Interval sorption kinetics in the system poly(methyl methacrylate)–methyl acetate

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Abstract

A series of interval absorption runs in the system poly(methyl methacrylate)–methyl acetate vapor at 30°C exhibiting non-Fickian behavior are presented. The relevant diffusion and viscous relaxation processes were studied separately by kinetic analysis of the first and second stage of two-stage sorption curves, respectively. Both processes were found to be much slower than that observed by Kishimoto et al. (J Phys Chem 1960;64:594) in nominally the same system. The concentration dependence of the diffusion coefficient was found to be well represented by the free volume theory of Vrentas and Duda. The second stage absorption was found to conform well to first-order relaxation kinetics. The corresponding relaxation frequencies exhibit a weak dependence on concentration, in contrast to the strong concentration dependence reported by Kishimoto et al. This difference is attributed to differences in polymer fine structure, reflected in the glass transition temperature of the polymer–penetrant system, which was found to be substantially higher in our case. As a result, Kishimoto et al.'s system undergoes glass transition in the upper region of experimental concentration range, while our system remains glassy throughout. Our data indicate that the S-shaped absorption curves observed at low concentrations are diffusion-, rather than relaxation-controlled. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Non-Fickian kinetics; Two-stage sorption; Poly(methyl methacrylate)

1. Introduction

Sorption kinetic experiments constitute the most common and convenient way of studying isothermal unidimensional diffusion of vapors in thin polymer films. In such experiments a polymer film of dry thickness $2l$ is typically pre-equilibrated at some vapor pressure $p = p_I$. Then, at time $t = 0$, p is raised (in the case of absorption) or lowered (in the case of desorption) to a new constant value p_F. The penetrant diffuses into (or out of) the film in the thickness direction and the weight gain or loss M_t (expressed here in g/g of dry polymer) is recorded as a function of time until a new equilibrium is established.

Studies of this kind on glassy polymer–organic vapor systems have revealed a variety of deviations from normal Fickian diffusion kinetics. The most extensive work in this respect is that reported by a group of Japanese workers (Fujita, Kishimoto, Odani et al.) who studied systematically

a considerable number of such systems in a series of "differential" or "interval" absorption experiments [1–5]. According to this experimental protocol, an initially dry film is subjected to a series of successive absorption runs covering narrow vapor pressure intervals $\Delta p = p_F - p_I$ (corresponding to concentration intervals $\Delta C = C_F - C_I$). As p_I (C_I) is raised, the observed deviations of the relevant M_t versus $t^{1/2}$ plots from the initially linear shape characteristic of Fickian diffusion, were found to follow a well-defined pattern. The most complete form of this pattern is:

S-shaped → pseudo-Fickian → two-stage → pseudo-Fickian or S-shaped → Fickian   (1)

Much the same results have been obtained in other studies of narrow interval absorption kinetics (e.g. Refs. [6–12]). The transition to two-stage absorption with increasing p_I (C_I) is a standard feature in all cases; but one (or more) of the preceding or following steps shown in (1) may be missing in particular instances. Thus Kishimoto et al. [2] pointed out that, for the semi-crystalline polymers studied by them, a final transition to Fickian kinetics could not be observed before the films became too tacky to maintain their mechanical integrity. Also, either one of the pseudo-Fickian or S-shaped steps preceding or following the aforementioned

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transition [2–4,9] or both of these steps [6,8] may be missing; and it is possible for the first-run curve to be pseudo-Fickian (maybe even Fickian) rather than S-shaped [2,11].

Non-Fickian kinetic behavior is commonly interpreted in terms of the viscoelastic response of the glassy polymer to the osmotic stress induced by the penetrant [13]. This is most clearly seen in two-stage sorption [1,4,6,8,9]. Here, the first stage corresponds to limited sorption and subsequent diffusion (with diffusion coefficient D) into the "elastically" swelling or "unrelaxed" polymer up to a quasi-equilibrium. The latter is determined by the extent to which the polymer can swell, under the prevailing osmotic stress, by fast (practically instantaneous) purely local chain segmental displacements. The second stage is the result of long-range chain rearrangements, which permit further ("delayed" or "viscous") swelling and are slow on the diffusion time scale. The rate of the aforementioned viscous relaxation (treated as a pseudo-first-order rate process governed by the relaxation frequency, or reciprocal relaxation time, β) relative to that of the diffusion process (governed by D/l^2) may be expressed mathematically [14,15] by the dimensionless parameter $\beta l^2/D$ (or by its reciprocal, the diffusion Deborah number $\tau D/l^2$, expressed in terms of the relaxation time $\tau = 1/\beta$ [16]). The condition for two-stage behavior, with well-separated first and second stage, is $\beta l^2 D \ll 1$. As $\beta l^2/D$ increases, the two stages tend to merge; yielding S-shaped absorption for M_t versus $t^{1/2}$ curves when $\beta l^2/D \sim 1$; and ultimately Fickian curves, when $\beta l^2 D \gg 1$. The aforementioned merging process is clearly seen in the two-stage curves of Kishimoto et al. [2] (in the form of a progressive shift of the second stage to the left on the relevant M_t versus $t^{1/2}$ plot), as the transition to pseudo-Fickian or S-shaped curves is approached; thus indicating that the said transition with rising C, is the result of β increasing more steeply than D.

