

The Effect of Camphorsulfonic Acid in TEMPO-Mediated Bulk and Dispersion Polymerization of Styrene

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Received November 13, 2004; Revised March 21, 2005

Abstract: The TEMPO-mediated living free-radical bulk and dispersion polymerization of styrene in the presence of camphorsulfonic acid (CSA) are investigated. In the absence of TEMPO and CSA in the bulk polymerization, a conversion of 93% is achieved within 6 hr of polymerization. When only TEMPO is involved in this polymerization, the pseudo-living free-radical polymerization is well achieved, however, the polymerization rate becomes quite slow. This retardation of the polymerization rate is solved by the addition of a low concentration of CSA. In the TEMPO-mediated dispersion polymerization in the presence of CSA, similar trends in the conversion, kinetics, and PDI are observed as those observed in the case of bulk polymerization. When only TEMPO is used in the dispersion polymerization, the resulting particle size becomes quite broad, due to the prolonged polymerization time. However, when a 1.0 molar ratio of CSA to TEMPO is added to the TEMPO-mediated dispersion polymerization, fairly mono-disperse PS microspheres having an average size of 5.83 μm and a CV of 3.4% are successfully obtained, due to the narrow molecular weight distribution of the intermediate oligomers and shortening of the polymerization time. This result indicates that the addition of CSA to the TEMPO-mediated bulk and the use of dispersion polymerization not only shortens the polymerization time, but also greatly improves the uniformity of the microspheres.

Keywords: nitroxide-mediated polymerization, camphorsulfonic acid, polystyrene, dispersion polymerization, microspheres.

Introduction

As the applications of polymeric materials have been expanded to more sophisticated areas, the precise molecular design of polymers has become very important. Among various polymerization methods to synthesize pre-determined molecular structure, the controlled radical polymerization (CRP) has received considerable attention due to their versatile and simple processes, thus a wide variety of polymers with complex structures has been successfully synthesized by several different CRP mechanisms.

Various strategies based on the common concept of alternating the activation and deactivation processes have been realized through the nitroxide-mediated polymerization (NMP),^{1,2} atom transfer radical polymerization (ATRP),^{3,4} and reversible addition-fragmentation chain transfer polymerization (RAFT).^{5,6} In these methods, the success of living free-radical procedures is essentially dependent on the iden-

tity of the mediating radical and various persistent or stable radicals have been discovered.^{7,8}

Certainly, the most widely studied and successful compounds are nitroxides and their associated alkylated derivatives. Since the stable nitroxide free-radicals favor to react with the growing carbon-centered radicals rather than to react with monomer, the reversible capping reaction drastically decreases the concentration of the radical chain ends. Due to the reduced radical concentration, the termination reaction is suppressed and the pseudo-living characteristics are achieved.⁹

Research interests in CRP are being devoted mainly to the synthesis of functional polymers¹⁰⁻¹³ and the application of CRP to various heterogeneous polymerization techniques such as (mini)emulsion, suspension, and dispersion polymerization.¹⁴⁻¹⁶ Among these heterogeneous polymerizations, miniemulsion and suspension polymerizations have been most frequently used. Since polymerization loci are monomer-swollen micelles in miniemulsion and monomer droplets stabilized by polymeric stabilizer in suspension polymerization, respectively, the pseudo-homogeneous reaction takes place in the polymerization loci. Therefore, strictly speaking, miniemulsion and suspension polymeriza-

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tions are not purely heterogeneous.

As another type of purely heterogeneous polymerization, dispersion polymerization provides a simple production route of polymer microspheres in the range of 1-10 μm , which is rarely achieved by other single step process.¹⁷ Such microspheres are recently being used as functional materials in information technology, electric, microelectronic, and bio-related applications.¹⁸⁻²⁰ The dispersion polymerization occurs in a complex manner in particle formation since it is a combination of homogeneous and heterogeneous reaction mechanisms. Initially, all reaction ingredients are dissolved in the reaction medium, then when the polymerization proceeds further, the polymeric particles are nucleated and precipitated upon reaching the critical limit of solubility of the oligomeric species in the medium. The precipitated particles are spherically stabilized by means of polymer stabilizers.^{17,21,22}

