HOLLOW GELULAR BEADS OF STYRENE-DIVINYLBENZENE COPOLYMER PREPARED BY SUSPENSION POLYMERIZATION

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Abstract—Hollow gelular beads of styrene-divinylbenzene copolymer have been prepared only by controlling the polymerization temperature and the amount of initiator. A mechanism for the formation of hollow beads is described. Copyright © 1996 Published by Elsevier Science Ltd.

INTRODUCTION
Styrene-divinylbenzene copolymers are widely used in many fields, particularly as ion-exchange resins, gel permeation chromatography column packings, specific sorbents, and catalyst or reagent supports [1–3]. Such polymers have therefore been the subject of a large number of studies. Although linear soluble polymers have been investigated as catalyst supports and can bring useful advantages in some applications [4], most systems have used crosslinked insoluble macromolecular networks. Furthermore, in terms of wide industrial applicability, spherical particulate materials are somewhat favored due to their physical characteristics, such as mechanical stability, narrow particle size distribution, and dynamic behavior. The morphology of styrene-divinylbenzene copolymers is very important for some applications. Resins are classified as gelular or macroporous [1]. In the dry state the porosity of gelular resin is very small, corresponding only to the distance between chains, and hence they are referred to as microporous. On addition of a good solvent, considerable porosity is re-established with some lightly crosslinked polymers being able to absorb many times their own weight of an appropriate solvent. So gelular resins are usually employed in the presence of a good solvent. In contrast, macroporous resins have a permanent porous structure often with a large surface area even in the dry state. The porosity of macroporous resins changes little on contact with a good solvent. Hence macroporous resins are generally applied in gas-phase reactions or liquid-phase reactions involving a poor solvent. Lightly crosslinked gelular beads are prepared via suspension polymerization of monomers containing only a small amount of crosslinking agent.

Macroporous beads are prepared in a similar way but with the addition of a pore-forming agent. Synthetic studies have been focused mainly on the characteristics of polymer beads in relation to the amount and type of porogenic agent and crosslinking agent used [5, 6]. The size distribution of polymer beads and its relationship to stirring speed and amount of surfactant employed have also been investigated [7]. The effect of temperature on polymer morphology has, however, hardly been studied at all. It is interesting that the new morphology described in this work has been obtained by controlling the temperature and the amount of initiator. The morphology is a hollow form having a large cavity at the center of the polymer bead. Hollow beads have been prepared before by Akar and Ersen in 1983 [8]. They described the preparation of hollow crosslinked poly(styrene-co-divinylbenzene) beads, obtained by coating a non-crosslinked primary bead, followed by solvent extraction of the soluble core.

In the present work, a very simple method has been developed which may have potential applications in many fields. The method involves only manipulation of the polymerization temperature and the amount of initiator. A mechanism for the formation of the hollow particles is also proposed.

EXPERIMENTAL
Suspension polymerization was carried out in a four-necked round-bottomed flask equipped with a mechanical stirrer, a condenser, nitrogen purge inlet, and reactant inlet. The stirrer has two impellers. Before stirring was started, the upper impeller was located at the interface of the organic and aqueous phases to avoid aggregation of monomer droplets during suspension polymerization. The other was located in the aqueous phase to obtain vertical motion in the reactor fluid. The aqueous phase consisted of distilled water (600 ml), poly(diallyldimethylammonium chloride) (Calgon Corp., Catno T) (20 ml) and gelatin (1 g) which was agitated at 40°C. Styrene and divinylbenzene (55% divinylbenzene isomers and 45% ethylnvinylbenzene) were washed alternately with aqueous sodium hydroxide solution (5 wt%) and distilled water three times to remove...
an inhibitor (4-tert-butylnatehlo). Azobisobutyronitrile (AIBN) or benzoyl peroxide (BPO) were added as initiator to the washed divinylbenzene (5 ml) and styrene (95 ml). The mixture was thoroughly stirred before being poured into the reactor. The reaction temperature was maintained at 40 °C for 30 min to stabilize the spherical monomer droplets, and the polymerization temperature was then increased to 60, 70 or 80 °C and kept at this temperature for 20 hr. The amount of AIBN was 0.2, 0.4 or 0.6 g, and the rate of temperature increase was 0.5 or 1 °C min. The product was washed with water only to preserve the morphology of the polymer beads and dried under reduced pressure. The morphology of the surface and cross-section of a single bead were observed using scanning electron microscopy. Swelling ratios in tetrahydrofuran (THF) were determined as the ratio of the volumes occupied by the same quantity of polymer bead swollen in THF and in the dry state.

