

Temperature dependence of methanol transport in spherical PMMA beads

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The effect of temperature on the kinetics of methanol transport in PMMA has been investigated for the first time in spherical sample geometry over the temperature range of 25–50°C. The observed penetration of methanol in PMMA beads of 1.045 ± 0.03 mm diameter exhibits a geometry-dependent Case II transport behaviour up to 50°C. This is characterized by an induction period followed by an extended region of linear front penetration before an acceleration of front movement towards the centre. This front acceleration, being absent in sheet samples, was shown to be characteristic of the solvent penetration behaviour in spheres. The induction period has been observed to decrease, whereas the front velocity to increase, with increasing temperature, consistent with their known dependencies on the solvent diffusivity and the viscosity of the polymer glass. Both the induction time and the velocity of the methanol front are thermally activated, with apparent activation energies of $27.8 \text{ kcal mol}^{-1}$ and $26.4 \text{ kcal mol}^{-1}$, respectively. No further increase in the PMMA bead diameter has been observed after the penetrating methanol fronts have met at the centre, suggesting a negligible concentration gradient behind the Case II swelling front. In addition, the continuous increase of PMMA bead diameter during the induction period for methanol front penetration provides new supporting evidence for the existence of a Fickian precursor penetrating ahead of the sharp Case II front in the PMMA–methanol system.

(Keywords: sorption; swelling; Case II transport; penetrating front; temperature effect; geometry effect; PMMA beads; poly(methyl methacrylate); methanol)

INTRODUCTION

The sorption of methanol in glassy poly(methyl methacrylate) (PMMA) is known to exhibit Case II behaviour¹. This occurs when the rate of polymer relaxation in response to the penetrating solvent is slow and rate-limiting. In sheet specimens, the Case II swelling is characterized by either a linear weight-gain kinetics or a constant velocity at the penetrating front. Such anomalous solvent transport in the PMMA–methanol system has been investigated extensively by Thomas and Windle^{2–4}, who reported that, below 30°C, there exists a typical Case II swelling behaviour and there is a negligible solvent concentration gradient behind the sharp swelling front. They also modelled such Case II swelling process in terms of the viscous response of the polymer glass to the osmotic swelling pressure generated by the penetrating solvent. Recent results obtained by Hui *et al.*^{5,6} based on Rutherford backscattering spectrometry appear to verify the existence of various essential features of Case II transport as predicted by the model of Thomas and Windle, especially the Fickian precursor penetrating ahead of the sharp front and the induction period before establishing a constant rate of front movement. More recently, results obtained by other investigators^{7,8} suggest that the Case II behaviour in the PMMA–methanol system may exist up to the 40–50°C range.

An accelerated Case II behaviour known as Super Case II transport was first reported in film samples of polystyrene undergoing n-hexane sorption⁹. It was characterized by a distinct acceleration of sample weight gain near the end of a Case II sorption process. Such Super Case II transport behaviour has been interpreted to be a result of the acceleration of swelling fronts before they meet at the centre of the film sample. However, a direct observation of such front acceleration has not been documented with the corresponding weight gain results. In the case of methanol transport in PMMA, Super Case II behaviour has not been conclusively demonstrated¹⁰.

Since most of the experimental results documenting Case II solvent transport were based on sheet specimens, the role of sample geometry in the interpretation of transport kinetics has largely been overlooked. Thus, despite the well known effect of sample thickness on Case II transport^{11,12}, the effect of sample geometry on such swelling behaviour, particularly the swelling front movement, has not been fully recognized. The lack of such information in the past has led to some questionable interpretations and analyses of relevant sorption results. For example, the apparent acceleration of water swelling front movement in spherical gelatin beads was incorrectly identified as Super Case II transport¹³. In another case, a constant swelling front velocity was incorporated a

priori into a theoretical model¹⁴ to describe the weight-gain kinetics in both flat and spherical samples undergoing Case II sorption. Not surprisingly, such a model is incapable of predicting any changes in the swelling front movement due to sample geometry.

