

## Supramolecular structure of gelation of atactic polystyrene/carbon disulphide solutions

Wang Yanxiang, Shen Deyan

Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing 100080, China

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### Summary

In this paper, atactic polystyrene/carbon disulphide (aPS/CS<sub>2</sub>) gel-dried film was prepared at low temperature. In such film, ordered structure was formed through stacks of some stereoregular segments by accepting TTGG type conformation, which strongly depended upon the interaction of CS<sub>2</sub> and polymer segments. The dynamics of interaction was studied by measuring FTIR spectra. With increasing temperature, the regular TTGG conformation transferred to less regular gauche TG conformation and the molecular chains relaxed.

### Introduction

The first observation of the ability of atactic polystyrene (aPS) solution to gelify by cooling was made by Tan et al.(1). It was the object of many further investigation and controversial interpretations(2-15). Indeed, aPS which is a stereo-irregular polymer is not expected to crystallise and physical gelation is generally believed to be the prerogative of the stereoregular polymers. Some models interpret the gelation of aPS in terms of a liquid-liquid demixing(5,8,9). The overall picture that emerges now is that gelation is due to intermolecular associations of chain segments in complex crystals including syndiotactic segments and solvent molecules(4,6,7). However, further investigations are needed to characterise the structure and the size of the crosslink domain and determine their number. Our laboratory has wide interest in microstructure of glassy polymer and its relationship with macroproperties(16,17). Studies in the gelation of glassy polystyrene may possibly disclose some important problems in polymer, such as the size of ordered structure which can form in glassy polymer and the minimum ordered size which is necessary to lead to crystallisation of polymer. In this paper, we prepared aPS/CS<sub>2</sub> gel dried film at low temperature and discussed its structure by FTIR, WAXD, TGA etc.

### Experimental

#### *Sample preparation*

The molecular weight of atactic polystyrene was  $1.69 \times 10^6$  with MW/MN=1.09 which was synthesised by anionic polymerisation. The tacticity of the molecular chain in the sample was calculated from <sup>13</sup>C NMR data obtained from a 12wt% solution in o-

dichlorobenzene-d at 140°C. The relative abundances of triads rr, mr, mm were 0.223, 0.502, 0.275 respectively. A 2.5wt% aPS/CS<sub>2</sub> solution sealed in a glass tube was kept at room temperature for two days, The solution was then transferred with a calibrated pipette into a shallow glass plate and quenched in a freezer at the temperature of -26°C. The thermal reversible gel was formed in this temperature and the film with proper thickness was obtained by slow volatilisation of solvent in the gel state within one week.

#### *FTIR measurements*

The infrared spectra of samples were recorded on Bruker Model IFS-113V spectrometer equipped with a Hg-Cd-Te detector cooled with liquid nitrogen. 256 co-added interferograms at a resolution of 2cm<sup>-1</sup> were used to obtain each spectrum. The curve analysis program (CAP) was made by our laboratory which analysed the spectra with the combination (80:20) of Lorentzian band shape and Gauss band shape. The function to be minimised in the CAP was the rms difference between real and synthesised spectra.

#### *Wide angle X-ray diffraction measurements*

Wide-angle X-ray diffractograms were obtained using a Rigaku DImax-313 Automatic X-ray Powder Diffractometer with Ni-filtered CuK Radiation(40KV, 30mA).

#### *Thermogravimetric analysis(TGA)*

Data were obtained from Perkin-Elmer 7 series thermal analysis system at a scan rate of 10°C/min.

### **Results and discussion**

In the IR spectra of atactic PS, the spectral region between 500 and 600cm<sup>-1</sup> has been discussed extensively by Monnerie et al. and it has been found that this region is specially sensitive to conformational behaviour of the polymer chains(18,19) and perhaps also to intrachain and interchain interactions(20,21,22). According to model compounds and spectral deconvolution analysis, several overlapped peaks are discovered and assigned in this region. The 540cm<sup>-1</sup> peak is assigned to the out-of-plane deformation mode of the phenyl ring in trans-conformation segments with 4 and more monomeric units, an overlapping higher-frequency component in this absorption region with the peak at 557cm<sup>-1</sup> is assigned to a similar vibrational model for higher conformation energy state involving gauche segments. Another overlapped band at 568cm<sup>-1</sup> is considered not to be sensitive to polymer chain conformation. Most recently, a band with the peak at 572cm<sup>-1</sup> was observed in the aPS/CS<sub>2</sub> gel(23). It was also assigned to the same vibrational mode as the peaks at 540cm<sup>-1</sup> and 557cm<sup>-1</sup>. It was assumed that the appearance of this band indicated the formation of regular TTGG sequence segments, and this was indeed approved by the studies of syndiotactic polystyrene (sPS) which could crystallise in helix TTGG conformation. Thus the 572cm<sup>-1</sup> peak was one of the conformational sensitive bands(24,25).

