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Diffusion of Dyes in Polycarbonate. A New Measurement Technique and Correlation with Shadow Areas

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ABSTRACT: Using a simple but novel technique, we have examined diffusion of an assortment of dyes in polycarbonate above its T_g (180.0 °C). The procedure yields precise diffusion constants at dye concentrations approximating infinite dilution. Our initial attempts to obtain a *Q*uantitative *S*tructure *A*ctivity *R*elationship (QSAR) between the measured diffusion constants and properties calculated for MOPAC optimized dye structures were unsuccessful. However, elongating or streamlining the structures yields a remarkably good QSAR with a single parameter, the log of the shadow area cast down the dye's long axis.

Introduction

The most commonly used techniques for quantifying diffusion of "large" molecules (penetrants) in polymers above T_g have serious limitations with respect to measurements of a wide variety of penetrants at low concentrations. To avoid confusion due to plasticization of the polymer by the penetrant, comparison of penetrant structural variations with measured diffusion constants should be made for the case of infinite dilution (D_o).

Both laser-induced holographic grating relaxation (LIHGR)[1] and pulsed field gradient NMR (PFGNMR)[2] techniques quantify diffusion of penetrants molecularly dispersed in a polymer. The LIHGR technique is suitable for diffusion measurements at low penetrant concentrations, but it requires a "photobleachable" chromophore in the penetrant. This severely limits the choice of penetrants. PFGNMR, has flexibility with regard to penetrant selection but requires chemical loadings in excess of ca. 10% and extrapolation to infinite dilution.

The inability to make precise diffusion measurements on a series of penetrants at low concentration has limited the progress of understanding of the diffusion process. Recently, Mauritz in a series of papers[3] has formulated a theory and the following equation to describe the diffusion of penetrants in amorphous polymers above their T_g

$$D = \frac{\mathrm{FV}^2}{6}\left(\frac{eRT}{\bar{M}_w}\right)^{1/2} \sum_{i=1}^{3}\left(\frac{1}{l_i A_i^2}\right) \exp\left(\frac{-E_a}{RT}\right) \qquad (1)$$

where D is the diffusion coefficient, FV is the free volume in the polymer, e is the base of the natural logarithm, R is the gas constant, T is temperature, $\bar{M}_w$ is the penetrant molecular weight, i is the designation for each of the three major axes in the penetrant, l_i is the length of the penetrant along the ith axis, A_i is the maximum cross-sectional area of the penetrant along the ith axis, and E_a is the activation energy to break the solvation binding for an incremental movement. The theory suggests that at constant temperature, the factors affecting a solute's diffusion are: (a) the penetrant's molecular weight ($\bar{M}_w^{-0.5}$), (b) the penetrant's "shape" (reciprocal of (length × cross-section areas^2)), and (c) the penetrant's "solvation" by the polymer (E_a).

Unfortunately, the experimental verification of the Mauritz theory rests on diffusion coefficients measured at very high solute concentrations (gravimetrically monitoring the incorporation of plasticizer into polymer immersed in neat plasticizer). The fit of the theoretical equation with experimental values is marginal[3d,e] even with the use of an activation energy term.

Recently, von Meerwall measured[2b] the diffusion of plasticizers heavily loaded in poly(vinyl chloride) using PFGNMR. Using penetrant loadings of 80% to 10%, von Meerwall extrapolated his results to infinite dilution to obtain D_o values. He reported a marginal correlation between log ($\bar{M}_w D_o$) and the "minimum frontal diameter", obtained from mechanical molecular models.

A subsequent collaboration between von Meerwall and Vaz of Tripos Assoc. has resulted in a more extensive attempt[4] to correlate the data. Using partial least squares analysis, Vaz found that there was no correlation between log(D_o) and any of his calculated molecular property descriptors; however, by excluding 2 of the 14 plasticizers, he could relate log(D_o) to 4 molecular descriptors with a rather poor cross-validated R^2 of 0.5. The most significant descriptors appeared to be related to molecular flexibility and shape. However, this result is not very satisfying in terms of a conceptually simple understanding of the important penetrant features affecting diffusion.

