

Regeneration of Nanoporous Crystalline Syndiotactic Polystyrene by Supercritical CO₂

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ABSTRACT: Guest desorption procedures for s-PS clathrate samples, leading to formation and regeneration of the nanoporous δ phase, are compared. An extraction procedure, based on supercritical carbon dioxide, allows an easy and fast recovery of the guest molecules operating under relatively mild conditions (90–200 bar, 40°C) and generates a completely empty δ form, also starting from the most stable s-PS clathrate forms. In agreement with a previously proposed crystal structure of the nanoporous δ form, X-ray diffraction patterns of δ form powders obtained by this procedure do not show the peak, which is reduced but still apparent in samples extracted with previous procedures based on boiling solvents. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2077–2082, 1999

Key words: syndiotactic polystyrene; clathrate; guest desorption; supercritical carbon dioxide extraction

INTRODUCTION

Syndiotactic polystyrene (s-PS) presents a very complex polymorphic behavior, which, after some simplification, can be described in terms of two crystalline forms, α and β , containing planar zig-zag chains and two forms, the γ and δ , containing s(2/1)2 helical chains.¹ In particular, the term “ δ -form” has been used to indicate different clathrate forms, for which the intensities and the precise locations of the crystalline reflections in the X-ray diffraction patterns change with the kind and amount of the included guest molecules.² Clathrate forms can be obtained by sorption of suitable compounds (mainly halogenated or aromatic hydrocarbons) in amorphous s-PS samples

as well as in semicrystalline s-PS samples being in the α or γ form.² By removal of the guest molecules from the clathrate forms,^{3,4} an empty form can be obtained, whose crystal structure has been described.⁵ The sizes and shapes of the cavities⁶ as well as host–guest interactions^{7,8} which are present in this nanoporous crystal phase have recently been modeled.

This emptied clathrate form of s-PS is able to absorb substantial amounts of some organic substances (to 20–30 wt %) also when present at low activities.^{3,9,10} Sorption studies from liquids and vapors into empty clathrate samples have suggested that this thermoplastic material is promising for applications in chemical separations as well as in water purification.^{3,9,10} For applications of these nanoporous materials, also relevant is their easy regeneration by removal and, possibly, recovery of the guest.

Since the nanoporous δ form is unstable above 100°C (being transformed into a mesomorphic and then into a γ form),⁴ thermal desorption pro-

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cedures are suitable only for some volatile guest molecules, which are more weakly bonded to the host polymer. For instance, carbon disulfide and 1,2-dichloroethane are nearly completely removed by thermal treatments at 50 and at 80°C,¹¹ respectively. In contrast, thermal desorption procedures are unsuitable for several clathrate forms like, for example, the one including styrene (obtained by bulk polymerization) as well as for the one including toluene (the most common product of solution polymerization).

A solvent-desorption procedure, using several hours of extraction by boiling ketones, is, instead, efficient for all guest molecules.³ However, this procedure also does not allow one to obtain completely empty samples. In fact, also after long-term extractions, the guest content remains close to 1 wt % and the diffraction peak $\bar{2} 10$ (located at $2\theta \approx 10.5^\circ$ for $\text{CuK}\alpha$ radiation) is still visible,^{3,5} although it is substantially null for the crystal structure which has been hypothesized for a completely empty δ form.⁵ Moreover, this regeneration procedure, which involves large amounts of boiling flammable solvents and does not allow an easy guest recovery, could be unsuitable for industrial developments.

A supercritical solvent is a compound working at a temperature and a pressure higher than its critical point. Therefore, it is in the gaseous state, but depending on the continuous modulation of the density, it can show liquidlike solvent power and large selectivity. Moreover, it maintains gaslike diffusivities. For these reasons, supercritical fluids and particularly supercritical CO_2 are widely used for selective extractions from complex matrices. For example, the extraction of essential oils, vegetable oils, fatty acids, and pharmaceutical compounds has been attempted from vegetable matter, fermentation broths, and preprocessed materials.^{12,13} Supercritical carbon dioxide has also sometimes been used to perform the selective desorption of compounds from various adsorbents. For example, selective desorption of terpenes has been obtained from silica gel^{12,14–16} and pollutants have been recovered from activated carbon.^{17,18}

