Control of Pore Size of Porous Silica by Means of Pyrolysis of an Organic–Inorganic Polymer Hybrid

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Pyrolysis of a silica gel hybrid with a starburst dendrimer gives porous silica, in which the pore-size is successfully controlled by the size of the organic component used.

Recently, we have explored new composite materials, *i.e.* molecular hybrids between silica gel and amide group-containing polymers such as polyoxazoline.[1] In these hybrids, amide groups in organic components were found to play an important role as an acceptor of hydrogen bonding. The molecular-level dispersion of the organic polymer in the framework of silica gel has been established, which is due to the hydrogen bonding between the organic polymer and silanol group of silica gel. Furthermore, porous silica was produced effectively from a polymer hybrid by pyrolysis at 600 °C, which is below the fusion point of silica gel. However, the size of pores of the produced porous silica could not be controlled by the degree of polymerization of polyoxazoline using these polymer hybrids. Here we describe the preparation of porous silica having controlled pore size by means of pyrolysis of polymer hybrids between silica gel and starburst dendrimers, which are known to have a spherical shape.

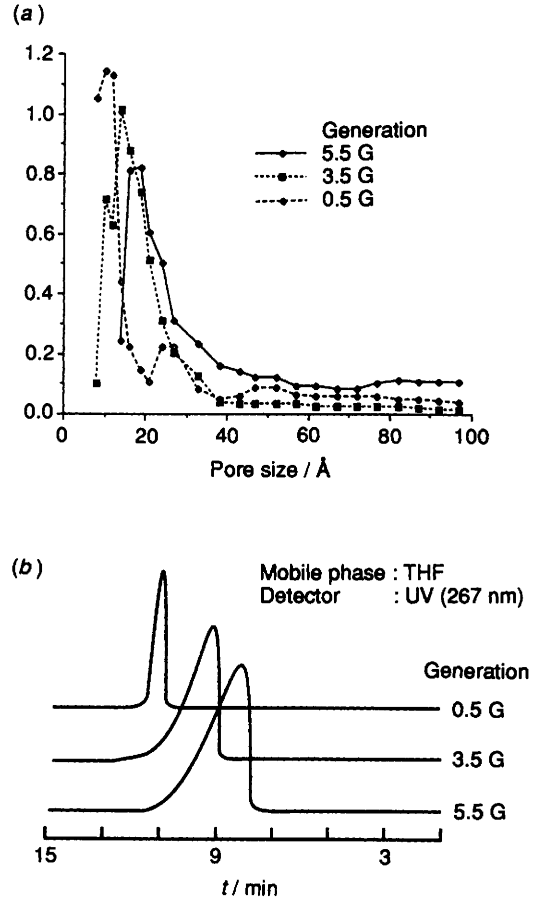

Fig. 1 (*a*) Pore-size distribution of porous silica; (*b*) GPC traces of starburst dendrimers

The starting starburst dendrimer was prepared according to the method reported by Tomalia;[2] ammonia was used as a core. Various starburst dendrimers having 0.5–5.5 generations were respectively synthesized by stepwise Michael-type addition of methyl acrylate and ester–amide exchange reaction using ethylenediamine. Scheme 1 shows the illustrative structure of the starburst dendrimer having various generations. It should be pointed out that these dendrimers contain an *N*-alkylamide group in the repeating units.

Organic–inorganic polymer hybrids were prepared by the acid-catalysed sol–gel reaction of tetramethoxysilane in the presence of various starburst dendrimers. Dendrimers having primary amino end groups (1.0, 2.0, 3.0, 4.0 and 5.0 generations) caused phase separation to produce only turbid or heterogeneous materials. On the other hand, by using dendrimers having ester end groups, the homogeneity of the polymer hybrids obtained was much improved. Especially, in the cases of 0.5–4.5 generations, completely transparent and homogeneous polymer hybrids were obtained in a wide range of generations. The results of preparation of polymer hybrids are summarized in Table 1.

These polymer hybrids were subjected to pyrolysis at 600 °C for 24 h. From the results of elemental analyses, the organic polymer segments (starburst dendrimers) were eliminated completely. As summarized in Table 1, the porous silica obtained by this procedure showed high surface area (200–610 m^2 g^{-1}). The results of pore-size distribution of the porous silica thus obtained are illustrated in Fig. 1 together with the traces of GPC measurement for each dendrimer. It is clear that the pore size of silica gel corresponds well to the size of spherical organic polymer, *i.e.*, to the generation of the starburst dendrimer used.† As a typical example, the radius of the dendrimer itself of 3.5 generation has been calculated by Tomalia[2] at 12.9 Å. The peak of the pore-size distribution curve of the corresponding porous silica after pyrolysis is located at about 13 Å.

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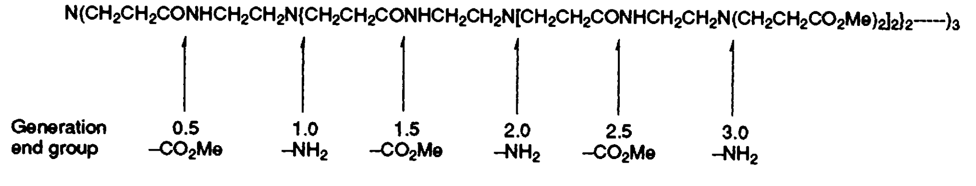
Footnote

† In Fig. 1, the silica formed from the 0.5 generation dendrimer showed a major peak around 10 Å together with minor peaks at 27 and 50 Å. These secondary peaks might be due to a small aggregation of dendrimers in the hybrid matrix. Although this observation should be


$$\mathrm{N(CH_2CH_2CONHCH_2CH_2N\{CH_2CH_2CONHCH_2CH_2N[CH_2CH_2CONHCH_2CH_2N(CH_2CH_2CO_2Me)_2]_2\}_2{-\!\!-\!\!-})_3}$$

Scheme 1 Starburst dendrimers

Table 1 Preparation and pyrolysis of silica–starburst dendrimer polymer hybrids

	Polymer hybrid				Porous silica		
Run	SBD[a] Generation	SBD : TMOS[b] (m/m)	Appearance	SBD Content (calc. from N%)	Surface area/ m^2 g^{-1}	Pore volume/ cm^3 g^{-1}	Pore size[c]/Å
1	0.5	1 : 10	Transparent	32.3	288	0.104	10
2	3.5	1 : 2	Transparent		613	0.484	13
3	4.5	1 : 10	Transparent		317	0.145	15
4	5.5	1 : 10	Translucent	28.6	203	0.088	18

[a] SBD = starburst dendrimer. [b] TMOS = tetramethoxysilane. [c] The highest concentration of pores.

clarified in future studies, a shift of pore size of silica with generations of dendrimers used is obviously demonstrated in Fig. 1.

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