Macromol. Symp. **2007**, 251, 1–10 DOI: 10.1002/masy.200750501

Structural Organization and Properties of Syndiotactic Polystyrene Gels

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Summary: In this manuscript, the structural organization of syndiotactic polystyrene (sPS) gels is reviewed with particular emphasis on the structure of molecular complexes (clathrates and intercalates) formed in sPS gels. Hereafter, results concerning macroscopic properties such as the rheological behaviour and the light transparency are reported and discussed on the basis of the gel molecular organization.

Keywords: gels; light transparency; rheological properties; structural organization; syndiotactic polystyrene

Introduction

Syndiotactic polystyrene (sPS) displays a complex polymorphic behaviour[1] and in the crystalline state four crystalline forms (designed by the acronyms α, β, γ, and δ) and numerous molecular complexes (clathrates[2] and intercalates[3]) can be obtained with low-molecular-mass compounds.

The two crystalline forms α,[4] and β[5] are characterized by zig-zag trans planar chains while the γ and δ[6] forms and the molecular complexes present s(2/1)2 helices.

All the crystalline structures of sPS clathrate and intercalate phases which have been determined[2,3] present several features common to the δ form. In fact, all known sPS molecular complexes are monoclinic with space group $P2_1/a$ and they are characterized by the same ac layers of close-packed enantiomorphous s(2/1)2 helices. However clathrates are characterized by a closer packing between the ac polymer layers. Thus for clathrates, guest molecules are enclosed into host cavities while for intercalates the guest molecules are not isolated into cavities but form layers of contiguous guest intercalated with mono-layers of enantiomorphous polymer helices.

SPS can also form thermoreversible gels with a large number of organic solvents and several studies focussing on the morphology, the thermal behaviour, or the molecular structure of sPS gels have been published in the literature.[7] Depending on the solvent-type and/or thermal treatments the crystalline junctions of sPS gels are characterized by s(2/1)2 helical polymer chain conformation[7a,b,f–h,j,k] or by the β phase with planar zigzag chain conformation.[7i,m]

The crystalline structure and in particular the stoichiometry of the s(2/1)2 helical molecular complex phases formed in sPS gels has been the matter of debate due to contradictory results of differential scanning calorimetry studies and diffraction analysis. In fact, some diffraction patterns of sPS gels are consistent with x-ray diffraction patterns obtained with the clathrate samples while the stoichiometry derived from differential scanning calorimetry (DSC) studies is found to be very different from the typical clathrate stoichiometry (i.e. 4 monomeric units/guest molecule).[7g,h,o,p]

In this contribution, the issue of the structural organization of sPS gels will be reviewed. Moreover the close relationship existing between gel structural organization and macroscopic properties such as the rheological behavior and light transparency will be shown.

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1. Structural Organization in sPS Gels

1.1. SPS Gels in Non-Complexing Solvents

It has been observed that solvents whose molecules are bulkier than 300 Å^3 generally are not able to form molecular complexes with sPS.[3b] However quenching of sPS solutions in these solvents can lead to the formation of gels.[7i,m]

In Figure 1, are reported, the FTIR spectrum (Figure 1A) and the x-ray diffraction

