

## SHORT COMMUNICATIONS

## Preparation of Porous Polymers by "in Situ Precipitation" Using Low Molecular Weight Gelators

Masahiro SUZUKI, Yasuhiko SAKAKIBARA,\* Satoshi KOBAYASHI,\* Mutsumi KIMURA,\*  
Hirofusa SHIRAI,\* and Kenji HANABUSA†

Graduate School of Science and Technology, Shinshu University,  
Ueda, Nagano 386–8567, Japan

\*Department of Functional Polymer Science, Faculty of Textile Science and Technology,  
Shinshu University, Ueda, Nagano 386–8567, Japan

(Received February 8, 2002; Accepted April 26, 2002)

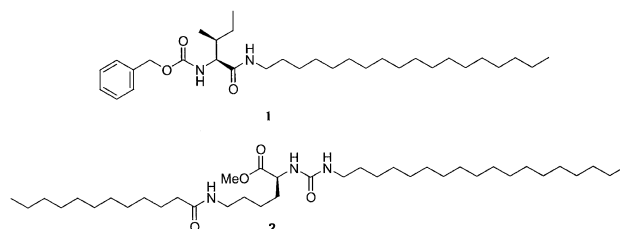
KEY WORDS Organogel / Gelator / Poly(styrene) / Supramolecular Chemistry / Polymer /

Highly porous polymer and inorganic materials with a well-defined pore size have been exploited in a wide range of applications such as chemical catalysis, ionic exchange resins, chemical sensors, and functional materials for selective binding and removal of drugs, peptides, and proteins.<sup>1,2</sup> The template-imprinting technique is very useful method in the preparation of these materials with size- and shape-specific binding sites. Often porous polymers have been prepared using reversible micelles as the templates,<sup>3</sup> especially sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in the mixture of water and many organic solvents,<sup>4</sup> because the size of the micelles can be controlled by changing the water content.<sup>3a,3b</sup>

On the other hand, low molecular weight compounds that can gel various organic fluids, gelators, have been considerably focused on their applications to the field of material chemistry.<sup>5</sup> In organic fluids, gelators form a hierarchical network of supramolecular nanofibers at the low concentration which is held together by relatively weak intermolecular forces including hydrogen bonding,  $\pi$ -stacking, and van der Waals interactions. Recently, the superstructures in organogels have been used as a template for sol-gel polymerization of tetraethoxysilane and tetraalkoxytitanium, resulting in novel silica and titania with a hollow fiber structures.<sup>6,7</sup> Furthermore, Shi *et al.* have reported the synthesis of new gelators that can gel supercritical CO<sub>2</sub> and fabrication of the porous polymers in supercritical CO<sub>2</sub>.<sup>8</sup> These studies are expected as new methods in the template-imprinting technique.

Here we describe the preparation of porous poly(styrene) from toluene gels made by gelators using

a new method, "in situ precipitation" and the characterization by scanning electron microscopy (SEM). The "in situ precipitation" is performed by replacing good solvent with poor solvent in polymer solution that is previously gelled by gelators. By this method, we can obtain the porous poly(styrene) that is almost keeping the shape and size of the original gels.



Scheme 1.

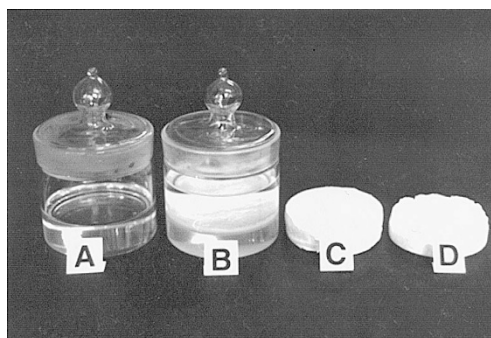
All reagents and solvents were obtained from Wako, TCI, or Aldrich. These reagents and solvents were analytically pure and were used without further purification. *N*-Carbobenzyloxy-*L*-isoleucylaminooctadecane (**1**)<sup>9</sup> and *N*<sup>ε</sup>-lauroyl-*N*<sup>α</sup>-stearylaminocarbonyl-*L*-lysine ethyl ester (**2**)<sup>5d</sup> were selected as the low molecular weight gelators illustrated in Scheme 1, which are excellent gelators for many organic solvents and form three-dimensional networks through nanofibers responsible for gelation. The porous poly(styrene)s were prepared by *in situ* precipitation, followed by removal of gelators with soaking a hot ethanol.<sup>10</sup>

