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Melting and recrystallization processes in a rubbery polymer detected by vapor sorption and temperature-modulated DSC methods

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Abstract

Series of successive absorption runs of *n*-hexane vapor in films of semi-crystalline poly(dimethylsilatrimethylene) at 25 °C are presented. Sorption overshoots were observed in the uptake kinetic curves of first series of absorption runs in as-prepared films. The said overshoots were absent in the second series of runs, conducted after desorption, while the sorption isotherms of the two series were identical. The overshoots are attributable to penetrant-induced melting and recrystallization phenomena. Strong support to this interpretation is given by temperature-modulated DSC data obtained from the pure polymer, which reveal similar thermally induced phenomena at slightly higher temperatures.

Keywords: Temperature-modulated DSC; Sorption overshoots; Poly(dimethylsilatrimethylene)

1. Introduction

One of the less common features of non-Fickian sorption kinetics observed in polymer-penetrant systems is the so-called 'sorption overshoot'. The term refers to a maximum in the penetrant uptake (M_t) vs time$^{1/2}$ ($t^{1/2}$) plot, observed before attainment of the final equilibrium uptake value M_∞ at t_∞. It is usually found during sorption of strongly interacting liquids or vapors in initially amorphous, crystallizable glassy polymers [1–3] and is attributed to solvent-induced crystallization (SINC) of the polymer, made possible by depression of its effective T_g by the penetrant below the experimental temperature. As the newly formed crystalline regions are impenetrable, part of the sorbed penetrant is expelled, thus producing the maximum in the sorption curve. The introduction of crystallinity is verified by DSC and density measurements [1–3], as well as by the fact that repetition of the sorption run does not produce an overshoot [1]. In certain cases, the phenomenon has also been observed in polymers in the rubbery state, as for example, during liquid cyclohexane sorption in isotactic polypropylene at ambient and sub-ambient temperatures [4], and during successive interval ethylbenzene vapor sorption runs in PEMA at 120 °C [5]. In the former case [4], it was attributed to crystallization of the initially smectic state of this particular polymer. This was confirmed by WAXD studies, as well as by the fact that equilibrium vapor sorption in as-received samples was higher than in samples previously immersed in cyclohexane. In the latter case, the overshoots were attributed to reversible slow relaxation processes of the polymer leading to a more compact structure. This interpretation, is in line with the facts that (i) no crystallinity was detected after desorption and (ii) a second series of interval sorption runs, conducted after desorption, was identical to the first [5].

A new powerful tool for the study of thermally induced structural reorganizations, such as primary and secondary crystallization and melting is the recent temperature-modulated DSC (TMDSC) technique; wherein a sample is subjected to a linear heating ramp with a superimposed low frequency temperature oscillation, resulting in modulation of the heating profile. The total heat flow (corresponding to the signal obtained from conventional DSC) is deconvoluted into a 'reversing' heat capacity-related component (identifying heat effects that can be reversed within the temperature range of the modulated amplitude), and a 'non-reversing' component. Glass transition and crystallization are present exclusively in the reversing and non-reversing signals, respectively, while melting may appear in both signals. In particular, reversing endotherms are attributed to partial melting of crystal lamellae, that are then able to rapidly recrystallize on existing crystals and endothermic non-reversing effects are attributed to melting

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of more perfect crystals that cannot recrystallize fast enough. The TMDSC method has been used to provide additional information (not obtainable by conventional DSC) on melting and recrystallization processes related to the metastability of polymer crystals [6,7].

Here, we present evidence of a new kind of sorption overshoot observed during sorption of *n*-hexane vapor in poly(dimethylsilatrimethylene), a semi-crystalline rubbery polymer. The overall observed sorption behavior was not consistent with either the reversible macromolecular relaxation, or the additional crystallization, effects referred to earlier. As demonstrated below, the said overshoots are attributable to penetrant-induced melting and recrystallization phenomena similar to those thermally induced in the dry polymer and revealed by the TMDSC technique.

2. Experimental

A sample of poly(dimethylsilatrimethylene) $[-(CH_2)_3-Si(CH_3)_2-]_n$ with $M_W = 1.1 \times 10^6$ was supplied by method published previously [8]. The T_g of the polymer (determined by conventional DSC at a heating rate of 10 °C min^{-1}) was −85 °C. The initial crystallinity of the polymer, as determined by WAXD, was ~50%, and its density was 0.908 g cm^{-3}. Polymer films were prepared by casting a chloroform solution of the polymer on a glass plate. After slow evaporation in an atmosphere partially saturated with chloroform vapor, the film was removed from the glass plate, evacuated for several days to ensure complete elimination of the casting solvent and then kept in a dessicator until required for use. Two film samples with dry film thickness $\ell = 386$ and 247 μm (designated in what follows as F386 and F247, respectively) were used in sorption experiments. Chloroform solutions of 15 and 5% wt/wt concentrations were used for the preparation of F386 and F247, respectively; *n*-hexane was of analytical reagent grade.

