Macromol. Symp. 2008, 273, 109–114 DOI: 10.1002/masy.200851315

Studies on the Effect of Glass Transition on the Crystalline Transition in Syndiotactic Polystyrene – Solvent Complexes

*Sudhakar Naidu, N. C. Ramesh**

Summary: Amorphous syndiotactic polystyrene (sPS) was crystallized at room temperature in Norbornadiene (bicyclo[2,2,1]-hepta-2,5-diene), Mesitylene (1,3,5-Trimethylbenzene), 3-Carene (3,7,7-trimethyl bicyclo[4,1,0]hept-3-ene) and DMN (1,4-Dimethylnaphthalene) to form the sPS-solvent complex (δ form) with respective solvent molecules. In situ HTFTIR studies showed that the δ form to γ form transformation temperature occurs well below the glass transition temperature of sPS, which is depressed due to the presence of solvent in the amorphous phase; higher the solvent content in the complex, lower the transition temperature. Glass transition temperatures determined by Modulated differential scanning calorimetry (MDSC) coincide with the transition temperatures, indicating that the δ form transforms into γ form at the glass transition temperature for these complexes. Such a behavior is very different from the behaviour of the sPS- solvent complexes formed by dichloromethane, chloroform, toluene, *o*-dichlorobenzene, decalin (cis-trans) etc. and for these complexes the transition occur well above the T_g.[1]

Keywords: crystallization; glass transition; infrared spectroscopy; syndiotactic polystyrene

Introduction

Syndiotactic polystyrene (sPS) in the semicrystalline form shows complex polymorphism and has four polymorphic forms, namely α, β, γ and δ. The α and β forms, both containing planar zigzag chains having T4 all trans conformation, can be obtained from the melt or glassy state of sPS under different thermal crystallization conditions.[2–5] In γ and δ forms, the chains have T2G2 helical conformation and are formed under conditions where solvents are used for crystallization.[6–8] The δ form has a clathrate structure where the guest, low molecular weight molecules, most often solvent molecules, are accommodated in the crystalline lattice. The clathrate δ form[8] can be obtained by the sorption of suitable compounds (methylene chloride, toluene, chloroform, iodine, dichlorobenzene, decalin etc.) in amorphous samples or semi crystalline samples having α or γ forms.

The polymorphs of sPS are shown to have varying degrees of stability and *in situ* high temperature X-ray diffraction studies have shown that the stability of δ form depends on the amount of solvent present in the clatharate.[1] However, the transition from γ form to α form is independent of the solvent used for the clathrate preparation[1] and occurs at about 200 °C. Guerra and coworkers[9] compared the d_{010} spacing of all sPS clathrates with known crystal structures. It is interesting to observe that the solvents may be classified into two groups based on the clathrate d_{010} spacing. Group A solvents show d_{010} d-spacing below 1.2 nm and includes methylene chloride, toluene, chloroform, iodine, dichlorobenzene, decalin etc. Group B solvents exhibit d-spacing above 1.3 nm and the solvents are Norbornadiene,

---

Division of Polymer Science and Engineering, National Chemical Laboratory, Pune 411008, India
E-mail: c.ramesh@ncl.res.in

Mesitylene, DMN, 3-Carene and Anthracene. Guerra et al[9,10] solved the structure of molecular complex of sPS with norbornadiene, 1, 4 dimethyl-naphthalene and 1,3,5-trimethyl-benzene. In these complexes the solvent molecules form a layer structure and intercalates with mono layers of enantiomorphous polymer helices and terms these sPS-solvent complexes as intercalates, while sPS-solvent complexes obtained from Group A solvents as clathrates.

Impetus for the present work came from the recent study[11] on the intercalates obtained from norbornadiene which showed δ form to γ form transition at temperatures well below the glass transitions temperature of pure sPS. Hence we examined the δ form to γ form transition as a function of the amount of solvent for the intercalates prepared from the Group B solvents and for the first time show the coincidence the δ form to γ form transition temperature for the intercalates and the glass transition temperature, which is depressed due to the presence of solvent in the amorphous phase.

