

Synthesis of Organic–Inorganic Polymer Hybrids by Means of Host–Guest Interaction Utilizing Cyclodextrin

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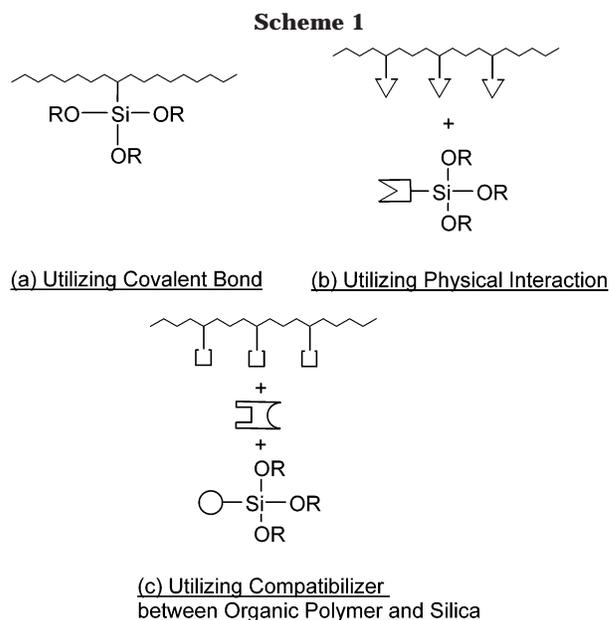
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ABSTRACT: Organic–inorganic polymer hybrids were synthesized utilizing the host–guest interaction. Cyclodextrins (CDs, α -, β -, γ -CD) could be dispersed in the silica gel matrix at a nanometer level because of the hydrogen-bonding interaction between hydroxyl moieties of CD and residual silanol groups of silica gel. It is known that β -CD forms a strong host–guest complex with 1-adamantanol in an aqueous solution. Thus, the organic polymer modified with an adamantane group at the side chain (ADA–PAA) and silica gel hybrids could be prepared by complexation of β -CD with ADA–PAA. β -CD played a role as a compatibilizer between ADA–PAA and silica gel to obtain transparent and homogeneous polymer hybrids. The evidence of the host–guest complex formation was confirmed by a fluorescence technique using a dansyl group. Furthermore, transparent and homogeneous CD–polymer complex/silica gel hybrids were prepared utilizing CDs formed polyrotaxane-type inclusion complexes with polymers, such as poly(ethylene glycol) and polyisobutylene.

Introduction

The construction of organic–inorganic polymer nanocomposites,^{1–5} which is the hybridization of organic polymer and inorganic materials on a molecular scale, is an area of extensive research in materials chemistry. These materials offer exceptional opportunities not only to combine the important properties from both fields but also to create new unique properties such as high gas barrier,⁶ flame resistance, transparency,⁷ excellent solvent resistance property,⁸ and so on. The sol–gel reaction of alkoxy silane is one of the most convenient methods for the preparation of organic–inorganic polymer hybrids. The sol–gel reaction comprises the hydrolysis of Si–OR groups to Si–OH (silanol) groups and the condensation of the silanol groups into –Si–O–Si– linkages.⁹ A three-dimensional silica gel network is constructed as the sol–gel reaction proceeds. One of the most attractive features of this method is its low processing temperature, which allows organic polymer to be incorporated into the silica matrix without decomposition.

To overcome problems of macro- and microphase separation between organic polymers and inorganic phases, organic–inorganic polymer hybrids have been mainly synthesized by three kinds of methods. The first method is that the organic–inorganic polymer hybrids could be prepared by utilizing the formation of the covalent bonds between organic polymers and inorganic phases.^{10–13} Alkoxy silane-modified polymers can be used as sol–gel precursors (Scheme 1a). The second one is utilizing physical interaction between organic polymer and silica gel (Scheme 1b). In our group, a large variety of organic–inorganic polymer hybrids have been prepared through physical interactions such as hydrogen bonding,^{14,15} aromatic,^{16,17} and ionic interactions¹⁸ between organic polymer and silica gel. The third one is “in-situ polymerization”, which means the polymerization of organic monomer and the formation of silica gel occurred at the same time.^{19,20} The polymer hybrids having interpenetrating polymer network structure have also been prepared by simultaneous formation of metal complex organic gel and silica gel²¹ or an in-situ

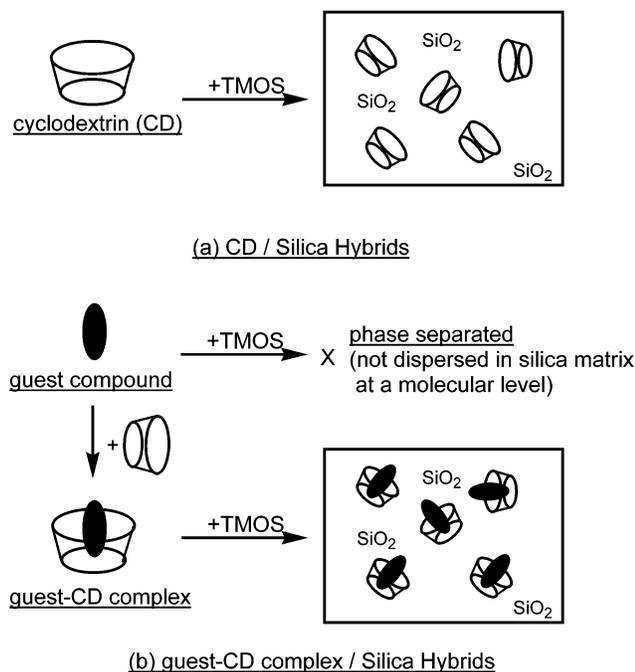


polymerization of vinyl monomers^{22,23} in a sol–gel reaction mixture. The advantage of the in-situ method is that the polymer hybrids could be prepared without any physical or chemical interactions between organic polymer and inorganic material.

