Colloid Polym Sci 279:931–935 (2001)

SHORT COMMUNICATION

M. Okubo
H. Minami
K. Morikawa

Production of micron-sized, monodisperse, transformable rugby-ball-like-shaped polymer particles

Received: 24 January 2001
Accepted: 18 April 2001

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

M. Okubo · K. Morikawa
Graduate School of Science
and Technology, Kobe University
Kobe 657-8501, Japan

Part CCXIII of the series "Studies on suspension and emulsion"

Abstract Micron-sized, monodisperse, "rugby-ball-like" polymer particles were produced by seeded polymerization for the dispersion of (divinylbenzene/vinylbiphenyl/xylene)-swollen polystyrene particles prepared by utilizing the dynamic swelling method which the authors proposed in 1991. The shape of the composite polymer particle was reversibly transformed between a rugby-ball-like shape and a spherical one by absorbing/releasing toluene.

Key words Micron size · Monodisperse · Hollow particle · Cross-linking · Rugby-ball-like

Introduction

Recently, many researchers studying polymer colloids have been concentrating their attention on the production of micron-sized, monodisperse polymer particles [1–5], which have been applied in the biomedical field, microelectronics, etc. We have also been producing micron-sized, monodisperse polymer particles having functional groups such as chloromethyl [6] and vinyl groups [7, 8] by seeded dispersion copolymerizations of styrene with chloromethylstyrene and divinylbenzene (DVB), respectively, in the presence of about 2-μm-sized, monodisperse polystyrene (PS) particles as seeds. In order to produce monodisperse particles having a diameter above 5 μm, we suggested seeded polymerization utilizing a novel swelling method to make seed polymer particles absorb with a large amount of monomer, which was named the dynamic swelling method (DSM) [9, 10]. Moreover, we produced micron-sized, monodisperse, cross-linked polymer particles having one hollow in the inside by utilizing seeded polymerization with the DSM, in which a hydrophobic solvent such as toluene or xylene was used for the formation of the hollow structure [11–13].

In general, emulsion, suspension, and dispersion polymerizations produce spherical particles within the limits of the resolution of electron microscopy. We have already produced various nonspherical composite polymer particles by utilizing seeded emulsion polymerization [14–21] and seeded dispersion polymerization [22, 23]. Moreover, in the process of the seeded polymerization for the production of hollow polymer particles just described, nonspherical polymer particles having rugby-ball-like and red-blood-corpuscle-like shapes, from which the solvent was removed by spontaneous evaporation, were observed at low conversions [13]. Afterward, the conditions to produce the red-blood-corpuscle-like polymer particles at the completion of the seeded polymerization were clarified [24].

In this article, the conditions to produce the rugby-ball-like polymer particles at the completion of the seeded polymerization is clarified. In addition, it is reported that the particle shape is reversibly transformable by absorbing and releasing solvent.

Experimental

Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB) and vinylbiphenyl (VBP) were supplied by Nippon Steel Chemical Co., Tokyo, Japan. The purity of DVB, which included ethylvinylbenzene, was 96%. The purity of VBP, which included ethylbiphenyl, methylbiphenyl and biphenyl, was 75%. DVB, VBP and vinyl toluene (VT) were washed with 1 N NaOH and deionized water to remove polymerization inhibitors before use. Reagent grade benzoyl peroxide (BPO) and 2,2′-azobis(isobutyronitrile) (AIBN) were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Poly(vinyl alcohol) (PVA), used as a colloidal stabilizer, was supplied by Nippon Synthetic Chemical Ind. Co, Osaka, Japan (Gohsenol GH-17: degree of polymerization, 1,700; degree of saponification, 88%). Poly(acrylic acid) (PAA), used as a colloidal stabilizer, was produced by solution polymerization of acrylic acid in 1,4-dioxane [6]. Reagent grade ethanol and analytical grade xylene, toluene, 1,4-dioxane, dodecyl alcohol and chlorobenzene were used as received.

Preparation of PS seed particles

Micron-sized, monodisperse PS seed particles were produced by dispersion polymerization of styrene in an ethanol/water (7/3 w/w) medium in the presence of PAA with AIBN as initiator at 70 °C for 24 h under a nitrogen atmosphere in a four-necked, round-bottomed flask according to the optimum conditions given in a previous article [6].

