Evaluation of the Amount and Composition of the Polymer-Rich and Polymer-Poor Phases of Syndiotactic Polystyrene Gels with Binary Solvent Mixtures

Christophe Daniel,* Davide Alfano, and Gaetano Guerra

Dipartimento di Chimica, Università di Salerno, Via S. Allende, 84081 Baronissi (SA), Italy

Pellegrino Musto

Institute of Chemistry and Technology of Polymers, National Research Council of Italy, Via Campi Flegrei 34, 80078 Pozzuoli (NA), Italy

Received April 4, 2003

ABSTRACT: Gels of syndiotactic polystyrene (sPS) in a binary mixture of 1,2-dichloroethane (DCE) and 1-chlorotetradecane (CTD) have been investigated by attenuated total reflectance−Fourier transform infrared spectroscopy. Host−guest interactions into the clathrate phase induce not only the well-known selectivity in favor of the trans conformer but also a well-defined shift of the CH_2 wagging mode of such conformer. Independent evaluations of the DCE content in the polymer-rich and polymer-poor phases, based on DCE conformer equilibrium and peak shift, give essentially identical results. As a consequence, an accurate evaluation of the amount and composition of the polymer-poor and polymer-rich phases of these gels from binary solvent mixtures can be achieved.

Introduction

In a previous work, attenuated total reflectance−Fourier transform infrared (FTIR-ATR) and wide-angle X-ray diffraction (WAXS) characterizations of syndiotactic polystyrene (sPS) gels and semicrystalline clathrate samples have allowed us to clarify the nature of the polymer-rich phase forming the cross-link domains in sPS/1,2-dichloroethane (DCE) and sPS/1-chloropropane (CP) gels.[1]

The choice of DCE and CP was motivated by the additional information which can be obtained from the study of their conformational equilibrium. Indeed, recent sorption studies have shown that the conformation equilibrium of guest molecules can be altered as a consequence of their sorption by sPS.[2] When DCE is absorbed in the clathrate phase, the trans conformer is largely prevailing mainly due to electrostatic attractive interactions with a quadrupolar cavity[3] while in the amorphous phase the trans and the gauche conformers are nearly equally populated.[2a,c] Conversely, no change of conformational equilibrium was observed for CP.[2c] Furthermore, by considering the different conformational equilibrium in the amorphous and in the clathrate phase, it was possible to evaluate the amount of DCE and diffusion kinetics in both phases.[2b]

The study of the solvent conformational equilibrium in sPS/DCE and sPS/CP gels and clathrates showed the occurrence of the same kind of conformational selectivity for DCE (in favor of the trans conformer) and the absence of conformational selectivity for CP for both gel and clathrate samples.[1] Moreover, for gels formed in DCE it was shown that the stoichiometry of the gel crystalline phase is nearly constant (3.6 ± 0.3)[1] in a large range of concentrations and is very close to the ratio (4) found for the sPS/DCE clathrate phase.[4] From these results it was concluded that the polymer-rich phase forming the cross-link domains of these gels is a crystalline clathrate phase.[1] It is worth noting that the stoichiometry of the crystalline phase of sPS/DCE gels was found to be quite different from the 1/1 monomeric unit/guest molecule stoichiometry determined for other sPS gels from differential scanning calorimetry (DSC) studies.[5]

In the previous study, relative to sPS/DCE gels, the polymer-rich phase of the gel was investigated by studying the conformational equilibrium of DCE guest molecules. However, although the investigated composition range was extended by considering desiccated gels, the maximum sPS concentration in the gel being suitable for our characterization study was ca. 60 wt % due to the experimental difficulties (mainly roughness of desiccated gels) to get spectra in the attenuated total reflectance mode.

Recently, we have reported on FTIR-ATR, WAXS, and rheological investigations relative to sPS gels formed in a binary mixture of DCE and 1-chlorotetradecane (CTD).[6] It has been shown that CTD is a compound too bulky to be included in the sPS clathrate phase, and when sPS/DCE + CTD gels are formed, all the CTD molecules are confined in the polymer-poor phase. Moreover, when a gel prepared in the binary mixture is maintained in air, the more volatile DCE can be progressively desorbed (and eventually the sPS/DCE clathrate phase which constitutes the polymer-rich phase is transformed into a γ phase) while the amount of CTD remains substantially constant. The retaining of CTD in the gel tri-dimensional network has the effect of maintaining the shape of the gel also after complete DCE desorption. This, of course, gives now the possibility (not available for gels with pure DCE) to study by FTIR-ATR spectroscopy the conformational equilibrium of DCE, and hence to get structural information relative to the polymer-rich phase, also for sPS gels where the DCE concentration is progressively reduced to zero.

Hence, in this paper, we report a FTIR-ATR investigation on sPS gels formed in binary mixtures of DCE and CTD by following the spectral changes associated

10.1021/ma034430w CCC: $25.00
Published on Web 07/03/2003

with the progressive DCE desorption. It will be shown that the quantitative analysis of some relevant guest and host peaks allows an accurate evaluation of the amount and composition of both polymer-rich and poor-phases which is possibly unprecedented for gels with binary solvent mixtures.

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 $\bar{M}_w = 3.2 \times 10^5$ g mol^{-1} with a polydispersity index $\bar{M}_w/\bar{M}_n = 3.9$. 1,2-Dichloroethane and 1-chlorotetradecane were purchased from Aldrich and used without further purification.

All sPS 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.

Techniques. Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Vector 22 FTIR spectrometer from Bruker and with a Perkin-Elmer System 2000 spectrometer. Both instruments were 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 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).

For gels with concentrations below ca. 0.10 g/g a piece of gel having the dimensions of the ATR crystal was prepared beforehand in a test tube. For higher concentration gels, data were obtained by solvent desorption.

Quantitative Analysis by ATR Spectroscopy. In ATR spectroscopy the relationship between absorbance, A, and concentration of the absorbing species, C, can be expressed as

$$A = \log \frac{I_0}{I} = -\log R = \alpha n d_p C \tag{1}$$

where I_0 is the incident intensity, I is the reflected intensity, R is the reflectivity, α is the absorption coefficient, d_p is the depth of penetration of the evanescent wave within the sample, and n is the number of reflections in the optical element.[7]

One major difference between eq 1 and the Beer−Lambert relationship employed in transmission measurements is that in the former case d_p depends on the wavenumber of the incident radiation according to

$$d_p = \frac{\lambda}{2\pi n_1}\left[\sin^2\theta - \left(\frac{n_2}{n_1}\right)^2\right]^{-1/2} \tag{2}$$

where λ is the wavelength of the incident radiation, n_1 and n_2 are respectively the refractive indices of the internal reflection element (IRE) and of the sample, and θ is the incident angle.[7,8]

Thus, contrary to transmission FTIR, in ATR spectroscopy any peak has a specific path length. To take into account this effect, quantitative analysis via ATR is generally performed by peak ratioing methods.[7,8] The use of this approach can also eliminate errors due to irreproducible sample contact with the IRE.

