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Measurement of Diffusion Coefficients of Oligomeric Penetrants in Rubbery Polymer Matrixes

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ABSTRACT: The diffusion coefficients of oligomeric radicals in monomer−polymer systems have a major influence on properties such as polymerization rates and molecular weight distributions. The present work reports the results of an extensive set of studies of diffusion coefficients of rubbery ternary systems comprising polymer, diluent, and oligomer, determined by pulsed-field-gradient NMR, at 25 and 40 °C. Oligomers of methyl methacrylate (MMA) and of butyl methacrylate (BMA) were synthesized by using a catalytic cobalt chain transfer agent to produce macromonomers with a terminal double bond. Where necessary, these were fractionated by preparative GPC to obtain samples ranging from dimeric to decameric; typical polydispersities were 1.08. Pulsed-field gradient NMR is facilitated by being able to monitor the proton NMR of the CH_2 hydrogens on the double bond. Matrixes used were high molecular weight polyMMA and polyBMA, the weight fraction of polymer (w_p) being varied by adding appropriate amounts of diluent (the saturated equivalents of MMA and BMA, viz., methyl isobutyrate and butyl isobutyrate). Above c^* (the concentration at which chains start to overlap), all data for diffusion coefficients D_i of an oligomer of degree of polymerization i could be fitted with acceptable accuracy by $D_1(w_p)/D_i(w_p) = i^{0.664 + 2.02w_p}$, for both BMA and MMA oligomers in both MMA and BMA matrixes; the same relation also fits earlier data on styrene oligomers in polystyrene. If more accurate scaling parameters are obtained experimentally for smaller oligomers, these can be used to predict data for higher oligomers with even better reliability. For MMA monomer in pMMA, where free-volume parameters are available, the predicted dependences of monomer diffusion coefficient on w_p and temperature are in accord with experiment.

Introduction

Diffusion of small species in a rubbery polymer is an important dynamical property. In particular, polymerization rates and molecular weight distributions in free-radical polymerizations are often influenced by diffusion.[1−3] In rubbery systems, where most polymer is formed, chemically controlled reactions such as transfer and propagation are diffusion-dependent; however, termination is likely to be diffusion-controlled.[2,3] In diffusion-controlled termination, the termination rate coefficient depends on the lengths of the growing chains undergoing termination as well as the percentage conversion of monomer to polymer. Modeling and understanding of these termination rate coefficients therefore require a knowledge of the diffusion coefficients $D_i(w_p)$ of radicals of different degrees of polymerization i, as a function of the weight-fraction of polymer, w_p.[2−4] In polymer/monomer systems that are above their glass transition temperature (T_g) and have a steady radical flux, it is thought that the termination rate is dominated by "short−long" events, where one chain is long and the other is short. The termination rate coefficient for such an event depends only on the length of the short chain and not on the length of the (long) chain with which it is terminating. As such, modeling termination (and hence rates and molecular weight distributions) requires accurate values of diffusion coefficients for short chains only, but this must include the dependence on the degree of polymerization i over a sufficient range, which might be (e.g.) up to 20-meric.[3−7]

At present, there are relatively few data for diffusion of small species as a function of both degree of polymerization and w_p. The system required for obtaining diffusion data of relevance to polymerization is ternary: polymer, small amounts of the oligomer as tracer, and a solvent (which is monomer in an actual polymerizing system). Data are available for the self-diffusion of larger chains in matrixes of the same molecular weight (of the same or a different polymer),[8−11] with limited data on diffusion of small species such as benzene, toluene, and tetrahydrofuran in a variety of polymers[12−14] as well as branched and star type species diffusion.[15,16] Only recently have data on the diffusion of oligomeric species over a range of w_p, such as styrene oligomers in a polystyrene matrix, begun to emerge.[17,18]

One of the major problems in determining diffusion data for oligomeric species in solutions of their own or other polymers is actually obtaining the small species themselves in sufficiently large quantities. In a normal polymerization reaction, even at very low monomer conversion, the minimum molecular weight formed tends to correspond to a species of anywhere between 100 and 1000 monomer units, while unfortunately it is expected that it is oligomeric species between 1 and 20 monomer units in length that are likely to be most important in the termination process. From the limited experimental data available for oligomeric species diffusion, diffusion as spheres or random coils is expected at infinite dilution,[19] and in very concentrated or entangled solutions it has been suggested that the reptation limit is significant.[8] Thus the diffusion coefficient D should progress from $D \sim i^{-0.5} - i^{-0.6}$ at infinite dilution through to $D \sim i^{-2}$ (or even[20] $i^{-2.1}$) in a concentrated matrix. A gradual progression with in-

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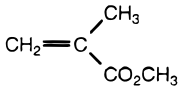
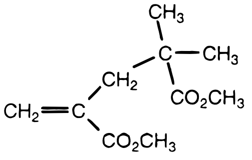
creasing weight fraction is expected. Studies by Torkelson and co-workers on diffusion coefficients between small penetrants and polymer in highly dilute solution[21] suggest that a simple 0.5 exponent for the dependence on penetrant molecular weight is often obeyed, while considerations such as aspect ratios can be used to understand the dependence of diffusion coefficients on penetrant molecular structure in undiluted rubbery polymers.[22]

The objective of the present study is to obtain experimental data on the dependence of diffusion coefficients on degree of polymerization, etc., in the nondilute region (recall this is a ternary system). Data will be obtained for a concentration range that covers the conditions which control much of the rates and molecular weight distributions in free-radical polymerizations, as shown, for example, by comparison between modeling and experimental data that are sensitive to termination events.[6]

Pulsed-field-gradient NMR[23] is an ideal means to obtain $D_i(w_p)$ for nonglassy systems,[17,24,25] being able to be used to obtain diffusion coefficients down to $\sim 10^{-10}$ $cm^2\ s^{-1}$. The basic idea is to align spins with an initial pulse and to interrogate with a subsequent sequence of pulses; spatial diffusion changes the resulting signal, and from the dependence of this signal on pulsing frequencies, the diffusion coefficient can be extracted. The means used to prepare the oligomers is through catalytic cobalt chain transfer agents (e.g., refs 26−32) to produce oligomers of methacrylates with a terminal double bond. The structures of MMA monomer and dimer are as follows:



MMA
I



dimer
II

Depending on the amount of catalyst, one can obtain virtually pure dimer to mixtures of oligomers, e.g., up to 16-meric. Where necessary, oligomers were fractionated by preparative GPC to obtain samples ranging from dimeric to decameric; some of these were mixtures of approximately equal amounts of tetra- and penta- or of penta- and hexameric, species. The use of catalytic cobalt chain transfer agents to produce suitable species is most easily applied to methacrylates, and so the present study is confined to macromonomers of both methyl and butyl methacrylate in both parent polymers. The desired w_p was achieved by preparing appropriate mixtures of a small amount of macromonomer, polymer, and a diluent, which mimics monomer: this diluent is chosen to be the corresponding saturated equivalent, methyl isobutyrate for MMA and butyl isobutyrate for BMA. Pulsed-field gradient NMR of these to obtain oligomer (macromonomer) diffusion coefficients is facilitated by being able to monitor the proton NMR of the CH_2 hydrogens on the macromonomer double bond, which is well separated from peaks of polymer and diluent.

