Synthesis of polystyrene and silica gel polymer hybrids *via* π–π interactions

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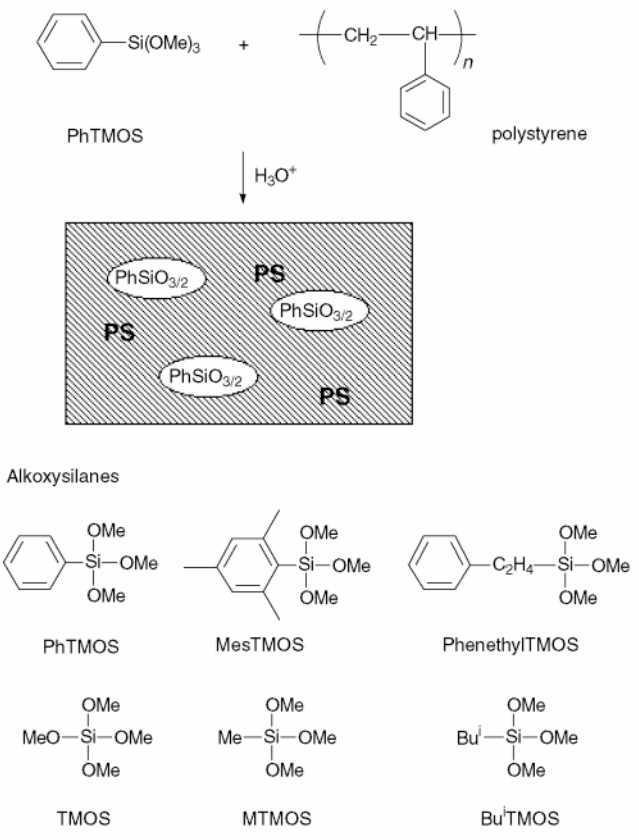
Homogeneous polystyrene and silica gel polymer hybrids have been prepared utilizing the sol–gel reaction of phenyltrimethoxysilane; π–π interactions between phenyl groups of the organic polymer and those of silica gel were found to play a critical role for the homogeneity.

In recent years a large variety of organic and inorganic polymer hybrids have been synthesized by the sol–gel technique utilizing alkoxysilanes.[1–4] A most noticeable characteristic of these hybrid materials is the molecular-level integration of organic and inorganic elements. The interactions that have been utilized to integrate organic and inorganic phases are generally classified into two groups; covalent bonding and hydrogen bonding interactions.[2] The former interaction is attained by the incorporation of silane coupling groups into organic segments.[5] The latter interaction is effective when organic segments have polar functional groups such as amide and urethane groups. The interaction acts between these functional groups and residual silanol groups of silica gel.[1] On the other hand, π–π interactions are known as one of the types of attractive non-covalent bonding interactions which play a critical role in, for example, the stabilization of the double helical structure of DNA and complexation in host–guest systems.[6] Here we introduce a new approach to synthesize homogeneous polymer hybrids utilizing π–π interactions. Homogeneous polymer hybrids of polystyrene and silica gel were successfully prepared by this method.

Polystyrene and silica gel polymer hybrids were prepared by utilizing a sol–gel reaction of phenyltrimethoxysilane (PhTMOS). The sol–gel reaction proceeds *via* hydrolysis and subsequent condensation of alkoxysilanes. When an alkyl-substituted alkoxysilane is used as a starting material, the alkyl group is introduced into silica gel since the Si–C bond does not undergo hydrolysis reaction. Thus, phenyl groups would be introduced into the silica gel by the sol–gel reaction of PhTMOS.

As shown in Scheme 1, the alkoxysilane was added to a THF solution of polystyrene (M_w = 24 500, M_n = 17 700, M_w/M_n = 1.39) followed by an addition of 0.1 M HCl as catalyst. The mixture was then heated at 30 °C and the temperature was gradually raised to 80 °C and the sample kept at this temperature for a week. For comparison, other alkoxysilanes such as tetramethoxysilane (TMOS) methyltrimethoxysilane (MTMOS) and isobutyltrimethoxysilane (Bu^iTMOS) were also used as starting materials. The mass ratio of alkoxysilane to polystyrene was 0.1 or 1.0. Homogeneity of the obtained polymer hybrids was evaluated optically. Transparency of the polymer hybrids is attained only when silica gel particles embedded within polystyrene are smaller than the wavelength of light.[2] As shown in Table 1, transparent polymer hybrids were obtained for both mass contents when PhTMOS was used as a starting material for the sol–gel reaction. In contrast, polymer hybrids became translucent or turbid when TMOS, MTMOS or Bu^iTMOS were used. Other alkoxysilanes containing a phenyl ring were also employed for the synthesis of the polymer hybrids. Mesityltrimethoxysilane (MesTMOS) gave homogeneous polymer hybrids when the mass ratio was 0.1. However, the homogeneity deteriorated as the mass ratio was increased to 1.0. The result might be attributed to methyl groups on the phenyl ring of MesTMOS, which are suspected to interrupt the π–π interaction. When phenethyltrimethoxysilane (PhenethylTMOS) was used as the starting material homogeneous polymer hybrids were obtained for both mass contents. These results demonstrate that a phenyl ring is necessary for the homogeneous dispersion of polystyrene and silica gel. In addition, as was observed for MesTMOS, spatial bulkiness on



