A Comparative Study on Gels and Clathrates of Syndiotactic Polystyrene: Solvent Mobility in Polymer−Solvent Compounds

C. S. J. van Hooy-Corstjens, P. C. M. M. Magusin, S. Rastogi,* and P. J. Lemstra

Department of Chemical Engineering, Dutch Polymer Institute/Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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ABSTRACT: Gels of syndiotactic polystyrene with different solvents have been compared to clathrates. Wide-angle X-ray diffraction results using toluene (good solvent for sPS) and decalin (relatively poor solvent for sPS) show that the structure of the crystalline junctions of the gels is similar to that of the clathrate δ-phase. A difference can be found in the width of the (010) reflection, which is, relative to the width of the ($\bar{2}$10) reflection, much broader for the gel than for the clathrate. This is caused by the difference in mechanism involved for crystal formation in gels and clathrates. Experiments performed on quenched samples of syndiotactic polystyrene with the monomer benzyl methacrylate show that also for this gel the structure of the crystalline part is similar to that of the clathrate phase. This means that solvent is present in both the crystalline and the amorphous part of the gel. By solid-state NMR studies, a clear difference in mobility of solvent molecules in the crystalline and amorphous parts of the gel has been observed.

1. Introduction

In contrast to the synthesis of isotactic polystyrene, which has been reported as early as 1955,[1] only recently have Ishihara et al. managed to prepare syndiotactic polystyrene (sPS).[2] Since then, four main crystalline structures have been found for sPS.[3,4] In the primary crystalline polymorphs, the α- and β- modifications,[5−8] the backbone of the polymer chain adopts an all-trans planar zigzag conformation, whereas the γ- and δ-phases[9,10] contain chains with a s(2/1)2 helical symmetry. The term δ-phase has been used to indicate different clathrate structures in which the helices of sPS form a crystalline lattice containing cavities in which solvent molecules are located. The chains are packed in a monoclinic unit cell according to the space group $P2_1/a$. An emptied clathrate phase (δ_e), which corresponds to a pure helical form of sPS free from guest molecules, can be obtained by extraction in boiling acetone or supercritical CO_2.[11,12] Because of the removal of solvent molecules, distinct cavities are present within the crystal lattice. The γ-phase, which is also free from solvent molecules, can be obtained by annealing the clathrate δ-phase above 100 °C. The structure of the γ-phase, which has not been solved yet, is different from that of the δ_e-phase. This suggests that two different helical phases, free from solvent molecules, exist in sPS.

Besides the crystallization into these four main crystal modifications, sPS can also form a physical gel in the presence of a solvent. Though the main constituent of the gel is a fluid, the material still maintains its shape as a result of polymer network formation. The connected junctions of the network can arise as a result of a phase transition, through some specific molecular association or as a result of entanglements.[13] For physical gels that are formed due to phase transitions, the junctions can be created and removed by cooling and heating, respectively. Therefore, this class of gels is often referred to as thermoreversible gels. During the past decade, several studies on thermoreversible gels of sPS with different solvents have been performed.[14−21] Mostly, the helical conformation is the structural element in these thermoreversible gels. The gelation process, which is a two-step mechanism,[22] consists of a coil-to-helix transition, followed by intermolecular associations of the helical chains.

Despite all research that has been performed so far on sPS/solvent gels, the structure of the crystalline junctions is still a matter of debate. The first part of this work aims to solve the structure of the gel. Gels of sPS with toluene and decalin are compared to clathrates with the same solvents. Also, the use of the monomer benzyl methacrylate (BzMA) will be discussed. The advantage of this monomer over the two other solvents is that it contains a C═C bond, which gives a possibility to convert the solvent into a polymer. In the second part of this article, the mobility of BzMA molecules present in different parts of the gels is investigated by nuclear magnetic resonance experiments.

2. Experimental Section

Materials and Sample Preparation. Syndiotactic polystyrene with a molar mass of 400 kg mol^{-1} with two different syndiotacticities (95% (commercial grade) and 99.1% (laboratory grade)) were supplied by Dow Chemical, Terneuzen (NL), in the form of pellets. For easy solubility, the material was ground into a fine powder. Toluene with a purity of 99.8%, benzyl methacrylate (96% pure), and the UV initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) were purchased from Aldrich. Decalin (mixture of cis and trans) with a purity of 99% was supplied by Merck. Clathrates of sPS with toluene were obtained by swelling thin amorphous pieces in the solvent at 60 °C. Clathrates of sPS with decalin could only be obtained by exposing the emptied clathrate to decalin at 65 °C.

Gels of sPS with toluene (3 wt % sPS), decalin (20 wt % sPS), and benzyl methacrylate (20 wt %) were obtained by preparing a homogeneous solution at temperatures close to the boiling point of the solvent and subsequent quenching of these homogeneous solutions in liquid nitrogen.

Samples for DSC were prepared by sealing the sPS powder and benzyl methacrylate (with 4-benzoquinone as inhibitor) in stainless steel pans with rubber O-rings. The total amount of material in the pans varied between 15 and 30 mg.

Techniques. Wide-angle X-ray diffraction (WAXS) patterns were obtained at the European Synchrotron Radiation Facility

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(ESRF) in Grenoble (France) at beamline ID11. The energy of the monochromatic beam, with a beam size of 300 × 300 μm, was tunable from 7 to 100 keV. In the described experiments different wavelengths between 0.7 Å (17.72 keV) and 0.8 Å (15.51 keV) were applied. Detection of the scattered photons was established by a Princeton CCD detector, and a grid was used to correct for spatial distortion of the detector. The powder diffraction rings of 2-D images were integrated to 1-D plots using FIT2D, a computational program obtained from ESRF. To perform an in-situ heating experiment, gels of sPS were transferred into a Lindemann capillary and subsequently sealed. The sealed capillary was placed in a holder which was fixed on a Linkam THMS 600 hot stage. This hot stage was controlled with a TMS-92 controller, and the sample was heated from room temperature to 230 °C at a rate of 5 °C min^{-1}.

