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Copper(0)-Mediated Living Radical Copolymerization of Styrene and Methyl Methacrylate at Ambient Temperature

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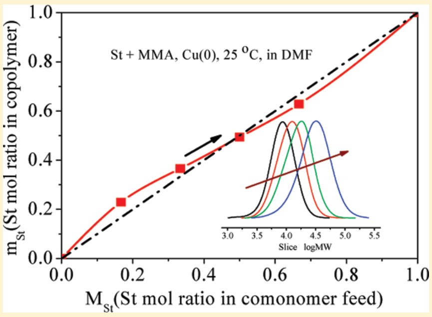
ABSTRACT: In this work, Cu(0)-mediated copolymerization of methyl methacrylate (MMA) and styrene (St) was explored. The polymerization was carried out at 25 °C with *N,N,N′,N′′,N′′*-pentamethyldiethylenetriamine as ligand and *N,N*-dimethylformamide as solvent. The copolymerization proceeded successfully while demonstrating characteristics of "living"/controlled radical polymerization. On the basis of the ^{1}H NMR spectra, the reactivity ratios of MMA and St were calculated to be 0.545 and 0.507, respectively, indicating a random copolymerization. In the case of dimethyl sulfoxide as the solvent, the copolymerization was out of control. The selection of initiator and concentration of Cu(0)/ligand were also important to the controlled process.



INTRODUCTION

The advent of "living"/controlled radical polymerization (CRP) over the past decade has enabled the synthesis of a wide range of macromolecules with well-defined architectures, compositions, and functionalities.[1−3] CRP combines the advantages of traditional free radical polymerization and living ionic polymerization.[4] To date, the most widely used CRPs include nitroxide-mediated radical polymerization (NMP),[5] atom transfer radical polymerization (ATRP),[1,6] reversible addition−fragmentation chain transfer (RAFT),[7,8] and single-electron transfer mediated LRP (SET-LRP).[9−15] Despite the continued debate over the mechanism of SET-LRP in the literature,[9,15] SET-LRP with Cu(0) as catalyst has shown its distinct advantages over other LRPs since its emergence in 2006,[9,10] including low temperature, small amount of catalyst, ultrafast polymerization and high molecular weight polymers with narrow molecular weight distributions. Matyjaszewski et al.[15] argued that SET-LRP was an activator regenerated by an electron transfer-ATRP mechanism, in which Cu(0) was used as a reducing agent. Irrespective of the undefined mechanism, the direct use of Cu(0) as the CRP catalyst is desirable since Cu(0) is cheaper and easier to handle than Cu(I) or Cu(II) complexes. In addition, Cu(0) is highly active and the polymerization temperature can be reduced to room temperature while maintaining a high polymerization rate. At room temperature, Cu(0)-mediated polymerization of MMA was reported with good control over the molecular weights with DMSO as solvent,[16−18] while the polymerization of styrene (St) was reported to be extremely slow with a poorly controlled process at equal reaction conditions.[19] The reason was possibly due to the sluggish initiation of St at room temperature.[19] Recently, Perrier et al. reported the Cu(0)-mediated living radical polymerization of St in toluene at 90 °C with well-controlled behavior.[20] In their communication, the proper selection of ligand was very important to a well-controlled process. *N,N,N′,N′′,N′′*-Pentamethyldiethylenetriamine (PMDETA) was superior to hexamethylene tris(2-aminoethyl)amine (Me_6TREN) and 4,4′-dinonyl-2,2′-bipyridine (diNbpy).[20] It was noteworthy that Me_6TREN and diNbpy were both highly effective ligands in ATRP. Perrier's report implied Cu(0)-mediated polymerization of St may be an intricate control process. In this work, we investigated the feasibility of copolymerization of MMA and St catalyzed by Cu(0) at room temperature. The polymerization rates and "living"/controlled features were stressed. The reactivity ratios of MMA and St were calculated and compared with the systems mediated by other CRP methods. This work would first exploit the copolymerization of MMA and St mediated by Cu(0), especially for those monomers which cannot be polymerized in a controlled manner.

