Articles

Synthesis of Organic−Inorganic Polymer Hybrids Having Interpenetrating Polymer Network Structure by Formation of Ruthenium−Bipyridyl Complex

Tomoki Ogoshi, Hideaki Itoh, Kyung-Min Kim, and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

Received May 10, 2001; Revised Manuscript Received October 15, 2001

ABSTRACT: Organic−inorganic polymer hybrids were prepared by an in-situ method. In the presence of ruthenium salt, the cross-linking reaction of bipyridyl-containing polymer was carried out together with the sol−gel reaction of tetramethoxysilane. This methodology includes the simultaneous formation of silica gel and organic gel. Using polystyrene or poly(ethylene oxide) having bipyridyl groups, organic−inorganic polymer hybrids could be prepared. The obtained polymer hybrids having IPN (interpenetrating polymer network) structure showed excellent solvent-resistant property.

Introduction

Nanocomposite materials of inorganic materials and organic polymers have received great attention.[1−3] The sol−gel technique of alkoxysilanes is one of the most popular methods to prepare organic−inorganic polymer hybird.[4−7] The advantage of the sol−gel technique is that the reaction proceeds at ambient temperature, while the conventional melt fusion technique for silica glass requires high temperature. Also, the reaction is performed in low-viscosity solution that allows high uniformity if the organic parts can be dissolved in the initial solution.

Generally, there are three kinds of structures of polymer hybrids available using the sol−gel reaction (Figure 1). The first utilizes the covalent bonds between the organic components and silica. These polymer hybrids are prepared by the sol−gel reaction in the presence of alkoxysilane-modified organic polymers.[8−10] The second is linear polymers dispersed in the three-dimensionally cross-linked silica network, a "semiinterpenetrating polymer network (semi-IPN)". The third one is an entangled combination of organic gel and silica gel, which is called a "complete IPN". We have recently explored two methods to prepare various structures of the organic−inorganic polymer hybrids as mentioned above.

Physical interactions, such as hydrogen bonding,[11−13] aromatic,[14] and ionic[15] interactions, between organic polymer and silica gel were explored to prepare semi-IPN polymer hybrids. The other approach is "in-situ polymerization", which means that the polymerization of organic monomer and the formation of silica gel occurred at the same time. The advantage of in-situ method is that the polymer hybrids could be prepared without any physical or chemical interactions between organic component and inorganic material. For example, using the in-situ method of styrene monomer and tetramethoxysilane, polystyrene can be uniformly dispersed in silica gel at a nanometer domain size without any aggregation.[16]

Also, there are two methods to prepare the IPN polymer hybrids. One is to make semi-IPN polymer hybrids using reactive functional groups modified organic polymers. The cross-linking reaction of organic polymers having reactive functional groups were conducted in silica matrix by photoirradiation[17,18] or heating[19] to prepare the IPN polymer hybrids. Another example utilizes the in-situ polymerization method in which radical copolymerization between vinyl monomers and bifunctional vinyl monomers were carried out simultaneously in the sol−gel reaction.[20,21] It is known that the IPN polymer hybrids show better solvent-resistant properties than semi-IPN polymer hybrids.[17,19−21]

In this study, we prepared polymer hybrids by utilizing a different type of in-situ method. It is known that it is difficult to make polymer hybrids using poly(ethylene oxide) and tetramethoxysilane because of the high crystallinity of organic components.[22] In the present research, ruthenium−bipyridyl complex formation between organic polymers with bipyridyl groups was utilized to obtain organic gel in a sol−gel reaction. Gelation of bipyridyl-modified polymers and formation of silica gel from tetramethoxysilane took place simultaneously. By utilizing this method, two different kinds of polymer hybrids of polymer gel and silica gel could be prepared. Furthermore, a ternary system of polymer hybrids, which is a mixture of hydrophobic polystyrene gel and hydrophilic poly(ethylene oxide) gel in the silica matrix, could also be obtained. Ruthenium−bipyridyl complexes are interesting as visible light-responsive photochemical devices or photocatalysts.[23,24] It is little known that the ruthenium−bipyridyl complex was dispersed in the silica gel matrix.

