Synthesis and Characterization of Crosslinked Phenolic-Typed Beads by Dispersion Polycondensation of 2-Phenoxyethanol with Formaldehyde

Chunnuan Ji, Jingxi Shi, Changmei Sun, Rongjun Qu, Chunhua Wang, Yanzhi Sun

School of Chemistry and Materials Science, Ludong University, Yantai, 264025, People's Republic of China

ABSTRACT: A novel dispersion polymerization of 2-phenoxyethanol (PE) with formaldehyde for the preparation of crosslinked phenolic-typed beads (CPBs) is reported. Monodisperse CPBs with particle sizes in the range 400–700 μm were obtained. The dispersion polymerization of PE with formaldehyde was conducted with hydroxyethyl cellulose, concentrated sulfuric acid, and formic acid as a stabilizer, catalyst, and solvent, respectively. The effects of reaction variables, including the polymerization temperature, agitation rate, molar ratio of formaldehyde to 2-phenoxyethanol (F/P), stabilizer concentration, and amount of the catalyst on the particle size, particle size distribution, and morphology, were investigated. Particularly, CPBs of a size 604 μm and a narrow particle size distribution (polydispersity index = 1.193) were prepared under the following conditions: polymerization temperature = 60°C, agitation rate = 700 rpm, stabilizer concentration = 2.5%, F/P = 3 : 1, and amount of catalyst = 8 mL. The resulting CPBs were characterized by scanning electron microscopy and laser particle analysis. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 216–221, 2010

Key words: polycondensation; resins; synthesis

INTRODUCTION

Recently, crosslinked polymer resins in particulate form have been attractive because of their many applications, including in absorption materials, chromatography, biomedical technology, controlled release of agrochemicals, and pharmaceuticals.[1–3] Many approaches have been reported to prepare monodisperse polymer microspheres with heterogeneous polymerization techniques, including suspension, dispersion, emulsion, and interfacial polymerization.[4–12] A comparison of various techniques used to produce nanospheres and microspheres was reviewed.[13] Among the aforementioned polymerization techniques, dispersion polymerization has been found to be an effective method for producing monodisperse polymer particles. It is evident that the formation of micrometer-size polymer particles reported so far have usually been conducted by the polymerization of vinyl monomers. The preparation of phenolic microspheres by dispersion polymerization is less published in the literature.

Generally, phenolic particles are prepared either by the cryogenic grinding of thermoplastic or thermosetting phenolic resin or by the suspension polymerization of phenolic prepolymer in aqueous or nonaqueous media.[14–20] The former usually needs heavy manual labor. More importantly, no regular phenolic particles with a narrow particle size distribution can be obtained. The latter often consists of two separate steps. In the first step, a phenolic prepolymer is produced through the reaction of phenol with formaldehyde in the presence of an acid or base catalyst. The obtained prepolymer is then allowed to crosslink and convert phenolic particles. In the second step, the stabilizer is used to prevent the coagulation of the phenolic prepolymer in the particle formation stage. To our knowledge, no study has been reported so far on the synthesis of crosslinked phenolic-typed beads (CPBs) via the dispersion polymerization of 2-phenoxyethanol (PE) with formaldehyde.

In this article, we report the synthesis of CPBs by dispersion polymerization with PE as novel polycondensable monomer and hydroxyethyl cellulose (HEC) as a stabilizer. The effects of the polycondensation temperature, agitation rate, molar ratio of formaldehyde to 2-phenoxyethanol (F/P), stabilizer concentration, and amount of sulfuric acid on the particle size and size distribution were investigated. The resulting CPBs were characterized with

Correspondence to: C. Ji (jichunnuan@126.com).

scanning electron microscopy (SEM) and laser particle analysis.

EXPERIMENTAL

Materials

PE (CR, Shanghai Lingfeng Chemical Reagents Co., Ltd., Shanghai, China), formaldehyde solution (37–41% w/v), sulfuric acid (> 98%, Laiyang Economic Development Zone Fine Chemical Factory, Laiyang, China), formic acid (AR, Tianjin Regent Chemicals Co., Ltd., Tianjin, China), and HEC (weight-average molecular weight = 4000, Shanghai Chemical Reagents of China Pharmaceutical Co., Shanghai, China) were used as received.

