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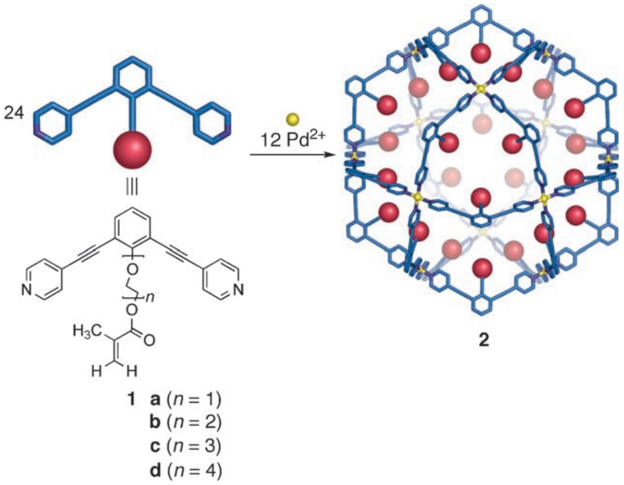
Molecular Nanoparticles

Nanometer-Sized Shell Molecules That Confine Endohedral Polymerizing Units**

Takashi Murase, Sota Sato, and Makoto Fujita*

Polymerization that proceeds in a restricted nanosized region under external stimuli, without any volumetric shrinkage, is a fascinating task in materials science because the physical and optical properties of the polymerized region dramatically change with nanoscale resolution, which has relevance to high-density data-storage materials, for example.[1] Polymerizations in zeolites,[2] porous organic crystalline hosts,[2] and porous coordination polymers[3] are currently active research fields. These host materials offer well-defined nanosized spaces or channels, but the nanometric regions are grouped together in a bundle. Therefore, it is impossible to handle them as soluble discrete scaffolds with high processability. Emulsion polymerization in a micelle is another approach to polymerization in spatially confined regions.[4] However, micelles do not have well-defined structures and shapes, and the number of monomers accommodated and polymerized in micelles is not precisely restricted.

Recently, we succeeded in the endohedral functionalization of a self-assembled spherical complex that consists of 12 metals and 24 ligands.[5–7] These complexes are regarded as a well-defined "molecular nanoparticle" with a precise chemical structure and uniform diameter (up to 4.6 nm). It is possible to position 24 functional groups precisely inward through suitable linkers in the spherical complex.[6,7] Herein, we report the preparation of molecular spheres that confine 24 methyl methacrylate (MMA) units at the interior (Scheme 1). We show the endohedral radical polymerization of MMA in the spheres, providing a new nanomolecular material that is potentially applicable to high-density data-storage materials.



Scheme 1. Self-assembly of $M_{12}L_{24}$ molecular nanoparticles **2** with 24 MMA units.

MMA-anchored ligands **1a–d** were prepared in high yields in three steps from 2,6-dibromophenol (pMeC$_6$H$_4$SO$_2$O(CH$_2$CH$_2$O)$_n$H/K$_2$CO$_3$ ($n = 1$–4), CH$_2$=C(CH$_3$)COCl/NEt$_3$; then 4-ethynylpyridine/[Pd(PhCN)$_2$Cl$_2$]/tBu$_3$P/(iPr)$_2$NH; see Supporting Information). When ligand **1a** (0.014 mmol) was treated with Pd(NO$_3$)$_2$ (0.007 mmol) in deuterated dimethyl sulfoxide ([D$_6$]DMSO, 0.7 mL) for 4 h at 70 °C, the formation of **2a** as a single product was observed by ^{1}H NMR spectroscopy. Spheres **2b–d** were prepared in a similar way from **1b–d**. After anion exchange from NO_3^- to $CF_3SO_3^-$, cold-spray ionization mass spectroscopy (CSI-MS)[8] of the complexes **2a–d** clearly confirmed an $M_{12}L_{24}$ composition with molecular weights of 14658, 15715, 16772, and 17830 Da, respectively.