RESULTS

The reactor temperature was maintained at 40 °C for 30 min in order to obtain good-shaped droplets and then increased up to 80 °C at a rate of 1 °C min. The amount of initiator was varied (0.2, 0.4 and 0.6 g). All the beads obtained under the above conditions have a hollow form, while the wall thickness decreased with the amount of initiator, as shown in Fig. 1.

Direct observation of the polymer morphology by scanning electron microscopy (Fig. 2) shows that the outer and inner surfaces consist of an aggregation of small microparticles similar to the structure of macroporous resins [6], while the cross-section shows evidence of aggregation of microparticles without any macropores (Fig. 3). The size of the microparticles decreases with the amount of initiator. In the case of BPO as initiator, the thickness of the wall is greater and the size of the microparticles aggregated on the surface of the hollow polymer bead is smaller than that using AIBN.

The polymerization temperature was varied from 60 to 70 and 80 °C, respectively. The thickness of the walls of the hollow polymer beads increased with a decrease in the polymerization temperature. Finally, the cavity at the center of the polymer bead was no longer observed when the polymerization temperature was reduced to 60 °C, as shown in Fig. 1. The wall thickness varied with the rate of increasing temperature from the initial value to the final polymerization temperature. In the case of increasing temperature at the rate of 0.5 °C min from 40 to

![Fig 1 Variation of the morphology of gelular polymer beads with polymerization conditions](image-url)
Hollow gelular beads of styrene-divinylbenzene copolymer

80°C, the cavity was not observed at the center of the bead as shown in Fig. 1. The specific surface area of these polymer beads is nearly zero, and the swelling ratio in THF is approximately 3.1 irrespective of the preparation conditions, as shown in Table I.

DISCUSSION

In the preparation of crosslinked beads, temperature effects have seldom been discussed. Considerable research has been applied to try to explain the mechanism of the formation of spherical crosslinked nodules in polymer beads in terms of the kinetics of polymerization and phase separation [10, 11]. In suspension polymerization, each droplet of the organic phase consists of monomer and initiator and behaves as an individual bulk polymerization reactor heated from an external wall. The product is a solid bead of copolymer. Because the first double bond in divinylbenzene is somewhat more reactive than that in styrene or ethylstyrene [12], a larger proportion of DVB will be found in the copolymer initially than in the monomer feed. This means that a polymer formed during the very early stages of the polymerization is composed of straight chains with a larger level of pendant vinyl groups than the average composition. A branch point occurs by reaction between the growing chains and the pendant vinyl groups. The corresponding radius of gyration of the highly branched polymer which is formed initially is lower than that of the linear polymer of the same molecular weight and produces very small domains of a polymer-rich phase called a nucleus. Once the nuclei are formed, they grow and produce a polymer-rich
phase. Within the same period of time, other nuclei grow within the same organic droplet and create another polymer-rich phase which grows until the monomer is completely consumed. Finally, the nuclei are aggregated with one another and produce an inhomogeneous gelular polymer bead which has many crosslinked nodules, as shown in Figs 2 and 3. The size of the polymer-rich domains and the distance between them depend on the extent of reaction and the rate of initiation. The size of crosslinked nodules in the polymer bead decreases with the amount of initiator, as shown in Fig 2. This means that the number of nuclei formed at the early stage of polymerization depends on the initiation rate. If the initiation rate is increased, the distance between polymer-rich domains decreases at a given extent of polymerization, developing a lot of nuclei at the initial stage. This distance decreases with time, and finally the polymer-rich domains tend to aggregate and produce an inhomogeneous polymer bead. As polymerization proceeds, growing chains contain a lower proportion of DVB residues than in the first phase of polymerization due to the decrease in the feed ratio resulting from the different reactivities of DVB and styrene. As the polymer-rich domains grow radially out from their centers with

