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# Synthesis of IPN polymer hybrids of polystyrene gel and silica gel by an *in-situ* radical polymerization method

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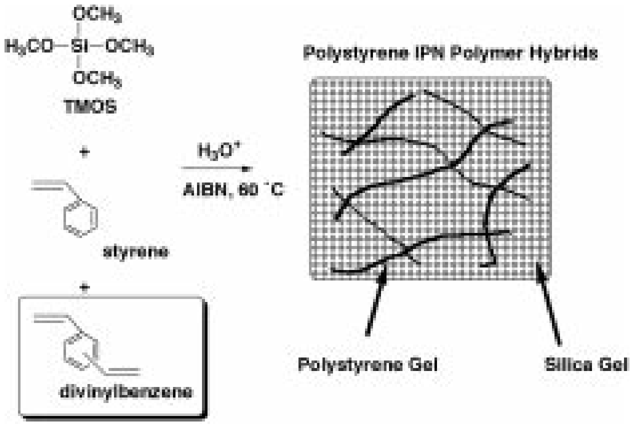
Homogeneous IPN polymer hybrids of polystyrene gel and silica gel were prepared by applying an *in-situ* polymerization method to styrene monomer and divinylbenzene. The monomers were mixed in the sol–gel reaction mixture of tetramethoxysilane and subjected to radical polymerization, resulting in transparent glassy materials. The homogeneity was confirmed by nitrogen porosimetry methods. The organic part was found to be dispersed at the nanometer scale. The obtained IPN polymer hybrids are highly solvent resistant.

In recent years a large variety of organic and inorganic polymer hybrids have been synthesized by utilizing the sol–gel technique with alkoxysilanes.[1,2] The sol–gel reaction comprises the hydrolysis and subsequent condensation reaction of alkoxysilanes.[3–7] When alkoxysilanes are used as precursors, Si–OH groups are formed by hydrolysis of alkoxy groups and Si–O–Si linkages are obtained by condensation of the hydroxyl groups. One of the interesting properties of the obtained silica gel is that it contains unreacted residual silanol groups even after gelation, which allow us to utilize hydrogen bonding interactions between the silanol groups and amide groups of organic polymers to obtain homogeneous organic–inorganic polymer hybrids. Poly(2-methyl-2-oxazoline), poly(*N*-vinyl-2-pyrrolidone) and poly(*N*,*N*-dimethylacrylamide) have been incorporated homogeneously by adding them into a sol–gel reaction mixture at an initial stage.[8–18]

On the other hand, we have successfully prepared homogeneous polymer hybrids of polystyrene, which has no polar functional groups, utilizing the *in-situ* radical polymerization of styrene monomer in the sol–gel reaction mixture.[19] In contrast to the prepolymer incorporation method used for poly(2-methyl-2-oxazoline), and the other polymers described above, hydrogen bonding interactions between silica gel and organic polymers are not so critical in this *in-situ* polymerization technique. It is, rather, confinement of the growing organic polymer by silica gel that affects the homogeneity.[20] Here, we have applied this *in-situ* polymerization method for the synthesis of polymer hybrids of polystyrene gel and silica gel with a so-called interpenetrating polymer network (IPN) structure. The polymer hybrids were expected to be highly solvent resistant because of the presence of cross-linking points in the organic network.

Polystyrene gel and silica gel polymer hybrids were prepared by the *in-situ* polymerization method as shown in Scheme 1. Divinylbenzene (DVB) was used to introduce cross-linking points in the organic network. Styrene and DVB were mixed with 0.01 equiv. of 2,2′-azobisisobutyronitrile (AIBN) and 1.0 g of tetramethoxysilane (TMOS) in 10 ml of acetone. The weight ratio of DVB and styrene was varied from 0 to 0.2 to control the density of cross-linking points, while the total weight of the organic monomers was fixed at 1.0 g (Table 1). 0.24 ml of 0.1 M HCl was added to the solution as a catalyst for the sol–gel reaction of TMOS. The mixture was stirred at room temperature for 5 h and subsequently heated at 60 °C under nitrogen for 1 week with an aluminium foil cover having a few pinholes. Sol–gel reaction of TMOS and radical polymerization of styrene and DVB were expected to proceed simultaneously, entrapping the organic network in the silica gel. After removal of the solvent, glassy materials were obtained.



