate the columns and obtain calibration curve (see Fig. S1 in Supplementary material). Equation of the polystyrene calibration curve has been given in Supplementary material (see Table S1) to allow any other laboratory to reproduce and compare GPC measurements. THF was used as an eluent with the flow rate of 1 ml min^{-1} at 35 °C. It should also be mentioned that as the solubility of PVAc macroinitiator and PMMA is almost comparable with that of polystyrene (see Mark–Houwink coefficients of THF solution of VAc, St and MMA in Table S2 of Supplementary material), it is expected that there is no significant difference between apparent and true values of molecular weight and polydispersity [38].

3. Results and discussion

3.1. Atom transfer radical homo- and copolymerization of St and MMA initiated with CCl₃-PVAc macroinitiator

Fig. 1 shows the ¹H NMR spectrum of PVAc telomer at the final conversion (70.6%) synthesized by radical telomerization of VAc in the presence of CHCl₃ as a telogen and AIBN as an initiator at 60 °C. Signals were assigned to the corresponding protons [29–31]. Number-average degree of polymerization ($\overline{DP}_n$), number-average molecular weight ($\overline{M}_n$) and telomer percentage (telomer %) were calculated from ¹H NMR spectrum by the following equations [39]:

$$\overline{DP}_n = \frac{I_{4.7-5.0} + (I_{3.9-4.1}/2) + I_{5.2-5.4}}{(I_{3.9-4.1}/2)} \quad (1)$$

$$\overline{M}_n = \overline{DP}_n \times 86.09 + [(Telomer\,\%/100) \times 119.38] + [\{1 - (Telomer\,\%/100)\} \times 69.10] \quad (2)$$

$$Telomer\,\% = \frac{I_{2.8-3.2}}{I_{3.9-4.1}} \quad (3)$$

in which I_{i-j} is the intensity of signal(s) appeared at the chemical shift between i and j. Term $1 - (telomer\,\%/100)$ indicates a fragment of chains initiated with the initiator derived radical. The numbers 86.09, 119.38 and 69.10 denote the molecular weights of VAc, CHCl₃ and initiator fragment incorporated into the PVAc polymer, respectively.
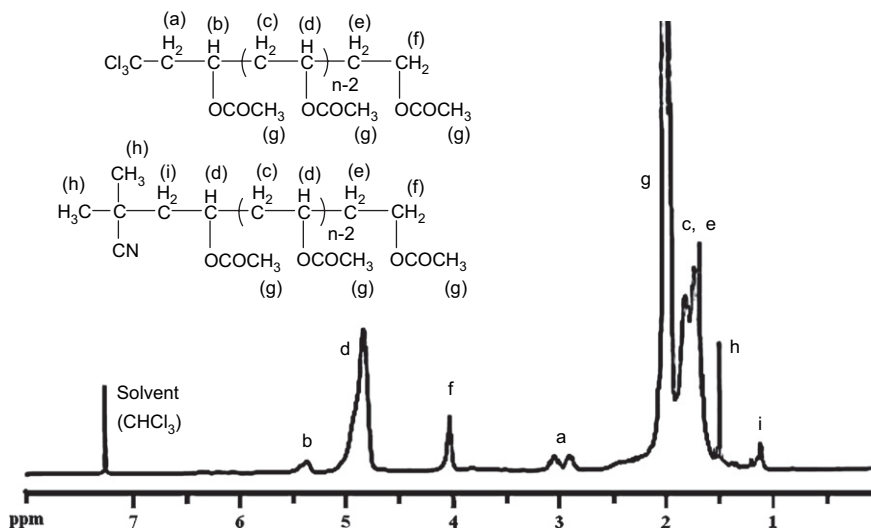
Fig. 1. ^{1}H NMR spectrum of CCl$_3$-terminated PVAc telomer at the final conversion ($X = 70.6\%$).

$\overline{M}_n$ and polydispersity index (PDI) of CCl$_3$-terminated PVAc telomer were measured by GPC. Results obtained from ^{1}H NMR and GPC analyses of telomer were presented in Section 2 (see also MS0.9(T) in Table 3). There is a good agreement between $\overline{M}_{n,NMR}$ and $\overline{M}_{n,GPC}$. It should be noted that $\overline{M}_n$ calculated from ^{1}H NMR data was used in all calculations.

CCl$_3$-terminated PVAc telomer has been used as a macro-initiator in the homopolymerization of various monomers such as St [29,32,36], MMA [30,31,34] and methyl acrylate (MA) [30,31] as well as in the copolymerization of MMA and MA [14,33,35] to synthesize PVAc-based block copolymers. In the present study, atom transfer radical homo- and copolymerization of St and MMA was performed in the presence of CCl$_3$-terminated PVAc telomer as a macroinitiator at 90 °C (Table 1). It should be noted that accurate amount of macroinitiator required for the reactions was calculated by considering the telomer percentage in the synthesized PVAc telomer. Overall mass conversion (X) as a function of time for all ATRP experiments (Table 1) is shown in Fig. 2. It should be mentioned that since the molecular weights of St (104.15 g mol^{-1}) and MMA (100.12 g mol^{-1}) are close to each other, the overall mass conversion would be almost same as the overall molar conversion (see the next section). It is clear from Fig. 2 that at the same condition, polymerization rate increases by increasing the mole fraction of MMA in the initial feed (f^0_{MMA}), which may be attributed to the higher propagation rate constant of MMA homopolymerization (k_p(MMA) = 1626 l mol^{-1} s^{-1} at 90 °C [40]) in comparison to that of St homopolymerization (k_p(St) = 900 l mol^{-1} s^{-1} at 90 °C [41]).

