Colloid Polym Sci (2007) 285:557–562
DOI 10.1007/s00396-006-1568-6

SHORT COMMUNICATION

Incorporation of nonionic emulsifier inside methacrylic polymer particles in emulsion polymerization

Amorn Chaiyasat · Hiroshi Kobayashi · Masayoshi Okubo

Received: 27 April 2006 / Accepted: 26 July 2006 / Published online: 9 November 2006

Abstract The incorporations of polyoxyethylene lauryl ether (Emulgen 109P) and polyoxyethylene nonylphenyl ether (Emulgen 911) nonionic emulsifiers inside poly (methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and poly(*iso*-butyl methacrylate) (P*i*-BMA) particles prepared by emulsifier-present emulsion polymerizations were examined. To measure the amounts of the incorporated nonionic emulsifiers, optimum compositions of 2-propanol aqueous solutions to remove the nonionic emulsifier from the particle surfaces without removal from the insides were determined. The amount of the incorporation measured by gel permeation chromatography was increased in the order of PMMA > PEMA > P*i*-BMA, which accorded with the order of miscibility between each polymer and the emulsifier.

Keywords Particles · Incorporation · Nonionic emulsifier · Emulsion polymerization

Introduction

Polymer particles prepared by emulsion polymerization were widely used as films in a variety of industrial applications, for example, paints, paper coatings, and adhesives.

In emulsion polymerization, emulsifier plays two important roles: the formation of polymer particles and the stabilization of the resulting polymer particles [1–3]. Nonionic emulsifiers were widely used in emulsion polymerization. We have carried out a series of investigations on the redistribution of carboxyl groups within carboxylated polymer particles stabilized with nonionic emulsifiers [4–8]. Throughout the studies it was found that multihollow polymer particles could be prepared by two-step posttreatment of styrene-butyl acrylate-methacrylic acid terpolymer particles with alkali and acid. This method was named the "stepwise alkali/acid method" [9–11]. Moreover, in the formation of the multihollow structure inside styrene-methacrylic acid copolymer [P(S-MAA)] (10 mol%) particles it was found that polyoxyethylene nonylphenyl ether (Emulgen 911) nonionic emulsifiers were incorporated inside the particles during emulsion polymerization [12, 13]. It is surprising to note that it corresponded to 75% of that used in the polymerization. The incorporation should induce the abatements of the colloid stability during the emulsion polymerization and of the water resistance of the product. These points are serious problems in the industrial applications. On the contrary, the incorporation acted positively for the preparation of the multihollow particles [12, 13]. In a previous article, it was also observed that both that polystyrene (PS) particles prepared by emulsion polymerizations with other two kinds of polyoxyethylene lauryl ether nonionic emulsifiers incorporated them in the insides [14]. That is, it seems that the incorporation is a general phenomenon in emulsion polymerization.

In this article, to clarify the incorporation phenomenon further in detail, the effect of the kind of base polymers on the incorporation of nonionic emulsifier inside particles will be studied.

A. Chaiyasat · H. Kobayashi · M. Okubo
Graduate School of Science and Technology,
Kobe University,
Kobe 657-8501, Japan

M. Okubo (✉)
Faculty of Engineering, Department of Chemical
Science and Engineering, Kobe University,
Kobe 657-8501, Japan
e-mail: okubo@kobe-u.ac.jp

Experimental

Materials

Methyl methacrylate (MMA), ethyl methacrylate (EMA), and *iso*-butyl methacrylate (*i*-BMA) were purified by distillation under reduced pressure in a nitrogen atmosphere. Analytical grade potassium persulfate (KPS, Nacalai Tesque, Kyoto, Japan) was purified by recrystallization. Guaranteed reagent grade tetrahydrofuran (THF, Nacalai Tesque) was used as received. Commercial grade polyoxyethylene lauryl ether nonionic emulsifier (Emulgen 109P) and polyoxyethylene nonylphenyl ether (Emulgen 911) (Kao, Tokyo, Japan) with formula $C_{12}H_{25}$–$O(CH_2CH_2O)_{9.2}H$ and C_9H_{19}–C_6H_4–$O(CH_2CH_2O)_{10.9}H$, respectively, were used as received. Deionized water with a specific resistance of 5×10^6 Ω cm was distilled before use.