Experimental Part

Syndiotactic polystyrene was kindly supplied by DOW Chemicals. The weight average molecular weight was 275000 and the melt index was 4.3. Amorphous films of thickness about 20 to 40μm were obtained by forming a thin melt film and then rapidly quenching in ice-water bath. The amorphous films were crystallized in the intercalate form by immersing in norbornadiene, mesitylene, DMN and 3-carene at room temperature for about a fortnight. Samples with different degrees of intercalation were obtained by extraction of the solvent molecules from the intercalate δ form samples in boiling acetone for different intervals of time.

Room temperature and high temperature infrared spectra of these samples were taken using Perkin-Elmer FTIR Spectrometer (model Spectrum GX) at a resolution of 2 cm^{-1} in the range of 450–1600 cm^{-1}. A total of 32 scans were used for signal averaging. The high temperature spectra were obtained by mounting the sample in the Mettler Toledo FP82HT hot stage and placing it in the sample compartment of the FTIR and aligned using the red laser light. The sample was heated at the rate of 5 °C/min. The spectra were collected while the sample temperature was held constant. The change in spectra was monitored during heating by scanning at regular temperature intervals until the sample melted. Once the sample started melting at about 270 °C, it moved out of the beam path and spectra could not be recorded with further increase in temperature. Grams AI software was used to process the FTIR spectra.

Perkin Elmer TGA-7 thermal analysis system was used to determine the amount of solvent trapped in the samples after drying. The samples were heated under flowing nitrogen atmosphere from 50 to 300 °C, with a scanning rate of 10 °C/min. and the weight loss was recorded. The calorimetric measurements were done using TA Instruments Q100 MDSC. The samples were heated at 5 °C/ min with an oscillation period of 60 s. The modulating amplitude is set by the instrument and is ±0.8 °C. The instrument was calibrated using the standard protocol. The nitrogen gas flow rate was 50 mL/min.

Results and Discussions

In general the heating thermogram of sPS-solvent complex is complicated because of the overlapping events of glass transition, solvent evaporation and the low temperature δ to γ form transition during heating and hence the exact position of the glass transition temperature and the first transition could not be seen clearly. However, MDSC, which is an extension of conventional DSC, which provides information about reversing and non reversing characteristics of the thermal events, separates the glass transition event from the other events. Figure 1 shows the typical MDSC

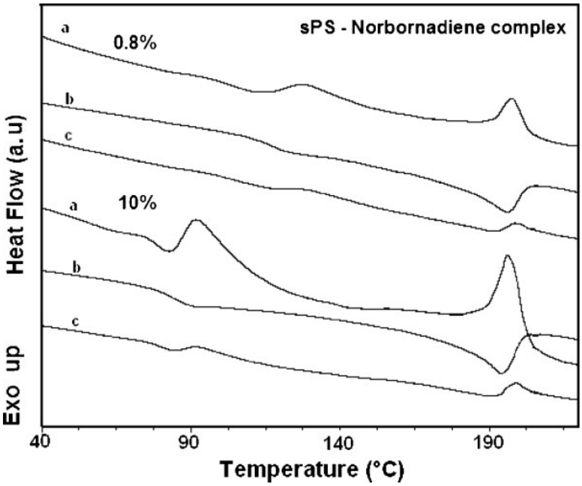

Figure 1.
MDSC thermograms during heating for sPS-Norbornadiene complex having 0.8% and 10% solvent content. a) Non reversing heat flow. b) Reversing heat flow. c) Total heat flow.

thermogram of the sPS- norbornadiene complex with 0.8 and 10% solvent. The T_g is well resolved in the reversing heat flow, while it is masked in the total heat flow.

