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The relationship between heterogeneous structures and phase separation in synthesis of uniform PolyDVB microspheres

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ABSTRACT

Polydivinylbenzene microspheres from microvoids, hollow to different porous structures were respectively fabricated by a combined route of membrane emulsification and suspension polymerization. The relationship between these structures and the phase separation behaviors in formation of these microspheres was investigated by in-situ tracking phototransmittance of polymerization system. Macrospores or hollow structure formed by non-solvating porogen often induced fast decline of transmittance and early phase separation, while micropores formed by solvating porogen lead to much slower declines of transmittance and later phase separation. Besides, the gelling point of polymerization system during phase separation process was found crucial to influence movements of phases in polymerization and thus the final heterogeneity of microspheres. The later gelling point occurred, the more heterogeneous structures such as hollow or microvoids of microspheres formed, while the early gelling point facilitated fabrication of small pores or non-porous structure.

1. Introduction

Polymer microspheres with heterogeneous structure possess versatile utilizations and distinctive properties. Porous microspheres with high specific surface areas and excellent absorption capacity provide various applications based on their different pore size, in hydrogen storage [1], versatile starting material for chromatographic columns [2], resin catalysts [3], or dialysis treatment [4]. Hollow microspheres with inner cavity and low density providing excellent thermal insulation and light scattering properties are thus widely used as architectural coatings, pigments, or floating drug delivery systems [5,6].

In the past decades, porous and hollow microspheres have been individually fabricated based on different research routes and chemical compositions. Microspheres with porous network involved polymerization of monomer mixture in the presence of inert diluents (also called porogen), which is soluble in the monomer mixture but a poor solvent for the copolymer. After monomer was completely converted to polymer matrix, diluent was removed from matrix leaving a porous structure [7]. Therefore, only suspension polymerization and its derivative techniques such as dynamic swelling polymerization can be carried out because of their facility to combine or absorb inert diluents [8–10]. Formation of hollow or void structures are often grouped into two routes, i.e. (1) synthesis of core–shell and then removal of the core, the related techniques including layer-by-layer self-assembly, swelling or template methods, interfacial condensation polymerization, etc. [5,11–13]; (2) encapsulation hydrocarbon in-situ polymerization of monomer, such as by seeded emulsion polymerization or suspension polymerization [14,15]. No matter porous or hollow structures, almost all the heterogeneity in microspheres comes from one basic formation mechanism of phase separation. Therefore, does it mean the transition between porous and hollow structures can be realized in one polymer microsphere just by manipulation of phase separation behavior? Obviously, suspension polymerization provides such possibility because of its direct encapsulation of inert diluents and easy manipulation of phase separation just in one step. Besides, compared with above methods, suspension polymerization has more universality to combine other size-controlling techniques such as membrane emulsification to synthesise uniform microspheres in large ranges from microns to tens of microns.

In suspension polymerization of porous microspheres, inert diluents have presented crucial roles in design of porous structure [16,17]. It is now well known that the thermodynamic affinity of diluent with polymer is mainly responsible for forming different porous structures. Generally, porous structures with small pores

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and high specific surface area were produced by good thermodynamic diluents for growing polymer network, while structures with larger pores and low specific surface area were produced by poor solvating diluents for polymer [18,19]. Recently, some poor solvating porogens were also found to construct hollow microspheres in different polymerization systems, such as petroleum ether (mixture of heptane and octane) in PST–DEGDA microsphere [20], hexadecane in PST–DMEMA microsphere [21], hexadecane or liner polystyrene of toluene solution in PolyDVB microsphere [22,23]. However, it is still unknown that what different phase behaviors make these diluents some act as porogens for porous structure and others as cores for hollow structure.

For free radical crosslinked microspheres prepared by suspension polymerization, macrosyneresis and microsyneresis have been recognized as the classical phase separation mechanism [7]. Macrosyneresis is related to that the growing gel deswells (or collapses) at the critical point separated from reaction mixture and becomes a microgel (nucleus), whereas the separated liquid remains as a continuous phase in the reaction mixture. As the polymerization and crosslinking proceed, new microgels are continuously generated due to the successive separation of the growing polymers, which react with each other through their pendant vinyl groups and radical centers located at their surfaces. These agglomeration processes result in the formation of a heterogeneous structure which consists of two continuous phases, a polymer and a diluent phase. Removal of the diluent creates voids (pores) of various sizes. That is the so-called macroporous polymer network. According to the model of microsyneresis, phase separation results in the formation of discontinuous liquid phase domains inside the polymer microspheres, and finally forms microspheres of non-porous surface.

Many phase separation behaviors of various porous microspheres in suspension polymerization have been understood quite well by above qualitative theories, but scarcely with quantitative treatments because of the difficulty to in-situ monitor phase separation process in one suspended microsphere [7]. However for bulk polymerization system, the proceeding of phase separation has been successfully monitored by turbidity change of polymerizing system [24,25]. Because the separated phases in polymerization system have different wavelength of scatter light which correspondingly give related opacity to the polymer system, the turbidity (transmittance) as a direct result of opacity can thus be used to describe the formation of polymer heterogeneities. Therefore if reaction in a suspended monomer droplet was regard as bulk polymerization, the phase separation behavior in one polymerizing microsphere can also be characterized by monitoring turbidity of bulk polymerization system (monomer–diluent mixture).

