ELSEVIER

Polymer 42 (2001) 4915–4923

polymer

www.elsevier.nl/locate/polymer

Estimating diffusion coefficients for small molecules in polymers and polymer solutions

O.J. Karlsson[1], J.M. Stubbs, L.E. Karlsson[1], D.C. Sundberg*

Polymer Research Group, Department of Chemical Engineering, University of New Hampshire, Durham, NH 03824, USA

Received 1 May 2000; received in revised form 27 September 2000; accepted 3 October 2000

Abstract

The diffusion coefficient for small molecules (solvent or monomer) through polymer solutions in the vicinity of the glass transition are known to change by as much as six orders of magnitude with only a small change in polymer concentration. Experimental measurements are difficult in this region and consequently there are data for only a limited number of systems. A rather simple method to estimate these diffusion coefficients for the rubbery, glass transition, and glassy regions as a function of polymer concentration and application temperature is presented. While the method is empirical in nature, it is based on carefully executed experimental studies, sound scaling laws, and agrees extremely well with free volume theories in the rubbery region. The method only requires a knowledge of the pure polymer glass transition temperature in order to estimate the diffusivity of molecules like styrenic and acrylic monomers (molecular weight of approximately 100 g/mol) at any polymer concentration and for temperatures above and below the polymer glass point. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Diffusion; Monomer; Polymer

---

1. Introduction

The diffusion of small molecules (solvents and monomers) and both oligomeric and high molecular weight polymers within a polymer phase is important to many chemical and physical processes. This includes polymerization reaction kinetics (particularly via the free radical mechanism) and the development of morphology in phase separated, composite polymers. Our own interest is in emulsion polymerization reactions and polymer particle morphology control where one must consider small and large molecule diffusion over a fairly wide range of polymer concentrations. When dealing with polymers whose glass transition temperatures (T_g) are higher than the process temperature (T_r), one is also confronted with the challenge of describing diffusion in the vicinity of the glass transition region. This has given us reason to find simple ways to estimate or predict diffusion coefficients in the so-called “rubbery” region, the glass transition region, and the glassy region.

The method employed in the present work involved the collection of previously reported experimental data for the diffusion of small molecules within a polymer such as poly(methyl methacrylate), PMMA. Unfortunately the available data are not always for the same diffusant molecule, obtained at the same temperature, or measured at the same polymer concentration. Thus we have resorted to scaling laws to bring the data to a single manipulated data set which spans the entire concentration range from pure solvent (or monomer) to pure polymer. In contrast, we compared the scaled data to predictions from the free volume theory and report on the differences and ease of computation or estimation. Our ultimate goal was to produce an empirical method to estimate the diffusion coefficient for molecules of a molecular size approximating common vinyl monomers (ca. 100 g/mol) diffusing through a variety of vinyl polymers at temperatures above and below the T_g of the polymers.

2. Free volume theory for prediction of diffusion coefficients

Free volume theory is by far the most widely used theory for predicting diffusion coefficients in polymers and polymer solutions. It has been shown to be capable of

---

* Corresponding author. Vice President for Research & Public Service, University of New Hampshire, Thompson Hall, 105 Main Street, Durham, NH 03824-3547, USA. Tel.: +1-603-862-1997; fax: +1-603-862-3617.

E-mail address: dsc@cisunix.unh.edu (D.C. Sundberg).

[1] Department of Polymer Science and Engineering, Lund University, PO Box 124, SE-22100 Lund, Sweden.

PII: S0032-3861(00)00765-5

accurately describing diffusion in many polymers and for many different diffusants [1–9]. The beauty of this theory is that it describes the very complex process of diffusion in polymers in a way that is based on realistic concepts, relying on parameters which have some relevant physical significance.

One problem is that it is often difficult to apply to certain systems due to the large number of parameters required for the model. Various methods have been proposed for estimating many of these parameters based on knowledge of the physical properties of the pure components [4–7,10]. These methods require physical property data such as density or viscosity as a function of temperature, thermal expansion coefficients both above and below the glass transition temperature, and Williams–Landel–Ferry (WLF) constants. Other parameters may be estimated from the equilibrium liquid volumes at 0 K, but these must be calculated based on group contribution methods as summarized by Haward [11]. It is quite common that for certain systems these physical data necessary to estimate many free volume parameters are not readily available. If the information is available some effort is required to estimate certain parameters from the physical property data, involving techniques such as non-linear regression analysis. In addition, it is usually necessary to have a few experimental data points in order to fit the model to the data and obtain the last few remaining parameters [5,7,12]. There are usually three remaining parameters (a pre-exponential term, an activation energy, and a term equal to the ratio of the molar volumes of the polymer and solvent jumping units) which are adjusted by nonlinear regression to fit the experimental diffusion data points [12].

If one is able to obtain or estimate all of the required parameters, free volume theory is able to provide excellent predictions of diffusion coefficients as a function of both polymer weight fraction and temperature in the rubbery regime. However, predicting the diffusion behavior in the vicinity of or below the glass transition temperature remains challenging. This is because glassy polymers possess an extra amount of free volume that is due to the fact that the entangled polymer chains are not able to easily relax to their equilibrium state when the polymer is in the glassy state. Vrentas and Vrentas have proposed an extension of the theory that should apply in the glassy state [6]. However, the parameters involved often cannot be directly related to physical properties as they depend on the specific history of the sample (annealing time, etc.) [6,10].