The dependence of T_g on the solvent present in the intercalate is shown in Figure 2. The T_g monotonically decreases with increasing solvent content but is independent of solvent nature as predicted.[12,13] Since T_g is controlled by the solvent molecules present in the amorphous phase and the continuous change in T_g with the solvent amount indicates that there exists an equilibrium between the solvent molecules in the crystalline lattice and the amorphous domains. However it is not the case with the clathrates obtained from DCB and toluene. In the case of DCB the T_g obtained for a solvent content of 22% is 54 °C, while for 12% it is 102 °C. This result indicates that the 12% solvent is present in

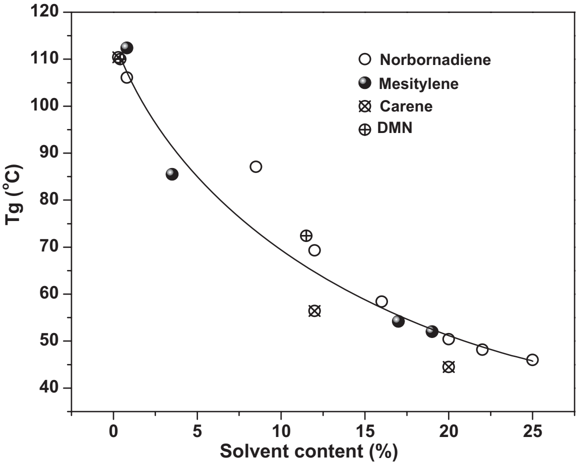

Figure 2.
Dependence of glass transition temperature on solvent content in the sPS-solvent intercalates.

the crystal lattice and not in the amorphous domains. Similarly in the case of toluene, the T_g obtained for 5% solvent content is 102 °C. The difference may be traced to the maximum amount of solvent present in the touch dry state, which is higher for DCB.[1]

Tashiro and co-workers[14–16] have shown that the 450–650 cm^{-1} infrared frequency region is sensitive to the chain packing mode in the crystalline forms of sPS (δ, δ_e and γ) having the same chain conformation.

The bands at 601 and 608 cm^{-1} are show subtle but definite change when δ form transforms to γ form on heating[14–16] and offer an alternative technique to monitor the crystalline transition. Figure 3 shows the spectra from 595 to 615cm^{-1} during heating for few representatives sPS-solvent complexes. The sPS-toluene clathrate sample contains 12% solvent and the bands at 600.7 and 608.5 cm^{-1} do not change on heating until 110 °C. But on heating to 120 °C these bands shifts to 600.2 and 608.8 cm^{-1} respectively, indicating the crystalline transition from δ phase to γ phase. The transition is confirmed by high temperature X-ray diffraction and discussed in detail elsewhere.[1] sPS-mesitylene intercalate sample which contains 0.6% solvent the subtle change in the band position occurs at 110 °C indicating the transition. Interestingly, the transition temperature 110 °C coincides with the glass transition temperature as measured by MDSC. The intercalate with 12% norbornadiene the shift is seen at