Recent data[33] show that the diffusion coefficient of a radical and its stable parent are close, but not the same: the difference can be as much as 25%, with the radical seeming to diffuse more slowly for aromatic-type species and more rapidly for aliphatic ones, although radical and nonradical diffusion coefficients seem to approach each other as the molecular weight increases. Given this *caveat*, the present data should prove of use in the modeling of diffusion coefficients of oligomeric radicals required for predicting and interpreting rate and molecular weight distribution data in rubbery systems.

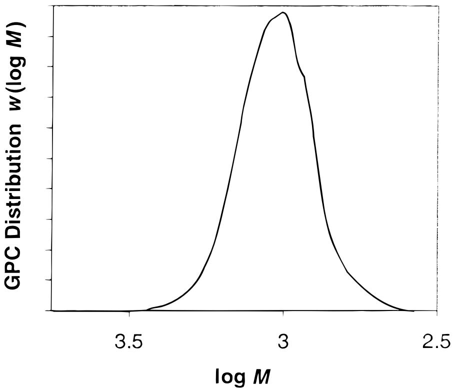


Figure 1. Analytic GPC trace of the decameric fraction obtained from preparative GPC of a mixture of MMA oligomers prepared by catalytic chain transfer agent; $\langle M_n \rangle = 1005$, polydispersity = 1.09.

In these studies, it will be useful to consider separately data below and above c^* (the concentration at which chains start to overlap); diffusion dynamics are likely to be different above and below c^*, and different again at conversions above and below the glass transition. For example, in the bulk free-radical polymerization of MMA at 50 °C, c^* occurs at a few percent polymer and the glass transition occurs at about 85% polymer.

Materials and Methods

The MMA-based oligomers were from a variety of sources. Monomer (Aldrich, 99%, inhibited with 10 ppm MEHQ) was purified by passing through an alumina column (Aldrich, active, basic) to remove the inhibitor, followed by distillation under reduced pressure (30 °C, 740 mmHg). Dimer and trimer, obtained by cobalt catalytic chain transfer agent,[26,34,35] were kindly supplied by the CSIRO Division of Chemicals and Polymers, Melbourne, Australia. Higher oligomers were synthesized via solution polymerization in THF[26,34−36] or emulsion polymerization[37] as macromonomer solutions using catalytic cobalt chain transfer agents.[31,32] The resulting macromonomers were separated into oligomeric fractions using a preparative GPC (DuPont Instruments) injector port and PLgel (50 Å, 10μ Styrogel) preparative column controlled via an Altex microprocessor, with a Waters R401 differential refractometer (64 × RI, negative polarity) as the detector. Redistilled THF was used as the eluent at a flow rate of 5 mL min^{-1}. All MMA oligomers were stored at 4 °C until used.

After separation, each oligomer was purified by passing through an alumina (Aldrich, active, neutral) column to remove residual chain transfer agent and the solvent stabilizer. One-dimensional proton NMR (Bruker, 400 MHz) of all oligomers obtained were run to confirm purity. Molecular weight distributions of macromonomers were obtained by analytical GPC (Waters Associates Liquid Chromatograph analytical GPC system), with a Waters 717 automatic sampler, three Waters μ-Styrogel columns in series (10^3, 100, and 50 Å), a Waters 410 differential refractometer (1 × RI, negative polarity), and Millenium (version 2.15) software. The flow rate was 1.0 mL min^{-1} with redistilled THF as eluent. Figure 1 gives some typical GPC data of these macromonomers.

BMA monomer (Aldrich, 99%, inhibited with 10 ppm MEHQ) was purified by passing through an alumina column

(Aldrich, active, basic) followed by distillation (68−70 °C, 744 mmHg). BMA was stored at 4 °C until required but was always used within 2 days of distillation, to reduce risk of thermal polymerization/autopolymerization occurring. The *n*-butyl methacrylate dimer was used as synthesized.

Matrix polymers (pMMA and pBMA) for use as matrixes in the macromer/diluent/polymer system were synthesized from purified monomer by emulsion polymerization using standard conditions (80 °C, AIBN or potassium persulfate initiator, etc.). Each polymer latex was purified by dialysis and repeated drying (in vacuo), dissolving (in THF), filtering, and precipitating (in methanol) of the polymer to remove the majority of the surfactant, small water-soluble species, and any cross-linked polymer present. Dried polymer was used in all sample preparations. Purified polymers were characterized by GPC and 200 MHz NMR. The matrix polymers had number average molecular weights ($\langle M_n \rangle$) of 1.04×10^5 and 1.5×10^5 for pMMA and pBMA respectively, with polydispersities of 2.5 and 1.9.

Methyl isobutyrate (MIB, Aldrich, 99%) was used as received as diluent in pMMA systems to obtain the desired w_p. MIB is a saturated MMA molecule and, as such, has about the same size and molecular weight as MMA and therefore approximately the same diffusion coefficient. For the purpose of diffusion, a solution of pMMA in MIB is assumed to behave much the same as a solution of pMMA in MMA. From an NMR point of view, MIB produces peaks in the same region as pMMA and will therefore not interfere with those peaks from the double bond of the oligomers. MIB is also stable to heating, so a solution of pMMA in MIB can be heated to facilitate removal of air bubbles (which lead to noise in the NMR spectra) and to accelerate sample preparation.

Butyl isobutyrate (BIB, TCI, 99%), was used as received. As with MIB, BIB is suited to studying the diffusion of BMA oligomers in pBMA solutions, as it is likely to diffuse in a manner similar to BMA due to structural similarity. As BIB is the saturated version of the BMA monomer it will not interfere with the olefinic peaks of interest in the NMR spectra. BIB is also heat stable.