EXPERIMENTAL SECTION

Materials. Methyl methacrylate (MMA) (>99%) and styrene (St) (>99%) monomers were purchased from Shanghai Chemical Reagents Co. (Shanghai, China). The monomers were washed three times with an aqueous solution of sodium hydroxide (5 wt %), followed by washes with deionized water until the solution was neutralized. The resulting solution was then dried over anhydrous magnesium sulfate, distilled twice at reduced pressure, and stored at −18 °C. Methyl 2-bromopropienate (MBP) (97%, Alfa Aesar Co.), 2,2-dichloroacetophenone (DCAP) (97%, Alfa Aesar Co.), *N,N,N′,N′′,N′′*-pentamethyldiethylenetriamine (PMDETA) (98%, Jiangsu Liyang Jiangdian Chemical Factory, China) was dried with 4 Å molecular sieves and distilled under vacuum. Copper (75 μm powder, 99%, Sigma-Aldrich), dimethyl sulfoxide (DMSO) (99.9%, Shanghai Chemical Reagents Co.) and *N,N*-dimethylformamide (DMF) (99.9%,

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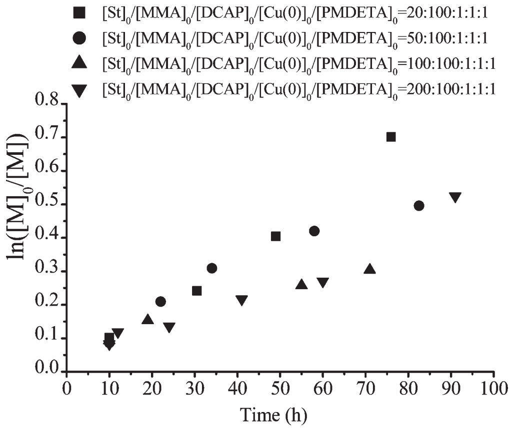

Figure 1. Kinetic investigation ($\ln([M]_0/[M])$ versus time) of Cu(0)-mediated copolymerization of MMA and St, using *N*,*N*-dimethylformamide (DMF) as solvent at various monomer mole ratios. $[St]_0/[MMA]_0/[DCAP]_0/[Cu(0)]_0/[PMDETA]_0$ = (20, 50, 100, 200):100:1:1:1, temperature = 25 °C. DMF = 1.00 mL, MMA = 1.20 mL.

Shanghai Chemical Reagents Co.) were used as received. All other chemicals were obtained from Shanghai Chemical Reagents Co. and used as received unless mentioned.

Characterization. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the resulting polymers were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Waters 2414), using HR 1, HR 2 and HR 4 (7.8 × 300 mm, 5 μm beads size) columns with molecular weights ranging from 10^2 to 5×10^5 g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min and 30 °C. GPC samples were injected using a Waters 717 plus autosampler and calibrated with poly(methyl methacrylate) standards purchased from Waters. The ^{1}H NMR spectrum of the precipitated copolymer was recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard.

Typical Procedures for Cu(0)-Mediated Polymerization. The monomers (MMA, 1.20 mL, 11 mmol; St, 1.30 mL, 11 mmol), solvent (DMF, 1.00 mL), initiator (DCAP, 15.7 μL, 0.11 mmol), catalyst (Cu(0), 7.00 mg, 0.11 mmol), and ligand (PMDETA, 23.4 μL, 0.11 mmol) were added to a 5.0-mL ampule in the following order: Cu(0), monomers, ligand, solvent, and initiator. The solution deoxygenated with three standard freeze−pump−thaw cycles. The ampule was then flame-sealed and placed in a stirred water bath equipped with a thermostat at 25 ± 0.1 °C. After the desired polymerization time, the ampule was cooled by immersion in ice water. Afterward, the ampule was opened, the contents dissolved in tetrahydrofuran (THF), and passed through a small basic Al_2O_3 chromatographic column to remove any unconsumed Cu(0) catalyst and Cu-ion compounds. The resulting solution was precipitated into a large amount methanol. The polymer was isolated by filtration and dried under vacuum until a constant weight at room temperature. The monomer conversion was determined gravimetrically.