For the polymer colloids prepared by the heterogeneous polymerizations, the particle size and their uniformity are considered as one of the most important factors controlling the final properties and applications. There exist a number of literature references on the dispersion polymerization employing CRP techniques to date.^{14a,16c,23,24} In these studies, it was observed that uniformity of the polymer microspheres was poor. The broadening of particle size is caused by the prolonged polymerization time due to reversible termination mechanism of CRPs. In general, a fast nucleation followed by uniform growth of the primary particles is essential to obtain monodisperse final particles by the dispersion polymerization.²⁵ It has been reported that some strong organic acids such as camphorsulfonic acid (CSA) and 2-fluoro-1-methylpyridinium *p*-toluenesulfonate (FMPTS) significantly accelerate the rate of nitroxide-mediated bulk, solution, and miniemulsion polymerizations.²⁶⁻²⁹

In this article, we report the effects of the CSA on the rate-acceleration, the change in the living characteristics and size variation of microspheres in nitroxide-mediated bulk and dispersion polymerization of styrene.

Experimental

Materials. 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), benzoyl peroxide (BPO), and racemic mixture of camphorsulfonic acid (CSA) were purchased from Aldrich, and used as received. Styrene (Junsei Chemicals, Japan) was purified using an inhibitor removal column (Aldrich) and stored at -5°C prior to use. Analytical grade of tripropylene glycol (TPG; Aldrich) was used after distillation off calcium hydride as the medium in the dispersion polymerization. Poly(*N*-vinylpyrrolidone) (PVP; weight-average molecular weight = 40,000; Sigma Chemical Co.) was used as a stabilizer and methylene chloride (Samchun, Korea) was used to purify the resultant polymer.

Polymerization. In the bulk polymerization, styrene (10 g; 96.015 mmol), 0.0413 mmol of TEMPO and 0.01 g

(0.0413 mmol) of BPO, and optionally 0.0206 mmol and 0.0413 mmol of CSA were charged into a reaction vessel. It is noted that the molar ratio of [TEMPO]/[BPO] equals to 1.0 and 0.5, and 1.0 molar ratio of [CSA]/[TEMPO] was used. After sufficient deaeration by dry nitrogen, the polymerization was conducted at 125°C for a desired time.

To perform TEMPO-mediated dispersion polymerization, 100 g of TPG was first charged to the reaction vessel. After complete dissolving of styrene (10 g; 96.01 mmol), BPO (0.1 g; 0.421 mmol), PVP (1 g), and CSA (0.206 and 0.413 mmol) in TPG, nitrogen was purged for deaeration. It is noted that the same molar ratios of [TEMPO]/[BPO] and [CSA]/[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. BPO was added at 70°C and aged for 1 hr under nitrogen. The temperature was then raised to 120°C . It is noted that the polymerization procedure was the same as that reported by Gabaston *et al.*^{14a} During the polymerization, 5 mL of sample was periodically taken from the reaction vessel in order to characterize the polymerization kinetics and products including the conversion, molecular weight, PDI, and particle size. After completion of the polymerization, the resultant product was repeatedly washed with methanol in order to remove the remaining PVP and dried *in vacuo* for 24 hrs.

Characterization. Conversion in bulk and dispersion polymerizations was measured gravimetrically. The molecular weight and PDI were measured using Waters GPC (gel permeation chromatography) equipped with 10^5 , 10^3 , and 10^2 Å μ -Styragel packed high-resolution columns and 510 differential refractometer and Viscotek T50 differential viscometer. Universal calibration curve was made using ten PS standard samples (Polymer Laboratories, UK) with molecular weights ranging 580-7,500,000 g/mole. For GPC measurement, an aliquot of the sample taken from the reaction vessel was repeatedly washed with excess of methanol and centrifuged at 13,000 rpm. Then, the polymer was dissolved in methylene chloride and re-precipitated from methanol, then dried *in vacuo* overnight at 50°C . The PS dissolved in THF was injected at a flow rate of 1.0 mL/min. The morphology of the PS particles was studied using scanning electron microscopy (SEM; Hitachi S-4300) and the number-average particle diameter, D_n , was measured using Scion Image[®] analyzer software by counting the individual 100 particles from SEM microphotographs.

