Atom Transfer Radical Homo- and Copolymerization of Styrene and Methyl Acrylate Initiated with Trichloromethyl- Terminated Poly(vinyl acetate) Macroinitiator: A Kinetic Study

Mohammad Ali Semsarzadeh, Mahdi Abdollahi

Polymer Engineering Group, Chemical Engineering Department, Faculty of Engineering,
Tarbiat Modares University, Tehran 14115-143, Iran

ABSTRACT: Atom transfer radical bulk copolymerization of styrene (St) and methyl acrylate (MA) initiated with trichloromethyl-terminated poly(vinyl acetate) macroinitiator was performed in the presence of CuCl/PMDETA as a catalyst system at 90°C. Linear dependence of $\ln[M]_0/[M]$ versus time data along with narrow polydispersity of molecular weight distribution revealed that all the homo- and copolymerization reactions proceed according to the controlled/living characteristic. To obtain more reliable monomer reactivity ratios, the cumulative average copolymer composition at moderate to high conversion was determined by ^{1}H-NMR spectroscopy. Reactivity ratios of St and MA were calculated by the extended Kelen-Tudos (KT) and Mao-Huglin (MH) methods to be $r_{St} = 1.018 \pm 0.060$, $r_{MA} = 0.177 \pm 0.025$ and $r_{St} = 1.016 \pm 0.053$, $r_{MA} = 0.179 \pm 0.023$, respectively, which are in a good agreement with those reported for the conventional free-radical copolymerization of St and MA. Good agreement between the theoretical and experimental composition drifts in the comonomer mixture and copolymer as a function of the overall monomer conversion were observed, indicating that the reactivity ratios calculated by copolymer composition at the moderate to high conversion are accurate. 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. However, MA-centered triad distribution results indicate that the spontaneous gradient copolymers can also be obtained when the mole fraction of MA in the initial comonomer mixture is high enough. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2509–2521, 2009

Key words: atom transfer radical copolymerization; styrene/methyl acrylate; poly(vinyl acetate) macroinitiator; monomer reactivity ratios; composition drifts; comonomer sequence length

INTRODUCTION

Synthesis of polymers with controlled architecture, molecular weight, and narrow molecular weight distribution by controlled/living radical polymerization (CLRP) is of interesting field in the polymer chemistry.[1–3] Among other 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]

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 minimize an extent of termination reactions. Thus, the equilibrium between halogenated polymer chain (dormant form) and growing free macroradical (active form) is the key step of ATRP, as simply described in the Scheme 1.[2]

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

Atom transfer radical copolymerization of various monomers has been performed 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
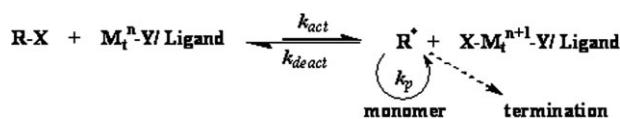
Scheme 1 Schematic illustration of ATRP mechanism.

radical copolymerization of various comonomer pairs[8–14] have been studied and the results did not show any significant difference in the monomer reactivity ratios, indicating that there are similarities between the mechanism of ATRP and conventional free-radical polymerization (Scheme 1).

Monomer reactivity ratios of styrene (St) and methyl acrylate (MA) in the conventional free-radical copolymerization have frequently been reported in the literature to be in the range of 0.73–0.9 and 0.07–0.24, respectively.[15–20] Monomer reactivity ratios in the controlled/living radical copolymerization of St and MA via nitroxide- mediated polymerization (NMP) have recently been reported.[21,22] It has been concluded by considering the calculated monomer reactivity ratios that nitroxide-mediated radical copolymerization of St and MA follows a free-radical polymerization mechanism. To our knowledge, there is no report in the literature on the atom transfer radical copolymerization of St and MA.

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.[23] Recently, controlled synthesis of poly(vinyl acetate) (PVAc) with respect to the molecular weight and its distribution as well as the chain end functionality via cobalt- mediated radical polymerization of VAc has been reported.[24] PVAc-based block copolymers are now readily obtained by combination of cobalt-mediated radical polymerization with a second type of controlled/living radical polymerization (for example, ATRP).[25,26] On the other hand, conventional free-radical polymerization techniques producing mono- or di-functional polymers can also be suitably combined with some CLRP systems to give novel block copolymers. For example, PVAc-based block copolymers have been synthesized by consecutive radical telomerization of VAc with chloroform or carbon tetrachloride and then ATRP of various monomers in the presence of trichloromethyl (CCl₃)- terminated PVAc telomer.[14,27–34] It has been found that PVAc telomer synthesized by conventional free-radical polymerization technique can be used as an effective macroinitiator in the ATRP of various monomers to prepare PVAc-based block copolymers. It has been reported that PVAc-based block copolymers can be used to prepare surfactant or membrane.[30]

Atom transfer radical homopolymerization of St[35,36] and MA[37] has been reported in the literature. However, to our knowledge, there is no report in the literature on the atom transfer radical copolymerization of St and MA. In this study, atom transfer radical homo- and copolymerization of St and MA is performed in the presence of CCl₃- terminated PVAc telomer as a macroinitiator. To obtain more reliable reactivity ratios of St and MA and compare them with those reported for the nitroxide-mediated and conventional free-radical copolymerizations, the copolymer composition at moderate to high conversion was measured by ¹H-NMR and then used to calculate monomer reactivity ratios.[14] Integrated intensities of the three observed peaks related to the oxymethyl (—OCH₃) group of MA in the ¹H-NMR spectra were used to calculate triad sequences in the copolymers. Theoretical composition drifts in the comonomer mixture and copolymer chains were also investigated by the monomer reactivity ratios calculated here. Results were compared with some experimental data to evaluate the accuracy of calculated reactivity ratios of St and MMA.

EXPERIMENTAL

Materials

Styrene (St) (Merck, >99%) and MA (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''-pentamethyldiethylenetriamine (PMDETA) (Merck, 99.8%) as a ligand and tetrahydrofuran (THF) as a solvent were used as received. CCl₃- terminated poly(vinyl acetate) telomer with 91.2% end functionality (i.e., telomer percentage), number-average molecular weight of 1370 g mol⁻¹ (calculated from ¹H-NMR, $\overline{M}_{n,GPC} = 1380$ g mol⁻¹) and polydispersity index of the molecular weight distribution of 1.85 (measured by gel permeation chromatography [GPC]) (see[14] for more details) was prepared by radical telomerization of VAc monomer in the presence of chloroform at 60°C for 5 h[14,27–29] and used as a macroinitiator in the atom transfer radical homo- and copolymerization of St and MA (Table I). Initial concentration of VAc in the reaction mixture was 2.42 M and the molar ratio of reaction ingredients [VAc]₀/[CHCl₃]₀/[AIBN]₀ was 1/4/0.01. Conversion of the reaction was 71.3% 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

Atom Transfer Radical Homo- and Copolymerization Recipes of St and MA Initiated with CCl3- Terminated PVAc Macroinitiator[a]

Exp. No.	$[St]_0$ (mol l^{-1})	$f_{St}^0 (f_{MA}^0)$
MS1.0[b]	8.59	1.0 (0.0)
MS0.9	7.90	0.9 (0.1)
MS0.7	6.43	0.7 (0.3)
MS0.5	4.81	0.5 (0.5)
MS0.3	3.03	0.3 (0.7)
MS0.1	1.06	0.1 (0.9)
MS0.0	0 (10.92)[c]	0.0 (1.0)

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

decompose traces of the unreacted AIBN initiator.[27–29] Finally, THF was evaporated at room temperature, and the polymer was dried under vacuum at 50°C up to a constant weight.