The calorimetric measurements on sPS/BzMA samples were performed with a Perkin-Elmer DSC-7. The samples were first heated to 250 °C and kept at this temperature for a few minutes to dissolve the sPS. After homogenization, the samples were quenched in the DSC to −20 °C. To measure phase transitions of the quenched samples, a constant heating rate of 5 °C min^{-1} was applied.

Magic-angle spinning (MAS) ^{1}H NMR spectra were obtained with a Bruker DMX500 operating at 500 MHz. MAS rates between 3 and 7 kHz were employed, and rotor-synchronized Hahn echo spectra were recorded. To get a good resolution, 64 or 128 scans were taken with a repetition time of 3 s. The number of experiments per relaxation measurement was approximately 16.

3. Results and Discussion

3.1. Crystal Structure in Gels. To clarify the crystal nature of the gels, a comparison with clathrates has been made. To understand the similarities and differences between the gels and the clathrates, several solvents have been studied.

Roels et al. have shown that the formation of the helical and planar zigzag phase upon cooling a homogeneous solution is dependent on the solvent quality for sPS.[19] In the case of a good solvent, the helical phase forms the stable phase at low polymer concentrations. For relatively poor solvents, the planar zigzag phase will be the most stable phase over the whole concentration region, and the helical phase can only be obtained by fast quenching.

In this article toluene and decalin are used as an example for a good and poor solvent, respectively. In addition, the use of benzyl methacrylate, containing a polymerizable unit, will be described.

3.1.1. Syndiotactic Polystyrene/Toluene Samples. The structure of the clathrate δ-phase of sPS including toluene has been solved several years ago by Chatani.[10] The WAXS pattern of such clathrate is depicted in Figure 1, and the corresponding Bragg distances are given in Table 1. To compare this diffraction pattern to that of a gel with low polymer content, a homogeneous solution containing 3 wt % sPS has been quenched in liquid nitrogen. The WAXS pattern of this gel, in which the sPS chains adopt a helical conformation, is depicted in Figure 2a. The diffraction pattern shows a very large halo around $2\theta = 8.0°$ ($d = 5.1$ Å) which is attributed to both the presence of a large amount of solvent and amorphous sPS. To compare the diffraction pattern of the gel to that of the clathrate with toluene, the diffraction pattern of pure toluene is subtracted from that of the gel, after proper scaling of maximum intensity (Figure 2b). The obtained diffraction pattern is similar to that of the clathrate phase. This suggests that the structure of the crystalline part of the gel is similar to that of the solvent-included δ-phase.

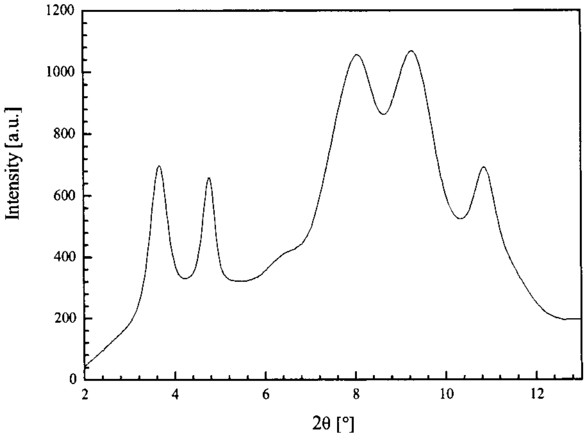

Figure 1. Wide-angle X-ray diffraction pattern ($\lambda = 0.718$ Å) of the clathrate δ-phase including toluene.

Table 1. Diffraction Angles and Bragg Distances of the Clathrate δ-Phase Including Toluene ($\lambda = 0.718$ Å)

	clathrate δ-phase with toluene		
(hkl)	$2\theta_{\text{obs}}$ [deg]	d_{obs} [Å] ([a])	d_{cal} [Å]
010	3.66	11.24 (s)	11.34
$\bar{2}10$	4.76	8.65 (s)	8.67
$\bar{1}11/101$	6.46	6.37 (w)	6.60/6.86
$111/\bar{1}21$	8.00	5.15 (vs)	5.34/4.99
$\bar{3}21/301/211$	9.26	4.45 (vs)	4.42/4.20/4.29
$\bar{4}11/\bar{4}21$	10.86	3.79 (m)	3.75/3.78

[a] vs = very strong, s = strong, m = medium, w = weak.

A closer look at the width of peak in the diffraction pattern shows a difference between the gel and the clathrate at low diffraction angles ($2\theta = 2-6°$) (Figure 2b). By comparing the first two reflections, it can be concluded that in the case of the gel the first peak, relative to the second peak, is much broader than in the case of the clathrate (Figure 1). For the clathrate, which is obtained by swelling amorphous sPS in toluene at 60 °C, the width of the (010) reflection is about the same as that of the ($\bar{2}10$) reflection, suggesting that the crystal size along the a-direction is similar to the size along the b-direction and that possible lattice distortions are the same in both directions. For the gel, however, the width of the (010) reflection is nearly 3 times larger than that of the ($\bar{2}10$) reflection.

