A New General Approach to Determine More Accurate Comonomer Reactivity Ratios in Controlled/Living Radical Copolymerization Systems

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ABSTRACT: In controlled/living radical copolymerization (atom transfer radical copolymerization in this study) and in any other living chain-growth copolymerization, the possible preferential addition of one of the comonomers onto the (macro)initiator-derived (macro)radical can affect the copolymer composition, especially at low conversion; this results in inaccurate comonomer reactivity ratio estimation by the classic approach. A new general approach is introduced in this article, which allowed us to exclude the influence of the possible preferential addition of one of the comonomers onto the (macro)initiator-derived (macro)-radical on the copolymer composition at any conversion. According to this approach, copolymer chain grown during time t ($t \neq 0$) is considered to be, in fact, the macroinitiator terminated with one of the comonomers under study, which will further grow during the time interval $\Delta t' = t' - t$ [where any reaction time t' is considered to be grater than reaction time t, i.e. $t' > t$] from a comonomer mixture with composition of $f(t)$ [where $f(t)$ is the molar ratio of comonomer i to comonomer j in the comonomer mixture] at time t. In such a situation, it is possible to obtain individual comonomer conversions [$x_i(\Delta t')$ and $x_j(\Delta t')$], the overall comonomer conversion [$x_{ov}(\Delta t')$], and the cumulative average copolymer composition for the copolymer formed during $\Delta t'$, from which more accurate comonomer reactivity ratios can be calculated by the various low- or high-conversion methods, depending on the overall comonomer conversion. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1341–1349, 2011

Key words: atom transfer radical polymerization (ATRP); copolymerization; kinetics (polym.); polymer synthesis and characterization

INTRODUCTION

Comonomer reactivity ratios are important parameters for the prediction of copolymer composition, and hence, the microstructure, polymerization rate, and ultimately, the molecular weight distribution in the case of copolymerization systems. This information, in conjunction with an appropriate model, can help in determining the reaction conditions to produce a desired product. When one is attempting to predict the product quality and production rates of multicomponent polymers, the accuracy of the monomer reactivity ratios has a significant impact on the model prediction. Poor predictions of the model can often be mistakenly attributed to a poor model when the cause is, in fact, inaccuracy in the comonomer reactivity ratios.

In conventional free-radical copolymerizations, the comonomer reactivity ratios are generally determined 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, the copolymer composition versus the initial comonomer composition is fitted with the differential copolymer composition equation.[1] To obtain statistically correct estimates of the reactivity ratios, nonlinear least square methods should be applied.

For conventional free-radical copolymerizations, such as the copolymerization of styrene (St) and methyl acrylate (MA), in which the copolymer composition and its microstructure is described by the terminal unit model,[2–5] the differential copolymer composition (Mayo–Lewis) equation is expressed as follows:[1]

$$F_i = \frac{r_i\left(f_i^0\right)^2 + f_i^0 f_j^0}{r_i\left(f_i^0\right)^2 + 2f_i^0 f_j^0 + r_j\left(f_j^0\right)^2} \tag{1}$$

where, r_i and r_j indicate reactivity ratios of comonomers i and j respectively. F_i is the instantaneous

molar fraction of comonomer i (St in this study) in the produced copolymer and f_i^0 and f_j^0 are the molar fraction of comonomers i and j (St and MA, respectively, in this study) in the initial comonomer mixture.

Equation (1) works only when copolymer chains are very long, to exclude the influence of the possible preferential addition of one of the comonomers onto the (macro)initiator-derived (macro)radical. However, in controlled/living radical copolymerizations, such as atom transfer radical polymerization (ATRP), the situation is completely different. As all copolymer chains are growing throughout the reaction time, it is not useful to determine the copolymer composition at low conversion because the chains are too short at the low conversion to allow accurate determination of the comonomer reactivity ratios because of the significant effect of the preferential addition of one of the comonomers onto the (macro)-initiator-derived (macro)radical on the copolymer composition. As a result, moderate to high conversion experiments should be carried out to accurately evaluate the comonomer reactivity ratios in ATRP.[6] Hence, one has to use the integrated form of the copolymerization equation (i.e., Meyer–Lowery equation[7]) or methods in which the effect of conversion is also considered in the calculation of comonomer reactivity ratios [e.g., extended Kelen–Tudos (KT)[8] and Mao–Huglin (MH)[9] methods].

In this work, a new approach is introduced for the first time to calculate more accurate comonomer reactivity ratios in controlled/living radical copolymerizations and in any other living chain-growth copolymerization system with the modified cumulative average copolymer composition [$\overline{F}(\Delta t')$] at either low or high conversion. According to this approach, the copolymer composition at least at two different overall molar conversions [$x_{ov}(t)$ and $x_{ov}(t')$ in which $t' > t$ and $t \neq 0$, where t is the time] for any initial comonomer mixture composition is determined. The copolymer chain grown during time t is considered to be, in fact, the macroinitiator terminated with one of the comonomers under study, which will further grow during the time interval $\Delta t' = t' - t$ from a comonomer mixture with a composition of $f(t)$ [where $f(t)$ is the molar ratio of comonomer i to comonomer j in the comonomer mixture] at time t. Thus, accurate $\overline{F}(\Delta t')$ and the individual [$x_i(\Delta t')$ and $x_j(\Delta t')$] and overall [$x_{ov}(\Delta t')$] comonomer conversions for the copolymer produced during $\Delta t'$ can be calculated at either low or high conversion by consideration of this fact that the initial comonomer mixture composition for the copolymer formed during this $\Delta t'$ is the composition of the comonomer mixture at time t [i.e. $f(t)$]. In such conditions, the influence of the possible preferential addition of one of the comonomers onto the (macro)initiator-derived (macro)-

radical on the copolymer composition is actually excluded.