■ RESULTS AND DISCUSSION

Copolymerization of Styrene and MMA. To investigate the feasibility of the copolymerization of MMA and St with Cu(0)-mediated at room temperature, a Cu(0)/PMDETA-catalyzed copolymerization was carried out at 25 °C in DMF with 2,2-dichloroacetophenone (DCAP) as an initiator. DCAP was reported to be an effective initiator for the Cu(0)-mediated polymerization of MMA.[9] The reaction conditions were as follows: $[St]_0/[MMA]_0/[DCAP]_0/[Cu(0)]_0/[PMDETA]_0$ = (20, 50, 100, 200):100:1:1:1, DMF = 1.00 mL, MMA = 1.20 mL. Cu(0) powder with a particle size of less than 75 μm was used as the primary activating species. The polymerization kinetics and living characteristics were studied. Figure 1 shows the kinetic data for the copolymerization in DMF. The polymerization proceeded smoothly, and the polymerization rate decreased with the increase of St monomer feed. This is may due to the much higher propagation rate constant of MMA homopolymerization[21] in comparison to that of St homopolymerization.[22] Similar results are also found in Ru(II)-mediated living radical copolymerization of St and MMA at 100 °C.[23]

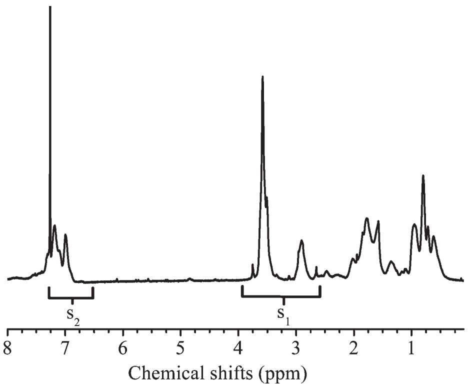

Figure 2. ^{1}H NMR spectra of the copolymer of MMA and St (M_n = 8050, conversion= 9.7%). ($[St]_0/[MMA]_0/[DCAP]_0/[Cu(0)]_0/[PMDETA]_0$ = 20/100/1/1/1, polymerization time =10 h, temperature = 25 °C, MMA = 1.20 mL, DMF = 1.00 mL). $CDCl_3$ was used as the solvent and tetramethylsilane (TMS) as the internal standard.

Figure 2 shows ^{1}H NMR spectra of the polymer obtained in the St/MMA/DCAP/Cu(0)/PMDETA system. In general, the signals in Figure 2 are broad and completely different from those of the homopolymers, indicating the formation of neither block copolymers nor homopolymer blends, but random copolymers.[23] Furthermore, the peak at about 2.85 ppm, which can not be found in the ^{1}H NMR spectra of both St and MMA homopolymers,[24,25] can be observed in the copolymer spectrum (Figure 2). This was assigned to the $-OCH_3$ groups of MMA units bonded to the St units.[26] Opresnik et al.[27] concluded that this peak was the indication of the formation of PS−PMMA random copolymer rather than PS−PMMA block copolymer. The peaks at 7.1 and 3.6 ppm were ascribed to the signals from $-C_6H_5$ and $-OCH_3$ in St and MMA repeat units, respectively. Hence, as shown in Figure 2, the molar unit ratio of St to MMA (copolymer composition) was obtained from the peak intensity ratio of the aromatic protons (6.5−7.3 ppm, 5H, integral value = S_2) for St units to $-OCH_3$ (2.5−3.8 ppm, 3H, integral value = S_1) in MMA repeat units. So we can use the following equation:[28]

$$[St]_{copolymer}/[MMA]_{copolymer} = 3S_2/5S_1 \qquad (1)$$

Figure 3 describes the number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) as functions of the overall monomers conversion at various $[St]_0/[MMA]_0$. The molecular weight of the copolymer increased with monomer conversion and the molecular weight distribution was below 1.50 in most cases (Figure 3a). The GPC traces of the copolymer showed unimodal profiles at different molar ratios of $[St]_0/[MMA]_0$ (Figure 3b − 3e). All of this evidence indicates that both monomers were incorporated into the copolymer chains and the copolymerization was well-controlled irrespective of the monomer feed ratio. It should be noted

