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A Novel Method for the Preparation of Octyl Bonded Styrene-divinylbenzene HPLC Packings

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Abstract: Monodisperse octyl bonded poly(styrene-divinylbenzene) (C8-PS-DVB) beads were prepared *via* a single-step swelling and polymerization method. Fourier transform infrared and chromatographic evaluation were used to confirm the reaction between the octene and divinylbenzene.

Keywords: Monodisperse, C8-PS-DVB, single-step swelling and polymerization.

In 1979 Ugelstad *et al.*[1] developed a technique named “activated multi-step swelling and polymerization” method, which made the preparation of monodisperse polymer beads possible. This method is excellent, but it seems rather complex because at least two steps are needed in the swelling process. In 1995, Ogino *et al.*[2] improved this method, they developed a single-step swelling and polymerization method which made the preparation very simple.

The synthesis of monodisperse alkyl bonded PS-DVB beads needs at least two steps. The first step is the preparation of monodisperse PS-DVB beads , the subsequent step is the modification of PS-DVB with alkyl. Friedel-Crafts reaction is the most common method to modify the polymer beads[3-6], but the structures of alkyl groups are not unitary. Indeed, isomerization of primary halides to secondary or tertiary halides occurs in the presence of aluminium chloride under the Friedel-Crafs reaction conditions. In this paper, the introduction of C8 and the synthesis of the polymer beads were completed in one step using a single-step swelling and polymerization method, without the Friedel-Crafts procedure.

According to the method reported by Zuo, *et al.*[7] monodisperse polystyrene seed particles were prepared by dispersion polymerization of styrene in ethanol medium. After centrifugal separation, the seed particle obtained were dispersed in an aqueous solution containing 1.0 % (w/w) poly(vinyl alcohol) (PVA) and made the content to be 0.02 g/mL. The size of the prepared particles was measured to be 1.7 μm by scanning electron microscopy.

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Octyl bonded PS-DVB was prepared as follows: A 30 g amount of a mixture, consisting of 1 g octene, 10 g divinylbenzene(55 %), 14 g toluene, 5 g dibutyl phthalate and 2 % (w/w) (based on the total monomer) of azobis(isobutyronitrile) initiator were emulsified in 300 mL water containing 0.4 g sodium *n*-dodecyl sulfate and 1.0 % (w/w) of PVA with an ultrasonic disrupter until the particle size of oil drops became at most 0.5 μm (observed by optical microscope). Then the emulsion was added dropwise to 10 mL dispersed PS seed solution mentioned above, with stirring. The mixture was stirred for 24-48 h at room temperature so that all the emulsified organic phase was absorbed by the polymer seeds. Then the polymerization was carried out at 70°C for 4 h, 75°C for 3 h, 80°C for 2 h, 85°C for 2 h, and 90°C for 2 h under a nitrogen atmosphere. The resulting polymer beads were washed successively with hot water, ethanol, and methanol; the beads were then dipped into the butyl acetate for 24 h to remove the porogens. The beads were washed with ethanol again and dried *in vacuo*. For comparison, porous poly(styrene-divinylbenzene) (PS-DVB) particles were prepared by the same method. **Figure 1** shows scanning electron micrographs of the prepared particles; they indicated that the prepared beads in this study are uniform in size and have a porous structure.

The FT-IR spectrum used to characterize the polymer beads is shown in **Figure 2**. For ST-DVB, absorption bands at 902, 989, and 1630 cm^{-1} are the typical peaks for unreacted vinyl groups[8,9]. The intensity of these bands decreases distinctly after modification with C8. This confirms that octene reacted with vinyl group of PS-DVB.