The diffusion of gaseous hydrocarbons across a polyisobutylene rubber membrane has been used to study[5] the effects of hydrocarbon shape on the diffusion coefficients. With the penetrant supplied to the membrane surface as a gas, there is no solvent, besides the penetrant, present to swell the membrane. Unfortunately, larger penetrants with poor or unknown volatilities require a solvent and typical solvents rapidly swell the host polymers.

We sought a solvent for the larger penetrants, which would not significantly swell or dissolve polymeric membranes of interest. We decided to examine polymeric fluids. The use of silicone oil to control the temperature of polymers (without swelling) has been known[6] for some time. However, *the selection of a polymeric fluid, which does not materially swell a rubbery polymer of interest, as a solvent for a penetrant appears to be a novel concept.*

We wish to illustrate the utility of this new procedure, which allows precise measurements of diffusion at low penetrant concentrations (approximating infinite dilution). The application of the procedure to diffusion of a variety of dyes in polycarbonate provides insight as to the penetrant properties that affect diffusion.

Results and Discussion

We have successfully measured diffusion of dyes across a high molecular weight (wt av 181 000) amorphous poly-

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(Bisphenol A carbonate) membrane above its T_g. The procedure simply involves monitoring the passage of dye from a stirred "infinite donor" reservoir at high dye concentration, through an isolating membrane, and into a stirred "receiver" reservoir at low dye concentration. We selected a dimethyl–phenylmethyl (50–50) siloxane copolymer of molecular weight ca. 2100 as a penetrant solvent for both donor and receiver baths. Incubation of polycarbonate membranes in this oil at 180 °C for 3 h revealed no detectable swell (<0.1%) by gravimetric analysis.

The determination of the diffusion coefficient is based upon Fick's law, which relates the flux of diffusing substance (penetrant) passing through a membrane to the diffusion coefficient and a concentration gradient.[7] Assuming that the concentration of dye in an infinitesimally thin element on the front boundary of a polymeric membrane is maintained near equilibrium, it may be approximated by the product of the equilibrium (polymer/oil) partition constant, K_{poly}, and the dye concentration, C_{oil}, in the donor bath. Under proper experimental conditions, the concentration term on the back boundary (receiver bath surface) may be neglected. The relationship is then expressed as

$$d(\mathrm{dye})/dt = D_{\mathrm{ss}}(K_{\mathrm{poly}})(C_{\mathrm{oil}})A/l \tag{2}$$

where $d(\mathrm{dye})/dt$ is the rate (mmol/s) of dye transport at steady state, D_{ss} is the steady state diffusion coefficient, K_{poly} is the equilibrium dye partition constant (polymer/oil), C_{oil} is the dye donor bath dye concentration, A is the exposed polymer area, and l is the polymer thickness.

To illustrate the utility of the technique, we examined diffusion of dye I in Figure 1 across a 20-μm polycarbonate membrane.

After sudden introduction of dye in the donor bath, the appearance of dye in the receiver bath was monitored with a fiber optic spectrometer. Figure 2 illustrates the results of a typical diffusion run at 201.8 °C. The steady state flux (slope; μmol/s) of such diffusion runs are quite precise (coefficient of variance (cv) is 0.8% for six determinations). However, over a period of months, reproducibility degrades to about ±5%, which is expected considering our limitations in temperature control (±0.1 to ±0.2 °C) and the very strong temperature dependence of the diffusion constant.

Stirring must be adequate to maintain the boundary conditions, but care must be taken to avoid introducing nonelastic distortions into the membranes. Our steady state flux measurements were independent of an 8-fold change in the bath stirring rates, indicating that the boundary dye concentrations were being properly maintained. However, our Daynes time lag values[8] (intercept with the abscissa in Figure 2) had considerably higher uncertainties (ca. 10%) than the steady state flux measurements, suggesting that complete mixing of dye in our donor bath during the early portions of the runs may have required a time comparable to the time lag.