These accurate data of copolymer composition can then be used to calculate more accurate comonomer reactivity ratios in any living chain-growth copolymerization, such as ATRP. $\Delta t'$ can be selected to be either short or long enough; thus, it is possible to calculate a more accurate comonomer reactivity by different low or high, respectively, conversion methods, such as the Finemann–Ross (FR),[10] KT,[11] extended KT,[8] Joshi–Joshi (JJ),[12] MH,[9] Tidwell–Mortimer (TM),[13] and error-in-variable[14] methods. It should be noted that this approach is also applicable to any living chain-growth copolymerization at any conversion range, either low or high.

In a previous work,[6] it was found that the copolymer composition at high conversion must be used to calculate accurate comonomer reactivity ratios in the controlled/living radical copolymerization of St and MA. However, the viscosity of the reaction medium can affect the reactivity of the comonomers and, hence, the comonomer reactivity ratios. This approach allows us to calculate an accurate copolymer composition at low conversion where there is no viscosity problem. On the other hand, the new approach introduced in this work can be used in any chain-growth copolymerization system to evaluate the possible conversion dependence of the comonomer reactivity ratios.

EXPERIMENTAL

Materials

St (Merck, >99%, Tehran, Iran) 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 *in vacuo*. N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA; Merck, 99.8%) as a ligand and tetrahydrofuran (THF) as a solvent were used as received. CCl$_3$-terminated poly(vinyl acetate) (PVAc) macroinitiator with 91.2% end functionality, a number-average molecular weight of 1370 g/mol (as calculated from ^{1}H-NMR), and a polydispersity index of the molecular weight distribution of 1.85 (as measured by gel permeation chromatography) was synthesized by the same procedure reported previously[6] via the radical telomerization of the vinyl acetate monomer in the presence of chloroform as a telogen.[15]

Atom transfer radical copolymerization (ATRCP) of St and MA

A required amount of CuCl was introduced into glass tubes equipped with a magnetic stirrer (Table I). The

TABLE I
Recipes for the ATRCP of St and MA Initiated with the CCl$_3$-Terminated PVAc Macroinitiator[a]

Experiment	[St]$_0$ (mol/L)	f_{St}^0 [b]
MS0.9[c]	7.90	0.90
MS0.7	6.43	0.70
MS0.5	4.81	0.50
MS0.3	3.03	0.30
MS0.1	1.06	0.10

[a] [CCl$_3$–PVAc]$_0$/[CuCl]$_0$/[PMDETA]$_0$/([St]$_0$+[MA]$_0$) = 1 : 1 : 2 : 300. Polymerization was carried out at 90 $\pm$ 0.1°C.
[b] f_{St}^0 = [St]$_0$/([St]$_0$ + [MA]$_0$).
[c] The number given in all the symbols indicates f_{St}^0.

glass tubes were sealed with rubber septums and were cycled between vacuum and nitrogen three times. Mixtures containing required amounts of St, MA, macroinitiator (CCl$_3$-terminated PVAc telomer), and ligand (PMDETA, Table I) were degassed by purging nitrogen for 20 min and then added via syringe to the glass tubes. The molar ratio of the 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 the comonomers was only variable in the experiments. A freeze–pump–thaw cycle was carried out three times to completely remove oxygen from the glass tubes. The glass tubes were sealed *in vacuo* and then immersed in a preheated oil bath at a desired temperature (i.e., 90 $\pm$ 0.1°C). The tubes (or a fraction of reaction mixture) were removed from the oil bath at the various $\Delta t''$s, and the reaction mixture was diluted with THF, filtered, and dried *in vacuo* at 40°C to a constant weight; 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 *in vacuo* at 40°C up to a constant weight and used in ^{1}H-NMR analysis.

Characterization

Overall mass conversion of the comonomers (X_{ov}) was calculated gravimetrically. PVAc-*block*-poly(St-*co*-MA) terpolymers were dissolved in CDCl$_3$ and characterized by 400-MHz ^{1}H-NMR spectroscopy (DRX 400 Bruker Avance) at ambient temperature.

Instrumentation

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 (25 s) and pulse angle (30°) allowed for a complete relaxation of the protons of both St and MA, which has been verified by determination of the longitudinal relaxation time.[6] The acquisition time was about 2 s. Under these conditions, the sum of the acquisition time and relaxation delay was at least five times greater than the longitudinal relaxation time, which was necessary for the best quantitative results. The polymer concentration in the CDCl$_3$ solution was about 2%.