Generally, polymerization rate (R_p) can be expressed by the following equation:

$$R_p = -\frac{d[M]}{dt} = \overline{k}_p[R^\bullet][M] \tag{4}$$

in which $\overline{k}_p$ is the average propagation rate constant (in the case of copolymerization) and [R$^\bullet$] and [M] are the instantaneous concentrations of radical and monomer, respectively. It will be shown later in this paper that for all initial feed compositions, drift in the co-monomer mixture composition with conversion is not significant at least up to moderate conversion. Therefore, by assuming that $\overline{k}_p$ and [R$^\bullet$] are constant during the reaction, Eq. (5) can be derived by integration of Eq. (4).

$$\ln\frac{[M]_0}{[M]} = \ln\left(\frac{1}{1-x}\right) = k_p^{app}.t \quad \text{where } k_p^{app} = \overline{k}_p[R^\bullet] \tag{5}$$

in which x is the overall molar conversion, k_p^{app} is the apparent polymerization rate constant and [M]$_0$ and [M] are the initial and instantaneous monomer concentrations, respectively. Fig. 3 shows the plots of $\ln(1/(1-x))$ as a function of time. It is clear from Fig. 3 that dependence of $\ln(1/(1-x))$ on time is linear for all homo- and
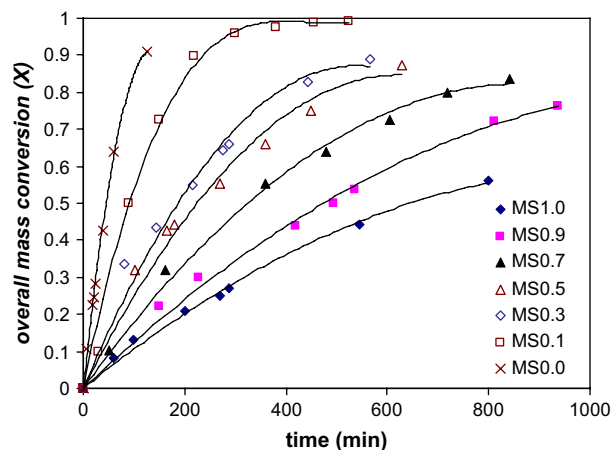
Table 3
GPC results obtained at the various conversions for the atom transfer radical copolymerization of St and MMA containing 0.9 mol fraction of St in the initial comonomer mixture (MS0.9 in Table 1)

Exp. No.	X (%)	$\overline{M}_{n,theor}$ (g mol^{-1})	$\overline{M}_{n,GPC}$ (g mol^{-1})	PDI
MS0.9(T)	0	1330[a,b]	1352[a]	1.83[a]
MS0.9(a)	29.72	10 580	12 270	1.69
MS0.9(b)	43.98	15 018	17 920	1.55
MS0.9(c)	53.81	18 078	20 960	1.49
MS0.9(d)	72.03	23 749	27 600	1.33

[a] Molecular weight and its distribution related to the CCl$_3$-terminated PVAc macroinitiator.
[b] This value has been calculated experimentally from ^{1}H NMR spectrum of the macroinitiator (see Fig. 1 and Eq. (2)).

Fig. 2. Overall mass conversion as a function of time for the atom transfer radical homo- and copolymerization of St and MMA containing various mole fractions of comonomers in the initial feed initiated with CCl$_3$-terminated PVAc macroinitiator at 90 °C (Table 1).
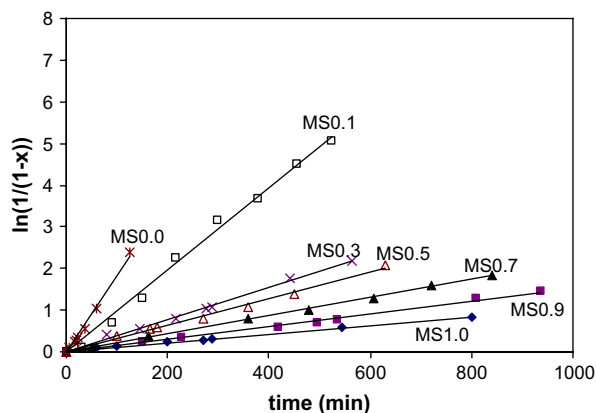
Fig. 3. $\ln(1/(1-x))$ versus time for the atom transfer radical homo- and co-polymerization of St and MMA containing various mole fractions of comonomers in the initial feed initiated with CCl_3-terminated PVAc macroinitiator (Table 1).

Fig. 4. Dependence of k_p^{app} on f_{St}^0 in the atom transfer radical homo- and co-polymerization of St and MMA initiated with CCl_3-terminated PVAc macroinitiator at 90 °C (Table 1).

copolymerization reactions, indicating that radical concentration is constant throughout the reaction and R_p is also proportional with the first order of monomer concentration. As the k_p values for the homopolymerizations of St and MMA at 90 °C have been reported in the literature to be 900 [41] and 1626 l mol^{-1} s^{-1} [40], respectively, it is possible to calculate steady state radical concentration ([R$^{\bullet}$]) for the homopolymerization reactions from the slope of the corresponding curves in Fig. 3 where the slope is equal to k_p^{app} (Eq. (5)) ($k_p^{app} = 1.928 \times 10^{-5}$ and 3.368×10^{-4} s^{-1} for St and MMA homopolymerizations, respectively). [R$^{\bullet}$] for St and MMA homopolymerizations was calculated to be 2.14×10^{-8} and 2.07×10^{-7} mol l^{-1}, respectively, indicating that radical concentration in both St and MMA homopolymerizations is low enough to minimize termination of macroradicals during the polymerization [42,43]. Consequently, reactions proceed up to high conversion as can be seen from Fig. 2.

Propagation involves the reaction of small monomer molecules and only one large radical, thus it is much less hindered during the reaction and propagation rate constant (k_p) remains almost unaffected until very high conversion. At very high conversion, the propagation reaction is assumed to be diffusion-controlled and decreases with conversion [44]. It should be mentioned that in controlled/living radical polymerization, bimolecular termination could be considered to be negligible.

However, radical concentration in the MMA homopolymerization is higher than that in the St homopolymerization, indicating that the monomer type affects ATRP equilibrium at the same condition. Similar results have been reported in the literature [42,43]. Therefore, although termination reactions in both St and MMA homopolymerizations are considered to be negligible, however, termination of some macroradicals may be occurred in the case of MMA homopolymerization. Therefore, it is expected that the PDI of PMMA formed in MMA homopolymerization will be relatively broader than that of PSt formed in the St homopolymerization [42,43] (see the next section).