As noted above, when one desires to apply the free volume theory to a system that has not been thoroughly studied there can be difficulty in obtaining or estimating all of the required parameters. Furthermore, if one needs estimates of diffusion coefficients in the vicinity of or below the glass transition, free volume theory may have difficulty providing accurate values. In order to predict latex particle morphology development [14], we find ourselves in need of diffusion coefficients for various vinyl monomers in a variety of different vinyl polymers and copolymers, and often need to do this in the vicinity of or below the glass transition. For these reasons it has been useful to us to develop a method to estimate these diffusion coefficients that is based on experimental diffusion coefficients and uses the guidance of free volume predictions in determining the shape of the various diffusion curves.

3. Estimating diffusion behavior based on experimental data

The first step towards constructing an approximate model was to assemble a series of experimentally measured diffusion coefficients for monomers, D_{mon}, which are available in the literature. The goal was to obtain values for D_{mon} in polymer solutions spanning the entire range of polymer weight fraction, w_{p}, for at least one polymer at one temperature. This provides a guide for the shape of the diffusion curve as a function of w_{p}, most importantly in the range of the glass transition. Various curves for different polymers at different temperatures should have the same general shape, but with the actual values adjusted accordingly, as described later. The assembly of experimentally measured diffusion coefficients is made more difficult by the fact that there are very little experimental data available, especially in the glassy region. This is because the diffusion coefficients in this range are so small, often as low as 10^{-14} cm^2/s. There are only a few methods that can directly measure these diffusion coefficients without introducing bulk perturbations to the system that may alter the physical nature of the polymer and produce erroneous results [15]. Pulsed Field Gradient NMR (PFG-NMR) can directly measure diffusion coefficients of small molecules such as monomers in polymers, but can only measure values above 10^{-10} cm^2/s, so it is only applicable in the rubbery regime [13]. Forced Rayleigh Scattering (FRS) is the most commonly used method to study diffusion in the glassy region but must use photosensitive dyes, most of which are much larger than vinyl monomer molecules, and therefore the results often require scaling to estimate the diffusion coefficients. It should also be noted that all reported methods of measuring diffusion coefficients must rely on Fick's law of diffusion in order to extract diffusion coefficients from the raw experimental data.

The system chosen to determine the overall shape of the D_{mon} versus w_{p} curve was that of PMMA solutions at 50°C, because for this system experimental values are available spanning almost the entire w_{p} range from 0 to 1. The first set of experimental diffusion coefficients used were those of Faldi et al. [13] for diffusion of MMA in PMMA/MMA solutions at 50°C and at w_{p}s ranging from 0 to 0.81. These points were measured using both PFG-NMR and FRS. Those measured using FRS were obtained using a tracer dye, 2-(4,5-dihydro-4,4-dimethyl-3(2H)-oxo-2-thienylidene)-4,5-dihydro-4,4-dimethyl-3(2H)-thiophenone (referred to as TTI),

Table 1
Diffusion coefficients for MMA in PMMA at 50°C from literature. Values are expressed in cm^2/s

w_p	D_{MMA}		
	Faldi, PFG-NMR	(Faldi, FRS)[a]	(Tonge, FRS)[b]
0	2.5×10^{-5}		
0.058	2.0×10^{-5}		
0.165	1.4×10^{-5}		
0.207	1.35×10^{-5}		
0.315	1.0×10^{-5}		
0.405	6.0×10^{-6}		
0.583	1.9×10^{-6}		
0.625	1.3×10^{-6}		
0.695	6.5×10^{-7}		
0.545		2.0×10^{-6}	
0.565		2.0×10^{-6}	
0.615		1.2×10^{-6}	
0.645		1.0×10^{-6}	
0.700		4.0×10^{-7}	
0.750		2.0×10^{-7}	
0.810		1.0×10^{-7}	
0.783			5.18×10^{-9}
0.82			1.36×10^{-9}
0.85			7.08×10^{-10}
0.875			1.03×10^{-12}
0.90			1.97×10^{-13}

[a] Estimated from diffusion coefficients for TTI in PMMA/MMA mixtures.

[b] Estimated from diffusion coefficients for CQ in PMMA/methyl isobutyrate mixtures.

which is about 70% larger than MMA [13]. The authors then scaled the values to those for MMA using a method based on free volume theory. The concentration of TTI in the mixture was always kept between 0.4 and 0.6% by weight, so that it does not represent an appreciable plasticizing agent in the mixture. This set of data is very useful because many of the points (those from PFG-NMR) represent direct measurements of a monomer molecule diffusing in a polymer at various weight fractions. When combined with the scaled data from FRS the data span the entire range of w_p in the rubbery regime.