RESULTS AND DISCUSSION

PVAc-*b*-poly(styrene-*co*-methyl acrylate) [P(St-*co*-MA)] terpolymers containing various molar fractions of St (or MA) were prepared by CCl$_3$-terminated PVAc telomer initiated ATRCP of St and MA with various

TABLE II
Copolymerization Data Obtained from Gravimetric and ^{1}H-NMR Analyses (Recorded at Two Different Reaction Times) for the ATRCP of St and MA Containing Various Initial Comonomer Mixture Compositions Initiated by the CCl$_3$-Terminated PVAc Macroinitiator at 90°C

Experiment	f^0	$X_{ov}(t)$ $X_{ov}(t')$	$\overline{F}(t)$ $\overline{F}(t')$	$x_{St}(t)$ $x_{St}(t')$	$x_{MA}(t)$ $x_{MA}(t')$	$x_{ov}(t)$ $x_{ov}(t')$	$f(t)$
MS0.9	9.0000[a]	0.060[a]	12.270[a]	0.061[a]	0.045[a]	0.059[a]	8.8468
		0.179	9.748	0.181	0.167	0.179	
MS0.7	2.3333[a]	0.113[a]	3.347[a]	0.123[a]	0.086[a]	0.112[a]	2.2385
		0.131	3.264	0.141	0.101	0.129	
MS0.5	1.0000[a]	0.065[a]	1.638[a]	0.079[a]	0.048[a]	0.064[a]	0.9676
		0.159	1.597	0.192	0.120	0.156	
MS0.3	0.4286[a]	0.074[a]	1.068[a]	0.123[a]	0.049[a]	0.071[a]	0.3954
		0.155	0.994	0.248	0.107	0.149	
MS0.1	0.1111[a]	0.032[a]	0.454[a]	0.097[a]	0.024[a]	0.031[a]	0.1028
		0.135	0.392	0.367	0.104	0.130	

$\overline{F}(t)$ and $\overline{F}(t')$ indicate cumulative average molar ratio of St to MA incorporated into the P(St-*co*-MA) copolymer chains at time t and ($t' > t$) respectively.
$x_{St}(t)$ and $x_{St}(t')$ indicate individual molar conversion of St at time t and t' respectively.
$x_{MA}(t)$ and $x_{MA}(t')$ indicate individual molar conversion of MA at time t and t' respectively.
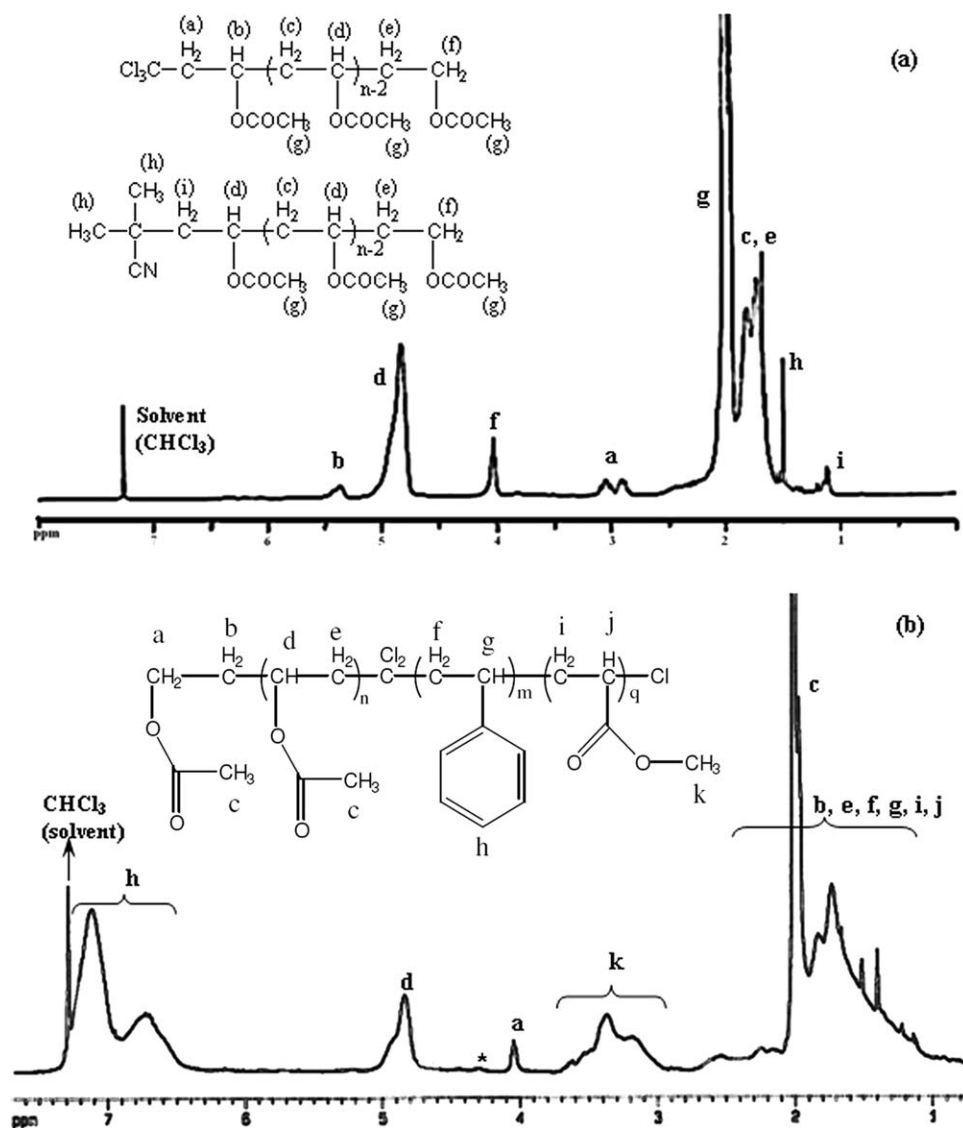[a] These data were used to calculate the reactivity ratios of St and MA at low conversion by the classic approach.

