1,2-Dichloroethane Conformation and Molecular Organization in Syndiotactic Polystyrene Gels

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SUMMARY The conformational equilibrium of 1,2-dichloroethane (DCE) in syndiotactic polystyrene (sPS)/DCE gels has been investigated by using Fourier transform infrared spectroscopy. Results show that the fraction of DCE in the *trans* conformation (X_T) increases with increasing polymer concentration. From these X_T values, by assuming that the crystalline phase in the gel presents the clathrate structure, the amount of DCE included in the crystalline phase and the fraction of polymer included in the crystalline phase were evaluated as a function of the gel composition.

Introduction

Since the synthesis of syndiotactic polystyrene (sPS) was reported, a large body of work has been focussed on the complex polymorphic behavior of this highly stereoregular polymer and four different crystalline forms have been identified1). In addition to the four main crystalline forms, several clathrate structures, for which the X-ray diffraction patterns change with the kind and the amount of guest molecules, have been also reported2). Complete removal of the guest molecules included in the clathrate structure can be achieved through suitable solvent treatments and the so-called δ form is obtained3).

Recent sorption studies have shown that the conformational equilibrium of guest molecules can be substantially altered as a consequence of clathration into the nanoporous δ form4). When 1,2-dichloroethane (DCE) and 1,2-dichloropropane (DCP) are absorbed in the clathrate phase, the *trans* conformer is largely prevailing while in the amorphous phase the *trans* and the *gauche* conformations are nearly equally populated4b). Conversely no change of conformational equilibrium was observed for 1-chloropropane (CP)4b). The high *trans* selectivity observed for DCE and DCP was explained by electrostatic attractive interactions5). Furthermore by considering the different conformational equilibrium in the amorphous and the clathrate phases it was possible to evaluate the amount of DCE present in both phases6).

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The gelation of sPS has been reported in many solvents and a number of studies have been published on sPS gels7). Even though a considerable amount of work has been devoted to this topic, the molecular organization of sPS gels is not yet fully understood.

In order to shed more light onto sPS gel structure, we studied sPS/DCE gels mainly by Fourier transform infra-red (FTIR) spectroscopy. This FTIR analysis should be in principle more informative than previous FTIR analyses7) since the conformational characterization of the polymer component can be associated with the conformational characterization of the solvent molecules.

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-dichloroethane was purchased from Aldrich and used without further purification.

All sPS solutions were prepared in hermetically sealed test tubes by heating the mixtures above the melting point of DCE until complete dissolution of the polymer and the appearance of a transparent and homogeneous solution had occurred.

Infrared spectra were obtained at a resolution of 4.0 cm^{-1} using a Perkin-Elmer System 2000 FTIR spectrometer, equipped with a deuterated triglycine sulfate detector and a Ge/KBr beam splitter. As transmission measurements are difficult to perform with gels, FTIR spectra were collected in the attenuated total reflectance mode (ATR) using an horizontal accessory (benchmark from SPECAC) equipped with a ZnSe crystal. With this sampling technique, it was always possible to maintain the analytic peaks within the range of absorbance linearity (less than 1.2 absorbance units).

For concentrations below c.a. 0.25 g/g a piece of gel with the ATR crystal dimensions was prepared beforehand in a test-tube. For higher concentrations, data were obtained by solvent desorption. The total concentration of DCE was then determined spectroscopically using a calibration curve constructed with precisely known polymer concentration gels.

Results and discussion

For the evaluation of the population of the DCE conformers, the CH_2 *wagging* of the *trans* conformer at 1234 cm^{-1} and the CH_2 *wagging* of the *gauche* conformer at 1285 cm^{-1} were used. As discussed in detail in ref.4a, the molar fraction of the *trans* conformer (X_T) can be evaluated by:

$$X_T = \frac{1}{\frac{N_g}{N_t} + 1} = \frac{1}{\frac{\varepsilon_{1234}}{\varepsilon_{1285}} \cdot \frac{A_{1285}}{A_{1234}} + 1}$$

where A is the absorbance height and ε the molar absorbivity.

The variation of the fraction of DCE being in the *trans* conformation (X_T) as a function of polymer concentration (X_{POL}) is reported in Fig. 1, for as prepared gels as well as for partially desiccated samples.