The second set of experimental diffusion coefficients used are from Tonge et al. [15]. These data were measured using FRS and are for camphorquinone (CQ) diffusing in PMMA/methylisobutyrate solutions with weight fractions between 0.78 and 0.9 and at temperatures ranging from 25 to 50°C (although only the data at 50°C were used here). Here the concentration of CQ was in the range of 0.5% by weight. These points are important because the conditions studied span both above and below the glass transition, and therefore complement the data of Faldi et al. [13] which are only in the rubbery region. The only difficulty with using these data is that they are for diffusion of camphorquinone, which is a larger molecule than MMA, and therefore will diffuse more slowly. This was overcome by scaling the diffusion coefficients based on the scaling law of Griffiths [16] given by Eq. (1)

$$D_i = \frac{D_{\text{mon}}}{i^{(0.664+2.02w_p)}} \tag{1}$$

This scaling law is based on measurements of diffusion coefficients for oligomers of various degrees of polymerization, i, ranging from 1 to 10 units. However, the degree of polymerization can also be expressed as the ratio of the polymer molecular weight over the molecular weight of an individual monomer unit. Since the size range of the oligomers studied by Griffiths covers the size range of both camphorquinone and MMA molecules, it was judged that Eq. (1) could also serve as a good approximation to scale the diffusion coefficients for camphorquinone to that for MMA, as follows:

$$D_{\text{MMA}} = D_{\text{CQ}}\left(\frac{\text{MW}_{\text{CQ}}}{\text{MW}_{\text{MMA}}}\right)^{(0.664+2.02w_p)} \tag{2}$$

where MW_{CQ} and MW_{MMA} refer to the molecular weights of the two molecules, which are 166 and 100 g/mol, respectively. This equation was used to estimate the values of D_{MMA} based on the measured values of D_{CQ}. The ratio of the experimental D_{CQ} values to the scaled D_{MMA} values varied slightly, between 3.62 and 3.78, for the different experimental points since the exponent in Eq. (2) is a function of polymer weight fraction. The values for the diffusion coefficients of MMA in PMMA at 50°C from both Tonge et al. [15] and Faldi et al. [13] are given in Table 1. The combination of these two sets of data represent nearly the complete range of monomer weight fractions for one type of polymer at one given temperature.

As noted by the authors, the data from Tonge et al. [15] are subject to some level of uncertainty due to the fact that the data span the region around the glass transition and this is the area where the diffusion coefficients are most sensitive to polymer weight fraction. Therefore, only a small error in either the w_p of the sample or the measured diffusion coefficient could significantly alter the shape of the D_{mon} versus w_p curve in this region. This is the region that is of most interest to us and thus we chose to obtain an additional set of experimental data that spanned the glass transition.

For this purpose the FRS data of Zhang and Wang [17], for diffusion of diacetyl in pure PMMA at temperatures ranging from 96 to 130°C, was used. Diacetyl is of a similar molecular weight and molecular size as MMA and therefore it was judged that no scaling for molecular size was required (this is also the reason we chose to focus on this data set rather than other similar data sets for larger molecule diffusants). However, the data are for diffusion in pure PMMA (the concentration of diacetyl was only about 0.9%) at temperatures spanning the T_g of pure PMMA, and what is needed are data for PMMA at various monomer concentrations at 50°C. In order to convert the data we assumed that the diffusion coefficients for different T_g polymers (or polymer/solvent solutions) will be the same as long as they are compared with respect to the difference between the

Table 2
Diffusion coefficients for diacetyl in PMMA from Zhang and Wang [17]

Temperature (°C)	D (cm^2/s)	Corresponding w_p at 50°C
96.00	2.10×10^{-14}	0.892
98.75	2.05×10^{-14}	0.886
107.2	3.57×10^{-14}	0.868
108.24	2.98×10^{-14}	0.866
110.58	1.80×10^{-13}	0.861
111.32	1.20×10^{-13}	0.859
112.06	1.00×10^{-12}	0.858
113.40	6.20×10^{-13}	0.855
114.30	9.50×10^{-12}	0.853
115.65	4.20×10^{-11}	0.850
115.80	4.20×10^{-11}	0.850
115.95	5.50×10^{-11}	0.850
116.11	5.80×10^{-11}	0.849
118.08	7.40×10^{-11}	0.845
119.46	7.60×10^{-11}	0.842
122.57	1.20×10^{-10}	0.835
125.88	1.50×10^{-10}	0.828

temperature of the measurement and the glass transition temperature of the system, or $T - T_g$. For instance, the diffusion coefficient in PMMA ($T_g = 119$°C) at 70°C should be the same as the diffusion coefficient in polystyrene ($T_g = 104$°C) at 55°C.

This assumption may not be completely true in all cases but has been used by several researchers in order to compare diffusion coefficients in different polymers [18–20]. In particular, experimental diffusion coefficients reported by Ehlich and Sillescu [19] for TTI diffusing in both pure polystyrene and in polystyrene with 10 wt% tricresyl phosphate, above and below the T_g, support this assumption. These polystyrene data sets also agree very well with data they reported for TTI diffusing in PMMA, when plotted versus $T - T_g$. In general, it is found that when diffusion coefficients in different polymers at various temperatures are plotted versus $T - T_g$, they all tend to fall on the same curve in the glass transition region. This technique is also used for time–temperature superposition [21]. It should also be noted that there are data sets for diffusion in other polymers that do not fall on the same curve. In another data set reported by Ehlich and Sillescu for diffusion of TTI in polyethylstyrene (PES), the diffusion coefficients were between 1 and 2 orders of magnitude greater, at the same $T - T_g$ values, than the values for TTI in the polystyrene and PMMA systems mentioned above. For this reason the method we are proposing for estimating diffusion coefficients will not necessarily be universal.

