

Dispersion Polymerization of Acrylamide in Methanol/Water Media

Ki-Chang Lee* and Seung-Eun Lee

Department of Polymer Sci. & Eng., Engineering Research Institute, Gyeongsang National University, Jinju 660-701, Korea

Bong-Keun Song

Pulp and Paper Research Lab., Korea Institute of Chemical Technology, P.O. BOX 107, Yusong, Taejeon 305-600, Korea

Received Dec. 18, 2001 ; Revised Mar. 2, 2002

Abstract: Dispersion polymerization of acrylamide was carried out in the media of methyl alcohol/H₂O mixtures using hydroxypropyl cellulose and ammonium persulfate as steric stabilizer and initiator, respectively. The effects of concentrations of initiator and steric stabilizer, amount of monomer, polymerization temperature, methyl alcohol/H₂O ratio, and purification of monomer and nitrogen purge on the particle size of the latices and molecular weight of the polymers were investigated. The average particle diameter increased with increasing concentration of initiator, water content in methyl alcohol/H₂O media, and polymerization temperature, but decreased with monomer and stabilizer concentrations. The viscosity average molecular weight increased with increasing concentrations of monomer, steric stabilizer, and water content in dispersion media, but decreased with initiator concentration and polymerization temperature. The PAM polymers prepared with the purified monomer and the nitrogen purging before the reaction showed the highest molecular weight.

Keywords : dispersion polymerization of acrylamide, methyl alcohol/H₂O media, particle size, viscosity average molecular weight.

Introduction

The dispersion polymerization process has recently received a great attention because of its easiness and convenience in preparing monodisperse polymer particles of large size (1~10 μm) in a single step.¹⁻¹⁵ Preparation of micron size-monodisperse particles of polystyrene (PSt)^{1-4,6,11,12} or poly(methylmethacrylate) (PMMA)^{1,7} has been studied intensely in polar media using steric stabilizers such as poly(vinylpyrrolidone) (PVP),^{6,7,9,11} hydroxypropyl cellulose (HPC),^{3,14} poly(acrylic acid),^{5,15} poly(vinylmethylether),¹⁶ etc. In fact, dispersion polymerization can be as a modified precipitation polymerization in which flocculation is prevented and particle size is controlled by the presence of the steric stabilizer. Dispersion polymerization usually involves the polymerization of a monomer dissolved in an aqueous or nonaqueous media in the presence of an amphiphatic polymeric stabilizer to produce insoluble polymer particles dispersed in the continuous phase. The first studies of this technique were carried out in nonaqueous dispersion systems [NAD]¹⁷⁻²⁰ to prepare the poly(methylmethacrylate) particles

in submicrometer size range by Barret.¹⁷ Later, Almog *et al.*¹ used this polymerization process in polar media to prepare monosize polystyrene and poly(methylmethacrylate) particles up to 5 μm . Most studies on dispersion polymerization deal with of non-polar monomers both in non-polar¹⁷⁻²⁰ and polar media.¹⁻¹⁶ However, studies on dispersion polymerization of water soluble monomers yielding water soluble polymers are rather scarce and poorly understood.^{16,21}

In the present study, we carried out the dispersion polymerization of acrylamide in methyl alcohol/water media using hydroxypropyl cellulose as the stabilizer, ammonium persulfate as the initiator and report the results on the effects of concentrations of monomer, initiator, and steric stabilizer, polymerization temperature, purification of monomer and nitrogen purge, *etc.*

Experimental

Materials. Acrylamide (AM, Junsei) and ammonium persulfate (APS, Shinyo) were used after recrystallization twice in chloroform and methanol, respectively. Hydroxypropyl cellulose (HPC, Aldrich, $\bar{M}_v=100,000$) was used without further purification. As the polymerization medium, methyl alcohol/distilled deionized-water mixtures were used.

*e-mail : kclee@nongae.gsnu.ac.kr

1598-5032/06/140-05 © 2002 Polymer Society of Korea

Dispersion Polymerization. All the ingredients as shown in Table I. were mixed and dissolved clearly in a cylindrical Corning glass tube [2.7(D) × 8.5(L)cm], and purged with O₂-free nitrogen gas for 5 min, after which the tubes were capped. The tubes were then placed in a carriage supported on a rotor submerged in a thermostated water bath at 40 °C and rotated end-over-end at 30 rpm for 48 hrs.

