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The structural organization in syndiotactic polystyrene film induced by toluene vapour sorption

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Abstract

Toluene vapour sorption behaviours in syndiotactic polystyrene (SPS) film were measured at 25°C by the quartz crystal microbalance method. The sorption isotherm of this system was concave toward the pressure axis below the activity of toluene vapour ($p/p_0 = 0.3$), indicating a strong interaction between toluene vapour and sorption sites in the mesophase consisting of TTGG conformation. On the other hand, the sorption isotherm of toluene vapour in atactic polystyrene film showed a normal good solvent type and could be described by Flory–Huggins thermodynamics. In addition, the structural changes in SPS film by toluene vapour sorption were characterized by Infrared spectroscopy. The absorbance at 933 cm^{-1}, which is assigned to TTGG conformation, was found to be constant below $p/p_0 = 0.3$; however, it increased above $p/p_0 = 0.3$ and was saturated above $p/p_0 = 0.6$. These results showed that toluene vapours penetrated into the pre-existing sorption sites composed of TTGG conformation to form the clathrate structure (δ form) below $p/p_0 = 0.3$. Furthermore, in the range of $p/p_0 =$ 0.3–0.6, the sorption of toluene vapour could induce a large increase in the ordered structure (δ form), i.e., TTGG confirmation. The changes in the non-clathrate structure with toluene (α form) composed of TT conformation, could be characterized by the absorbance at 1222 cm^{-1}. It was confirmed that the α form could be also increased by toluene vapour sorption above $p/p_0 = 0.4$. The sorption enthalpy of toluene vapour (ΔH_s), estimated from sorption isotherms showed a negative value below $p/p_0 = 0.6$, but showed a positive value above $p/p_0 = 0.6$, even though the polymer–good solvent pair. This result also supports the structural organization in SPS film by toluene vapour sorption. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Syndiotactic polystyrene; Toluene vapour sorption; δ form (clathrate structure)

1. Introduction

It is well known that sorption of vapours and liquids into polymeric films can cause significant plasticization resulting in substantial decreases in the glass transition temperature (T_g) [1,2]. If the reduction of T_g of the used crystalline polymer is large enough to put the system in the crystallization temperature region, the polymer chains rearrange themselves into a lower free energy state [3,4]. For example, some workers reported on the soaking of polyethylene terephthalate and polycarbonate films into acetone and observed the crystallization of these polymers [5–7]. Moreover, it was said that nylon with low crystallinity content swollen by water could crystallize further. Kambour et al. investigated kinetic and equilibrium phenomena in an acetone vapour–polycarbonate system, as a system in which crystallization could be induced by vapour–polymer interaction [8]. It was observed from their study that sorption isotherms showed an inflection point at or near the depressed glass transition and the sorption amount of acetone decreases by crystallization of polycarbonate.

Gases like CO_2 with a high critical temperature are considerably more soluble, particularly in glassy polymers, as described in a number of previous publications and can induce plasticization [9–11]. Wang et al. have investigated the reduction of T_g from measurements of the mechanical relaxation of polystyrene exposed to CO_2 and showed that high pressure CO_2 could act as a plasticizer [12]. Chiou et al. pointed out that the plasticization by CO_2 sorption induced crystallization of crystalline polymers [13–15]. Such penetrant molecules as organic vapours and CO_2 are possible to change the structural organization of the permeation phase and make it more complex to understand sorption behaviours. Kamiya et al. have investigated plasticization of glassy polymers due to addition of low-molecular weight substances such as organic solvents and plasticizers, and

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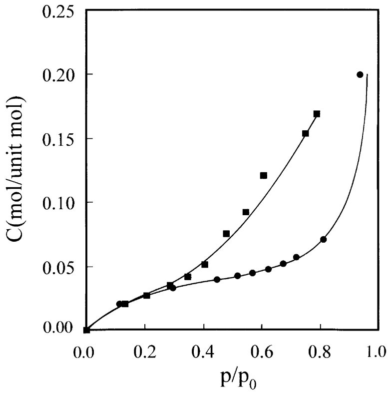

Fig. 1. Sorption isotherms of toluene vapour in 1T170 (●) and 1T140 (APS) (■) at 25°C.

their isothermal glass transition by means of volumetric, sorption kinetic, and dynamic mechanical measurements and analysed the sorption isotherms according to the extended dual-mode sorption model [16–18].