Samples with a weight fraction of pMMA or pBMA up to 40% were prepared by dissolving the polymers in MIB in 9 mm (outer diameter), flat-bottomed, precision NMR tubes (Wilmad). The tubes were then sealed with Teflon plugs and Parafilm and heated in a water bath at 50−55 °C, until the desired weight fraction, without air bubbles, was achieved (2 days to 4 weeks). After this time 20−40 mg of oligomer was added and the pMMA matrix samples were stored at about 4 °C (to reduce even further the very small risk of autopolymerization of the oligomers[38]) for 2−4 days to allow the oligomer to diffuse to give a homogeneous solution. The pBMA matrix samples were left at room temperature for 2−4 days, as refrigeration of these samples leads to the pBMA passing through its glass transition point ($T_g \sim 20$ °C) and becoming a glassy polymer, hampering diffusion. The total amount of solution per tube was approximately 0.5 g.

Samples with a weight fraction of pBMA up to 40% were prepared as for the MMA oligomer samples but using BIB instead of MIB as the solvent; pMMA matrix samples could not be studied, as pMMA is insoluble in BIB.

The protons on the double bond of the monomer or macromonomer used as tracers in the present study, being attached to an sp^2 carbon, give NMR signals shifted significantly downfield from the remaining proton peaks in the sample and are thus easily distinguished. Since these protons are bonded to the same carbon atom and the double bond cannot rotate, the two protons are not identical and so give rise to two individual signals, each of which can be used independently.

The PFG NMR technique itself has been described elsewhere (e.g., refs 17 and 25). A static magnetic field aligns magnetization vectors of the nuclei along the z axis, and a pulse is applied to rotate these vectors by 90° into the xy plane. A field gradient is applied for a time δ, causing the nuclei to precess at different frequencies depending on the field they experience, which is related to their position and hence is influenced by diffusion. Another pulse is applied to turn the vectors 180° around the x axis where they will rephase with application of a second field-gradient pulse of the same magnitude and duration as the first. The attenuation of the resulting "echo peak" is monitored as δ is increased. The diffusion coefficient is calculated from[24]

$$\ln\left(\frac{I}{I_0}\right) = -\gamma^2 D_i(w_p) G^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right) \tag{1}$$

where I is the intensity at a certain value of δ, I_0 is its value at $\delta = 0$, γ is the magnetogyric ratio of the nucleus (here ^{1}H), G is the magnitude of the field-gradient pulse and Δ is the time between pulses. D is obtained from a plot of $\ln(I/I_0)$ against $\delta^2(\Delta - \delta/3)$; these plots were found to be highly linear for the present systems.

Results

Collected results of diffusion studies for MMA-based oligomers in pMMA and pBMA and of BMA oligomers in pBMA are given in Table 1. The diffusion coefficients at $w_p \geq 0.4$ for oligomers longer than trimeric were unable to be measured for the pMMA matrix due to swamping effects from the polymer peaks present in the spectra. In the case of the pBMA matrix all diffusion coefficients at $w_p = 0.4$ except for the decameric sample were able to be measured without undue interference from the polymer peaks.

As illustrated in Figures 2 and 3, which show $D_i(w_p)$ for MMA and for BMA oligomers in the parent polymers at 25 °C, the w_p dependences of the diffusion coefficients suggest a change in character as infinite dilution is approached. This apparent change at infinite dilution has been observed previously[11] and may be due to changes in the dynamics of diffusion above c^*.

The weight fraction at overlap, w_p^* (equivalent to c^*) is found from[39]

$$w_p^* = \frac{3\langle M_n \rangle}{4\pi d_M {R_g}^3 \boldsymbol{N}_A} \tag{2}$$

where d_M is the density of monomer, N_A is Avogadro's constant, and the radius of gyration is given in terms of the expansion factor C_∞ by[40]

$${R_g}^2 = \frac{1}{6} C_\infty \frac{\langle M_n \rangle}{M_0} l^2 \tag{3}$$

where M_0 is the molecular weight of monomer and l is the length between two monomer units. Taking $\langle M_n \rangle = 10^5$, $l = 2(\text{C}-\text{C}$ bond length$) = 2 \times 1.54$ Å, and $C_\infty = 7$,[40] gives $w_p^* \approx 0.03$ for MMA. Hence the observation of an apparent change in diffusion behavior between 0 and 10% polymer exhibited in Figures 2 and 3 is not unexpected.

The data at infinite dilution ($w_p = 0$), given in Figure 4, show the dependence of the diffusion coefficient on oligomer length that has been seen in many other such data sets, viz., that $D_i(w_p{=}0) \propto i^{-(0.5-0.6)}$.[41] Specifically, the data for MMA oligomers in MIB obey $D_i(w_p{=}0) \propto i^{-(0.56\pm0.08)}$ and $i^{-(0.53\pm0.13)}$ at 25 and 40 °C, respectively (there are only two data points each for BMA in BIB, so the exponents obtained from the data, 0.96 and 0.90 for 25 and 40 °C, respectively, are not statistically meaningful).

To examine the dependence of the diffusion coefficient on oligomer length above c^*, it is informative to plot a normalized diffusion coefficient, i.e., the diffusion coef-

Table 1. Diffusion Coefficients/10^{-9} m^2 s^{-1} (Values Averaged over Several Readings)

MMA Oligomers as Diffusing Species

	degree of polymerization													
	1		2		3		4 + 5		5 + 6		7		10	
w_p	25 °C	40 °C	25 °C	40 °C	25 °C	40 °C	25 °C	40 °C	25 °C	40 °C	25 °C	40 °C	25 °C	40 °C
PMMA Matrix														
0.00	3.06	6.41	1.94	3.43	1.35	4.43			0.937	2.33	0.863	2.22	0.964	
0.02	2.08													
0.05	1.88	2.35												
0.10	1.67	2.12	0.903	1.15	0.645	0.793	0.383	0.490	0.291	0.379	0.263	0.358	0.255	0.326
0.20	1.18	1.54	0.573	0.815	0.361	0.541	0.261	0.398	0.183	0.270	0.117	0.186	0.135	0.184
0.30	0.789	1.12	0.367	0.516	0.183	0.282			0.058	0.098	0.062	0.083		
0.40	0.428	0.703	0.165	0.287	0.122	0.157								
PBMA Matrix														
0.00	3.06	6.41	1.94	3.43	1.35	4.43			0.937	2.33	0.863	2.22	0.964	
0.10	1.77	2.47	0.989	1.35	0.671	1.03	0.489	0.699	0.362	0.553	0.294	0.483	0.250	0.419
0.20	1.30	1.77	0.685	0.890	0.461	0.711	0.239		0.200	0.265	0.152	0.218		
0.30	1.01	1.31	0.432	0.626	0.262	0.355		0.183	0.097	0.139	0.074	0.110	0.071	0.117
0.40	0.728	0.949	0.278	0.376	0.148	0.226	0.064	0.089	0.045	0.077	0.042	0.062		

