Physical Gelation of Syndiotactic Polystyrene in the Presence of Large Molar Volume Solvents Induced by Volatile Guests of Clathrate Phases

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ABSTRACT: Cooling of syndiotactic polystyrene (s-PS) solutions with bulky solvents, unsuitable as guests of s-PS clathrate phases, results in the formation of pastelike gels characterized by a trans-planar chain conformation and poor mechanical properties. Strong elastic gels with s(2/1)2 helical polymer chains forming a three-dimensional network can be, instead, obtained with the same bulky solvents by the temporary presence of a volatile solvent which is instead a suitable guest for a s-PS clathrate phase. After gel formation, the volatile solvent can be easily removed without breaking the gel structure, and the big size solvent molecules remain entrapped in the three-dimensional polymer network. The gel structures have been investigated by Fourier transform infrared spectroscopy, wide-angle X-ray diffraction, and rheological measurements.

Introduction

Gels consist of a three-dimensional network structure swollen by a liquid. For chemical gels, the cross-links that give rise to this network are covalent bonds while for physical gels the connectedness between polymer chains is achieved by intermolecular physical bonding forming junction zones (polymer-rich phase) which can be created and removed by cooling and heating, respectively.[1]

It is well-known that syndiotactic polystyrene (s-PS) easily forms physical gels with several organic compounds.[2] Particularly stable are gels where the polymer-rich phase is characterized by the helical s(2/1)2 conformation.[3] In a recent study it has been clarified that such polymer-rich phases are substantially consisting of clathrate phases,[4] which include guest molecules in well-defined positions of generally monoclinic crystal structures.[5]

Solvents whose molecules are bulkier than 160−165 Å^3 generally are not able to form s-PS clathrates phases.[6] Quenching of s-PS solutions in these solvents gives rise to the so-called gels of type II,[7] which present in the polymer-rich phase trans-planar s-PS chains[8] and much lower elasticity.

In this contribution we describe a procedure to achieve, with these bulky solvents, s-PS gels presenting in the polymer-rich phase s(2/1)2 helical chains which are more elastic than those presenting trans-planar chains, especially for lower polymer concentrations. This procedure is based on the temporary presence of a volatile guest of a s-PS clathrate phase.

Guest molecules, like 1,2-dichloroethane (DCE), whose conformational equilibrium is substantially altered as a consequence of inclusion into the clathrate phase, can be particularly informative as for the solvent distribution between the polymer-rich and the polymer-poor phase.[4,9]

Hence, in the present study, DCE has been used as volatile component of s-PS gels while 1-chlorotetradecane (CTD), that is, a solvent of s-PS whose molecules are too large to be included in s-PS clathrates and whose FTIR bands do not superimpose to the conformational sensitive bands of DCE and s-PS, has been chosen as the main nonvolatile component of the gels.

Experimental Part

Materials and Sample Preparation. 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%. Mass average molar mass obtained by gel permeation chromotography (GPC) in trichlorobenzene at 135 °C was found to be $M_w = 3.2 \times 10^5$ g mol^{-1} with a polydispersity index $M_w/M_n = 3.9$. 1,2-Dichloroethane and 1-chlorotetradecane were purchased from Aldrich and used without further purification.

Native s-PS gel samples were prepared in hermetically sealed test tubes by heating the mixtures until complete dissolution of the polymer and the appearance of a transparent and homogeneous solution had occurred. Then the hot solution was cooled to room temperature where gelation occurred. Desiccated gel samples were prepared by solvent evaporation in air.

For native and desiccated gel samples, the concentrations of CTD, s-PS, and DCE will be expressed as weight percentage.

Techniques. X-ray diffraction patterns were obtained on powder samples with nickel-filtered Cu Kα radiation with an automatic Philips diffractometer (PW1710).

Rheological experiments were performed at $T = 25$ °C with the rotational stress rheometer, SR5000 (Rheometric Inc.), in a plate−plate configuration ($\phi = 40$ mm) under a N$_2$ atmosphere.

Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Vector 22 FTIR spectrometer from Bruker, equipped with a deuterated triglycine sulfate (DTGS) detector and a KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He−Ne reference laser. Collection of meaningful infrared spectra of gels in the transmission mode is a difficult task, especially if one is interested in measuring the absorbance of medium-strong solvent peaks. This would require the use of extremely thin liquid cells (few microns) which are difficult to fill and to clean. Therefore, FTIR spectra

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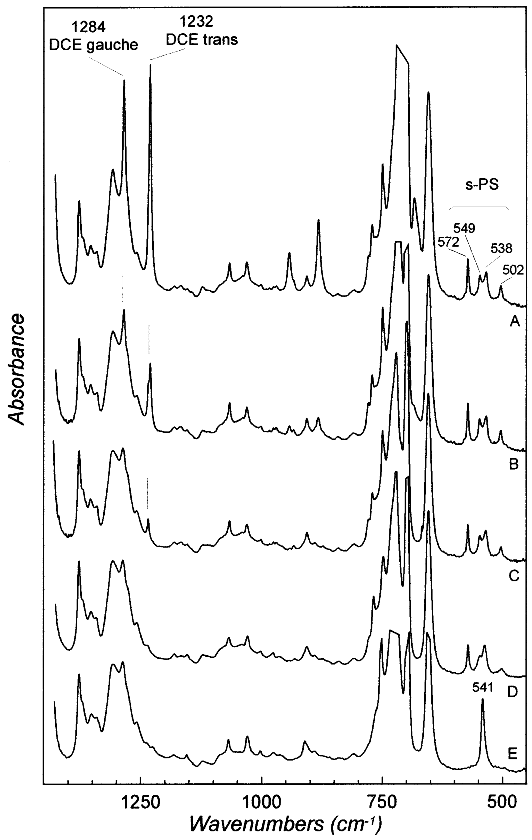

Figure 1. FTIR spectra for samples obtained from (A–D) 4 wt % s-PS solution prepared into a 50/50 wt mixture of DCE and CTD quenched at room temperature followed by progressive DCE desorption: (A) 28 wt % of DCE; (B) 10 wt % of DCE; (C) 1.3 wt % of DCE; (D) 0 wt % of DCE (DCE completely desorbed); (E) 10 wt % s-PS solution prepared in CTD quenched at room temperature. For all samples the CTD/s-PS weight ratio is close to 10.

were collected in the attenuated total reflectance mode (ATR) using a multiple reflection ATR accessory (Benchmark from SPECAC, UK) with horizontal geometry equipped with a KRS-5 crystal. (The angle of incidence was 45°, and the number of reflections was equal to 6.) With this sampling technique, it was always possible to maintain the analytical peaks within the range of absorbance linearity (less than 1.2 absorbance units).

Results

FTIR spectra of s-PS gels prepared by dissolving at ca. 170 °C 4 wt % of s-PS into a 50/50 wt mixture of DCE and CTD (composition s-PS/CTD/DCE: 4/48/48), then cooling rapidly the solution at room temperature, and finally maintaining the gel in air, thus allowing the more volatile DCE to be progressively desorbed, are reported in Figure 1A–D. During the progressive desorption of DCE from the native gel sample, the concentrations of CTD, sPS, and DCE were recalculated and expressed as percentage.

The reduction of the absorbance bands at 1232 and 1284 cm^{-1} typical of the CH$_2$ wagging modes of the trans and gauche DCE conformers,[10] respectively, clearly indicates the progressive DCE desorption from 28% (A), 10% (B), 1.3% (C) to zero (D), while the CTD/s-PS weight ratio remains nearly constant. All the FTIR spectra of Figure 1A–D show the absorption bands at 572, 549, 538, and 502 cm^{-1}, which are characteristic of the s(2/1)2 helical conformation,[11] independent of the presence of DCE, that is, of a guest suitable for a possible clathrate formation. The polymer weight fraction in the helical conformation (and hence in the polymer-rich phase) as determined by the relative intensity of the conformationally sensitive bands is nearly constant for the samples of Figure 1A–D and close to 60%.