In this study, a combining route of SPG membrane emulsification and suspension polymerization was designed to fabricate uniform microspheres with different heterogeneity from hollow to porous structures. Because SPG membrane emulsification can effectively narrow the size distribution of emulsion droplet and thus microspheres, volume effect on structure development in suspension polymerization of microspheres was expected to be avoided. The relationship between morphology of microspheres and phase separation was investigated by following polymerization system: monomer of DVB and its typical non-solvating and solvating diluents. Correspondingly, their phase separation behaviors were characterized by in-situ monitored turbidity (transmittance) of polymerization system including monomer and various diluents. Further because phase's mobility in polymerizing microsphere has been proved important in formation of final structure [26], the gelling point when the polymerization system changes from liquid to solid-like state was also investigated simultaneously with phase separation monitoring.

Table 1
Standard recipe for membrane emulsification.

Oil phase (dispersed phase)	Content (g)	Aqueous phase (continuous phase)	Content (g)
Divinylbenzene (DVB)	7.00	Deionized water	300.00
Benzoyl peroxide (BPO)	0.4107	Polyvinyl alcohol (PVA)	2.7000
Porogen (selected)	7.00	Sodium dodecyl sulfate (SDS)	0.1330
Lauryl alcohol (selected)	0.70	Na_2SO_4	0.0667
		Hydroquinone (HQ)	0.0750

2. Experimental

2.1. Materials

Divinylbenzene (DVB, 55 wt%, Dongda Chemical Engineering Group Co., China) was washed with 5 wt% aqueous sodium hydroxide solution and deionized water, and dried by anhydrous sodium sulfate. Sodium dodecyl sulfate (SDS, biochemical grade) was purchased from Merck. Sodium sulfate (Na_2SO_4), benzoyl peroxide (BPO, with 25 wt% moisture content, reagent grade), heptane (A.R.), toluene (A.R.), liquid paraffin, hexadecane (A.R.), hydroquinone (HQ) were purchased from Beijing Chemical Reagents Company. Lauryl alcohol (LOH) was purchased from Tokyo Kasei Kogyo Co. Ltd. Polyvinyl alcohol (PVA, degree of polymerization 1700, degree of hydrolysis 88.5%) was kindly provided by Kuraray (Japan).

2.2. Methods

2.2.1. Emulsification

A standard recipe of SPG emulsification conditions is shown in Table 1. The mixture of monomer and porogen dissolving BPO initiator and lauryl alcohol as interface stabilizer was used as a dispersed phase. The aqueous solution of PVA (stabilizer), SDS (surfactant), Na_2SO_4 (electrolyte), and HQ (inhibitor) was used as continuous phase. The dispersed phase was pressed through the pores of the SPG membrane into the aqueous phase continuously by applying nitrogen gas pressure. A 5.2 μm membrane (SPG Technology, Japan) was chosen in this study. The size of emulsion droplet is about four to six times as large as the pore size of the membrane. The detailed SPG membrane emulsification process was described elsewhere [27]. The porogen was selected from some typical hydrocarbon diluents. Their physical properties are listed in Table 2.

2.2.2. Polymerization

The obtained emulsion was transferred to a four-neck glass separator flask equipped with a semicircular anchor type blade, a condenser and a nitrogen inlet nozzle. The emulsion was bubbled with nitrogen gas for 1 h. Then, the nozzle was lifted and the temperature was elevated to 75 °C gradually. The polymerization was carried out for 24 h under nitrogen atmosphere. The prepared microspheres were collected and washed with hot water and ethanol for four times, then extracted in Soxhlet apparatus with acetone, and dried in a vacuum.

Table 2
Physical properties of all diluents used in this work.

Diluents	Density (g/ml)	Dielectric constant[a]	Viscosity (mPa·s)	Refractive index[b]
DVB	0.919	2.4737[c]	1.967	1.561
Heptane	0.710	1.9209	0.461	1.397
Paraffin	0.842	1.9853–2.0578	10.612	1.450
Hexadecane	0.783	2.0460	3.032	1.441
Toluene	0.870	2.379	0.523	1.496

[a] From CRC Handbook, 87th.

[b] From Lange's Handbook of Chemistry, 13th.

[c] Refer to the value of polystyrene.

2.2.3. Observation of surface feature of microspheres

The morphology and porous feature of microspheres were observed respectively by an optical microscope (XSZ-H3, Coic, China), and scanning electron microscopy (JSM-6700F, JEOL, Japan).

2.2.4. Measurement of transmittance and gelling point

The transmittances of polymerization system (monomer, diluents, BPO) were determined according to a modified method described by Okubo et al. [23]. Briefly, the transmittances were measured by a temperature-controlled visible spectrophotometer (SP-721, Spectrum Instruments Co. Ltd., Shanghai, China) at 550 nm. The solution of DVB, diluents and BPO initiator were sealed in a spectrophotometer cell and polymerized at controlled temperature 75 °C. The real time data of transmittance for mixed solution were recorded per 30 s to 1 min with polymerization proceeding until the reading did not change in 5 min. Simultaneously, the observation of gelling point for above polymerization system was also carried out in another water bath at 75 °C, and determined by test tube inverting method [28].

