JOURNAL OF MATERIALS SCIENCE **35** (2000) 3237–3243

# Effect of addition of polymeric species with ether moieties on porous structure of silica prepared by sol-gel method

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The authors have investigated the effect of the addition of polymeric species (polyethyleneglycol, polypropyleneglycol and polytetramethyleneoxide) containing ether moieties in their main chain on the silica porous structure yielded via the sol-gel method. The obtained silica porous structures were characterized by nitrogen adsorption/desorption and SEM. Introducing those polymeric species apparently enhanced the pore formation. The enhancement is more noticeable for higher concentrations of the polymeric species, distributed from the microporous to mesoporous regions. The pore diameter at which the pore enhancement is induced by adding the polymeric species reduces with the fraction of ether moiety. Adding the polymeric species prior to the onset of the hydrolysis of tetraethylorthosilicate (TEOS) was necessary for the enhancement in the mesoporous region to takes place. The pore enhancement was more outstanding when HCL was used as the catalyst for the hydrolysis of the alkoxide than $NH_3$. The mutual affinity between the added polymeric and silica species is considered as an important factor of the pore generation in the micro- and meso-porous regions.

## 1. Introduction

The sol-gel method is a promising and practical way to produce porous materials by a relatively simple process [1]. The link between the processing conditions and the finally obtained micro- or mesoscopic porous structures have attracted interest particularly from the practical viewpoints and been extensively investigated [2–11]. However, it is not easy to manipulate the porous structure in the micro- or mesoscopic spatial scales only by the variation of macroscopic processing conditions such as compositions of the reacting agents, pH or the species of diluents. As a prescription for this point, there have been proposals of the sol-gel method incorporated with hybridization of silica and organic polymeric species, the latter of which can later be eliminated by combustion [12–14]. Polymeric species containing oxazoline, pyridone or acrylamide functions have been revealed to form hybrids in the molecular scale combined with silanol functions due to the presence of hydrogen bonds [12]. Eliminating these polymeric species by combustion yields fine pores reflecting the mixture structure of the polymer-silica hybrids. This indicates the possibility of the variation of the porous structure of silica materials on the spatial scale of 1–100 nm utilizing the molecular interaction between the polymeric and silica species. As a further step, it is of interest to investigate how the presence of those polymeric species affects the pore generation depending on the way in which the relevant chemical moieties in those polymeric species are involved. Specifically, the concentration of the introduced polymeric species and the fraction of the relevant chemical moieties which are likely to interact with silica are expected to influence the size or extent at which the pore generation is induced. To

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grasp the effect of the polymeric species and their concentrations giving a variation in the above point, the authors prepared silica porous materials by the sol-gel method incorporated with the hybridization with three polymeric species, which were anticipated to interact attractively with silica due to the presence of ether moieties causing hydrogen bond.

## 2. Experimental procedure

### 2.1. Materials

Tetraethylorthosilicate (TEOS) and $NH_3$ were used as provided (Nacalai Tesque, Kyoto, Japan). Polyethyleneglycol (PEG), polypropyleneglycol (PPG), polytetramethyleneoxide (PTMO), tetrahydrofuran (THF) and HCl were also used as provided (Wako Pure Chemical Industries, Osaka, Japan). The number-average molecular weight was approximately 2000 for each polymeric species. Water was purified by ion-exchange followed by distillation.

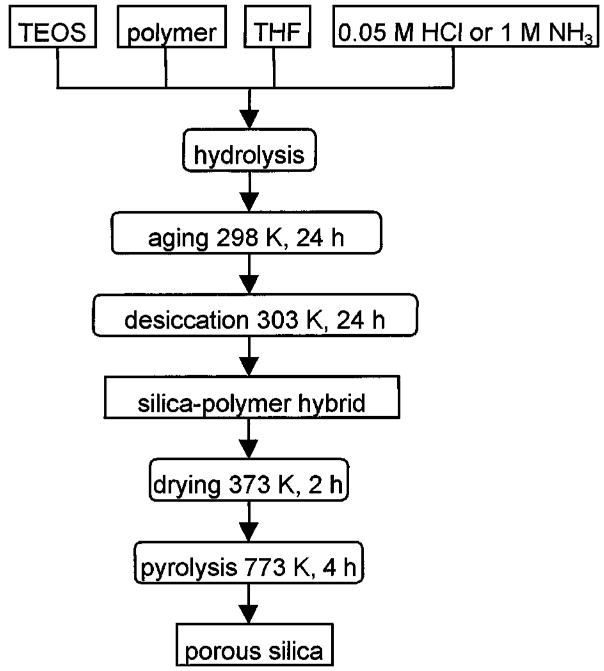

*Figure 1* Schematic of the sample preparation of porous silica from the starting solutions.