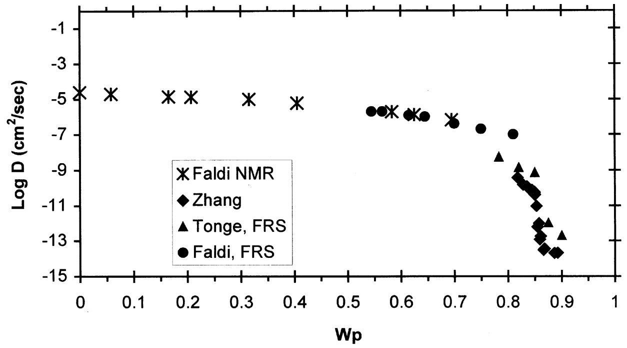

Fig. 1. Experimental diffusion coefficients (adjusted via scaling for molecular size and temperature) for MMA diffusion in PMMA as a function of w_p at 50°C.

In order to scale these data of Zhang and Wang [17] to PMMA at 50°C it is necessary to have an expression relating the glass transition temperature of the polymer/monomer solution to the weight fraction of polymer. This relationship has been presented by Faldi [13] based on differential scanning calorimetry (DSC) measurements of the T_g for PMMA/MMA solutions at various weight fractions. These data points were fit using the Kelley–Bueche relation [22]. This relationship between T_g and w_p for the PMMA/MMA solutions reported by Faldi agrees almost exactly with limiting conversion versus temperature reported by Hamielec and Friis [23] if one assumes that the limiting conversion is reached at the glass transition. It is clear from both sets of data that the T_g exhibits a nearly linear dependence on w_p over the range of T_gs that would be comparable to most common emulsion polymerization reaction temperatures (50–100°C). Vrentas has also used a linear relationship to describe the dependence of the T_g of polymer solutions on polymer weight fraction [6]. Therefore, it was judged that a linear expression relating T_g to w_p would be sufficient in the present case, and was estimated from the DSC data of Faldi to be

$$T_g(°\mathrm{C}) = 464w_p - 345 \qquad 0.7 \leq w_p \leq 1.0 \tag{3}$$

This equation gives a T_g for pure PMMA ($w_p = 1$) of 119°C, which agrees with the value commonly reported in the literature [24].

It should be noted here that the rate of decrease of the T_g of the polymer solution upon the addition of solvent is a function of the solvent type, because different solvents add different amounts of free volumes depending on their size. We have not considered the effect of solvent type on the T_g of the polymer solvent solution in Eq. (3). While this simplification is not completely valid, we are interested in applying this method for common vinyl monomers having similar molecular weights close to 100 g/mol, and we consider it to be adequate for our purposes. A possible improvement to this method would be to use the Kelley–Bueche equation [22] to determine relationships between the T_g of the polymer solution and the polymer weight fraction that are dependent on the type of monomer. However, this equation requires a value for the glass transition temperature of the monomer as well as a value, α_m, which is equal to the difference between the coefficients for volumetric expansion for the monomer in the rubbery and glassy states. Neither of these values for the monomer are readily available [25].

Eq. (3) was used to scale the data of Zhang and Wang [17] to a system of PMMA/MMA at 50°C; the method is as follows. For any of the experimental points, the difference between the temperature of the measurement and the glass transition temperature of PMMA, or $T - T_g$, was calculated. For this step, a value of 115°C for the T_g of PMMA was used since this is the value reported by Zhang and Wang [17] for their particular experimental PMMA samples. Then the value of T_g was calculated for a PMMA/MMA solution that would give the same $T - T_g$ when the temperature was 50°C. Finally, Eq. (3) was used to calculate the value of w_p that would correspond to this value of T_g. The data of Zhang and Wang, along with the calculated w_p values that give the same corresponding values for $T - T_g$ at 50°C, are shown in Table 2. All of these experimental diffusion coefficients, from both Tables 1 and 2, are plotted together in Fig. 1 as a function of w_p.

Upon examination of the data in Fig. 1 there are a number of points that become clear. The first is that at low weight fractions of polymer, when the system is well within the rubbery regime, the dependence of the diffusion coefficient on w_p is rather weak. This is in accord with the predictions of free volume theory [10]. There is one data point from Faldi et al. [13] in Fig. 1 which is in disagreement with the data of Tonge et al. [15] and Zhang and Wang [17] at similar weight fractions (w_p just above 0.8). It should be noted that these points from Faldi at w_ps approaching 0.8 are measurements of TTI diffusing in PMMA, and have been scaled to represent diffusion of MMA. The size difference between MMA and TTI is even greater than between MMA and camphorquinone [18] and the scaling relationship used by Faldi was established from points at lower w_ps, thus further below the T_g. It is possible that this scaling relationship is no longer valid at these higher w_ps due to the approaching onset of the glass transition. With this in mind, this point should be viewed with some caution.