Atom transfer radical homo- and copolymerization of St and MA initiated with CCl3- terminated PVAc macroinitiator

A required amount of CuCl was introduced to glass tubes equipped with a magnetic stirrer (Table I). The glass tubes were sealed with a rubber septum and were cycled between vacuum and nitrogen three times. Mixtures containing required amounts of St, MA, macroinitiator (CCl3- terminated PVAc telomer) and ligand (PMDETA) (Table I) were degassed by purging nitrogen for 20 min and then added to the glass tubes. The molar ratio of reaction ingredients $[St + MA]_0/[PMDETA]_0/[CuCl]_0/[PVAc-CCl_3]_0$ was kept constant for all experiments (300/2/1/1) (Table I). 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°C ± 0.1°C). The tubes were removed from the oil bath at the various time intervals, and reaction mixture was diluted with 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 (Table III in the next section).

Characterization

Overall mass conversion of comonomers (X) was calculated gravimetrically. Poly(vinyl acetate)-block-poly(St-co-MA) 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 (D1) (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[38]) molecular weight and polydispersity of the terpolymers dissolved in THF was determined by a Waters 150C GPC equipped with a 10^4, 10^3, and 500 Å set of Ultrastyragel columns and a refractive index 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 (Figure S1 in Supporting Information). Equation of the polystyrene calibration curve has been given in the Supporting Information (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 at 35°C. It should also be mentioned that as the solubility of PVAc macroinitiator and PMA is almost comparable with that of polystyrene (see Mark- Houwink coefficients of THF solution of VAc, St and MA in Table S2 of Supporting Information), it is expected that there are no significant difference between apparent and true values of molecular weight and polydispersity.[39] Moreover, it has been reported in a previous study on the St/MA copolymers that hydrodynamic volume is independent of copolymer composition.[40]

RESULTS AND DISCUSSION

Atom transfer radical homo- and copolymerization of St and MA initiated with CCl3- terminated PVAc macroinitiator

CCl3- terminated PVAc telomer has been used as a macroinitiator in the homopolymerization of various
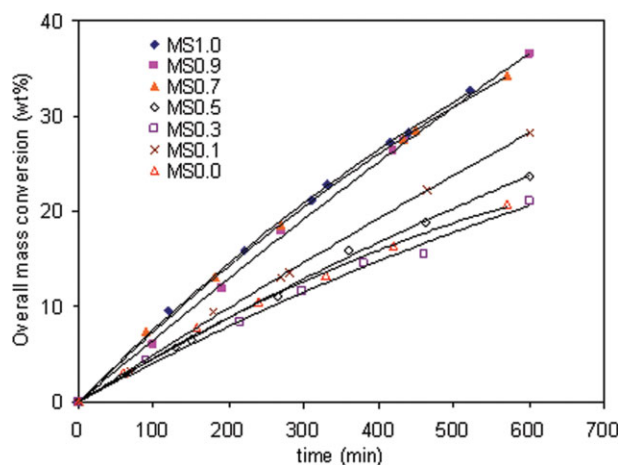
Figure 1 Overall mass conversion as a function of time for the atom transfer radical homo- and copolymerization of St and MA containing various mole fractions of comonomers in the initial feed initiated with CCl_3- terminated PVAc macroinitiator at 90°C (Table I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

monomers such as St,[27,30,34] MMA[28,29,32] and MA[28,29] as well as in the copolymerization of MMA/MA[13,31,33] and St/MMA[14] to synthesize PVAc-based block copolymers. In this study, atom transfer radical homo- and copolymerization of St and MA was performed in the presence of CCl_3- terminated PVAc telomer as a macroinitiator at 90°C (Table I). 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 I) is shown in Figure 1. It should be mentioned that since the molecular weights of St (104.15 g mol^{-1}) and MA (86.09 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 Figure 1 that at the same condition, polymerization rate decreases by increasing the mole fraction of MA in the initial feed (f_{MA}^0) from zero up to 0.7 and then increases for the reaction mixture containing 0.9 mole fraction of MA in the initial feed. Finally, polymerization rate decreases again in the case of MA homopolymerization (f_{MA}^0 =1.0). Therefore, there is no specific trend for the effect of initial comonomer composition on the polymerization rate, which will be discussed in detail in the next section.

Generally, polymerization rate (R_p) can be expressed by eq. (1).

$$R_p = -\frac{d[M]}{dt} = \bar{k}_p[R^\bullet][M] \quad (1)$$

in which $\bar{k}_p$ is the average propagation rate constant (in the case of copolymerization) and $[R^\bullet]$ and $[M]$

are the instantaneous concentration of radical and monomer respectively. It will be shown later in this article that for all initial feed compositions, drift in the comonomer mixture composition with conversion is not significant at least up to moderate conversion. Therefore, by assuming that $\bar{k}_p$ and $[R^\bullet]$ are constant during the reaction, eq. (2) can be derived by integration from eq. (1).

$$\ln\frac{[M]_0}{[M]} = \ln\left(\frac{1}{1-x}\right) = k_p^{app}.t \quad \text{where } k_p^{app} = \bar{k}_p[R^\bullet] \quad (2)$$

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 concentration, respectively. Figure 2 shows the plots of $\ln(1/(1-x))$ as a function of time. It is clear from Figure 2 that dependence of $\ln(1/(1-x))$ on time is linear for all homo- and 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 MA and St at 90°C have been reported in the literature to be 56,000[41] and 900 l mol^{-1} s^{-1}[42], respectively, it is possible to calculate steady state radical concentration ($[R^\bullet]$) for the homopolymerization reactions from the slope of the corresponding curves in Figure 2 where slope is equal to k_p^{app} [eq. (2)] (k_p^{app} = 1.276×10^{-5} and 7.069×10^{-6} s^{-1} for St and MA homopolymerizations respectively). $[R^\bullet]$ for St and MA homopolymerizations was calculated to be 1.42×10^{-8} and 1.26×10^{-10} mol l^{-1} respectively, indicating that radical concentration in both St and MA homopolymerizations are low enough to minimize termination of macroradicals during the
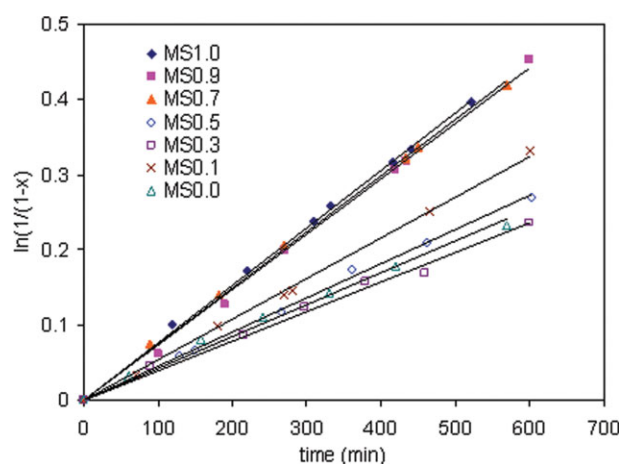

