The imbibition of carbon disulphide by poly(methyl methacrylate) latex particles†

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A light scattering study of the imbibition of carbon disulphide by poly(methyl methacrylate) latex particles is presented. It is shown that, by monitoring the time dependence of the scattered light intensity at a fixed angle, it is possible to determine penetrant diffusion coefficients and polymer segmental relaxation constants using a two stage model. It is found that the penetrant diffusion coefficients are typical of those for diffusion in glassy polymers and the segmental relaxation constants are independent of colloid particle size.

(Keywords: polymer latices; light scattering; sorption kinetics; diffusion; segmental relaxations)

INTRODUCTION

The swelling of polymers caused by the imbibition of penetrant molecules is an interesting and important phenomenon and polymer latices provide useful model systems for studying the kinetics and mechanism of this process. Polymer latex particles are of uniform size and usually have spherical geometry. As a consequence, it is possible to describe the diffusion of penetrant molecules into (or out of) the polymer particles using relatively simple expressions[1]. More importantly however, because of the relatively short path along which the penetrant molecules diffuse (roughly the diameter of the latex particle), diffusion equilibrium is reached quickly. Thus, a uniform concentration of penetrant is rapidly established throughout the whole of the polymer particle. This eliminates the possibility of Case II or anomalous diffusion, and consequently the data analysis is greatly simplified[2].

It is possible to use radiation scattering to study the process. This is a non-intrusive technique and both neutron[3] and light scattering[4,5] have been used.

In this paper, a light scattering study of the imbibition of carbon disulphide by poly(methyl methacrylate) latices is reported. This is an important system which finds many applications. For example, concentrated dispersions of these latices have been studied by light scattering and the time-average interparticle structure factor has been measured[6]. In addition, the wavevector dependent diffusion coefficient has been studied[7,8].

In all of these experiments, CS_2 was used in a binary solvent mixture in order to match the refractive index of the dispersion medium with that of the dispersed particles. In this way, it was possible to eliminate the complicating experimental problem of multiple scattering. However, this paper illustrates that the use of CS_2 as a cosolvent can lead to penetration of the poly(methyl methacrylate) latex particles.

EXPERIMENTAL

Materials

Hexane and dodecane were purchased from BDH Ltd. All other materials were kindly supplied by ICI Paints Division, Slough. The stabilizer was supplied as a solution in a low boiling aliphatic hydrocarbon ester mixture.

Preparation of PMMA latices

Polymer latices were prepared by dispersion polymerization[9]. During the course of the present work three latices were studied; their particle sizes are listed in *Table 1*. The latex preparation was as follows: azo-bis-isobutyronitrile was dissolved in *ca.* 5 cm^3 of monomer and the stabilizer solution was then mixed with the remaining monomer. These solutions, together with the octyl mercaptan and methacrylic acid were added to a round bottom flask immersed in an oil bath and fitted with an overhead stirrer and a dropping funnel. The remaining reactants were added and the reaction mixture was maintained at 80°C for *ca.* 2 h. After this time, the reaction mixture had become highly turbid indicating the presence of colloidal particles. These colloidal particles were stable against coagulation owing to the physical adsorption of the graft copolymer.

The stabilizer used was a comb-like graft copolymer, with a backbone of methyl methacrylate and glycidyl methacrylate and 'teeth' of poly(12-hydroxystearic acid). The amphipathic nature of the copolymer resulted in its adsorption onto the latex particle surface. However, to ensure stability the stabilizer was chemically locked onto the particle surface by an esterification reaction. The base catalyst, dimethyl ethanolamine, was added to the reaction mixture (0.2 wt %) and the mixture heated to *ca.* 120°C for *ca.* 3 h. During this stage of the preparation the hexane was removed by distillation and replaced by an equal volume of dodecane. As a check for completion of the reaction, a small aliquot of the reaction mixture was removed and added to a small volume of toluene. When the latex appeared to dissolve but was recovered on the addition of an excess of dodecane indicating that

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Table 1 Properties of the three systems studied

Latex	Diameter (μm)	Latex concentration (g cm^{-3})
L1	0.166	0.05
L2	1.20	0.088
L3	0.34	0.03

extensive crosslinking had occurred at the surface of the particles it was concluded that the reaction was complete. Precipitation of the polymer would have indicated inadequate surface crosslinking and hence inadequate chemical bonding of the stabilizer onto the particle surface.

