

Preparation of Silica/Plloxamer Composite by Sol–Gel Process and Pore Control of Silica Gel Obtained from the Composite

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ABSTRACT: Silica gels that controlled the pore size were prepared by calcination of silica/organic polymer (50/50 wt %) composites prepared by the sol–gel process. Poly(ethylene oxide) (PEO)–poly(propylene oxide) (PPO)–PEO triblock copolymers, which are called plloxamers, were used as an organic polymer. The pore control of the silica gels was carried out by changing the molecular weight of PEO or PPO in the plloxamers. The silica gels obtained by the above procedure had a dual pore size of around 4 nm and below 2 nm in diameter, and the specific surface area was 500–1000 m²/g. The plloxamer molecules were supposed to be dispersed monomolecularly in the composites. Therefore, the pore structure of the silica gels reflected the structure of the plloxamer and, particularly, the radius of gyration of PPO in the composites. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 763–768, 1997

Key words: sol–gel process; plloxamer; silica gel; pore size; monomolecular domain

INTRODUCTION

Many studies concerning the preparation of inorganic/organic hybrid materials by the sol–gel process and its application have been carried out, as reviewed by Wen and Wilkes.¹ We studied the preparation of porous silica gels by calcination of silica/organic polymer composites obtained by the sol–gel process.^{2–4} In the case of using silica/poly(vinyl alcohol) (PVA) composites, the pore structure of the silica gel was varied by changing the PVA content or by the drawing of the composite before calcination.^{2,3} On the other hand, the pore size was controlled by changing the molecular weight (MW) of the poly(ethylene glycol) (PEG) in the silica/PEG composite.⁴ From the values of the pore size, we found that PEG molecules will be dispersed approximately monomolecularly in the composites.

In this study, using poly(ethylene oxide) (PEO)–poly(propylene oxide) (PPO) ABA-type block copolymers as the organic polymer, the composites with silica were prepared by the sol–gel process. Also, the pore control of the silica gels obtained by calcination of the composites was carried out. The block copolymers are nonionic surface-active agents which consist of the hydrophilic part of PEO chain and the hydrophobic part of PPO chain and are called plloxamers.^{5,6} By changing the MW of PEO or PPO in the plloxamer, the effect of the MW of each chain for the pore size of the silica gel was investigated using the methods of the fluorescence probe technique, electron spectroscopy for chemical analysis (ESCA), and nitrogen adsorption.

EXPERIMENTAL

Materials

Tetraethoxysilane (TEOS) and hydrochloric acid (HCl), which were the starting compounds to pre-

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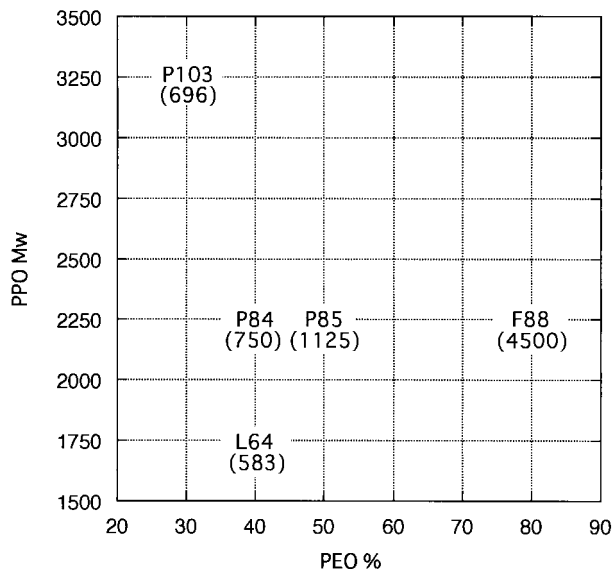
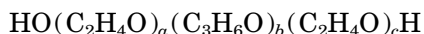


Figure 1 Classification of poloxamer. The MW of PEO in the poloxamer are designated in parentheses.

pare the silica gels, were obtained from the Shinetsu Kagaku Co. and the Kanto Chemical Co., respectively, and used without any purification. Poloxamers with the general formula of



were provided by the Asahi Denka Co., and $a \cong c$ in them. Figure 1 shows the classification of the poloxamers used in this study. The symbols L, P, and F in this figure indicate the liquid, paste, and flake states at room temperature, respectively. The MW of blocks a and/or c in PEO is shown in parentheses. The samples of P84, P85, and F88 have the same MW as that of PPO (MW = 2250) but differ from the MW of PEO. On the other hand, the MW of PEO and those of L64, P84, and P103 were almost similar, but the MW of PPO and those of these samples were different.