Conversion and Particle Size. The final conversion of the samples was determined gravimetrically after removing unreacted monomer and excessive steric stabilizer by washing in excess amount of acetone. The PAM dispersions (about 10 mL) were treated with acetone (50 mL). The particles were then centrifuged out. The isolated particles were redispersed in acetone (50 mL) and sedimented again by centrifugation. The sedimented particles were dried in a vacuum oven at 40 °C for 48 hrs. The particle sizes were examined by scanning electron microscopy (SEM, Jeol Jsm 6400). A drop of the PAM dispersion was diluted in about 2~3 mL of acetone and one drop of the diluted dispersion was coated on the aluminum stud and was dried at room temperature overnight. The samples were sputter coated with gold, and examined at 15 kV. The particle size of the latices was measured on photographs and particle size distributions (PSD) were determined from the ratio of number (\bar{D}_n)- and weight (\bar{D}_w)-average diameters as follows.⁹

$$\bar{D}_n = \frac{\sum_{i=0}^N D_i}{N}$$

$$\bar{D}_w = \frac{\sum_{i=0}^N D_i^4}{\sum_{i=0}^N D_i^3}$$

$$\text{Polydispersity Index (PDI)} = \frac{\bar{D}_w}{\bar{D}_n}$$

where, N is the total number of particles counted (about 100 particles) and D_i is the diameter of particle i .

Viscosity-average Molecular Weight. The intrinsic viscosity was measured in 0.5 NaCl at 25 °C using an Ubbelohde viscometer. The following equation²² was used to calculate bar \bar{M}_v from $[\eta]$:

$$[\eta] = (7.19 \times 10^{-6})(\bar{M}_v)^{0.77}$$

Results and Discussion

Dispersion Polymerization. In order to investigate the effect of polymerization parameters, dispersion polymerizations with numerous reaction factors were carried out based on the standard recipe as shown in Table I. Most of the polymerizations showed almost 100% conversion to polymer

Table I. Standard Recipe Used in Dispersion Polymerization of Acrylamide

Ingredients	w/v (%)	Amount (g)
AM	5	0.5
HPC	2	0.2
APS	0.0035 ^a	0.008
MeOH/H ₂ O	50/50 ^b	4.0/5.0

Polymerization conditions: 40 °C (polymerization temp.), 30 rpm (revolution speed).

^amol/L. ^bv/v (%).

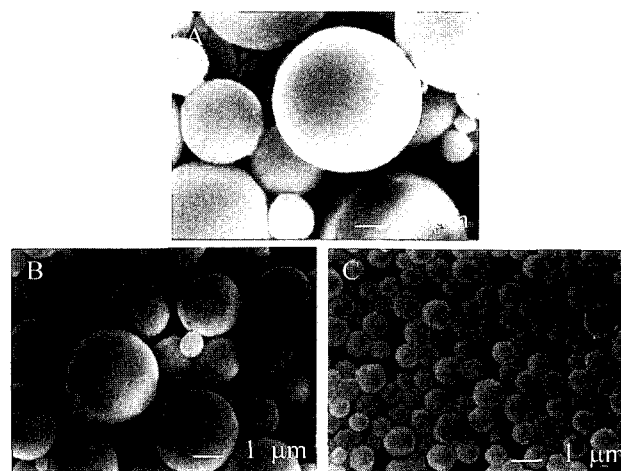


Figure 1. SEM photographs of PAM particles prepared with 3 different HPC concentrations. (A) 1 wt% HPC, (B) 2 wt% HPC, and (C) 4 wt% HPC.

with negligible amount of coagulum.

Effect of Stabilizer Concentration. The polymerizations were performed with three different HPC concentrations (i.e., 1.0, 2.0, and 4.0% w/v) at a constant APS initiator concentration of 0.0035 mol/L in a dispersion medium containing methyl alcohol and H₂O (50/50% v/v) based on the polymerization conditions as described in Table I. Figure 1 and Figure 2 show the photographs of PAM particles prepared with three different stabilizer concentrations and the log-log plots of particle diameter (\bar{D}_n) vs stabilizer concentration and of viscosity average molecular weight vs stabilizer concentration, respectively. The average particle diameter decreased and the viscosity average molecular weight increased with increasing stabilizer concentration, resulting in $\bar{D}_n \propto [\text{HPC}]^{-1.0}$ and $\bar{M}_v \propto [\text{HPC}]^{0.5}$ relationships. The theoretical analysis of Paine²³ predicted an exponent of -0.5 for the dependence of the particle diameter on the stabilizer concentration for the grafting mechanism of stabilization by both the full and adsorption models. On the other hand, stabilization by the homopolymer adsorption mechanism suggested an exponent of -1. The exponent in this work was about -1, suggesting that the stabilization be achieved by the

