Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 6633–6639 **6633**
DOI: 10.1021/ma9011335

Molecular Compounds from Ternary Systems of Syndiotactic Polystyrene

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Received May 25, 2009; Revised Manuscript Received June 29, 2009

ABSTRACT: The temperature−concentration phase diagrams as well as the structure and the morphology of ternary systems sPS/solvent 1/solvent 2, where sPS is syndiotactic polystyrene, solvent 1 is naphthalene, and solvent 2 is either benzene or biphenyl, are reported. The binary solvents have been chosen for two reasons: (i) They usually produce different molecular compound forms in binary systems: sPS/naphthalene gives clathrate compounds (δ_c form) and sPS/biphenyl forms intercalate compounds (δ_i form), while in case of sPS/benzene both forms occur depending on temperature and concentration. (ii) The binary solvent mixtures form themselves molecular compounds. The main outcomes of this investigation are threefold: (i) existence of ternary compounds, (ii) possibly another new compound form, and (iii) intercalates are still formed for low content of naphthalene in sPS/naphthalene/benzene systems, while they no longer occur in sPS/naphthalene/biphenyl systems.

Introduction

Syndiotactic polystyrene (sPS) has received growing interest since its synthesis in the late 1980s thanks to its high crystallization rate[1,2] but also thanks to its propensity to form polymer−solvent molecular compounds with a wide range of organic solvents (these compounds are also designated sometimes as crystallosolvates or solvated crystals, intercalates, or clathrates).[3−18] sPS possesses a very complex polymorphic behavior, which, for the sake of simplicity, can be described in terms of two nonsolvated crystalline forms, α and β, containing all-trans conformation with identity period 0.51 nm and several forms containing a 2_1 helical chain conformation with identity period of 0.77 nm (δ, γ, ε) of which several are solvated, and the other are produced from solvated forms.[19] Four types of solvated systems have been observed so far: the clathrates (or δ_c), first described by Chatani et al.,[8] the intercalates (or δ_i), first observed by Daniel et al. with benzene[11] but later described by Petraccone et al.,[18] a liquid-crystalline type (or δ_N), and more recently a new type of clathrate where guest molecules are located in the channels typical of the ε form (δ_ε form).[20,21] The latter is formed with highly polar solvents, such as nitrobenzene, through special procedures while the former, clathrates and intercalates, are produced with far less or even nonpolar solvents, such as toluene, chloroform, benzene, etc. sPS clathrates are less solvated than intercalates[19] (as a rule 1/4 against 1/2 solvent molecules/monomers). The reason why some solvents give one type of compound and other another type remains unclear. In particular, intercalates, namely the more solvated crystals, are chiefly obtained from solvents with rather large molar volume (biphenyl, benzophenone, etc.)[22,23] which are usually poor solvents for the atactic counterpart (benzene is a notable exception). Clearly, one would expect intercalates to be formed chiefly with good solvents, solvents that rather possess a small molar volume unlike what is currently observed. In order to cast some light on the role of the solvent in the formation of either clathrates or intercalates, we have attempted to tackle the question of ternary systems, namely sPS/solvent 1/solvent 2, where solvent 1 produces clathrates and solvent 2 intercalates. In addition, we have chosen couples of solvent 1 and solvent 2 whose mixtures form molecular compounds as will be shown in this paper. So far such systems have not been investigated, yet their study is believed to add interest in view of the wealth of crystalline structures of sPS and its versatility for preparing nanoporous materials.[24,25]

Experimental Section

1. Materials. The syndiotactic polystyrene (sPS) samples were synthesized following the method devised by Zambelli and coworkers using hydrogenous monomer (sPSH) or perdeuterated monomer (sPSD), the latter to be used for neutron diffraction purposes. The content of syndiotactic triads characterized by ^{1}H NMR was found to be over 99%. The molecular weight characterization was performed by self-exclusion chromatography (SEC) in dichlorobenzene at 140 °C and yielded the following: sPSH: $M_w = 1.0 \times 10^5$ with $M_w/M_n = 4.4$; sPSD: $M_w = 4.3 \times 10^4$ with $M_w/M_n = 3.6$.

2. Sample Preparation. For the sPS−naphthalene/benzene system, first the binary solvent mixtures (with different weight fractions) containing benzene and naphthalene were prepared under the desired proportions. The gels were prepared in hermetically closed test tubes by heating sPS and appropriate weight fraction of the binary solvent to get the homogeneous solution, which were cooled rapidly to room temperature. For the sPS−naphthalene/biphenyl system, sPS, naphthalene, and biphenyl having appropriate weight fractions were melted together at high temperature and then cooled to room temperature.

3. Techniques. *Differential Scanning Calorimetry*. The thermal behavior of the systems was investigated by means of Perkin-Elmer DSC Pyrhis. The systems were prepared before in test tubes as described above and were then transferred to into "stainless steel" pans that were hermetically sealed. The systems containing sPS/naphthalene/benzene were systematically melted at 150 to 200 °C (depending upon the polymer concentration) for 10 min and then cooled down to −30 °C at a rate of 10 °C/min. The system containing sPS/naphthalene/biphenyl were systematically melted at 200 °C for 10 min and

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then cooled down to −10 °C at a rate of 10 °C/min. In both systems the thermograms were recorded with heating rates ranging from 5 to 10 °C/min. In all cases the phase diagrams were mapped out by using the results obtained at 10 °C/min. The weight of the pans containing the samples was checked after each experiment, and the instrument was calibrated with indium before investigating the next polymer concentration.

