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The synthesis and characterizations of monodisperse cross-linked polymer microspheres with carboxyl on the surface

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Abstract

Monodisperse cross-linked polymer microspheres with carboxyl groups on their surface were prepared by means of emulsifier-free emulsion copolymerization. The characterizations by X-ray photoelectron spectroscopy and conductometric titration indicate that most carboxyl groups are located on the surface of microspheres. Their swelling degree or cross-linking degree has been investigated by an in situ swelling method. Moreover, these microspheres can be easily and quickly self-organized into two- or three-dimensional ordered multilayer films or latex crystals. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Emulsifier-free; Cross-linked polymer microsphere; Colloidal crystal

1. Introduction

Monodisperse colloids, especially polymer latex with surface functional groups [1–12] such as carboxyl, hydroxyl, amino and aldehyde, whose diameter ranges from nanometer to submicrometer, have been attracting considerable attention for their potential applications [13–23] in the field of optics, magnetics, electronics, colloidal chemistry, biochemistry and medicine. Recently, the studies on colloids or latexes are focusing on manipulating the chemistry of colloid formation, especially on manipulating functional groups on the surface to control stability, solubility and biologic compatibility of the latexes [24–29], and on constructing templates of functional materials such as photon band gap materials from monodisperse colloids [10–16,30–33]. On the other hand, cross-linked polymer microspheres [34–37], allowing changes in size (swelling and deswelling) which may be induced by changes in temperature and solvent, is of growing interest in a number of applications, in particular for rheological control [38,39] and thermal-sensitive microgels [40–43]. In this work, cross-linked polymer microspheres with well-defined microsphere size and functional carboxyl groups on the surface were prepared via an emulsifier-free emulsion copolymerization. Their swelling ratio and cross-linking degree were measured using an in situ swelling method. These microspheres could easily and quickly self-organize into latex crystals due to their monodispersity and carboxyl groups on the surface. All these will be highly desired in the field of biochemistry, functional material and chemical industry.

2. Experimental section

2.1. Materials

Styrene and methacrylate acid were distilled under reduced pressure before use. 4,4′-isopropylidenediphenol bimethacrylate was used as cross-linker and prepared in our laboratory. Potassium persulfate ($K_2S_2O_8$) and other reagents were utilized without further purification. Deionized water was applied for all polymerization and treatment processes.

2.2. Preparation of microspheres

Cross-linked polystyrene microspheres with carboxyl groups were synthesized using an emulsifier-free emulsion copolymerization. All polymerizations were carried out in an atmosphere of nitrogen for 12 h in a 500-ml four-necked flask fitted with a reflux condenser and a stirrer. Styrene was used as the major monomer, methacrylic acid as functional monomer to provide carboxyl groups on the surface of microspheres, and 4,4′-isopropylidenediphenol bimethacrylate as cross-linker. Potassium persulfate ($K_2S_2O_8$) served as

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initiator and no emulsifier was used in the polymerization. During polymerizations, a definite amount of $NaHCO_3$ was added to partially ionize carboxyl groups. The resulting emulsion was purified by the processes of filtering, ion exchanging and dialyzing in deionized water.

2.3. Swelling of the microspheres

A typical swelling procedure was employed as follows: 0.5 ml of emulsion (0.5 wt% of solid content) were added into 3.0 ml of water, ethanol or THF, respectively. Then they were sonicated in an ultrasonic bath at room temperature for 5 min. All swelling processes were performed under the same concentration of microspheres.

2.4. Characterization

FTIR spectra were measured in the wavenumber range 4000–400 cm^{-1} at a resolution of 4 cm^{-1} using a Nicolet Avatar 360 FTIR spectrophotometer. The number of carboxyl groups and the molar fraction of C and O on the surface of microspheres were determined by conductometric titration and X-ray photoelectron spectroscopy (XPS) (VG ESCALAB MK II), respectively. The morphology of cross-linked microspheres was investigated by transmission electron microscopy (TEM) using a JEOL JEM2010 at an accelerator voltage of 200 kV. The average diameter and size distribution of microspheres was determined by Zetasizer 3000HS and from TEM image. Surface topography of latex crystals was collected using atomic force microscopy (AFM) (Digital Instrument, Nanoscope IIIa, Multimode) in a tapping mode and scanning electron microscopy (SEM) (JEOL JSM-840 microanalyzer). The samples of SEM were sputter-coated with Au film prior to examination.