k_p^{app} for all experiments were obtained directly from slope of the curves plotted in Fig. 3. Fig. 4 shows k_p^{app} versus the mole fraction of St in the initial feed (f_{St}^0). It can be seen from Fig. 4 that k_p^{app} decreases suddenly by increasing f_{St}^0 from 0 up to 0.3 and then remains almost constant with further increase in f_{St}^0. Similar trend has been observed in the literature for variations of $\bar{k}_p$ versus f_{St}^0 in the conventional free-radical copolymerization of St and MMA [45,46], indicating that average propagation rate constant in the radical copolymerization of St and MMA does not follow the terminal unit model (TUM) [15,47]. It has frequently been reported that kinetics of radical copolymerization of systems such as St and MMA can be
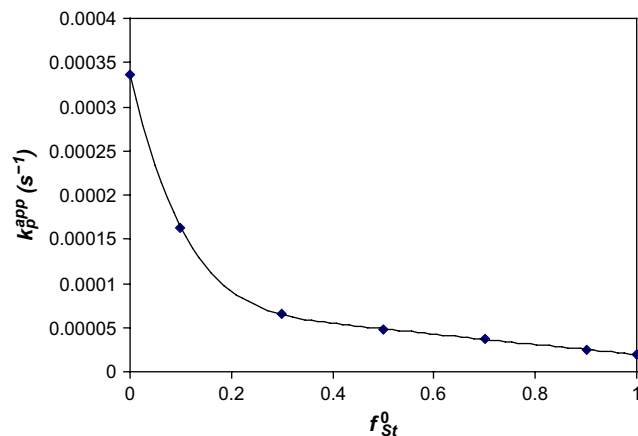
explained by the restricted (implicit) penultimate unit model (PUM) where the copolymer composition and microstructure could be explained by TUM while average propagation rate constant ($\bar{k}_p$) of copolymerization is affected by penultimate unit [45,46,48].

Table 2 shows the results obtained from GPC and ^{1}H NMR for poly(St-co-MMA) copolymers blocked with PVAc. There is a relatively good agreement between the theoretical and experimental values of $\bar{M}_n$ (Fig. 5). However, experimental $\bar{M}_n$ is relatively greater than the theoretical one. It may be attributed to the occurrence of termination of macroradicals to some extent, low macroinitiator efficiency or the calibration of GPC columns by polystyrene standards. PDI of terpolymers increases slightly by increasing the mole fraction of MMA in the initial feed probably due to the increase in the termination of macroradicals as well as increase in the average propagation rate constant. Termination of growing macroradicals is pronounced in the initial stage of ATRP reaction where concentration of Cu^{II} (see Scheme 1) is very low. Occurrence of termination of macroradicals may be reflected in the broadening of PDI of PVAc-b-P(St-co-MMA) terpolymers. Although experimental $\bar{M}_n$ is relatively greater than theoretical one, however, dependence of experimental $\bar{M}_n$ on x is linear (Fig. 5), indicating that all reactions proceed according to the controlled/living characteristic.

Samples from experiment MS0.9 at the various conversions were subjected to the GPC analysis (Table 3 and Figs. 6 and 7). It is
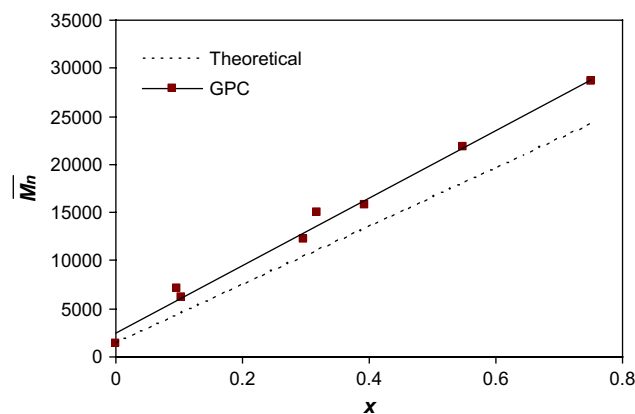

Fig. 5. Experimental and theoretical $\bar{M}_n$ (Table 3) as a function of x for PVAc-based block copolymers synthesized by atom transfer radical homo- and copolymerization of St and MMA initiated with CCl_3-terminated PVAc macroinitiator ([CCl$_3$-PVAc]$_0$:[CuCl]$_0$:[PMDETA]$_0$:([St]$_0$ + [MMA]$_0$) = 1:1:2:300 with various concentrations of styrene in the initial feed (see Table 1)).
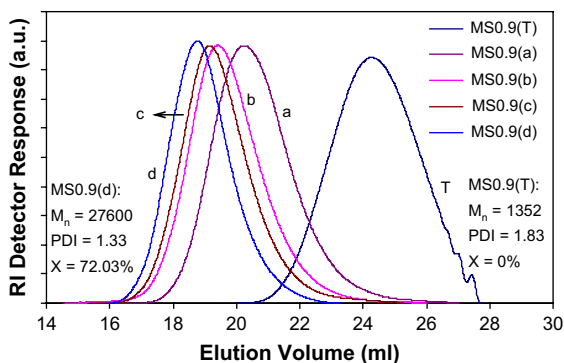
Fig. 6. GPC chromatograms of PVAc-*b*-P(St-*co*-MMA) terpolymers obtained at the various conversions for experiment MS0.9 (Table 4).

clear from Figs. 6 and 7 that, as it is expected, PDI decreases gradually from 1.83 for CCl$_3$-terminated PVAc macroinitiator at zero conversion to 1.33 for PVAc-*b*-P(St-*co*-MMA) at $X = 72.03$, which is in the expected range of PDI for the controlled/living polymerizations. However, relatively higher PDI for PVAc-*b*-PMMA block copolymer (MS0.0 in Table 2) at higher monomer conversion ($X = 76.72\%$) was observed, indicating that macroradical termination may be significant to some extent in the case of MMA homopolymerization. Results in Fig. 7 indicate again that there is a linear relationship between experimental $\overline{M}_n$ and *x*. Thus, polymerization proceeds according to the controlled/living characteristic.

3.2. Determination of the reactivity ratios of St and MMA

In conventional free-radical copolymerization, monomer 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 ^{1}H NMR. Then, copolymer composition versus initial comonomer composition is fitted with the differential copolymer composition (Mayo–Lewis) equation [15]. To obtain statistically correct estimates of the monomer reactivity ratios, non-linear least square methods should be applied.