For the case of a sPS gel with DCE and CTD, the following relationships can be written:

$$A_T = \alpha_T n d_{p,T} C_T \tag{3}$$

$$A_G = \alpha_G n d_{p,G} C_G \tag{4}$$

$$A_S = \alpha_S n d_{p,S} C_S A_G = \alpha_G n d_{p,G} C_G \tag{5}$$

$$A_{CTD} = \alpha_{CTD} n d_{p,CTD} C_{CTD} \tag{6}$$

where the subscripts T and G refer to the trans and gauche conformers of DCE, and the subscripts S and CTD refer to the styrene monomeric units and to the CTD molecules, respectively.

Recalling that

$$C_{DCE} = C_T + C_G = \frac{1}{\alpha_T n d_{p,T}}\left(A_T + \frac{\alpha_T d_{p,T}}{\alpha_G d_{p,G}} A_G\right) \tag{7}$$

one obtains

$$\frac{C_S}{C_{DCE}} = \frac{N_S}{N_{DCE}} = \frac{\alpha_T d_{p,T}}{\alpha_S d_{p,S}} \frac{A_S}{A_T + \frac{\alpha_T d_{p,T}}{\alpha_G d_{p,G}} A_G} \tag{8}$$

where N indicates the number of moles.

From eqs 5 and 6 we have

$$\frac{C_S}{C_{CTD}} = \frac{N_S}{N_{CTD}} = \frac{\alpha_{CTD} d_{p,CTD}}{\alpha_S d_{p,S}} \frac{A_S}{A_{CTD}} \tag{9}$$

Figure 1a,b displays a plot of N_S/N_{DCE} vs $A_S/[A_T + (\alpha_T d_{p,T})/(\alpha_G d_{p,G})A_G]$ and N_S/N_{CTD} vs A_S/A_{CTD} constructed by several gel samples having precisely known concentration ratios. In order to obtain a polymer concentration at the surface of the samples close to the bulk concentration, solvent evaporation was minimized, and the pressure applied to the sample was maintained very low to avoid the formation of a solvent layer on the crystal surface.

By assuming that the absorption coefficients of DCE peaks remain unchanged in pure DCE or when DCE is in solution with another solvent,[9] one can estimate the value of $\alpha_T d_{p,T}/\alpha_G d_{p,G}$ in the mixture DCE/CTD from the ATR spectrum of liquid DCE and from the knowledge of the C_T/C_G ratio characteristic of liquid DCE at 25 °C (0.35).[10] As predicted by eqs 8 and 9, the plots are linear through the origin, which allows one to evaluate spectroscopically the concentration of CTD and DCE in any gel sample.

The analytical peaks employed in the present investigation were the CH_2 wagging modes of the trans and gauche DCE conformers at 1232 and 1284 cm^{-1},[10] respectively, the absorption peak of CTD at 1377 cm^{-1}, and the conformationally insensitive mode of sPS at 1493 cm^{-1}.

Evaluation of the Fraction of Monomeric Units Assuming the s(2/1)2 Helical Conformation in sPS/DCE + CTD Gels. The s(2/1)2 helical conformation of sPS exhibits various characteristic IR absorption peaks, and for a few of them, a critical sequence length (CSL), which is defined as the lower sequence length necessary for the appearance of the sensitive band, has been recently estimated. For example, for the absorption peaks centered at 1355 and 572 cm^{-1}, the values of CSL, expressed as the number of monomeric units constituting the sequence, are respectively $m = 12-15$ and $m = 20-30$.[11]

The fraction of styrene monomeric units accommodated in any ordered s(2/1)2 helical sequences ($x_{S,s(2/1)2}$) can be estimated

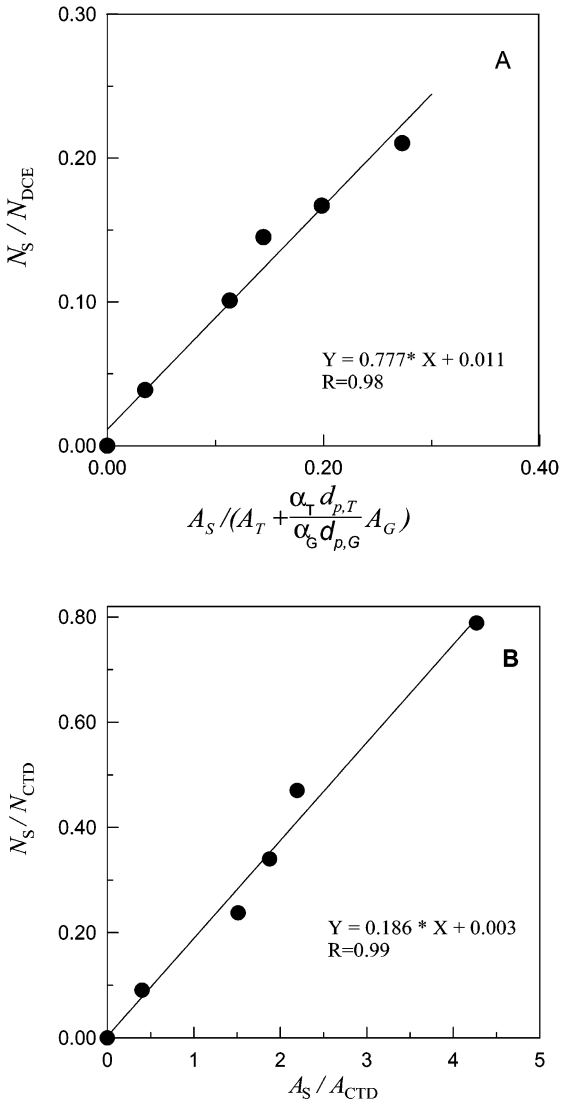

Figure 1. Calibration curves for the spectroscopical determination of the concentration ratios of DCE (curve A) and CTD (curve B) in sPS/DCE + CTD gels.

for sPS/DCE + CTD gel samples in the entire range of compositions by ATR spectroscopy.

In fact, from the relationship

$$\frac{A_{s(2/1)2}}{A_{reference}} = \frac{\alpha_{s(2/1)2} d_{p,s(2/1)2}}{\alpha_{reference} d_{p,reference}} x_{S,s(2/1)2} = K x_{S,s(2/1)2} \quad (10)$$

it is possible to evaluate $x_{S,s(2/1)2}$ for any sample from its ATR spectrum once the value of the constant K has been determined.