Two-stage absorption data are of special interest, because they afford the opportunity to study the relevant diffusion and viscous relaxation process independently of one another. The results obtained by Fujita et al., in this respect [1,2,4] indicate that β is, in general, a function of C as well as of ΔC. On the other hand, two-stage data available on the cellulose acetate–acetone system [6,8] referred to above indicate very little dependence of β on C coupled with substantial dependence of β on ΔC. Little attention has been given to full kinetic analysis of second-stage sorption until recently, when good conformity to first-order kinetics was shown for sufficiently small ΔC, in cellulose acetate penetrated by acetone or methanol [8,9]. Similar analyses of other systems is obviously of interest.

The S-shape of the M_t versus $t^{1/2}$ absorption curves obtained at the low concentration end of the series of interval runs, is usually attributed to a viscous relaxation process [1,4,6,17]. However, systematic investigation of the cellulose acetate–acetone system has shown [8,12] that the said curves are diffusion-controlled. It is of interest to investigate the relevant behavior of other systems.

Accordingly, the poly(methyl methacryrate)–methyl acetate (PMMA–MAc) system studied previously by Kishimoto et al. [2] was chosen by us for further investigation and analysis. In the course of this investigation we found that the kinetic behavior of the PMMA–MAc system studied by us showed significant differences from the behavior of nominally the same system studied by Kishimoto et al. These differences are also discussed below.

2. Experimental

Poly(methyl methacrylate) of average MW 996k, supplied by Aldrich (code No 18226-5) was used. The T_g of the dry polymer, determined by DSC, was found to be 115°C (onset of glass transition at 108°C). A film of thickness 9.5 μm was cast from a 12 wt% solution of PMMA in acetone on a glass plate. After evaporation of the solvent, the film was removed from the glass plate by immersion in distilled water and dried overnight at 90°C. The methyl acetate used was of analytical reagent grade.

Sorption experiments were carried out at 30°C in a vacuum sorption apparatus using a Cahn 2000 Electrobalance. A blind run showed that substantial amounts of penetrant were absorbed by the balance itself, resulting in a readout much larger than that expected in the case of an interval sorption experiment. After cleaning of the balance arms to remove all polymeric adhesives, a blank run showed less than 10 μg sorption at $p_F = 175$ Torr. A film sample of dry weight 11.315 mg was used in the sorption experiments. Since at the maximum vapor pressure of 140 Torr used in our experiments the total weight gain of the PMMA sample was ∼1.4 mg, sorption by the balance itself amounted to an error of less than 1%.

3. Results and discussion

The film was first subjected to a series of four interval absorption runs (series S1) up to a final pressure of 80 Torr. At the end of the fourth run (run No S1R4), due to a leak in the apparatus, the whole system was exposed to atmospheric pressure. Hence, it was re-evacuated and a new series of runs was performed (series S2), consisting of eight runs, up to a final pressure of 140 Torr. After complete desorption, effected by a series of interval desorption runs, an additional series of absorption runs was performed up to the same final pressure but consisting of fewer runs, in order to examine the effect of the magnitude of ΔC on sorption kinetics.

The sorption isotherm obtained from the equilibrium uptake data is shown in Fig. 1. The data from different series are quite reproducible. However, comparison with the corresponding data of Kishimoto et al. [2] (see filled points in Fig. 1) shows considerably higher sorption at lower concentrations in the polymer sample used by us, consistent with the presence of a higher fraction of excess free volume.
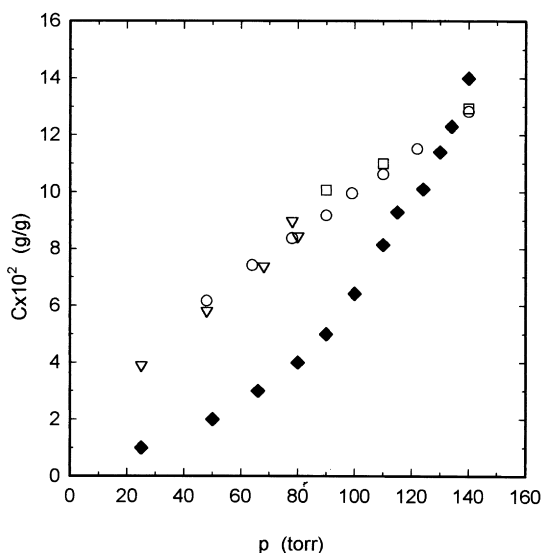
Fig. 1. Absorption isotherm for the system PMMA–MAc at 30°C including data from series S1 ($\triangledown$), S2 ($\bigcirc$), S3 ($\square$), in comparison with the absorption isotherm of Kishimoto et al. [2] ($\blacklozenge$).