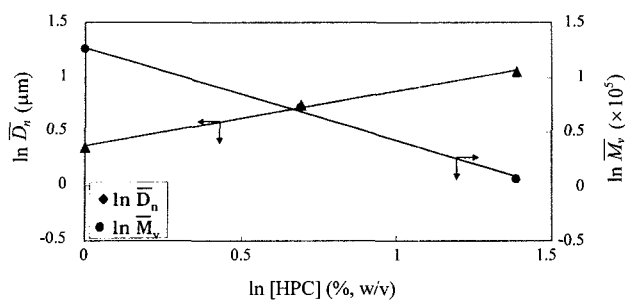


Figure 2. Particle size and \bar{M}_v change as a function of HPC concentration.

latter. To make a comparison, an exponent of -0.78^{16} was reported in a dispersion polymerization of acrylamide using a *t*-butyl alcohol-water medium and poly(vinylmethylether) as the stabilizer. A higher stabilizer concentration provides larger adsorption area onto stabilizing particles, resulting in a greater number of particles of smaller size. The increase in molecular weight with increasing stabilizer concentration suggests considerable polymerization taking place inside the particles due to higher monomer concentration and larger surface area.

Effect of Initiator Concentration. In order to investigate the effect of initiator concentration, the polymerizations were carried out with three different APS concentrations (i.e., 0.0015, 0.0035, and 0.006 mol/L) at a constant HPC concentration of 2% (w/v) in a dispersion medium containing methyl alcohol and H₂O (50/50% v/v) based on the polymerization conditions as described in Table I. Figure 3 and Figure 4 show the photographs of PAM particles prepared with three different initiator concentrations and the log-log plots of particle diameter (\bar{D}_n) vs initiator concentration and of viscosity average molecular weight vs initiator concentration, respectively. The average particle diameter

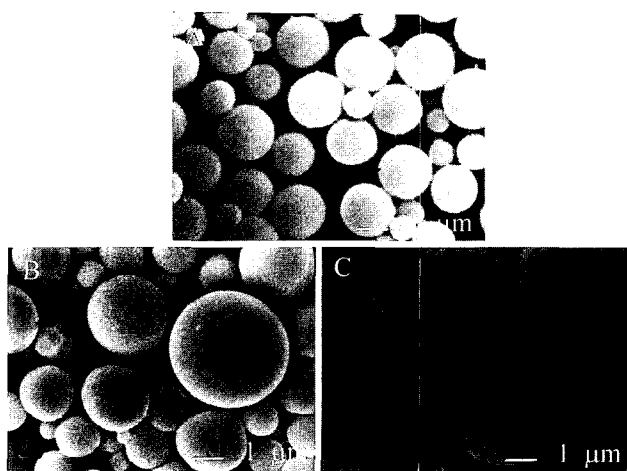


Figure 3. SEM photographs of PAM particles prepared with 3 different APS concentrations. (A) 0.0015 mol/L APS, (B) 0.0035 mol/L APS, and (C) 0.006 mol/L APS.

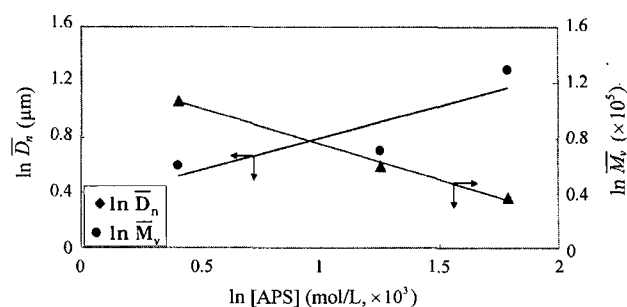


Figure 4. Particle size and \bar{M}_v change as a function of APS concentration.

increased and the viscosity average molecular weight decreased with increasing initiator concentration, resulting in $\bar{D}_n \propto [\text{APS}]^{0.47}$ and $\bar{M}_v \propto [\text{APS}]^{0.5}$ relationships. To make a comparison, an exponent value of $0.4^{11,12}$ has been reported for the dispersion polymerization of styrene. The increase in the initiator concentration causes an increase in the number of free radicals for polymerization. This led to low molecular weight polymer chains which had good solubility in the medium. In dispersion polymerization, the nucleation occurs when the polymer chains reach a certain molecular weight in which they become insoluble in the dispersion medium. At high initiator concentration, due to low concentration of high molecular weight chains in the medium, a few nuclei were produced, leading to a few larger size.

