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Influence of Supercritical Carbon Dioxide Extraction Temperature on the Crystalline Structure and the Morphology of Syndiotactic Polystyrene Aerogels

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Summary: In this manuscript the influence of supercritical carbon dioxide extraction temperature on the morphology, the porosity, and the crystalline structure of syndiotactic polystyrene aerogels is investigated. Results show that depending on the extraction temperature, δ-form, γ-form, and β-form high porosity aerogels characterized by a fibrillar morphology can be obtained.

Keywords: supercritical carbon dioxide extraction; syndiotactic polystyrene aerogels

Introduction

Syndiotactic polystyrene (sPS) displays a complex polymorphic behaviour and in the crystalline state five crystalline forms (designed by the acronyms α,[1a] β,[1b] γ,[1c] δ,[1d] and ε [1e–f]) and numerous co-crystal phases (clathrates[2] and intercalates[3]) can be obtained with low-molecular-mass compounds.

SPS can also form thermoreversible gels with a large number of organic solvents and depending on the solvent-type and/or thermal treatments different type of gels can be obtained. Strong elastic gels with the co-crystal crystalline junctions[4] are obtained with solvent molecules capable to form co-crystals while past-like pseudo gels with the β-form crystalline phase are obtained with bulky solvents.[5]

It has been shown recently that high porosity sPS aerogels can be obtained by supercritical CO_2 extraction of the solvent present in the native sPS physical gels[6a–b] or by sublimation of the solvent.[6c,d] The crystalline phase of the aerogels as well as their structure depend on the crystalline structure (co-crystalline or β) of the junction zones of the starting gel. Solvent extraction of sPS gels with co-crystal phases leads to aerogels characterized by semi-crystalline nanofibrils (fibril diameter range between 30–200 nm) exhibiting the nanoporous crystalline δ-phase[6a–b] while for the gels with the β phase, the corresponding aerogels are characterized by β-phase interconnected lamellar crystals (thickness in the range 200–400 nm).[6a–b]

It is well known that treatments by supercritical CO_2 can induce crystal-to-crystal transformations in sPS,[7] and more specifically that high temperature supercritical CO_2 treatments can induce, in sPS co-crystalline films, transformation of co-crystalline phases in γ and β-phases.[7c]

High temperature supercritical CO_2 extraction procedures were also applied to sPS gels and results about the influence of the extraction temperature on the crystalline structure, the porosity, and the morphology of the obtained aerogels will be reported in this report.

Experimental Part

The syndiotactic polystyrene used in this study was manufactured by Dow Chemicals under the trademark Questra 101. ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic triads was over 98%. The mass average molar mass obtained by gel permeation chromotography (GPC) in

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trichlorobenzene at 135 °C was found to be $M_w = 3.2 \cdot 10^5$ g mol^{-1} with a polydispersity index $M_w/M_n = 3.9$. Solvents used to prepare the gels were purchased from Aldrich and used without further purification.

All sPS gel samples were prepared in hermetically sealed test tubes by heating the mixtures above the boiling point of the solvent until complete dissolution of the polymer and the appearance of a transparent and homogeneous solution had occurred. Then the hot solution was cooled down to room temperature where gelation occurred.

Aerogel samples were obtained by treating sPS gels with a SFX 200 supercritical carbon dioxide extractor (ISCO Inc.) at a pressure of 200 bar.

The porosity P of aerogel samples can be expressed as a function of the aerogel apparent density ρ as:

$$P = 100\left(1 - \frac{\rho}{\rho_S}\right)$$

where ρ_S is the density of the polymer

X-rays diffraction patterns were obtained on a Phillips PW1710 automatic diffractometer operating with a nickel-filtered Cu K_α radiation. Scanning electron micrographs were obtained using a Leica 440 scanning electron microscope.

Results and Discussion

The porosity of aerogels obtained by solvent extraction from gels in dichloroethane (DCE) and toluene ($C_{pol} = 5$ wt%) at 40 °C, 130 °C, and 150 °C, are reported in Table 1.

Data reported in Table 1 show that supercritical CO_2 extraction in the temperature range 40–130 °C of sPS gels allows to obtain high-porosity aerogels independently of the solvent used to prepare the gel. At 150 °C a collapse of the gel prepared with toluene was observed while high porosity aerogel was still obtained with the sPS/DCE gel. This different behaviour could be possibly explained by the lower melting temperature of the gel formed in toluene. In fact, the melting temperature at ambient pressure of a sPS/toluene gel at $C_{pol} = 5$wt% is c.a. 100 °C[4f] while the sPS/DCE gel melting temperature is c.a. 140°C.[4j]

Table 1.
Porosity of sPS aerogels obtained from gels prepared in DCE and toluene at $C_{pol} = 5$wt%, after supercritical CO_2 extraction at 40 °C, 130 °C, and 150 °C.

	sPS/DCE	sPS/Toluene
T = 40 °C	93	94
T = 130 °C	92	93
T = 150 °C	91	n.d.[a]

[a] The porosity of the aerogel was not determined due to the total collapse of the sample during the extraction.