10.1021/ma010819c CCC: $22.00

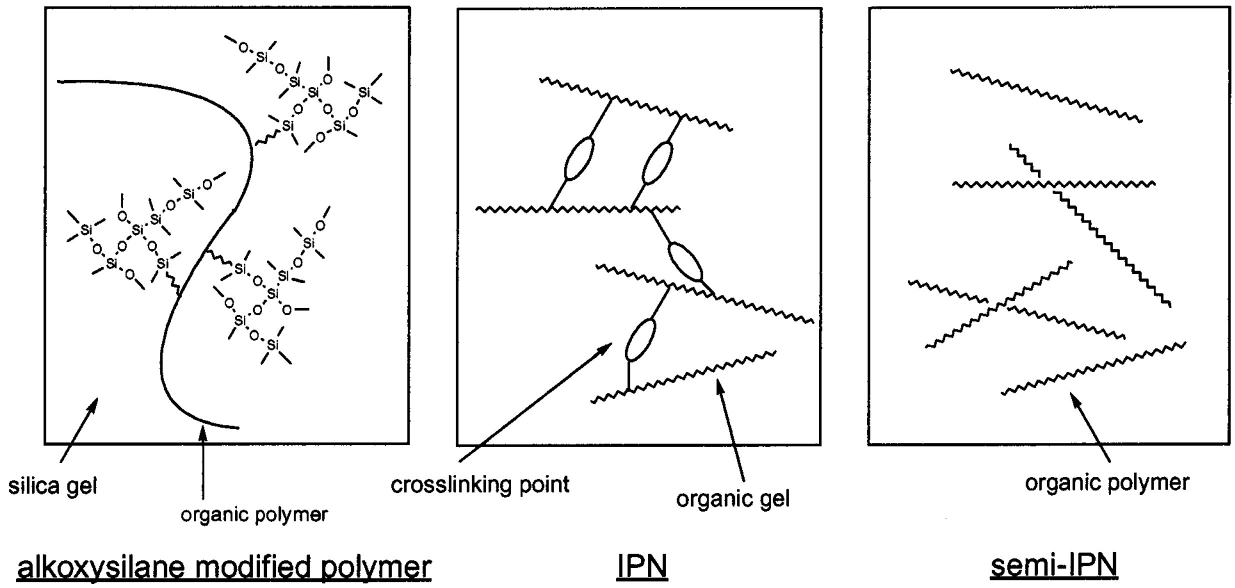
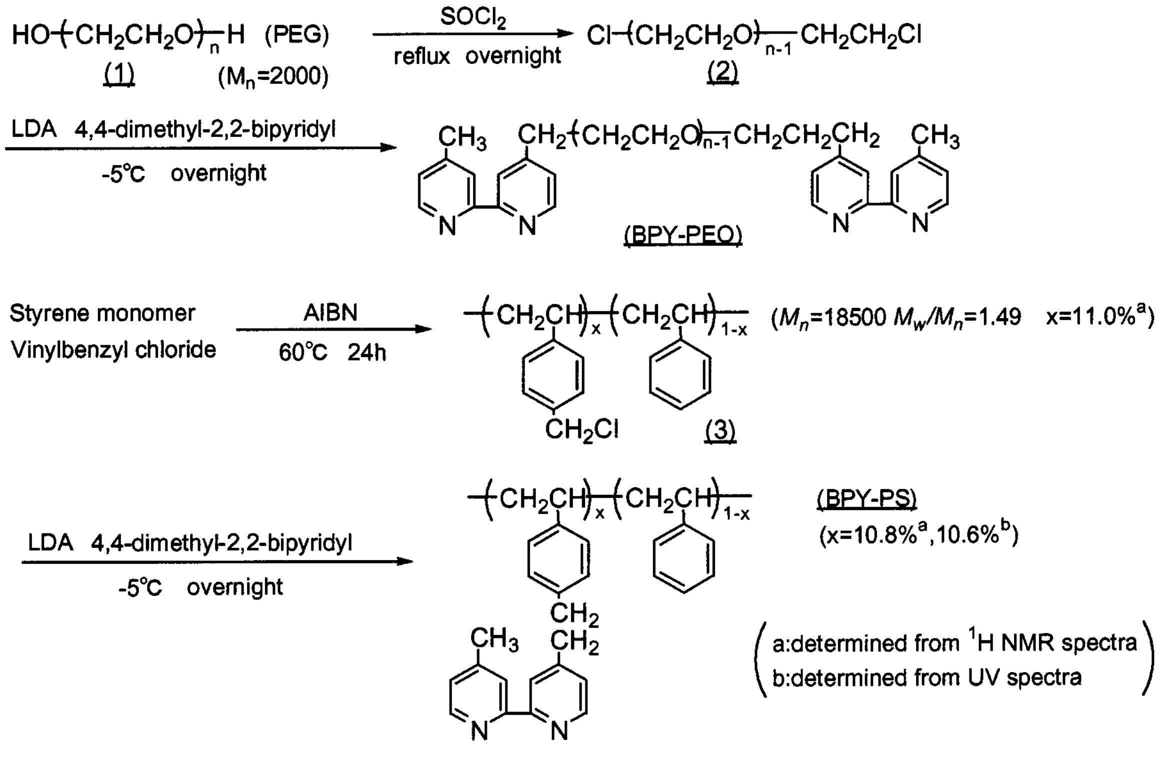