Broadening of a peak in the diffraction pattern is normally associated with a decrease in crystal size or an increase in distortion of the crystal lattice. Such peak broadening can be explained by the mechanism for gel formation as proposed by Berghmans et al.[22] They showed that compound formation is a two-step mechanism. Cooling first results in a coil-to-helix transition followed by intermolecular associations of the helical chains. Considering this mechanism, the presence of a large amount of solvent is likely to hinder the well-ordered intermolecular association along the b-axis, as solvent molecules sit along this axis of the unit cell. Along the a-axis the influence is expected to be less, because in this direction the polymer chains are more closely packed without the intervention of any solvent. Hindering of the packing would cause a decrease in periodicity (long-range order) along the b-direction of the crystal, resulting in a broad reflection for the (010) plane. Moreover, the limited time which is given to the chains to organize due to fast quenching from homoge-

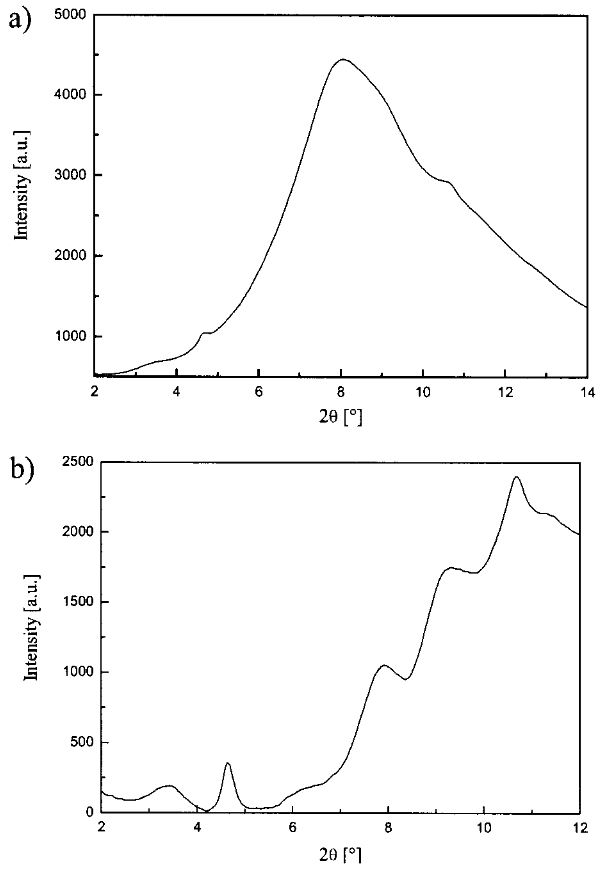

Figure 2. Wide-angle X-ray diffraction patterns ($\lambda = 0.718$ Å) of (a) a gel of sPS in toluene and (b) a gel corrected for toluene.

neous solution can cause a larger distortion of the crystal lattice. The presence of solvent molecules along the *b*-axis results in distortions in this direction. This is more difficult along the *a*-direction due to the stronger interactions between the chains. The distortion in the *b*-direction could result in additional broadening of the (010) reflection.

3.1.2. Syndiotactic Polystyrene/Decalin Samples. To strengthen the conclusion on the sPS/toluene system, also experiments with the solvent decalin have been performed. Compared to toluene, decalin is a relatively poor solvent for sPS, implying that clathrate formation from decalin is more difficult. Our experiments show that a clathrate phase with decalin can be obtained by swelling δ_e in the solvent at 65 °C. The obtained diffraction pattern is depicted in Figure 3, and the corresponding diffraction angles with Bragg distances are given in Table 2.

Similar to the clathrate with toluene, the first two reflections are attributed to the (010) and ($\bar{2}10$) planes, respectively, while the strong reflection at $d = 5.45$ Å, arising from the packing of the phenyl groups, is attributed to the (111) plane. By comparing the diffraction angles of the clathrate with decalin (Table 2) to those of the clathrate with toluene (Table 1), it can be concluded that the *d* value of the (010) reflection increases about 10%. This is caused by the increase in solvent size. Since solvent molecules are placed along the *b*-axis of the unit cell, this result is self-explanatory.

For the preparation of the gel, a homogeneous solution of sPS in decalin is prepared by heating the system close to the boiling point of the solvent (187 °C), similar to the sPS/toluene system. Upon quenching the homogeneous solution in liquid nitrogen, a white, milky sample is obtained. Pushing the quenched solution out of the pipet does not change the shape of the material (Figure 4a). This implies that connectivity between the crystalline zones, needed for the formation of a gel, is present. Thus, similar to the sPS/toluene system, this material can be regarded as a physical gel.[13] The presence of a relatively strong reflection at 800 cm^{-1} in the Raman spectrum of this gel (Figure 4b) indicates that the chains adopt a helical conformation.[15]

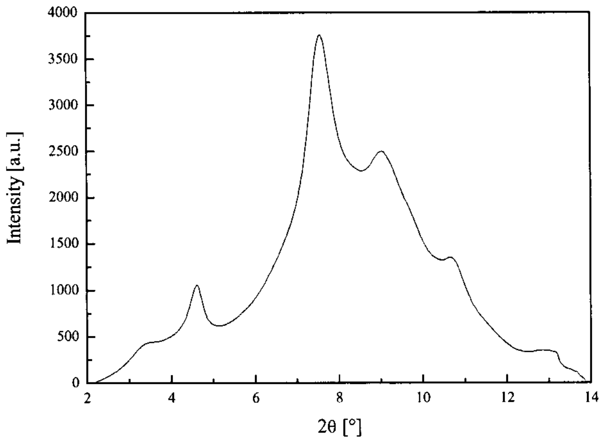

Figure 3. Wide-angle X-ray diffraction pattern ($\lambda = 0.718$ Å) of δ_e swollen in decalin.

