Some Monomer Reactivity Ratios of Styrene and (Meth)Acrylates in the Presence of TEMPO

Huang Jianying, Chu Jiayan, Zhuang Jiaming, Chen Yihong, Dai Lizong, Zou Yousi

Department of Material Science and Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, People's Republic of China

ABSTRACT: The living free-radical copolymerizations of styrene (St) with the polar monomers (methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), 2-hydroxyethyl acrylate (HEA), and vinyl acetate (VAc)) mediated by TEMPO and BPO as initiator at 125°C had been analyzed by ^{1}H NMR and gel permeation chromatography (GPC). The data from GPC showed that the polydispersities of the resulted copolymers were below 1.5, and the rate of polymerization increased, while the polydispersity declined with increase in St molar fraction in the feed. Monomer reactivity ratios had been determined by expanded Kelen–Tüdos method. $r_{St} = 1.32$, $r_{MA} = 0.14$; $r_{St} = 1.17$, $r_{EA} = 0.23$; $r_{St} = 0.83$, $r_{BA} = 0.20$; $r_{St} = 0.74$, $r_{MMA} = 0.25$; $r_{St} = 0.76$, $r_{EMA} = 0.30$; $r_{St} = 1.27$, $r_{BMA} = 0.59$; $r_{St} = 1.67$, $r_{VAc} = 1.05$; and $r_{St} = 0.28$, $r_{HEA} = 0.43$. In the copolymerization of St with acrylates the monomer reactivity ratio $r1$ (St) decreases and in the copolymerization of St with methacrylates the monomer reactivity ratio $r1$ (St) increases while the length of the substituted group increases. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3531–3535, 2006

Key words: monomer reactivity ratio; copolymerization; living free-radical polymerization

INTRODUCTION

Free-radical polymerization is an extensively useful polymerization technique because of its easy manipulation and can be applied to a great variety of monomers. Additionally, in free radical random copolymerization, the range of accessible structures and properties is much broader, covering an unlimited field of possible applications. So as an alternative to the high demanding polymerization techniques employing living ionic chain ends, much interest of current researches is focused on the development of the controlled or living free-radical polymerization processes.

Polymers of predetermined molecular weights, narrow molecular weight distribution (with M_w/M_n below the theoretical limit of 1.5), and well-defined block structure[1,2] can be obtained by controlled radical polymerization without the need of special precautions, such as anhydrous conditions and high purity monomers. One of the methods developed for controlled radical copolymerization is stable free-radical polymerization (SFRP). SFRP is a polymerization with reversible termination coupling. Currently, the best example is alkoxyamine-initiated or nitroxide-mediated polymerization, which was first described by Solomon et al.[3] and was later developed by Georges and coworkers[4,5] and Hawker.[6]

To our knowledge, although the comonomer fraction effects on the polymerization rate, molecular weight, and polydispersity in copolymerization have been reported widely for various monomers,[7–15] such as acrylonitrile, methyl methacrylate (MMA), butyl methacrylate (BMA), methyl acrylate (MA), and butyl acrylate (BA), the monomer reactivity ratio on the polymerization of these pairs have not been studied in detail, except by Cuervo-Rodriguez et al.[16] They examined that the monomer reactivity ratios of the statistical copolymerization of styrene (St) and BMA initiated by 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyl-oxy) ethane (PETEMPO) are $r_{St} = 0.44 \pm 0.02$ and $r_{BMA} = 0.55 \pm 0.02$, respectively.

Monomer reactivity ratios are important quantitative values to predict the copolymer composition for any starting feed and to understand the kinetic and mechanistic aspects of copolymerization. They are considered as a possible mechanistic probe, as they express the effects of rate constants. Steric, electronic, and relative hydrophobicity will clearly have different effects with either anionic or radical propagation. It is reasonable to assume that the relative changes in the rate constants of propagation and cross propagation for two monomers will not necessarily be exactly the same for different mechanisms. Usually, monomer reactivity ratios are obtained by establishing the relationship of the composition between the monomer

feed and the copolymer, such as the extended Kelen–Tüdos method.[17]

Therefore, this article is devoted to studying the monomer reactivity ratios of the living free-radical copolymerization of St with MMA, BMA, ethyl methacrylate (EMA), MA, ethyl acrylate (EA), BA, 2-hydroxyethyl acrylate (HEA), and vinyl acetate (VAc). We obtained the well-defined random copolymers mediated by TEMPO and analyzed monomer reactivity ratios of SFRP according to the Kelen–Tüdos method,[17] which is similar to that of conventional free-radical polymerization.

EXPERIMENTAL

Materials

TEMPO was purchased from Aldrich and used as received without purification. All the other reagents were purchased from Shanghai Chemical Reagent Corp. The monomers were distilled immediately before use. The solvent for the gel permeation chromatography (GPC) samples was tetrahydrofuran (THF), which was distilled twice immediately before use.

