

SHORT COMMUNICATIONS

## A Two-Step Stirring Process of Producing Granular Polymers with Uniform Fine Particle Size for High-Performance Liquid Chromatography

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In recent years, finding a technique for obtaining granular resins with a uniform particle size has become important in aqueous suspension polymerization. Examples of uses for such resins are as polymers for various toners, biomaterials, pharmaceutical reagents and separation media for various kinds of chromatographies. The packing materials for high-performance liquid chromatography (HPLC) used now are mostly spherical porous polymers or silicas that have a uniform particle size of about  $10\ \mu\text{m}$  or less<sup>1-3</sup>; this need requires techniques for producing granular polymers with a highly uniform particle size distribution (PSD).

Various attempts have been made to produce such granular polymers, such as changing the ratio of the monomer to water, combining a suspension agent and suspension assistant,<sup>4</sup> using agitating blades, and changing the number of revolutions of the agitator. However, it is difficult to produce polymer beads with a particle size of about  $10\ \mu\text{m}$  at a high yield. Even if the agitation system is adjusted to the most suitable conditions, it is difficult to make the oil drop distribution completely uniform at the initial stage of polymerization. It is known that the process

of stirring with high speed shearing at normal temperature for preliminary dispersion has some effect on producing small particle beads.<sup>5,6</sup> However, it is also difficult to inhibit the non-uniform growth of oil drops at the stage of polymerization completely, due to discrepancies in their coalescing and dispersion speeds.

The packing materials for high-performance gel permeation chromatography (GPC) for the analysis of organic polymeric materials are spherical porous polymers of styrene-divinylbenzene<sup>7,8</sup> that have a uniform particle size of about  $10\ \mu\text{m}$ . In this article, we describe a two-step stirring process for producing a granular polymer of styrene-divinylbenzene with a fine particle size of about  $10\ \mu\text{m}$  that is done by conducting aqueous suspension polymerization in the presence of a suspension agent, a suspension assistant and/or non-reactive organic solvents.

In this process, polymerization should be carried out for a certain period from the beginning of polymerization under stirring accompanied with high speed shearing at a shear force of  $10^5$ — $5 \times 10^6\ \text{min}^{-1}$  acts of the polymerization system. A preferable rate of

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shearing is  $3 \times 10^5$ — $2 \times 10^6 \text{ min}^{-1}$ . Apparatuses that produce high speed shearing incorporate a turbine pump. In our study, a table-type homomixer<sup>9</sup> manufactured by Tokushukika Kogyo was used.

When the percentage conversion is between 1% and 50%, or more exactly between 5% and 30%, polymerization under stirring with high speed shearing is stopped and transferred to a stirring system for polymerization that is not accompanied with high speed mechanical cutting or grinding. In this process, we use a stirrer with an H-type blade (H-type stirrer) manufactured by Hitachi Chemical and chosen for its chemical engineering characteristics.

The materials (A) shown in Table I were placed in a 1-liter four-necked separable flask equipped with a thermometer, a bimetal relay, reflex condenser and homomixer, and stirred with accompanying high speed shearing (rate of shear, about  $1.3 \times 10^6 \text{ min}^{-1}$ ). The contents were heated to 70—75°C by a mantle heater during dispersion, and polymerization was carried out for two hours. The percentage conversion as identified by gas chromatography was 30%. Subsequently, the reaction solution was quickly removed to another 1-liter four-necked separable flask and polymerization was continued using the H-type stirrer at 80—85°C for 4 h with a stirring rate of

500—600 rpm.

During polymerization, the contents were often sampled so that the particle size of the beads was measured by optical microscope. Ten percent tricalcium phosphate (TCP) was intermittently added to the reaction solution in order to make the dispersions stable and to keep the particle size small. The spherical beads produced were filtered, washed with a diluted hydrochloric acid solution and dried. Microphotographs of the beads were taken, and their particle size was measured. The PSD of the beads was deduced in terms of percentage by weight. The resulting PSD is shown in Figure 1(a). The average particle size ( $\bar{x}$ ) was 11.6  $\mu\text{m}$ , and the standard deviation ( $s$ ) was 6.0. The yield of  $10 \pm 5 \mu\text{m}$  beads was 54%. By using the optical and electron microscopes, there was

Table I. Materials<sup>a</sup> for production used in this study

Materials/g	(A)	(B)	(C)
Styrene	67.2	72	—
60% DVB	17.2	40	100
BPO	0.52	1.2	5.0
10% TCP	23.4	60	100
1% DA	1.26	2.4	—
Toluene	—	40	36
DEB	—	20	36
IAA	—	—	150
0.5% MA	—	—	800
Water	420	560	—

<sup>a</sup> Abbreviations: DVB, divinylbenzene; BPO, benzoyl peroxide; TCP, tricalcium phosphate; DA, sodium dodecylbenzenesulfonate; DEB, diethylbenzene; IAA, isoamyl alcohol; MA, methyl cellulose.