Recently, we have resolved the fundamental issue of whether a penetrating solvent front will maintain a constant rate throughout a sphere or a cylinder under conditions where the front penetrating behaviour in a sheet sample of identical polymer composition and comparable dimension is completely Case II¹⁵. Similar concerns on the effect of geometry in systems with known Fickian and non-Fickian sorption behaviour have also been addressed. Both the theoretical and experimental results of that study reveal that only the initial stage of the solvent penetration behaviour is independent of sample geometry. In addition, the apparent acceleration of solvent front penetration towards the core in spheres and cylinders has been shown to be a natural outcome of the radially symmetric geometry rather than a Super Case II behaviour, and it occurs independently of the transport mechanisms involved.

In this article, we report for the first time the temperature dependence of methanol transport in spherical PMMA beads. In addition to presenting evidence of a geometry-dependent Case II transport behaviour in such a PMMA-methanol system up to the 40–50°C range, the effect of temperature on the movement of methanol front in spherical PMMA beads and the apparent activation energies for both the induction time and the penetrating front velocity are also examined.

EXPERIMENTAL

Synthesis of polymer beads

PMMA beads were prepared by free radical suspension polymerization of freshly distilled methyl methacrylate at 70°C for 3 h using t-butyl peroxy-2-ethylhexanoate as the initiator and freshly precipitated Mg(OH)₂ as the suspending agent. After the completion of polymerization, concentrated HCl was added to remove the suspending agent, and these beads were filtered and extracted in a Soxhlet with methanol before being dried to a constant weight in a vacuum oven, typically at 70–80°C for 3–5 days. In the present study, these PMMA beads of average diameter 1.045 ± 0.03 mm were further annealed at 130°C for 3 h and cooled under ambient condition prior to each swelling experiment. These drying and annealing steps ensured a solvent-free condition in the present PMMA beads. Based on the intrinsic viscosity data in acetone obtained on a Ubbelohde viscometer, the average molecular weight for the present PMMA beads was estimated to be about 5.2×10^5 from the Mark-Houwink equation.

Swelling measurements

The swelling of PMMA beads by methanol was measured in a sealed cuvette immersed in a constant temperature water bath (Haake D8-G; accurate to $\pm 0.02^\circ\text{C}$). The penetrating front movement and the associated dimensional changes were observed with a Wild M420 stereomicroscope using a digital optical measuring accessory (Wild MMS 235; accurate to ± 0.001 mm).

RESULTS AND DISCUSSION

The dynamic swelling behaviour and transient dimensional changes of the present PMMA beads were investigated by following the progression of the methanol swelling front and the outer bead diameter at 25, 30, 40, and 50°C. In all cases, a sharp penetrating solvent front separating the swollen shell from the unpenetrated glassy core was clearly visible during methanol sorption. Figure 1 is a typical photograph of such methanol front penetration in a spherical PMMA bead. The temperature dependence of the methanol front movement in spherical PMMA beads is shown in Figures 2a and 2b for temperatures

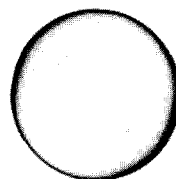


Figure 1 Photograph showing a typical methanol front penetration in spherical PMMA beads