3. Results and discussion

3.1. Non-solvating diluent effects on microsphere morphology

3.1.1. Diluent types

A series of non-solvents with different hydrocarbon chain length were chosen to fabricate heterogeneous microspheres at a fixed porogen/monomer ratio (1:1, wt:wt). Fig. 1 showed that the heterogeneity of microsphere shifted from porous to hollow structure with increasing chain length of diluents. Heptane prepared porous surface is composed by innumerable nuclei (also see Fig. 4). Comparatively, liquid paraffin formed both multiple microvoids and hollow structures, while hexadecane with longest hydrocarbon chain led to hollow void which can be observed by obvious inner circle and collapsing part of the microspheres in Fig. 1c.

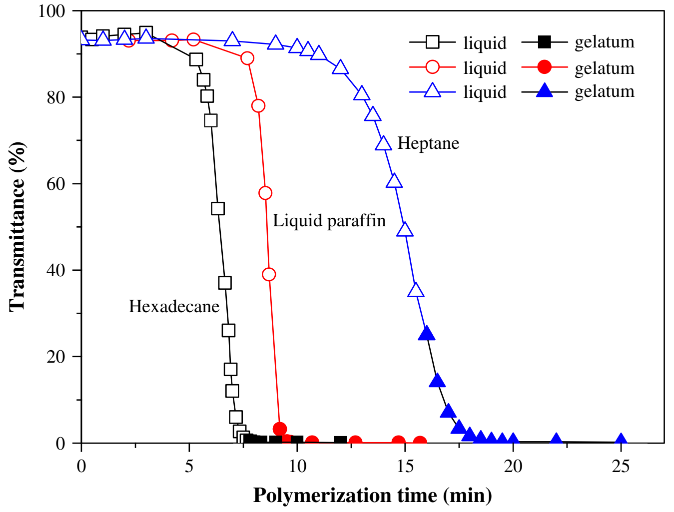
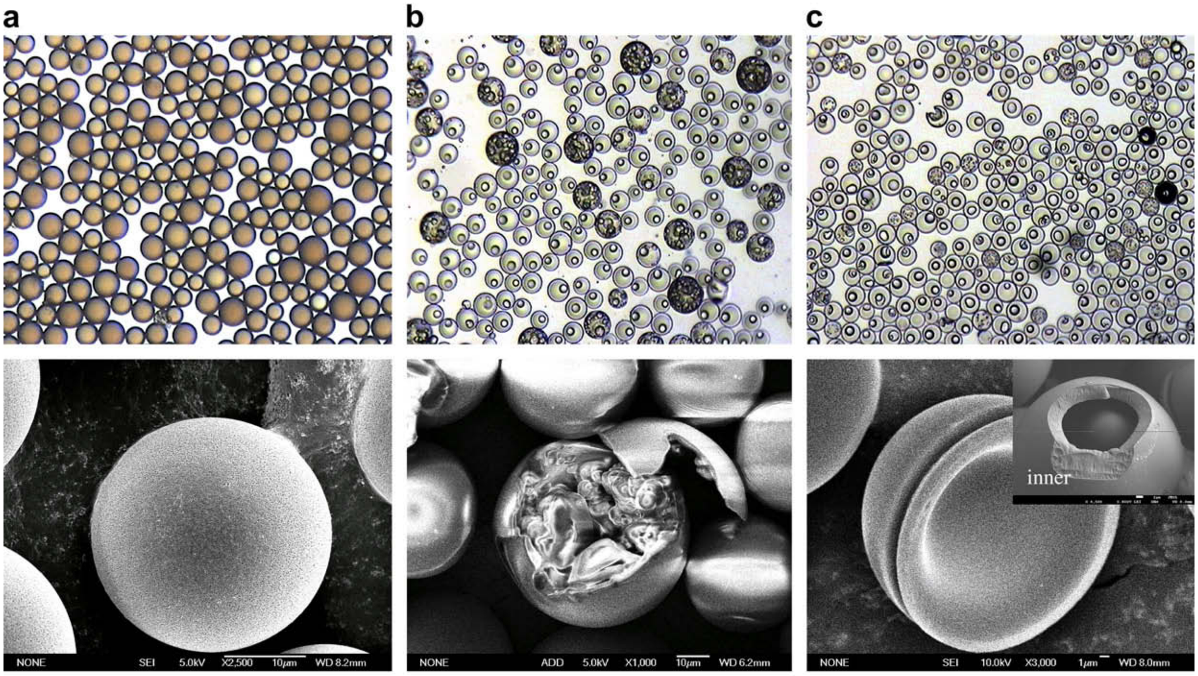


Fig. 2. Transmittance development with polymerization time for different diluents (hexadecane, liquid paraffin, heptane).

