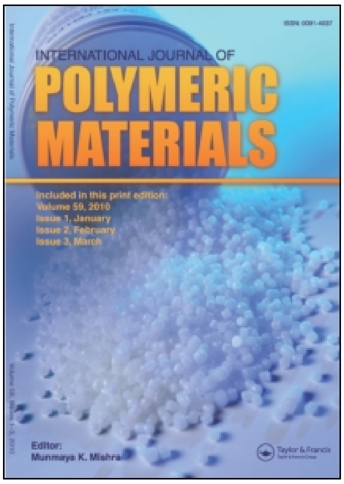

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Heterogeneous Structures in the Synthesis of Hydrophobic Lauryl Acrylate-Styrene-Ethylene Glycol Dimethacrylate Copolymer Particles

Ye Li[a]; Haijing Ren[b]; Zhaokun Luan[a]
[a] Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China [b] Institute of Environment and Sustainable Development in Agriculture, CAAS, Beijing, China

To cite this Article Li, Ye , Ren, Haijing and Luan, Zhaokun(2010) 'Heterogeneous Structures in the Synthesis of Hydrophobic Lauryl Acrylate-Styrene-Ethylene Glycol Dimethacrylate Copolymer Particles', International Journal of Polymeric Materials, 59: 9, 710 — 724

To link to this Article: DOI: 10.1080/00914037.2010.483213

URL: http://dx.doi.org/10.1080/00914037.2010.483213

International Journal of Polymeric Materials, 59:710–724, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914037.2010.483213

Heterogeneous Structures in the Synthesis of Hydrophobic Lauryl Acrylate-Styrene-Ethylene Glycol Dimethacrylate Copolymer Particles

Ye Li,[1] Haijing Ren,[2] and Zhaokun Luan[1]

[1]Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China
[2]Institute of Environment and Sustainable Development in Agriculture, CAAS, Beijing, China

Novel crosslinked hydrophobic lauryl acrylate-styrene-ethylene glycol dimethacrylate copolymer particles were synthesized with heterogeneous structures by radical suspension copolymerization with benzoyl peroxide as the initiator. Ethylene glycol dimethacrylate was used as a crosslinking agent; toluene, cyclohexanol, 1-octanol and liquid paraffin were used as porogens. The effects of the crosslinking monomer and porogens on the morphologies of the copolymer microspheres were investigated. The copolymers were characterized by FTIR, SEM and swelling in toluene. Permanent pores remained in the dried polymeric particles prepared with nonsolvating porogens at certain crosslink densities as indicated by SEM pictures. The results of swelling revealed that 1-octanol was the most effective porogen, leading to the LA-S-EGDMA copolymer particles with maximum porosity and optimized spheric morphology. Furthermore, lower crosslink density and higher porogen contents promote the formation of porous morphology.

Received 6 January 2010; accepted 12 March 2010.
The authors gratefully acknowledge the financial support of the National Science and Technology Support Program of China (Grant no. 2006BAJ08B05) and the National Natural Science Foundation of China (Grant no. 50678169).
Address correspondence to Zhaokun Luan, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: luanzk@rcees.ac.cn; luanzk@mail.rcees.ac.cn

Keywords heterogeneous structures, LA-S-EGDMA copolymer, phase separation, porous particles

INTRODUCTION

The applications of methacrylic ester crosslinked polymers with permanently porous structures have attracted increasing attention all over the world. Exploitation occurs in areas a diverse as chromatography, polymer-supported catalysts, ion recovery [1], water treatment and purification [2–5]. For many applications it is important to utilize a porous resin with a high surface area. The formation conditions of porous (heterogeneous) structures in resin have been the subject of both applied and fundamental research for many years. As early as the end of the 1950s, Dušek [6], Kunin [7,8], and Millar et al. [9–11] had already discovered this polymerization technique. According to the present reports [12–24], it was concluded that porous matrices can be obtained by suspension copolymerization, using monovinylic monomers and crosslinking reagents in the presence of inert porogens. These porogens may be extracted after polymerization, leaving holes or pores in the copolymer structures. Good solvents, nonsolvents, polymeric solvents, or mixtures of them may be used as porogens, leading to different kinds of pore size distributions.

A variety of acrylic ester resins with different specific areas and porosity had been prepared by varying the type and ratio of porogen at a given condition [13,25–29]. However, the preparation of perfusion particles was complicated, and this method was most used in trimethylolpropane trimethacrylate, 2-hydroxyethyl methacrylate, EGDMA, or methacrylate systems, and long alkyl chain acrylates systems have not been reported. Furthermore, the choice of polymerization conditions and experimental optimization must be specific for each chosen monomer system [20]. So it is necessary to further study.

In our work, a novel hydrophobic porous copolymer, lauryl acrylate-styrene-ethylene glycol dimethacrylate copolymer, was prepared by the suspension polymerization technique in the presence of porogens. The effect of the independent variables of synthesis on the morphology of LA-S-EGDMA copolymer was investigated in details, such as the relationship between the porous structure and the porogens or crosslink agent, and the interaction parameters of the components. By the way, the polymeric solvents were not considered as porogens, because of the difficulty of removal from the final product [30]. Low-molecular-weight solvents were used as porogens, i.e., toluent, cyclohexanol, 1-octanol and liquid paraffin. The effects of the crosslinking agent and porogens concentration on the properties of LA-S-EGDMA copolymer particles were studied. If the LA-S-EGDMA copolymer particles are to be used as adsorbents in oily waste water, it is necessary to know their behavior in organic solvents. So we investigated their swelling ability in toluene.

