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Rich-Syndiotacticity of Poly(Ethyl Methacrylate) Prepared by Modified Microemulsion Polymerization

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Nanoscale poly(ethyl methacrylate) (PEMA) particles were prepared by a monomer post-added microemulsion polymerization procedure. ^1H NMR analysis suggested that the PEMA samples were rich in syndiotactic content (58–64% rr) and lower in isotactic content (4–6% mm). The glass transition temperatures (Tg's) of the products were also higher than those of the PEMA samples prepared by ordinary free-radical polymerization. The polymer properties, such as particle size, molecular weight, tacticity, and Tg were affected by the reaction conditions. The smaller the particle size, the higher the syndiotacticity, the lower the isotacticity, the greater the molecular weight, then the higher the Tg of PEMA. A possible mechanism of rich-syndiotacticity was also discussed primarily.

Keywords modified microemulsion polymerization, poly(ethyl methacrylate), nanoparticles, syndiotacticity

Introduction

Microemulsion polymerization has been widely studied since the first studies by Stoffer (1) and Gan et al. (2) in the early 1980's, and this procedure can yield stable polymer latexes with a particle size of about 10 to 50 nm. However, traditional microemulsion processes require high surfactant concentration (up to 20 wt% of the total reactor charge) to form stable polymer latexes with a polymer content of less than 10 wt%. Low polymer/surfactant ratios (usually less than 1) and low polymer contents limit the application of microemulsion latexes in industry. Recently, our laboratory developed a modified microemulsion polymerization procedure and nanosize (15–50 nm) poly (methyl methacrylate) latex with low surfactant content (1–2 wt%) and high polymer content (15–35 wt%) was prepared (3, 4). The resulting PMMA samples had higher glass transition temperatures (greater than 120°C) and were rich in syndiotactic content (55–61% rr). Poly(ethyl methacrylate) (PEMA) latex also could be prepared by this

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modified microemulsion polymerization process. The reaction conditions which affect PEMA properties, including particle size, molecular weight, tacticity, and Tg, etc. were discussed and the possible mechanism was proposed in this paper.

Experimental

Materials

EMA from Shanghai Chemical Reagent Co. was distilled under reduced pressure before polymerization. Sodium dodecyl sulfate (SDS), purchased from Shanghai Shenggong Bioengineering Corp., was used as received. Ammonium persulfate (APS) from Shanghai Aijian Reagent Factory was purified by recrystallization in water. Pentanol (POH) from Shanghai Chemical Reagent Co. was used as received. Ascorbic acid from Shanghai Chemical Reagent Co. and a 30% hydrogen peroxide solution from Shanghai Taopu Chemical Factory were used as received. Methanol was purchased from Shanghai Zhenxing Reagent Factory and used as received. Deionized water was used for all experiments.

Polymerization

The recipes of modified microemulsion polymerizations under various conditions are shown in Table 1. A typical procedure with SDS/POH as surfactant/cosurfactant and APS as initiator can be described as follows. The premicroemulsion, composed of the entire amount of surfactant, auxiliary surfactant, water, and a small fraction of monomer was added into a 100 mL, three-necked flask equipped with a reflux condenser, an addition funnel, a nitrogen gas inlet and outlet, and a magnetic stirring bar. The premicroemulsion was heated to 70 ± 2°C for APS initiator (35 ± 2°C for redox initiators) and stirred under a nitrogen atmosphere. Then, the requisite amount of initiator, which was dissolved in a minimum quantity of water, was added. When the polymerization started, the rest of the monomer in the addition funnel was added dropwise into the reaction flask.

The polymer particles were precipitated in methanol. The precipitated polymer was vacuum-filtered, washed successively with methanol and water, then dried in a vacuum desiccator for 24 h at normal temperature.

Characterization

Particle size and size distribution were determined by dynamic light scattering (DLS) on a Malvern 4700 from Malvern Instruments, Ltd. Molecular weight and molecular weight distribution were measured by Agilent 1100 gel permeation chromatography (GPC) apparatus. The shape of the particles was observed by a Hitachi H-600 transmission electron microscope (TEM).

A Bruker DMX 500 NMR spectrometer was used for ^1H NMR analysis with $CDCl_3$ as a solvent. The Tg values of the samples were measured by a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC). Wide-angle X-ray diffraction (WAXRD) was performed by a Brukerd & Advance diffractometer with Cu Kα radiation.