The recently synthesized syndiotactic polystyrene (SPS) with very highly tacticity is characterized by the clathrate formation with various organic molecules. The clathrate structure is called δ form, which exhibits TTGG helix conformation [19–21]. As a result of this, organic vapour sorption behaviours of SPS are expected to be very complex due to the clathration with penetrant molecules, different from the system in which penetrant molecules are excluded from the crystal lattice when crystallization occurs. SPS films can form the characteristic morphology and it is expected that organic vapour sorption has a strong influence with the morphology of the SPS films. But, there have been few reports on sorption behaviour such SPS-organic vapours [22,23]. Even in the case of organic molecules, sorption behaviours at low activity are expected to be reflected by morphology of the membrane. It is known that the δ form is transformed into the γ form by thermal treatment [24,25] (the γ form is free of solvent). We recently concluded that the transition from the δ to the γ form occurred through a mesophase in our previous article [26]. The mesophase is defined as the phase which has not a crystalline regularity but a conformational order. Taking the formation mechanism of the mesophase into consideration, it is possible that the sorption sites in the mesophase memorize solvent size and properties. Accordingly, sorption behaviours in the SPS–toluene vapour system at low activity may be influenced strongly by such clathrate structures of SPS films. So we will investigate the sorption mechanism in SPS–toluene vapour system and the effect of such clathrate structures of SPS films on the toluene sorption behaviours in this article.

2. Experimental

Syndiotactic polystyrene (SPS) was kindly supplied by Idemitsu Petrochemical Co., and was used without further purification. The weight-averaged molecular weight is $M_w = 211\,000$ ($M_w/M_n = 3.45$). Atactic polystyrene (APS) was purchased by Aldrich, and the weight-averaged molecular weight was $M_w = 280\,000$. The SPS film cast from a toluene solution was annealed at 170°C for 1 h (abbreviated as 1T170). The APS film cast from toluene solution was annealed at 140°C for 1 h (abbreviated as 1T140 (APS)). It was confirmed that there were no solvents in either sample by thermogravimetric analysis (t.g.a).

Differential scanning calorimetry (d.s.c.) thermograms in the range 25–300°C were performed using a Perkin-Elmer DSC 7 at the heating rate of 2°C/min under a nitrogen gas purge. Thermogravimetric analysis (t.g.a) data in the range of 25–300°C were obtained using a Seiko TG/DTA220 at the heating rate of 2°C/min under a nitrogen gas purge. Infrared (i.r.) spectra were obtained using a Jasco IR-700 type i.r. spectrometer with the 1 cm^{-1} resolution in the range 4000–400 cm^{-1} and one scan was performed per spectrum. The SPS films sorbed by toluene vapour at various activities were used for i.r. measurement.

Toluene vapour sorption isotherms at 25°C were obtained by the quartz crystal microbalance (QCM) method. QCM has become a popular method for the detection of a very small amount of weight because its resonance frequency can sensitively decrease upon the increase of mass on the QCM in the nanogram level [27]. The thin films were coated on the electrode on the quartz crystal oscillator by spin-casting and annealed under the appropriate conditions. Sorption amount of toluene vapour (C mol/styrene unit mol) is plotted against activity (p/p_0); p and p_0 are actual and saturated pressure of toluene vapour at 25°C, respectively.

3. Results and discussion

3.1. Toluene vapour sorption isotherm of the annealed cast SPS film

Fig. 1 shows a toluene vapour sorption isotherm of 1T170 at 25°C. This sorption data is not corrected based on the crystalline content of the film. Atactic polystyrene (APS), which is annealed at 140°C for 1 h (1T140 (APS)), is also shown in Fig. 1. The isotherm of 1T140 (APS) is typical as seen in amorphous polymer–organic vapour systems. On the other hand, the isotherm of 1T170 is a sigmoid-type isotherm and concave toward the pressure axis at low activity. Such an isotherm is seen in polar polymer–water systems, whose isotherm is a local-site type, and polymer gases like CO_2 with a high critical temperature, whose isotherm exhibit a point of inflection that means glass transition. Here, we suggest that the isotherm in SPS–toluene system may be a local-type isotherm judging from the morphology of the SPS films. We reported the morphology of 1T170 in a previous article [26] as follows: thermal and spectral analyses of annealed cast-SPS films were performed and it was suggested that the films annealed at