For conventional free-radical copolymerization of St and MMA, it has been known that copolymer composition and its microstructure are well-described by the TUM [45,46,48]. Therefore, differential copolymer composition equation [15] for
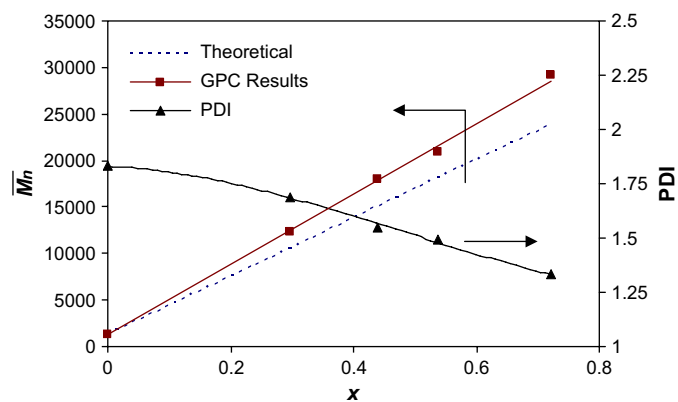

Fig. 7. Dependence of experimental $\overline{M}_n$ and PDI (Table 4) on *x* for atom transfer radical copolymerization of St and MMA containing 0.9 mol fraction of styrene in the initial feed (experiment MS0.9 in Table 1).

copolymerization of St and MMA is expressed by the following equation:

$$F_{St} = \frac{r_{St}\left(f_{St}^0\right)^2 + f_{St}^0 f_{MMA}^0}{r_{St}\left(f_{St}^0\right)^2 + 2f_{St}^0 f_{MMA}^0 + r_{MMA}\left(f_{MMA}^0\right)^2} \tag{6}$$

in which F_{St} is the instantaneous mole fraction of comonomer St in the produced copolymer and f_i^0 is the mole fraction of comonomer i in the initial reaction mixture.

Eq. (6) holds only when polymer chains are very long to exclude the influence of possible preferential addition of one of the comonomers onto the (macro)initiator-derived (macro)radical. However, in the controlled/living radical polymerizations such as ATRP, the situation is completely different. As all polymer chains are growing throughout the reaction time, it is not useful to determine copolymer composition at low conversion because the chains are too short at the low conversion to allow accurate determination of monomer reactivity ratios. As a result, moderate to high conversion experiments should be carried out in order to accurately evaluate the monomer reactivity ratios in ATRP. Hence, one has to use the integrated form of the copolymerization equation (i.e., Meyer–Lowery equation [49], see the next section) or methods in which the effect of conversion is also considered in the calculation of monomer reactivity ratios. Consequently, extended KT and MH methods are chosen in the present study to calculate the monomer reactivity ratios in such situation. Then, Meyer–Lowery equation is used to evaluate accuracy of the calculated reactivity ratios.

PVAc-*b*-P(St-*co*-MMA) terpolymers containing various mole fractions of St (or MMA) were prepared by CCl$_3$-terminated PVAc telomer initiated atom transfer radical bulk copolymerization of St and MMA with various mole fractions of comonomers in the initial reaction mixture (Table 1) at 90 °C. ^{1}H NMR spectroscopic technique was used to characterize copolymer composition at the moderate to high conversion. Fig. 8 shows ^{1}H NMR spectrum for terpolymer MS0.5 containing 0.515 mole fraction of St in the P(St-*co*-MMA) copolymer at overall mass conversion of 31.80% (Table 2). ^{1}H NMR signals were assigned to the corresponding protons [21,50].

From ^{1}H NMR spectrum, it is possible to calculate the cumulative average mole fraction of St ($\overline{F}_{St}$) and cumulative molar ratio of St to MMA ($\overline{F}_{St}/\overline{F}_{MMA}$) incorporated into the P(St-*co*-MMA) copolymer chains by Eqs. (7) and (8), respectively.

$$\overline{F}_{St} = \frac{I_{1H(St)}}{I_{1H(St)} + I_{1H(MMA)}} \tag{7}$$

$$\overline{F} = \frac{\overline{F}_{St}}{\overline{F}_{MMA}} = \frac{I_{1H(St)}}{I_{1H(MMA)}} \tag{8}$$

where

$$I_{1H(MMA)} = \{I_{0.4-3.4} - (5 \times [I_{4.7-5.0} + I_{4-4.2}]) - (0.6 \times I_{6.3-7.3})\}/8 \tag{9}$$

$$I_{1H(St)} = I_{6.3-7.3}/5 \tag{10}$$

in which $\overline{F}$ is defined as the cumulative molar ratio of St to MMA in the produced copolymer chains and $I_{1H(i)}$ is signal intensity equivalent to the one proton from comonomer i incorporated into the copolymer. The numbers 5 (5/1, in fact) and 0.6 (3/5, in fact) in Eq. (9) denote the relative numbers of VAc and St, respectively, protons appeared at the chemical shift range of 0.4–3.4 ppm (overlapped with each other as well as with the signals of all eight protons of MMA) to those appeared at the chemical shift ranges other than 0.4–3.4 ppm. The number 5 in Eq. (10) indicates the number of
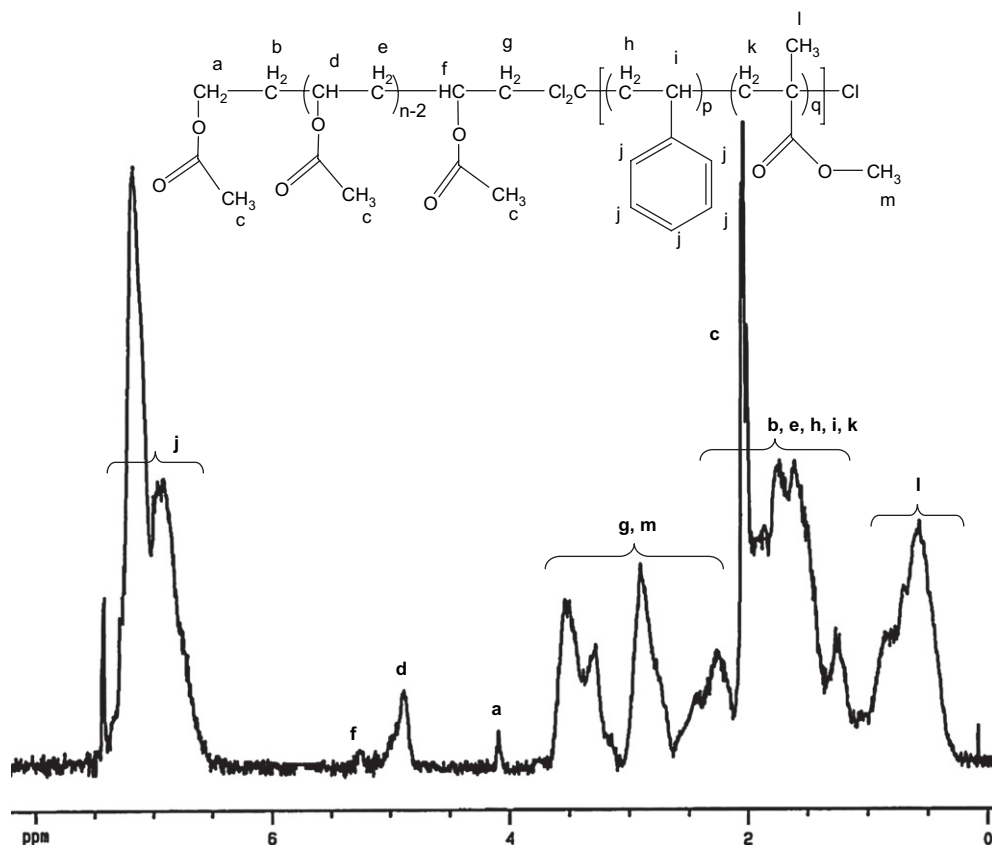
Fig. 8. Typical ^{1}H NMR spectrum of PVAc-*b*-P(St-*co*-MMA) terpolymer synthesized by atom transfer radical copolymerization of St and MMA containing 0.515 mol fraction of styrene in the P(St-*co*-MMA) copolymer (experiment MS0.5 in Table 4) at the conversion of 31.80%.