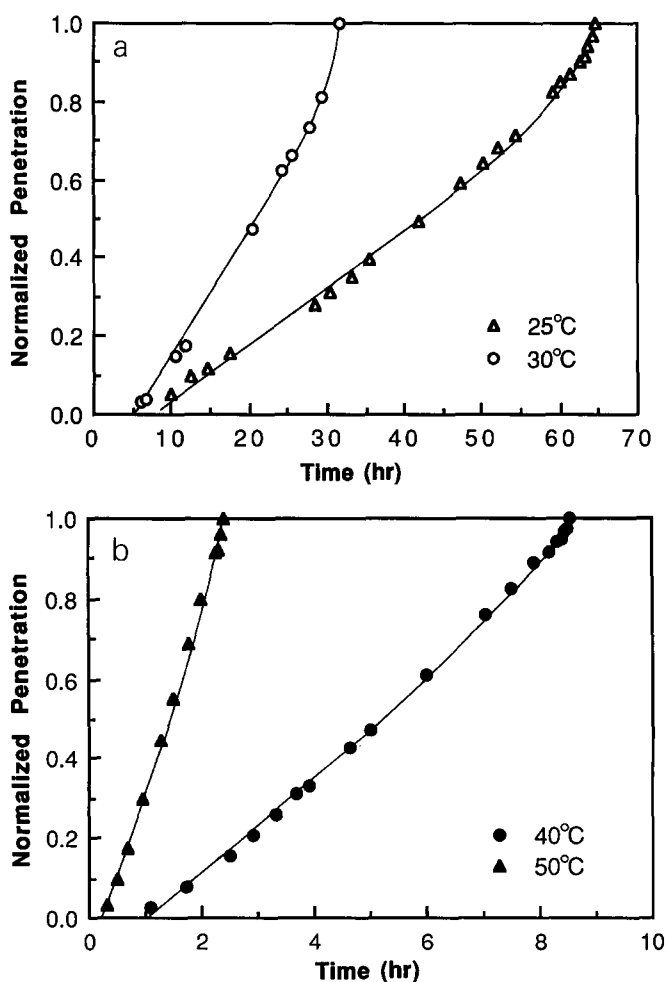


Figure 2 Effect of temperature on the methanol front penetration in spherical PMMA beads: (a) 25°C and 30°C; (b) 40°C and 50°C

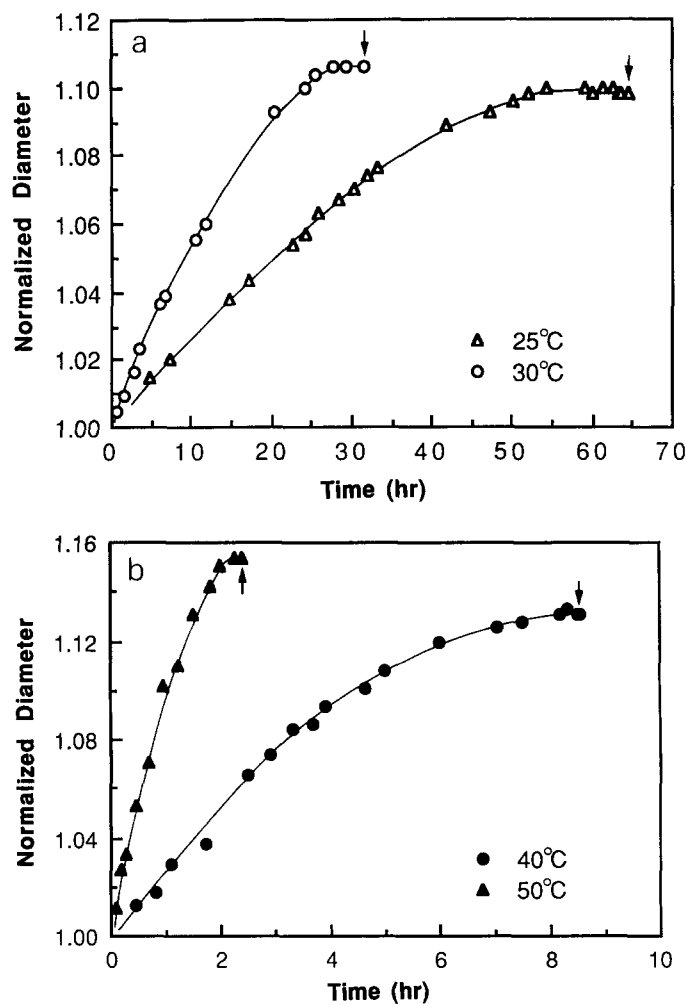


Figure 3 Effect of temperature on the dimensional changes in spherical PMMA beads, corresponding to the methanol front penetration (Figure 2: (a) 25°C and 30°C; (b) 40°C and 50°C. ↓: solvent fronts meet)

ranging from 25°C to 50°C, where the front penetration, defined as the thickness of the gel or swollen region, has been normalized to the overall penetration thickness. The corresponding transient dimensional changes in PMMA beads are presented in Figures 3a and 3b with the diameter normalized to the original bead size.

