Rate-acceleration of TEMPO-mediated Polymerization of Styrene in the Presence of Various Acids

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Abstract: The acceleration effect of various organic acids, such as methanesulfonic acid (MSA), ethanesulfonic acid (ESA), 4,4'-sulfonyldibenzoic acid (SDA), diphenylacetic acid (DPAA), and *p*-toluenesulfonic acid (TSA), on the rate of styrene bulk polymerization with 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and benzoyl peroxide (BPO) was investigated. The addition of organic acids significantly accelerated the rate. Among these organic acids, DPAA showed an efficient rate-accelerating effect with living nature of polymerization. When DPAA was used as a rate-accelerating additive for TEMPO-mediated living free radical polymerization (LFRP), the rate of polymerization was dramatically enhanced, the linearity of reaction kinetics was successfully maintained, and the polydispersity was effectively controlled.

Keywords: living polymerization, TEMPO-mediated, polymerization rate, organic acid, rate-acceleration.

Introduction

The desire for accurate control of macromolecular structure with well-defined molecular weight and low polydispersity is a continuing focus in polymer science. Conventionally, well-controlled polymer architectures were only available from ionic polymerization techniques. While these techniques are successful, they are limited by rigorous synthetic requirements and incompatibility with a variety of functional groups.[1] To overcome these drawbacks, new polymerization techniques based on living free radical polymerization (LFRP) have been developed. The field of LFRP has rapidly expanded with major advances occurring in nitroxide-mediated polymerization (NMP),[2-7] atom transfer radical polymerization (ATRP),[8,9] and reversible addition-fragmentation chain transfer polymerization (RAFT).[10,11]

Among the LFRP's, the NMP have attracted considerable interest and a variety of well-defined and complex macromolecular architectures has been successfully synthesized using the NMP technique. The success of this approach can be related to the ability of stable nitroxide free radicals, such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), to react with the carbon-centered free radical of the growing polymer chain end in a thermally reversible process.[4] The working mechanism of TEMPO-mediated LFRP of styrene using

benzoyl peroxide (BPO) is illustrated in Scheme I. The initiation radicals and growing polymer radicals could be capped by a stable TEMPO radical and form dormant chains, then the termination reaction by radical coupling would be retarded due to the reduced radical concentration.[12] This mechanism involves the equilibrium between dormant and active polymer chains called growing radicals. Because the dormant chains are thermally labile, homolytic dissociation of the C-ON bond at high temperatures yields an active polymeric radical and a TEMPO radical.[13] The active polymer radicals can undergo chain extension with monomer and the degree of polymerization has increased. Recombination of active polymer chains with TEMPO free radicals then gives dormant species. This process is believed to be responsible for the living nature of TEMPO-mediated LFRP.

However, one of the major deficiencies of TEMPO-mediated LFRP process was the long reaction time. Usually, 36-72 h may be required to reach completion and obtain large polymers. Long reaction times of the order of 36-72 h are not economically attractive. It has been reported that the rate of TEMPO-mediated LFRP could be raised by the addition of organic acid, such as camphor sulfonic acid (CSA) and 2-fluoro-1-methylpyridinium *p*-toluenesulfonate (FMPTS), glucose, malononitrile, and dodecylbenzenesulfonic acid.[14-19] In the presence of CSA, a higher molecular weight was obtained in less time but a broadening of the polydispersity was observed if the CSA concentration was too

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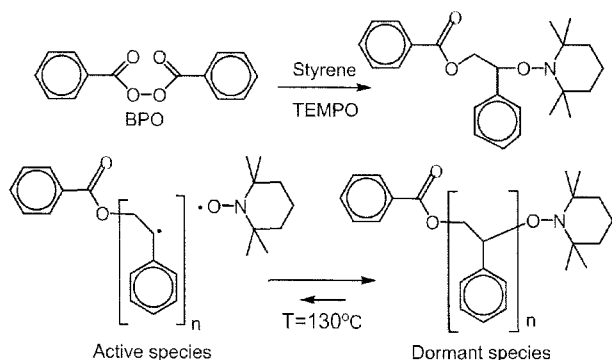
**Scheme I.** Working mechanism of TEMPO-mediated polymerization.