Atomic Force Microscopy. AFM experiments were carried out at room temperature in air using a Nanoscope III instrument (Digital Instruments, Santa Barbara, CA). Images were taken by means of tapping mode with a silicon nitride cantilever (Scientec, France) having a spring constant of 25−50 N/m and a rotating frequency of 280−365 kHz. Films were prepared by careful deposition of hot, homogeneous solution onto a glass slide in closed environment (to prevent solvent loss prior to gel formation) and then finally allowing the solvent to sublimate. The observation of the surface topography of the films was performed with a scanning rate varying from 1 to 2 Hz.

X-ray Diffraction. The X-ray experiments were performed on beamline BM2 at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The energy of the beam was monitored to 15.8 keV which corresponds to a wavelength of $\lambda = 7.86 \times 10^{-2}$ nm. At the sample position the collimated beam was focused with a typical cross section of 0.1×0.3 mm^2. The scattered photons were collected onto a two-dimensional CCD detector developed by Princeton Instruments, presently Roper Scientific. Typical acquisition times were of about 10 s, which allows time-resolved experiments to be carried out at 2 °C/min.

The sample-to-detector distance was about 0.2 m, corresponding to a momentum transfer vector q range of $1 < q$ (nm^{-1}) < 17, with $q = (4\pi/\lambda)\sin(\theta/2)$, where λ and θ are the wavelength and the scattering angle, respectively (further information available at http://www.esrf.fr).

The scattering intensities obtained were corrected for the detector response, the dark current, the empty cell, the sample transmission, and the sample thickness. The data were radially regrouped to obtain a one-dimensional X-ray pattern out of the two-dimensional digitalized pictures. A silver behonate sample was used for determining the actual values of the momenta transfer q.

Approximately 300 mg of the sPS/solvent systems prepared as described above was transferred into glass tubes of 3 mm inner diameter and wall thickness 0.1 mm. These tubes were then sealed from the atmosphere while keeping them at low temperature through a quench in liquid nitrogen in order to prevent from solvent loss. Homogeneous solution was obtained again by heating and was eventually cooled to room temperature for producing the crystallized samples.

Neutron Diffraction. Neutron diffraction experiments were carried out on G-6-1, a diffraction camera located at nuclear reactor Orphée (Laboratoire Léon Brillouin, Saclay, France). G-6-1 is a two-axis spectrometer equipped with a banana-type BF_3 detector composed of 400 cells with an angular resolution of 0.2°. The spectrometer operates at a wavelength $\lambda = 0.474$ nm obtained by diffraction of the neutron beam onto a graphite monocrystal oriented under Bragg condition (further details available at http://www.llb.fr). The following q range was used:

$$1.5 \text{ nm} < q < 10 \text{ nm}^{-1} \text{ with } q = (4\pi/\lambda)\sin(\theta/2)$$

Detector normalization was achieved by means of a vanadium sample.

The samples were introduced into amorphous quartz tubes of 4 mm inner diameter after having been prepared as described above. The cell was sealed hermetically from atmosphere and then heated so as to obtain a homogeneous solution. The mixtures were then rapidly cooled to room temperature. Only the system where benzene/naphthalene = 0.78/0.22 and C_{sPSD} = 0.2 g/g was investigated with four combinations of labeled species: sPSD/benzeneH/naphthaleneH, sPSD/benzeneD/naphthaleneH, sPSD/benzeneH/naphthaleneD, sPSD/benzeneD/naphthaleneD.

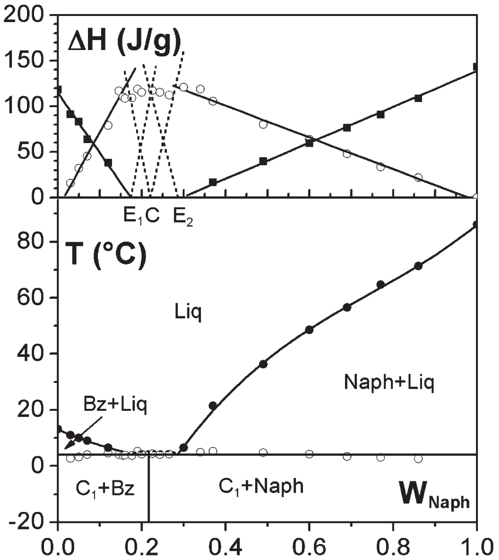

Figure 1. Temperature−concentration phase diagram (T vs W_{Naph}) and Tamman's diagram (ΔH vs W_{Naph}) for the binary system naphthalene/benzene.