The equilibrium partition constant for equilibration of dye between the polycarbonate membrane and the oil was obtained through a timed series of extended exposures of membranes to the dye donor bath. The membranes were quantitatively extracted with acetone to allow spectral analysis for incorporated dye and thus the dye concentrations in the polymer. The equilibrations were assumed complete when further change was undetectable. Reproducibility was about 1% cv. Analysis of the equilibrating bath yielded the partition constant, K_{poly}.

With the high molecular weight polycarbonate used (T_g ca. 150 °C and flow point ca. 230 °C), the useful temperature range is ca. 170–210 °C. Below 170 °C the rates are agonizingly slow, and above about 200 °C the membrane distortions become serious contributors to the error.

Table I. Concentration Dependence of Dye I Diffusion Coefficients in Polycarbonate at 201.8 °C

wt % dye[a]	dye conc (M)[a]	K_{poly}[b]	$10^9 D_{\mathrm{ss}}$ (cm^2/s)
0.06	1.83×10^{-3}	6.3(0)	8.5
0.16	4.64×10^{-3}	6.3(6)	8.6
0.42	1.21×10^{-2}	6.4(2)	8.6
1.16	3.31×10^{-2}	6.6(0)	8.5

[a] Dye concentration in front surface of the membrane. [b] Equilibrium dye partition (polymer/oil) constant.

Table II. Dye I Diffusion in Polycarbonate vs Temperature

temp		steady state diffusion coefficient (cm^2/s)
°C	K	
201.8	475	$8.5(8) \times 10^{-9}$
191.8	465	$3.3(5) \times 10^{-9}$
186.8	460	$1.6(1) \times 10^{-9}$
181.8	455	$8.2(5) \times 10^{-10}$
180.0	453.2	$6.4(9) \times 10^{-10}$
176.8	450	$3.5(0) \times 10^{-10}$
171.8	445	$1.2(9) \times 10^{-10}$

