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Thermoreversible Gelation of Syndiotactic Polystyrene in Naphthalene

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Summary: Investigation into syndiotactic polystyrene/naphthalene systems of concentrations ranging from 0 to 78% (w/w) have been carried out by electron microscopy, DSC, and neutron diffraction. It is found that a fibrillar morphology is produced in this solvent, similar to that observed for thermoreversible gels. The temperature-concentration phase diagram suggests the existence of two compounds of differing stoichiometries. Neutron diffraction experiments confirm the existence of compounds in this system.

Keywords: polymer-solvent complex; syndiotactic polystyrene; T-C phase diagram; thermoreversible gel

Introduction

Syndiotactic polystyrene (sPS) has received great interest as an attractive material due to its high crystallization rate, high melting temperature, low specific gravity and good chemical resistance [1]. sPS possesses very complex polymorphic behaviour, which, by simplification, can be described in terms of two crystalline forms, α and β, containing all trans conformation with identity period 5.1Å and two forms, δ and γ, containing helical chain conformation with identity period of 7.7Å [2] sPS has a tendency to form polymer-solvent compounds (also designated sometimes as crystallosolvates, intercalates or chlathrates), which are due to formation of solvent-induced crystalline δ-form, with a large variety of solvents such as benzene [3], toluene [4], chloroform, bromoform [5], decalin etc. by exposing solid polymer in the liquid solvent or vapour (solvent-induced-process) [6] or by cooling homogeneous solution (solution-cast-process) [7]. In previous reports, sPS complexes were prepared from solvents that are liquid at room temperature and also toxic. For the sake of using safer solvents, we have considered here naphthalene that is far less harmful to human body, and which is easier

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to handle as it is in the solid state in room temperature. Naphthalene possesses well-known sublimation property.

Experimental

Syndiotactic polystyrene (sPS) samples, hydrogenated and deuterated, were synthesized following a method devised by Zambelli and co-workers [8]. The content of syndiotactic triads characterized by ^{13}C-NMR was found to be over 99%. The molecular weight characterization of these samples was performed by GPC in dichlorobenzene at 140°C and yielded the following data: $M_w = 1.0 \times 10^5$ g/mol with $M_w/M_n = 4.4$ for sPSH; $M_w = 4.3 \times 10^4$ g/mol with $M_w/M_n = 3.6$ for sPSD.

Naphthalene was purchased from Aldrich and used without further purification.

The thermal behaviour of the gel was investigated by means of Perkin Elmer DSC 7. Pieces of gel prepared beforehand in test tube were introduced into "volatile sample" pans that were hermetically sealed. The systems were melted so as to obtain a homogeneous solution, and then cooled to 20°C. The thermograms were recorded at a scan rate of 5°C/min. The weight of the sample was checked after each experiment and the instrument was calibrated with indium before each set of experiment.

A film of sPS/naphthalene was dried in vacuum at room temperature and was coated with gold by sputtering technique under argon atmosphere and observed under microscope (Hitachi S-2300) operating voltage ranging from 15 kV to 25 kV.

Neutron diffraction experiments were carried out on D16, a diffractometer located at Institut Laue Langevin, Grenoble, France. It is a two circle diffractometer equipped with a position sensitive ^{3}He multidetector made up with 128x128 wires. The distance between consecutive wires is 2 mm. The diffractometer operates at wavelength $\lambda = 0.454$ nm obtained by diffraction of the neutron beam onto a pyrolytic graphite mosaic-crystal (mosaicity = 0.7°) oriented under Bragg condition. Momentum transfer $q = (4\pi/\lambda)\sin(\theta/2)$ were ranging from $q = 2$ to 12 nm^{-1}. Detector normalization and correction of cell efficiency were achieved with the spectrum given off by water. The samples were prepared directly in quartz tubes of 3 mm inner diameter. After introducing a mixture of polymer (sPSD) and solvent these tubes were sealed from atmosphere. Homogeneous solution were obtained by heating and were then quenched to room temperature.

Results and Discussion

Samples from sPS in naphthalene are solid in the room temperature but become transparent above the melting temperature of pure naphthalene (82°C), and possess all the characteristics of thermoreversible gels. The morphology of this system, as observed by SEM, does reveal a fibrillar network morphology (see fig. 1) similar to that reported for thermoreversible gels [7]. The mesh size is in the micrometer range while the fibrils cross-sections are in the nanometer range (around 20-40 nm).

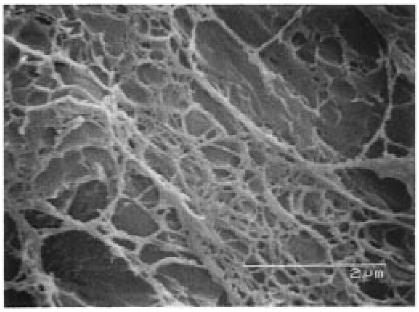

Figure 1. Scanning electron micrograph of 30%(w/w) sPS-naphthalene dries gels.

