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ORIGINAL CONTRIBUTION

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Multiporous hollow polymer particles

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Abstract Hollow particles with interconnected cavities have been prepared by a simple modified suspension polymerization of acrylate monomers in the incorporation of a phase inversion process and polymerizable emulsifier. The morphology of particles has been characterized by scanning electron micrographs (SEMs). Based on observations made using an optical microscope equipped with a digital camera and SEM images of particles obtained under different conditions, the formation mechanisms for multiporous hollow particles are discussed.

Keywords Suspension polymerization · Structure · Phase inversion · Polymerizable emulsifier

Introduction

Recently, control of the morphology of colloidal particles has become an intensive area in research of emulsion polymer science and various fields of technology. The synthesis of core-shell, microdomain, interpenetrating network, and hollow particles is now possible. The porous and hollow particles are more widely used because they can be used as toners, inks, cosmetics, coatings, supports for medical assays, enzyme immobilization carrier, chromatographic packing, and sound damping and absorption materials [1].

Some approaches have been reported to prepare hollow and porous polymer particles [1–11]. Okubo and coworkers [2–4] prepared submicrometer-sized multihollow particles via alkali swelling procedure (ASP) and dynamic swelling method (DSM). Schlarb et al. [5] used copolymer containing acrylic acid as emulsifier for the second-step emulsion polymerization in the presence of organic solvents. After the residual solvents were removed, the porous structures were yielded. Skovby and Kops [6] prepared porous beads by adding a porogen into the polymerization. Shouldice et al. [7] prepared porous particles by a three-step synthetic route, including emulsifier-free latex preparation, aggregation and aggregation stabilization, and coalescence. Omi et al. produced hollow particles by two-stage suspension polymerization using a Shirasu porous glass (SPG) membrane [8]. Generally speaking, those methods involve some drawbacks: tedious treatment procedures or producing lots of waste, which leads to more time-intensive and higher cost. According to Garti, double emulsions are prepared by two-step mode: hydrophobic emulsifier for the W/O inner droplets and hydrophilic emulsifiers for the external O/W emulsion [9]. Kim et al. [10] prepared poly(methylmethacrylate) (PMMA) multihollow particles by W/O/W emulsion polymerization technique. It is crucial to choose a suitable emulsifier for both inner and external emulsion and prevent the coalescence of the inherently unstable droplets. Instead, Yang et al. [11] prepared micrometer-sized multihollow spheres of epoxy resin by a phase inversion technique; however, it needed posttreatment for curing.

In this report, a new approach was developed to prepare multiporous hollow polymer particles by modified suspension polymerization, with the distinct advantage that no organic solvents are involved. From the viewpoint of practical application, this method is very attractive to achieve porous–hollow polymer particles owing to its simplicity, low cost, and environment friendliness. The fine porous structure features and formation mechanism of the particle were discussed in detail.

Experimental

Materials

Isophorone diisocyanate (IPDI) were vacuum-distilled before use. Dimethylopropionic acid (DMPA; Kelong Chemical Factory), 2-hydroxyethylmethacrylate (HEMA; Tianjing Chemical Co.), polypropylene oxide glycol (N210, Mw=1.0×10^3; Gaoqiao Co.), triethylamine (TEA; Tianjing), 2,2-azobisisobutyronitrile (AIBN; Tianjing), sodium hydrogen phosphate (Na_2HPO_4), di (ethylene glycol) diacrylate (DEGDA; Tianjiao Chemical Co.), sodium dodecyl benzene sulfonate (SDBS), and poly (vinyl alcohol) (PVA; 1788, saponificating value, ca. 88%) were used as received. Methylmethacrylate (MMA) and butyl acrylate (BA, Tianjing) were distilled under reduced pressure before polymerization.

Synthesis of polymerizable emulsifier

The oligomer PUA was synthesized by the stepwise reaction procedure. Firstly, after dissolving 1 wt.% of dibutyltin dilaurate (DBTDL), 1 mol of DMPA dissolved in dimethylformamide (DMF) was reacted with 2 mol of IPDI at 80 °C for 4 h. Then, 0.5 mol of N_{210} was poured into a reactor to react for another 4 h. After dissolving 1 wt.% of DBTDL into the reactor again, 2 mol of HEMA was reacted with the residual NCO groups at 45 °C for 6 h, which capped the molecular ends with the reactive vinyl groups. The schematic molecular structure of product is represented in Scheme 1. Carboxylic acid group of PUA was ionized with appropriate amount of TEA at room temperature for 0.5 h, and then the final product was named as IPUA.