Figure 1 Typical ^{1}H-NMR spectra of (a) the CCl$_3$-terminated PVAc macroinitiator and (b) the PVAc-b-P(St-co-MA) terpolymer with a 0.621 molar fraction of St ($\overline{F}$ = 1.638) in the P(St-co-MA) copolymer (experiment MS0.5 in Table II) at the overall comonomer (molar) conversion of 6.37%.

molar fractions of comonomers in the initial reaction mixture (Table I) at 90°C. The ^{1}H-NMR spectroscopy technique was used to obtain the copolymer composition (Table II). Figure 1 shows the typical ^{1}H-NMR spectra for the CCl$_3$-terminated PVAc macroinitiator and terpolymer containing a 0.6209 molar fraction of St in the P(St-co-MA) copolymer [MS0.5 in Table II, where the number after "MS" indicates the molar fraction of St in the initial feed (f_{St}^0)] at an overall molar conversion of 6.37%. ^{1}H-NMR signals were assigned to the corresponding protons.[3,16] It is clear from Figure 1 that the peaks appearing in the chemical shift range of about 1.0–2.6 ppm overlapped with each other. Therefore, precise assignment of these overlapped peaks to the corresponding protons was not possible. Moreover, —CH$_2$—CCl$_3$ protons of the macroinitiator [a in Fig. 1(a)] appeared in the chemi-

cal shift at about 2.8–3.2 ppm (see peak a in the ^{1}H-NMR spectrum of the macroinitiator). These methylene protons (—CH$_2$—CCl$_2$—) in the terpolymer should have appeared in the chemical shift at about 2.5–2.8 ppm.[16] However, because of the weak and wide intensity of these methylene protons and possible overlapping with other peaks, the corresponding peak in the ^{1}H-NMR spectrum of terpolymer was not visible. It should also be mentioned that a weak peak appeared in the chemical shift at about 4.3 ppm [shown by a star sign in Fig. 1(b)] and corresponded to the j or g protons present at the ω end of terpolymer chains (i.e., >CH—Cl); this indicated the livingness of the terpolymer chains.[16]

A broad peak [shown as k in Fig. 1(b)] appearing in the chemical shift range of about 3.0–3.7 ppm was due to the methoxy protons of MA units

incorporated into the copolymer.[3,16] The methoxy region could be subdivided into the three subregions, 3.5–3.7, 3.3–3.5, and 3.0–3.3 ppm, which could be assigned to the MA-centered triads of MA/MA/MA, MA/MA/St, and St/MA/St, respectively (see refs. [3] and [16] for more details).

From the ^{1}H-NMR spectrum recorded at any time t, it was possible to calculate the cumulative average molar fraction of St $[\bar{F}_{St}(t)]$ and the cumulative average molar ratio of St to MA $[\bar{F}(t) = \bar{F}_{St}(t)/\bar{F}_{MA}(t)]$ incorporated into the P(St-co-MA) copolymer chains with eqs. (2) and (3), respectively:

$$\bar{F}_{St}(t) = \frac{3I_h(t)}{3I_h(t) + 5I_k(t)} \quad (2)$$

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

where $I_h(t)$ and $I_k(t)$ indicate the peak areas of the aromatic (from St) and methoxy (from MA) proton resonances, respectively, from the ^{1}H-NMR spectra recorded at any time t. The results of the calculations are given in Table II.

Now, $x_{ov}(t)$ and the individual molar conversion of comonomers i [St in this case; $x_i(t)$] and j [MA in this case; $x_j(t)$] could be calculated by known values of overall mass conversion $[X_{ov}(t)]$, molar ratio of comonomer i to comonomer j in the initial comonomer mixture (f^0), and $\bar{F}(t)$ via the following equations:[6]

$$x_j(t) = \frac{X_{ov}(t)[\mu + f^0]}{[\mu + \bar{F}(t)]} \quad (4)$$

$$x_i(t) = x_j(t)[\bar{F}(t)/f^0] \quad (5)$$

$$x_{ov}(t) = f_i^0 \times x_i(t) + f_j^0 \times x_j(t) \quad (6)$$

in which μ is the molecular weight ratio of comonomer j (86.09 g/mol for MA in this study) to comonomer i (104.15 g/mol for St in this study). The results of the calculations are given in Table II.

Determination of the comonomer reactivity ratios via the new approach

In the previous study,[16] we carried out ATRCP of St and MA initiated with a trichloromethyl-terminated PVAc macroinitiator in the presence of CuCl/PMDETA as a catalyst system at 90°C. Kinetic studies and gel permeation chromatography results showed that all reactions proceeded according to the controlled/living characteristic.[16] To obtain reliable comonomer reactivity ratios, $\bar{F}(\Delta t')$ at moderate conversion (>13%) was determined by ^{1}H-NMR spectroscopy. The reactivity ratios of St(r_{St}) and MA (r_{MA}) were then calculated by the extended KT and MH methods to be $r_{St} = 1.018 \pm 0.060$ and $r_{MA} =$

0.177 ± 0.025 and $r_{St} = 1.016 \pm 0.053$ and $r_{MA} = 0.179 \pm 0.023$, respectively.[16] In this article, the possibility of calculating more accurate comonomer reactivity ratios with the new approach introduced in this work is discussed for the ATRCP of St and MA initiated with CCl$_3$-terminated PVAc macroinitiator.