A comparison of the ^{1}H NMR spectra of spherical complexes **2a–d** revealed their endohedrally functionalized structures. While the signals derived from the aromatic protons of the shell are almost identical, those from the MMA units are shifted downfield with an increase in length of the oligo(ethylene oxide) linker, suggesting the aggregation of MMA units at the core of the sphere. Diffusion-ordered NMR spectroscopy (DOSY) experiments in [D$_6$]DMSO revealed the same diffusion coefficient ($\log D = -10.45$) for complexes **2a–d**, indicating that all MMA units tethered to the shell are confined in the spherical shell and do not come out of the shell.[9] Molecular modeling of complexes **2a–d** using the Cerius^2 program clearly shows that the effective concentration of MMA units in the sphere is strictly controlled by the linker length (Figure 1).

Radical polymerization was carried out in the spherical complex **2c** (0.788 mM) in DMSO at 70 °C for 17 h using 2,2′-azobis(isobutyronitrile) (AIBN, 8.3 mol% per MMA unit) as radical initiator.[10] Figure 2 shows the ^{1}H NMR spectra of the complex before and after polymerization. The intensity of the signals of the vinyl protons ($\delta = 5.7$ and 5.4 ppm) decreased and the signals from protons on sp^3 carbon atoms appeared after the polymerization. The conversion of MMA units into PMMA segments was calculated from the ratio of the area under the peaks corresponding to MMA units and those

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[*] T. Murase, Dr. S. Sato, Prof. Dr. M. Fujita
Department of Applied Chemistry
School of Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
Fax: (+81) 3-5841-7257
E-mail: mfujita@appchem.t.u-tokyo.ac.jp

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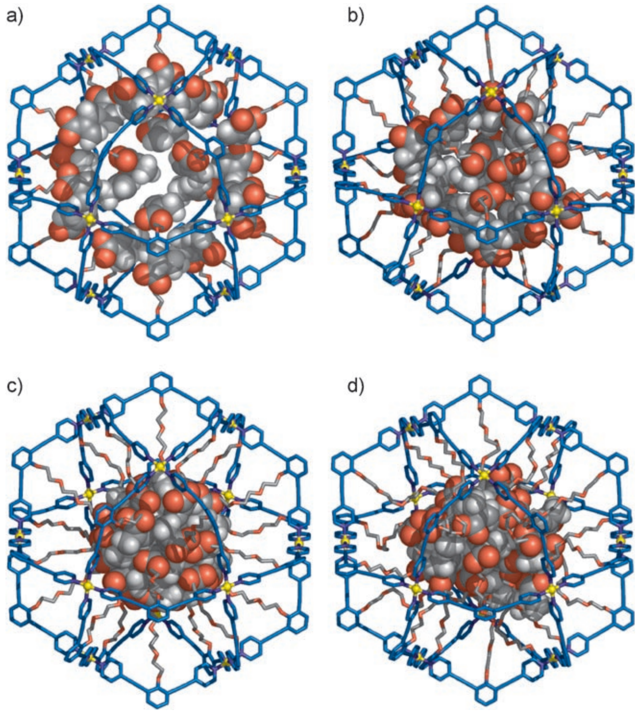

Figure 1. Molecular models of a) **2a**, b) **2b**, c) **2c**, and d) **2d** optimized using a force-field calculation with Cerius^2 3.5. MMA units are shown in space-filling representation (aromatic shell blue, Pd yellow, O red, C gray, H white).

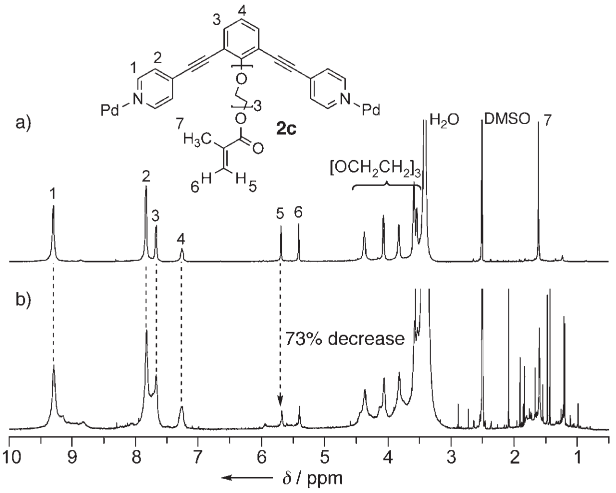

Figure 2. ^{1}H NMR spectra of complex **2c** a) before and b) after polymerization (500 MHz, [D$_6$]DMSO, 300 K, tetramethylsilane).

corresponding to the outer aromatic shell. It was found that 73% of the MMA units were converted into PMMA oligomers. No new peaks appeared around the aromatic region after the polymerization, indicating that the structure of the outer shell was maintained during the polymerization.[11] With prolonged reaction time (31 h), the conversion was increased to 85% but the shell was partially decomposed. The conversion was also increased to 81% by increasing the amount of AIBN used (42 mol% per MMA unit).