high. It was also reported that acetic anhydride could be used to shorten the reaction time of nitroxide-mediated LFRP, and the mechanisms to explain the acceleration rate of polymerization were proposed.[13]

In this study, we report the rate accelerating effect of several organic acids such as methanesulfonic acid (MSA), ethanesulfonic acid (ESA), 4,4'-sulfonyldibenzoic acid (SDA), diphenylacetic acid (DPAA), and p-toluenesulfonic acid (TSA), for TEMPO-mediated LFRP. The effects of the organic acids on the rate of styrene bulk polymerization with TEMPO and benzoyl peroxide (BPO) are discussed.

Experimental

Materials. Styrene (Junsei Chemicals, Japan) was purified using an inhibitor-removal column (Aldrich, USA) and stored at -5 °C prior to use. 2,2,6,6-tetramethyl-piperidinyloxy (TEMPO, Aldrich) and benzoyl peroxide (BPO, Aldrich) were used without further purification. Methanesulfonic acid (MSA), ethanesulfonic acid (ESA), 4,4'-sulfonyldibenzoic acid (SDA), diphenylacetic acid (DPAA), and p-toluenesulfonic acid (TSA) were used as received. The chemical formulas of the organic acid used as the rate-accelerating additives in this study are presented in Figure 1.

Polymerization. Styrene (10 g, 96.015 mmol), 0.0413 mmol of TEMPO and 0.0413 mmol of BPO, and optionally 0.0206,
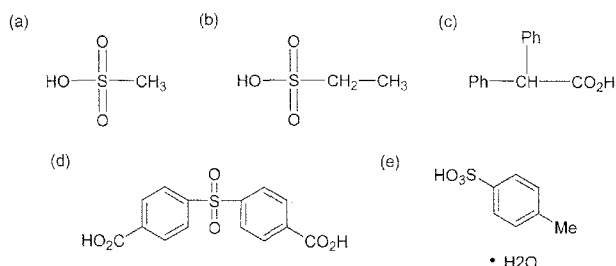
Figure 1. Chemical formulas of acids: (a) methanesulfonic acid (MSA), (b) ethanesulfonic acid (ESA), (c) 4,4'-sulfonyldibenzoic acid (SDA), (d) diphenylacetic acid (DPAA), and (e) p-toluenesulfonic acid (TSA).

0.0413 and 0.0629 mmol of organic acids were charged into a reaction vessel. It is noted that 1.0 molar ratio of [TEMPO]/[BPO], and 0.5, 1.0 and 1.5 molar ratio of [acids]/[TEMPO] were used. The reaction mixture was heated at 125 °C and the polymerization was conducted under nitrogen atmosphere at a constant agitation speed of 200 rpm for a desired time. During the polymerization, aliquots of the sample were periodically taken from the reaction vessel in order to characterize the polymerization products including the conversion, molecular weight and polydispersity.

Characterization. The conversion was calculated gravimetrically. The molecular weight and polydispersity index (PDI) were measured using a Viscotek Gel Permeation Chromatography (GPC). Universal calibration curve was made using ten PS standard samples (Polymer Laboratories) with molecular weights of 580-7,500,000 g/mole. The PS dissolved in THF was injected at a flow rate of 1.0 mL/min.

Results and Discussion

The effect of TEMPO on the bulk polymerization of styrene is represented in Table I. In the absence of TEMPO, the high conversion of 93% was achieved for 6 h and the number-average of molecular weight (M_n) is 51,819 g/mol with the PDI of 2.56, which is a typical value obtained from conventional radical polymerizations. It is noted that the molecular weight of the product was measured using GPC calibrated with PS standards with the range of molecular weights of 580-7,500,000 g/mole. However, in the presence of 1.0 molar ratio of [TEMPO]/[BPO], the reaction rate became much slower and the conversion barely reached 75% for 70 h. The M_n dramatically decreased to 18,348 g/mol and the PDI was well-controlled to 1.15. In the presence of nitroxide such as TEMPO, it was possible to achieve controlled polydispersity and molecular weight by bulk polymerization, as expected. However, the long reaction time and retarded polymerization rate have been great disadvantages in TEMPO-mediated polymerization due to reversible termination mechanism. A definite need for the development of rate accelerating additives therefore exists.