### 2.2. Sample preparation

The scheme of the sample preparation is shown in Fig. 1. The concentrations of the starting solutions are shown in Table I. The ratio $r_{X/T}$ signifies the molar ratio of X species (PEG, PPG, PTMO, water or catalyst) to TEOS. Mostly, 0.05 M HCl aq. was used as the catalyst, otherwise 1 M $NH_3$ aq. was used. The materials were mixed and hydrolyzed under vigorous stirring until the mixture looked homogeneous by naked eye. The polymeric species was added after the hydrolysis exceptionally in E7. The solutions were aged at 298 K for 24 hours with a cover to prevent vaporization prior to desiccation at 303 K for 24 hours. The obtained silica-polymer hybrids were dried at 373 K for 2 hours. Finally, the hybrids were calcined at 773 K for 4 hours in air to eliminate the polymeric species.

### 2.3. Analysis

Adsorption/desorption nitrogen isotherms were measured at 77 K using SA3100+ (Coulter, USA). The pore size distribution was evaluated by the *t*-plot and the Dollimore-Heal method for the microporous (pore diameter: ∼2 nm) and mesoporous (pore diameter: 2–50 nm) region, respectively. The surface of the obtained samples was observed by scanning electron microscopy (SEM) using JSM-6340FS (Nippon Denshi Datum, Japan). The gyration radius of the polymer chain dissolved in methanol at 298 K was evaluated from the self-diffusion coefficient obtained by dynamic light scattering (DLS) using ALV-5000E (ALV Vertriebsgeselschaft, Germany).

## 3. Results and discussion

Fig. 2 shows nitrogen adsorption/desorption isotherms of the silica materials prepared without (Fig. 2a) and

TABLE I Composition (molar ratio) of the starting solutions

| Sample | TEOS | Polymer | | | THF | | Catalyst | | | Water | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $M_T$[a] | | $r_{P/T}$[b] | $M_P$[a] | $r_{H/T}$[b] | $M_H$[a] | | $r_{C/T}$[b] | $M_C$[a] | $r_{W/T}$[b] | $M_W$[a] |
| X1 | 2.2 | — | 0 | 0 | 2 | 4.4 | HCl | 0.005 | 0.011 | 5.5 | 12.2 |
| X2 | 2.2 | — | 0 | 0 | 2 | 4.4 | $NH_3$ | 0.1 | 0.22 | 5.5 | 8.8 |
| E1 | 2.1 | PEG | 0.5 | 1.1 | 2 | 4.2 | HCl | 0.005 | 0.011 | 5.5 | 11.7 |
| E2 | 2.0 | PEG | 1.0 | 2.0 | 2 | 4.0 | HCl | 0.005 | 0.010 | 5.5 | 11.2 |
| E3 | 1.8 | PEG | 2.0 | 3.7 | 2 | 3.7 | HCl | 0.005 | 0.009 | 5.5 | 10.2 |
| E4 | 2.1 | PEG | 0.5 | 1.1 | 2 | 4.2 | $NH_3$ | 0.1 | 0.21 | 5.5 | 8.4 |
| E5 | 2.0 | PEG | 1.0 | 2.0 | 2 | 4.0 | $NH_3$ | 0.1 | 0.20 | 5.5 | 8.0 |
| E6 | 1.8 | PEG | 2.0 | 3.7 | 2 | 3.7 | $NH_3$ | 0.1 | 0.18 | 5.5 | 7.4 |
| E7[c] | 1.8 | PEG | 2.0 | 3.7 | 2 | 3.7 | HCl | 0.005 | 0.009 | 5.5 | 10.2 |
| P1 | 2.1 | PPG | 0.5 | 1.0 | 2 | 4.2 | HCl | 0.005 | 0.010 | 5.5 | 11.5 |
| P2 | 2.0 | PPG | 1.0 | 2.0 | 2 | 3.9 | HCl | 0.005 | 0.010 | 5.5 | 10.8 |
| P3 | 1.8 | PPG | 2.0 | 3.5 | 2 | 3.5 | HCl | 0.005 | 0.009 | 5.5 | 9.7 |
| T1 | 2.0 | PTMO | 0.5 | 1.0 | 2 | 4.1 | HCl | 0.005 | 0.010 | 5.5 | 11.3 |
| T2 | 1.9 | PTMO | 1.0 | 1.9 | 2 | 3.8 | HCl | 0.005 | 0.010 | 5.5 | 10.6 |
| T3 | 1.7 | PTMO | 2.0 | 3.4 | 2 | 3.4 | HCl | 0.005 | 0.008 | 5.5 | 9.3 |

[a] $M_X$, weight molar concentration (mol/kg) of X species.

