

Water sorption of poly(methyl methacrylate): 1. Effects of molecular weight

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A sample of poly(methyl methacrylate), PMMA, of low molecular weight (10^4 D) took up less water (1.2%) than samples of high molecular weight (10^6 D: 2.0%). In contrast, the uptake of water was only slightly dependent on molecular weight for samples made by radiolysis in the glassy state. It is concluded that uptake of water depends on the closer molecular packing possible in polymers of lower molecular weight. However during radiolysis in the glassy state, this potential is not fully realized because of limited mobility. In more detail, the small changes in the diffusion coefficient and uptake of water in irradiated samples were consistent with closer packing in samples with $M_n \leq 10000$. It is concluded that molecular packing proceeds more readily below the critical molecular weight for formation of an entangled network.

(Keywords: poly(methyl methacrylate); water sorption; diffusion of water; molecular weight; radiolysis; molecular packing; entanglements)

INTRODUCTION

Relatively little work has been done on the influence of molecular weight on the water sorption of polymers¹⁻⁴. Sheppard and Newsome noted that 'There is some evidence, which will not be stressed at this time, that the moisture regain, or water absorption, of cellulose is progressively lowered by treatments which degrade the cellulose'. Degradation was monitored by measurements of solution viscosity^{5,6}. Independently, Kargin pointed out that a decrease in molecular weight might result in closer molecular packing in the glassy state and hence to a lower sorptive capacity. As an extreme case, he contrasted the sorption of water vapour by glasses of cellulose and by crystalline glucose. At low vapour pressures, the polysaccharide takes up water into pores whereas the close-packed monosaccharide does not. Such a difference in sorptive capacity is not limited to water as penetrant and a similar contrast was demonstrated on contacting ethyl benzene vapour with high polymers and with oligomers of styrene⁷.

In respect of the kinetics of sorption Rogers cited data showing that, generally, 'The molecular weight of a polymer has been found to have little effect on the rates of diffusion and permeation'⁸⁻¹¹.

The purpose of the present work is to study the influence of molecular weight on the sorption of water by glassy poly(methyl methacrylate), PMMA. Previously Brauer and Sweeney found water sorption to be little influenced by molecular weight in the range $0.18-1.56 \times 10^6$ D, at temperatures from 4 to 60°C⁹. Bueche found water diffusion to be independent of molecular weight in the range investigated, from $0.2-1.0 \times 10^6$ D¹⁰. In order to extend this previous work to much lower

molecular weights, samples of high molecular weight PMMA were exposed to γ -rays. This results in random fracture of the macromolecular backbone yet with negligible concurrent crosslinking¹¹. Previously this technique has been used in studies of the influence of molecular weight of PMMA on fracture surface energy¹², fracture morphology¹³, glass transition temperature^{14,15} and tensile strength¹⁶.

EXPERIMENTAL

A PMMA powder described as of 'average molecular weight 12000' (Aldrich, Milwaukee, WI) was heated at 65°C for several weeks in vacuum. After this treatment the powder no longer smelt of residual monomer or transfer agent. Glass transition temperatures were determined by differential scanning calorimetry, at 20°C/min, using a DuPont 990 Thermal Analyzer: before heating, $T_g = 80^\circ\text{C}$; after heating, $T_g = 82^\circ\text{C}$.

Another PMMA powder from Aldrich, provided as a secondary molecular weight standard of $M_w = 60\,600$ and $M_n = 33\,200$, was heated at 75°C for 6 h in vacuum.