Much effort has been made to enhance the rate of TEMPO-mediated LFRP and it has been reported that the rate improvement can be achieved by the addition of strong organic acids, such as CSA,[14,15,17,20] which was added in an attempt to suppress autopolymerization.[21] We chose five kinds of organic acids, such as MSA, ESA, SDA, DPAA, and TSA, for styrene bulk polymerization to develop new

Table I. The Effect of TEMPO on Bulk Polymerization of Styrene at 125 °C

	Reaction time (h)	M_n (g/mol)	PDI	Conversion (%)
TEMPO=1	70	18,348	1.15	75
TEMPO=0	6	51,819	2.56	93
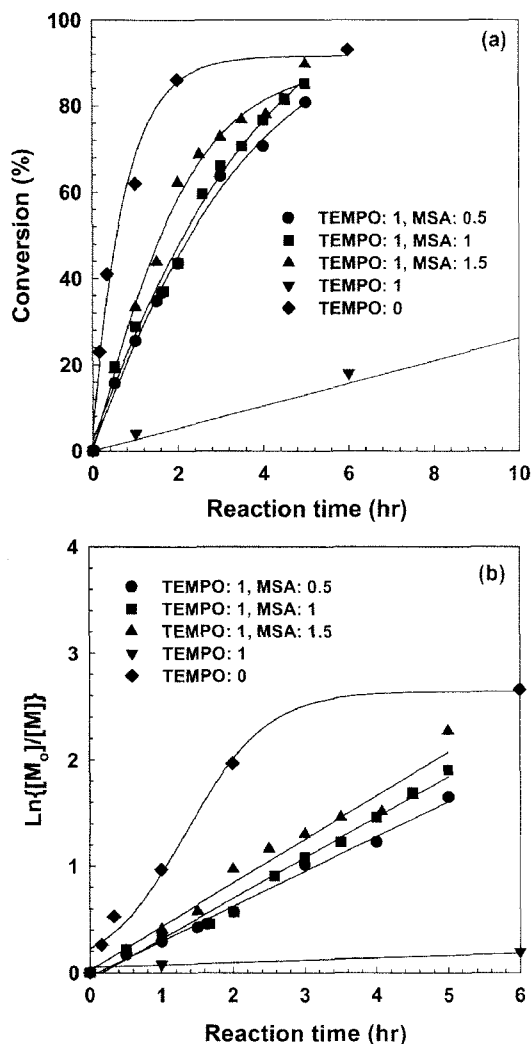
Figure 2. Polymerization characteristics of TEMPO-mediated bulk polymerization of styrene in the presence of various amounts of methanesulfonic acid (MSA). [TEMPO]/[BPO]=0 and 1, [MSA]/[TEMPO]=0.5, 1, and 1.5.

rate-accelerating additives for TEMPO-mediated LFRP.

Figure 2 shows the conversion and polymerization kinetics of TEMPO mediated bulk polymerization of styrene in the absence or presence of TEMPO and MSA as a function

of the reaction time. When neither TEMPO nor an organic acid was used, the polymerization reaction was almost completed for 2 h due to the high reaction temperature of 125 °C. However, when 1.0 molar ratio of [TEMPO]/[BPO] without the acids was used, the reaction rate was retarded and low conversion of 18.5% was obtained for 6 h. To overcome the retardation of reaction rate in the presence of TEMPO, MSA was added and the effect of concentration on the rate acceleration was then studied. As shown in Figure 2(a), when the MSA concentration was increased from 0.5 to 1.5 molar ratio of [MSA]/[TEMPO], there was a distinct increase in the rate of polymerization. The rate enhancement mechanism due to organic acids such as CSA in nitroxide-mediated polymerization involves the consumption of nitroxide radicals.[14] The lower nitroxide concentration drives the equilibrium to favor the formation of active radicals, increasing the number of growing chains, and hence increasing the polymerization rate. In addition to direct consumption of the TEMPO radicals, it was suggested that the rate constant for the deactivation between an active radical and nitroxide radical decreases in the presence of acids.[22] It was also reported that the weakening of the C-ON bond in the alkoxyamine could significantly increase the rate of polymerization.[13,23]