Emulsion polymerization

Emulsifier-free and emulsifier-incorporated poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and poly(*iso*-butyl methacrylate) (P*i*-BMA) particles were prepared by emulsifier-free and emulsifier-present emulsion polymerizations, respectively, under the conditions shown in Table 1. The emulsion polymerizations were carried out at 70 °C in a 1-l round bottom flask that was equipped with a two-blade paddle stirrer at a stirring rate of 120 rpm.

Characterizations

Weight- and number-average particle diameters (D_w and D_n, respectively) were detected by dynamic light scattering (FPAR-1000 RK, Fiber-optics particle analyzer, Photal Otsuka Electronics, Kyoto, Japan). Weight- and number-average molecular weights (M_w and M_n, respectively) were determined by gel permeation chromatography (GPC, Tosoh, Japan). The glass transition temperature (T_g) of the polymer particles was measured using a power compensative differential scanning calorimeter (DSC 6200, Seiko Instrument, Japan).

Incorporation of nonionic emulsifier

To measure the amount of incorporated emulsifier inside particles prepared by emulsifier-present emulsion polymerization, the emulsifier adsorbed on particle surfaces must be removed without removal from the insides. Appropriate washing solution was examined as follows. Nonionic emulsifier was added to polymer emulsions prepared by emulsifier-free emulsion polymerization. The emulsifier-added emulsions and polymer emulsions prepared by emulsifier-present emulsion polymerization were centrifugally washed three times with 2-propanol aqueous solutions having different compositions at about 20,000 rpm The washed particles were dried in a vacuum oven at room temperature overnight. The dried particles of 50 mg were dissolved in 4.95 g of THF. The sample solutions were filtered with 0.45 μm of polytetrafluoroethylene membrane before GPC measurement with two styrene/divinylbenzene gel columns (Tosoh, TSK gel GMH_{HR}-H, 7.8 mm i.d. × 30 cm) using THF as eluent at 40 °C at a flow rate of 1.0 ml/min employing refractive index detector (RI 8020). The columns were calibrated with six standard PS samples$\left(1.05\times10^{3}5.48\times10^{6},M_w/M_n=1.051.15\right)$. The amounts of nonionic emulsifier incorporated inside particles were obtained from peak areas due to nonionic emulsifier using the calibration curves of corresponding emulsifier standards.

Cloud point

Excess amounts of MMA, EMA, and *i*-BMA were separately added to water and kept at 70 °C for 3 h. The saturated monomer aqueous solutions were withdrawn and then emulsifier was added to the aqueous solutions in

Table 1 Methacrylic polymer particles prepared by emulsifier-free and emulsifier-present emulsion polymerizations

Ingredients	Emulsifier-free			Emulsifier-present		
	MMA	EMA	*i*-BMA	MMA	EMA	*i*-BMA
MMA (g)	60.10	–	–	60.03	–	–
EMA (g)	–	60.00	–	–	60.00	–
i-BMA (g)	–	–	60.03	–	–	60.00
KPS (g)	0.25	0.25	0.25	0.25	0.25	0.25
Emulgen 109P (g)	–	–	–	3.05	3.05	3.05
Water (g)	540	540	540	540	540	540
D_w (nm)	293	298	402	330	390	160
D_w/D_n	1.05	1.09	1.18	1.14	1.11	1.36
M_w ($\times10^5$ g/mol)	6.07	3.64	2.81	5.98	4.65	4.41
M_w/M_n	3.55	2.28	2.46	3.76	3.37	3.77

which the emulsifier concentration was 1 wt%. Cloud point determination was carried out using a spectrophotometer (Shimadzu UV-2500) at 550 nm with a temperature controller at a heating rate of 1.0 °C/min from 30 to 85 °C. The cloud point was determined as the temperature at which the transmittance of the aqueous solution was 90% [15].

Partition ratio

Partition ratio of nonionic emulsifier between monomer and aqueous phases in which the composition was the same as the polymerization recipe was measured as follows. The mixture in which the emulsifier had been dissolved in the monomer was stirred and kept at 70 °C until the two phases were separated completely and then about 50 mg and 2 g of samples were obtained from the monomer and aqueous phases, respectively. The amounts of the emulsifier in the monomer and the aqueous phases were determined by GPC and gravimetry, respectively.