Effect of Monomer Concentration. In this set of experiment, the concentration of monomer was varied with three different AM concentrations (i.e., 5, 20, and 34% w/v) and the amount of the other components were the same as those listed in Table I. Table II and Figure 5 show the results of polymerization experiments and the SEM photographs of PAM particles, respectively. The average particle diameter decreased and the viscosity average molecular weight increased with increasing monomer concentration. As far as the average particle diameter is concerned, it is the inverse of what was observed for the dispersion polymerization of nonpolar monomers in polar solvents. That is, the particle diameter in the present case was proportional to the solubility parameter (δ) of the medium. δ of the medium (Methanol : H₂O = 50 : 50 wt%) and acrylamide are 19.2 and $9.5 \sim 14.5^{24}$ (cal/cm³)^{1/2}, respectively. Since other ingredients besides the

Table II. Effect of AM Concentration in Bottle-Polymerization

Samples	[AM] (% w/v)	\bar{D}_n (μm)	PDI	\bar{M}_v ($\times 10^5$)
A	5	2.25	1.38	1.87
B	20	1.51	1.45	4.18
C	34	0.62	1.53	4.97

Polymerization conditions : [APS] : 3.5 mol/L ($\times 10^{-3}$), [HPC] : 2% (w/v), 40°C, Tumbler, 30 rpm.

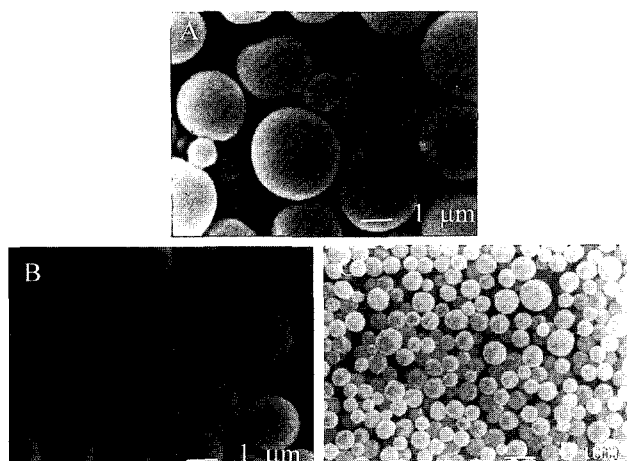


Figure 5. SEM photographs of PAM particles prepared with 3 different AM concentrations: (A) 5 wt% AM, (B) 20 wt% AM, and (C) 34 wt% AM.

solvent components were used in small quantities, the contributions of only methanol and water were taken into account in the solubility evaluation. Thus, the increase in the monomer concentration would result in the decrease in δ of the medium, and at the same time result in the decrease in the solvency of the medium toward the HPC stabilizer. As a result, the adsorption of the stabilizer would be more facile, resulting in the facilitation of primary stabilization and leading to a great number of primary stabilized particles and hence a lower ultimate particle size as the monomer concentration is increased. The increase in molecular weight with an increasing monomer concentration suggests that considerable polymerization has taken place inside the particles through the capture of oligomeric radicals from the continuous phase by the particles. These radicals subsequently underwent polymerization inside the particles and grew to higher molecular weights due to the gel effect.