The sorption apparatus included a liquid vapor generator continuously stirred and thermostated to ±0.05 °C, a mercury manometer for vapor pressure measurements and a jacketed glass vessel (thermostated to 25 ± 0.05 °C) containing the polymer film. The latter was suspended from a quartz spring (of sensitivity ca. 27 cm g^{-1}), the elongation of which was monitored by a cathetometer (reading to 0.01 mm). Vacuum, provided by a two-stage rotary pump, was of the order of 10^{-3} Torr.

TMDSC measurements (TA Instruments, Model MDSC 2920) were performed using a heating ramp of 2 °C min^{-1} and a temperature modulation of ±0.32 °C every 60 s. The temperature modulation amplitude is small relative to the underlying heating rate, and the modulated profile was obtained by heating only.

3. Results and discussion

Sample F386 was subjected to a series of four successive absorption runs, covering narrow *n*-hexane vapor pressure intervals, up to a final pressure of 97 Torr. An attempt to perform a fifth run up to 123 Torr, led to dissolution of the film during the sorption process. Accordingly, the first four runs were repeated with sample F247, and after complete evacuation, a second identical series of runs was performed.

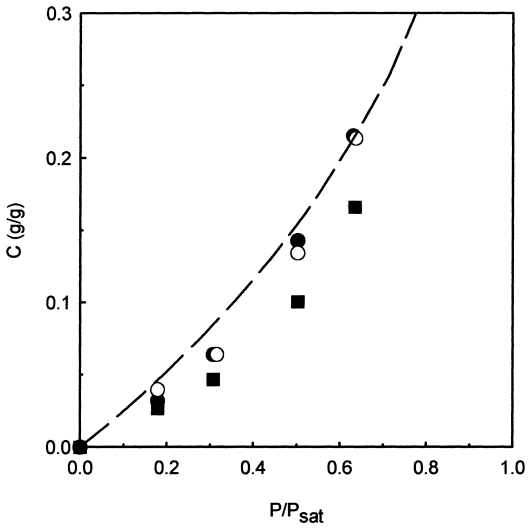

Fig. 1. Absorption isotherm for the system *n*-hexane vapor-poly(dimethylsilatrimethylene) at 25 °C, including data from polymer sample F247 (circles) and F386 (squares). Data from first series of absorption runs are indicated by dark points and data from second series by open points. Dashed line is the calculated isotherm using inverse gas chromatography data [9].

As shown in Fig. 1, the sorption isotherms (obtained from the equilibrium uptake data) resulting from the first and second series of runs in sample F247 agree fairly well. They also agree with sorption isotherm line obtained from inverse gas chromatography data [9], but lie slightly above the isotherm obtained from sample F386 (see latter).

The results of the uptake kinetic curves M_t/M_∞ vs. $t^{1/2}/\ell$ for F386 and F247 are presented in Figs. 2 and 3, respectively. The first series of uptake kinetic curves for both film samples exhibit the same features, i.e. sorption overshoots, which are just discernible during the third run, but become very pronounced during the fourth one. F386 exhibits relatively less intense sorption overshoots by comparison with F247; the maximum fractional uptake M_t/M_∞ during the fourth run is ~2.5 for F386 and ~3 for F247. This, in conjunction with the fact (noted earlier) that the sorption isotherm of F386 lies below that of F247, points to a higher degree (and possibly perfection) of initial crystallinity in F386, most probably due to differences in the preparation conditions of these samples.

