

Chemical composition and its distribution of emulsion copolymers composed of styrene and ethyl acrylate as hydrophobic and hydrophilic comonomers

Minoru Kobayashi (✉), Shiho Ohuchi, Hisaya Sato

Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan
E-mail: Mikoba3@aol.com; Fax: +81 (72) 689-1918

Received: 13 December 2005 / Revised version: 15 April 2006 / Accepted: 24 April 2006
Published online: 5 May 2006 – © Springer-Verlag 2006

Summary

Chemical composition and its distribution of styrene (St)-ethyl acrylate (EA) copolymers synthesized by emulsion copolymerization under different monomer ratios and polymerization conditions were examined by $^1\text{H-NMR}$ and high-performance liquid chromatography (HPLC), respectively, and compared with those of bulk copolymers. It was newly found that the chemical composition of copolymer at early stage is affected by the concentration of emulsifier (SDS, sodium dodecyl sulfate) and monomer/water ratio, and is almost independent of the concentration of initiator or polymerization temperature. The EA fraction decreased with the increase of SDS concentration and converged to the value calculated using distribution factor (f_d) when SDS concentration was extrapolated to zero. These results indicate that the EA fraction in micelle decreased compared to the expected value from f_d due to the interaction of EA monomer with emulsifier. From HPLC, it was found that each copolymer showed a sharp single peak at an early stage of polymerization indicating that no homopolymer or copolymer with different composition was produced.

Introduction

In emulsion copolymerization of hydrophobic and hydrophilic vinyl monomers, such as styrene (St) and acrylonitrile, or St and lower alkyl acrylate such as methyl acrylate (MA) and ethyl acrylate (EA), specific phenomena frequently arise because of their different solubility in water. The chemical composition and its distribution (CCD) in such copolymers, therefore, can be very complex. So far, many studies on such copolymers have been reported [1-7]. For example, Ramirez et al. [2] and Djekhaba et al. [3] studied emulsion copolymerizations of St-MA and St-EA, respectively, found that the MA or EA fractions at low conversion were higher than those of bulk copolymers, and estimated that aqueous polymerization of MA or EA can not be neglected. Van Doremale et al. [4] studied emulsion copolymerizations of St and MA, found that the CCD patterns for the copolymers prepared under the conditions of high polymerization rates were bimodal containing MA-richer copolymer. Xu et al. [5] reported that the MA fractions at low conversions of St-MA copolymers prepared

by irradiation with gamma ray were lower than those of bulk copolymers, which is different from the results of Ramirez et al. [2] mentioned above.

In this manner, the chemical composition or CCD at an early stage of St and lower alkyl acrylate emulsion copolymer seems to be different depending on the polymerization conditions, and the mechanism in such phenomena is yet unclear. In the present report, therefore, the effects of monomer ratios and polymerization conditions on the chemical compositions and CCD of St-EA emulsion copolymers were investigated. In this study, it was newly found that the copolymer compositions at early stage are influenced by the concentration of emulsifier and by the monomer/water ratio.

Experimental

Bulk copolymerization

Copolymer was synthesized by bulk copolymerization of mixture of Styrene (St) and ethyl acrylate (EA) purified by distillation. The polymerization was conducted using benzoyl peroxide (0.2 mol % based on monomers) as initiator at 60 °C in nitrogen atmosphere. The sample was dried under reduced pressure after precipitation with n-hexane. The conversion was calculated from the yield of sample.

Emulsion copolymerization

A mixture of sodium dodecyl sulfate (SDS) as emulsifier and deionized water was charged into a 0.3 L four-necked flask equipped with stirrer, thermometer, and a tube for introducing nitrogen gas. A mixture of each monomer purified by distillation and 1-dodecanethiol (0.066 mol % based on monomers) were added. The polymerization by the batch method was conducted under stirring (250 rpm) after adding a deionized water solution of ammonium peroxydisulfate (APS) as an initiator. The intermediate conversion was determined with solid content analysis by sampling about 1 ml of emulsion, diluting with about 3 ml of acetone, drying by heat, and weighing the solid materials. The polymerization rate (R_p , wt.%/min.) was obtained as an average rate in initial stage based on the conversion curve (0 ~ 16 wt.%) against polymerization time. Polymers for NMR and HPLC measurements were obtained by salting-out and centrifugation. The reaction mixture was diluted with two fold amount of methanol and salted out using hydrochloric acid (3.5 wt%), standing still for 24 hours, and centrifugally separated. The sample was dried under reduced pressure after purification by reprecipitation with chloroform/n-hexane. It was confirmed that the water layer did not contain any polymers by drying the volatile materials and weighing the residue.