The method for preparation of polymer hybrids in this article is utilizing cyclodextrin as a compatibilizer between organic polymer and silica gel (Scheme 1c). It is possible that the mixing order of the obtained organic–inorganic composites could be controlled from micro- to nanoorder according to the increase of the weights of the compound used as a compatibilizer.

In the present research, cyclodextrins (CDs) are used as the compatibilizer. CDs are a series of cyclic oligosaccharides containing six to eight glucose units linked by α -1,4-linkages. The outside of the CD is hydrophilic depending on a large number of hydroxyl groups, while the inside of the CD is hydrophobic resulting from the alkyl moiety. Thus, CDs form inclusion complexes with various hydrophobic compounds in an aqueous solution.

Scheme 2

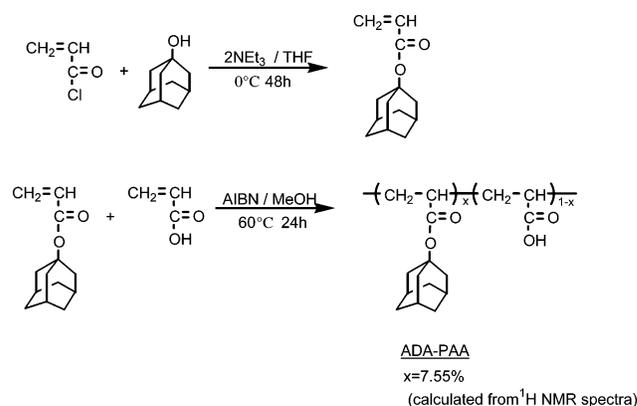


It is known that the adamantane moiety forms a strong complex with β -CD.²⁴ Furthermore, Harada reported that CDs formed polyrotaxane-type inclusion complexes not only with hydrophilic polymers such as poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), and poly(methyl vinyl ether) (PMVE) but also with hydrophobic polymers such as oligoethylene, polypropylene (PP), and polyisobutylene (PIB).^{25–29} In this study, transparent polymer hybrids were prepared by utilizing these guest–CD complexes.

Transparent and homogeneous hybrids of CDs and silica gel can be obtained because the outside of CDs has many hydroxyl groups as the strong hydrogen acceptor (Scheme 2a). Thus, the formation of transparent polymer hybrids of the complex of the guest with CD and silica gel can be expected, while the guest alone (without CD) cannot be dispersed in silica matrix at the molecular level (Scheme 2b). The advantage of utilizing CD as a compatibilizer is that transparent polymer hybrids can be prepared by utilizing hydrophobic interaction. Because hydrophobic interaction usually exists in a hydrophilic environment, the phase separation between hydrophobic and hydrophilic parts should take place. On the other hand, it is possible to disperse organic polymer in the silica matrix at the nanometer level utilizing CD. The CD is expected to play a role as a nanosize host compound in a nanoscale field of the hydrophobic interaction. It is the first example that the transparent and homogeneous polymer hybrids could be prepared utilizing host–guest interactions.

The organic–inorganic polymer hybrids of the guest modified polymer and silica gel are prepared utilizing the complexation of the guest with CD. Polyrotaxane-type polymer–CD complex/silica hybrids were also prepared by using a similar method. It is interesting to note that the organic–inorganic polymer hybrids of polyolefin and silica gel can be prepared by utilizing the main-chain-type polymer–CD complex. It is little known that the polyolefin is dispersed in a silica matrix at the nanometer level because there is no interaction between polyolefin and silica gel.

Scheme 3



Experimental Section

Materials. Poly(vinyl alcohol) (PVA) (DP = 500) and poly(ethylene glycol) (PEG) of average molecular weight 2000 were purchased by Nakarai Tesque Inc. Poly(acrylic acid) (PAA) of average molecular weight 5000 were obtained from Wako Pure Chemical Industries, Ltd. Polyisobutylene (PIB) ($M_w = 1350$) was obtained from Polysciences, Inc. Poly(2-methyl-2-oxazoline) (POZO) ($M_n = 6300$, $M_w/M_n = 1.64$) polystyrene standard; eluent, DMF) was prepared by the ring-opening polymerization of 2-methyl-2-oxazoline initiated by methyl *p*-toluenesulfonate. Tetramethoxysilane (TMOS) was distilled and stored under nitrogen. Dimethylformamide (DMF) was dried and distilled over magnesium sulfate under reduced pressure and stored under nitrogen. Tetrahydrofuran (THF) was dried and distilled over sodium under nitrogen. Acryloyl chloride and acrylic acid were distilled under reduced pressure and stored under nitrogen. Triethylamine was dried and distilled over calcium hydride under nitrogen. Methanol was dried and distilled from magnesium methoxide. The other solvents and reagents were used as supplied.

Measurements. The ¹H NMR spectra were recorded on a 270 MHz JEOL-JNM-GX270 NMR spectrometer. Thermogravimetric analysis (TGA) was performed using a TG/DTA6200, SEIKO Instruments, Inc., with a heating rate of 10 °C min⁻¹ in air. Scanning electron microscopy (SEM) measurements were conducted using a JEOL JNM-5310/LV system. Nitrogen adsorption porosimetry was conducted with a BEL Japan Inc. Powder X-ray diffraction patterns were taken by using Cu K α radiation with a Shimadzu XRD-600. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer.