The influence of the possible preferential addition of one of the comonomers onto the (macro)initiator-derived (macro)radical on the copolymer composition in any living chain-growth copolymerization system can be excluded via determination of the $\bar{F}(\Delta t')$ at least at any two different conversions $[x_{ov}(t)$ and $x_{ov}(t')]$ for the same initial comonomer mixture composition and then calculation of a new $\bar{F}(\Delta t')$ related to the copolymer formed during $\Delta t'$. When the overall molar conversion of the comonomers during $\Delta t'$ $[x_{ov}(\Delta t')]$ is selected to be low enough, $\bar{F}(\Delta t')$ will then be equal to the instantaneous copolymer composition $[F(\Delta t')]$. In such a situation, the accurate comonomer reactivity ratios can be calculated by the low conversion methods. However, this approach may also be extended to high conversion data when the $x_{ov}(\Delta t')$ under study is selected to be high enough. Then, the accurate comonomer reactivity ratios should be calculated by the high conversion methods, such as extended KT and MH methods, where drift in the copolymer composition with conversion is also considered in the calculations. Moreover, the new approach can be used to determine the $\bar{F}(\Delta t')$ values at almost the same values but in various ranges (from low to high) of $x_{ov}(t)$ and $x_{ov}(t')$ for the various initial comonomer mixture compositions, from which the possible dependence of comonomer reactivity ratios on the conversion (or equivalently on the medium viscosity) can be evaluated for any chain-growth copolymerization system.

By known values of $x_i(t)$, $x_j(t)$, and $f(t)$ at any time t $(t \neq 0)$ and those at any time t' $(t' > t)$, it is possible to exclude the influence of the possible preferential addition of one of the comonomers onto the (macro)initiator-derived (macro)radical on the copolymer composition via the following equations:

$$f(t) = \frac{f_i(t)}{f_j(t)} = \frac{[1 - x_i(t)]}{[1 - x_j(t)]} f^0 \quad (7)$$

$$x_i(\Delta t') = \frac{x_i(t') - x_i(t)}{1 - x_i(t)} \quad (8)$$

$$x_j(\Delta t') = \frac{x_j(t') - x_j(t)}{1 - x_j(t)} \quad (9)$$

$$x_{ov}(\Delta t') = f_i(t) \times x_i(\Delta t') + f_j(t) \times x_j(\Delta t') \quad (10)$$

$$\bar{F}_i(\Delta t') = \frac{f(t) \times x_i(\Delta t')}{f(t) \times x_i(\Delta t') + x_j(\Delta t')} \quad (11)$$

Individual [$x_{St}(\Delta t')$ and $x_{MA}(\Delta t')$] and Overall [$x_{ov}(\Delta t')$] Comonomer Conversions and $\bar{F}(\Delta t')$ Obtained by the New Approach Introduced in this Work from the Data Given in Table II for the ATRCP of St and MA Containing Various Initial Comonomer Mixture Compositions Initiated by the CCl$_3$-Terminated PVAc Macroinitiator at 90°C

Experiment	$f(t)$	$x_{St}(\Delta t')$	$x_{MA}(\Delta t')$	$x_{ov}(\Delta t')$	$\bar{F}(\Delta t')$
MS0.9	8.8468	0.1273	0.1277	0.1273	8.8218 (8.8511[a])
MS0.7	2.2385	0.0211	0.0168	0.0198	2.8053 (2.8326[a])
MS0.5	0.9676	0.1222	0.0754	0.0984	1.5689 (1.5766[a])
MS0.3	0.3954	0.1423	0.0604	0.0836	0.9315 (0.9275[a])
MS0.1	0.1028	0.2990	0.0823	0.1025	0.3734 (0.3747[a])

[a] Values giving inside the parentheses were directly calculated from ^{1}H-NMR spectra by eq. (14).

$$\bar{F}(\Delta t') = \frac{F_i(\Delta t')}{F_j(\Delta t')} = \frac{x_i(\Delta t')}{x_j(\Delta t')} f(t) \qquad (12)$$

where t is any time during the polymerization reaction ($t \neq 0$) and t' is also any time after time t ($t' > t$). The molar ratio of comonomer i (St in this work) to comonomer j (MA in this work) in the comonomer mixture at time t [i.e., $f(t)$] and that in the copolymer chains produced during $\Delta t'$ between times t' and t [i.e., $\bar{F}(\Delta t')$] and the corresponding individual [$x_{St}(\Delta t'$ and $x_{MA}(\Delta t')$] and overall [$x_{ov}(\Delta t')$] monomer conversions during this $\Delta t'$ for experiments performed at the various initial comonomer mixture compositions are given in Table III. It is clear from Table III that $\bar{F}(\Delta t')$ obtained by the new approach was related to the low conversion.

$\bar{F}(\Delta t')$ in eq. (12) means that the amount of comonomers incorporated into the copolymer chains during the time t was deducted from the amount of comonomers incorporated into the copolymer chains during time t' ($t' > t$). In other words, $\bar{F}(\Delta t')$ was related only to the molar fraction of comonomers incorporated into the copolymer chains during $\Delta t'$ by consideration of the fact that the initial comonomer mixture composition for the copolymer chains grown during $\Delta t'$ with composition of $\bar{F}(\Delta t')$ was the comonomer mixture composition at time t [i.e., $f(t)$]. Therefore, this approach allowed us to exclude the influence of possible preferential addition of one of the comonomers onto the (macro)initiator-derived (macro)radical on the copolymer composition. In fact, the copolymer chains produced during time t with an ω-end containing one of the comonomers under study was considered in this approach to be as a macroinitiator for further copolymerization of the comonomers present in the comonomer mixture at time t with a composition of $f(t)$. Therefore, the new approach introduced here allowed us to obtain a more accurate copolymer composition and corresponding initial comonomer mixture composition and individual and overall comonomer conversions, from which more accurate comonomer reactivity ratios could then be calculated.