Preparation of Silica/Poloxamer (50/50 Wt %) Composite

A silica sol was prepared by hydrolysis and polycondensation by adding dropwise a hydrochloric acid (HCl) aqueous solution (mol ratio of $[\text{HCl}]/[\text{TEOS}] = 0.01$, $[\text{H}_2\text{O}]/[\text{TEOS}] = 4$) to TEOS with stirring at a temperature near 0°C . The poloxamer was added to the silica sol in a drying weight ratio of silica : poloxamer = 1 : 1, and the mixture to prepare the silica/poloxamer blend viscous sol was warmed in a water bath of 50°C

for 2 h. The blend sol was cast and dried on a polystyrene Petri dish at 40°C without the aging process to prepare the wet gel. A silica gel prepared by this method without adding the poloxamer was a nonporous material in spite of being calcined at 600°C .

Apparatus and Procedures

The polar evaluation of the silica/poloxamer blend sol at 50°C was performed by the fluorescence probe technique (fluorescence spectrophotometer Hitachi F-4010) using pyrene (about $3 \times 10^{-6}M$) as a fluorescent dye. The excitation wavelength was 340 nm.

The distribution of silicon, carbon, and oxygen for the depth direction in the composite was measured by ESCA (Shimadzu ESCA 1000). (X-ray [Mg], 10 kV–30 mA; ion gun [Ar+], 2 kV–20 mA; etching time; 0.10 min/div.) The calcination of the composite was performed at 600°C in air for 1 h using an electric furnace, similarly to the case of the silica/PEG composites.⁴

The nitrogen adsorption isotherms (-196°C) of the silica gels were measured by a volumetric apparatus. The pore volume (v) was determined from the nitrogen adsorption amount which was obtained by an extrapolation from the value of above 0.95 of relative pressure to unity. The specific surface area (S) and the average pore diameter (\bar{d}), which was determined by assuming a cylindrical pore shape, were calculated from the adsorption isotherms by applying the finite-layer BET equation.⁷ The pore-size distribution (PSD) curve was obtained from the adsorption isotherm by the Cranston–Inkley method.⁸

RESULTS AND DISCUSSION

The Polar Evaluation of Silica/Poloxamer Blend Viscous Sol with Pyrene

Figure 2 shows the fluorescence spectrum of pyrene in a silica/P84 (50/50 wt %) blend viscous sol at 50°C . It is known that the degree of the polarity around pyrene in the medium is evaluated from the ratio (I_1/I_3) of the intensity of first (I_1) and third (I_3) peaks.^{9,10} If the hydrophobic domain exists in the medium, the values of I_1/I_3 are decreased because pyrene becomes incorporated in it. Table I shows the values of I_1/I_3 for each silica/poloxamer blend viscous sol. As a comparison, the values of the silica/PEG (MW