3. Results and discussion

3.1. Synthesis of monodisperse cross-linked microspheres

In Refs. [36,37,42–45], divinylbenzene or ethylene glycol dimethacrylate was used as cross-linker in the preparation of cross-linked polymer microspheres. But because of the short length of the chain between the two double bonds, it is difficult for divinylbenzene to react completely in the emulsifier-free emulsion polymerization. Instead, we used 4,4′-isopropylidenediphenol bimethacrylate, a longer chain cross-linker. Examination of the FTIR spectrum of Fig. 1 has confirmed the presence of the copolymer of 4,4′-isopropylidenediphenol bimethacrylate, methacrylate acid and styrene. In addition, Fig. 1 shows that the IR absorbance of the C=C double bonds at 1630 cm^{-1} could hardly be detected due to its low concentration in the resulting microspheres, which indicates that almost all of the double bonds including that of the cross-linker, react completely. Some other factors that can affect the size of microspheres, such as the content of methacrylate acid and the amount of cross-linker, were discussed in Refs. [1,2,36,37]. Some typical ingredient recipes for the preparation of monodisperse cross-linked microsphere are listed in Table 1, which shows that the monodisperse cross-linked microspheres can be prepared at a wide range of synthesis conditions. A typical TEM image of Fig. 3(a) indicates that these cross-linked polymer microspheres are spherical in shape and monodisperse. The average diameter is 188.0 nm and the polydispersity is 0.05. In good agreement with the TEM examinations, the average diameter and the polydispersity of the same microsphere sample were measured to be 196.2 nm and 0.04, respectively, by Zetasizer 3000HS. Moreover, cross-linking had no effect on the monodispersity and shape of the resulting cross-linked microspheres by comparison with the same situation of microsphere without cross-linking.

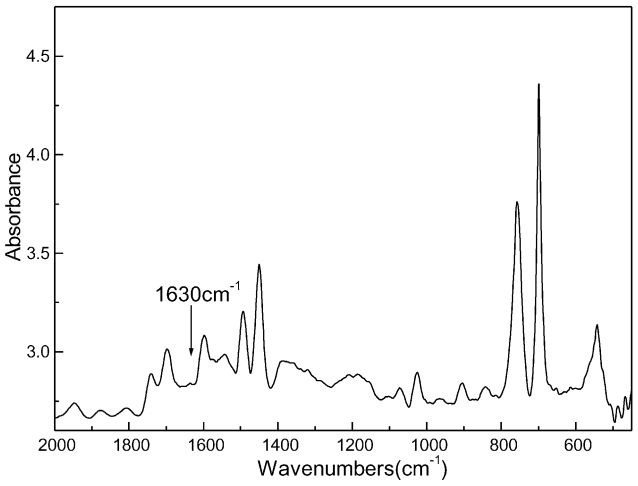

Fig. 1. FTIR spectra of cross-linked polystyrene microspheres with carboxyl groups on the surface.

Table 1
Typical ingredient recipes of the preparation of cross-linked monodisperse microspheres with carboxyl on the surface via an emulsifier-free emulsion polymerization

Ingredient	Weight (g) at 75 °C		
Styrene	9.0	9.0	9.0
Methacrylic acid	1.0	1.0	1.2
Cross-linker[a]	0.5	0.6	0.5
Potassium persulfate	0.08	0.08	0.08
$NaHCO_3$[b]	0.24	0.24	0.24
Deionized water	100	100	100
Diameter (nm)[c]	196.2	228.8	246.5
PDI	0.05	0.012	0.039

[a] Cross-linker is 4,4′-isopropylidenediphenol bimethacrylate.
[b] $NaHCO_3$ could be instead with NaOH or $NH_3{\cdot}H_2O$.
[c] The diameter and polydispersity index (PDI) of microspheres were measured by Zetasizer 3000HS under the solid content 0.5 wt% at room temperature.