The signal appearing in the chemical shift range 4.7–5.0 ppm was due to the methine proton in the repeat units of the CCl$_3$-terminated PVAC macroinitiator and inactive PVAc (Fig. 1). This signal could be considered as a reference signal in the ^{1}H-NMR spectra of PVAc-b-P(St-co-MA) terpolymers because the methine proton in PVAc remained unchanged during the ATRCP of St and MA. Therefore, in addition to the general approach introduced previously, $\bar{F}(\Delta t')$ was also calculated via eq. (13) in this work, where there was the same reference signal in all ^{1}H-NMR spectra recorded for the same initial comonomer mixture composition at the various times:

$$\bar{F}(\Delta t') = \frac{\bar{F}_{St}(\Delta t')}{\bar{F}_{MA}(\Delta t')}$$
$$= \frac{3 \times [[I_h(t')/I_{4.7-5.0}(t')] - [I_h(t)/I_{4.7-5.0}(t)]]}{5 \times [[I_k(t')/I_{4.7-5.0}(t')] - [I_k(t)/I_{4.7-5.0}(t)]]}$$
$$(13)$$

where $\bar{F}(\Delta t')$ is defined as the cumulative average molar ratio of St to MA incorporated into the copolymer chains during any $\Delta t'$. $I_h(t)$ and $I_k(t)$ indicate the signal intensities of the aromatic (from St) and methoxy (from MA) proton resonances, respectively, at any time t ($t \neq 0$). If $I_{4.7-5.0}$ is normalized to be equal to 1 in all of the spectra, eq. (13) can be rewritten as eq. (14):

$$\bar{F}(\Delta t') = \frac{\bar{F}_{St}(\Delta t')}{\bar{F}_{MA}(\Delta t')} = \frac{3 \times [I_h(t') - I_h(t)]}{5 \times [I_k(t') - I_k(t)]} \qquad (14)$$

The results of the calculation of $\bar{F}(\Delta t')$ by eq. (14) are given in Table III. There was very good agreement between the $\bar{F}(\Delta t')$ values determined by eqs. (12) and (14); this suggested that the new general approach introduced in this work could be used to accurately determine $\bar{F}(\Delta t')$, $x_i(\Delta t')$, $x_j(\Delta t')$, and $x_{ov}(\Delta t')$, from which the more accurate comonomer reactivity ratios could then be calculated.

The values of $f(t)$, $\bar{F}(\Delta t')$, $x_{St}(\Delta t')$, $x_{MA}(\Delta t')$, and $x_{ov}(\Delta t')$ given in Table III were used to calculate the reactivity ratios of St and MA by different methods

TABLE IV
Summary of the Reactivity Ratios Calculated by the New Approach and by the Classic Approach[16] for ATRCP of St and MA Along with Those Reported in the Literature

Method	Conversion	r_{St}	r_{MA}	Reference
Bulk ATRP				
FR	<13% (<11%[a])	0.905 (1.102[a])	0.187 (0.164[a])	This work
JJ	<13% (<11%[a])	0.909 (1.199[a])	0.190 (0.223[a])	This work
KT	<13% (<11%[a])	0.911 ± 0.029 (1.167 ± 0.261[a])	0.192 ± 0.015 (0.185 ± 0.122[a])	This work
Extended KT	<13% (<11%[a])	0.904 ± 0.009 (1.179 ± 0.263[a])	0.170 ± 0.004 (0.178 ± 0.117[a])	This work
MH[b]	<13% (<11%[a])	0.904 ± 0.009 (1.179 ± 0.256[a])	0.170 ± 0.004 (0.176 ± 0.114[a])	This work
TM[b]	<13% (<11%[a])	0.926 (1.085[a])	0.194 (0.161[a])	This work
Extended KT	Moderate (>13%)	1.018 ± 0.060	0.177 ± 0.025	16
MH	Moderate (>13%)	1.016 ± 0.053	0.179 ± 0.023	16
Bulk NMP[c]				
Extended KT	<30%	0.89	0.22	17
Extended KT	<30%	1.32	0.14	18
CFRP[d]				
KT	<10% (bulk)	0.84 ± 0.08	0.21 ± 0.05	2
KT	<15% (solution)	0.73 ± 0.05	0.19 ± 0.05	3
—	—	0.75	0.18	4 and 19
—	—	0.825	0.238	20
—	—	0.82	0.24	21
—	—	0.9	0.07	21
—	—	0.871 ± 0.022	0.148 ± 0.026	21

[a] Values inside the parentheses are related to the calculation of the reactivity ratios by the classic approach.
[b] With initial guesses of $r_{St} = r_{MA} = 1$ for the MH method and $r_{St} = 1$ and $r_{MA} = 0$ for the TM method.
[c] Nitroxide-mediated polymerization.
[d] CFRP, conventional free-radical polymerization.