Shape-keeping precipitation, which is referred to "in situ precipitation" was performed by addition of poor solvent onto the resulting gels of poly(styrene) solution. The *in situ* precipitation gave the precipitate of

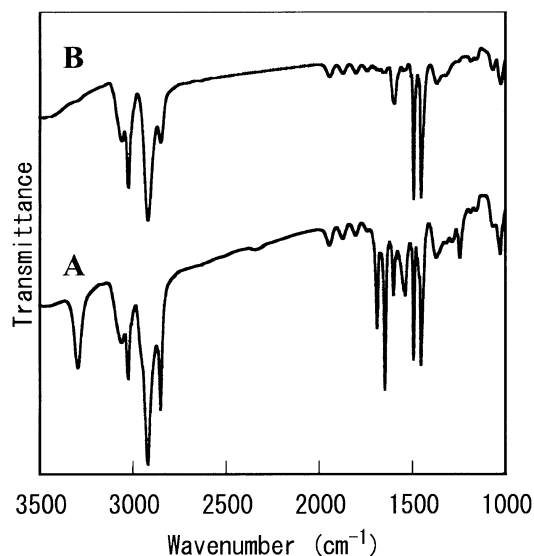
†To whom correspondence should be addressed (Fax: +81-268-24-7248, E-mail: hanaken@giptc.shinshu-u.ac.jp).

**Table I.** Condition of *in situ* precipitation and weight change of obtained poly(styrene) before and after soaking in ethanol

Poly(styrene)	Gelator 1	Toluene	Yield before soaking	Yield after soaking
g	mg	mL	g	g
2.00	0	20	—	1.33
2.00	200	20	2.00	1.83
2.00	500	20	2.27	1.89
2.00	750	20	2.53	1.89
2.00	1000	20	2.70	1.84

**Figure 1.** Photographs of four states of samples during *in situ* precipitation: (A) toluene gels consisting of poly(styrene) and gelator 1, (B) immediately after the replacement of toluene with hexane, (C) poly(styrene) obtained by *in situ* precipitation, and (D) porous poly(styrene) after removal of the gelator by soaking in ethanol.

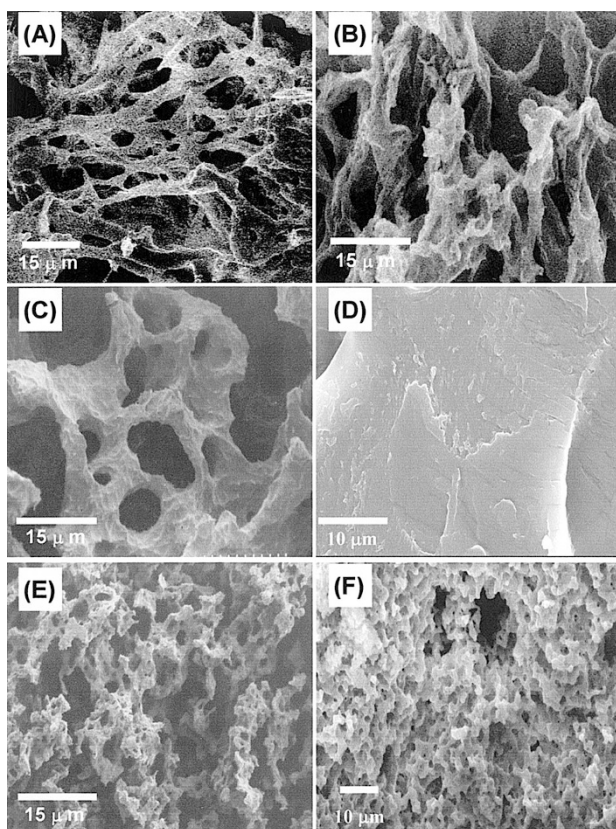
poly(styrene) that kept the shape and size of the original gels. Figure 1 shows the photographs of four states of samples during *in situ* precipitation process; (A) toluene gels consisting of poly(styrene) and gelator 1, (B) immediately after the replacement of toluene with hexane, (C) poly(styrene) containing the gelator obtained by *in situ* precipitation, and (D) porous poly(styrene) after removal of the gelator by soaking in ethanol. When hexane was poured onto the transparent toluene gels, the gels became gradually opaque, indicating that poly(styrene) began to precipitate (B). After completion of *in situ* precipitation, poly(styrene) containing the gelator was obtained (C), and finally, the cylindrical porous poly(styrene) was obtained after soaking in a hot ethanol (D). It is noteworthy that poly(styrene) obtained by *in situ* precipitation almost keeps both the cylindrical shape and size of the polymer gel macroscopically, even after soaking in ethanol. For comparison, ordinary reprecipitation that the toluene solution of poly(styrene) was poured into hexane and precipitation by the same procedure as *in situ* precipitation were carried out under the same condition, but without the gelator. Poly(styrene) by the former and the latter methods was powder and large mass, respectively, and both did not possess porous structure at all. Consequently, *in situ* precipitation from the gels is an excellent method for preparation of porous poly(styrene). The porous poly(styrene) is very stable not only in ethanol but also in the solvents, that the poly(styrene)