Results and Discussion

TEMPO-Mediated Bulk Polymerization in the Presence of CSA. It has been reported that FMPTS or CSA reduces the concentration of active TEMPO radical,^{26,27} therefore, the rate-acceleration originates from the consumption of TEMPO radicals by FMPTS or CSA in TEMPO-mediated polymeri-

zation. However, when CSA was used in bulk polymerization of styrene, the rate-acceleration was not observed.³⁰

In Figure 1, the polymerization kinetics is represented as $\text{Ln}\{[M_0]/[M]\}$ vs the reaction time of TEMPO-mediated bulk polymerization of styrene in the absence or presence of TEMPO and CSA at 125°C. In this figure, as expected, non-linear behavior of the polymerization rate is observed when TEMPO is not added. On the other hand, when 1.0 molar ratio of $[\text{TEMPO}]/[\text{BPO}]$ is used, the polymerization rate became much slower and shows a fair linearity in $\text{Ln}\{[M_0]/[M]\}$ vs reaction time, which gives characteristics typical living polymerization. The linearity is achieved since the number of radicals is maintained constant throughout the polymerization. More importantly, when 0.5 and 1 molar ratios of $[\text{CSA}]/[\text{TEMPO}]$ are added, the linearity is successfully observed, indicating that living nature of the polymerization is maintained at the fast reaction by addition of CSA. It is noted that both 0.5 and 1.0 molar ratios of $[\text{CSA}]/[\text{TEMPO}]$ give the similar rate of polymerization to that of TEMPO-absent system. The result implies that the rate of polymerization is greatly enhanced even at a low concentration of CSA.

Figure 2 shows the molecular weight evolution of polystyrene during the bulk polymerization in the absence or presence of TEMPO and CSA. The molecular weight evolution as a function of conversion without TEMPO shows a typical shape of free-radical polymerization. With 93% of conversion, the number-average of molecular weight (M_n) is 51,820 g/mol. However, in the presence of 1.0 molar ratio of $[\text{TEMPO}]/[\text{BPO}]$, the M_n dramatically decreases to 18,350 g/mol at 75% of conversion. The theoretically calculated molecular weight (solid line) shows a good agreement

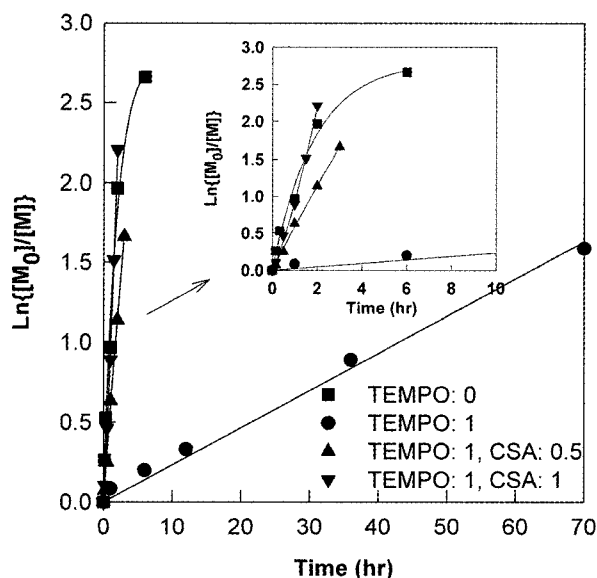


Figure 1. Kinetics of bulk polymerization of styrene in the absence or presence of TEMPO and CSA at 125°C.

with the experimental data for the system where 1.0 molar ratio of $[\text{TEMPO}]/[\text{BPO}]$ is used. When 0.5 and 1.0 molar ratios of $[\text{CSA}]/[\text{TEMPO}]$ are used, the molecular weights increase to 29,060 and 38,460 g/mol at 83 and 89% conversion, respectively. This indicates that the concentration of CSA increases the molecular weight of polystyrene and reduces the reaction time. The increased molecular weight originates from the reduced radical concentration since CSA