Typical dispersion polycondensation procedure

A typical procedure for the polycondensation was as follows: PE (25.00 mL, 27.74 g), formaldehyde solution (37% w/w solution, 50.00 mL, 53.33 g), formic acid (50.00 mL, 61.00 g), and HEC (1.144 g) were mixed in a 250-mL, three-necked flask, attached to a mechanical stirrer, a reflux condenser, and dropping funnel. After HEC was dissolved thoroughly, 8.0 mL of sulfuric acid (98%, w/w) was added dropwise over 0.5 h. The reaction mixture was then allowed to react at predetermined temperature for 14 h. After the polycondensation reaction, the resulting polymeric beads were separated by filtration and washed with water, a 5% NaOH aqueous solution, water, and ethanol in that order. Then, the polymeric beads were moved to a Soxhlet extraction apparatus for reflux extraction in 95% ethanol for 4 h and were finally dried *in vacuo* at 50°C for 48 h. The polymer conversion was determined gravimetrically.

Characterization

The surface morphology of the particle was recorded by SEM (JSM-5610LV, JEOL, Tokyo, Japan). The samples were sputter-coated with gold before analysis. The mean particle size of the CPBs was manually calculated from each sample micrograph by computerized imagine analysis.[21] Two types of mean particle size were calculated: number-average mean particle size (D_n) and weight-average mean particle size (D_w). The polydispersity index (PDI) was obtained as follows:[22]

$$D_n = \sum_{i=1}^{n} d_i \Big/ \sum_{i=1}^{n} n_i; \ D_w = \sum_{i=1}^{n} d_i^4 \Big/ \sum_{i=1}^{n} d_i^3;$$

$$\mathrm{PDI} = D_w/D_n$$

where D_n is the number-average diameter, D_w is the weight-average diameter, n_i is the number of particle i, and d_i is the diameter of particle i.

The D_n and size distribution coefficient values of the particles were measured with a laser particle size analyzer (LS13320, Becjman Coulter, Los Angeles, CA). The samples were dispersed in ethanol under ultrasonic vibration before measurement.

RESULTS AND DISCUSSION

In this article, the reaction mixture, consisting of PE, formaldehyde solution, formic acid, and HEC, was homogeneous. After the sulfuric acid was added, the polycondensation of PE with formaldehyde took place immediately. Initially, the polymerization occurred in the continuous phase. When the polymer chain grew too long to be dissolved in the solution, the oligomer precipitated from the continuous phase to form nuclei. The primary nuclei were unstable and tended to aggregate with each other. During the aggregation process, the nuclei could adsorb HEC, and then, stable particles were formed. The possible crosslinked structure of the CPBs is shown in Scheme 1 In following sections, the effects of the reaction variables on the particle size and size distribution, together with the particle morphology and yield, are discussed in detail.

Effect of the polycondensation temperature

The particle size and size distribution of CPBs prepared under different polycondensation temperatures are tabulated in Table 1 When the polycondensation temperature was 50°C, no polymeric beads were obtained. Once the polycondensation temperature was raised to 60–80°C, CPBs in the size range 406–661 μm were formed. These experimental results illustrate that the polycondensation temperature had an important effect on the particle formation during the
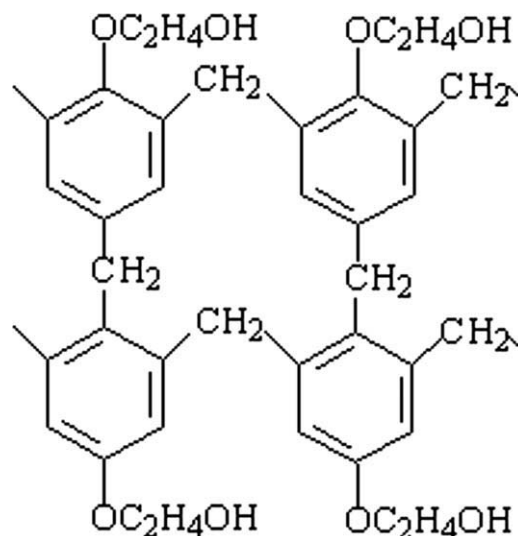
Scheme 1 Structure of the CPBs.