The phase separations of the above three microspheres were reflected by development of transmittance development in Fig. 2. The decrease of transmittance indicated the separation of heterogeneous phases from polymerization solution (monomer–diluent–BPO mixture). The hollow dots in transmittance curves denote the observed reaction system still in liquid state, and the solid dots indicate the gelling of reaction system changed to solid-like state (gelatum), which came from the simultaneous observation results of gelling point for polymerization solution. Among three curves, hexadecane induced most rapid decrease of transmittance and late appearance of solid dots at the end of transmittance curves. Based on this, the formation of hollow structures was speculated as follows. Plenty of hexadecane-rich phases and PolyDVB-rich phases were quickly separated from polymerization solution at early stage



Heptane Liquid paraffin Hexadecane

Fig. 1. Optical (above) and SEM (down) micrographs of polydivinylbenzene microspheres prepared by various non-solvating diluents.

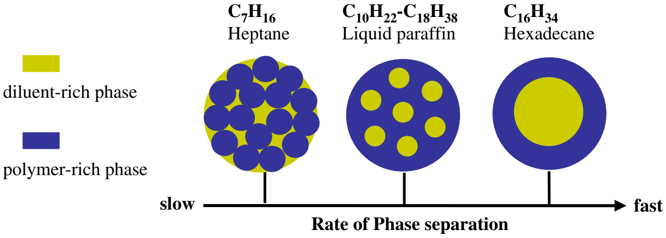


Fig. 3. Schematic of phase separation distribution for three microspheres.

of polymerization with low conversion. The new generated polymer microgels in polymer-rich phases with low molecular weight would make interior of microsphere in liquid and mobile state until to gelling point. Such long-term mobility in 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 microsphere suspended in water during suspension polymerization, highly hydrophobic hexadecane-rich phases tended to move into center of microsphere and combined each other into one bulky liquid core. Consequently, a core–shell conformation was constructed as illustrated in Fig. 3, which speculated the final diverse distributions of phases for above three microspheres.

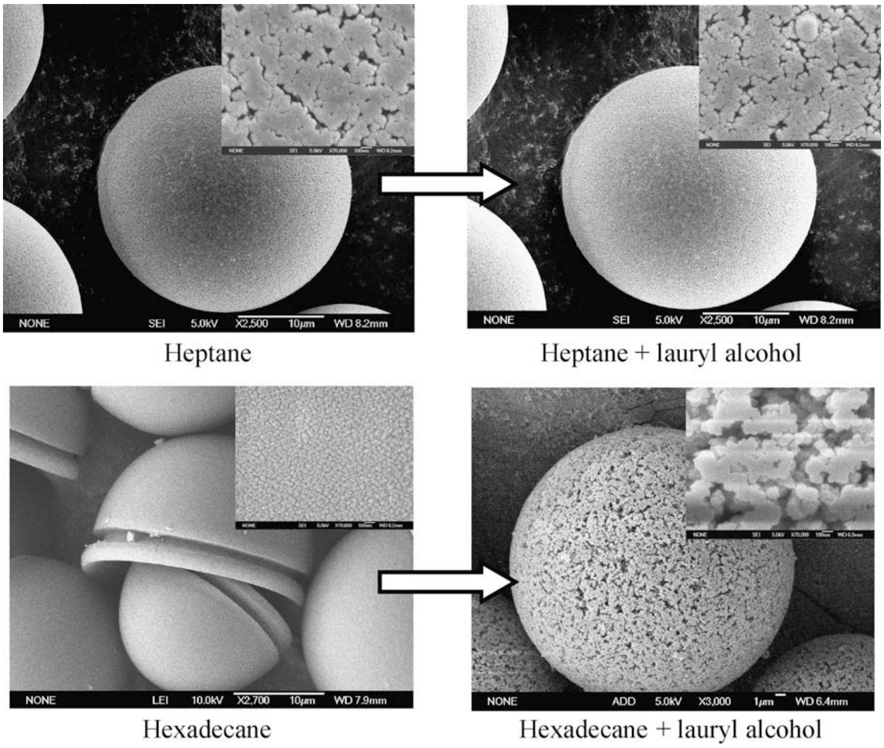
Liquid paraffin proceeded with a slightly later decline of transmittance and earlier gelation of reaction system than hexadecane, which finally led to both hollow and multivoid structures. Comparatively, most multivoid structures existed in slightly larger microspheres. It seemed that the volume effect was too strong to be effectively avoided even after membrane emulsification has greatly unified the size of reaction droplets. For larger microsphere, diffusion distance of components would be increased, which resulted in more difficulties for diluent-rich phases and polymer-rich phases to transport and aggregate. Until to the gelation stage of polymerization system, because the viscosity of polymerization environment was greatly enhanced, the diluent-rich phases were gradually restricted in discontinuous microdomains as shown in Fig. 3. Consequently multivoids were formed in microsphere of large diameter.

Comparatively, the transmittance for heptane decreased much later than the above two diluents, and the gelation point occurred earlier in decreasing of transmittance. It indicated that the polymer system was already solidified during phase separation process. So the subsequent polymerization and uncompleted phase separation, the growth of microgels into nuclei, and the fusion of nuclei into skeleton of porous matrix all had to proceed locally in gelation microdomain. Finally, such structure was constructed with diluent and nuclei homogeneously distributed in microsphere as illustrated in Fig. 3c. After removal of the diluent, a porous matrix with numerous polymer nuclei was created.