Preparation of porous–hollow particles

The composition for the production of PMMA/BA porous–hollow particles is listed in Table 1. All ingredients of composition A were dissolved as homogeneous solution. Monomer compositions of B were charged into a round-bottomed reaction kettle equipped with a mechanical stirrer, a reflux condenser, thermocouples, and an N_2 inlet system. Solution A was dropped slowly into the reaction kettle at a given agitation speed. The polymerization was carried out continuously at 65 °C for 4 h. The supernatant was then decanted, and the remaining precipitate was washed with butyl alcohol repeatedly and dried at ambient temperature overnight in vacuo.

Table 1 Composition for preparation of modified suspension polymerization

Mixture	Ingredients	Weight (g)	
		Run 11	Run 21
A	SDBS	0.5	0
	Na_2HPO_4	1.2	1.2
	PVA	0.2	0.2
	Water	220	220
B	MMA	6	6
	BA	4	4
	DEGDA	4.5	4.5
	PUA	2.5	0
	IPUA	0	2.5
	AIBN	0.2	0.2

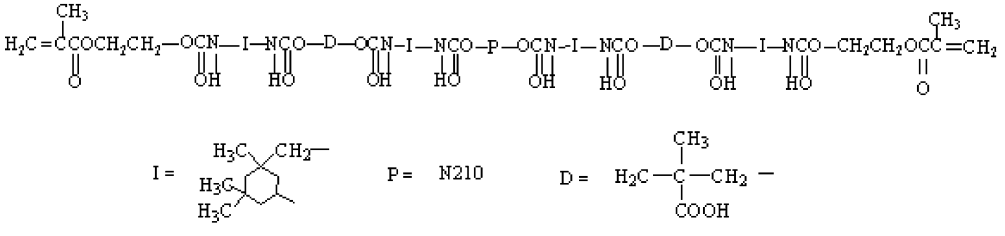
Measurements

The electrical properties were monitored by directly reading the current impedance value measured with a DDS-12A digital conductivity tester (Xiaoshang Analytical Instruments Factory), which was connected with well-designed electrodes fully immersed in the reactive mixture. When a continuous phase inversion from the oil phase to the water phase had occurred, this critical water content is defined as the phase inversion point (PIP).

For optical microscopic observation, samples of the emulsion taken at varied times were spread on a slide glass without a coverglass. Morphology of droplets was recorded using a digital camera (Canon PowerShot A70) attached to an optical microscope (OM; SDRE-IA optical microscope).

To verify the hollow structure, the produced particles were placed onto a coverglass and diluted with a drop of toluene (n=1.4967), which has a similar refractive index to

Scheme 1 The molecular structure of PUA oligomer



that of PMMA (n=1.4893) and poly(butyl acrylate) (PBA) (n=1.4740). Then, particles were observed with OM. The dried particles were sputtered with Au and observed with a scanning electron microscope (JSM-5900, JEOL).

Detailed information of multiporous hollow particles (such as surface area) is determined by BET (Brunauer–Emmett–Teller) method using SA 3100 (Beckman Coulter, USA).