After cooling, the dispersion medium was changed from dodecane to dekalin by centrifugation of the particles (typically 2 h at *ca.* 15000 rpm in a MSE high speed centrifuge), with exchange of the supernatant and subsequent redispersion in the new solvent. The process was repeated at least twice to ensure that unused reactants were removed.

The latices were filtered through sintered glass filters to remove any extraneous dust particles.

Particle size determination

The particle size was determined by light scattering. A FORTRAN computer program was written to calculate the Rayleigh ratio for a dispersion of concentric sphere particles using the full electromagnetic solution of the problem[10]. Knowing the necessary refractive indices, i.e. particle core, shell and solvent, it was possible to fit the experimental data, obtained from a dilute dispersion in dekalin, by varying the particle dimensions. The experimental Rayleigh ratio was determined as a function of scattering angle using a Brice Phoenix Universal Light Scattering Photometer, Series 2000 as has been previously described[11]. Before the measurements were made the angular alignment of the instrument was checked. The raw data were converted into absolute values using benzene as a standard and correcting for: variation in scattering volume with angle; attenuation of the light beam as it traversed the cell; refraction of the emergent rays and the scattering by the background solvent. All measurements were made at room temperature (*ca.* 18°C).

Light scattering measurements

The intensity of the light scattered by a dispersion of polymer particles was measured as a function of time at a fixed angle. A stop watch was used to monitor the time and after the addition of CS_2 readings were taken every half minute for the first twenty minutes and then every 5 min. The intensity at zero time was obtained by extrapolating the short time data back to the origin.

The latices were dispersed in dekalin and the addition of CS_2 was made in a dust free cabinet. The physical process of adding the CS_2 to the samples excluded a short time period from the light scattering measurements. That is, to ensure complete mixing of the dekalin and CS_2 the sample was shaken vigorously before being transferred to the Brice Phoenix instrument. The whole process, from the beginning of the CS_2 addition to taking the first measurement, took about 1 to $1\frac{1}{2}$ min. This time interval was thus precluded from experimental observation.

The experiment was stopped when there was little further change in the scattered intensity with time.

THEORY

Light scattering analysis

When the refractive index of a particle, n_p, is very close to that of the solvent within which it is dispersed, n_0, the intensity of the scattered light follows the form[12]

$$I_{90}(t) \sim (n_p^2(t) - n_0^2(t))^2 V_p^2(t) \tag{1}$$

where $I_{90}(t)$ is defined as the time dependent scattered intensity measured at a fixed scattering angle of 90° and $(n_p^2(t) - n_0^2(t))$ is the time dependent refractive index difference between the particle and the solvent. $V_p(t)$ is the time dependent particle volume.

From equation (1) it follows that

$$[I_{90}(t)]^{1/2} \sim |n_p^2(t) - n_0^2(t)| V_p(t) \tag{2}$$

Now we define

$$v_t = \frac{[I_{90}(t)]^{1/2} - [I_{90}(0)]^{1/2}}{[I_{90}(\infty)]^{1/2} - [I_{90}(0)]^{1/2}} \tag{3}$$

where $I_{90}(\infty)$ is the equilibrium (long time) value of the scattered intensity and $I_{90}(0)$ is the scattered intensity at $t = 0$.

If we assume a small change in particle volume then the change in scattered intensity, or equivalently v_t, will mainly be due to the change in particle refractive index, assuming n_0 will be approximately constant. Since the change in refractive index will be proportional to the mass transfer we can assume that v_t reflects the mass uptake process.

Temporal separation of the diffusion-relaxation process

The imbibition of small molecules by a glassy polymer involves Fickian diffusion of the small molecules into the polymer matrix. This concentration gradient driven diffusion results in penetrant molecules occupying the available free volume frozen in the glassy polymer matrix. The occupancy of the free volume causes the polymer chains to redistribute themselves in an attempt to relieve the swelling stress and to attain their new equilibrium state. These polymer relaxations involve slow, large scale segmental motion.