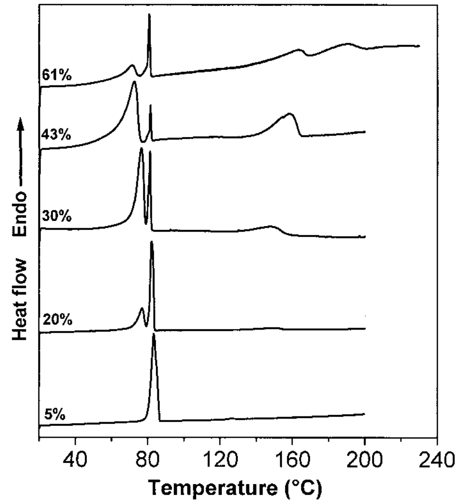

Figure 2. The representative DSC traces of sPS-naphthalene system at indicated concentration.

Typical differential scanning calorimetry (DSC) thermograms of sPS in naphthalene at indicated polymer concentration are presented in Figure 2. As can be seen there are two domains, a low temperature region and a high temperature region. The temperature associated with the first domain is due to the melting of the free naphthalene present in the system. It is interesting to note that the peaks due to naphthalene melting at the temperature range 82 – 68°C are bifurcated at polymer concentration (C_{pol}) 20-66% (g/g). The reason of bifurcation of the solvent peak is probably due to the fact that increasing the polymer concentration produces smaller and smaller free solvent domains with a melting point lower than that of infinite crystals .

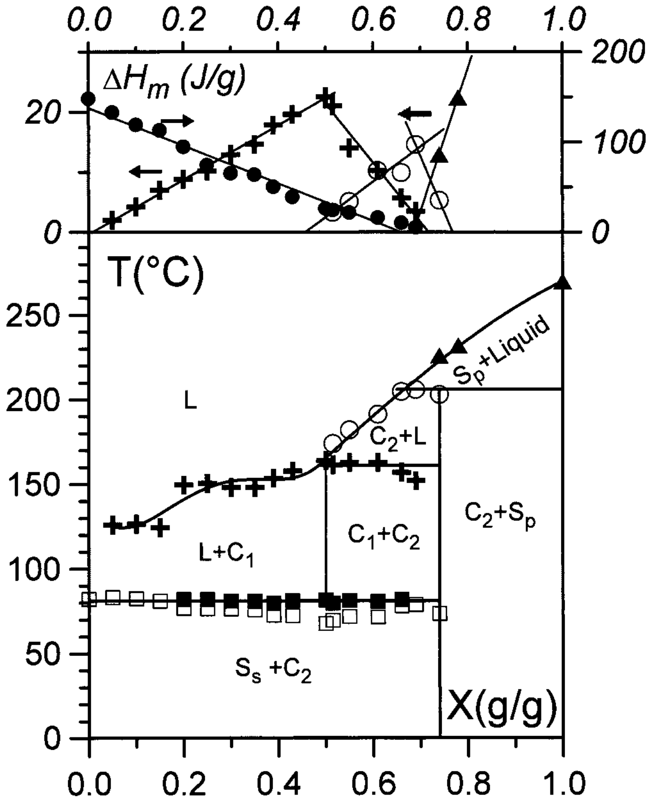

Figure 3. Temperature-concentration phase diagram and Tamman's diagram for sPS-naphthalene systems.

In the high temperature domain, one melting endotherm (low-melting endotherm) is observed up to a concentration C_P = 50% (w/w) while for the high concentrated systems a second melting endotherm (high-melting endotherm) appears at higher temperature. The temperature associated with low-melting endotherm, initially , remains constant up to $C_P = 15\%$, after this it jumps to 149°C at $C_P = 20\%$, and then increases with increasing concentration. The temperature associated with high-melting endotherm increases continuously with increasing concentration of sPS investigated here. The temperature- concentration phase diagram drawn in figure 3 presents these different types of behaviour. The variations of the enthalpies associated with each endotherm as function of polymer concentration (Tamman's diagram) are presented in the same figure.

The enthalpy associated with the melting of naphthalene is gradually decreasing with increasing polymer concentration and becomes zero at $C_P = 70\%$. The enthalpy associated with low melting endotherm at high temperature region increases linearly up to a polymer concentration $C_P = 50\%$ and then decreases to become zero at about $C_P = 74\%$. On the other hand, the enthalpy associated with high melting endotherm increases continuously. The enthalpy variations together with the shape of phase diagram are consistent with the existence of the two compounds C_1 and C_2 of different stoichiometries. C_1 is a singularly melting compound that transforms to C_2 at low temperature. The stoichiometry of the compound C_1 is determined by the maximum of the enthalpy associated with T_{low}, namely about 0.9 naphthalene molecules per monomer unit. The stoichiometry of compound C_2 is given by the concentration at which the enthalpy of low melting endotherm goes to zero ($C_P = 74\%$) , namely one naphthalene molecule per four monomeric unit, and is incongruently-melting compound.