Figure 2 $\ln(1/(1-x))$ as a function of time for the atom transfer radical homo- and copolymerization of St and MA containing various mole fractions of comonomers in the initial feed initiated with CCl_3- terminated PVAc macroinitiator (Table I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
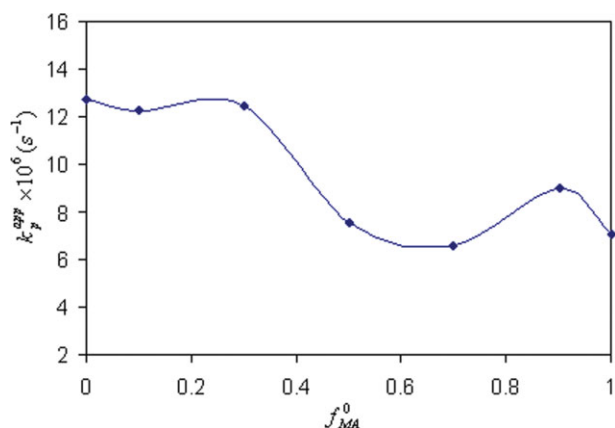
Figure 3 Dependence of k_p^{app} on f_{MA}^0 in the atom transfer radical homo- and copolymerization of St and MA initiated with CCl₃- terminated PVAc macroinitiator at 90°C (Table I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymerization. Consequently, reactions can proceed up to high conversion. However, radical concentration in the St homopolymerization is higher than that in the MA homopolymerization, indicating that the monomer type affects ATRP equilibrium at the same condition. The similar results have been reported in the literature for the homopolymerizations of St and MA at the same condition.[35–37]

k_p^{app} for all experiments were obtained directly from slope of the curves plotted in Figure 2. Figure 3 shows k_p^{app} versus the mole fraction of MA in the initial feed (f_{MA}^0). Apparently, there is no general trend for variation of k_p^{app} as a function of f_{MA}^0. Hence, to better understanding the effect of initial feed composition on k_p^{app} value, it is necessary to individually evaluate the $\bar{k}_p$ and $[R^\bullet]$ [see eq. (2)]. It has been reported that kinetics of radical copolymerization of St and MA 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 of copolymerization ($\bar{k}_{p,\mathrm{cop}}$) is affected by the penultimate unit.[43] It should also be mentioned that controlled/living (nitroxide-mediated) radical copolymerization of St and MA has been reported to follow the free-radical polymerization mechanism.[21,22] Therefore, $\bar{k}_{p,\mathrm{cop}}$ value for radical copolymerization of the St/MA can be calculated by the known values of radical and monomer reactivity ratios via the implicit penultimate unit model [eq. (3)].

$$\bar{k}_{p,\mathrm{cop}} = \frac{r_i f_i^2 + 2 f_i f_j + r_j f_j^2}{\frac{r_i f_i}{k_{ii}} + \frac{r_j f_j}{k_{jj}}} \quad (3)$$

TABLE II
$\bar{k}_{p,\mathrm{cop}}$ and $[R^\bullet]$ Values Estimated for the Atom Transfer Radical Homo- and Copolymerization of St and Ma Initiated with CCl₃- Terminated PVAc Macroinitiator

Exp. No.	$f_{\mathrm{St}}^0 (f_{\mathrm{MA}}^0)$	$\bar{k}_{p,\mathrm{cop}}$ (l mol⁻¹ s⁻¹)	$[R^\bullet]$ (mol l⁻¹)
MS1.0	1.0 (0.0)	900	1.42×10^{-8}
MS0.9	0.9 (0.1)	980	1.25×10^{-8}
MS0.7	0.7 (0.3)	1148	1.08×10^{-8}
MS0.5	0.5 (0.5)	1343	5.64×10^{-9}
MS0.3	0.3 (0.7)	1625	4.04×10^{-9}
MS0.1	0.1 (0.9)	2555	3.53×10^{-9}
MS0.0	0.0 (1.0)	56,000	1.26×10^{-10}

$$\bar{k}_{ii} = \frac{k_{iii}(r_i f_i + f_j)}{r_i f_i + (f_j / s_i)} \quad (4)$$

where f_i is the mole fraction of monomer i in the feed, r_i and s_i are the reactivity ratio of monomer and radical i, respectively.[7] k_{iii} is identified with the propagation rate constant in the homopolymerization of the pure monomer i. $\bar{k}_{p,\mathrm{cop}}$ values for the radical copolymerization St and MA were estimated from eq. (3) by using the monomer reactivity ratios of St and MA obtained in this study ($r_{\mathrm{St}} = 1.016$ and $r_{\mathrm{MA}} = 0.179$ by Mao-Huglin method, see the next section) in conjunction with the reported values of radical reactivity ratios ($S_{\mathrm{St}} = 0.94$ and $S_{\mathrm{MA}} = 0.11$) for the free-radical copolymerization of St and MA at 60°C[43] and propagation rate constants of St (900 l mol⁻¹ s⁻¹ at 90°C[42]) and MA (56,000 l mol⁻¹ s⁻¹ at 90°C[41]) homopolymerizations. Then, $[R^\bullet]$ was calculated from eq. (2) by known values of k_p^{app} and $\bar{k}_{p,\mathrm{cop}}$ of all the homo- and copolymerization reactions of St and MA (Table II).

Figure 4 shows variations in $\bar{k}_{p,\mathrm{cop}}$ and $[R^\bullet]$ values with f_{MA}^0. It is clear from Figure 4 that $[R^\bullet]$ decreases gradually by increasing k_{MA}^0 from 0 to 0.5 and then remains almost constant up to $f_{\mathrm{MA}}^0 = 0.9$, followed by
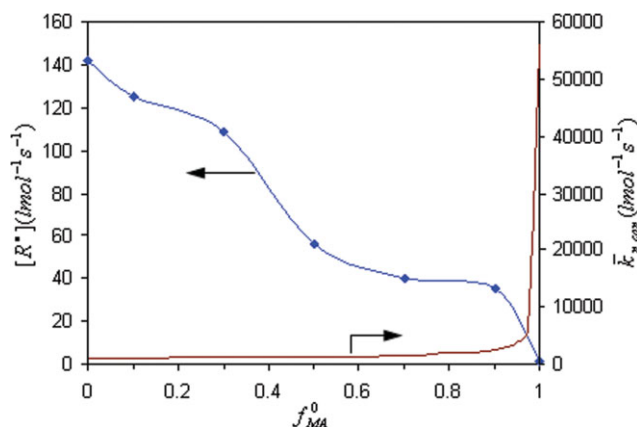

Figure 4 Dependence of $\bar{k}_{p,\mathrm{cop}}$ and $[R^\bullet]$ on f_{MA}^0 in the atom transfer radical homo- and copolymerization of St and MA initiated with CCl₃- terminated PVAc macroinitiator at 90°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rapidly decrease in $[R^\bullet]$ by increasing f^0_{MA} from 0.9 to 1.0. Generally, $[R^\bullet]$ decreases by increasing the f^0_{MA}, indicating that the equilibrium constant between the halogenated polymer chain (dormant form) and growing free-(macro)radical (active form) in the ATRP reaction is affected by the monomer type. At the same condition, the equilibrium constant between the active and dormant species in the ATRP of MA has been reported to be much smaller than that in the ATRP of styrene.[37] Consequently, decrease in $[R^\bullet]$ by increasing the f^0_{MA} and thereby observed trend of k^{app}_p versus f^0_{MA} seems to be reasonable.