The glass transition for PMMA at 50°C, according to Eq. (3), occurs at a w_p of 0.85. Fig. 1 shows that in this region, from a w_p of about 0.7 to 0.9, the diffusion coefficients change by about 8 orders of magnitude. This is in accord with the predictions of free volume theory that the diffusion coefficient is most sensitive to w_p near the glass transition. However, as noted by Zeilinski and Duda [10], a few percent change in the solvent concentration near the glass transition can change the diffusion coefficient about 3 orders of magnitude. Clearly the total change in Fig. 1 is much greater than 3 orders of magnitude. In fact, further examination of Fig. 1 indicates that there may actually be two distinct regions making up the total decrease in D between w_p of 0.7 and 0.9. The first region is in the area approaching the glass transition from the rubbery side. Starting at a w_p of about 0.7 the diffusion coefficient starts to decrease more rapidly than at lower w_ps, but not so rapidly that a few percent change in the solvent concentration would result in the diffusion coefficient decreasing by 3 orders of magnitude. This is indicated both by the data of Tonge at w_ps of 0.78, 0.82 and 0.85, and also by the data of Zhang and Wang at lower w_ps below the glass transition point of $w_p = 0.85$. Other investigations of diffusion in polymers have also reported diffusion coefficients starting to decrease more rapidly before the glass transition as it is approached from the rubbery side [12,26].

The second apparent region in this total range spanning the large decrease in the diffusion coefficients comes directly after the glass transition is crossed, here at $w_p = 0.85$. In this region the values decrease much more rapidly than in the range of w_p from 0.7 to 0.85. This is indicated by the difference between the values from Tonge at w_p of 0.85 and 0.875, and also by the rate of decrease of the scaled values from Zhang and Wang between about 0.85 and 0.87. In both instances the values decrease by 3–4 orders of magnitude over regions where the percent polymer changes by only about 2%. It is likely that this is the rapid decrease in the diffusion coefficients near the glass transition that was referred to by Zeilinski and Duda [10].

The final point that is indicated by Fig. 1 is that at higher w_ps, when the system is further into the glassy region, the diffusion coefficients seem to level off at a value close to 10^{-14} cm^2/s. This is indicated strongly by the data of Zhang and Wang, which is plotted in Fig. 2 as D_{mon} versus $T - T_g$. These data represent the direct experimental measurements in pure PMMA and have not been scaled in any way. From this figure it is clear that within the range of 5°C above to 5°C below the glass transition the diffusion coefficients decrease rapidly, changing by over 3 orders of magnitude. However, after the temperature is more than 5°C below the T_g the change in the diffusion coefficient with further decreases in temperature is minimal. From about 7°C below the T_g to about 19°C below, the measured diffusion coefficient remains essentially unchanged.

Also included in Fig. 2 is a prediction from free volume theory, made using the same form of the free volume equations and the specific parameters used by Faldi et al. [13]. Unlike the experimental diffusion coefficients, which decrease rapidly at the glass transition and then level off below the T_g, free volume predicts a steady decrease in the diffusion coefficients through the T_g which continues well into the glassy region. It is noted that the form of the free volume equations used to make the prediction in Fig. 2 is only applicable in the rubbery region and has been used here to make predictions in the glassy regime as well. Predictions have not been made here using these "glassy" free volume equations proposed by Vrentas and Vrentas [6] because several of the 10–15 required parameters are not readily available. These "glassy" free volume equations would predict values that are even larger in the glassy region than the predictions shown here, due to the extra free volume in the glassy state, and would therefore be further from the experimental values. In addition, even if the appropriate free volume equations for the glassy state were used, they would not predict the rapid decrease in the diffusion coefficients at the T_g that is observed in the experimental data of Zhang and Wang, and would also not predict the flat area further into the glassy region.

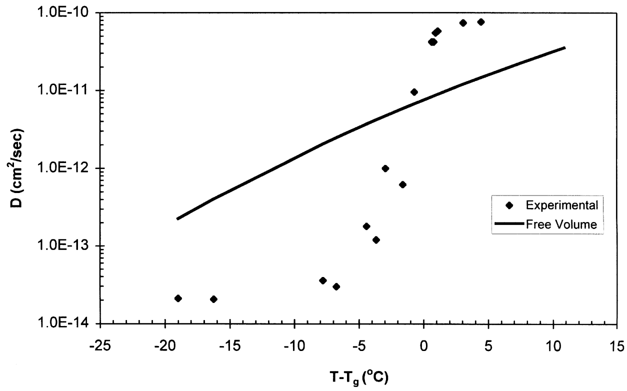

Fig. 2. Experimental diffusion coefficients from Zhang and Wang [17] plotted against the difference between the measurement temperature and the T_g of PMMA (115°C as reported by Zhang and Wang). The solid line represents predictions from the free volume theory.

We have chosen to focus our attention on the data from Zhang and Wang for diacetyl because no scaling for the molecular size of the diffusing molecule is required for our purposes. Since conditions change so rapidly in the vicinity of the glass transition, we felt it was important to use a data set in this region that required the least amount of manipulation in order to estimate the diffusion coefficients in Fig. 1. As mentioned earlier, there are a few other data sets available for diffusion coefficients spanning the glass transition for molecules such as TTI [18,19]. These molecules are considerably larger than most vinyl monomers we are interested in. It is noted here that some of these data sets for larger diffusing molecules show somewhat different behavior near the glass transition than shown in Fig. 2 (the decrease in D near the T_g is not quite so steep and more gradual before T_g is reached). However, if we had chosen to focus on these data sets it would have been necessary to adjust the values to account for the difference in molecular size in addition to adjusting the values to represent a system with solvent at 50°C, which is the condition for the data in Fig. 1 (only the latter adjustments were required for the data from Zhang and Wang for diacetyl).