BMA Oligomers as Diffusing Species

	degree of polymerization			
	1		2	
w_p	25 °C	40 °C	25 °C	40 °C
0.00	1.56	3.75	0.798	2.03
0.10	0.912	1.28	0.479	0.726
0.20	0.695	0.957	0.325	0.465
0.30	0.504	0.665	0.211	0.309
0.40	0.330	0.489	0.120	0.185
0.90	0.059			

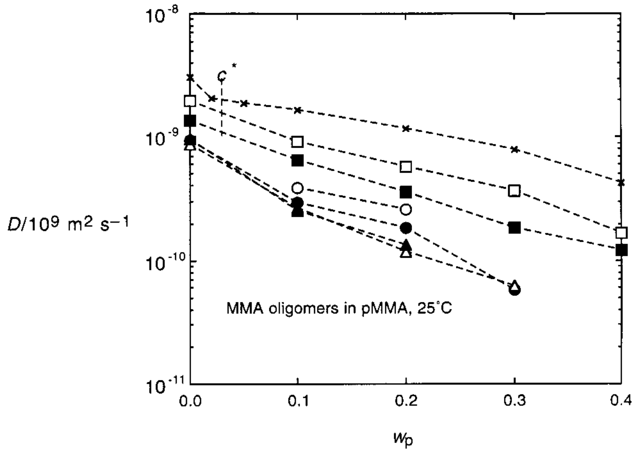


Figure 2. Some of the data from Table 1, viz., $D_i(w_p)$ for MMA oligomers of the indicated degrees of polymerization i in pMMA at 25 °C: monomer (×), dimer (□), trimer (■), tetra- and pentamer (○), penta- and hexamer (●), heptamer (△), decamer (▲). Lines joining data points are only as a visual guide. The approximate value of c^* is also shown.

ficient for each oligomer at a particular weight fraction divided by the diffusion coefficient of the monomer at the same w_p, as a function of degree of polymerization i: $D_i(w_p)/D_1(w_p) \equiv D_i(w_p)/D_{mon}(w_p)$, as given for MMA oligomers in a pBMA matrix in Figure 5. In this case, the points are semiquantitatively described by a power law dependence on i:

$$D_i(w_p)/D_{mon}(w_p) = a i^{u(w_p)} \tag{4}$$

where the values of the exponent u are given in Table 2. While an unrestrained least-squares power-law fit to the data does not yield $a = 1$ exactly, Figure 5 shows that this holds to a reasonable approximation.

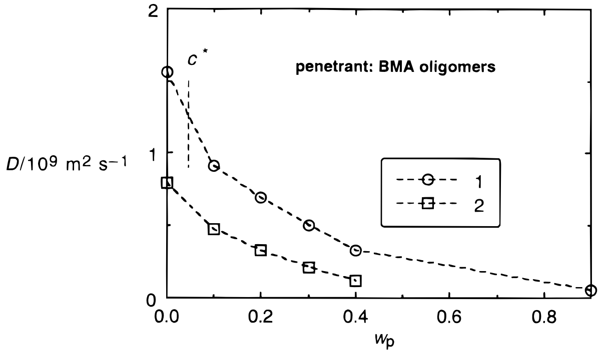


Figure 3. $D_i(w_p)$ for BMA monomer and dimer in pBMA at 25 °C. Lines joining data points are only as a visual guide. The approximate value of c^* is also shown.

Empirical Scaling Fit to MMA Oligomer Data. A reasonable place to begin expressing the observed dependence of oligomeric diffusion coefficients on degree of polymerization and on w_p is a simple empirical approach,[17] where the dependence on oligomer length changes gradually with increasing weight fraction of polymer:

$$u(w_p) = c_0 + c_1 w_p \tag{5}$$

Note that the linearity of the exponent assumed in eq 5 can only hold for a rubbery system, since when w_p increases to the extent that the system becomes glassy (given that the temperature is below the T_g of the polymer matrix), one expects the exponent to follow the reptation value of 2, independent of w_p.

Scaling exponents for all the data for MMA oligomers in both matrixes and at both temperatures are now considered. In calculating $u(w_p)$, the data for $w_p = 0$ were omitted, in line with the earlier observation that the diffusion behavior at infinite dilution seems signifi-

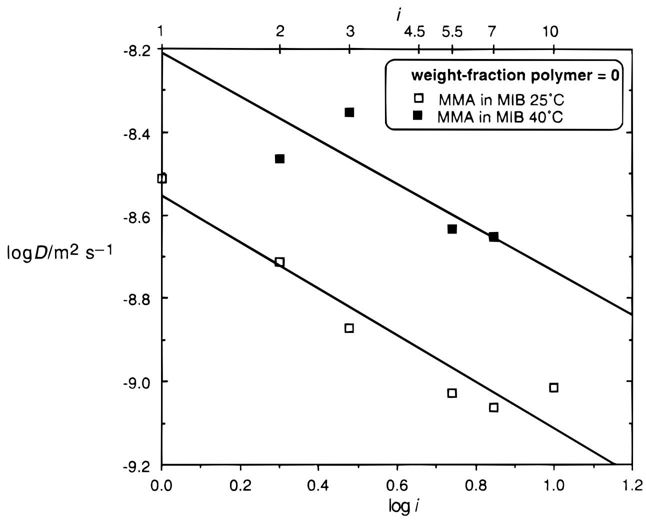


Figure 4. log/log plot of infinite-dilution ($w_p = 0$) diffusion coefficients for various MMA-based oligomers in MIB diluent (the saturated equivalent of the monomer), at 25 and 40 °C. The lines of best fit are also shown.

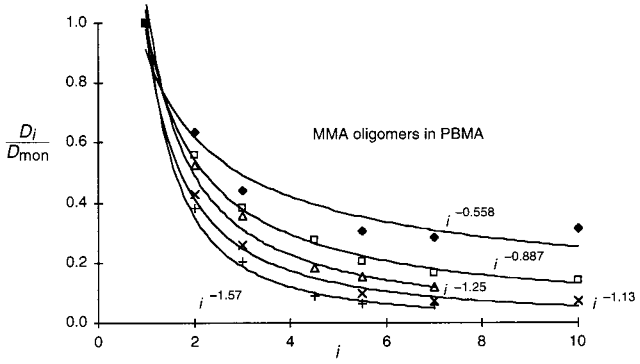


Figure 5. Oligomeric diffusion coefficients normalized by that of the monomer, $D_i(w_p)/D_{mon}(w_p)$, for various w_p for MMA oligomers in pBMA at 25 °C ($w_p = 0$, ◆; = 0.1, □; = 0.2, △; = 0.3, ×; = 0.4, +), together with corresponding power-law fits, $D_i(w_p)/D_{mon}(w_p) = a/i^u$. Note that the power-law fits were not constrained to give $a = 1$, although they do so to a good approximation.