Relatively high concentration of growing (macro)-radical ($[R^\bullet]$) in the range of $f^0_{MA} = 0.0 - 0.9$ (i.e., until styrene comonomer exists in the initial reaction mixture) may be attributed to the ability of styrene monomer to generate styrene ended-growing (macro)radicals. In the absence of styrene (i.e., $f^0_{MA} = 1.0$), $[R^\bullet]$ decreases suddenly due to the smaller equilibrium constant between active and dormant species, which in turn results in the lower concentration of active species (i.e., methyl acrylate ended-growing macroradicals.[37]

Table III shows the results obtained from GPC and ^{1}H-NMR for poly(St-co-MA) copolymers blocked with PVAc. There is a good agreement between the theoretical and experimental values of $\overline{M}_n$ (Table III). Decreased PDI of terpolymers (Table III) in comparison with the PDI of CCl$_3$-PVAc macroinitiator (1.85) as well as the linear dependence of experimental $\overline{M}_n$ on x (Fig. 5) indicates that all reactions proceed according to the controlled/living characteristic.

Figure 5 Experimental $\overline{M}_n$ (Tables III and IV) as a function of conversion for PVA- based block copolymers synthesized by atom transfer radical homo- and copolymerization of St and MA initiated with of CCl$_3$- terminated PVAc macroinitiator ([CC13-PVAc]$_0$: [CuCl]$_0$: [PMDETA]$_0$: ([St]$_0$ + [MA]$_0$) = 1 : 1 : 2 : 300 with various concentration of styrene in the initial feed (Table I)). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Samples from experiment MS0.9 at the various conversions were subjected to the GPC analysis (Table IV and Figures 6 and 7). It is clear from Figures 6 and 7 that, as it is expected, PDI decreases gradually from 1.85 for CCl$_3$- terminated PVAc macroinitiator at zero conversion to 1.37 for PVAc-b-P(St-co-MA) at $X = 36.40\%$, which is in the expected range of PDI for the controlled/living polymerizations. Results in Figure 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.

Determination of the reactivity ratios of St and MA

In conventional free-radical copolymerization, monomer reactivity ratios are generally determined by performing experiments at low conversion where composition drift in the comonomer mixture can be

TABLE III
Data Obtained for the Atom Transfer Radical Homo- and Copolymerization of St and MA Initiate with CCl$_3$- Terminated PVAc Macroinitiator at 90°C (Table I)

Exp. No.	X (%)[a]	$\overline{M}_{n,\text{theor}}$ [b] (g mol^{-1})	$\overline{M}_{n,\text{GPC}}$ (g mol^{-1})	PDI
MS1.0	32.71 (32.15)[c]	11,590	11,359	1.41
MS0.9	36.40	12,545	11,608	1.37
MS0.7	28.59	9838	10,139	1.37
MS0.5	18.85	6748	6676	1.33
MS0.3	21.03	7143	6875	1.33
MS0.1	28.23	8815	8696	1.27
MS0.0	20.72 (20.52)[c]	6723	7232	1.34

[a] Overall mass conversion was obtained gravimetrically.
[b] $\overline{M}_{n,\text{theor}} = \sum \left[\left(\frac{[M_i]_0}{[CCl_3 - PVAc]_0} \right) \times x_i \times M_{n,M_i} \right] + \overline{M}_{n,\text{macroinitiator}}$ in which $\overline{M}_{n,\text{macroinitiator}}$ is the number-average molecular weight of CCl$_3$- terminated PVAc telomer ($M^{\text{Telomer}}_{n,\text{NMR}} = 1370$ 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 V) and molecular weight of comonomer i respectively.
[c] Values given inside the parenthesis were obtained from ^{1}H-NMR spectrum of the reaction mixture containing both unreacted monomer and produced polymer.
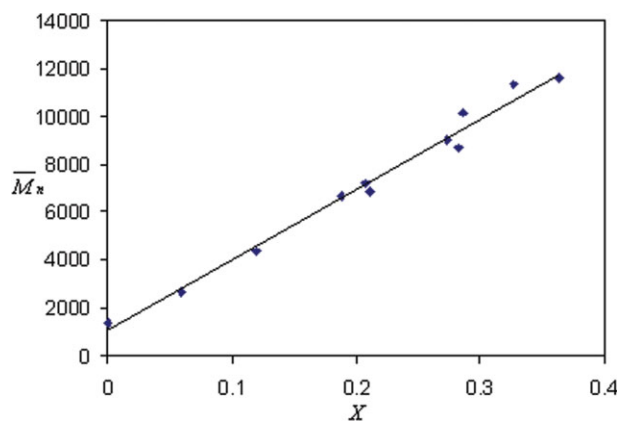
TABLE IV
GPC Results Obtained at the Various Conversions for the Atom Transfer Radical Copolymerization of St and MA Containing 0.9 Mole Fraction of St in the Initial Comonomer Mixture (MS0.9 in Table I)

Exp. No.	X (%)	$\overline{M}_{n,\text{GPC}}$ (g mol^{-1})	PDI
MS0.9(T)	0	1380[a]	1.85[a]
MS0.9(a)	5.96	2674	1.64
MS0.9(b)	11.91	4342	1.59
MS0.9(c)	27.30	9033	1.46
MS0.9(d)	36.40	11,600	1.37

[a] Molecular weight and its distribution related to the CCl$_3$- terminated PVAc macroinitiator were obtained by GPC analysis.
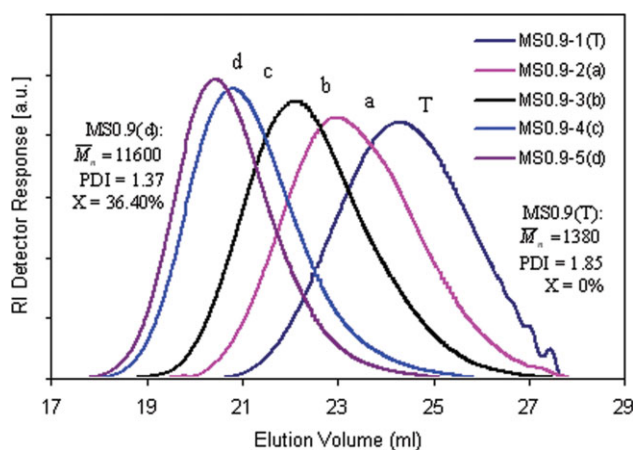
Figure 6 GPC chromatograms of PVAc-b-P(St-*co*-MA) terpolymers obtained at the various conversions for experiment MS0.9 (Table V). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

considered to be negligible. The average chemical composition of the resulting copolymer is analyzed by various methods such as ¹H-NMR. Then, copolymer composition versus initial comonomer composition is fitted with the differential copolymer composition (Mayo- Lewis) equation.[44]

For conventional free-radical copolymerization of St and MA, it has been known that copolymer composition and its microstructure is well-described by the TUM.[15–19,43] Therefore, differential copolymer composition equation[44] for copolymerization of St and MA is expressed by eq. (5).

$$F_{St} = \frac{r_{St}\left(f_{St}^0\right)^2 + f_{St}^0 f_{MA}^0}{r_{St}\left(f_{St}^0\right)^2 + 2f_{St}^0 f_{MA}^0 + r_{MA}\left(f_{MA}^0\right)^2} \quad (5)$$

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.