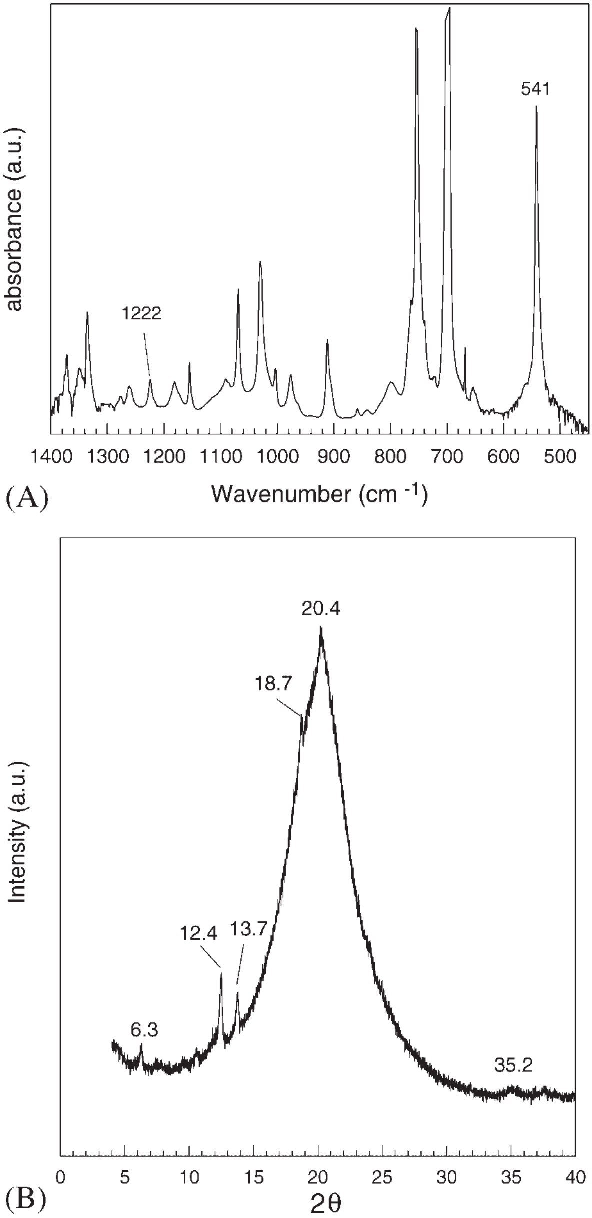

Figure 1.
(A) FTIR spectrum of a gel prepared in CTD at $C_{pol} = 0.10$ g/g after subtraction of the CTD contribution; (B) X-ray diffraction pattern for a gel prepared in CTD at $C_{pol} = 0.20$ g/g.

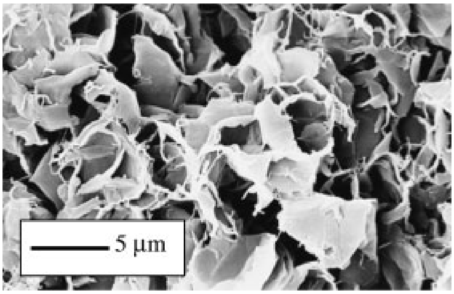

Figure 2.
Scanning micrographs of an aerogel obtained from a gel prepared at $C_{pol} = 0.10$ g/g in CTD.

pattern (Figure 1B) of a gel prepared in chlorotetradecane (CTD, $V_m = 450$ Å^3) at $C_{pol} = 0.10$ g/g.

The FTIR spectrum (Figure 1A) shows absorption bands at 541 and 1222 cm^{-1} which are characteristic of the all-trans planar conformation[8] of sPS while the x-ray diffraction pattern (Figure 1B) displays reflections at $2\theta = 6.1°$, 12.3°, 13.6°, 18.5° and 20.2° thus indicating the formation of the orthorhombic β-form,[5] in the gel.

The morphology of sPS gel polymer-rich domains can be easily observed, after solvent extraction procedures by a supercritical fluid leading to the corresponding aerogels.[9] In fact these procedures generally allow to avoid the collapse of the gel structure and thus preserve the morphology of polymer-rich phase of the native gel.[10]

In Figure 2 is reported the scanning electron micrograph of a gel prepared at $C_{pol} = 0.10$ g/g in CTD after solvent extraction with supercritical carbon dioxide.

The micrograph shows that the polymer-rich phase of sPS gels obtained with non-complexing solvent molecules consist in interconnected lamellar crystals.

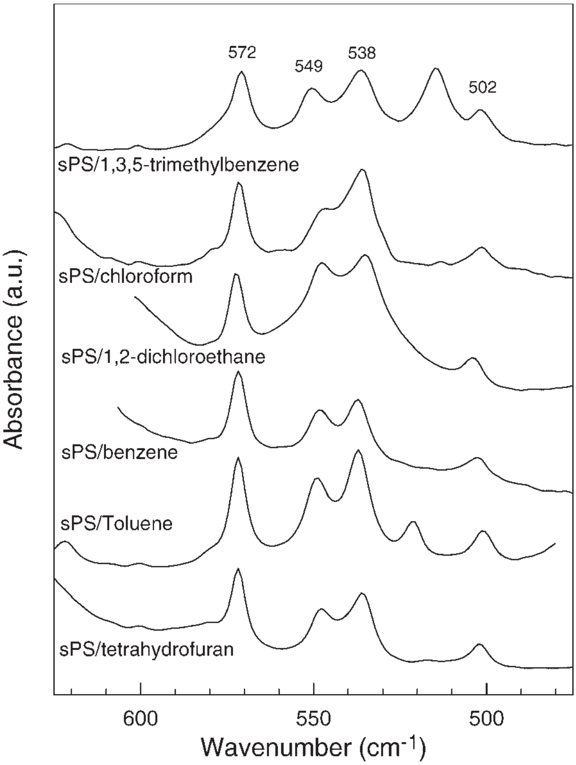

Figure 3.
FTIR spectra for the wavenumber range 625–475 cm^{-1} of sPS gels prepared in various complexing solvent molecules.