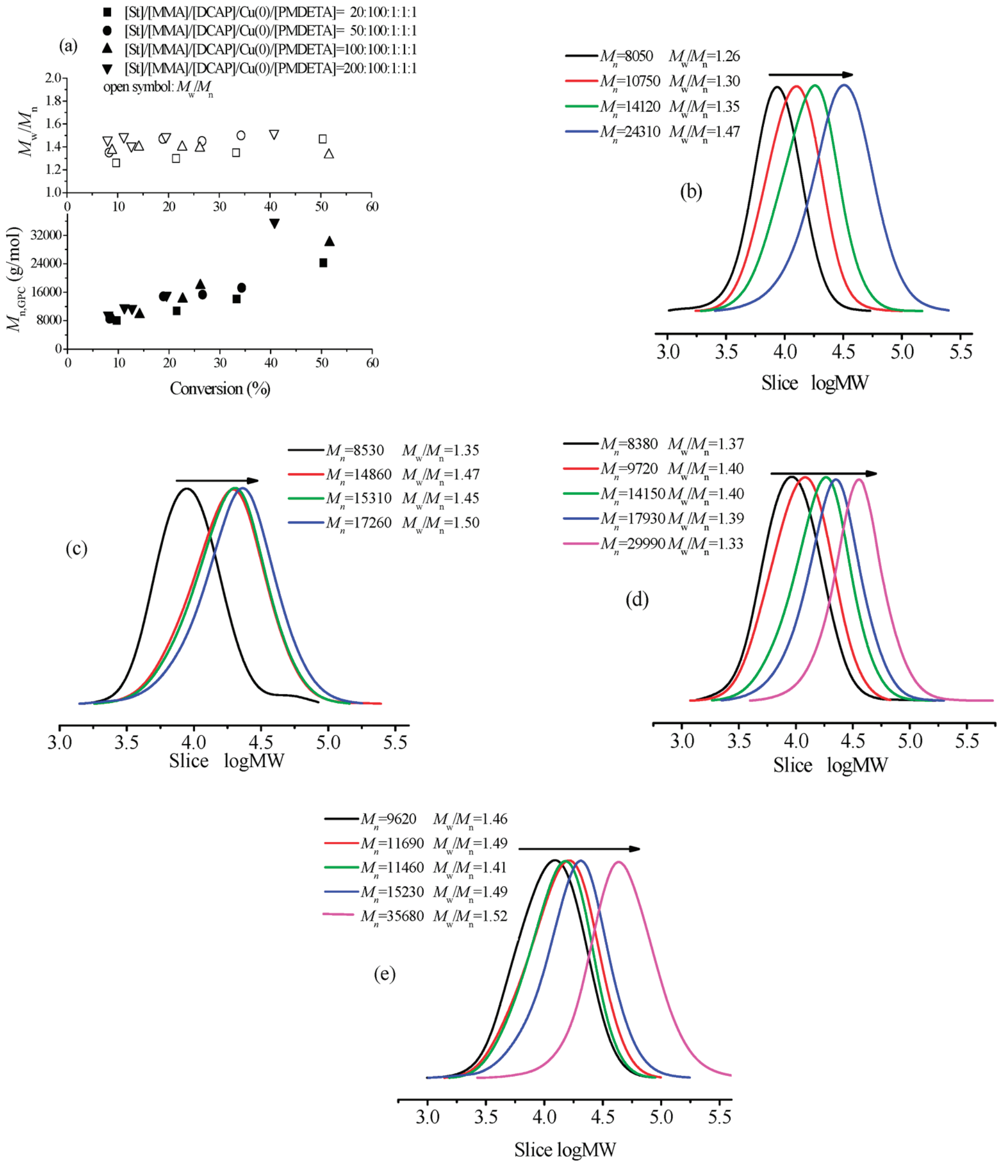

Figure 3. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the copolymer from Cu(0)-mediated living radical polymerization versus the conversion at various $[St]_0/[MMA]_0$. Parts b−e are GPC curves. Reaction conditions are the same as in Figure 1. The ratios of $[St]_0/[MMA]_0/[DCAP]_0/[Cu(0)]_0/[PMDETA]_0$ are 20:100:1:1:1 for part b, 50:100:1:1:1 for part c, 100:100:1:1:1 for part d, and 200:100:1:1:1 for part e, respectively. In all cases of experiments, temperature = 25 °C. DMF = 1.00 mL, and MMA = 1.20 mL.