**Figure 2.** FT-IR spectra of poly(styrene) obtained by *in situ* precipitation using gelator 1: (A) before soaking in ethanol, (B) after soaking in ethanol.

is insoluble, such as hexane, alcohols, acetonitrile, water and so on. Thus, the porous poly(styrene) may have potential applications to various reactions in these solvents.

Condition of *in situ* precipitation and weight change of obtained poly(styrene) before and after soaking in ethanol are summarized in Table I. The porous poly(styrene) can be obtained by *in situ* precipitation from the gels with the high yield, compared with that from the solution. The weight of poly(styrene) obtained by *in situ* precipitation decreased after soaking in ethanol and the weight change almost corresponded to removal of the gelators.

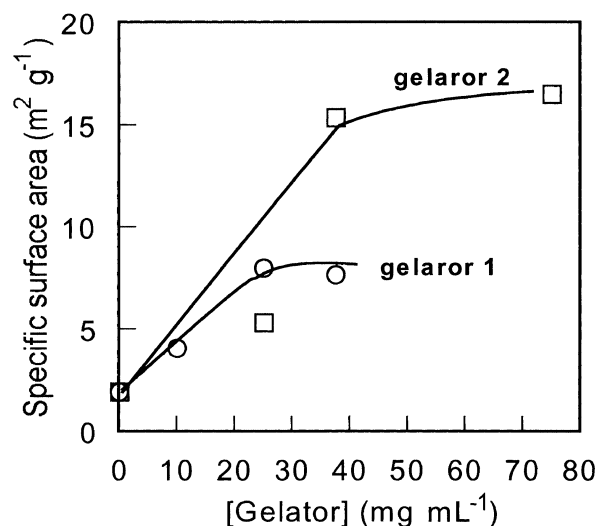
Figure 2 shows FT-IR spectra of poly(styrene) by *in situ* precipitation using gelator 1, before and after soaking in ethanol. The FT-IR spectrum of poly(styrene) before soaking in ethanol appeared the peaks at  $3290\text{ cm}^{-1}$  ( $\nu$  N-H), and  $1690\text{ cm}^{-1}$  ( $\nu$  C=O for urethane), and  $1645\text{ cm}^{-1}$  ( $\nu$  C=O for amide), indicating the existence of the gelator 1. The disappearance of these peaks after soaking demonstrated that the gelators were completely removed by soaking. It should be mentioned that porous poly(methyl methacrylate), poly(ethylene), and poly(sulfone) were also obtained by the similar *in situ* precipitation.



**Figure 3.** SEM images of xerogels prepared from cyclohexane gels of 1 (A) and 2 (B) using a freeze-drying technique, poly(styrene) (C, E, F) which was prepared by *in situ* precipitation, followed by soaking in EtOH. For comparison Figure 3 also contains that of powdered poly(styrene) (D) prepared in the absence of the gelator. It is obvious from Figure 3 that the porous poly(styrene) with the pore size of micrometer scale is obtained by *in situ* precipitation. Very interestingly, the pore size of the porous poly(styrene) (E, F) is *ca.* 1  $\mu\text{m}$ , which is almost consistent with the size of the gelator (A, B) (0.5  $\mu\text{m}$ –1  $\mu\text{m}$ ). This indicates that the supramolecular structures formed by the gelators are imprinted in polystyrene. Furthermore, the pore size significantly depends on the concentration of the gelators; the pore size is *ca.* 13  $\mu\text{m}$  at the low gelator concentration (C) and *ca.* 1  $\mu\text{m}$  at the high concentration (E). Since gelator forms a closer network structure with increasing concentration of the gelator,<sup>5</sup> the pore size of poly(styrene) can be controlled by the concentration of the gelator. In contrast, the poly(styrene) obtained in the absence of the gelators has a very smooth surface and is never porous (D).