Effect of the Composition of the Medium. Table III shows the results of the polymerization experiments in which the methanol concentration was varied from 50 to 90 vol%, while the concentrations of the other components were kept constant as shown in Table I. The viscosity average molecular weight of the PAM and the particle size increased with a decrease in methanol concentration. Methanol is a nonsolvent for PAM, but water is a good solvent. Addition of methanol to water makes the solvent increasingly poorer for PAM, such that the polymer becomes insoluble at methanol concentrations greater than 40 vol%. Thus, the solvency of the medium toward the PAM and the HPC stabilizer would decrease gradually with an increase in methanol concentration in the present dispersion polymerization (50~90 vol%). As a result, the adsorption of the stabilizer would be more facile from solvents richer in methanol. This would lead to a lower ultimate particle size as the methanol concentration is increased. In regard to the effect of the medium on the

Table III. Effect of Methyl Alcohol Content in Polymerization Medium

Samples	MeOH/H ₂ O (% v/v)	δ (cal/cm ³) ^{1/2}	\bar{D}_n (μ m)	PDI	\bar{M}_v ($\times 10^5$)
A	50/50	19.2	2.78	1.39	2.10
B	70/30	17.5	2.01	1.18	1.26
C	90/10	15.6	1.64	1.29	0.83

Polymerization conditions : [AM] : 5%(w/v), [HPC] : 2%(w/v), [APS] : 3.5 mol/L ($\times 10^{-3}$), 40 °C, Tumbler, 30 rpm.

Table VI. Effect of Polymerization Temperature

Samples	Temp. (°C)	\bar{D}_n (μ m)	PDI	\bar{M}_v ($\times 10^5$)
A	30	0.98	1.20	3.31
B	40	2.14	1.58	2.16
C	50	3.83	1.15	1.16

Polymerization conditions : [AM] : 5%(w/v), [HPC] 2%(w/v), [APS] : 3.5 mol/L ($\times 10^{-3}$), Tumbler, 30 rpm.

molecular weight, the results are found to be against the general trend of higher molecular weight associated with smaller particle size. For the general heterogeneous polymerizations, the transport process of the monomer into the particles during the polymerization is very important and sensitive to the molecular weight of the resulting polymer. For the present case, the transport of acrylamide monomer into particles occurs through the solvent channels of the swollen particles. As mentioned above, methanol is a non-solvent for PAM and an increase in the methanol content of the medium would decrease the extent of swelling for the polymerizing-PAM particles and thus the concentration of AM monomer in the particles. This effect would result in a decrease the polymerization inside the particles and in a decrease of molecular weight with an increase in methanol content.

Effect of the Polymerization Temperature. Table VI shows the results of the polymerization experiments on the effect of the polymerization temperature. The polymerization recipe used was as same as that in Table I except that the polymerization temperature was varied from 30 to 50 °C. The average particle diameter increased and the viscosity average molecular weight decreased with increasing the polymerization temperature. The increase in the polymerization temperature causes an increase in the number of free radicals generated during the polymerization. This led to low molecular weight polymer chains which had good solubility in the medium. In dispersion polymerization, the nucleation occurs when the polymer chains reach a certain molecular weight in which they become insoluble in the dispersion medium. At high initiator concentration, due to low concentration of high molecular weight chains in the medium, a few nuclei were produced, leading to a few

Table V. Effect of Purification of the Polymerization System

Samples	N ₂ Purging AM Purification	\bar{D}_n (μm)	PDI	\bar{M}_v ($\times 10^5$)
A	N ₂ purging AM purification	1.93	1.79	2.01
B	Without N ₂ purging AM purification	1.67	1.81	1.68
C	N ₂ purging Without AM purification	1.53	1.83	1.18
D	Without N ₂ purging Without AM purification	2.17	1.84	0.85

Polymerization conditions : [AM] : 5%(w/v), [HPC] : 2%(w/v), [APS] : 3.5 mol/L($\times 10^{-3}$), 40 °C.

larger size.

Effect of the Purification of the Polymerization System. In spite of recent studies, the mechanisms involved in dispersion polymerization are still poorly understood. The dispersion polymerization depends on numerous reaction parameters, and the process is highly sensitive to small changes in reaction parameters. In this experiment, the dispersion polymerization of acrylamide was further investigated by studying the effect of the nitrogen purge and monomer purification. Table V shows the results of the polymerization experiments on the effect of the purification of the polymerization system. The polymers prepared with the purified monomer and the nitrogen purging before the reaction showed the highest viscous average molecular weight. However, the PAM latexes prepared in these experiment showed the similar particle size distributions. The presence of inhibitor in unpurified monomer and of oxygen in the polymerization system would reduce the concentration of high molecular weight free radicals in the medium, resulting in the formation of lower molecular weight polymer.