[b] $r_{X/T}$, molar ratio to TEOS of X species.

[c] PEG was added after hydrolysis.

The subscripts P, T, C and W denote polymer, THF, catalyst and water, respectively.

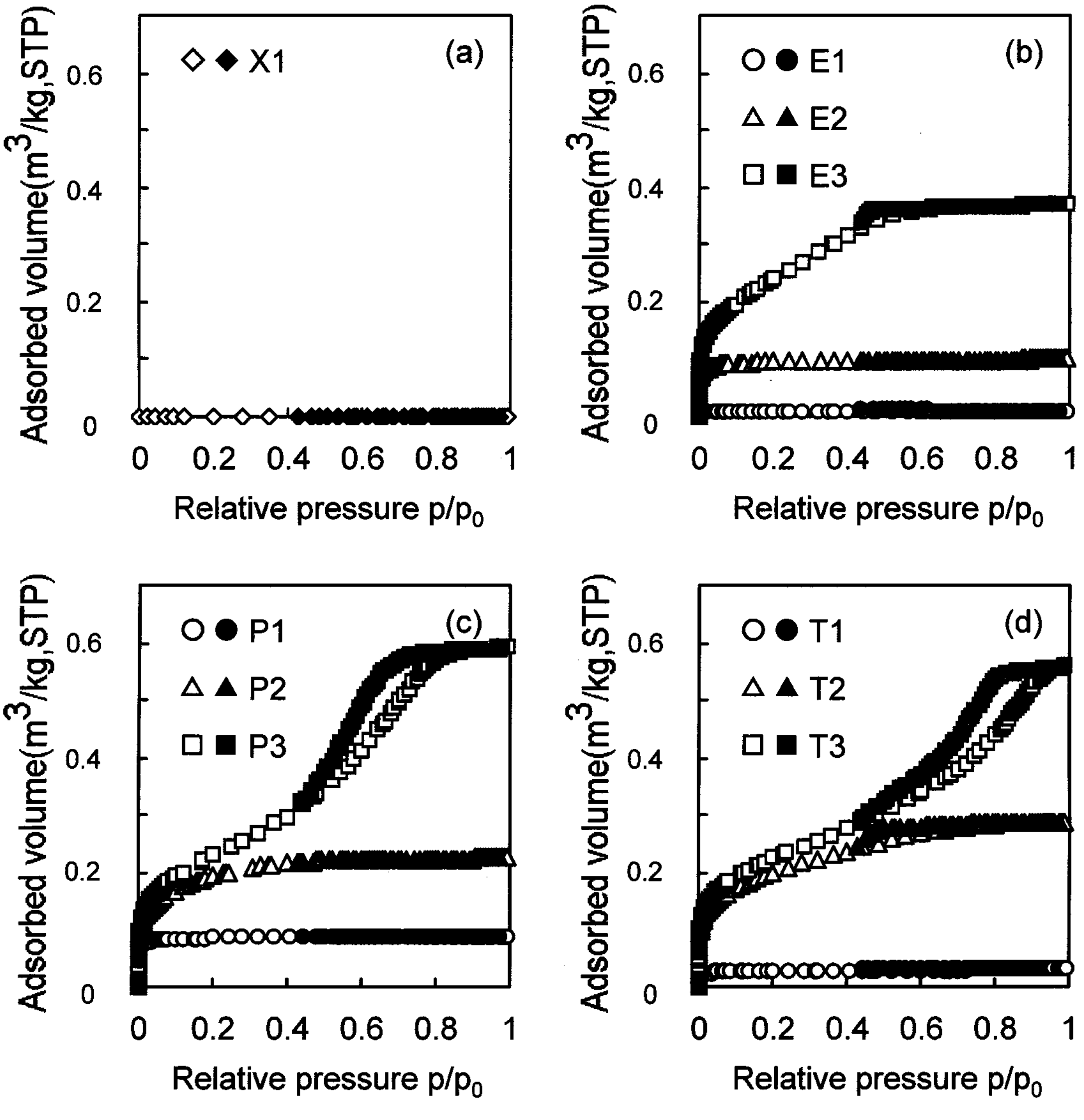

*Figure 2* Nitrogen adsorption/desorption isotherms of the porous silica prepared with HCl catalyst at different polymer concentrations; $r_{P/T}$: (◇, ◆) 0, (○, ●) 0.05, (△, ▲) 0.1 and (□, ■) 0.2 (a) without polymer, (b) with PEG, (c) with PPG, (d) with PTMO Open and filled markers are adsorption and desorption data respectively.

incorporated with three polymeric species, PEG, PPG and PTMO (Fig. 2b–d) at three prescribed concentrations shown in Table I. Here, the samples were prepared with HCl as the catalyst, and the polymeric species were introduced prior to the onset of the hydrolysis of TEOS. Pores are scarcely yielded in the silica material prepared without adding the polymeric species (Fig. 2a). The formation of non-porous monolithic structure is also indicated from the appearance of the obtained sample which looks black due to residual carbon enclosed in silica matrix. The effect of adding polymeric species is apparent for each sample prepared incorporated with those polymeric species (Fig. 2b–d). For each polymeric species, the increase in the added polymer content resulted in the enhancement of the pore formation. Fig. 3 shows the pore size distributions of those samples. The effect of adding the polymeric species, PEG, PPG and PTMO, is obvious. When PEG is