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A New Preparation Method for Well-Controlled 3D Skeletal Epoxy Resin-Based Polymer Monoliths

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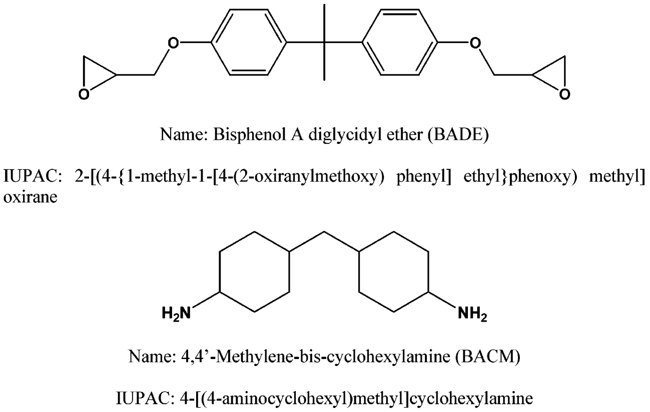
In the past decade, polymer-based skeletal and macroporous "monoliths" having micrometer size macro-through-pores have been utilized as chromatographic separation media, purification devices, adsorption media, and even synthetic media in combinatorial chemistry. As the separation media in high-performance liquid chromatography (HPLC), those polymer-based monoliths realize good separation efficiency with low column pressure drop due to a combination of micron size polymer skeleton and relatively large macro-through-pores. In fact, some better separations of relatively large molecules such as proteins using ordinary polymer-based monolithic separation media have been reported so far compared with that on separation media packed with usual particle type stationary phases.[1−4] The preparation methods of those polymer-based monolithic media were first reported in early 1990s, and surprisingly, rather simple and easy methods were utilized for the preparations.[5,6] Usually, those polymer-based monoliths were prepared using a typical radical polymerization of monomer(s) with cross-linking agent in some porogenic solvents. The polymerization is thermally initiated, but in some cases, photoinduced polymerization is also utilized.[7−10] The photoinduced polymerization can be achieved at lower temperature compared with that of radical polymerization. Recently, the irradiation ionization method was reported to prepare polymer-based monoliths.[11,12] This polymerization system does not require an initiator; in addition, relatively fast polymerization at any temperature could be done. The irradiation method was reported to prepare wider dimensions of polymer monoliths in comparison to those prepared using photoinduced polymerization because of longer effective penetration depth by the irradiation method than that by photoinduced polymerization. Living radical polymerization was also reported to afford polymer-based monolith having rather controlled macro-through-pores compared with those by the usual free radical polymerization method.[13] In addition, ring-opening methathesis copolymerization was also applied for preparation of monolithic separation media.[14]

In the above-mentioned cases, as porogenic solvent, binary or ternary mixtures of poor and/or good solvents are occasionally used for controlling a variety of pore



Name: Bisphenol A diglycidyl ether (BADE)

IUPAC: 2-[(4-{1-methyl-1-[4-(2-oxiranylmethoxy) phenyl] ethyl}phenoxy) methyl] oxirane

Name: 4,4'-Methylene-bis-cyclohexylamine (BACM)

IUPAC: 4-[(4-aminocyclohexyl)methyl]cyclohexylamine

Figure 1. Structures of monomers.

Table 1. Polymerization Conditions

condition	PEG M_w	porogen (g)	temp (°C)
1	200	7.2	120
2	150	6	160
3	300	7	80

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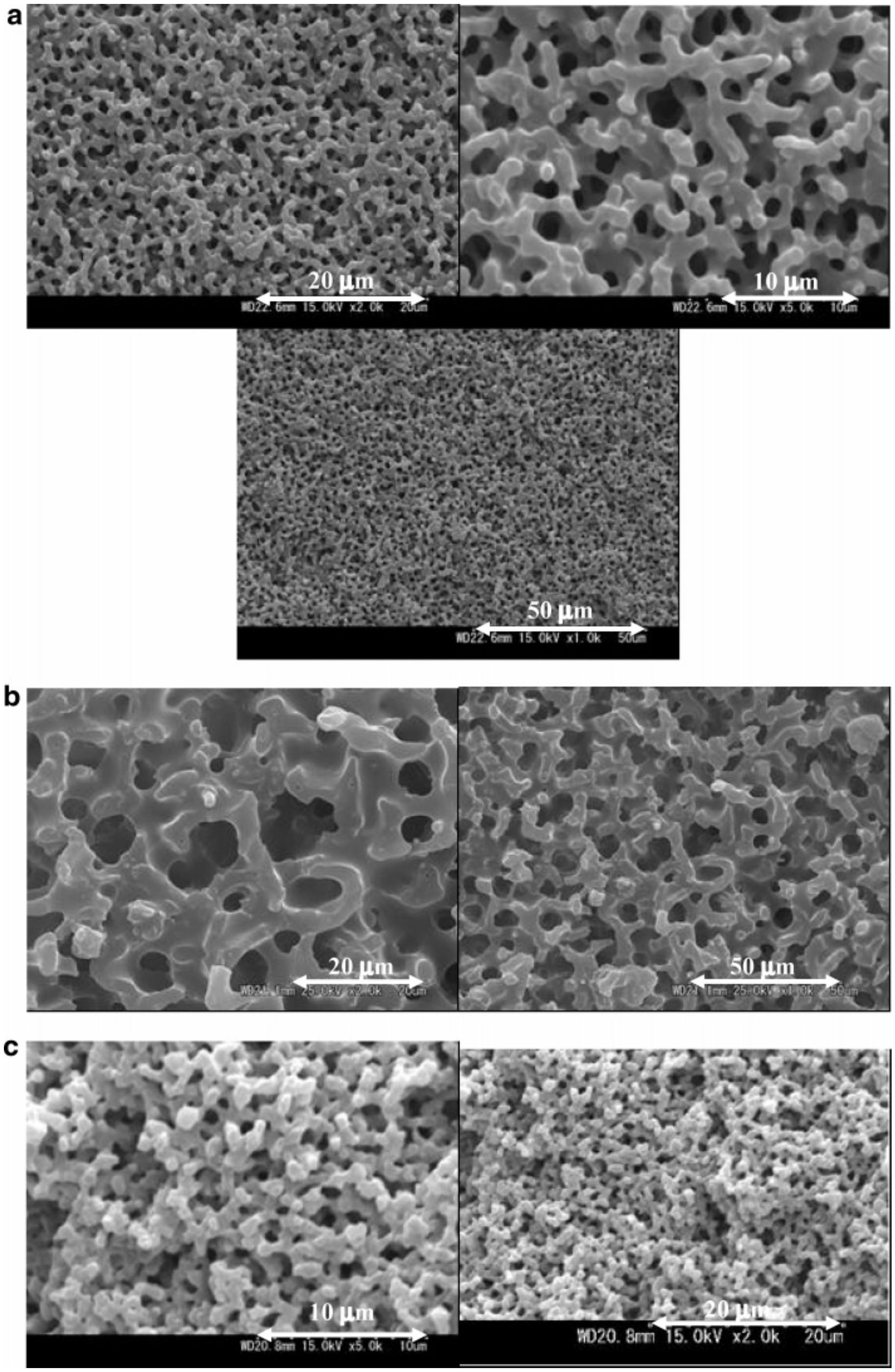