Synthesis of Adamantane-Modified Acrylic Acid (ADA–AA). The synthetic route is shown in Scheme 3. Under a nitrogen atmosphere, 1-adamantanol (3.78 g, 24.7 mmol) and triethylamine (7.00 mL, 50.2 mmol) were dissolved in 25 mL of THF. The resulting mixture was cooled to 0 °C, and then 25 mL of THF containing acryloyl chloride (2.50 mL, 30.8 mmol) was added dropwise over a 30 min period. The mixture was stirred for 48 h. After removal of insoluble salts by filtration, the filtrate was concentrated under reduced pressure. The residue was washed with water to remove triethylamine·HCl salts. The white solid (ADA–AA) (2.67 g, 13.0 mmol, yield 52.3%) was obtained. ¹H NMR (CDCl₃): δ 6.29 (d, 1H, vinyl), 6.01 (q, 1H, vinyl), 5.78 (d, 1H, vinyl), 2.16 (s, 3H, adamantane), 1.76 (s, 6H, adamantane), 1.63 (s, 6H, adamantane).

Synthesis of Adamantane-Modified Poly(acrylic acid) (ADA–PAA). The synthetic route is shown in Scheme 3. Under a nitrogen atmosphere, ADA–AA (1.00 g, 4.85 mmol), acrylic acid (2.99 mL, 43.7 mmol), and AIBN (0.16 g, 0.97 mmol) were dissolved in 20 mL of methanol, and the mixture was stirred at 60 °C for 24 h under a nitrogen atmosphere. The resulting solution was poured into chloroform. The white precipitate was collected by filtration and dried in a vacuum to produce the white solid (ADA–PAA) (4.12 g, 48.2 mmol, yield ~100%). The degree of substitution of the adamantane

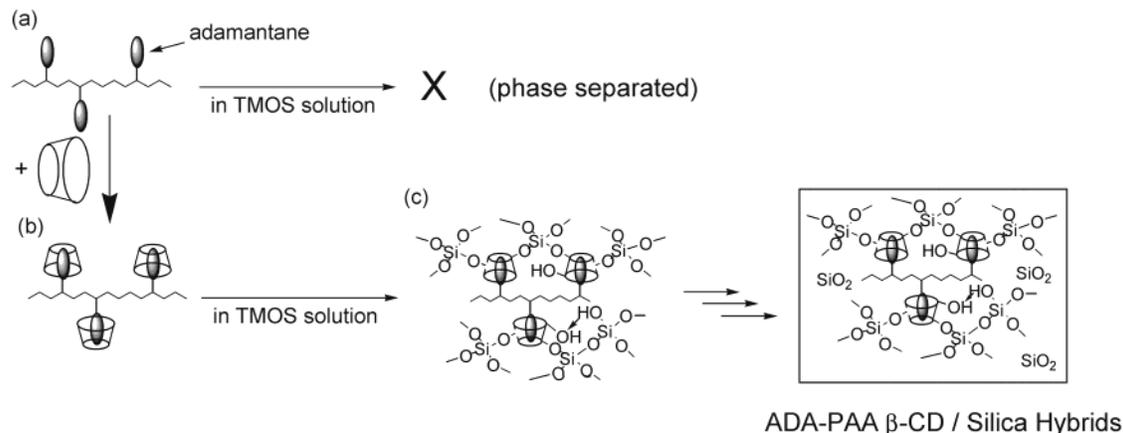


Figure 1. Synthetic route of organic-inorganic polymer hybrids from ADA-PAA- β -CD.

group determined by ^1H NMR was found to be 7.17%. ^1H NMR (CDCl_3): δ 2.44 (m, $\text{CH}_2\text{-CH-COO}$), 2.15 (m, adamantane), 1.93–1.34 (m, $\text{CH}_2\text{-CH-COO}$ and adamantane).

Synthesis of the Inclusion Complexes of Poly(ethylene glycol) with β -CD (β -CD-PEG) and Polyisobutylene with γ -CD (γ -CD-PIB). A polyrotaxane-type CD-polymer complex was synthesized according to the literature.²⁷ The polymer samples were put into tubes. A saturated aqueous solution of CD was added at room temperature, and the mixtures were ultrasonically agitated for 10 min and then allowed to stand overnight at room temperature. The precipitated products were collected by centrifugation, washed with THF, and then dried in a vacuum at 60 °C to make the complexes.

Synthesis of Organic-Inorganic Polymer Hybrids in an Aqueous Solution. When TMOS was put into an aqueous solution, two separated TMOS/water phases were observed because of poor solubility of TMOS in an aqueous solution. But the phase-separated solution became transparent and homogeneous solution by vigorously stirring for some time. ADA-PAA and β -CD were dispersed in an aqueous solution (Figure 1a). ADA-PAA was not easily dissolved in an aqueous solution because of poor solubility of adamantane moiety. Then the aqueous solution suspended with ADA-PAA became transparent solution by sonication (Figure 1b). It means that the strong host-guest complex is formed in an aqueous solution between ADA-PAA and β -CD. TMOS was added to the mixture, and the resulting mixture was stirred in a sealed bottle for 72 h before allowing the solvent to evaporate at room temperature (Figure 1c). The resulting samples were dried in a vacuum oven at 80 °C to remove solvents completely.