1.2. SPS Gels in Complexing Solvents

In Figure 3 are reported the FTIR spectra for the wavenumber range 625–475 cm^{-1} of sPS gels prepared in various solvents forming a molecular complex phase (clathrate or intercalate) with sPS.

The FTIR spectra of the different gels show absorption bands at 502, 538, 549, and 572 cm^{-1} which are characteristic of the ordered s(2/1)2 helical conformation.[8]

1.2.1 SPS Gels with a Clathrate Phase

The presence of molecular complex phases in gels obtained with solvents capable to form a clathrate phase with sPS has been

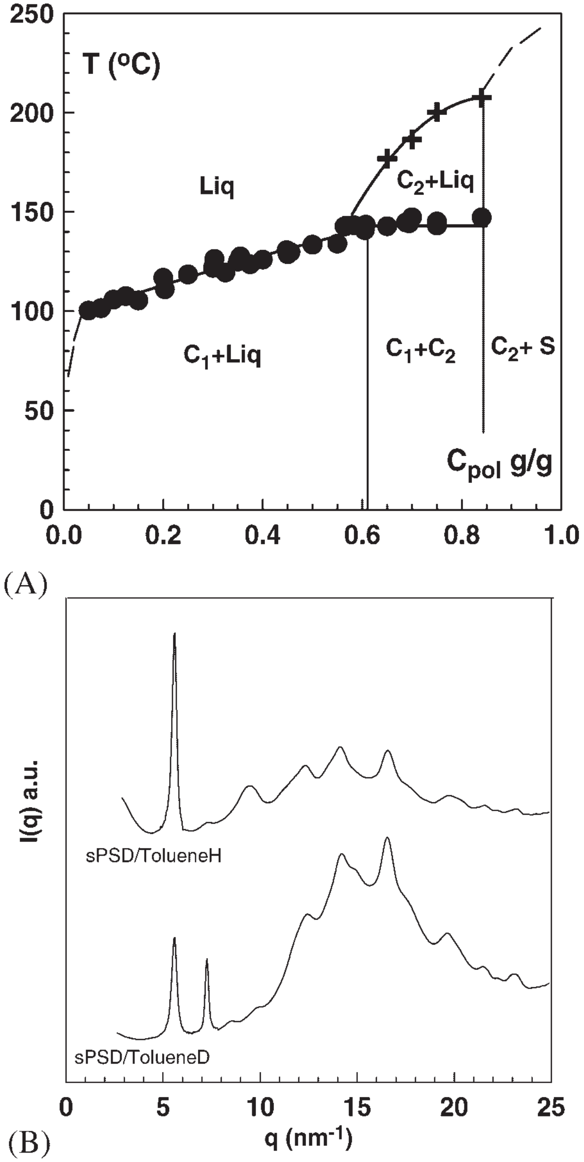

Figure 4.

(A) Temperature-concentration phase diagram for sPS/toluene gels. (B) Neutron diffraction patterns for sPS/toluene gels prepared at $C_{pol} = 0.60$ g/g (corresponding to the stoichiometry of compound C_1). Top: deuterated polystyrene in hydrogenous toluene; bottom: deuterated polystyrene in deuterated toluene.

clearly established from the gel temperature-concentration phase diagrams and from neutron diffraction experiments.[7g,h,o,p]

For instance, the temperature-phase diagram for sPS/toluene gels[7h] is reported in Figure 4A and the neutron diffraction patterns obtained with sPS/toluene gels prepared at $C_{pol} = 0.6$ g/ with different isotopic solvent labeling[7h] is reported in Figure 4B.

The temperature-concentration phase diagram shows the formation of two polymer-solvent compounds C_1 and C_2 of different stoichiometries. C_1 is an incongruently melting compound with a stoichiometry about 1.25 monomer unit per 1 toluene molecule while the stoichiometry of C_2 is about 4 monomeric units per 1 toluene molecule.