Table 2
Contents of C and O from XPS and the calculated value of microspheres of different diameters in Table 1

Ingredient	*A* (196.2 nm)		*B* (228.8 nm)		*C* (194.6 nm)	
	XPS (%)	Calculated[a] (%)	XPS (%)	Calculated[a] (%)	XPS (%)	Calculated[a] (%)
C	91.98	96.43	90.0	96.28	91.28	96.43
O	8.02	3.53	10.0	3.72	8.72	3.53

[a] For the calculated value it was assumed that the copolymer chain was random and that carboxyl groups were uniformly distributed in the microspheres.

3.2. Concentration of surface carboxyl groups

Controlling the surface functionalization is important and challenging in the synthesis of microsphere. In this paper, the carboxyl groups on the surface are one of important factors influencing the stability and ability of self-organization of microspheres. The amount of carboxyl groups was determined by conductometric titration [46,47] with the aqueous solution of NaOH in an atmosphere of nitrogen after emulsion was purified through filtering, ion changing, and dialyzing. Measurements of conductometric titration have shown that the content of carboxyl groups on the surface is 0.255 mmol/g of microsphere and reaches 20.6% of the total amount of the carboxyl groups. When the specific surface areas of microspheres were calculated from average diameter of 196.2 nm determined by Zetasizer 3000HS, and the microsphere density was taken to be 1.05 g/cm^3, the number of carboxyl group on the surface of one microsphere is about 0.5 millions. The contents of C and O from XPS measurement of microsphere with different diameters are listed in Table 2 and compared with the calculated value. Results in Table 2 indicates that the molar ratios of C/O on the surface of microspheres are smaller than the calculated values based on assumption that the monomer was randomly distributed on the copolymer chain and that carboxyl groups were uniformly distributed in the microsphere. This indicates that carboxyl groups are mainly distributed on the surface of the microspheres, and it is true for microspheres with different diameters and different cross-linker content. All the above depend on the facts that the polarity of styrene is smaller than that of the hydrophilic carboxyl groups, and carboxyl groups have a tendency to distribute in the outside region of microspheres. Of course, there are some carboxyl groups, which are buried inside the microspheres [1,2].

3.3. The swelling behavior of cross-linked microspheres

Cross-linking of polymer microspheres with nanometer and submicrometer diameters is of practical importance in enhancing the performance of other polymer materials and constructing some microstructures. Swelling is a classical and simple method for measuring the cross-linking degree of the bulk cross-linked polymer [36,37,44,45], but it cannot be directly applied to measure the cross-linking degree of polymer microspheres of nanometer and submicrometer because of their smaller size. Here the in situ swelling and size-determining method was used to study the swelling behavior of cross-linked polymer microspheres. In order to investigate the effects of solvents on swelling ratio, concentrations of the microspheres were held constant and different swelling reagents were used. Fig. 2 shows that the average diameter of the swelling microspheres will increase by prolonging the swelling time (Fig. 2(a)) as well as increasing the concentration of the swelling reagent

