

Using $^1\text{H-NMR}$ Spectroscopy for the Kinetic Study of the *In Situ* Solution Free-Radical Copolymerization of Styrene and Ethyl Acrylate

Mahdi Abdollahi,¹ Shahram Mehdipour-Ataei,² Farshid Ziaee²

¹Department of Polymer Engineering, Faculty of Engineering, Tarbiat Modares University, P.O. Box 14155/143, Tehran, Iran

²Iran Polymer and Petrochemical Institute, P.O. Box 14965/115, Tehran, Iran

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ABSTRACT: The free-radical copolymerization of styrene and ethyl acrylate in benzene- d_6 as the solvent in the presence of benzoyl peroxide as an initiator at 70°C was studied by online $^1\text{H-NMR}$ spectroscopy. The chemical composition of the copolymer at different reaction times was calculated from the conversion of the monomers to the copolymer, and then the reactivity ratios of styrene and ethyl acrylate were determined at both low and high conversions. Data for the overall monomer conversion versus the time were used to estimate the ratio $k_p k_t^{-0.5}$ for different compositions of the initial feed (k_p is the propagation rate constant, and k_t is the termination rate constant). $k_p k_t^{-0.5}$ increased with an increasing molar fraction of ethyl

acrylate in the initial feed. The monomer mixture and copolymer compositions versus the overall monomer conversion were calculated with the data of $^1\text{H-NMR}$ spectra. The incorporation of the styrene monomer into the copolymer structure was more favored than that of the ethyl acrylate monomer. Reducing the molar fraction of styrene in the initial feed intensified this. Drawing the molar fraction of styrene (or ethyl acrylate) in the copolymer chains versus that in the initial feed showed a tendency of the system toward random copolymerization. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2588–2597, 2007

Key words: copolymerization; NMR; kinetics (polym.)

INTRODUCTION

During the past 20 years, more attention has been focused on the copolymerization of styrene (St) and ethyl acrylate (EA).^{1–6} The kinetics of this reaction have been studied widely in bulk, solution, and emulsion. However, to the best of our knowledge, not all the kinetic parameters of this copolymerization, especially at high temperatures, have been determined yet.

The determination of the reactivity ratio has been the major focus of studies described in the open literature for this copolymerization system.^{7–17} The results of numerous studies in which the reactivity ratios have been calculated are summarized in Table I. The reactivity ratios for EA (r_{EA}) and St (r_{St}) are in the range of about 0.13–0.23 and 0.69–1.36, respectively.

$^1\text{H-NMR}$ spectroscopy has proven to be one of the most important techniques for studying the copolymer composition.^{14,18–20} Online $^1\text{H-NMR}$ spectroscopy has been successfully used for the kinetic study of free-radical homopolymerization.²¹ This research

deals with the kinetic study of the St–EA copolymerization reaction using online $^1\text{H-NMR}$ spectroscopy. Monomer reactivity ratios in the solution system were calculated by different methods at both low and high conversions with data obtained from online $^1\text{H-NMR}$ spectroscopy. To obtain further kinetic information, data of the overall monomer conversions versus the progress of the reaction were used to estimate the ratio of the propagation rate constant to the average square root of the termination rate constant ($k_p k_t^{-0.5}$). The compositions of the monomer mixture and copolymer were plotted as a function of the overall monomer conversion, and the results were evaluated by terminal model equations.

EXPERIMENTAL

Materials

The monomers, St stabilized with 4-*tert*-butyl catechol and EA stabilized with monoethyl ether hydroquinone (Merck Chemical Co., Darmstadt, Germany), were washed three times with a 5% sodium hydroxide solution and then three times with distilled water to remove their inhibitors and dried over calcium chloride. Benzene- d_6 (BZ- d_6) as the solvent was purchased from Armar Chemicals (Döttingen, Switzerland). Benzoyl peroxide (BPO; Fluka

Correspondence to: S. Mehdipour-Ataei (s.mehdipour@ippi.ac.ir).

TABLE I
Literature Values of r_{St} and r_{EA}

r_{EA}	r_{St}	Condition	Reference
0.22	0.71	Emulsion/50°C	3
0.19	0.78	Solution/50°C	7
0.18	0.79	Solution/50°C	7
0.17	0.77		8
0.138	0.698		9
0.152 ± 0.006	0.787 ± 0.023	Solution/50°C	10
0.194	0.828	Solution/50°C	5
0.17	0.94	Bulk	11
0.17	0.9	Emulsion/60°C	12, 13
0.171	0.781	Bulk/40°C	4
0.22 ± 0.04	1.16 ± 0.20	Bulk/BPO/70°C	14
0.160	1.010		15
0.190	0.790		15
0.200	0.800		15
0.480	0.800		15
0.128	0.717	Bulk/azobisisobutyronitrile/50°C	16
0.2071	0.8996	Bulk/ <i>tert</i> -butyl perbenzoate/100°C	17
0.2219	0.9129	Bulk/ <i>tert</i> -butyl perbenzoate/130°C	17
0.1997	0.8895	Bulk/thermal/100°C	17
0.2224	0.9742	Bulk/thermal/130°C	17
0.2125	0.9014	30 wt % <i>m</i> -xylene/100°C	17
0.2083	0.9066	60 wt % <i>m</i> -xylene/100°C	17
0.1969	0.8802	30 wt % <i>p</i> -xylene/100°C	17
0.2100	0.9826	60 wt % <i>p</i> -xylene/100°C	17
0.2221	0.9293	30 wt % <i>m</i> -xylene/130°C	17
0.1996	0.9305	60 wt % <i>m</i> -xylene/130°C	17
0.2342	0.9058	30 wt % <i>p</i> -xylene/130°C	17
0.2353	0.9426	60 wt % <i>p</i> -xylene/130°C	17

Chemical Co., Dottingen, Switzerland) was used as the initiator without further purification.