Figure 1. Structures of organic–inorganic polymer hybrids.

Scheme 1



Experimental Section

Materials. All solvents and reagents were used as supplied except the following. Tetramethoxysilane (TMOS) was distilled and stored under nitrogen. Benzene was dried and distilled over magnesium sulfate and then 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. Ethanol was dried and distilled from magnesium ethoxide.

Measurements. The ^{1}H NMR spectra were recorded on a 270 MHz JEOL-JNM-GX270 NMR spectrometer. The UV absorption spectra were obtained on a JASCO V-530 spectrophotometer. Thermogravimetric analysis (TGA) was performed using a TG/DTA6200, SEIKO Instruments, Inc., with heating rate of 10 °C min^{-1} in air. Scanning electron microscopy (SEM) measurements were conducted using a JEOL JNM-5310/LV system. The FT-IR spectra were obtained using a Perkin-Elmer 1600 infrared spectrometer.

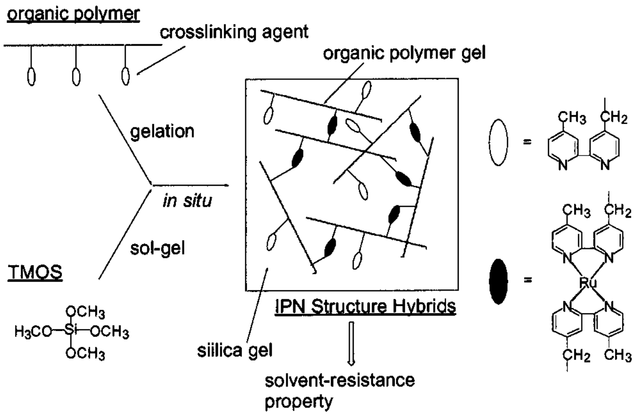
Synthesis of Bipyridyl-Modified Poly(ethylene oxide) (BPY-PEO). The synthetic route is shown in Scheme 1. A mixture of poly(ethylene oxide) (**1**) (5 g, 2.5 mmol, $M_n = 2000$) and thionyl chloride (10 mL) was refluxed for 17 h, and then excess thionyl chloride was removed by evaporation and freeze-dried with 2 mL of benzene. The white solid (**2**) was obtained. Under a nitrogen atmosphere, 4,4′-dimethyl-2,2′-bipyridyl (3.68 g, 20 mmol) was dissolved in 300 mL of THF. The resulting mixture was cooled to −10 °C, and then 10 mL of 2.0 M lithium diisopropylamide (LDA) (20 mmol) was added over a 10 min period by syringe. The mixture was cooled to −78 °C for 1 h. **2** in 50 mL of THF and 60 mL of benzene were added to the dark black solution over a 50 min period by syringe. The mixture was stirred overnight. The reaction was quenched using a small portion of methanol. The dark black