Scheme 1

The conversion of the monomer to polymer was confirmed by thermogravimetric analysis (TGA), which shows the onset of polymer decomposition around 350 °C (Fig. 1).[19] The weight loss at around 100 °C corresponds to residual solvent. The polymer hybrids obtained were ground and subjected to $CHCl_3$ extraction using a Soxhlet apparatus. The contents of organic polymer in the hybrids after $CHCl_3$ extraction were confirmed by TGA as the weight loss at 900 °C. As shown in Fig. 1, the polymer contents decreased dramatically after the extraction in the polymer hybrid prepared without DVB. The polymer contents before and after the extraction were 48% and 17%, respectively (Table 1). The results indicate 64% of polystyrene was extracted from the polymer hybrid prepared without DVB. On the other hand, the polymer contents hardly changed before and after extraction when 0.1 equiv. of DVB was used (Fig. 2). In this case, the polymer contents before and after extraction were 53% and 50%, respectively. The loss of organic polymer was only 6%. For clarity the polymer loss was plotted against DVB contents as illustrated in Fig. 3. The plot shows the considerable improvement of the resistivity to solvent extraction with increasing DVB content and the extraction was almost prevented above 10 wt.% of DVB. The results indicate polystyrene formed a percolation network in silica gel with 10 wt.% of DVB, resulting in strong resistance to dissolution in chloroform.

The homogeneity of IPN polymer hybrids could be estimated by optical observation. Since the refractive indices of organic and inorganic parts have different values, *i.e.* 1.46 and 1.60 at 20 °C for polystyrene and silica gel respectively, the composites would become opaque when the domain of each component is larger than wavelength of visible radiation.[2] As shown in

**Table 1** Synthesis of polystyrene IPN polymer hybrids[a]

| run | DVB/St | homogeneity[b] | polym. cont.[c] before(%) | polym. cont.[c] after(%) | weight loss[c] (%) |
|---|---|---|---|---|---|
| 1 | 0 | transparent | 48.0 | 17.4 | 63.8 |
| 2 | 0.05 | transparent | 49.5 | 40.3 | 18.9 |
| 3 | 0.1 | transparent | 53.0 | 49.7 | 6.2 |
| 4 | 0.2 | transparent | 55.8 | 51.9 | 7.0 |

[a] Each hybrid was prepared with 0.01 equiv. of AIBN, 1.0 g of TMOS, 0.24 ml of 0.1 M HCl in 10 ml of acetone. The total amount of DVB and St was 1.0 g. The mixture was heated at 60 °C under nitrogen. [b] Homogeneity was evaluated optically. [c] The polymer contents in the hybrids were calculated by TGA. [d] Weight loss of the organic part was calculated as follows: weight loss = {polym.cont.(before) − polym.cont.(after)}/polym.cont.(before) × 100.

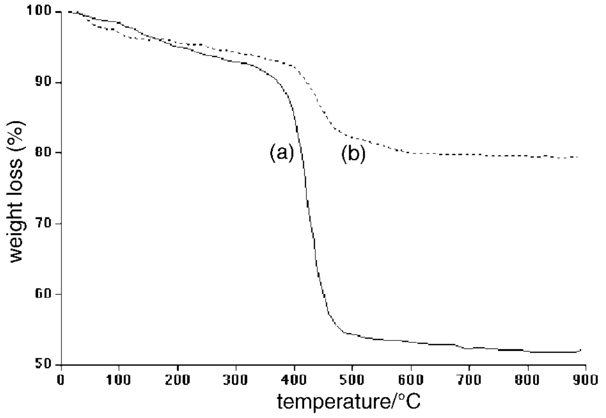


**Fig. 1** TGA traces of polystyrene–silica gel IPN polymer hybrid (DVB/styrene = 0) before (a) and after (b) $CHCl_3$ extraction

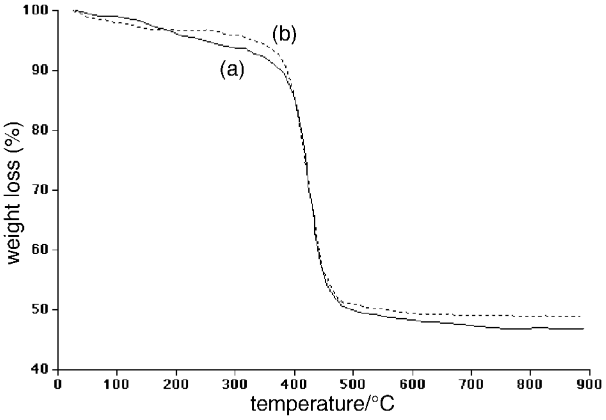


**Fig. 2** TGA traces of polystyrene–silica gel IPN polymer hybrid (DVB/styrene = 0.1) before (a) and after (b) $CHCl_3$ extraction

