



Janus-like Hollow Polymer Spheres Prepared from Emulsion Droplets by the Solvent Evaporation Method

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Polystyrene/poly(vinylbenzylchloride) hollow spheres with Janus-like morphology were produced from emulsion droplets *via* evaporation of the organic solvent followed by extraction of internal phase water. The effect of the organic solvent and the weight ratio of polystyrene: poly(vinylbenzylchloride) on the morphology were discussed. Benzene, 1,2-dichloroethane (1,2-DCE), fluorobenzene, benzene-1,2-dichloroethane mixture were used as oil phase solvent respectively and variety of polymer with different weight ratio of polystyrene/poly(vinylbenzylchloride) were tested. When benzene-1,2-dichloroethane mixture used as oil phase solvent and the weight ratio of polystyrene: poly(vinylbenzylchloride). Solvent fixed at 2:4:94, the obtained hollow spheres formed the morphology of Janus-like. The two-dimensional infrared images results showed the hollow spheres generated polystyrene-rich and poly(vinylbenzylchloride)-rich hemispheres.

Key Words: Hollow spheres, Polystyrene, Infrared images, Phase separation.

INTRODUCTION

Inertial confinement fusion (ICF) is one of the most promising directions of controlled thermonuclear fusion. Polystyrene (PS) hollow spheres with the features of low density and low atomic often used as pellet material in inertial confinement fusion. The radius of the compressed fuel plasma, which is measured by the argon (Ar) X-ray image from the compressed core (fuel and pusher) plasma is an important parameter in inertial confinement fusion. When the thickness of the pusher plasma is not negligibly small in comparison with that of the fuel plasma, the Ar X-ray image does not show the boundary of the fuel plasma¹. Doping with specific elements and measuring its characteristic X-rays can solve this problem.

Ryusuke and Yasushi² prepared polystyrene hollow microspheres doped with Al₂O₃ by emulsion techniques, Li and Fen³ prepared polystyrene hollow microspheres doped with Si *via* microencapsulation method and diethoxydimethylsilane interfacial polymerization technology. Liu *et al.*⁴ achieved ferrum doped with polystyrene through the copolymerization of polystyrene and ethylferrocene. In this paper, polystyrene hollow spheres doped with chlorine were generated by using polystyrene and poly(vinylbenzylchloride) as materials. Furthermore, the spheres formed polystyrene-rich and poly(vinylbenzylchloride)-rich hemispheres so that could be used to compare the effect of doping in the same inertial

confinement fusion experiment, with the result that eliminating the background errors and improving the measure accuracy.

EXPERIMENTAL

Water was used as w₁ phase after distillation. Polystyrene (PS, MW-250000, Acros Organics Company) and Poly(vinylbenzylchloride) (PVBC, MW-100000, Sigma-Aldrich Company) dissolved in organic solvent were used as oil phase. Benzene, fluorobenzene, 1,2-dichloroethane (1,2-DCE) of analytical reagent grade were used as received. Poly(vinyl alcohol) (PVA, MW 13000-23000, Sigma-Aldrich Company) dissolved in distilled water (PVA/water = 2/98 w/w) was used as w₂ phase.

Preparation of polystyrene/poly(vinylbenzylchloride) hollow spheres. In this paper, polystyrene/poly(vinylbenzylchloride) hollow spheres were made in a three-step process (Fig. 1), by first generating w₁/o/w₂ emulsion with an homemade microfluidics device and then solidifying the droplets in a rotating glass bottle, finally drying the droplets to remove the inner water. During the solidification, the organic solvent diffused to the outer water phase, inducing phase separation of the polystyrene-poly(vinylbenzylchloride) mixture and then formatted the polystyrene-rich and poly(vinylbenzylchloride)-rich hemispheres. Some conditions did not change in the experiment: the inner water phase was always distilled water and the outer water phase was 2 wt %

PVA solution; the solidification time and temperature fixed at 24 h and 20 °C respectively; the drying process lasted 48 h at 45 °C, ensuring that inner water can be removed and the morphology of the spheres did not change. The weight ratio of polymer [polystyrene and poly(vinylbenzylchloride)]/organic solvent was fixed at 6/94, but we changed the weight ratio of polystyrene/poly(vinylbenzylchloride) (W_{PS}/W_{PVBC}) and used different organic solvent to generate spheres of different morphologies.