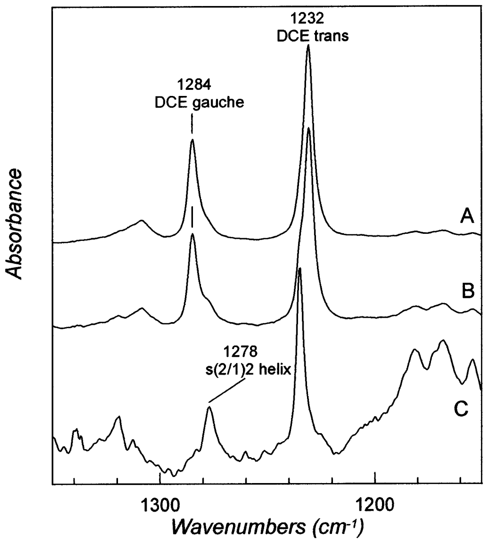

Figure 2. Comparison of the FTIR spectra shown in Figure 1A–C in the spectral region sensitive to DCE conformation. For the sake of comparison, the contribution of CTD has been subtracted, and the spectra have been normalized with respect to the trans DCE band at 1232 cm^{-1}.

For the sake of comparison, the FTIR spectrum of a sample, presenting a composition close to that one of the gel sample of Figure 1D, but obtained by dissolving at ca. 230 °C, 10 wt % of s-PS in CTD and then quenching the solution at room temperature, is shown in Figure 1E. The spectrum shows an absorption band at 541 cm^{-1} which is characteristic of the all-trans-planar conformation of s-PS.[11] The polymer weight fraction in the trans-planar conformation (and hence in the polymer-rich phase), as estimated by a spectral subtraction analysis is not far from 60%.

Details in the range 1150–1350 cm^{-1} of the FTIR spectra of Figure 1A–C after subtraction of the CTD contribution and normalization with respect to the band at 1232 cm^{-1} characteristic of the trans DCE conformer are shown in Figure 2A–C.

The spectra of Figure 2 clearly show the faster disappearance of the band at 1284 cm^{-1} characteristic of the gauche DCE conformer.[10]

In particular, for the spectrum of Figure 2C (and Figure 1C) which corresponds to a gel with 1.3% of DCE, the relative intensities of the DCE conformational bands clearly indicate that the remaining DCE is essentially only in the trans conformation and hence only included in the clathrate phase.[4,9]

X-ray diffraction patterns of s-PS gels whose FTIR spectra are presented in parts C, D, and E of Figure 1 are shown in parts A, B, and C of Figure 3, respectively. Because of the presence of very strong amorphous halos nearly centered at $2\theta = 20°$ (Cu Kα radiation), only the more informative part of the pattern with $2\theta < 15°$ is reported.

In agreement with the FTIR results indicating the presence of essentially only the trans conformer of DCE (Figures 1C and 2C), being completely included into the polymer-rich phase, the X-ray diffraction pattern of the gel sample obtained by quenching of s-PS/DCE/CTD