The irreversible nature of the aforementioned overshoots is shown by their absence during the second series of sorption runs on F247 (see Fig. 3). However, their interpretation in terms of irreversible penetrant-induced crystallization of previously amorphous regions of the polymer (see earlier), is here contradicted by the coincidence of

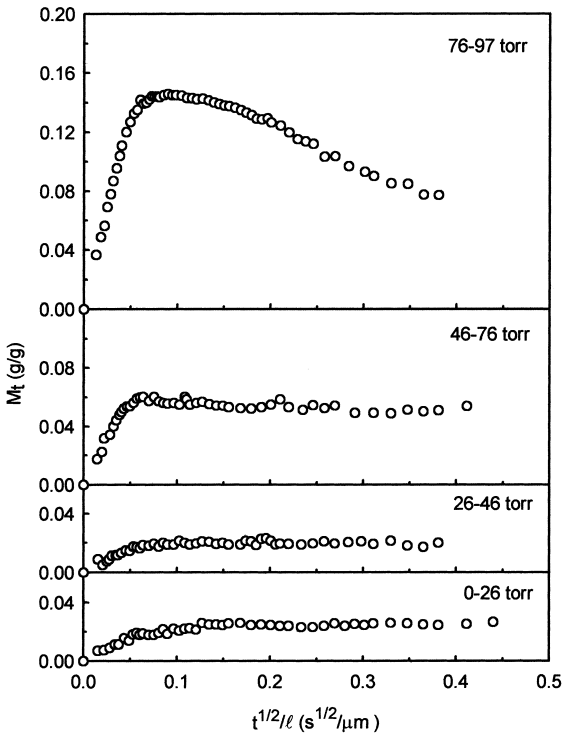

Fig. 2. First series of successive interval absorption kinetic runs of *n*-hexane vapor in poly(dimethylsilatrimethylene) film F386, at 25 °C.

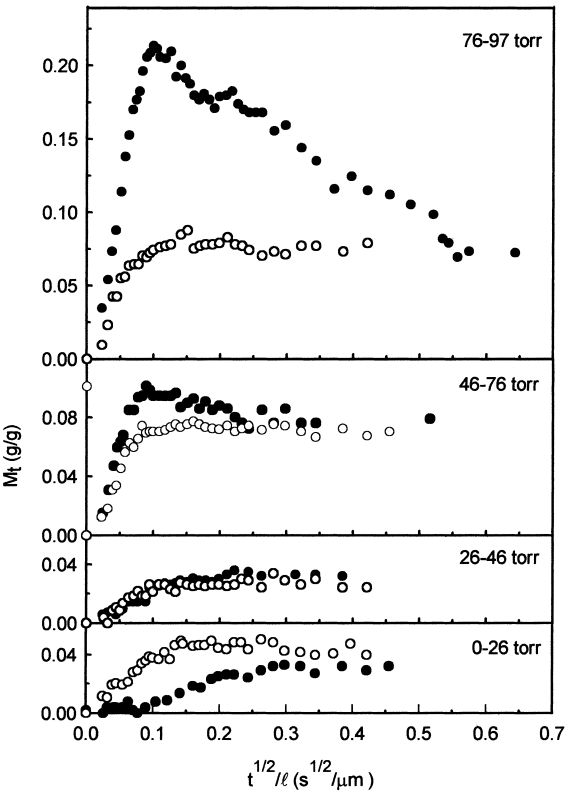

Fig. 3. First (dark points) and second (open points) series of successive interval absorption kinetic runs of *n*-hexane vapor in poly(dimethylsilatrimethylene) film F247, at 25 °C.

sorption isotherms of the first and second series of sorption runs (noted earlier) at all concentrations. This means that the degree of crystallinity of the polymer at sorption equilibrium remains practically unaffected by the occurrence of the overshoot. A plausible explanation of this behavior is that, during the first sorption series the high degree of plasticization of the polymer prevailing at the third, and more so at the fourth run leads to melting of more labile crystallites followed by recrystallization in a more stable crystal structure. Partial melting permits excess uptake of penetrant in previously inaccessible regions of the structure. Then, as recrystallization progresses, excess sorbed solvent is gradually expelled from the reformed, more stable ordered regions, thus producing the aforementioned sorption overshoots. Thanks to its higher stability, the new ordered structure remains practically unaffected by subsequent desorption and resorption processes, within the same concentration range (but will, of course, melt at still higher concentrations as shown by the abortive fifth sorption run on F386). The absence of overshoots during the second series of sorption runs is thus convincingly explained.

Strong evidence for the above interpretation is provided by the TMDSC data obtained from the pure polymer. In Fig. 4, we present (a) a TMDSC run on an as-prepared polymer film (not subjected to *n*-hexane sorption) and (b) a corresponding run conducted on hexane-treated F247 film (namely the F247 film resulting from the aforementioned two series of absorption experiments and subsequent elimination of the absorbed *n*-hexane).