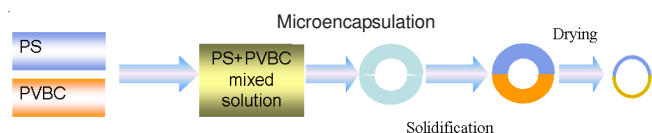


Fig. 1. Scheme of preparation polystyrene/poly(vinylbenzylchloride) hollow spheres

Characterization: After the process of solidification, the emulsion droplets changed to microspheres. The size, shape, surface and phase separation of the microspheres can be observed under a microscope (vix-60, reynce company). The solid particles changed to hollow spheres after the drying process. The hollow spheres were placed on the KBR salt-chip, scanned under Spotlight-150 IR Imaging System (Perkin-Elmer Company) with transmission mode. The scanning generated a two-dimensional infrared image, which can provide more phase separation information.

RESULTS AND DISCUSSION

The effect of organic solvent on phase separation. In this series of experiments, benzene, 1,2-dichloroethane, fluorobenzene, benzene-1,2-dichloroethane ($w/w = 1$) mix solvent were used as oil-phase solvent respectively. The weight ratio of polystyrene: poly(vinylbenzylchloride): solvent was fixed at 4:2:94.

As shown in Fig. 2, various microspheres were obtained by changing the type of solvent. When benzene (Fig. 2a) or 1,2-dichloroethane (Fig. 2b) used alone, the obtained microspheres did not occur phase separation that can be observed by microscope. With fluorobenzene as the oil phase solvent (Fig. 2c), the microspheres occurred phase separation, but some droplets changed to solid particles, which have no value in inertial confinement fusion experiments. The microspheres, which have clear phase separation interface of polystyrene-poly(vinylbenzylchloride) and smooth surface were obtained by using benzene-1,2 dichloroethane ($w:w = 1$) mixture as oil phase solvent (Fig. 2d).

From the view point of thermodynamics, phase separation depends on the interaction of polystyrene-poly(vinylbenzylchloride) (χ_{23}), solvent-polystyrene (χ_{12}), solvent-poly(vinylbenzylchloride) (χ_{13}) in the polystyrene-poly(vinylbenzylchloride)-solvent system. In this series of experiments, χ_{23} can be considered identical because of the same weight ratio of polystyrene:poly(vinylbenzylchloride). According to the solubility parameter theory, solvent-polymer interaction parameter can be estimated as $\chi_{li} = V_1(\delta_1 - \delta_i)^2/RT$, δ is the solubility parameter and V_1 is partial molal volume of solvent, the specific values shown in Table-1. Zeman and Patterson⁵ proved that phase separation in ternary systems was strongly

promoted by any asymmetry in the polymer-solvent interactions ($\chi_{12} \neq \chi_{13}$) and the effect increase with the greater difference value of $|\chi_{12} - \chi_{13}|$. As shown in Table-1, when fluorobenzene used as oil-phase solvent, $|\chi_{12} - \chi_{13}|$ has the maximum value, the obtained microspheres shown in Fig. 2c indicated that theory consistent with experiment. Kinetic factors determine whether the microspheres can achieve the thermodynamically favoured state, therefore also strongly affect the phase separation of microspheres. Due to the high molecular weight of polystyrene and poly(vinylbenzylchloride), the viscosity of the polymer solution increase sharply with organic solvents spreading to the external water phase, results polymer chains move with difficulty. In the process of solidification, the viscosity and diffusion rate of O-phase determine the mobility of polymer chains. As shown in Table-1, the solubility in water and viscosity of fluorobenzene is smaller than benzene and 1,2-dichloroethane, indicating that polystyrene and poly(vinylbenzylchloride) easier to move and have more accumulation time in it. However, it is noted that the special case of polystyrene-poly(vinylbenzylchloride)-benzene-dichloro-ethane system, which has a small value of $|\chi_{12} - \chi_{13}|$ but good conditions of phase separation. This particular example can be explained as follows: when benzene/1,2-dichloroethane mixture used as oil-phase solvent, the dissolution of polystyrene and poly(vinylbenzylchloride) have more selectivity than in single solvent [polystyrene tend to dissolve in benzene and poly(vinylbenzylchloride) in 1,2-dichloroethane]. This selective dissolution is equivalent to generating two nuclear at the beginning of phase separation, reducing the energy barrier of phase separation, results the system easier to phase separation.