Table 2. Diffraction Angles and Bragg Distances of the Clathrate δ-Phase Including Decalin ($\lambda = 0.718$ Å)

(*hkl*)	$2\theta_{obs}$ [deg]	d_{obs} [Å]	d_{cal} [Å]^c	I^a
010^b	3.36	12.24		w
$\bar{2}10^b$	4.61	8.93		m
$\bar{1}11^b$	7.56	5.45		vs
$\bar{3}21^c$	9.01	4.57	4.56	s
$\bar{4}21^c$	10.66	3.86	3.86	m

[a] vs = very strong, s = strong, m = medium, w = weak. [b] Assigned on the basis of the sPS/toluene system. [c] Possible assignment based on a monoclinic unit cell for which the dimensions are calculated from the first three reflections, with $c = 7.71$ Å.

WAXS patterns upon heating the quenched solution are given in Figure 5a, while Figure 5b gives a representation at low diffraction angles. In the quenched solution a large halo is present around $2\theta = 7.5°$. Similar to the sPS/toluene system, this halo is attributed to the presence of both a large amount of solvent and amorphous sPS. Besides this large halo, two reflections are present at lower angles ($2\theta = 3.36°$ ($d = 12.24$ Å), $2\theta = 4.61°$ ($d = 8.93$ Å)). Since the position of these reflections is the same as for the clathrate of sPS with decalin, it seems that the structure of the crystalline part of the gel is similar to the structure of the clathrate. Therefore, the two reflections are attributed to the (010) and ($\bar{2}10$) plane, respectively. However, the first reflection (010) is so broad that it can be hardly distinguished. As discussed earlier for the sPS/toluene system, the broadening of this reflection is caused by either a smaller crystal size or a larger lattice distortion along the *b*-direction of the unit cell. Both phenomena result from the presence of a large amount of solvent in the gel. Upon heating the sample, the (010) reflection gets more pronounced (Figure 5b, $T = 100$ °C). The increase in intensity could be a result of an increased mobility of the polymer on heating, which favors the removal of lattice distortions.

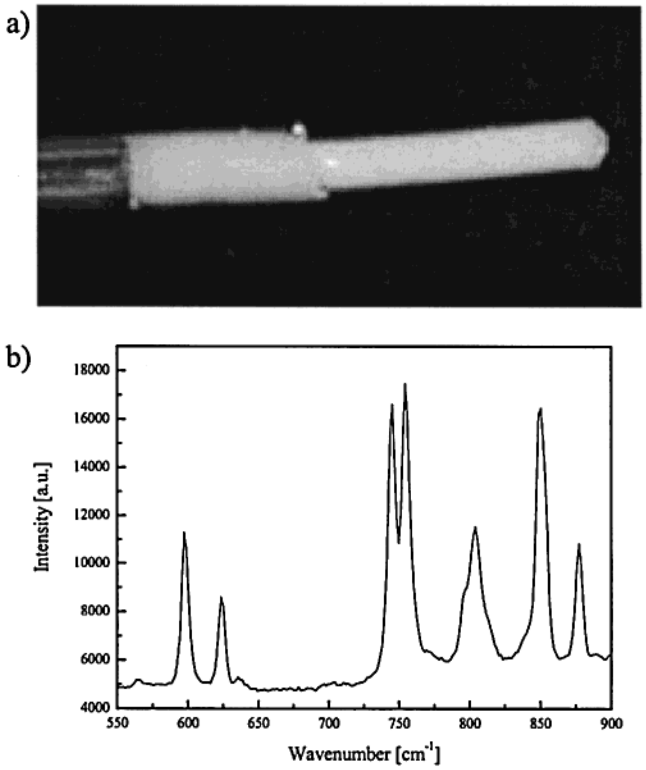

Figure 4. (a) Appearance of a quenched solution of 20 wt % sPS in decalin. (b) Raman spectra of a quenched solution of 20 wt % sPS in decalin.

Our observations on toluene and decalin samples show that the structure of the crystal junctions in the gel is similar to that of the clathrate phase. Differences exist in the crystal dimensions; i.e., crystals in the crystalline domains of the gel are much smaller than in clathrates, especially along the *b*-axis.

Structural Changes upon Heating. On continuous heating above 100 °C, the broad reflection at $2\theta = 3.36°$ disappears around 115 °C, while the second reflection (at $2\theta = 4.61°$) shifts to $2\theta = 4.39°$ ($d = 9.4$ Å) and gets more asymmetric. Since the large amount of solvent and amorphous material dominate the diffraction pattern, changes at higher diffraction angles cannot be observed. The changes at low diffraction angles match to a transition into the solvent-free γ-phase (see Table 3). This result is in agreement with structural changes which occur upon heating the clathrate δ-phase, as first described by Immirizi et al.[24]

As apparent by the incoming of several relatively sharp reflections, the sample transforms into the β-phase above 140 °C.

3.1.3. Syndiotactic Polystyrene/Benzyl Methacrylate Samples. From the results on toluene and decalin gels it can be concluded that the crystalline junctions possess a structure similar to that of clathrates. The next step is to investigate gels consisting of sPS and the monomer BzMA. The advantage of BzMA is that it can be polymerized due to the presence of a C=C bond.