Measurement of the solubilities of DVB, VT and VBP in an ethanol/water medium

A large amount of DVB, VT or VBP was added to an ethanol/water (7/43 w/w) medium (50 g) in 100 ml glass cylindrical reactors, and these reactors were left at 25 °C for 4 h. The amount of DVB, VT or VBP dissolved in the ethanol/water medium was measured by gas chromatography (GC-18APFsc, Shimadzu, Kyoto, Japan) with helium as a carrier gas.

Swelling of seed particles with monomers and xylene utilizing the DSM

The swelling of the PS seed particles with DVB, VBP (or VT) and xylene was carried out utilizing the DSM under the conditions described in Table 1 (or 2). The PS seed particles were dispersed in the homogeneous ethanol/water (7/3 w/w) solution dissolving DVB, VBP (or VT), BPO and PVA. Water (40 g) was added to the dispersion with a microfeeder at a rate of 2.66 ml/h under stirring with a magnetic stirrer for 15 h at room temperature.

Seeded polymerization

Seeded polymerization for the dispersions of (monomers/solvent)-swollen PS particles was carried out in sealed glass tubes under a nitrogen atmosphere at 70 °C for 24 h. The tubes were shaken horizontally at 60 cycles/min (3-cm strokes). The conversion was measured by gas chromatography with helium as a carrier gas. Dodecyl alcohol (or chlorobenzene) and 1,4-dioxane were used as standard reagent and solvent, respectively. Droplets in the dispersion were observed on a slide glass, which was covered with a cover glass, with a Nikon MICROPHOT-FXA optical microscope.

Electron microscopy

A Hitachi H7100-TE electron microscope and a Hitachi S-2500 electron microscope were used for transmission electron microscopy (TEM) and scanning electron microscopy (SEM) observations, respectively. For the TEM samples, each emulsion was diluted and a drop was placed onto a carbon-coated grid. For the SEM samples, each emulsion was dropped onto an aluminum plate. The samples were allowed to dry at room temperature in a desiccator.

Table 1 Recipes for the productions of polystyrene (*PS*)/poly(divinylbenzene–vinylbiphenyl [*P(DVB–VBP)*] composite particles by seeded copolymerizations (in a sealed tube: 70 °C; 48 h; N_2; shaking rate, 60 cycles/min, 3-cm strokes) for the dispersions of (DVB/VBP/xylene)-swollen PS particles prepared by utilizing the dynamic swelling method

DVB/VBP (w/w)	1/7	1/8	1/9	1/11	1/12	1/16
PS particles (mg)[a]	30	30	30	30	30	30
96-DVB (mg)[b]	11.3	10.0	9.0	7.5	6.9	5.3
VBP (mg)	78.8	80.0	81.0	82.5	83.1	84.7
Xylene (mg)	360	360	360	360	360	360
Benzoyl peroxide (mg)	1.8	1.8	1.8	1.8	1.8	1.8
Poly(vinyl alcohol) (mg)	15	15	15	15	15	15
Ethanol (g)	7	7	7	7	7	7
Water (g)[c]	43	43	43	43	43	43

[a] D_n, 1.7 μm; C_v, 2.2%
[b] Purity, 96% (by catalog)
[c] Water (40 g) was added afterward at a rate of 2.66 ml/h using a microfeeder

Table 2 Recipes for the productions of PS/poly(DVB–vinyl toluene) [*P(DVB–VT)*] composite particles by seeded copolymerizations (in a sealed tube: 70 °C; 48 h; N_2; shaking rate, 60 cycles/min, 3-cm strokes) for the dispersions of (DVB/VT/xylene)-swollen PS particles prepared by utilizing the dynamic swelling method

DVB/VT (w/w)	1/6	1/12	1/16
PS particles (mg)[a]	30	30	30
96-DVB (mg)[b]	12.9	6.9	5.3
VT (mg)	77.1	83.1	84.7
Xylene (mg)	360	360	360
Benzoyl peroxide (mg)	1.8	1.8	1.8
Poly(vinyl alcohol) (mg)	15	15	15
Ethanol (g)	7	7	7
Water (g)[c]	43	43	43

[a] D_n, 1.7 μm; C_v, 2.2%
[b] Purity, 96% (by catalog)
[c] Water (40 g) was post-added at a rate of 2.66 ml/h using a microfeeder

Results and discussion

TEM photograph of the PS seed particles produced by dispersion polymerization under the conditions listed in Table 3 are shown in Fig. 1. The PS particles were spherical and monodisperse: the number-average diameter (D_n) and coefficient of variation (C_v) were 1.71 μm and 2.2%, respectively, which were determined from the particle observation on TEM photographs with a Personal Image Analysis System (PIAS Co., LA-525, Osaka, Japan).