3.1.2. *Cosurfactant*

Previously, cosurfactant of lauryl alcohol (LOH) was often regarded as efficient additive to increase interface stability and monodispersity of emulsion in preparation of uniform microspheres by SPG membrane emulsification [27]. However, the influence of LOH on the structure of polymer microspheres was scarcely discussed. In this study, we compared the effect of lauryl alcohol on two structures respectively prepared by hexadecane and heptane. Fig. 4 shows that porous structure prepared by heptane was almost maintained after adding LOH (10 wt%), while hollow structure by hexadecane was dramatically transformed to macroporous polymer.

Fig. 5 compared their phase separation behaviors before and after adding LOH by tracking the development of turbidity. No obvious change in phase separation mode was observed for heptane. It demonstrated that LOH has not great disturbance on porous structure. However, for hexadecane system, LOH delayed the decline of transmittance curve and shifted the gelling point ahead before turbidity fell to the lowest. As previously discussed,



Heptane

Heptane + lauryl alcohol

Hexadecane

Hexadecane + lauryl alcohol

Fig. 4. SEM micrographs of polydivinylbenzene microspheres before and after addition of lauryl alcohol (top right – surface structure at 70 000 magnifications).

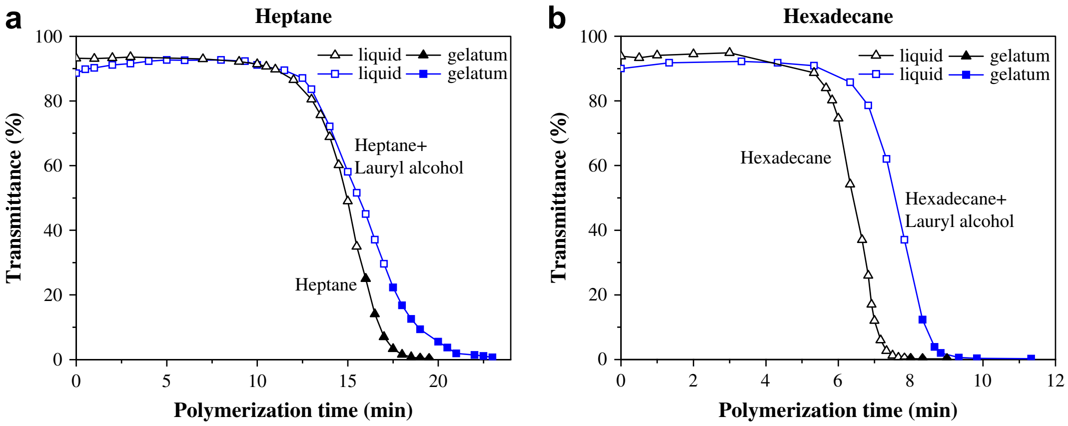


Fig. 5. Turbidity development with polymerization time before and after addition of lauryl alcohol.

the earlier gelling would induce the separation and arrangement of phases in microsphere at solidified environment. Because the mass transport in microsphere was greatly retarded at this case, the diluent phases had to be restrained discontinuously in polymer channels built up with numerous nuclei. Finally by extraction of diluent, macroporous network was formed. It should be noted that hydroxyl group of LOH might become another important contribution for formation of porous morphology. By introducing hydroxyl group, the hydrophobicity of hexadecane-rich phase (dissolved with LOH) was lowered, and its movement to microsphere interior was also reduced. Therefore a configuration with diluent homogeneously distributed in matrix of microsphere seems more favorable as heptane illustrated in Fig. 3.

3.1.3. Diluent amount

The amount effect of non-solvating diluent on morphology of PolyDVB microspheres was investigated with heptane as porogen. As heptane increased, both pores and nuclei on microsphere's skeleton were obviously enlarged (see Fig. 6). Correspondingly, Fig. 7 shows that decline of transmittance curves also went ahead and the gelling point was postponed with increasing heptane. This tendency demonstrated that increase of non-solvent porogen accelerated phase separation between porogen and growing polymer because of its poor thermodynamic affinity with polymer network. Since phase separation had occurred early with low conversion when heptane increased, the formed microgels were swollen with a high concentration of monomer which caused not only fusing of the microgel particles but also significant in-filling of small pores between microgels. Also because the gelling point was put off in phase separation with increase of heptane, the separated microgels gained much time to move and congregated into larger nuclei. Consequently, a polymer matrix with larger nuclei and pores was built up at high addition of heptane. An extreme case can be speculated as follows: if continue to postpone the gelling point at later stage than above, the polymer-rich phases would obtain more mobility and finally arrange into outer shell of hollow microsphere as previous discussion of hexadecane.

3.2. Solvating diluent effects on microsphere morphology

Most good solvating diluents have demonstrated abilities to fabricate small pores in polymerization of porous materials [18,29], but scarcely construct hollow or macroporous structures if without specially mixing other non-solvating diluent. In this study, toluene was chosen as typical solvating diluent to investigate its effect on porous structure evolution and phase behaviors in preparation of PolyDVB microspheres. Fig. 8 showed that porous feature for toluene can only appear above a high addition (the toluene/monomer wt. ratio 2.0), and with much smaller pores and nuclei than non-solvating diluent. With further increasing toluene, both pores and nuclei were enlarged.