Synthesis of Organic-Inorganic Polymer Hybrids Utilizing β -CD-PEG and γ -CD-PIB. The β -CD-PEG or γ -CD-PIB complex was dissolved in DMF with prescribed amounts of TMOS and 0.1 M HCl_{aq} . The resulting mixture was stirred in a sealed bottle for 5 h before allowing the solvent to evaporate at 60 °C. To prevent the evaporation of TMOS, the preparation of polymer hybrids was carried out in a bottle covered with an aluminum foil having a few pinholes. The resulting samples were dried in a vacuum oven at 80 °C to remove solvents completely.

Nitrogen Adsorption Porosimetry. The powder of polymer hybrids was heated at 600 °C in an ambient atmosphere for 24 h to remove organic components. The sample was dried at 150 °C for 2 h at reduced pressure under a nitrogen atmosphere before porosimetry measurements. The surface area was calculated with the Brunauer-Emmet-Teller (BET) equation³⁰ in the range of 0.05–0.30 (p/p_0), and the pore size distribution was calculated by the MP method³¹ or the Barrett-Joyner-Halenda (BJH) method.³²

Results and Discussion

Synthesis of Organic-Inorganic Polymer Hybrids in an Aqueous Solution. The hydrogen-bonding

Table 1. Synthesis of Organic-Inorganic Polymer Hybrids in an Aqueous Solution

run	organic component ^a (mg)	TMOS (mg)	H ₂ O (mL)	appearance
1	PVA 50	250	3	transparent
2	PAA 100	500	3.5	phase separated
3	POZO 100	500	3.5	precipitated
4	PEG 100	500	3.5	precipitated
5	α -CD 150	1500	20	transparent
6	β -CD 150	1500	20	transparent
7	γ -CD 150	1500	20	transparent

^a PVA = poly(vinyl alcohol), PAA = poly(acrylic acid), POZO = poly(2-methyl-2-oxazoline), and CD = cyclodextrin.

interaction between silanol groups resulting from hydrolysis of TMOS and organic polymers is a key to be achieving homogeneous dispersion of organic polymers in the silica gel matrix. Organic polymers having strong hydrogen-accepting groups such as amide groups could be incorporated into a silica gel matrix at the molecular level. For example, transparent polymer hybrids were obtained using POZO or PEG as organic polymers with TMOS in a wide range in the case of methanol used as a solvent for the sol-gel reaction.^{14,15} In the present experiment, organic-inorganic polymer hybrids were prepared in an aqueous solution. It was generally thought that the preparation of polymer hybrids in aqueous solution was difficult because TMOS could not be easily mixed with water.⁹ But the heterogeneous aqueous solution of TMOS became a homogeneous solution by vigorous stirring of the mixture. It is recognized that the hydrolysis of TMOS occurs at the interface between TMOS and water by vigorous stirring. Thus, the suspended aqueous solution of TMOS brings about transparent aqueous solution as the hydrolysis of TMOS at the interface with the water is proceeded. Then the organic polymer or CDs were dissolved in the homogeneous sol-gel solution. The results are shown in Table 1.

In the case of poly(2-methyl-2-oxazoline) (POZO) and poly(ethylene glycol) (PEG) used as an organic component, transparent polymer hybrids could not be obtained in an aqueous solution (runs 3 and 4). The hydrogen-bonding interaction between organic polymers containing amide or ether groups and silanol groups should be weaker in an aqueous solution than in methanol. On the other hand, homogeneous and transparent polymer hybrids utilizing poly(vinyl alcohol) (PVA) (run 1) and CDs (run 5–7) could be prepared in an aqueous solution without any difficulties. In the case of DMF used as a solvent, γ -CD/silica hybrids were translucent. The hy-

Table 2. Synthesis of Organic–Inorganic Polymer Hybrids Utilizing CD

run	ADA–PAA (mg)	β -CD (mg)	TMOS (mg)	stirring time (h)	appearance
8	50	50	250	1	turbid
9	50	50	250	72	transparent
10	50		250		not dissolved
11	50	α -CD 50	250		not dissolved
12	50	γ -CD 50	250		not dissolved

droxyl groups in both PVA chain and CDs form a stronger hydrogen-bonding interaction with silanol groups than that of amide groups with silanol groups of silica gel. Thus, it is considered that the self-aggregation of PVA or CDs from intramolecular interaction of hydroxyl groups occurred in the case of DMF or methanol used as a solvent. But the self-aggregation of PVA or CDs should be decreased in an aqueous solution and hydrogen-bonding interaction between hydroxyl groups and silanol groups would be more effective. Thus, transparent and homogeneous polymer hybrids utilizing PVA or CDs could be prepared in an aqueous solution. The transparent polymer hybrids could not be obtained from PAA in an aqueous solution (run 2). In the case of methanol used as a solvent, PAA/silica hybrids also brought about translucent polymer hybrids. The hydrogen-bonding interaction between carbonyl groups of PAA and silanol groups would be weaker compared to amide groups and hydroxyl groups.

Synthesis of Adamantane-Modified Poly(acrylic acid) (ADA–PAA). Poly(acrylic acid) having adamantane groups (ADA–PAA) was synthesized following the route depicted in Scheme 3. Adamantane-modified vinyl monomer (ADA–AA) was first prepared, and then the copolymer of ADA–AA and acrylic acid was synthesized by radical copolymerization initiated by AIBN. In the ^1H NMR, the vinyl group peaks ($\delta = 6.30\text{--}5.74$ ppm) derived from ADA–AA and acrylic acid completely disappeared after radical copolymerization. The degree of adamantane groups determined from ^1H NMR was 7.17%. The structure of ADA–PAA was characterized by ^1H NMR and FT-IR.