aromatic protons appeared at the chemical shift range of 6.3–7.3 ppm. Results of cumulative copolymer composition calculations are given in Table 4.

Now, overall molar conversion (x) as well as individual molar conversion of St (x_{St}) and MMA (x_{MMA}) can be calculated by known values of X (overall mass conversion), f^0 (initial molar ratio of St to MMA in the initial comonomer mixture) and $\overline{F}$ via the following equations [16]:

$$x_{MMA} = \frac{X\left(\mu + f^0\right)}{(\mu + \overline{F})} \tag{11}$$

$$x_{St} = x_{MMA}\left(\overline{F}/f^0\right) \tag{12}$$

Table 4
Data of the overall mass (X) and molar (x) conversion of comonomers, individual St (x_{St}) and MMA (x_{MMA}) conversions and mole fraction of St in the initial feed (f^0_{St}) and copolymer ($\overline{F}_{St}$) used for the calculation of reactivity ratios of St and MMA in the atom transfer radical copolymerization of St and MMA initiated with CCl$_3$-terminated PVAc macroinitiator (Table 1)

Exp. No.	X	f^0_{St}	$\overline{F}_{St}$	x_{St}	x_{MMA}	x
MS0.9	0.2972	0.90	0.8679	0.2870	0.3931	0.2976
MS0.9	0.4398	0.90	0.8792	0.4300	0.5317	0.4402
MS0.7	0.1044	0.70	0.6585	0.0984	0.1190	0.1046
MS0.7	0.3190	0.70	0.6772	0.3089	0.3436	0.3193
MS0.5	0.3180	0.50	0.5150	0.3274	0.3082	0.3178
MS0.5	0.4252	0.50	0.5254	0.4463	0.4032	0.4248
MS0.3	0.5363	0.30	0.3691	0.6580	0.4820	0.5348
MS0.3	0.6424	0.30	0.3416	0.7303	0.6032	0.6413
MS0.1	0.0979	0.10	0.1788	0.1745	0.0890	0.0976
MS0.1	0.7246	0.10	0.1277	0.9246	0.7015	0.7238

$$x = f^0_{St} \times x_{St} + f^0_{MMA} \times x_{MMA} \tag{13}$$

in which μ is the molecular weight ratio of MMA (100.12 g mol^{-1}) to St (104.15 g mol^{-1}). Results of the calculations are given in Table 4.

By data collected in Table 4, reactivity ratios of St and MMA were calculated by extended KT (see Fig. S2 in Supplementary material) and MH (see Table S3 in Supplementary material) methods to be $r_{St} = 0.605 \pm 0.058$, $r_{MMA} = 0.429 \pm 0.042$ and $r_{St} = 0.602 \pm 0.043$, $r_{MMA} = 0.430 \pm 0.032$, respectively (Table 5). It is clear from Table 5 that r_{St} and r_{MMA} obtained in the present study are different from those reported in the literature for atom transfer radical copolymerization of St and MMA. This difference may be attributed to the calculation of r_{St} and r_{St} in the previous studies by using copolymer composition measured at low conversion, which in turn can result in less reliable estimates of monomer reactivity ratios. As mentioned before, for controlled/living radical copolymerization of comonomers (St and MMA in the present study), monomer reactivity ratios obtained from moderate to high conversion experiments are more accurate than those obtained from low conversion experiments. Data collected in Table 5 also indicate that there is a relatively good agreement between the reactivity ratios calculated here for atom transfer radical copolymerization of St and MMA and those reported in the literature for conventional free-radical copolymerization of St and MMA. As a result, one can conclude that ATRP reactions proceed via a mechanism similar to the radical polymerization mechanism as shown in Scheme 1.

Simple confidence intervals for estimated reactivity ratios do not clearly convey the message of which pair of parameters is consistent with data since monomer reactivity ratios must be simultaneously determined and therefore, cannot be considered statistically independent. On the other hand, the specification of

Table 5
Summary of the reactivity ratios of St and MMA obtained in the present work along with those reported in the literature for various copolymerization systems of St and MMA

Method	Conversion	r_{St}	r_{MMA}	Reference
Bulk ATRP				
Extended KT	Moderate to high	0.605 ± 0.058	0.429 ± 0.042	This work
MH	Moderate to high	0.602 ± 0.043	0.430 ± 0.032	This work
FR	Low	0.60	0.63	[20]
Inverted FR	Low	0.70	0.72	[20]
KT	<15%	0.64 ± 0.08	0.63 ± 0.08	[21]
EVM	<15%	0.66	0.65	[21]
Bulk CFRP				
Fitting to TUM	<6%	0.523	0.460	[45]
Fitting to TUM	<1%	0.517	0.420	[48]
–	Moderate to high	0.56 ± 0.04	0.44 ± 0.04	[51]
–	–	0.585 ± 0.007	0.478 ± 0.011	[52]
–	–	0.57	0.41	[52]
–	–	0.52	0.46	[52]
KT	3–5%	0.50 ± 0.03	0.45 ± 0.3	[53]
Fitting to TUM	<3%	0.48 ± 0.03	0.42 ± 0.09	[54]

joint confidence limits, within which the correct values are believed to exist, properly conveys some idea of the goodness of the experiment and data. The smaller the experimental error and the better the experimental design, the smaller the area of uncertainty.