Table 1
Compositions and particle sizes of the PEMA samples[a]

Sample	Surfactant (g)[b] SDS/POH	Initiator (g)	EMA (g)[c]	H_2O (mL)	Time[d] (min)	Dz (nm)
A1	1.05/0.15	APS(0.114)	1+3	42	72	20
A2	1.05/0.15	APS(0.114)	1+4	42	96	21
A3	1.05/0.15	APS(0.114)	1+5	42	120	21
A4	1.05/0.15	APS(0.114)	1+13	42	312	33
A5	1.05/0.15	APS(0.2)	1+5	42	120	25
A6	1.05/0.15	APS(0.5)	1+5	42	120	31
A7	2.1/0.3	APS(0.114)	1+5	42	120	22
A8	1.4/0.2	APS(0.114)	1+5	42	30	23
B1[e]	1.05/0.15	H_2O_2/asorbic acid (0.06/0.09)	1+5	42	120	13
B2[e]	1.8/0.3	H_2O_2/asorbic acid (0.06/0.09)	1+5	42	12	16
C[f]	5.4/0.7	APS(0.114)	1	42	—	21
D[g]	1.05/0.15	APS(0.114)	1+5	42	120	25

[a] The polymerization temperature was 70°C, if not specialized.
[b] N-pentanol (POH) was used as a cosurfactant.
[c] The first part of the monomer was in the initial microemulsion and the second part was post-added.
[d] Feeding time of the post-added EMA monomer.
[e] The polymerization temperature was 35°C.
[f] The sample was polymerized by traditional microemulsion polymerization.
[g] The polymerization temperature was 80°C.

Results and Discussion

The particle sizes (Dz), molecular weights (Mw, Mn), molecular weight distributions (Mw/Mn), glass transition temperatures (Tg) and tacticities of PEMA samples polymerized in various conditions were listed in Tables 1 and 2. These various polymerization conditions were as follows: various amounts of monomer post-added (A1, A2, A3, A4), various speeds of monomer post-addition (A3, A8; B1, B2), various amounts of initiator (A3, A5, A6) and surfactant (A3, A7), various polymerization temperatures (A3, B1, D).

Effect of Polymerization Conditions On Particle Size of PEMA Microlatexes

The recipes of EMA polymerization under various conditions and the corresponding particle sizes of PEMA microlatexes are shown in Table 1. The particle sizes barely changed as the amount of post-added monomer increased from 3 g to 5 g (A1, A2, A3). When the amount of post-added monomer increased to 13 g (A4), the particle size increased dramatically, but were still in the range of nanoscale. The TEM photograph of sample A4 (Fig. 1) shows that the resulting PEMA microlatexes were uniform spheric particles with the size of about 30 nm, which was approximate to the DLS value. A possible explanation is that "homogeneous nucleation" was the major nucleation

Table 2
Molecular weights, Tg's, and tacticities of the PEMA samples

Sample	Mw (10^{-5})	Mn (10^{-5})	Mw/Mn	Tg (°C)	rr	mr	mm
A1	0.58	0.34	1.7	79.9	0.62	0.35	0.03
A2	0.48	0.29	1.7	78.8	0.60	0.36	0.04
A3	0.51	0.26	2.0	78.2	0.60	0.35	0.05
A4	0.73	0.46	1.6	77.3	0.59	0.37	0.04
A5	0.40	0.31	1.3	76.3	0.59	0.35	0.06
A6	0.30	0.23	1.3	74.4	0.58	0.36	0.06
A7	0.63	0.42	1.5	76.5	0.59	0.35	0.06
A8	5.98	2.17	2.7	81.6	0.61	0.34	0.05
B1	0.56	0.39	1.4	80.3	0.64	0.31	0.05
B2	2.76	0.91	3.0	82.5	0.64	0.31	0.05
C[a]	6.78	3.46	2.0	76.2	0.58	0.35	0.07
D	0.52	0.19	2.8	77.2	0.59	0.35	0.06

[a] The sample was polymerized by traditional microemulsion polymerization.

mode (5). Through diffusion equilibrium, the emulsifier was absorbed rapidly to the surface of newly formed particles and stabilized them. Therefore, the particle size changed very little with the increasing amount of monomer post-added. A similar phenomenon had been observed by our group in the modified microemulsion polymerization of MMA (6). With a further increase of monomer post-added, the emulsifier would be severely short and insufficient to protect the newly formed particles from aggregation. Then, the particle size increased dramatically as the large particles formed by aggregation of the small ones.