Equation (5) 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 to accurately evaluate the monomer reactivity ratios in ATRP.[14] Hence, one has to use the integrated form of the copolymerization equation (i.e., Meyer-Lowery equation,[45] 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 this study to calculate the monomer reactivity ratios in such situation. Then, Meyer-Lowery equation is used to evaluate accuracy of the calculated reactivity ratios as well as to investigate composition drift in the comonomer mixture with conversion.

¹H-NMR spectroscopy technique was used to characterize composition of P(St-*co*-MA) copolymers blocked with PVAc at the moderate to high conversion. Figure 8 shows ¹H-NMR spectra for PVAc-b-P(St-*co*-MA) terpolymers containing various mole
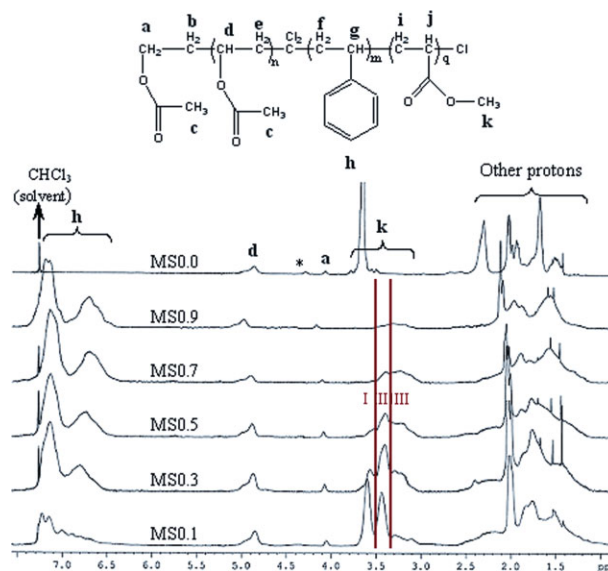
Figure 8 ¹H-NMR spectra of PVAc-b-P(St-*co*-MA) terpolymers containing various mole fractions of styrene in the P(St-*co*-MA) copolymers at the corresponding conversions (Table III) synthesized by atom transfer radical copolymerization of St and MA initiated with CCl₃- terminated PVAc macroinitiator. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
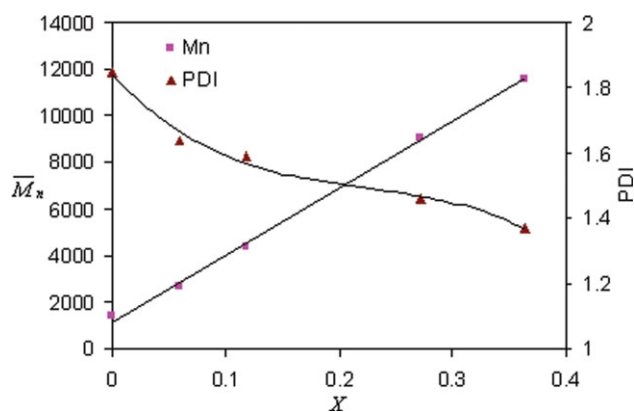

Figure 7 Dependence of experimental $\overline{M}_n$ and PDI (Table V) on X for atom transfer radical copolymerization of St and MA containing 0.9 mole fraction of styrene in the initial feed (experiment MS0.9 in Table I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Exp. No.	X	f_{St}^0	$\overline{F}_{St}$	x_{St}	x_{MA}	x
MS0.9	0.1794	0.90	0.9070	0.1806	0.1667	0.1792
MS0.9	0.3640	0.90	0.9105	0.3676	0.3251	0.3633
MS0.7	0.2859	0.70	0.7614	0.3075	0.2248	0.2827
MS0.7	0.1307	0.70	0.7506	0.1389	0.1076	0.1295
MS0.5	0.1593	0.50	0.6149	0.1917	0.1201	0.1559
MS0.5	0.1885	0.50	0.6129	0.2262	0.1428	0.1845
MS0.3	0.1549	0.30	0.4986	0.2477	0.1068	0.1490
MS0.3	0.2103	0.30	0.4794	0.3246	0.1510	0.2031
MS0.1	0.1352	0.10	0.2815	0.3669	0.1041	0.1304
MS0.1	0.2823	0.10	0.2486	0.6812	0.2287	0.2740

fractions of St in the P(St-*co*-MA) copolymers at the corresponding overall mass conversion (Table III). ^{1}H-NMR signals were assigned to the corresponding protons.[16,21] It should be mentioned that a weak peak appeared at the chemical shift of about 4.3 ppm corresponds to the j or g protons present at the ω-end of terpolymer chains (i.e., >CH—Cl), indicating the livingness of the terpolymer chains.

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 MA ($\overline{F}_{St}/\overline{F}_{MA}$) incorporated into the P(St-*co*-MA) copolymer chains by eqs. (6) and (7) respectively.

$$\overline{F}_{St} = \frac{3I_h}{3I_h + 5I_k} \quad (6)$$

$$\overline{F} = \frac{\overline{F}_{St}}{\overline{F}_{MA}} = \frac{3I_h}{5I_k} \quad (7)$$

in which $\overline{F}$ is defined as the cumulative molar ratio of St to MA in the produced copolymer chains. I_h and I_k indicate the peak areas of the aromatic (from St) and methoxy (from MA) protons resonance, respectively. Results of the cumulative copolymer composition calculations are given in Table V.

Now, the overall molar conversion (x) as well as the individual molar conversion of St (x_{St}) and MA (x_{MA}) can be calculated by known values of X (overall mass conversion), f^0 (initial molar ratio of St to MA in the initial comonomer mixture) and $\overline{f}$ via the following equations[14]:

$$x_{MA} = \frac{X(\mu + f^0)}{(\mu + \overline{F})} \quad (8)$$

$$x_{St} = x_{MA}(\overline{F}/f^0) \quad (9)$$

$$x = f_{St}^0 \times x_{St} + f_{MA}^0 \times x_{MA} \quad (10)$$

in which μ is the molecular weight ratio of MA (86.09 g mol^{-1}) to St (104.15 g mol^{-1}). Results of the calculations are given in Table V.

By data collected in Table V, reactivity ratios of St and MA were calculated by extended KT (Fig. S2 in Supporting Information) and MH (Table S3 in Supporting Information) methods to be r_{St} = 1.018 ± 0.060, r_{MA} = 0.177 ± 0.025 and r_{St} = 1.016 ± 0.053, r_{MA} = 0.179 ± 0.023, respectively (Table VI). It is clear from Table VI that r_{St} and r_{MA} obtained in this study are in a relatively good agreement with those