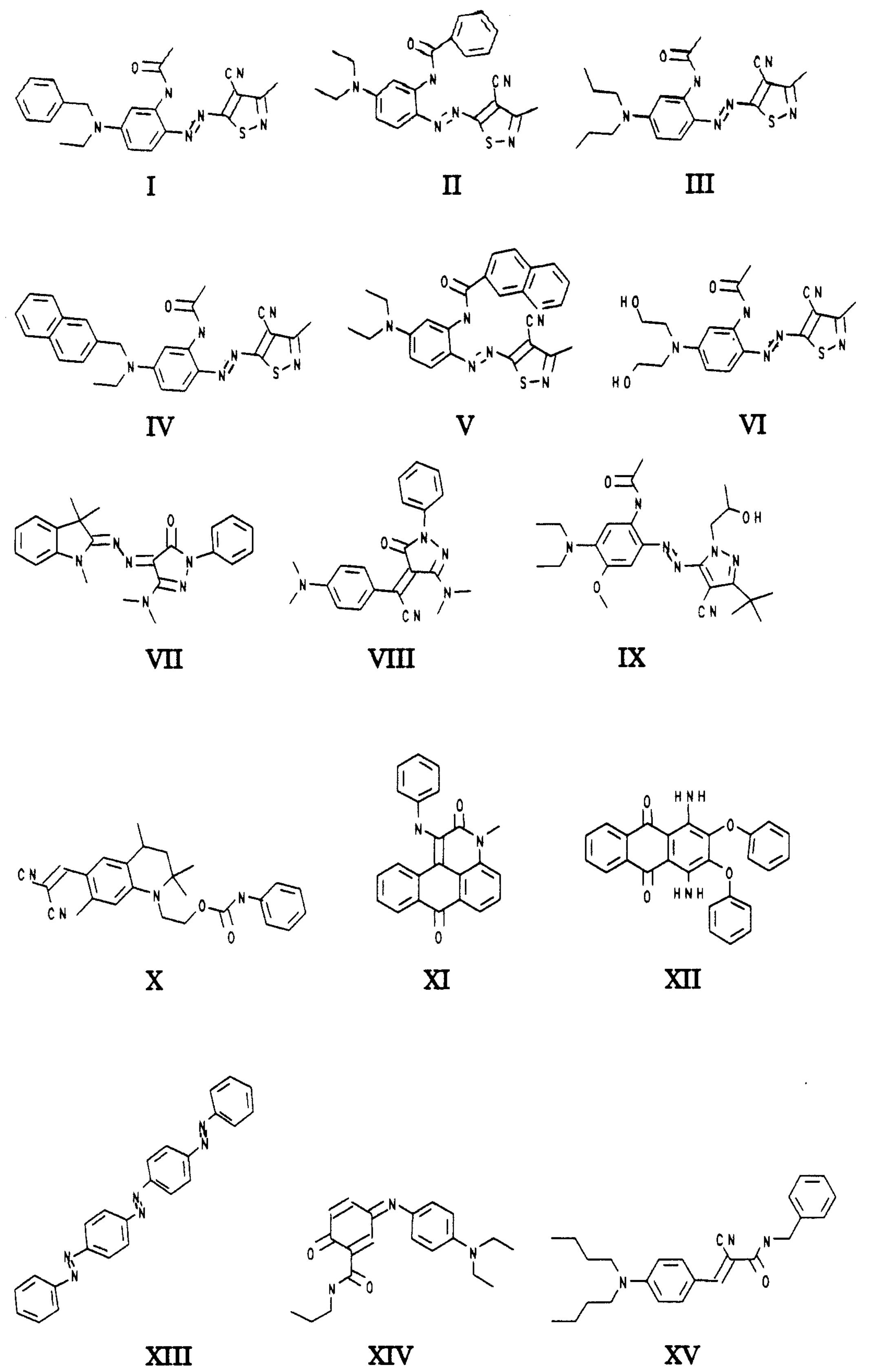
Work by Wang examining diffusion in poly(methyl methacrylate)[1a] and poly(α-methylstyrene)[1b] indicates that the diffusion constants in these polymers are independent of concentration when the penetrant loadings are less than ca. 0.5 wt%. We have examined the effects of the concentration of dye I at the front surface of the membrane on measured diffusion constants (see Table I) at 201.8 °C. Dye donor bath concentrations were varied more than 1 order of magnitude to yield front surface dye concentrations, estimated using the partition constants (K_{poly}), ranging from 2×10^{-3} to 3×10^{-2} M (0.06–1.2 wt%). As can be seen in Table I, the diffusion constants obtained were essentially constant and independent of dye concentration; however, small changes in the partition constants are apparent. It should be recalled that the front surface dye concentrations noted in Table I and present in equilibrated samples (K_{poly} determinations) are at the top of a declining concentration profile for each membrane in the diffusion experiments. Our experiments are typically run at ca. 10^{-2} M or ca. 0.4 wt% dye *at the front surface*, where the measured diffusion coefficient, D_{ss}, should approximate D_0.

Wang[9] has found that the temperature dependence of camphorquinone diffusion in polycarbonate is well described with the *W*illiams, *L*andel, and *F*erry (WLF) temperature shift equation[10]

$$\log(DT_0/D_0T) = c_{1\mathrm{d}}(T - T_0)/(c_{2\mathrm{d}} + T - T_0) \tag{3}$$

where D is the diffusion coefficient, T is temperature in Kelvin, subscript zero refers to a reference temperature, $c_{1\mathrm{d}}$ is an adjustable parameter, and $c_{2\mathrm{d}}$ is an adjustable parameter that corresponds to the c_2 value obtained from viscoelastic measurements. According to theory,[11] the $c_{1\mathrm{d}}$ parameter differs from the viscoelastic c_1 values in that it contains a contribution from the nature or size of the diffusing penetrant.

For dye I we have measured the dependence of the diffusion coefficient upon temperature and collected the results in Table II. Nonlinear regression was used to determine the optimum $c_{1\mathrm{d}}$ and $c_{2\mathrm{d}}$ values fitting the data in Table II to eq 3. As expected, the fit of the data to eq 3 using 445 K (171.8 °C) as the reference temperature is excellent. However, the optimum value obtained for $c_{2\mathrm{d}}$ is 28 (reference temperature 150 °C) with wide 95%



I II III

IV V VI

VII VIII IX

X XI XII

XIII XIV XV

Figure 1. Dye structural variations for diffusion coefficient correlations.

confidence limits (18-38). This value is smaller than the values of 37 and 39 reported by Wang[9] in his LIHGR study of camphorquinone diffusion in a moderately low molecular weight (20 000) polycarbonate. Wang points out that Ishida and Matsuoka[12] have obtained a similar result (38 with 150 °C reference temperature) using dielectric relaxation of moderate $\bar{M}_w$ (ca. 40 000) polycarbonate.