The neutron diffraction patterns obtained with sPS/toluene gels (Figure 4B) prepared at $C_{pol} = 0.6$ g/g show a clear variation of the peak intensities when solvent labeling is modified. This clearly confirms the formation of a polymer-solvent compound with the presence of solvent molecules in the crystalline lattice of sPS/toluene gels.

The presence of molecular complexes was also clearly established in gels obtained with other solvents known to form a clathrate structure with sPS.[7e,h,o,p] In Table 1 are reported the stoichiometries determined from temperature-concentration phase diagrams of the complexes formed in different gel systems.

The values reported in Table 1 show that the stoichiometries of the molecular complexes forming the cross-link domains are quite different from the typical 4/1 monomer unit/guest molecule stoichiometry determined for clathrate crystalline structures, by x-ray diffraction studies on fiber samples while the gel diffraction patterns were found to be qualitatively consistent with x-ray diffraction patterns obtained with clathrate samples.

In particular in Figure 5, are compared the neutron diffraction pattern of a gel prepared in deuterated toluene at $C_{pol} = 0.6$ g/g and the x-ray diffraction pattern of a sPS/toluene clathrate sample obtained by sorption of toluene in an amorphous film.

Figure 5 shows that the diffraction patterns of the gel and the clathrate obtained with toluene present the diffraction peaks located at the same position $2\theta = 7.85$, 10.20, 17.55, 20.05, 23.46, and 27.9°. This result suggests the formation of the same crystalline structure (and thus the same stoichiometry) in both samples.

It is worth adding that the stoichiometry of the polymer-rich phase of sPS/1,2-dichloroethane (DCE) was also evaluated from Fourier transform infrared spectroscopy (FTIR) study of the conformational equilibrium of DCE.[7k] It was shown that the polymer rich phase of sPS/DCE gels presents a stoichiometry nearly constant for the entire composition range and is substantially coincident with the typical stoichiometry of the clathrate crystalline structure.

Recently, different explanations have been proposed to rationalize the discrepancy between the stoichiometry determined from the phase diagram and that deduced from structural data (x-rays or FTIR). The discrepancy may arise from the degree of solvation of the amorphous phase[7q] or to the formation of the β phase.[7n]

With regard to morphology, SEM micrographs of areogels obtained after solvent

Table 1.
Stoichiometry of molecular complexes formed in sPS gels determined from temperature-concentration phase diagrams.

Solvent	Molecular complex stoichiometry
chloroform[7h]	1 monomer unit/ 1 solvent molecule
trans-decalin[7p]	1 monomer unit/ 1 solvent molecule
naphatalene[7o]	1 monomer unit/ 0.8 solvent molecule
	3 monomer units/ 1 solvent molecule
benzene[7g]	1 monomer unit/ 4 solvent molecules
	1 monomer unit/ 1 solvent molecules

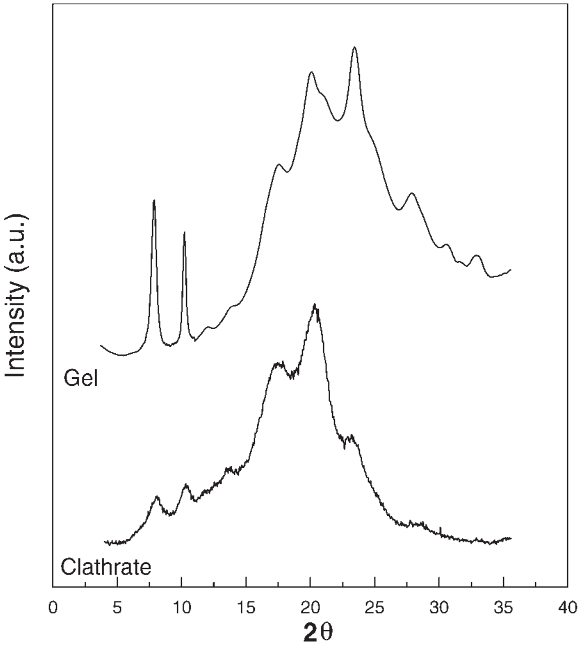

Figure 5.
Neutron diffraction pattern of a gel prepared with deuterated polystyrene in deuterated toluene at $C_{pol} = 0.60$ g/g and x-ray diffraction pattern of a clathrate sample obtained by sorption of toluene in an amorphous film.