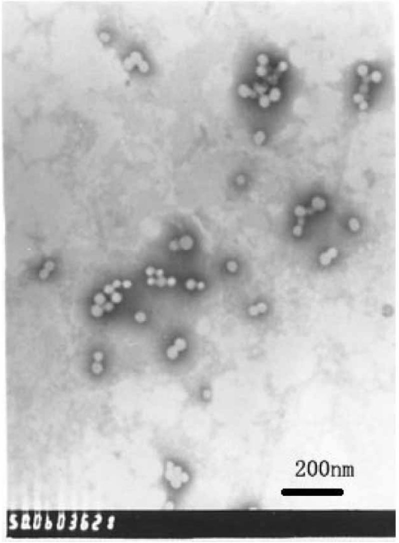

Figure 1. TEM photographs of PEMA sample A4.

As shown in Table 1, the particle sizes didn't vary much with the increasing speed of monomer post-addition (from 5 g/120 min (A3) to 5 g/30 min (A8)). The same phenomenon was observed for sample B1and B2 (from 5 g/120 min to 5 g/12 min). It seems that homogeneous nucleation was the dominating nucleation mode even at rather rapid post-addition speeds. Emulsifier, through diffusion equilibrium, was adsorbed rapidly to the particle surface and stabilized the particles.

Particle sizes of PEMA microlatexes increased gradually as the amount of APS varied from 0.114 g to 0.5 g (A3, A5, A6). This result may be due to the occurrence of interparticle aggregation, i.e., at high initiator concentration, the number of initiation center and reaction center increased, and accordingly, the number of nuclear particles was very large. In a thermal initiated system, as the number of nuclear particles increased in the initial steps, the possibility of collision and aggregation was higher and larger particles were formed.

The particle sizes didn't change much with the increase amount of emulsifier (A3, A7), but the stability of the PEMA microlatexes increased.

The PEMA particle sizes varied dramatically with the reaction temperature. The particle sizes of PEMA prepared by redox initiators (B1, B2) were smaller than those of the PEMA prepared by thermal initiators (A3, D). It seems that smaller particles are liable to be formed at a lower reaction temperature. This may be attributed to the reduced possibility of aggregation between the nuclear particles at lower temperature.

Effect of Polymerization Conditions on Molecular Weight of PEMA Microlatexes

As shown in Table 2, the PEMA particles produced by modified microemulsion polymerization generally had the weight-average molecular weights (Mw) of about $3-6 \times 10^4$, except the ones polymerized at rapid monomer post-addition speeds (A8, B2), which had the Mw of about $3-6 \times 10^5$. The molecular weight polydispersities (Mw/Mn) were from 1 to 3. A possible explanation is that the monomer post-addition process was a "monomer starved" procedure (6). When the post-addition speed was very slow, the monomer supply couldn't satisfy the need of propagation in the lifetime of the propagating chain radicals and the chain radicals died in starving, then the resulting polymer had a low Mw of $3-6 \times 10^4$. As the post-addition was applied at a proper speed and the need of propagating chain radicals was satisfied, the Mw of PEMA increased dramatically to $3-6 \times 10^5$, which was comparable with the Mw of PEMA prepared by traditional microemulsion polymerization (C), but the polymer/surfactant ratio and polymer content were remarkably higher than the latter. We can conclude that in order to obtain PEMA products with high molecular weight, adjusting the monomer post addition to a proper speed is very important in this modified microemulsion polymerization procedure.

Effect of Polymerization Conditions on Tacticity of PEMA Microlatexes

Table 2 shows that the Tg's of PEMA samples prepared by modified microemulsion polymerization were generally higher than the Tg value reported (by the ordinary radical polymerization, 68°C) (7). To explain the high Tg's, ^{1}H NMR analysis was carried out to determine the rr, mr and mm triad ratios of PEMA samples. Figure 2 presents the ^{1}H NMR spectrum of PEMA sample A3. The contents of rr, mr and mm triad were calculated according to the literature (8). The tacticity composition of PEMA was determined from the relative intensity of R-CH_3 resonances due to rr, mr and mm