EXPERIMENTAL

Materials

Lauryl acrylate (LA), styrene (S), and ethylene glycol dimethacrylate (EGDMA) were washed with 5% aqueous solution of NaOH to remove the inhibitor and washed with deionized water five times to remove the remaining hydroxyl ions. Then, it was dried over anhydrous sodium, and finally vacuum distilled. Benzoyl peroxide (BPO), poly(vinyl alcohol) (PVA), NaCl, toluene, 1-octanol, cyclohexanol, and liquid paraffin were used as received without further purification.

Preparation of Copolymer Particles

The copolymers were prepared by the suspension copolymerization method with inert porogen. A standard recipe of the polymerization conditions appears in Table 1. The mixture of LA (monomer), S (monomer), and EGDMA (crosslinking agent) dissolving BPO initiator was employed as a dispersed phase. For the copolymerization of LA, S, and EGDMA, an aqueous solution of PVA (stablizer) and NaCl (electrolyte) was used as a continuous phase. An emulsion was prepared by dispersing the organic phase into the aqueous phase in a double-walled reactor fitted with an anchor-type agitator, condenser and nitrogen inlet at room temperature, the stirring rate of agitator was 150 rpm. After 30 min of nitrogen passing through the reactor, the temperature was elevated to 80°C~85°C for polymerization. The polymerization was carried out for 8 h under an agitation speed of 280 rpm and in a nitrogen atmosphere. The polymer particles obtained were washed by deionized water, and then were extracted with a Soxhlet apparatus by acetone for 24 h. Finally, the copolymeric particles were dried in a vacuum oven at 50°C for 24 h.

Table 1: Standard recipe for suspension polymerization.

Oil phase (dispersed phase)	Content (g)	Aqueous phase (continuous phase)	Content (g)
Lauryl acrylate (LA)	3.75	Deionized water	300.00
Styrene (S)	3.75	Polyvinyl alcohol (PVA)	0.30
Ethylene glycol dimethacrylate (EGDMA)	7.50	NaCl	6.00
Benzoyl peroxide (BPO)	0.30		
Porogens (selected)	15.00		

FTIR

The FTIR spectra of copolymer samples were recorded in the range 400–4000 cm^{-1} in KBr pellet, and the liquid monomer and crosslinking agent were cast onto the KBr pellet. All samples were analyzed by a Nicolet Nexus 670 spectrophotometer.

SEM

The diameter and surface features of polymer particles after drying were observed by an S-3000N Scanning Electron Microscope (Hitachi, Japan). Particles were fixed to the substrate, using double-sided Scotch tape, and were uniformly coated with a gold layer. The inner particle structure was revealed by cutting them in half with a razor blade prior to their fixation on the substrate.

Swellabilities of LA-S-EGDMA Copolymer Particles

In order to exhibit swellabilities of the particles, swelling ratios of the particles were obtained as follows [24]: Swelling (%) in toluene was measured with a 5 g oven-dried sample in a stoppered test tube. The sample was soaked with 20 mL of toluene for 24 h at the ambient temperature. Toluene was filtered, and the particles were patted dry with filter paper and weighed:

$$Swelling\ (\%) = \left[\frac{Increase\ in\ the\ weight\ of\ the\ particles}{Original\ weight\ of\ the\ particles}\right] \times 100\%$$

RESULTS AND DISCUSSION

FTIR

Figure 1 demonstrates the FTIR transmission spectra of the LA-S-EGDMA copolymer, the monomers and crosslinking agent. Figure 1(a) shows the characteristic peaks of styrene at 3000–3100 cm^{-1} (aromatic CH stretching vibration), 1630 cm^{-1} (C=C stretching vibration), 1601 cm^{-1} (ring quadrant stretching vibration), 1494 cm^{-1} (ring semicircle stretching vibration), 1448 cm^{-1} (ring semicircle stretching +CH_2 symmetric (scissors) deformation vibration), 775 cm^{-1} (mono-substituted ring in phase bending), and 696 cm^{-1} (mono-substituted ring out-of-plane bending). Figure 1(b) shows the characteristic peaks of LA at 2924 cm^{-1} ($-CH_3$ symmetric stretching vibration), 1728 cm^{-1} (C=O stretching vibration), 1637 cm^{-1} (doublet, C=C stretching vibration), 1191 cm^{-1} (C–O–C stretching vibration), 985 cm^{-1} (vinyl twisting vibration) and 965 cm^{-1} (vinyl CH_2 wagging vibration). Figure 1(c) shows