It is particularly interesting that the spherical complex can "concentrate" 24 MMA monomer units. When radical polymerization was carried out using ligand **1c** at the same concentration of MMA units (18.9 mM) as in the case of complex **2c**, the reaction hardly proceeded. With an internal diameter of 3.7 nm for the spherical complex **2c** and a capacity of 24 MMA units, the concentration of MMA units in the complex is approximately 1.5 M. Therefore, polymerization is efficiently promoted inside the spherical complex even at very low concentrations of monomer.

When radical polymerization was carried out in the other MMA-containing complexes, **2a**, **2b**, and **2d**, under the same polymerization conditions, 22, 29, and 62% conversion, respectively, of MMA into PMMA was observed. Therefore, complex **2c** with a tri(ethylene oxide) linker afforded the best efficiency (73% conversion). These results are in good agreement with the molecular models of the complexes (Figure 1). The 24 MMA units are the most closely packed at the core of complex **2c**, thus providing the most desirable arrangement of the MMA units for polymerization. The mono and di(ethylene oxide) linkers seem to be slightly too short for polymerization in the spherical complex, preventing the frequent close approach of MMA units. When the tetra(ethylene oxide) linker is used (**2d**), MMA units repel each other and lie away from the center of the complex because the linker is too long.

To examine the degree of polymerization of the polymerized sample, the PMMA segments tethered to the shell were cleaved by hydrolysis and converted into the methyl ester. From the sample obtained in **2c** with 81% conversion, the resulting oligomer was revealed by gel permeation chromatography (GPC) analysis to have a number-average molecular weight (M_n) of 1315 relative to PMMA standards and a polydispersity index (M_w/M_n) of 1.60.

In summary, we have prepared a spherical complex containing 24 MMA units in which radical polymerization can be effectively promoted. The complex has the ability to concentrate monomer units at the core of the complex. The present method is widely applicable to the preparation of other complexes that contain reactive monomers. For example, by attaching photochemically polymerizing functionalities at the interior surfaces of complexes, a photopolymer-incarcerated sphere can be obtained. Studies on such a photoresponsive sphere are in progress in our laboratory.

Experimental Section

PMMA cleavage[12] and GPC analysis: The polymerized complex **2c** (81% conversion) was precipitated by adding ethyl acetate and dried under reduced pressure. The PMMA segments tethered to the shell were cleaved by hydrolysis using concentrated H_2SO_4 (0.5 mL) at room temperature for 5 days, then the resulting solution was poured into ice water to precipitate the product. The precipitated polymethacrylic acid was esterified with trimethylsilyldiazomethane (0.1 mL, 2.0 M in hexane) in CH_3OH/THF (0.2 and 0.7 mL, respectively) at room temperature for 12 h to yield PMMA oligomer. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the obtained and standard PMMA were measured with GPC (Japan Analytical Industry LC-918) with refractive index detection. The columns were the connection of two Tosoh TSK-GEL G2000H$_{XL}$.

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THF was used as eluent, with a flow rate of 1.0 $\mathrm{mL\,min^{-1}}$ at 35 °C. See Supporting Information for a list of the physical properties of complexes **2a**–**d**.

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[9] The non-tethered (hollow) spherical complex also showed the same diffusion coefficient. Therefore, the sizes of the spherical complexes are uniform and do not depend on the contents.

[10] Although MMA monomers are concentrated in the complex, AIBN is not. Therefore, a relatively large amount of AIBN is required in the present study. Presumably, AIBN enters through the portals of the shell framework under equilibrium.

[11] The diffusion coefficient of the complex did not change before and after polymerization, indicating that the polymerization proceeded only in the complex. See Supporting Information.

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