TABLE I
Effect of the Reaction Temperature on the Particle Size and Particle Size Distribution

Run	Temperature (°C)	D_n (μm)	PDI	Yield (%)[a]	Particle morphology
A1	50	—	—	—	Coagulum
A2	60	661.046	1.175	43.54	Bead
A3	70	406.423	1.320	48.32	Bead
A4	80	462.226	1.512	50.63	Bead

The reaction conditions were as follows: 27.74 g of PE, 53.33 g of a formaldehyde solution, 1.14 g of HEC, 8 mL of sulfuric acid, 61.00 g of formic acid, 14 h, and 700 rpm.
[a] Determined gravimetrically (the spherical beads were weighted).

polycondensation process of PE with formaldehyde. The particle size first decreased with increasing polycondensation temperature and then increased later. The decrease of the average particle size of the CPBs with increasing polycondensation temperature might be attributed to the increase in the rate constant of propagation and the concentration of precipitated chains.[23] These factors facilitated the formation of more primary nuclei and stable particles, which resulted in smaller beads. On the other hand, the increase in the polycondensation temperature might also have induced a decrease in the amount of adsorbed stabilizer because of the decreased viscosity of the medium and the increase in the growth rate of the existing particles. As a result, the particle size of the CPBs increased. Also, the polycondensation temperature had an important effect on the particle size distribution. CPBs with a narrow size distribution (PDI = 1.175) were obtained when the polycondensation temperature was 60°C. The particle size distribution of CPBs produced at higher polycondensation temperatures was broader. The phenomenon could be explained as follows: at higher polycondensation temperatures, the specific surface area of the CPBs increased because of the increase in the number of the nuclei formed at the earlier stage of nucleation. The stabilizer was not able to provide sufficient protection against particle aggregation, which led to the intensification of coalescence. The experimental results tabulated in Table I also demonstrate that no significant change in the yields of the CPBs was observed when the temperature was varied in the range 60–80°C. Thus, the effect of the reaction parameters on the yield of CPBs are no longer discussed for the following experiment.

The SEM images in Figure 1 show that CPBs had a spherical shape and a smooth surface. No pores were found on the surface of these particles, even at higher magnification, which confirmed the absence of macropores.

Effect of the agitation rate

The relation between the size and size distribution of CPBs and the agitation rate is shown in Figure 2. As shown in Figure 2, the particle size of the CPBs first increased slightly and then decreased sharply when the agitation rate varied from 500 to 800 rpm. Meanwhile, the particle size distribution became broader as the agitation rate increased. These results could be explained as follows: the stress field derived from stirring increased with increasing agitation rate. At a higher agitation rate, the mechanical force acting across the nuclei was higher, which reduced the extent of aggregation and increased the number of nuclei. As a result, smaller CPBs were obtained.[19] However, when the agitation rate was too high, the formation and growing process of
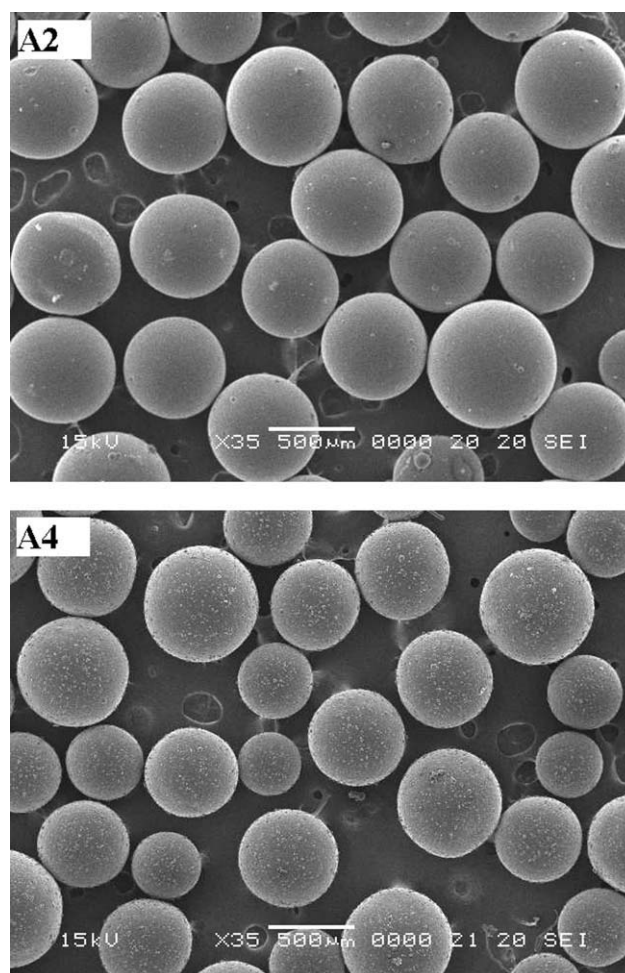