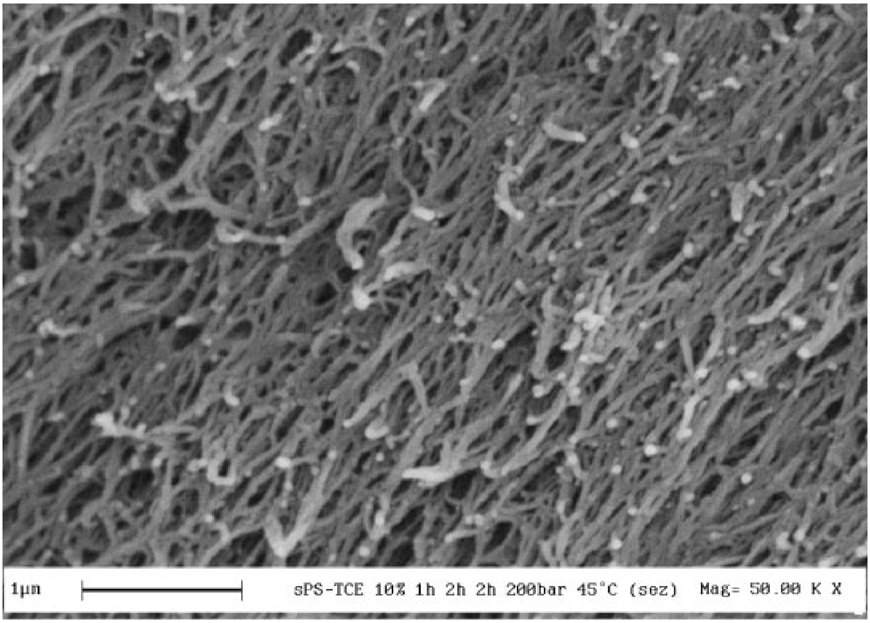

Figure 6.
Scanning micrographs of an aerogel obtained from a gel prepared at $C_{pol} = 0.10$ g/g in 1,2-dichloroethane.

extraction from gels have shown that sPS gels with a clathrate phase present a similar fibrillar morphology.[7r]

This is shown, for example, in Figure 6 for an aerogel obtained from a gel prepared in 1,2-dichloroethane at $C_{pol} = 0.10$ g/g.

1.2.2 SPS Gels with an Intercalate Phase

As mentioned above, it has been observed that, in addition to clathrates, sPS can also form a different type of molecular complex defined as intercalate.[3]

In Figure 7 the x-ray diffraction pattern of a gel prepared in norbornadiene at $C_{pol} = 0.15$ g/g (curve a) is compared with the diffraction patterns of a desiccated gel (curve b) and of a semicrystalline intercalate sample obtained by norbornadiene sorption into amorphous sPS[3a] (curve c).

The diffraction patterns of both gels (native gel and desiccated gel) present diffraction peaks located at c.a. the same positions than the diffraction peaks of the film with an intercalate phase.

This result suggests that the crystalline phase of the cross-link domains of sPS/norbornadiene gels is an intercalate phase. It is worth adding that diffraction data suggest also the existence of intercalate phases in gels formed in various solvents such as benzene,[7g] benzylmethacrylate,[7j] cyclohexylmethacrylate,[7j] benzophenone,[7q] biphenyl,[7q] diphenylmethane,[7q] 1,3,5-trimethylbenzene,[11] and 1,4-dimethylnaphthalene.[11] For sPS/benzene gels, both the intercalate and the clathrate phase can be obtained depending on the gel polymer concentration.[7g]

The morphology of sPS gels with an intercalate phase was also observed and SEM micrographs have shown that sPS gels with an intercalate phase are generally characterized by a fibrillar morphology.[7e,q,r]

2. Properties of sPS Gels

2.1 Rheological Behaviour

In Figure 8 are reported the dynamic moduli G′ and G″ measured at 25 °C for sPS gels prepared at $C_{pol} = 0.02$ g/g with the

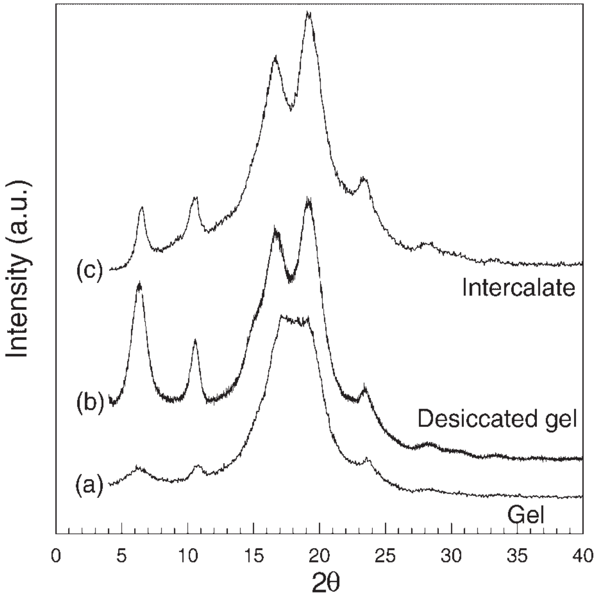

Figure 7.