The reversing signal of the as-prepared film (Fig. 4(a)) shows a small melting endotherm at ~28 °C (indicative of an ordered structure, which should be very labile at the temperature of the sorption experiments) followed by a stronger one at ~35 °C (consistent with a substantial degree of more stable crystallinity). The small endotherm is coupled with an exotherm of similar magnitude in the non-reversing signal, implying recrystallization presumably into the aforementioned more stable crystal structure. The second exotherm on the non-reversing signal provides evidence of recrystallization processes during melting of the more stable crystallites at ~35 °C.

The hexane-treated film (Fig. 4(b)) is characterized by (i) absence of exotherms in the non-reversing signal and hence absence of substantial amount of the recrystallizable crystalline material, which characterized the as-prepared film; (ii) absence of the more labile ordered structure of melting point (mp) ~28 °C seen in the as-prepared film; (iii) greatly diminished presence of the more stable crystallinity of mp ~35 °C seen in the as-prepared film; and (iv) appearance of a substantial amount of new crystallinity of greater stability (mp ~44 °C). The fact that the magnitude of the reversing endotherm (indicative of imperfect crystals able to melt and recrystallize easily) is much greater in Fig. 4(a) than in Fig. 4(b) is also consistent with a greater crystal stability and perfection in the latter case.

The picture presented earlier leaves little room for doubt

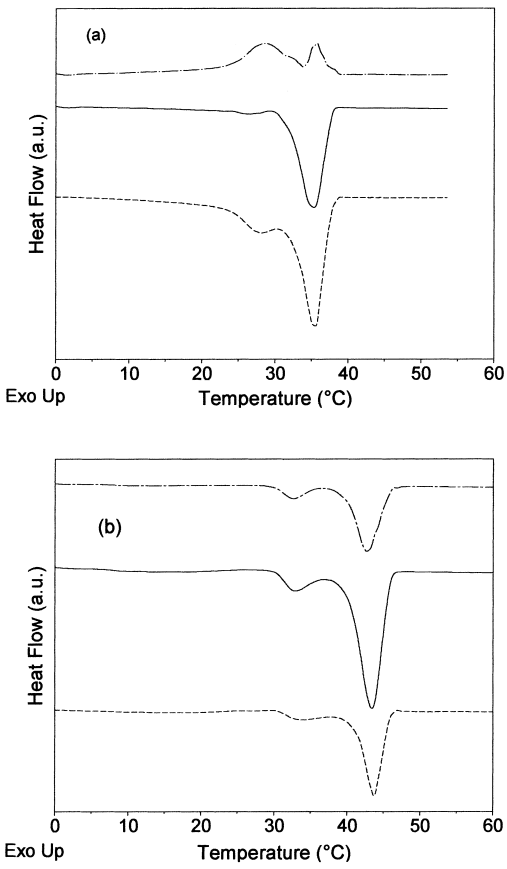

Fig. 4. Total (solid curve), reversing (dashed curve) and non-reversing (dot–dashed curve) TMDSC data on dry poly(dimethylsilatrimethylene) film samples: (a) as-prepared film; (b) F247 film subjected to *n*-hexane vapor sorption and subsequent desorption (see text). Melting temperatures: (a) 28 and 35 °C: (b) 34 and 44 °C. ΔH (J g^{-1}) deduced from integration of both peaks in (i) total signal: (a) +42; (b) +56, (ii) reversing signal: (a) +72; (b) +29, and (iii) non-reversing signal: (a) −30; (b) +27. Modulation: ±0.32 °C every 60 s; ramp: 2 °C min^{-1}.

that the basic process responsible for the prominent sorption overshoots observed in the present work is penetrant-induced melting of the crystallites of mp ~35 °C present in the as-prepared polymer film, followed by slow recrystallization to the more stable and perfect crystals of mp ~44 °C.

4. Conclusions

The present work presents an example of the application of the TMDSC method for the interpretation of anomalous sorption behavior in polymer films. In particular, the information provided by TMDSC (not obtainable by conventional DSC) on simultaneous melting and recrystallization processes of as-prepared and *n*-hexane-treated poly(dimethylsilatrimethylene) films, indicates that the sorption overshoots observed, when the films were first exposed to *n*-hexane vapor, are primarily attributable to penetrant-induced melting crystallites of mp ~35 °C, followed by slow recrystallization to a more stable crystalline structure of mp ~44 °C. Further work planned for the future, involves WAXD studies of poly(dimethylsilatrimethylene) films in the presence of *n*-hexane vapor and TMDSC studies on the effect of thermal annealing on the recrystallization process of the as-prepared films.

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