introduced (Fig. 3a), the pore formation takes place in the region smaller than 2 nm in the pore diameter for $r_{P/T} = 0.05$ (E1) and 0.1 (E2) corresponding to the micropores. When $r_{P/T}$ is increased up to 0.2 (E3), the pore formation is simultaneously promoted in the mesoporous region (3–4 nm) corresponding to the rise in the adsorbed volume in $0.1 < p/p_0 < 0.4$ seen in Fig. 2b for E3. Therefore, the enhancement of the pore formation due to the addition of the polymeric species shifts to larger diameters as more PEG is introduced. This trend is fundamentally common to the influence of adding PPG and PTMO (Fig. 3b and c). However, it should be noted that the enhancement occurs at larger pore diameters (5–10 nm) than when PEG is introduced corresponding to $0.4 < p/p_0 < 0.7$ in the isotherms.

As the general trend, the addition of polymeric species containing hydrophilic moieties in its main chain has been shown to promote the formation of pores in the silica materials when catalyzed by HCl [12]. In this regard, the present work shows basically similar results. Several features in the pore generation can be discussed as follows in terms of the relation among the promoted pore diameter, the polymeric chemical species and its quantity. Since the gyration radius of each polymer chain dissolved in methanol has been estimated to be approximately 1 nm by DLS, the enhancement in the region smaller than 2 nm in diameter is considered to stem from voids which are yielded after individual