¹H-NMR measurement

The copolymer composition was determined by ¹H-NMR (500 MHz). The copolymer sample was dissolved in deuterium chloroform to a 2.5 wt% solution, and tetramethylsilane was added as an internal standard. The composition was determined from the intensity ratio of phenyl ring protons (δ : 6.3 ~ 7.3 ppm) in St and methylene protons of ethoxy group (δ : 3.4 ~ 4.2 ppm) in EA.

HPLC measurement

HPLC was carried out according to the method reported earlier [8,9]. Highly cross-linked styrene gel was prepared as HPLC packing material. The gel was prepared by suspension copolymerization of St with divinylbenzene (St-DVB gel). St-DVB gel was packed into a stainless steel column with 4.6 mm i.d. and 25 cm length by the slurry method. The number of theoretical plates (25 cm) of column was 2,700. HPLC was carried out at room temperature using JASCO PU-980 pump and using the gradient elution method. The combination of dichloromethane/acetonitrile and St-DVB gel (reversed phase condition) was used. The two solvents were mixed downstream from two pumps at a flow rate of 0.5 ml/min., and the proportion of dichloromethane was linearly increased over 30 minutes. The column effluent was monitored with a UV detector (JASCO PU-980) or an evaporative mass detector (Applied Chromatography Systems Co. Ltd., United Kingdom, Model 750/14).

Measurement of molecular weights

Average molecular weights were determined by gel permeation chromatography (GPC, JASCO PU-980). Chloroform was used as the mobile phase. Cross-linked polystyrene gel was used as the packing materials. Average molecular weights were obtained from a polystyrene calibration curve.

Measurement of distribution factor (f_d)

St, EA, and deuterium oxide (D_2O , 99.9 atom% D, CISCOTEC Inc., USA) with or without SDS were fully mixed, and then centrifugally separated (10,000 rpm, 10 min.) for the mixtures containing SDS. Distribution factor (f_d) was determined from the concentration of each monomer dissolved in D_2O layer by 1H -NMR. Known amount of dioxane was added as an internal standard to determine the proton contents as HDO contained in D_2O . The concentration of HDO (c_H : mol in 100 g of D_2O) was obtained by:

$$c_H = \frac{s_1 \times 8}{s_2} \times \frac{w}{88.12} \quad (1)$$

where, s_1 and s_2 are protons in HDO (δ : 4.6 ~ 4.7 ppm) and dioxane (δ : 3.5 ppm), respectively, and w is weight (g) of dioxane added to 100 g of D_2O . Concentrations (mol) of St (c_{St}) and EA (c_{EA}) in 100 g of D_2O were obtained by:

$$c_{St} = c_H \times \frac{s_3}{s_1 \times 5} \quad (2)$$

$$c_{EA} = c_H \times \frac{s_4}{s_1 \times 2} \quad (3)$$

where, s_3 and s_4 are phenyl ring protons (δ : 7.3 ~ 7.4 ppm) in St and methylene protons (δ : 4.2 ppm) of ethoxy group in EA, respectively. Molar ratio after partitioning (in organic phase), f_{St}/f_{EA} , was determined by:

$$\frac{f'_{St}}{f'_{EA}} = \frac{\alpha \times f_{St} - c_{St}}{\alpha \times f_{EA} - c_{EA}} \quad (4)$$

$$\left(\alpha = \frac{m}{104.15 \times f_{St} + 100.11 \times f_{EA}} \right)$$

where, f_{St} and f_{EA} are molar fraction of St and EA in feed, respectively and m is total weight (g) of St and EA added to 100 g of D_2O . The f_d was calculated by equation (5).

$$f_d = \frac{f'_{St}}{f'_{EA}} \times \left(\frac{f_{St}}{f_{EA}} \right)^{-1} \quad (5)$$

Results

Chemical composition of bulk copolymers

For comparison with emulsion copolymerizations, St-EA bulk copolymerizations were carried out with different monomer fractions in feed. The molar fractions of EA unit (F_{EA}) in copolymer were determined by 1H -NMR. In Figures 1 and 2, F_{EA} values are plotted against monomer molar fraction of EA in feed (f_{EA}) and conversions, respectively. The monomer reactivity ratios determined by Fineman-Ross method [10] using f_{EA} and F_{EA} values were $r_{St} = 0.87 \pm 0.01$ and $r_{EA} = 0.20 \pm 0.01$. The instantaneous theoretical copolymer composition was calculated using r_{St} and r_{EA} by the copolymerization theory [11]. The composition at each conversion was obtained by accumulating the calculated values for every 1 % conversion. The results are shown in Figures 1 and 2. The observed F_{EA} agreed with the theoretical values within a margin of ± 1.4 %.