TEM photographs of PS/P(DVB–VT) composite particles produced by seeded polymerizations for the dispersions of (DVB/VT/xylene)-swollen PS particles prepared by utilizing the DSM under the conditions listed in Table 2 are shown in Fig. 2. The ratios on the photographs indicate the weight ratios of DVB/VT. These particles should have different cross-linking densities and the same shell thickness as the particles having rugby-ball-like shape prepared at 33% conversion in previous work [13]. At the DVB/VT weight rations of 1/6 and 1/12, the dried composite particles had nonspherical shapes, which were produced at completion of the seeded polymerization. At the DVB/VT weight ratio of 1/16, the dried composite particles had a spherical shape because the cross-linked shell was not formed. In each system, a lot of 150 nm-sized by-product particles were observed with TEM as shown in Fig. 2, though they were not observed with an optical microscope. The amounts of the by-product particles were determined to be above 30% of the total monomers (DVB and VT) by gravimetric analysis. This indicates that the polymerization did not always proceed in the swollen particles, which presented difficulty to control the cross-linking density and the shell thickness of the composite polymer particles. This seems to be based on the high solubility of VT in the polymerization medium compared with DVB as shown in Table 4. In order to depress the formation of by-product particles, VBP, which has low solubility in the medium as shown in Table 4, was used in place of VT.

Table 3 Recipe for the preparation of micron-sized monodisperse PS seed particles by dispersion polymerization. 70 °C; 24 h; N_2; stirring rate, 60 rpm

Ingredient	Amount (g)
Styrene	140
2,2′-Azobis(isobutyronitrile)	2.35
Poly(acrylic acid)	16.8
Ethanol	959
Water	280

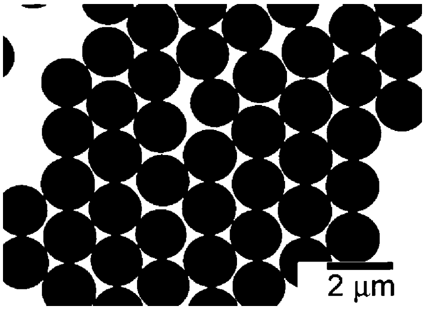


Fig. 1 A transmission electron microscopy (*TEM*) photograph of polystyrene (*PS*) seed particles produced by dispersion polymerization under the condition listed in Table 3

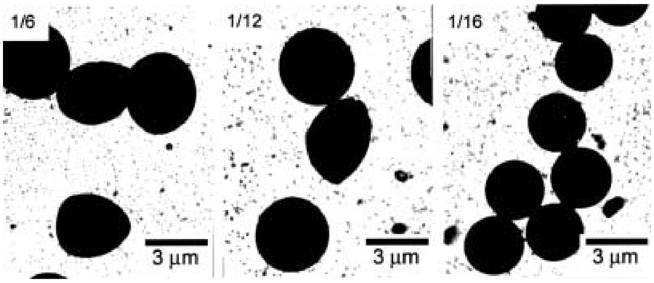


Fig. 2 TEM photographs of PS/poly(divinylbenzene–vinyl toluene) [P(DVB–VT)] composite particles produced by seeded copolymerizations for the dispersions of (DVB/VT/xylene)-swollen PS particles prepared by utilizing the dynamic swelling method (*DSM*) under the conditions listed in Table 2. The *ratios* on the photographs indicate the weight ratios of DVB/VT

