

Synthesis of polystyrene/silica gel polymer hybrids by in-situ polymerization method

Ryo Tamaki, Kensuke Naka, Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-01, Japan

Received: 8 July 1997/Revised version: 29 July 1997/Accepted: 1 August 1997

Summary

Homogeneous polystyrene and silica gel polymer hybrids were prepared by in-situ radical polymerization method. Styrene monomer was introduced into a sol-gel reaction mixture of tetramethoxysilane (TMOS) and the polymerization was initiated by Azobisisobutyronitrile (AIBN), while sol-gel reaction of TMOS proceeded to form a silica gel. The homogeneity of the hybrids was found to be dependent on the amount of the acid catalyst. The homogeneity was confirmed quantitatively by measuring porosity of charred hybrids with nitrogen porosimetry method. It was found that polystyrene was dispersed at a nano-meter level in the silica gel matrix.

Introduction

By incorporation of organic polymers at initial stage of sol-gel reaction of alkoxy silanes, organic-inorganic polymer hybrids with a wide range of functionality have been obtained [1-12]. Sol-gel technique of metal alkoxides is the most efficient method for preparation of the composite materials. The method comprises initial hydrolysis of those metal alkoxides and subsequent condensation, resulting in the formation of metal oxides [13-18]. An advantage of the sol-gel technique is a fact that the reactions can be carried out at ambient temperature, while conventional melt fusion techniques of silica glasses need high temperature. Thus, it enables introduction of organic elements into inorganic materials without deteriorating their functionality. Another feature of the reaction is that silica gels obtained by the sol-gel reaction contain a large amount of residual hydroxyl groups.

To synthesize homogeneous polymer hybrids, organic polymers with functional groups that have specific interaction with silica gels were chosen. In our group, organic polymers such as poly(2-methyl-2-oxazoline), poly(N-vinylpyrrolidone) or poly(N,N-dimethylacrylamide) were incorporated homogeneously into silica gels, utilizing the hydrogen bonding interaction between the silanol groups and amide groups of the organic polymers. Those polymers were added to sol-gel reaction mixtures to give transparent polymer hybrids [19-28].

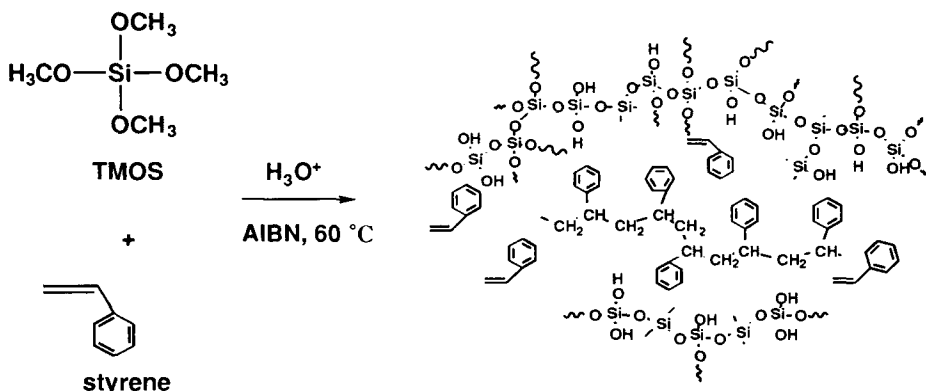
Here we demonstrate the synthesis of homogeneous polymer hybrids starting from polystyrene. The polymer does not possess the hydrogen bonding accepting groups. As such, it is difficult to obtain homogeneous polystyrene and silica gel polymer hybrids by the method used for the polymers with amide groups. On the other hand, we recently reported another method for the synthesis of poly(N,N-dimethylacrylamide) hybrids [29]. The method utilizes in-situ radical polymerization of the vinyl monomer in sol-gel reaction mixtures. It was found that gelation degree of silica gels at a moment of radical

* Corresponding author

polymerization, i.e., the mobility of the monomer in the solution plays an important role for homogeneous dispersion of the resulting polymer in the hybrids. We have applied the same method for the synthesis of polystyrene and silica gel hybrids, expecting the suppression of aggregation by the same effect.