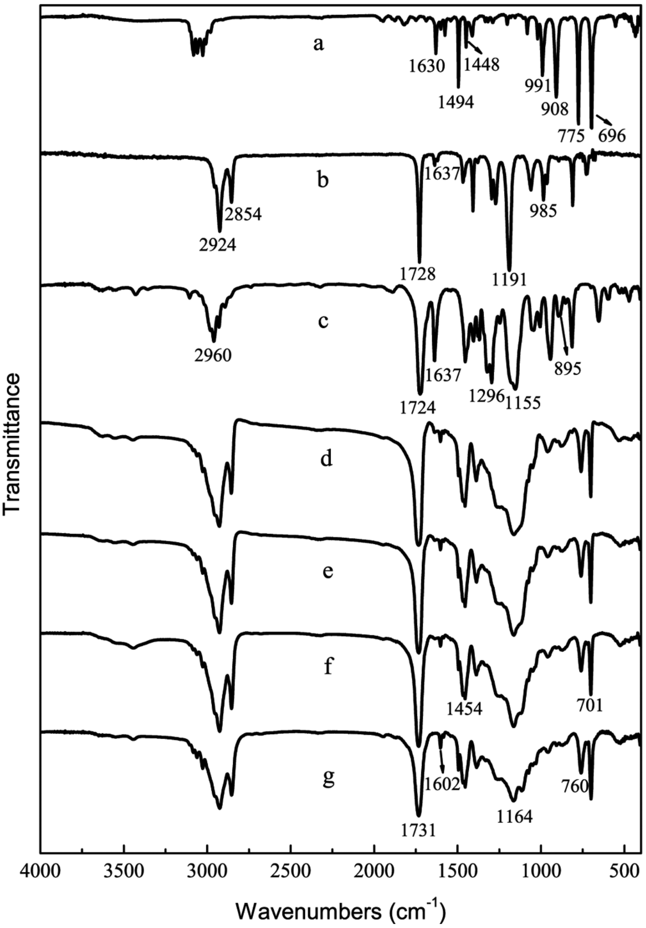

Figure 1: FTIR transmittance spectra: (a) styrene, (b) LA, (c) EGDMA, and (d)–(g) copolymers prepared with 50%, 40%, 30%, 20% EGDMA feed ratios, respectively.

the characteristic peak of EGDMA at 2960 cm^{-1} ($-CH_3$ asymmetric stretching), 1724 cm^{-1} (C=O stretching vibration), 1637 cm^{-1} (singlet, C=C stretching vibration), 1454 cm^{-1} (ring semicircle stretching $+CH_2$ symmetric (scissors) deformation vibration), 1155 cm^{-1} (C−O−C stretching vibration), 943 cm^{-1} (vinyl wagging vibration). The peak at 1630 cm^{-1} in Figure 1(a) and the peaks at 1637 in Figure 1(b) and (c), which are due to the C=C stretching, disappeared in the copolymers as shown in Figure 1(d)–(h). In addition, the peak at 991 cm^{-1} in Figure 1(a), the peaks at 985 and 965 cm^{-1} in Figure 1(b), and the peak at 943 cm^{-1} in Figure 1(c), which are attributed to the vinyl twisting and wagging, disappeared in Figure 1(d)–(g). In Figure 1(g), several peaks at the 3000–3100 cm^{-1} region are due to the CH stretching in the aromatic ring, and the peaks at 1602, 1494, 1454, 760, and 701 cm^{-1} also originate from the aromatic ring in styrene. The characteristic peaks of the LA unit are observed at 1728 and 1191 cm^{-1} and the characteristic peaks of EGDMA, such as 1724, 1454, 1155 cm^{-1}, were also exhibited in the FTIR spectra of LA-S-EGDMA copolymer. Thus, the very strong peak at 1731 cm^{-1} in Figure 1(g) is due to the C=O stretching in acrylate, and the less intense peak at 1189 cm^{-1} is designated to the C–O–C stretching in acrylate. Considering Figure 1(d)–(g), it is observed that the intensity of the peaks of EGDMA decreases with decrement of the concentration of EGDMA, but that of the peaks due to S and LA increases.

Effect of Porogen Types on Structures

A series of porogens were chosen to fabricate heterogeneous microspheres at a fixed porogen/(reaction mixture) ratio (1:1, wt:wt). Several physical parameters of the porogens are listed in Table 2 [16]. Figures 2–5 show the LA-S-EGDMA copolymer prepared with toluene, cyclohexanol, 1-octanol and liquid paraffin as the porogen. These porogens are characterized by differences in the polarity, chemical structure, functional behaviors, and solvent–polymer interaction values [31] that will lead to networks with a large variety of porous structures. The correlated characteristic of the copolymers particles were listed in Table 3. From Figure 2, when toluene was added in the oil phase in order to synthesize porous structures, the surface of the particles was very smooth and there weren't any details that could be observed at all. It can be concluded that toluene is a good solvent for the copolymers. An expanded structure with micro and mesopores was formed during the polymerization. The expanded particles thus formed collapsed during the removal of the porogen after its synthesis. That resulted in the disappearance of pores.

Figures 3–5 show the heterogeneous structures of copolymer particles prepared with cyclohexanol, 1-octanol and liquid paraffin, respectively. It is found that all three porogens can produce porous networks. Moreover from Figures 3(b), 4(b), and 5(c), the interior of the particles becomes looser and rougher; the pores inside the particles become bigger. This indicates that

Table 2: Physical properties of the porogens.

Solvent	Boiling point (°C)	Solubility parameter δ ($(MPa)^{1/2}$)	Solubility (water)/%
Toluent	110	18.1	0.045 (20°C)
Cyclohexanol	161	23.3	3.6 (20°C)
1-octanol	195	21.1	0.01~0.05
Liquid paraffin	≥300*	–	–

*Refer to the specification of liquid paraffin.