In the present article, for s-PS clathrate samples including toluene and styrene, a guest desorption procedure based on supercritical carbon dioxide is described and compared with the boiling acetone-extraction procedure. The desorption of these guests is not only relevant for preparation of nanoporous crystalline materials but also for their regeneration. In fact, aromatic hydrocar-

bons are often major components of industrial wastewaters.¹⁹

EXPERIMENTAL

The styrene/s-PS clathrate sample was obtained by bulk polymerization of the monomer, using a homogeneous catalyst consisting of CpTiCl_3 and methylalumoxane (MAO). The as-polymerized powder presents a surface area of nearly 4 m^2/g and a styrene content close to 15 wt %.

The toluene/s-PS clathrate sample was obtained by a 2-h treatment by boiling toluene of a γ form powder sample, in turn, obtained by treatment at 160°C of the as polymerized s-PS powder. Its toluene content is close to 16 wt %.

Wide-angle X-ray diffraction patterns were obtained on powder samples with nickel-filtered $\text{CuK}\alpha$ radiation using an automatic PW1710 Philips diffractometer. The thermogravimetric analyses were carried out with a Mettler TG50 thermobalance in a flowing nitrogen atmosphere at a heating rate of 10 K/min. The solvent-extraction procedures were conducted with a Soxhlet extractor using boiling acetone.

Supercritical and liquid CO_2 desorption tests were performed in a laboratory apparatus consisting mainly of a 200- cm^3 desorption vessel that was loaded with about 70 g of polymer containing the guest compound and of a separator operated at lower pressure that had a conical bottom connected to a Pyrex vessel by a regulating valve. This arrangement allowed the discharge of the desorbed matter at fixed-time intervals. The separator was also cooled to reduce the vapor pressure of the desorbed compound to reduce or eliminate the loss in the gaseous CO_2 at the exit of the apparatus. CO_2 was delivered by a high-pressure diaphragm pump capable of operating at pressures up to 500 bar and of delivering up to 4 kg/h of the solvent. The instantaneous CO_2 flow rate and the total quantity of solvent delivered were measured by a calibrated rotameter (Matheson, Model 604) and a dry test meter (Sim Brunt, Model B10). More details on the apparatus were published elsewhere.²⁰

RESULTS AND DISCUSSION

The X-ray diffraction pattern of a clathrate s-PS sample including 16 wt % of toluene is shown by curve a in Figure 1. This is a typical pattern of