The optimum c_{1d} value for dye I diffusion in high $\bar{M}_w$ polycarbonate is 8.5, using a 150 °C reference temperature. This is larger than the viscoelastic c_1 value (5.1) obtained by Ishida and Matsuoka.[12] Vrentas and Duda have argued[13] that the c_{1d}/c_1 ratio for *small penetrants* is the ratio of the solute molar volume to that of the critical molar free volume of the polymer segmental jump unit. However, for larger molecules, where diffusion is expected to proceed in steps that are fractional increments of the penetrant's dimensions, these correlations with penetrant volume break down.[14,15]

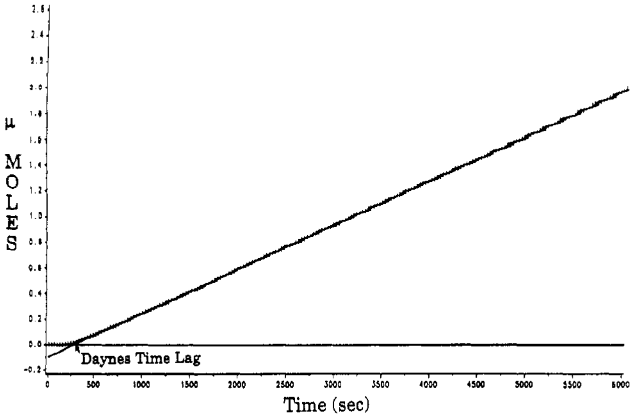


Figure 2. Example of dye I flux measurements at 201.8 °C through polycarbonate.

Table III. Measured Diffusion Coefficients for Dyes in Polycarbonate at 180.0 °C

dye	$\bar{M}_W$	D_{ss} (cm²/s)
I	419	6.5×10^{-10}
II	419	4.4×10^{-10}
III	385	7.8×10^{-10}
IV	469	4.4×10^{-10}
V	469	2.8×10^{-10}
VI	388	6.8×10^{-10}
VII	387	4.9×10^{-10}
VIII	359	6.5×10^{-10}
IX	470	3.4×10^{-10}
X	429	6.8×10^{-10}
XI	366	5.8×10^{-10}
XII	422	8.4×10^{-10}
XIII	390	$1.8(4) \times 10^{-9}$
XIV	339	$1.1(3) \times 10^{-9}$
XV	390	6.7×10^{-10}

To evaluate the penetrant features that affect diffusion, we have examined the remaining dyes in Figure 1 at 180.0 °C.

Dyes I-VI (Figure 1) compose a set of penetrants with chromophores common to dye I but designed to probe the effects of pendant aromatic moieties (on the "end" vs a branch). Also in this set is a comparison to assess the impact of intermolecular H-bond donating groups. Dye XIII is an example of an elongated chromophore. Dye X is an example of a reasonably flexible dye, while dye XI is quite rigid. The molecular weights vary from 340 to 470.

Dye XV showed evidence of photochromism, which would normally confuse the spectral analyses. However, we have used multiple regression curve fitting to analyze the isomer mixtures. The results of the diffusion measurements for all of the dyes in Figure 1 are collected in Table III.

Quick examination of Table III reveals diffusion coefficients ranging 6.5-fold ($(2.8\text{–}18) \times 10^{-10}$ cm²/s) with most of the values ranging from 4 to 8×10^{-10}.

To initiate a *Q*uantitative *S*tructure *A*ctivity *R*elationship (QSAR) search, the dye structures were entered into MOPAC input data files and optimized using MOPAC (version 6.00) software[16] with the PM3 Hamiltonian. Although the structures appear visually rational, we made no additional attempts to ensure that the MOPAC optimizations had found the global minima.