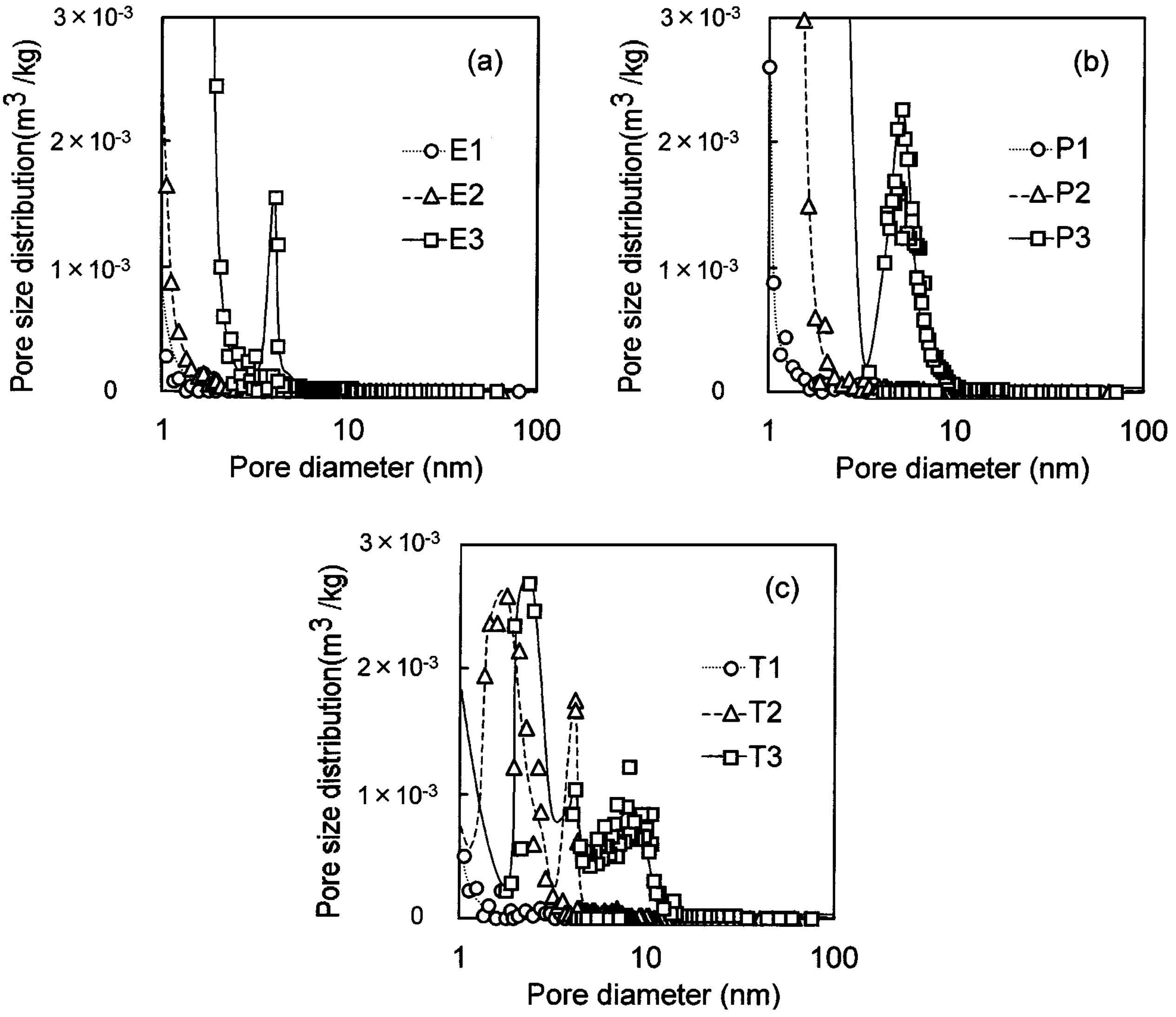

*Figure 3* Pore size distributions of the porous silica prepared with HCl catalyst at different polymer concentrations; $r_{P/T}$: (○) 0.05, (△) 0.1 and (□) 0.2; (a) PEG, (b) PPG, (c) PTMO.

polymer molecules are removed by combustion. This mechanism is expected to be present considering that those polymeric species have high affinity with silica or silanol as the precursory moiety because of the presence of hydrogen bonds. Similarly, the observed result that pores larger than 2 nm are formed should be ascribed to introducing those polymeric species, because they cannot be considered to stem from the inherent property of silica judging from the results of the nearly nonporous sample prepared free of the polymeric species (Fig. 2a). Furthermore, since the size of the secondarily appearing pores over 2 nm in diameter is larger than the molecular size of the polymer chains, they should be attributed to an effect which is induced by those polymer chains in some collective mechanism. As seen in the isotherms in Fig. 3 in the order of E3, P3 and T3, the secondarily appearing pore becomes larger as the fraction of the ether moiety in the polymer chain decreases (PEG→PPG→PTMO). Since the ether moiety is expected to be mainly responsible for the affinity between the polymeric and silica species, the enlargement of the secondarily appearing pore is explained by considering that the size of the density fluctuation contributing to the pore formation over 2 nm increases as the polymeric species has less affinity with the silica species in the above order shown above.

Fig. 4 shows SEM images of the samples prepared incorporated with the polymeric species at $r_{P/T} = 0.05$ and 0.2. Although these samples are free of cracks observed with the naked eye, the surface has many crack-like patterns ranging from 10 to 100 nm. However, the crack-like patterns do not affect the pore-size distribution in volume shown in Fig. 3. There are two possible reasons for it as follows; 1) Even monodispersed spherical particles as dense as fumed silica in the body-centered cubic array yields $1.3\times10^{-4}$m$^3$/kg of vacancy. Actually, the void volume corresponding to the crack-like patterns is anticipated to be smaller than the above value, thus, the crack-like patterns scarcely affects the pore size distribution. 2) The crack-like patterns correspond to macropores with the diameter ranging from 50 nm to 100 nm as in the SEM observation. Those macropores are possibly quite difficult to detect by nitrogen sorptometry because their saturation relative nitrogen pressure is approximately 0.99. P3 and T3 (Fig. 4d and f, respectively) show a distinct appearance from others, where they have less uniform structure apparently comprised of aggregates of smaller particulate