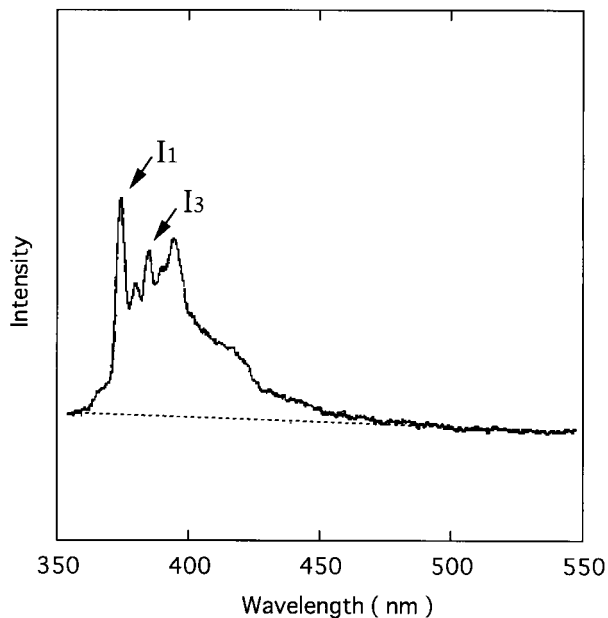


Figure 2 Excitation and fluorescence spectrum of pyrene in silica/P84 (50/50 wt %) blend viscous sol at 50°C.

= 2000) blend sol and water are also shown in this table. The water, which is polar solvent, showed a high value (1.75). The values of the silica/poloxamer blend sol were lower than those of the silica/PEG blend sol which had no PPO chain in the matrix. Also, a tendency was observed in that the values of I_1/I_3 decreased with increasing PPO content and/or MW of PPO in the poloxamer. From these results, we considered that the hydrophobic domain of PPO will exist in the silica/poloxamer blend viscous sol. But the domain size was not able to be evaluated by this method.

Table I The Values of the Intensity Ratio (I_1/I_3) of Silica/Poloxamer (50/50 wt %) Blend Viscous Sol at 50°C

Sample	I_1/I_3^a	PPO Content in Poloxamer (%)
Silica/L64	1.35	60
Silica/P84	1.31	60
Silica/P85	1.31	50
Silica/F88	1.37	20
Silica/P103	1.25	70
Silica/PEG ^b	1.45	0
Water	1.75	—

^a Intensity ratio of pyrene fluorescence at 374 nm (I_1) and 385 nm (I_3) for silica/poloxamer blend viscous sol at 50°C.

^b Silica/PEG (MW = 2000) (50/50 wt %).

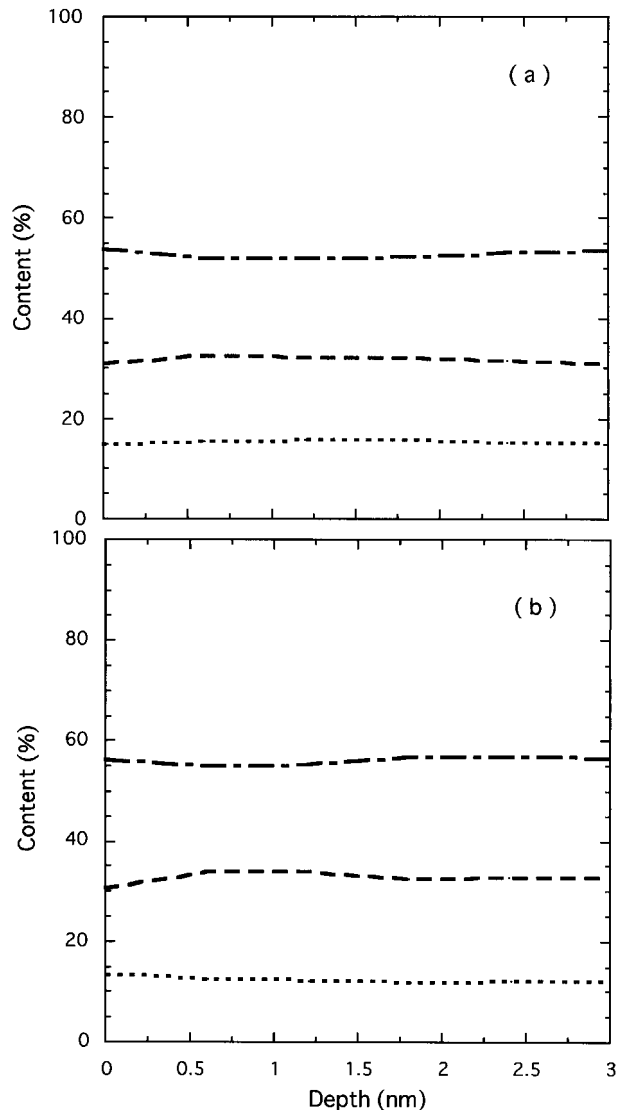


Figure 3 Distribution profiles of the elements from the (a) front and (b) back sides of silica/P84 (50/50 wt %) composite by ESCA measurement: (.....) C (1s); (---) Si (2p); (- - -) O (1s).