In Figure 1 are reported the X-ray diffraction patterns of aerogels obtained from gels prepared in DCE at $C_{pol} = 5$ wt%, after supercritical carbon dioxide extraction at 40 °C (a), 130 °C (b) and 150 °C (c). Similar X-ray diffraction patterns are also observed for aerogels obtained by the same extraction procedures from toluene-based gels.

The X-ray diffraction pattern of the aerogel obtained by extraction at 40 °C (Figure 1a) displays the strong reflections

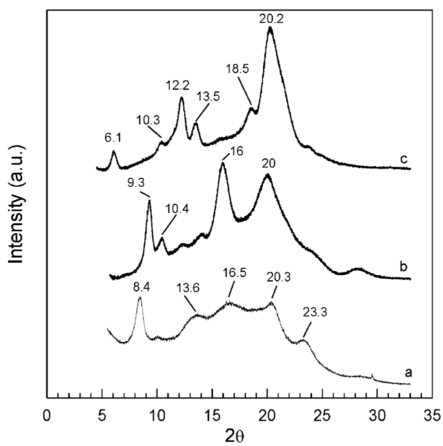

Figure 1.
X-ray diffraction patterns of sPS aerogels obtained from gels prepared in DCE at $C_{pol} = 5$ wt%, after supercritical carbon dioxide extraction at 40 °C (a), 130 °C (b) and 150 °C (c).

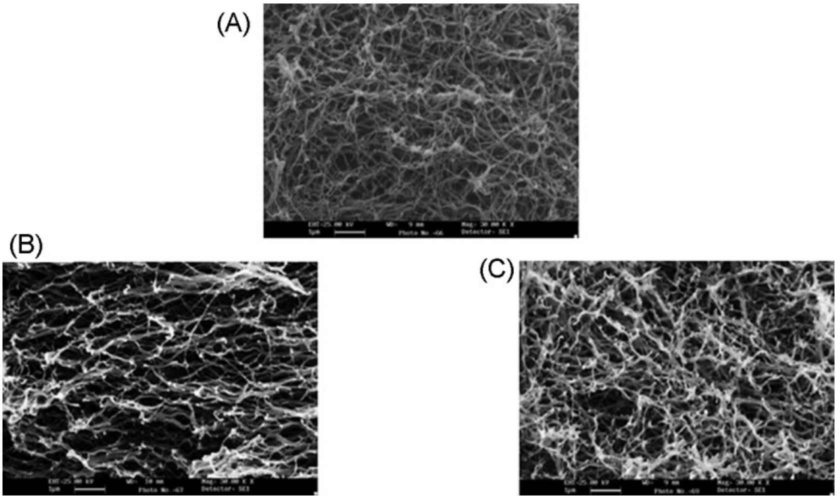

Figure 2.
Electron micrographs of δ-form(Figure A), γ-form (Figure B) and β-form (Figure C) aerogels obtained from gels prepared in DCE at $C_{pol} = 5$ wt% after supercritical carbon dioxide extraction at 40 °C, 130 °C and 150 °C. Magnification x30000 for all micrographs; scale as indicated.

at $2\theta = 8.4, 13.6, 16.5, 20.3$ and 23.1° that are typical of the δ-form.[1d] The X-ray diffraction pattern of the sample obtained after extraction at 130 °C (Figure 1b) displays strong reflections at $2\theta = 9.4$, 10.4, 16 and 20° thus indicating the formation of a γ-form[1c] aerogel, while the reflections at $2\theta = 6.1$, 10.5, 12.3, 13.5, 18.6 and 20.2° observed for the sample obtained after extraction at 150°C (Figure 1c) indicate the formation of a β -form[1b] aerogel.

The influence of extraction temperature on aerogel morphology was also investigated and the SEM micrographs of the δ-form, γ-form, and β-form high-porosity aerogels obtained from gels prepared in DCE after supercritical carbon dioxide extraction at 40°, 130 °C, and 150 °C, are reported in Figure 2.

The micrographs clearly show that, for the entire range of temperature, surpercritical CO_2 extraction leads to aerogels with a fibrillar morphology with fibril diameters in the range 30–150 nm. Thus, supercritical carbon dioxide extraction allows to obtain aerogels where the polymer essentially preserves the morphology of the native gels.

Conclusion

In this paper, the influence supercritical carbon dioxide extraction temperature on the crystalline structure, the morphology and the porosity of sPS aerogels has been investigated.

The variation of the supercritical CO_2 extraction temperature allows to obtain high-porosity aerogels characterized by different crystalline forms. At 40 °C, aerogels with the nanoporous δ-form are obtained while at 130 °C and 150 °C and γ-form and β-form aerogels are obtained. Moreover, in the whole range of temperature investigated (40–150 °C) the supercritical carbon dioxide extractions preserve the morphology occurring in the native gels and lead to aerogels with a fibrillar morphology with fibril diameters in the range 30–150 nm.

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