The linearity in $Ln\{[M_o]/[M]\}$ versus polymerization time is a typical characteristic of living polymerization, since the number of growing oligomeric radicals is maintained constant throughout the polymerization. When TEMPO was not added in the bulk polymerization of styrene, a nonlinear behavior of the polymerization kinetics, which is a characteristic of conventional radical polymerization, was observed as shown in Figure 2(b). On the other hand, in the presence of TEMPO only, a fair linearity of polymerization kinetics was observed and polymerization rate became much slower. More importantly, when MSA was added as a rate-accelerating additive, it was observed that the polymerization rate was greatly enhanced and the linearity of reaction kinetics was successfully maintained for all MSA concentrations during TEMPO-mediated polymerization. However, when 1.0 and 1.5 molar ratio of [MSA]/[TEMPO] were added, the molecular weights were 86.475 and 102,739 g/mol and PDI values were 1.682 and 1.768 at 85.1 and 89.7% conversion, respectively, shown in Table II. This implies that the use of

Table II. Conversion and Molecular Weight Evolution of Polystyrene Synthesized by TEMPO-Mediated Bulk Polymerization in the Presence of Various Amounts of Acids for 5 h

| Acid	[TEMPO] : [Acids] = 1 : 1			[TEMPO] : [Acids] = 1 : 1.5		
	M_n (g/mol)	PDI	Conversion (%)	M_n (g/mol)	PDI	Conversion (%)
MSA	86,475	1.682	85.1	102,739	1.768	89.7
ESA	85,614	1.675	98.7	83,513	1.784	99.7
SDA	57,251	1.682	79.1	50,371	1.791	97.2
DPAA	50,497	1.626	96.6	71,020	1.500	83.2
TSA	84,787	1.705	81.1	92,618	2.122	60.2
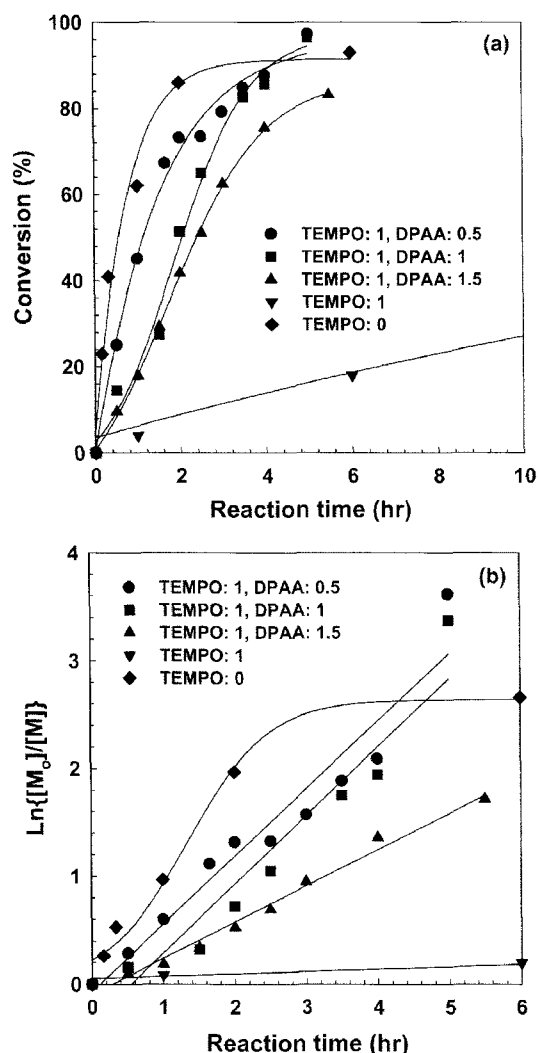
Figure 3. Polymerization characteristics of TEMPO-mediated bulk polymerization of styrene in the presence of various amounts of diphenylacetic acid (DPAA). [TEMPO]/[BPO]=0 and 1, [DPAA]/[TEMPO]=0.5, 1, and 1.5.