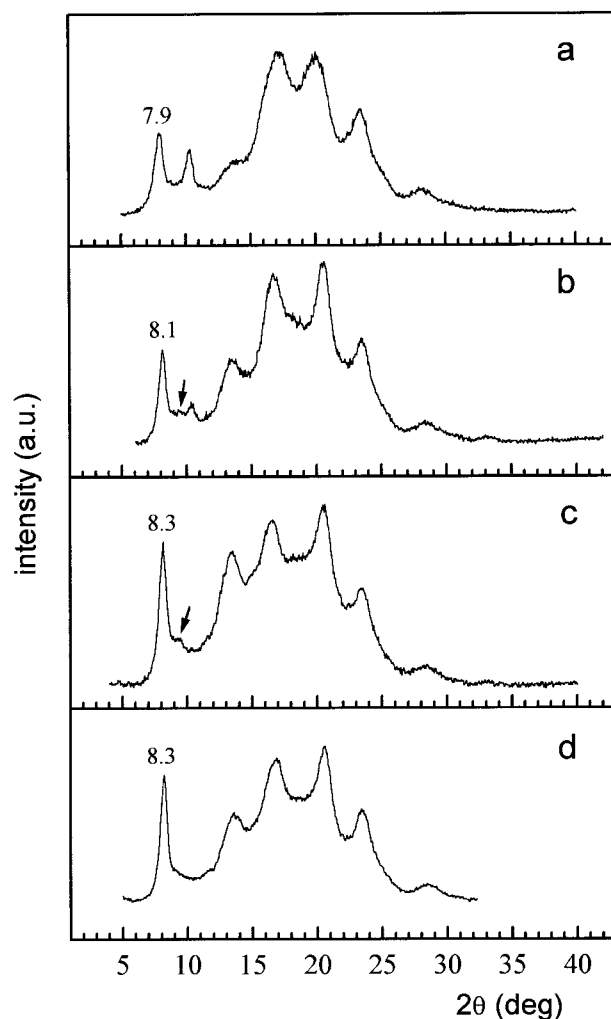


Figure 1 X-ray diffraction patterns of a clathrate s-PS sample initially including 16 wt % of toluene: (a) untreated; (b) after an 8-h extraction by boiling acetone; (c) after acetone extraction and followed by thermal treatment at 50°C for 2 h; (d) after extraction by CO₂ at 40°C and 200 bars for 5 h.

filled clathrate, presenting similar intensities of the 010 and reflections (located, for CuK α radiation, at $2\theta \approx 7.9^\circ$ and 10.5° , respectively) as well as low intensities of the 101 and $\bar{1}11$ reflections (both located at $2\theta \approx 13^\circ$).⁵

The X-ray diffraction pattern of the clathrate powder after an 8-h extraction procedure by boiling acetone is shown by curve b in Figure 1. The reduction of the peak at $2\theta \approx 10.5^\circ$ and the increase of the peak at $2\theta \approx 13^\circ$ indicate the occurrence of a partial guest removal. The appearance of a small diffraction peak at $2\theta \approx 9^\circ$ (marked by an arrow in Fig. 1), which is typical of the γ form of s-PS, indicates that the boiling acetone treat-

ment produces a partial transformation of the clathrate form into the γ form. Let us recall that the γ form of s-PS is not nanoporous and is transformed into clathrate forms only in the presence of suitable guests at high activities, while it is unable to clathrate guests from dilute solutions.⁹ It is also worth noting that infrared spectroscopy measurements indicate (e.g., by the presence of the typical carbonyl band) that the polymer sample included acetone, which would be removed by thermal treatments above 50°C.

The X-ray diffraction pattern of the acetone-extracted sample of Figure 1(b) after a thermal treatment at 50°C for 2 h, shown by curve c in Figure 1, indicates that the thermal treatment produces a nearly complete guest removal. In fact, the peak (at $2\theta \approx 10.5^\circ$) is very weak while the 010 peak is stronger than in the clathrate sample and is shifted upward to 8.3 Å. The residual content of low molecular mass molecules (essentially, toluene) in the polymer sample, as evaluated by thermogravimetric analysis, was reduced to 1 wt %.

The extraction procedures by carbon dioxide in supercritical conditions are more efficient. For instance, the same toluene clathrate sample of Figure 1(a), after an extraction by CO₂ at 40°C at a pressure of 200 bars for 5 h, presents a toluene content lower than 1 wt % and the X-ray diffraction pattern shown in curve d of Figure 1. This pattern does not present any peak in the range of 2θ between 8.5° and 11° , indicating that the only crystalline phase which is present in the polymer sample is a completely empty δ form.

A typical desorption kinetic curve obtained using supercritical CO₂ is shown in Figure 2, where the desorption yield of toluene is reported against the time for an experiment performed at 200 bar, 40°C, 0.4 kg/h CO₂ on a polymer sample loaded with 16% wt of toluene. The complete desorption of the guest molecule is obtained in about 200 min. When we operated at higher CO₂ flow rates, we obtained even shorter desorption times. For example, using a CO₂ flow rate of 0.8 kg/h and operating at the same conditions as in Figure 2, only about 120 min were required to desorb 16 % wt of toluene.