Figure 1 SEM micrographs of CPBs at different polycondensation temperatures.
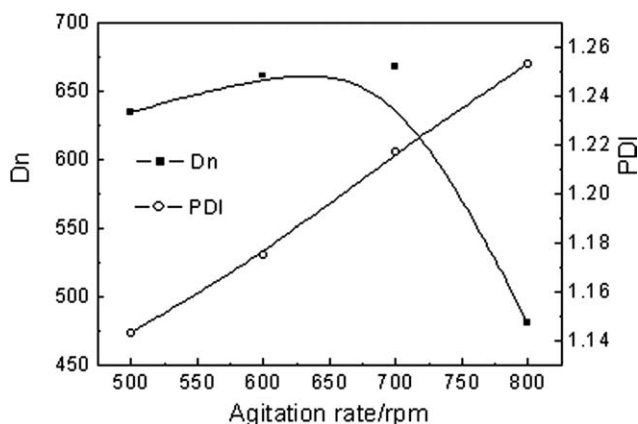
Figure 2 Effect of the agitation rate on the particle size and size distribution (reaction conditions: 27.74 g of PE, 53.33 g of a formaldehyde solution, 61.00 g of formic acid, 1.14 g of HEC, 8 mL of sulfuric acid, 14 h, and 60°C).

microspheres might have been disturbed because the steric stabilization of HEC was seriously destroyed by the fierce agitation.[24] This might have upset the uniformity of the primary nuclei, which resulted in a broader particle size distribution. Although dispersion polymerization is less sensitive to the agitation rate than suspension polymerization and emulsion polymerization, the proper agitation rate should be selected to reduce the coacervation effect.

Effect of the stabilizer concentration

The stabilizer plays a crucial role in dispersion polymerization.[23,25,26] It provides a protective effect to prevent aggregation during the particle-formation process. In this study, HEC was chosen as a stabilizer in the dispersion polycondensation of PE with formaldehyde. The effects of HEC concentration on the particle size and size distribution were studied, and the results are shown in Figure 3. The average particle
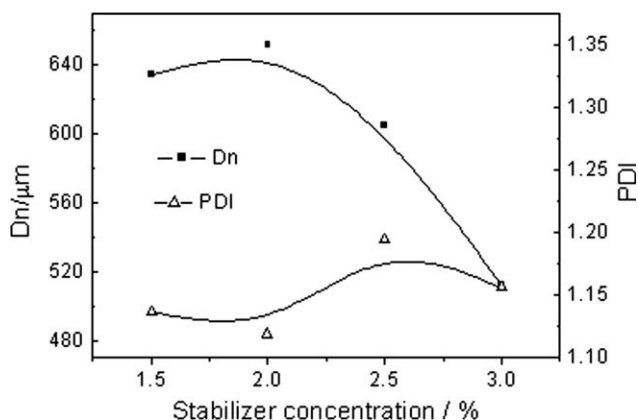
size varied from 634 to 513 μm as the HEC concentration increased from 1.5 to 3.5 wt %. The influence of the stabilizer concentration on the particle size was straightforward. When the HEC concentration was increased, the viscosity of the continuous phase, the rate of physical adsorption of stabilizer molecules, and the number of nuclei increased. As a result, the extent of nuclei aggregation decreased, and the number of stable nuclei increased. Correspondingly, smaller CPBs were obtained. As shown in Figure 3, an increase in the stabilizer concentration also had little effect on the particle size distribution.