Table 1. Synthesis of Poly(ethylene oxide)/Silica Hybrids

run	BPY-PEO x (h)	$RuCl_3 \cdot 3H_2O$ x (h)	stirring time x' (h)	appearance
1	0[a]	0[a]	0	turbid
2	0[a]	0[a]	1	transparent
3	0[a]	0[a]	3	phase separated
4	0[a]	0.5[a]	1	phase separated
5	1[a]	0[a]	2	turbid
6	1[a]	1[a]	2	phase separated

[a] Adding time of materials.

Scheme 2



solution turned to yellow. Then the resulting solution was concentrated under reduced pressure. The residue was purified by reprecipitation from chloroform into methyl *tert*-butyl ether (MTBE) twice. A white-yellow solid (BPY-PEO) (4.12 g, yield 69.6%) was obtained. ^{1}H NMR ($CDCl_3$): δ 2.43 (s, 3H, Ar$-CH_3$), 2.78 (t, 2H, Ar$-CH_2$), 3.30−3.70 (m, $-CH_2CH_2O-$), 7.12 (m, 4H, bpy), 8.22 (m, 4H, bpy), 8.52 (m, 4H, bpy); UV/vis (CH_3OH): 281 nm [bpy].

Synthesis of Bipyridyl-Modified Polystyrene (BPY-PS). The synthetic route is shown in Scheme 1. Styrene (8.0 mL, 70.4 mmol), vinylbenzyl chloride (1.10 mL), and AIBN (0.128 g, 78.2 mmol) were dissolved in 20 mL of toluene, and the mixture was stirred at 60 °C for 24 h under a nitrogen atmosphere. The resulting solution was poured into methanol. A white solid (**3**) (6.02 g, 55.3 mmol, yield 78.6%) was obtained. The content of the chloromethyl group determined by ^{1}H NMR was found to be 11.0%. Under a nitrogen atmosphere, 4,4′-dimethyl-2,2′-bipyridyl (2.0 g,10 mmol) was dissolved in 150 mL of THF. The resulting mixture was cooled to −10 °C, and 5 mL of 2.0 M lithium diisopropylamide (LDA) (10 mmol) was added over a 10 min period by syringe. Then, the mixture was cooled to −78 °C for 1 h. **2** (3.0 g, 27.6 mmol) in 30 mL of THF was added to the dark black solution over a 30 min period by syringe, and the mixture was stirred overnight. The reaction was quenched using a small portion of methanol. The dark black solution turned to yellow. Then the resulting solution was concentrated under reduced pressure. The residue was purified by reprecipitation from chloroform into methanol. A white-yellow solid (BPY-PS) (3.29 g, 26.3 mmol, yield 95.3%) was obtained. The contents of the bipyridyl group determined by ^{1}H NMR and UV spectra were 10.6% and 10.8%, respectively (THF: $\lambda_{max} = 281$ nm [bpy]), so introduction efficiency was almost quantitative. ^{1}H NMR ($CDCl_3$): δ 1.00−2.00 (m, Ar$-CHCH_2$), 2.43 (m, CH_3-bpy), 2.87 (m, Ph$-CH_2CH_2-$bpy), 6.20−7.20 (m, Ar and bpy), 8.25 (m, bpy), 8.52 (m, bpy).