Thus the imbibition of solvent by a latex particle is viewed as involving Fickian diffusion of the imbibing molecules, coupled with large scale segmental relaxations of the glassy polymer. For relatively small latex particles, these two stages can be considered as occurring independently. This is because the Fickian diffusion occurs on a time scale much shorter than that of the segmental relaxations. The characteristic time scale for Fickian diffusion is directly proportional to the particle diameter[1]. Thus, the Fickian diffusion is considered to be complete before there is any relaxation of the polymer segments. As a consequence, it is possible to separate the two contributions to the sorption process. This is the basis of a model due to Berens and Hopfenberg[13,14]. This model expresses the amount of sorptive uptake at a time t, M_t, relative to the amount of sorption at infinite time, i.e. equilibrium, M_∞, as the sum of contributions from

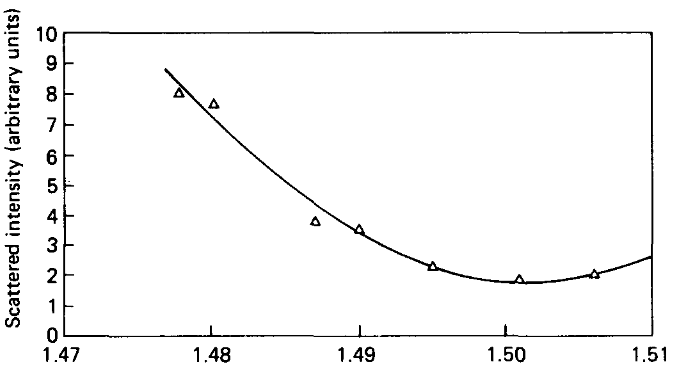

Figure 1 Intensity of light scattered as a function of solvent refractive index for polymer latex particles dispersed in dekalin/CS_2 mixed solvents

Fickian diffusion and a first order relaxation process. The resulting expression is

$$M_t/M_\infty = 1-\phi_F\left\{(6/\pi^2)\sum_{n=1}^{\infty}(1/n^2)\exp(-n^2k_Ft)\right\} - \phi_R\exp(-k_Rt) \qquad (4)$$

where ϕ_F and ϕ_R are the fractional contributions to the sorption process due to Fickian diffusion and relaxation processes respectively. k_R is a first order relaxation constant and k_F is given by

$$k_F = 4\pi^2D/d^2 \qquad (5)$$

where d is the particle diameter and D is the diffusion coefficient. To exploit this model equation (4) is re-written in the following form:

$$v_t = 1-\phi_F\left\{(6/\pi^2)\sum_{n=1}^{\infty}(1/n^2)\exp(-n^2k_Ft)\right\} - \phi_R\exp(-k_Rt) \qquad (6)$$

where v_t is given by equation (3).

For long times, equation (6) can be written as

$$(1-v_t) \sim \phi_R\exp(-k_Rt) \qquad (7)$$

and

$$-\ln(1-v_1) \sim \ln\phi_R + k_Rt \qquad (8)$$

Hence, by plotting the experimental data according to equation (8), i.e. as $-\ln(1-v_t)$ against t, it is possible to determine k_R and ϕ_R.

EXPERIMENTAL EVIDENCE FOR THE SORPTION OF CS_2 BY PMMA LATEX PARTICLES

Optical matching of PMMA latices in dekalin/CS_2 mixed solvents

It is possible to determine the refractive index of colloidal particles by varying the refractive index of the solvent in which they are dispersed. When the refractive index of the solvent is equal to that of the dispersed particles the intensity of the scattered light is at its minimum value.

Figure 1 shows the results obtained from a series of experiments using the latex L2 dispersed in solvents of varying proportions of dekalin and CS_2. From these data it is apparent that a minimum in the scattered intensity occurs at a solvent refractive index of *ca.* 1.502.