¹H-NMR experiments

All NMR experiments reported in this study were carried out on a Bruker Avance 400-MHz NMR spectrometer (Bruker Instruments, Darmstadt, Germany). The sample cavity was equilibrated at 70°C (i.e., the temperature at which all the kinetic NMR experiments were carried out) by a BVT 3000 (±0.1°C) temperature control unit. A typical ¹H-NMR kinetic experiment consisted of the following sequence of steps.

First, the cavity was set to the desired reaction temperature (i.e., 70°C), and a sample containing only BZ-*d*₆ (the solvent) was introduced into the sample cavity and allowed to equilibrate for approximately 10 min. The magnet was then thoroughly shimmed with the BZ-*d*₆ sample. The 5-mm-diameter NMR tube containing the reaction mixture was inserted into the sample chamber after degassing with nitrogen gas and sealed with a rubber septum, and the start time was recorded. The spin of the tube in the sample chamber was 30 rpm during the experiment. The sample containing the reaction mixture was allowed to equilibrate for 5 min. The first

recorded spectrum (after the sample tube containing the reaction mixture was inserted into the cavity) was regarded as the spectrum representing the zero overall monomer conversion. Although approximately 5 min passed from the insertion of the sample into the cavity to the first scan, negligible conversion occurred because of the low overall rate of reaction. All samples contained high amounts of BZ-*d*₆. This high amount of BZ-*d*₆ had to be used because of better thermal conductivity (isothermal condition) and to avoid an excessive viscosity increase at higher conversions.

RESULTS AND DISCUSSION

A typical ¹H-NMR spectrum of the initial reaction mixture containing a molar fraction of St in the initial feed (f_{St}^0) of 0.5480 (sample St-EA-3 in Table II) at an overall monomer conversion of 45 mol % with the signal assignments is shown in Figure 1. From this figure, it is clear that the signals related to the —CH^{*a*} (or —CH^{*b*}) proton of St and the —CH^{*g*} (or —CH^{*h*} and —CH^{*i*}) proton of EA could be used to follow the reaction progress. In all spectra of each sample, the overall integral for —CH₂^{*f*} and —CH₂^{*f*} proton signals of EA (4–4.5 ppm in Fig. 1) existing in the monomer mixture and produced copolymer

TABLE II
Concentrations of the Components in the Initial Reaction Mixture^a

Sample	[M] (mol/L)	f_{St}^0	[BPO] (mol/L)	$(n_{St} + n_{EA})/V_{BZ-d6}$ (mol/L)	$n_{BPO}/(n_{St} + n_{EA})$ (mol/mol)
St-EA-1	0.9037	0.166771	0.0450	1.004	0.04984
St-EA-2	0.9286	0.270769	0.0448	1.035	0.04826
St-EA-3	0.9450	0.548017	0.0466	1.058	0.04723
St-EA-4	0.9260	0.714729	0.0447	1.035	0.04826
St-EA-5	0.8900	0.893580	0.0448	0.9914	0.05038

^a The reaction temperature was 70°C. The solutions in the NMR tubes were degassed with nitrogen gas (99.9% pure) to exclude oxygen from the solutions.

n_{St} , moles of styrene; n_{BPO} , moles of benzoyl peroxide; n_{EA} , moles of ethyl acrylate; and V_{BZ-d6} , volume of benzene- d_6 .

chain, respectively, was adjusted to an arbitrary value of 2.0000. The integral for the signals of other protons in the same spectrum was automatically scaled accordingly to this value. All other spectra recorded at various time intervals for each sample were then scaled similarly so that the overall integrals of all proton signals in the other spectra for each sample were equal to the first spectrum of that sample. Thus, the individual and overall monomer conversions as well as the monomer mixture and copolymer compositions could be monitored as a function of the reaction time via the following equations:

$$x_{St}^t = \frac{I(-CH^a)_0 - I(-CH^a)_t}{I(-CH^a)_0} \quad (1)$$

$$x_{EA}^t = \frac{I(-CH^g)_0 - I(-CH^g)_t}{I(-CH^g)_0} \quad (2)$$

$$x^t = 1 - \frac{I(-CH^a)_t + I(-CH^g)_t}{I(-CH^a)_0 + I(-CH^g)_0} \quad (3)$$

$$f_{St}^t = \frac{I(-CH^a)_t}{I(-CH^a)_t + I(-CH^g)_t} \quad (4)$$

$$F_{St}^t = \frac{I(-CH^a)_0 - I(-CH^a)_t}{I(-CH^a)_0 + I(-CH^g)_0 - I(-CH^a)_t - I(-CH^g)_t} \quad (5)$$

where x_{St}^t and x_{EA}^t are the individual conversions of St and EA at reaction time t , respectively; x^t is the overall monomer conversion at time t ; f_{St}^t and F_{St}^t are the molar fractions of St in the monomer mixture and produced copolymer chain at time t , respectively; $I(-CH^a)_0$ and $I(-CH^a)_t$ indicate the intensities of the $-CH^a$ proton signal of the St monomer at the initial state and at time t , respectively; and $I(-CH^g)_0$ and $I(-CH^g)_t$ indicate the intensities of the $-CH^g$ proton signal of the EA monomer at the initial state and at time t , respectively.

The online 1H -NMR spectra recorded for sample St-EA-1 as a function of the reaction time are shown in Figure 2. It is clear that by the progress of the copolymerization reaction, the intensities of the peaks

related to the aliphatic protons of the produced copolymer chains (ca. 1.5–3.2 and 4–4.4 ppm) increased. Therefore, the progress of the reaction could be followed with time. As a result, it was possible to investigate the kinetics of the St/EA copolymerization reaction. Furthermore, a low rate of copolymerization and a large amount of the solvent were applied to maintain the isothermal conditions of the system during the reaction.