Preparation of Organic−Inorganic Polymer Hybrids from BPY-PEO and BPY-PS. An ethanol solution of BPY-PEO was added to TMOS, hydrochloric acid (0.1 M, 4 equiv to TMOS), and an ethanol solution (250 mg/25 mL) of ruthenium(III) chloride hydrate. The resulting mixture was stirred in a sealed bottle for a certain time (Table 1) before allowing the solvent to evaporate in air. In the case of BPY-PS, DMF was used as a solvent, and the mixture was heated at 60 °C to evaporate the solvent.

Solvent-Resistant Property of Polymer Hybrids. The powdered hybrids were put in cellulose timbers (28 mm × 100 mm, Whatman Int., Ltd.) and extracted with chloroform and pyridine. After extraction for 1 week, the samples were dried in a vacuum oven at 100 °C.

Results and Discussion

The synthetic route for poly(ethylene oxide) and polystyrene having bipyridyl groups is shown in Scheme 1. In the ^{1}H NMR, in the case of bipyridyl-modified polystyrene, the chloromethyl group peak ($\delta = 4.50$ ppm) derived from the precursor (**3**) completely disappeared after substitution reaction with 4,4′-dimethyl-2,2′-bipyridyl and a bipyridyl group peak appeared at the same time. In **3** (Scheme 1), the content of the chloromethyl group determined from ^{1}H NMR was 11.0%, and in BPY-PS (Scheme 1), the degree of the bipyridyl group calculated from ^{1}H NMR and UV spectra was 10.6% and 10.8%, respectively. So the introduction efficiency of bipyridyl groups was almost quantitative. The structures of BPY-PS and BPY-PEO were characterized by ^{1}H NMR, UV, and FT-IR.

The in-situ method was employed for the synthesis of homogeneous organic gel and silica gel polymer hybrids, which comprises simultaneous gelation of bipyridyl modified organic polymer and formation of silica gel (Scheme 2). Homogeneous and glassy transparent materials were obtained after removal of the solvent.

Generally, the preparation of poly(ethylene oxide)/silica hybrids is difficult because of its high crystallinity. In this study, the polymer hybrids of BPY-PEO/silica were prepared by in-situ methods. As shown in Scheme 2, in the presence of ruthenium salt, the cross-linking reaction of bipyridyl-containing polymer was carried out together with the sol−gel reaction of tetramethoxysilane. The results of the preparation of polymer hybrids (weight of organic/inorganic = 1/8) are summarized in Table 1. In run 1, BPY-PEO, ruthenium salt, TMOS, and HCl_{aq} (0.1 M) were dissolved in EtOH, and then the solvent was evaporated at room temperature. The obtained polymer hybrids were turbid, which means that the sol−gel reaction proceeded imperfectly. It is because poly(ethylene oxide) was highly crystalline, so the sol−gel reaction could not proceed. On the other hand, in run 3, the obtained polymer hybrids were phase separated in two components of poly(ethylene oxide) gel and silica gel. It is confirmed that formation of the organic gel is faster than that of silica gel. In run 2, the obtained polymer hybrids were transparent. The rate of formation of silica gel depended on stirring time

Scheme 3

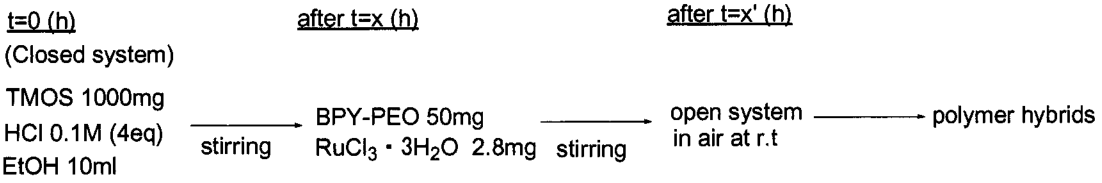


Table 2. Synthesis of Organic−Inorganic Polymer Hybrids[a]

run	BPY-PS (mg)	PBY-PEO (mg)	TMOS (mg)	appearance	polymer content (wt %) calcd	polymer content (wt %) obsd[c]
7	50	0	500	transparent	19.8	50.6
8	100	0	500	transparent	33.1	40.0
9	25	25	500	transparent	19.8	28.0
10 (Cl-PS)	50	0	500	translucent		
11[b]	50	0	500	phase separated		

[a] $RuCl_3{\cdot}3H_2O$ 2.0 mg, HCl_{aq} (0.1 M) 4 equiv to TMOS. [b] Without $RuCl_3{\cdot}3H_2O$. [c] Determined from TGA.

