

Porous Silica Obtained from Biodegradable and Biocompatible Inorganic-Organic Hybrid Materials

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Abstract.

Porous silicas have been successfully prepared from poly(ϵ -caprolactone) (PCL)-silica hybrid materials based on the template approach. The final texture of the porous silica can be tailored by the PCL template, i.e., molecular weight and molecular weight distribution, content, type and number of reactive end-groups per chain. Porosity has been investigated by nitrogen adsorption-desorption technique and small angle X-ray scattering (SAXS).

Keywords: porous silica, inorganic-organic hybrid, pyrolysis, texture characterization

1. Introduction

Porous materials, such as silica [1-3], are emerging as a new area of great technological and scientific interest. One method to obtain porous silica is the template-based approach [2, 5], in which porosity is created by removing the incorporated template from the silica network. The porosity is therefore tailored by the design of the template. Recently, we have reported on novel biodegradable and biocompatible inorganic-organic hybrid materials prepared by the sol-gel process [6-9]. Poly(ϵ -caprolactone) (PCL), well-known for its biocompatibility, permeability and biodegradability, has been successfully incorporated into silica network. The organic (PCL) and inorganic (SiO_2) constitutive components are associated not only by covalent bonds (in case of end-reactive PCL) but also by hydrogen bonding (between the carbonyl groups of PCL and the residual OH groups on silica) [8]. "In vitro" cell culture and biodegradation tests have demonstrated that these new inorganic-organic hybrid materials are biomaterials with biodegradable and biocompatible properties [7]. Dynamic mechanical properties and the phase morphology of these new hybrid materials have also been reported elsewhere [9]. In this paper, we report on the preparation of porous silicas by the template approach involving the deliberate removal of the organic component, i.e., PCL chains.

2. Experimental

Synthesis of α, ω -hydroxyl PCL ($M_n = 2000$ and 4000) and α, ω -triethoxysilane PCL ($M_n = 2000$) has been detailed elsewhere [8]. PCL-diol ($M_n = 12.50$) and PCL-triol ($M_n = 900$) (Aldrich) were used as received. PCL/TEOS (tetraethoxysilane (Janssen)) mixtures of various compositions were dissolved in THF (20 wt%) and hydrolyzed by a stoichiometric amount of water with respect to the alkoxide functions. HCl was used as a catalyst with a 0.05/1 HCl/TEOS molar ratio. A representative synthesis was as follows: 1.5 g TEOS was added to the α, ϵ -triethoxysilane PCL (0.5 g, $M_n = 2000$) solution in THF (10.0 ml) and thoroughly mixed until a homogeneous solution was formed. Then deionized water (0.54 ml), ethanol (0.80 ml) and HCl (0.01 ml) were added with rapid stirring at ambient temperature for ca., 10 min. The clear solution was then cast into a plastic Petri dish and covered with a Parafilm for several days, depending on the PCL end-groups (hydroxyl or triethoxysilane) [5]. The gelified material was then dried under ambient conditions for one week and finally cured at 100°C for 2 days.

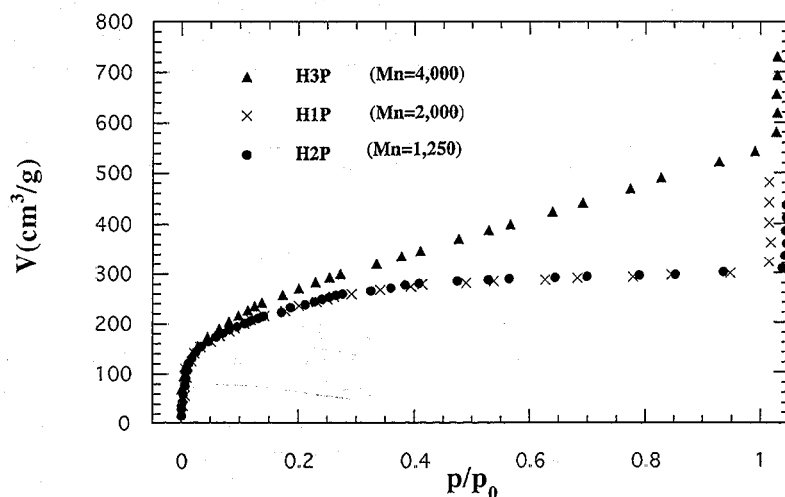


Figure 1. Nitrogen adsorption-desorption isotherms for the silica/ α,ω -hydroxyl PCL samples after pyrolysis: effect of the PCL molecular weight