Table 2. Value of Exponent u Fitting $D_i(w_p)/D_{mon}(w_p) = ai^u$, for MMA-Based Oligomers in Both Matrixes at 25 and 40 °C

	pMMA Matrix		pBMA Matrix	
w_p	25 °C	40 °C	25 °C	40 °C
0.0	−0.669	−0.525	−0.558	−0.573
0.1	−0.897	−0.879	−0.887	−0.803
0.2	−1.03	−0.991	−1.13	−1.10
0.3	−1.42	−1.40	−1.25	−1.18
0.4	*a*	*a*	−1.57	−1.47

[a] Insufficient values for representative power law fit.

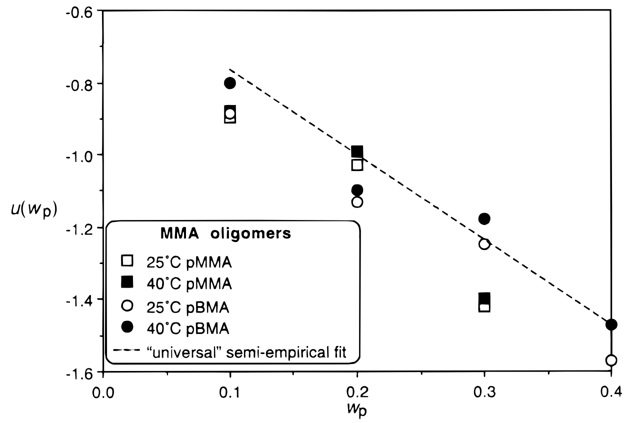


Figure 6. Points: exponents $u(w_p)$ for power-law fit (MMA oligomers in both pMMA and pBMA matrixes at 25 and 40 °C). Line: approximate fitting by $u(w_p) = -0.664 - 2.02w_p$.

cantly different from that at higher w_p (above c^*). In the limit of $w_p = 0$, c_0 will be approximately 0.5−0.6, in line with infinite dilution diffusion results, but may take any value if the infinite dilution regime is excluded. Both c_0 and c_1 might depend on a number of variables such as temperature, the type of oligomer, or the type of matrix through which the oligomers are diffusing. Fits for $u(w_p)$ were calculated for both 25 and 40 °C and also for the two temperatures combined. These are plotted in Figure 6, from which it is clear that there is little dependence of $u(w_p)$ on the temperature for MMA oligomers diffusing in either matrix, at least over the small temperature range considered in this study, although over a wider temperature range, $u(w_p)$ could well depend significantly on temperature.

It is not unreasonable to expect the structure of the matrix polymer to affect the diffusion of small species through it (and, indeed, various ideas for such dependences have been put forward[18,22]). In every case the unnormalized pBMA matrix diffusion coefficients are slightly larger than those for pMMA, as expected: it is well-known that the butyl side chain in pBMA acts as an internal plasticizing agent. However, Figure 6 suggests that there is no significant dependence of the scaling exponent for the *normalized* diffusion coefficients on the matrix, at least for MMA oligomers in either pMMA or pBMA matrixes. The lack of matrix dependence in the *normalized* diffusion coefficients (D_i/D_{mon}) implies that the differences between the matrixes is largely accounted for by the diffusion coefficient of the monomer. However, the difference in the gradients of the fits of $u(w_p)$ for the two matrixes implies that it is possible that, at higher w_p, the two fits may diverge.

It is useful to see if estimates of the values for the diffusion coefficients for higher oligomers can be obtained by extrapolating data only for dimer and trimer (reduced data). Comparison between the two $u(w_p)$ equations for each matrix should give some indication of whether it is necessary to measure experimentally as far as a decamer to be able to predict diffusion behavior accurately for systems such as MMA. The values of c_0 and c_1 for the dimer/trimer fits were used to predict extrapolated reduced diffusion coefficients in Figure 7, which shows that the empirical exponents obtained from fitting the data for all MMA oligomers (di- to decameric) from w_p just above c^* to the maximum studied here (approximately 0.4), can also be estimated adequately with dimer and trimer data alone. As the diffusion coefficients for both matrixes were well fitted by full and reduced $u(w_p)$ equations, for systems such as MMA it should only be necessary to measure diffusion coefficients of the smallest species to be able to predict those for the larger species. In the two closely related matrixes used in this study, the type of matrix does not influence $u(w_p)$ significantly, as illustrated by the similarity of the exponents using both matrix-dependent and matrix-independent $u(w_p)$ equations. The empirical scaling exponent in the normalized diffusion coefficient, $D_i(w_p)/D_{mon}(w_p)$, seems to depend only on w_p and not on either the temperature or the matrix type in diffusion of oligomers based on the same monomer unit in closely related matrixes. The effects of temper-

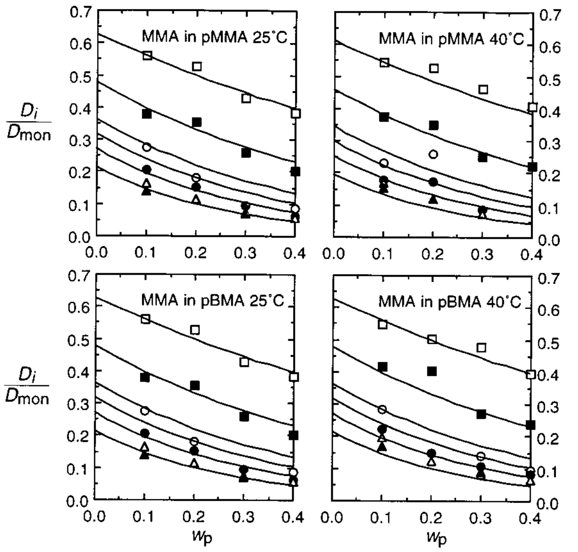


Figure 7. Points: normalized diffusion coefficients for MMA oligomers in both pMMA and pBMA at 25 and 40°C (same symbol code as in Figure 2). Lines: extrapolated fits using the power law estimated only from data from dimer and trimer.

