Anomalous Sorption in Poly(ethyl Methacrylate)

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Synopsis

Vapor sorption data were obtained for the ethylbenzene–poly(ethyl methacrylate) system at 120°C. Successive step-change sorption experiments carried out at two-film thicknesses indicate the presence of maxima in the sorption curves. The fractional amount of overshoot decreased as the final pressure or weight fraction of the experiment increased and as the sample thickness increased. It is proposed that the maxima in the sorption curves are caused by structural rearrangements produced by relaxation of polymer chains.

INTRODUCTION

It is well known[1,2] that sorption processes for polymer–solvent systems frequently do not conform to the behavior expected from the classical theory of diffusion. The slow reorientation of polymer molecules can lead to a wide variety of anomalous effects for both permeation and sorption experiments, particularly when such experiments are conducted near or below the glass transition temperature of the system. The sluggish polymeric relaxation process not only affects the transport of solvent through the polymer but also determines the rate at which equilibrium is established at a polymer-fluid interface during a sorption experiment. For example, for a sorption process with a glassy polymer, Long and Richman[3] have shown that the concentration of a polymer film does not immediately attain the equilibrium value consistent with the new solvent pressure in the gas phase. Since the rearrangement of polymer molecules needed to accommodate the equilibrium penetrant concentration can be a slow process, a two-stage sorption curve can be observed, and the significant structural rearrangements of the polymer occur during the second stage.

In this paper, we report anomalous sorption behavior in an amorphous polymer, poly(ethyl methacrylate) (PEMA), at 120°C, more than 50°C above the glass transition temperature of the pure polymer. Not only is the presence of non-Fickian sorption behavior rather unusual at a temperature this far above the glass transition temperature, but the sorption curves exhibit an overshoot in the weight pickup before leveling off to the equilibrium value. The sorption experiments are described in the second section of this paper, and the data are presented and interpreted in the third section.

EXPERIMENTAL

The vapor sorption data were collected using a glass high-temperature sorption column[4] with samples placed in quartz buckets and suspended from quartz

springs. The penetrant was fed to the column with a temperature-controlled solvent flask, and temperature control for the column was maintained with a condensing vapor system. The weight pickup M, the total mass of solvent per unit area which has entered the polymer sample at time t during a step-change experiment, was determined using the calibrations of the quartz springs. The gas pressure p in the column was measured directly with a quartz Bourdon null gauge. In all cases, the pressure–time curve was an excellent approximation to the desired step-change forcing function for p. More details of the apparatus and experimental procedure are given elsewhere.[4]

The polymer used in this study was a commercial sample of PEMA with a number-average molecular weight of 126,000 and a weight-average molecular weight of 340,000.

RESULTS AND DISCUSSION

Step-change sorption experiments were carried out at 120°C for the ethylbenzene–PEMA system in the pressure range 0–402 mm Hg. This pressure range was covered using five successive step-change experiments, and experiments were conducted using two values of L, the initial sample thickness, $L = 0.025$ cm and $L = 0.050$ cm. For a Fickian diffusion process, the sorption curves for all values of L should form a single curve when plotted as M/M_∞ vs. $t^{1/2}/L$, where M_∞ is the value of M achieved at infinite time. Consequently, the data collected in this study were plotted in this manner in Figures 1 and 2. Since a large number of data points were obtained for each run in the vapor sorption experiment, it
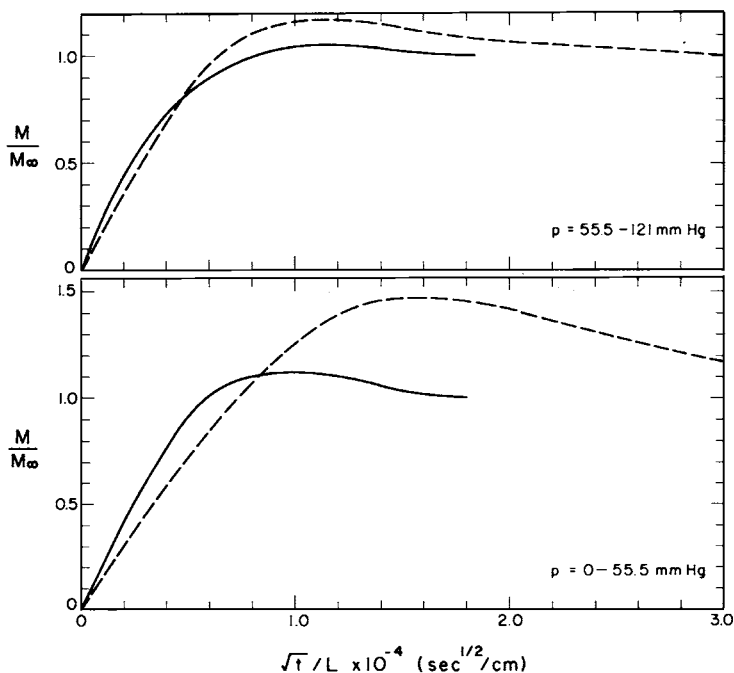