The 95% joint confidence limits for the reactivity ratios of St/MMA system have been shown in Fig. 9. It is clear from Fig. 9 that the area of uncertainty 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 St and MMA are required, reactivity ratios obtained by MH method will be used preferentially.

3.3. Composition drifts in the comonomer mixture and copolymer

Other important information about St/MMA copolymerization system can be obtained via plots of the comonomer mixture and copolymer compositions versus the overall monomer conversion. The instantaneous copolymer composition equation of Mayo–Lewis [15] is expressed by Eq. (6). Integration from Eq. (6) leads to the Meyer–Lowry equation [49] as follows:
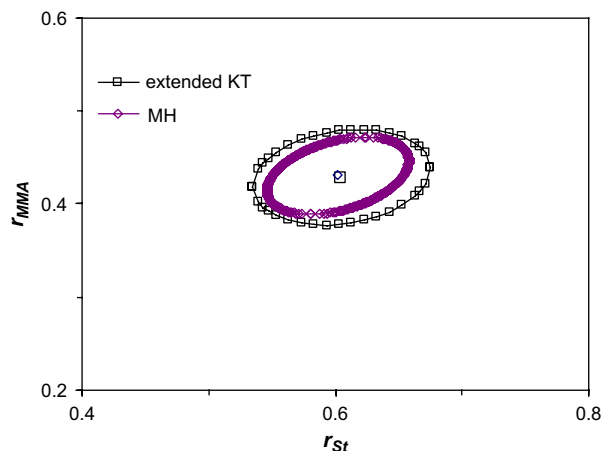
$$x = 1 - \left(\frac{f_i}{f_i^0}\right)^{\alpha} \left(\frac{1-f_i}{1-f_i^0}\right)^{\beta} \left(\frac{f_i^0 - \delta}{f_i - \delta}\right)^{\gamma} \tag{14}$$

where

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

$$\text{and } \delta = \frac{1 - r_j}{2 - r_i - r_j} \tag{15}$$

in which f_i is the instantaneous mole fraction of comonomer i in the reaction mixture, f_i^0 is f_i in the initial state. According to the Meyer–Lowry equation, the overall molar conversion (x) is related to the comonomer composition in the reaction mixture and monomer reactivity ratios. Some of these parameters are also related by a material balance in the following equation, where $\overline{F}_i$ is the cumulative average mole fraction of comonomer i (St or MMA) incorporated into the copolymer.

$$\overline{F}_i = \frac{f_i^0 - f_i(1 - x)}{x} \tag{16}$$

By using the Meyer–Lowry equation (Eq. (14)) in conjunction with Eq. (16), theoretical f_i and $\overline{F}_i$ were obtained as a function of overall monomer conversion for the various initial feed compositions, as shown in Figs. 10 and 11, respectively. Monomer reactivity ratios obtained by MH method were preferentially used in the Meyer–Lowry equation.

Fig. 10 shows changes in the theoretical (along with some experimental data) comonomer mixture composition versus the overall monomer conversion for various mole fractions of St (or MMA) in the initial reaction mixture. Fig. 10 reveals that in the various mole fractions of St in the initial feed, both comonomers polymerize at approximately the same rates to give virtually "azeotropic" random copolymers that are also living or long-lives and thus possess controlled molecular weights and narrow PDI.

It is expected that changes in the cumulative copolymer composition will be less pronounced when changes in the comonomer composition in the comonomer mixture are not considerable, as shown in Fig. 11. The theoretical values along with the some experimental data in Fig. 11 reveal that until changes in the comonomer composition are not significant, the copolymer composition drift is not considerable. In other words, when the amount of MMA (or St) in the monomer mixture reduces drastically, the copolymer composition will be changed significantly with increasing the overall monomer conversion.
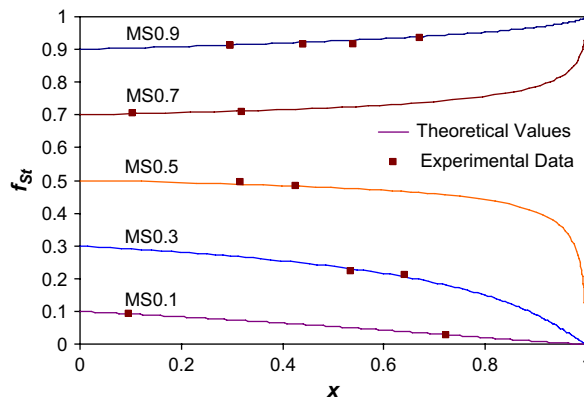

Fig. 9. Monomer reactivity ratios and 95% joint confidence limits for the reactivity ratios of St and MMA obtained in this work by extended KT and MH methods.

Fig. 10. Comonomer mixture composition as a function of the overall monomer conversion for the various mole fractions of St in the initial feed calculated by Meyer–Lowry equation (Eq. (14)) using reactivity ratios of the MH method.
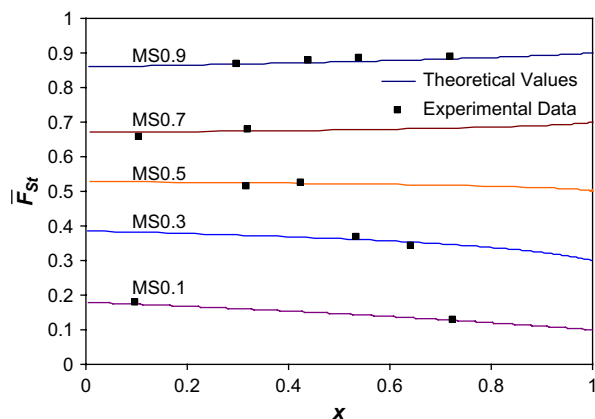
Fig. 11. Plots of the cumulative average copolymer composition versus the overall monomer conversion for the various mole fractions of St in the initial reaction mixture calculated by the Meyer–Lowry equation (Eq. (14)) in conjunction with the material balance equation (Eq. (16)) using reactivity ratios of the MH method.