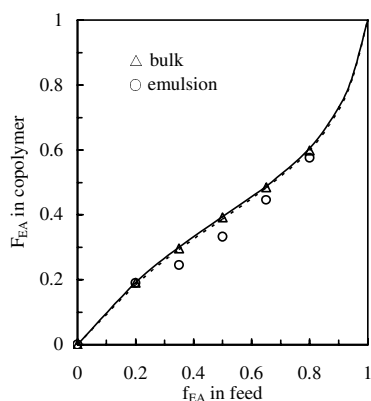


Figure 1. Composition curves in St-EA copolymerization at low conversion. The solid line indicates the values calculated using only monomer reactivity ratios at conversion of 8%. The broken line indicates the values calculated using monomer reactivity ratios and distribution factor ($f_d=1.05$).

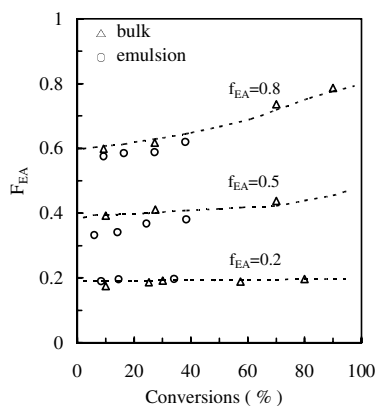


Figure 2. Relation between conversions and copolymer compositions (F_{EA}) in St-EA copolymerizations. The broken line indicates the values calculated by using monomer reactivity ratios.

Chemical composition of emulsion copolymer

St-EA emulsion copolymerizations were carried out with different monomer ratios and polymerization conditions. The F_{EA} values of copolymers at low conversions (<12 %) determined by $^1\text{H-NMR}$ are shown in Table 1. In Figures 1 and 2, the F_{EA} values of copolymers at low and high conversions prepared under the same polymerization conditions are shown, respectively.

Table 1. St-EA Emulsion copolymerizations

No.	f_{EA} in feed	Monomer /water (wt/wt)	Emulsifier [SDS] (mol/l)	Initiator (APS) (mol% ^a)	Temp. (°C)	Conversion (%)	Polymzn. rate, R_p (wt%/min) ^b	F_{EA} obsd. in copolym.	Molecular weights ^c , ($/10^5$)	
									Mw	Mn
E1	0.20	0.250	0.0148	0.058	65	8.5	0.13	0.190	7.1	3.4
E2	0.35	0.250	0.0148	0.058	65	6.7	0.67	0.245		
E3	0.50	0.250	0.0148	0.058	65	6.2	0.80	0.332	6.6	2.6
E4	0.65	0.250	0.0148	0.058	68	12.3	0.25	0.446		
E5	0.80	0.250	0.0148	0.058	65	9.3	0.23	0.575	10.7	2.9
E6	0.50	0.250	0.0296	0.058	70	8.5	1.40	0.329		
E7	0.50	0.250	0.0074	0.058	74	8.3	0.42	0.340		
E8	0.50	0.250	0.0015	0.058	74	8.9	0.15	0.354		
E9	0.80	0.250	0.0296	0.058	65	10.1	1.68	0.565		
E10	0.80	0.250	0.0444	0.058	64	9.8	2.88	0.559		
E11	0.80	0.250	0.0444	0.580	62	12.2	3.10	0.560		
E12	0.80	0.111	0.0148	0.058	65	8.6	0.20	0.557		
E13	0.80	0.250	0.0148	0.058	70	10.0	2.10	0.577		
E14	0.80	0.250	0.0148	0.058	75	11.8	3.93	0.578		

^a Based on the amounts of monomers in feed; ^b Observed in 0-16% conversions; ^c Mw: weight average molecular weights, Mn: number average molecular weights.