3.1. General characteristics of sorption curves

Series S2 of interval absorption kinetic runs, extending over the same vapor pressure and concentration range as the corresponding data of Kishimoto et al. [2] ($p_F^{max} =$ 140 Torr) is presented in Fig. 2. The observed rates of sorption were much lower than those found by the aforementioned authors. This meant that the time scale of our experiments was much more protracted than originally expected, even though our film sample was made as thin as possible. The characteristics of the M_t versus $t^{1/2}$ curves follow the normal sequence: S-shaped (run No. S2R1), pseudo-Fickian (run No. S2R2) and two-stage (run Nos. S2R3–S2R8); but no tendency towards the transition: two-stage $\rightarrow$ pseudo-Fickian $\rightarrow$ Fickian, observed by Kishimoto et al. [2] is discernible.

In fact, the time scale of second-stage sorption, as represented by the relevant half-life t_{h2} (i.e. the time required to absorb half the equilibrium quantity of penetrant), appears to vary only to a small extent in the range 64–140 Torr (corresponding to $C_I = 0.074$–0.125 g/g), as illustrated in Fig. 3, where the relevant data of series S2 together with those of S1 and subsequent series are presented. In this respect, the present PMMA–MAc system shows a much closer resemblance to those of cellulose acetate–acetone and cellulose acetate–methanol studied previously by us [8,9] than to the PMMA–MAc system of Kishimoto et al. [2].

On the other hand, the corresponding first-stage half-life t_{h1} exhibits a substantial tendency to decrease with rising concentration (see Fig. 3), indicating that diffusion into the film is governed by a diffusion coefficient exhibiting substantial concentration dependence.

Fig. 3 further shows that the behavior of the half-life t_{hS} of
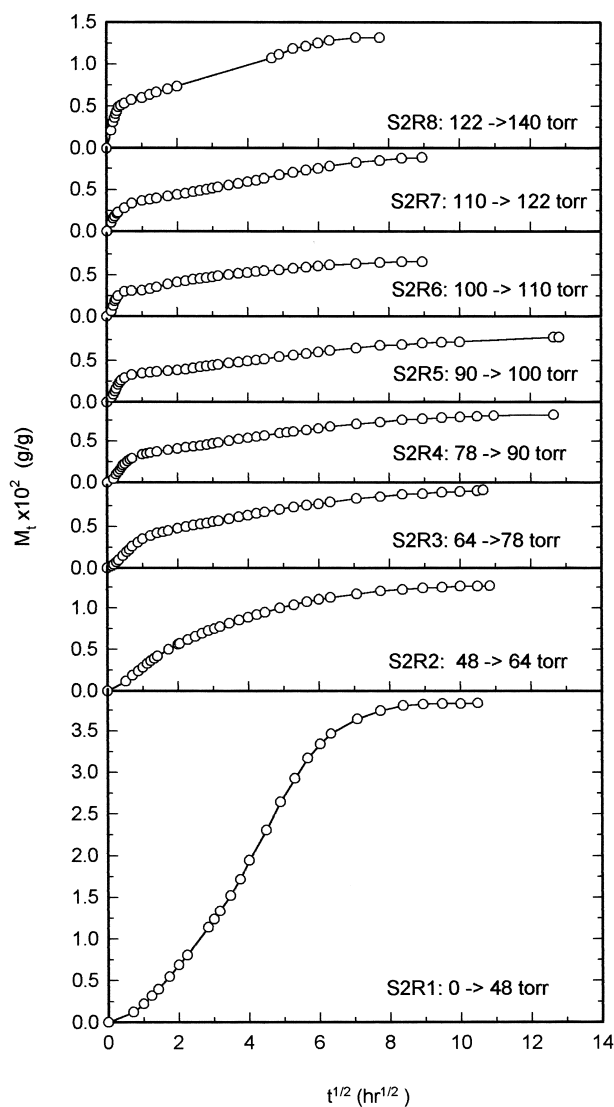

Fig. 2. Series S2 of successive absorption kinetic runs of MAc in PMMA at 30°C; with C_I(g/g) = 0.024 (S2R1); 0.061 (S2R2); 0.074 (S2R3); 0.083 (S2R4); 0.092 (S2R5); 0.099 (S2R6); 0.106 (S2R7); 0.115 (S2R8).