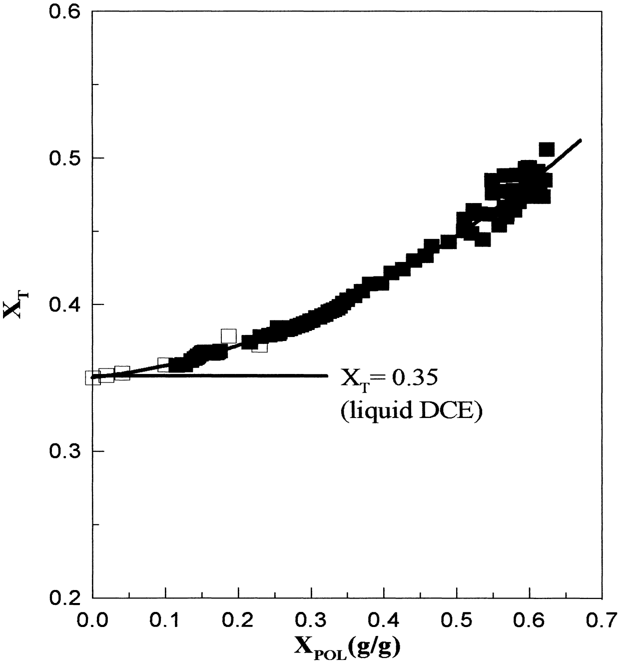

Fig.1 : Variation of the fraction of *trans* conformer as a function of polymer concentration. □ : data obtained from gels prepared at a given polymer concentration; ■ :data obtained by desorption measurements

The fraction of *trans* conformer increases steadily with increasing polymer concentration. This can be interpreted by an increase of the fraction of solvent included in the crystalline phase. For low polymer concentrations, a small amount of crystallites is formed and only a small proportion of the solvent is included in the crystalline phase. As a consequence, the fraction of

DCE being in the *trans* conformation is very close to the liquid state equilibrium, i.e. $X_T = 0.35$. When the polymer concentration increases, more crystallites are formed in the gel (differential scanning calorimetry measurements showed that the melting enthalpy increases with increasing polymer concentration (not shown here)) and the amount of DCE included in the crystalline phase increases. As a result, the fraction of *trans* conformer increases with increasing polymer concentration.

The fraction of DCE in the crystalline phase $(X_{DCE})_c$ can be estimated from the X_T values reported in Fig. 1 by considering two species of solvent molecules : some solvent molecules are included in the crystalline domains while other molecules are merely entrapped in the gel network. For the former molecules, the fraction of *trans* conformer is assumed to be equal to the highest experimental value observed in the clathrates, i.e. $X_T = 0.94$[4)]. For the latter molecules, we considered in a first approximation that the fraction of *trans* conformer is equal to the conformational equilibrium observed in the liquid state, i.e. $X_T = 0.35$.

The variation of $(X_{DCE})_c$ as a function of polymer concentration is shown in Fig. 2.

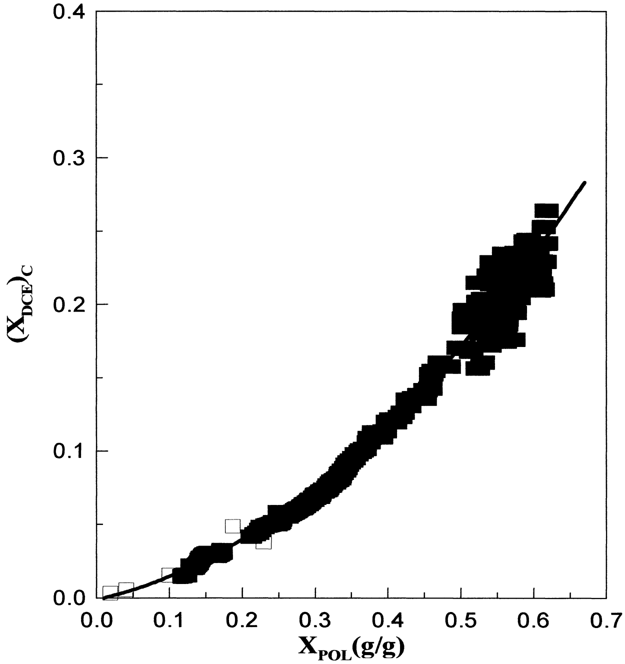

Fig.2 : Variation of the fraction of DCE included in the crystalline phase as a function of polymer concentration. □ : data obtained from gels prepared at a given polymer concentration; ■ :data obtained by desorption measurements.

