Chinese Chemical Letters Vol. 15, No. 2, pp 242 – 245, 2004
http://www.imm.ac.cn/journal/ccl.html

The Surface Imprinted Polystyrene Beads Prepared *via* Emulsion Templates

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Abstract: In this paper, the surface imprinted cross-linked polystyrene beads were prepared *via* suspension polymerization with styrene (St), divinylbezene (DVB), polyvinyl alcohol (PVA1788), the mixture of Span 85 and xylene or the mixture of Span 85 and paraffin as monomer, cross-linking agent, dispersion stabilizer and templates, respectively. The results indicate that there are dense cavities on the surface of beads, and the diameter and density of cavity are related with the composition and amount of emulsion template. The forming mechanism of cavity from thermodynamics and dynamics was proposed.

Keywords: Emulsion template, surface imprinted polystyrene beads, suspension polymerization.

Recently, the template technique for preparing originating from the biomimetic ideas has attracted much attention. According to structures and properties of substance to be recognized, separated or catalyzed and that of material to be prepared, the molecules[1,2], molecule assembles[3], surfactant[4], bacteria[5], emulsion[6], metal ions and metal complex[7-9] are used as templates. The functional material with special groups and structures can be obtained after templates are extracted. Yoshida *et al*.[8] employed this surface imprinting technique to prepare Zn (II)-imprinted polymer beads. The reactions of the functional group and the substance separated on the surfaces of beads were sensitive and fast.

The emulsion template techniques are divided into intra-template and extra-template technique[10]. Emulsion negative template technique refers to the technique that products are prepared in the microspaces of molecule assembles. For example, the water pools of reverse microemulsion micelles can be used to prepare various nanoparticles[11,12]. Emulsion positive template technique refers to the technique that materials are prepared by assembling on the regular and uniform emulsion drops or particles those are used as template. The template is extracted after polymerization from the polymer to leave regular cavities in the polymer network. Up to date, emulsion positive template methods including emulsion drops template[13] and surfactant template [3,4,13,14], have been used to prepare porous materials owing to the advantages of simple operation and controllable diameter and distribution of the pores.

In this work, a modified emulsion template surface imprinted technique was developed to prepare the cross-linked polystyrene (CPS) beads with many cavities on

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their surfaces by suspension polymerization.

Experimental

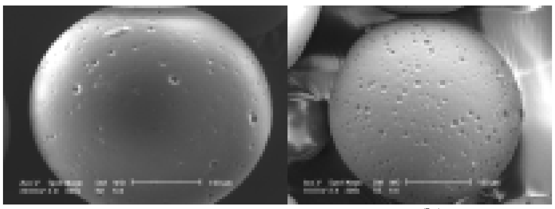
Xylene, paraffin, styrene (St), divinylbenzene (DVB) and azo-bis-isobutyronitrile (AIBN) of analytical grades and Span 85 (Sorbitan oleate), PVA1788 (poly (vinyl alcohol)) of chemical grade were used for this work. The morphology of the surface and section of the CPS beads were analyzed by Philips XL30 scanning electronic microscope (SEM).

The CPS beads were prepared by emulsion template imprinting technique. 90 mL deionized water was added into a round-bottomed flask equipped with a thermometer and a stirrer, and was heated to 70℃ in the water bath. 0.27 g of PVA was added and dissolved fully. Then 22.65 g of St, 4.50 g of DVB, 0.10 g of AIBN and the mixture of Span 85 and xylene or paraffin were added sequentially. The suspension polymerization was carried at 70℃ for 10 hours under the flow of nitrogen. The resulted polymer beads were washed with de-ionized water and then filtered until the filtrate is colorless. Then the beads were washed three times with boiling water and dried at 50℃.