Determination of the monomer reactivity ratios

The monomer reactivity ratios are important factors for predicting the copolymer composition for each initial mixture of monomers and for understanding the kinetics and mechanism of the copolymerization. In general, the reactivity ratios of the monomers are determined at low conversions. In the classic terminal model of copolymerization, it has been suggested that for a given pair of monomers, the composition of the copolymer is just a function of the instantaneous composition of the feed.^{22,23}

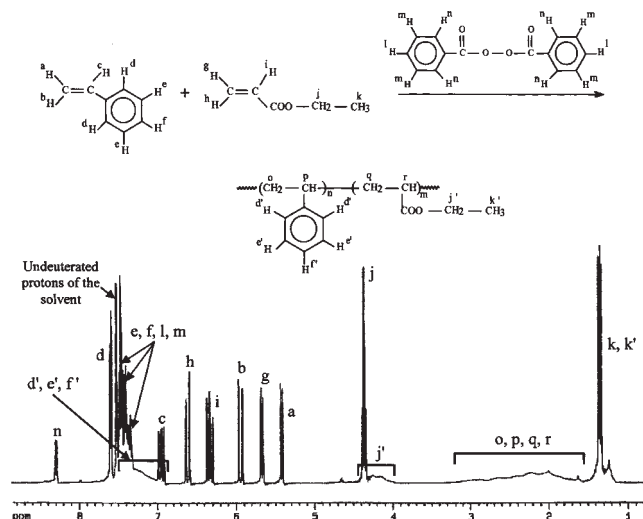


Figure 1 Typical 1H -NMR spectrum of the mixture of the monomers and produced copolymer after an overall monomer conversion of 45 mol % for sample St-EA-3.

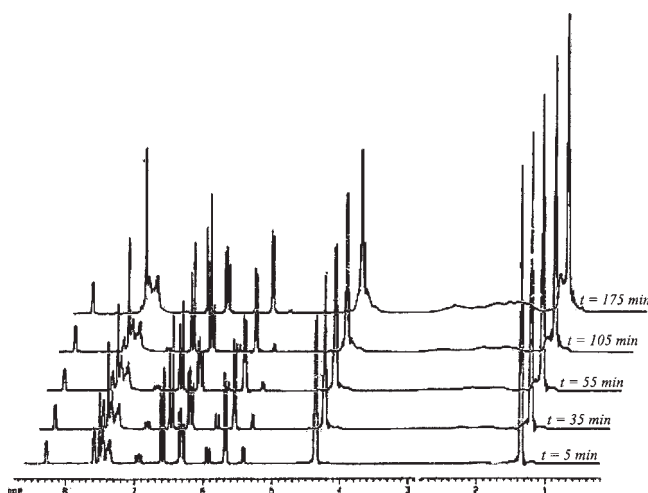


Figure 2 Progress of the copolymerization reaction as a function of time for sample St-EA-1.

Among several methods for the determination of the monomer reactivity ratios, the following methods are extensively used for obtaining monomer reactivity ratios at low conversions: the Mayo-Lewis,²² Finemann-Ross,²⁴ inverted Finemann-Ross,²⁵ Kelen-Tudos,²⁶ extended Kelen-Tudos,²⁷⁻²⁹ Joshi-Joshi,³⁰ Mao-Huglin,³¹ and Tidwell-Mortimer³² methods. The Mayo-Lewis, extended Kelen-Tudos, and Mao-Huglin methods are applicable for high conversions, too.

Mahdavian et al.²¹ successively applied online ¹H-NMR spectroscopy to the kinetic study of the free-radical homopolymerization of acrylamide and derived all kinetic parameter of this system. Davis and coworkers^{33,34} applied this technique to the copolymerization of St with itaconic acid and St with *m*-isopropenyl- α,α' -dimethylbenzyl isocyanate and calculated the overall rate constant of copolymerization ($k_p k_t^{-0.5}$).

As mentioned before, the composition of the monomer mixture, the individual and overall conversions

TABLE III
Data Obtained from ¹H-NMR Spectra at Low Conversions in the Free-Radical Copolymerization of St and EA

f_0^a	F^b	x_{St}	x_{EA}	x
0.200150	0.564596	0.238949	0.084708	0.110431
0.371308	0.948744	0.177496	0.0694661	0.0987172
1.212472	2.558234	0.0499372	0.0236677	0.0380638
2.505435	4.544601	0.129905	0.0716167	0.113277
8.396725	15.196362	0.0514598	0.028434	0.0490094

^a Molar ratio of St to EA in the initial monomer mixture.

^b Molar ratio of St to EA in the produced copolymer chains.

TABLE IV
Data Obtained from ¹H-NMR Spectra at High Conversions in the Free-Radical Copolymerization of St and EA

f_0	F	x_{St}	x_{EA}	x
0.200150	0.400065	0.89276	0.446643	0.521043
0.371308	0.74866	0.67522	0.334884	0.427036
1.212472	1.711258	0.521108	0.369219	0.452457
2.505435	3.121469	0.372773	0.299204	0.351786
8.396725	8.514511	0.343103	0.338357	0.342598

of the monomers, and the composition of the copolymer can be determined as functions of the reaction time by a comparison of all the spectra with the first spectrum in each sample. The results at both low and high conversions are given in Tables III and IV, respectively. With these data at low and high conversions, the monomer reactivity ratios can be calculated by the different mentioned methods. The results of the calculation of r_{St} and r_{EA} with these methods are shown in Table V. The 95% joint confidence limits obtained for the monomer pair are shown in Figure 3. The confidence limits for all reactivity ratios (with the exception of the reactivity ratios obtained from the extended Kelen-Tudos and Mao-Huglin methods at high conversions, which omitted in Fig. 3 because of the very broad joint confidence limits) are narrow, justifying the high degree of certainty in the numerical values of the monomer reactivity ratios. These observations indicate that the reactivity ratios calculated with low-conversion data were more accurate than ones calculated with high-conversion data. Furthermore, it is believed that the monomer reactivity ratios obtained by the nonlinear Tidwell-Mortimer method are more accurate than those of the linear methods. For this reason, the reactivity ratios of the nonlinear method will be preferentially used later for evaluating the composition drifts in the monomer mixture and produced copolymer.