The effect of pressure on the desorption process was assessed during tests performed on a clathrate s-PS sample including 12 wt % of toluene, at pressures between 90 and 200 bar. The efficiency of the desorption increases with pressure as illustrated in Figure 3, where a test performed at increasing pressure is reported. The first part of

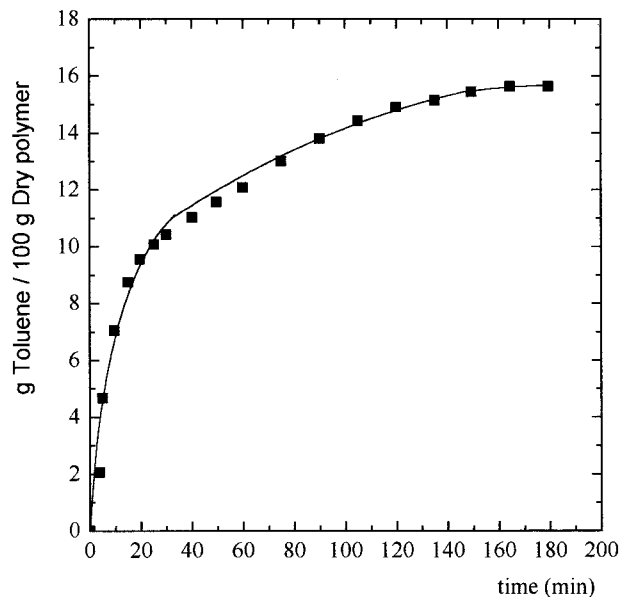


Figure 2 Desorption kinetics of a clathrate s-PS sample loaded with 16 wt % of toluene, for a 0.4-kg/h CO₂ flow rate, at 200 bar and 40°C.

the operation (up to 60 min) was performed at 90 bar: a very long tail of the desorption curve was expected to obtain the complete recovery of the adsorbate. When pressure was increased to 200 bar, a fast completion of the regeneration process

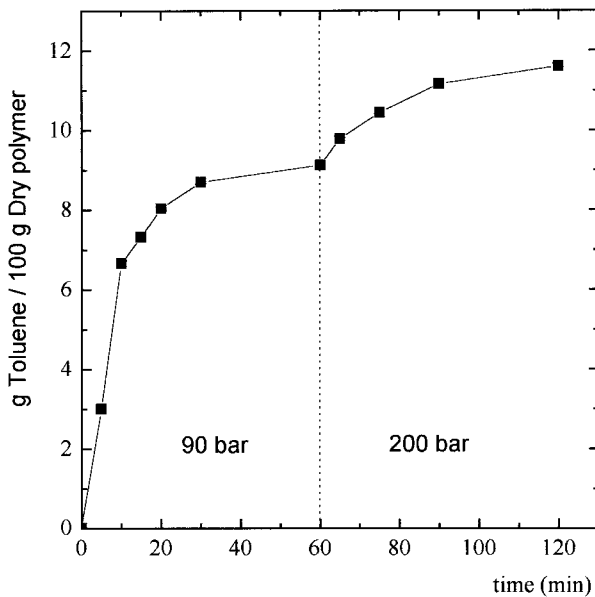


Figure 3 Desorption kinetics relative to clathrate s-PS sample loaded with 12 wt % of toluene. The first stage of the operation (up to 60 min) was performed at 90 bar and the second stage at 200 bar.