X-ray diffraction patterns for gels prepared in norbornadiene and for a film presenting a sPS/norbornadiene intercalate phase: (a) gel prepared at $C_{pol} = 0.15$ g/g; (b) desiccated gel ($C_{pol} = 0.80$ g/g) obtained from a gel prepared at $C_{pol} = 0.20$ g/g; (c) film with an intercalate phase obtained by sorption of norbornadiene into amorphous sPS.

trans-planar and a s(2/1)2 helical polymer-rich phase.[7m]

For the gel with the s(2/1)2 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 solid like behaviour. For the sample with the trans planar rich phase, the storage modulus G′ is much lower than for the gel with the helical crystalline phase and a cross-over between G′ and G″ can be observed at low frequency. The sample prepared with the trans-planar rich phase displays rather a liquid like rheological behaviour.

These two different rheological behaviours can be attributed to a different morphology. For sPS gels with a molecular complex phase, the polymer rich phase of the gel is made of fibrils leading to the formation of a three-dimensional network (see Figure 6) and thus the gel displays a solid like behaviour while for sPS gels with a trans-planar rich phase, the morphology is lamellar (see Figure 2) and hence the system should be described as a suspension of crystals rather than a gel.

2.2. Light Transparency

Depending on solvent-type, sPS gels with s(2/1)2 helical molecular complex phases can be either turbid (in decahydronaphtalene[7e] or o-xylene[7d]) or transparent (in benzene,[7b] toluene,[7e] carbon tetrachloride,[7b] or chloroform[7b]).

In particular in Figure 9, is shown the visual aspect of a gel prepared at $C_{pol} = 0.10$ g/g in benzene (Figure 9A) and in 1,2-dichloroethane (Figure 9B).

In order to quantitatively compare the transparency of sPS gels, light transmission measurements in the visible wavelength have been carried out with gels prepared at $C_{pol} = 0.1$ g/g in various solvents leading to the formation of s(2/1)2 helical molecular complex (clathrate and intercalate) phases.[7r] It was observed that the light transmittance calculated by integration of the transmission curved in the range 400–750 nm can vary between 79% (gel obtained with benzene) and 0.6% (gel obtained with 1,2-dichloroethane).

It has been shown that the differences in light transmittance cannot be explained by differences in refractive index between the solvent and the polymer-rich phase neither

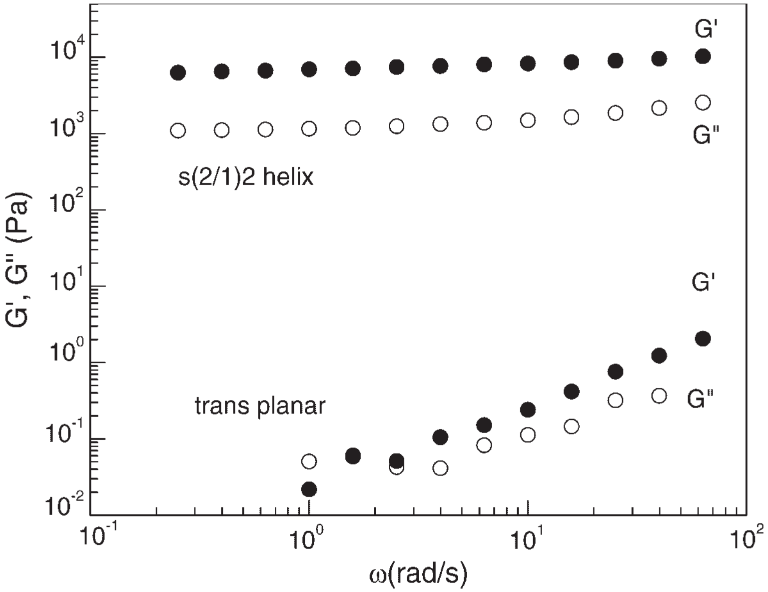

Figure 8.