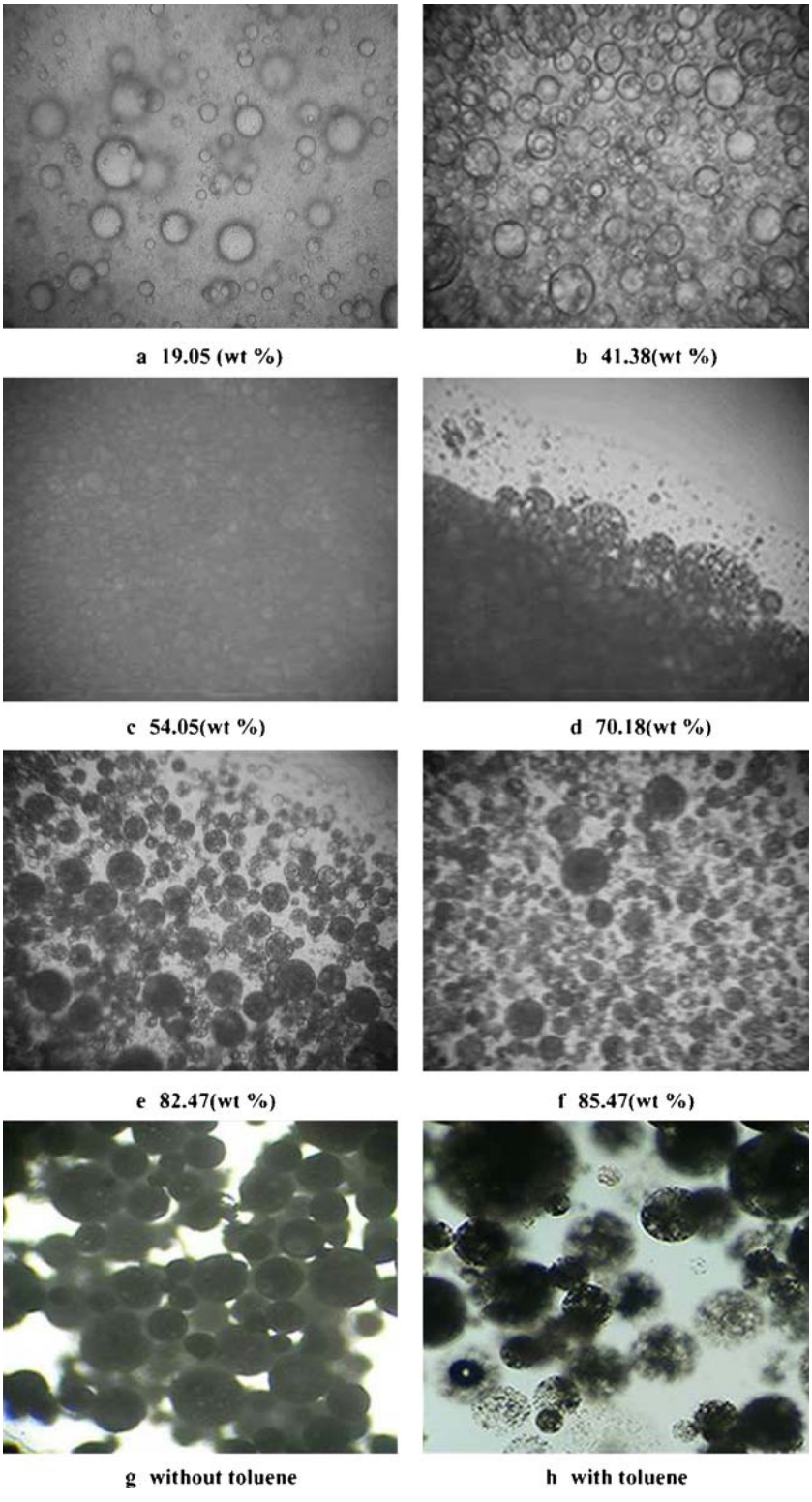


Fig. 1 **a**–**f** Morphological evolution (×100) during a phase inversion process with varied water content. **g**, **h** Representative OM micrographs of the porous–hollow particles prepared in run 11

Results and discussion

Phase inversion process during the formation of porous–hollow particles

Because of the solubility of PMMA/BA in its monomer, it is impossible to prepare porous PMMA/BA by conventional suspension polymerization. Furthermore, only small homogeneous (solid) particles are formed when acrylate monomer is polymerized by common emulsion process. To understand the formation process of the porous–hollow particles during the modified suspension polymerization with the polymerizable oligomer PUA and added emulsifier (SDBS) in run 11, the morphological evolution was traced by observing the representative samples with an OM-equipped camera during the phase inversion process, as shown in Fig. 1. As can be seen in Fig. 1a, when the water content is 19.05%, it is found that some bigger water drops coexist with smaller water droplets. The interface between water droplet and oil phase can be maintained clearly as aqueous solution is added (before PIP), seen in Fig. 1b. On increasing water content, for example to 54.05%, an unclear biphase-continuous fine structure can be found. Then, the local phase inversion occurs, and the interconnected structure is formed by the coalescence among the bigger water drops (Fig. 1c). When the water content reaches 70.18%, the critical water content at PIP (Fig. 1d), the continuous phase is completely inverted from the oil phase into the aqueous phase. It can be seen that lots of smaller water droplets are trapped in the bigger waterborne structure. Therefore, a W/O/W complex dispersion is obtained. As shown in Fig. 1e, the colloid structures become spherical and then experiences a slow curing progress. Some interconnected networks within the spheres are seen in Fig. 1e,f. Repeating the experiments, which show that the process is repeatable, attained similar results.