The usual film thickness was 0.1-1 mm. Porous silica was prepared by pyrolysis of the silica-PCL hybrid materials at 400°C under an air flow (100 ml/min) until no weight loss was detected by thermogravimetric analysis (TGA). Nitrogen adsorption-desorption isotherms were measured at the boiling temperature (77 K) of liquid nitrogen (99,98%) with a Sorptomatic Carlo Erba 1900 Small-angle X-ray scattering (SAXS) measurements were carried out at the "Laboratoire pour l'Utilisation du Rayonnement Electromagnetique" (LURE; Oisay France) on DCI (D24 station). The size of the X-ray beam ($\lambda = 1.488 \text{ \AA}$) at the sample was smaller than 1 mm^2 , so that no desmearing of the data was required. The scattered X-rays were detected with an Argon-CO₂ gas-filled, one-dimensional position-sensitive detector (with a resolution of 0,4444 mm). The sample-to-detector distance (1151 mm) allowed SAXS data to be recorded in the 0.02 to 0.8 nm⁻¹ s range. These data were plotted as relative intensity versus s after correction for parasitic scattering and sample absorption. The background scattering was corrected in the standard manner.

3. Results and Discussion

The effect of molecular weight of the PCL template on the final texture of porous silica has been studied. Figure 1 shows the nitrogen adsorption-desorption isotherms for samples H1P, H2P and H3P, that contain 46.5 wt% α,ω -PCL template of different molecular weights M_n , i.e., 1250, 2000 and 4000, respectively (Table 1).

Table 1. Main characteristics of the PCL-templated porous silica.

Samples	End-groups of PCL chains	M_n of PCL	M_w/M_n of PCL	PCL wt%	a_{SBEI} (m ² /g)	a_{VT} (cm ³ /g)	a_{WDR} (cm ³ /g)	a_{R_g} (nm)	(nm)	α_p
H1	PCL-diol	1250	1.45	46.5	844	0.785	0.449	0.97 ± 0.22	6.70	2.90
H2	α,ω -hydroxyl	2000	1.50	46.5	876	0.634	0.452	0.93 ± 0.30	6.50	3.80
H3	α,ω -hydroxyl	4000	1.50	46.5	1017	1.132	0.668	1.49 ± 0.48	5.05	2.60
H4	α,ω -hydroxyl	4000	1.50	27.8	515	0.536	9.232	0.72 ± 0.16	3.60	2.50
H5	α,ω -hydroxyl	4000	1.50	15.5	94	0.390	0.043	-	-	-
H6	α,ω -triethoxysilane	2000	1.50	45.8	653	0.58	0.309	0.83 ± 0.21	4.95	2.70
H7	PCL-triol	900	1.40	46.5	870	0.626	0.415	0.67 ± 0.33	6.40	2.80
H8	α,ω -methyl	4000	1.25	46.5	872	0.640	0.544	0.89 ± 0.21	6.17	2.60

^a indicate textural characteristics after pyrolysis.

The isotherms of the H1P and H2P samples can be clearly identified as type I isotherm according to the BDDT classification [10], which is characteristic of microporous materials (pore width $w < 2 \text{ nm}$). For the sample H3P, the isotherm cannot be clearly identified with one of the typical BDDT isotherms. t -Plots [11] (Fig. 2) exhibit downward deviations with respect to the straight line passing through the

origin for the three samples. Nevertheless, the H3P deviation is more gradual and appears at a higher adsorbed volume than for H2P and H1P. This feature indicates that pores are larger and their size distribution is broader in H3P compared to the pores in the other two samples H2P and H1P. Table 1 shows the BET specific surface area (S_{BET}) obtained by the BET technique [11] in the classical range (0.05-0.20); the porous volume (V_p) calculated from the adsorbed volume at saturation; the microporous volume (W_{DR}) calculated by the Dubinin-Raduskevich equation [11] and the mean pore size and corresponding standard deviations calculated by the Brunauer's method [11]. These results show that pyrolysis of the H1P, H2P, H3P samples leads to very heterogeneous microporous materials, in which the mean pore size, the pore size distribution, the specific surface area, the microporous volume and the total volume, increase with the molecular weight of the PCL template.