The overall shape of the curve in Fig. 1, with a gradual decrease in the diffusion coefficient at low w_p followed by a rapid decrease near T_g and then leveling off near 10^{-14} cm²/s in the glassy region, is similar to that used previously by other authors [14,27]. It is also consistent with the shape suggested by swelling experiments of polystyrene latex with isoprene [28].

4. Construction of the empirical model to estimate diffusion in various systems

For the reasons discussed above, we have divided the diffusion curve into four distinct regions, and approximated the dependence of $\log D$ on w_p within each region by a linear function. The first region is at low w_p where the slope of $\log D$ versus w_p is small and the line was determined directly by fitting the data of Faldi (Table 1) in the rubbery regime, for w_p values between 0 and 0.75. However, we also made the slope in region 1 a function of the difference between the temperature of application and the glass temperature of the pure polymer, or $T - T_g$. This was done because the free volume theory for diffusion in various polymers in the rubbery regime shows that the slope of $\log D$ versus w_p is a function of $T - T_g$. At a given temperature this slope is more significant for polymers with smaller values of $T - T_g$. For the sake of simplicity, we have made the slope of the line in region 1 to be a linear function of $T - T_g$. It should be noted that this slope does not change greatly even for polymers having vastly different T_gs. Since we are usually interested in obtaining estimates at high polymer weight fractions typical of semicontinuous polymerizations, the diffusion behavior in region 1 has been of lesser importance to us compared to the behavior of the diffusion coefficients in the regions surrounding the glass transition.

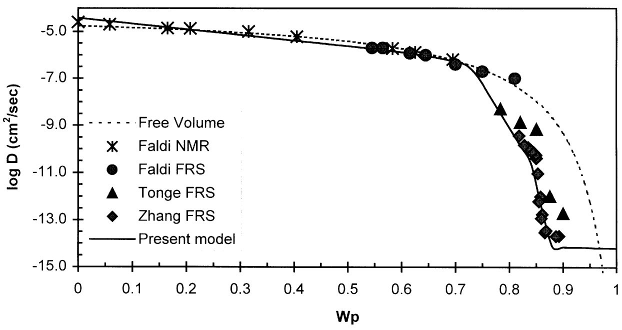

Fig. 3. Fitted curve for the diffusion coefficient of MMA in PMMA at 50°C as a function of polymer weight fraction, w_p. Also shown is a prediction from the free volume theory.

The second region is at w_ps before the glass transition, on the rubbery side, where $\log D$ starts to decrease more rapidly with w_p. For the system shown in Fig. 1 this occurs between w_p values of 0.75 and 0.85. The slope in region 2 was taken to be the same as that used by Ivarsson [29] in previous work in order to estimate diffusion coefficients in the glass transition region. The third region is just after the glass transition is crossed where the system becomes glassy, and the diffusion coefficient decreases rapidly with w_p. The slope of the line in this region was determined by fitting a line to the data of Zhang and Wang in Fig. 1 between w_ps of 0.85 and 0.87. The fourth and final region is at higher w_p in the glassy region, above 0.87 in Fig. 1, where the diffusion coefficient levels off at about 10^{-14} cm²/s and the slope, which is negligible in comparison to that in the other regions, was estimated by the data of Zhang and Wang at the lowest temperatures studied. The final shape of the diffusion curve thus obtained for PMMA at 50°C, along with the data points from Fig. 1 for comparison, is shown in Fig. 3.

Also shown in Fig. 3 is a prediction from free volume theory, again using the form of the free volume equations

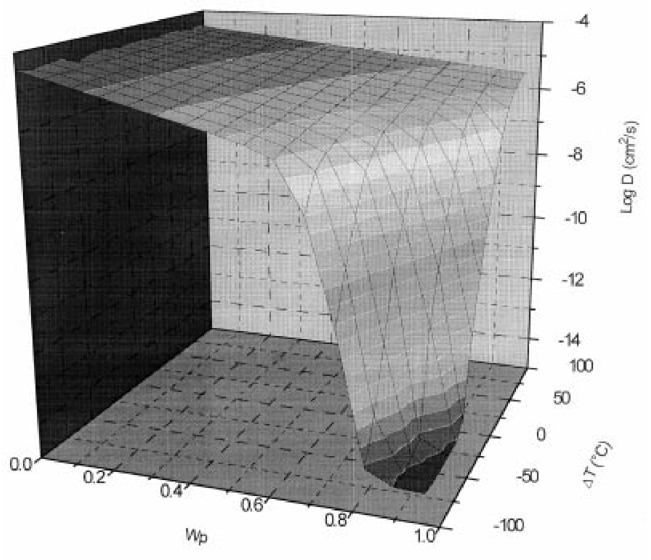

Fig. 4. Diffusion coefficients, log *D*, for small molecules in polymers as a function of weight fraction of polymer, w_p, and $\Delta T = T - T_g$.

and parameters used by Faldi and for the predictions in Fig. 2. This clearly shows that the predictions of free volume theory agree very well with the experimental data in the rubbery regime, but they do not agree well in the glassy regime. As noted earlier, these equations are not actually valid in the glassy regime, and the "glassy" form of the free volume equations proposed by Vrentas and Vrentas [6] should actually be used here. However, as was the case in Fig. 2, had these equations been used to make predictions in the glassy regime, the decrease in the free volume predictions would be less rapid in the glassy regime than they are in Fig. 3. This again would result in an even greater difference between the free volume predictions and the experimental measurements.