The thinnest available sheets of PMMA were used in order to reduce the time to water saturation to a few weeks (1/32 inch Plexiglas, Rohm and Haas Company, Philadelphia, PA). Subsequently, this material was withdrawn from the market and further experiments had to be curtailed. An approximate value of $M_n = 6 \times 10^5$ was calculated from solution viscosity data, assuming a random molecular weight distribution: $T_g = 103^\circ\text{C}$. Samples of dimensions $7.5\text{ cm} \times 2.5\text{ cm} \times 0.07\text{ cm}$ were machined and exposed in air to γ -rays from a ^{137}Cs source: the dose rate was 0.8 Mrad/hour; ambient

Table 1 Approximate values of M_n and T_g for irradiated samples of PMMA

Dose (Mrad)	0	5.7	17.7	36.6	55.5	74.7	93.9
M_n (D)	6×10^5	8.4×10^4	3.0×10^4	1.5×10^4	9.8×10^3	7.3×10^3	5.9×10^3
T_g (°C)	103	—	94	87	81	75	70

temperature = 35°C. After irradiation, samples were degassed at room temperature, in vacuum, for 1 week. Approximate values of M_n were calculated assuming 1.7 random main chain fractures per 100 eV energy deposition ($1 \text{ Mrad} = 6 \times 10^{19} \text{ eV/g}$)¹¹. Approximate values of T_g were estimated from a pertinent experimental relationship between T_g and radiation dose, in the range which allows interpolation¹⁵ (Table 1).

Attempts to prepare sheets from solutions of the lowest molecular weight (12 000 D) were unsuccessful because cracking occurred during the evaporation of solvent. Instead, sheets were made by compression moulding of the powder between tin foils. The mould cavity (diameter = 3.8 cm; thickness = 0.1 cm) was slightly overfilled with powder and then heated to 150°C. After many closures, to allow air to escape, the mould was kept at 150°C under a load of 1000 lb for 20 min. The temperature was allowed to drop to 90°C, under load, and the sample quenched in water. This procedure gave flawless transparent samples with minimal crack formation. In some cases, fortuitously, a single circular crack was formed which provided samples with a diameter only slightly smaller than the cavity diameter; such samples were used for studies of water sorption.

A solution of the powder of highly molecular weight ($M_n = 33\,200 \text{ D}$) in methylene chloride was strained through lens tissue paper. Portions (6 ml) were allowed to evaporate very slowly (many weeks) from aluminium trays. Resultant films retained sufficient solvent to allow trimming to provide flawless films of dimensions ca. 6 cm × 1.5 cm × 0.035 cm. The trimmed films were heated at 65°C for several weeks in vacuum to remove solvent.

All samples were dried to constant weight (W_0) over anhydrous calcium sulphate (Drierite, W. R. Hammond, Ohio) in air. The thickness, $2l$, was taken as the mean of 8 micrometer readings. Dried samples were immersed in distilled water at $24.2 \pm 0.7^\circ\text{C}$. They were periodically removed, mopped dry, and weighed (W_t) using a Mettler Digital Balance of precision $\pm 0.05 \text{ mg}$ up to a limiting value (W_∞). A few samples were studied further in a desorption cycle over the same desiccant.

A diffusion coefficient, D , was obtained by reference to Stefan's approximation of the appropriate solution of Ficks' law for plane sheet geometry (equation (1)): $M_t = W_t - W_0$; $M_\infty = W_\infty - W_0$ ¹⁷.

$$\frac{M_t}{M_\infty} = 2 \left(\frac{Dt}{\pi l^2} \right)^{1/2} \quad (1)$$

Density measurements were made by Archimedes' method¹⁸.

RESULTS

Sorption data for moulded samples of low molecular weight (12 000 D) conform approximately to equation (1) (Figure 1). One sample, designated by the open circles,

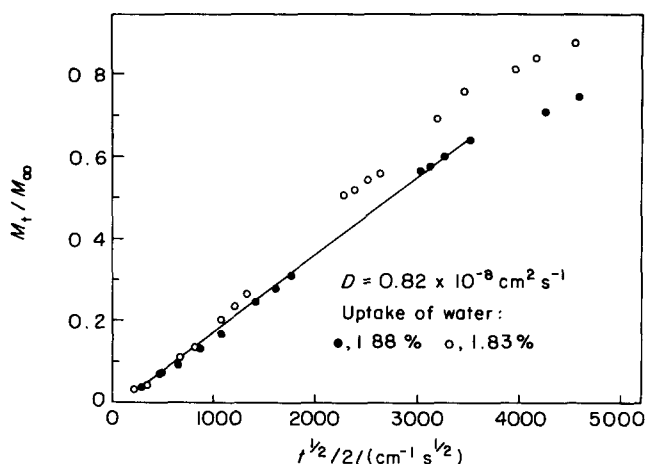


Figure 1 Sorption kinetics of moulded specimens ($M = 12\,000 \text{ D}$). Crack formation was observed in one of the specimens (○) in the course of water sorption. Thickness: ○, 0.1280 cm; ●, 0.0967 cm