TABLE VI
Summary of the Reactivity Ratios of St and Ma Obtained in This Work Along with those Reported in the Literature for Various copolymerization systems of St and MA

| Method	Conversion	r_{St}	r_{MA}	Reference
Bulk ATRP				
Extended KT	Moderate to high	1.018 ± 0.060	0.177 ± 0.025	This work
MH	Moderate to high	1.016 ± 0.053	0.179 ± 0.023	This work
Bulk NMP				
Finemann-Ross	<30%	0.89	0.22	21
Extended KT	<30%	0.89	0.22	21
Extended KT	<30%	1.32	0.14	22
CFRP				
KT	<10% (bulk)	0.84 ± 0.08	0.21 ± 0.05	15
Tidwell-Mortimer	<10% (bulk)	0.84	0.21	15
KT	<15% (solution)	0.73 ± 0.05	0.19 ± 0.05	16
–	–	0.75	0.18	17,18
–	–	0.825	0.238	19
–	–	0.82	0.24	20
–	–	0.722	0.168	20
–	–	0.9	0.07	20
–	–	0.871 ± 0.022	0.148 ± 0.026	20
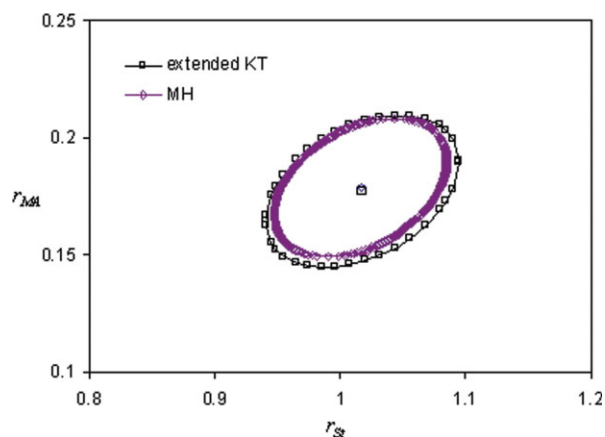
Figure 9 Monomer reactivity ratios and 95% joint confidence limits for the reactivity ratios of St and MA obtained in this work by extended KT and MH methods. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

reported in the literature for nitroxide-mediated radical copolymerization of St and MA. Data collected in Table VI also indicate that there is a relatively good agreement between the reactivity ratios calculated here for atom transfer radical copolymerization of St and MA and those reported in the literature for conventional free-radical copolymerization of St and MA. As a result, one can conclude that ATRP reactions proceed via a mechanism similar to the radical polymerization mechanism as shown in Scheme 1. However, there is a small but important difference between the r_{St} calculated for ATRP in this study and that reported for both conventional free-radical and nitroxide-mediated radical copolymerizations, which may be attributed to the different reaction conditions.

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

Composition drifts in the comonomer mixture and copolymer

The instantaneous copolymer composition equation of Mayo-Lewis[44] is expressed by eq. (5). Integration from eq. (5) leads to the Meyer-Lowry equation[45] as follows:

$$x = 1 - \left(\frac{f_i}{f_i^0}\right)^\alpha \left(\frac{1-f_i}{1-f_i^0}\right)^\beta \left(\frac{f_i^0 - \delta}{f_i - \delta}\right)^\gamma \quad (11)$$

where

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

$$\delta = \frac{1 - r_j}{2 - r_i - r_j} \quad (12)$$

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 $\bar{F}_i$ is the cumulative average mole fraction of comonomer i (St or MA) incorporated into the copolymer.

$$\bar{F}_i = \frac{f_i^0 - f_i(1 - x)}{x} \quad (13)$$

By using the Meyer-Lowry equation [eq. (11)] in conjunction with eq. (13), theoretical f_i and $\bar{F}_i$ were obtained as a function of overall monomer conversion for the various initial feed compositions, as shown in Figures 10 and 11 respectively. Monomer reactivity ratios obtained by MH method was preferentially used in the Meyer-Lowry equation.

Figure 10 shows changes in the theoretical (along with the some experimental data) comonomer mixture composition versus the overall monomer conversion for various mole fractions of St (or MA) in the initial reaction mixture. Figure 10 reveals that in the various mole fractions of St in the initial feed, the incorporation of St comonomer into the copolymer chain is more favor than that of MA comonomer. Moreover, this difference in the rate of incorporation of comonomers into the copolymer
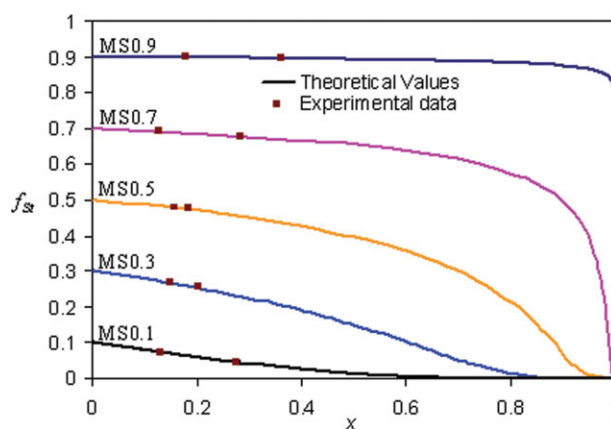

Figure 10 Comonomer mixture composition as a function of the overall monomer conversion for the various mole fractions of St in the initial feed calculated by Meyer-Lowry equation [eq. (11)] using reactivity ratios of the MH method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
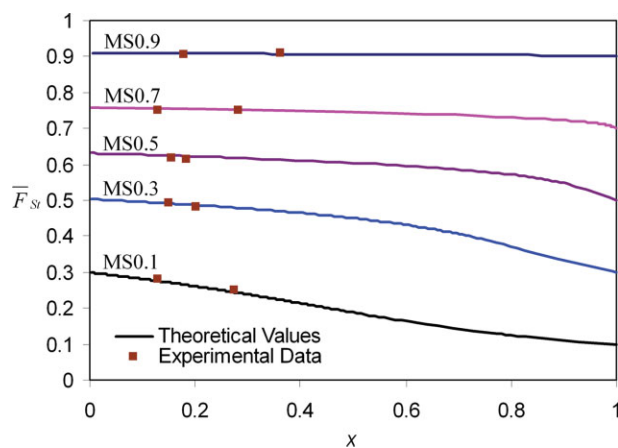
Figure 11 Plots of the cumulative average copolymer composition versus the overall monomer conversion for the various mole fractions of St in the initial reaction mixture calculated by the Meyer-Lowry equation [eq. (11)] in conjunction with the material balance equation [eq. (13)] using reactivity ratios of the MH method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

chain increases by decreasing the mole fraction of St in the initial feed, indicating that P(St-co-MA) copolymer chain formed during the ATRP reaction will be intramolecularly heterogeneous.

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

The theoretical instantaneous copolymer composition curve obtained from the differential copolymer composition equation of Mayo-Lewis [eq. (5)] by using monomer reactivity ratios of MH method is shown in Figure 12. Copolymerization system of St/MA shows no azeotropic point.

The instantaneous number-average sequence length of comonomers incorporated into the copolymer chains can be related to the monomer reactivity ratios as follow[14]:

$$\bar{n}_{St} = r_{St}\frac{f_{St}}{f_{MA}} + 1 \tag{14}$$

$$\bar{n}_{MA} = r_{MA}\frac{f_{MA}}{f_{St}} + 1 \tag{15}$$

Instantaneous number-average sequence lengths of both comonomers incorporated into the copoly-

mer chains as a function of overall molar conversion were calculated from eqs. (14) and (15) by using reactivity ratios of MH method and instantaneous comonomer mixture composition (calculated from eq. (11)). Results have been shown in Figure 13. Under conditions of $r_i > 1$ and $r_j < 1$ as be in the case of St/MA pair comonomers, both adduct radicals incline to react with the comonomer i (St in the present case). Thus, when the radical M_i^* is formed, it inclines to reacts with comonomer i and generates the radical M_i^*. This later radical inclines to react with the comonomer i and generates again M_i^*. In other words, at low conversion, mole fraction of more reactive comonomer i (St in this study) in the copolymer will be higher than that in the comonomer mixture (Figs. 10 and 11 as well as Fig. 12). Thus, it is expected that at low conversion, number-average sequence length of comonomer i incorporated into the copolymer chain will be significantly higher than that of comonomer j (Fig. 13). By progress of the reaction, mole fraction of the more reactive comonomer i in the comonomer mixture and thereby in the copolymer chain decreases. As all copolymer chains are growing throughout the reaction time of the controlled/living radical copolymerizations such as ATRP, copolymer formed under such condition will therefore be a random copolymer with intramolecularly heterogeneous chain and without azeotropic point.