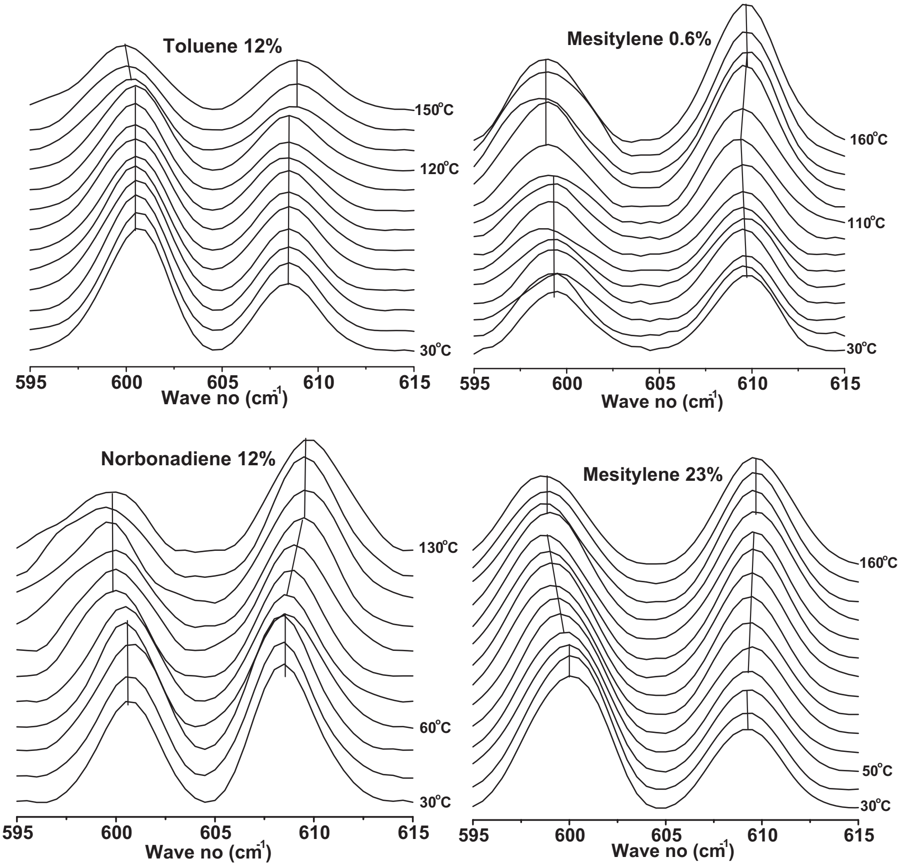

Figure 3.
The overlay of FTIR spectra in of the region 595 to 615 cm^{-1} on heating from room temperature for various sPS-solvent complexes.

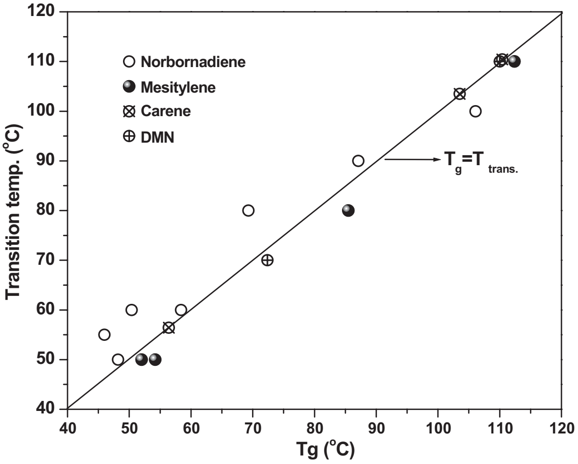

Figure 4.
The relationship between the δ phase to γ phase transition temperature and the glass transition temperature of the intercalates.

its glass transition temperature, 60 °C; depressed from 97 °C due to the presence of solvent. The mesitylene 23% sample the transition occurs still at lower temperature, 50 °C, the depressed glass transition temperature.

Figure 4 shows the correlation between the T_g and the transition temperature for various intercalates obtained from Group B solvents. The data points scattered around the $T_g = T_{trans}$ line indicating that the glass transition triggers the δ phase to γ phase transition. This is at variance with the behavior of clathrates, obtained from Group A solvents, which transform into γ phase at temperatures well above the Tg of pristine sPS.[1] However, it may be noted that the emptied clathrate sample, δ form transforms into γ phase at T_g, like the emptied intercalates from Group B solvents. The difference in the crystalline transition behaviour of clathrate (Group A solvents) and intercalate (Group B solvents) samples is consistent with the difference in the crystal structure of intercalate and clathrate samples.[9,10]

The T_g of the clathrate/intercalate samples depend on the amount of solvent present in the polymer-solvent complex, however, some degree of morphological information may be obtained from the T_g of the emptied samples. The glass transition temperatures of the emptied δ phase, γ phase and α phase were measured in three successive heating cycles. In the first heating T_g of the emptied δ phase was measured and by heating up to 150 °C, the δ phase was converted in to the γ phase. Cooling to room temperature and in the second heating to 220 °C, the T_g of the γ phase was determined and the sample was converted in to α phase. Again cooled to room temperature and the T_g of the α phase was measured during the third heating. Table 1 list the measured T_g's of various emptied clathrates/intercalates and other phases. The emptied intercalates of Group

Table 1.
The glass transition temperature measured for the various phases.

SOLVENT	T_g (°C)		
	α	γ	δ
Norbornadiene	103	103	106
Mesitylene	102	106	109
DMN	103	110	110
3-Carene	102	108	109
DCB	103.	108	100
Toluene	101	104	98

- T_g of the amorphous sPS was 97 °C.
- DSC was run MDSC mode and the heating rate was 5 °C/min

B solvents show higher T_g values; emptied intercalate of Norbornadiene shows 106 °C while emptied intercalates of other Group B solvents show a value of 110 °C.