departed from the expected linearity of Stefan's approximation, which holds up to values of M_t/M_∞ of about 0.5. It is believed that this was due to initiation and growth of a crack which eventually caused separation of the sample into two fragments. The initial slope selected to represent both sets of data is shown by the full line and corresponds to a value of $D = 0.82 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. Values obtained for water uptake, referred to initial dry weight, of the two samples were 1.88 and 1.83 wt %. The density of the wet sample (1.1852 g cm^{-3}) was only slightly greater than that of the dry sample (1.1803 g cm^{-3}).

After storage in closed bottles for one year all the moulded samples were found to be turbid. Examination under an optical microscope revealed a network of microcracks. The moulding conditions had been chosen carefully so as to effect complete coalescence of the particles of PMMA in the powder^{19,20}. For this reason it is believed that microcracking is not associated with exfoliation of particles, such a seems to have occurred in some of the experiments of Brauer and Sweeney⁹.

Changes in weight of films of PMMA ($M_n = 33\,200 \text{ D}$) cast from methylene chloride pass through a maximum value in the course of prolonged immersion in water (Figure 2). Presumably, despite storage for several further weeks after formation of a brittle film, residual solvent remains which subsequently leaches out concurrently with water sorption. However, residual solvent can be removed effectively as shown by a limiting, plateau, value of weight increase which is little changed by variation of the time of preheating in vacuum. The limiting uptake of water is about 1.2% (Figure 2). The kinetics of sorption conform to equation (1) but subsequent desorption is distinctly anomalous (Figure 3). In a reversal of usual behaviour for PMMA^{10,18}, the rate of desorption is not greater than the rate of sorption. Another anomaly is an abrupt increase in the rate of desorption which was observed to correspond to onset of a turbidity which

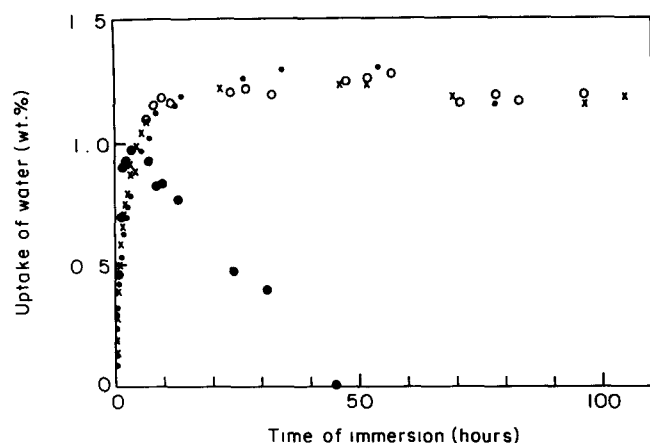


Figure 2 Uptake of water of specimens cast from solution ($M_w = 60\,600$; $M_n = 33\,200$). Thickness range = 0.035–0.045 cm. Drying conditions prior to test: ●, in air at room temperature; other specimens in vacuum at 65°C–75°C for several days