Miscibility of nonionic emulsifier in methacrylic polymers

PMMA, PEMA, and P*i*-BMA films containing different concentrations of the nonionic emulsifier were prepared by casting in a desiccator for 24 h from THF solutions in which various amounts of the nonionic emulsifier and each polymer prepared by emulsifier-free emulsion polymerization were dissolved and further dried under vacuum for 2 days at room temperature. The thickness of each film was measured with a micrometer (Mitutoyo, Japan). The miscibilities of the nonionic emulsifier in the polymers were estimated by measuring the percent transmittance of the films at a wavelength of 550 nm with a spectrophotometer.

Results and discussion

In previous articles, the amounts of Emulgen 911 nonionic emulsifier were incorporated inside P(S-MAA) particles [12, 13] and those of polyoxyethylene lauryl ether nonionic emulsifiers with averages of 9.2 (Emulgen 109P) and 47.4 (Emulgen 150) ethylene oxides per molecule inside PS particles [14]. The former was indirectly obtained from the subtraction of the total amounts by the amounts in the medium and the amounts at the surfaces, which were measured with ^{1}H NMR and soap titration, respectively. The latter was directly obtained by using ^{1}H NMR measurement after washing by 2-propanol.

In this article, the ^{1}H NMR measurement could not be applied to measure the amounts of Emulgen 109P nonionic emulsifier incorporated inside various methacrylic polymers because ^{1}H NMR spectra of the nonionic emulsifier and the methacrylic polymer were overlapped. Therefore, it was directly measured with GPC after completely removing nonionic emulsifier from the particle surfaces without removal from the insides. For this purpose, optimum solvents had to be used. When methanol, ethanol, and 2-propanol were used for washing the particles prepared by emulsifier-present emulsion polymerization, the nonionic emulsifier was removed not only from the particle surface but also from the inside. To depress the swelling of the particles with solvent for washing, which should decrease the removal of the emulsifier from the inside of the particles, 2-propanol aqueous solutions having various compositions were used for the washing.

Figure 1 shows percentages of Emulgen109P that remained inside/on PMMA particles after washing as a function of 2-propanol content. An increase in the 2-propanol content led to a decrease in the amount of nonionic emulsifier that remained at the PMMA particle surfaces, on which the nonionic emulsifier had been adsorbed by postaddition to emulsifier-free PMMA particles. At 2-propanol content of 20%, the adsorbed nonionic emulsifier was completely removed. On the other hand, in the case of PMMA particles prepared by the emulsifier-present emulsion polymerization, 28% of the nonionic emulsifier used still remained in the inside after washing with 20% of 2-propanol aqueous solution. Although it is not clear whether any emulsifier was not removed from the inside by the washing, we determined the optimum composition for the washing. Similar experiments were carried out for PEMA and P*i*-BMA particles (data

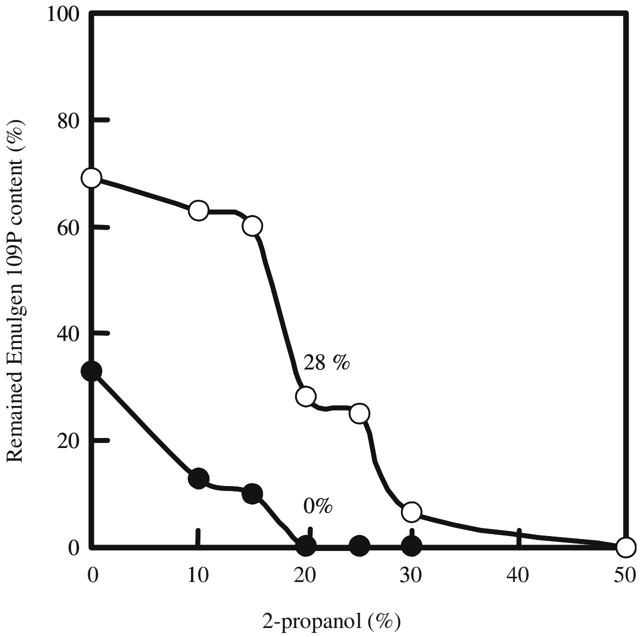

Fig. 1 Emulgen 109P inside/on PMMA particles that remained, which were prepared by emulsifier-present emulsion polymerization (*open circles*) and obtained from a mixture of Emulgen 109P and emulsifier-free PMMA particles (*filled circles*), after washing with various compositions of 2-propanol aqueous solutions

not shown). The results show that the optimum 2-propanol contents for PMMA, PEMA, and P*i*-BMA particles were 20, 25, and 25 wt%, respectively.