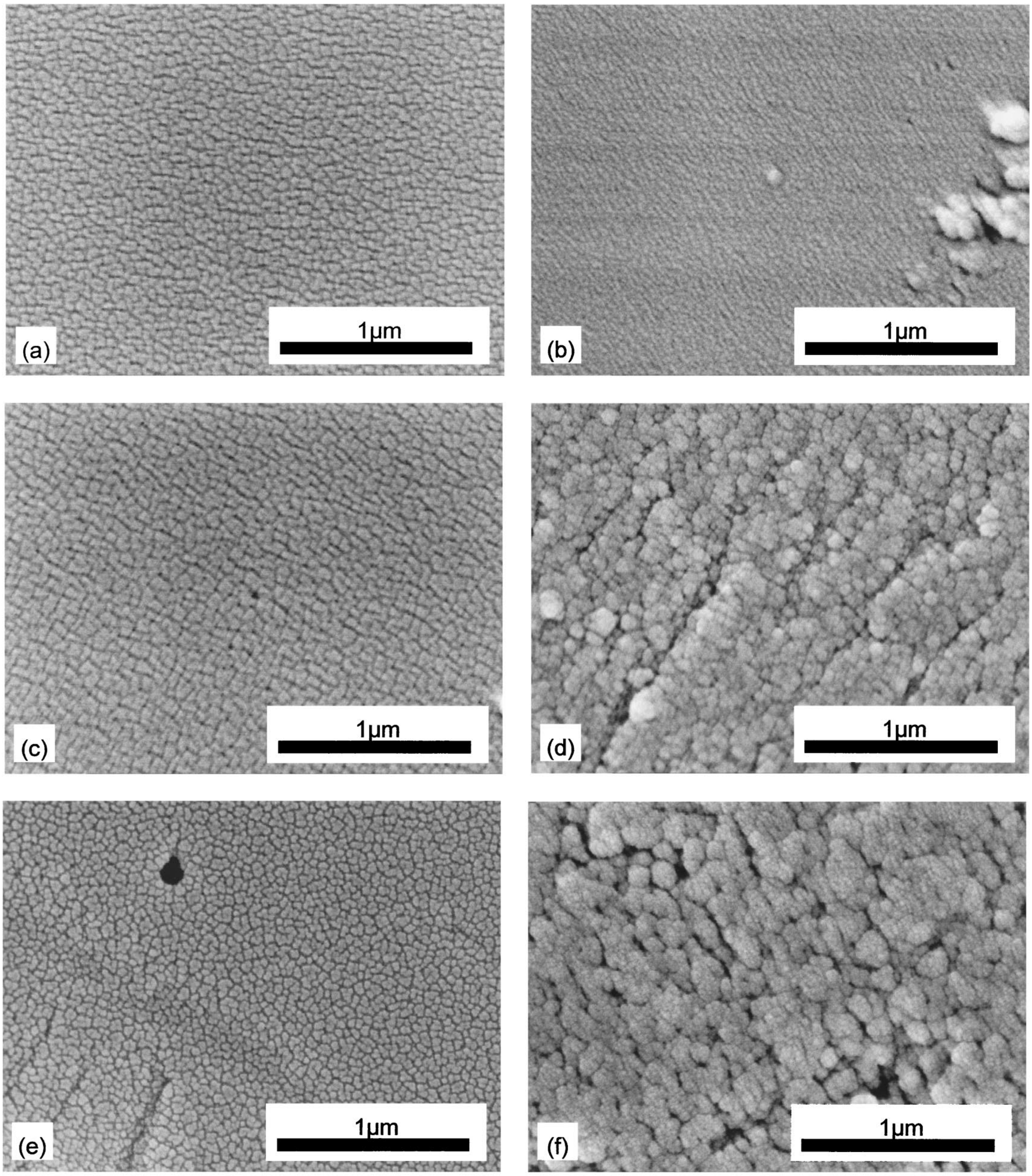

*Figure 4* SEM images of the porous silica prepared with HCl catalyst; (a) E1, (b) E3, (c) P1, (d) P3, (e) T1, (f) T3.

structures. The less uniform appearance of P3 and T3 is suggestive of concentration fluctuations of PPG or PTMO induced by the increase in their overall content. As pointed out in the discussion of the pore size distribution in volume (Fig. 3), those fluctuations are considered to be converted into mesopores after the polymer is removed by combustion.