Neutron diffraction is an appropriate tool for studying polymer-solvent compound as deuterium-labelling of either component allows one to get four structure factors without significant change in the molecular arrangement. The existence of polymer-solvent compounds can be therefore confirmed from neutron diffraction as is illustrated by the general expression for the intensity diffracted by a binary system composed of polymer(p) and solvent(s) [9,10]:

$$I(q) = \overline{A}_P^2(q)S_p(q) + \overline{A}_s^2(q)S_s(q) + 2A_p(q)A_s(q)S_{ps}(q) \qquad (1)$$

where $A(q)$ and $S(q)$ with appropriate subscripts are the coherent scattering amplitude and the structure factor of the polymer and of the solvent, and $S_{ps}(q)$ is a cross-term between polymer and solvent. This term is only meaningful when polymer-solvent compound are dealt with, which results in an alteration of the ratio of diffracted intensities with respect to one another when different labelled species are used. Conversely, if no complex is formed, this cross term vanishes and the diffraction pattern of the crystallized polymer is independent of labelling. Therefore, if significant variation of this ratio is observed when replacing one species by its labelled counterpart then polymer- solvent compounds are present beyond doubt.

Here we shall discuss only the qualitative aspect of the diffraction patterns that are presented in figure 4 and figure 5 for C_P = 20 wt % and C_P = 73 wt % respectively. As can be seen in figure 4 , the intensity ratio does vary with the solvent labelling. For instant, the reflection at 7.3 nm^{-1} (indicated by arrow) is much stronger for sPSD/napD (curve a) than that for sPSD/napH (curve b) while that at 5.4 nm^{-1} varies little. This clearly supports the existence of a sPS/Naphthalene compounds. Note that the strong reflection at 8.7 nm^{-1} arises from the free, crystallized naphthalene and it vanishes when the system is heated above 80°C (curve c).

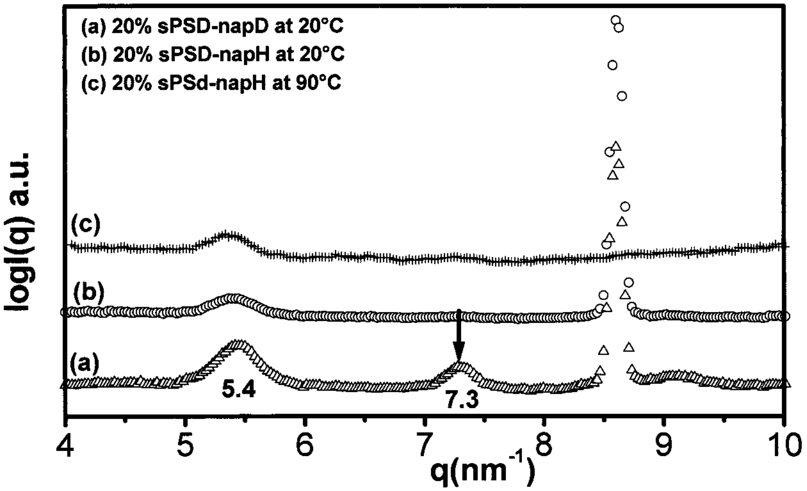

Figure 4. Neutron diffraction pattern for 20% sPS-naphthalene system for different isotopic solvent labelling (as indicated).

In figure 5 the relative intensities of the peaks at q = 5.4 nm^{-1} and q = 7.3 nm^{-1} are significantly altered with changing solvent labelling. This indicates clearly the presence of another complex at C_p = 74% (g/g) in the sPS/naphthalene system. This indication supports the phase diagram as well as the existence of two polymer-solvent compound in this system.

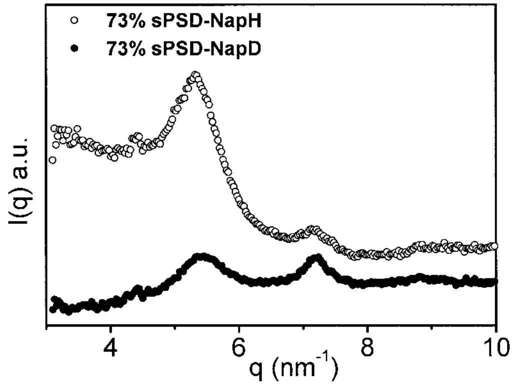

Figure 5. Neutron diffraction pattern for 74% sPS-naphthalene system for different isotopic solvent labelling (as indicated).

Conclusion

Syndiotactic polystyrene/naphthalene forms fibrillar structures quite reminiscent of thermoreversible gels. From the phase diagram two compounds have been identified with different stoichiometries. The neutron diffraction study also supports the presence of polymer-solvent compound as derived from the phase diagram.

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