The final issue to be resolved over the use of the fitted diffusion curve, is how to use it for different polymers with various T_gs and at different reaction temperatures. Here the assumption was made that the slope of a graph of T_g versus w_p, as given by Eq. (3) for MMA in PMMA from the DSC data of Faldi, will be the same for other polymers and solvents. The difference will be that the intercept of Eq. (3) will be different for other polymers. This intercept can be determined by taking advantage of the fact that the T_g of the pure polymer, or at $w_p = 1$, is known. Therefore, the intercept is given by

$$\text{intercept} = T_g(\text{pure polymer}) - 464 \quad (4)$$

where T_g is expressed as degrees Celsius. By combining Eqs. (3) and (4), a relationship between T_g and w_p can be estimated for any polymer. This allows the w_p corresponding to the glass transition to be estimated for any polymer, and at any application temperature. To provide consistency between the various diffusion curves, we chose to follow the assumption made by Ivarsson [29] that the the diffusion coefficient at the glass transition is always equal to 10^{-11} cm^2/s. This agrees with the value measured by Zhang and Wang [17] at the T_g of pure PMMA, and is consistent with the fact that when plotted versus $T - T_g$, the diffusion coefficients in different polymers tend to fall on the same curve [18–20]. This assumption sets the point of the intersection between the two regions spanning the glass transition. With this point set, and knowing the slopes of the lines of log *D* versus w_p in all four regions, a diffusion curve as in Fig. 3 can be estimated for different polymers at a variety of application temperatures.

The assumption that the diffusion coefficient at the T_g is the same for different systems will not be completely valid as it assumes that all polymers and polymer solutions have the same free volume at their glass transition, and it is likely that this is not the case. There is also some experimental evidence, as shown by Vrentas [5], that the diffusion coefficient at the glass transition for polymer solvent solutions with different concentrations is a function of the concentration and increases as the solvent concentration increases. This leaves a possible area for improvement of this method for estimating diffusion coefficients. Instead of making the assumption that the diffusion coefficient at the T_g is always equal to 10^{-11} cm^2/s, it should be possible to estimate how the diffusion coefficient at the T_g varies with solvent concentration based on the data given by Vrentas [5]. This relationship could then be used to set the point of intersection between regions 2 and 3 on the diffusion curve. We have not yet attempted this modification, but will likely do so as we attempt to improve this method for estimating diffusion coefficients in polymers. However, it may be that more experimental data will be needed for this to prove useful.

After the assumptions made above, the general diffusion curve plot will have three axes and the diffusion coefficient will be expressed as a function of both the weight fraction of polymer, w_p, and also $T - T_g$. The equation expressing

Table 3
Coefficients for calculating the diffusion coefficients in the four different regions using Eq. (5)

	C_1	C_2	C_3	C_4
Region 1	-4.428	1.842	0	8.12×10^{-3}
Region 2	26.0	37.0	0.0797	0
Region 3	159.0	170.0	0.3664	0
Region 4	-13.7	0.500	0	0

$\log D$ in the four regions of the diffusion curve is given in the general form in Eq. (5), and the respective coefficients are given in Table 3

$$\log D(w_{\mathrm{p}},\Delta T) = [C_1 - w_{\mathrm{p}}C_2] + [\Delta T C_3] + [w_{\mathrm{p}}\Delta T C_4] \qquad (5)$$

A specific example is included in Appendix A to illustrate the use of Eq. (5). It should be noted that our assumption that the diffusion coefficient equals $10^{-11}\,\mathrm{cm}^2/\mathrm{s}$ at the T_{g} is inherently incorporated into the model through the values of the constants in Table 3. By applying Eq. (5) in the four regions of the diffusion curve and generating the $\log D$ data points using a simple computer program for large intervals of ΔT and w_{p}, it is possible to plot the diffusion coefficient as the three-dimensional (3D) surface seen in Fig. 4. The diffusivity expressed as a 3D surface is very useful for the purpose of easily estimating the diffusion coefficient in a polymer. An advantage of this estimation method is that there are no adjustable parameters and that all the data needed for determining the diffusivity will always be known or possible to calculate, i.e. temperature, T_{g} and weight fraction of polymer. Using this rather simple approach to express the dependency of the diffusion coefficient on w_{p} and T_{g} of the polymer we have found it possible to simulate free radical polymerization kinetics successfully, as will be reported in the future.

5. Concluding remarks

The original purpose of this work was to develop an approximation for the diffusion of monomers through a second, host polymer phase. We have found great utility in Fig. 4 and the ease with which we can estimate reasonable values for monomer diffusivity in a variety of polymers at different reaction temperatures. While Fig. 4 is entirely empirical, it is based on sound scaling laws, agrees very well with predictions from free volume theory in the rubbery region, and provides realistic values through the transition to the glassy region.