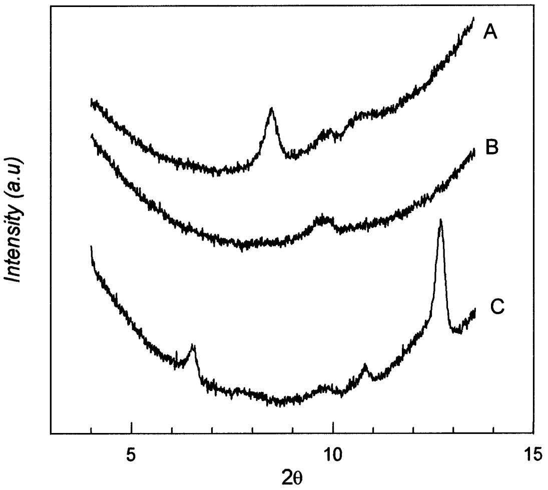

Figure 3. X-ray diffraction patterns in the 2θ range 5°−15° for (A) 4 wt % s-PS solution prepared into a 50/50 wt mixture of DCE and CTD quenched at room temperature followed by desorption of the DCE included in the polymer poor phase (1.3 wt % of DCE), (B) sample A after complete DCE desorption, and (C) 10 wt % s-PS solution prepared in CTD quenched at room temperature.

solutions (Figure 3A) shows reflections located at 2θ = 8.5° and 10.7° which can be attributed to (010) and ($\bar{2}$10) reflections of the s-PS/DCE clathrate form.[5c] However, the weak peak located at 2θ = 9.8° also indicates the presence of a minor amount of the solvent-free helical γ phase.[12]

The X-ray diffraction pattern of the gel sample obtained after a complete desorption of DCE presents only one peak located 2θ = 9.8° (Figure 3B). Hence, X-ray diffraction data confirm the FTIR evidence that the helical conformation is maintained during the desorption of DCE molecules from the clathrate phase while show in addition a transformation of the clathrate phase into the γ phase.

It is worth noting that the extraction of guest molecules from the clathrate phase generally leads to the formation of the kinetically stable nanoporous δ form[4,13] which substantially retains the crystal structure of the clathrate phase, but for the guest molecules which are replaced by empty cavities.[12] The different behavior observed during the desorption of DCE from these mixed solvent gels may be possibly explained by the higher mobility of polymer chains which should be assured by the maintenance of CTD in the polymer-poor phase of the gel. This higher chain mobility should lead to an easier transition toward the γ phase which is more stable than the δ phase, in the absence of suitable guest molecules.

The X-ray diffraction patterns of s-PS samples prepared by quenching of CTD solutions (Figure 3C) show the presence of typical (020), (110), and (040) reflections of the orthorhombic β form[15] and thus indicate that the trans-planar chains which are pointed out by FTIR experiments (Figure 1E) are organized in small β form crystals.

In summary, the combined X-ray diffraction and FTIR data indicate that all considered gels can be approximately described as composed by a crystalline phase including ca. 60% of the polymer and by a polymer-poor phase which would contain all the CTD molecules and nearly 40% of the polymer. However, the nature of the crystalline phase can be completely different. For instance, for the gel samples presenting the FTIR spectra of Figure 1C−E and the WAXS patterns of Figure 3A−C, the polymer-rich phase consists of DCE clathrate, γ, and β crystallites, respectively.