Results and Discussion

For the sake of clarity, we shall present separately the two systems, namely sPS/naphthalene/benzene and sPS/naphthalene/biphenyl. The sPS/naphthalene mixtures are known to produce clathrates and sPS/biphenyl mixtures give intercalates[22] while sPS/benzene can produce both forms depending upon polymer concentration and temperature.[11] In the latter system, for $C_p \leq 0.26$ g/g, only the intercalate form (δ_i) is obtained, while for 0.26 g/g $\leq C_p \leq 0.57$ g/g both forms coexist (δ_i and δ_c), and finally for $C_p \geq 0.57$ g/g only the clathrates form (δ_c) is observed.[11] Note that benzene possesses a molar volume significantly smaller than that of naphthalene (89 cm^3/mol vs 133 cm^3/mol) whereas biphenyl molar volume (156 cm^3/mol) differs only slightly from that of naphthalene.

1. sPS/Naphthalene/Benzene. The temperature−concentration phase diagram of the binary naphthalene/benzene systems as mapped out by DSC is given in Figure 1. This diagram suggests the existence of a congruently melting compound of stoichiometry of 1/6. The reasons for considering the occurrence of a compound are twofold: (i) the linear variations of the enthalpies of the terminal melting do not extrapolate to zero at the same composition (0.17 vs 0.30) as would be the case for an eutectic, and (ii) the melting enthalpy associated with the nonvariant event at $T = 4$ °C is virtually constant in the range 0.15−0.30. The latter point suggests that this enthalpy is actually the sum of two terms as highlighted with dashed lines on the Tamman's diagram.

The outcome from the phase diagram is further borne out by X-ray diffraction as shown in Figure 2. The diffraction pattern of the system of composition 0.22/0.78 is not simply the sum of the diffraction pattern of each component. In particular, two new reflections are observed at $q = 13.6$ nm^{-1} (labeled 1) and $q = 15.4$ nm^{-1} (labeled 2).

In view of the phase diagram of Figure 1, the following three naphthalene/benzene compositions have been considered for studying the ternary systems: 0.1/0.9, 0.22/0.78, and 0.3/0.7. One composition corresponds to the stoichiometry

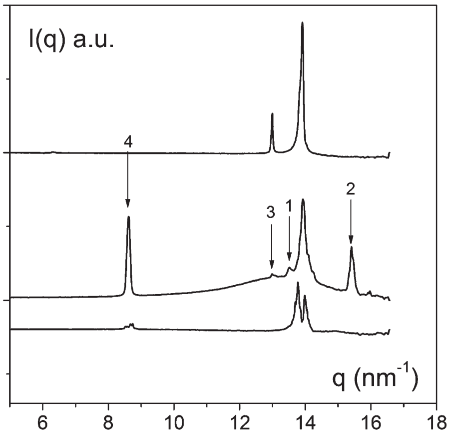

Figure 2. Diffraction patterns: top, benzene; bottom, naphthalene at 0 °C; middle, naphthalene/benzene mixture 0.22/0.78 at 0 °C. Numbers highlight the additional or enhanced diffraction peaks.

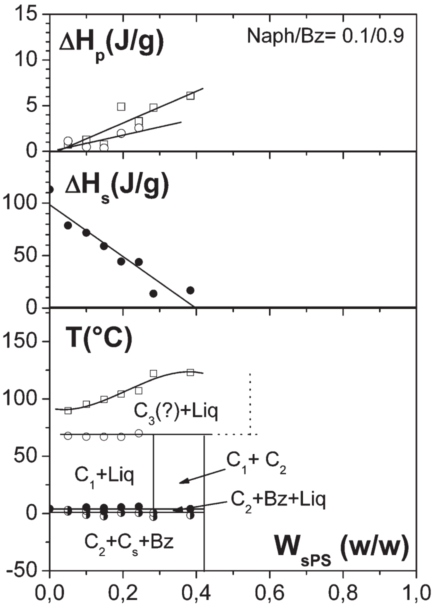

Figure 3. Temperature–concentration phase diagram and Tamman's diagrams for sPS/naphthalene/benzene systems (composition as indicated). C_s corresponds to the solvents binary compound.

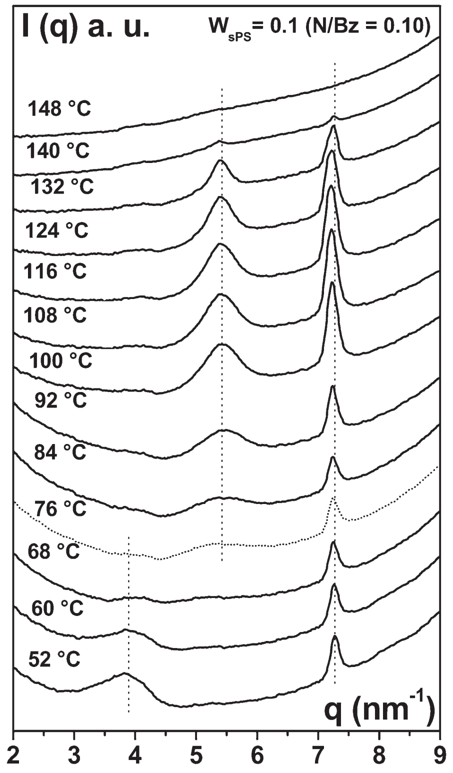

Figure 4. Time-resolved X-ray diffraction patterns. The dotted spectrum highlights the transition observed in the $T-C$ diagram of Figure 3 (composition and polymer concentration as indicated).