first-run S-shaped curves bears little relation to that of t_{h2} but fits neatly in the pattern exhibited by t_{h1}. This behavior suggests that first-run S-shaped curves are diffusion-, rather than relaxation-controlled in conformity with our previous findings in the cellulose acetate–acetone vapor system [8,12]. The S-shape of these curves is thus attributable, not to the effect of viscoelastic relaxation, but to that of differential swelling stresses; which are generated by (and closely follow the build up and decay of) concentration gradients during the sorption experiment [8,12,18,19]. It is worth noting that a similar explanation is applicable to the S-shaped M_t versus $t^{1/2}$ curves observed in a study of sorption of liquid methanol by ethylene–vinyl alcohol copolymers [20].

The S2 series of interval sorption runs was complemented with a series of interval desorption runs starting at $p_I =$ 140 Torr and ending at $p_F = 0$ Torr. Each of these runs
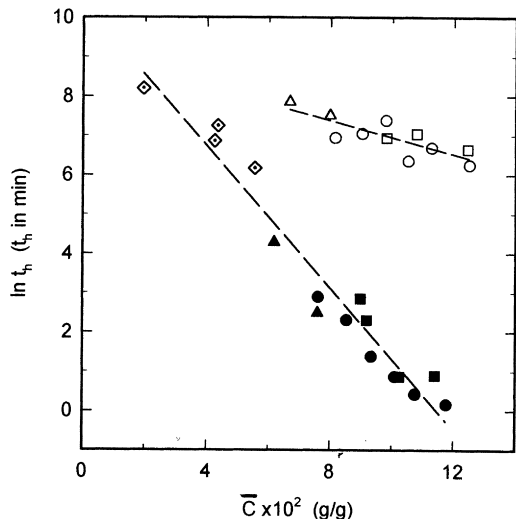
Fig. 3. Dependence of the half times (t_h) of absorption M_t versus $t^{1/2}$ curves on the relevant mean concentration: $\diamond$, t_{hs} (low concentration, S-shaped curves) versus $\bar{C} = 0.5\ (C_I + C_F)$; filled symbols, t_{h1} (first stage of two-stage curves) versus $\bar{C}_1 = 0.5\ (C_I + C_q)$; open symbols, t_{h2} (second stage of two-stage curves) versus $\bar{C}_2 = 0.5\ (C_q + C_F)$. Two-stage data from series: S1 ($\triangle$, $\blacktriangle$); S2 ($\bigcirc$, $\bullet$); S3 ($\square$, $\blacksquare$).

was continued as far as practically possible; but, because of the unexpectedly protracted experimental time scale referred to above, it was not considered worthwhile to insist on making sure that full final equilibrium had been attained in every case, before the next run was started. The crucial point of interest here is that, in the higher concentration region, these desorption runs also exhibit two-stage character (Fig. 4). This feature constitutes useful confirmatory evidence that the system under investigation here conforms to the usual physical picture of two-stage sorption [8,12]; which, as mentioned above, involves a practically uniform concentration of penetrant across the film C_2 gradually relaxing from an initial value $C_2 = C_q$ to the final one $C_2 = C_F$ (as against the alternative interpretation in terms of a Case II diffusion mechanism advanced by Kwei [21]).

3.2. Analysis of diffusion-controlled sorption kinetics

Diffusion coefficients in a polymer-fixed frame of reference, D_P, were deduced from the first stage of the two-stage curves, using the formula

$$M_t/M_q = 2(D_P t/\pi l^2)^{1/2}$$

Here we use M_q and M_∞ to designate the amount of penetrant corresponding to the quasi-equilibrium attained at the end of the first stage (corresponding concentration C_q) and to the final equilibrium (corresponding concentration C_F), respectively. M_q was estimated by the method described in Refs. [8,9]. M_q/M_∞ was found to be practically independent of C_I. The resulting diffusion coefficients are presented in Fig. 5 as a function of the mean concentration of the first stage $\bar{C}_1 = 0.5(C_q + C_I)$. It will be noted that satisfactory reproducibility was generally obtained between different series of absorption runs, as well as between absorption and desorption runs in series S2.