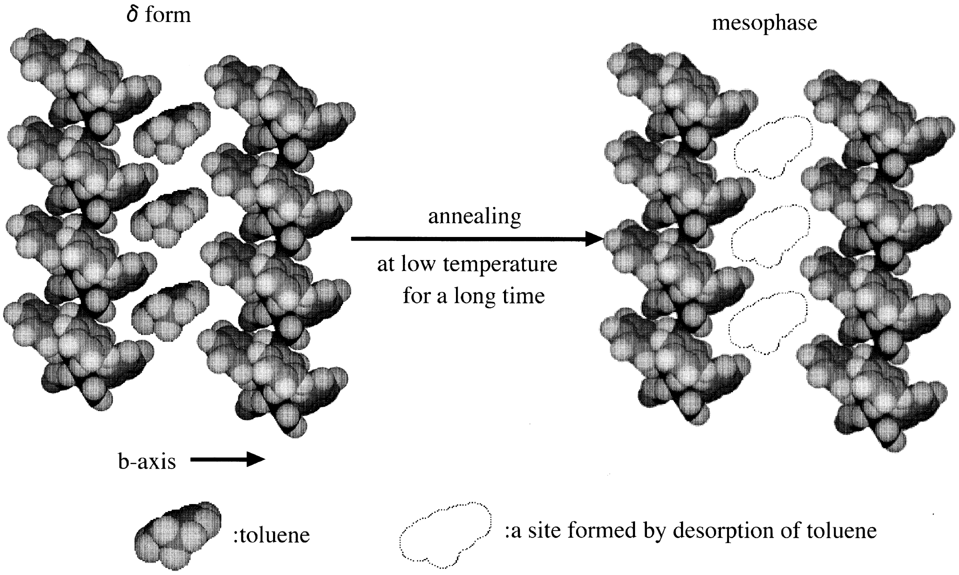

Fig. 2. Schematic representation of reorganization from δ form to mesophase in SPS–toluene system.

lower temperature exhibited an ordered conformation but a lack of crystalline regularity. This structure was defined as a mesophase. From CO_2 sorption measurement, it was apparent that the films annealed at lower temperature contained many solvent desorption sites as nanopores in the mesophase. From these reported results, we suggest that the concaveness toward the pressure axis at low activity for 1T170 is due to the preferential sorption of toluene vapour into the solvent desorption sites in the mesophase. Taking the formation mechanism of the solvent desorption sites into consideration, it is possible that the sites memorize solvent size and properties (Fig. 2) and the preferential sorption into such the sites may occur at low activity.

3.2. The structural organization of SPS films induced by toluene vapour sorption

It is well-known that organic vapours are able to plasticize to some extent an amorphous part of a crystalline polymer and make it crystallizable due to much more mobility. Accordingly, toluene vapour can change the structural organization of the SPS matrix. Fig. 3 shows a sorption isotherm of toluene vapour in 1T170 which has been dried in vacuum at 25°C for a long time after sorption measurement (second run). The sorption amount of toluene at $p/p_0 = 0$ in second run was not 0, i.e. this means toluene vapour may clathrate with SPS. For 1T140 (APS), the sorption amount of toluene at $p/p_0 = 0$ in the second run was almost 0. There were 0.035 mol/unit mol of toluene vapour in the SPS matrix after full drying under vacuum at 25°C as seen in Fig. 3. Fig. 4 shows a t.g.a. curve and a d.s.c. thermogram of 1T170 after first run (i.e. 1T170 saturated by toluene vapour at $p/p_0 = 0.9$). The rapid weight loss of the film can be seen from 100 to 150°C. There is also an endothermal peak in the same temperature range within the d.s.c. thermogram. These behaviours are due to the desorption of the clathrated solvents forming the δ form with SPS, because their thermal behaviours were characteristic of the SPS films which contain the δ form, such as the cast films, that cannot be seen in the case of 1T140 (APS). The number of moles of the clathrated solvent with SPS can be the sorption amount of toluene vapour for 1T170 after full drying under vacuum at 25°C (0.035 mol/unit mol). These results show the clathration of toluene vapour with SPS during first run. The sorption isotherm denoted by (▲) in Fig. 3 is obtained by subtracting 0.035 mol/unit mol from the sorption amount of second run and is not more concave at low activity than that of first run. This is because the sorption sites in the mesophase may be saturated after first run, which may suggest the preferential sorption into the sites in the mesophase at low activity. Fig. 5 shows first, second, third, and fourth runs of toluene sorption isotherms at 25°C. Full drying under vacuum was done after each sorption measurement. Judging from the

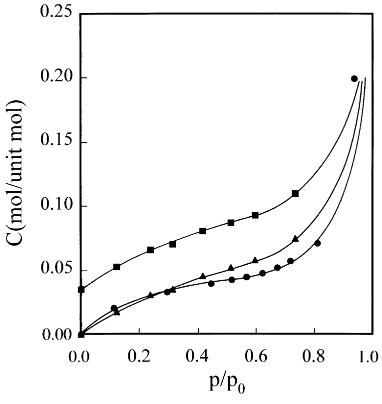

Fig. 3. Sorption isotherms of toluene vapour in 1T170 at 25°C; first run (●) and second run (■). The isotherm denoted by (▲) is obtained by subtracting 0.035 (mol/unit mol) from the sorption amount of second run (■).