On the other hand emptied clathrates of DCB and Toluene, Group A solvents, show a value close to 100 °C. The T_g of γ phase obtained from the emptied intercalate of Group B solvents either shows a minor decrease or remains unaltered. In the case Group A solvents T_g increases and approaches the value of Group B solvents. The similar values of T_g for the δ and γ phases of intercalate samples indicate that the amorphous phase is not reorganized during the transition for the intercalates. On the other hand, in the case of clathrate samples the transition leads to higher T_g values indicating a change in the amorphous phase structure. Once converted into α phase, the samples show similar T_g values indicating that all samples have similar semicrystalline morphology in the α phase, irrespective of the starting morphology of the emptied δ phase. Furthermore, the change in T_g during the γ to α phase transition seems natural because during the transition, the helical conformation transforms into linear zigzag conformation involving amorphous phase reorganization. Hence, the γ to α phase transition may be considered as a rapid melting and recrystallization process.

Conclusions

The crystalline transition behavior of the sPS-solvent complex depends on the solvent and may be divided onto two groups depending on the solvents used. When Group A solvents are used clathrate structure is formed, while use of Group B solvents result in intercalates. It has been observed for the first time the glass transition induced crystalline transition in intercalates, which is distinctly different from the clathrates. In sPS-solvent intercalates the phase transition temperature and the glass transition temperature decreases with increasing solvent content. The glass transition temperature depends on the amount of solvent present in the sample but not on the nature of the solvent.

Acknowledgements: The authors wish to thank Dr. S. Sivaram, Director, National Chemical Laboratory for his keen interest and encouragement during the course of this work. Authors also thank Dow Chemical Company, USA, for the sPS samples.

[1] E. B. Gowd, S. S. Nair, C. Ramesh, *Macromolecules* **2002**, *35*, 8509.
[2] E. M. Woo, Y. S. Sun, M. L. Lee, *Polymer* **1999**, *40*, 4425.
[3] V. Vittoria, A. R. Filho, F. De Candia, *J. Macromol. Sci. – Phys.* **1990**, *B29*(4), 411.
[4] S. Cimmino, E. Di. Pace, E. Martuscelli, C. Silvestre, *Polymer* **1991**, *32*, 1080.
[5] C. De Rosa, M. Rapacciuolo, G. Guerra, V. Petraccone, *Polymer* **1992**, *33*, 1423.
[6] G. Guerra, E. Vitagliano, C. De Rosa, V. Petraccone, V. Vittoria, *Macromolecules* **1990**, *23*, 1539.
[7] S. Rastogi, J. G. P. Goossens, P. J. Lemstra, *Macromolecules* **1998**, *31*, 2983.
[8] A. Immirzi, F. De Candia, P. Iannelli, A. Zambelli, V. Vittoria, *Makromol. Chem. Rapid Commun.* **1988**, *9*, 761.
[9] O. Tarallo, V. Petraccone, V. Venditto, G. Guerra, *Polymer* **2006**, *47*, 2402.
[10] V. Petraccone, O. Tarallo, V. Venditto, G. Guerra, *Macromolecules* **2005**, *38*, 6955.
[11] E. B. Gowd, K. Tashiro, C. Ramesh, *Polymer preprints, Jpn*, **2007**, *56*, 3412.
[12] E. A. Di Marzio, C. Castellano, A. Yang, *J. Polym Sci Polym Phys* **1996**, *34*, 535.
[13] T. S. Chow, *Macromolecules* **1980**, *13*, 362.
[14] A. Yoshioka, K. Tashiro, *Macromolecules* **2003**, *36*, 3001.
[15] E. B. Gowd, S. S. Nair, C. Ramesh, K. Tashiro, *Macromolecules* **2003**, *36*, 7388.
[16] E. B. Gowd, N. Shibayama, K. Tashiro, *Macromolecules* **2006**, *39*, 8412.