Preparation of glycerol dimethacrylate-based polymer monolith with unusual porous properties achieved via viscoelastic phase separation induced by monodisperse ultra high molecular weight poly(styrene) as a porogen

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Abstract

The preparation of polymer-based monolith capillary was examined by the use of glycerol dimethacrylate (GDMA) as monomer and monodisperse standard polystyrene (PS) solution in chlorobenzene as porogen. Poly-GDMA monoliths were prepared in situ in test tubes with standard PS having the variety of molecular weight (defined as Mw hereafter) from 50,000 to 3,840,000, and their morphology was compared to that of poly-GDMA monolith prepared in situ with a poor porogenic solvent of GDMA. According to scanning electron micrograph (SEM) observation, the structure of poly-GDMA monolith prepared in situ with toluene as a poor porogenic solvent showed a typical agglomerated globular structure, whereas the morphology of poly-GDMA monolith prepared in situ with the polymer (PS) porogenic solution was transformed from the aggregated globule form to three dimensionally (3D) continuous skeletal structure with the increase of Mw of standard PS utilized. Along with this morphological transformation or change, in the case of poly-GDMA monolith prepared in situ with ultra high Mw standard PS porogenic solution, the pore size distribution showed a sharp bimodal distribution, with one peak being located around 4 nm in the mesopore range (2–50 nm) and the other peak located around 1–2 μm in the macropore range (>50 nm), respectively. The poly-GDMA capillaries were prepared in situ with toluene, low Mw (50,000, 600,000) PS solution in chlorobenzene and the above mentioned ultra high Mw PS solution in chlorobenzene as a porogen, respectively, and measured by μ-HPLC with benzene and *n*-alkyl phenyl ketone as solutes for the evaluation in aqueous methanol (MeOH/H$_2$O = 50/50–80/20, v/v). The permeability of capillaries prepared in situ with ultra high Mw standard PS polymer porogenic solution was much larger, compared to those of the capillaries prepared in situ with low Mw standard PS polymer porogenic solution or with toluene as porogen. On the other hand, the column efficiency was better in the case of the capillary prepared in situ with the ultra high Mw PS solution than in the latter capillaries. Those observations indicated that the ultra high Mw standard PS polymer porogenic solution should delay dynamically the phase separation of polymerizing mixture because of its visco-elasticity and should contribute to the creation of three dimensionally continuous skeletal monolith structure better to afford high separation efficiency.
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1. Introduction

Conventionally, polymer monoliths have been prepared by in situ polymerization of functional monomer(s), crosslinking agent, and initiator in porogenic solvent (pore forming diluent).

As porogenic solvent, binary or ternary mixtures of poor and/or good solvents are occasionally used for controlling a variety of pore size and its structure [1]. The porogenic solvent dominantly selected for the preparation of monolith type media are usually poor solvents of the monomers utilized to form macro through-pores required for liquid flow. In the case of the porogenic poor solvents, the growing polymer chains tend to aggregate each other because van der Waals attraction surmounts the steric hindrance mutually expelling the polymer chains [2]. Thus, in the case of the 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. The inherent disadvantages of these heterogeneous macroporous monolith are cited by the adverse effects, such as larger eddy diffusion through irregular interstitial channels (increase of A term of the van Deemter equation), low permeability, monolith compressibility at high pressure drops [3], and limited pore surface area for molecular recognition site, especially for small molecules.

For that reason, our examination has been made on the preparation of polymer monolith from the perspective of the control of phase separation induced by polymerization, in order to realize a polymer monolith having a more skeletal continuous structure. Also, such examination on polymer monolith preparation should be based on the material design concept of the hierarchical porous structure of mesopores (2–50 nm in diameter) and macropores (larger than 50 nm in diameter). The mesopores provide molecular recognition sites and the latter macropores do flow through channels for effective mobile phase transport, and also for solute transfer between mobile phase and stationary phase, which is also important for the size exclusion effect for larger protein molecules.

Monolithic continuous skeletal network has been successfully realized as silica monoliths prepared in situ through spinodal decomposition with sol–gel transformation by Minakuchi et al. [4]. Their silica monoliths showed the controlled skeletal structure with skeleton in μm size and 14–25 nm size mesopores of specific surface area of 170–370 m^2/g. The separation efficiency was demonstrated with low plate heights of 10–20 μm for aromatic hydrocarbons in 80% aqueous methanol.