Diffusion coefficients, D_P, determined similarly from the corresponding two-stage absorption curves of Kishimoto et al. (Fig. 1 of Ref. [2]) are also presented in Fig. 5. The two sets of results in Fig. 5 follow a similar trend with increasing concentration, but their numerical values differ by almost two orders of magnitude, reflecting the aforementioned considerably slower diffusion rates characteristic of our system. This trend is, furthermore, shown in Fig. 5 to follow reasonably faithfully that predicted by Eqs. (1)–(3), applied previously by Durning [17] to the same penetrant–polymer system

$$D_M = GD_{01} \exp\{ -[\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)/\hat{V}_F]\} \tag{1}$$

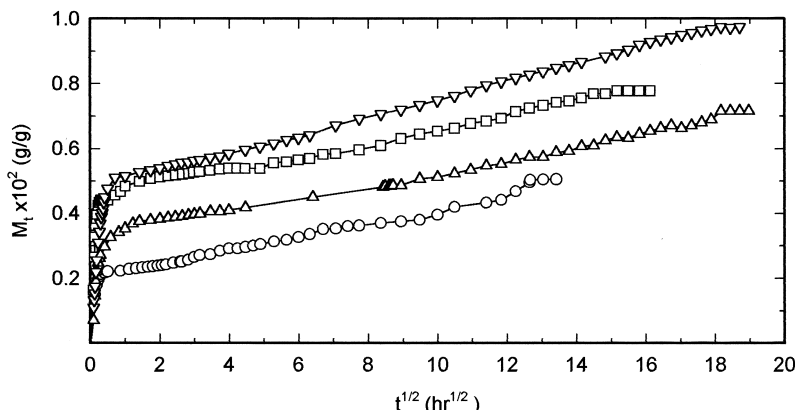$$G = \frac{\rho_2 \hat{V}_2}{RT}\left(\frac{\partial \mu_1}{\partial \ln \rho_1}\right) \tag{2}$$

Fig. 4. Examples of two-stage desorption kinetic runs of MAc in PMMA at 30°C with $p_I \to p_F$ (Torr): $140 \to 122$ ($\bigcirc$); $110 \to 78$ ($\square$); $78 \to 71$ ($\triangle$); $68 \to 50$ ($\triangledown$).
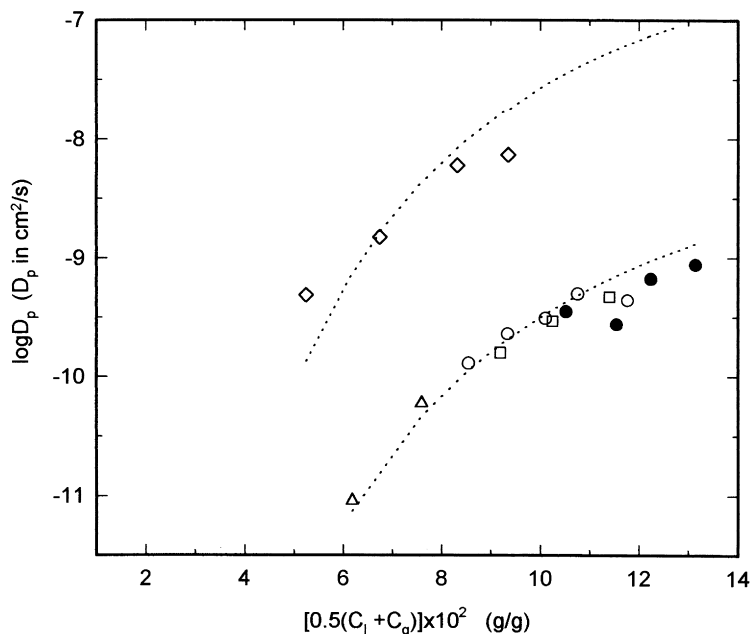
Fig. 5. Diffusion coefficients of MAc in PMMA at 30°C determined from the first stage of two-stage curves and plotted as a function of the relevant mean concentration $\bar{C}_1 = 0.5\,(C_I + C_q)$: (a) from absorption run series S1 ($\triangle$); S2 ($\bigcirc$); S3 ($\square$) and from desorption run series S2 ($\bullet$) and (b) from the corresponding series of absorption runs of Kishimoto et al. (Fig. 1 of Ref. [2]) ($\diamondsuit$). The lines were calculated by fitting the above data to Eq. (1) using $D_{01} = 5.8 \times 10^{-6}$ or 4.9×10^{-4} cm^2/s to fit lower or upper points, respectively.

$$\frac{\hat{V}_F}{\gamma} = \omega_1\left(\frac{K_{11}}{\gamma}\right)(K_{21} - T_{g1} + T)$$
$$+ \omega_2\left(\frac{K_{12}}{\gamma}\right)(K_{22} - T_{g2} + T) \qquad (3)$$