Results and Discussion

We employed in-situ radical polymerization method for the synthesis of homogeneous polystyrene and silica gel polymer hybrids, which comprises initial introduction of vinyl monomers into sol-gel reaction mixtures and simultaneous polymerization of the monomers with the formation of silica gel. Styrene monomer was incorporated into CH₃CN solution of TMOS and AIBN. The reaction mixture was then heated at 60 °C to initiate the radical polymerization. (Scheme 1) It was observed that the reaction proceeded homogeneously and glassy transparent materials were obtained after removal of the solvent.



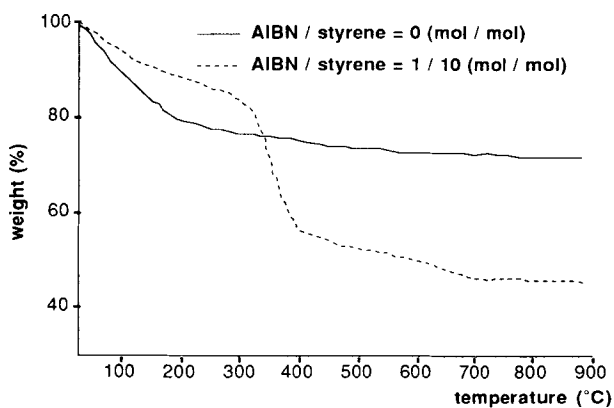
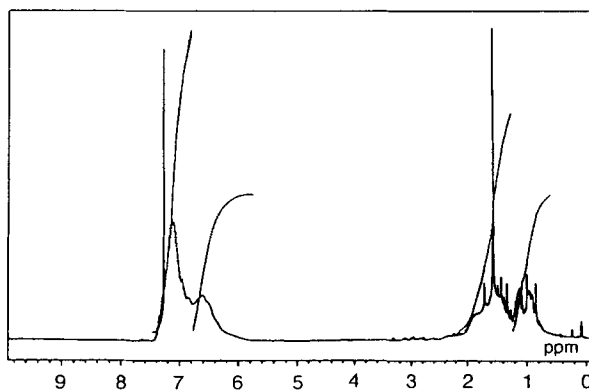
Scheme 1

The amount of AIBN was altered from 0 to 0.10 equivalent to styrene (Table I). The degree of polymerization was confirmed both by thermogravimetric analysis (TGA) and gel permeation chromatography (GPC). As shown in Figure 1, the decomposition started soon after the heating in the hybrid prepared without AIBN, indicating no polymerization occurred in this case. In contrast, the onset of decomposition temperature as well as T_{20} shifted to higher temperature when the amount of AIBN was increased above 0.01 equivalent to styrene monomer (Table I). The results support the formation of polystyrene. GPC measurement was in good agreement with the results; the weight-average molecular weight of polystyrene formed was found to be 4,540 in run 3 and 1,390 in run 4. The polymerization of styrene monomer was also confirmed by ¹H-NMR spectrum. Polystyrene extracted from the polymer hybrid in run 4 also showed effective conversion of the monomer; olefin protons disappeared completely as shown in Figure 2.