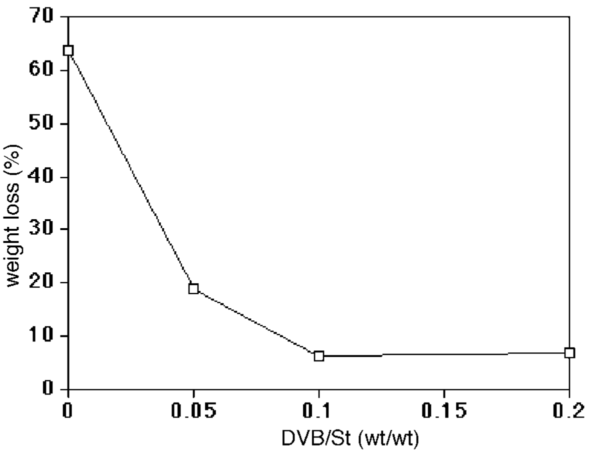
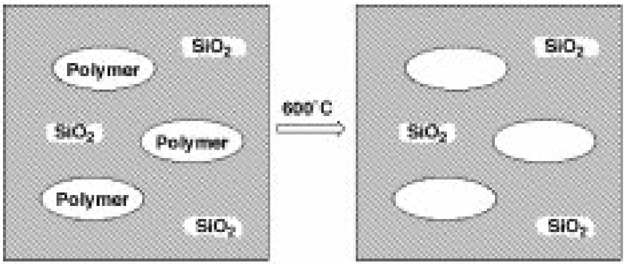


**Fig. 3** Weight loss by $CHCl_3$ extraction for 1 week



**Scheme 2**

Table 1, the obtained polymer hybrids were all transparent, indicating the homogeneous dispersion of the organic domain in the silica matrix. The homogeneity of the polymer hybrids was also evaluated quantitatively by nitrogen porosimetry of porous silica obtained from the polymer hybrids. The organic polymer was removed from the polymer hybrids by charring at 600 °C for 24 h, resulting in porous silica with pores of comparable size to the organic domains in the polymer hybrids (Scheme 2).[18] Therefore the dispersity of organic polymers in the hybrids could be evaluated by measuring the pores.[18] The BET method was applied to the isotherm curves to calculate surface areas and pore volumes of porous silicas.[21] As shown in Table 2, it was found that the porous silica obtained from these polymer hybrids had surface areas of more than 200 $m^2 g^{-1}$. If an aggregation of the organic segment occurred, the porous silica would have much smaller values for surface area and pore volume.[20] The pore size was calculated by the BJH method from the desorption isotherm curve from which the pore radius ($R_p$) was obtained assuming cylindrical pores.[22] The results are illustrated in Fig. 4 and Table 2. Although the pore size is larger than that of porous silica obtained from a polymer hybrid of linear polystyrene and silica gel, the pore size distribution plot for the porous silica obtained from the polymer hybrids prepared with 10 and 20 wt.% DVB exhibited peaks at 1.9 and 2.7 nm, respectively. As the pore of the silica obtained from polymer hybrids corresponds to the domain size of the organic segment, it seems reasonable to say that the polystyrene gel was dispersed at a nanometer level in these polymer hybrids. This is very interesting for the organic segment which does not possess hydrogen bond accepting groups and has poor solubility in the solvent. The homogeneity could be attributed to confinement of the polystyrene network

**Table 2** Pore volume and surface area of porous silica[a]

| run | DVB/ St | pore volume[b]/ ml $g^{-1}$ | surface area[b]/ $m^2 g^{-1}$ | pore radius[c]/ nm |
|---|---|---|---|---|
| 1 | 0 | 63.6 | 277 | 1.8 |
| 2 | 0.1 | 64.7 | 282 | 1.9 |
| 3 | 0.2 | 67.9 | 295 | 2.7 |

[a] The porous silicas were obtained by charring the polymer hybrids at 600 °C for 24 h. [b] Calculated by BET method. [c] Calculated by BJH method from desorption curve.

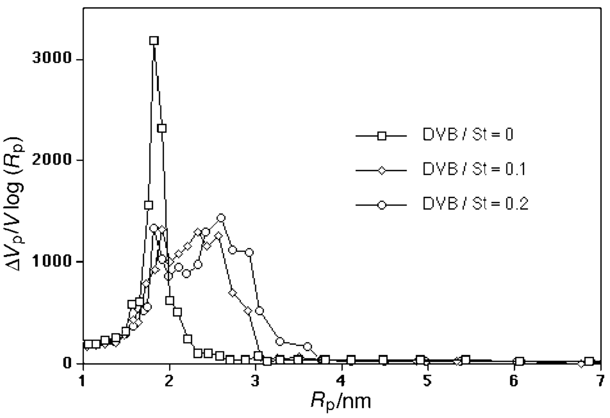


**Fig. 4** Pore size distribution plots of porous silica gels

within the silica gel matrix. The formation of polystyrene gel and silica gel proceeded simultaneously resulting in an IPN structure in this *in-situ* polymerization method. It was, thus, expected that the rigid structure of silica gel suppressed the mobility of polystyrene and then prevented aggregation of the organic segment.

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