Figure 2 shows T_g values of PMMA particles, which had been prepared by emulsifier-free emulsion polymerization and obtained from a mixture of the emulsifier-free PMMA emulsion and the Emulgen 109P aqueous solution after washing with various compositions of 2-propanol aqueous solutions. The T_g measurement was carried out with DSC at the dry state. The T_g was increased with increasing 2-propanol content and attained 115 °C at 20 wt%, which was the same as that of the emulsifier-free emulsion PMMA particles. This also indicates that the nonionic emulsifier was completely removed from the PMMA particle surfaces.

Figure 3 shows the percentage of the nonionic emulsifiers incorporated inside the methacrylic polymer particles prepared by the emulsion polymerizations. The Emulgen 109P incorporated inside PEMA and P*i*-BMA particles were zero, while that for PMMA particles was 28 wt% based on the used ones. The incorporation of Emulgen 911 inside polymer particles was increased in the order of PMMA > PEMA > P*i*-BMA, which were 78, 11, and 9%, respectively. The significant difference in the percentage of the incorporation between both emulsifiers seems to be based on the difference in the affinity between the emulsifiers, the monomers and the polymers.

Figure 4 shows the variations of transmittance of the nonionic emulsifier aqueous solutions in which MMA, EMA, or *i*-BMA was saturated as a function of temperature. The cloud point obviously decreased in order of MMA < EMA < *i*-BMA. This indicates that high polar monomer decreases the hydration of the nonionic emulsifiers in the aqueous solutions. The polymerization temperature of 70 °C was much higher than the cloud point in the MMA-saturated aqueous solution, which might make the largest

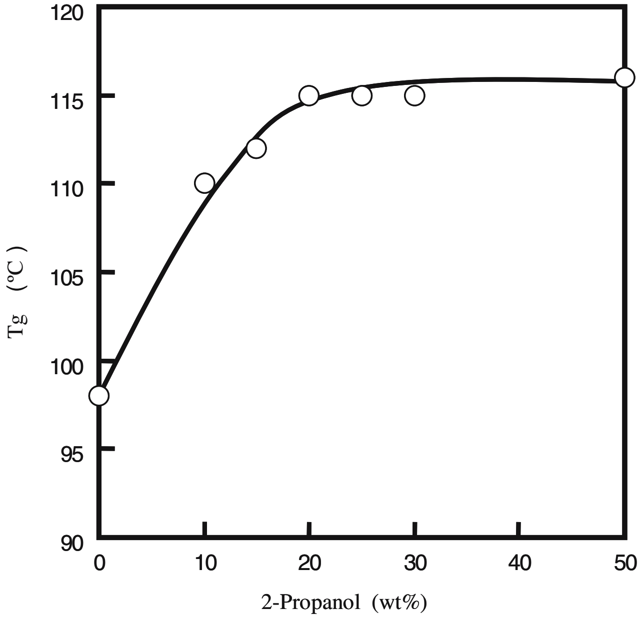

Fig. 2 T_g values of PMMA particles, which had been prepared by emulsifier-free emulsion polymerization and obtained from a mixture of the emulsifier-free emulsion and the Emulgen 109P aqueous solution after washing with various compositions of 2-propanol aqueous solution

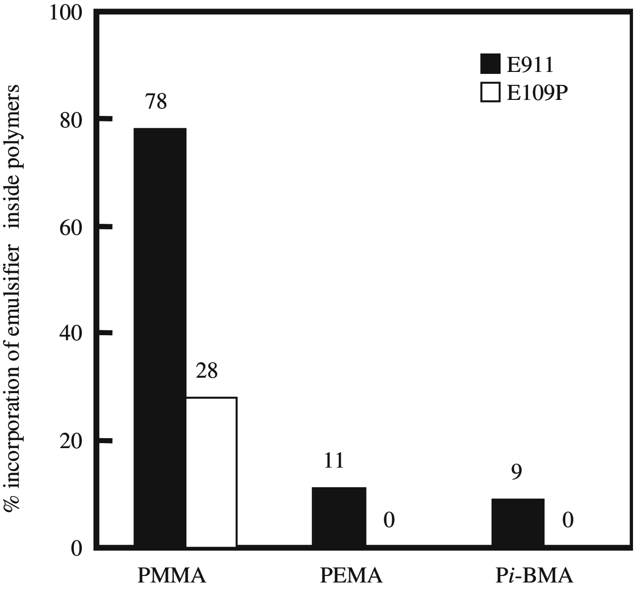

Fig. 3 The percent of incorporation of emulsifier inside the different type of polymers