The latex L2 has a core diameter of 1.20 μm and an absorbed layer thickness of *ca.* 9 nm. Thus, to a very good approximation, the refractive index of the latex particles can be assumed to be equal to that of bulk PMMA. At the wavelength of the incident light used in the experiments (546 nm) the refractive index of PMMA is 1.493.[15]

The fact that the average value of the refractive index of the particles was found to be greater than that for PMMA was interpreted as indicating that the CS_2 had penetrated into the PMMA core of the particles, thus raising its refractive index.

Time dependent scattered light intensity

Figure 2 shows the time dependence of the scattered light intensity. It can be seen that it changes over a relatively long period and can increase considerably from its initial value.

The experimental data shown in *Figure 2* were plotted according to equation (8) so that k_R and ϕ_R and consequently ϕ_F (since $\phi_R + \phi_F = 1$) could be determined. Knowing these three parameters in the theoretical model, the only unknown parameter was the diffusion coefficient, which was determined by fitting the original data, plotted in reduced form, with the theoretical model.

The logarithmic plots of $(1-v_t)$ against time are shown in *Figure 3*. From the long time linear region ($\geqslant 25$ min) the quantities k_R and ϕ_R were determined. Using these values (and those for ϕ_F) it was possible to fit the reduced experimental data with the theoretical model by varying the diffusion coefficient only. These fits are shown in *Figures 4*, *5* and *6* for the three latices studied and the fitting parameters used are summarized in *Table 2*.

D.s.c. measurements

A sample of a polymer latex previously unexposed to CS_2 and prepared in exactly the same manner as the

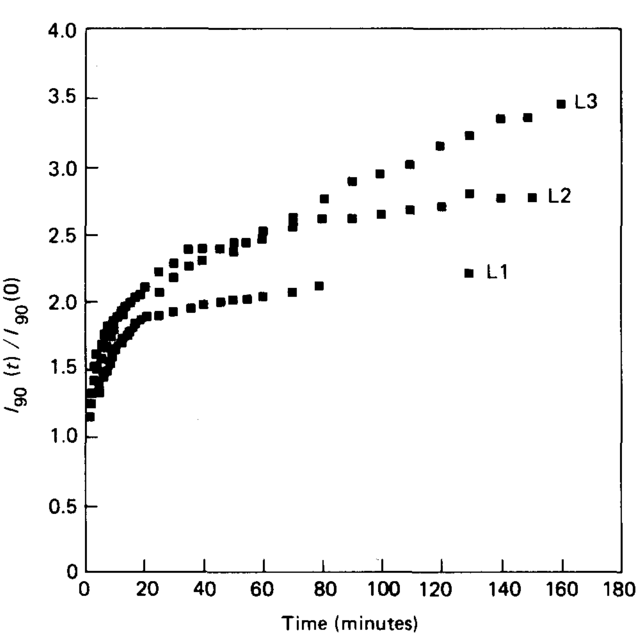

Figure 2 Time dependence of the light scattered by the latices L1, L2 and L3 measured at a fixed angle of 90°

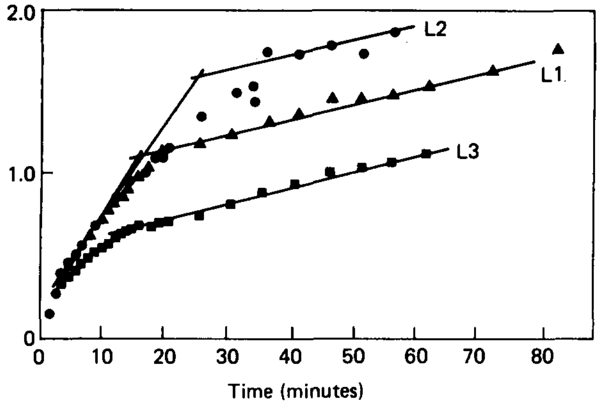

Figure 3 Plots to determine the relaxation constant k_R and the constant ϕ_R for the three latices L1, L2 and L3