of the compound naphthalene/benzene (0.22/0.78), while the other two bracket this value.

a. sPS/Naphthalene/Benzene 0.1/0.9. For samples of lowest composition in naphthalene, the temperature–concentration phase diagram (here the concentration is that of the polymer) is much reminiscent of the binary phase diagram sPS/benzene, which is the existence of two compounds C_1 and C_2 of differing stoichiometries[11] (Figure 3). In view of the stoichiometries derived from the $T-C$ phase diagram, two compounds correspond to the clathrates (C_2) and to the intercalates (C_1). Worth noticing is the stoichiometric concentration given by extrapolation of the solvent melting enthalpy ($C_p \approx 0.4$ g/g) is significantly lower than that obtained from the binary system ($C_p = 0.57$ w/w). The occurrence of a third compound C_3 at higher temperature at the temperature where C_1 melts incongruently may be worth considering. This conclusion is also suggested by the X-ray diffraction data.

The time-resolved diffraction data drawn in Figures 4 and 5 show the evolution of the molecular structure on either side of the stoichiometry of compound C_1 ($C_p = 0.26$ w/w). For $W_{sPS} = 0.1$ w/w one does observe the transformation of one compound into the other (C_1 into C_3 using the labeling of the phase diagram) as the peak at $q = 3.9$ nm^{-1}, which characterizes the sPS intercalates,[11,16,17] shifts to $q = 5.5$ nm^{-1}, which corresponds to the sPS clathrates. For $W_{sPS} = 0.3$ w/w, where the phase diagram indicates the coexistence of C_1 and C_2, two peaks are indeed seen yet at $q = 3.9$ nm^{-1} and $q = 5.2$ nm^{-1}. On heating the first peak disappears, as expected again from the phase diagram, while the second peak is slightly shifted to higher q values ($q = 5.5$ nm^{-1}), which corresponds to C_3. This suggests, as already proposed above, that C_2 and C_3 are different compounds whose main difference lies either in their stoichiometry, with C_2 being slightly more solvated than C_3, or in their solvent composition if ternary compounds are dealt with. Note that four phases are present at the nonvariant event at $T = 69$ °C, which still complies with Gibbs phase rules as we are presently dealing with a ternary mixture.

b. sPS/Naphthalene/Benzene 0.22/0.78. This composition corresponds to the stoichiometric composition of the compound naphthalene/benzene as derived from the $T-C$ phase diagram of Figure 1. The $T-C$ phase diagram for the ternary system is drawn in Figure 6. Surprisingly, the nonvariant event observed at 69 °C for the previous system, which corresponded to a compound–compound transformation, is conspicuously absent. This suggests that there is either only one compound, in which case it should be a ternary compound, sPS/naphthalene/benzene, or two binary compounds. In the latter case one could have C_1 = sPS/naphthalene and C_2 = sPS/benzene with virtually the same stoichiometry corresponding to the usual clathrate form. Diffraction data from time-resolved experiments that are plotted in Figure 7 reveal the occurrence of two peaks at $q = 4.2$ nm^{-1} and $q = 5.4$ nm^{-1} that persist until the complete melting of the sample. As the $T-C$ phase diagram and the Tamman's diagram both point to a

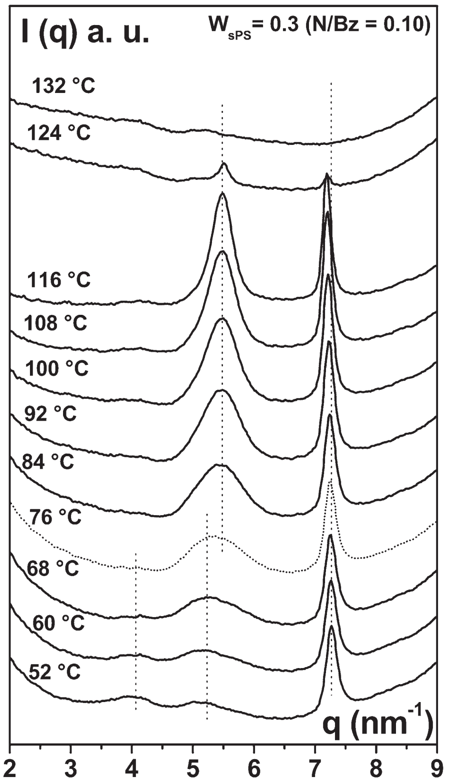

Figure 5. Time-resolved X-ray diffraction patterns. The dotted spectrum highlights the transition in the $T-C$ diagram of Figure 3 (composition and polymer concentration as indicated).