(see Table IV and Figures S1–S3 and Tables S1 and S2 in the Supporting Information). The results in Table IV indicate that the reactivity ratios of St and MA calculated by the new approach were in good agreement with those reported in the literature for the conventional free-radical copolymerization of St and MA ($r_{St} < 1$ and $r_{MA} < 1$ in Table IV); this suggests that the ATRCP of St and MA proceeded via a mechanism similar to the free-radical copolymerization.[6]

A slightly difference between the comonomer reactivity ratios calculated by the new approach introduced here and those calculated in a previous study[16] by the copolymer composition at the overall comonomer conversion greater than 13% (moderate conversion) was observed (Table IV). This may have been due to the slight but significant influence of the possible preferential addition of one of the comonomers onto the (macro)initiator-derived (macro)radical on the copolymer composition in the previous study, where the copolymer composition was obtained by the classic approach for the copolymer chains formed during time t [i.e., $\overline{F}(t)$] instead of $\overline{F}(\Delta t')$ introduced in the new approach. Therefore, it is not possible in the classic approach to actually exclude the influence of the possible preferential addition of one of the comonomers onto the (macro)-initiator-derived (macro)radical on the copolymer composition unless conversion is selected to be high enough, where the aforementioned influence can be

considered to be negligible. However, the viscosity of the reaction medium at high conversion can affect the reactivity ratios. Therefore, new approach was introduced here, which allows one to exclude the aforementioned influences on the copolymer composition and, thereby, on the reactivity ratios.

The results suggest that more accurate comonomer reactivity ratios from low conversion data in the controlled/living radical copolymerizations can be calculated from copolymer composition measured by the new approach. This approach is also applicable in any other living chain-growth copolymerization system. This approach is believed to be applicable for any living chain-growth copolymerization system at any conversion range (or equivalently at any $\Delta t'$), from low to high. According to this approach, the copolymer compositions and the individual and overall comonomer conversions are obtained at any two different reaction times (e.g., t and t' with $t' > t$ and $t \leq 0$), either toward or away from each other, from which the modified $\overline{F}(\Delta t')$ and the individual [$x_i(\Delta t')$ and $x_j(\Delta t')$] and overall [$x_{ov}(\Delta t')$] comonomer conversions related to the copolymer formed during $\Delta t'$ are calculated at either low or high conversion, respectively. In such a situation, the influence of possible preferential addition of one of the comonomers onto the (macro)initiator-derived (macro)radical on the copolymer composition is really excluded. These accurate data of
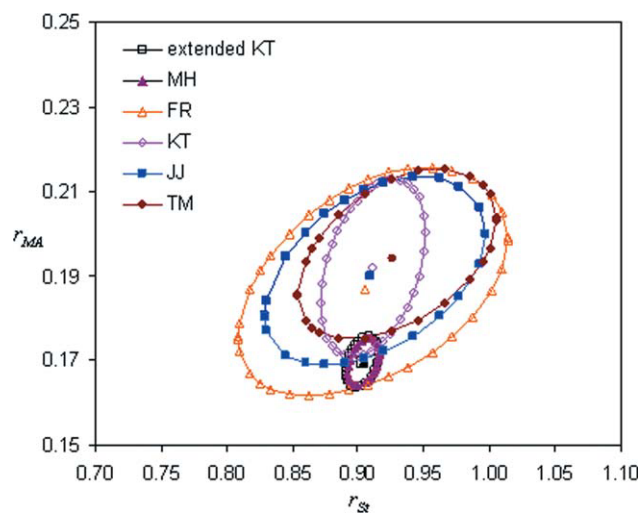
Figure 2 Comonomer reactivity ratios and 95% joint confidence limits for the reactivity ratios of St and MA obtained in this work by the new approach [(▲) MH, (◆) TM, (◇) KT, (□) extended KT, (■) JJ, and (△) FR methods]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

copolymer composition are then used to calculate the more accurate comonomer reactivity ratios. Moreover, the new approach introduced in this work can be used in any chain-growth copolymerization system to evaluate the possible conversion dependence of comonomer reactivity ratios when the copolymer compositions at the almost same, but various overall conversion ranges are obtained for the various initial comonomer mixture compositions and are then used to calculate reactivity ratios.

It should be noted that existence of dead chains at very high conversions did not affect the accuracy of the reactivity ratios calculated by the new approach because, according to this approach, these dead chains formed during time t were excluded from the chains growing during $\Delta t' = t' - t$ ($t' > t$). In other words, although the number of growing macroradicals may have decreased slightly with reaction progress, the nature of the growing macroradicals did not change with the reaction progress.

Joint confidence limits

In the calculation of simple intervals, reactivity ratios are considered to be statistically independent. On the other hand, the reactivity ratios are simultaneously calculated and, therefore, cannot be considered statistically independent. Therefore, simple intervals do not clearly convey the message of which a pair of parameters is consistent with the data. The specification of joint confidence limits, within which the correct values are believed to exist, properly conveys some idea of the goodness of the experiment and data. The smaller the experimental error is and the

better the experimental design is, the smaller the area of uncertainty is.

The 95% joint confidence limits for the reactivity ratios of St and MA calculated in this work are shown in Figure 2. It is clear from Figure 2 that the area of uncertainty was small enough for all methods. Therefore, all methods resulted in more reliable comonomer reactivity ratios. However, the most precise estimates were obtained by extended KT and MH methods, where the effect of conversion on the copolymer composition drift was also considered in the calculations. The results indicate that drifts in the copolymer composition were significant, even at low conversion. Therefore, one should consider the effect of conversion on the copolymer composition drift to calculate the most accurate comonomer reactivity ratios. It should be noted that in all calculations where the reactivity ratios of St and MA were required, the reactivity ratios obtained by the MH method were preferentially used.