Effect of the amount of sulfuric acid

The effects of the amount of sulfuric acid on the particle size and size distribution were also investigated. The experimental results are ere given in Figure 4. As shown in Figure 4, the average particle size of the CPBs decreased as the catalyst amount increased. The particle size of the CPBs decreased from 704 to 466 μm as the volume of concentrated sulfuric acid increased from 6 to 12 mL. These results could be explained as follows: the increase in the amount of sulfuric acid might have caused an increase in the rate constant of propagation, which, in turn, resulted in a short nucleation period at the early stage, where the particle number reached its final value.[27] Consequently, smaller CPBs were performed. On the other hand, the particle size distribution became broader with increasing catalyst amount, which indicated that the increase in the rate constant of propagation might have resulted in a broader particle size distribution. The SEM images of CPBs obtained under different amounts of sulfuric acid are shown in Figure 5, which further identifies the effect of the amount of sulfuric acid on the particle size and particle morphology.
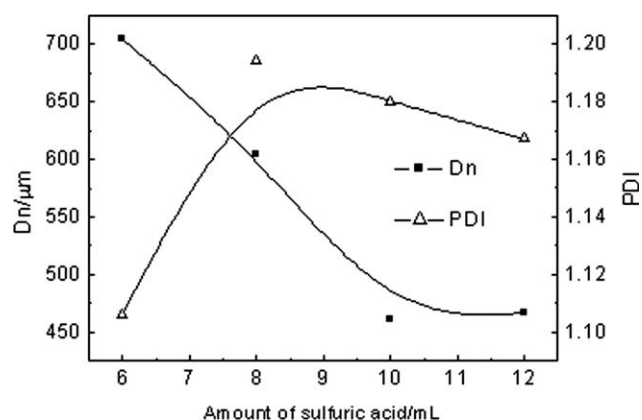

Figure 3 Effect of the stabilizer concentration on the particle size and size distribution (reaction conditions: 27.74 g of PE, 53.33 g of a formaldehyde solution, 8 mL of sulfuric acid, 61.00 g of formic acid, 14 h, 60°C, and 700 rpm).

Figure 4 Effect of the amount of sulfuric acid on the particle size and size distribution (reaction conditions: 27.74 g of PE, 53.33 g of a formaldehyde solution, 61.00 g of formic acid, 1.14 g of HEC, 14 h, 60°C, and 700 rpm).
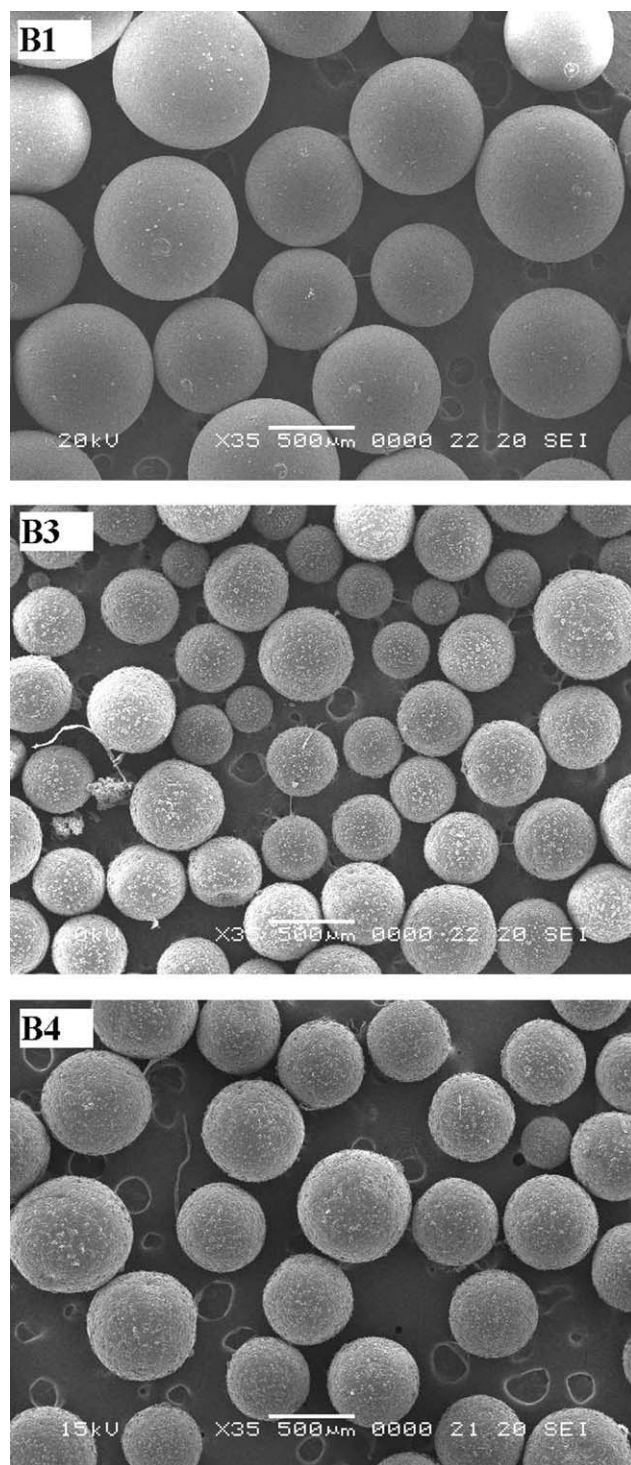
Figure 6 Effect of the F/P molar ratio on the particle size and size distribution (reaction conditions: 8 mL of sulfuric acid, 61.00 g of formic acid, 1.14 g of HEC, 14 h, 60°C, and 700 rpm).