Several specific features of the observed dynamic swelling behaviour should be noted. It is evident from Figures 2a and 2b that, after a characteristic induction period, the penetration of methanol in PMMA beads proceeds linearly with time up to over 60% of the total penetration followed by an apparent acceleration of front movement towards the core at all the temperatures studied. These trends are in excellent agreement with the Case II front penetration behaviour predicted for spheres¹⁵. Thus, these results provide direct evidence of a Case II transport behaviour in the present PMMA-methanol system up to 50°C. The apparent acceleration of solvent front movement near the core has previously been shown to be a natural outcome of the spherical geometry rather than a Super Case II transport behaviour¹⁵. This latter aspect is further supported by Figures 3a and 3b, where the PMMA bead diameter is seen to have almost reached its final equilibrium value prior to the onset of front acceleration. As a result, the acceleration of penetrating front near the core does not lead to an accelerated methanol uptake as would be

expected in Super Case II sorption. In this case, the equilibrium PMMA bead diameter also increases with increasing temperature (see also Table 1). It should be noted that the lack of further increases in PMMA bead diameter after the penetrating methanol fronts have met suggests a negligible concentration gradient behind the swelling front, consistent with the findings of Thomas and Windle² on sheet specimens of PMMA.

The induction period before establishing a constant-rate front movement, as seen in Figures 2a and 2b, has been recognized as one of the most important features of Case II transport^{16,17}. It arises because the surface concentration of penetrant does not immediately reach an equilibrium value in a glassy polymer. Rather, a finite amount of time is required to reach a critical surface concentration before the Case II front develops. Since the induction time has been shown to depend only on the viscous (or creep) behaviour of the polymer glass⁴, its temperature dependence should follow similar behaviour as that of the viscous component in the Case II transport process. Indeed, the induction time is observed to decrease with increasing temperature (Figures 2a and 2b). On the other hand, the front velocity has been shown to scale with the square root of the ratio of the solvent diffusivity to the polymer flow viscosity in the glassy state^{4,17}. Therefore, it is reasonable that the front velocity is observed to increase with temperature. Since the total sorption time required for the penetrating methanol fronts to meet at the centre of a PMMA bead is a sum of the induction time and the time needed for the sharp fronts to traverse from the surface to the centre of the bead, it is expected that this total sorption time also decreases with increasing temperature as shown in Figures 2a and 2b.

The measured temperature dependence of these parameters, including the induction time, total sorption time, front velocity and the equilibrium bead diameter, are summarized in Table 1. These results suggest that both the induction time and the velocity of the methanol front are thermally activated. Arrhenius plots for these two parameters, as shown in Figures 4a and 4b, yield an apparent activation energy of 27.8 kcal mol⁻¹ for the induction time, and 26.4 kcal mol⁻¹ for the front velocity in the present PMMA-methanol system. These are well within the range of activation energy values reported for creep in glassy PMMA¹⁸ and are similar to those reported by Thomas and Windle⁴ (i.e. 28.7 kcal mol⁻¹ for the induction time and 27.0 kcal mol⁻¹ for the front velocity).

Another important feature of Case II transport is the Fickian precursor penetrating ahead of the sharp front. This aspect has been verified by Hui *et al.*^{5,6}, who measured concentration profiles of iodohexane diffusing into polystyrene using Rutherford backscattering spectrometry. Although this feature was originally

Table 1 Characteristic parameters for methanol transport in spherical PMMA beads

Temp. (°C)	Induction time (h)	Total sorption time (h)	Velocity of Case II front (μm/h)	Normalized eq. diameter
25	8.5	64.5	8.7	1.100
30	5.0	31.4	18.2	1.106
40	1.0	8.5	74.4	1.131
50	0.23	2.4	274.6	1.154