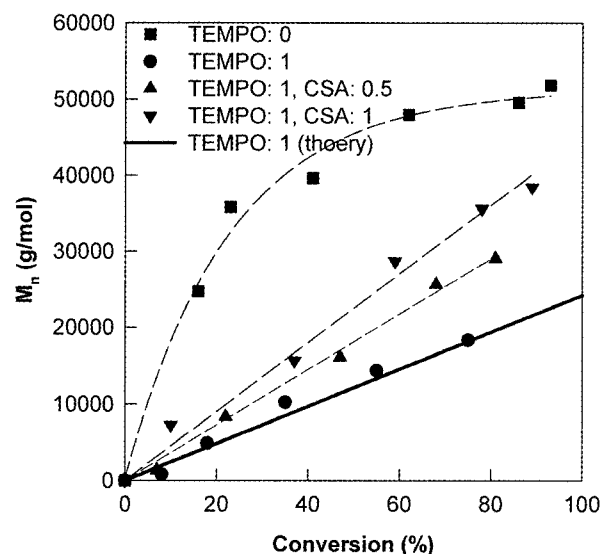


Figure 2. Molecular weight evolution of polystyrene prepared by bulk polymerization without and in the presence of TEMPO and CSA at 125°C. $M_{n(\text{theory})} = (M_{0,\text{styrene}} \times \text{conversion})/[\text{TEMPO}]$.

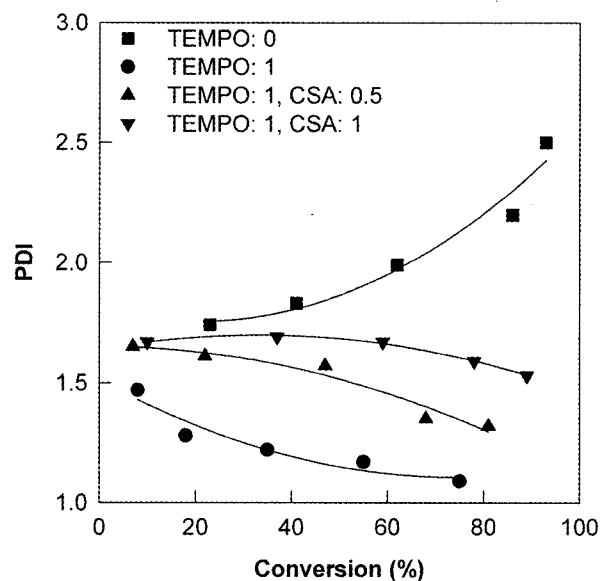


Figure 3. PDI vs conversion of polystyrene prepared by bulk polymerization in the absence or presence of TEMPO and CSA at 125°C.

consumes TEMPO radicals.²⁸

In Figure 3, the PDI of the polystyrene resin prepared by bulk polymerization in the absence or presence of TEMPO and CSA is represented as a function of conversion. Without TEMPO and CSA, the PDI increases from 1.74 to 2.50 between 23 and 93% of conversion, which is a typical value obtained from conventional radical polymerizations. As 1.0 molar ratio of [TEMPO]/[BPO] is added, the PDI decreases from 1.47 to 1.09 with the conversion between 10 and 75%. This is an indicative of the living behavior using nitroxide-mediated polymerization. When 0.5 and 1.0 molar ratios of [CSA]/[TEMPO] are added together with the fixed 1.0 molar ratio of [TEMPO]/[BPO], the PDI decreases from 1.65 and 1.67 to 1.31 and 1.51, respectively. In the case with CSA, a significant lowering in the PDI is observed compared with the TEMPO-absent system. The polymerization results are summarized in Table I. These polymerization characteristics reveal that the addition of CSA effectively accelerate the polymerization rate while the living nature of the polymerization is slightly affected. Based on the results, 0.5 and 1.0 molar ratios of [CSA]/[TEMPO] with the 1.0 molar ratio of [TEMPO]/[BPO] is used in the subsequent dispersion polymerization.

Effects of CSA on TEMPO-Mediated Dispersion Polymerization. It is noted that the amount of BPO was increased 10 fold compared to that in bulk polymerization since higher concentration of BPO was needed to achieve satisfactory conversion in the dispersion polymerization. And the concentrations of TEMPO and CSA were adjusted according to the increased concentration of BPO. When neither TEMPO nor CSA is used, i.e. typical dispersion polymerization, the high conversion of 92% is achieved for 3 hrs due to the high polymerization temperature, but when 1.0 molar ratio of [TEMPO]/[BPO] is used, a quite low conversion of 63% was obtained for 48 hrs as shown in Table II.