Chemical composition distribution (CCD) of St-EA copolymers

The CCD's of copolymers were determined by HPLC using the gradient elution method under reversed phase conditions (nonpolar column: St-DVB gel) [8,9]. Examples of HPLC charts for the bulk and emulsion copolymers at low conversions are shown in Figure 3. Each copolymer was eluted in EA-richer order. It is known that nonpolar sample elutes earlier than polar one with normal phase conditions, while providing opposite elution order with reversed phase conditions [8,9]. Therefore, these results show that the EA-rich copolymer is more polar than the St-rich copolymer. As seen in Figure 3, the CCD patterns of bulk and emulsion copolymers are almost same in each f_{EA} except for the shift to EA-poorer side in emulsion copolymers, corresponding to the lower EA fraction for emulsion copolymer as described above. The HPLC chart showed only one peak by the separate sample injection. This finding indicates that EA-richer copolymer and EA homopolymer were not produced in bulk and emulsion copolymerizations. Other copolymers showed fundamentally same CCD patterns as those in Figure 3.

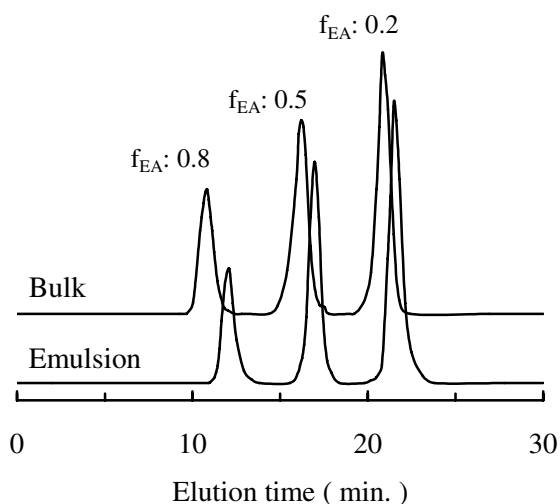


Figure 3. HPLC charts of St-EA copolymers. HPLC was measured by reversed phase and UV detector.

Distribution factor

The distribution factors in the mixtures composed of St, EA and water were determined by $^1\text{H-NMR}$ to measure the solubility of the monomers in deuterium oxide (D_2O , as replacement of water) with or without emulsifier: SDS. The distribution factor (f_d) was calculated by equation (5). The experiments were carried out with monomer/water ratio of 0.25 (weight ratio). The results observed for $f_{EA}=0.2$ and 0.8 are shown in Table 2. The f_d values tends to slightly decrease with the addition of SDS and with an increase in the mixing temperature. The f_d in the system containing SDS at 65 °C, which is closed to the actual system, could not be determined because of operational restrictions in centrifugal separation. Taking the small temperature effect shown in Table 2 into account, f_d at 65 °C is assumed to be close to the value at 25 °C.

Thus, $f_d = 1.05$ was used in the following calculations at monomer/water ratio of 0.25. From this value, the f_d at monomer/water ratio of 0.111 was calculated to be 1.12.

Table 2. Distribution factor (f_d) observed ^a

EA/(St+EA) in feed (mol/mol)	Emulsifier [SDS] (mol/l)	Mixing temp. (°C)	Monomer conc. in D ₂ O (g/l)		Distribution factor: f_d
			St	EA	
0.200	-	25	0.18	2.6	1.059
0.200	0.0148	25	0.17	2.0	1.052
0.800	-	25	0.00	10.2	1.056
0.800	0.0148	25	0.00	9.6	1.052
0.800	-	65	0.00	8.5	1.044

^a Composition of mixtures: (St+EA)/D₂O = 0.250 (wt/wt).

Discussion

Effect of monomer ratio in feed on copolymer composition

As seen in Figure 1, the F_{EA} values of bulk copolymers at low conversions agreed with the theoretical values, independent of f_{EA} . On the other hand, the F_{EA} values of emulsion copolymers at low conversions were 2 ~ 6 mol % lower than corresponding values in bulk copolymerization except for E1 copolymer ($f_{EA}=0.2$), which had almost the same composition with the corresponding copolymer by bulk method. With an increase in conversion, as seen in Figure 2, the F_{EA} values converged to their theoretical values. Furthermore, EA-richer copolymer and EA homopolymer were not observed in HPLC as seen in Figure 3. These results indicate that EA monomer does not homopolymerize or copolymerize in aqueous phase but copolymerizes in micelle.

