

NOTES

Surface Structure Control of Macroporous Silica Gel by Atom Transfer Radical Polymerization

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The Synthesis of polymer grafting from a silica surface is significantly important for application to organic and inorganic hybrid materials with functions. The methods involving a controlled polymerization technique, such as ring-opening metathesis polymerization (ROMP) and atom transfer radical polymerization (ATRP), using an immobilized initiator on a silicon wafer and silica gel have been successfully accomplished and many studies have been reported.^{1–4}

ATRP, mediated by metal complexes, is of considerable interest and has realized various architectural macromolecular designs and syntheses, because it is versatile and useful for constructing well-defined functional polymers.⁵ The preparations of the silica gel-tethered polymers by the ATRP method using a variety of silica gels as the starting material have been reported;³ however, little attention has been paid to silica gels with a large pore. The macroporous silica gel is widely used, for example, as a supporting material of a stationary phase for high-performance liquid chromatography (HPLC).⁶ Therefore, the control of the surface structure and further functionalization may be important and contribute to generating novel functions and materials. On the other hand, the living manner during the grafting ATRP inside and outside of the pores of the silica gel should be significantly affected by its pore size.

In this study, macroporous silica gel (particle size: 7 μm , pore size: 1000 \AA , surface area: 30 $\text{m}^2 \text{g}^{-1}$) was employed as the starting material bearing immobilized initiators, and the grafting polymerization of vinyl monomers by the ATRP technique with the copper(I) chloride/4,4'-di-*n*-heptyl-2,2'-bipyridine (DHBP) or *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) complex was carried out.

EXPERIMENTAL

Materials

Solvents, reagents, and monomers were purified by general methods or used as received. Macroporous silica gel (Daisogel SP-1000, particle size: 7 μm , pore size: 1000 \AA , surface area: 30 $\text{m}^2 \text{g}^{-1}$) was a kind gift by Diso, Osaka. The silica gel-initiator **1** was prepared as follows:

Silica gel (20.6 g) was treated with *N*-methylaminopropyltrimethoxysilane (10 mL) and dry pyridine (1 mL) in dry benzene (200 mL). After heating at 90°C for 15 h, the mixture was washed with methanol, filtered, and dried *in vacuo* to produce a gel (20.7 g). Based on the elemental analysis (C: 0.49%, H: 0.06%, N: 0.13%), the estimated loading was *ca.* 8.9 $\times 10^{-5} \text{ mol g}^{-1}$ based on the [N] content. To the obtained gel (9.0 g) in tetrahydrofuran (THF) (100 mL) was added 4-chloromethylbenzoyl chloride (1.8 g, 10 mmol) and triethylamine (2.0 mL, 14 mmol). The reaction was carried out at 50°C for 18 h, and subsequent washing with methanol and filtration gave **1** (9.0 g). The loading value calculated based on that of the starting gel, 8.8 $\times 10^{-5} \text{ mol g}^{-1}$, was approximately comparable with the value estimated by thermogravimetric analysis (TGA), 9.7 $\times 10^{-5} \text{ mol g}^{-1}$ (Scheme 1). The scanning electron microscope (SEM) images of **1** are shown in Figure 1.

Polymerization (Typical Procedure)

ATRP was carried out according to the reported procedure.³ DHBP or PMDETA was used as a ligand for CuCl (Scheme 2). The polymerization was typically carried out using a monomer, CuCl, a ligand, and an initiator [500/1/2/1 (mol)] under a N₂ atmosphere. The