The theoretical instantaneous copolymer composition curve obtained from the differential copolymer composition equation of Mayo–Lewis (Eq. (6)) by using monomer reactivity ratios of MH method is shown in Fig. 12. Copolymerization system of St/MMA shows an unstable azeotropic point with a composition of $f_{St}^0 = F_{St} = (1 - r_{MMA})/(2 - r_{St} - r_{MMA}) = 0.589$ (calculated by reactivity ratios of MH method).

The instantaneous number-average sequence length of comonomers incorporated into the copolymer chains can be related to the monomer reactivity ratios as follows [55]:

$$\overline{n}_{St} = r_{St} \frac{f_{St}}{f_{MMA}} + 1 \qquad (17)$$

$$\overline{n}_{MMA} = r_{MMA} \frac{f_{MMA}}{f_{St}} + 1 \qquad (18)$$

Instantaneous number-average sequence lengths of both comonomers incorporated into the copolymer chains as a function of overall molar conversion were calculated from Eqs. (17) and (18) by using reactivity ratios of MH method and instantaneous comonomer mixture composition (calculated from Eq. (14)). Results have been shown in Fig. 13. Under conditions of $r_i < 1$ and $r_j < 1$ as in the case of St/MMA pair comonomers, both adduct radicals incline to react with the contrary comonomers. Thus, when the radical M_j^* is formed, it inclines to reacts with comonomer i and
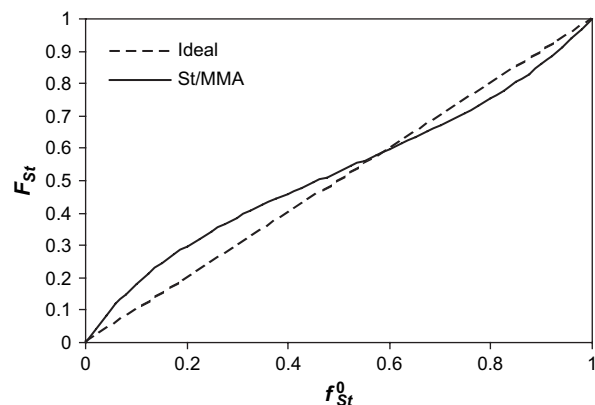

Fig. 12. Theoretical variation of the instantaneous copolymer composition (F_{St}) as a function of the mole fraction of St in the initial feed (f_{St}^0) for St/MMA copolymerization (theoretical values were calculated from the copolymer composition equation (Eq. (6)) by using reactivity ratios of MH method).
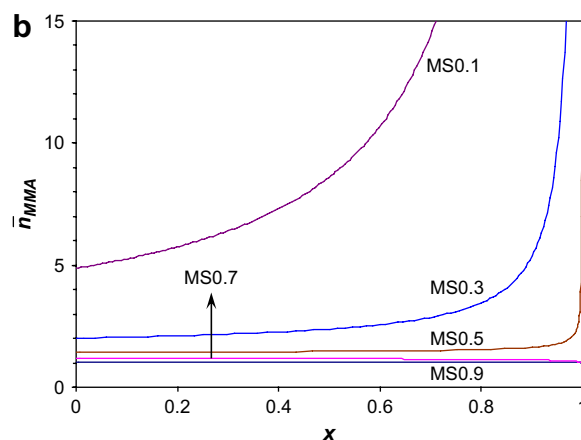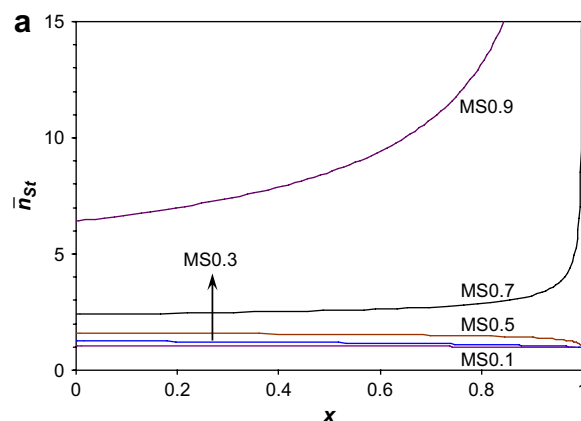

Fig. 13. Theoretical instantaneous number-average sequence length of comonomers St (a) and MMA (b) incorporated into the copolymer chains as a function of overall molar conversion calculated from Eqs. (17) and (18), respectively, by using reactivity ratios of MH method.

generates the radical M_i^*. This latter radical inclines to react with the comonomer j and generates M_j^*. In other words, both M_i and M_j tend to randomly copolymerize. It is clear from Figs. 12 and 13 that St and MMA tend to copolymerize randomly [20].

4. Conclusions

Atom transfer radical bulk copolymerization of styrene (St) and methyl methacrylate (MMA) was performed successfully in the presence of CuCl/PMDETA as a catalyst system and CCl₃-terminated PVAc telomer as a macroinitiator at 90 °C. Cumulative average copolymer composition at moderate to high conversion was determined by ¹H NMR spectroscopy and then used to calculate reactivity ratios of St and MMA by using extended KT and MH methods. It was found that to obtain more reliable reactivity ratios in the controlled/living radical polymerization systems such as ATRP, moderate to high conversion experiments should be carried out. Monomer reactivity ratios obtained in the present study were in relatively good agreement with those reported for the conventional free-radical copolymerization of St and MMA, indicating that atom transfer radical copolymerization of St and MMA proceeds via radical polymerization mechanism. The 95% joint confidence limits showed that MH method results in most precise reactivity ratios. Accuracy of the monomer reactivity ratios was further confirmed by investigating the theoretical and experimental composition drifts in the comonomer mixture and copolymer as a function of the overall monomer conversion. Instantaneous copolymer composition curve as well as the instantaneous number-average sequence length of comonomers incorporated into the copolymer

chains indicated that the St/MMA copolymerization system tends to produce a random copolymer.

Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.polymer.2008.04.059.