The difference in the composition between bulk and emulsion copolymers: δF_{EA} ($\delta F_{EA}=F_{EA}$ in emulsion - F_{EA} in bulk) can be explained by taking the water solubility of St and EA (0.5 and 26 g/l at 45 °C, respectively [12]) into account. Therefore, the distribution factor (f_d) in the mixtures composed of St, EA and water was determined to estimate the monomer ratio in micelle. If the monomer ratio in micelle (f'_{EA}) was dependent only f_{EA} and f_d , the F_{EA} value at an early stage can be calculated by f_{EA} , f_d and monomer reactivity ratios (r_{St} and r_{EA}). The values of f'_{EA} calculated using f_d ($=1.05$) and equation (5) are shown in Table 3. The copolymer molar fractions of EA in emulsion copolymerization (F'_{EA}) calculated using f'_{EA} , r_{St} and r_{EA} are shown in Table 3.

Table 3. Calculation of monomer (f'_{EA}) and polymer (F'_{EA}) compositions in micelle using distribution factor ($f_d=1.05$)

No.	E1	E2	E3	E4	E5
f_{EA} in feed	0.200	0.350	0.500	0.650	0.800
f'_{EA} in micelle ^a	0.192	0.339	0.487	0.639	0.792
F_{EA} obsd.	0.190	0.245	0.332	0.446	0.575
F'_{EA} calcd. in micelle ^b	0.184	0.291	0.386	0.482	0.598
F_{EA} calcd. ^c	0.191	0.299	0.394	0.490	0.606

^a Calculated using monomer fraction and $f_d = 1.05$; ^b Calculated using f'_{EA} , r_{St} (0.87) and r_{EA} (0.20) in the same conversions as those observed; ^c Calculated using f_{EA} , r_{St} and r_{EA} in the same conversions as those observed.

The copolymer composition curve for emulsion copolymerization is obtained by plotting F'_{EA} against f_{EA} as shown in Figure 1. As seen in Figure 1, the calculated F'_{EA} are 0.7 ~ 0.8 mol % lower than the calculated F_{EA} which correspond to the value with $f_d = 1.00$, in the range of $f_{EA}=0.2 \sim 0.8$. The F_{EA} observed in E2 ~ E5 copolymers are even about 2 ~ 5 mol % lower than F'_{EA} . These results mean that the chemical compositions of E2 ~ E5 copolymers in the early stages cannot be explained only by the distribution factor (f_d).

Djekhaba et al. [3] and Guillot [13] found by gas chromatography analysis that the EA fractions in St-EA emulsion copolymer at low conversions were higher than those of bulk copolymers. They explained the higher EA fraction by the aqueous polymerization of EA, which can not be neglected and this effect is enhanced by high dilution of monomers (monomer/water<0.2). Their results were contrary to our results. In our experiments, we could not observe even at higher dilution of monomers (monomer/water=0.111: E12 in Table 1). The differences between their results and ours may be caused by different polymerization conditions.

Effect of polymerization conditions on copolymer composition

To examine the factor affecting the difference of composition between bulk and emulsion copolymers, copolymerization was carried out under different polymerization conditions with the same f_{EA} of 0.5 or 0.8. As seen in Table 1, the R_p decreases with decreased emulsifier concentrations. The R_p value is plotted against emulsifier concentration ([SDS]) in double logarithm scale in Figure 4. The plots for $f_{EA} = 0.5$ fell in a straight line with a slope of 3.2/5, showing that the relation approximately follows to Smith-Ewart rule (3/5) observed in emulsion polymerization of St [14]. These results indicate that the emulsion copolymerization proceeded by the same mechanism regardless of emulsifier concentration.

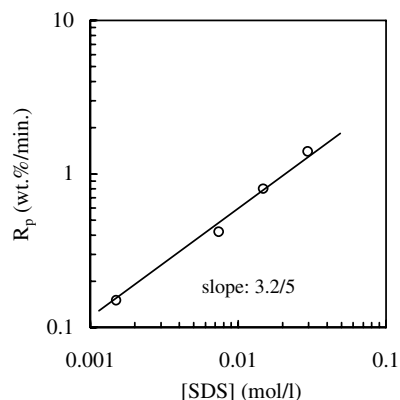


Figure 4. Relation between emulsifier concentration ([SDS]) and polymerization rate (R_p) in St-EA emulsion copolymerizations ($f_{EA}=0.5$).