The procedure reported in a previous work[1] to evaluate the fraction of styrene monomeric units accommodated in s(2/1)2 helical sequences in semicrystalline clathrate samples obtained by immersion of an amorphous film in DCE from the 1355 cm^{-1} peak was extended to the 572 cm^{-1} peak. In these samples, the fraction of monomeric units included in short and long helical sequences from the peaks at 572 and 1355 cm^{-1} was found to be equal to $x_{S,572} \approx 32\%$ and $x_{S,1355} \approx 65\%$, respectively. By comparing the reduced intensity of the peaks at 572 and 1355 cm^{-1} for gels and semicrystalline clathrate samples, it emerged that the fractions of helical sequences in sPS/DCE + CTD gels prepared at $C_{pol} = 0.07$ g/g in a 50/50 wt mixture of DCE and CTD are equal to $x_{S,572} \approx 43\%$ and $x_{S,1355} \approx 67\%$. Since for these gel samples FTIR-ATR spectroscopy gives $A_{1355}/A_{reference} \approx 0.078$ and $A_{572}/A_{reference} \approx 0.42$, we obtain, according to eq 10, K values of 0.116 and 0.977 for the 1355 and 572 cm^{-1} peaks, respectively.

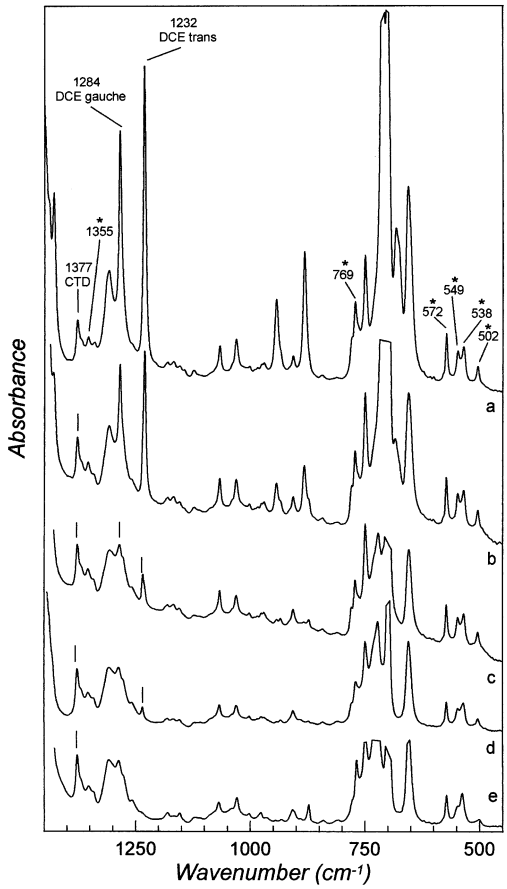

Figure 2. FTIR-ATR spectra collected at different times during DCE desorption of a sPS/DCE + CTD gel prepared at $C_{pol} = 0.07$ g/g in a 50/50 wt mixture of DCE and CTD. Some absorption peaks of the sPS helical conformation are indicated with asterisks.

Results

In Figure 2 are reported the spectra collected at various times of a gel prepared at $C_{pol} = 0.07$ g/g subjected to isothermal desorption at $T = 25$ °C. As already reported in ref 5 for a gel prepared at $C_{pol} = 0.04$ g/g, the progressive reduction of the absorbance peaks characteristic of the DCE (see in particular the peaks at 1232 and 1284 cm^{-1}) clearly shows the progressive DCE desorption, while at the same time the invariability of the CTD peaks (see in particular the peak at 1377 cm^{-1}) indicates that the amount of CTD remains substantially unchanged.

This behavior is illustrated in Figure 3 where the variation of the concentration of DCE and CTD is reported as a function of time. While the concentration of CTD remains constant within experimental uncertainty over the whole investigated time range, the DCE concentration decreases continuously with time. We can also observe that the desorption of DCE proceeds at two different rates. In the early stage of the process (i.e., interval time 0−300 min), the DCE desorption rate is ca. 2.2 g of DCE/100 g of dry polymer/min, while for longer times the desorption rate is about 50 times slower. It is also worth noting that the change in the desorption rate occurs at ca. $N_{DCE}/N_S \sim 0.23$, which is not too far from the stoichiometric ratio of the sPS/DCE clathrate phase ($N_{DCE}/N_S = 0.25$).[4]

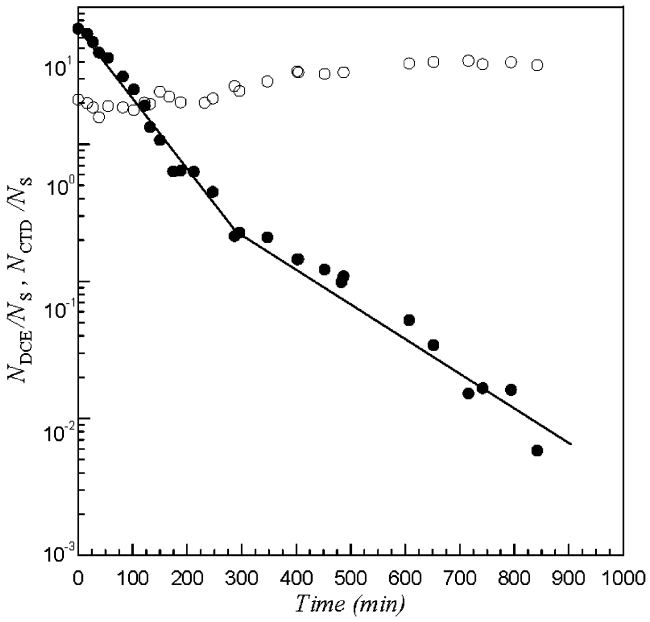

Figure 3. Molar ratios N_{DCE}/N_S and N_{CTD}/N_S as a function of the desorption time. Lines are drawn to guide eyes.

The fast desorption process occurring first (0−300 min) can be attributed to the DCE desorption from the gel polymer-poor phase, while the much slower desorption phenomenon which takes place later (after 300 min) can be attributed to the desorption from the clathrate phase which leads to a nearly complete removal of DCE after longer times (ca. 900 min).

Structural Information from the Spectrum of the Polymer Host. As can be observed in Figure 2, characteristic peaks of the s(2/1)2 helical conformation can be observed in the FT-ATR spectra independent of the amount of DCE present in the gel (for instance, at 769, 572, 548, 538, and 502 cm^{-1}).[13] Among the different peaks sensitive to the helical conformation, we considered those located at 1355 and 572 cm^{-1}. These peaks allowed us to investigate the amount of short and long TTGG sequences as the 572 cm^{-1} peak is associated with long helical sequences (critical sequence length CSL: $m = 20-30$[11]) while the 1355 cm^{-1} peak is associated with short helical sequences (CSL: $m = 12-15$[11]).

The reduced intensity of the 1355 and 572 cm^{-1} peaks for a sPS/DCE + CTD gel prepared at $C_{pol} = 0.07$ g/g in a 50/50 wt mixture of DCE and CTD is reported in Figure 4A,B (shown on the left scale) as a function of the molar ratio of monomeric units X_S' ($X_S' = N_S/(N_S + N_{DCE})$). Following the procedure reported in the last section of the Experimental Part, the fraction of monomeric units included in the helical sequences associated with both peaks ($x_{S,1355}$ and $x_{S,572}$) was determined, and values of $x_{S,1355}$ and $x_{S,572}$ are also reported in parts A and B of Figure 4, respectively (shown on the right scale).