Gels of sPS and BzMA have already been studied by us some years ago, and some salient features will be recalled here. On the basis of the knowledge obtained with the toluene and decalin systems, the experimental results will be explained slightly different than in the previous article.[21] The wide-angle X-ray diffraction pattern after quenching a homogeneous 20/80 wt % sPS/BzMA solution is depicted in Figure 6a. Raman spectroscopy shows that in the quenched sample the chains adopt a helical conformation, implying that either the γ- or δ-phase is formed. The diffraction pattern does not match with the data of the γ-phase, and therefore it is likely that, similar as for the toluene and decalin gels, the clathrate δ-phase is formed. However, the clathrate δ-phase shows two reflections in the region of small 2θ (2−6°), attributed to the (010) and ($\bar{2}$10) planes, while for the quenched gel only one reflection is observed.[17] The reflection at $2\theta = 5.1°$ ($d = 8.59$ Å) matches close to the ($\bar{2}$10) reflection of the clathrates, including toluene ($d = 8.65$ Å) or decalin ($d = 8.93$ Å). Since the position of this reflection only slightly changes with solvent size, for the sPS/BzMA system the reflection at $d = 8.59$ Å is again attributed to the ($\bar{2}$10) plane. This means that

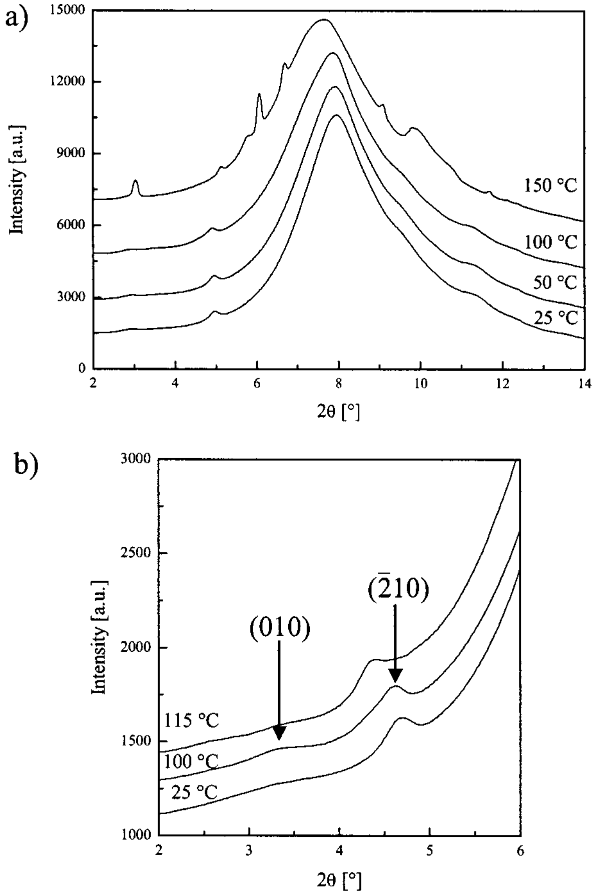

Figure 5. Wide-angle X-ray diffraction patterns ($\lambda = 0.718$ Å) upon heating a quenched solution of 20 wt % sPS in decalin: (a) 2-D representation, (b) low diffraction angles.

Table 3. Diffraction Angles and Bragg Distances of a 20/80 wt % SPS/BzMA Gel Which Has Been Heated until 110 °C ($\lambda = 0.757$ Å)[21] Together with the Bragg Distances of the γ-Phase[24]

gel heated until 110 °C			γ-phase	
2θ [deg]	d [Å]	I^a	d [Å]	I^a
4.62	9.39	s	9.5	s
7.97	5.45	s	8.6	w
8.89	4.88	m		
9.69	4.48	m	5.5	vs
11.11	3.91	w	4.5	s
12.41	3.50	w	3.7	vw
			3.2	w

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

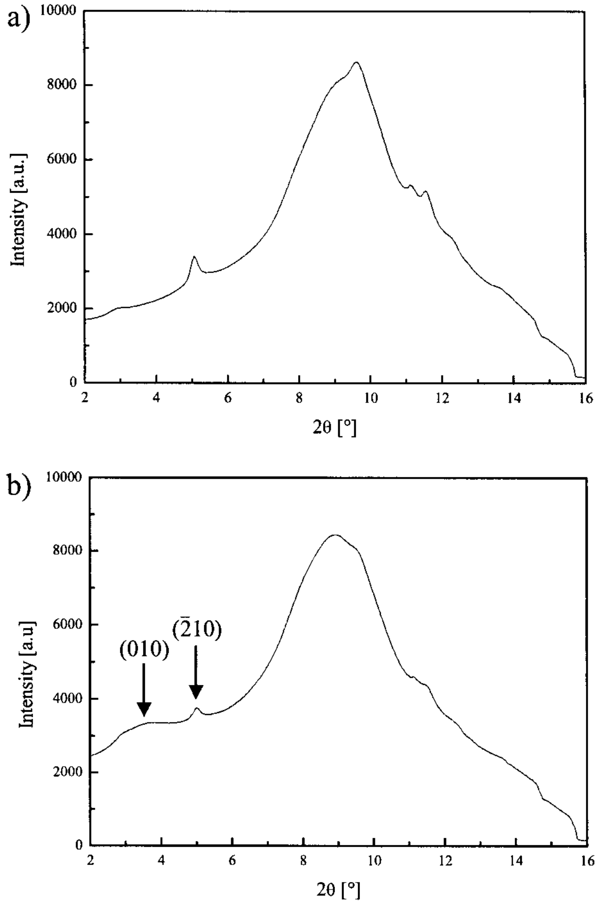

Figure 6. Wide-angle X-ray diffraction patterns ($\lambda = 0.757$ Å) upon quenching a homogeneous 20/80 wt % sPS/BzMA solution: (a) room temperature, (b) $T = 60$ °C.[21]