Synthesis of Organic–Inorganic Polymer Hybrids in an Aqueous Solution Utilizing Complexation of Adamantane– β -CD (Side Chain Type). Organic–inorganic polymer hybrids were synthesized by the host–guest interaction. Transparent polymer hybrids of the guest compound and silica gel were successfully prepared by the complexation of the guest compound with CDs, which could be dispersed in a silica gel matrix at the molecular level. In this method, transparent and homogeneous polymer hybrids of the guest compound–CD complex and silica gel were obtained even if the guest compound could not be dispersed in a silica gel matrix. In this case, ADA–PAA was used as the polymer having a guest compound. The results are shown in Table 2.

Transparent and homogeneous polymer hybrids were obtained (run 9). On the other hand, the samples with α -CD (run 11) and γ -CD (run 12) and without CD (run 10) did not give transparent polymer hybrids because these samples were not dissolved in aqueous solution by sonication. Among three (α -, β -, γ -) CDs, the strongest host–guest complex with adamantane groups was formed by β -CD.²⁴ Thus, the sample utilizing β -CD could form the complex by sonication and afforded transparent polymer hybrids, while the other samples could not

form the complexes and afforded no transparent polymer hybrids.

Evidence of the Host–Guest Complex Formation by the Fluorescence Technique Utilizing a Dansyl Group. The complexation of ADA–PAA with β -CD in a silica gel matrix was checked by fluorescence spectra utilizing a dansyl group. The dansyl group is a typical fluorescence probe; it is very sensitive to the environment and exhibits strong fluorescence in a hydrophobic environment, and its fluorescence intensity is weakened in bulk water. Thus, strong fluorescence appears in the case of a complex of dansyl with β -CD because of high hydrophobicity of the β -CD cavity.³³ Figure 2 shows fluorescence spectra of the mixture of β -CD and dansyl groups with various concentrations of ADA–PAA in an aqueous solution.

The intensity of the fluorescence peak at around 480 nm decreased with increasing concentration of ADA–PAA, suggesting that the dansyl groups are excluded from the hydrophobic β -CD cavity to the outside bulk aqueous solution with the accommodation of ADA–PAA as a guest in the cavity because the complexation ability of adamantane groups with β -CD is stronger than that of dansyl groups.

The fluorescence spectra of the polymer hybrids were also measured (Figure 3). The polymer hybrid films for fluorescence measurement were prepared on a quartz by casting the reaction mixture. The fluorescence peak of the polymer hybrid was quenched. On the other hand, the fluorescence peak appeared in the case of the sample without ADA–PAA. These results confirm the complex of ADA–PAA with β -CD in a silica gel matrix.

Synthesis of Organic–Inorganic Polymer Hybrids Utilizing Polyrotaxane-Type Polymer–CD Complex in DMF (Main Chain Type). Organic–inorganic polymer hybrids were also prepared utilizing a polyrotaxane-type polymer–CD complex. The results are shown in Table 3. Transparent and homogeneous polymer hybrids from the PIB– γ -CD complex were obtained (runs 13 and 14). On the other hand, the polymer hybrids from PIB and silica gel resulted in the phase separation because PIB was not dissolved in DMF (run 16). The polymer hybrids from γ -CD used as a host compound were also translucent utilizing DMF (run 18). The results mean that the transparent polymer hybrids can be only prepared by complexation of PIB with γ -CD (Figure 5). It is conceivable that the PIB– γ -CD complex disturbs the self-aggregation of γ -CD in DMF. γ -CD would be aggregated as the sol–gel reaction proceeds. But the self-aggregation of γ -CD in the PIB– γ -CD complex should be prevented compared to only γ -CD (without PIB). The physical entrapment of PIB– γ -CD by the silica cage would effectively deter self-aggregation of γ -CD. It is also thought that the local concentration of γ -CD should be decreased by formation of the PIB– γ -CD complex because the PIB– γ -CD complex is found to be 3:1 (monomer unit: γ -CD).

The PEG– β -CD/silica hybrid was translucent, although transparent polymer hybrid of PEG and silica gel was obtained (runs 15 and 17). The hybrid of β -CD and silica gel, as well as the hybrid of γ -CD and silica, resulted in translucent polymer hybrids in DMF (run 19). It is considered that β -CD might be removed from the PEG– β -CD complex due to the high solubility of PEG in DMF, resulting in the self-aggregation of β -CD. In contrast, PIB was not dissolved in DMF, so the PIB– γ -CD complex would be stable in DMF.