TABLE V
Results of the Calculations of r_{St} and r_{EA}

Method		r_{St}	r_{EA}
Low conversion	Finemann-Ross	1.749561	0.311034
	Inverted Finemann-Ross	1.714764	0.274642
	Kelen-Tudos	1.707671	0.273218
	Extended Kelen-Tudos	1.724785	0.245106
	Joshi-Joshi	1.704692	0.275499
	Tidwell-Mortimer ^a	1.705075	0.273861
High conversion	Mao-Huglin ^a	1.738663	0.297168
	Mayo-Lewis	1.725044	0.267362
	Extended Kelen-Tudos	0.947978	0.183988
	Mayo-Lewis	0.977160	0.324510
	Mao-Huglin ^a	0.918648	0.153328

^a With an initial guess of $r_{St} = r_{EA} = 1$.

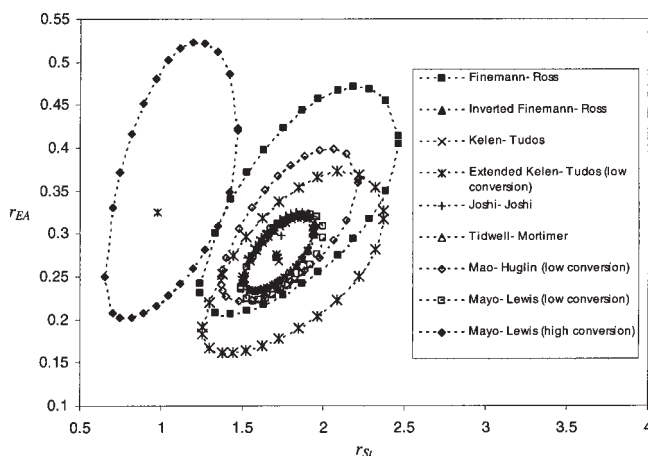


Figure 3 Ninety five percent joint confidence limits for the reactivity ratios of the St/EA system.

r_{St} and r_{EA} increase with increasing reaction temperature, as shown in Table I. Sahloul and Penlidis¹⁷ investigated the dependence of r_{St} and r_{EA} on the temperature. They observed r_{St} and r_{EA} increasing with increasing temperature. However, the sensitivity of r_{St} to the temperature was less than the sensitivity of r_{EA} . Brar and Sunita¹⁴ studied the bulk polymerization of these monomers at 70°C in the presence of BPO and found $r_{St} = 1.16 \pm 0.20$ and $r_{EA} = 0.22 \pm 0.04$ for this system at a low conversion. These data were closer than those of the other studies to the calculated reactivity ratios at low conversions in this study for the solution copolymerization of St/EA in the presence of BZ- d_6 at 70°C. The difference in the values of the reactivity ratios might be due to the differences in the procedure of polymerization and the difference in the technique used for the determination of the copolymer composition. The monomer reactivity ratios obtained with high-conversion data were in good agreement with the values reported in the literature, whereas the reactivity ratios obtained with low-conversion data were noticeably different from those reported in the literature. This difference might be due to the effect of equipment noise on the peak intensities at low conversions because the decrease in the intensity of peaks related to the monomers protons was small at the beginning of the reaction [see eqs. (1–5)]. In other words, with increasing conversion, the area of the peaks related to the monomers protons decreased significantly, so more accurate data were obtained from ¹H-NMR spectra.

Estimation of the overall polymerization rate coefficient

The individual conversions of monomers St and EA as a function of the reaction time were calculated by

an analysis of ¹H-NMR spectra through eqs. (1) and (2). Figure 4 shows the individual monomer conversions versus the time for copolymerization systems containing 0.1668 (St-EA-1) and 0.5480 (St-EA-3) molar fractions of St in the initial reaction mixture. The reaction was performed at 70°C, and the concentration of the initiator in all cases was about 0.045M. The curves of the individual monomer conversions versus the time for St and EA show clearly that both monomers were polymerized (most likely copolymerized) and that EA was incorporated into the copolymer at a slower rate than St.

In all the initial reaction mixture compositions, similar curves for individual conversions of the monomers versus the time were observed. This means that St was incorporated preferably into the copolymer chains. These curves of the individual conversions versus the time can be used to calculate the overall monomer conversions versus the reaction time via eq. (3) and to derive changes in the compositions of the monomer mixture and copolymer as a function of time (or overall monomer conversion). The calculation of changes in the compositions of the monomer mixture and copolymer versus the overall monomer conversion is discussed later.

The overall monomer conversions as a function of the reaction time for different molar fractions of St in the initial reaction mixture are shown in Figure 5. The rate of the reaction decreased considerably with an increasing amount of St in the reaction mixture, as shown in Figure 4 by the reduced slope of the individual monomer conversion curves. Similar results have been reported over the full conversion range.¹⁶ This trend was predictable because the homopolymerization of St is slower than that of EA

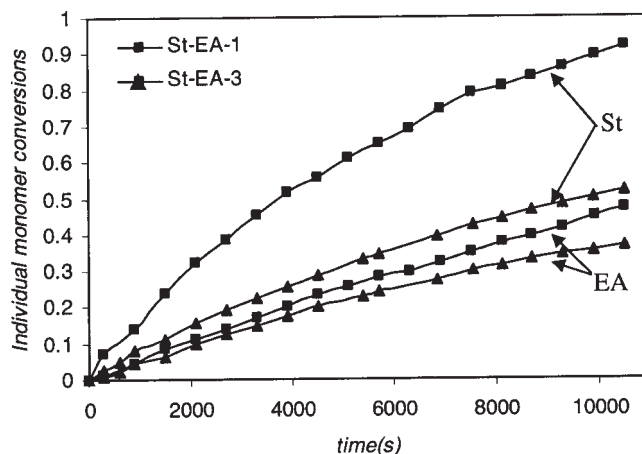


Figure 4 Individual monomer conversions of St and EA versus the reaction time for the free-radical copolymerization of the St/EA system calculated by ¹H-NMR spectroscopy data.