Table 1. Data for Calculating Reactivity Ratios

entry[a]	M_{St}	M_{MMA}	m_{St}	m_{MMA}	f	F	f/F^2	$(f-1)/F$
1	0.167	0.833	0.229	0.771	0.297	0.2	7.425	−3.515
2	0.333	0.667	0.366	0.634	0.577	0.5	2.309	−0.845
3	0.5	0.5	0.494	0.506	0.976	1	0.976	−0.024
4	0.667	0.333	0.628	0.372	1.688	2	0.422	0.344

[a] Copolymers obtained at low conversation (about 10%) from different monomer feed compositions ($[St]_0/[MMA]_0$ = 20/100, 50/100, 100/100, 200/100). m_{St} and m_{MMA} refer to the St and MMA composition in the copolymer, respectively. M_{St} and M_{MMA} refer to the feed compositions of St and MMA monomer, respectively. $f = m_{St}/m_{MMA}$, $F = M_{St}/M_{MMA}$.

that a general trend in the GPC traces seemed to be an increase in M_w/M_n value with conversion and with increasing styrene feed. The cause may be due to $Cu(II)X_2$ catalyzed termination of the styrenic radical chain ends (β-H elimination).[29] Recent report from Matyjaszewski et al. also indicated that dead chain fraction increased with conversion, resulting from the increased propagating radical.[30]

Calculation of Monomer Reactivity Ratio (*r*). The random copolymerizations of St and MMA catalyzed by Cu(0)/PMDETA at 25 °C were performed with varying monomer feed compositions. The parameters for calculating reactivity ratios with Fineman−Ross method[31] are concluded in Table 1. From Table 1, we find that at any feed composition, both monomers were consumed almost at the same rates.

The relationship between copolymer compositions versus monomer mixture composition is shown in Figure 4. The dashed line is the linear fit for comparison. In the various mole fractions of St in the initial feed, both comonomers polymerized approximately at the same rates, and the calculated copolymer compositions were found to be close to the monomer feed ratios. This suggests that both monomers can copolymerize at similar rates. This result agreed well with the copolymerization by other CRP methods.[23,28] As a result, the composition of the copolymer can be easily predetermined by monomer feed composition. Thus, random copolymers of St and MMA with controlled composition and molecular weights can be readily prepared by the Cu(0)-mediated "living"/controlled radical copolymerization at 25 °C. It was noteworthy that the homopolymerization of St by Cu(0)-mediated at 25 °C was extremely slow and uncontrolled.[19]

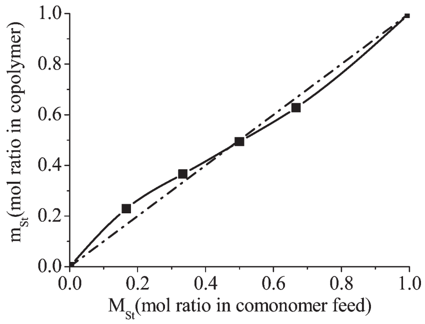

Figure 4. Copolymer composition (m_{St}) as a function of the molar fraction of St in the initial feed (M_{St}) for St/MMA copolymerization.

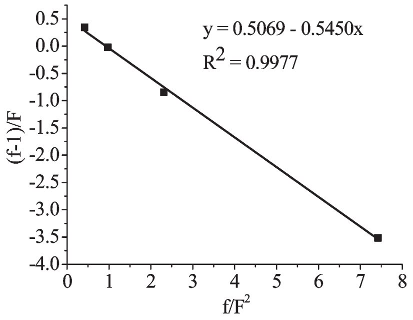

Figure 5. Plot of $(f - 1)/F$ vs f/F^2 for St (M_1) and MMA (M_2) copolymerization with least-squares straight line in Cu(0)-mediated "living"/controlled radical copolymerization.

Based on Fineman–Ross method,[31] the calculation equation is depicted as the following eq 2, where the slope is the negative of the reactivity ratio of MMA ($-r_{MMA}$), and the intercept is reactivity ratio of St (r_{St}).

$$(f - 1)/F = -r_{MMA} \times f/F^2 + r_{St} \quad (2)$$

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The Fineman–Ross method was used to calculate the values for r_{St} and r_{MMA} of the copolymer obtained in the initial stages of copolymerization (<10% conversion). The results were r_{St} = 0.507 and r_{MMA} = 0.545, respectively (see Figure 5).