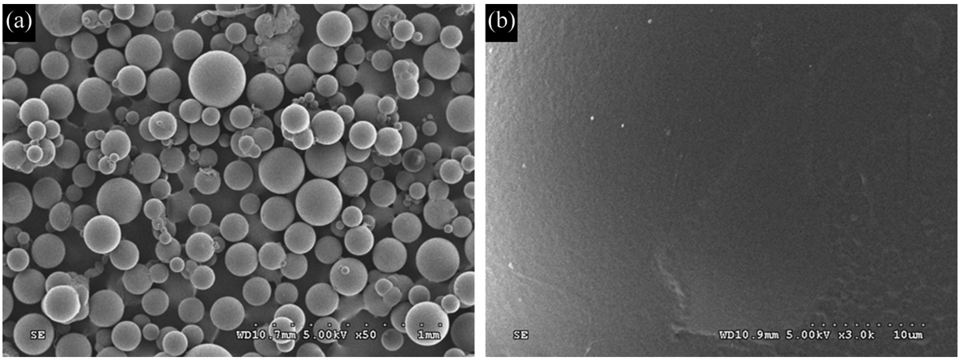

Figure 2: SEM of particles with toluene as diluent; (a) particles and (b) particle surface.

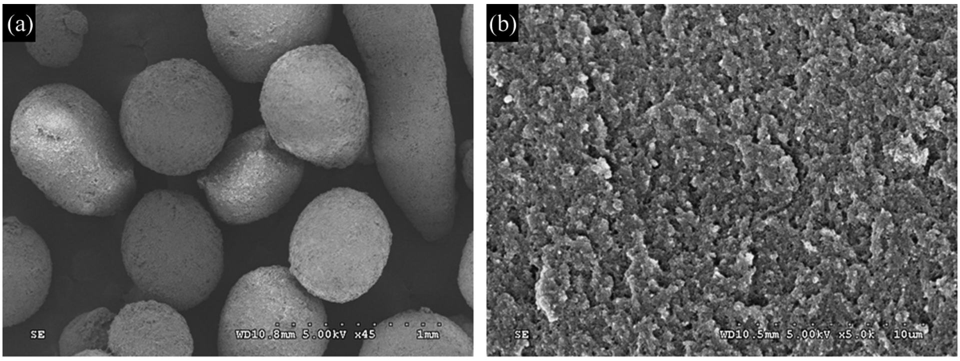

Figure 3: SEM of particles with cyclohexanol as diluent; (a) particles and (b) interior structure.

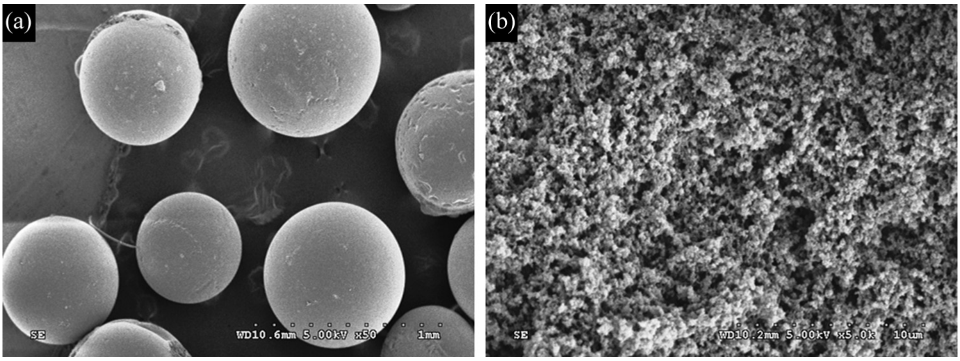

Figure 4: SEM of particles with 1-octanol as diluent; (a) particles and (b) interior structure.

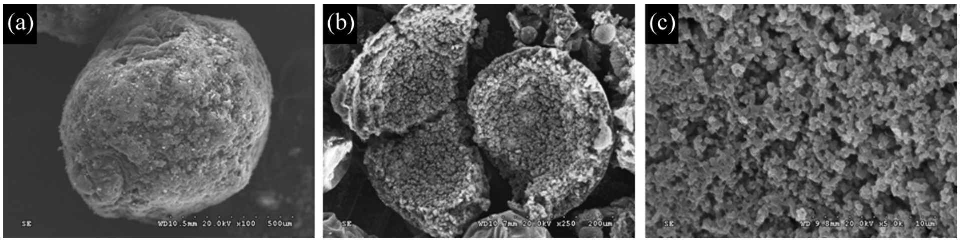

Figure 5: SEM of particles with liquid paraffin as diluent; (a) particles, (b) hollow morphology and (c) interior structure.

the phase separation occurs during the crosslinking polymerization in the presence of porogens. Phase separation depends on the following main factors [32]: the molar volumes of the individual components, the initial solvent and crosslinking agent concentrations, the polymerization conversion, and the interaction parameters of the components. The first three factors remained constant, when the samples of Figures 3–5 were synthesized. The fourth factor was variable, because different type of porogens were added in the polymerization system. These interaction parameters are affected by the changes in the thermodynamic quality of the porogens. The deterioration of the porogens' thermodynamic quality results in the phase separation at much lower polymerization conversion, and microspheres (or their aggregates) preferentially solvated by the monomer, then grow to larger dimensions and induce bigger pores [13]. So the porous structures prepared with 1-octanol and liquid paraffin was superior to those prepared with toluene and cyclohexanol.