Fig. 1. Sorption curves for ethylbenzene–PEMA system at 120°C: (- - -) $L = 0.025$ cm; (——) $L = 0.050$ cm.
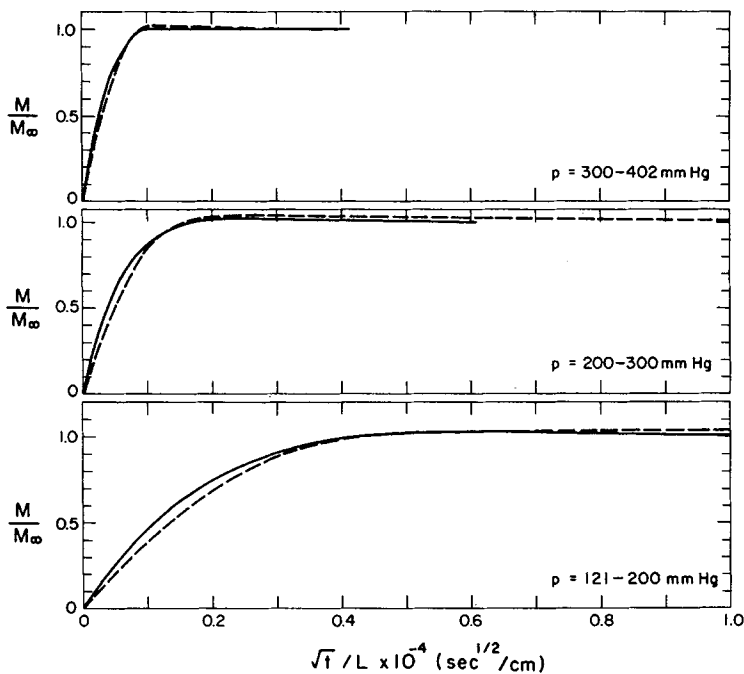
Fig. 2. Sorption curves for ethylbenzene–PEMA system at 120°C: (- - -) $L = 0.025$ cm; (——) $L = 0.050$ cm.

is convenient to present the data in Figures 1 and 2 as smooth curves. The equilibrium pressure-weight fraction relationship for the ethylbenzene–PEMA system at 120°C (based on the values of M_∞) is presented for both values of L in Figure 3.

From the data presented in Figures 1–3, the following observations can be made:

1. All sorption runs exhibited a maximum in the M/M_∞ vs. $t^{1/2}/L$ curve. The fractional amount of overshoot, $[M(\text{max}) - M_\infty]/M_\infty$, decreased as the final
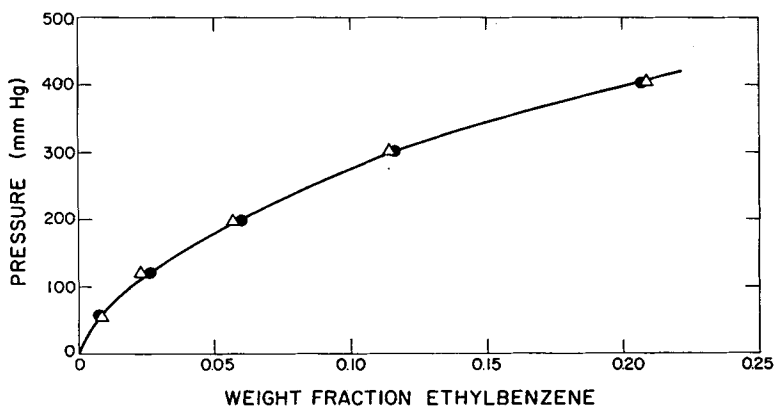

Fig. 3. Equilibrium pressure-solvent weight fraction curve for ethylbenzene–PEMA system at 120°C: (△) $L = 0.025$ cm; (●) $L = 0.050$ cm.

pressure or weight fraction of the experiment increased and as the sample thickness increased. These trends are depicted in Figure 4.