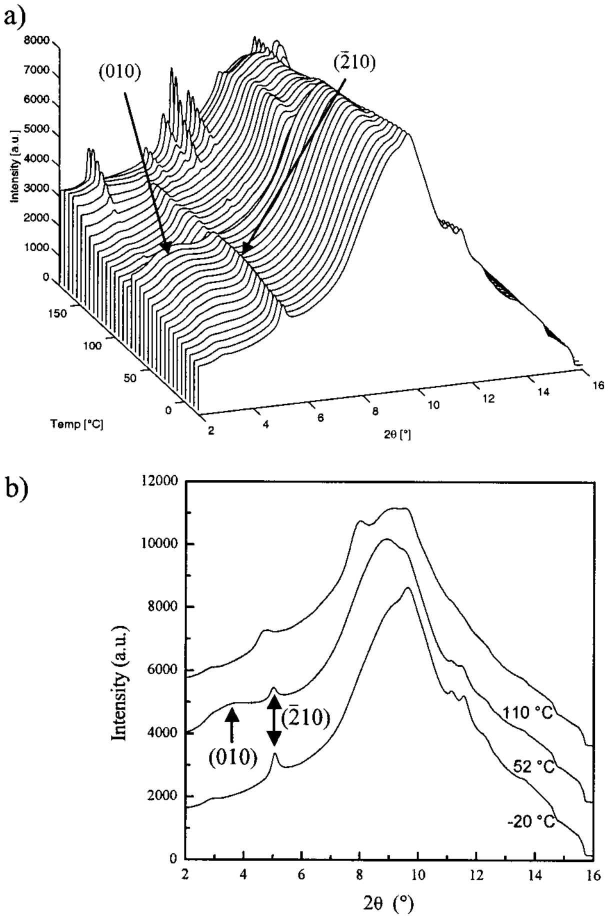

Figure 7. Heating run of a quenched 20/80 wt % sPS/BzMA sample: (a) 3-D WAXS plot, (b) 2-D WAXS plot ($\lambda = 0.757$ Å).

no reflection corresponding to the (010) plane is observed.

As mentioned, the (010) reflection of the gel is very broad due to either a small crystal size along the *b*-axis of the unit cell or a large distortion along this plane. A possible explanation for the absence of the (010) reflection in the sPS/BzMA gels can be that this reflection is too broad to be distinguished. Figure 6b shows the wide-angle X-ray diffraction pattern of a 20/80 wt % sPS/BzMA gel at 60 °C. At this temperature a broad hump appears in the WAXS pattern around 12.8 Å. This broad reflection is attributed to the (010) plane. With the two reflections the dimensions of a possible unit cell can be calculated, assuming a monoclinic unit cell with γ varying between 120° and 130° and c set to 7.71 Å. The result is $a = 17.3-17.4$ Å, $b = 14.8-16.7$ Å, $c = 7.71$ Å, and $\gamma = 120°-130°$. Assuming two BzMA molecules per unit cell, the calculated cell dimensions result in a density between 1.15 and 1.16 g cm^{-3}. This value is of the same magnitude as normally found for filled clathrate structures[10,18] and therefore seems acceptable.[19] On the basis of the three reflections assigned in Table 2, for the sPS/decalin system we found that the unit cell dimensions are $a = 17.94$ Å, $b = 14.5$ Å, $c = 7.71$ Å, and $\gamma = 122.6°$. In principle, the size of the cavity between the sPS chains is determined by the size of the solvent molecule. To compare both systems, the van der Waals volumes of the two solvent molecules are calculated according to the method described by Bondi.[20] For decalin the volume is 156.5 Å^3 per molecule, whereas for benzyl methacrylate the calculated value is 170 Å^3. This result suggests that in the case of BzMA the cavity, and therefore the *b*-axis of the unit cell, should be larger than in the case of decalin. This is in agreement with the suggested cell dimensions for both systems.

Structural Changes upon Heating. Upon heating the 20/80 wt % sPS/BzMA sample above 110 °C, several changes in the diffraction pattern can be followed (Figure 7). First of all, the reflection at $d = 8.59$ Å ($2\theta = 5.05°$) shifts to 9.39 Å ($2\theta = 4.62°$), whereas the reflection at $d = 12.8$ Å ($2\theta = 3.39°$) disappears. Simultaneously, the reflection at $d = 4.5$ Å ($2\theta = 9.65°$) shifts to slightly higher Bragg distance ($d = 4.88$ Å, $2\theta = 8.89°$), and a new reflection appears at $d = 5.45$ Å ($2\theta = 7.97°$). The reflections that are present in the sPS/BzMA sample at 110 °C are summarized in Table 3.

The Bragg distances as observed around 110 °C for the sPS/BzMA sample are in close accordance with the values found for the γ-phase of sPS. The changes upon heating will therefore be explained by a transition from the solvent-included δ-phase to the solvent-free γ-phase. This means that, above this temperature, solvent will only be present in the amorphous part of the material. The reflection at $d = 9.39$ Å is asymmetric, which can be caused by overlapping of the two reflections at $d = 9.5$ and 8.6 Å, as observed for the γ-phase of sPS.

On heating the sample beyond 140 °C, the reflections corresponding to the helical γ-phase disappear, while the incoming of several sharp reflections is observed. These reflections match the d values of the β-phase.[21] This implies that a transition from the helical phase into the planar zigzag phase occurs around 140 °C.