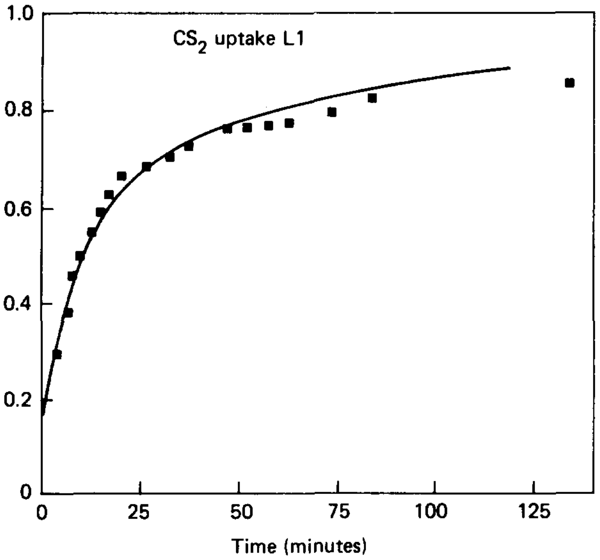

Figure 4 Comparison of the reduced form of the time dependent scattered light intensity with the theoretical calculation for the latex L1. $k_R = 1.50 \times 10^{-4}\,s^{-1}$; $D = 1.26 \times 10^{-14}\,cm^2\,s^{-1}$; $\phi_R = 0.38$; $\phi_F = 0.62$

latices studied in the present work was dried of solvent in a vacuum oven. The glass transition temperature, T_g, of the dried particles was determined by differential scanning calorimetry (d.s.c.). The T_g was found to be 107°C which is typical for PMMA[16].

DISCUSSION

In this paper we have shown that the imbibition of carbon disulphide by poly(methyl methacrylate) latex particles can be described using a simple two stage model. From the experimental data we have extracted values of the diffusion coefficient, D, for carbon disulphide in the latex particles and found that the values are typical of the diffusion of penetrants in glassy polymers. Additionally, the experimental results obtained for k_R (*Table 2*) indicate that the segmental relaxations involved in the imbibition process are independent of particle size.

The T_g of the latex particles was found to be close to that expected for bulk PMMA. This suggests that little, if any, stabilizer is occluded into the core of the latex particle. Moreover, the values of the diffusion coefficients are typical of penetrant diffusion in a glassy polymer matrix. These data indicate that a core–shell model is an adequate description of the particle morphology. This may not always be the case and may depend upon the particular system studied. For example, luminescence data obtained from non-aqueous dispersions of poly(methyl methacrylate) stabilized by poly(isobutylene) have been interpreted in terms of a 'microphase' model[17].

Given that carbon disulphide penetrates the latex core and induces segmental redistribution of the poly(methyl

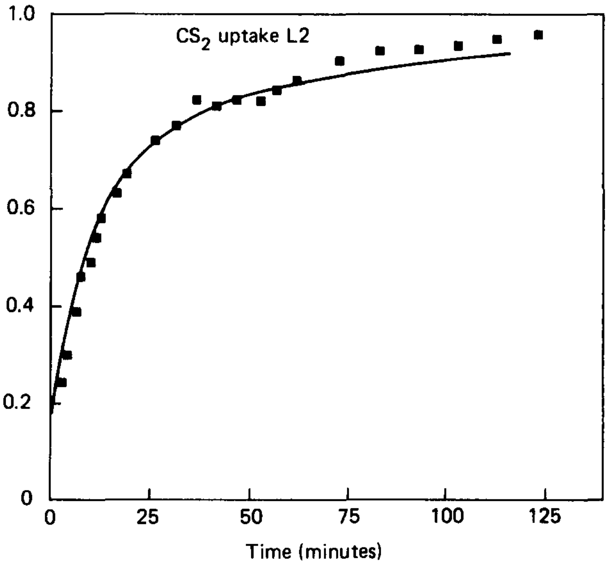

Figure 5 Comparison of the reduced form of the time dependent scattered light intensity with the theoretical calculation for the latex L2. $k_R = 1.55 \times 10^{-4}\,s^{-1}$; $D = 4.38 \times 10^{-13}\,cm^2\,s^{-1}$; $\phi_R = 0.25$; $\phi_F = 0.75$