Table 1: Polymerization conditions and characteristics of the bead

<table>
<thead>
<tr>
<th>Run</th>
<th>Initiator</th>
<th>Temperature (°C)</th>
<th>Morphology</th>
<th>Swelling ratio in THF</th>
<th>( t )</th>
<th>P*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.60 g AIBN</td>
<td>40</td>
<td>80</td>
<td>1 C min</td>
<td>hollow</td>
<td>3.1</td>
</tr>
<tr>
<td>B</td>
<td>0.40 g AIBN</td>
<td>40</td>
<td>80</td>
<td>1 C min</td>
<td>hollow</td>
<td>3.2</td>
</tr>
<tr>
<td>C</td>
<td>0.30 g AIBN</td>
<td>40</td>
<td>80</td>
<td>1 C min</td>
<td>hollow</td>
<td>3.2</td>
</tr>
<tr>
<td>D</td>
<td>0.60 g AIBN</td>
<td>40</td>
<td>70</td>
<td>1 C min</td>
<td>hollow</td>
<td>3.1</td>
</tr>
<tr>
<td>E</td>
<td>0.40 g AIBN</td>
<td>40</td>
<td>70</td>
<td>1 C min</td>
<td>hollow</td>
<td>3.1</td>
</tr>
<tr>
<td>F</td>
<td>0.20 g AIBN</td>
<td>40</td>
<td>70</td>
<td>1 C min</td>
<td>filled</td>
<td>3.1</td>
</tr>
<tr>
<td>G</td>
<td>0.60 g AIBN</td>
<td>40</td>
<td>60</td>
<td>1 C min</td>
<td>filled</td>
<td>3.1</td>
</tr>
<tr>
<td>H</td>
<td>0.60 g AIBN</td>
<td>40</td>
<td>80</td>
<td>0.5 C min</td>
<td>filled</td>
<td>3.2</td>
</tr>
<tr>
<td>I</td>
<td>0.89 g BPO</td>
<td>30</td>
<td>80</td>
<td>1 C min</td>
<td>hollow</td>
<td>3.0</td>
</tr>
<tr>
<td>J</td>
<td>0.89 g BPO</td>
<td>40</td>
<td>80</td>
<td>1 C min</td>
<td>hollow</td>
<td>3.2</td>
</tr>
</tbody>
</table>

*The ratio of wall thickness to the radius of the bead.
concentrated polymer in the center of the polymerization, which might cause a local acceleration of polymerization, which in turn leads to highly concentrated polymer in the center of the polymer-rich domain. The latter are swollen by monomer and the swelling ratio increases from the center to the periphery. In the situation where the swelling ratio of the polymer at the periphery of the polymer-rich domain is higher than a certain value at the time the polymer domains aggregate, the periphery of the copolymer behaves, in some respects, like a liquid and the polymer-rich domains collapse on each other and produce a gelular bead which has no porous structure. However, generally the level of crosslinking agent is high enough for hardening of the polymer-rich domain to occur before aggregation, in which case a macroporous structure will be obtained even though a porogenic agent is absent [14].

A mechanism for the formation of hollow gelular polymer beads is proposed in Fig. 4. The important factors are the volume contraction on polymerization and the aggregation of polymer-rich domains near the interface of the suspension medium and the organic droplet. Heat transfer from suspension medium to the organic droplet means that the initiator begins to decompose and generate radicals most efficiently at the surface of particles, where polymer also forms more quickly. Hence a polymer concentration gradient exists along the radial dimension of each organic droplet, and the volume fraction of polymer increases with the polymerization time. This phenomenon, where polymer forms more quickly at the particle surface, is most likely with a sharp increase in temperature of the suspension medium. The process is essentially a bulk polymerization near the surface. This tends to reduce the polymerization at the center of the organic droplet. Increasing polymer concentration also decreases the translocation diffusion of polymer chains to the center of the polymer droplet as the reaction medium becomes more viscous [16]. The size of the organic droplet is reduced by contraction during polymerization until the nuclei at the surface become aggregated with one another, and the concentration of polymer reaches the glass point. The condition describing a high $T_\text{g}$ polymer phase reaching its glass point can be estimated as follows [17]:

$$T_\text{g} = \frac{\alpha_p \phi_p T_{\text{mp}} + \alpha_m (1 - \phi_p) T_{\text{sm}}}{\alpha_p \phi_p + \alpha_m (1 - \phi_p)}$$

where $T_\text{g}$ is the reaction temperature (°C), $T_{\text{mp}}$ and $T_{\text{sm}}$ are the glass transition temperature (°C) of the pure polymer and monomer, respectively; $\phi_p$ is the volume fraction of polymer in the glassy phase, $\alpha_p$ is the difference between the coefficient of volumetric expansion of the polymer in the melt and glassy state, and $\alpha_m$ is the corresponding difference for the monomer. When the volume fraction of polymer at the surface of the organic droplet is such that the glass point is approached, the volume contraction cannot be replenished by polymer or monomer because of the inhibition of translational motion. This effect gradually generates a cavity at the center of the polymer bead. The wall thickness of this hollow gelular polymer bead can be controlled by the temperature increment, the concentration of initiator and the polymerization temperature. If the temperature is increased slowly, hollow gelular beads are not formed. However, a rapid increment in the temperature yields hollow spherical polymer beads as shown in Fig. 1. Control can also be achieved by changing the amount of initiator. The hollow domain can be roughly defined by a line in a map where the abscissa is reaction temperature and the ordinate is the amount of initiator, as shown in Fig. 5. Depending on the rate of increase of temperature and the decomposition properties of initiators, the position of the line may be different. Provided the suspension polymerization conditions are close to the boundary of the hollow domain, the wall thickness of the
hollow bead formed increases as shown in the SEM images of Fig. 1.

Using RPO instead of AIBN under the same reaction conditions, the walls become thicker and the size of the aggregated microparticles becomes smaller, as shown in Fig. 2. RPO decomposes more rapidly at a lower temperature than AIBN. This may cause initiation and polymerization to occur more easily in the center of the organic droplet, with many nuclei developed during the early part of the polymerization. This may explain the thicker wall and smaller microparticles.

Considering the volume change of the organic phase on polymerization, the minimum ratio of the wall thickness to the radius of bead is approximated by mass conservation as follows:

$$l/R = 1 - \sqrt{1 - \rho_m/\rho_p}$$

where $R$ is the radius of the polymer bead and $l$ is its wall thickness, $\rho_p$ and $\rho_m$ are the real density of polymer and monomer, respectively. If the density changes from $\rho_m = 0.906$ to $\rho_p = 1.050$ on polymerization, the minimum value of $l/R$ will be 0.48. It is interesting, however, that the actual wall thickness of hollow gelular beads is smaller than that calculated from the above equation. This may be attributed to the effect of tangential stress at the surface of the organic droplet by the suspension of fluid and the generation of nitrogen by decomposition of initiator.

The tangential stress may increase when the polymerization changes the effective viscosity $\mu^*$ of the suspension medium. The relation between $l/R$, polymerization changes from $\mu^*$ = 0.70 N sec/m$^2$ for styrene) can be described as follows [18]:

$$\mu^* = 1 + 2\left(\frac{\mu + 0.5\mu}{\mu + \mu_0}\right)$$

Under the experimental conditions used, the effective viscosity changes from 1.101 to 1.208 N sec/m$^2$. The tangential stress and nitrogen generated by decomposition of the initiator will expand the organic droplet during the suspension polymerization and the droplet remains expanded until the bead becomes hard. As a result the thickness of the wall is thinner than expected.

The swelling ratio of the polymer bead in THF is approximately 3.0 independent of reaction conditions (Table 1). Hence the swelling properties of the polymer phase in the product seem to be independent of the preparation conditions and depend only on the chemical composition of the polymer bead.

**CONCLUSIONS**

Hollow beads of styrene-divinylbenzene copolymer were prepared. The size of a polymer bead can be controlled by varying the stirring speed [7], and the wall thickness of a hollow bead is also controlled by the method described in this work. Therefore, the physical characteristics of a hollow gelular polymer bead for suitable applications can be easily obtained by controlling the polymerization conditions. Hollow polymer beads may have potential applications as a light packing material, new catalyst or reagent supports and an encapsulator of macromolecules such as enzymes. It also has high potential for application as a membrane reactor.

**REFERENCES**