To further investigating the microstructure of synthesized copolymers and its dependence on the initial comonomer mixture compositions and conversion, it would be useful to evaluate the triad distribution of comonomers. The ^{1}H-NMR spectra of the copolymers P(St-co-MA) blocked with PVAc synthesized with various mole fractions of comonomers
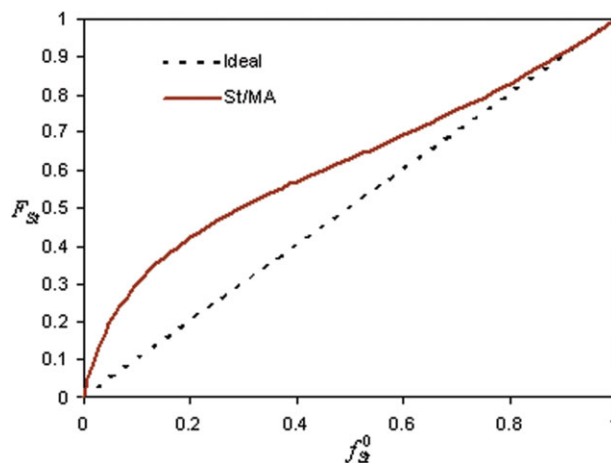

Figure 12 Theoretical variation of the instantaneous copolymer composition (F_{St}) as a function of the mole fraction of St in the initial feed (f_{St}^0) for St/MA copolymerization (theoretical values were calculated from the copolymer composition equation [eq. (5)] by using reactivity ratios of MH method). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
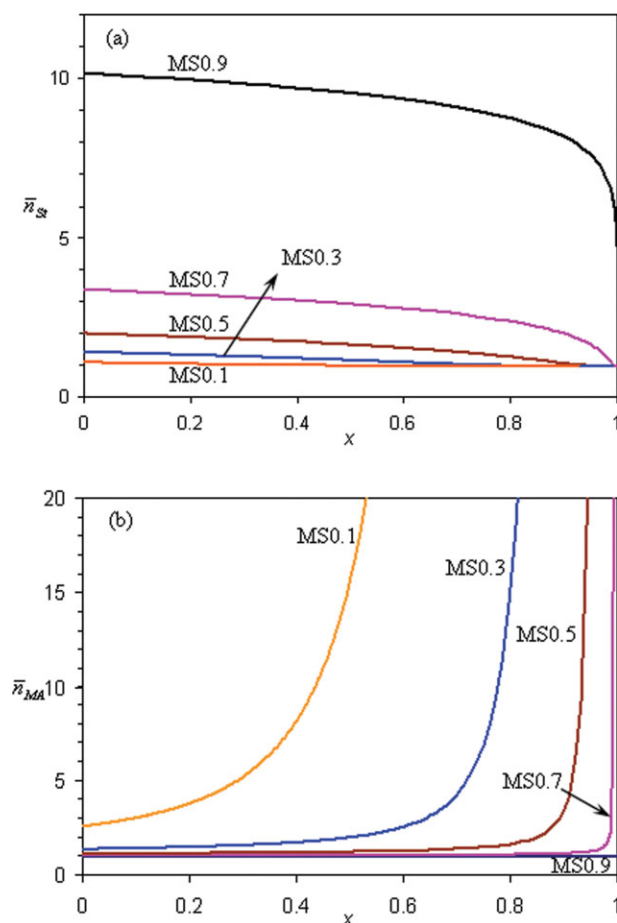
Figure 13 Theoretical instantaneous number-average sequence length of comonomers St (a) and MA (b) incorporated into the copolymer chains as a function of overall molar conversion calculated from eqs. (14) and (15), respectively, by using reactivity ratios of MH method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in the initial comonomer mixture are compared in Figure 8. It is clear from Figure 8 that the evolution of peaks of the aromatic and methoxy protons is related to the copolymer composition, distribution of the comonomer units and polymer tacticity. Broad signal appeared at the chemical shift range of about 3.0–3.7 ppm is due to the methoxy protons of methyl acrylate units.[16] The methoxy region can be subdivided into the three subregion I (3.5–3.7 ppm), II (3.3–3.5 ppm) and III (3.0–3.3 ppm), which can respectively be assigned to the MA-centered triads of MA/MA/MA (MMM for simplicity) (homopolymer), MA/MA/St (MMS for simplicity) (random) and St/MA/St (SMS for simplicity) (alternating). Intensity of peak I increases significantly by increasing the mole fraction of MA in the initial feed (Fig. 8). Moreover, three distinct peaks I, II and III in the range of 3.0–3.7 ppm can be observed only for the copolymer prepared at the high mole fraction of MA in the initial feed (i.e., MS0.1 with $f^0_{MA} = 0.9$). For other copolymers,

methoxy region peaks overlapped with each other and also overlapping of peaks increases by decreasing the mole fraction of MA in the initial feed.

The probability distribution for the diad of the comonomer sequence can be calculated from the reactivity ratio of comonomers according to the Ito and Yamashita method developed for styrene-methyl methacrylate (St/MMA) copolymers.[46] This method can be used to determine the ratio of three comonomer (MA or St)-centered triads as previously described for St/MA comonomer pair.[16,21] The instantaneous MA-centered triad distribution can be calculated by eqs. (16)–(18).

$$F_{MMM} = (P_{MM})^2 \qquad (16)$$

$$F_{MMS} = 2P_{MM}(1 - P_{MM}) \qquad (17)$$

$$F_{SMS} = (1 - P_{MM})^2 \qquad (18)$$

$$\text{where } P_{MM} = \frac{(r_{MA}/f)}{1 + (r_{MA}/f)} \qquad (19)$$

In which F represents the number fraction of triads normalized to unity and P_{MM} is the probability of a growing chain having an MA-type chain end to add comonomer MA. It is clear from eq. (19) that all these instantaneous triad fractions can be predicted by using the instantaneous comonomer mixture composition ($f = [St]/[MA]$) and reactivity ratio values.

To obtain the cumulative triad distribution which varies with conversion, it is necessary to integrate F_{MMM}, F_{MMS} and F_{SMS} between x_0 and any conversion x ($x > x_0$). Then, theoretical cumulative triad distribution ($\overline{F}_{MMM}$, $\overline{F}_{MMS}$, and $\overline{F}_{SMS}$) can directly be compared with experimental one obtained from ¹H-NMR results. The theoretical values of $\overline{F}_{MMM}$, $\overline{F}_{MMS}$, and $\overline{F}_{SMS}$ along with some experimental ones are shown in Figure 14 for the comonomer mixture containing $f^0_{MA} = 0.9$ (MS0.1). There is a good agreement between the theoretical and experimental values. It should be mentioned that in a more complete and detailed work, it is necessary to consider not only the composition of triad but also the tacticity of triad. However, since agreement between the theoretical and experimental values of cumulative triad distribution is good, it is expected that Figure 14 can reflect the evolution of the composition from one end to the other end of the growing chain during the progress of atom transfer radical copolymerization of St and MA.