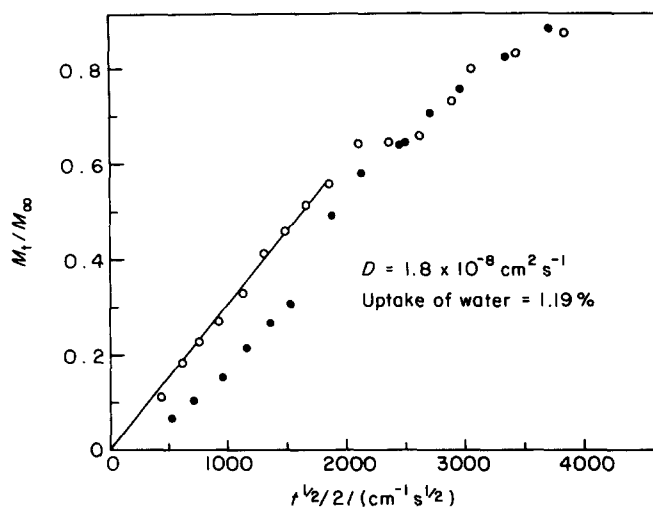


Figure 3 Sorption kinetics of specimens cast from solution ($M_w = 60\,000$). Turbidity observed in the course of run 2 (desorption, ●); onset near $M_t/M_\infty = 0.3$. Thickness: 0.03625 cm

became progressively more marked with further drying. The sample resumed its transparency on saturation with water. Presumably voids are formed which are sufficiently large to cause turbidity ($> 300 \text{ \AA}$) but these can be filled with water.

Because of the difficulties encountered with polymers of low molecular weight, attention was concentrated on the more convenient radiation technique. Good conformity to equation (1) and reproducibility of data was obtained for all samples, as exemplified by typical results in Figure 4. The dependence of values of water uptake and diffusion coefficient on radiation dose is shown in Figure 5. After the sorption experiments, samples were dried in vacuum and then heated for several days at 65°C. Unfortunately, this resulted in considerable bubble formation in samples which had been irradiated.

DISCUSSION

It is difficult to interpret the water sorption of samples of PMMA of low molecular weight because volumetric changes, though small, can cause microcracking or void formation. Such changes might increase both diffusion

and uptake of water. Nevertheless, there are observations from uptake data which are consistent with the occurrence of closer molecular packing. First, samples of low molecular weight ($M_w = 60\,600$, $M_n = 33\,200$) take up only 1.2% water, as compared with samples of high molecular weight ($M_w > 10^6$) which take up to 2.0%^{9,18}. Second, although the other sample of low molecular weight (12 000) took up as much as 1.8–1.9% water, yet it differs from high molecular weight PMMA in increasing only slightly in density on saturation. In the case of high molecular weight PMMA it was calculated, from changes in density, that the increase in volume accounted for about only half the uptake of water. The discrepancy was attributed to accommodation of about 50% of the water uptake in microvoids¹⁸. The same line of reasoning suggests that only 15% water is accommodated in microvoids in the low molecular weight sample. A decreased microvoid volume would be consistent with closer molecular packing. For an explicit example of the way in which a penetrant molecule might be accommodated in a microvoid the reader is referred to the work of Barrer *et al.* on gas sorption by glassy ethyl cellulose which, like PMMA, has stiff and bulky macromolecules²¹. Their depiction of a penetrant

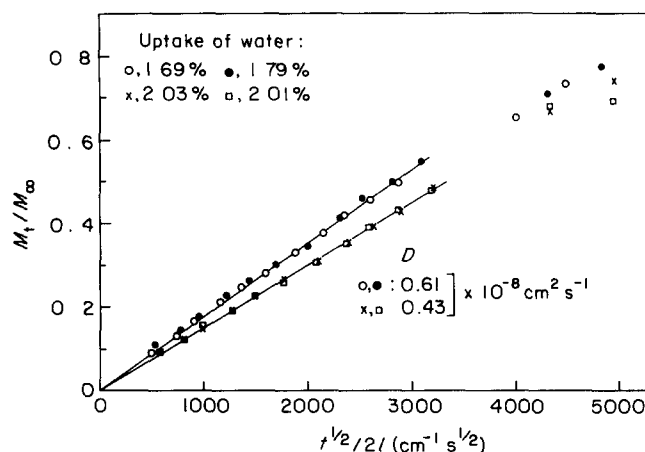


Figure 4 Sorption kinetics of specimens cut from proprietary sheets. Unirradiated specimens: ○ (0.07467 cm), ● (0.06967 cm). Irradiated specimens (dose = 55.5 Mrad): □ (0.06775 cm), × (0.0679 cm)