Copolymerization of St and other monomers

Polymerizations were carried out in glass ampoules with length of 10 cm and outer diameter of 1.3 cm. The monomer mixture of St and another comonomers, the initiator BPO and TEMPO radical (molar ratio of TEMPO/BPO = 1.2) were mixed, and moved into several numbered tubes. The contents were degassed by argon, sealed off, and immersed in an oil bath thermostated at 125°C for specified times. To measure monomer reactivity ratios, the yield of the copolymerization was controlled below 30%. To measure molecular weight, the yield of the copolymerization was controlled to high conversion.

Measurements of polymers

The structures of the copolymers were analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra were recorded on a Varian Unity Plus-500 spectrometer for 5% (w/v) polymer solution in CDCl$_3$ at 298 K, and tetramethylsilane (TMS) was used as internal standard. The number- and weight-average molecular weights of the polymers were evaluated by GPC at 40°C, using a Waters 410 instrument equipped with four Waters Ultrasytragel columns of pore size 10^4, 2 × 500, and 100 Å, and used polystyrene standards for calibration. THF was used as eluent at a flow rate of 1 mL/min.

RESULTS AND DISCUSSION

Living free-radical copolymerization of St and other monomers

TEMPO is the first and most commonly used nitroxide in living free-radical polymerization. It shows good results with styrenes and styrene-analogues. And a random copolymerization with a wide range of other monomers mediated by TEMPO is possible.

Copolymerization of St and various (meth)acrylates were prepared in glass tubes with mixture of both monomers in different compositions, BPO and TEMPO, in which the molar fraction of St in the feed was varied from 0.9 to 0.1. The tubes were sealed off and immersed in an oil bath thermostated at 125°C for specified times. After polymerization, the contents of each tube were diluted with THF, and the solution was poured under stirring into an excess of methanol. The precipitated polymers were reprecipitated with methanol from THF solutions, isolated by filtration, washed with methanol, and dried at reduced pressure. Conversion were determined gravimetrically and reported in Table I, along with the copolymer compositions and GPC analysis.

GPC measurements

In most systems, except St/HEA copolymerization, the polydispersity indices kept narrow (PD < 1.5), which is the character of living polymerization. Both in the copolymerization of St with methacrylates and the copolymerization of St with acrylates, copolymerization rate increased with the St molar fraction increasing in the feed, which was attributed to continuous thermal self-initiation of St. The decrease in copolymerization rate was correlated with a loss of reaction control, since the polydispersity index became larger as the St molar fraction in the feed decreases, which is the same as in the study of Hawker et al. [10] and Butz et al.[12] In those systems, the character of the copolymerization of St with HEA was different from the others, and the polydispersities of the St/HEA were all above 1.5. That may be the result of the substituted hydroxyl in the HEA monomer. After a short polymerization time, TEMPO caught the hydrogen atom of the hydroxyl group in HEA and converted it to 2,2,6,6-tetramethyl-4-piperidinol, as shown in Scheme 1.

From the data of Table I, we can conclude that most copolymerizations were living free-radical polymerization, except the system of St/HEA copolymerization.

Monomer reactivity ratios

Most of the methods to determine the monomer reactivity ratio are appropriate at low conversion. Only the Mayo-Lewis[18] and the extended Kelen–Tüdos[17] meth-

TABLE I
Copolymerizations of St and Polar Monomers Mediated by TEMPO[a]

Pairs	f_{St}	Time (h)	Conv. (%)	F_{St}	PD	M_n(exp.)/10^{-3}
St–MMA	0.2	10	10.3	0.35	1.68	8.82
	0.4	10	22.4	0.50	1.52	13.61
	0.6	10	41.8	0.66	1.31	16.76
	0.9	10	75.6	0.89	1.26	18.90
St–EMA	0.3	30.5	33.3	0.43	1.59	8.11
	0.4	28	44.5	0.50	1.46	15.19
	0.5	24.5	47.5	0.57	1.35	16.21
	0.8	16	63.0	0.77	1.22	16.94
St–BMA	0.3	7	11.3	0.38	1.21	5.09
	0.4	7	15.3	0.49	1.20	5.70
	0.5	7	17.0	0.59	1.20	6.22
	0.8	7	28.2	0.59	1.14	7.55
St–MA	0.2	124	57.2	0.39	1.33	10.68
	0.3	61	54.8	0.48	1.32	10.27
	0.4	42	55.4	0.58	1.18	10.41
	0.5	34.5	58.5	0.66	1.15	13.66
	0.6	17	43.1	0.73	1.12	10.10
St–EA	0.3	29	26.6	0.47	1.26	7.13
	0.5	29	54.7	0.58	1.28	10.30
	0.6	12.5	67.4	0.68	1.18	11.53
	0.8	12.5	70.6	0.85	1.16	11.72
St–BA	0.2	146.5	47.2	0.37	1.30	8.44
	0.4	12.5	43.0	0.51	1.33	6.00
	0.5	12.5	55.6	0.60	1.26	12.07
	0.8	12.5	55.4	0.83	1.22	17.32
St–HEA	0.2	63	88.9	0.27	2.19	4.78
	0.4	34.5	66.7	0.42	3.06	5.84
	0.6	22.5	93.6	0.55	3.02	7.65
	0.8	22.5	87.4	0.68	5.68	4.36
St–Vac	0.5	31	52.8	0.97	1.22	11.88
	0.6	31	55.2	0.98	1.23	26.40
	0.8	20	61.6	0.99	1.11	25.89