Up to a polymer concentration $X_S' = 0.85$ mol/mol the reduced intensity of both peaks remains constant. In this concentration range, the fraction of monomeric units included in the short and long helical sequences is equal to $x_{S,1355} = 0.67 \pm 0.04$ and $x_{S,572} = 0.43 \pm 0.05$, respectively. However, for polymer concentrations larger than $X_S' = 0.85$ mol/mol, the fraction of monomeric units included in the short sequences decreases progressively with increasing polymer concentration reaching the same value observed for the fraction of monomeric units included in the longer sequences.

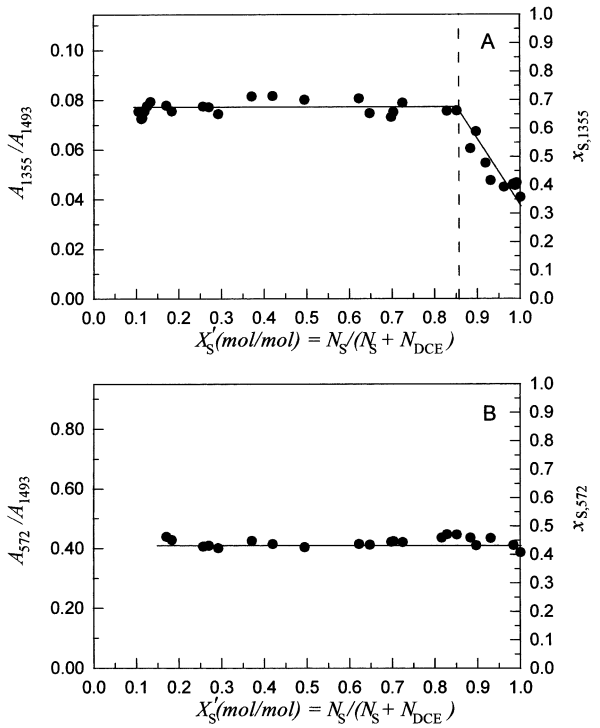

Figure 4. (A) Reduced intensity of the 1355 cm^{-1} peak (left scale) and fraction of styrene units included in short helical sequences ($x_{S,1355}$, right scale) as a function of X_S'. (B) Reduced intensity of the 572 cm^{-1} peak (left scale) and fraction of monomeric units included in long helical sequences ($x_{S,572}$, right scale) as a function of X_S'.

In a recent study we have shown that, during the desorption of DCE molecules from the crystalline phase of gels formed in binary mixtures of DCE and CTD, there is a transition of the clathrate phase into the helical γ phase rather than into the nanoporous δ phase, as generally observed for clathrate samples.[6] The decrease of short helical sequences during guest desorption may be explained by assuming that when DCE guest molecules are desorbed from the gel crystalline phase, the short helical sequences corresponding to less perfect crystalline regions would be broken while the long helical sequences corresponding to more perfect crystalline regions would recrystallize into γ-form crystallites. However, we have to keep in mind that the molar absorption coefficients of the helical conformation peaks may also vary during the transformation of the clathrate phase into the solvent-free helical γ phase. This variation may also play a role in the decrease of the reduced intensity of the 1355 cm^{-1} peak for X_S' values larger than 0.85 mol/mol.

Structural Information from Guest Peaks. *(i) Study of the Conformational Equilibrium.* For the evaluation of the amount of DCE conformers, we used the CH_2 wagging mode of the gauche conformer at 1284 cm^{-1} and the CH_2 wagging mode of the trans conformer at 1232 cm^{-1}.[10]

The molar fraction of the trans conformer (x_T) was then evaluated by

$$x_T = \frac{1}{1 + \frac{N_G}{N_T}} = \frac{1}{1 + \frac{\alpha_T d_{p,T}}{\alpha_G d_{p,G}} \frac{A_G}{A_T}} \qquad (11)$$

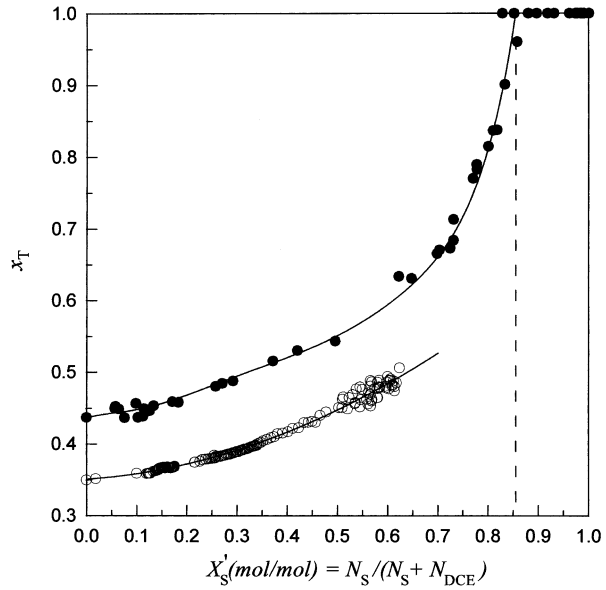

Figure 5. Fraction of DCE trans conformer (x_T) as a function of the molar ratio of styrene units (X_S'): ●, sPS gels prepared in the binary mixture DCE + CTD; ○, sPS gels prepared in pure DCE (data by Daniel et al.[1]).

In Figure 5 the fraction of DCE being in the trans conformation (x_T) is reported as a function of the molar ratio of monomeric units X_S' for different gel samples initially prepared at $C_{pol} = 0.07$ g/g. For the sake of comparison, the fraction of trans conformer previously obtained for gels prepared in pure DCE[1] is also reported (open symbols).

We can observe that for both types of gels the molar fraction of trans conformer presents a similar increase with increasing the polymer concentration. The only difference is a constant shift of the x_T values which is due to a different conformer equilibrium of DCE in the pure liquid and in the mixture. This feature suggests the existence of the same conformational selectivity in the sPS/DCE gels and sPS/DCE + CTD gels.

The regular increase of x_T can be attributed to an increase of the fraction of DCE being included in the polymer-rich phase due to the faster desorption kinetics from the polymer-poor phase. For low polymer concentration gels, only a very small fraction of DCE is included in the crystalline phase, and as a consequence, the measured x_T value is very close to the conformer equilibrium of DCE when mixed to CTD in a weight ratio 1:1, i.e., $x_T = 0.43$. When the polymer fraction in the gel increases, the fraction of DCE included in the crystalline phase increases and hence the fraction of DCE trans conformer increases also.

The region of the plot with $X_S' > 0.6$ mol/mol, which was not accessible for sPS/DCE gels,[1] comes out to be very informative. In fact, we can observe that the molar fraction of trans conformer reaches a x_T value equal to 1 for polymer concentrations larger than $X_S' = 0.85$ mol/mol. As a value of x_T close to 1 is typical of the DCE in the clathrate phase,[2a,b] we can conclude that for polymer concentrations larger than 0.85 mol/mol all the residual DCE in the gel is included into the clathrate phase.