Table I The Effect of AIBN Content on the Conversion of Styrene

| Run ^{a)} | molar ratio of AIBN / styrene | appearance | weight loss (%) ^{b)} | T_{20} ($^{\circ}\text{C}$) ^{b)} | conversion(%) TGA ^{c)} | Mw ^{d)} | Mn ^{d)} | Mw / Mn |
|-------------------|-------------------------------|-------------|-------------------------------|---|---------------------------------|------------------|------------------|---------|
| 1 | 0 | transparent | 29.0 | 190 | ~0 | 210 | 180 | 1.19 |
| 2 | 0.001 | translucent | 35.5 | 144 | ~0 | 190 | 160 | 1.19 |
| 3 | 0.01 | translucent | 42.7 | 221 | 45.9 | 4,540 | 2,770 | 1.64 |
| 4 | 0.1 | transparent | 55.0 | 335 | 73.6 | 1,390 | 940 | 1.48 |

^{a)} 20ml of CH_3CN was used as solvent. The weight ratio of styrene to TMOS was 1 / 2 (styrene = 1.0 g, TMOS = 2.0 g). 2.06 ml of 0.1N HCl was used. ^{b)} Calculated by TGA. ^{c)} Weight % of polymer in total weight loss. ^{d)} Calculated by GPC.

**Figure 1** TGA traces of the polymer hybrids.**Figure 2.** ^1H -NMR spectrum of polystyrene extracted from hybrid in run 4 of Table I.

It should be mentioned that environment of the reaction mixture, especially the viscosity, changes drastically due to gelation of TMOS while polymerization of styrene monomer proceeds. It may affect the degree of polymerization and dispersion of the polymer, since the movement of the monomer would be restricted by the forming silica gels. It has been shown that the rate of gelation is affected by some parameters such as reaction temperature, [30] solvents, [31] pH [15,16,32] as well as the amount of water [33-35].

Here amounts of acid catalyst were altered to investigate the effect of gelation degree on the homogeneity. As is shown in Table II, the conversion of styrene monomer was found to be independent of the acid content, which was almost quantitative for all the case. The molecular weight of polystyrene had also the same tendency. The results imply that the gelation degree did not affect the polymerization of the monomer. Of considerable interest was the observation that the homogeneity was improved with the increase of the acid content. With 1.6 ml of 0.1N HCl, the polymer hybrid became optically transparent that suggested homogeneous dispersion of each segment. As was reported, gelation of TMOS completed faster with 1.6 ml of 0.1N HCl aq than that with less acid content [15,16,32-34,36-38]. It is assumed that styrene monomer was entrapped inside the growing silica matrix and the polymerization followed inside the cage due to the rapid gelation of silica gels in run 4. As such, aggregation of the resulting polymer was suppressed and the homogeneous polystyrene polymer hybrids were produced. On the contrary, gelation would proceed more slowly with less acid catalyst, resulting in polymerization of styrene monomer 'outside' the silica matrix, i.e. in the solvent. Polystyrene that produced in the solvent would aggregate to form large domains with growth of silica matrix and afford phase-separated polymer hybrids. These results imply that physical entrapment of the monomer inside the silica matrix played a critical role on the homogeneity of the polymer hybrids. Thermal stability of the polymer hybrids was also affected by the acid content. As shown in Table II, T_{10} in TGA traces shifted from 272 to 287 °C. The results could be attributed to the improved dispersion of the polymer in the thermally stable inorganic matrix.

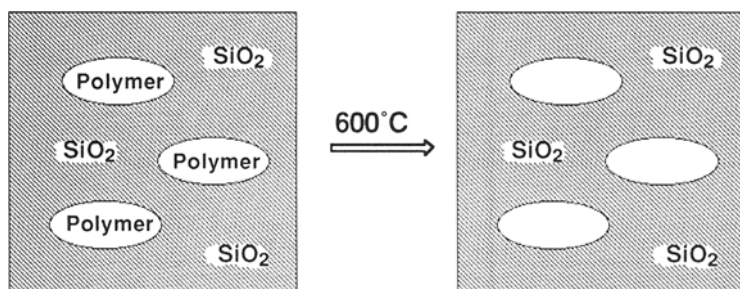
Table II The Effect of Acid Content on the Homogeneity