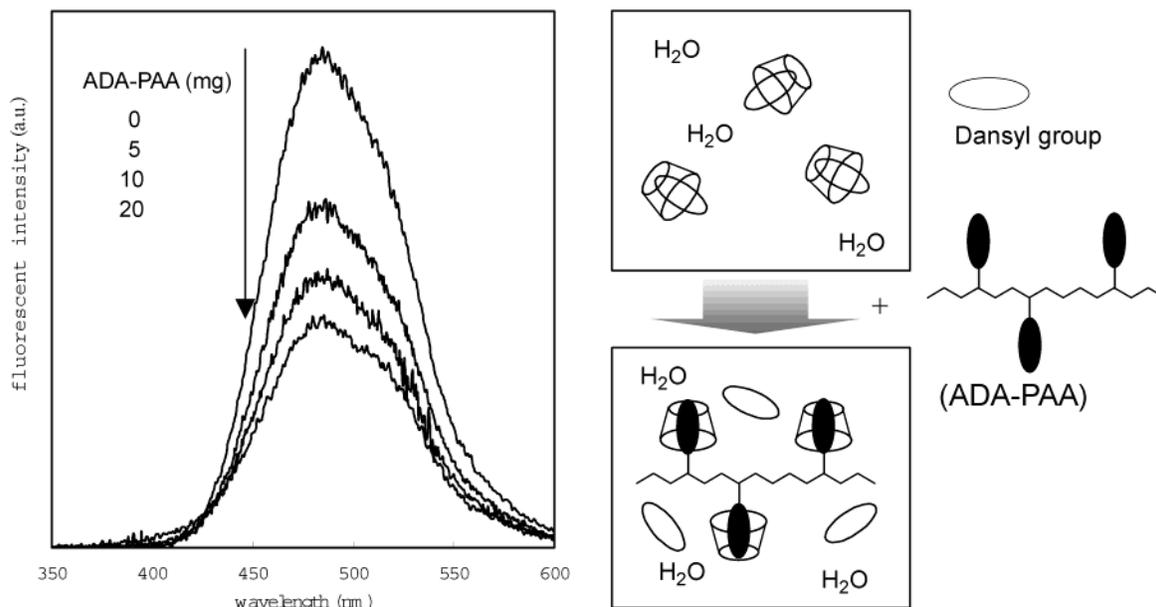


Figure 2. Fluorescence emission spectra of the dansyl chloride (5 mg) and β -CD (100 mg) in 10 mL of aqueous solution and in the presence of various concentrations of ADA-PAA (excitation at 340 nm).

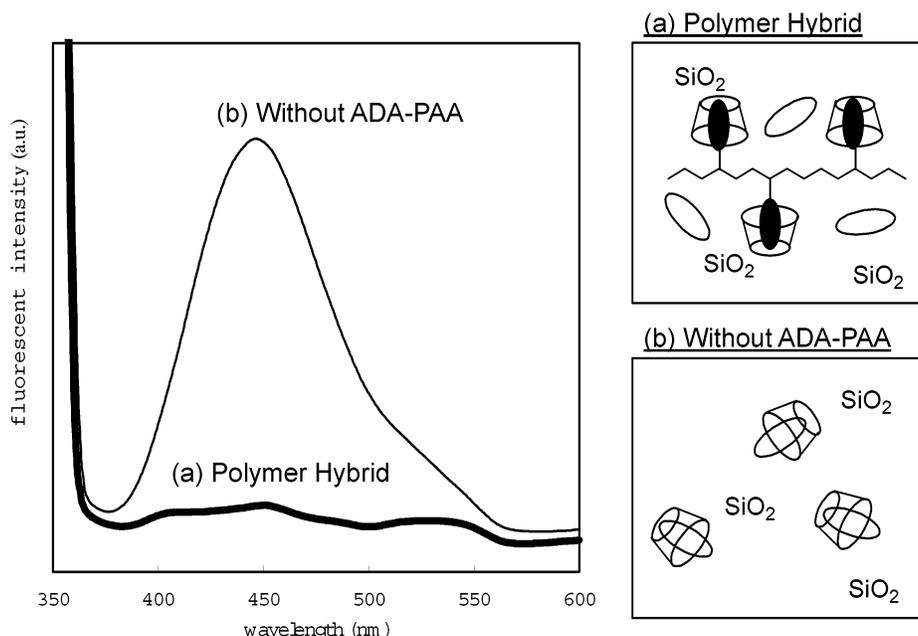


Figure 3. Fluorescence emission spectra of (a) the polymer hybrid film (casting from the 10 mL aqueous solution of dansyl chloride, 1 mg; β -CD, 100 mg; TMOS, 250 mg; and ADA-PAA, 50 mg) and (b) the film without ADA-PAA (excitation at 340 nm).

Table 3. Synthesis of Organic-Inorganic Polymer Hybrids Utilizing CD (Main Chain Type)^a

run	organic component (mg)	TMOS (mg)	DMF (mL)	appearance	organic content (wt %)	
					calcd	obsd
13	PIB ^b - γ -CD complex 20	200	10	transparent	20.0	31.9
14	PIB ^b - γ -CD complex 40	200	15	transparent	33.3	39.8
15	PEG ^c - β -CD complex 20	200	5	translucent		
16	PIB20	200	10	not dissolved		
17	PEG 20	200	5	transparent	20.0	33.8
18	γ -CD 20	200	5	translucent		
19	β -CD 20	200	5	translucent		

^a 0.1 M HCl_{aq} 0.03 mL, stirring time 5 h, evaporating temperature at 60 °C. ^b Polyisobutylene $M_w = 1350$. ^c Poly(ethylene glycol) $M_w = 2000$.

XRD Pattern of Organic-Inorganic Polymer Hybrids (Main Chain Type). The XRD pattern of organic-inorganic polymer hybrids was measured (Figure 5). In the case of the polymer hybrid (Table 3, run

13), the characteristic broad peak appeared around 25° (Figure 5a). This is a halo peak resulting from the amorphous state of silica. In contrast, X-ray pattern of the PIB-CD complex was observed (Figure 5b). It

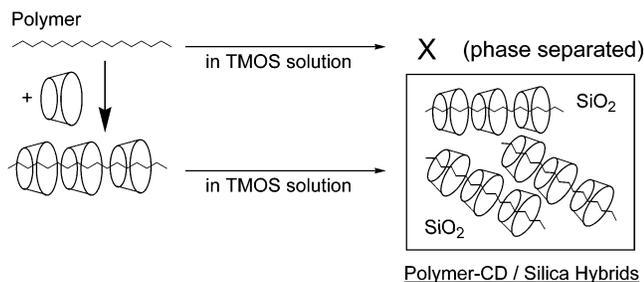


Figure 4. Method of synthesis of polymer hybrids from main-chain type polymer–CD complex.