[a] St and monomers at 125°C using a 1 : 1.2 molar mixture of BPO and TEMPO.

ods consider the drift in the comonomer and copolymer compositions with conversion. Usually, in conventional free-radical copolymerization, monomers reactivity ratios are measured by fitting the copolymer composition at low conversion as a function of initial monomer feed composition. However, in living/controlled free-radical polymerization, the copolymer chain slowly formed throughout the reaction and measurements of the copolymer chain composition at low conversion could be affected by the structure of the initiator, which may preferentially react with one comonomer. Therefore, to obtain reliable results, it is necessary to measure the cumulative copolymer composition from 10–20% to high conversion.
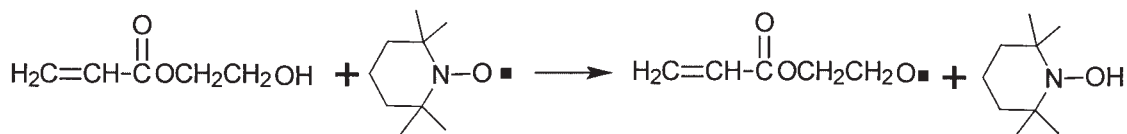
The extended Kelen–Tüdos (K–T) method[17] is the right choice to measure the monomer reactivity ratios in such situation, which can be expressed by the following equations:

$$\eta = (r1 + r2/\alpha)\xi - r2/\alpha$$

where

$$\eta = G/(d+F) \quad \xi = F/(\alpha+F) \quad \alpha = (F_{min}F_{max})^{1/2}$$

$$F = Y/Z^2 \quad G = (Y-1)/Z \quad Z = \log(1-\xi_1)/\log(1-\xi_2)$$

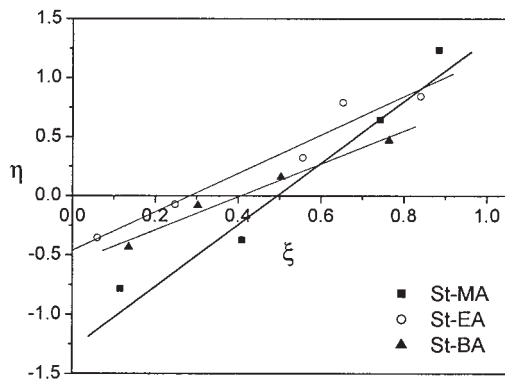**Scheme 1** The reaction of HEA and TEMPO.

Figure 1 Kelen–Tüdos diagram for the bulk copolymerization of St with various acrylates in the presence of TEMPO at 125°C.

where $\xi_2 = W(u+X)/(u+Y)$ and $\xi_1 = \xi_2(Y/X)$
where X and Y represent the molar ratios of monomer 1 to monomer 2 in the comonomers feed and the resulting copolymer, respectively. In addition, W represents the conversion of the copolymerization and μ equals the weight proportion of monomer 2 to that of monomer 1.

Table I contains the relevant data for monomer mixture composition and copolymer composition. Copolymer compositions were determined by ^{1}H NMR from the relative areas of aromatic proton (6.8–7.2 ppm) resonances of the St unit and those of the aliphatic protons (2.8–4.1 ppm) corresponding to (meth)acrylate units (MMA, EMA, BMA: 2.8–4.1 ppm; MA: 3.0–3.8 ppm; EA: 3.4–4.2 ppm; and BA: 3.4–4.2 ppm). The monomer reactivity ratios were obtained from the compositions of copolymers with the conversions less than 30% with the extended Kelen–Tüdos[17] method, in which the variation of the monomer feed composition with conversion is considered.