Figure 1 Scanning electron micrographs of the monosized porous beads

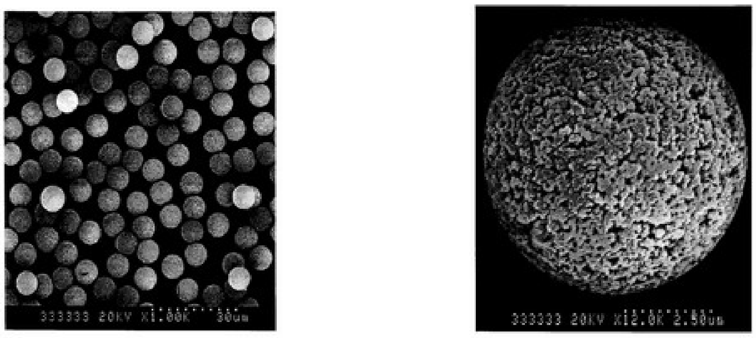


Figure 2a FT-IR spectra of ST-DVB beads

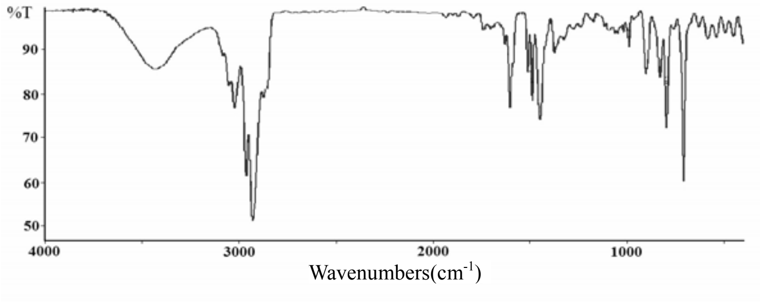


Figure 2b FT-IR spectra of C8-ST-DVB beads

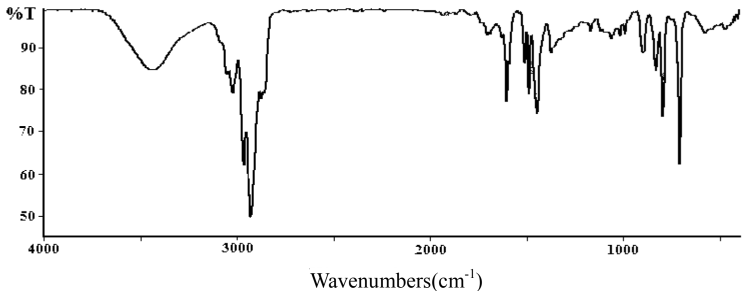
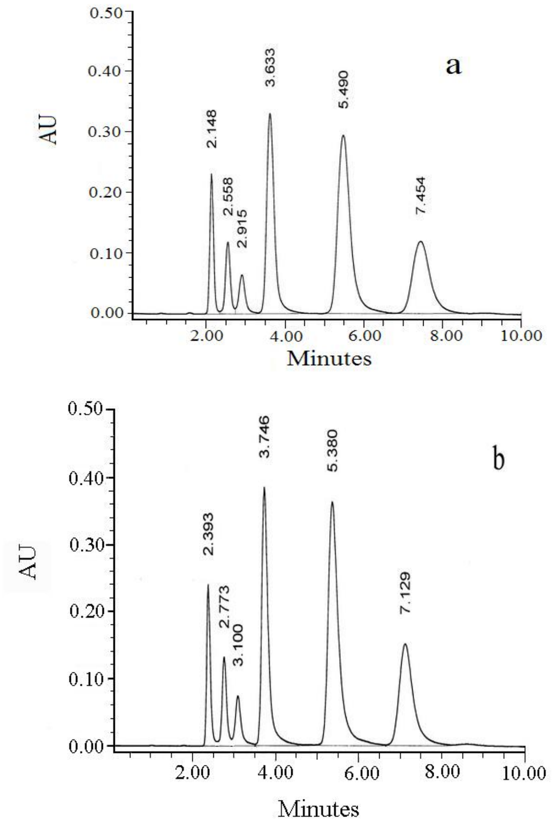


Figure 3 Separation of basic compounds on (a) PS-DVB and (b) C8-PS-DVB.



Analysis conditions: eluants, 80% acetonitrile/water; flow rates, 1.0 mL/min; ambient temperature; detection, UV at 254 nm; sample, 1) pyridine, 2) aniline, 3) o-methylaniline, 4) N-methylaniline, 5) N,N-dimethylaniline, 6) N,N-diethylaniline

C8-PS-DVB and PS-DVB beads were packed into stainless columns (150×4.6 mm). Using these two columns, we separated some basic compounds. It is clear that the chromatographic characteristics on the C8-ST-DVB are better than those on the unmodified PS-DVB (for pyridine, the theoretical plate number of C8-PS-DVB is

26077/m, and that of PS-DVB is 16954/m). This can also verify that the polymer beads contain C8 functionalities that have been bonded to a polymer matrix. The presence of the C8 groups alters capacity factors (k′ values) of these compounds compared with underivatized materials (for N,N-diethylaniline, $k'_{\text{ST-DVB}} = 6.96$, $k'_{\text{C8-ST-DVB}} = 6.53$). Consequently, the analysis time on C8-PS-DVB is shorter than that of underivatized polymers (**Figure 3)**.

Acknowledgments

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