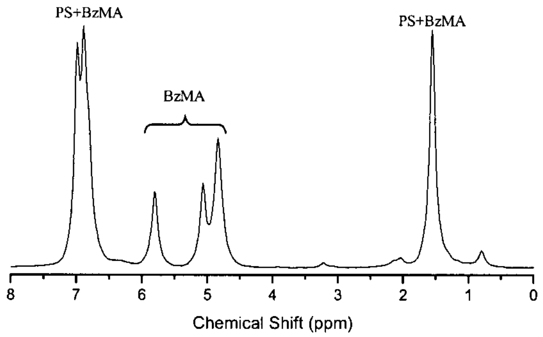

Figure 8. ^1H NMR spectrum of a quenched 20/80 wt % sPS/BzMA sample.

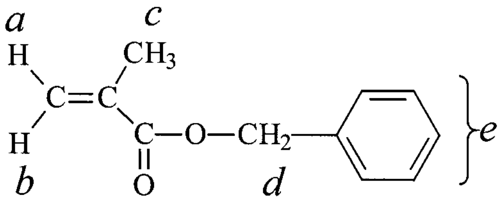

Figure 9. Chemical structure of BzMA.

Table 4. Peak Positions in the ^1H NMR Spectrum of BzMA Together with the Corresponding Protons

chemical shift [ppm]	proton	chemical shift [ppm]	proton
1.6	c	5.8	b
4.8	d	6.9−7	e
5.1	a		

3.2. Solvent Mobility. Two different modifications in which the sPS chains adopt a helical conformation have been assigned to the sPS/BzMA system. In the quenched gel the δ-phase is obtained, and solvent is assumed to be present in both the crystalline and amorphous part of the material. In the γ-phase, obtained around 110 °C, solvent is expected to be located only in the amorphous part of the sample. To confirm these hypotheses, solid-state nuclear magnetic resonance (NMR) experiments have been performed at room temperature for as-prepared gels (δ-phase) and samples heated to 110 °C (γ-phase).

NMR relaxation experiments provide information about molecular motions in the system.[21,22] The different surroundings of the solvent in the crystalline and the amorphous phases are expected to lead to a different mobility. In this study mobility information is obtained from the transverse relaxation caused by dipolar interactions between the protons in the polymer/solvent system. These dipolar interactions are strong, and thus the resulting transverse relaxation times T_2 are short, for rigid polymer systems. The larger the motional amplitude, the smaller the residual dipolar interaction and the longer the observed proton T_2.

Figure 8 presents the ^1H NMR spectrum of a 20/80 wt % sPS/BzMA gel. The peak positions with the matching protons (Figure 9) are listed in Table 4. For polystyrene, peaks are found between 1 and 2.4 ppm (methyl group) and between 6.6 and 7.2 ppm (phenyl group). This implies that for the sPS/BzMA sample the peaks at 1.6 and 7 ppm are assigned to both solvent and polymer. However, the peaks at the positions 4.8, 5.1, and 5.8 ppm can exclusively be assigned to the solvent. Since the peak at 5.8 ppm is not overlapping with other peaks, the intensity of this peak will be used to study the molecular motion of the solvent.

Table 5. $T_2(^1H)$ Relaxation Times of the δ- and γ-Phase for Varying SPS Concentrations

concentration sPS	$T_2(^1H)$ [ms]	
	δ-phase	γ-phase
0	50.6	50.6
6	55.3	
12	31	
19	14.7	
22		39.9
28	17.7	
29		37.1
30	12.4	
38		32.5

For a single solvent population (as expected in the γ-phase) the transverse relaxation can be described with a monoexponential decay:

$$M = A\,\exp(-t/T_2) \tag{1}$$

In the δ-phase two different solvent populations, with relaxation times $T_{2,A}$ and $T_{2,C}$ present in the amorphous and crystalline part of the gel, respectively, are expected to be observed. In the case of slowly exchanging solvent populations (average residence time $\tau \gg T_{2,A}$, $T_{2,C}$), the magnetization shows a biexponential decay. This decay can be described according to

$$M = A\,\exp(-t/T_{2,A}) + C\,\exp(-t/T_{2,C}) \tag{2}$$

For fast exchange between the two solvent populations ($\tau \ll T_{2,A}$, $T_{2,C}$), the two relaxation times will not be separated anymore. A single relaxation time will be found, which is a weighted average over the solvent in the two different phases:

$$\frac{1}{T_2} = \frac{\nu_A}{T_{2,A}} + \frac{\nu_C}{T_{2,C}} \tag{3}$$

In this equation ν_A and ν_C are the fraction of the solvent being present in the amorphous and crystalline phase, respectively ($\nu_A + \nu_C = 1$).

For samples with a polymer concentration up to 40 wt %, the results for both the δ- and γ-phase can be described with a monoexponential decay (Table 5).

By comparing the relaxation times of samples with roughly the same polymer concentration, it is observed that for the δ-phase much shorter relaxation times are obtained than for the γ-phase. These low $T_2(^1H)$ values imply that the overall mobility of the solvent molecules is less than for solvent in the γ-phase. Assuming the amorphous part of the samples to be similar in the δ- and γ-phase, the difference in relaxation times suggests that solvent in the crystalline phase has a short relaxation time. According to the proposed model, this is due to trapping of the solvent molecules in small cavities, which reduces the rotational mobility of the solvent. As the relaxation data of the δ-phase can be fit with a monoexponential decay, the exchange between the two populations must be fast.