Dynamic moduli measured at 25 °C prepared at $C_{pol} = 0.02$ g/g with a s(2/1)2 helical and the trans-planar polymer-rich phase as evaluated for different frequencies.

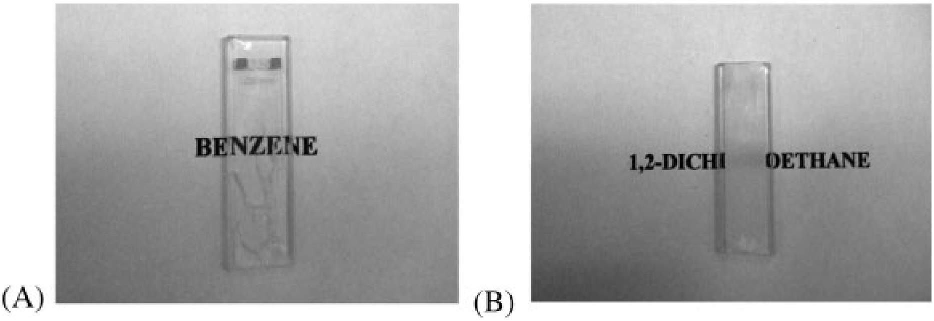

Figure 9.
Visual aspect of a gel prepared at $C_{pol} = 0.10$ g/g in benzene (A) and in 1,2-dichloroethane (B).

by the occurrence of different gel morphology (always fibrillar) nor by the size of the polymer-rich domains.

On the other hand it has been established, for a large variety of solvents, that sPS light transparency is strongly dependent on the structural order in gel crystalline domains.

In Figure 5, the gel light transmittance data are reported versus the correlation length perpendicular to the *ac* planes (D_{010}).[7r]

Results clearly show that the gel light transmittance regularly decreases with increasing the structural order along the direction perpendicular to (010) planes.

Conclusions

The structural organization of sPS gels is strongly correlated to sPS polymorphic behaviour. In non complexing solvent molecules, the gel junction zones consist

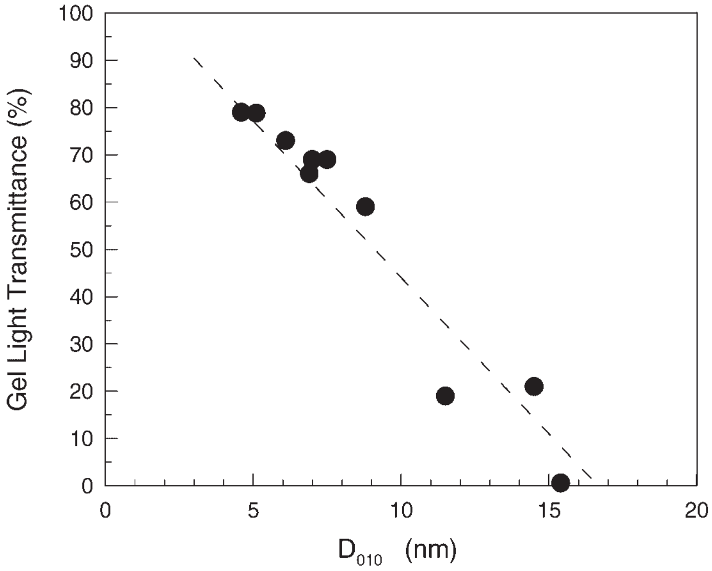

Figure 10.
Variation of the gel light transmittance ($C_{pol} = 0.10$ g/g, thickness = 1.0 mm) .vs the correlation length of (010) planes D_{010}.

of the solvent-free β phase and a lamellar morphology is obtained. With solvents capable to form a s(2/1)2 helical molecular complex phase (clathrate or intercalate) with sPS, the same molecular complex phases are obtained in the gel and a fibrillar morphology is generally observed.

Results reported in this communication also show that the molecular organization can strongly influences gel macroscopic properties such as the rhelogical behaviour and the light transparency.

Acknowledgements: The author is greatly indebted to Prof. Gaetano Guerra and Prof. Jean-Michel Guenet. Financial support of the ''Ministero dell'Istruzione, dell'Università e della Ricerca'' (Prin 2004) and of Regione Campania (Legge 5 and Centro di Competenza) is gratefully acknowledged.

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