Figure 2. SEM photographs of the polymers prepared.

size and its structure. The porogenic solvent dominantly selected for preparation of monolith type media is usually poor solvent for the monomers utilized to form macro-through-pores required for liquid flow. In the case of poor solvent as the porogenic solvent, the growing polymer chains tend to aggregate each other because van der Waals attraction surmounts steric hindrance mutually expelling the polymer chains. Thus, in the case of ordinary polymer monolith preparations, the phase separation between growing polymer chains and porogenic solvent proceeds so fast and the coarsening of monolithic structure inherently leads to heterogeneous macroporous structures composed of tiny micron size globular particles.

As mentioned above, the majority of polymerization methods for the preparation of polymer-based monolith are so-called vinyl polymerizations utilizing vinyl or (metha)acrylate monomers. Although various polymerization techniques can be utilized, the polymerization system cannot be changed because of the above-mentioned reasons. Therefore, to change our view of monomers utilized for monolithic media, our study in this paper mainly focuses on a new polymerization method using a polycondensation reaction with an epoxy compound and an amino compound. This is also a simple method; for example, both monomers are just mixed with porogenic solvent at a prescribed polymerization temperature to afford an epoxy resin-based polymer monolith. We varied the polymerization temperature, varieties, as well as amount of porogenic solvent to evaluate morphological changes such as pore size of the monoliths and size of skeletal polymer network.

4-[(4-Aminocyclohexyl)methyl]cyclohexylamine (BACM) (0.52 g ,2.47 mmol) was dissolved in poly(ethylene glycol) (PEG), and then 2.33 g (6.84 mmol) of 2-[(4-{1-methyl-1-[4-(2-oxiranylmethoxy)phenyl]ethyl}phenoxy)-methyl]oxirane (BADE) was added into this solution with stirring. This polymerization mixture was poured into a glass test tube having 12 mm inner diameter. The polymerization took place in oil bath at the prescribed temperature for 3 h. The structures of monomers utilized and the amount of monomers as well as porogen are shown in Figure 1 and Table 1, respectively. The resulting polymers were removed form the test tube to be washed with water followed by acetone and then dried at 60 °C for 24 h. We have prepared three types of polymers with different molecular weight PEG and polymerization temperature.

We assumed that cross-linking took place in the resin; therefore, we started this experiment with an epoxy: amine ratio = 2:1. However, for some reason, the ratio mentioned in this study (2.77) afforded nicely controlled monolith structure. At this moment, this reason has not been clear, but viscosity during the polymerization might prevent effective formation of network structure, which induces phase searation; therefore, excess of epoxy group was utilized.

As shown in Figure 2, the polymerization conditions studied in this paper nicely afforded 3D skeletal monolithic polymers. The polymerization condition 1 formed 1.8 μm polymeric skeletons with 2.5 μm macro-through-pores, as shown in Figure 2a. Interestingly, the condition 2 employing lower molecular weight PEG and higher polymerization temperature changed the structure of polymer (skeleton: 6 μm, macro-through-pores: 4 μm) (Figure 2b). On the other hand, higher molecular weight of PEG and lower polymerization temperature (condition 3) afforded thinner polymer skeleton and narrower macro-through-pores, as shown in Figure 2c. Those observations suggest that, by the change of molecular weight of the porogen as well as polymerization temperature, the structure of monolithic polymer can be changed. Usually, to change skeletal structure of polymer monolith, the ratios of monomers and porogenic solvents are changed. However, in this method, molecular weight of porogen (PEG) and polymerization temperature are the dominant factors to realize skeletal changes, while the ratios of monomers and porogenic solvents are slightly changed. Detailed studies for the reaction mechanism, physical measurements, chemical characterization, and possible applications are now in progress.

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