Furthermore, as illustrated in Figure 5(b), the sample prepared with liquid paraffin as porogen had a cavity in the center of the particles. It was speculated as follows. Plenty of liquid paraffin-rich phases and copolymer-rich

Table 3: Synthesis and characterization of LA-S-EGDMA copolymer particles.

			Particles (dry status)	
No.	**Porogens ratios**[a]		**Shape**	**Transparent**
1	Toluent	1:1	Beads	Yes
2	Cyclohexanol	1:1	Beads, Irregulars[b]	No
3	1-Octanol	1:1	Beads	No
4	1-Octanol	0.8:1	Beads	No
5	1-Octanol	0.6:1	Beads	No
6	1-Octanol	0.4:1	Beads	No
7	1-Octanol	0.2:1	Beads	Translucent
8	Liquid paraffin	1:1	Irregulars	No

[a] The ratios are with respect to the total weight of LA, S, and EGDMA, and the oil phase/aqueous phase ratio was kept constant.
[b] The shape of the product is not a regular sphere.

phases were quickly separated from the polymerization solution at the early stage of the polymerization with low conversion. The new generated polymer microgels in copolymer-rich phases with low molecular weight would make an interior of microsphere in a liquid and mobile state until the gelling point. Such long-term mobility in a reaction environment provided much possibility for plenty of phases to rearrange into more stable conformation with thermodynamic equilibrium and lowest interfacial free energy. For one polymerizing droplet suspended in water during suspension polymerization, highly hydrophobic porogen phases tended to move into the center of the microsphere and combined each other into one bulky liquid core. The polymer will precipitate in the droplet, migrate to the interface, and eventually envelope the inert hydrophobic solvents (liquid paraffin) [33,34]. Thus, hollow copolymer microspheres were obtained after liquid paraffin was removed.

Effect of Porogen Types on Apparent Shapes

The spherical shape of the copolymer particles synthesized by suspended polymerization is another important characterization. Figures 2(a)–5(a) show the shape of the samples prepared with different porogens. It is found that if the porogen was toluene or 1-octanol, with limited solubility in water, then predominantly spherical particles are formed. In contrast, cyclohexanol, which is readily soluble in water, when used as a porogen lead to the formation of the irregular particles polymerization product [Figure 3(a)]. The formation of irregular particles may be connected with a change in the mechanism of the polymerization as a consequence of increased solubility of the initiator in the aqueous phase if the porogen concentration in this phase is high. The participation of solution precipitation copolymerization in this phase could then increase [14]. This process results in the formation of the irregular particles. However, liquid paraffin is a mixture of $C_{16}\sim C_{20}$ hydrocarbons, thus the interaction in the dispersed phase between liquid paraffin and copolymer was multiple and complicated. It was speculated that the complicated interaction mechanism was responsible for the irregular shapes of copolymer particles.

Effect of Porogen Amount

Figure 6 shows the interior structures became rougher gradually as the ratios of 1-octanol/(LA + S + EGDMA) increased from 0.2:1 to 0.8:1. During the polymerization process, 1-octanol could produce a porous network structure due to the phase separation. Furthermore, more holes, voids, and microdefects were left with the increasing of 1-octanol. These results are in agreement with the reported literature [17,24].

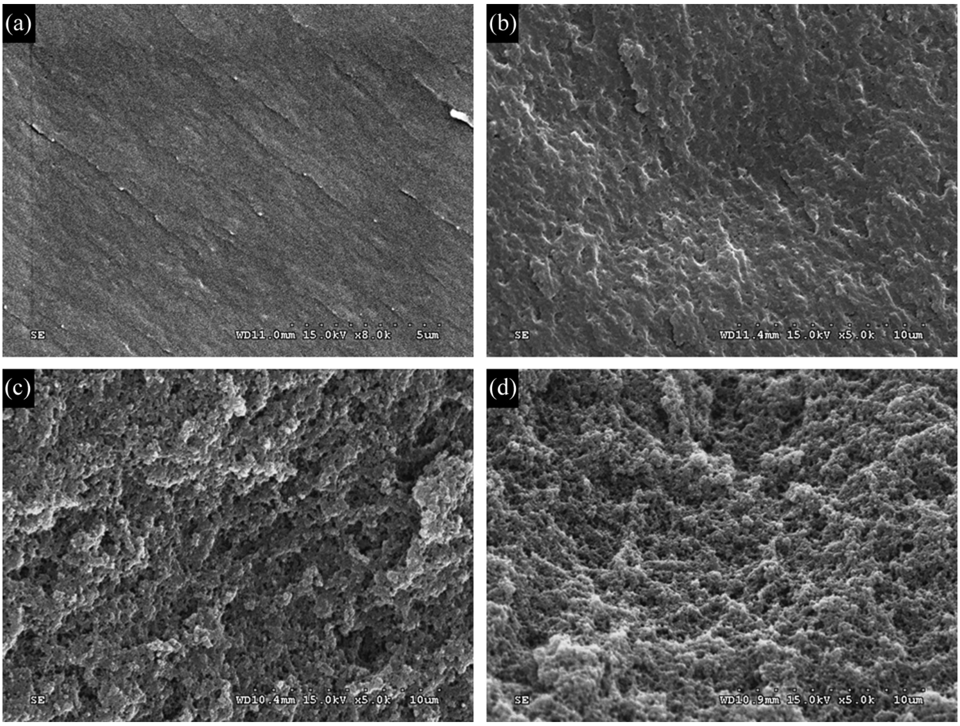

Figure 6: Interior structure of the particles prepared with different 1-octanol content; (a) 0.2:1, (b) 0.4:1, (c) 0.6:1, and (d) 0.8:1.