The infra-red spectrum of aPS/CS<sub>2</sub> gel dried film was measured. it was almost the same as that of normal aPS film, but a peak at 572cm<sup>-1</sup> was observed clearly(Figure 1), which did not exist in the IR spectra of normal aPS film. This band didn't disappear even one month later at -26°C. This suggested that in such film, some syndiotactic

segments segregated in helix form conformation, but short stereoregular sequence length in the aPS sample prevented the formation of long regular sequences of TTGG conformation or crystallisation, because in its IR spectra, only one of TTGG conformational sensitive bands at  $572\text{cm}^{-1}$  could be detected. However, the formation of sequences of a particular conformation suggested that, compared to glassy polymer, some more ordered structure existed in such noncrystallizable polymer. This was also approved by the wide angle X-ray scattering study of this film.

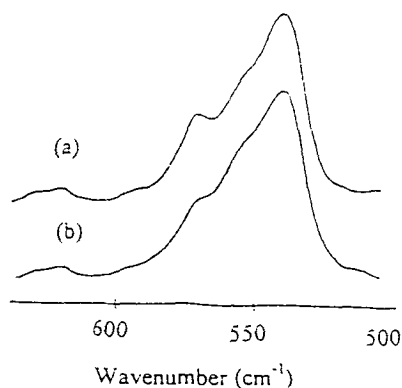


Figure 1. (a) FTIR spectra of aPS/CS<sub>2</sub> gel-dried film. (b) aPS cyclohexane solution cast film

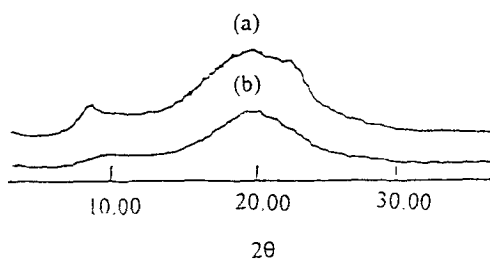


Figure 2. Wide angle X-ray scattering pattern of aPS/CS<sub>2</sub> gel dried film. (a) just formed film. (b) after thermal treatment at  $80^{\circ}\text{C}$  for 60 minutes

Wide angle X-ray scattering from glassy polymer usually shows rather diffuse halos without distinguished structure. In the case of bulk aPS, characteristically broadened amorphous diffraction peaks are observed at  $2\theta$  of about  $10^{\circ}$  and  $20^{\circ}$  in the X-ray diffraction patterns. They have been assigned as follows(26,27,28): the peak at  $20^{\circ}$  corresponds to the contribution of the distance between intermolecular methylene-methylene, methylene-phenyl, and phenyl-phenyl groups, and the peak at  $10^{\circ}$ , the so-called 'prepeak', may be related to the existence of main chains, whose origin is however not well understood at present. Mitchell et al. pointed out that the peak at  $10^{\circ}$  perhaps reflected a form of microsegregation of phenyl groups in neighbouring chains whereby they were associated in stacks. The wide angle X-ray scattering intensity profiles,  $I_{\text{ex}}(2\theta)$ s of aPS/CS<sub>2</sub> gel-dried film are shown in Figure 2, which are characteristic of amorphous polymer. But the intensity of the peak at  $10^{\circ}$  for curve (a) is more intense, shaper and transferred to lower  $2\theta$  angle compared to that of ordinary glassy polystyrene, indicating that in this noncrystallised film, the stack of chains was more ordered. Also, a new shoulder peak appearing at  $2\theta$  of about  $22^{\circ}$  are not well understood now. The X-ray scattering pattern after heat treatment at  $80^{\circ}\text{C}$  for 60 minutes is the same as that of ordinary aPS. That is to say, the characteristic segregation structure of the film is unstable, and strongly related to the nonequilibrium formation process due to the slow volatilisation process of solvent under gel state.

It should be pointed out that such ordered segregation structure strongly depended upon the existence of remaining solvent. The CS<sub>2</sub> solvent in this film could stand a long time at low temperature and the peak at  $572\text{cm}^{-1}$  also remained stable. When this film

stayed at room temperature,  $\text{CS}_2$  would escape from the film gradually with time and the band characterising the  $\text{CS}_2$  molecule disappeared. Therefore, the solvent molecule should have some more intense interaction with polymer chains. It was possible that they only interacted with parts of segments with regular TTGG type conformation. Also, such interaction was a dynamic process that the interaction between  $\text{CS}_2$  and polymer segments decreased with increasing temperature. It may be concluded that the above ordered structure in such glassy film was maintained due to the interaction of  $\text{CS}_2$  solvent molecule and the segments with TTGG conformation.