Also, in the field of polymer monolith, the similar pore size distribution concept has been already disclosed in the US patent by Frechet and Svec [5]. The binary pore size distribution claimed by this patent is characterized with small size pores ranging below 200 nm and the larger pores above 600 nm. This patent claim on the bimodal pore size distribution was applied to the preparation of polymer monoliths, for example, styrene-co-divinybenzene-based monolith or methacrylate-based monolith with glycidyl methacrylate and ethylene dimethacrylate as a functional monomer and a cross-linking agent, respectively.

However, in the case of the polymer monolith preparation exemplified above, it is very difficult to suppress the inherent tendency of the aggregated globular monolith structure due to the use of a poor solvent as porogen as explained above. In view of the phase separation control of polymerization system, the delayed phase separation dynamics may enhance the freezing of the three dimensionally continuous structure induced by spinodal decomposition.

From the perspective of the controlled phase separation, our examination has been also made on a new concept of the phase separation of binary polymer solution proposed theoretically and verified experimentally [6,7]. This phase separation is called "viscoelastic phase separation". According to this theoretically proposed phase separation, the viscoelastic behavior of polymer solution plays a key role in delaying spinodal decomposition dynamics and inducing the transient three dimensional (3D)

polymer network structure. For example, in the case where the large difference of molecular dynamics or mobility may exist between solvent molecules and polymeric molecules, the polymer rich phase becomes rapidly a transient gel because of the "swift" solvent molecule diffusion out into solvent rich phase and this transient gel has its temporal relaxation modulus, "viscoelasticity", resisting the phase separation until the complete relaxation [7]. This viscoelastic phenomenon may decay with a long relaxation time especially in a highly viscous solution. In this paper, the freezing of this transient polymer network structure induced by viscoelastic phase separation has been attempted by chemical cross-linking and proposed as a practical way for the realization of the skeletal structure observed in the silica monolith. More specifically, the use of ultra high molecular weight monodisperse PS solution as a polymer porogenic solution is examined extensively because the highly viscous polymer porogen is expected to enhance the polymerizing system's viscoelasticity, as mentioned above. In such view of our experiment, the preparation of polymer monolith capillary has been carried out and the prepared capillaries have been chromatographically evaluated.

Our polymerization system is composed of a rather hydrophilic dimethacrylate monomer, GDMA because of a hydroxyl group in the middle of the structure, and polymer porogenic solution, which is a standard polystyrene solution in chlorobenzene, and azo-type initiator. Recently, the authors measured in real time the gelation of GDMA in toluene as porogen by dynamic light scattering (DLS) together with those of rather hydrophobic ethylene dimethacrylate, EDMA and 1,6-hexanediol dimethacrylate, HDMA and showed that the gelation of GDMA also may proceed through hydrogen bondings at the initial stage of the gelation [8]. This was discussed in terms of three dimensionally continuous morphology of poly-GDMA with 1–2 μm homogeneously dispersed macropores prepared in a hydrophobic solvent like toluene.

The use of polymeric porogen was described extensively for the preparation of uniformly sized porous poly(styrene-*co*-divinylbenzene) beads back in early 90s by Wang and Svec and coworkers [9]. They already indicated that the molecular weight of polymer and its concentration in organic phase strongly effected on the pore size and its distribution of polymer beads. Also, they reported that the high concentration of polymer porogen was favorable for the preparation of the macroporous polymer beads that are useful for the size exclusion of PS standards and protein separation also in reversed phase mode. Horak et al. [10] used extensively poly(styrene) or poly(methyl methacrylate) (PMMA) as polymer porogen co-existing with toluene for the preparation of porous beads of poly(glycidyl-*co*-ethylene dimethacrylate). They examined the effects of PS or PMMA molecular weight and the content in porogenic system on the porous feature of the beads through the phase separation. Also, they commented on the use of high molecular weight of PMMA around 1,440,000 with the large polydispersity. Their system seems to be quite heterogeneous due to the incomplete dissolution in monomers of PMMA.

Recently, the porous morphology control for poly(divinylbenzene) resin has been reported by Macintyre and Sherrington