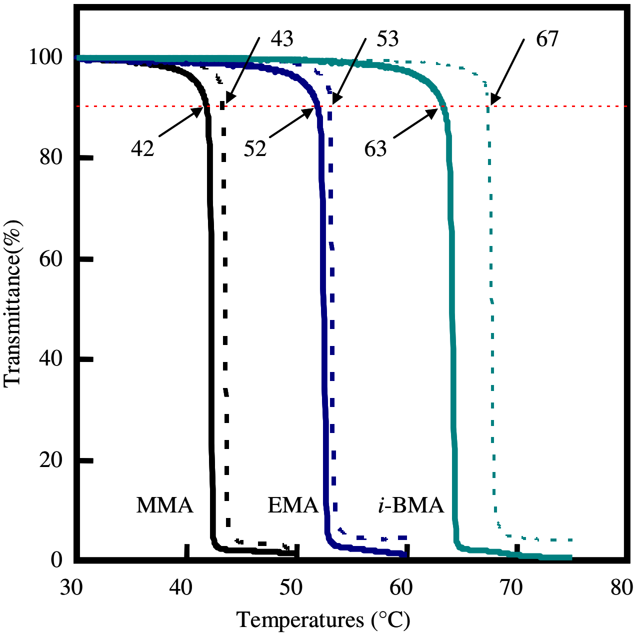

Fig. 4 Variations of transmittance of Emulgen 911 (*solid lines*, 14 mM) and Emulgen 109P (*dashed lines*, 17 mM) aqueous solutions in which MMA, EMA, or *i*-BMA was saturated as a function of temperature

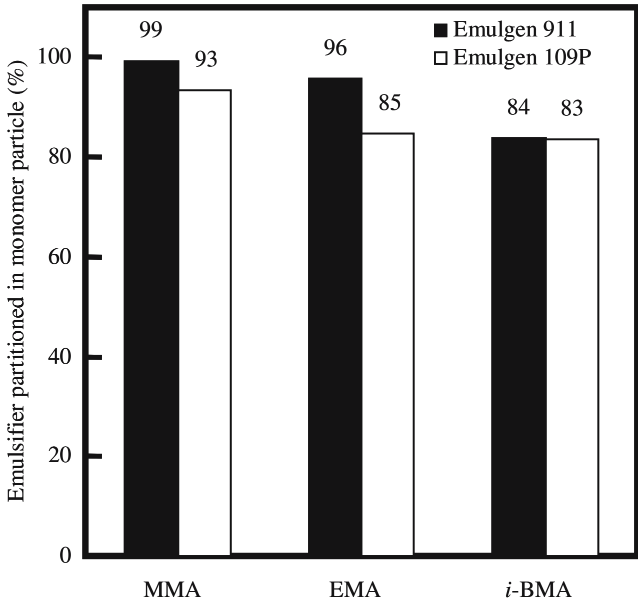

Fig. 5 The relationship between methacrylate monomers and the amount of Emulgen 109P and Emulgen 911 in monomer phase (Emulsifiers: monomer: H_2O; 0.05: 1: 9)

amount of the nonionic emulsifier incorporate into the inside of the PMMA particles.

Figure 5 shows the percentages of Emulgen 109P and Emulgen 911 partitioned in the monomer phases at the same ratio of emulsifier/monomer/H_2O at 70 °C. The percentage increased in the order of PMMA > PEMA > P*i*-BMA. This indicates that the concentration of the nonionic emulsifiers in the monomer phases increased with the increase in the polarity of the monomers.