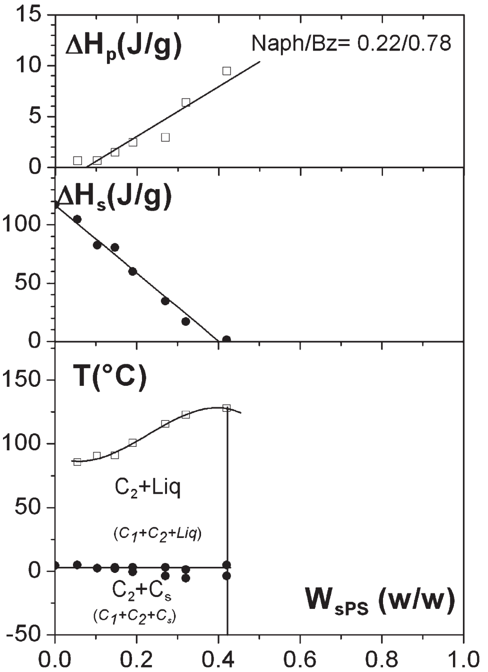

Figure 6. Temperature–concentration phase diagram and Tamman's diagrams for sPS/naphthalene/benzene systems (composition as indicated). C_s corresponds to the solvents binary compound.

stoichiometry close to that of the usual clathrates, the peak at $q = 4.2$ nm^{-1} is most probably not arising from the intercalate form usually located at $q = 3.9$ nm^{-1}. This result rather suggests the existence of a ternary molecular compound sPS/naphthalene/benzene as opposed to two binary compounds. The existence of a ternary compound makes sense in view of the composition of the binary solvent, which corresponds to the stoichiometry of the binary naphthalene/benzene compound.

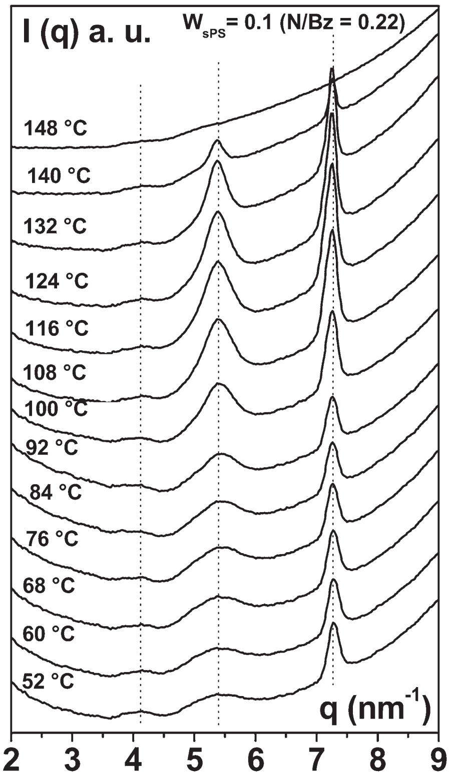

Figure 7. Time-resolved X-ray diffraction patterns. Polymer concentration and solvent composition as indicated.

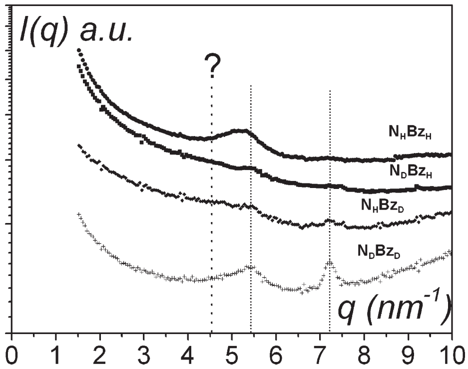

Figure 8. Neutron diffraction patterns obtained for napthalene/benzene = 0.22/0.78, and C_{sPSD} = 0.2 g/cm^3. The different types of labeling are indicated. The positions of the expected reflections[8] for the 010 plane (q = 5.5 nm^{-1}) and the $2\bar{1}0$ plane (q = 7.3 nm^{-1}) are shown as well as that of the reflection seen by X-ray diffraction.

In order to test the validity of this statement, neutron diffraction experiments have been carried out. By using different combinations of deuterated polymer and deuterated or hydrogenous solvents, four systems were studied (see Figure 8). As has been shown in other papers, the neutron diffraction method is quite suited for studying polymer–solvent molecular compound as the diffraction pattern depends strongly on the labeling of the different species.[11,15,16,22] Here, we have focused the study on two reflections at q = 5.5 nm^{-1} and q = 7.3 nm^{-1}, which correspond to the 010 and the $2\bar{1}0$ planes, respectively, in the lattice derived by Chatani and co-workers[8] (see sketch in Figure 9). In binary systems

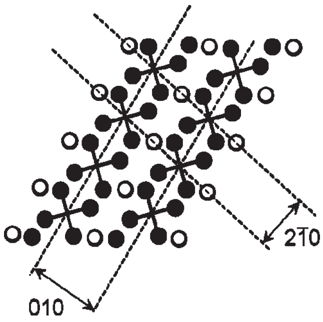

Figure 9. Sketch of the Chatani's crystalline lattice[8] as seen parallel to the sPS 2_1 helix axis (helices are crosses and solvent molecules are open circles).