In Eq. (1), D_M is the mutual diffusion coefficient; the exponential factor on the right-hand side of Eq. (1) represents the concentration dependence of the self-diffusion coefficient as derived from the free volume theory of Vrentas and Duda [22,23]; $\hat{V}_1^*$ is the specific critical local hole free volume required for a penetrant molecule to jump to a new position; $\hat{V}_2^*$ is the specific critical local hole free volume required for the displacement of a polymer jumping unit; $\hat{V}_F$ is the specific average hole free volume of the mixture; γ is the free volume overlap factor; ξ is the ratio of penetrant to polymer critical molar volumes; ω_1 and ω_2 represent the weight fractions of penetrant and polymer, respectively; and D_{01} serves as an adjustable constant. In Eq. (2), μ_1 is the chemical potential of the penetrant; ρ_1 and ρ_2 are the densities of penetrant and polymer, respectively; and $\hat{V}_2$ is the specific volume of the pure penetrant. In Eq. (3), T_{g1} and T_{g2} are the glass transition temperatures of the penetrant and the polymer, respectively, and K_{11}, K_{12}, K_{22} and K_{21} are related to the WLF equation constants of the two components. D_P is related to D_M by

$$D_P = D_M(1 - \phi_1)^2$$

where $\phi_1$is and the volume fraction of the penetrant. The calculations were performed using the values of $\hat{V}_1^*$, $\hat{V}_2^*$,

K_{11}/γ, K_{12}/γ, $(K_{21} - T_{g1})$ and $(K_{22} - T_{g2})$ suggested by Durning [17]. G was evaluated from the respective isotherm data. The dashed curves in Fig. 5 represent the results with $D_{01} = 5.8 \times 10^{-6}$ and 4.9×10^{-4} cm^2/s for our and Kishimoto's data, respectively. As it can be seen, Eq. (1) represents our data fairly well. The corresponding D_{01} value is very close to the value 5×10^{-6} cm^2/s calculated by Durning [17] for the same system. The D_{01} value deduced by us from Kishimoto's data is of the same order of magnitude as the value 1.2×10^{-4} cm^2/s determined in Ref. [24] for the same system from diffusion coefficients measured by capillary column inverse gas chromatography.

The difference in the diffusivity between the two systems can be qualitatively explained on the basis of the dual mode transport mechanism [25], which was originally applied to gas–glassy polymer systems in the absence of plasticization effects, but later extended to systems exhibiting plasticization phenomena [26]. According to this model, the penetrant molecules dissolved in a glassy polymer consist of two distinct populations: one dissolved by a simple, Henry's law mode of dissolution in the dense polymer matrix, and one adsorbed by a Langmuir mode in fixed microcavities dispersed in the said matrix. The microcavities constitute the excess free volume of a glassy polymer. The Langmuir population is assumed to be totally or partially immobilized, and experimental data on glassy polymer–gas systems indicate that the diffusion coefficient of the Langmuir population can be of more than an order of magnitude lower than the diffusion coefficient of the Henry's law population [27]. Since the isotherm data of Fig. 1 indicate that a higher
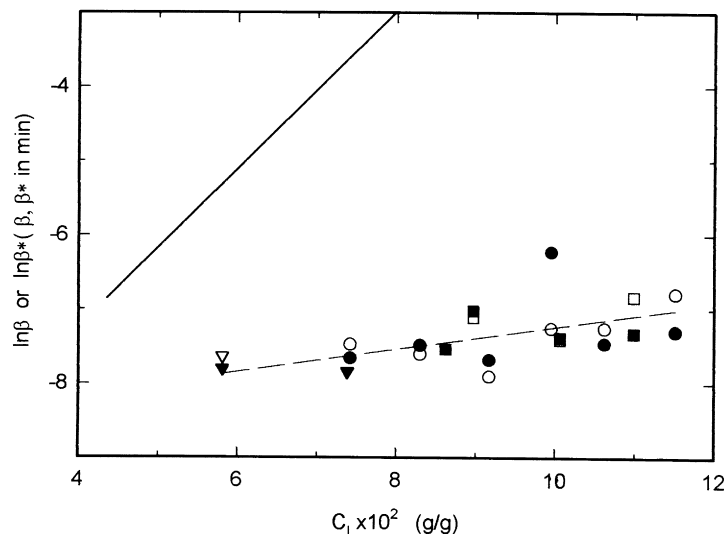
Fig. 6. Concentration dependence of relaxation frequencies β deduced from first-order plots (open symbols) or $\beta^* = 1/2t^*$ (filled symbols) deduced from the inflection point of the second stage of two-stage absorption runs of series S1 ($\triangledown$, $\blacktriangledown$); S2 ($\bigcirc$, $\bullet$); S3 ($\square$, $\blacksquare$). The solid line represents the β^* values deduced from the corresponding data of Kishimoto et al. (Fig. 4 of Ref. [2]).

fraction of excess free volume is present in our polymer sample as compared to the sample of Kishimoto et al. [2], one may attribute the lower diffusion coefficients observed in the former, to the higher contribution of the Langmuir population to the overall effective diffusion coefficient of the system.