2. None of the runs exhibited superposition of the sorption curves for the two values of L. However, superposition of the curves for different thicknesses was approached as the final concentration of the experiment increased.

3. The equilibrium weight fraction of solvent corresponding to a particular pressure in the gas phase is independent of sample thickness, as is evident from Figure 3.

It seems reasonable to propose an explanation of the above anomalous sorption behavior which is based on slow relaxation processes in the polymer–solvent mixture. Apparently, solvent can be absorbed into the sample before the polymer chains have a chance to completely relax, and the structural rearrangements which the sample experiences as the chains eventually reorient themselves lead to rejection of some of the solvent from the sample. This partial exclusion of the penetrant will be more pronounced in instances when the diffusion rate is faster than the rate of chain relaxation since most of the solvent absorption is into an unrelaxed polymer network.

The relative rates of diffusion and polymer relaxation can conveniently be examined using the diffusion Deborah number $(DEB)_D$, which is defined[5] as the ratio of the characteristic time λ_m of the fluid to the characteristic time θ_D of the diffusion process:

$$(DEB)_D = \lambda_m/\theta_D \qquad (1)$$

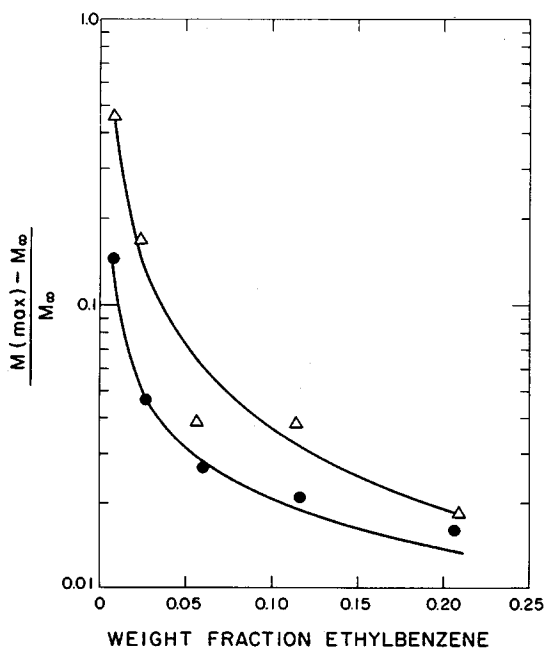An average characteristic diffusion time for unsteady, 1-dimensional mass

Fig. 4. Fractional overshoot in sorption curves for ethylbenzene–PEMA system at 120°C: ($\triangle$) $L = 0.025$ cm; ($\bullet$) $L = 0.050$ cm.

transfer in polymer films can be defined as

$$\theta_D = L^2/D* \tag{2}$$

where $D*$ is an appropriate diffusion coefficient for diffusional transport in the polymer–solvent mixture. A reasonable and convenient definition of the characteristic relaxation time of a polymer–solvent system is

$$\lambda_m = \int_0^\infty tG(t)\,dt \Big/ \int_0^\infty G(t)\,dt \tag{3}$$

where $G(t)$ is the shear relaxation modulus. Since λ_m and $D*$ are concentration-dependent, it is clear that a single value of the Deborah number for a step-change experiment will provide an appropriate average only if the concentration interval of the experiment is suitably small. For high Deborah numbers, anomalous sorption behavior can be expected because the rate of rearrangement of polymer molecules is slower than the diffusion rate, whereas classical diffusion can be expected in the limit of low Deborah numbers.

It is evident from eqs. (1) and (2) that the Deborah number increases as L decreases, and, hence, solvent rejection should be more pronounced for thinner samples since a significant amount of absorption occurs before the polymer chains can relax. Furthermore, as will be shown below, the decrease of λ_m with increasing solvent mass fraction leads to a decrease of the Deborah number as solvent is added. Hence, a more pronounced sorption maximum is expected at low solvent concentrations because chain relaxation is slower for such samples and a significant amount of solvent is absorbed before significant structural rearrangements take place. Clearly, anomalous effects should diminish as the experiments go from the lowest concentration or pressure range studied (0–55.5 mm Hg) to the highest (300–402 mm Hg). Since low Deborah numbers can be obtained for sufficiently high solvent concentrations, it is to be expected that such sorption runs should produce sorption curves with no maxima, and there should be a superposition of sorption curves measured using different thicknesses. Finally, since all the chains will eventually relax after a sufficiently long period of time, the solvent weight fraction consistent with an equilibrium polymer–solvent configuration will be reached in the long time limit. Furthermore, the equilibrium solvent mass fraction should in no way depend on the sample thickness. It is evident that the picture of solvent rejection caused by chain relaxation predicts qualitative trends which are consistent with the observed data.