In conclusion, the short $T_2(^1H)$ in the δ-phase results from a fast exchange between solvent present in the amorphous ($T_{2,A}$ similar as in the γ-phase) and the crystalline part of the material ($T_{2,C} < T_{2,A}$).

The slight decrease in $T_2(^1H)$ with increasing polymer concentration as observed for the γ-phase is attributed to the increased viscosity of the system. A linear curve can be fit on the data, and the result is used to describe the amorphous part of gels containing the δ-phase. As shown in Table 5, the decrease in $T_2(^1H)$ with increasing polymer concentration is for the δ-phase is much larger than for γ-phase. Hence, for the δ-phase we expect also other factors than changes in viscosity of the system to play a role.

For the samples presented in Table 5, the glass-transition temperature is lower than room temperature, resulting in a relatively high mobility of the system. This permits fast exchange of solvent molecules between the crystalline and amorphous phases. To gain more insight into the relaxation within the crystalline part of the δ-phase, another set of experiments has been performed. In these experiments 20/80 wt % sPS/BzMA samples were dried in a vacuum oven at 50 °C for different times. In this way two samples (sPS/BzMA 61/39 and sPS/BzMA 80/20) are obtained for which the T_g is higher than room temperature. This means that during the solid-state NMR measurements, which are performed at room temperature, these samples are in the glassy state. Because of the reduced mobility in the glassy state, it is now possible to separate the two different solvent populations, and therefore the relaxation curve can be decribed with a biexponential decay.[31] To find a proper description for the δ-phase, the fit of this biexponential decay according to eq 2 is coupled with the fit of the monoexponential decay for samples for which the glass-transition temperature is lower than room temperature (Table 5). In this fitting the following assumptions have been made: (1) for the crystalline phase, one solvent molecule per four monomer units is present (model Chatani[10]);[32] (2) the crystallinity, which is defined as the fraction of the polymer in the crystalline phase, is constant for all samples; (3) after saturation of the crystalline phase, the remaining of the solvent is placed in the amorphous part of the gel; (4) the relaxation time of the crystalline phase is independent of the physical state of the amorphous phase, and therefore $T_{2,C}$ is the same for all samples; (5) for the rigid samples (T_g > 25 °C) the relaxation time of the amorphous phase is constant; (6) the relaxation time of the amorphous phase ($T_{2,A}$) for samples for which the glass transition is lower than room temperature is described with the linear fit as found for the γ-phase.

With these assumptions a coupled fit is performed for the samples with sPS concentration between 6 and 80 wt %. This results in a crystallinity of 54% and a relaxation time of solvent in the crystalline phase of 1.9 ms. Here, the crystallinity is defined as the fraction of the polymer in the crystalline phase (excluding the solvent).

By comparing this relaxation time to the value as found for the γ-phase, it can be concluded that the solvent mobility of the crystalline phase is indeed highly reduced due to trapping of the solvent molecules within small cavities.

It should be noted that the relaxation times as found by this coupled fit can differ from the values as presented in Table 5. The values in this table are obtained by fitting all monoexponential decays separately without any restrictions. To show the quality of the fitting, Figure 10 depicts the relaxation times as presented in Table 5 and the theoretical curve, based on a crystallinity of 54% and a relaxation time of the crystalline phase of 1.9 ms.

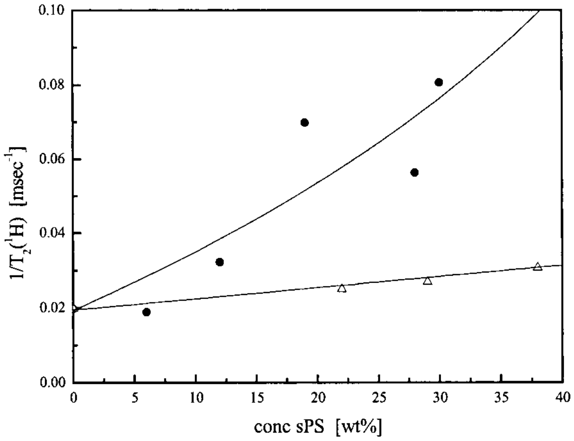

Figure 10. $1/T_2(^1H)$ vs sPS concentration for sPS/BzMA samples: (●) δ-phase; with theoretical result of coupled fit, (△) γ-phase with result of linear fit.

4. Concluding Remarks

To understand the crystal structure of the gels, a comparison with different clathrate phases has been made. From these results several conclusions can be drawn:

1. The structure of the crystalline junctions of the gels is similar to the structure of the clathrate δ-phase.
2. Differences between the gel and the clathrates can be found in the crystal dimensions; i.e., the crystal domains of the gels are much smaller than in clathrates. This is especially the case for the *b*-direction of the unit cell, along which the solvent molecules are placed.
3. Upon heating the gels, the γ-phase is obtained around 110 °C, followed by a transformation into the β-phase at higher temperatures.
4. From NMR results it has been concluded that solvent molecules present in the crystalline part has a much lower mobility than solvent molecules in the amorphous part of the gel. This is due to intercalation of solvent molecules in isolated holes present within the crystalline lattice.

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(27) We are aware that in principle it is possible to get a different kind of crystal structure with a different solvent. However, the above calculation of a monoclinic unit cell is based on the assumption that for different solvents a similar unit cell would be obtained, and it is only performed to get some feeling for possible dimensions.

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(32) Results based on a polymer/solvent ratio of 1:1 have been published by Spevaçek (*Macromol. Symp.* **1999**, *138*, 123−129). On the basis of our X-ray results, we apply a polymer:solvent ratio of 4:1.

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