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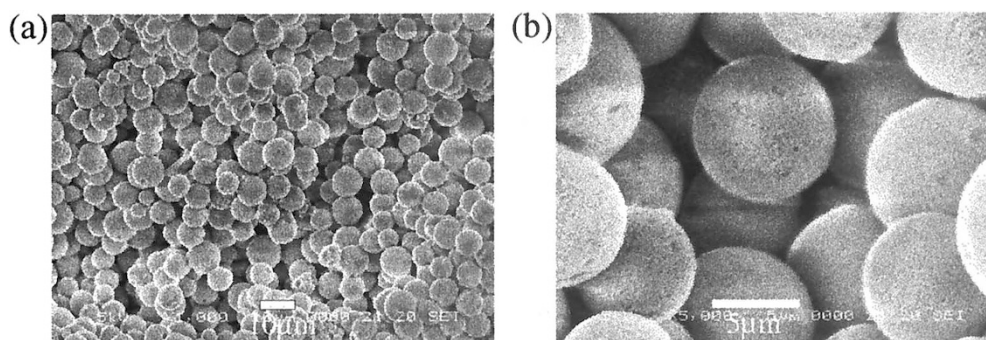
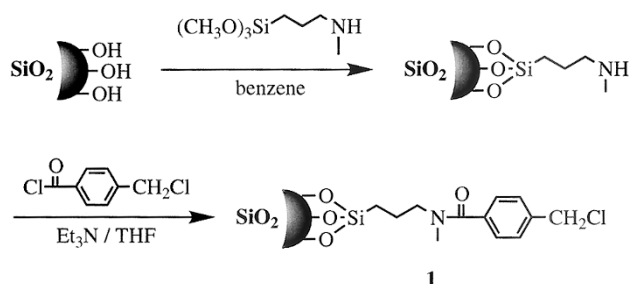
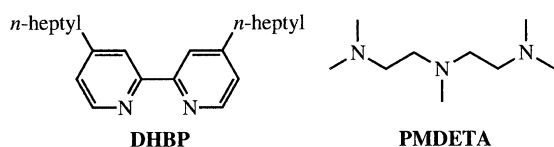


Figure 1. SEM images of **1**.



Scheme 1.



Scheme 2.

gel was collected after repeatedly washing with THF and methanol, then decantation, and drying *in vacuo*.

The obtained gel was treated with a mixture of 1N NaOH aq. and THF [1/3 (v/v)]. After stirring at room temperature for 48 h, 1N HCl was added to neutralize the mixture. The solvents were evaporated, and a THF soluble part was collected for analysis.

Measurement

The SEM was carried out using a JEOL JSL-5600. The TGA thermogram was taken using a Seiko EXS-TRA6000 system. The size exclusion chromatographic (SEC) analysis was performed on a JASCO-BORWIN GPC equipped with JASCO UV-970 and JASCO RI-930 detectors using Tosoh TSKgel G7000HHR and G3000HHR columns connected in series and CHCl_3 was used as the eluent. Calibration was carried out using standard polystyrenes.

RESULTS AND DISCUSSION

The results of the ATRP of styrene (St) and methyl methacrylate (MMA) using **1** are listed in Table I. Poly(St) and poly(MMA) chains were effectively im-

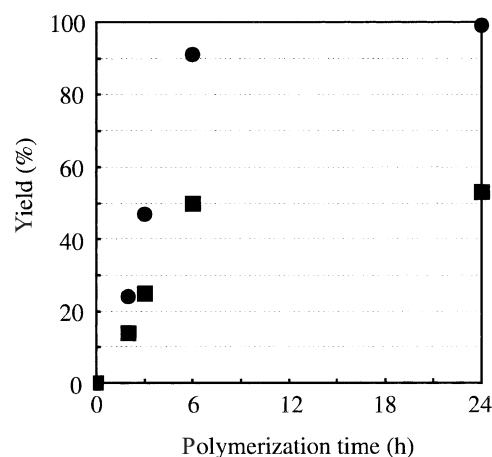


Figure 2. Plots of time vs. yield of the immobilized polymer (■) and total yield (●) for ATRP of St using PMDETA ligand (entries 2–5).

mobilized on the macroporous silica gel. The polymerization of St using the CuCl-DHBP complex at 130°C ($[\text{St}]/[\text{initiator}] = 500/1$) proceeded with 7% yield (calculated based on the amount of immobilized polymer on the silica gel) after 3 h (entry 1). The immobilized poly(St) chain was cleaved by hydrolysis under basic conditions and analyzed by SEC, showing a molecular weight distribution of $M_w/M_n = 1.58$. Although the value seems to be broad, the polymer chains grafted by ATRP on solid supports generally have a relatively broader M_w/M_n value than those of the polymers prepared using normal soluble initiator systems and the polymerization proceeds in a controlled manner.^{3,7}