MSA in TEMPO-mediated polymerization of styrene is useful in reducing the reaction time but it is not efficient for controlling the polydispersity. It is thought that the added acids with aromatic rings and strong acidity interact with the radical in the active species allowing the resonance-induced stabilization during the TEMPO-mediated polymerization. Thus, the organic acids without aromatic ring and strong acidity show the poor control in the polydispersity.

We varied the amount of all the organic acids for TEMPO-mediated bulk polymerization of styrene and observed the influence on the rate of polymerization. The molecular weight, PDI values and conversion are given in Table II. Among these organic acids, DPAA enhanced the rate of polymerization with better controlled PDI values.

The conversion and polymerization kinetics of TEMPO mediated bulk polymerization with DPAA are shown in
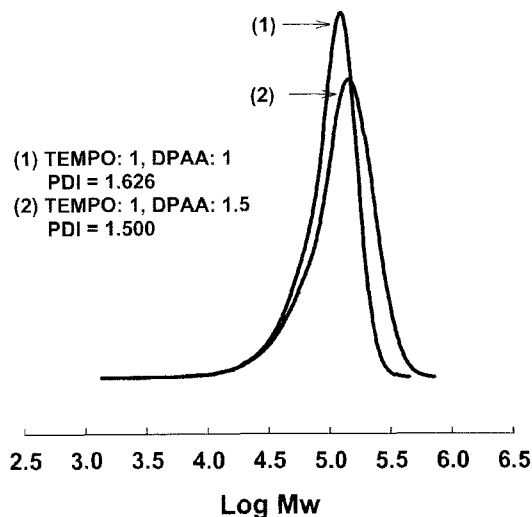
Figure 4. Molecular weight evolution of polystyrene synthesized by TEMPO-mediated bulk polymerization in the presence of different amounts of diphenylacetic acid (DPAA). [TEMPO]/[BPO] =1, [DPAA]/[TEMPO]=1, and 1.5.

Figure 3 as a function of the reaction time. The plots of 0 and 1.0 molar ratio of [TEMPO]/[BPO] are the same as in Figure 2 where MSA was used. By adding DPAA to the TEMPO mediated polymerization, the polymerization rates are efficiently accelerated. And the first order kinetics is well observed for all concentration of DPAA, which indicates the polymerization occurs in a controlled manner. When 1.5 molar ratio of [DPAA]/[TEMPO] was used, the molecular weight of polystyrene was 71,020 g/mol and the PDI was 1.500 with a conversion of 83.2%, shown in Table II. As the molar ratio of [DPAA]/[TEMPO] increased from 1.0 to 1.5, the PDI decreased from 1.626 to 1.500 as shown in Figure 4. It is indicated that the DPAA additive not only increases the rate of polymerization to obtain substantially high conversion, but also gives effective control of the molecular weight and polydispersity of polystyrene. From our experimental results, diphenylacetic acid (DPAA) is believed to act as an efficient rate-accelerating additive for TEMPO-mediated LFRP.

Conclusions

In this study, the effect of various organic acids, such as MSA, ESA, SDA, DPAA, and TSA, as accelerating agents on the rate of TEMPO-mediated bulk polymerization of styrene was investigated. The significant rate-acceleration was observed by adding various organic acids in TEMPO-mediated polymerization. Among these additives, DPAA showed efficient rate-accelerating effects with controlled PDI for TEMPO-mediated LFRP. The rate of polymerization was dramatically enhanced by the addition of DPAA and the linearity of reaction kinetics was successfully maintained for

all the concentrations, which is a characteristic of living polymerization. When 1.5 molar ratio of [DPAA]/[TEMPO] was added, the molecular weight of polystyrene was 71,020 g/mol and the PDI was controlled to 1.500 with a conversion of 83.2%.