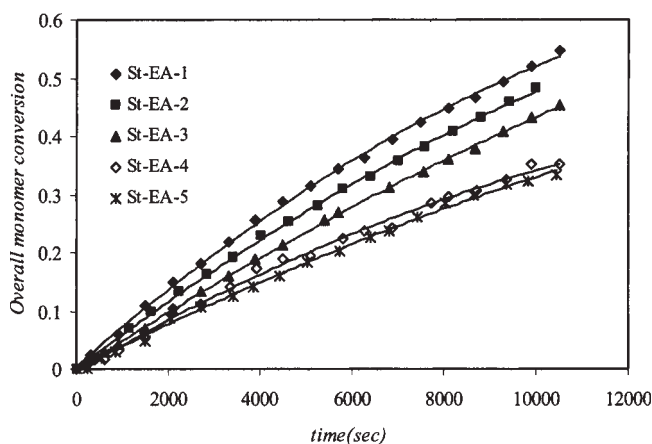


Figure 5 Overall monomer conversion as a function of the reaction time for various molar fractions of St in the initial reaction mixture calculated by $^1\text{H-NMR}$ spectroscopy data.

under similar conditions.^{6,16} This observation is in agreement with the reported data for the coefficients of propagation and termination rates for St and EA, which will be studied later.

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

$$R_p = k_p[M] \left(\frac{R_i}{2k_t} \right)^{1/2} \quad (6)$$

where R_i is the initiation rate, k_t is the coefficient of the termination rate (average), k_p is the coefficient of the propagation rate (average), and $[M]$ is the overall concentration of the monomers.

Because R_p (or equivalently slopes of the curves in Fig. 5) is proportional to $k_p k_t^{-0.5}$, Figure 5 shows that from pure EA to pure St, an overall decrease in R_p and therefore a decrease in the overall rate constants (or $k_p k_t^{-0.5}$) are expected. To investigate the effect of the amount of St in the initial reaction mixture on R_p (and then on $k_p k_t^{-0.5}$), the linear parts of the curves of the overall monomer conversion versus time (according to Fig. 5, all the curves up to about 10,000 s are almost linear) were plotted as first-order curves [which were derived by the integration of eq. (6)] via the following equation:

$$\ln \left(\frac{1}{1-x} \right) = k_{\text{obs}} \times t \quad \text{where} \quad k_{\text{obs}} = k_p \left(\frac{f'k_d[I]}{k_t} \right)^{1/2} \quad (7)$$

where x is the overall monomer conversion, f' is the efficiency of the initiator, k_d is the rate constant of initiator decomposition, and k_{obs} is the observed

polymerization rate constant. k_{obs} is equal to the slope of the $\ln[1/(1-x)]$ -time curve. The corresponding curves are shown in Figure 6.

The straight lines in Figure 6 were obtained through the fitting of eq. (7) with data sets. Because f' , the decomposition rate constant of BPO, and its concentration are known, eq. (7) can be used to estimate $k_p k_t^{-0.5}$ from experimental data of k_{obs} obtained from the slope of the curves in Figure 6. The value of f' (for BPO) under the specified conditions used in this study is assumed to be close to 0.7.³⁵ Fehervari et al.¹ observed that the group of initiation rate constants ($2f'k_d$) in the copolymerization of St and EA was linearly related to the molar fraction of the monomers in solution. Ma et al.⁶ investigated the free-radical copolymerization of St and EA in bulk at 40° in the presence of a 2,2'-azobisisobutyronitrile (AIBN) initiator and estimated the dependence of $2f'k_d$ on the molar fraction of styrene in the feed (f_{St}) with the following linear equation:

$$2f'k_d(\text{s}^{-1}) \times 10^6 = 0.537 + 0.209 f_{\text{St}} \quad (8)$$

Similar results have been published for St/EA/50°C and St/EA/BZ/50°C systems.³⁶ As a result, the dependence of $2f'k_d$ on f_{St} in the solution and bulk is similar. Therefore, by knowing the values of $2f'k_d$ for both homopolymerizations of St and EA, we can estimate the dependence of the group of initiation rate constants on the molar fraction of the monomers for copolymerization with this assumption, that $2f'k_d$ has a linear relation with the monomer composition. To the best of our knowledge, the value of $2f'k_d$ for EA/BPO at 70°C does not exist. Furthermore, for St/BPO at 70°C, only k_d has been reported ($k_d = 9.9 \times 10^{-6}/\text{s}$).¹⁵ By supposing that the dependence of $2f'k_d$ on the feed composition for the St/EA/BPO system is similar to that for St/EA/AIBN and that f' is independent of the feed composition and equal

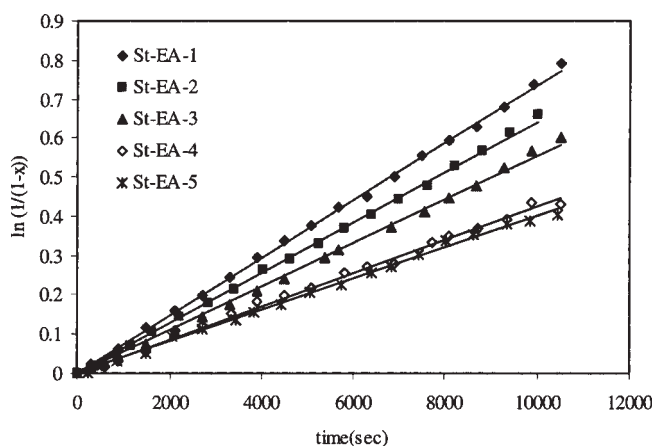


Figure 6 Dependence of $\ln[1/(1-x)]$ versus time for the molar fractions of St (or EA) in the initial reaction mixture.