TEM and SEM photographs of PS/P(DVB–VBP) composite particles produced by seeded polymerization for the dispersion of (DVB/VBP/xylene)-swollen PS particles prepared by utilizing the DSM, under the conditions listed in Table 1, are shown in Figs. 3 and 4, respectively. The ratios on the photographs indicate the weight ratios of DVB/VBP. As shown in Fig. 3, by-product particles were hardly observed in all systems. This suggests that the polymerization proceeded effectively in the swollen particles and that the cross-linking density and the shell thickness of the composite polymer particles were controlled. As shown in Fig. 4, all the composite particles were nonspherical at the completion of seeded polymerization. The cave became bigger with a decrease in the cross-linking density. This suggests that the shell strength of the composite polymer particle decreased with the decrease in the cross-linking density. When the ratios of DVB/VBP were 1/11–1/16 (w/w),

Table 4 Solubilities of monomers in an ethanol/water medium (14/86 w/w) at 25 °C

Monomer	Solubility (%)
DVB	0.005
VT	0.016
VBP	~0

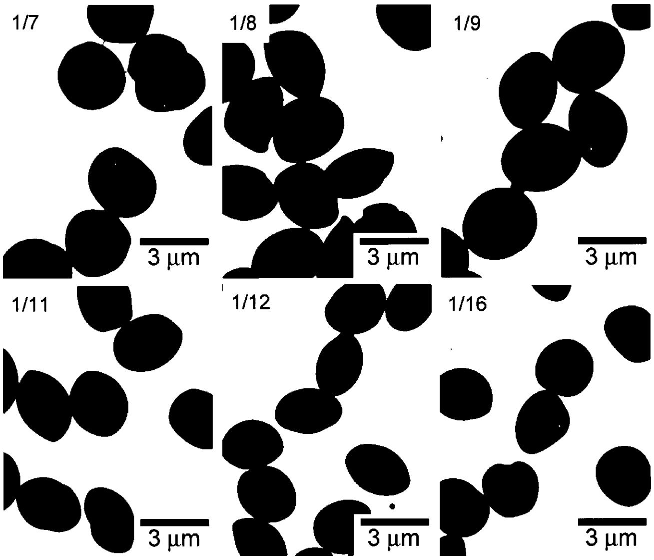


Fig. 3 TEM photographs of PS/poly(DVB–vinylbiphenyl) [*P(DVB–VBP)*] composite particles produced by seeded copolymerizations for the dispersions of (DVB/VBP/xylene)-swollen PS particles prepared by utilizing the DSM under the conditions listed in Table 1. The *ratios* on the photographs indicate the weight ratios of DVB/VBP

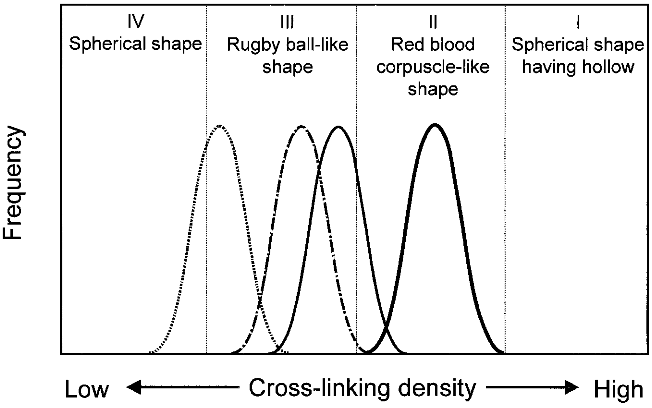
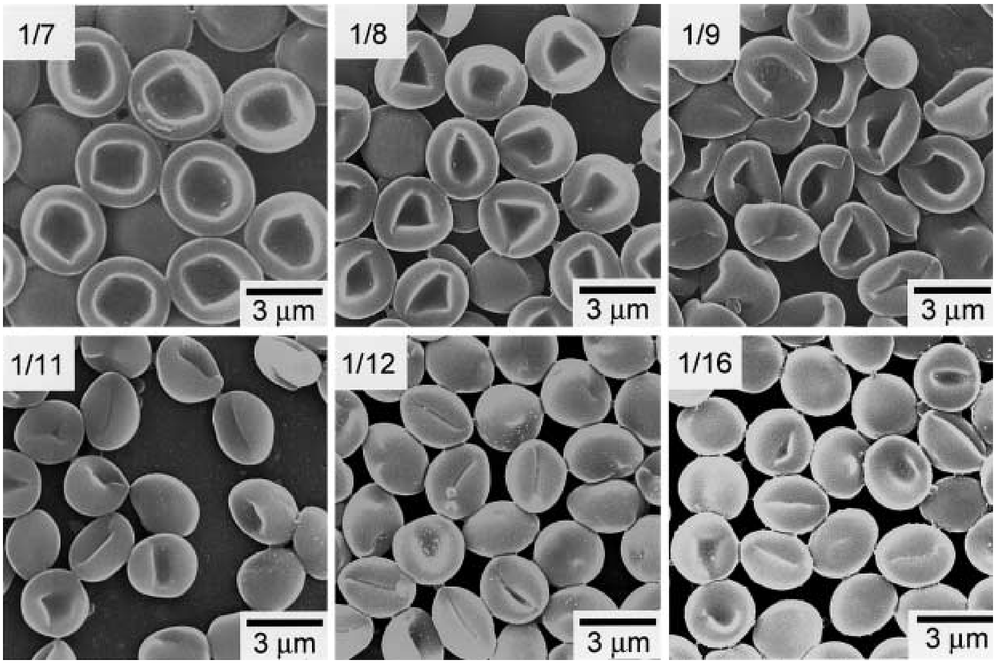