| Run ^{a)} | 0.1N HCl (ml) | solvent | appearance | weight loss (%) ^{b)} | T_{10} (°C) ^{b)} | conversion(%) TGA ^{c)} | M _w ^{d)} | M _n ^{d)} | M _w / M _n |
|-------------------|---------------|--------------------|-------------|-------------------------------|-----------------------------|---------------------------------|------------------------------|------------------------------|---------------------------------|
| 1 | 0.48 | CH ₃ CN | translucent | 51.5 | 272 | ~100 | 1,114 | 657 | 1.70 |
| 2 | 0.96 | CH ₃ CN | translucent | 50.8 | 284 | ~100 | 1,470 | 784 | 1.87 |
| 3 | 1.47 | CH ₃ CN | translucent | 47.5 | 282 | ~100 | 1,080 | 682 | 1.58 |
| 4 | 1.87 | CH ₃ CN | transparent | 50.9 | 287 | ~100 | 1,027 | 734 | 1.40 |
| 5 ^{e)} | 1.96 | CH ₃ CN | turbid | - | - | - | - | - | - |
| 6 ^{f)} | 1.96 | THF | turbid | - | - | - | - | - | - |

^{a)} Condition: weight ratio of styrene / TMOS = 1 / 2. TMOS = 2.0 g, Styrene = 1.0 g. Solvent = 20 ml. Molar ratio of AIBN / styrene = 1 / 10. ^{b)} Calculated by TGA. ^{c)} Weight % of polymer in total weight loss. ^{d)} Calculated by GPC. ^{e)} Polystyrene extracted from the polymer hybrid of run 4. ^{f)} Polystyrene (M_w = 2,300).

The polystyrene and silica gel polymer composites were also prepared by introducing preformed polystyrene into a sol-gel reaction mixture. In the reaction, two different polystyrenes were used; a polystyrene extracted from the polymer hybrid that prepared by in-situ polymerization method (Table II, run 4) and a polystyrene with molecular weight of 2,300 produced by radical polymerization with AIBN in THF. These low molecular weight polystyrenes were chosen to confirm the effect of end groups of the polymer chains. Since the polymerization was initiated with AIBN, the obtained polystyrene had isobutyronitrile unit at the end of the polymer. It might affect compatibility of the polystyrene with silica gel. The obtained polymer hybrids were, though, both turbid (Table II, run 5 and 6), suggesting that homogeneity of the obtained polymer hybrids prepared by the in-situ polymerization method was rather dependent on gelation degree of silica gels than on the effect of the end groups.

Homogeneity of the obtained polymer hybrids was investigated quantitatively by measuring pore sizes of porous silicas that obtained by charring the polystyrene hybrids at 600 °C. The organic parts would be removed from polymer hybrids by sintering the hybrids at 600 °C without affecting its morphology (Scheme 2) [28,39]. Thus, homogeneity of original polymer hybrids would be verified by measuring pore size distribution of the obtained porous silicas.



Scheme 2

A surface area and a pore volume were determined by BET method and a pore size was calculated by BJH method [28,40,41]. As is shown in Table III, the porous silica that obtained from the homogeneous polymer hybrid (Table II, run 4) was found to have quite a large surface area and a pore volume. It was also observed that the porous silica had a sharp pore size distribution at 1.8 nm (Figure 3). The results showed the presence of nano pores. All these results indicate that polystyrene was homogeneously dispersed at a nano-meter level inside the silica matrix.

Table III Porosity of the Silica ^{a)}

| Run | acid content 0.1N HCl (ml) | pore volume ^{b)} (ml / g) | surface area ^{b)} (m ² / g) | pore radius ^{c)} (nm) (desorption) |
|-----|-------------------------------|---------------------------------------|--|---|
| 1 | 1.87 ^{d)} | 50.87 | 221.4 | 1.8 |

^{a)} The porous silica was obtained by charring the silica at 600 °C for 24 h. ^{b)} Calculated by BET method.