TABLE VI
Dependence of the Rate Constants of St/EA Copolymerization on f_{St}^0

	f_{St}^0	$k_{obs} \times 10^5$ (s^{-1})	$k_p k_t^{-0.5} \times 10^2$ ($L^{0.5} mol^{-0.5} s^{-0.5}$)	k_p ($L mol^{-1} s^{-1}$)	$k_t \times 10^{-7}$ ($L mol^{-1} s^{-1}$)
Pure EA	0	—	96.1538 ^a	3190.59	1.10000
St-EA-1	0.166771	7.36716	13.2760	776.210	3.41841
St-EA-2	0.270769	6.40279	11.5547	649.782	3.16239
St-EA-3	0.548017	5.55727	9.81260	536.080	2.98464
St-EA-4	0.714729	4.27827	7.70339	508.208	4.35230
St-EA-5	0.893580	4.01045	7.20337	489.187	4.61189
Pure St	1	—	4.44343 ^a	480.857	11.7110

^a Data reported in the literature.

to 0.7,³⁵ we can obtain an equation similar to eq. (8) for St/EA/BPO/70°C:

$$2f' \cdot k_d(s^{-1}) \times 10^6 = 13.651 + 0.209 f_{St} \quad \text{where} \\ f' = 0.7 = \text{cte} \quad (9)$$

From these values, the half-life of the initiator is calculated to be close to 50,010 s for pure St and 50,776 for pure EA.

The ratio of $k_p k_t^{-0.5}$ can be obtained now by the insertion of these values of $f' k_d$ together with the concentration of the initiator (Table II) into eq. (7). The results are listed in Table VI and plotted as a function of the molar fraction of St in the initial reaction mixture in Figure 7.

In Figure 7, the value of $k_p k_t^{-0.5}$ decreases with an increasing amount of St in the initial feed, and this indicates that the square root of k_t decreases less than corresponding k_p . This is expected from the known values of k_p and k_t for the homopolymerizations of St and EA (discussed later).

From the experimental data at hand, it is possible to calculate the ratio $k_p k_t^{-0.5}$ for the polymerization of pure St and EA. k_p and k_t values for the free-radical homopolymerization of St at 70°C have been reported to be 480.857³⁷ and $1.171 \times 10^8 L mol^{-1} s^{-1}$,³⁸ respectively. Therefore, the value of $k_p k_t^{-0.5}$ for the homopolymerization of St at 70°C is calculated to be $0.0444 L^{0.5} mol^{-0.5} s^{-0.5}$. k_p and k_t values for the homopolymerization of EA at 70°C have not been reported. However, the value of $k_p k_t^{-0.5}$ at 70°C for the free-radical homopolymerization of EA in benzene is reported to be $0.962 L^{-0.5} mol^{-0.5} s^{-0.5}$.³⁹

Now, to calculate the individual values of k_p and k_t for pure EA, the value of one of them should be known. The values of k_p and k_t at 40°C for EA/benzene have been reported.⁶ Generally, in free-radical homopolymerization, k_t is almost independent of the temperature and monomer concentration. For example, the value of $k_t(70^\circ C)/k_t(40^\circ C)$ for the homopolymerization of St is calculated to be 1.189,³⁸ therefore, the k_t value at 70°C does not have a significant difference from that at 40°C. Because the k_t

value of EA at 70°C has not been reported in the literature, we compulsorily used the k_t value of EA at 40°C, although the difference between the k_t values at 70 and 40°C may be relatively considerable. Hence, from the $k_p k_t^{-0.5}$ and k_t values, the value of k_p can be estimated. The value of k_t at 40°C for the homopolymerization of EA in toluene has been reported to be $1.1 \times 10^7 L mol^{-1} s^{-1}$.⁶ Using these data, we have calculated the value of k_p for the homopolymerization of EA at 70°C to be $3.191 \times 10^3 L mol^{-1} s^{-1}$.

A comparison of this value of k_p for EA with k_p of the homopolymerization of ethyl methacrylate at 70°C, which is almost $1116.4 L mol^{-1} s^{-1}$ [$k_p = 10^{6.61} L mol^{-1} s^{-1} \exp(\frac{-23.4 kJ mol^{-1}}{RT})$],⁴⁰ shows that the calculated k_p value for pure EA is reasonable because the k_p value for the homopolymerization of EA should be more than this value for ethyl methacrylate. The value of k_t (complete bimolecular composition) for the bulk polymerization of pure St at 70°C has been reported to be $1.171 \times 10^8 L mol^{-1} s^{-1}$, whereas the k_t value for EA is almost $1.1 \times 10^7 L mol^{-1} s^{-1}$. Lower k_p and higher k_t values for the homopolymerization of St in comparison with the homopolymerization of EA may be due to the hard and bulky phenyl groups in the St monomer. The larger the side group is of the monomer, the slower the rate will be of monomer addition to a macro-

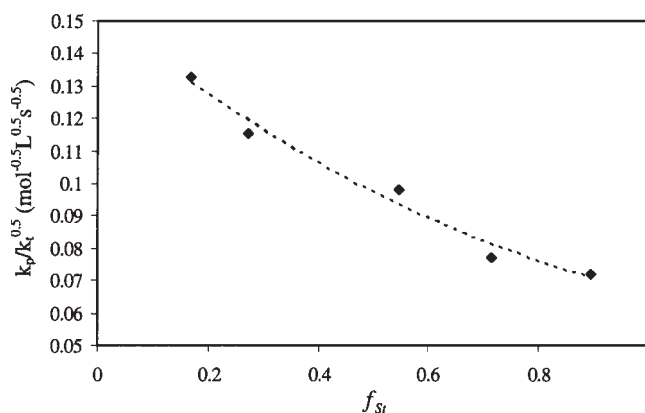


Figure 7 Plot of the ratio $k_p k_t^{-0.5}$ as a function of f_{St}^0 .

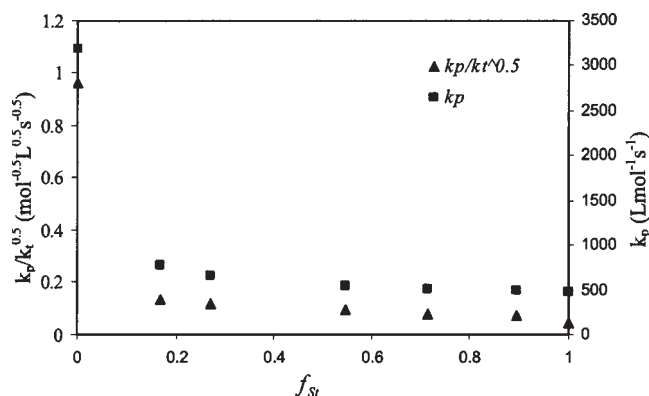


Figure 8 Experimental $k_p k_t^{-0.5}$ and calculated k_p values versus the molar fraction of St in the initial reaction mixture.

radical with a terminal unit of the corresponding monomer. This may result in low and high rates of propagation and termination, respectively.