We calculated a number of the dye molecular descriptors including various mathematical forms of the molecular weight ($\bar{M}_w$, $\bar{M}_w^{-1}$, $\bar{M}_w^{-0.5}$, log $\bar{M}_w$). We calculated the shadow areas (Å²) cast by the dyes down their principal axes using procedures described[17] by Jurs. None of these descriptors provided a useful model.

Table IV. Calculated Changes before and after Structure Elongation

	heat of formation (kcal/mol)			SABC[a]		
dye	before[b]	after[c]	Δ	before[b]	after[c]	%[d]
I	101	109	8	73.4	57.3	22
II	102	106	4	69.2	67.6	2.3
III	56.5	66.8	10.3	58.7	54.5	7.1
IV	122	131	9	94.3	63.3	33
V	120	122	2	72.3	72.4	0
VI	-11.8	-1.1	10.7	55.3	54.8	0.9
VII	74.9	80.4	5.5	62.4	59.4	4.8
VIII	116	117	1	56.1	55.9	0.3
IX	-10.3	-2.3	8	74.2	69.7	6.1
X	31.4	36.3	4.9	74.6	59.6	20
XI	15.4	20.3	4.9	63.1	59.3	6.0
XII	-11.7	-1.5	10.2	63.9	51.0	20
XIII	22.6	22.6	0.0	25.7	25.7	0.0
XIV	-21.9	-17.5	4.4	43.8	44.5	-1.6
XV	26.8	33.6	6.8	66.1	56.8	14

[a] Shadow area (Å²) cast down the A (long) axis. [b] MOPAC structure before manipulation. [c] Structure after bond rotations to elongate the structure. [d] Percent reduction.

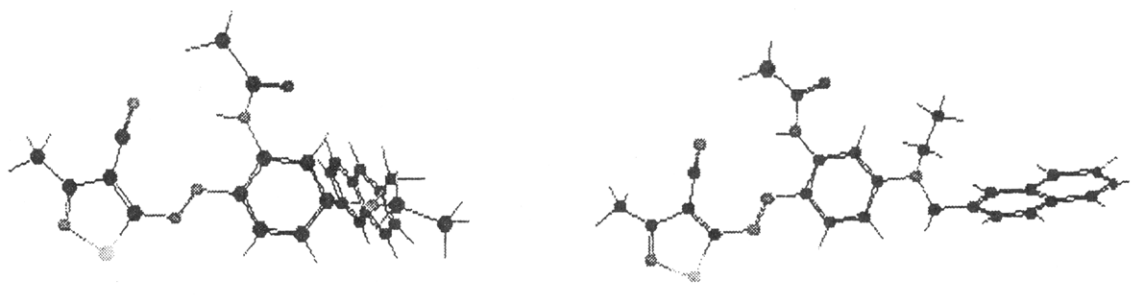
We suspected that our MOPAC optimized conformations may not be relevant for diffusion at 180 °C. Because of the hypothesis of von Meerwall[2b] and Mauritz,[3] that diffusion of large molecules occurs primarily along their long axis and may be dependent upon penetrant shape, we determined to examine accessible conformations that would elongate (streamline) each of the MOPAC dye structures.

Selected bonds of the MOPAC optimized dye structures were rotated to create conformations that minimized the cross-sections and the shadows cast down the long axis (as viewed from the ends of the molecules). Normally, two or three bonds were rotated and in no occasion did the number exceed five. The "elongated" structures were submitted to an additional MOPAC calculation (1SCF) to quantify any introduced strains, van der Waals repulsions, etc. The heats of formation before and after elongation were compared, and elongated structures were rejected if the enthalpy of formation increased beyond our arbitrarily set limit of about 10 kcal/mol.