To reduce the retardation effect of TEMPO, 0.5 and 1.0 molar ratios of [CSA]/[TEMPO] are employed, then 71.1 and 78.5 % conversions are obtained for 6 hrs. This implies that the use of CSA in TEMPO-mediated dispersion polymerization efficiently accelerates the polymerization rate.

Figure 4 shows the kinetics of the TEMPO-mediated dispersion polymerization of styrene using CSA as the rate-acceleration agent. The linearity in $\text{Ln}\{[M_0]/[M]\}$ vs reaction time is observed and this is characteristics of living nature of polymerization since the number of growing radicals is maintained constant throughout the polymerization.

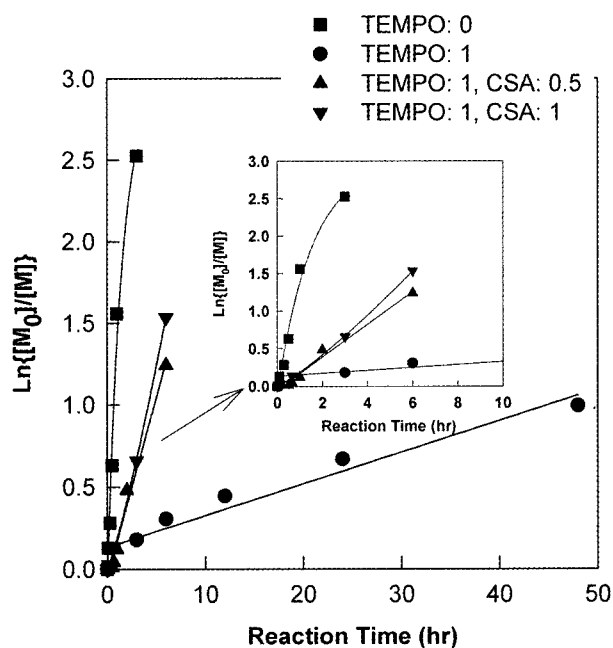


Figure 4. The kinetics of TEMPO-mediated dispersion polymerization of styrene with CSA in tripropylene glycol at 125 °C.

Table I. The Characteristics of PS Prepared by Bulk Polymerization with Various Concentrations of TEMPO and CSA

[TEMPO]/[BPO]	[CSA]/[TEMPO]	Time(hr)	Conversion(%)	M_n (g/mol)	PDI
0	0	6	93.0	51,820	2.50
1.0	0	70	75.0	18,350	1.09
1.0	0.5	3	81.0	29,060	1.31
1.0	1.0	2	89.2	38,460	1.51

Table II. Properties of Resultant PS Microspheres Prepared by Dispersion Polymerization with Various Concentrations of TEMPO and CSA

[TEMPO]/[BPO]	[CSA]/[TEMPO]	Time(hr)	Conversion(%)	M_n (g/mol)	PDI	D_n (μm)	CV(%)
0	0	3	92.0	51,250	2.84	0.65	11.7
1.0	0	48	63.0	16,350	1.16	1.44	35.1
1.0	0.5	6	71.1	30,126	1.30	2.37	36.4
1.0	1.0	6	78.5	38,980	1.38	5.83	3.4

In the absence of TEMPO and CSA, a non-linear kinetics is observed, while pseudo-first order kinetics is obtained in the presence of 1.0 molar ratio of [TEMPO]/[BPO] and 0.5 and 1 molar ratios of [CSA]/[TEMPO]. The molecular weight evolution without and in the presence of CSA during the TEMPO-mediated dispersion polymerization of styrene shows that the experimentally measured M_n is marginally higher than the theoretically calculated M_n molecular weight where 1.0 molar ratio of [TEMPO]/[BPO] is used. The higher experimental molecular weight results from the grafting of PVP with polystyrene since dispersion polymerization is initiated on the stabilizer molecules by abstraction of labile hydrogen.³¹

The PDI of the PS microspheres prepared in the presence of CSA is demonstrated in Figure 5. In the absence of TEMPO, the PDI continuously increases up to 2.9. When 1.0 molar ratio of [TEMPO]/[BPO] is used, the PDI decreases to 1.22 with 63% of conversion. In the cases where CSA is incorporated, the PDI increases to 1.38 and 1.46 for 0.5 and 1.0 molar ratios of [CSA]/[TEMPO], respectively. However, the values are substantially lower than that of TEMPO-absent system. Thus, CSA is working as an efficient rate-enhancing agent in the TEMPO-mediated dispersion polymerization with minimizing the deterioration of the living nature of the polymerization.