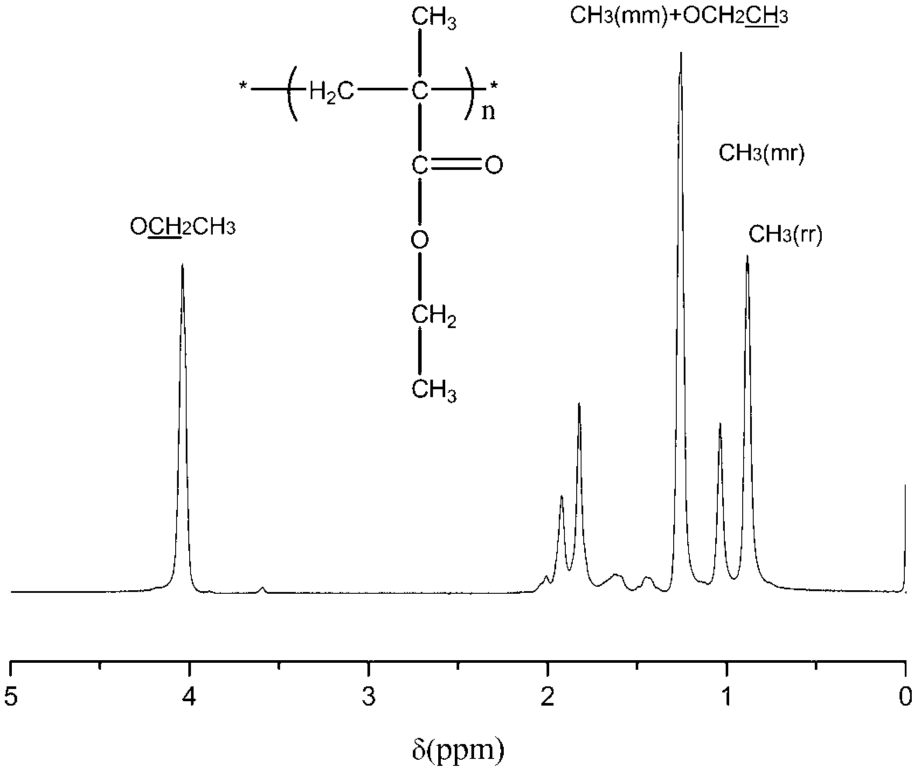

Figure 2. ^{1}H-NMR spectrum (500 MHz) of PEMA sample A3.

triads. The intensities of mm, mr, and rr triad resonances in every spectrum of the ^{1}H-NMR data were measured by integrating the spectral regions of 1.18–1.28, 0.98–1.07, and 0.82–0.92 ppm, respectively. The ester CH_3 resonance at 1.23 ppm overlapped with the R-CH_3 resonance due to mm triad, and thus the intensity of mm triad resonance was evaluated by subtracting 1.5 times the intensity of the ester OCH_2 resonance at 3.92–4.06 ppm from the intensity of the spectral region from 1.18 to 1.28 ppm (see Fig. 2) because the theoretical relative intensity of ester CH_3 and OCH_2 resonances is 1.5 : 1.0.

^{1}H NMR analysis shows that the PEMA samples prepared by modified microemulsion polymerization were rich in syndiotacticity. The content of rr triad ranged from 58–64% and the content of mm triad was only 3–6%. The rr content decreased and the particle size increased with an increased amount of monomer post-added (A1, A2, A3, A4). Both the rr content and the particle size remained almost the same as the speed of post-addition increased (A3 to A8, B1 to B2). A decreasing rr content and increasing particle size were also observed with an increasing amount of initiator (A3, A5, A6). As the amount of emulsifier increased (A3, A7), the particle size increased, the rr content decreased slightly and the mm content increased accordingly. The rr contents of samples polymerized by redox initiated systems (B1, B2) were greater than those of the samples polymerized by thermal initiated ones (A3, A8), with the particle size of the former far smaller than the latter.

As shown in Table 2, the PEMA samples prepared by modified microemulsion polymerization were rich-syndiotactic. We wondered if confinement of the monomer in the small volume of a microemulsion might influence the microstructure of the resulting polymer. In the small volume of a latex particle formed in microemulsion, the polymer chain must have more awkward conformations than in its unperturbed state, especially near the surface of the particle, the path of its random walk would be forced to turn back into the particle (9). Therefore, the polymer formed in a microemulsion was conformationally restricted and the potential energy was higher. To compensate for this effect, the propagating chain would be liable to have a smaller root-mean-square end-to-end distance and lower potential energy during the propagation process (10). According to the discussions above, we can assume that the rr contents of the PEMA samples would be affected by the particle sizes, as was validated by the experimental results. With the increase of particle size (A3, A5, A6), the restriction of the confined space to chain propagation decreased, and the rr content decreased correspondingly. The particle size of sample B1 was far smaller than that of A3, and the rr content of B1 was dramatically higher than that of A3.