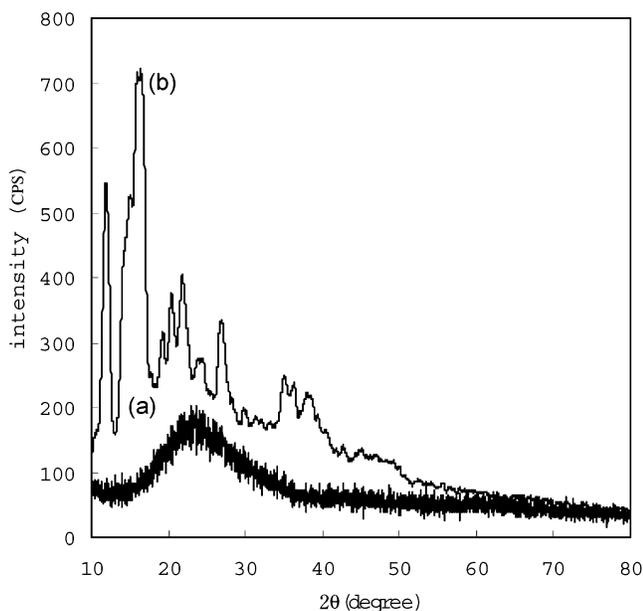


Figure 5. XRD pattern of (a) PIB– γ -CD complex/silica hybrid (Table 4, run 13) and (b) PIB– γ -CD complex.

means that high crystalline PIB–CD complex is dispersed in silica gel matrix.

SEM Images of Organic–Inorganic Polymer Hybrids. The dispersity of two phases between organic polymer and silica gel was examined by SEM (Figure 6). Phase separation of translucent polymer hybrid (run 15) was observed (Figure 6a). Bright spots indicated silica, and the size of silica domain was calculated to be 0.5 μm . In contrast, in the case of the samples of both the ADA–PAA complex/silica hybrid (run 9) and PIB–CD complex/silica hybrid (run 13), the bright spot is dispersed completely (Figure 6b,c). It is thus expected that silica is dispersed at the nanometer level. The size of the organic polymer domain in silica gel matrix was measured by the nitrogen adsorption of porous silica prepared from polymer hybrids.

Pore Size Distribution of Porous Silica Obtained from Organic–Inorganic Polymer Hybrids. The homogeneous polymer hybrids were investigated by measuring the pore size of porous silica obtained by charring polymer hybrids at 600 $^{\circ}\text{C}$ in an ambient atmosphere for 24 h (Figure 7). The organic parts would be removed from polymer hybrids by sintering the hybrids at 600 $^{\circ}\text{C}$. The silica gel lattice is so rigid that it would not be affected at this temperature. Therefore, the size of the remained pores is expected to be comparable to the size of the domain of CDs or organic polymer. A surface area and a pore volume were calculated by the BET method,³⁰ and a pore size was determined by the MP method³¹ or the BJH method³²

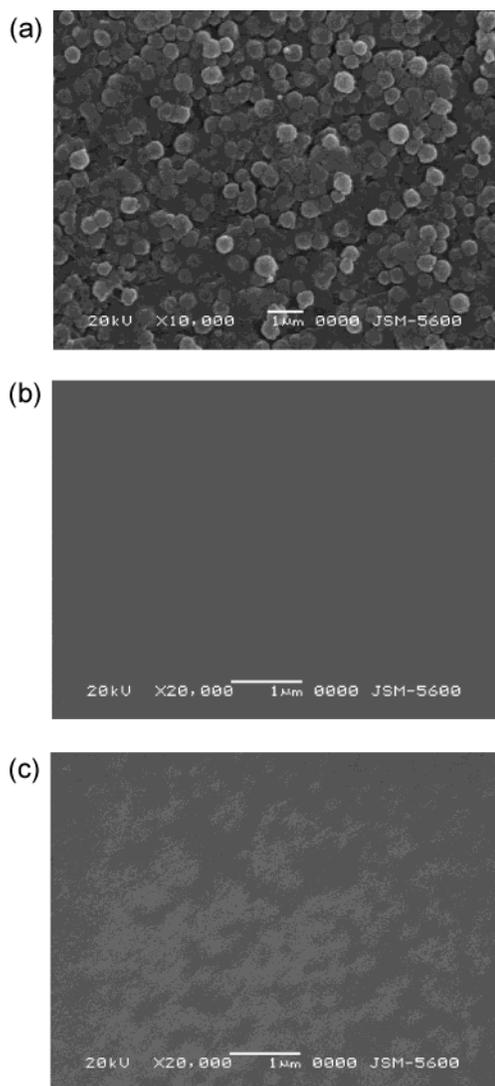


Figure 6. SEM images of the polymer hybrids from (a) PEG– β -CD complex (Table 3, run 15), (b) PIB– γ -CD complex (Table 3, run 13), and (c) ADA–PAA– β -CD complex (Table 2, run 9).