To check the accuracy level in the comonomer reactivity ratios estimated via the classic approach, the reactivity ratios of St and MA were calculated by the copolymer composition at low overall comonomer conversion (<11%, see Table II). The results of the calculations are given in Table IV (see the values given inside the parentheses). The corresponding 95% joint confidence limits are shown in Figure S4 of the Supporting Information. It is clear from Figure S4 that the area of uncertainty in the 95% joint confidence limits was significantly larger than that of Figure 2; this suggests that the comonomer reactivity ratios calculated by the new approach were more accurate than those calculated by the classic approach at low conversion. Moreover, as the reactivity ratios obtained by the classic approach at low conversion were almost same as those obtained by the classic approach at moderate conversion (>13%), one can conclude that the moderate conversion also was not enough to obtain an accurate copolymer composition. Therefore, to calculate more accurate comonomer reactivity ratios, it is necessary to obtain the copolymer composition at high conversion by the classic approach [i.e., $\overline{F}(t)$][6] or, preferentially, the copolymer composition at any $\Delta t'$, either short or long, by the new approach introduced in this work [i.e., $F(\Delta t')$ or $\overline{F}(\Delta t')$, respectively].

Figure 3 shows the theoretical instantaneous copolymer composition curves obtained from eq. (1) with the comonomer reactivity ratios calculated by the new approach and classic approach, both at low conversion (<13 and <11%, respectively), along with the experimental data obtained by the new approach. It is clear from Figure 3 that when the comonomer reactivity ratios calculated by the classic approach at low conversion (<11%) and at moderate conversion (>13%; the corresponding curve has been
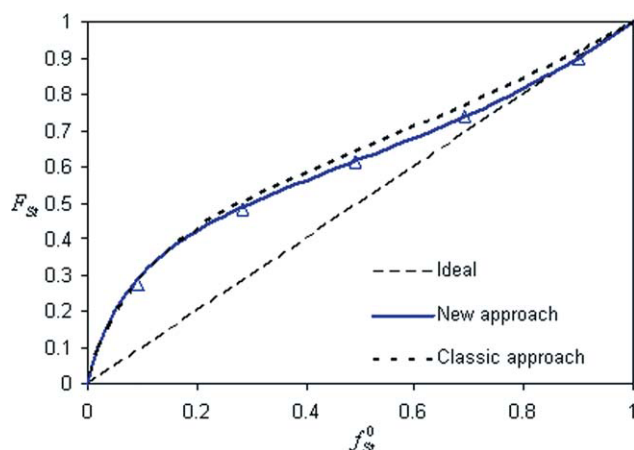
Figure 3 Experimental ($\triangle$, Table III) and theoretical variation of the instantaneous copolymer composition (F_{St}) versus f_{St}^0 for ATRCP of St and MA [the theoretical values were calculated from eq. (1) with the reactivity ratios of the MH method estimated from the copolymerization data of the new approach and the classic approach]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

omitted in Fig. 3, but it was between the two curves shown in Fig. 3) were used to plot the instantaneous copolymer composition curve, the instantaneous molar fraction of St in the copolymer at the same initial comonomer mixture composition was predicted to be always higher than that predicted by the comonomer reactivity ratios of the new approach. In other words, the results in Figure 3 indicate that St was preferentially added to the (macro)initiator-derived (macro)radical; this resulted in a higher molar fraction of St in the copolymer, especially at the low conversion. It is clear from Figure 3 that the influence of the preferential addition of St onto the (macro)initiator-derived (macro)radical on the copolymer composition could be neglected for the reaction mixture containing low f_{St}^0. However, the significance of this influence would be increased with increasing f_{St}^0. Therefore, with the new approach, the influence of the preferential addition of St onto the (macro)initiator-derived (macro)radical on the copolymer composition was excluded, and thereby, an accurate copolymer composition was obtained, from which more accurate comonomer reactivity ratios were calculated.

CONCLUSIONS

In controlled/living radical copolymerization systems, possible preferential addition of one of the comonomers onto the (macro)initiator-derived (macro)radical can affect the copolymer composition, especially at low conversion and, hence, the comonomer reactivity ratios calculated via the classic approach. ATRCP of St and MA was performed in bulk in the presence of a CCl$_3$-terminated PVAc

telomer as a macroinitiator and CuCl/PMDETA as a catalyst system at 90°C. A new approach was introduced in this work, allowing us to exclude the influence of the possible preferential addition of one of the comonomers onto the (macro)initiator-derived (macro)radical on the copolymer composition. In addition to this approach, $\overline{F}(\Delta t')$ was directly calculated from ^{1}H-NMR spectra. There was a very good agreement between the $\overline{F}(\Delta t')$ values calculated by the two different methods; this confirmed the accuracy of the new approach for evaluating the copolymer composition. The 95% joint confidence limits confirmed the higher accuracy of the reactivity ratios calculated by the new approach. As a result, this approach could be used as a general method to calculate more accurate comonomer reactivity ratios in controlled/living radical copolymerizations and in any other living copolymerization system.

Supporting information

The Supporting Information includes detailed results of the reactivity ratios of St and MA calculated by the new approach and the 95% joint confidence limits of the reactivity ratios of St and MA calculated by the classic approach.

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