ESCA Observations for Silica/Poloxamer Composite

Figure 3 shows the results of the elemental analysis of the silica/P84 composite for the depth direction by ESCA. The measurements were taken on the front (air side) and back (polystyrene dish side) sides of the composite. The distribution of the elements for each side was almost constant, although the depth was shallow within 3 nm. Also, the composition of the front and back sides showed good agreement. Consequently, it is confirmed that silica and the poloxamer were intimately mixed together without the separationlike

Table II Pore Characterizations of Silica Gels Obtained by Calcination (600°C, 1 h) of Silica/Poloxamer Composites

Poloxamer	Pore Volume (mL/g)	Surface Area (m ² /g)	Average Pore Diameter (nm)
P84	0.593	721	3.3
P85	0.590	730	3.2
F88	0.527	706	3.0

layer for the depth direction in the composite obtained.

Pore Control of Silica Gel Obtained by Calcination of Silica/Poloxamer Composite

Effect of MW of PEO in Poloxamer

Table II shows the values of v , S , and \bar{d} of silica gels obtained by calcination of the poloxamer (P84, P85, and F88) in the composites. The value of v decreased and the value of \bar{d} increased with increasing MW of PEO in the poloxamer. (The MW of PPO was constant.) The change of the value of S was not observed. Figure 4 shows the PSD curves of the silica gels obtained. The pore was distributed into two regions which were around 4 nm (mesopore region) and below 2 nm (micropore region) of the pore diameter. The peak

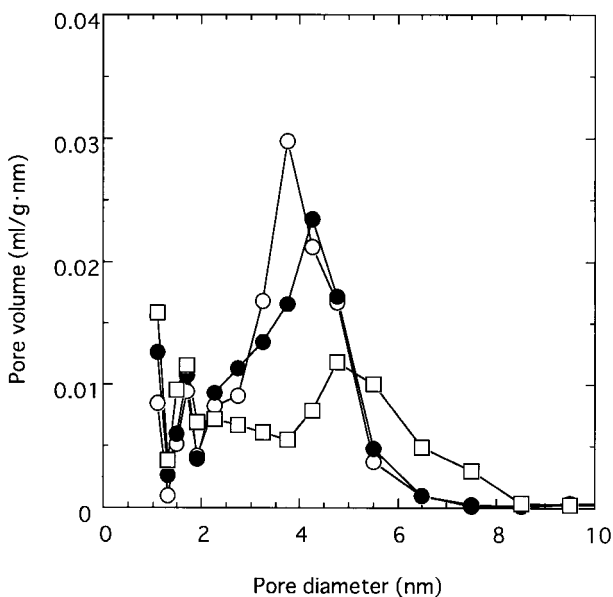


Figure 4 PSD curves for silica gels obtained by calcination of silica/poloxamer (50/50 wt %) composites. Poloxamer: (○) P84; (●) P85; (□) F88.

Table III Pore Characterizations of Silica Gels Obtained by Calcination (600°C, 1 h) of Silica/Poloxamer Composites

Poloxamer	Pore Volume (mL/g)	Surface Area (m ² /g)	Average Pore Diameter (nm)
L64	0.572	944	2.4
P84	0.593	721	3.3
P103	0.597	547	4.4

in the mesopore region was shifted to a large pore size with increasing MW of the PEO in the poloxamer. Also, the pore volume was decreased, but it was increased in the micropore region. The values of \bar{d} in Table II reflect the average values of both pore regions.