complicated influence on the particle size and size distribution. When F/P was below 4 : 1, the particle size increased with increasing F/P. In the case of particle size distribution, no significant changes were observed. When F/P varied from 4 : 1 to 5 : 1, smaller CPBs with broader particle size distributions were formed. Obviously, the changes in F/P might have affected the rate constant of propagation and nucleation during the particle-formation process. These effects could be clarified as follows: the increase in F/P might have caused the following changes: (1) a decrease in the rate of physical adsorption because of the increase in the solubility of HEC, (2) a decrease in the solubility of the oligomer chains, and (3) a decrease in the critical chain length and the concentration of precipitated chains. The increase in the particle size with increasing F/P indicated the dominant influence of the first change. On the other hand, the average particle size of the CPBs decreased with increasing F/P, which might have been due to the decrease in both the critical length and the concentration of precipitated chains.

CONCLUSIONS

A novel polycondensable monomer (PE) and formaldehyde were successfully used to prepare CPBs by dispersion polycondensation. The effects of the reaction parameters, including the polycondensation temperature, agitation rate, HEC concentration, amount of sulfuric acid, and F/P, on the particle size and particle size distribution were investigated. The particle size of the CPBs decreased as the stabilizer concentration, agitation rate, and amount of sulfuric acid increased. The particle size of the CPBs was also affected by the polycondensation temperature and F/P. In this study, CPBs with a particle

Figure 5 SEM micrographs of CPBs with different amounts of sulfuric acid in the range of 6–12 mL: (B1) 6, (B3) 10, and (B4) 12 mL (reaction conditions: 27.74 g of PE, 53.33 g of a formaldehyde solution, 61.00 g of formic acid, 1.14 g of HEC, 14 h, 60°C, and 700 rpm).

Effect of F/P

In comparison to the other reaction variables, including temperature, agitation rate, stabilizer concentration, and amount of the catalyst, F/P had a more
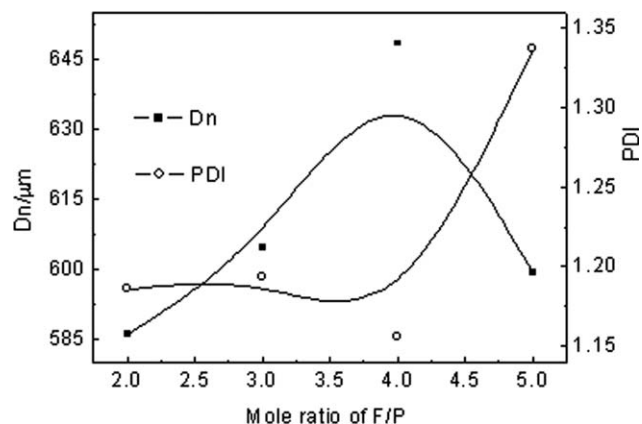
size of 604 μm as and a narrow particle size distribution (PDI = 1.193) were obtained under the following conditions: polymerization temperature = 60°C, agitation rate = 700 rpm, stabilizer concentration = 2.5%, F/P = 3 : 1, and amount of catalyst = 8 mL. Further studies are in progress to fully elucidate the mechanism of the particle and other effects such as the solvent and types of stabilizers on the particle size and particle size distribution.