The obtained reactivity ratios in this work (r_{St} = 0.507, r_{MMA} = 0.545) are different from that of reported by conventional free radical polymerizations (r_{St} = 0.48–0.52, r_{MMA} = 0.42–0.46).[33–37] The terminal-unit-model or Kelen–Tudos calculation methods were used for conventional free radical copolymerizations of St and MMA, while the Fineman–Ross method was used for this study. It was reported that different calculation methods could result in different values.[23,38,39] The reported reactivity ratios for the ATRP copolymerization of St and MMA calculated by the Fineman–Ross method were 0.60 and 0.63 respectively.[23] The deviation of reactivity ratios between ATRP and our work may be due to the different reaction temperature (100 °C in ATRP), reaction media (bulk in ATRP), as well as possible mechanistic differences.

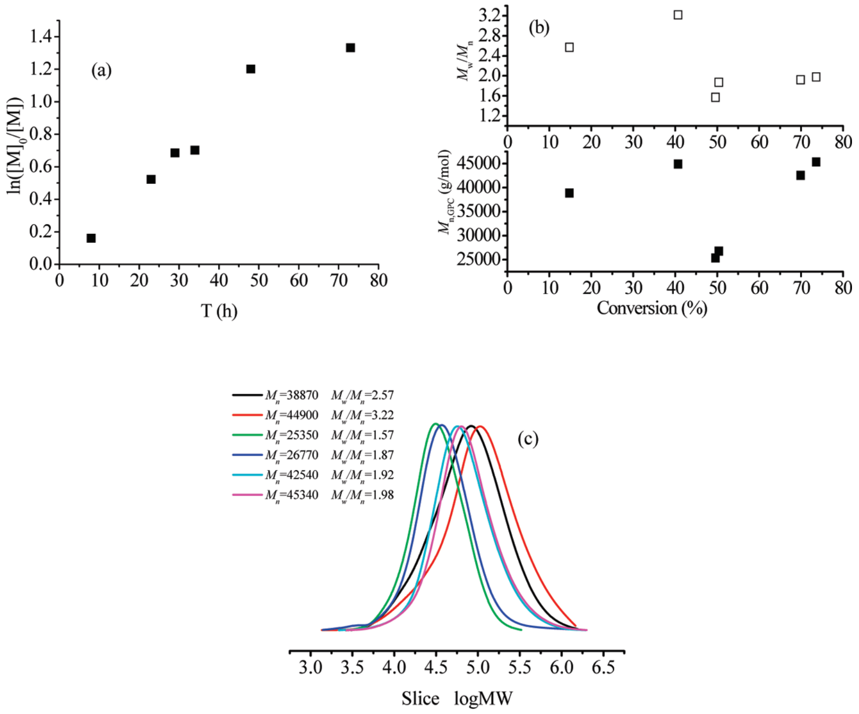

Figure 6. (a) Kinetic investigation (ln([M]$_0$/[M]) versus time) of Cu(0)-mediated living radical copolymerization of MMA and St, DMSO as solvent. (b) Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the copolymer from the polymerization versus the conversion. (c) GPC curves. $[St]_0/[MMA]_0/[DCAP]_0/[Cu(0)]_0/[PMDETA]_0$ = 20:100:1:1:1; temperature = 25 °C. DMSO = 1.00 mL; MMA = 1.20 mL.

Table 2. Effects of Initiator and Catalyst Concentration on the Copolymerization

entry[a]	$[St]_0/[MMA]_0/[initiator]_0/[Cu(0)]_0/[PMDETA]_0$	convn (%)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	100:100:1:0.1:0.1	2.2	3800	1.16
2	100:100:1:0.2:0.2	3.4	5900	1.18
3	100:100:1:0.5:0.5	7.1	6790	1.23
4	100:100:1:1:1	22.7	24 250	1.57
5	100:100:1:2:2	20.4	51 450	2.99
6[b]	20:100:1:1:1	14.9	bimodal	---
7	50:100:1:1:1	11.2	bimodal	---
8	100:100:1:1:1	21.8	bimodal	---

[a] Temperature = 25 °C. Entries 1−5: initiator = DCAP, St = 1.30 mL, MMA = 1.20 mL, DMF = 1.00 mL, and time = 28 h. [b] Entries 6−8: initiator = methyl 2-bromopropienate (MBP), MMA = 1.20 mL, and DMF = 1.00 mL. Entry 6: time = 23 h, St = 0.30 mL. Entry 7: time = 22 h; St = 0.60 mL. Entry 8: time = 34 h; St = 1.30 mL.