Figs 5 and 6 show the adsorption/desorption isotherm and pore size distribution, respectively, when PEG was introduced after the hydrolysis of TEOS (E7). The other preparation conditions are the same as the case of E3. The effect of PEG on the pore formation differs in two regards. First, the pore formation over 2 nm in the diameter is less apparent when PEG is added after hydrolysis than before. Secondly, the total amount of the adsorption and desorption reduces, that is, the effect of the pore enhancement becomes less significant. They indicate that the effect of the hybridization of PEG and silica species on the molecular scale prior to the hydrolysis of TEOS is a key factor for the pore enhancement. PEG and the silica species are less likely to be mixed on the molecular scale after TEOS is already largely converted into silica.

Figs 7 and 8 shows the results when samples were prepared with PEG and $NH_3$ as the catalyst (X2, E4, E5, E6) in the place of HCl in X1, E1, E2 and E3. The pore formation is somewhat promoted by the presence of PEG. However, the effect is much less significant than when HCl is used. It should also be pointed out that the overall features of the isotherm (Fig. 7) scarcely alter

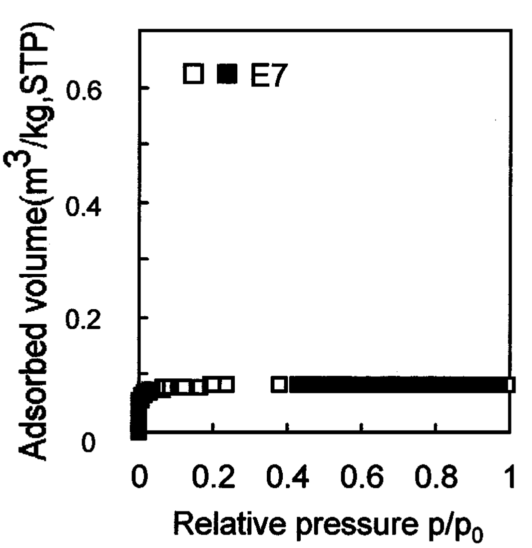

*Figure 5* Nitrogen adsorption/desorption isotherm of the porous silica prepared with HCl catalyst. PEG ($r_{P/T} = 0.2$) was added after the hydrolysis. Open and filled markers are adsorption and desorption data respectively.

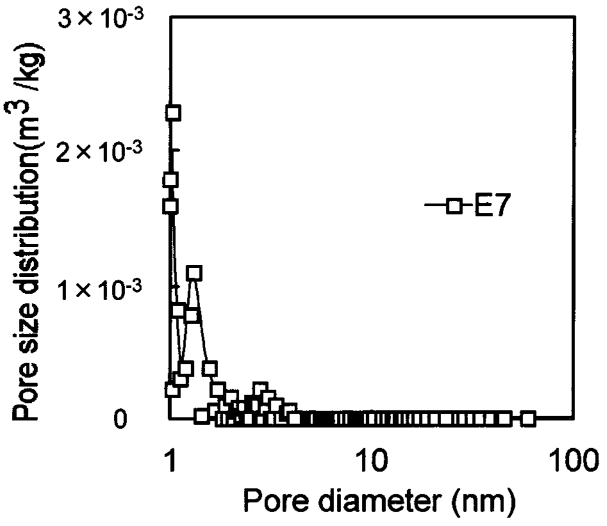

*Figure 6* Pore size distribution of the porous silica with HCL catalyst. PEG ($r_{P/T} = 0.2$) was added after the hydrolysis.