Effect of Crosslinking Agent Amount

As shown in Figure 7, the interior porosity increased with crosslinking agent concentration increasing. The EGDMA amount and characteristic of the particles were list in Table 4. According to Dušek [35], the heterogeneous pores may appear as a result of the interaction of the polymer and the solvent when a poor solvent (χ-induced syneresis) is used, or by increasing the crosslink density (ν-induced syneresis). Although the crosslinking agent concentration was relative low (20% and 30%) in Figures 7(a) and (b), the permanent pores were generated because the porogen concentration was too high to be completely absorbed by the polymeric networks, which resulted in the dispersion of the free porogens (separated phase, χ-induced syneresis) in the copolymer particles. As the polymerization proceeds, the porogen was immobilized by the crosslinking networks [23]. Then the porous structure was formed after extraction and drying. In this case, the porogen exsists in these voids result in permanent pores, whereas the rest of the porogen, absorbed by the polymeric network, lead to "expanded pores" [21] and these pores would collapse or shrink during the drying operation. However, they can be recovered during swelling. This can

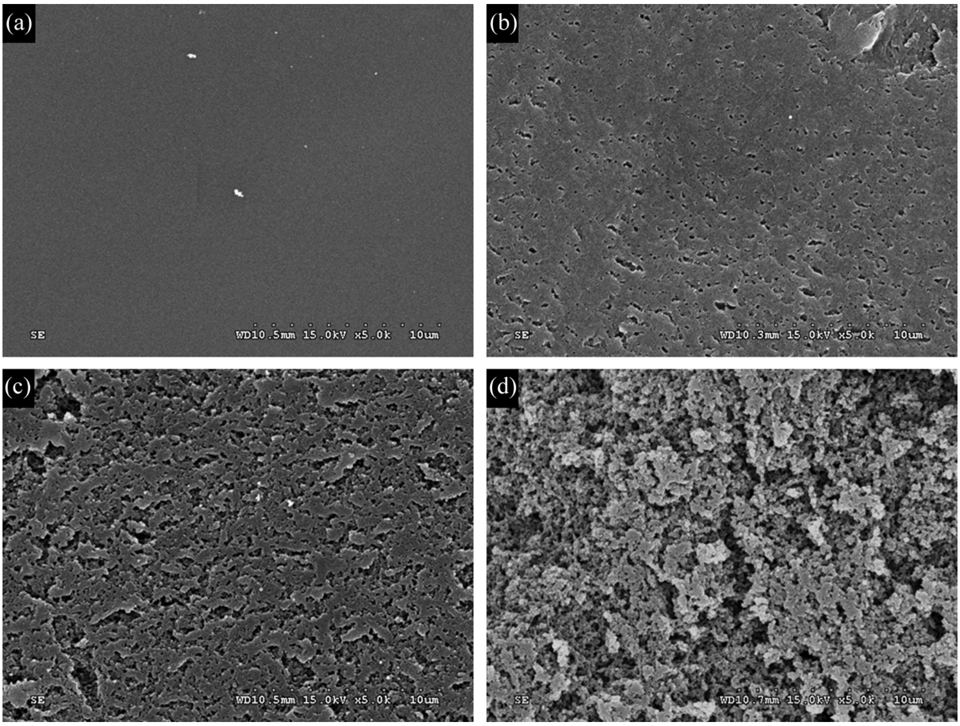

Figure 7: Interior structure of particles prepared with different EGDMA content: (a)10wt%, (b) 20wt%, (c) 30wt%, and (d) 40wt%.

be concluded from the swelling capability of the LA-S-EGDMA copolymer particles (Figure 8).

The mechanism of the phase separation will be the ν-induced syneresis if the crosslink density keeps increasing [17]. From Figures 7(c) and (d) the permanent pores formed by the agglomeration of many microgels can be observed with a higher crosslinking agent concentration (40% and 50%).

Table 4: Effect of crosslinking agent on polymer particles synthesis.

No.	1-Octanol ratio	EGDMA contents[a] (wt%)	Particles (dry status)	
			Hardness	Transparent
1	1:1	50	Yes	No
2		40	Yes	No
3		30	Yes	No
4		20	Yes	Translucent
5		10	No[b]	Yes

[a] The content is with respect to the total weight of the oil phase except porogen.
[b] The particles are elastic and viscous.

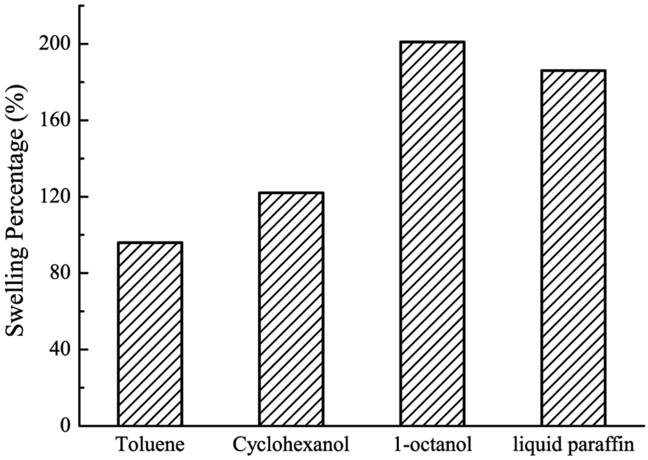

Figure 8: Effect of LA-S-EGDMA copolymers synthesized with different porogens on the swelling ability.