(ii) Study of Guest Peak Shift. A closer look to the FTIR-ATR spectra reported in Figure 2 shows that, during the progressive desorption of DCE, the reduction of the DCE trans conformer peak at 1232 cm^{-1} is accompanied by a splitting of the peak in two components at 1232 and 1235 cm^{-1} (see Figure 6, curves b−e). This feature is not present in the spectrum of the 50/50 wt mixture of DCE and CTD, which displays only a fully resolved peak at 1232 cm^{-1} (curve a). Moreover, we can observe that during DCE desorption the peak at 1232 cm^{-1} vanishes well before the peak at 1235 cm^{-1} (Figure 6).

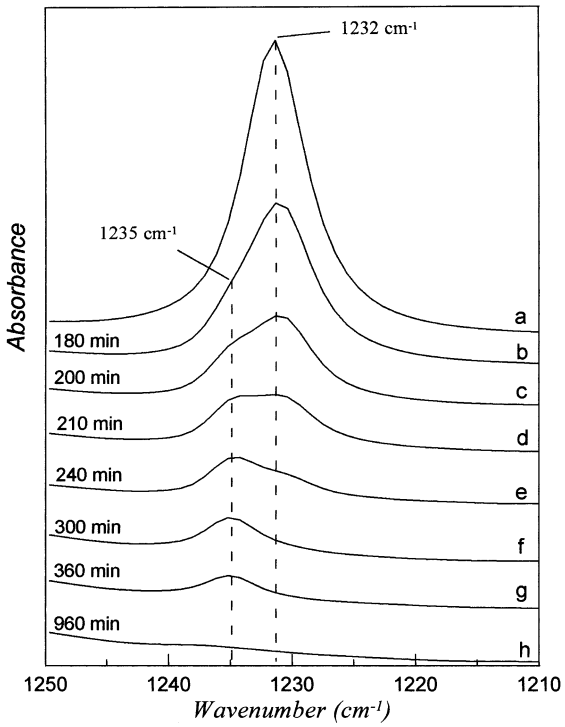

Figure 6. FTIR-ATR spectrum in the 1250−1210 cm^{-1} region of a 50/50 wt mixture of DCE and CTD (curve a) and FTIR-ATR spectra collected at different times during DCE desorption of a sPS/DCE + CTD gel prepared at $C_{pol} = 0.07$ g/g in a 50/50 wt mixture of DCE and CTD (curves b−h).

This behavior can be explained by considering two types of trans DCE molecules in the gel: guest molecules included in the gel crystalline phase (characterized by the peak at 1235 cm^{-1}) and free molecules included in the polymer-poor phase (characterized by the peak at 1232 cm^{-1}). At the initial stages of the desorption the amount of DCE included in the polymer-poor phase is much larger than the amount of DCE included in the clathrate phase, and thus the peak at 1232 cm^{-1} is largely prevailing (Figure 6, curve b). Then, as the DCE desorption from the polymer-poor phase proceeds at a higher rate than from the polymer-rich phase, we observe a strong decrease of the 1232 cm^{-1} peak which vanishes well before the 1235 cm^{-1} peak.

It is worth noting that analogous peak shifting attributed to specific host−guest interactions has been observed for chloroform in the sPS clathrate phase[14] as well as for para-disubstituted benzene forming clathrate structures with poly(ethylene oxide).[15]

In Figure 7 are reported the full width at half-height (fwhh) of the peaks at 1232 and 1235 cm^{-1} for various gel compositions. As the two peaks are highly overlapped, a spectral subtraction procedure was applied to separate them when necessary. This was accomplished by subtraction of the spectra of parts a and g of Figure 6 for the peaks at 1235 and 1232 cm^{-1}, respectively.

We can observe that for both peaks fwhh remains substantially constant with $fwhh_{1232} = 6.5 \pm 0.2$ cm^{-1} and $fwhh_{1235} = 4.6 \pm 0.3$ cm^{-1}. Since the full width at

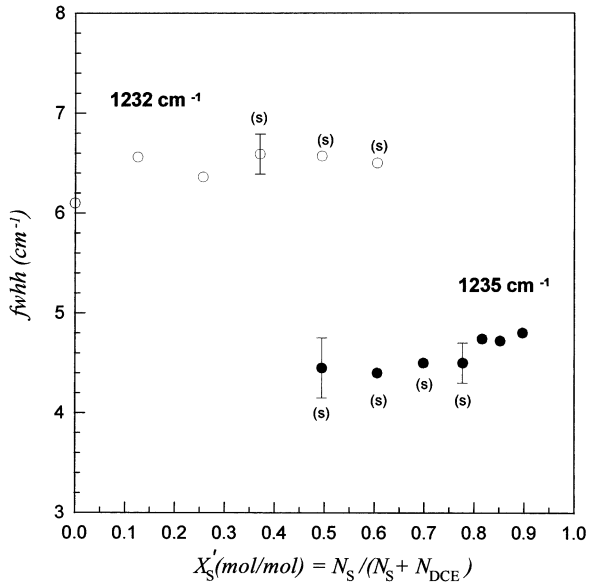

Figure 7. Full width at half-height (fwhh) of the peaks at 1232 and 1235 cm^{-1} as a function of X_S'. The symbol *s* indicates when a spectral subtraction procedure was applied to separate the two peaks.

half-height of an infrared peak is inversely proportional to the relaxation time of the motion of the groups associated with this vibrational peak,[16] we can conclude that the DCE trans conformer associated with the 1232 cm^{-1} peak displays smaller relaxation time (i.e., larger molecular motion) than the DCE trans conformer associated with the 1235 cm^{-1} peak. This result is consistent with the assumption that the 1235 cm^{-1} peak is associated with the DCE trans molecules included in the gel crystalline clathrate phase while the 1232 cm^{-1} peak is associated with the DCE trans molecules included in the polymer-poor phase.

(iii) Determination of the Fraction of DCE Molecules Included in the Polymer-Rich and the Polymer-Poor Phases. As reported in a previous paper,[1] the fraction of DCE molecules included in the crystalline phase can be estimated from the x_T values by considering two species of solvent molecules: guest molecules included in the polymer-rich phase forming the junction zones and free molecules merely entrapped with CTD molecules in the gel network. For the crystalline phase nearly all DCE molecules are in the trans conformation ($x_{T,c} = 1$) while for the free molecules in the polymer-poor phase, we assumed for DCE the conformational equilibrium of DCE when mixed to CTD in a ratio 1:1 ($x_{T,free} = 0.43$).

The fractions of DCE included in the gel crystalline phase ($x_{DCE,c}$) and in the gel network ($x_{DCE,free}$) are evaluated as follows:

$$x_{DCE,c} = \frac{N_{T,c} + N_{G,c}}{N_{DCE}} = \frac{N_{T,c}}{N_{DCE}}$$

$$x_{DCE,free} = \frac{N_{T,free} + N_{G,free}}{N_{DCE}} \qquad (12)$$

where $N_{T,c}$ and $N_{T,free}$ represent the number of moles of trans conformer in the crystalline phase and in the gel network, $N_{G,free}$ is the number of moles of gauche conformer in the gel network, and N_{DCE} is the total number of moles of DCE in the gel.