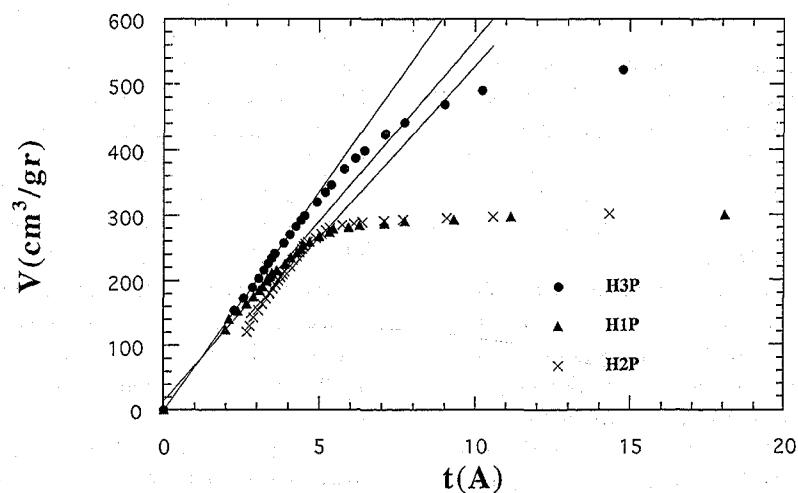


Figure 2. t -Plots for the samples H1P, H2P and H3P (see Table 1).

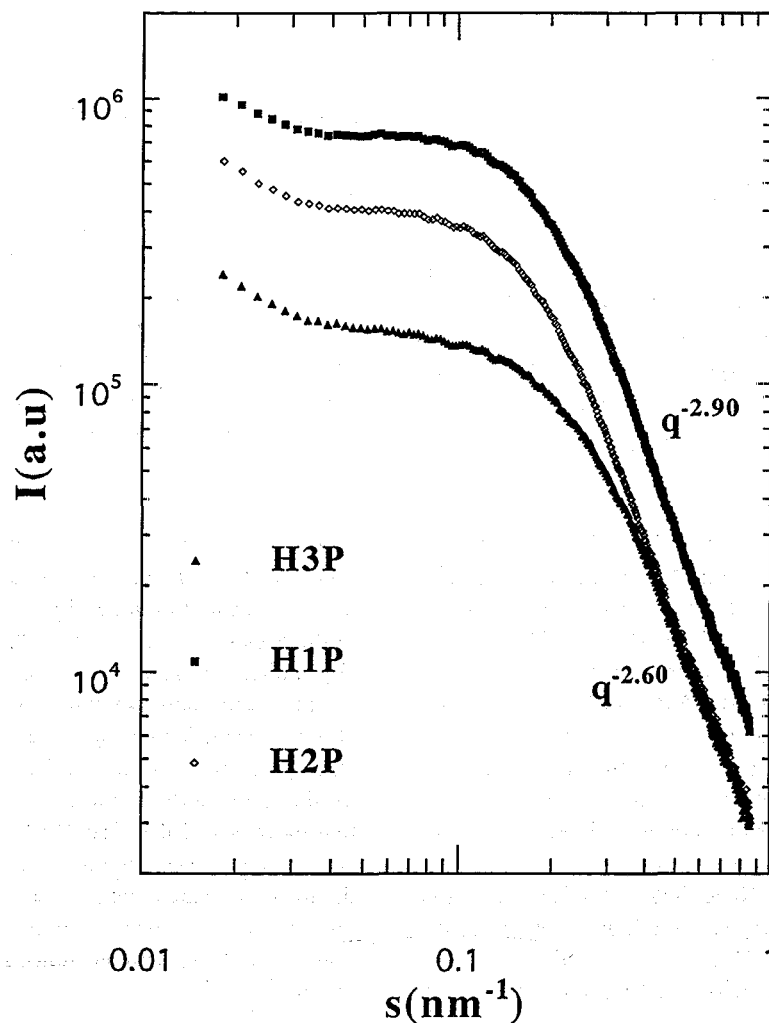


Figure 3. SAXS profiles for the samples H1P, H2P and H3P (see Table 1).