The values of $k_p k_t^{-0.5}$, k_{pr} , and k_t for the homopolymerizations of pure St and EA at 70°C are shown in Table VI. According to the terminal model, the average copolymerization rate constant for systems containing two monomers can be calculated with the following equation:⁴¹

$$\bar{k}_p = \frac{r_i f_i^2 + 2f_i f_j + r_j f_j^2}{\frac{r_i f_i}{k_{p,ii}} + \frac{r_j f_j}{k_{p,jj}}} \quad (10)$$

where f_i is the molar fraction of monomer i in the initial feed, r_i is the reactivity ratio of monomer i , $k_{p,ii}$ is the propagation rate constant for the homopolymerization of monomer i , and \bar{k}_p is the average propagation rate constant for the copolymerization of monomers i and j . According to eq. (10), \bar{k}_p at a low conversion can be calculated from the composition of the initial feed, the reactivity ratios of the monomers, and the propagation rate coefficients of homopolymerizations. Therefore, the value of \bar{k}_p can be easily calculated for any composition of the feed, and then from $k_p k_t^{-0.5}$, the value of \bar{k}_t for different molar fractions of the monomers in the initial reaction mixture can be obtained. The results of these calculations for \bar{k}_p and \bar{k}_t are shown in Table VI and plotted in Figures 8 and 9, respectively. We believe that our method is an adequately reliable procedure for the determination of $k_p k_t^{-0.5}$. Therefore, with an accurate k_p value, the value of k_t can be obtained with good reliability.

Figure 8 shows that the decrease in the polymerization rate coefficient for molar fractions of St in the reaction mixture from 0 to 0.1668 is more intense than that for the other molar fractions. Qualitatively, the same conclusions have been reported for an St/EA/40°C system.⁶

In Figure 9, the values of k_t calculated by experimental data are shown as a function of f_{St} . All the copolymerization data points fall between $k_{t,St}$ and $k_{t,EA}$, indicating that the termination process is controlled by diffusion. Ma et al.⁶ observed similar results and concluded that the Ito-like diffusion model equation ($k_t^{-1} = F_{St} k_{t,St}^{-1} + F_{EA} k_{t,EA}^{-1}$) describes the experimental data better than the equation of the North diffusion model ($\bar{k}_t = F_{St} k_{t,St} + F_{EA} k_{t,EA}$),⁶ as shown in Figure 9. It is clear from Figure 9 that although both the Ito-like and North diffusion models did not fit the experimental data, the results of the Ito-like model were much better and with good estimations fitted the data.

Composition drifts in the monomer mixture and copolymer

Other important information about the St/EA copolymerization system can be obtained via plots of the comonomer and copolymer compositions versus the overall monomer conversion. These data can be calculated with eqs. (3–5). Figure 10 shows the experimental changes in the comonomer composition in the reaction mixture versus the overall monomer conversion up to 55 mol % for different amounts of St (or EA) in the initial reaction mixture. It is obvious from this figure that with increasing amounts of EA in the initial monomer mixture, the tendency of St for incorporation into the copolymer chains increases, although the overall changes in the experimental monomer mixture composition with increasing conversion is small.

The experimental changes in the copolymer composition as a function of the overall monomer conversion of the reaction for different amounts of St (or EA) in the initial monomer mixture up to a 55 mol % conversion are shown in Figure 11. It is clear that with increasing amounts of EA in the

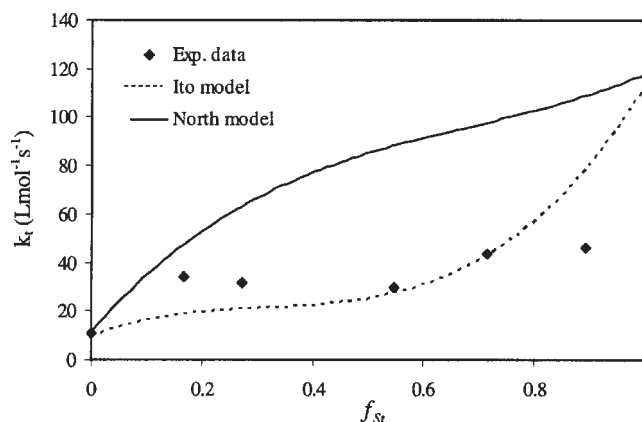


Figure 9 Calculated k_t values versus f_{St}^0 for the solution copolymerization of St and EA.

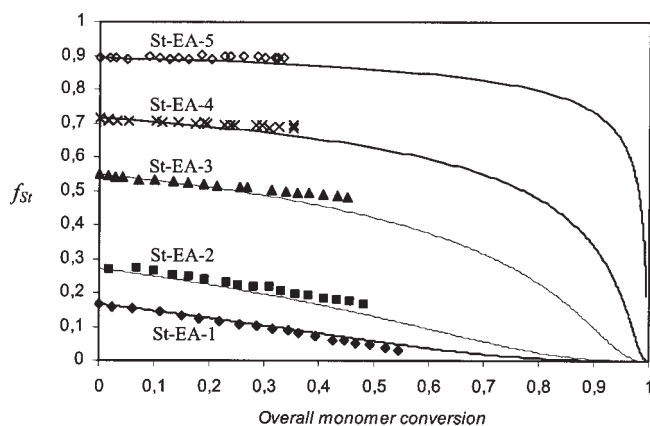


Figure 10 Monomer mixture composition as a function of the overall monomer conversion [the symbols show the experimental data, and the solid curves indicate the theoretical data calculated by eq. (11) with the reactivity ratios of the Tidwell–Mortimer method].

comonomer mixture, the tendency of St to incorporate into the copolymer increases. This result is in good agreement with the data in Figure 10.