As mentioned in the previous section, cumulative copolymer composition measured at moderate to high conversion was used to calculate more reliable reactivity ratios of St and MA. Therefore, experimental values of $\overline{F}_I$, $\overline{F}_{II}$, and $\overline{F}_{III}$ corresponding to the
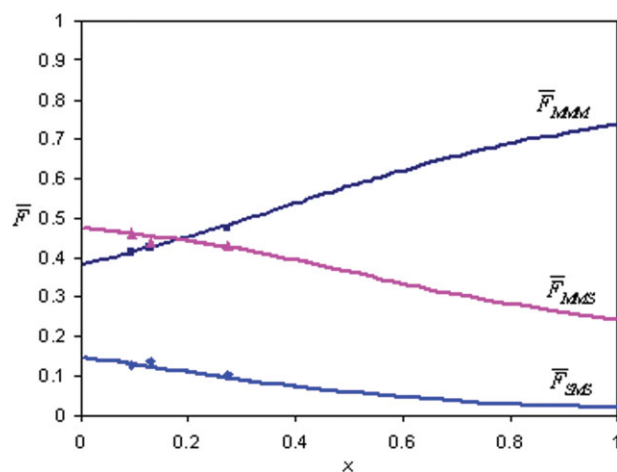
Figure 14 Theoretical (solid lines) and experimental (points) values of $\overline{F}_{MMM}$ (■), $\overline{F}_{MMS}$ (▲) and $\overline{F}_{SMS}$ (◆) as a function of conversion for the comonomer mixture containing $f^0_{MA} = 0.9$ (MS0.1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fractions of three subregions *I*, *II*, and *III* of the methoxy region (Fig. 8) are in fact cumulative ones. Hence, it is not possible to estimate the value of coisotactic parameter (σ), which is necessary parameter for complete and detailed investigation of the experimental triad distribution via the following equations introduced by Ito and Yamashita.[46]

$$F_I = F_{MMM} + (1 - \sigma)F_{MMS} + (1 - \sigma)^2 F_{SMS} \quad (20)$$

$$F_{II} = \sigma F_{MMS} + 2\sigma(1 - \sigma)F_{SMS} \quad (21)$$

$$F_{III} = \sigma^2 F_{SMS} \quad (22)$$

in which F_I, F_{II} and F_{III} represent the fractions of the areas *I*, *II* and *III* of the methoxy resonance of the copolymer at low conversion.

Moreover, a coisotacticity degree close to unity (σ = 0.9) has been reported for the free-radical solution copolymerization of St and MA via the well-known Ito and Yamashita assignment.[16,46] Results of the reactivity ratios of St and MA obtained in this study with those reported for the conventional free-radical copolymerization of St and MA (Table VI) indicate that the microstructure (triad distribution and tacticity parameter, σ) of St/MA copolymers obtained by conventional free-radical and atom transfer radical copolymerizations are almost the same. Consequently, on may assume σ ≈ 1 for the atom transfer radical copolymerization of St and MA. Then, eqs. (20)–(22) are simplified to the following equations.

$$F_I = F_{MMM}, F_{II} = F_{MMS} \text{ and } F_{III} = F_{SMS} \quad (23)$$

Results in Figure 14 indicate that eq. (23) may be used to predict the experimental values of cumula-

tive triad distribution ($\overline{F}_{MMM}$, $\overline{F}_{MMS}$, and $\overline{F}_{SMS}$) by experimental values of $\overline{F}_I$, $\overline{F}_{II}$ and $\overline{F}_{III}$ in this study. In other words, σ in this system seems to be close to unity.

Theoretical changes in the cumulative MA-centered triad distribution as a function of conversion were evaluated for various mole fractions of St (or equivalently MA) in the initial feed (Fig. 14 as well as Fig. S3 in Supporting Information). It was observed that for $f^0_{St} = 0.9$ (MS0.9), $f^0_{St} = 0.7$ (MS0.7) and $f^0_{St} = 0.5$ (MS0.5), the proportion of random triad MMS ($\overline{F}_{MMS}$) is much lower than that of alternating triad SMS ($\overline{F}_{SMS}$). The proportion of homopolymer triad MMM ($\overline{F}_{MMM}$) is also negligible. This behavior indicates that in the low mole fraction of MA in the initial feed, the MA-centered triad in the synthesized copolymer has a high tendency to alternate.

The predominant structure for $f^0_{St} = 0.1$ (MS0.1) is the homopolymer triad MMM ($\overline{F}_{MMM}$), which also further increases with conversion, indicating that the MA-centered triad in the synthesized copolymer has a tendency to homopolymerize. Moreover, drift in the cumulative triad distribution is more pronounced when the mole fraction of MA in the initial comonomer mixture is high enough (MS0.3 and more especially MS0.1). For copolymerization systems MS0.3 and more especially MS0.1, significant drift in the cumulative triad distribution with conversion is also expected from changes in the instantaneous number-average sequence length of MA incorporated into the copolymer ($\overline{n}_{MA}$) with conversion [Fig. 13(b)]. Such behavior in the living/controlled radical copolymerizations (ATRP in this study) results in the generation of "spontaneous gradient copolymers" in the growing macromolecular chains with the progress of the classical batch copolymerization. The spontaneous gradient in the chain prepared by living/controlled radical batch copolymerization is obtained through the variation of comonomer mixture composition with conversion [see eq. (11)] due to the large difference between the monomer reactivity ratios as well as to the large difference between the mole fraction of comonomers in the initial feed with very low fraction of more reactive comonomer (St in this study) in the initial comonomer mixture (MS0.1 in this study).

On the other hand, random St/MA copolymers can be obtained by lowering the mole fraction of MA in the initial feed. Consequently, depending on the mole fraction of MA in the initial feed, random or gradient copolymers can be obtained by atom transfer radical batch copolymerization of St and MA. The similar results have been have been reported for the nitroxide-mediated batch copolymerization of St and MA.[21]

CONCLUSIONS

Atom transfer radical bulk copolymerization of styrene (St) and MA was performed successfully in the presence of CuCl/PMDETA as a catalyst system and CCl$_3$- terminated PVAc telomer as a macroinitiator at 90°C. Conversion versus time data and GPC results confirmed the controlled/living characteristic of all the reactions. Cumulative average copolymer composition at moderate to high conversion was determined by ^{1}H-NMR spectroscopy and then used to calculate more reliable reactivity ratios of St and MA by using extended KT and MH methods. Monomer reactivity ratios obtained in this study were in a relatively good agreement with those reported for the conventional free-radical and nitroxide-mediated radical copolymerizations of St and MA, indicating that atom transfer radical copolymerization of St and MA proceed via radical polymerization mechanism. 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 showed that the atom transfer radical copolymerization of St/MA system tends to produce a random copolymer. However, MA-centered triad distribution results indicate that the spontaneous gradient copolymers (rich in St in the low to medium conversion, followed by rich in MA in the medium to high conversion) can also be obtained when the mole fraction of MA in the initial comonomer mixture is high enough.

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