Figure 3 shows the SEM photographs of xerogels prepared from cyclohexane gels of 1 (A) and 2 (B) using a freeze-drying technique, poly(styrene) (C, E, F) which was prepared by *in situ* precipitation, followed by soaking in EtOH. For comparison Figure 3 also contains that of powdered poly(styrene) (D) prepared in the absence of the gelator. It is obvious from Figure 3 that the porous poly(styrene) with the pore size of micrometer scale is obtained by *in situ* precipitation. Very interestingly, the pore size of the porous poly(styrene) (E, F) is *ca.* 1  $\mu\text{m}$ , which is almost consistent with the size of the gelator (A, B) (0.5  $\mu\text{m}$ –1  $\mu\text{m}$ ). This indicates that the supramolecular structures formed by the gelators are imprinted in polystyrene. Furthermore, the pore size significantly depends on the concentration of the gelators; the pore size is *ca.* 13  $\mu\text{m}$  at the low gelator concentration (C) and *ca.* 1  $\mu\text{m}$  at the high concentration (E). Since gelator forms a closer network structure with increasing concentration of the gelator,<sup>5</sup> the pore size of poly(styrene) can be controlled by the concentration of the gelator. In contrast, the poly(styrene) obtained in the absence of the gelators has a very smooth surface and is never porous (D).

Figure 4 shows the dependence of the surface area



**Figure 4.** Dependence of the specific surface area of porous poly(styrene)s obtained by *in situ* precipitation on the concentration of the gelators: gelator 1 (○) and gelator 2 (□).

of porous poly(styrene) determined by a BET method on the concentration of the gelators. The surface area of porous poly(styrene) increases with increasing the gelator concentration. In particular, the specific surface area of poly(styrene) obtained by *in situ* precipitation using the gel comprised of toluene (20 mL), poly(styrene) (2.00 g), and gelator 2 (800 mg), after removal of the gelator, is *ca.* 16 m<sup>2</sup> g<sup>-1</sup>. This specific surface area is about 8 times as large as that of poly(styrene) obtained by the ordinary reprecipitation.<sup>11</sup> These facts support the result obtained from SEM observation.

## CONCLUSION

We reveal the preparation of porous poly(styrene) by a new method, "*in situ* precipitation", using the gelators which forms three-dimensional networks in organic solvents. The characteristic of *in situ* precipitation is to afford the precipitates of polymers, almost keeping the shape and size of the original gels macroscopically. Upon subsequent soaking in a hot EtOH the gelators are removed, resulting in the porous polymers. SEM observations show that the supramolecular structures formed by the gelators are microscopically imprinted in the poly(styrene). The size of pores is controllable by the concentration of gelators. The current "*in situ* precipitation method" may open up new pathways to prepare porous polymers as one of the template-imprinting techniques. Moreover, porous polymers by *in situ* precipitation may find unique applicants as high-efficiency absorbent, carrier for catalysts, or support for tissue engineering, although the applications are limited by the solvents to some extent due to solubility of porous polymers.

*Acknowledgment.* This work was supported by Grant-in-Aid for COE Research (10CE2003) and a grant (No. 12450369) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