Figure 2 indicates that, when the water content (wt.%) is near 70%, the impedance of the emulsion system will change abruptly and reach a constant value. The consistent morphological and impedance change effectively identified that perfect phase inversions have taken place during the polymerization process, and it provides a way to track phase inversion in this method.

Representative OM micrographs of the porous–hollow acrylate particles are shown in Fig. 1g,h. It is obvious that the particles are porous–hollow. The cavities inside were further confirmed by redispersing the dried particles in toluene. Because the refractive index of the PMMA/BA is close to that of toluene, the inner voids filled with air display a different contrast from the PMMA/BA polymer phase as shown in Fig. 1h. It can be seen that the cavities are interconnected within the particles.

It should be noted that the fraction of multiporous hollow particles is about 75.40% of total monomer in run 11 and 85.1% in run 21, which indicates that the multiporous hollow particles are the dominative product, although a small quantity of homogeneous colloid latex or particles is formed (about 15.3 and 8.1% in runs 11 and 21, respectively).

Mechanism analysis of the porous–hollow particle formation

There are considerably fewer data in the literature identifying the mechanism or principles behind the formation of voided latex particles [1]. The Smoluchowski [12] theory developed by Davis and Rideal [13] mainly represents how the interaction of two phases influences the strength of interfacial films and then controlled the whole process of phase inversion. Although it is suitable in explaining the process of phase inversion, it meets difficulties when applied to explain how the inner structures form. On the basis of multiple pronounced phenomena in polymerization and unique transitional morphology during the formation procedure of particles, the formation mechanism is discussed here.

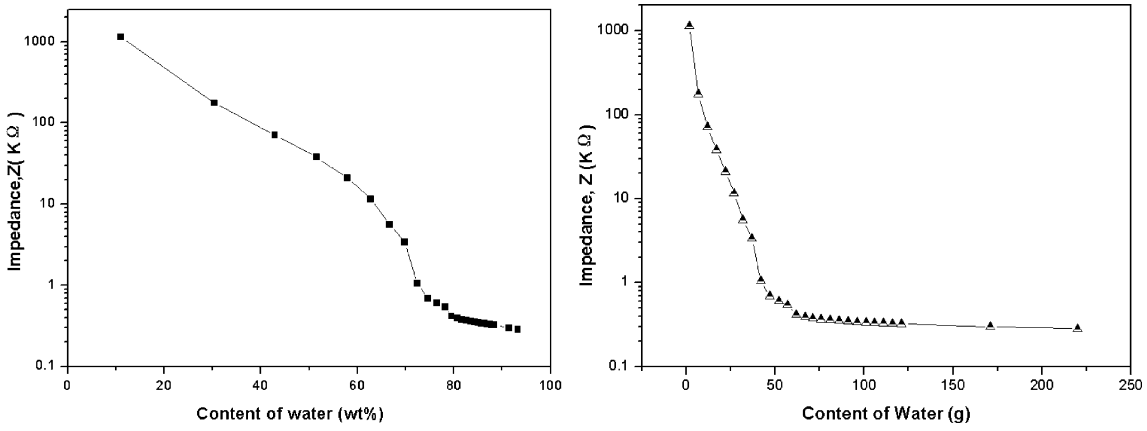


Fig. 2 Changes of the electrical properties with water content during phase inversion evolution

At the beginning of emulsification of MMA/BA/DEGDA/PUA mixtures, emulsifier molecules of SDBS within water solution are dispersed onto the water–oil interfaces to stabilize the water droplets. Aqueous phase is broken-up into very small droplets under shear field. Although the separated aqueous phase in the form of small droplets will coalesce to form larger ones, which gradually leads to a new continuous phase, those small droplets that do not coalesce will be kept in the oil matrix, which at last leads to cavities. On the other hand, while the hydrophilic carboxylic acid groups diffuse toward the aqueous phase, PUA formed in situ cross-linking membrane across the water–oil interfaces through reactive vinyl groups. A three-dimensional network is formed (gel formation) in the W/O emulsion right at the same time of the forming of a microphase-separated structure. Thus, the biphase-continuous fine structure of emulsions is achieved as shown in Fig. 1c. Next, with the content increase in water solution, the degree of microphase separation between water and oil phases will increase until enough water phases and shear field finally cause a phase inversion at PIP. The microstructure of gels is stabilized and maintained after PIP, as shown in Fig. 1d,e. In other words, shear field just changed the macrostructure of the gels, but not the microstructure. SEM micrographs in Fig. 3c show that porous–hollow particles have some obvious biphase-continuous structure. Smooth surfaces and cavities of these microparticles indicate a typical microphase-separated structure formed during the reaction process, which in fact is the gelation related above. It should be noted that when the microphase-separated structure forms, the gelation should happen at that very moment to obtain porous structures.