The calculation of $(DEB)_D$ for the ethylbenzene–PEMA system can be carried out using a procedure discussed elsewhere.[5] If $D*$ is defined in terms of the self-diffusion coefficient for the solvent, D_1, and the self-diffusion coefficient for the polymer, D_2, then it can be shown[5] that the concentration dependence of $(DEB)_D$ at any temperature T can be computed from the following expression:

$$(DEB)_D = \left[\frac{x_2 D_1(T,\omega_1)}{D_2(T,\omega_1)} + x_1\right]\frac{D_2(T,0)\lambda_{m0}}{L^2} \tag{4}$$

Here ω_1 is the solvent mass fraction, x_1 is the solvent mole fraction, x_2 is the polymer mole fraction, and λ_{m0} is the characteristic time of the pure polymer at T. Free volume theory[5] can be used to compute D_1 and D_2, and λ_{m0} can be

determined using appropriate stress–relaxation data[6] by utilizing an approximate estimate for the molecular weight dependence. The $(DEB)_D$ vs. ω_1 relationship for the ethylbenzene–PEMA system at 120°C is presented in Figure 5 for the two sample thicknesses used in the experiments of this investigation. As noted previously, the diffusion Deborah number decreases substantially as solvent is added to the sample. Furthermore, since classical or Fickian diffusion can be expected only when $(DEB)_D$ is significantly less than unity (say 0.1), it is evident that anomalous behavior can be expected for the ethylbenzene–PEMA system for practically all of the concentration range considered in this investigation. Only the final experiment with $L = 0.050$ cm has a chance of being free of anomalous diffusion effects, and Figures 2 and 4 show that it is this experiment which most closely approaches a Fickian diffusion process.

In Figure 5, we have also presented $(DEB)_D$ vs. ω_1 curves for the ethylbenzene–polystyrene system at 160°C (60°C above the glass transition temperature of polystyrene) for $L = 0.025$ cm and $L = 0.050$ cm. In this case, the diffusion Deborah numbers are sufficiently low so that Fickian diffusion can be expected
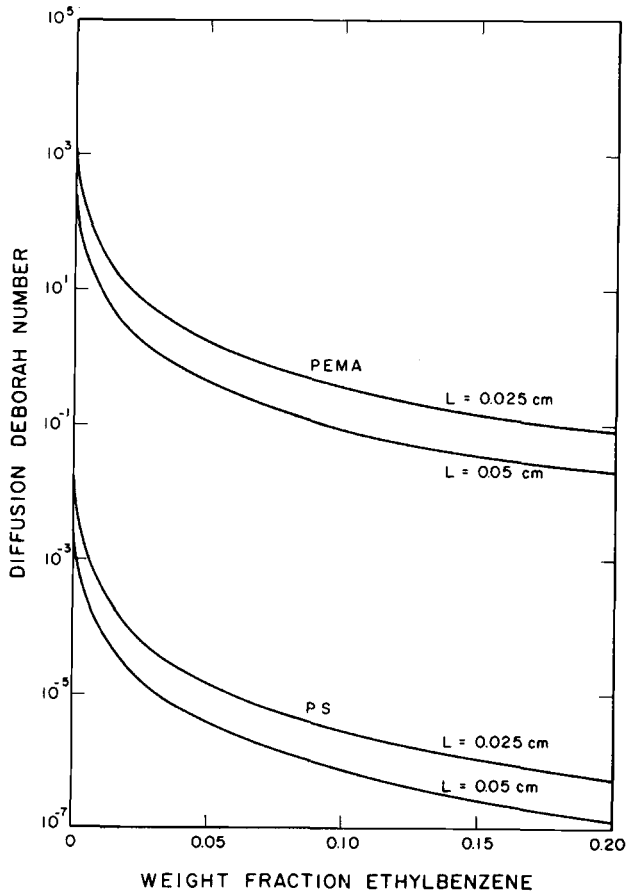

Fig. 5. Dependence of Deborah number on solvent mass fraction for ethylbenzene–PEMA system at 120°C and for ethylbenzene–polystyrene system at 160°C. The polystyrene molecular weight is 3×10^5.

over the complete concentration range. Indeed, sorption experiments[7] for the ethylbenzene–polystyrene system at 160°C indicate that a Fickian diffusion process exists for this polymer–solvent system at this temperature. The great differences in the sorption behavior of these two polymer–penetrant mixtures (at comparable temperature differences above the respective glass transition temperatures of the pure polymers) can thus be anticipated and explained by using the Deborah number concept.