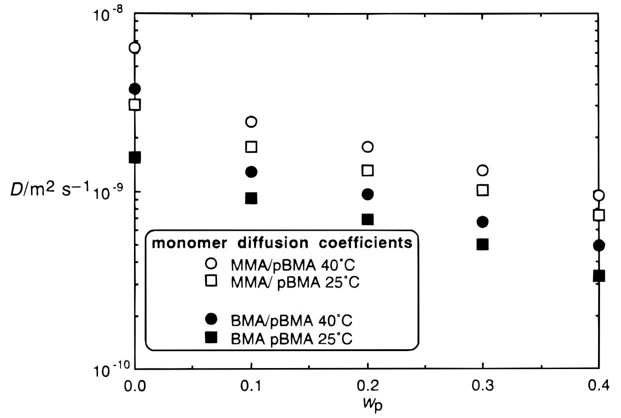


Figure 8. Diffusion coefficients of MMA and of BMA monomers in pBMA matrixes at 25 and 40 °C.

ature and matrix type in $D_i(w_p)$ seem therefore to be accounted for by the monomer diffusion coefficient.

BMA Data. The behavior of the BMA-based oligomers is similar to that of the MMA-based ones. As shown in Figure 3, a change in character between diffusion coefficients at $w_p = 0.0$ and 0.1 is observed, which again is ascribed to the transition through c^*.

As seen in Figure 8, the magnitude of the diffusion coefficient of the two monomer types is considerably different in the same matrix. MMA monomer diffuses considerably faster than does BMA, which can be rationalized on the basis of size; it has been established that diffusion of monomer in such monomer/polymer binary systems can be quantitatively fitted by free-volume theory.[42,43]

Figure 9 compares the reduced diffusion coefficients, $D_2(w_p)/D_{mon}(w_p)$, for BMA dimer in pBMA and MMA dimer in pMMA. It can be seen that the reduced diffusion coefficients for these two oligomer/polymer systems do not depend strongly on either temperature or composition (with again the exception of very low w_p). This suggests the possibility of a "universal", albeit approximate, scaling law.

"Universal" Semiempirical Fit to Reduced Diffusion Coefficients. In an attempt to find an approximate "universal" scaling law, all reduced diffusion coefficient data for all oligomers, both temperatures, and all w_p above c^* were least-squares fitted to the form of eqs 4 and 5. The result is

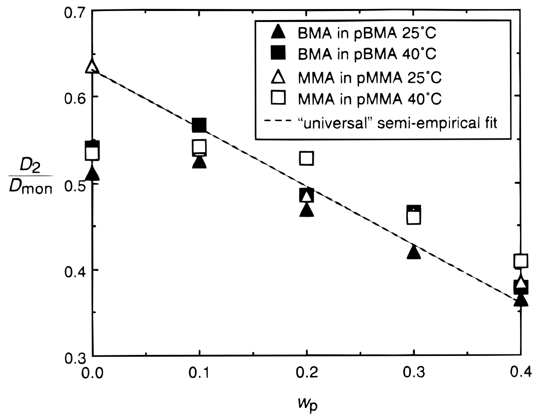


Figure 9. Reduced diffusion coefficients, $D_2(w_p)/D_{mon}(w_p)$, for BMA dimer in pBMA and MMA dimer in pMMA, at 25 and 40 °C.

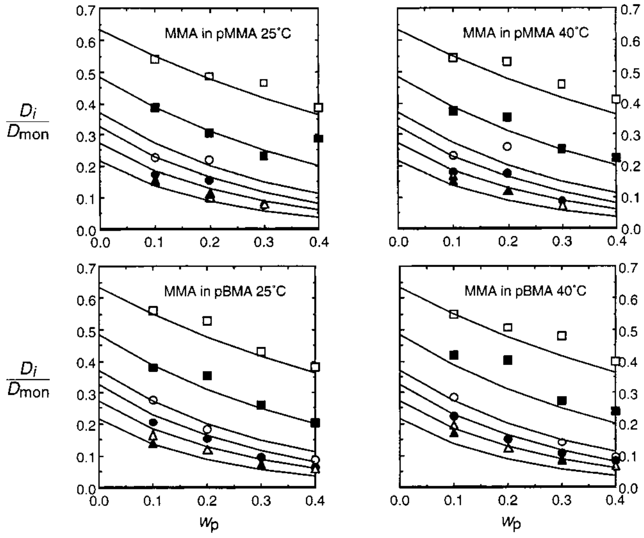


Figure 10. Points: normalized diffusion coefficients for MMA oligomers in both pMMA and pBMA at 25 and 40 °C (same symbol code as in Figure 2). Lines: predictions using the "universal" power law, eq 6.

$$\frac{D_i(w_p)}{D_{mon}(w_p)} = i^{-(0.664 + 2.02w_p)} \tag{6}$$

As shown in Figures 6 and 10, the accumulated data for MMA oligomers at both 25 and 40 °C in both pMMA and pBMA matrixes in the range $0.4 \geq w_p \geq 0.1$ can be fitted adequately, although imperfectly, by eq 6. Diffusion coefficients at $w_p = 0$ are predicted poorly by these c_0 and c_1, as expected. Similarly, the BMA dimer data can also be represented moderately well by this relation, as shown in Figure 9.

Comparison with Predictions of Various Models

The present data have the potential to provide critical tests for various models for $D_i(w_p)$, since a truly "molecular-level" theory (i.e., one that claims to predict data from parameters such as inter- and intramolecular potentials) should be able to predict oligomer results from those for monomer, since the potential functions

Table 3. Free Volume Parameters for PMMA and MMA[a]

parameter	Faldi et al.[52]	Waggoner et al.[14]
$\hat{V}_1$* (cm^3 g^{-1})	0.87	0.771
$\hat{V}_2$* (cm^3 g^{-1})	0.757	0.788
K_{11}/γ (cm^3 g^{-1} K^{-1})	8.15×10^{-4}	1.17×10^{-3}
$K_{21} - T_{g1}$ (K)	0	−51.37
K_{12}/γ (cm^3 g^{-1} K^{-1})	4.77×10^{-4}	3.05×10^{-4}
$K_{22} - T_{g2}$ (K)	−339.6	−301
D_{01} (cm^2 s^{-1})	1.61×10^{-3} (adjusted to 2.74×10^{-3})	9×10^{-5}
E (J mol^{-1})	3255	0
ξ	0.60	0.92

[a] The value quoted by Faldi et al. for D_{01} (1.61×10^{-3} cm^2 s^{-1}) was adjusted to 2.74×10^{-3} cm^2 s^{-1} to give improved agreement with the present data.

should be essentially the same apart from allowing for the connectivity of the oligomers.