these two reflections are seen when both components are deuterated, while the second reflection is absent when dealing with hydrogenous solvent. This makes sense as the 2$\bar{1}$0 plane contains only solvent molecules, so that the diffracted intensity is lowered if hydrogenous species are used instead of deuterated species. In the present case the same type of result is unsurprisingly retrieved: (i) when both solvents are deuterated, both reflections are seen, while (ii) when both solvents are protonated, only the $q = 5.5$ nm^{-1} reflection is observed. The other two cases, namely when one solvent is deuterated and the other one protonated, are much more interesting as both reflections virtually vanish. Note that this is not due to a difference in degree of crystallinity as the measured enthalpies are the same for all the samples within experimental uncertainties. Vanishing of the second reflection definitely confirms the existence of a ternary compound. Indeed, if one were dealing with binary compounds, on should observe this reflection when benzene is deuterated as this is a major component of the solvent mixture. If we had only a sPS/naphthalene binary compound, the same reasoning holds. To be sure, there is no reason why we should not find the same results as those found when both solvents are deuterated. What is more surprising is the quasi-disappearance of the first reflection although the polymer is deuterated. Again, the above reasoning applies, as this reflection must be present independently of the solvent labeling. Here it should have the same magnitude as that seen when both solvents are deuterated or both are hydrogenous. Does this suggest that the placement of the solvent molecules is at variance with that of Chatani's original lattice? Also, the reflection at $q = 4.5$ nm^{-1} observed with WAXS is hardly, even not, visible at all. What is the significance of this effect?

Clearly, while neutron diffraction outcomes bear out the existence of a ternary compound, they also point to another possible solvent arrangement in the crystalline lattice or even a somehow variant of this lattice.

c. sPS/Naphthalene/Benzene 0.3/0.7. The $T-C$ phase diagram of Figure 10 also suggests the occurrence of only one type of compound. The fact that the enthalpies of the two nonvariant transformations ($T = 0$ °C and $T = 20$ °C) extrapolate to zero at the same sPS concentration is consistent with this statement. Most probably this is again a ternary compound as one would otherwise observe four phases in the domain located between the two nonvariant events, which is forbidden by Gibbs phase rules (four phases cannot coexist in a 2-D domain of the phase diagram).

The time-resolved X-ray diffraction data shown in Figure 11 exhibit only the characteristic reflections of the clathrate form, namely at $q = 5.4$ nm^{-1} and $q = 7.3$ nm^{-1}.

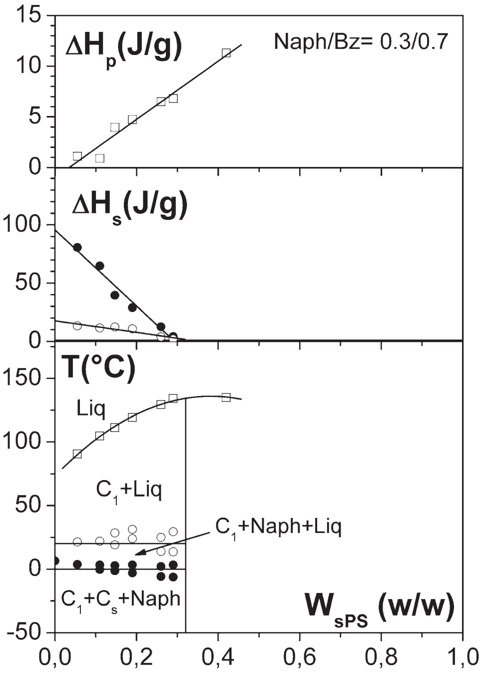

Figure 10. Temperature−concentration phase diagram and Tamman's diagrams for sPS/naphthalene/benzene systems (composition as indicated).

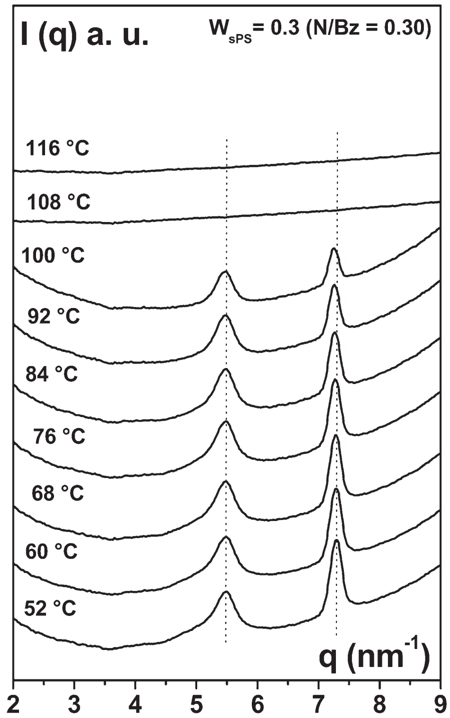

Figure 11. Time-resolved X-ray diffraction patterns. Polymer concentration and solvent composition as indicated. The vertical dotted lines highlight the diffraction peak for intercalates and for clathrates (see text).

To summarize the results on sPS/naphthalene/benzene systems, the $T-C$ phase diagrams, the time-resolved X-ray diffraction data, and the neutron diffraction data are consistent with the existence of ternary compounds. Diffraction data further suggest that the Chatani's crystalline lattice may need some reappraisal.