Investigation of Reaction Conditions on the Copolymerization. It has been reported that the solvent plays an important role in the Cu(0)-mediated "living"/controlled radical polymerizations. In this work, DMSO, a widely used solvent in Cu(0)-mediated "living"/controlled radical polymerization, was used as the solvent instead of DMF. The results are concluded in Figure 6. As in Figure 6a, the polymerization rate was slightly elevated (73 h, 73.6%) comparison with DMF as solvent at the equal reaction conditions ($[St]_0/[MMA]_0/[DCAP]_0/[Cu(0)]_0/[PMDETA]_0$ = 20:100:1:1:1, Figure 1), however, the molecular weights of the copolymer did not increase with monomer conversion and most of the M_w/M_n values were higher than 1.50 (Figure 6b). All of these indicated that the molecular weights were poorly controlled in case of DMSO as solvent. This evidence confirmed that DMF was much better than DMSO in the copolymerization of St and MMA catalyzed by Cu(0). The reason is not clear at present.

We investigated the effect of initiator structure on the polymerization. Methyl 2-bromopropienate (MBP) was selected as the model initiator. The results with MBP as initiator are summarized in Table 2 (entries 6−8). It was found that the copolymerizations were uncontrolled irrespective of the comonomer feed concentration. The reason may be due to MBP being a poor initiator for MMA, despite it being a good initiator for St.[32] Thus, it can be deduced that in the Cu(0)-mediated "living"/controlled radical copolymerization, the selected initiator should match both comonomers. The effects of Cu(0)/PMDETA concentration on the copolymerization were also explored. It can be found from Table 2 (entries 1−5) that the copolymerization rates increased with increasing concentration of Cu(0)/PMDETA. In Cu(0)-mediated "living"/controlled radical polymerization, an increase in Cu(0) concentration can result in elevation of the polymerization rate since Cu(0) acts as an activator. However, when Cu(0) concentration was too high to keep the equilibrium, the Cu(II) species formed in situ cannot deactivate the propagating radical effectively. Therefore, the polymerization lost its controllability. Thus, the catalyst concentration should be chosen to provide a balance between polymerization rate and controllability.

CONCLUSION

The Cu(0)-mediated "living"/controlled radical copolymerization of MMA and St at 25 °C proceeded smoothly with the features of a "living"/controlled radical polymerization. The polymerization was found to be a random copolymerization. Reactivity ratios of MMA and St in the system were 0.545 and 0.507, respectively. The solvent was found to have an important role on the copolymerization, with DMF giving a more controlled copolymerization than DMSO. The selected initiator should match both monomers for a good control over the copolymerization. Suitable concentration of Cu(0)/PMDETA should be used to balance the polymerization rate with polymerization controllability.

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REFERENCES

(1) Matyjaszewski, K.; Gnanou, Y.; Leibler, L. *Macromolecular Engineering. Precise Synthesis, Materials Properties*, Applications; Wiley-VCH: Weinheim, Germany, 2007.

(2) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93–146.

(3) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2006**, *59*, 669–692.

(4) Szwarc, M. *Nature* **1956**, *178*, 1168–1175.

(5) Hawker, C. *J. Acc. Chem. Res.* **1997**, *30*, 373–382.

(6) Matyjaszewski, K.; Xia *J. Chem. Rev.* **2001**, *101*, 2921–2990.

(7) Chiefari, J.; Chong, Y. K.; Ercole, F.; Kristina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559–5562.

(8) Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. Int. Pat. 980478; *Chem. Abstr.* **1998**, *128*, 115390.

(9) Percec, V.; Guliashvili, T.; Ladislaw, J. S.; Wistrand, A.; Stjerndahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. *J. Am. Chem. Soc.* **2006**, *128*, 14156–14165.