CSA as a Particle Size Uniformity-Controlling Agent.

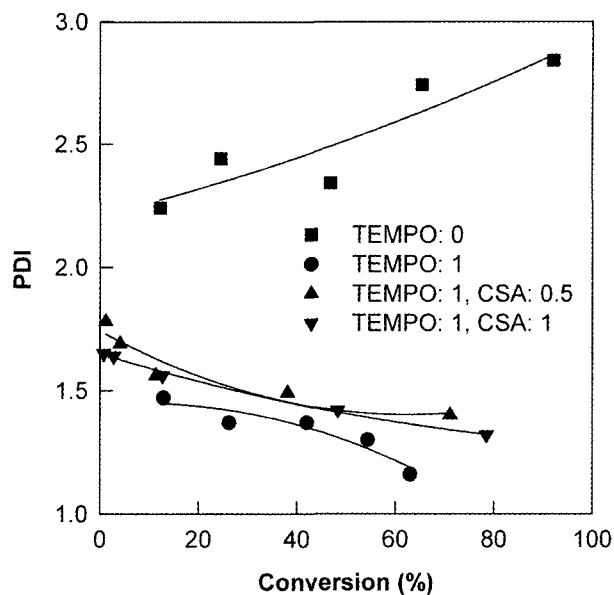


Figure 5. The influence of the addition of CSA on the PDI of PS microspheres prepared by the TEMPO-mediated dispersion polymerization of styrene in tripropylene glycol at 125°C.

The SEM microphotographs of the PS microspheres prepared by various concentrations of TEMPO and CSA are

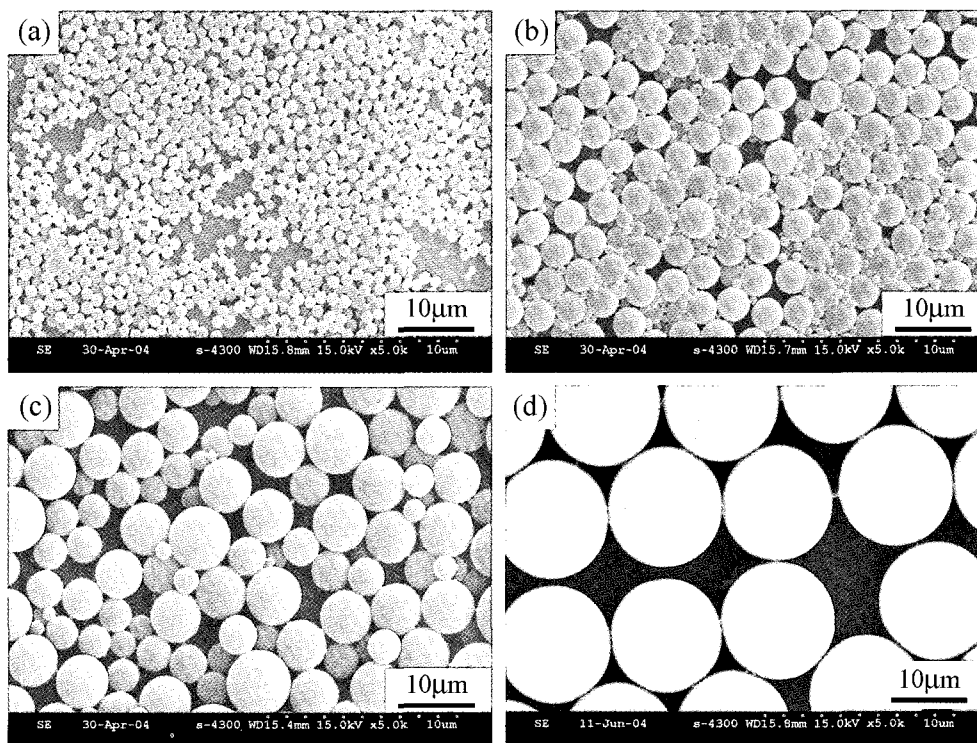


Figure 6. SEM photographs of PS beads prepared under various conditions by dispersion polymerization in tripropylene glycol at 125 °C. (a) [TEMPO]/[BPO] = 0, [CSA] = 0; (b) [TEMPO]/[BPO] = 1, [CSA] = 0; (c) [TEMPO]/[BPO] = 1, [CSA]/[BPO] = 0.5; and (d) [TEMPO]/[BPO] = 1, [CSA]/[TEMPO] = 1.