The permanent pores are the heterogeneous pores when the copolymer particles are in the dry state. The porous morphology illustrates the heterogeneity as a result of the agglomeration of a large amount of separated microgels. According to Okay [17], a higher crosslink density results in the microgels that are separated earlier than the original gel point without being greatly swollen by the solvents or the reaction mixture. In this case, the organic phase remains as a continuous phase, which is full of the separated microgels. As the reaction proceeds, more microgels are continuously generated and agglomerate to form the heterogeneous gel, which consists of two continuous phases, a gel and a porogen phase. The voids between the agglomerated gels are occupied by the porogen to form permanent pores after the porogen is removed from the copolymer particles.

Swelling Measurements

Acording to Tuncel et al. [21], the distribution of the porogen between network and porogen phases (porogen in the pores) at the end of the polymerization determines the total porosity of the resulting polymer and their swelling ratios in solvents. So the swelling capability of the LA-S-EGDMA copolymer particles was investigated for further illuminating the effect of the porogen on the porous morphology. Toluene was selected as the solvent for determining the swelling ability of the LA-S-EGDMA copolymer particles. As shown in Figure 8, a higher swelling percentage (201%) was achieved in LA-S-EGDMA copolymers synthesized with higher 1-octanol content (100%). Furthermore, higher toluene as a porogen produced copolymers with minimum swelling (96%). These values indicate that nonsolvating porogens (e.g., 1-octanol) produced more pores.

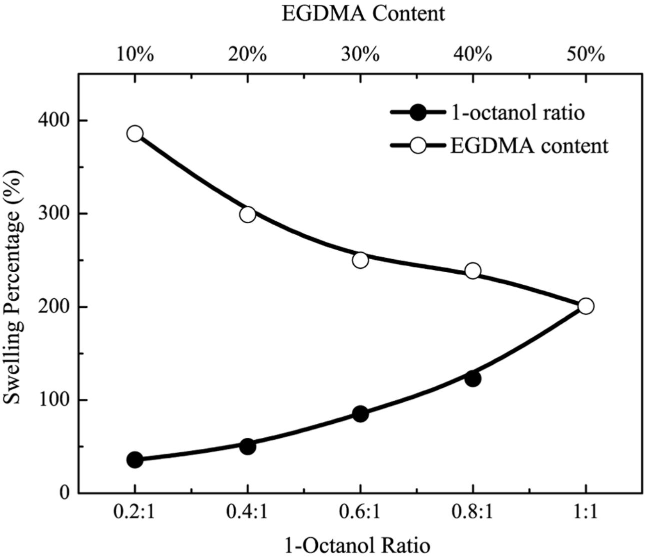

Figure 9: Effect of LA-S-EGDMA copolymers synthesized with different EGDMA content or 1-octanol/(LA+S+EGDMA) ratios on the swelling ability.

However, solvating porogens (toluene) resulted in poor porosity of copolymer particles, as indicated by lower swelling percentage values. These conclusions are identical with the results of SEM pictures (Figures 2–5).

Figure 9 shows that the swelling percentage increases with the amount of the 1-octanol increasing, but decreases with the amount of EGDMA increasing, because more porogen (1-octanol) leads to higher porosity of the particles at a constant crosslinking agent content (50% EGDMA). On the other hand, more crosslinking agent content can create a denser polymeric network, which restricts the relaxation of the polymeric chain and induces the reduction of the expanded pores [23,36]. This will result in a decreasing swelling capacity. Furthermore, the swelling capacity is higher at a lower crosslink density and higher porogen contents since more expanded pores can be produced.

Generally, the swelling capacity was greatly enhanced because of the presence of a highly porous structure (permanent and expanded pores) and loose polymeric networks. Thus, copolymer particles with higher swelling capacity were obtained under high 1-octanol and low EGDMA content [24,37].

CONCLUSIONS

Different morphologies of LA-S-EGDMA copolymer particles were synthesized by free radical suspension polymerization with toluene, cyclohexanol, 1-octanol and liquid paraffin as porogens, respectively. The crosslink density, the porogens' properties and content strongly influence the porous structure, the particles' morphology and the swelling capacity.

The porosity of the copolymer particles increases with corosslink agent concentration and porogens content increasing. The copolymer particles boasted an excellent porous network and regular spherical shapes when 1-octanol was the porogen, and the optimum content of 1-octanol and EGDMA was 100% and 50%. And there was a cavity in the center of the particles while liquid paraffin was porogen. However, if 100% toluene was used as porogen, nonporous copolymer particles were obtained with a smooth surface and translucent appearance.

The swelling capacity of these particles in toluene at room temperature correlates with the porous structure and the crosslink density of the polymeric networks. The copolymer particles synthesized under higher porosity and lower crosslink density will have a higher swelling capacity. The maximum swelling capacity of copolymer particles in toluene was achieved when 100% 1-octanol and 10% EGDMA was added in the polymerization process. And the minimum swelling capability was obtained when 100% toluent and 50% EGDMA was added.