After finishing the extended Kelen–Tüdos plots in Figures 1 and 2, the intercepts at $\xi = 0$ and $\xi = 1$ of the ξ versus η plots gave $r_{St} = 1.32$, $r_{MA} = 0.14$; $r_{St} = 1.17$,
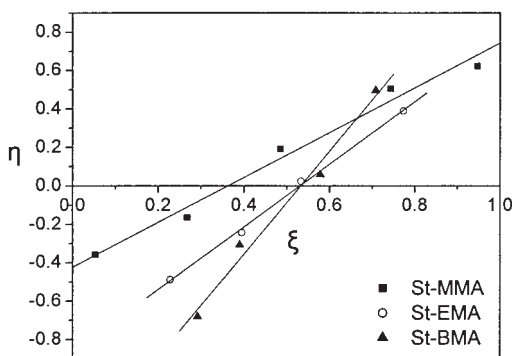

Figure 2 Kelen–Tüdos diagram for the bulk copolymerization of St with various methacrylates in the presence of TEMPO at 125°C.
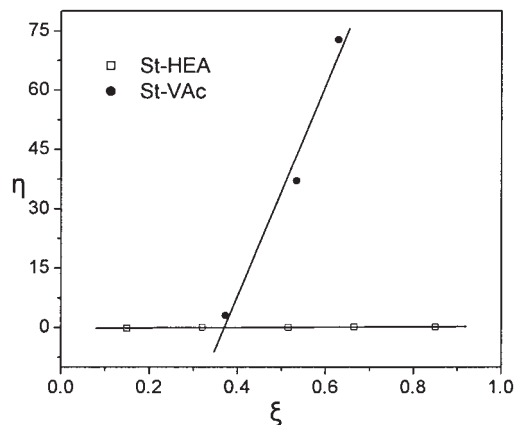

Figure 3 Kelen–Tüdos diagram for the bulk copolymerization of St with VAc and HEA in the presence of TEMPO at 125°C.

$r_{EA} = 0.23$; $r_{St} = 0.83$, $r_{BA} = 0.20$; $r_{St} = 0.74$, $r_{MMA} = 0.25$; $r_{St} = 0.76$, $r_{EMA} = 0.30$; $r_{St} = 1.27$, $r_{BMA} = 0.59$, respectively. These data confirmed that the St was more active than the (meth)acrylate in NMRP.

For the copolymerizations of St with VAc and HEA, some data are not available, and so the monomer reactivity ratios of St with VAc and that with HEA for SFRP were also determined. Copolymer compositions were determined by ^{1}H NMR from the relative areas of aromatic proton (6.8–7.2 ppm) resonances of the St unit and those of the aliphatic protons corresponding to VAc (3.2–3.8 ppm), and HEA (3.4–4.2 ppm). Figure 3 gave the copolymerization data, the monomer reactivity ratios are $r_{St} = 1.67$, $r_{VAc} = 1.05$; $r_{St} = 0.28$, $r_{HEA} = 0.43$, respectively.

The results were summarized along with those of previous work and other works in Table II to compare the monomer reactivity ratios in conventional free-radical polymerization (CFRP). In the living copolymerization of St with acrylates, the monomer reactivity ratios of acrylates (MA, EA, and BA) kept with value as in CFRP, but that of St decreased with the second monomer changing from MA to EA and BA. In the living copolymerization of St with methacrylates (MMA, EMA, and BMA), there was a difference between CFRP and SFRP. The monomer reactivity ratios of methacrylates and that of St increased when the length of the substituted groups of methacrylate increased in SFRP. Methacrylates and acrylates exhibited different characters in the living copolymerization with St. And in all the copolymerizations, the monomer reactivity ratio of St was higher than that of the other comonomer that confirmed St is more active than methacrylates and acrylates in SFRP, which is similar to the conventional copolymerization.

CONCLUSIONS

Living free-radical copolymerizations of St and polar comonomers were prepared in the presence of

TABLE II
Compare of Reactivity Ratio in the Systems

Conventional free-radical copolymerization				Living free-radical copolymerization			
Pairs	$r1$	$r2$	Ref.	Pairs	$r1$	$r2$	Ref.
St–MMA	0.59	0.536	19	St–MMA	0.74	0.25	This paper
St–EMA	0.65	0.29	20	St–EMA	0.76	0.30	This paper
St–BMA	0.54	0.64	20	St–BMA	1.25	0.56	This paper
St–MA	0.825	0.238	19	St–MA	1.32	0.14	This paper
St–EA	0.8	0.2	21	St–EA	1.17	0.23	This paper
St–BA	0.82	0.21	22	St–BA	0.83	0.20	This paper

TEMPO and BPO. The polydispersities of most copolymers were below 1.5, indicating a controlled process during the polymerization, except the copolymerization of St with HEA. By increasing the St molar fraction in the feed, the rate of polymerization increased, while polydispersity indices declined. The monomer reactivity ratios have been reported for SFRP systems, and most of them are first reported. When St is polymerized with acrylates, the monomer reactivity ratio $r1$ (St) decreased, and when St is polymerized with methacrylates, the monomer reactivity ratio $r1$ (St) increased, with the increase in the length of the substituted group. In the presence of TEMPO, living free-radical copolymerization of St with polar comonomers follows a free-radical mechanism.

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