^{c)} Calculated by BJH method. ^{d)} 20 ml of CH₃CN was used. Styrene = 1.0 g, TMOS = 2.0 g.

It is of considerable interest that a polymer without hydrogen bonding accepting groups would be dispersed in the silica gel at a nano-meter domain size. Physical entrapment of polystyrene by the silica cage deterred aggregation of the polymer and then afforded the homogeneous polymer hybrids. The results suggest the possibility that the technique could be applied for a large variety of other vinyl polymers that have poor affinity with a silica gel.

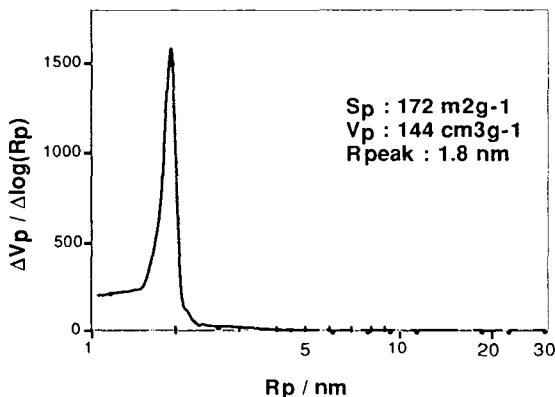


Figure 3. Pore size distribution plot of a porous silica obtained from polymer hybrid (Table I, run 4). Pore size was calculated by BJH method.

Experimental Section

General Procedures: ^1H NMR spectra were measured on a JEOL EX270 spectrometer using chloroform- d . Thermogravimetric analysis was conducted on Shimadzu TG-30, TGC-30 with the heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Nitrogen absorption porosimetry was conducted with BEL JAPAN INC. The reactions were carried out under nitrogen unless mentioned. GPC analysis was conducted with HLC-8020 (Tosoh), UV-8010 (Tosoh) with TSKgel G3000H $_{\text{XL}}$ (Tosoh) column.

Materials: All solvents and reagents were used as supplied except the following materials. CH_3CN , THF, and styrene were dried and distilled under nitrogen. AIBN was recrystallized from ethanol at $35\text{ }^\circ\text{C}$. TMOS was distilled under nitrogen.

Polystyrene polymer hybrids: To reaction mixture of styrene (1.0 g), TMOS (2.0 g) and 0.1N HCl (1.96 ml) in 20 ml of CH_3CN , 0, 1/1000, 1/100 or 1/10 equivalents of AIBN were added. The resulting mixture was kept stirring at room temperature for 5 h and was heated at $60\text{ }^\circ\text{C}$ for 2 weeks. The obtained polymer hybrids were crashed into powder and subjected to the further analysis. Similar procedure was employed for the other solvents.

Soxhlet Extraction: The powdered hybrids were put into cellulose timbers and were extracted with CH_3CN for 3 days in a Soxhlet extraction apparatus.

Nitrogen Absorption Porosimetry: The powder of the hybrid was heated at 600 °C under ambient atmosphere to remove the organic parts. The sample was then dried at 200 °C for 2 h at reduced pressure under nitrogen atmosphere. A surface area was calculated with BET equation in the range of 0.05 to 0.30 (p/p_0) and a pore size distribution was calculated by BJH method [40,41].