The phase separation behaviors of above microspheres prepared by toluene were reflected in Fig. 9. Compared with previous non-solvating diluents, toluene showed much slower decline of transmittance and much earlier appearance of gelling point in descending stage of transmittance curves. It suggested that the proceeding of phase separation was obviously restrained after addition of solvating diluent, which resulted in difficult precipitation of polymer-rich phases. This late phase separation and early occurrence of gelling made the whole reaction mixture solidified into homogenous gel. At such gel environment, the following process including vinyl polymerization, phase separation and even microgel fusion (and aggregation) has to be in-situ finished, because most diffusion and movement of materials have been

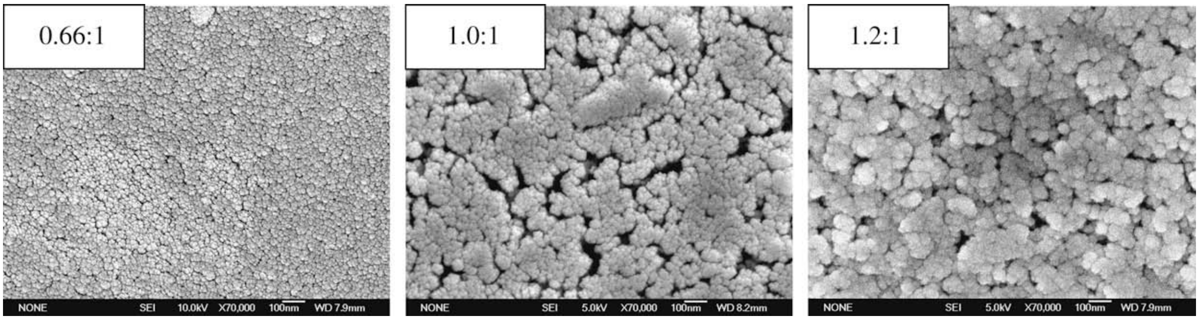


Fig. 6. SEM micrographs of polydivinylbenzene microspheres for heptane at different porogen/monomer ratios.

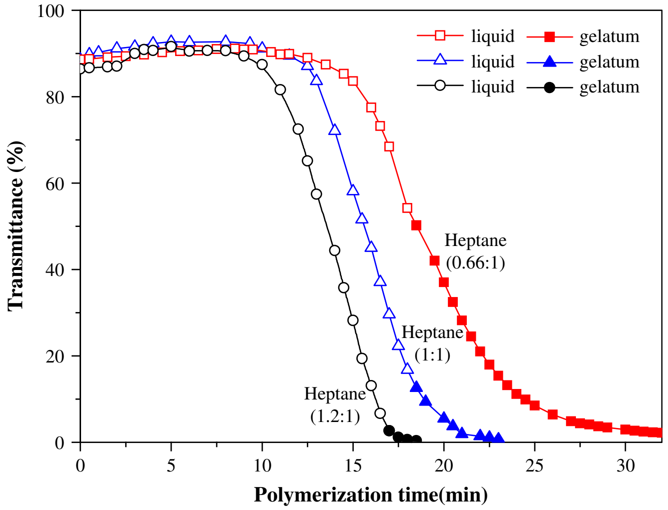


Fig. 7. Turbidity development with polymerization time for heptane at different porogen/monomer ratios.

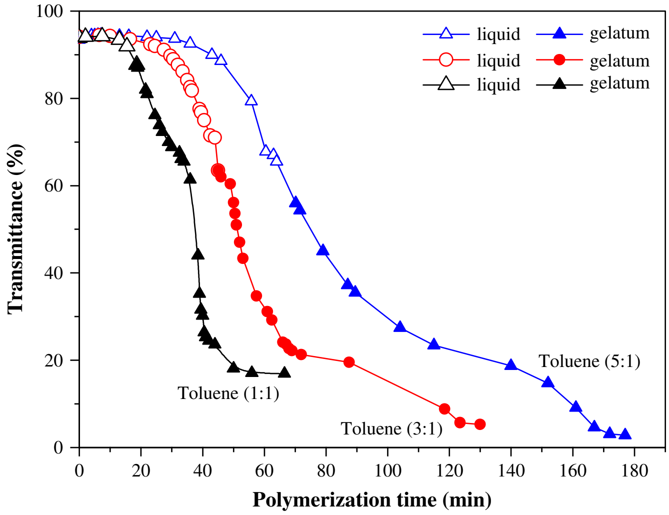


Fig. 9. Turbidity development with polymerization time for toluene.

greatly limited at gelation point as previously discussed. Consequently, the polymerized microgels cannot aggregate into larger nuclei and small pores were constructed in the final polymer network. If continue increasing the amount of toluene, both the transmittance curve and the gelling point were postponed, which means the phase separation was put off with increasing amount of the efficient swelling solvent, and larger pores can be formed because of the late gelling point facilitating formation of larger polymer nuclei. Moreover, all the transmittance curves were not smooth as previous non-solvent diluents created. It might result from the formation of many irregular cracks on bulk polymer in spectrophotometer cell, which made the disturbance on the continuous development of transmittance.