Free Volume Theory. While there are a number of models for penetrant diffusion in rubbery polymer systems,[13,14,44–46] the dominant current model is that of free volume,[47,48] which assumes that the ability to diffuse depends on the amount of empty space in the system.[48] Extensive modifications of this idea to apply to polymeric systems have been presented, especially by Duda, Vrentas, and co-workers.[42,49–51] Their expression for D in a solvent/polymer binary system is

$$D = D_{01}e^{-E/RT}\exp\left(-\gamma\frac{(1-w_p)\hat{V}_1^* + w_p\xi\hat{V}_2^*}{\hat{V}_{FH}}\right) \quad (7)$$

where 1 and 2 refer to solvent and polymer, respectively, E is the attractive energy between the penetrant and its neighbors, D_{01} is a preexponential factor, γ corrects for free-volume overlap, $\hat{V}_i^*$ is the specific critical hole free volume of component i, ξ is the ratio of the critical molar volume of the solvent jumping unit to that of the polymer jumping unit, and

$$\hat{V}_{FH}/\gamma = (1-w_p)\frac{K_{11}}{\gamma}(K_{21}+T-T_{g1}) + w_p\frac{K_{12}}{\gamma}(K_{22}+T-T_{g2}) \quad (8)$$

where K_{ij} are various parameters and T_{gi} is the glass transition temperature for that component. It is claimed that one can obtain the values of the many parameters from independent experiments, making the theory semiquantitatively predictive.[42,43]

Free volume parameters have been reported for pMMA and MMA[14,52] and are given in Table 3. Since no data are available for MIB, it will be assumed that the free-volume parameters for MIB can be approximated by those for MMA, and for this pseudobinary system of MMA monomer diffusion in pMMA, the monomer diffusion coefficients were obtained by using eq 8. These are compared with present experimental values, and with earlier MMA/pMMA data of Waggoner et al. at 25 °C, in Figure 11. It is seen that there is good accord with the present monomer diffusion data and those of these authors.

The free-volume predictions using the parameters of Faldi et al.[52] and of Waggoner et al.[14] give a reasonable although imperfect agreement with the experimental values, with the marked exception of the $w_p = 0.0$ case, where the experimentally observed rapid increase in diffusion coefficient is not predicted by the model.

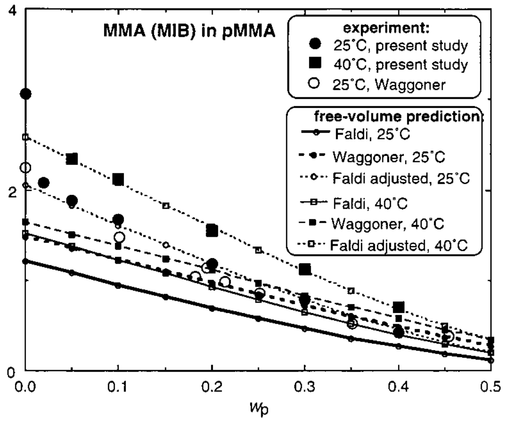


Figure 11. Diffusion coefficients for MIB (the saturated analogue of MMA) in pMMA. Points: experiment, showing values from present study at 25 and 40 °C, and values for MMA in pMMA at 25 °C from Waggoner et al.[14] The experimental value for $w_p = 0$ at 40 °C from the present study, $\sim 6 \times 10^{-9}$ m^2 s^{-1}, is off-scale and not shown. Lines: predicted from free-volume theory with parameters of Table 3, including values calculated both with the parameters given by Faldi et al.[11] and recalculated with an adjusted value of D_{01} and with the parameter values of Waggoner et al.[14]

Accord with experiment above c* can be obtained by minor adjustment of the free-volume parameters: e.g., changing the value of D_{01} in the parameters of Faldi et al. as indicated gave good agreement, with the exception of the value at 40 °C at the highest w_p.

The monomer diffusion data for MMA in pBMA and BMA in pBMA have been used elsewhere to test and refine free-volume parameters.[53]

An extension of free-volume theory to a ternary system is available;[42] however, as oligomeric species of MMA have not previously been studied extensively and are not available in large quantities, the parameters required for such a calculation for the current systems are not available.

In the recent theory presented by Petit et al.[18] diffusion of relatively small species in a hydrophilic polymer system were studied. The results suggested a functional form such that the experimental data could be fitted using two parameters related to the quality of the solvent (ν) and the size of the diffusing molecule and the temperature ($k\beta^2$).[18] Unfortunately, this model has yet to be extended to *ternary* systems such as the present one.

It would appear that no current theories (with the presumed exception of laborious molecular dynamics simulations) are able to predict or rationalize the present data for oligomer (as distinct from monomer) diffusion in these ternary systems.

Activation Energy for Monomer Diffusion Above c*. Given the insensitivity of the reduced diffusion coefficients to temperature, matrix, and penetrant type (for a given w_p), it is apparent that the temperature dependence of oligomer diffusion coefficients can, to acceptable accuracy, be obtained from that for monomer alone. As the present data are only for two relatively close temperatures, the activation energy from the monomer data will obviously be subject to high uncertainty. Given this warning, activation energies for monomer diffusion as a function of w_p are shown in Figure 12. Again it is seen that the values below c* are anomalous, with the size of this anomaly being much greater than the uncertainty in the data. Activation energies for all systems at a given w_p above c* lie within

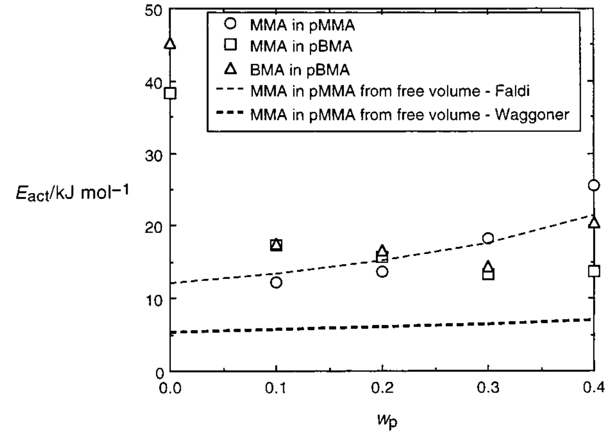


Figure 12. Experimental activation energies for monomers (MMA and BMA) diffusing in pMMA and pBMA, and values calculated for MMA in pMMA from the free-volume parameters in Table 3, with parameters from Faldi et al.[52] and from Waggoner et al.[14]

each other's experimental uncertainty, with averages varying from 14.7 kJ mol^{-1} at $w_p = 0.1$ to 16.2 kJ mol^{-1} at $w_p = 0.4$.