Results and Discussion

Figure 1 shows the ESEM photograph of a bead surface with Span 85/xylene emulsion as template. It can be seen that there are dense cavities on the beads surface. When the amount of 2% wt Span 85 was used and increased the amount of xylene, the number of cavity on beads surfaces increased and their diameters became more uniform. The

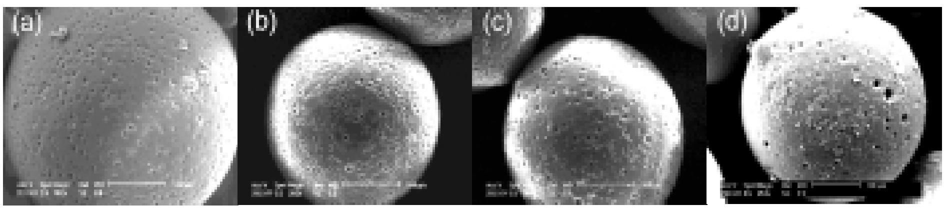
Figure 1 Surface of the beads with xylene and 2% wt Span 85 as template (the bar is 100 μm)



(a) (b)

(a) 8% wt xylene, (b) 20% wt xylene

Figure 2 Surface of the beads with 19% paraffin and Span 85 as template (the bar is 100 μm)



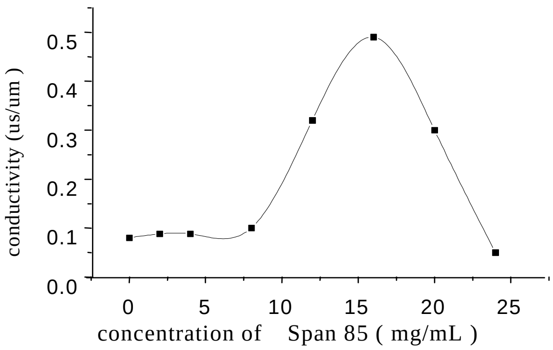
(a) 2% wt Span 85 (b) 4% wt Span 85 (c) 8% wt Span 85 (d) 16% wt Span 85

SEM photograph of a bead using Span 85/paraffin as emulsion templates is shown in **Figure 2.** To remain the amount of paraffin at 19% wt and increase the amount of Span 85 from 2%wt to 16% wt in step, the cavities on bead surfaces enhanced at first and then reduced in number with the increase of Span 85, but the cavities came into being deeper or perforative pores. In addition, the cavity density on bead surface at the condition of using Span 85/paraffin as template was larger than that using Span 85/xylene as template. The observation of the section morphology of the CPS beads showed that the density of pores inside of the beads is less than that on the surfaces. This phenomenon can be named emulsion template surface imprinting.

In order to investigate the forming mechanism of the cavities on surfaces of beads, the resolvability of Span 85 in St was performed. The result is shown in **Figure 3**. It can be seen that Span 85 can self-assembly to micelle and form emulsion structure in St[12]. So the forming mechanism was proposed for the cavities on surfaces of beads as follows.

When the amount of Span 85 is appropriate, the shape of xylence or paraffin microdrops in monomer and polymer beads are spherical because of the characters of self-assembling and emulsifiability. With the increase of the content of xylene or paraffin,the amount of spherical beads increase, which cause the cavities on the surface of beads to be denser. However, the shape of emulsion drops is not spherical when the amount of emulsifier approaches to some degree. During the polymerization, the monomer gradually translated into polymer and phase separation arose obviously in the emulsion template/monomer/polymer beads. In the same time, the stirring caused the emulsion template/monomer/polymer beads to circumgyrate, which bring on the centrifugal force occurring. The emulsion drops in polymer has the tendency to transfer from insides toward surfaces of the beads during the phase separation. The viscidity of the emulsion template/monomer/polymer beads increases with polymerization, which cause the viscous force to turn into the major resistence during the migration of the emulsion drops from insides of polymer to the surface. Meantime, the viscous force was the one of reasons that the emulsion drops could exist on the polymer bead surface. Therefore, the emulsion-imprinted cavities are formed on the polymer bead surface when the equilibrium is achieved among the force of microphase separation, centrifugal force

Figure 3 The correlation of the conductivity and the construction of the Span 85



and viscous force. When the content of emulsifier is appropriate, the emulsion drops increase with the increase of inert solvent, which result in the more surface-imprinted cavities.

Conclusion

The surface imprinted polystyrene beads bearing lots of cavities were prepared *via* suspension polymerization using xylene/Span 85 and paraffin/Span 85 as emulsion templates respectively. The cavity density on bead surface using paraffin/Span 85 as template is larger than that using xylene/Span 85 as template.

Acknowlegment

The authors would like to thank the National Natural Science Foundation of China (grant number: 29906008) for financial support.

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Received 11 February, 2003