References

[1] Kamigato M, Ando T, Sawamoto M. Chem Rev 2001;101:3689–745.
[2] Matyjaszewski K, Xia J. Chem Rev 2001;101:2921–90.
[3] Braunecker WA, Matyjaszewski K. Prog Polym Sci 2007;32:93–146.
[4] Guillaneuf Y, Gigmes D, Marque SRA, Astolfi P, Greci L, Tordo P, et al. Macromolecules 2007;40:3108–14.
[5] Noda T, Grice AJ, Levere ME, Haddleton DM. Eur Polym J 2007;43:2321–30.
[6] Krishnan R, Srinivasan KSV. Eur Polym J 2004;40:2269–76.
[7] Vidts KRM, Dervaux B, Du Prez FE. Polymer 2006;47:6028–37.
[8] Ramakrishnan A, Dhamodharan R. Macromolecules 2003;36:1039–46.
[9] Fuente JL, Fernandez-García M, Fernandez-Sanz M, Madruga EL. Macromol Rapid Commun 2001;22:1415–21.
[10] Ydens I, Degée P, Haddleton DM, Dubois P. Eur Polym J 2005;41:2255–63.
[11] Bisht HS, Ray SS, Chatterjee AK. Eur Polym J 2003;39:1413–20.
[12] Demirelli K, Coskun M, Kaya E. J Polym Sci Part A Polym Chem 2004;42:5964–73.
[13] Demirelli K, Kaya E, Coskun M. J Appl Polym Sci 2006;99:3344–54.
[14] Semsarzadeh MA, Rostami Daronkola MR, Abdollahi M. J Macromol Sci Part A Pure Appl Chem 2007;44:953–61.
[15] Mayo FP, Lewis FM. J Am Chem Soc 1944;66:1594–601.
[16] Kelen T, Tudos F. J Macromol Sci 1981;A16:1283–97.
[17] Mao R, Huglin MB. Polymer 1993;34:1709–15.
[18] Jianying H, Jiayan C, Jiaming Z, Yihong C, Lizong D, Yousi Z. J Appl Polym Sci 2006;100:3531–5.
[19] Chambard G. Control of monomer sequence distribution: strategic approaches based on novel insights in atom transfer radical copolymerization. Ph.D. thesis, Eindhoven University of Technology; 2000.
[20] Kotani Y, Kamigaito M, Sawamoto M. Macromolecules 1998;31:5582–7.
[21] Brar AS, Puneeta. J Polym Sci Part A Polym Chem 2006;44:2076–85.
[22] Fineman M, Ross SD. J Polym Sci 1950;5:259–62.
[23] Kelen T, Tudos F. J Macromol Sci 1975;A9:1–27.
[24] Dube M, Amin Sanayei R, Penlidis A, O'Driscoll KF, Reilly PM. J Polym Sci Part A Polym Chem 1991;29:703–8.
[25] Xia J, Paik HJ, Matyjaszewski K. Macromolecules 1999;32:8310–4.
[26] Bryaskova R, Detrembleur C, Debuigne A, Jerome R. Macromolecules 2006;39:8263–8.
[27] Bryaskova R, Willet N, Debuigne A, Jerome R, Detrembleur C. J Polym Sci Part A Polym Chem 2007;45:81–9.
[28] Kaneyoshi H, Matyjaszewski K. J Polym Sci Part A Polym Chem 2007;45:447–59.
[29] Destarac M, Pees B, Boutevin B. Macromol Chem Phys 2000;201:1189–99.
[30] Semsarzadeh MA, Mirzaei A, Vasheghani-Farahani E, Nekoomanesh Haghighi M. Eur Polym J 2003;39:2193–201.
[31] Semsarzadeh MA, Mirzaei A. Iran Polym J 2003;12:67–75.
[32] Li GH, Cho CG. Colloid Polym Sci 2005;283:946–53.
[33] Semsarzadeh MA, Rostami Daronkola MR. Iran Polym J 2006;15:829–39.
[34] Li H, Zhang YM, Liu YG. J Appl Polym Sci 2006;101:1089–94.
[35] Semsarzadeh MA, Rostami Daronkola MR. Iran Polym J 2007;16:47–56.
[36] Paik HJ, Teodorescu M, Xia J, Matyjaszewski K. Macromolecules 1999;32:7023–31.
[37] Netopilik M, Kratochvil P. Polymer 2003;44:3431–6.
[38] Guillaneuf Y, Castignolles P. J Polym Sci Part A Polym Chem 2008;46:897–911.
[39] Semsarzadeh MA, Abdollahi M, Ziaee F, Nouri A. Iran Polym J 2008;17(2):141–54.
[40] Beuermann S, Buback M, Davis TP, Gilbert RG, Hutchinson RA, Olaj OF, et al. Macromol Chem Phys 1997;198:1545–60.
[41] Buback M, Gilbert RG, Hutchinson RA, Klumperman B, Kuchta FD, Manders BG, et al. Macromol Chem Phys 1995;196:3267–80.
[42] Matyjaszewski K, Patten TE, Xia J. J Am Chem Soc 1997;119:674–80.
[43] Zhu S, Yan D. J Polym Sci Part A Polym Chem 2000;38:4308–14.
[44] Achilias DS. Macromol Theory Simul 2007;16:319–47.
[45] Fukuda T, Ma YD, Inagaki H. Macromolecules 1985;18:17–26.
[46] Olaj OF, Schnoll-Bitai I, Kremminger P. Eur Polym J 1989;25:535–41.
[47] Alfery G, Goldfinger J. J Chem Phys 1944;12:205–9.
[48] Willemse RXE, van Herk AM. J Am Chem Soc 2006;128:4471–80.
[49] Meyer VE, Lowry GG. J Polym Sci Part A 1965;3:2843–51.
[50] Aerdts AM, de Haan JW, German AL. Macromolecules 1993;26:1965–71.
[51] Johnson M, Karmo TS, Smith R. Eur Polym J 1978;14:409–14.
[52] Greenly RZ. Free radical copolymerization reactivity ratios. In: Brandrup J, Immergut EH, Grulke AE, editors. Polymer handbook. 4th ed. New York: Wiley; 1999. p. II/234–5.
[53] Uebel JJ, Dinan FJ. J Polym Sci Polym Chem Ed 1983;21:2427–38.
[54] Maxwell IA, Aerdts AM, German AL. Macromolecules 1993;26:1956–64.
[55] Jaacks V. Die Makromol Chem 1972;161:161–72.