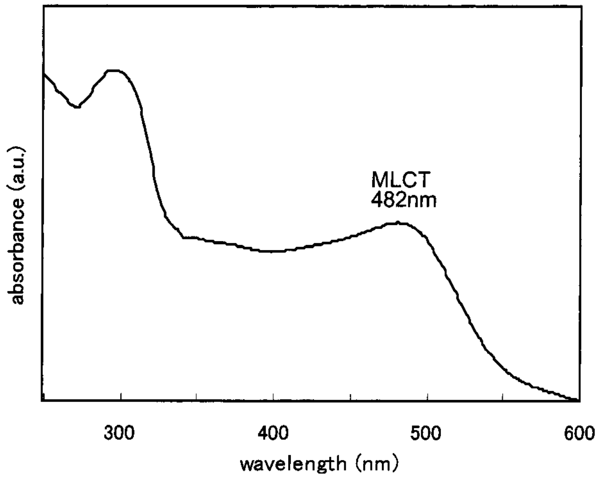


Figure 2. UV spectrum of the hybrid (Table 1, run 2).

(under a closed system), and the rate of gelation of the organic gel depended on putting time of ruthenium salts in this system. So it is considered that the gelation of organic gel by the ruthenium−bipyridyl complex and the formation of silica gel occurred simultaneously in good harmony with each other, so transparent and homogeneous polymer hybrids were obtained. The polymer content calculated was almost same to that measured from TGA analysis in air, which means the sol−gel reaction was accelerated perfectly. The UV spectrum of polymer hybrids is shown in Figure 2. The characteristic absorption around 400−500 nm ($\lambda_{max} = 482$ nm) can be assigned to a metal-to-ligand charge transfer-(MLCT) absorption.[24] This absorption appeared in the case of organic gel without silica gel, so the ruthenium−bipyridyl complex is assumed to form completely in the polymer hybrids. It was considered that the organic polymer was cross-linked by the formation of the ruthenium−bipyridyl complex in the silica matrix.

The IPN structure of bipyridyl-modified polystyrene and silica gel was constructed by the same manner of making poly(ethylene oxide)/silica hybrids (Table 2). Homogeneous and transparent polymer hybrids were prepared by controlling the stirring time and adding time of ruthenium salt. To prevent from evaporating of TMOS, polymer hybrids were prepared and covered with aluminum foil a few pinholes and heated in air at 60 °C, but a little TMOS was evaporated before gelation of TMOS. So organic polymer contents by TGA were different from calculated values. In this system, BPY-PS/Ru ratios were 4. As BPY/Ru ratios was decreased, transparent polymer hybrids could not be obtained. It was considered that organic gel was formed faster than silica gel. The dispersity of two phases was examined by SEM. As shown in Figure 3a, the sample using polystyrene without a bipyridyl group (run 11) showed phase separation resulting from an aggregation of polystyrene in the silica matrix, because there is no interaction between polystyrene and silica gel, and the sample without ruthenium salt (run 10) also showed phase separation between silica gel and the organic polymer. Bright spots indicate silica, from which the size of silica domain could be estimated to be about 10 μm (Figure 3b). On the other hand, in the case of the sample (run 7), the bright spot disappeared completely (Figure 3c), so it was considered that silica was dispersed at the nanometer level. From these results, it was confirmed that the ruthenium−bipyridyl complex plays a role as a cross-linking point in the preparation of homogeneous polymer hybrids.