## REFERENCES

1. a) M. J. Sundell, E. O. Pajunen, O. E. O. Hormi, and H. J. Näsman, *Chem. Mater.*, **5**, 372 (1993).  
b) V. Smigol, F. Svec, and J. M. J. Fréchet, *Macromolecules*, **26**, 5615 (1993).
2. a) A. I. Cooper and A. B. Holmes, *Adv. Mater.*, **11**, 1270 (1999).  
b) R. Seshadri and F. C. Meldrum, *Adv. Mater.*, **12**, 1149 (2000) and references therein.
3. a) F. M. Menger, T. Tsuno, and G. S. Hammond, *J. Am. Chem. Soc.*, **112**, 1263 (1990).  
b) F. M. Menger and T. Tsuno, *J. Am. Chem. Soc.*, **112**, 6723 (1990).  
c) X. X. Zhu, K. Banana, and R. Yen, *Macromolecules*, **30**, 3031 (1997).  
d) X. X. Zhu, K. Banana, H. Y. Liu, M. Krause, and M. Yang, *Macromolecules*, **32**, 277 (1999).  
e) T. H. Chieng, L. M. Gan, C. H. Chew, and S. C. Ng, *Polymer*, **36**, 1941 (1995).  
f) T. H. Chieng, L. M. Gan, C. H. Chew, S. C. Ng, and K. L. Pey, *Langmuir*, **12**, 319 (1996).
4. a) E. Bardez, E. Monnier, and B. Valeur, *J. Phys. Chem.*, **89**, 5031 (1985).  
b) T. K. Jain, M. Varshney, and A. Maitra, *J. Phys. Chem.*, **93**, 7409 (1989).
5. a) P. Terech and R. G. Weiss, *Chem. Rev.*, **97**, 3313 (1997).  
b) J. H. van Esch and B. L. Feringa, *Angew. Chem. Int. Ed.*, **39**, 2263 (2000).  
c) D. J. Abdallah and R. G. Weiss, *Adv. Mater.*, **12**, 1237 (2000).  
d) K. Hanabusa, H. Nakayama, M. Kimura, and H. Shirai, *Chem. Lett.*, **2000**, 1070.  
e) X. Luo, C. Li, and Y. Liang, *Chem. Commun.*, **2000**, 2091.  
f) J. Brinksma, B. L. Feringa, R. M. Kellogg, R. Vreeker, and J. van Esch, *Langmuir*, **16**, 9249 (2000).  
g) K. S. Partridge, D. K. Smith, G. M. Dykes, and P. T. McGrail, *Chem. Commun.*, **2001**, 319.  
h) M. de Loos, J. van Esch, R. M. Kellogg, and B. L. Feringa, *Angew. Chem. Int. Ed.*, **40**, 613 (2001).  
i) R. P. Lyon and W. M. Atkins, *J. Am. Chem. Soc.*, **123**, 4408 (2001).
6. a) J. H. Jung, Y. Ono, and S. Shinkai, *Langmuir*, **16**, 1643 (2000).  
b) J. H. Jung, Y. Ono, and S. Shinkai, *Chem. Eur. J.*, **6**, 4552 (2000).  
c) J. H. Jung, Y. Ono, K. Hanabusa, and S. Shinkai, *J. Am. Chem. Soc.*, **122**, 5008 (2000).
7. a) S. Kobayashi, K. Hanabusa, N. Hamasaki, M. Kimura, H. Shirai, and S. Shinkai, *Chem. Mater.*, **12**, 1523 (2000).  
b) S. Kobayashi, K. Hanabusa, M. Suzuki, M. Kimura, and H. Shirai, *Bull. Chem. Soc. Jpn.*, **73**, 1913 (2000).
8. C. Shi, Z. Huang, S. Kikic, J. Xu, R. M. Enick, E. J. Beckman, A. J. Carr, R. E. Melendez, and A. D. Hamilton, *Science*, **286**, 1540 (1999).
9. K. Hanabusa, K. Hiratsuka, M. Kimura, and H. Shirai, *Chem. Mater.*, **11**, 649 (1999).
10. A typical procedure for *in situ* precipitation is as follows: poly(styrene) (2.0 g) was dissolved in toluene (20 mL) in a weighing bottle and then the gelator (200 mg) was dissolved with heating. The hot homogeneous solutions were allowed to cool to room temperature for 2 h, during which time the gels were formed. Hexane as poor solvent was slowly poured onto the formed toluene gels. Poly(styrene) including the gelators was gradually precipitated with replacement of toluene in the gel with hexane. The supernatant hexane mixed with toluene was renewed several times. After completion of precipitation, white solid was dried in vacuum overnight. Porous poly(styrene) was obtained in a yield of 2.00 g. In order to remove the gelator, the white solid was immersed at 50°C into ethanol (150 mL) overnight. Drying in vacuum after washing with ethanol gave 1.83 g of porous poly(styrene).
11. This surface area was smaller than that of conventional inorganic porous materials such as molecular sieves and sintered glasses.