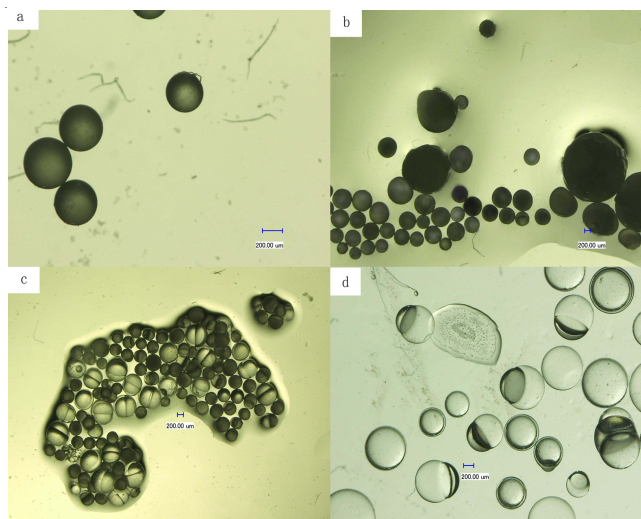


Fig. 2. Micrographs of the polystyrene-poly(vinylbenzylchloride) (weight ratio: 2:1) microspheres obtained from various oil solution: (a) Benzene; (b) 1,2-Dichloroethane; (c) Fluorobenzene; (d) Benzene-1,2-dichloroethane ($w/w=1$) mix solvent

The effect of polymer composition on phase separation. In this series of experiments, benzene/1,2-dichloroethane ($w/w = 1$) were used as O-phase solvent, the total weight ratio of polymer (polystyrene and poly(vinylbenzylchloride))/solvent was fixed at 6/94. We changed the weight ratio of polystyrene/poly(vinylbenzylchloride) from 4 to 0.25 in order to research the effect of polymer composition.

TABLE-1
PARAMETERS OF POLYMER AND SOLVENT USED IN THE PRESENT REPORT

	Molar volume (cm ³ /mol)	Solubility parameter (J/M ³) ^{0.5}	PS-Solvent interaction parameter	PVBC-Solvent interaction parameter	Solubility parameter (g/100 mL, 20 °C)	Viscosity (mPa s, 20 °C)
PS	114.69	$9.1 \times 2.046 \times 10^3$				
PVBC	114.69	$10.2 \times 2.046 \times 10^3$				
1,2-DCE	79.00	$9.8 \times 2.046 \times 10^3$	0.407	0.344	0.86	0.840
Benzene	89.40	$9.15 \times 2.046 \times 10^3$	0.340	0.510	0.18	0.647
Fluorobenzene	93.60	$9.01 \times 2.046 \times 10^3$	0.341	0.568	0.15	0.577
Benzene/1,2DCE (w/w=1)	84.81	$9.42 \times 2.046 \times 10^3$	0.355	0.429		

In this series of experiments, the same kind and amount of organic solvent were used, so the miscibility of polystyrene and poly(vinylbenzylchloride) dominated the phase separation of microspheres. When W_{PS}/W_{PVBC} is 4 (Fig. 3a), clearly phase separation can not be observed under microscopy. On the contrary, reducing the value of W_{PS}/W_{PVBC} to 2 (Fig. 3b) and 0.5 (Fig. 3c), the morphology of microspheres changed to double-hemisphere. When W_{PS}/W_{PVBC} fixed at 0.25 (Fig. 3d), the morphology of microspheres changed to a typical sea-island shape: a polymer dispersed in a continuous polymer phase in the form of small island-like areas. The results showed that the miscibility of polystyrene-poly(vinylbenzylchloride) has the following characteristics: when polystyrene or poly(vinylbenzylchloride) has the high mass fraction, the miscibility is good; when polystyrene and poly(vinylbenzylchloride) has the close mass fraction, the miscibility is poor. Compared Fig. 3a with Fig. 3d, the microspheres showed a clear phase separation when $W_{PS}/W_{PVBC} = 0.25$ and the opposite results when $W_{PS}/W_{PVBC} = 4$. These results suggest that the phase separation region is not symmetrical along the mass fraction, but mainly located in the region of high mass fraction of poly(vinylbenzylchloride). It should be noted that kinetic factors also strongly affect the morphology of microspheres. Owing to the low stability of double emulsion droplets, experiments carried out at 20 °C, which is far below the glass transition temperature. With the diffusion of solvent, the viscosity of polymer will increase and the mobility of polymer chain will decrease. As the viscosity of polystyrene more than poly(vinylbenzylchloride), the mixture contains more polystyrene components will halt molecular chain movement in a shorter time. Fig. 3b showed clear phase separation, indicating that component b and lower viscosity component c, component d have enough time to form a double hemisphere microspheres, so the sea-island morphology of component d is determined by the miscibility of polystyrene and poly(vinylbenzylchloride) instead of kinetic factors.