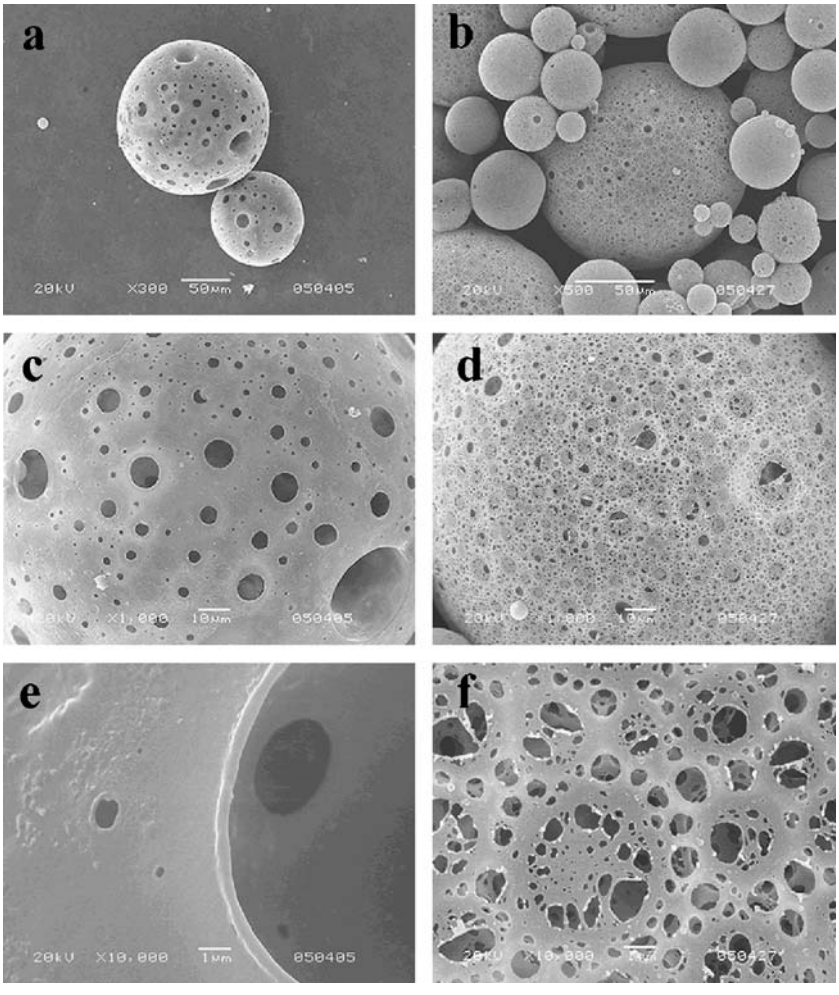


Fig. 3 SEM micrographs of multiporous hollow particles prepared with PUA (**a**, **c**, and **e**) and IPUA (**b**, **d**, and **f**)

Structure control of the porous–hollow particles

Through a series of experiments in run 21 with polymerizable emulsifier IPUA instead of SDBS, particles with fine porous structure are obtained by the said suspension polymerization techniques. Interestingly, both phase inversion and impedance change are also observed. However, it is found that the appearances of final products are quite different from those with PUA in microstructures, as shown in Fig. 3e,f. To reveal the reason for such structure difference in these particles, the so-called mechanism of AGD (the atomic group drive) is proposed here. Because IPUA molecules have more hydrophilic structures of group "$-COO^{-}HN^{+}(C_2H_5)_3$" (shown as an oval in Fig. 4) and long hydrophobic molecular chains (shown as a straight line in Fig. 4), it can function as an emulsifier. To distinguish from the added emulsifier (SDBS), IPUA is termed as polymerizable emulsifier.