Kambour et al.,[8] Titow et al.,[9] and Overbergh et al.[10] observed maxima in sorption curves for solvent diffusion in crystallizable polymers. They attributed the overshoots to crystallization induced by the presence of a solvent. The ordered regions formed during the sorption process reject the solvent which was absorbed before these ordered regions existed. Overbergh et al.[10] also noted that the fractional overshoot increased as the sample thickness decreased since most of the sorption occurs before the onset of crystallization in a thin sample.

A method which can be used to distinguish between the chain relaxation and crystallization mechanisms is to conduct a repeat sorption experiment after a first sorption run is carried out. Suppose that an untreated sample goes through a maximum in the sorption curve for a single run, ultimately reaching the sorption weight consistent with an equilibrium liquid structure. If we now desorb the sample, the polymer should eventually reach an equilibrium conformation consistent with zero solvent if the chain relaxation mechanism is operative since the experiment is conducted above the glass transition temperature of the pure polymer. If we repeat the sorption experiment, then a sorption curve identical to the initial sorption curve should be produced. If, on the other hand, the maximum in the first sorption curve can be attributed to exclusion of solvent caused by solvent-induced crystallization, then the second sorption curve should be substantially different than the first. It is reasonable to expect that the ordered regions will remain intact during the desorption process following the initial sorption experiment. Hence, there should be little or no additional solvent exclusion in the second sorption run which should thus no longer exhibit a maximum. Titow et al.[9] have observed this type of behavior for sorption curves with solvent-induced crystallization.

In Figure 6, we have plotted both the first and the repeat sorption curves for the ethylbenzene–PEMA system at 120°C. Since the two curves are quite close to each other, it seems reasonable to exclude the possibility of the formation of ordered regions in PEMA in this particular experiment. Furthermore, data taken using a differential scanning calorimeter indicate no melting of crystals up to 200°C. Since it is not likely that the commercial sample of PEMA is totally atactic,[11] the above experiment was done to check for the possibility of ordered regions in this polymer. However, it is quite reasonable to expect the absence of crystalline regions in the commercial polymer because of the lack of a high degree of stereoregularity.

From the data obtained in this study and from the above discussion, it appears reasonable to propose that the overshoots in the sorption curves are caused by structural rearrangements produced by relaxation of polymer chains. Under comparable conditions, PEMA relaxes much more slowly than a polymer like polystyrene (as is evident from the time dependence of the relaxation modulus). This slower relaxation of PEMA is due to greater steric hindrances for polymers
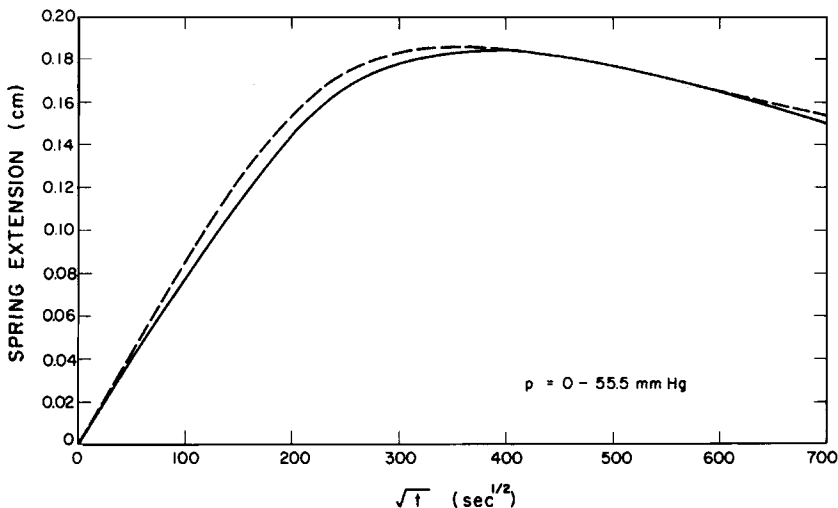
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Fig. 6. Raw data for first and repeat sorption runs for ethylbenzene–PEMA system at 120°C with $L = 0.025$ cm: (——) first sorption run; (- - -) repeat sorption run.

with disubstituted backbone chain atoms (PEMA) than for polymers with monosubstituted backbone atoms (polystyrene).   It should be noted, however, that there is no direct evidence for the above proposed explanation to the anomalous sorption curves.

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