3.3. Evolution process of heterogeneous structure in suspension polymerization

In order to speculate the mobility and mass transfer during heterogeneous structure formation, the rheology (solution viscosity) changes of monomer solutions during polymerization are also described in Fig. 10. It showed that viscosities of polymerization system including hexadecane, paraffin, heptane and toluene all presented sharp increase in 1 min near the gelation point. Especially for toluene system, the viscosity presented the rapidest increase. This great leap of viscosity resulted in much mass transport difficulty in polymerization system. So it demonstrated that the inner structure of microspheres at gelatum point has a determination effect on final heterogeneous structure of microspheres.

According to previous analysis about turbid (transmission), gelling point and viscosity in polymerization, it can be summarized that final heterogeneity of microspheres mainly depended on competition of three dynamics in polymerization, i.e. polymerization kinetics, interfacial energy between phases, and mass transport rate governed by gelation, which recently have been demonstrated much contribution for manipulating porous structures in reaction-induced phase separation process [30–32].

As shown in Fig. 11, in an initial polymerizing droplet before gelling point, both the new polymer-rich phases and diluent-rich phases could move freely without limitation. At this moment, if the diluent has good affinity for polymer (solvating diluent), slow phase separation and early gelation of polymer system would occur. So resistance of mass transfer became dominant factor in following phase separation, which caused final separated microgels in polymer-rich phases mostly polymerized in solidified microdomains as illustrated of toluene in Fig. 8a. Consequently, approximately homogenous morphologies with few pores or small pores were prepared. If the diluent has poor affinity for polymer (non-solvating diluent), fast phase separation and late gelation of polymer system occurred. So the early separated polymer and diluent phases obtained sufficient mobility. At this case without mass transfer limitation, interfacial energy between phases become dominant factor to manipulate phases arranged into stable distribution. Consequently, with increasing the hydrophobic chain of diluent such as heptane, liquid paraffin and hexadecane, more heterogeneous distribution of phases from macroporous, multivoid to hollow structure would form in final microspheres as shown in Fig. 8b–c.

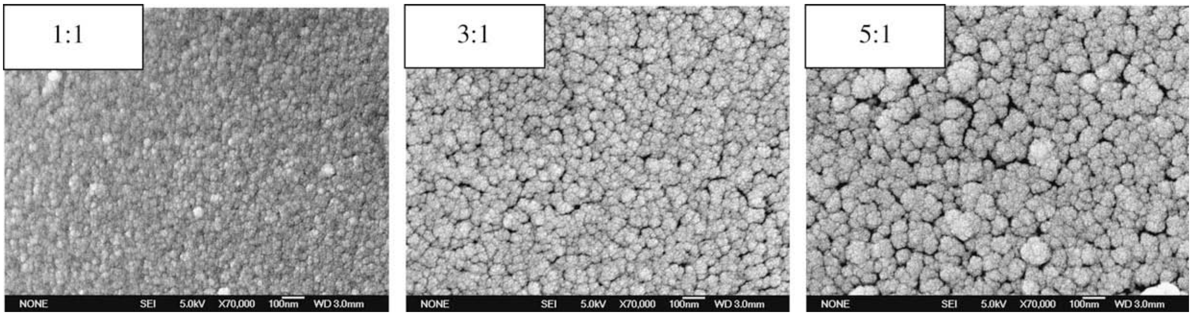


Fig. 8. SEM micrographs of polydivinylbenzene microspheres for toluene at different porogen/monomer ratios.