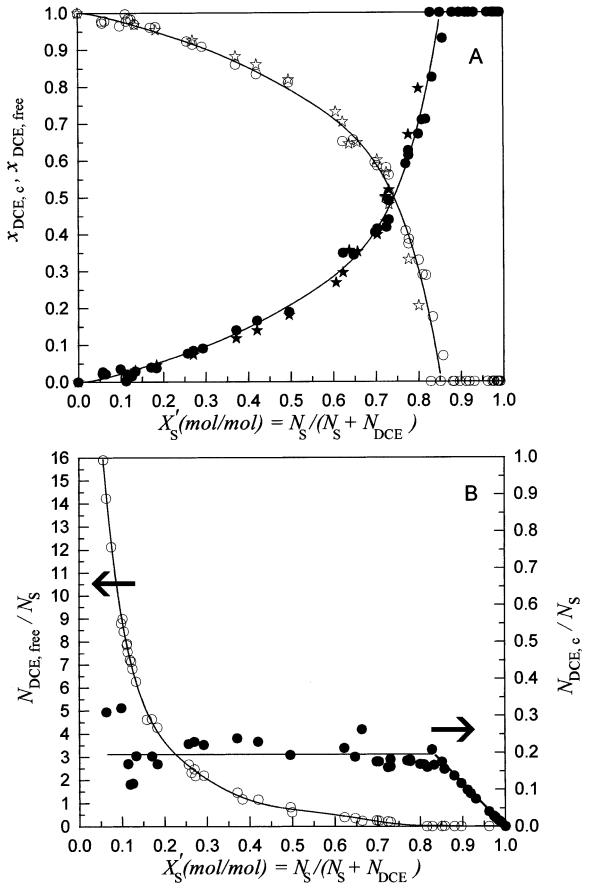

Figure 8. (A) Fraction of DCE included in the gel crystalline phase ($x_{DCE,c}$, ● and ★) or merely entrapped in the gel network ($x_{DCE,free}$, ○ and ☆) vs X_S'. (B) Molar ratios $N_{DCE,c}/N_S$ and $N_{DCE,free}/N_S$ vs X_S'. $N_{DCE,c}$ is the number of DCE molecules included in the crystalline phase, and $N_{DCE,free}$ is the number of DCE molecules included in the polymer-poor phase of the gel.

Recalling that

$$x_{T,free} = \frac{N_{T,free}}{N_{T,free} + N_{G,free}} = 0.43$$

$$x_{T,c} = 1$$

$$x_T = \frac{N_T}{N_{DCE}} = \frac{N_{T,c} + N_{T,free}}{N_{DCE}}$$

$$x_{DCE,c} + x_{DCE,free} = 1 \qquad (13)$$

one obtains

$$x_{DCE,c} = \frac{1 - x_{T,free}}{x_{T,c} - x_{T,free}}\left(1 - \frac{1 - x_T}{1 - x_{T,free}}\right) = \frac{x_T - 0.43}{0.57}$$

$$x_{DCE,free} = 1 - x_{DCE,c} = \frac{1 - x_T}{0.57} \qquad (14)$$

The variation of $x_{DCE,free}$ and $x_{DCE,c}$ as a function of X_S' is shown in Figure 8A (circle symbols). We can observe that the fraction of DCE included in the crystalline phase increases with increasing polymer concentration, while at the same time the fraction of free DCE in the gel network decreases.

As mentioned above, during the DCE desorption, the absorbance peak of the CH_2 wagging mode of the trans DCE conformer at 1232 cm^{-1} is split into two compo-

nents which may be attributed to the DCE trans population included in the gel crystalline phase and to the DCE trans population entrapped in the gel network, respectively.

Thus, the fraction of DCE in the gel crystalline phase ($x_{DCE,c}$) and in the gel network ($x_{DCE,free}$) can be also evaluated independently as follows:

$$N_{T,c} = \alpha_{T,c} d^{c}_{p,T} A_{T,c} = \alpha_{1235} d_{p,1235} A_{1235}$$

$$N_{T,free} = \alpha_{T,free} d^{free}_{p,T} A_{T,free} = \alpha_{1232} d_{p,1232} A_{1232} \quad (15)$$

Assuming that the absorption coefficient and the depth of penetration are identical for both DCE trans absorption peaks, one obtains

$$\frac{N_{T,free}}{N_{T,c}} = \frac{A_{1232}}{A_{1235}} \quad (16)$$

Recalling that

$$N_{T,c} + N_{T,free} = N_T = x_T N_{DCE}$$

$$x_{DCE,c} = \frac{N_{DCE,c}}{N_{DCE}} = \frac{N_{T,c}}{N_{DCE}} \quad (17)$$

we get

$$x_{DCE,c} = \frac{x_T}{1 + \frac{A_{1232}}{A_{1235}}} \quad (18)$$

The variation of $x_{DCE,free}$ and $x_{DCE,c}$ estimated from the two peaks at 1235 and 1232 cm^{-1} is also reported in Figure 8A (star symbols).

We can observe that there is a good agreement between the two independent methods of evaluation of $x_{DCE,free}$ and $x_{DCE,c}$ in the entire range of polymer compositions. This result shows that the assumption made by considering two species of solvent molecules, namely, guest molecules included in the polymer-rich phase forming the junction zones, and free molecules merely entrapped in the gel network can be considered valid for all the considered gel compositions.

From $x_{DCE,free}$ and $x_{DCE,c}$ it is possible to evaluate the ratios $N_{DCE,\ c}/N_S$ and $N_{DCE,free}/N_S$, where $N_{DCE,c}$ is the number of DCE molecules included in the crystalline phase and $N_{DCE,free}$ is the number of DCE molecules included in the gel network, and values of both ratios are reported in Figure 8B vs the molar fraction X_S'.