Conclusions

Dispersion polymerization of acrylamide was carried out in the media of methyl alcohol/H₂O mixtures using hydroxypropyl cellulose and ammonium persulfate as steric stabilizer and initiator, respectively, to investigate the effects of concentrations of initiator and steric stabilizer, amount of monomer, polymerization temperature, methyl alcohol/H₂O ratio, and purification of monomer and nitrogen purge on the particle diameter of the latices and molecular weight of the polymers. Important results are as follows.

1. The average particle diameter increased with increasing concentration of initiator, water content in methyl alcohol/H₂O media, and polymerization temperature, but decreased with monomer and stabilizer concentrations.

2. The viscosity average molecular weight increased with

increasing concentrations of monomer, steric stabilizer, and water content in dispersion media, but decreased with initiator concentration and polymerization temperature.

3. $\bar{D}_n \propto [\text{HPC}]^{-1.0}$, $\bar{D}_n \propto [\text{APS}]^{0.47}$, $\bar{M}_v \propto [\text{HPC}]^{0.5}$, and $\bar{M}_v \propto [\text{APS}]^{-0.5}$ relationships were found from the log-log plots.

4. The PAM polymers prepared with both purified monomer and the nitrogen purging before the reaction showed the highest molecular weight.

5. PAM latices of about 1~3 μm with 80,000~500,000 in \bar{M}_v were prepared throughout the study and the resulting latices were all dissolved in water instantly.

Acknowledgment. This work was carried out during the sabbatical year of 2001.

References

- (1) Y. Almog, S. Reich, and M. Levy, *Br. Polym. J.*, **14**, 131 (1982).
- (2) A. Tuncel, R. Kahraman, and E. Piskin, *J. Appl. Polym. Sci.*, **50**, 303 (1993).
- (3) K. P. Lok and C. K. Ober, *Can. J. Chem.*, **63**, 209 (1985).
- (4) C. K. Ober and H. L. Hair, *J. Polym. Sci. Polym. Chem. Ed.*, **25**, 1395 (1987).
- (5) C. K. Ober and K. P. Lok, *Macromolecules*, **20**, 268 (1987).
- (6) A. J. Paine, *J. Polym. Sci. Polym. Chem. Ed.*, **28**, 2485 (1990).
- (7) S. Shen, E. D. Sudal, and M. S. El-Aasser, *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 1393 (1993).
- (8) R. Hu, V. L. Dimonie, E. D. Sudal, and M. S. El-Aasser, *J. Appl. Polym. Sci.*, **55**, 1411 (1995).
- (9) J. M. Saenz and J. M. Asua, *J. Polym. Sci. Polym. Chem. Ed.*, **33**, 1511 (1995).
- (10) D. Horak, F. Svec, and J. M. J. Frechet, *J. Polym. Sci. Polym. Chem. Ed.*, **33**, 2329 (1995).
- (11) C. M. Tseng, Y. Y. Lu, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 2995 (1986).
- (12) A. J. Paine, W. Luymes, and J. McNulty, *Macromolecules*, **23**, 3104 (1990).
- (13) K. C. Lee, H. J. Seo, and J. M. Park, *Korea Polym. J.*, **6**(5), 405 (1998).
- (14) A. J. Paine, *J. Colloid Interf. Sci.*, **138**, 157 (1990).
- (15) T. Corner, *Colloid Surf.*, **3**, 119 (1981).
- (16) B. Bay and B. M. Mandal, *Langmuir*, **13**(8), 2191 (1997).
- (17) K. E. J. Barrett, Ed., *Dispersion Polymerization in Organic Media*, Wiley, New York, 1975.
- (18) A. J. Backhouse, *J. Coatings Tech.*, **54**(693), 83 (1982).
- (19) K. C. Lee, M. A. Winnik, and T. C. Jao, *J. Polym. Sci. Polym. Chem. Ed.*, **32**, 2333 (1994).
- (20) K. C. Lee, N. J. Heo, S. E. Lee, K. S. Kim, and Y. C. Kim, *Polymer (Korea)*, **21**, 173 (1997).
- (21) D. Horak, M. Krystufek, and J. Spevacek, *J. Polym. Sci. Polym. Chem. Ed.*, **38**, 653 (2000).
- (22) J. Klein and K. P. Conrad, *Makromol. Chem.*, **181**, 227 (1980).
- (23) A. J. Paine, *Macromolecules*, **23**, 3109 (1990).
- (24) A. F. M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Florida, 1983, pp 288.