The scattered intensity, I , has also been measured over a range of scattering vectors s defined as $s = 2\lambda^{-1}\sin(\theta/2)$, where λ is the wavelength of the incident photons and θ is the total scattering angle. Porod's law, $I\alpha s^{-P}$, is valid for scattering between sharp surfaces. For $1 < P < 3$ the material has a mass/pore fractal structure of dimension $D_{m/p} = P$. If $3 < P < 4$, there is a surface fractal structure of dimension $D_S = 6 - P$ [12]. The limiting values $P = 3$ and 4 are characteristic of uniformly dense structures and smooth surfaces, respectively. Figure 3 compares the SAXS curves for pyrolyzed PCL-silica hybrid materials that originally contained PCL of different molecular weights (samples H1P, H2P and H3P). For the low s regime the SAXS curves are almost flat indicating the absence of any structure. From Guinier's law [12], the particulate radius of gyration, R_g , has been calculated (Table 1). For high s values, a linear regime extends over a length scale that depends on the molecular weight of the PCL template. Upon increasing molecular weight of PCL R_g decreases from 7 to 5 nm and P from 2.90 to 2.60. These values agree with a mass/pores fractal structure. Finally, taking into account the pore size distribution for the samples as obtained from adsorption-desorption measurements and the R_g values (Table 1), we can infer that the microporosity is intra-particle in the H1P and H2P samples and it could be intra- and inter-particle in the H3P sample.

The amount of the PCL template ($M_n = 4000$) has also been varied (46.5, 27.8 to 15.5 wt% in samples H.3P, H4P and H5P, respectively), see Table 1. For the non-porous H5P material (shown by the adsorption-desorption isotherm), a decrease in the amount of PCL template yields microporous materials that contain less micropores. These micropores are smaller in size and have a narrower size distribution. This is consistent with the SBET, V_T and W_{DR} data (Table 1). SAXS profiles confirm the adsorption results, since both the R_g and the fractal dimension value (P) decrease as the amount of PCL decreases.

The effect of the PCL template end-groups, and their number per chain, on the final texture of the porous silica has been studied by comparing the H1P, H2P, H6P, H7P and H8P samples (Table 1). As reported previously [8], when the amount of PCL is kept constant, an increase in the reactivity and number of the PCL end-groups favors the incorporation of PCL into the silica network. After pyrolysis, it is observed that increasing either the reactivity of the PCL end-groups or their number per PCL chain has the same effect on the final texture of the porous silica (see samples H2P and H6P, samples H1P and H7P in Table 1). The adsorption-desorption isotherms, the *t*-plots, and the SAXS measurements (not shown) indicate that the microporous silica templated with PCL α,ω -hydroxyl PCL rather than α,ω -triethoxysilane PCL has a broader pore size distribution, which however excludes small pores and a possible sieve effect. The same conclusion holds when PCL-diol and PCL-triol are compared. Table 1 shows that all the experimental sizes are larger for samples H2P and H1P than for samples H6P and H7P, respectively, indicating a more open porosity. However, the reverse behavior is observed for samples H3P (α,ω -hydroxyl PCL template) and H8P (α,ω -methyl PCL template which is non-reactive in the sol-gel process), see Table 1. Indeed, a broader pore size distribution (at the exclusion of small pores with sieve effect) is promoted by the hydroxy terminated PCL in contrast to the α,ω -methyl PCL template. This indicates that the reactivity of the PCL template end-groups is not as important as the molecular weight distribution of the template (see Table 1, samples H3P and H8P). As expected, microporous silica templated with PCL of a narrower molecular weight distribution has a smaller microporous size with a narrow size distribution and, smaller S_{BET} , V_T and W_{DR} values (Table 1, samples H8P and H3P).

4. Conclusion

Porous silicas have been successfully prepared by pyrolysis of silica-PCL hybrid materials based on the template approach. This structure has been analyzed by two independent characterization methods. The silica microporosity can be tailored by the amount of the PCL template, molecular weight and molecular weight distribution of the PCL template and by the reactivity and number of the PCL end-groups.

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