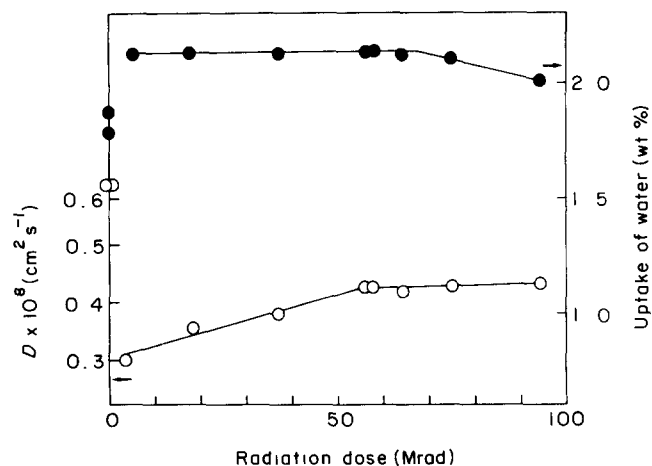


Figure 5 Dependence of diffusion coefficient and uptake of water on radiation dose. ○, diffusion coefficient (D); ●, uptake of water. Thickness: 0.05625–0.08017 cm

accommodation site (Figure 4 of ref. 21) can be regarded as one example of an entanglement site mentioned below.

The influence of radiation dose on water sorption can be divided into three regions. The marked changes in both the rate and extent of water uptake after a dose as little as 5.7 Mrad may be attributed to radiation-induced polymerization of small amounts of residual monomer (ca. 1%) which remain in many commercially available cast sheets of PMMA. Residual monomer is expected to act as a plasticizer so that its removal by irradiation might account for a decrease in D , as in Figure 5. It is more difficult to rationalize the accompanying increase in uptake of water, and the effect of relatively small doses of radiation calls for further investigation. However, given the present focus of attention, it will suffice to take the position that the changes in region 1 are too marked to be attributed to relatively small changes in molecular weight (c.f. Table 1).

Regions 2 and 3 are distinguished by a change of slope, near 55 Mrad, which is more evident for plots of D . A dose of 55 Mrad is calculated to reduce the molecular weight to about $M_n = 10000$ (Table 1). This, for PMMA, is the entanglement molecular weight, M_e^{22} , at which some physical properties change abruptly when plotted against molecular weight¹²⁻¹⁶. Molecular packing should be favoured especially below M_e , but this potential is but little realized as judged by Figure 5. This may be because of limited macromolecular mobility in the glassy state, at least 35° below T_g (Table 1). However there is the possibility of some mobility, as judged by experiments in which the creep rate of glassy polymers, including PMMA, was found to increase during irradiation²³.

In region 2 ($M > M_e$; $55 > R > 5.7$ Mrad) a dominant competing process must be invoked to account for an increase in D with radiation dose. It is suggested that water diffusion increases because of the increase in free volume associated with chain ends formed by radiation-induced fracture. Previously a suggestion of this kind was made to account for the observation that gas permeability increases as a result of irradiating PMMA²⁴. Presumably in region 3 the opposing influences on D of chain ends and entanglements are compensatory.

CONCLUSIONS

(1) Samples of PMMA of low molecular weight ($10^4 D$) may take up less water (1.2 wt%) than samples of normally high molecular weight ($10^6 D$: 2.0 wt%).

(2) From density changes accompanying water sorption it is estimated that a low molecular weight sample accommodated only 15% water in microvoids, as compared with 50% for samples of high molecular weight.

(3) Conclusions (1) and (2) are consistent with the hypothesis that, in glassy polymers, closer molecular

packing may be effected in samples of low molecular weight.

(4) Prolonged exposure of PMMA to γ -rays results in great decreases in molecular weight, yet changes in water sorption are quite small. This is interpreted to mean that close molecular packing, which is difficult to realize in the glassy state, is the primary factor affecting water sorption rather than molecular weight *per se*.

(5) Plots of diffusion coefficient and uptake of water versus radiation dose exhibit a change in slope at $M_n = 10000$. This is interpreted to mean that molecular packing occurs more readily below the critical molecular weight required to form an entangled network.

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