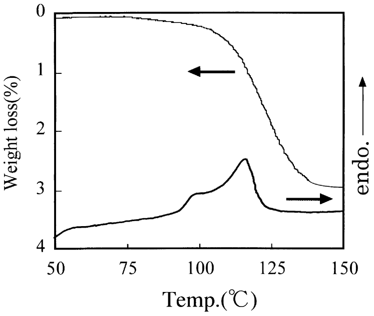

Fig. 4. T_g curve and d.s.c. thermogram of 1T170 which has been dried in vacuum at 25°C for a long time after sorption measurement.

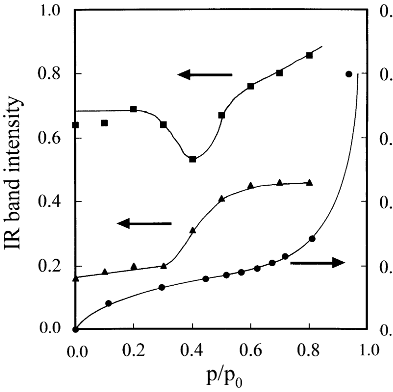

Fig. 6. Effect of toluene activity (p/p_0) on chain conformation and sorption amount (●) for 1T170. The relative absorbance ($A_{933\ cm^{-1}}/A_{1180\ cm^{-1}}$ (▲) and $A_{1222\ cm^{-1}}/A_{1180\ cm^{-1}}$ (■)) characterize the relative amounts of SPS in the TT and TTGG conformation, respectively.

same sorption isotherms, the structural reorganization of SPS may not occur in second, third, fourth runs, whose concaveness towards the pressure axis at low activity is due to the desorption site of toluene vapour formed in amorphous part during vacuum drying at 25°C.

I.r. measurement is a very useful method to investigate the structural organization of SPS in this case, because two-crystal structures (δ form and α form) of SPS are i.r. active. We examined i.r. spectra to detect the conformational change by sorbed vapour. I.r. absorbances at 933 and 1222 cm^{-1} are assigned to the TTGG (δ form) and TT (α form) conformations, respectively. Fig. 6 shows the absorbance value of 933 and 1222 cm^{-1} of 1T170 sorbed at each activity versus toluene vapour activity with sorption amount at each activity. The absorbance value at 933 and 1222 cm^{-1} are normalized by the absorbance value at 1183 cm^{-1} as an internal standard to correct for the film thickness. The absorbance value of 933 cm^{-1} is constant until $p/p_0 = 0.4$ and then increases from $p/p_0 = 0.4$ to 0.6 and is again constant. The absorbance value of 1222 cm^{-1} is constant as well as that of 933 cm^{-1}, and then decreases from $p/p_0 = 0.2$ to 0.4 and increases from $p/p_0 = 0.4$. The constant of the absorbance value seen in Fig. 6 is due to the preferential sorption into the sorption sites in the mesophase. Accordingly, the structural organization of SPS may not occur in this activity region. After the sorption sites in the mesophase are saturated, toluene vapour can plasticize SPS and the structural organization of SPS can occur. From these results, toluene vapour may sorb SPS and clathrate and form the δ form. Simultaneously, toluene vapour may plasticize SPS and influence the α form. In higher activity, the α form can be formed as shown in Fig. 6.