The δF_{EA} values are plotted against [SDS] in Figure 5. It was found that the F_{EA} decreased with the increase of [SDS], and converged to the calculated F'_{EA} when [SDS] was extrapolated to zero. These results indicate that when the emulsifier increases, the monomer composition in micelle deviated from the value expected

assuming that the composition depends only on f_{EA} and f_d . In order to examine the initiator concentration, copolymerization was carried out with 10 times of initiator (E11 in Table 1). The polymerization rate did not change as expected from emulsion polymerization theory. The copolymer composition changed negligibly as shown by an open triangle in Figure 5. The ratio of monomer/water was changed from 0.250 to 0.111 (E12 in Table 1). The value of δF_{EA} changed from -0.024 to -0.042. Because the value of δF_{EA} calculated using f_d changed from 0.008 to 0.020, this shift can be explained by the decrease of EA monomer fraction in micelle. The copolymerization was carried out at 65, 70, and 75°C (E5, E13, and E14 in Table 1) to examine the temperature effect. The value of δF_{EA} changed negligibly in the range from -0.024 to -0.021. It is noteworthy that the composition did not depend on temperature, although polymerization rate increased from 0.23 to 3.93 wt%/min by increasing the temperature. The detail of mechanism in the relation between copolymer composition and emulsifier concentration, however, is not clear.

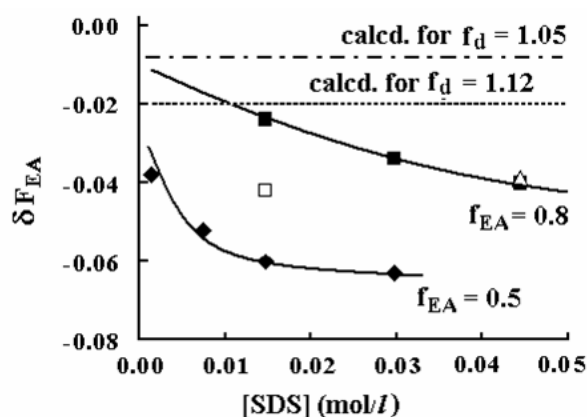


Figure 5. Relation between emulsifier concentration ($[SDS]$) and difference of composition of emulsion and bulk copolymers (δF_{EA}) in St-EA emulsion copolymerizations. ■, ◆: initiator(APS)=0.058 (mol%) and monomers/water(wt)=0.250 ($f_d=1.05$), ▲: APS=0.58 and monomers/water=0.250 ($f_d=1.05$), and □: $f_{EA}=0.8$, APS=0.058, and monomers/water=0.111 ($f_d=1.12$).

Conclusions

The effects of the monomer ratios in feed and polymerization conditions on the chemical compositions and those distributions (CCD) of emulsion copolymers were investigated using St and EA as hydrophobic and hydrophilic comonomers and sodium dodecyl sulfate (SDS) as an emulsifier. It was found that the chemical composition of copolymer at early stage was affected by SDS concentration and monomer/water ratio, and that it was independent of polymerization temperature or initiator concentration. The EA fraction decreased with the increase of SDS concentration and converged to the value calculated using distribution factor (f_d) when SDS concentration was extrapolated to zero. From HPLC, it was found that each copolymer showed a sharp single peak at an early stage of polymerization indicating that no homopolymer or copolymer with different composition was produced.

References

1. Ohtsuka Y, Kawaguchi H, Sugi Y (1981) *J Appl Polym Sci* 26:1637
2. Ramirez W, Guillot J (1988) *J Makromol Chem* 189:361
3. Djekhaba S, Graillat C, Guillot J (1988) *Eur Polym J* 24:109
4. Van Doremale GHJ, Van Herk AM, Ammerdorffer JL, German AL (1988) *Polym Comm* 29:299
5. Xu X, Ge X, Zhang Z, Zhang M (1998) *Polymer* 39:5321
6. Lee KC, Gan LM, Chew CH, Ng SC (1995) *Polymer* 36:3719
7. Sanghvi PG, Patel AC, Gopalkrishnan KS, Devi S (2000) *Eur Polym J* 36:2275
8. Sato H, Takeuchi H, Tanaka Y (1984) *Makromol Chem Rapid Commun* 5:719
9. Sato H, Takeuchi H, Tanaka Y (1986) *Macromolecules* 19:2613
10. Fineman M, Ross SD (1950) *J Polym Sci* 5:269
11. Yamashita Y, Ito K (1975) *Copolymerization*. Baifukan Tokyo, vol. 1
12. Eliseeva VI (1981) *Emulsion polymerization and its application in industry*. Plenum New York
13. Guillot J (1990) *Makromol Chem Macromol Symp* 35/36:269-289
14. Bartholome EO, Gerrens H, Herbeck R, Weitz HM (1956) *Z Electrochem* 60:334