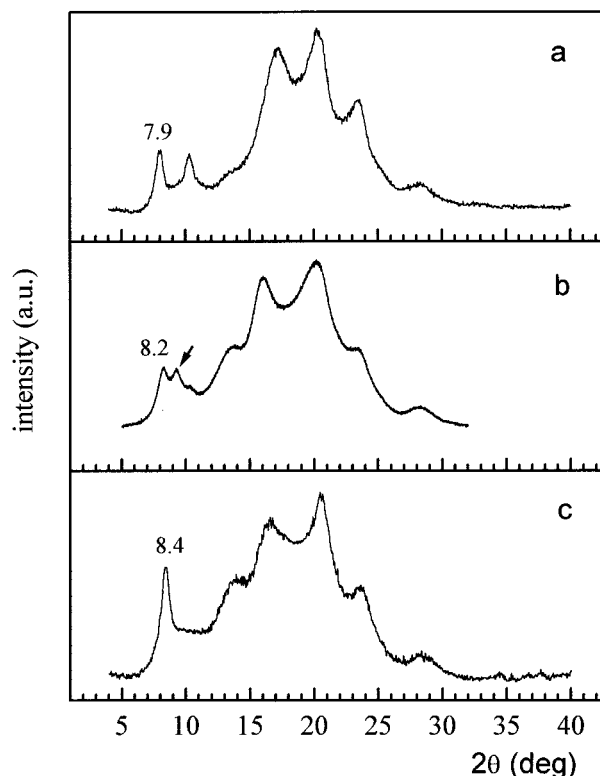


Figure 4 X-ray diffraction patterns of a clathrate s-PS sample initially including 15 wt % of styrene: (a) untreated; (b) after an 8-h extraction procedure by boiling acetone and thermal treatment at 50°C for 2 h; (c) after extraction by CO₂ at 40°C at 200 bars for 5 h.

was obtained. The higher efficiency for guest removal of the extraction procedures based on supercritical carbon dioxide was even more clearly apparent by extraction studies relative to bulk-polymerized samples which present an s-PS/styrene clathrate phase.

The X-ray diffraction pattern of a clathrate s-PS sample including 15 wt % of styrene is shown by curve a in Figure 4 and is similar to that of the toluene/s-PS clathrate [Fig.1(a)]. The X-ray diffraction pattern of the clathrate powder after 48 h of the extraction procedure by boiling acetone, followed by thermal treatment at 50°C for 2 h, is shown by curve b in Figure 4. Although the diffraction peak at $2\theta \approx 9^\circ$, typical of the γ form of s-PS, is already present, this treatment was not sufficient for complete guest removal (peak at $2\theta \approx 10.5^\circ$ still present).

On the other hand, extraction procedures on the styrene/s-PS clathrate sample of Figure 4(a), by carbon dioxide in supercritical conditions, can lead to completely empty δ form samples, without

any transition toward the γ form. For instance, the same styrene clathrate sample of Figure 4(a), after extraction by CO_2 at 40°C at a pressure of 200 bars for 2 h, presented a styrene content lower than 1 wt % and the X-ray diffraction pattern shown in curve c of Figure 4 (typical of a completely empty δ form and very similar to curve d of Fig. 1). Similar results were obtained using other guest molecules, when the corresponding pure compounds were characterized by a large solubility or complete miscibility in supercritical CO_2 .

A desorption test was also performed using liquid CO_2 . The scope of this experiment was to assess if the efficiency of the desorption process depends on the physical status of the solvent (gaseous versus liquid). Indeed, CO_2 can produce the swelling of several polymers independently of its physical state, but the different diffusivities that characterize liquid and supercritical conditions can also play an important role in the fast desorption of the guest molecules.

To operate at comparable conditions, we performed the liquid CO_2 desorption test on the polymer loaded with toluene at a 0.4 kg/h CO_2 flow rate and at 27°C , 130 bar, at which the CO_2 density is 0.84 g/cm^3 , that is, the same density as in the test illustrated in Figure 3. Although we performed a very long experiment (420 min), a residual solvent content larger than 3 wt % was observed. This result indicates that the efficiency of the desorption process largely depends on the higher diffusivities that characterize the supercritical fluid.

CONCLUSIONS

Regeneration procedures of nanoporous crystalline syndiotactic polystyrene, based on extractions by liquid, weakly clathrating solvents (like acetone and carbon disulfide), can be efficient also for strongly bonded guest molecules (like chlorinated and aromatic hydrocarbons). However, these procedures, for guests forming highly stable clathrates, lead to substantial guest removal only in drastic conditions: several hours of treatments by boiling solvents. These conditions can produce partial transformation of the nanoporous δ form into the γ form, which is unsuitable for chemical separations. In particular, this problem occurs for the clathrate forms with styrene and toluene which are generally present in as prepared sam-

ples by bulk and solution polymerizations, respectively.

On the other hand, extraction procedures based on supercritical carbon dioxide generate, at shorter times and lower temperatures, completely empty δ form samples, without any transition toward the γ form, also for the most stable s-PS clathrates. In fact, X-ray diffraction patterns of powder clathrate samples extracted with this procedure do not show the peak typical of the filled clathrates. It is also worth noting that these kinds of extractions allow an easy recovery of the guest molecules by reducing the fluid pressure and putting carbon dioxide in the gas phase.

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