Figure 4a shows the state of oil phase without added water, in which it can be seen that amphiphilic molecules of IPUA are dispersed into the oil phase at random. Once water is added into the homogeneous oil phase, hydrophilic groups of IPUA will intensively orient toward aqueous phase to protect the newly formed interface (shown in Fig. 4b).

As the amount of water rises, small droplets will coalesce to form bigger ones or clusters, as shown in Fig. 4c, while the very small ones can maintain the shapes of spheres because the gel cross-linked in oil phase, which form a network that links the dispersed water globules. The increase in aqueous phase will finally lead to the phase inversion at PIP. After that, the intense orientation of hydrophilic groups toward aqueous phase will shape the separated oil droplets into particles. What's more, the orientation toward water phase in the viscous oil droplets will cause lots of pores and cavities, which are much smaller than the small water droplets in the polymer matrix. This explains why the cavities of porous–hollow particles prepared with IPUA are much smaller in size and much denser than those prepared with PUA (shown in Fig. 3). The intensive orientation of hydrophilic group introduced by IPUA toward aqueous phase is the dominant drive force to form fine porous structure of particles. The specific surface area and pore volume of the particles are listed in Table 2. It is obvious that the results are quite consistent with the SEM pictures.

Moreover, it indicates that the morphology of particles prepared by this method can be regulated as needed. It will be helpful to enhance the applications of the particles in various fields such as sound damping and absorption.

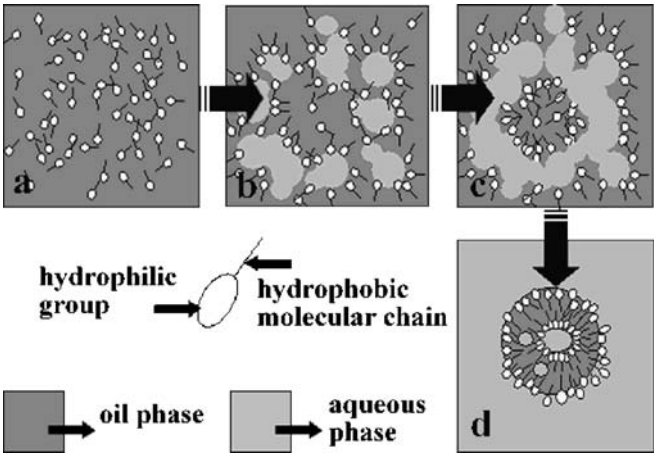


Fig. 4 Schematic illustration of the formation of porous–hollow spheres with IPUA by AGD

Table 2 Characterization of multiporous hollow polymer particles

Symbol	Average size (μm)	Surface area (m^2/g)	Pore volume (ml/g)
Run 11	68.27	2.172	0.0072
Run 21	41.32	6.603	0.0197

Conclusion

By incorporating a phase inversion process and a certain polymerizable emulsifier (IPUA) into emulsion polymerization, PMMA/BA multiporous hollow particles have been fabricated. The results obtained during this study suggest that the method could also be extended to other polymer particles. Phase-separated-gels formation and amphiphilic group drive mechanism are presented as preliminary understandings for the formation of particles. It is validated that phase inversion and IPUA played an important role in the structure formation of porous particles.

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References

1. Charles JM, Michael JD (2002) Adv Colloid Interface Sci 99:181
2. Okubo M, Ito A, Hashiba A (1996) Colloid Polym Sci 274:428
3. Okubo M, Mori H (1997) Colloid Polym Sci 275:634
4. Okubo M, Minami H (1997) Colloid Polym Sci 275:992
5. Schlarb B, Rau MG, Haremz S (1995) Prog Org Coat 26:207
6. Skovby MHB, Kops J (1990) J Appl Polym Sci 39:169
7. Shouldice GTD, Rudin A, Paine AJ (1996) J Polym Sci A Polym Chem 34:3061
8. Omi S, Ma GH, Nagai M (2000) Macromol Symp 151:319
9. Garti N (1998) Acta Polym 49:606
10. Kim BS, Kim JW, Suh KD (1999) Colloid Polym Sci 277:252
11. Yang Z, Zhao D, Xu M et al (2000) Macromol Rapid Commun 21: 574–578
12. Smoluchowski MV (1916) Phys Z 17:557
13. Davis JT, Rideal EK (1963) Interfacial phenomena, 2nd edn. Academic, New York, p 344