Hydrophilicity-controllable Microporous Hybrid Materials by Anion Exchange

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Poly(acrylic acid) (PAA)/silica hybrids having imidazolium chloride [IL(Cl^-)] moieties could be prepared by utilizing ionic interactions between anionic carboxylic acid groups of PAA and cationic imidazolium groups of silica phase. By removing PAA from the obtained hybrids, we could obtain hydrophilicity-controllable microporous hybrids by means of anion-exchange reaction of imidazolium moieties.

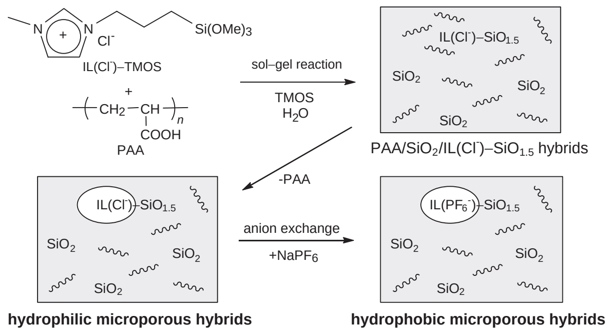
Recently, a large variety of organic–inorganic polymer hybrids have been synthesized by the sol–gel reaction utilizing alkoxysilanes.[1] A most noticeable characteristic of these hybrids is the molecular level integration of organic and inorganic elements. These hybrids usually exhibit improved properties compared with conventional composites, in which two components are mixed on macroscopic scale (>μm).[2] For example, nanoscale organic–inorganic hybrid materials show transparency, gas barrier,[3] and flame resistance properties, which are different from those in micron scale composites.

A key point for the elaboration of organic–inorganic nanocomposites is improving the affinity of the interface between organic and inorganic phases. The low compatibility between them results in aggregation of organic polymer in a silica matrix during the formation of the silica gel, and then the appearance of the obtained composite materials is turbid or phase separated. To obtain transparent polymer hybrids, it is necessary to introduce covalent bond[4] or some appropriate physical interactions between organic polymer and silica gel.

The physical interaction is especially effective when organic segments have polar functional groups such as amide groups. Our group has elaborated novel hydrophilic polymer hybrids by utilizing physical interactions such as hydrogen bonding[5] and ionic interactions[6] between organic polymer and silica gel. For example, the hydrogen-bonding interaction between residual silanol groups from sol–gel reaction and organic polymer having strong hydrogen-accepting groups such as poly(2-methyl-2-oxazoline) (POZO), poly(*N*,*N*-dimethylacrylamide) (PDMAAm), and poly(*N*-vinylpyrrolidone) (PVP) resulted in the molecular dispersion in silica gel matrix. Although various applications of these hybrids have been desired and widely studied owing to the excellent properties such as optical transparency and high thermal durability, an intrinsic drawback of poor water resistance is not negligible.

To overcome this drawback, we have developed a new approach to synthesize novel polymer hybrids utilizing π–π interactions.[7] Hydrophobic polymer hybrids of polystyrene and phenyl groups-modified silica gel could be prepared by this method. The novel methodologies to hydrophobic hybrid materials can broaden the scope of the sol–gel hybrid materials chemistry, but few approaches are known until now.

In this study, we describe a novel approach for the construction of hydrophobic polymer hybrids based on anion-exchange reaction of imidazolium groups. It was already reported that the property of imidazolium-based ionic liquids depends on the appropriate counter anions. In other words, the miscibility of the ionic liquids with water is controllable by selecting the kinds of the counter anions. Our new concept consists of three steps: (i) Preparation of poly(acrylic acid) (PAA)/silica hybrids by utilizing ionic interactions between carboxylic acid groups of PAA and cationic imidazolium groups of silica phase. (ii) Creation of imidazolium groups-induced microporous hybrids by removing PAA from the original hybrids. (iii) Anion-exchange reaction of imidazolium groups at the surface of the micropores (Scheme 1).



Scheme 1. Hydrophilicity-controllable microporous hybrid materials.

A typical preparation method of PAA/silica hybrids is as follows. The prescribed amount of PAA ($M_w = 25000$), tetramethoxysilane (TMOS), and IL(Cl^-)-modified alkoxysilane[8] [IL(Cl^-)–TMOS] were dissolved in solvent. Then, the resulting solution was stirred for 1 h at room temperature in a sealed bottle to proceed the sol–gel reaction. The mixture was placed in a polypropylene container covered with a paper towel and left at room temperature for 3 h. Then, the container was placed in a 60-°C oven to evaporate the solvent. Finally, the resulting hybrids were heated under reduced pressure at 80 °C to remove the remaining solvents and to complete the sol–gel reaction. The results of hybridization are shown in Table 1.

The solvents used for the synthesis of polymer hybrids were H_2O, MeOH, and DMF, all of which can dissolve PAA. It was found that the type of solvent has a great influence on the transparency of the polymer hybrids produced. When MeOH or

Table 1. PAA/SiO_2 hybrids with organic groups modified alkoxysilanes[a]

Run	R–TMOS	Solvent	Appearance	Ceramic calcd.	yield/wt % obsd.[b]
1	IL(Cl^-)–TMOS	H_2O	transparent	62.3	65.1
2	IL(Cl^-)–TMOS	MeOH	turbid	—	—
3	IL(Cl^-)–TMOS	DMF	turbid	—	—
4	Cl–TMOS	H_2O	turbid	—	—

[a] PAA/SiO_2/R–$SiO_{1.5}$ = 1/2.4/0.75 (wt %). [b] Determined by TGA.