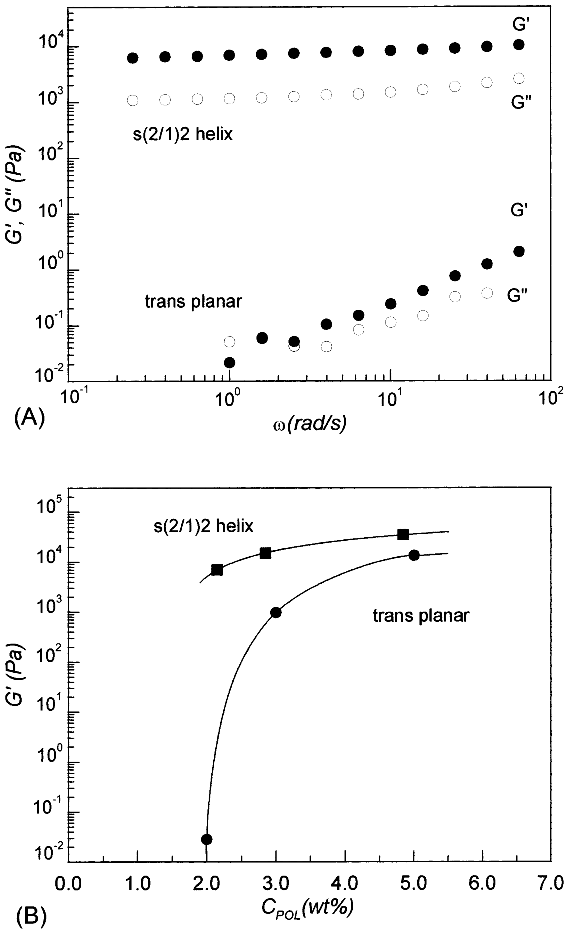

Figure 4. (A) Dynamic moduli measured at 25 °C for s-PS/CTD samples prepared at C_{pol} = 2 wt % with the helical and the trans-planar polymer-rich phase as evaluated for different frequencies. (B) Values of the storage modulus measured at 25 °C and 1 rad/s for both types of s-PS/CTD samples for different gel compositions.

Substantial differences between the physical properties of s-PS/CTD gel samples with helical (clathrate or γ) and trans-planar (β) polymer-rich phases (like those of parts D and E of Figure 1, respectively) are pointed out by rheological measurements.

As an example, the dynamic moduli G' and G'' measured at 25 °C, for s-PS/CTD samples prepared at C_{pol} = 2.0 wt %, which present the helical and the trans-planar polymer-rich phase, are compared in Figure 4A. For the gel with the helical crystalline phase, G' is much larger than G'' throughout the entire range of investigated frequencies. This feature agrees with the mechanical definition of a gel which should display a solidlike behavior.[16] We can also observe that the gel displays a weak relaxation behavior since G' varies as w^m, where the value of m is equal to 0.080. This value is similar to exponent values observed with other physical gels.[17] For the sample with the trans-planar polymer-rich phase, the storage modulus G' is much lower than for the gel with the helical crystalline phase, and a crossover between G' and G'' can be observed at low frequency. The sample prepared directly in CTD displays a liquid-like rheological behavior and hence could be described as a suspension of β form crystals rather than a gel.

The values of the dynamic storage modulus *G*′ measured at 1 rad/s for both types of gels prepared at different polymer concentrations are compared in Figure 4B. We can observe that for higher polymer concentrations the values of the storage modulus *G*′ for gels with helical crystalline phase remain larger than for gels with trans-planar crystalline phase, although differences are reduced.

Conclusions

In conclusion, we present here the first example, to our knowledge, of gelation of a solvent (which is nongelling from diluted solutions) being induced by the temporary presence of a volatile solvent. When the s-PS gel formation occurs in the binary mixture, the big size molecules (in our case CTD) are confined to the polymer-poor phase while the polymer-rich phase is a clathrate phase which includes only the solvent which is suitable as guest (in our case DCE). Also, when the volatile guest is totally desorbed, the resulting gel maintains strong solidlike properties associated with the maintenance of a crystalline helical polymer phase. X-ray diffraction studies have shown that the clathrate phase of these mixed solvent gels as a consequence of the gradual desorption of the guest molecules is transformed into a γ phase, rather than into the other helical nanoporous δ phase, as generally observed for guest desorption from solid clathrate samples as well as for single solvent helical gels.

The ability of s-PS gels to also entrap big size molecules, as induced by the addition of volatile guest molecules, generates new soft materials which could be potentially helpful in addressing environmental pollution issues such as oil spills and leaking oils or could possibly find applications in the treatment of industrial wastes (e.g., recovery of organic solvents).

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Supporting Information Available: Text detailing the quantitative analysis by ATR spectroscopy and the construction of the calibration curves used to evaluate spectroscopically the concentration of CTD and DCE in any gel sample. This material is available free of charge via the Internet at http://pubs.acs.org.

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