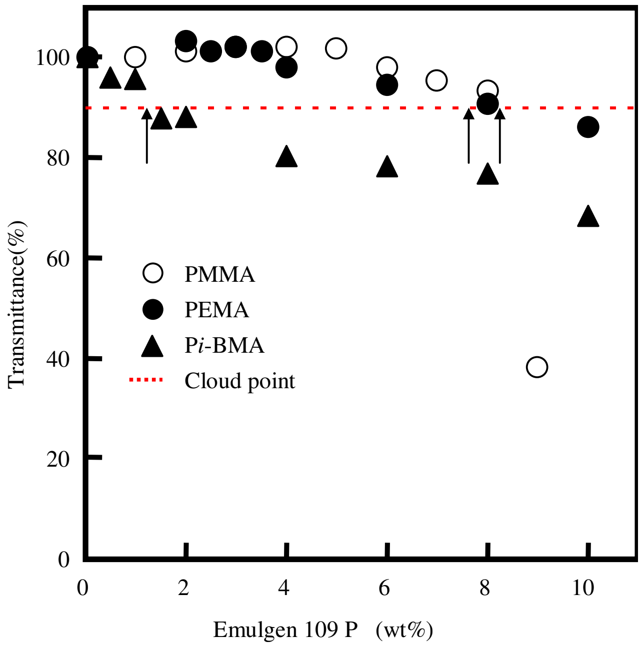

Fig. 6 The transmittance of polymethacrylate polymers films containing various amounts of Emulgen 109P

Figure 6 shows the transmittance of PMMA, PEMA, and P*i*-BMA films containing various concentrations of Emulgen 109P. All films were prepared from THF solutions in which polymers prepared by emulsifier-free emulsion polymerization and various amounts of Emulgen 109P were dissolved. The maximum content of Emulgen 109P at which a transparent film was obtained (taken as the point where the transmittance was 90% at 550 nm) increased in the order of PMMA > PEMA > P*i*-BMA.

Conclusions

PMMA, PEMA, and P*i*-BMA emulsions were prepared by emulsion polymerizations using two kinds of the nonionic emulsifiers having different hydrophilic–lipophilic balance values separately. The GPC analysis was used for the determination of the amounts of nonionic emulsifiers incorporated inside the polymer particles. The optimal 2-propanol contents of the aqueous solutions to remove the adsorbed nonionic emulsifier from the particle surfaces without removal from the inside seemed to be 20, 25, and 25 wt% for PMMA, PEMA, and P*i*-BMA particles, respectively. The percentage of Emulgen 109P incorporated inside PMMA particles was 28% while PEMA and P*i*-BMA particles were not incorporated, which were directly determined by GPC analysis after removal of adsorbed ones by washing with the optimum 2-propanol aqueous solution. That of Emulgen 911 was increased in order of PMMA (79%) > PEMA (11%) > P*i*-BMA (9%). That is, there was an obvious effect of the kind of base polymers on the incorporation of the nonionic emulsifiers inside particles. The percentage seems to be base on the affinity between emulsifier and the polymers (monomers).

Acknowledgement This work was partially supported by Creation and Support program for Start-up from Universities (no. 1509) from the Japan Science and Technology Agency.

References

1. Gilbert RG (1995) Emulsion polymerization: a mechanistic approach. Academic, London
2. El-Aasser MS, Sudol ED (1997) Features of emulsion polymerization. In: Lovell PA, El-Aasser MS (eds) Emulsion polymerization and emulsion polymers. Wiley, London, p 37
3. Asua JM (2004) J Polym Sci A Polym Chem 42:1025
4. Matsumoto T, Okubo M, Yasui M (1974) Kobunshi Ronbunshu 31:112

5. Okubo M, Nakamura Y, Matsumoto T (1976) Kobunshi Ronbunshu 39:473
6. Okubo M, Miyanaga M, Nakamura Y, Matsumoto T (1983) Kobunshi Ronbunshu 40:707
7. Okubo M, Xu DH, Kanaida K, Matsumoto T (1987) Colloid Polym Sci 265:246
8. Okubo M, Kanaida K, Matsumoto T (1987) J Appl Polym Sci 33:1511
9. Okubo M, Kanaida K, Fujimura M (1990) Chem Express 5:797
10. Okubo M, Ichikawa K, Fujimura M (1991) Colloid Polym Sci 269:1257
11. Okubo M, Ichikawa K (1994) Colloid Polym Sci 272:933
12. Okubo M, Furukawa Y, Shiba K, Matoba T (2003) Colloid Polym Sci 281:82
13. Okada M, Matoba T, Okubo M (2003) Colloid Polym Sci 282:193
14. Okubo M, Kobayashi H, Matoba T, Oshima Y, Langmuir, in press
15. Boutris C, Chatzi EG, Kiparissides C (1997) Polymer 38:2567