As expected the fraction of solvent molecules included in the crystalline phase increases with polymer concentration. While for low polymer concentrations $(X_{DCE})_c$ is almost nought, about 25% of the DCE is included in the crystalline phase at $X_{POL} = 0.60$ g/g.

The fraction of polymer included in the crystalline phase $(X_{POL})_c$ can be estimated by assuming for the crystalline phase of the gel a stoichiometry of four monomer units per solvent molecule, as observed for the clathrate phase[2]. The variation of $(X_{POL})_c$ as a function of the polymer concentration is reported in Fig. 3.

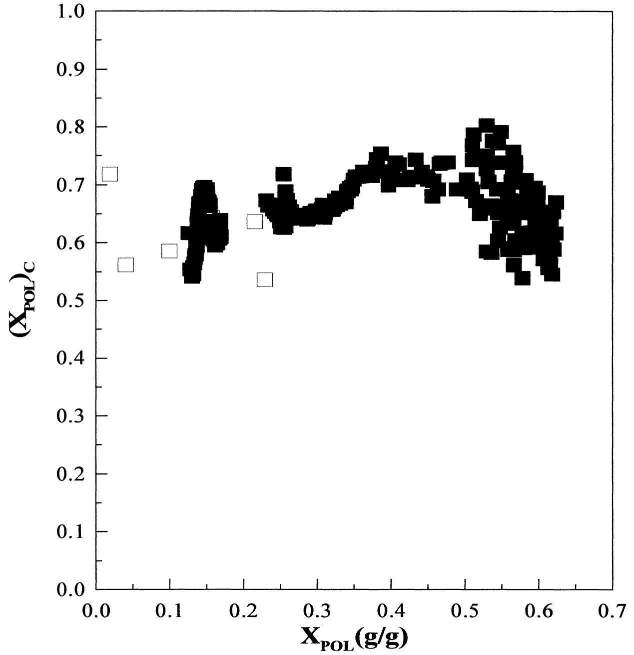

Fig.3 : Variation of the fraction of polymer included in the crystalline phase as a function of polymer concentration. □ : data obtained from gels prepared at a given polymer concentration; ■ :data obtained by desorption measurements.

Throughout the entire investigated range of compositions, $(X_{POL})_c$ is substantially constant within experimental uncertainties, with $(X_{POL})_c = 0.65 \pm 0.05$. This result is consistent with FTIR results that showed that the fraction of 2_1 helix remains roughly constant for X_{POL} in the range 0.05-0.60 g/g (not shown here). The high fraction of polymer included in the gel crystalline phase may be rather surprising as this value is larger than the crystallinity observed for sPS samples, which is generally lower than 50 %. However, it is worth noting that a high value of $(X_{POL})_c$ has been also reported for syndiotactic poly(methyl methacrylate) gels formed in toluene. In these gels, it was found, through high resolution ^{1}H NMR measurements, that c.a. 80% of the polymer chains are included in the crystalline phase8).of gels with a polymer fraction in the range 0.02-0.30 g/g.

Conclusions

In this paper by reflectance infra-red spectroscopy measurements we have shown that the fraction of *trans* conformer in sPS/DCE gels increases with increasing polymer concentration. The variation of the solvent conformational equilibrium can be explained by an increase of the fraction of DCE molecules included into the crystalline phase of the gel. By assuming that the crystalline phase in the gel presents the clathrate structure, it has been possible to evaluate the fraction of polymer included in the crystalline phase. We found that for the whole range of investigated compositions the fraction of polymer included in the crystalline phase remains always in the range $(X_{POL})_c = 0.65 \pm 0.05$. To our knowledge, this is the first time that the fraction of polymer included in crystalline phase has been evaluated for a wide range of gel composition.

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