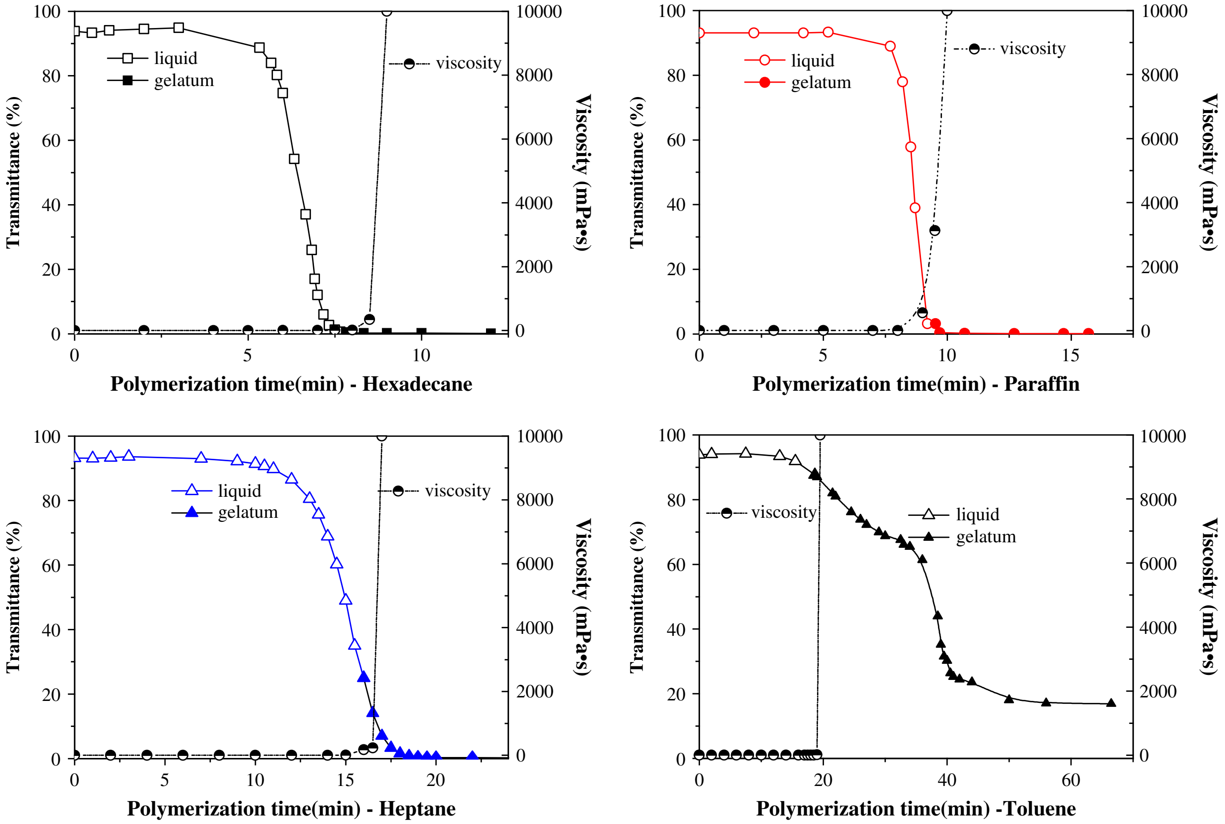


Fig. 10. Viscosity changes of reaction solutions during polymerization.

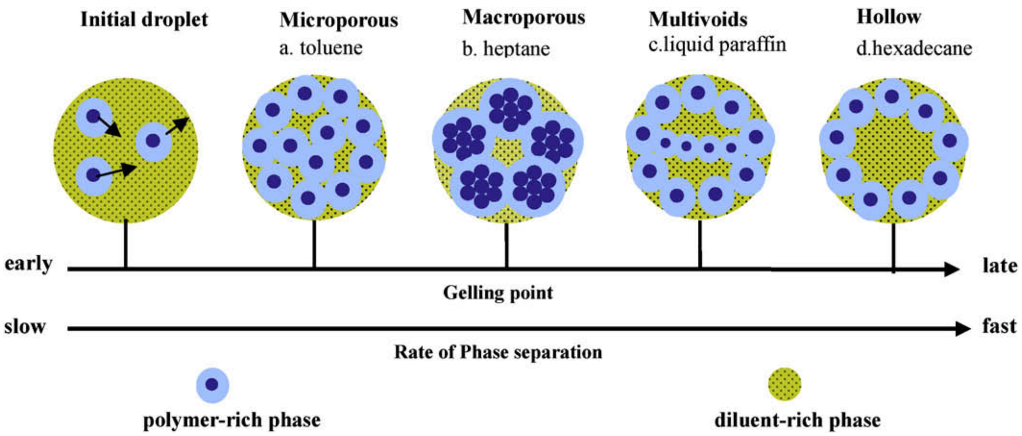


Fig. 11. Schematic of formation of heterogeneous structure in phase separation.

To summarize above phase separation by syneresis theory [7,33], it can be found that both heptane and toluene presented obvious macrosyneresis feature, i.e. formation of two continuous phases of nucleus agglomeration and diluent phase which finally lead to porous structures. Comparatively, the pore structure formed by toluene led to more ordered and smaller agglomerates than formed by heptane, which corresponded to the phase separation description of non-solvating induced polymer–solvent interaction syneresis mechanism and solvating diluent induced crosslink-density syneresis mechanism proposed by Okay [7]. In this study, by tracking development of transmittance, gelation and viscosity in polymerization, it showed that these diversity of structure and mechanism result from different occurrence of gelation in phase separation process of these two diluents. As to liquid paraffin and hexadecane, both of them showed microsyneresis behavior. They existed in the form of the dispersed microdomains in microspheres and finally combined into bulk phase which lead to hollow and multivoid structures. It could be speculated that their late gelation and high hydrophobicity contribute much for their microsyneresis behavior.

4. Conclusions

Uniform PolyDVB microspheres with hollow, multivoids or different porous structures were prepared by membrane emulsification and suspension polymerization. Such evolutions of heterogeneous structures were speculated as results of their diverse phase distribution in final polymer microsphere. The final phase distribution in microsphere depended on separation rate between polymer-rich and diluent-rich phases, and also gelling point of polymer system. These phase separation behavior can be indirectly reflected by real time tracking transmission of polymer system. It showed that movement of transmittance was influenced by the affinity of inert diluents with polymer. Non-solvating diluents with poor affinity for PolyDVB such as alkanes made early declines of transmittance and fast phase separation, while solvating diluents led to late declines of transmittance and slow phase separation. Moreover, it showed the occurrence of gelling point of reaction system during phase separation process contributed much for diverse structures of microspheres. If the reaction system was solidified at earlier stage in phase separation process, homogenous structure as non-porous or small pores was more likely formed. With further postponing occurrence of gelling point, macroporous, microvoids and hollow structures were respectively formed. This relationship provides a convenient criterion for selecting suitable components to manipulating targeted structure in fabrication of various heterogeneous polymer microsphere.

Acknowledgments

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