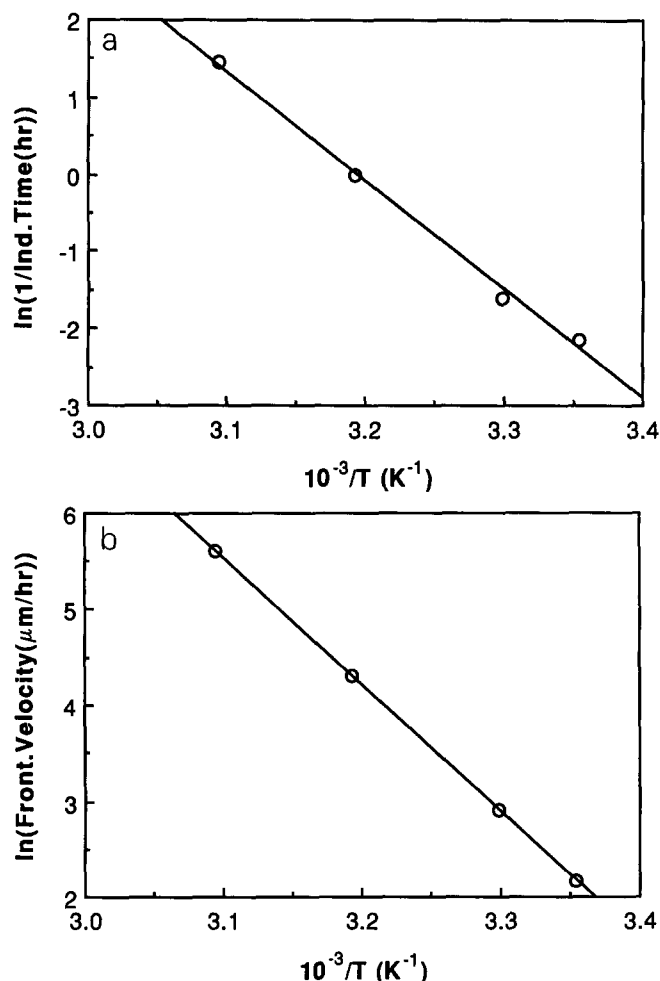


Figure 4 Arrhenius plots, showing the temperature dependence of (a) induction time and (b) penetrating front velocity, for the methanol transport in spherical PMMA beads

predicted by Thomas and Windle for the PMMA–methanol system, direct confirmation of methanol diffusion ahead of the penetrating front in PMMA is still lacking. In the present study, the ability to monitor simultaneous changes in the penetrating front position and the bead diameter has resulted in new supporting evidence for the existence of such a Fickian precursor of methanol in PMMA. For example, it is clear that, despite the induction period required to build up a critical surface concentration of methanol before Case II penetration begins (Figures 2a and 2b), the corresponding sizes of these PMMA beads continue to increase during this induction period without any noticeable delay (Figures 3a and 3b). This translates to a continuous weight gain, which is directly attributable to the continuous penetration of the Fickian precursor of methanol during the induction period.

CONCLUSION

The temperature dependence of methanol transport in spherical PMMA beads has been studied over the temperature range of 25–50°C. The observed methanol penetration in PMMA beads of 1.045 ± 0.03 mm diameter

exhibits a geometry-dependent Case II transport behaviour up to 50°C. This is characterized by an induction period followed by a major region of linear front penetration before an accelerated front movement towards the core, in excellent agreement with the predicted Case II front penetration behaviour in spheres. The induction period has been observed to decrease, whereas the front velocity to increase, with increasing temperatures, consistent with their known dependencies on the solvent diffusivity and the viscosity of the polymer glass. Both the induction time and the velocity of the methanol front are thermally activated, with apparent activation energies of $27.8 \text{ kcal mol}^{-1}$ and $26.4 \text{ kcal mol}^{-1}$, respectively. These values are well within the range of activation energy values reported for creep in glassy PMMA and are similar to those reported by Thomas and Windle.

In the present study, the ability to monitor simultaneous changes in the penetrating front position and the bead diameter has resulted in new supporting evidence for various essential features of the Case II transport. For example, the lack of further increases in PMMA bead size after the methanol fronts have met suggests a negligible concentration gradient behind the sharp swelling front. Similarly, the observation of a continuous increase of PMMA bead size during the induction period for methanol front penetration supports the existence of a Fickian precursor penetrating ahead of the Case II front in the PMMA–methanol system.

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