3.3. Analysis of viscous relaxation-controlled sorption kinetics

On the basis of the close correspondence of second-stage sorption with mechanical creep, Fujita et al. [1,4] characterized second-stage sorption rates by means of relaxation times $\tau^* = 2t^*$ (where t^* is the time corresponding to the inflection point of the second-stage M_t versus $t^{1/2}$ plot, which is not very different from the half-life t_{h2} used above). Analogous values of $\beta^* = 1/\tau^*$ for the present system are shown in Fig. 6 plotted as a function of concentration in comparison with the corresponding data of Kishimoto et al. [2].

The markedly different behavior of these two sets of data already noted above, is attributable to differences in polymer fine structure. An example of such an effect is provided by the aforementioned study of Kishimoto et al. [2], wherein the concentration dependence of $\beta(C)$ was found to be far steeper for atactic polystyrene–benzene than for highly crystalline polystyrene–benzene. The precise nature of the structural differences between our PMMA sample and that of Kishimoto et al. [2] cannot be tracked down because the latter was a laboratory sample which had not been characterized in any detail. However, strong (weak) dependence of β on C may reasonably be expected when the system is close to (far from) $T_g(C)$. The transition to Fickian behavior observed by Kishimoto et al. [2] occurred at $p_I \sim 130$ Torr,

corresponding to $C_I \sim 0.11$ g/g. This value of C_I compares well in their case, with the concentration (interpolated [2] from $T_g(C)$ versus C data), at which the $T_g(C)$ of the PMMA–MAc mixture is reduced to the temperature of the sorption experiments. Accordingly, if the above reasoning is correct our system should still be well in the glassy state under these conditions. This expectation was confirmed by DSC measurements, which indicated onset of glass transition for $C_1 = 0.11$ g/g in our system at 42°C, well above the temperature of our sorption experiments.

Certain recent findings reported by Tang et al. [10] on the two-stage sorption behavior of the polystyrene–ethylbenzene system at 40°C are relevant in this connection. These results show the second stage of sorption to be insensitive to concentration in the region of $C < 0.05$ g/g and then shift increasingly to the left (i.e. towards higher sorption rates), in the higher concentration region up to the point of glass transition (at $C \sim 0.1$ g/g [7]). The authors tended to regard the low-concentration behavior as the result of the difficulty of attaining final equilibrium, due to the extremely protracted time scale of the experiments. However, the relevant experimental curves extend in all cases beyond the point of inflection of the second stage (which is related to the relaxation frequencies β^* considered in this work), and this inflection point is insensitive to C for $C < 0.05$ g/g. Hence, one may justifiably conclude that, here too, and independent of the non-attainment of final equilibrium, the relevant relaxation frequencies β^* are practically independent of the concentration, as long as the system remains well within the glassy state; and become increasingly concentration dependent as $T_g(C)$ is approached.

A more rigorous way to determine the value of β is to check first that the second-stage sorption rate conforms
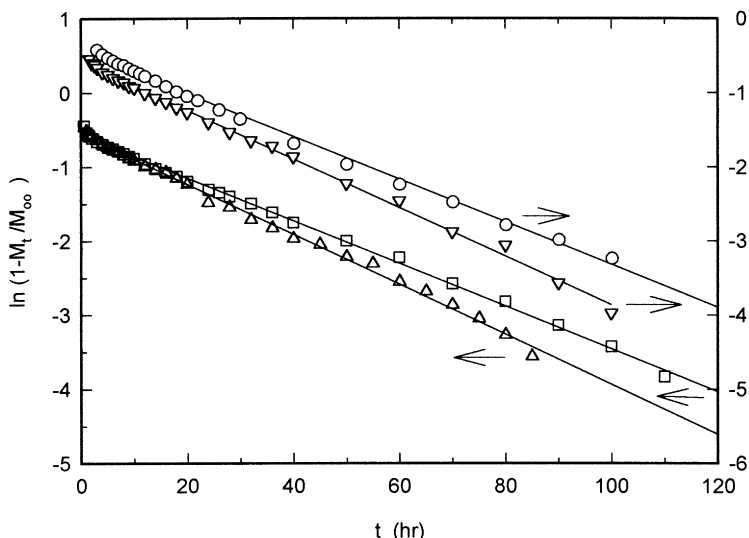
Fig. 7. First-order kinetic plots of the second stage of two-stage absorption runs, with $p_I \rightarrow p_F$ (Torr): $48 \rightarrow 58$, S1R3 ($\bigcirc$); $64 \rightarrow 78$, S2R3 ($\triangledown$); $78 \rightarrow 90$, S2R4 ($\square$); $80 \rightarrow 105$, S4R3 ($\triangledown$).

satisfactorily to first-order kinetics, namely

$$\partial C / \partial t = \beta (C_F - C_2) \qquad (4)$$

and then evaluate β from the slope of the appropriate first order plot. As shown in Fig. 7, our data conform reasonably well to first-order kinetics. The resulting values of β, which have been included in Fig. 6, do not differ materially from the corresponding β^* values. The said relaxation frequencies β also exhibit a weak dependence on magnitude of the concentration interval ΔC covered by the respective two-stage absorption experiments, as shown in Fig. 8.