The gel-dried film kept in a freezer for one month was analysed by TGA. The change in its weight with increasing temperature is shown in Figure 3. It can be seen that during this process, the weight of sample reduced approximately 2% gradually with the volatilisation of  $\text{CS}_2$ . Also, a small transition at about  $138^\circ\text{C}$  may be detected. At this temperature, the film contracted greatly in size. This transition might be attributed to nonequilibrium

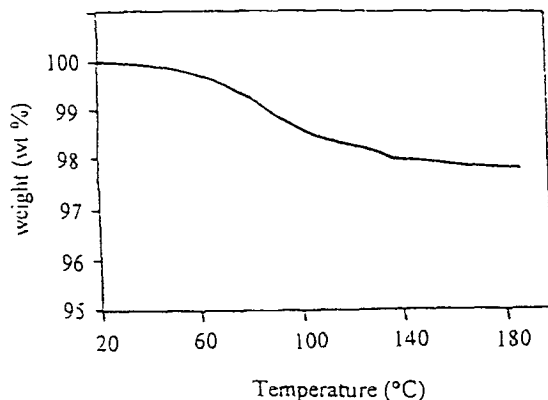


Figure 3. The TGA scan of aPS/ $\text{CS}_2$  gel-dried film

formation process of the film due to slow volatilisation of solvent in gel state. In such gel-dried film, the chains stayed in a stiff nonequilibrium state which was maintained by some physical crosslink points comprising these ordered segregation domains. With increasing temperature, these ordered domains were destroyed and the polymer chains were also activated and become movable, resulting in their relaxation. Previous studies neglected this ordered segregation form because the solvent was always dispelled completely by every possible means during sample preparation(11). However, the ordered segregation form was destroyed during this process.

In order to investigate the structure change during this process in aPS/ $\text{CS}_2$  gel-dried film, infrared spectra in the  $500\text{-}600\text{cm}^{-1}$  region, which was sensitive to chain conformation, was analysed with a program made in our laboratory. As shown in Figure 4, in this region, the spectra were analysed with four bands at  $572\text{cm}^{-1}$ ,  $568\text{cm}^{-1}$ ,  $555\text{cm}^{-1}$  and  $540\text{cm}^{-1}$ . The relative intensity change of each band with increasing temperature is shown in Figure 5. In this process, the relative intensities at  $555\text{cm}^{-1}$  and  $572\text{cm}^{-1}$  change apparently. Corresponding to Figure 3, the intensity at  $572\text{cm}^{-1}$  characterising the regular TTGG conformation reduces and the intensity at  $555\text{cm}^{-1}$ , which is sensitive to TG conformation, increases. That is to say, with increasing temperature, the solvent escapes from the bulk film, and at the same time, the regular TTGG type conformation changes to the less ordered TG type conformation.

From the above discussion, it was concluded that some ordered segregation existed in our sample which was constructed through interaction of  $\text{CS}_2$  and some short syndiotactic segments with TTGG type conformation. This segregation state was stable only at low temperature. With increasing temperature,  $\text{CS}_2$  escaped from the glassy

film, the regular TTGG conformation changed to the less regular TG type conformation and the polymer chains relaxed.

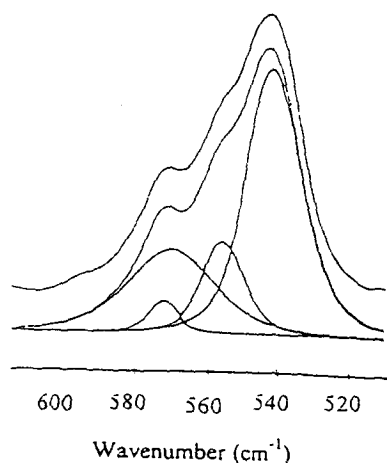


Figure 4. Curve analysis of 500-600 $\text{cm}^{-1}$  region of aPS/CS<sub>2</sub> gel dried film

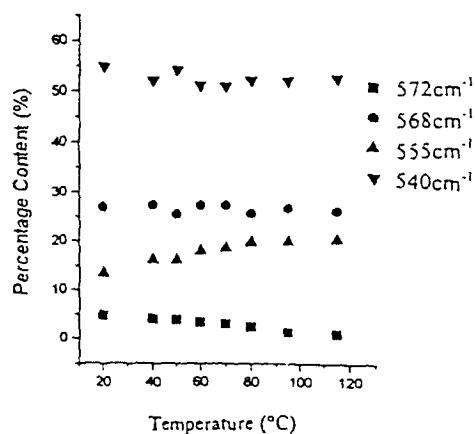


Figure 5. Relative intensity changes of bands characteristic of local conformation

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