Figure 12 also shows the monomer-in-polymer activation energy predicted for MMA in pMMA with the free-volume parameters of Table 3 (the predicted activation energy is of course independent of the value of the parameter D_{01}). Again, with the exception of below c^*, the magnitude and trend of the free-volume prediction are consistent with observation. However, the free-volume parameters of Faldi et al.,[11] where the value of the parameter E is nonzero, give better agreement with the (widely scattered) experimental activation-energy data than do the parameter values of Waggoner et al.[14] who used $E = 0$.

Wider Applicability of Semiempirical Scaling Relation. As the scaling given in eq 6 for MMA and BMA oligomers appears to be independent of temperature and matrix type, it might also be possible to use eq 6 with data for different sorts of systems. To investigate further the observed matrix and oligomer type independence of the $u(w_p)$ equations, diffusion coefficients for a polystyrene system were predicted using the matrix-independent full $u(w_p)$ equation. Data have been obtained by Piton et al.[17] for the diffusion at 50 °C through a polystyrene matrix of toluene and benzene (both of which should be a close approximation to the diffusion of styrene monomer), of a dimer-like species and of an unfractionated, commercial polystyrene pentamer standard. The pentameric species was a mixture of oligomers, which gave a peak molecular weight of 580.

Diffusion coefficients were predicted for the dimeric and pentameric species as follows. The "monomer" data were fitted to a polynomial

$$\ln(D_{mon}/\mathrm{m}^2\ \mathrm{s}^{-1}) = -19.982 - 4.4073w_p + 8.2787w_p^2 - 13.719w_p^3 \quad (9)$$

after which "dimer" and "pentamer" diffusion coefficients were predicted using eq 6. The results are shown in Figure 13.

From Figure 13 it seems that the $u(w_p)$ semiempirical scaling calculated for the methacrylate-based systems is able to predict diffusion behavior with acceptable accuracy in a polystyrene system. This result shows that $u(w_p)$ is not heavily dependent on, e.g., the type of functional group present in a polymer, as the methacrylate and styrene systems are structurally dissimilar. This extends the range of systems for which diffusion coefficients can be predicted using the empirical approach.

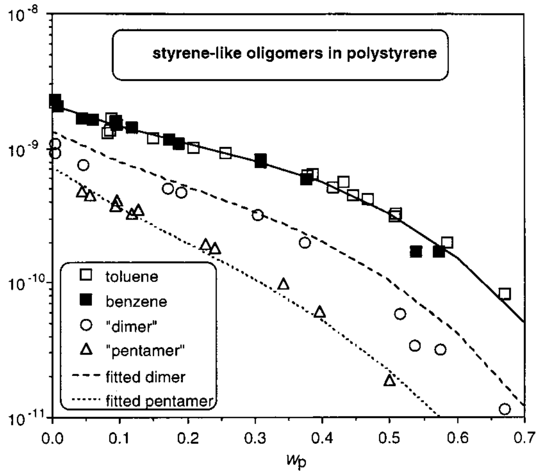


Figure 13. Observed[17] (points) and calculated (lines) diffusion coefficients for styrene-like penetrants in polystyrene at 50 °C. The calculated values for "monomer" are the least-squares fit values of eq 9; those for "dimer" and "pentamer" are obtained from these fitted values for "monomer" together with eq 6.

Conclusions

Diffusion coefficients for both BMA- and MMA-based oligomers can be measured successfully over a wide range of weight fractions in rubbery systems using pulsed field gradient NMR. The results are reproducible and internally consistent.

The observed dependence of the diffusion coefficients on degree of polymerization at very low polymer concentrations (below c^*, where chain overlap commences) follows expected scaling laws, within concepts such as the Zimm model.[41,54-57]

For the purposes of understanding and modeling rates and molecular weight distributions in free-radical polymerizations, it is, however, far more important to know the dependence on degree of polymerization from c^* to high conversion.

As the polymer concentration increases above c^*, a change in diffusion behavior is observed. This is assumed to arise because above c^*, the polymer chains greatly interfere with the small species diffusion, whereas below c^* the small species are relatively free to diffuse between chains. The precise origin of this changeover is unknown, although some hints are beginning to emerge[58] from molecular dynamics simulations. To date there seems to be no theory (apart from full molecular dynamics simulations) that can predict diffusion coefficients accurately both below and above c^*, due to the significant change in diffusion behavior above and below c^*.

The present data cover a significant part of this range in the "intermediate conversion" regime. The dependence observed here for monomer diffusion coefficients on polymer fraction and temperature above c^* is in accord with free-volume theory, certainly at least where parameters for this dependence are available. However, neither free-volume theory nor an alternative due to Petit et al.[18] are able to model a priori a ternary system such as those studied here, comprising polymer, penetrant of varying degrees of polymerization, and monomer-like diluent.

A fruitful approach to encapsulating the data for oligomer diffusion obtained here is a semiempirical scaling fit, exemplified in eqs 4 and 6. This enables the dependence of oligomer diffusion coefficients on degree of polymerization, matrix, polymer fraction, and temperature to be expressed in terms of the dependences of *monomer* diffusion coefficients on matrix, polymer fraction, and temperature (which as stated are consistent with free-volume precepts) and a scaling exponent. It is found that these exponents may be expressed with varying degrees of sophistication. At one level, it is found that an accurate measurement of this exponent, for each w_p, matrix, and temperature, for dimer and trimer alone seems sufficient to predict the behavior of oligomers of higher degrees of polymerization (Table 2). Since small oligomers are often relatively easy to synthesize with low polydispersity, this observation suggests that future experimental PFG NMR data obtained from small species could be used with acceptable reliability to predict data for higher degrees of polymerization.

A surprising result is that a particularly simple "universal" scaling law, eq 6, provides an adequate, although imperfect, fit for a range of temperatures, oligomers, degrees of polymerization, and matrixes (oligomers of MMA in both pMMA and pBMA, BMA dimer in pBMA, and styrene oligomers in polystyrene). Thus, it seems that, above c^*, the scaling exponent of the normalized diffusion coefficient is insensitive to the type of oligomer diffusing as well as insensitive to temperature and matrix. That is, any dependence on the type of oligomer diffusing can be accounted for in the monomer diffusion coefficient. This is a very useful (if puzzling) result for modeling and interpreting rates and molecular weight distributions in free-radical polymerizations. The reason for this observed approximate "universal" scaling is not apparent and does not appear to be explained by current theories, although it is noted that hints from simulations are starting to emerge.[59] The exploration of reasons for this observation is seen as a fruitful area for theory.

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