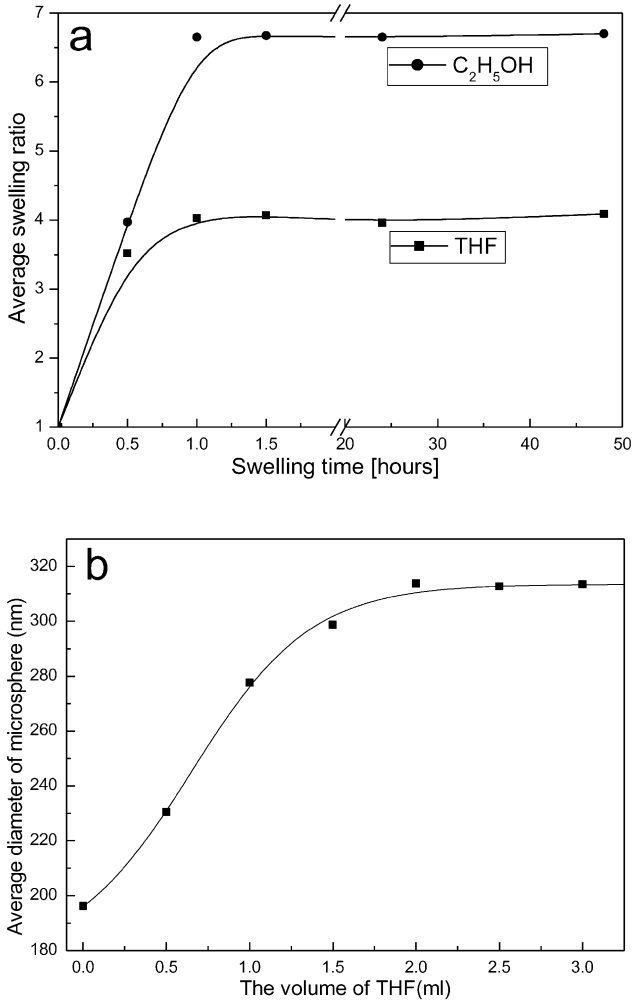

Fig. 2. (a) The plot of swelling ratio in different reagent versus swelling time. (b) Effect of swelling reagent concentration on the diameter of microsphere. Mixture is consisting of 3.0 ml different swelling solvent and 1.0 ml of emulsion with solid content of 0.5 wt% at room temperature.

(Fig. 2(b)). Fig. 2(a) indicates that swelling equilibrium can be reached quickly within 1 h due to their small size, and once reaching the swelling equilibrium in a certain swelling reagent, the maximal swelling ratio is definite. For example, in comparison with the initial diameter of 196.2 nm with polydispersity of 0.05, the average diameter and polydispersity will be 313.7 nm and 0.042, respectively, in the mixture of THF and water. The swelling ratio and M_c (the number-average molecular weight of the network chain between two cross-linking sites, which was used to characterize the cross-linking degree) of the microspheres with 196.2 nm in diameter in alcohol and THF are listed in Table 3. Herein swelling ratio is determined using volume method [44,45] as follows: swelling ratio $= (V_1 - V_0)/V_0$, where V_1 is the volume of swollen microspheres and V_0 the volume of unswollen microspheres. Based on the data in Table 3, when alcohol and THF served as swelling reagent, M_c of the microspheres is obtained to be about 4.53×10^3 and 4.06×10^3, respectively, according to the reports [36,37,48]. While, based on the idealized 100% conversion of double bonds, the value of M_c in theory calculation should be 3.65×10^3. Further, we performed this method under the same conditions to determine M_c of the microsphere with 228.8 nm in diameter in Table 1, the resulting M_c is about 6.10×10^3 and the theoretical calculated value is 4.55×10^3. The M_c value measured by this method is higher than and close to the theoretical calculated value, which is in agreement with the fact that there still remains a double bond with no reaction, as shown in the IR spectrum. All these indicate that the in situ swelling method could be used to measure the swelling ratio and the cross-linking degree of submicrometer microspheres and even nanometer polymer particles.

3.4. Self-organization of the microspheres and swelling behavior of ordered structure

There has been a variety of works [30–33] on constructing colloidal crystals, however, most reports indicated that the speed of formation of colloidal crystal was slow. In this paper, three-dimensional colloidal crystal was easily and quickly created in a short time when the resulting emulsion was placed on mica or silica slides and dried at room temperature or at 70 °C. For example, latex crystals could be obtained within 10 min at 70 °C. SEM micrographs of surface and cross-section of latex crystals are shown in Fig. 3(b) and (c). Self-organization of microspheres results in a close-packed structure, in which the majority displays

Table 3
Final average diameters, PDI and M_c of microspheres in different swelling mixtures

Mixture[a]	Diameter (nm)	PDI	Swelling ratio	M_c[b]
Water	196.2	0.050		
Alcohol/water	369.0	0.038	6.65	4.53×10^3
THF/water	313.7	0.042	4.10	4.06×10^3

[a] Mixture is consisting of 3.0 ml different swelling solvents and 1.0 ml emulsion with solid content 0.5 wt%.