Fig. 7 shows the thermal dependence of sorption isotherms of toluene vapour in 1T170. The sorption amount of toluene vapour is smaller at low activity as the measurement temperature is higher, but the temperature dependence becomes opposite at high activity. The temperature dependence seen at high activity is observed in such a system in which the dynamic structural change can induce the increase of the sorption site (for example, the glass transition temperature). We estimated the sorption enthalpy (ΔH_s) from the thermal dependence of sorption isotherms of 1T170 to investigate the structural reorganization during sorption. We can use the following relation (Calusius–Clapeylon's equation) to calculate ΔH_s,

$$\left(\frac{\mathrm{d}\ln x}{\mathrm{d}T}\right) = \frac{Q_v}{pVT} - \frac{L}{p_0TV_0} \tag{1}$$

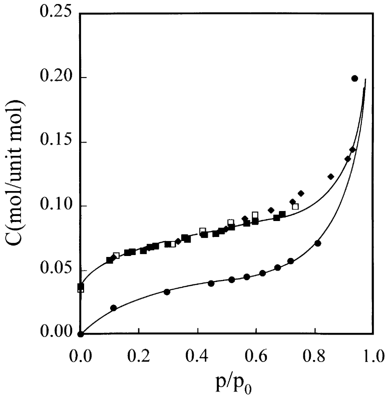

Fig. 5. Sorption isotherms of toluene vapour in 1T170 at 25°C; first run (●), second run (□), third run (■), fourth run (◆).

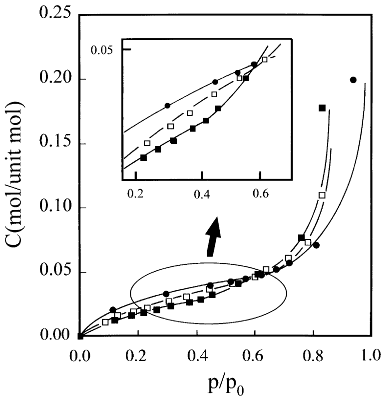

Fig. 7. Sorption isotherms of toluene vapour in 1T170 at 25°C (●), 27°C (□) and 30°C (■).

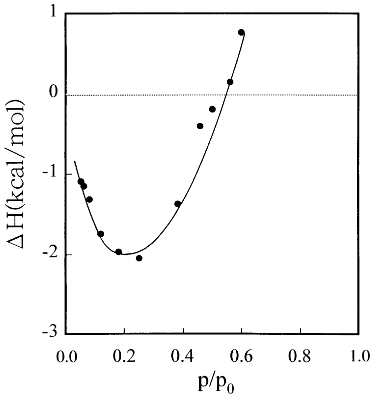

Fig. 8. The plot of sorption enthalpy of toluene vapour (ΔH_s) vs activity (p/p_0) for 1T170.

where $x = p/p_0$, V and V_0 are the volumes of vapour at p and p_0, respectively, and Q_v and L are the differential heat of sorption and the heat of vapourization from gas state. We apply ideal gas's equation to Eq. (1).

$$Q_l = RT^2\left(\frac{\mathrm{d}\ln x}{\mathrm{d}T}\right) = -R\left(\frac{\mathrm{d}\ln p/p_0}{\mathrm{d}(1/T)}\right) \tag{2}$$

where Q_l is the differential heat of sorption from liquid state. If the sorption from liquid state. If the sorption amount at different x_1 and x_2 in the two sorption isotherms at T_1 and T_2 (the difference between T_1 and T_2 is little) is the same, Eq. (2) is transformed in the following,

$$Q_l = \frac{RT_1T_2}{T_2 - T_1}\ln\frac{x_2}{x_1} \tag{3}$$

From Eq. (3) and the relation of $\Delta H_s = -Q_l$, the differential enthalpy of sorption (ΔH_s) can be calculated. Fig. 8 shows the plot of ΔH_s of toluene vapour versus p/p_0 for 1T170. The ΔH_s showed a negative value below $p/p_0 = 0.6$, but showed a positive value from $p/p_0 = 0.6$, even though the polymer–good solvent pair. This result also supports the structural reorganization in SPS film by toluene vapour sorption and is different in polymer–organic vapour systems. One of the most important reasons may be the structural reorganization by plasticization of toluene vapour, because it needs large amounts of heat (for example, crystal transition of the α form).

4. Conclusion

We investigated the toluene vapour sorption behaviours in SPS film and suggest the sorption mechanism.

The toluene vapour isotherm of 1T170 was concave toward the pressure axis below $p/p_0 = 0.3$ different from 1T140 (APS). The results of i.r. measurement for 1T170 showed the preferential sorption into sorption sites in the mesophase and that crystal transition of the α form occurred at low activity and formed at high activity by plasticization of toluene vapour.

This study showed that the sorption sites in the mesophase was effected on the sorption behaviours of toluene vapour at low activity. From these obtained results, we suggest the possibility that the sorption sites in the mesophase memorize solvent size and properties. It will be cleared by the investigation of the sorption behaviours of SPS films containing different sorption sites in the mesophase formed by preparing with a variety of solvents.

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