The polymerization of St was carried out using the CuCl-PMDETA complex at 130°C for various polymerization times (entries 2–5). Figure 2 demonstrates the time-yield plots of these results. The yield of the immobilized polymer increased almost linearly during the first 6 h, and reached to a plateau value. The increase in the yield as a measure of the amount of immobilized polymer on the silica gel was hardly observed even after 24 h. The obtained gel with 50% yield (entry 4) contained about 2.3 g of poly(St) immobilized on a silica gel surface (1.0 g). On the other

Table I. Radical polymerization of St and MMA^a

Entry	Ligand	Monomer	Time h	Yield ^b %	M_n^c $\times 10^4$	M_w/M_n^c
1	DHBP	St	3	7 (3)	6.9	1.58
2	PMDETA	St	2	14 (10)	13.5	7.85
3	PMDETA	St	3	25 (22)	13.8	6.60
4	PMDETA	St	6	50 (41)	22.0	7.46
5	PMDETA	St	24	53(>46)	21.2	8.70
6	DHBP	MMA	3	21 (2)	14.3	4.08

^aConditions: [monomer]/[initiator] = 500/1, [initiator]/[CuCl]/[ligand] = 1/1/2, temp = 130°C (for St) and 90°C (for MMA). ^bThe yield was calculated based on the weights of the immobilized polymer and the monomer in feed. The yield of THF-soluble and MeOH-insoluble part is shown in parentheses.

^cDetermined by SEC after cleavage of the polymer-chain (CHCl₃, poly(St) standard).

hand, the polymerization system also gave a polymer as a THF-soluble and methanol-insoluble fraction,⁸ which may be produced by the chain-transfer reaction or thermal polymerization, and the result indicates that the polymerization for 24 h (entry 5) quantitatively proceeded. The cleaved polymer chains showed much broader M_w/M_n values, suggesting that some of the growing chains lost the chance to add monomers in a living fashion, probably because the pores were filled with the grafted polymers. Therefore, the molecular weight of the polymer produced in the pore may depend on the size of the pore. This may cause the broad molecular weight distribution of the polymer.

The obtained hybrid gel (entry 4) was again used as an initiator for the ATRP of St using the CuCl–PMDETA system at 130°C for 3 h ([St]/[initiator]/[CuCl]/[PMDETA] = 500/1/1/2). The polymerization resulted in a 5% yield ($M_n = 23.1 \times 10^4$, $M_w/M_n = 9.71$), a value which is much lower than that (25% yield, entry 3) of the polymerization using **1** under the same conditions.

The specific surface areas of the obtained gels were measured by BET experiments (N₂ desorption) and the results are plotted as the yield of the immobilized polymer (Figure 3). **1** showed a surface area of 25.7 m² g⁻¹, which is approximately comparable with the value of the starting macroporous silica gel. The observed surface area values were dramatically decreased with the degree of polymerization (increasing the yield). The gel prepared by the 6 h polymerization (entry 4) had a surface area of 3.1 m² g⁻¹ and little change was observed in comparison to that of the polymer obtained by the 3 h polymerization (entry 3, 3.5 m² g⁻¹). These results suggest that the pores of the silica gel were almost filled after the graft polymerization progressed with a 25% yield [about 1.2 g of poly(St) on 1 g of silica gel surface].