To produce a further explanation of rich-syndiotacticity of the PEMA samples, we discuss here the difference in activation enthalpy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) between the isotactic and syndiotactic specific propagations. According to the literature (11), $\Delta H^{\ddagger}$and $\Delta S^{\ddagger}$ can be determined by the plot according to the following equation:

$$\ln\left(\frac{P_i}{Ps}\right) = \frac{\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}}{R} - \frac{\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}}{RT}$$

Where Pi and Ps are the mole fractions of isotactic and syndiotactic dyads (square root value of mm and rr content), respectively, R is the gas constant ($1.987\,\mathrm{cal/mol \cdot K}$), T is the polymerization temperature (K). Figure 3 is the plot of ln(Pi/Ps) to 1/T (sample D, A3, B1).

It can be obtained from the plot that $\Delta H_s^{\ddagger} - \Delta H^{\ddagger} = -972\,\mathrm{cal/mol}$, $\Delta S_s^{\ddagger} - \Delta S_i^{\ddagger} = -0.37\,\mathrm{cal/mol \cdot K}$. The rather large negative value of $\Delta H_s^{\ddagger} - \Delta H_i^{\ddagger} = -972\,\mathrm{cal/mol}$ indicated that in a restricted volume, the propagating chain end was restricted during polymerization, and the syndiotactic propagation was favored by enthalpy.

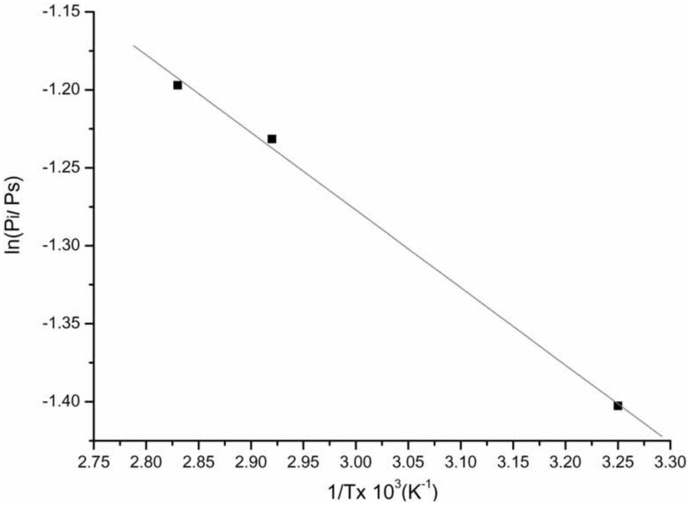

Figure 3. Plots for the polymerizations of EMA under different polymerization temperatures.

Although the small negative value of $\Delta S_s^\ddagger - \Delta S_i^\ddagger$ indicated that the syndiotactic propagation was slightly disadvantaged by entropy, it was favored by activation energy as we took both enthalpy and entropy into account.

Effect of Polymerization Conditions on Glass Transition Temperature of PEMA Samples

As we have discussed above, the polymerization conditions can affect the particle sizes, molecular weights and tacticities of PEMA samples. The glass transition temperatures are affected by all of them. It is shown in Table 2 that the ratio of triads (rr, mr, mm) is the major influencing factor of the glass transition temperature. The higher the content of rr triad, the lower the content of mm triad, the higher the Tg. And according to our former discussion, the major influencing factor of the ratio of triads (rr, mr, mm) is the particle size. If the ratio of triads (rr, mr, mm) is the same (B1, B2), the greater the molecular weight, the higher the Tg value.

WAXRD Graphs of PEMA Samples

WAXRD observations are shown in Fig. 4. Three diffraction peaks ($2\theta = 27^\circ, 35^\circ, 41^\circ$) in the PEMA samples polymerized by modified microemulsion polymerization and traditional microemulsion polymerization are shown. These peaks indicated that there were some ordered regions in the resulting PEMA particles. WAXRD graphs of PMMA samples polymerized by modified microemulsion polymerization (4) also showed two diffraction peaks ($2\theta = 21^\circ, 23^\circ$). It seems that poly(methacrylate)s prepared by modified microemulsion polymerization generally have some kind of order.