REFERENCES

[1] Arai, T., and Hozumi, Y. *Chem. Lett.* **27**, 1153 (1998).

[2] Aiken, G. R., Thurman, E. M., Malcolm, R. L., and Walton, H. F. *Anal. Chem.* **51**, 1799 (1979).

[3] Payne, G. F., Payne, N. N., Ninomiya, Y., and Shuler, M. L. *Sep. Sci. Technol.* **24**, 457 (1989).

[4] Brown, J. L., Chen, T., Embree, H. D., and Payne, G. F. *Ind. Eng. Chem. Res.* **41**, 5058 (2002).

[5] Yang, W. B., Li, A., Fan, J., Yang, L., and Zhang, Q. *Chemosphere* **64**, 984 (2006).

[6] Dušek, K. *J. Polym. Sci., Part B: Polym. Lett.* **3**, 209 (1965).

[7] Kunin, R., Meitzner, E., and Bortnick, N. *J. Am. Chem. Soc.* **84**, 305 (1962).

[8] Kunin, R., Meitzner, E. A., Oline, J. A., Fisher, S. A., and Frisch, N. *I&EC Prod. Res. Dev.* **1**, 140 (1962).

[9] Millar, J. R., Smith, D. G., Marr, W. E., and Kressman, T. R. E. *J. Chem. Soc.* 218 (1963).

[10] Millar, J. R., Smith, D. G., Marr, W. E., and Kressma, T. R. E. *J. Chem. Soc.* 2740 (1964).

[11] Millar, J. R., Smith, D. G., and Kressma, T. R. E. *J. Chem. Soc.* 304 (1965).

[12] Horák, D., Pelzbauer, Z., Bleha, M., Ilavský, M., Scaronvec, F., and Kálal, J. *J. Appl. Polym. Sci.* **26**, 411 (1981).

[13] Horák, D., Lednický, F., Řehák, V., and Švec, F. *J. Appl. Polym. Sci.* **49**, 2041 (1993).

[14] Poinescu, I. C., Beldie, C., and Vlad, C. *J. Appl. Polym. Sci.* **29**, 23 (1984).

[15] Takeda, K., Akiyama, M., and Yamamizu, T. *Angew. Makromol. Chem.* **157**, 123 (1988).

[16] Okay, O., and Gürün, Ç. *J. Appl. Polym. Sci.* **46**, 421 (1992).

[17] Okay, O. *Prog. Polym. Sci.* **25**, 711 (2000).

[18] Erbay, E., and Okay, O. *Polym. Bull.* **41**, 379 (1998).

[19] Okay, O. *Polymer* **40**, 4117 (1999).

[20] Svec, F., and Fréchet, J. M. J. *Macromolecules* **28**, 7580 (1995).

[21] Gomez, C. G., Alvarez, C. I., Strumia, M. C., Rivas, B. L., and Reyes, P. *J. Appl. Polym. Sci.* **79**, 920 (2001).

[22] Tang, F., Fudouzi, H., Uchikoshi, T., and Sakka, Y. J. *Eur. Ceram. Soc.* **24**, 341 (2004).

[23] Fang, D. Y., Pan, Q. M., and Rempel, G. L. *J. Appl. Polym. Sci.* **103**, 707 (2007).

[24] Tank, R., Beldar, A., Saxena, A., and Gupta, D. C. *J. Appl. Polym. Sci.* **108**, 1531 (2008).

[25] Rosenberg, J. E., and Flodin, P. *Macromolecules* **19**, 1543 (1986).

[26] Rosenberg, J. E., and Flodin, P. *Macromolecules* **20**, 1518 (1987).

[27] Kotha, A., Raman, R. C., Ponrathnam, S., and Shewale, J. G. *React. Funct. Polym.* **28**, 227 (1996).

[28] Kolarz, B. N., Jermakowicz-Bartkowiak, D., and Trochimczuk, A. *Eur. Polym. J.* **34**, 1191 (1998).

[29] Hebb, A. K., Senoo, K., Bhat, R., and Cooper, A. I. *Chem. Mater.* **15**, 2061 (2003).

[30] Horák, D., Labskýa, J., Pilařa, J., Blehaa, M., Pelzbauera, Z., and Šveca, F. *Polymer* **34**, 3481 (1993).

[31] Knill, C. J., and Kennedy, J. F. *Carbohydr. Polym.* **46**, 295 (2001).

[32] Scholz, E. *Fresenius. J. Anal. Chem.* **312**, 462 (1982).

[33] Omi, S., Ma, G. H., and Nagai, M. *Macromol. Symp.* **151**, 319 (2000).

[34] Hao, D. X., Gong, F. L., Hu, G. H., Lei, J. D., Ma, G. H., and Su, Z. G. *Polymer* **50**, 3188 (2009).

[35] Dušek, K. (1971). In *Polymer Networks. Structure and Mechanical Properties*, A. J. Chompff and S. Newman, Eds., Plenum Press, New York.

[36] Yan, J., Wang, X., and Cao, Z. *React. Funct. Polym.* **46**, 127 (2000).

[37] Tuncel, A., and Pişkin, E. *J. Appl. Polym. Sci.* **62**, 789 (1996).