Fig. 5 Schematic diagram showing the relationship between the cross-linking density and the shape for the PS/P(DVB–VBP) composite particles having the same shell thickness. The *curves* indicate the distribution of the cross-linking density among the composite particles: DVB/VBP (w/w): 1/7, —; 1/11, —; 1/12, -·-; 1/16, ····

PS/P(DVB–VBP) composite particles having a rugby-ball-like shape were produced successfully. Some particles having a red-blood-corpuscle-like or a spherical shape rather than the rugby-ball-like shape were also observed at ratios of 1/11 and 1/16, respectively. This indicates that the cross-linking density had a distribution among the composite particles, which was already discussed in previous articles [13, 25]. The schematic diagram of the relation between the cross-linking density and the particle shape is shown in Fig. 5. For the same shell thickness (the shell thickness also affects the particle shape), as the cross-linking density decreases, the shape changes in the order hollow spherical (I), red-blood-corpuscle-like (II), rugby-ball-like (III) and spherical (IV) shapes, though the boundaries are not clear. The cross-linking densities of the composite particles

Fig. 4 Scanning electron microscopy photographs of PS/P(DVB–VBP) composite particles produced by seeded copolymerizations for the dispersions of (DVB/VBP/xylene)-swollen PS particles prepared by utilizing the DSM under the conditions listed in Table 1. The *ratios* on the photographs indicate the weight ratios of DVB/VBP



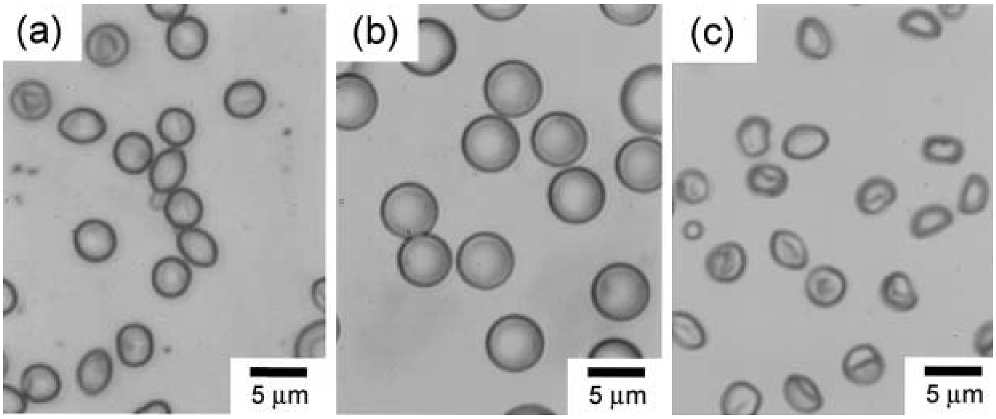


Fig. 6 Optical micrographs of PS/P(DVB–VBP) (DVB/VBP = 1/12) composite particles at various conditions: **a** original state; **b** toluene-absorbed state; **c** toluene-released state

produced at the DVB/VBP weight ratios of 1/7 and 1/12 are contained in single regions II and III, respectively. On the other hand the cross-linking for the 1/11 and 1/16 systems, respectively, ranges from regions II to III and regions III to IV, which result in a mixture of particles having different shapes in each system.