Acknowledgements

We are thankful for financial support from the University of New Hampshire Latex Morphology Industrial Consortium (BASF, Elf Atochem, Mitsubishi Chemical, Zeneca (now Avecia)), and the Swedish Foundation for International Cooperation in Research and Higher Education (STINT) for O.J.K.

Appendix A

The procedure for constructing the curve of $\log D$ versus w_{p} for a given polymer at a certain temperature from Eq. (5) is illustrated here. Diffusion in polystyrene ($T_{\mathrm{g}} = 104°\mathrm{C}$) at a temperature of 70°C is used as an example, so for this system $\Delta T = -34°\mathrm{C}$. Combining Eq. (5) with the coefficients listed in Table 3 gives rise to four different linear equations, each valid in a different "region", or range of w_{p} values. For the present system these equations are:

Region 1 : $\log D = -4.428 - 1.842w_{\mathrm{p}}$

Region 2 : $\log D = 23.290 - 37.0w_{\mathrm{p}}$

Region 3 : $\log D = 146.542 - 170.0w_{\mathrm{p}}$

Region 4 : $\log D = -13.7 - 0.5w_{\mathrm{p}}$

Once these equations have been obtained it only remains to determine the w_{p} ranges over which each equation should be used. The w_{p} value that separates regions 1 and 2 is calculated simply by equating the right-hand sides of the equations for regions 1 and 2. The same procedure is followed to determine the w_{p} values separating regions 2 and 3, and regions 3 and 4. For the present system this leads to the following w_{p} ranges:

Region 1 : $0 \le w_{\mathrm{p}} < 0.795$

Region 2 : $0.795 \le w_{\mathrm{p}} < 0.927$

Region 3 : $0.927 \le w_{\mathrm{p}} < 0.945$

Region 4 : $0.945 \le w_{\mathrm{p}} < 1$

References

[1] Vrentas J, Duda J, Ling H. J Polym Sci: Polym Phys Ed 1985;23:275.

[2] Vrentas J, Duda J. Diffusion. In: Mark HF, Bikales NM, Overberger CG, Menges G, editors. Encyclopedia of polymer science and engineering, vol. 5. 2nd ed. New York: Wiley, 1986. p. 36–68.

[3] Vrentas J, Duda J, Ling H. J Polym Sci: Polym Phys Ed 1988;26:1059.

[4] Vrentas J, Vrentas C. Macromolecules 1993;26:1277–81.

[5] Vrentas J, Vrentas C. Macromolecules 1994;27:4684–90.

[6] Vrentas J, Vrentas C. Macromolecules 1994;27:5570–6.

[7] Vrentas J, Vrentas C, Faridi N. Macromolecules 1996;29:3272–6.

[8] Hong S-U. Ind Engng Chem Res 1995;34:2536–44.

[9] Hong S-U. J Appl Polym Sci 1996;61:833–41.

[10] Duda J, Zeilinski J. Free volume theory. In: Neogi P, editor. Diffusion in polymers. New York: Marcel Dekker, 1996. p. 143–71.

[11] Haward RJ. Macromol Sci: Rev Macromol Chem 1970;C4:191.

[12] Frick T, Huang W, Tirrell M, Lodge T. J Polym Sci Part B: Polym Phys 1990;28:2629–49.
[13] Faldi A, Tirrell M, Lodge T, von Meerwall E. Macromolecules 1994;27:4184–92.
[14] Stubbs JM, Karlsson OJ, Sundberg EJ, Durant YG, Jonsson JE, Sundberg DC. Colloids Surf A Physiochem Engng Aspects 1999;153:255–70.
[15] Tonge MP, Stubbs JM, Sundberg DC, Gilbert RG. Polymer 2000;41:3659–70.
[16] Griffiths MC, Strauch J, Monteiro MJ, Gilbert RG. Macromolecules 1998;31(22):7835–44.
[17] Zhang J, Wang C. Macromolecules 1987;20:683–5.
[18] Chapman B, Gochanour C, Paoulaitis M. Macromolecules 1996;29:5635–49.
[19] Ehlich D, Sillescu H. Macromolecules 1990;23:1600–10.
[20] Kim H, Waldow DA, Han CC, Tran-Cong Q, Yamamoto M. Polym Commun 1991;32(4):108–12.
[21] Schultz J. Polymer materials science. Englewood Cliffs, NJ: Prentice-Hall, 1974 (p. 366–71).
[22] Bueche F. Physical properties of polymers. New York: Wiley-Interscience, 1962 (p. 116).
[23] Hamielec A, Friis N. Short Course on Polymer Production Technology, McMaster University, Hamilton, Ontario, Canada, 1976.
[24] Polymer handbook. New York: Wiley, 1989. p. 102, other.
[25] Sundberg D, James D. J Polym Sci: Polym Chem Ed 1978;16:523–9.
[26] Zhang J, Wang C, Ehlich D. Macromolecules 1986;19:1390–4.
[27] Mills MF, Gilbert RG, Napper DH. Macromolecules 1990;23:4247–57.
[28] Karlsson O, Wesslen B. J Appl Polym Sci 1998;70:2041–51.
[29] Ivarsson L.M.S. Thesis, Lund Institute of Technology, 1997.