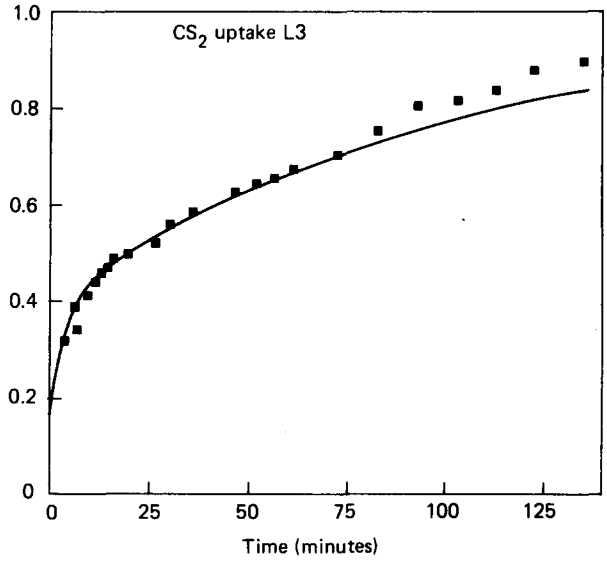

Figure 6 Comparisons of the reduced form of the time dependent scattered light intensity with the theoretical calculation for the latex L3. $k_R = 1.60 \times 10^{-4}\,s^{-1}$; $D = 1.46 \times 10^{-13}\,cm^2\,s^{-1}$; $\phi_R = 0.61$; $\phi_F = 0.39$

Table 2 Experimental parameters for the sorption process

Latex	k_R (s^{-1})	ϕ_R	ϕ_F	D ($cm^2\,s^{-1}$)
L1	1.50×10^{-4}	0.38	0.62	1.26×10^{-14}
L2	1.55×10^{-4}	0.25	0.75	4.38×10^{-13}
L3	1.60×10^{-4}	0.61	0.39	1.46×10^{-13}

methacrylate), there is the possibility that swelling of the latex particles might occur. Clearly, the extent of penetration and swelling of the latex particles will depend on a number of factors, including the penetrant activity and the polymer–penetrant affinity. Also, the influence of the absorbed polymer layer on the imbibition process may be of importance where such factors as adsorbed polymer layer thickness, density and mobility can influence the mass transport process.

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REFERENCES

1 Crank, J. 'The Mathematics of Diffusion', Clarendon Press, Oxford, 1956

2 Frisch, H. L. *Polym. Eng. Sci.* 1980, **20**, 2

3 Goodwin, J. W., Ottewill, R. H., Harris, N. M. and Tabony, J. *J. Coll. Int. Sci.* 1980, **78**, 253

4 Liang, S.-L. and Fitch, R. M. *J. Coll. Int. Sci.* 1982, **90**, 51

5 Liang, S-L., Fitch, R. M. and Ugelstad, J. *J. Coll. Int. Sci.* 1984, **97**, 336

6 Livsey, I. and Ottewill, R. H., to be published

7 Pusey, P. N. and van Megen, W. *J. Physique* 1983, **44**, 285

8 van Megen, W., Ottewill, R. H., Owens, S. M. and Pusey, P. N. *J. Chem. Phys.* 1985, **82**, 508

9 Barrett, K. E. J. (Ed.) 'Dispersion Polymerisation in Organic Media', Wiley, 1975

10 Aden, A. L. and Kerker, M. *J. Appl. Phys.* 1951, **22**, 1242

11 Ottewill, R. H. and Richardson, R. A. *Colloid Polym. Sci.* 1982, **260**, 1580

12 Kerker, M. 'The Scattering of Light and Other Electromagnetic Radiation', Academic Press, 1969

13 Berens, A. R. and Hopfenberg, H. B. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **17**, 253

14 Berens, A. R. and Hopfenberg, H. B. *Polymer* 1978, **19**, 489

15 Goodwin, J. W., Ottewill, R. H. and Parentich, A. *J. Phys. Chem.* 1980, **84**, 1580

16 'Polymer Handbook', (Eds. J. Brandrup and E. H. Immergut), Wiley Interscience,1966

17 Winnik, M. A. *Polym. Eng. Sci.* 1984, **24**, 87