Crystalline Organization in Syndiotactic Polystyrene Gels and Aerogels

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Summary: The crystalline structure of syndiotactic polystyrene gels and aerogels has been investigated by using x-ray diffraction. Results show that, depending on the solvent, the crystalline structure of the junction zones of the gels is a clathrate phase or the solvent free orthorhombic β-form. For aerogels obtained from gels with a clathrate phase, the aerogel crystalline phase consists of the nanoporous δ-form while for aerogels obtained from gels with the β-form, the original crystalline structure is maintained.

Keywords: aerogels; crystalline structure; gels; syndiotactic polystyrene

Introduction

Syndiotactic polystyrene (sPS) displays a complex polymorphic behaviour and in the crystalline state four crystalline forms, designed by the acronyms α, β, γ, and δ, can be obtained.[1] The polymer chains adopt the all-trans planar zig-zag structure in the α– and the β–form while the s(2/1)2 helical conformation is present in the γ– and δ–forms. In addition to these four crystalline forms, semicrystalline clathrate structures characterized by the helical chain conformation can be obtained by sorption of suitable compounds (mainly halogenated or aromatic) in amorphous sPS samples as well as in sPS samples being in the α-, γ-, or δ-form.

It is well-known that sPS easily forms physical gels with several organic solvents and many reports focussing on the molecular structure, the morphology, the thermal behaviour and the crystalline structure have been published.[2] Depending on solvent-type and/or thermal treatments, the polymer-rich phase of the gels is characterized by the s(2/1)2 helical [2a,b,f,h] or the planar zigzag[2c,g,j] chain conformations.

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It has been recently observed that complete removal of the solvent from sPS gels with the polymer-rich phase characterized by the s(2/1)2 helical or the planar zigzag chain conformations can be achieved by an extraction procedure based on supercritical carbon dioxide and high porosity physical aerogels can be obtained.[3]

In this paper we report on x-ray diffraction investigations relative to gels obtained with 1,2-dichloroethane (DCE) and 1,2-chlorotetradecane (CTD) and aerogels obtained from these different gel samples. In sPS/DCE gels polymer chains assume the s(2/1)2 helical conformation[2h] while in sPS/CTD gels polymer chains assume the planar zigzag chain conformation.[2j]

Experimental Part

The syndiotactic polystyrene used in this study was manufactured by Dow Chemicals under the trademark Questra 101. The ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic triads was over 98%. 1,2-dicloroethane (DCE) and 1-chlorotetradecane (CTD) 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 native gels with a SFX 200 supercritical carbon dioxide extractor (ISCO Inc.) using the following conditions: T= 45°C, P = 200 bar, extraction time t = 60 min (sPS/DCE gel), t = 180 min (sPS/CTD gel).

X-ray diffraction patterns were obtained on powder samples with nickel-filtered Cu K_α radiation with automatic diffractometers PW1710 (Phillips) and D8 (Bruker). Gel samples prepared beforehand in test tube and aerogels were reduced in fine powder before data collection was performed.

Results and discussion

In Figure 1, x-ray diffraction patterns of sPS/DCE gels prepared at different polymer concentrations are reported.

For polymer concentrations below 0.05 g/g, the amount of crystallites formed in gels is too small and diffraction patterns do not display any Bragg peak. By increasing the polymer concentration, the crystallinity of gel samples increases and for a gel prepared at 0.15 g/g weak peaks can be observed at $2\theta \approx 18$, 21, 22, and 29°. By increasing further the polymer concentration, diffraction peaks become sharper and more intense and for a gel prepared at 0.35 g/g, the diffraction pattern displays Bragg peaks located at $2\theta = 8.2$, 10.8, 18, 21, 24, and 29°. The location of the reflections which is substantially identical to that of sPS/DCE clathrate[2h,4] indicates that the cross-links domains of sPS/DCE gels is a crystalline clathrate phase.

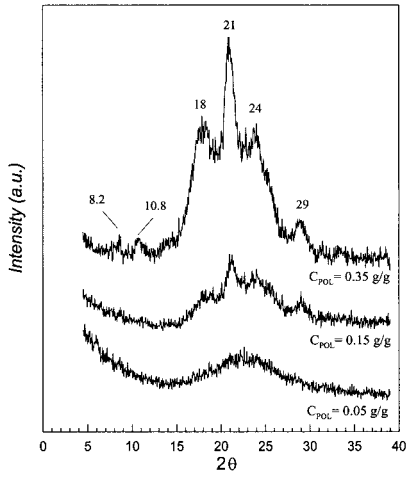

Figure 1. X-ray diffraction patterns for gels obtained in DCE. Concentrations are expressed as polymer weight fraction.

It is worth adding that similar x-ray diffraction patterns were obtained with sPS gels prepared with various solvents capable to form a clathrate phase (in particular chloropropane, toluene, decahydronaphthalene).