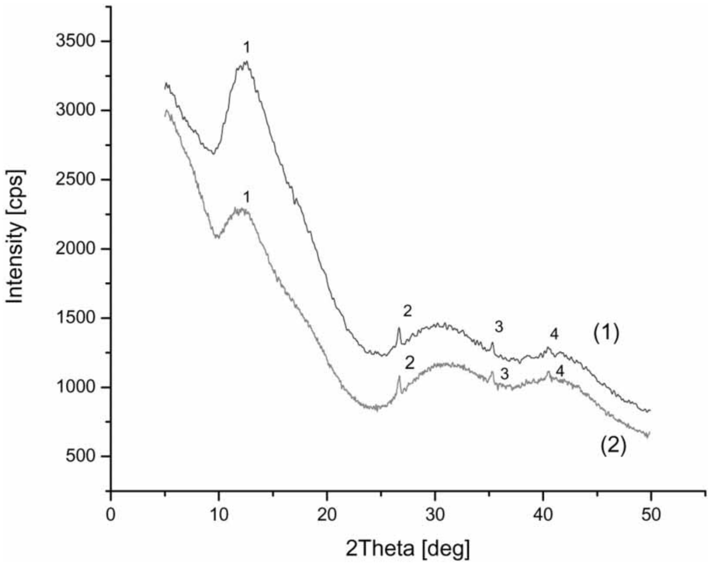

Figure 4. XRD curves of PEMA: (1) C, (2) A3.

Conclusions

Nanosize PEMA latexes with polymer/surfactant weight ratios up to 14 could easily be produced from modified microemulsion polymerization. The resulting PEMA samples had higher Tg's and were rich in syndiotacticity. Tacticities of the polymers were influenced by the reaction temperatures, smaller particles with higher syndiotacticities and Tg's were prepared at lower reaction temperatures. The particle size, molecular weight, triad (rr, mr, mm) ratio and Tg of the PEMA sample were influenced by the reaction conditions. The smaller the particle size, the higher the syndiotacticity, the lower the isotacticity, the greater the molecular weight, then the higher the Tg of PEMA.

Acknowledgments

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References

1. Stoffer, J.O. and Bone, T. (1980) Polymerization in water-in-oil microemulsion systems I. *J. Polym. Sci.: Polym. Chem. Ed.*, 18: 2641–2648.
2. Gan, L.M. and Chew, C.H. (1983) Polymerization of styrene in water-alcohol-ionic surfactant solutions. *J. Macromol. Sci. Chem.*, 19 (5): 739–756.
3. Ming, W.H., Jones, F.N., and Fu, S.K. (1998) Synthesis of nanosize poly(methyl methacrylate) microlatexes with high polymer content by a modified microemulsion polymerization. *Polymer Bulletin (Berlin)*, 40: 749–756.
4. Jiang, W., Yang, W.L., Zeng, X.B., and Fu, S.K. (2004) Structure and properties of poly(methyl methacrylate) particles prepared by a modified microemulsion polymerization. *J. Polymer Sci.: Polym. Chem.*, 42: 733–741.
5. Gan, L.M., Chew, C.H., Ng, S.C., and Loh, S.E. (1993) Polymerization of methyl methacrylate in ternary systems: Emulsion and microemulsion. *Langmuir*, 9: 2799–2803.
6. Ming, W.H., Jones, F.N., and Fu, S.K. (1998) High solids-content nanosize polymer latexes made by microemulsion polymerization. *Macromol. Chem. Physic.*, 199 (6): 1075–1079.
7. Gaur, U., Lau, S.F., Wunderlich, B.B., and Wunderlich, B. (1982) Heat-capacity and other thermodynamic properties of linear macromolecules. 6. Acrylic polymers. *J. Phys. Chem. Ref. Data*, 11 (4): 1065–1089.
8. Kitayama, T., Janco, M., Ute, K., Niimi, R., Hatada, K., and Berek, D. (2000) Analysis of poly(ethyl methacrylate)s by on-line hyphenation of liquid chromatography at the critical adsorption point and nuclear magnetic resonance spectroscopy. *Anal. Chem.*, 72: 1518–1522.
9. Pilcher, S.C. and Ford, W.T. (1998) Structures and properties of poly(methyl methacrylate) latexes formed in microemulsions. *Macromolecules*, 31: 3454–3460.
10. Yan, D.Y. and Zhou, Z.P. (1999) Configurational-conformational statistics of stereoirregular poly(methyl methacrylate)s. *J. Macromol. Sci. Phys. B*, 38 (3): 217–225.
11. Isobe, Y., Yamada, K., Nakano, T., and Okamoto, Y. (1999) Stereospecific free-radical polymerization of methacrylates using fluoroalcohols as solvents. *Macromolecules*, 32: 5979–5981.