Effect of MW of PPO in Poloxamer

Table III shows the values of v , S , and \bar{d} of silica gels obtained by calcination of the composites which were prepared by using L64, P84, and P103. The decrease of the value of S and the increase of the value of \bar{d} were remarkable with increasing MW of the PPO in the poloxamer. Also, the value of v tended to increase slightly. Figure 5 shows the PSD curves. Similarly to Figure 4, the pore was in the micropore and mesopore regions. The peak in the mesopore region was

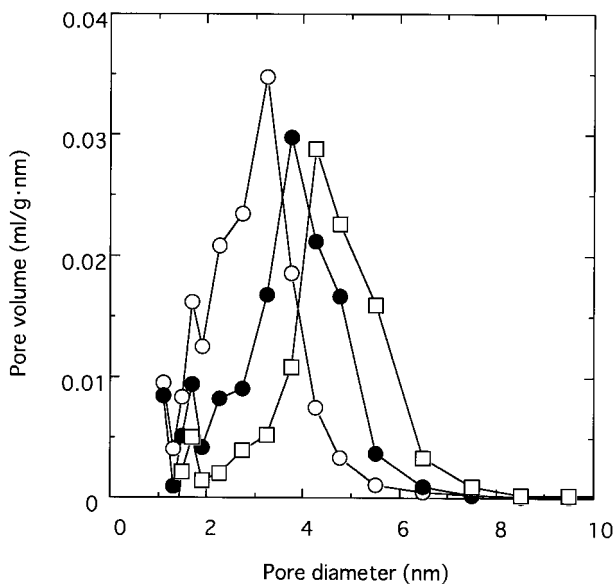


Figure 5 PSD curves for silica gels obtained by calcination of silica/poloxamer (50/50 wt %) composites. Poloxamer: (○) L64; (●) P84; (□) P103.

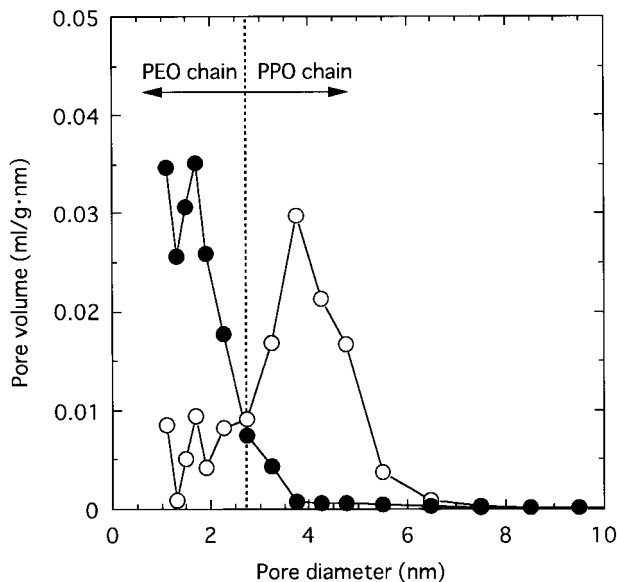


Figure 6 Comparison of PSD curves of silica gels obtained by calcination of (○) silica/P84 (50/50 wt %) and (●) silica/PEG (MW: 2000) (50/50 wt %) composites.

shifted to the right with increasing MW of the PPO in the poloxamer. The pore volume in the micropore region became very large with a smaller MW of PPO.

The Evaluation of the PSD Curves

As mentioned above, the silica gels obtained from the silica/poloxamer composites had a dual range pore size. To evaluate these PSD curves, as shown in Figure 6, they were compared with the PSD curve of the silica gel obtained from the silica/PEG (MW = 2000) composite. The value of \bar{d} of the silica gel was 1.33 nm, which corresponds to the diameter of one molecular chain coil of PEG.⁴ Thus, we judged that PEG molecules will be dispersed monomolecularly in the composite.

To be able to apply above concept for the silica/poloxamer system in the same way, the PSD curve of the silica gel obtained was separated into two regions at around 2.7 nm (dotted line) in Figure 6, i.e., the left and right sides of the dotted line correspond to PEO and PPO chains in the poloxamer, respectively. Hence, the pore volume in the micropore region depended on the PEO content in a unit weight of the poloxamer: It increased with increasing PEO content (see Figs. 3 and 4).