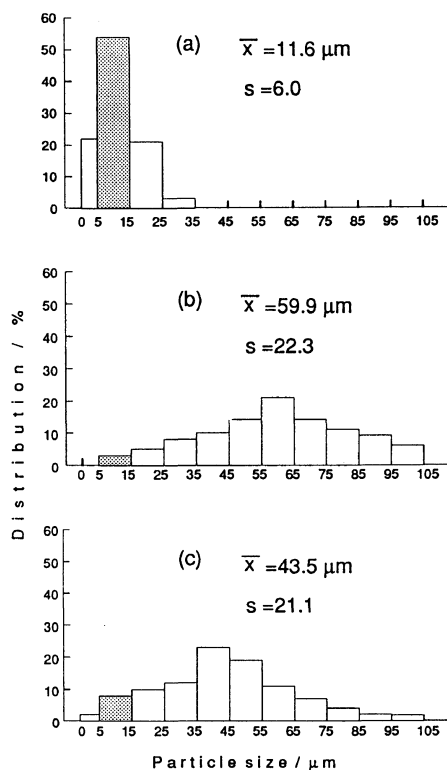


Figure 1. PSD of the beads produced from materials (A). a) two-step process; b) H-type stirrer only; c) preliminary dispersion by homomixer and polymerization by H-type stirrer.

no observation of submicron size beads, which might have been produced if the concurrence of emulsion polymerization had occurred.

As the control experiments for the two-step stirring process described above, three polymerization processes were carried out using the materials (A) shown in Table I. First, the process was repeated under the same conditions described above, but without the homomixer, that is, the H-type stirrer was used throughout the procedure. The resulting PSD is shown in Figure 1(b). The yield of  $10 \pm 5 \mu\text{m}$  beads was only 2.5%.

Second, the materials (A) were placed and stirred with high speed shearing (rate of shear, about  $1.3 \times 10^6 \text{ min}^{-1}$ ) at normal temperature (20–30°C) for 20–30 min for preliminary dispersion (percentage conversion was 0%). Subsequently, the resulting dispersion was removed to the separable flask equipped with the H-type stirrer and polymerization was carried out at 70–75°C for 2 h and 80–85°C for 4 h with a stirring rate of 500–600 rpm. The resulting PSD is shown in Figure 1(c). The yield of  $10 \pm 5 \mu\text{m}$  beads was 8%.

Third, the process was repeated using the same conditions described above, but without the H-type stirrer, that is, the homomixer was used throughout the procedure. After three to four hours from the beginning of polymerization (the percentage conversion was about 60%), the spherical beads appeared to be broken down by the homomixer, clogging the apparatus and terminating the reaction.

The results of Figure 1 clearly indicate that the PSD of (a) is quite narrow and highly uniform at about  $10 \mu\text{m}$  in comparison with (b) and (c). The process of stirring with high speed shearing at normal temperature for preliminary dispersion<sup>5–6</sup> has some effect on producing small particle beads, but is not useful in producing beads with a narrow PSD.

Two other examinations were carried out by the two-step processes using materials (B) and (C) listed in Table I. Polymerization was carried out at 70–75°C for 1.5–3 h with a homomixer

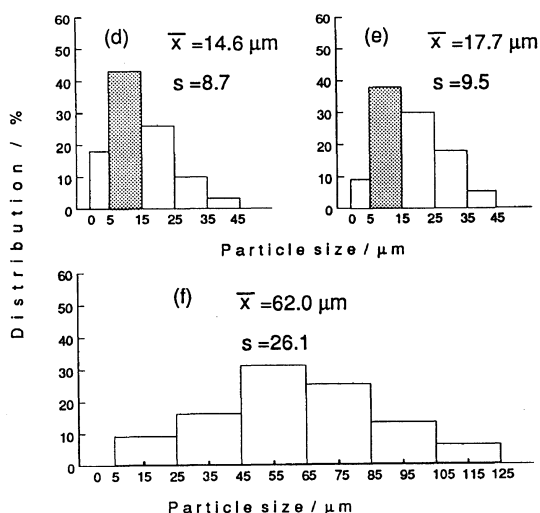


Figure 2. PSD of the beads produced from materials (B) and (C).

d) two-step process from materials (B); e) two-step process from materials (C); f) H-type stirrer only from materials (B).

(percentage conversion was about 20–25%). Subsequently, polymerization was continued at 80–85°C for 5 h using the H-type stirrer at a rate of 400–450 rpm. The results are shown in Figure 2(d) and (e). The yields of  $10 \pm 5 \mu\text{m}$  beads were 43% and 38%, respectively.

As the control experiments, the processes were repeated under the same conditions described above, but without the homomixer, that is, the H-type stirrer was used throughout the procedure. The resulting PSD produced from materials (B) is shown in Figure 2(f). As polymerization from materials (C) was unstable, the resulting beads had particle sizes of 100–1000  $\mu\text{m}$ .

In these polymerizations, non-reactive organic solvents, such as toluene, diethylbenzene and isoamyl alcohol, were used to produce highly porous beads with micro pores. It is reasonable that the PSD of (d) and (e) shown in Figure 2 were slightly larger than that of (a) shown in Figure 1, because there was a tendency for the particle size of the beads to grow when non-reactive organic solvents were used. However, as shown in Figure 2, even with

conventional polymerization, which is unsuitable for producing fine particle beads method, this two-step stirring process provides a high yield of fine particle beads.

This new process is applicable to the polymerization of other granular polymers for HPLC with a uniform fine particle size and its distribution can be regulated by selecting the chemical engineering characteristics of the homomixer and the H-type stirrer. These problems are being studied further and will be the subject of a subsequent paper.

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