References

1. Klampfl, C. W.; Buchberger, W.; Rieder, G.; Bonn, G. K. J Chromatogr A 1997, 770, 23.
2. Ugelstand, J.; Mørk, P. C.; Schmid, R.; Ellingsen, T.; Berge, A. Polym Int 1993, 30, 157.
3. Ugelstand, J.; Berge, A.; Ellingsen, T.; Schmid, R.; Nilsen, T.-N.; Mørk, P. C.; Stenstad, P.; Hornes, E.; Olsvik, Ø. Prog Polym Sci 1992, 17, 87.
4. Arshady, R.; George, M. H. Polym Eng Sci 1993, 33, 865.
5. Horák, D. Acta Polym 1996, 47, 20.
6. Shen, S.; Sudol, E. D.; El-Aasser, M. S. J Polym Sci Part A: Polym Chem 1993, 31, 1393.
7. Cui, H. L.; Chen, H.; Qu, R. J.; Wang, C. H.; Ji, C. N.; Sun, C. M.; Zhou, W. Y.; Yu, M. M. J Appl Polym Sci 2008, 107, 3909.
8. Li, K.; Stöver, H. D. H. J Polym Sci Part A: Polym Chem 1993, 31, 3257.
9. Song, J.-S.; Chagal, L.; Winnik, M. A. Macromolecules 2006, 39, 5729.
10. Bai, F.; Yang, X. L.; Huang, W. Q. Macromolecules 2004, 37, 9746.
11. Luo, Y. D.; Chiu, W. Y.; Dai, C. A. Polym Eng Sci 2009, 49, 1043.
12. Wang, J.; Liu, C. S.; Chi, P. J Biomed Mater Res B 2009, 89, 45.
13. Arshady, R. J Microencapsul 1980, 5, 101.
14. Yang, J. B.; Ling, L. C.; Liu, L.; Kang, F. Y. Carbon Technol 2000, 4, 35.
15. Ma, Q. L.; Lu, M. L. Ion Exch Adsorption 2000, 16, 239.
16. Brode, G. L. J Macromol Sci Chem 1985, 22, 897.
17. Ma, Q. L.; Lu, M. L. Ion Exch Adsorption 2000, 16, 239.
18. Zhou, H.; Huang, G. S.; Gao, P.; Long, C. Q. Polym Adv Technol 2007, 18, 582.
19. Singh, A.; Lai, D. J Appl Polym Sci 2006, 100, 2323.
20. Singh, A.; Yadav, R. K.; Srivastava, A. J Appl Polym Sci 2009, 112, 1005.
21. Strikovsky, A.; Hardil, J.; Wulff, G. React Funct Polym 2003, 54, 49.
22. Lee, D. H.; Kim, J. W.; Suh, K. D. J Mater Sci 2000, 35, 6181.
23. Shen, S.; Sudol, E. D.; El-Aasser, M. S. J Polym Sci Part A: Polym Chem 1994, 32, 1087.
24. Song, J. S.; Tronc, F.; Winnik, M. A. J Am Chem Soc 2004, 126, 6562.
25. Ramanathan, L. S.; Shukla, P. G.; Sivaram, S. Pure Appl Chem 1998, 70, 1295.
26. Ramanathan, L. S.; Baskaran, D.; Sivaram, S. Macromol Chem Phys 2002, 203, 998.
27. Kawaguchi, S.; Winnik, M. A.; Ito, K. Macromolecules 1995, 28, 1159.