The instantaneous copolymer composition equation of Mayo and Lewis²² can be expressed as eq. (11):

$$F_i = \frac{r_i f_i^2 + f_i f_j}{r_i f_i^2 + 2f_i f_j + r_i f_j^2} \quad (11)$$

where F_i is the instantaneous molar fraction of monomer i (methyl acrylate) (MA) in the produced copolymer. In eq. (5), it is the cumulative average molar fraction of monomer i in the copolymer chain.

An integration of eq. (11) leads to the Meyer–Lowry⁴² equation:

$$x = 1 - \left(\frac{f_i}{f_i^0} \right)^\alpha \left(\frac{1-f_i}{1-f_i^0} \right)^\beta \left(\frac{f_i^0 - \delta}{f_i - \delta} \right)^\gamma \quad (12)$$

where

$$\alpha = \frac{r_j}{1-r_j}$$

$$\beta = \frac{r_i}{1-r_i}$$

$$\gamma = \frac{1-r_i r_j}{(1-r_i)(1-r_j)}$$

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

f_i is the instantaneous molar fraction of monomer i in the feed, and f_i^0 is f_i in the initial state. According to the Meyer–Lowry equation, the overall monomer

conversion (x) is related to the monomer composition in the reaction mixture and reactivity ratios.

Some of these parameters are related by a material balance in the following equation, where \bar{F}_i is the cumulative average molar fraction of MA in the copolymer:

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

Using the Meyer–Lowry equation⁴² in conjunction with eq. (13), we obtained theoretical f_i and \bar{F}_i values as functions of the overall monomer conversion for different comonomer mixture compositions and compared them with the corresponding experimental data in Figures 10 and 11. As mentioned before, the monomer reactivity ratios obtained by the Tidwell–Mortimer method were preferentially used in the Meyer–Lowry equation. The fitting of the theoretical values of f_i and \bar{F}_i versus x with the corresponding experimental data was good, indicating the accuracy of the monomer reactivity ratios obtained here.

The theoretical composition curve obtained from the copolymer composition equation of Mayo and Lewis²² [eq. (11)] with the monomer reactivity ratios of the Tidwell–Mortimer method is shown in Figure 12. The experimental data are in good agreement with the theoretical curve, and this means that the composition of this copolymerization system conforms to the terminal model. This behavior has been observed for the St/EA/50°C, St/EA/benzene/50°C,⁴³ and St/EA/40°C⁶ systems. The concave shape of the curves in Figure 12 indicates that the monomer distribution is statistical in nature and that the random copolymer is formed by the copolymerization of St and EA.

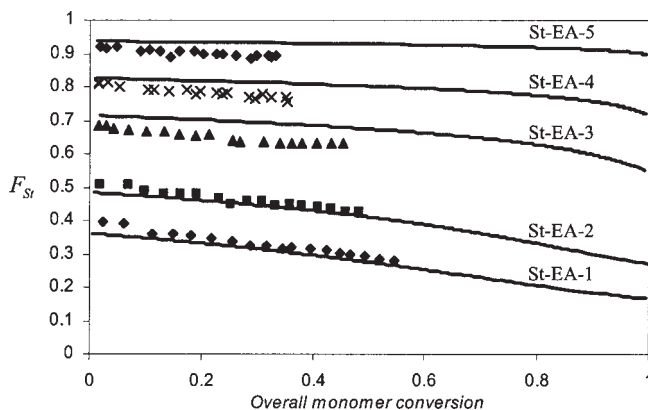


Figure 11 Changes in the copolymer composition as a function of the overall monomer conversion [the symbols show the experimental data, and the solid curves indicate the theoretical data calculated by eq. (11) with the reactivity ratios of the Tidwell–Mortimer method].

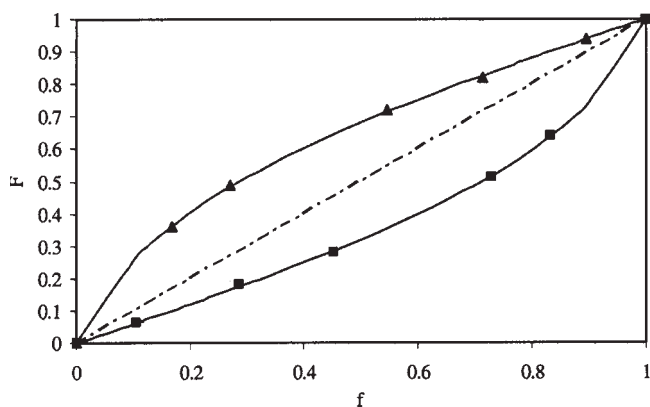


Figure 12 Variation of the copolymer composition [(\blacktriangle) F_{St} and (\blacksquare) F_{EA}] as a function of the monomer composition expressed as f_{St} for St/EA copolymerization (the symbols show the experimental data, and the solid curves indicate the theoretical data calculated by the terminal model copolymer composition equation).

CONCLUSIONS

The *in situ* solution free-radical copolymerization of EA and St at 70°C was studied by $^1\text{H-NMR}$ spectroscopy. In all the experiments, the total molar concentrations of the monomers and initiator were constant, and the only variable under study was the composition of the initial monomer mixture. The monomer reactivity ratios were calculated by different linear and nonlinear methods at both low and high conversions. It was found that the monomer reactivity ratios obtained by high-conversion data were in good agreement with the literature values. The ratio $k_p k_t^{-0.5}$ was estimated from the overall monomer conversion versus the time. This ratio decreased with increasing amounts of St in the initial monomer mixture, and this was reflected in the reduced rate of copolymerization. Composition drifts in the monomer mixture and copolymer versus the overall monomer conversion were also evaluated experimentally and theoretically via reactivity ratios calculated in this work. The fitting of the experimental and theoretical values was appropriate. A tendency of the system toward random copolymerization was observed from an instantaneous copolymer composition curve.

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