[b] Experimental value; all diameter and PDI of microspheres were measured by Zetasizer 3000HS at room temperature.

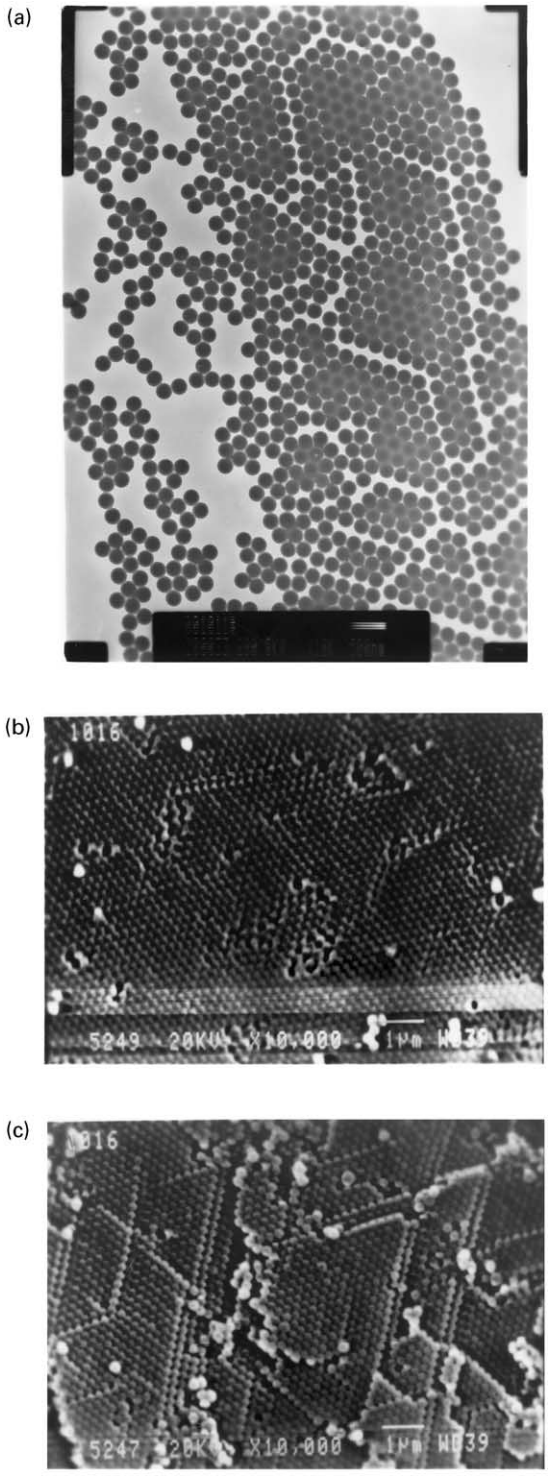

Fig. 3. (a) Typical TEM image of the polymeric microspheres; SEM images of (b) the surface; (c) the section of colloidal crystal. The sample was prepared by drying emulsion of solid content 5.0 wt% under humidity atmosphere at 60 °C.

hexagonal packing in plane of the surface. Here we think the formation of latex crystal is not only the result of the entropy driven packing of hydrophilic microspheres, which was enhanced by capillary adhesion during evaporation of the dispersed water; but also the result of the cooperative association of the electrostatic interaction and hydrogen bond between carboxyl groups. In addition, we studied the effects of swelling behavior on original ordered structure (Fig. 4(a)) by AFM. When latex crystal on the glass slide was immersed into THF for a few minutes, the average diameter of the microspheres will increase from 196.2 to 220.0 nm, and sphere shape of some polymer microspheres became flattened but they still kept original ordered structure (Fig. 4(b)).