displayed in Figure 6 and the results are summarized in Table II. When TEMPO and CSA are not involved like conventional dispersion polymerization, the PS microspheres having the D_n of 0.65 μm and CV (coefficient of variation) of 11.7% are produced. In general dispersion polymerization, primary particles are generated from the precipitation of relatively large oligomeric species, and they subsequently grow as microspheres by absorbing oligomers and monomer from the medium. This is shown in Figure 6(a), which indicated the birth of secondary particles during the polymerization. Therefore, the final monodisperse microspheres could be readily produced if the precipitating oligomers have the same molecular weight. In this process, long polymerization time should be avoided since the molecular weight of oligomers is not perfectly identical (PDI of polymers from NMP is not exactly unity).

When 1.0 molar ratio of [TEMPO]/[CSA] is incorporated, the D_n increase to 1.44 μm with broad particle size distribution having the CV of 35.1% (Figure 6(b)) due to the prolonged polymerization time. However with 1.0 molar ratios of [TEMPO]/[BPO] and [CSA]/[TEMPO], fairly monodisperse PS microspheres with 5.83 μm in average size and 3.4% CV are successfully achieved as seen in Figure 6(d). The monodisperse microspheres could be produced due to a narrow molecular weight of intermediate oligomers and shortening of the polymerization time by effectively suppressing the generation of secondary particles. Although the PDI and polymerization rate of 1.0 [CSA]/[TEMPO] system seem similar to those of 0.5 [CSA]/[TEMPO] system, the uniform particles for the former system are resulted by the shortening of nucleation period, i.e. the formation of precursor particles. Since the addition of CSA accelerates the rate of polymerization as shown in Figures 1 and 4, it is suggested that the nucleation period be accordingly shortened.

This result obviously indicates that the addition of CSA in TEMPO-mediated dispersion polymerization not only shortens the polymerization time to obtain substantially high conversion and narrow molecular weight distribution, but also improves the uniformity of the microspheres. However, the marginally affected living nature due to the presence of CSA is left a further work in the bulk and dispersion polymerization.

Conclusions

The TEMPO-mediated living free-radical bulk and dispersion polymerization of styrene are studied in the presence of camphorsulfonic acid (CSA). In the bulk polymerization, the conversion of 93% is achieved within 6 hrs of polymerization in the absence of TEMPO and CSA. However, when TEMPO is solely involved, the pseudo-living free-radical polymerization is well achieved with quite slow polymerization rate. In addition, the addition of CSA effectively

accelerate the bulk polymerization rate while the living nature of the polymerization is slightly affected. Thus, the retardation of the polymerization rate is solved by addition of 0.5 and 1.0 molar ratios of CSA to TEMPO with minimizing the deterioration of the living nature.

In the TEMPO-mediated dispersion polymerization with low concentration of CSA, the similar trends in the conversion, kinetics, and PDI are observed as those observed in the bulk polymerization. The same 0.5 and 1.0 molar ratios of CSA to TEMPO is used, the polymerization time is substantially shortened maintaining the living characteristics and broad particle size distribution due to the prolonged polymerization time. However, with the addition of 1.0 molar ratio of CSA to TEMPO, the fairly monodisperse PS microspheres having 5.83 μm in average size and 3.4% CV are successfully achieved. This is resulted by the shortening of nucleation period, i.e. the formation of precursor particles because CSA accelerates the polymerization rate, followed by the shortening the nucleation period.

Thus, the addition of CSA in TEMPO-mediated dispersion polymerization not only shortens the polymerization time to obtain substantially high conversion and narrow molecular weight distribution, but also greatly improves the uniformity of the microspheres.

Acknowledgements. This work is financially supported by Korean Ministry of Science and Technology as a NRL project (grant no.: M10203000026-02J0000-01410) in the years of 2002-2007.

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