Figure 8B clearly shows that the behavior of these two populations of solvent molecules differs completely from each other. While the amount of free DCE decreases continuously with increasing polymer concentration reaching zero for X_S' values larger than 0.80 mol/mol, the amount of DCE included in the gel crystalline phase remains substantially constant within experimental uncertainty (0.186 ± 0.033) up to $X_S' = 0.85$ mol/mol and then linearly decreases to zero with increasing polymer concentration. Hence, up to $X_S' = 0.85$ mol/mol, desorption of DCE occurs only in the polymer-poor phase of the gel while desorption of DCE from the clathrate phase takes place only after complete DCE desorption from the polymer-poor phase. It is worth noting that the constant value of $N_{DCE,c}/N_S$ (0.186 ± 0.033) is not far from the guest/host molar ratio typical of the sPS/DCE clathrate phase.[4]

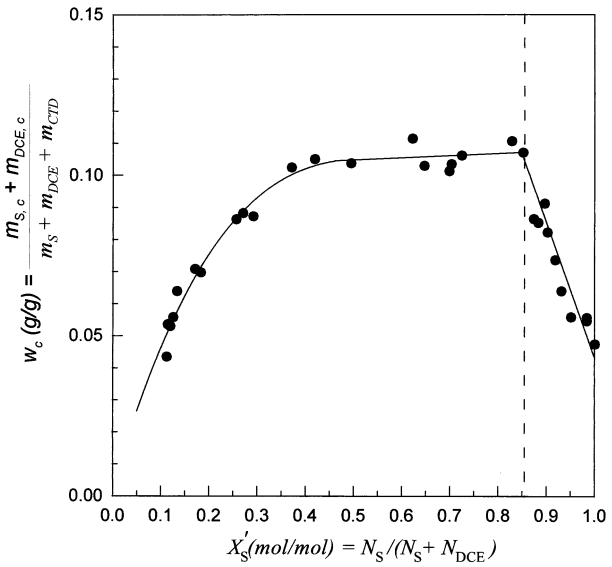

Figure 9. Variation of the weight fraction of the gel polymer-rich phase during the progressive desorption of DCE from a gel prepared at $C_{pol} = 0.07$ g/g in a 50/50 wt mixture of DCE and CTD.

We can also note that $X_S' = 0.85$ mol/mol nearly corresponds to the X_S' value which can be calculated by assuming that all helical chains are included into the sPS/DCE clathrate phase and that DCE is not present in the polymer-poor phase:

$$X_S' = \frac{1}{1 + \frac{X_c}{R}} \quad (19)$$

where R is the stoichiometry of the gel crystalline phase and X_c is the polymer fraction in the gel presenting the helical conformation.

If we consider a stoichiometry of the cross-links domains of 4 monomeric units/DCE molecule and X_c value equal to 67% (i.e., amount of short helical sequences ($x_{S,1355}$) evaluated in Figure 4A), we obtain $X_S' = 0.86$ mol/mol.

Hence, we can conclude from the data of Figures 5 and 8 that, for these gels formed with a binary mixture of DCE and CTD, a complete removal of DCE from the polymer-poor phase can be achieved, and correspondingly the polymer-rich phase is constituted by a 4/1 stoichiometric sPS/DCE clathrate phase.

Amount and Composition of Polymer-Poor and Polymer-Rich Phases. The weight fraction (w_c) of the polymer-rich phase during the DCE desorption can be estimated from the ratio $(m_{S,c} + m_{DCE,c})/(m_S + m_{DCE} + m_{CTD})$, where $m_{S,c}$ and $m_{DCE,c}$ are the mass of polymer and DCE included in the gel crystalline phase and m_S, m_{DCE}, and m_{CTD} are the total mass of polymer, DCE, and CTD in the gel. The ratio w_c can be easily evaluated in the assumption that all the sPS monomeric units being in the short helical sequences are included in the gel crystalline phase.

In particular, for a gel prepared at $C_{pol} = 0.07$ g/g, w_c values calculated on the basis of the fraction of polymer constitutional units in short helical sequences ($x_{S,1355}$ data of Figure 4A) and of $x_{DCE,c}$ data of Figure 8A are reported vs X_S' in Figure 9.

We can observe that w_c gradually increases with DCE desorption reaching a plateau regime at ca. $X_S' = 0.40$ mol/mol. Then w_c remains substantially constant with

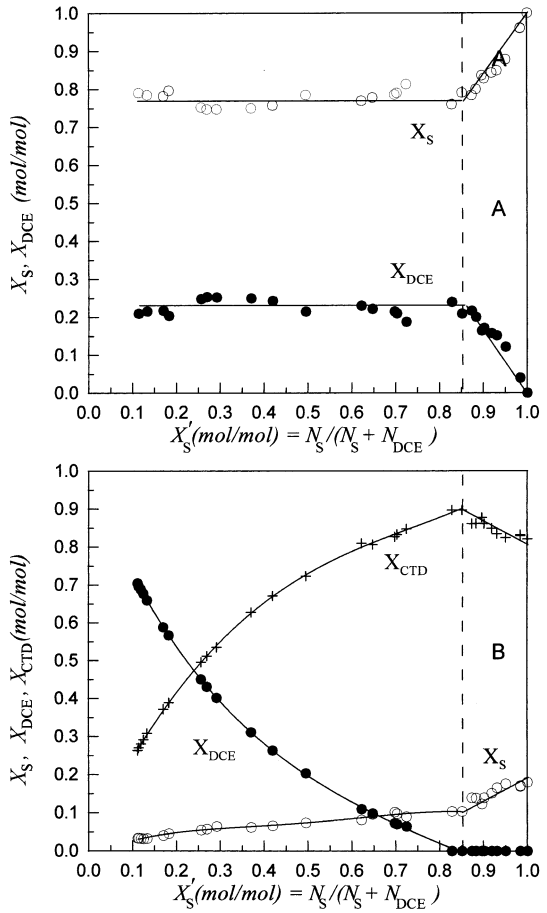

Figure 10. Variation during DCE desorption of the composition of the polymer-rich (A) and polymer-poor phases (B) of a gel prepared at $C_{pol} = 0.07$ g/g in a 50/50 wt mixture of DCE and CTD: (X_{DCE}, ●) mole fraction of DCE; (X_S, ○) mole fraction of styrene monomeric units; (X_{CTD}, +) mole fraction of CTD.

$w_c \approx 0.10$ before decreasing for X_S' above 0.85 mol/mol. Finally after complete DCE desorption, the polymer-rich phase represents about 4 wt % of the gel.

The initial increase of w_c is due to the desorption of DCE from the gel polymer-poor phase. As can be seen in Figure 8B, the number of DCE molecules included in the polymer-poor phase decreases by a factor 10 from $X_S' = 0.10$ mol/mol and $X_S' = 0.40$ mol/mol. Then, for X_S' values between 0.50 and 0.85 mol/mol, the desorption from the polymer-poor phase proceeds at a slower rate, and as a consequence w_c remains substantially constant. For X_S' above 0.85 mol/mol, the gradual decreases is due both to the desorption of DCE from the gel crystalline phase and to a reduction of the crystallinity.

The composition of the polymer-rich and the polymer-poor phases of these binary gels was also evaluated for the entire range of DCE concentrations, and results are reported in parts A and B of Figure 10, respectively.