Table 2. Solvent extraction efficiencies[a]

$MeOH^b$	H_2O^b	1 M HCl_{aq} for 4 h[c]	1 M HCl_{aq} for 24 h[c]
0	13.6	48.4	79.9

[a] The polymer content of Run 1 hybrid before and after extraction (P_b and P_a, respectively) was calculated from TGA in air, and the solvent extraction efficiency **E** was calculated according to the equation: $\mathbf{E} = (P_b - P_a)/P_b(1 - P_a)$. [b] Values obtained after MeOH or H_2O Soxhlet extraction for 7 days. [c] Values obtained after extraction at rt with sonication.

DMF was used as a solvent, the polymer hybrids brought about turbid (Runs 2 and 3). In contrast to these results, the polymer hybrid obtained in H_2O was optically transparent (Run 1). The difference in transparency of the polymer hybrids could be attributed to the different dielectric constants of the solvents. The dielectric constants of H_2O, MeOH, and DMF are 78.3, 33.1, and 36.7 (25 °C), respectively.[9] The solvents with high dielectric constants can solvate ionic pairs via stronger electrostatic interaction. This indicates that only H_2O can dissociate carboxylic acid groups of PAA sufficiently, which enabled the formation of transparent polymer hybrid by effective ionic interactions between anionic carboxylic acid groups of PAA and cationic imidazolium groups of silica phase. In addition, the obtained material with 3-chloropropyltrimethoxysilane (Cl-TMOS), which was not reacted with 1-methylimidazole, also brought about turbid due to the poor compatibility between organic and inorganic phases (Run 4).

To construct hydrophilicity-controllable microporous hybrid materials, solvent-extraction experiments were conducted. The obtained polymer hybrids were crushed into powders, which were extracted with MeOH, H_2O, and aqueous 1 M HCl solution. The results are summarized in Table 2.

Very little organic component could be extracted with MeOH and H_2O. On the other hand, in the case of using 1 M HCl_{aq} as a solvent, the solvent extraction efficiencies dramatically increased. This result clearly indicates that only 1 M HCl_{aq} can dissociate the ionic interactions between anionic carboxylic acid groups of PAA and cationic imidazolium groups of silica phase, resulted in efficient PAA extraction. The successful extractions were also confirmed by FT-IR and nitrogen adsorption porosimetry studies.

In the FT-IR spectra (Figure 1), a reduction in the intensity of the peak at 1727 cm^{-1} arising from the C=O stretching vibrations of PAA can clearly be seen after the solvent extraction. Furthermore, nitrogen sorption isotherm curves showed type I curves, indicating that the hybrids after the solvent extraction had nano-pores. Figure 2 shows the pore size distribution plots (estimated by the MP method[10]) of the hybrids after the solvent extraction. The increase in the pore volume can clearly be seen with increasing the solvent extraction time. These results indicate the successful extractions of PAA from the original hybrids.

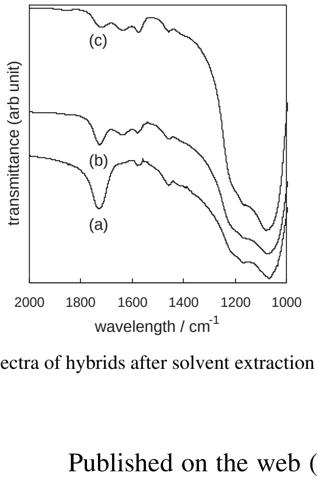


Figure 1. FT-IR spectra of hybrids after solvent extraction for (a) 0, (b) 4, and (c) 24 h.

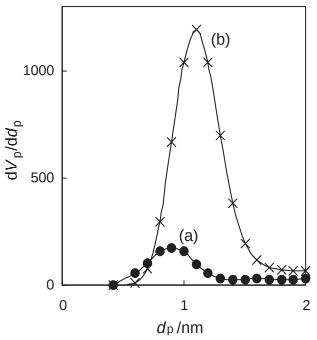


Figure 2. MP-plots of hybrids after solvent extraction for (a) 4 and (b) 24 h.

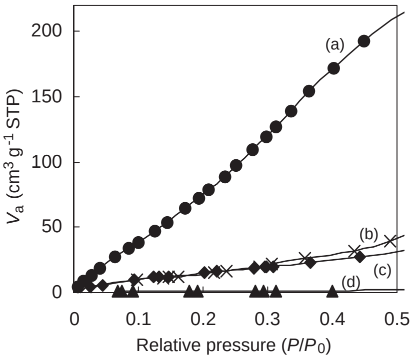


Figure 3. Water vapor (25 °C) adsorption isotherm curves of hybrids after anion-exchange reaction with $NaPF_6$ in H_2O for (a) 0, (b) 0.5, (c) 6, and (d) 48 h.

To achieve hydrophobic hybrid materials, anion-exchange reaction was conducted. It is known that ionic liquids having PF_6^- as a counter anion exhibit hydrophobic property. Thus, by changing counter anion of imidazolium cation from Cl^- to PF_6^- on the surface of nano-pores, the hydrophilicity of the hybrids would be largely exchangeable. To investigate the changes of the hydrophilicity, water vapor adsorption study was conducted. Water vapor adsorption studies were carried out at 25 °C from 0 to 0.99 ($P/P_0, P_0$ = saturated water vapor pressure) for adsorption process. As shown in Figure 3, the amount of water vapor adsorption was gradually decreased with increasing of anion-exchange reaction time. Especially, when anion-exchange reaction was completed (confirmed by elemental analyses), we could not observe any amount of water vapor adsorption, which resulted in the desired hydrophobic material (Figure 3d).

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