Scheme 1

Table 1 Effect of alkyl groups on homogeneity of silica gel hybrids

Run	$RSi(OMe)_3$[a]	$RSi(OMe)_3$ /PS[a]	0.1 M HCl/ml	Appearance
1	Ph	0.1	0.045	Transparent
2	Ph	1	0.045	Transparent
3	OMe	0.1	0.059	Turbid
4	OMe	1	0.059	Turbid
5	Me	0.1	0.078	Turbid
6	Me	1	0.078	Turbid
7	Bu^i	0.1	0.052	Turbid
8	Bu^i	1	0.052	Turbid
9	Mesityl	0.1	0.037	Transparent
10	Mesityl	1	0.037	Turbid
11	Phenethyl	0.1	0.040	Transparent
12	Phenethyl	1	0.040	Transparent

[a] 0.5 g of PS was dissolved in 5 ml of THF with $RSi(OR)_3$ and acid catalyst. The mixture was heated at 30–80 °C in an oven.

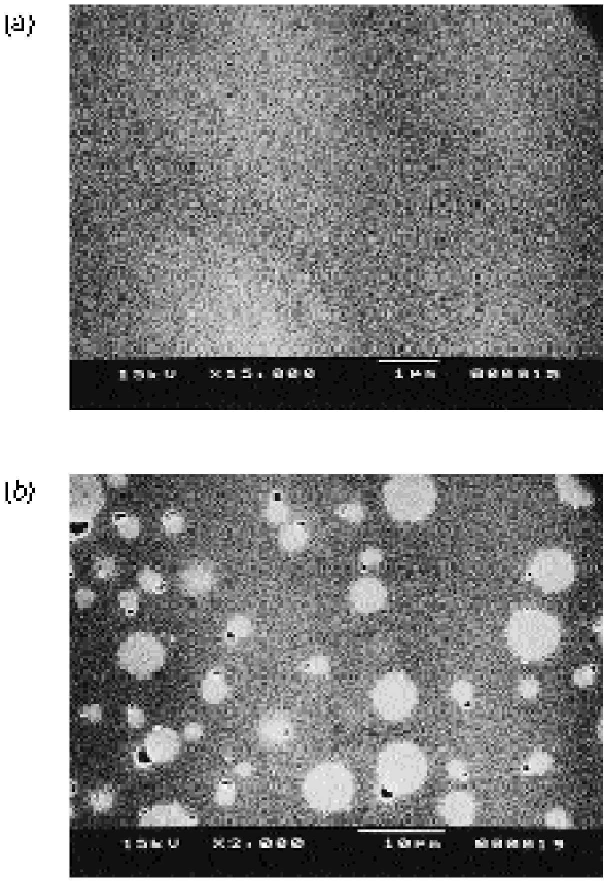


Fig. 1 Scanning electron micrographs of (*a*) a polymer hybrid prepared from PhTMOS and PS (*b*) a polymer hybrid prepared from MTMOS and PS

the phenyl rings was found to lead to deterioration of the homogeneity. Considering these results, it is expected that the stacking between phenyl rings of polystyrene and silica gel, rather than hydrophobic interactions, is critical for the homogeneous dispersion of the polymer and silica gel. Clear differences were observed in SEM measurements. As shown in Fig. 1, phase separation appeared in the polymer hybrid prepared from MTMOS with a mass ratio of 0.1 and silica gel domains of $\geqslant 5$ μm were observed. On the other hand, a polymer hybrid prepared from PhTMOS showed no recognizable segregation at this level. As the mass ratio of alkoxysilanes was increased to 1.0, the size of silica gel domains increased to 50 μm in the polymer hybrid prepared from MTMOS, while the polymer hybrid prepared from PhTMOS still showed a uniform image.

We also carried out the synthesis of polymer hybrids starting from poly(diallylphthalate) and polycarbonate as organic components which also have phenyl rings as repeating units. As observed in the case of polystyrene, transparent polymer hybrids were obtained when PhTMOS or PhenethylTMOS was used as a starting reagent for the inorganic part, while other alkoxysilanes such as TMOS, MTMOS or Bu^{i}TMOS gave only inhomogeneous polymer hybrids.[7] These results indicate that π–π interactions are quite effective for the synthesis of homogeneous polymer hybrids of aromatic polymers and silica gel.

Notes and References

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