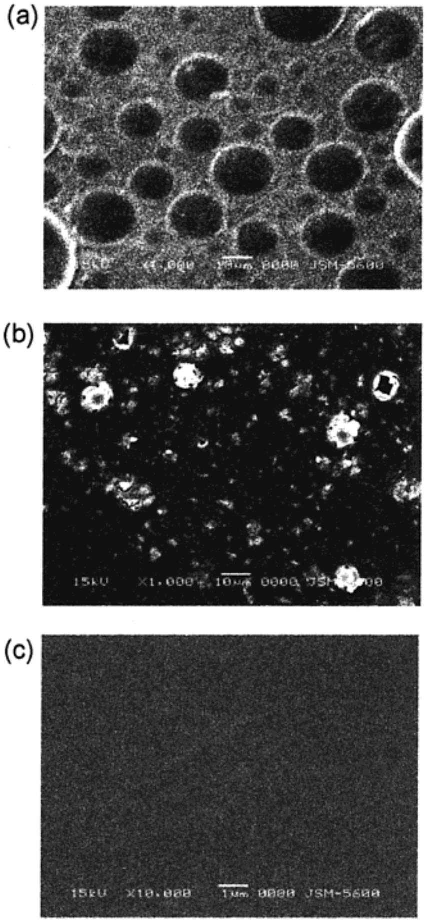


Figure 3. SEM images of the samples: (a) Table 2, run 10; (b) Table 2, run 11; (c) Table 2, run 7.

TGA study of the obtained polymer hybrids is shown Figure 4. In polymer hybrids of **1**, T_{10} was 357 °C, and in the BPY-PS gel of **3**, T_{10} was 313 °C; the polymer hybrids showed higher thermal stability than BPY-PS gel.

The polymer hybrids of polystyrene/poly(ethylene oxide) gel and silica gel were also prepared (run 9). Transparent polymer hybrids were obtained. It was thought that hydrophobic polystyrene gel and hydrophilic poly(ethylene oxide) gel coexisted with highly

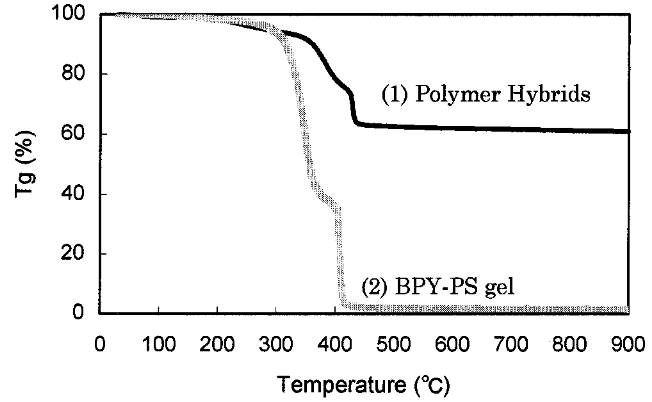


Figure 4. TGA of (1) polymer hybrids (Table 2, run 8) and (2) BPY–PS gel (without silica gel) in air.

Table 3. Solvent-Resistance Property[a]

run	solvent	solvent extraction efficiency (%)	polymer content (wt %)[b]	
			P_a	P_b
8	$CHCl_3$	0.41	39.9	40.0
8	pyridine	9.62	37.6	40.0

[a] The polymer content in polymer hybrids before (P_b) and after (P_a), solvent extraction efficiency E was calculated according to the equation $E = 100(P_b - P_a)/P_b(1 - P_a)$. [b] Measured by TGA.

homogeneous dispersion in the silica matrix. The nanostructure of this polymer hybrids is now under investigation.

The UV spectra of BPY-PS/silica hybrids were also measured. The characteristic absorption peak appeared at around 480 nm. This peak appeared in the case of polystyrene gel by utilizing the ruthenium–bipyridyl complex without silica. The formation of the bipyridyl–ruthenium complex was confirmed in the silica gel matrix.