As can be seen in Figure 10A, the composition of the gel polymer-rich phase remains substantially unchanged during DCE desorption for polymer compositions below $X_S' = 0.85$ mol/mol while for larger polymer concentrations the molar fraction of polymer increases. This increase is, of course, due to the progressive removal of DCE from the polymer-rich phase. It is also worth noting that, before DCE desorption from the gel crystalline phase has started, the stoichiometric ratio of the polymer-rich phase remains constant with experimental uncertainty (3.50 ± 0.40). This value is very close to the stoichiometry of the gel crystalline phase obtained in a previous paper with sPS gels formed in pure DCE (3.60 ± 0.30).[1]

For the gel polymer-poor phase (Figure 10B), for X_S' below 0.85 mol/mol, the fraction of DCE included in the polymer-poor phase gradually decreases while at the same time the fraction of s-PS and CTD increases. For larger polymer concentrations, when all the DCE initially present in the polymer-poor phase is totally desorbed, the fraction of CTD in the polymer-poor phase decreases slightly while the fraction of polymer increases. This behavior is due to a diminution of the gel crystallinity.

It is also worth noting that the variations of the concentration of the different species which are presented in Figure 10 show discontinuities associated with the clathrate phase stoichiometry (i.e., at $X_S' = 0.85$ mol/mol).

Concluding Remarks

The FTIR-ATR characterization of sPS gels including a binary mixture of DCE and CTD resulted to be particularly informative. In fact, host−guest interactions into the clathrate phase (which corresponds to the polymer-rich phase of the gel) induce not only the well-known selectivity in favor of the DCE trans conformer[2] but also a well-defined shift of the CH_2 wagging mode of such a conformer.

As a consequence, two independent evaluation methods of the DCE content in the polymer-rich and polymer-poor phases (one based on DCE conformational equilibrium and the other one on the resolution of the two CH_2 wagging components) are available. Since these two independent methods give essentially identical results for a broad gel composition range, the model assuming two kinds of DCE molecules, namely, guest molecules included in the clathrate polymer-rich phase forming the junction zones and free molecules merely entrapped in the gel network, has been validated.

It is also shown that when the second solvent is not suitable as guest of sPS clathrate phases (e.g., too bulky, like chlorotetradecane) an accurate evaluation of the amount and composition of both polymer-poor and polymer-rich phases of these gels can be achieved. In our knowledge this is the first study where the amount and composition of both phases of a gel with a binary solvent mixture has been established.

This characterization approach which can be in principle applied to any sPS gel obtained in mixtures of DCE with solvents which are not suitable as guests of sPS clathrate phases could be also easily extended to gels where DCE is replaced by other sPS clathrate guests, whose conformational equilibrium is modified by clathration (like e.g. 1,2-dichloropropane[2c]) or presenting some FTIR peak shift or splitting associated with host−guest interactions (like e.g. chloroform[14]).

Finally, it is worth noting that a discontinuity in several independent structural parameters is clearly apparent at a molar ratio corresponding to the stoichiometry of the sPS/DCE clathrate phase (Figures 4A and 8). This suggests that the proposed approach provides a method to determine the stoichiometric ratio for sPS clathrate phases and more in general for other gels where the polymer-rich phase would be a clathrate phase.

Acknowledgment. C.D. was supported by a grant cofinanced by EEC (European Social Fund). The financial support of MURST of Italy (Grants PRIN 2002 and Cluster 26) and Regione Campania (Legge 41 and Centro di Competenza Regionale CdCR "Nuove Tecnologie per le Attività Produttive") is also acknowledged. We thank Dow Chemicals for the gift of Questra 101.

References and Notes

(1) Daniel, C.; Guerra, G.; Musto, P. *Macromolecules* **2002**, *35*, 2243.
(2) (a) Guerra, G.; Manfredi, C.; Musto, P.; Tavone, S. *Macromolecules* **1998**, *31*, 1329. (b) Musto, P.; Manzari, M.; Guerra, G. *Macromolecules* **1999**, *32*, 2770. (c) Musto, P.; Manzari, M.; Guerra, G. *Macromolecules* **2000**, *33*, 143.
(3) (a) Guerra, G.; Milano, G.; Venditto, V.; Musto, P.; De Rosa, C.; Cavallo, L. *Chem. Mater.* **2000**, *12*, 363. (b) Milano, G.; Guerra, G.; Cavallo, L. *Macromol. Theory Simul.* **2001**, *10*, 349.
(4) De Rosa, C.; Rizzo, P.; Ruiz de Ballesteros, O.; Petraccone, V.; Guerra, G. *Polymer* **1999**, *40*, 2103.
(5) (a) Daniel, C.; Deluca, M. D.; Guenet, J. M.; Brulet, A.; Menelle, A. *Polymer* **1996**, *7*, 1273. (b) Daniel, C.; Menelle, A.; Brulet, A.; Guenet, J. M. *Polymer* **1997**, *16*, 4193.
(6) Daniel, C.; Alfano, D.; Guerra, G.; Musto, P. *Macromolecules* **2003**, *36*, 1713.
(7) Harrick, N. J. *Internal Reflection Spectroscopy;* Harrick Scientific Corp.; New York, 1967.
(8) Mirabella, F. M. *Appl. Spectrosc. Rev.* **1985**, *21*, 45.
(9) (a) Naobumi, O.; Coetzee, J. F. *J. Am. Chem. Soc.* **1969**, *91*, 2478. (b) El Bermani, M. F.; Woodward, A. J.; Jonathan, N. *J. Am. Chem. Soc.* 19**70**, *92*, 6750. (c) Wiberg, K. B.; Keith, T. A.; Frisch, M. J.; Murcko, M. *J. Phys. Chem.* **1995**, *99*, 9079. (d) Stolov, A. A.; Remizov, A. B. *Spectrochim. Acta* **1995**, *51*, 1919. (e) Herrebout, W. A.; van der Veken, B. J. *J. Phys. Chem.* **1996**, *100*, 9671. Kato, M.; Abe, I.; Taniguchi, Y. *J. Chem. Phys.* **1999**, *110*, 11982. (f) Cappelli, C.; Corni, S.; Tomasi, J. *J. Phys. Chem. A* **2001**, *105*, 10807.
(10) Tanabe, K. *Spectrochim. Acta* **1972**, *28A*, 407.
(11) Tashiro, K.; Ueno, Y.; Yoshioka, A.; Kaneko, F.; Kobayashi, M. *Macromolecules* **2001**, *34*, 310.
(12) (a) Kobayashi, M.; Yoshioka, T.; Imai, M.; Itoh, Y. *Macromolecules* **1995**, *28*, 7376. (b) Kobayashi, M. *Macromol. Symp.* **1997**, *114*, 1. (c) Tashiro, K.; Ueno, Y.; Yoshioka, A.; Kaneko, F.; Kobayashi, M. *Macromol. Symp.* **1999**, *141*, 33.
(13) Guerra, G.; Musto, P.; Karaz, F. E.; MacKnight, W. J. *Makromol. Chem.* **1990**, *191*, 2111.
(14) Musto, P.; Mensitieri, S.; Cotugno, S.; Guerra, G.; Venditto, V. *Macromolecules* **2002**, *35*, 2296.
(15) Point, J. J.; Jasse, B.; Dosiere, M. *J. Phys. Chem.* **1986**, *90*, 3273.
(16) Fröhlich, H. *Theory of Dielectrics*, 2nd version; Oxford: London, 1960.

MA034430W