4. Conclusion

Cross-linked monodisperse polymer microspheres with carboxyl on the surface have been synthesized and characterized, and their swelling behavior and cross-linking degree were measured via the in situ swelling method. In addition, these microspheres could be fabricated into ordered structure or colloidal crystal quickly and easily. The order of latex crystals from the microspheres may depend on the monodispersity of microspheres and microsphere interactions including the electrostatic interaction and hydrogen bond between carboxyl groups on the surface.

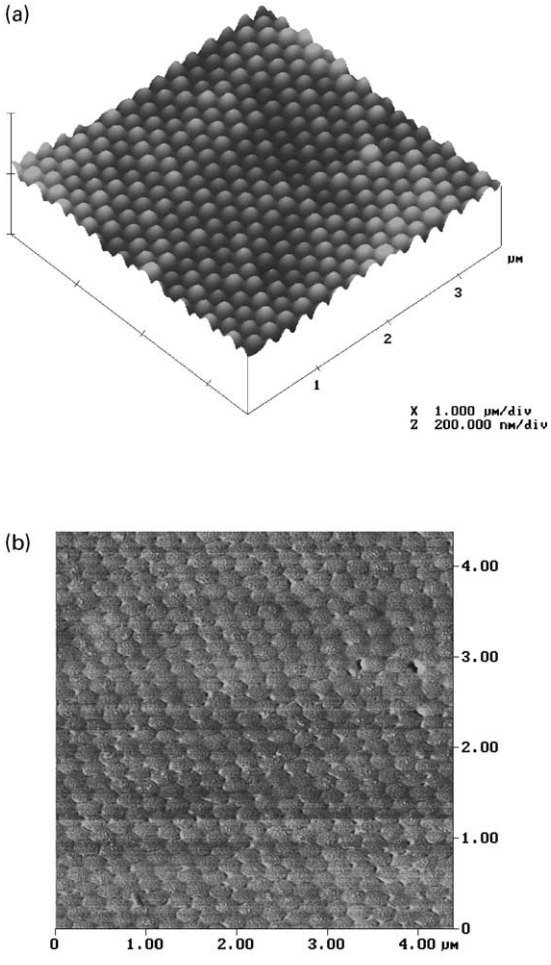

Fig. 4. (a) AFM image of the surface of the colloidal crystal in a tapping mode; (b) AFM image of the surface of ordered structure of the microspheres after swelling in THF.