Figure 4 demonstrates the SEM images of the obtained gels (entries 1–4). The pores are observed for the gels with a polymer prepared with low yields (en-

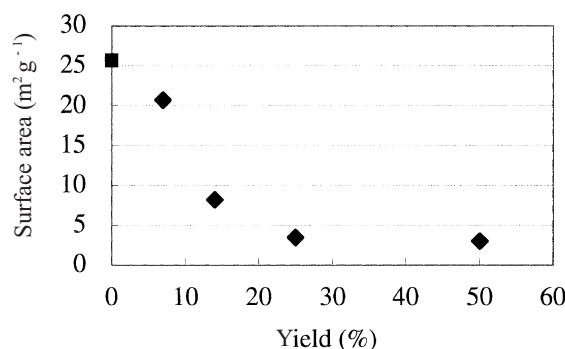


Figure 3. Plots of surface area of **1** (■) and the obtained gels by ATRP of St (◆: entries 1–4) vs. yield of the immobilized polymer.

tries 1 and 2), whereas the surface structure of the gels for a polymer with a higher yield (entries 3 and 4) looks quite different. The silica gel surface seems to be fully covered by poly(St) and no more clear pores are observed. The gel diameter of (d) looks larger than the others. These observations explain the results of the polymerization and BET measurements of the obtained gels.

In conclusion, the ATRP grafting from macroporous silica gel effectively immobilized a vinyl polymer chain to some extent. Although the polymerization may proceed in a controlled manner during the initial low monomer conversion, the polymerization in macropores seems to be significantly influenced by the size of the pore. Therefore, the surface area and pore size of the silica gel were effectively varied by this method.

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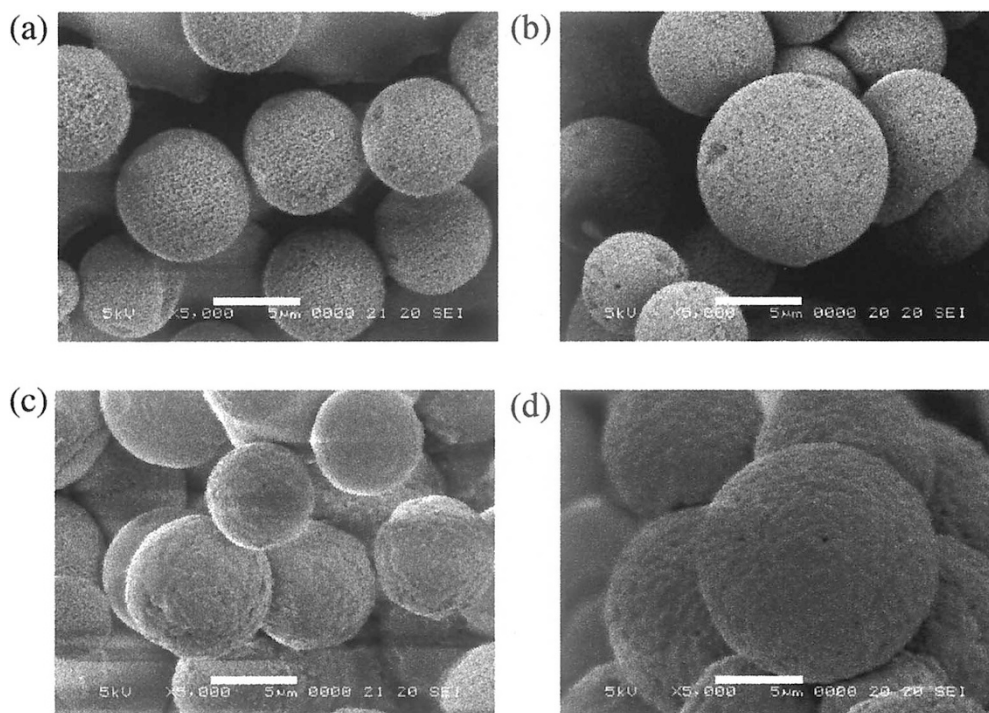


Figure 4. SEM images of the obtained gels by ATRP of St: (a) entry 1, (b) entry 2, (c) entry 3, and (d) entry 4 (white bar indicates 5 μm).

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- $M_n = 0.8\text{--}9.3 \times 10^4$, $M_w/M_n = 2.1\text{--}2.6$ [Measured by SEC (CHCl_3 , poly(St) standard)].