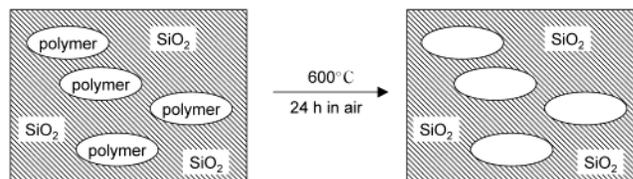


Figure 7. Formation of porous silica from the polymer hybrid.

Table 4. Porosity of the Silica Obtained from Polymer Hybrids

run	pore vol ^a (mL/g)	surf. area ^a (m ² /g)	pore radius ^b (nm)
1	62.4	271.4	1.7
5	48.4	210.6	0.50
6	45.2	196.8	0.50
7	52.1	226.6	0.53
9	42.8	186.1	0.56, 1.6
13	43.8	188.3	>2.0 ^c

^a Calculated by BET. ^b Calculated by MP or BJH methods. ^c Porous silica from run 13 had a pore below 2 nm.

(Table 4). As shown in Table 4, all of the porous silica obtained from transparent polymer hybrids had a quite large pore volume and a surface area. The porous radius of the porous silica calculated from MP or BJH methods

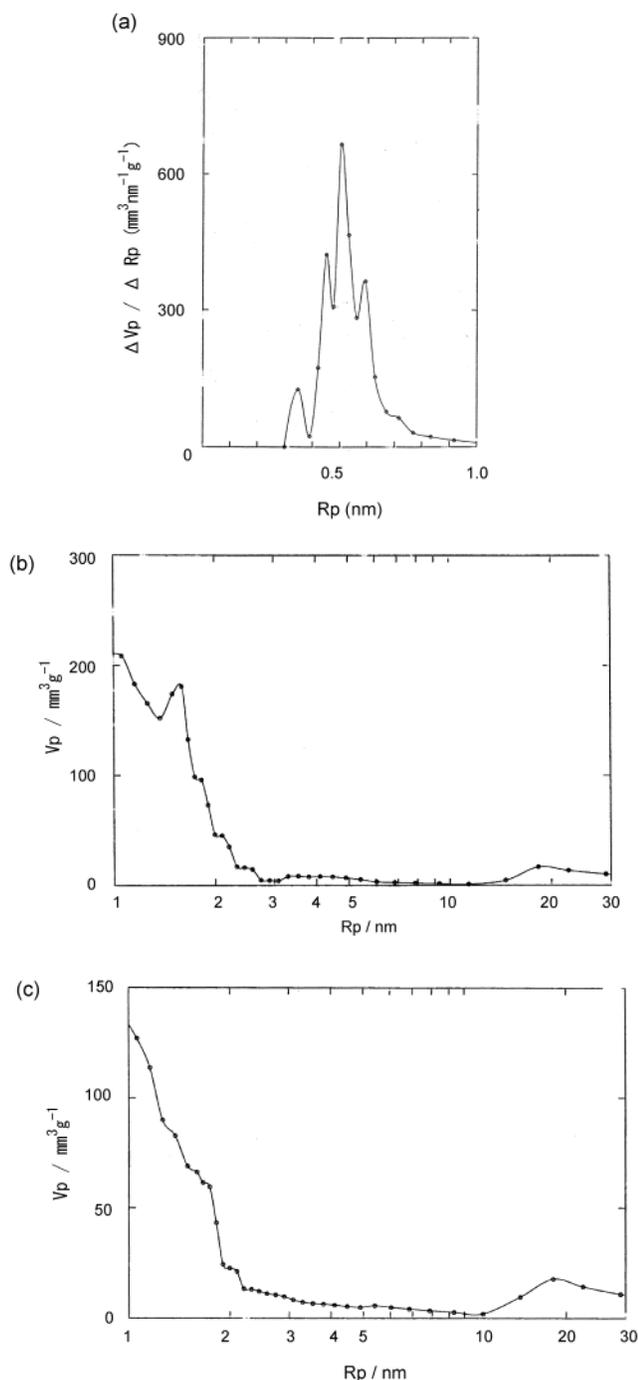


Figure 8. Pore size distribution plots of porous silica obtained from (a) β -CD/silica hybrid (Table 1, run 6), (b) polymer hybrid of ADA-PAA- β -CD complex/silica (Table 2, run 9), and (c) PIB- γ -CD/silica hybrid (Table 4, run 13).

was below 2.0 nm. The results show the presence of nanopores in the silica matrix. It is considered that CDs or organic polymer are dispersed in a silica matrix at the molecular level because the pore size is consistent to the domain of the CDs or organic polymer. In the case of porous silica from CDs and silica hybrids (runs 5–7), the pore size calculated from the MP method was almost equal to the cavity size (Figure 8a). The size of the porous silica from organic polymer/silica hybrids calculated from the BJH method was from 1 to 2 nm (Figure 8b,c). It is assumed that the pore size might be compa-

table to the domain size of organic polymer in the polymer hybrids.

Conclusions

Transparent and homogeneous polymer hybrids were prepared utilizing the ADA-PAA- β -CD complex or the polyrotaxane-type PIB-CD complex. The complexation of ADA-PAA- β -CD in a silica matrix was measured by the fluorescence-probe using dansyl moiety. CD played a role as a compatibilizer between organic polymer and silica gel because only ADA-PAA or PIB was not dispersed in silica gel matrix. The obtained porous silica by calcination of polymer hybrids had nanopores. It is thought that the polymer-CD complexes are dispersed in a silica gel matrix at the nanometer level.

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