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References

[1] Sakota K, Okaya T. J Appl Polym Sci 1977;21(4):1025–43.
[2] Ceska GW. J Appl Polym Sci 1974;18(8):2493–9.
[3] Charleux B, Pichot C, Llauro MF. Polymer 1993;34(20):4352–9.
[4] Charreyre M, Razafindrakoto V, Veron L, Delai T, Pichot C. Macromol Chem Phys 1994;195(6):2153–67.
[5] Lee K, Winnik MA, Jao T. J Polym Sci, Part A: Polym Chem 1994;32(12):2333–44.
[6] Liu LJ, Krieger IM. J Polym Sci, Polym Chem Ed 1981;19(11):825–30.
[7] Delair T, Marguet V, Pichot C, Mandrand B. Colloid Polym Sci 1994;272(8):962–70.
[8] Charleux B, Pichot C. Makromol Chem 1992;193(1):187–203.
[9] Yan C, Zhang X, Sun Z, Kitano H, Ise N. J Appl Polym Sci 1990;40(1):89–98.
[10] Okubo M, Kondo Y, Takahashi M. Colloid Polym Sci 1993;271(2):109–13.
[11] Okubo M, Fukami N, Ito A. J Appl Polym Sci 1997;66(8):1461–4.
[12] Kamei S, Okubo M, Matsuda T, Mastsumoto T. Colloid Polym Sci 1986;264(9):743–7.
[13] Jiang P, Bertone JF, Colvin VL. Science 2001;291(5503):453–7.
[14] Xia YN, Gates B, Yin Y, Lu Y. Adv Mater 2000;12(10):693–713.
[15] Tessier PM, Velev OD, Kalambur AT, Rabolt JF, Lenhoff AM, Kaler EW. J Am Chem Soc 2000;122(34):9554–5.
[16] Jiang P, Cizeron J, Bertone JF, Colvin VL. J Am Chem Soc 1999;121(39):7957–8.
[17] Kondo Y, Takayanagi K. Science 2000;289(5479):604–6.
[18] Fuchs H. Langmuir 1997;123(26):7121–4.
[19] Rogach AL, Kotov NA, Koktysh DS, Ostrander JW, Ragoisha GA. Chem Mater 2000;12(9):2721–6.
[20] Xia YN. Adv Mater 2001;13(6):369.
[21] Braybrook JH, Hall LD. Prog Polym Sci 1990;15(8):715–43.
[22] Tuncel A, Kahraman R, Piskin E. J Appl Polym Sci 1994;51(5):1485–98.
[23] Ishizu K. Prog Polym Sci 1998;23(8):1383–408.
[24] Bruinsma PJ, Smith PA, Bunke BC. J Phys Chem B 1997;101(50):8410–7.
[25] Sing C, Pockett G, Zhulina E. J Phys Chem B 1997;101(42):10614–24.
[26] Brouwer WM, Vegt MVD, Haeren PV. Eur Polym J 1990;26(1):35–39.
[27] Watts JF. Langmuir 1996;12(16):3866–75.
[28] Wang Q, Fu S, Yu T. Prog Polym Sci 1994;19(4):703–53.
[29] Zhang G, Li X, Jiang M, Wu C. Langmuir 2000;16(24):9205–7.
[30] Chen Y, Ford WT, Materer NF, Teeters D. J Am Chem Soc 2000;122(42):10472–3.
[31] Holland BT, Blanford CF, Stein A. Science 1998;281(5376):538–40.

[32] Subramanian G, Manoharan VN, Thorne JD, Pine D. J Adv Mater 1999;11(15):1261–5.
[33] Cardoso AH, Leite CAP, Galembeck F. Langmuir 1999; 15(13):4447–53.
[34] Durant YG, Sundberg EJ, Sundberg DC. Macromolecules 1997; 30(4):1028–32.
[35] Durant YG, Sundberg DC. Macromolecules 1996;29(26):8466–72.
[36] Zeeuw EA, Sagis LMC, Koper Ger JM. Macromolecules 1996; 29(2):801–3.
[37] Kan CC, Blackson JH. Macromolecules 1996;29(21):6853–64.
[38] Bradna P, Quadrat SP, Sparch J. J Colloid Polym Sci 1995; 273(4):324–30.
[39] He C, Donaldand AM, Butler MF. Macromolecules 1998;31(1):58–64.
[40] Dowding PJ, Bincent B, Williams E. J Colloid Interface Sci 2000; 422(2):268–72.
[41] Gold D, Onyenemezu C, Miller WG. Macromolecules 1996; 29(17):5710–6.
[42] Shibayama M, Norisuye T, Nomura S. Macromolecules 1996; 29(27):8746–50.
[43] Daly E, Saunders BR. Langmuir 2000;16(13):5546–52.
[44] Tuncel A, Piskin E. J Appl Polym Sci 1996;62(5):789–98.
[45] Wironen J, Shen C, Yan J, Batich C. J Appl Polym Sci 1996; 59(5):825–30.
[46] Li P, Xu J, Wang Q, Wu C. Langmuir 2000;16(9):4141–7.
[47] Greene BW. J Colloid Interface Sci 1973;43(2):449–72.
[48] Mark HF, Bikales NM, Overberger CG, Menges G, Kroschwitz JI. Encyclopedia of polymer science and engineering, Emulsion polymerization to fibers, manufacture, vol. 6. New York: Wiley, 1986. p. 30–5.