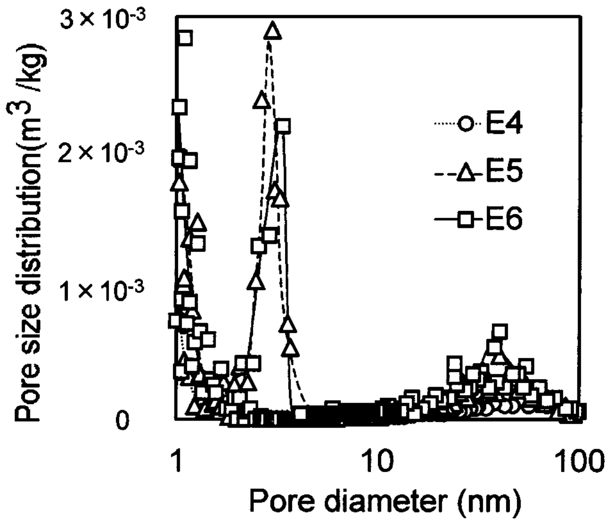

*Figure 8* Pore size distributions of the porous silica prepared with $NH_3$ catalyst at different polymer concentrations. $r_{P/T}$: (○) 0.05, (△) 0.1 and (□) 0.2.

depending on the quantity of the added PEG. Therefore, the use of $NH_3$ as the catalyst is primarily influential compared to the effect of introducing PEG. The affinity of the ether moiety with the silica species via hydrogen bond is not sufficient to affect the morphology of silica when $NH_3$ is used as the catalyst for the condensation process. This is in clear contrast with the case of HCl catalyst where the condensation process is expected to proceed under the molecular molphological influence of the hybrid by the polymeric species.

## 4. Conclusion

Porous silica materials were prepared from the hybridized state of silica and polymeric species (PEG, PPG and PTMO) with ether moieties. These polymeric species played a significant role in the generation of pores by the hybridization with silica on the molecular scale due to hydrogen bonds taking place at the ether moieties. The volume of micro- or mesopore was

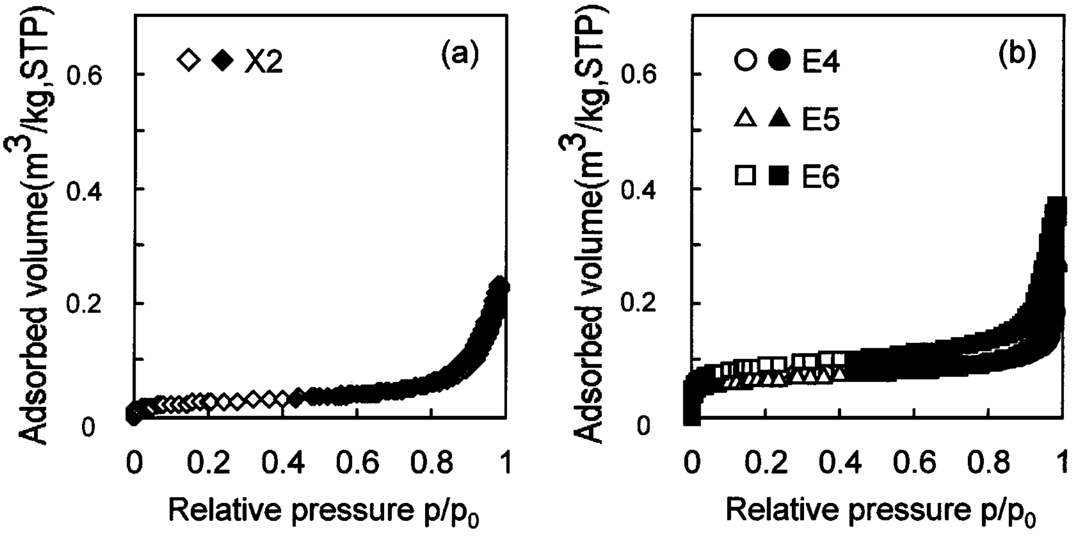

*Figure 7* Nitrogen adsorption/desorption isotherms of the porous silica prepared with $NH_3$ catalyst at different polymer concentrations. Open and filled markers are adsorption and desorption data respectivelty; (◇, ◆) 0, (○, ●) 0.05, (△, ▲) 0.1 and (□, ■) 0.2. (a) without polymer, (b) with PEG. Open and filled markers are adsorption and desorption data respectively.

shown to be varied by the concentration of the polymeric species. The addition of the polymeric species was much less influential when $NH_3$ was used as the catalyst than when HCl was used. The polymeric species were more responsible for the formation of mesopores when incorporating with the silica structure from the primary stage of the polymerization condensation by being mixed with TEOS prior to the onset of the hydrolysis than posterior.

## Acknowledgements

One of the authors, ANCHALEEPORN WARITSWAT LOTHONGKUM, gratefully acknowledge Japan Society for the Promotion of Science, the Hitachi Scholarship Foundation and Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang for the supports of this research work.

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*Received 28 July*
*and accepted 22 December 1999*