References and Notes

1. Sur G S, Mark J E (1985) *Eur Polym J* 21:1051
2. Mark J E, Sur G S (1985) *Polym Bull* 14:325
3. Clarson S J, Mark J E (1987) *Polym Commun* 28:249
4. Sun C -C, Mark J E (1989) *Polymer* 30:104
5. Mark J E (1989) *Chemtech* April:230
6. Wung C J, Pang Y, Prassad P N, Karasz F E (1991) *Polymer* 32:605
7. Motakef S, Suratwala T, Roncone R L, Boulton J M, Teowee G, Neilson G F, Uhlmann D R (1994) *J Non-Cryst Solids* 178:31
8. Motakef S, Suratwala T, Roncone R L, Boulton J M, Teowee G, Uhlmann D R (1994) *J Non-Cryst Solids* 178:37
9. Yoshida M, Prassad P N (1996) *Applied Optics* 35:1500
10. Dave B C, Dunn B, Valentine J S, Zink J I (1994) *Anal Chem* 66:1120
11. Philipp G, Schmidt H (1984) *J Non-Crystal Solids* 63:283
12. Claude C, Garetz B, Okamoto Y, Tripathy S (1992) *Mater Lett* 14:336
13. Schmidt H, Scholze H, Kaiser A (1984) *J Non-Cryst Solids* 63:1
14. Brinker C J, Keefer K D, Schaefer D W, Assink R A, Kay B D, Ashley C S (1984) *J Non-Cryst Solids* 63:45
15. Orgaz F, Rawson H (1986) *J Non-Cryst Solids* 82:57
16. Kelts L W, Ejjinger N J, Melpolder S M (1986) *J Non-Cryst Solids* 83:353
17. Brinker C J, Scherer G W (1985) *J Non-Cryst Solids* 70:301
18. Brinker C J, Scherer G W (1990) *Sol-Gel Science*; Harcourt Brace & Co., Publishers, Boston, 1990
19. Chujo Y, Ihara E, Kure S, Saegusa T (1993) *Macromolecules* 26:5681
20. Toki M, Chow T Y, Ohnaka T, Samura H, Saegusa T (1992) *Polym Bull* 29:653
21. Saegusa T, Chujo Y (1990) *J Macromol Sci -Chem* A27:1603
22. Chujo Y, Saegusa T (1992) *Adv Polym Sci* 100:11
23. Chujo Y, Ihara E, Kure S, Suzuki N, Saegusa T (1991) *Makromol Chem, Macromol Symp* 42/43:303
24. Chujo Y (1996) *Encyclp Poly Sci Tech*, CRC Press, Boca Raton, 1996; Vol 6, pp 4793.
25. Chujo Y (1996) *Polym Mater Sci Eng* 74:65
26. Saegusa T, Chujo Y (1991) *Makromol Chem, Macromol Symp* 51:1
27. Saegusa T, Chujo Y (1992) *Makromol Chem, Macromol Symp* 64:1
28. Chujo Y, Matsuki H, Kure S, Saegusa T, Yazawa T (1994) *J Chem Soc, Chem Commun* 635
29. Tamaki R, Naka K, Chujo Y (1996) *Polym. Prep. Jpn.* 45:E984
30. Colby M W, Osaka A, Mackenzie J D (1986) *J Non-Cryst Solids* 82:37
31. Sharp K G (1995) *Hybrid Organic-Inorganic Composites* 163
32. Zerda T W, Artaki I, Jonas J (1986) *J Non-Cryst Solids* 81:365

33. Yamane M, Inoue S, Yasumori A (1984) *J Non-Cryst Solids* 63:13
34. Sakka S, Kozuka H (1988) *J Non-Cryst Solids* 100:142
35. Sakka S, Kamiya K, Makita K, Yamamoto Y (1984) *J Non-Cryst Solids* 63:223
36. Sakka S, Tanaka Y, Kokubo T (1986) *J Non-Cryst Solids* 82:24
37. Hasegawa I, Sakka S (1988) *J Non-Cryst Solids* 100:201
38. Strawbridge I, Craievich A F, James P F (1985) *J Non-Cryst Solids* 72:139
39. Loy D A, Shea K J (1995) *Chem Rev* 95:1431
40. Kondo S, Ishikawa T, Abe I (1991) *Science of Adsorption (Kyutyaku no Kagaku)*; 1 ed; Maruzen, Tokyo, 1991; Vol 228.
41. Gregg S J, Sing K S W (1982) *Adsorption, Surface Area and Porosity*; Second ed; New York, 1982