Characterization of two-dimensional infrared images. The structure of poly(vinylbenzylchloride) is similar to polystyrene except -CH₂Cl instead of a benzene ring -C-H bond. The spectra of polystyrene and poly(vinylbenzylchloride) (Fig. 4), the C-Cl bond of poly(vinylbenzylchloride) has a strong peak at 1260 cm⁻¹ while polystyrene has not and both polystyrene and poly(vinylbenzylchloride) have a stable peak of benzene ring near 1600 cm⁻¹. Define $Arb = \text{peak area} (1260 \text{ cm}^{-1}) : \text{peak area} (1600 \text{ cm}^{-1})$, the value of Arb close to 0 in the pure polystyrene while close to 2 in the pure poly(vinylbenzylchloride). Tested the microspheres with two-dimensional infrared scanning and represented the value of Arb with colour, there-

fore the relative distribution of polystyrene and poly(vinylbenzylchloride) can be shown in the form of an image.

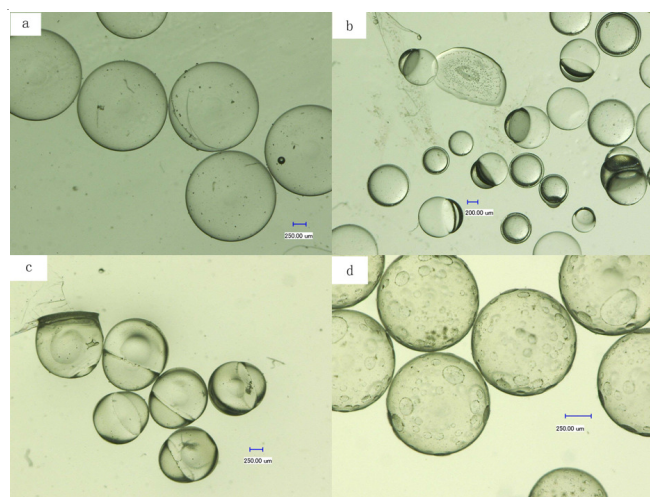


Fig. 3. Micrographs of the polystyrene-poly(vinylbenzylchloride) microspheres obtained from various weight ratio of polystyrene/poly(vinylbenzylchloride): (a) 4 (b) 2 (c) 0.5 (d) 0.25

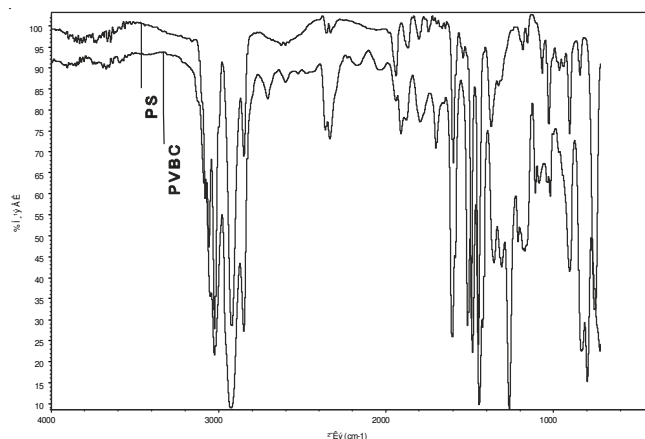


Fig. 4. IR spectra of polystyrene and poly(vinylbenzylchloride)

The IR image of a hollow microsphere obtained from Fig. 3c shown as Fig. 5, mark1 and mark3 labeled the same hemisphere (hemisphere-a) of microsphere, so did mark 2 and mark 4 (hemisphere-b). Fig. 5a was the total infrared absorption image of microsphere and the relationship between absorption and colour expressed with a histogram. Fig. 5b showed the distribution of Arb in the microsphere, a higher value of Arb meant the higher ratio of poly(vinylbenzylchloride):polystyrene. It was easy to see from the image that the major component of hemisphere-a was poly(vinylbenzylchloride) while hemisphere-

b was polystyrene. The values of Arb of hemisphere-a and hemisphere-b were inconsistent with pure materials, indicating that polystyrene and poly(vinylbenzylchloride) could not be completely separated under the experimental conditions.