The D_P and β^* values of Figs. 5 and 6, respectively, were used to calculate the corresponding parameter $\beta l^2/D$ for our as well as Kishimoto's, two-stage absorption curves. The gradual merging of the two stages as C_I increases observed

by Kishimoto et al., is reflected in the progressive increase of $\beta l^2/D$ from ~ 0.0075 at $C_I \sim 0.04$ g/g (which corresponds to a two-stage curve with well-separated two stages) to ~ 0.25 at $C_I \sim 0.092$ g/g (which corresponds to the last two-stage curve with partly overlapping first and second stages, observed before the transition to Fickian kinetics). On the other hand, the two-stage curves observed by us for C_I ranging from ~ 0.05 to ~ 0.11 g/g, are characterized by well-separated two stages with values of $\beta l^2/D \ll 1$, ranging from 0.0052 to 0.025.

4. Conclusions

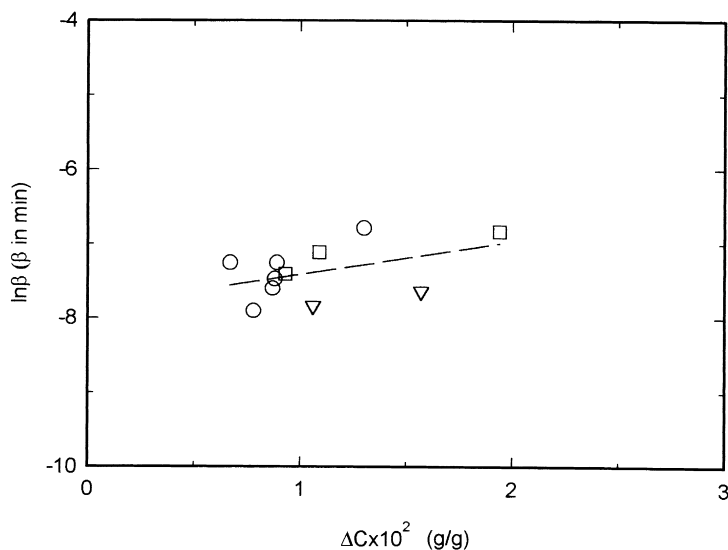The series of interval absorption M_t versus $t^{1/2}$ curves of

Fig. 8. Relaxation frequencies β deduced from the second stage of two-stage absorption runs versus the magnitude of concentration interval of the run $\Delta C = C_F - C_I$. Notations as in Fig. 6.

the PMMA–MAc system studied here, show the familiar progressive change from S-shaped at the low-, to two-stage at the high-concentration end. This behavior is usually interpreted uniformly in terms of slow viscous molecular relaxations of the polymer in response to penetrant-induced osmotic stresses. In line with this interpretation, two-stage desorption curves were also observed at the high-concentration end. In addition, kinetic analysis of the second stage of two-stage absorption curves has (in accordance with our previous results in this respect for cellulose acetate–acetone or methanol) shown good conformity to first-order kinetics, thus confirming the constitutive relation for the viscous relaxation process adopted in the relevant theoretical model [15] (cf. Eq. (4) above). However, comparison of the magnitude and concentration dependence of the sorption rates of the S-shaped M_t versus $t^{1/2}$ absorption curves observed at low concentrations, with the respective rates of the first and the second stage of two-stage absorption curves observed at higher concentrations, indicate that the former curves are diffusion-, rather than relaxation-controlled. This result points to differential swelling stresses, rather than viscous relaxation as the mechanism responsible for the S-shape of the absorption curves in the low C region, in line with our previous findings in the case of cellulose acetate–acetone or methanol.

An important finding of this work concerns the effect of polymer fine structure on non-Fickian sorption behavior. Thus, the PMMA–MAc system studied here was found to exhibit substantially different sorption isotherm, as well as much lower penetrant diffusion and polymer relaxation rates, relative to that studied by Kishimoto et al. [2]. The concentration dependence of the diffusion coefficient was found to be much the same and in keeping with the behavior predicted by a previous application of the Vrentas–Duda free volume theory to this system. However, the concentration dependence of the relaxation frequency observed by us was much smaller than that found by Kishimoto et al. We have shown that these differences in behavior can be understood in terms of the higher glass transition temperature $T_g(C)$ noted here; as a result of which the system studied by Kishimoto et al. undergoes glass transition in the upper region of the experimental concentration range, while our system remains glassy throughout.

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