References

(1) K. Ueda, A. Hirao, and S. Nakahama, *Macromolecules,* **26**, 2145 (1993).

(2) R. P. N. Veregin, P. G. Odell, L. M. Michalak, and M. K. Georges, *Macromolecules,* **29**, 2746 (1996).

(3) R. P. N. Veregin, P. G. Odell, L. M. Michalak, and M. K. Georges, *Macromolecules*, **29**, 3346 (1996).

(4) C. J. Hawker, G. G. Barclay, A. Orellana, J. Dao, and W. Devonport, *Macromolecules*, **29**, 5245 (1996). S. Abraham, J. H. Choi, J. K. Lee, and I. Kim, *Macromol. Res.*, **15**, 324 (2007). S. Oh, G. Kim, N. Ko, S. E. Shim, and S. Choe, *Macromol. Res.*, **13**, 187 (2007).

(5) E. Malmstrom and C. J. Hawker, *Macromol. Chem. Phys.*, **199**, 923 (1998).

(6) M. Rodlert, E. Harth, I. Rees, and C. J. Hawker, *J. Polym. Sci. Part A: Polym. Chem.*, **38**, 4749 (2000).

(7) R. B. Grubbs, J. M. Dean, M. E. Broz, and F. S. Bates, *Macromolecules*, **33**, 9522 (2000).

(8) K. Matyjaszewski, D. A. Shipp, G. P. McNurthy, S. G. Gaynor, and T. Pakula, *J. Polym. Sci. Part A: Polym. Chem.*, **38**, 2023 (2000).

(9) U. Uegaki, M. Kanigaito, and M. Sawamoto, *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 3003 (1999).

(10) C. P. R. Nair, P. Chaumont, and D. Charmot, *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 2511 (1999).

(11) R. T. A. Mayadunne, E. Rizzardo, J. Chiefari, J. Krstina, G. Moad, A. Postama, and S. H. Thang, *Macromolecules*, **33**, 243 (2000).

(12) C. J. Hawker, *Trends Polym. Sci.*, **4**, 183 (1996).

(13) E. Malmstrom, R. D. Miller, and C. J. Hawker, *Tetrahedron*, **53**, 15225 (1997).

(14) M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer, and M. Saban, *Macromolecules*, **27**, 7228 (1994).

(15) R. P. N. Veregin, P. G. Odell, L. M. Michalak, and M. K. Georges, *Macromolecules*, **29**, 4161 (1996).

(16) P. G. Odell, R. P. N. Veregin, L. M. Michalak, and M. K. Georges, *Macromolecules*, **30**, 2232 (1997).

(17) S. OH, K. Kim, B. H. Lee, S. E. Shim, and S. Choe, *J. Polym. Sci. Part A: Polym. Chem.*, **44**, 62 (2006).

(18) J. Huang, L. Jian, M. Lin, Q. Lin, L. Dai, and Y. Zou, *J. Polym. Sci. Part A: Polym. Chem.*, **43**, 5246 (2005).

(19) K. C. Cheng, J. J. Chen, W. Y. Chiu, L. Y. Wang, and P. C. Wang, *J. Polym. Sci. Part A: Polym. Chem.*, **43**, 42 (2005).

(20) M. F. Cunningham, K. Tortosa, M. Lin, B. Keoshkerian, and M. K. Georges, *J. Polym. Sci. Part A: Polym. Chem.*, **40**, 2828 (2002).

(21) W. C. Buzanowski, J. D. Graham, D. B. Priddy, and E. Shero, *Polymer,* **33**, 3055 (1992).

(22) M. V. Baldavi, N. Mohat, and J. C. Scaiano, *Macromolecules,* **29**, 5497 (1996).

(23) H. Jianying, L. Jian, L. Minghua, L. Qiang, D. Lizong, and Z. Yousi, *J. Polym. Sci. Part A: Polym. Chem.*, **43**, 5246 (2005).