(10) Rosen, B. M.; Percec, V. *Chem. Rev.* **2009**, *109*, 5069–5119.

(11) Nguyen, N. H.; Rosen, B. M.; Lligadas, G.; Percec, V. *Macromolecules* **2009**, *42*, 2379–2386.

(12) Fleischmann, S.; Percec, V. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 4884–4888.

(13) Wright, P. M.; Mantovani, G.; Haddleton, D. M. *J. Polym. Sci., Part A.: Polym. Chem.* **2008**, *46*, 7376–7385.

(14) Martin, E. L.; Ian, W.; Stephen, O.; Anne, D. C.; Anthony, J. G.; Christopher, F.; C, R. B.; David, M. H. *Polym. Chem.* **2010**, *1*, 1086–1094.

(15) (a) Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Wei, M. L.; Woodworth, B. E. *Macromolecules* **1997**, *30*, 7348–7350. (b) Matyjaszewski, K.; Tsarevsky, N. V.; Braunecker, W. A.; Dong, H.; Huang, J.; Jakubowski, W.; Kwak, Y.; Nicolay, R.; Tang, W.; Yoon, J. A. *Macromolecules* **2007**, *40*, 7795–7806. (c) Lin, C. Y.; Coote, M. L.; Gennaro, A.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2008**, *130*, 12762–12774.

(16) Percec, V.; Grigoras, C. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5609–5619.

(17) Zhang, Z. B.; Wang, W. X.; Xia, H. D.; Zhu, J.; Zhang, W.; Zhu, X. L. *Macromolecules* **2009**, *42*, 7360–7366.

(18) Wang, W. X.; Zhang, Z. B.; Zhu, J.; Zhou, N. C.; Zhu, X. L. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 6316–6327.

(19) Subramanian, S. H.; Babu, R. P.; Dhamodharan, R. *Macromolecules* **2008**, *41*, 262–265.

(20) Jessica, T.; Ben, H.; Andrew, W.; Simon, H.; Sébastien, P. *Polym. Chem.* **2010**, *1*, 420–422.

(21) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Olaj, O. F. *Macromol. Chem. Phys.* **1997**, *198*, 1545–1560.

(22) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F. D.; Manders, B. G. *Macromol. Chem. Phys.* **1995**, *196*, 3267–3280.

(23) Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 5582–5587.

(24) Kongkeaw, A.; Wootthikanokkhan, J. *J. Appl. Polym. Sci.* **2000**, *75*, 938–944.

(25) Kongkeaw, A.; Wootthikanokkhan, J. *Sci. Asia* **1999**, *25*, 35–41.

(26) Randall, J. C. *Polymer Sequence Determination*; Academic: New York, 1977; p 109.

(27) Opresnik, M.; Sebenik, A. *Polym. Int.* **1995**, *36*, 13–22.

(28) Na Songkhla, P.; Wootthikanokkhan, J. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 562–571.

(29) Lutz, J. F.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 897–910.

(30) Zhong, M. J.; Matyjaszewski, K. *Macromolecules* **2011**, 10.1021/ma102834s.

(31) Finema, M.; Sidney, D.; Ross *J. Polym. Sci.* **1950**, *5*, 259–265.

(32) Rosen, B. M.; Percec, V. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5663–5697.

(33) Fukuda, T.; Ma, Y. D.; Inagaki, H. *Macromolecules* **1985**, *18*, 17–26.

(34) Willemse, R. X. E.; Herk, V. A. *J. Am. Chem. Soc.* **2006**, *128*, 4471–4480.

(35) Johnson, M.; Karmo, T. S.; Smith, R. *Eur. Polym. J.* **1978**, *14*, 409–414.

(36) Maxwell, I. A.; Aerdts, A. M.; German, A. L. *Macromolecules* **1993**, *26*, 1956–1964.

(37) Uebel, J. J.; Dinan, F. J. *J. Polym. Sci.: Polym. Chem.* **1983**, *21*, 2427–2438.

(38) Brar, A. S.; Puneeta. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2076–2085.

(39) Semsarzadeh, M. A.; Abdollahi, M. *Polymer* **2008**, *49*, 3060–3069.