It is worth emphasizing that the visual aspect of these systems, namely nearly transparent bluish aspect, is definitely that of a fibrillar gel.[19] The morphology as observed by

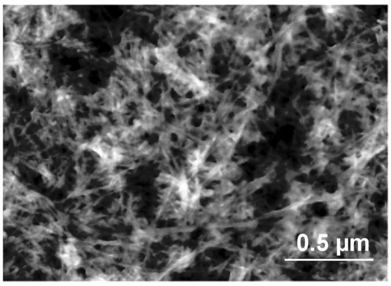

Figure 12. AFM picture of a 0.22/0.78 naphthalene/benzene system (W_{sPS} = 0.2).

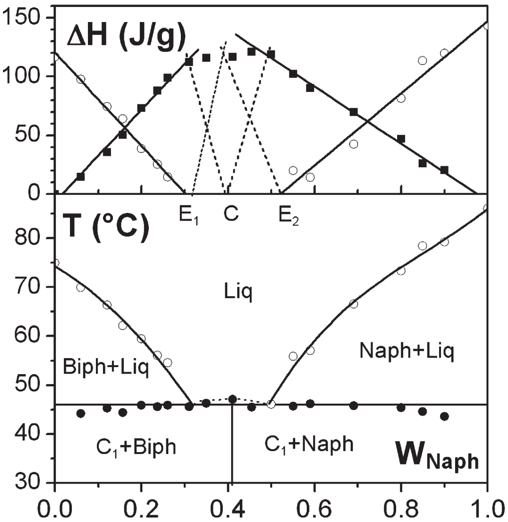

Figure 13. Temperature−concentration phase diagram (T vs W_{Naph}) and Tamman's diagram (ΔH vs W_{Naph}) for the binary system naphthalene/biphenyl.

AFM does reveal the presence of fibrils (Figure 12) as has already been reported for sPS/benzene and sPS/naphthalene systems.[11,16]

2. sPS/Naphthalene/Biphenyl. As a reminder, biphenyl produces intercalates with sPS.[22] Upon heating, these intercalates transform within a short temperature domain into the δ_N mesophase and finally into the nonsolvated β form. The $T-C$ phase diagram does not show the occurrence of the clathrate form unlike what was reported for sPS/benzene systems.

The temperature−composition phase diagram of the binary naphthalene/biphenyl systems (Figure 13) is much reminiscent of that of Figure 1 for naphthalene/benzene systems. Here again, the values of the compositions obtained after extrapolation to zero of the terminal melting enthalpies, together with the virtually constant value of the enthalpy associated with the nonvariant event at 46 °C in the composition range 0.3−0.5, suggest the existence of a molecular compound. The estimated stoichiometry of this compound is 1/1. X-ray diffraction investigations support this outcome as is shown in Figure 14: the diffraction pattern of the mixture 0.42/0.58 is not the simple superimposition of the diffraction pattern each components as new peaks are seen (q = 0.86, 13.2, 14.9, and 16.5 nm^{-1}).

As with the previous system, the sPS/naphthalene/biphenyl systems have been studied at the stoichiometric composition of the naphthalene/biphenyl compound (0.42/0.58) and at a composition containing a lesser amount of naphthalene (0.2/0.8).

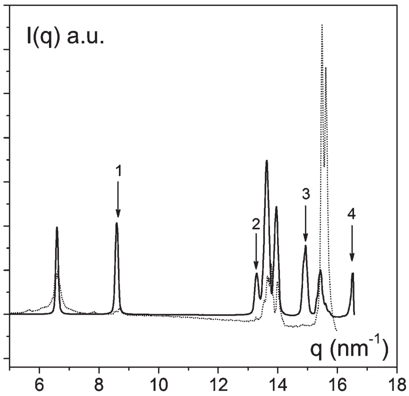

Figure 14. X-ray diffraction patterns: full line, 0.4/0.6 naphthalene/biphenyl mixture (stoichiometric composition); dotted line, addition of the diffraction patterns of pure naphthalene + pure biphenyl in the same proportion. Numbers highlight the additional or enhanced diffraction peaks.

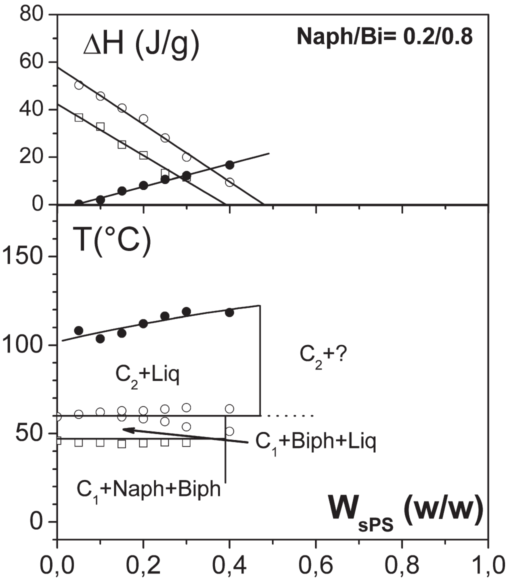

Figure 15. Temperature−concentration phase diagram and Tamman's diagrams for sPS/naphthalene/biphenyl systems (composition as indicated).

a. sPS/Naphthalene/Biphenyl 0.2/0.8. The temperature−concentration phase diagram is plotted in Figure 15. The results suggest the existence of only one compound with a change of stoichiometry at 60 °C, which corresponds to the transition where all solid solvent molecules become liquid. This compound is therefore probably a ternary compound, and it is likely that the transformation occurring at 60 °C is rather a change of the compound composition, possibly releasing biphenyl molecules.