In the drying process, xylene in the hollow evaporated faster than the medium. The medium should penetrate into the hollow through the hydrophobic shell because the hollow space is evacuated; however, the penetration rate of the medium into the hollow through the shell is much slower than the evaporation rate of xylene from the hollow. As a result, when they had low cross-linking density or thin shells, which are not enough to withstand the water pressure, a part of the shell caved in during drying as discussed in a previous article [24].

These rugby-ball-like PS/P(DVB–VBP) (DVB/VBP = 1/12, weight ratio) composite particles transformed from a spherical shape after the polymer dispersion was kept in a capless vessel for 24 h as shown in Fig. 6a. To absorb toluene, which is good solvent for the polymer, 200 μl toluene was added to 10 ml of the dispersion of the nonspherical composite particles, and the dispersion was left for 3 h under stirring with a magnetic stirrer at room temperature. Interestingly, the composite particles in the original state changed from the rugby-ball-like shape (Fig. 6a) to a spherical one (Fig. 6b). Moreover, the spherical shape was changed to the rugby-ball-like shape by releasing toluene again (Fig. 6c).

From these results, we clarified that the micron-sized, monodisperse, rugby-ball-like polymer particles could be produced by the seeded polymerization for (DVB/VBP/xylene)-swollen PS particles prepared by utilizing the DSM at the optimum conditions: monomers/xylene = 1/4 and DVB/VBP = 1/11–1/16 (weight ratios). Moreover, the unique shape was reversibly transformable by absorbing/ releasing toluene.

References

1. Coner T (1981) Colloids Surf 3:119
2. Ugelstad J (1978) Makromol Chem 179:815
3. Ugelstad J, Kaggerud KH, Hansen, Berge A (1979) Adv Makromol Chem 180:737
4. Ugelstad J, Mørk, PC, Kaggerud KH, Ellingsen T, Berge A (1980) Adv Colloid Interface Sci 13:101
5. Vanderhoff JW, El-Aasser MS, Micale FJ, Sudol ED, Tseng CM, Silwanowicz A, Kornfeld DM, Vincent FA (1984) J Dispersion Sci Technol 5:231
6. Okubo M, Ikegami K, Yamamoto Y (1989) Colloid Polym Sci 267:193
7. Okubo M, Katayama K, Yamamoto Y (1991) Colloid Polym Sci 269:217
8. Yamamoto Y, Okubo M, Iwasaki Y (1991) Colloid Polym Sci 269:1126
9. Okubo M, Shiozaki M, Tsujihiro M, Tsukuda Y (1991) Colloid Polym Sci 269:222
10. Okubo M, Shiozaki M (1993) Polym Int 30:469
11. Okubo M, Minami H, Yamashita T (1996) Makromol Chem Macromol Symp 101:509
12. Okubo M, Minami H (1996) Colloid Polym Sci 274:433
13. Okubo M, Minami H (1997) Colloid Polym Sci 275:992
14. Matsumoto T, Okubo M, Shibao S (1976) Kobunshi Ronbunshu 33:575
15. Okubo M, Katsuta Y, Yamada A, Matsumoto T (1979) Kobunshi Ronbunshu 36:459
16. Okubo M, Ando M, Yamada A, Katsuta Y, Matsumoto T (1981) J Polym Sci Polym Chem Ed 18:481
17. Okubo M, Ando M, Yamada A, Katsuta Y, Matsumoto T (1981) J Polym Sci Polym Lett Ed 19:143
18. Okubo M, Katsuta M, Matsumoto T (1982) J Polym Sci Polym Lett Ed 20:45
19. Okubo M, Kanaida K, Matsumoto T (1987) Colloid Polym Sci 265:876
20. Okubo M, Murakami Y, Tsukuda Y (1993) Chem Express 8:253
21. Okubo M, Murakami Y, Fujiwara T (1996) Colloid Polym Sci 274:520
22. Okubo M, Nakagawa T, Yamashita T, Tsuji M (1995) Macromol Symp 92:83
23. Okubo M, Hosotani T, Yamashita T (1996) Colloid Polym Sci 274:279
24. Okubo M, Minami H (2000) Macromol Symp 150:201
25. Okubo M, Nakagawa T (1994) Colloid Polym Sci 272:530