From the results of the fluorescence spectra, the presence of the hydrophobic domain of PPO

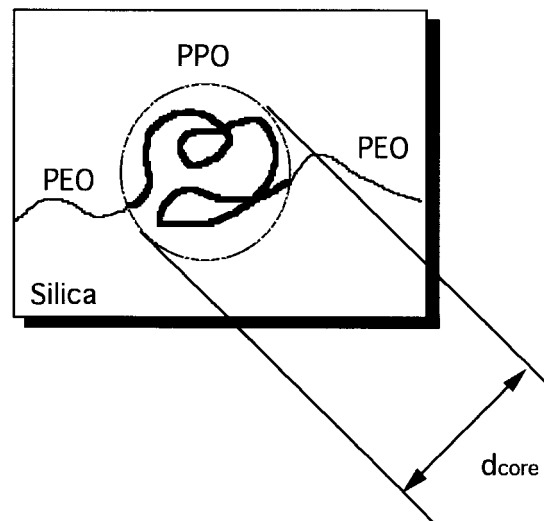


Figure 7 Schematic illustration of the structure of the poloxamer in the composite.

was confirmed in the blend sol. By the assumption that the structure of the blend sol will be kept by the composite to a certain extent, the form of the poloxamer molecule in the composite will be considered as in Figure 7. The monomolecular domain of PPO will be formed as a random coil. Therefore, the diameter (d_{core}) could be approximately evaluated from the top of the peak at the mesopore region of the PSD curve. Table IV shows the values of the d_{core} of each sample. The values of the d_{core} increased with increasing MW of PEO for the combination of P84, P85, and F88 or increasing MW of PPO for the combination of L64, P84, and P103. We considered that the radii of gyration of PPO in the blend sols became greater with increasing MW of PEO (when the MW of PPO is constant) or increasing MW of PPO (when the MW of PEO is constant), and these results are reflected on in Table III.

Using eqs. (1) and (2), Zhou and Chu calculated a lower limit micelle volume (V_c) which assumed the spherical shape of the liquid PPO ho-

Table IV The Values of d_{core} Obtained from the PSD Curves

Poloxamer	d_{core} (nm)
P84	3.75
P85	4.25
F88	4.75
L64	3.25
P103	4.25

mopolymer.¹¹ The estimate neglects the possible penetration of the solvent and so on:

$$V_c = \frac{4}{3} \pi \left(\frac{d_{\text{PPO}}}{2} \right)^3 = \alpha \bar{n} v_{\text{PO}} \quad (1)$$

$$v_{\text{PO}} = M_0 / (\rho N_A) \quad (2)$$

where d_{PPO} is a lower limit micelle diameter; α , the number of propylene oxide (PO); \bar{n} , the aggregation number of PPO; v_{PO} , the mean volume of the PO unit; M_0 , the MW of the PO monomer (=58); ρ , the density of liquid PPO (taken as 1.01 g/mL); and N_A , Avogadro's number. The values of d_{PPO} were calculated as $\bar{n} = 1$. In the case of the MW of 1750, 2250, and 3250, the values of d_{PPO} were 1.76, 1.92, and 2.16 nm, respectively. These values were about one-half or less than the values of d_{core} in Table III. But, considering the spread of the domain size by the existing silica sol (solvent; water/ethanol mixture) and PEO chain, we considered that the values of d_{core} were reasonable for the monomolecular domain of PPO without molecular aggregation.

CONCLUSION

The porous silica gels were prepared by the calcination of silica/poloxamer composites prepared by the sol-gel process. The pore control was carried out by changing the MW of PEO or PPO in the poloxamers. We considered that the poloxamers were dispersed monomolecularly and the state of the spherical monomolecular domain of PPO was formed in the composites. The silica gels obtained had a dual pore size: below 2 nm and

around 4 nm, corresponding to the PEO chain and the monomolecular domain of PPO, respectively. The domain size increased with increasing MW of the PPO when the MW of the PEO is constant or increasing MW of PEO when the MW of PPO is constant. Thus, the pore control was achieved mainly by variation of the domain size of PPO in the poloxamer. The silica gels obtained are to be expected to be used for adsorbents, separation membranes, catalysts, and carriers.

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