This conclusion is borne out by time-resolved diffraction data that show the occurrence of the only clathrate form as the typical reflections of this form are seen at $q = 5.4$ nm^{-1} and $q = 7.3$ nm^{-1} (Figure 16). These outcomes therefore indicate that for very low amounts of naphthalene the intercalate form, which occurs for pure biphenyl, does not exist any longer. This is clearly at variance with the previous system (i.e., naphthalene/benzene).

b. sPS/Naphthalene/Biphenyl 0.42/0.58. This composition corresponds to the stoichiometric composition. The temperature−concentration phase diagram drawn in Figure 17 highlights the occurrence of only one compound whose stoichiometry changes slightly at the "solvent" melting (T = 49 °C). Again, this may correspond to a change of compound composition as a ternary compound is most

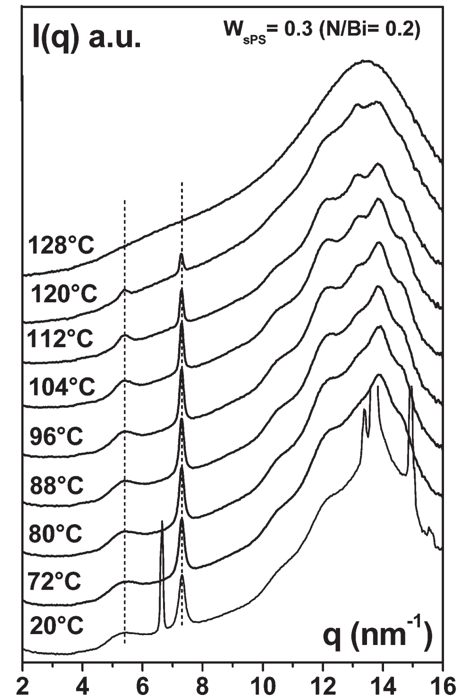

Figure 16. Time-resolved X-ray diffraction patterns. Polymer concentration and solvent composition as indicated.

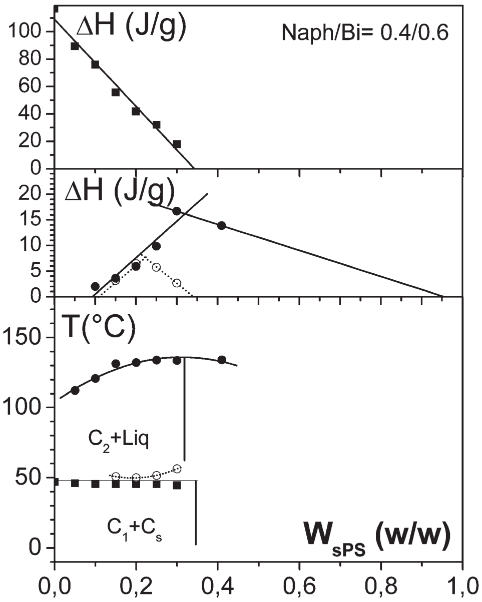

Figure 17. Temperature–concentration phase diagram and Tamman's diagrams for sPS/naphthalene/biphenyl systems (composition as indicated).

probably dealt with. As with the above system, the time-resolved X-ray experiments reveal only those diffraction peaks related to the clathrates form ($q = 5.5\ nm^{-1}$ and $q = 7.3\ nm^{-1}$, spectra not shown). So, in spite of the solvent composition, the dominant system is again the clathrate form to the detriment of the intercalate form. It is, however, worth noting that the compound seems to be of the congruently melting type as opposed to what has been observed so far.

Concluding Remarks

The investigation of ternary systems of syndiotactic polystyrene has suggested the existence of ternary molecular compounds. Three forms have been identified: the usual clathrates and intercalates and a seemingly new form in the case of sPS/naphthalene/benzene compounds. Interestingly, the intercalate form is still produced in sPS/naphthalene/benzene systems for significant contents of naphthalene while it is absent in the case of sPS/naphthalene/biphenyl systems. This suggest either that no binary compounds are formed in this systems or that intercalate sPS/biphenyl cannot form under these conditions. The former assumption is probably more likely. If so, this would mean that small amounts of naphthalene are sufficient to prevent from intercalate formation in sPS/naphthalene/biphenyl systems. These results and assumption need now to be confirmed by further investigations together with other techniques.

Acknowledgment. Arnab DAWN is indebted to CNRS for a postdoctoral fellowship through a Joint European Laboratory Institut Charles Sadron-MPI für Polymerforschung. Time-resolved X-ray experiments have been carried out on the French beamline CRG-D2AM (ESRF, Grenoble, France). Neutron diffraction experiments have been carried out at Laboratoire Léon Brillouin (CEA Saclay, France). The authors are grateful to Dr. Isabelle Mirebeau for assistance on spectrometer G6-1 and for processing the neutron data, to C. Saettel for the DSC experiments, and to C. Contal for AFM investigations.

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