The solvent-resistant property by the formation of IPN structure was estimated by means of solvent extraction experiments. The obtained hybrids were crushed into powders, which were then extracted with $CHCl_3$ and pyridine. The results are shown in Table 3. Very little organic component was extracted with $CHCl_3$ and pyridine. In the case of using pyridine compared with $CHCl_3$ as a solvent, more organic polymer was extracted. It might be considered that pyridine coordinated to form a ruthenium–pyridine complex. But the coordination ability of the bipyridyl–ruthenium complex was stronger than ruthenium–pyridine complex, so a little organic component was extracted. As shown in Table 3, the polymer hybrids showed excellent solvent-resistant property, so it was considered that the polymer hybrids formed a complete-IPN structure.

Conclusions

Organic–inorganic polymer hybrids having complete-IPN structure were prepared by the in-situ method. Homogeneous polymer hybrids could be obtained by controlling the factors such as adding time of ruthenium salt and the stirring time. Furthermore, the polymer hybrids having hydrophobic and hydrophilic polymer gels at the same time in the silica matrix could be prepared. The obtained polymer hybrids showed an MLCT absorption peak and excellent solvent-resistant property. In conclusion, the IPN polymer hybrids could be prepared by cross-linking reaction by the formation of the ruthenium–bipyridyl complex in the silica matrix.

References and Notes

(1) Special issues of nanostructured materials. *Chem. Mater.* **1996**, *8*, 8.
(2) Beecroft, L. L.; Ober, C. K. *Chem. Mater.* **1997**, *9*, 1302.
(3) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; Wiley: New York, 1983.
(4) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422.
(5) Schubert, U.; Hüsing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010.
(6) Schmidt, H.; Scholze, H.; Kaiser, A. *J. Non-Cryst. Solids* **1984**, *63*, 1.
(7) Brinker, C. J.; Scherer, G. W. *J. Non-Cryst. Solids* **1985**, *70*, 301.
(8) Huang, H.-H.; Orler, B.; Wilkes, G. L. *Macromolecules* **1987**, *20*, 1322.
(9) Wei, Y.; Yang, D.; Tang, L.; Hutchins, M. K. *J. Mater. Res.* **1993**, *8*, 1143.
(10) Wei, Y.; Yeh, J.-M.; Jia, X.; Wang, J. *Chem. Mater.* **1995**, *7*, 969.
(11) Chujo, Y.; Saegusa, T. *Adv. Polym. Sci.* **1992**, *100*, 11.
(12) Saegusa, T.; Chujo, Y. *Makromol. Chem., Macromol. Symp.* **1991**, *51*, 1.
(13) Chujo, Y.; Matsuki, H.; Kure, S.; Saegusa, T.; Yazawa, T. *J. Chem. Soc., Chem. Commun.* **1994**, 635.
(14) Tamaki, R.; Samura, K.; Chujo, Y. *Chem. Commun.* **1998**, 1131.
(15) Tamaki, R.; Chujo, Y. *Chem. Mater.* **1999**, *7*, 1719.
(16) Tamaki, R.; Naka, K.; Chujo, Y. *Polym. Bull.* **1997**, *39*, 303.
(17) Imai, Y.; Naka, K.; Chujo, Y. *Polym. J.* **1998**, *12*, 990.
(18) Imai, Y.; Naka, K.; Chujo, Y. *Macromolecules* **1971**, *4*, 1013.
(19) Imai, Y.; Itoh, H.; Naka, K.; Chujo, Y. *Macromolecules* **2000**, *12*, 4343.
(20) Tamaki, R.; Chujo, Y. *J. Mater. Chem.* **1998**, *5*, 1113.
(21) Tamaki, R.; Horiguchi, T.; Chujo, Y. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2749.
(22) Takahashi, R.; Nakanishi, K.; Soga, N. *J. Sol-Gel Sci. Technol.* **2000**, *17*, 7.
(23) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroi, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26.
(24) Schröder, M.; Stephenson, T. A. Ruthenium. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987.

MA010819C