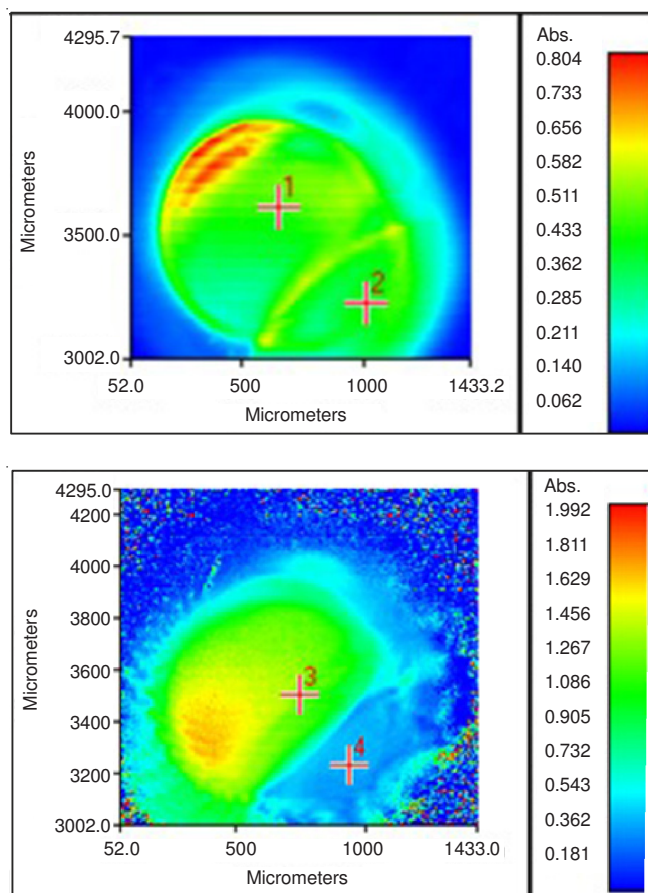


Fig. 5. Two-dimensional infrared images of polystyrene/poly(vinylbenzylchloride) microsphere

Conclusion

In conclusion, we have demonstrated that polystyrene/poly(vinylbenzylchloride) Janus-like hollow spheres could be produced by the solvent evaporation method. Experiments showed that the *o*-phase solvent and the weight ratio of polystyrene:poly(vinylbenzylchloride) strongly influenced the phase separation morphology of microspheres. When solidification temperature fixed at 20 °C, benzene-1,2-dichloroethane (w:w = 1) mixture used as organic solvent, the weight ratio of polystyrene: poly(vinylbenzylchloride): Solvent fixed at 2:4:94, Janus-like hollow spheres with good conditions of phase separation could be produced. The characterization of two-dimensional infrared images indicated that hollow microspheres indeed formed polystyrene-Rich hemisphere and poly(vinylbenzylchloride)-rich hemisphere, but two hemispheres both contain another polymer because of kinetic factors. Improve the degree of phase separation from dynamic factors without destroying the emulsion stability will be the focus of future research.

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REFERENCES

1. S.P. Regan and J.A. Delettrez, Characterization of Direct-drive-implosion Core Conditions on OMEGA with Time-Resolved Ar K-Shell Spectroscopy. LLE Review Quarterly Report. University of Rochester (2001).
2. T. Ryusuke and O. Yasushi, *Fusion Engg. Design*, **34-35**, 811 (1997).
3. B. Li and S.F. Cheng, *High Power Laser Particle Beams*, **16**, 8 (2004).
4. C.L. Liu, L. Zhang and Y.J. Tang, *Mate. Rev.*, **9**, 301 (1995).
5. L. Zeman and D. Patterson, *Polym. Incompatib.*, **5**, 513 (1972).