In Figure 2, x-ray diffraction patterns of sPS/CTD gels prepared at different polymer concentrations are reported.

Conversely to the gel obtained with DCE, we can observe diffraction peaks for a polymer concentration as low as 0.05 g/g (in particular at $2\theta \approx 12.5$ and 13.5°). This can be attributed to a higher gel crystallinity or a larger crystallite size. By increasing the polymer

concentration as low as 0.05 g/g (in particular at $2\theta \approx 12.5$ and 13.5°). This can be attributed to a higher gel crystallinity or a larger crystallite size. By increasing the polymer concentration, diffraction peaks become sharper and more intense and for a gel prepared at 0.20 g/g, the diffraction pattern displays Bragg peaks located at 2θ = 6.3, 10.5, 12.5, 13.7, 18.7, and 20.4 thus indicating the presence in the gel of the orthorhombic β-form.[5]

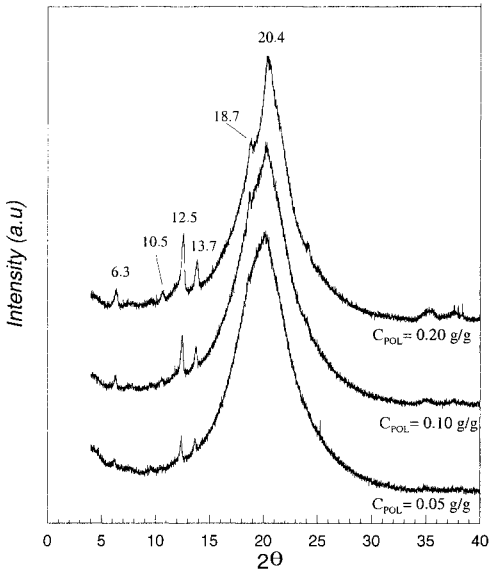

Figure 2. X-ray diffraction patterns for gels obtained in CTD. Concentrations are expressed as polymer weight fraction.

It has been recently observed that complete removal of the solvent from sPS gels can be achieved by an extraction procedure based on supercritical carbon dioxide and high porosity physical aerogels can be easily obtained.[3]

In Figure 3 are reported the x-ray diffraction patterns of aerogels obtained from gels prepared in DCE and in CTD at C_{POL} = 0.10 g/g.

The x-ray diffraction pattern of the aerogel obtained from the sPS/DCE gel displays strong reflections located at 2θ (CuKα) 8.3°, 13.5°, 16.8°, 20.7°, 23.5° and the absence of a diffraction peak at $2\theta \cong 10.6°$, thus indicating that the CO_2 treatment has extracted DCE also from the clathrate phase correspondingly producing a nanoporous δ–phase.[6] Aerogels with

the nanoporous δ-phase were also obtained with gels prepared in solvent capable to form a sPS clathrate phase (in particular toluene, benzene, chloroform).

The diffraction pattern of the aerogel obtained from the sPS/CTD gel displays strong reflections at 2θ = 6.1°, 10.4°, 12.3°, 13.6°, 18.5° and 20.2° thus indicating the maintenance in the aerogel of the orthorhombic β-form, being already present in the starting gel.

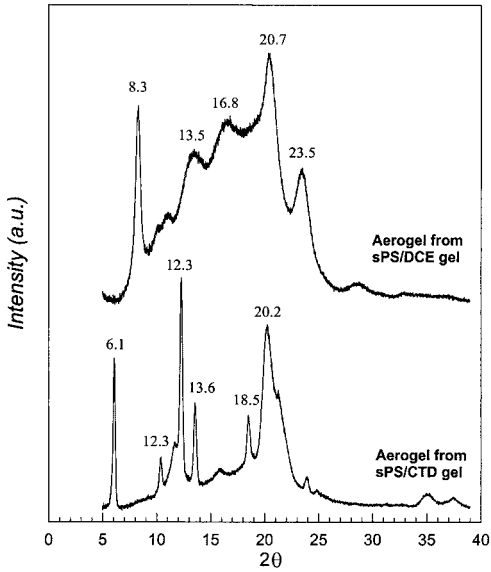

Figure 3. X-ray diffraction patterns for aerogels obtained from gels prepared in DCE and in CTD at C_{POL} = 0.10 g/g.

Conclusion

In this short communication x-ray diffraction chracterization of sPS gels prepared in DCE and CTD and of corresponding aerogels has been presented. In the former gels, the junction zones consist of a clathrate phase while for gels prepared with CTD the β-form is obtained. When the polymer rich phase of the physical gel is a clathrate phase, the corresponding aerogel is characterized by the nanoporous crystalline δ-phase while for aerogels obtained from the other type of gels the β-form is maintained.

It is worth adding that aerogels with the nanoporous δ-form are very promising for industrial applications on chemical separation and water purification as they present the high sorption capacity typical of s-PS δ–form samples associated with the high sorption kinetics typical of aerogels (due to the high porosity).[3]

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