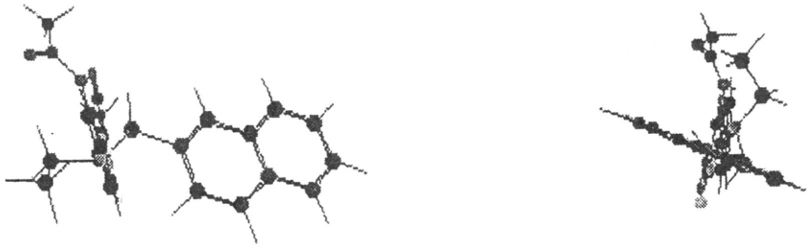
Changes in the calculated properties, enthalpy of formation, and shadow area cast down the dye's long axis, are collected in Table IV. As may be noted, the shadow areas cast down the long axis onto a perpendicular plane, SABC, range from a 2% increase to a 33% decrease. Figure 3 illustrates the changes for the most strongly altered dye, dye IV. It may be noted in Figure 3 that the pendant naphthalene moiety in dye IV has been moved from a position roughly perpendicular to the long axis of the chromophore (MOPAC structure) to a position aligned with the axis.

The ability and patience of an investigator will certainly affect the reproducibility of these structural manipulations. The ideal search for structures with minimum SABC values would be performed through manipulation of structure optimization software, which is beyond the scope of this report. It should be emphasized that *our structural manipulations were completed prior to statistical evaluation* of the data.

Using the elongated structures yields **a remarkably good correlation between the diffusion coefficients and the shadow areas, SABC.** This single parameter (+ intercept) model has a cross-validated R^2 of 0.90 and accommodates 95% of the response variance. The **logarithm of SABC gives an even better one parameter model** with a cross-validated R^2 of 0.96 and accommodates



"MOPAC" - Side View "Elongated" - Side View



"MOPAC" - End View "Elongated" - End View

Figure 3. Dye IV before conformational manipulation "MOPAC" and after conformational manipulation "Elongated".

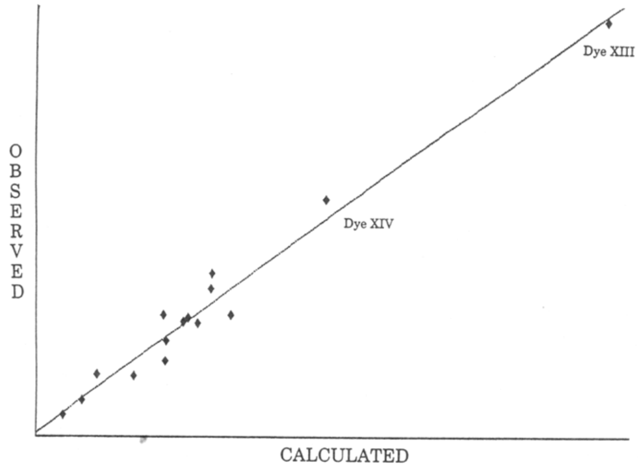


Figure 4. Calculated vs observed D_{SS} values for the log(SABC) model.

97% of the variance (Figure 4). The quality of the fit is dramatic for a one parameter model.

Using log(SABC), the modeling equation for diffusion at 180 °C in polycarbonate is as follows:

$$D_{ss} = (6.81 \times 10^{-9}) - (3.50 \times 10^{-9})(\log(\mathrm{SABC})) \quad (4)$$

It is evident from the calculated vs observed plot (Figure 4) that the fit is heavily weighted by two points (dye XIII and dye XIV). The heavy loading on these two points may explain why the model accommodates 97+% of the response variance, when we expect about 5% error in the measurements and some contribution from the manipulation of the structures.

Despite this caveat about the distribution of points, the fits are remarkably good. Excluding the various forms of SABC (log, etc.), we have found no other single parameter models with cross-validated R^2 values above 0.5. Unlike many QSAR models, this one is simple and has obvious physical significance. The lack of a suitable model using the MOPAC structures and the excellent model obtained with the elongated structures strongly suggests that the molecules assume an elongated conformation during molecular translation along their long axis. Mauritz[3d] has speculated that higher energy conformations of flexible molecules may diffuse more readily, which our work appears to confirm.

Recalling the temperature-dependent WLF behavior for dye I, we hypothesize that we are modeling the free volume fluctuation requirements, which allow translation along the dye's long axis. It is not clear why log(SABC) provides a better model than SABC.

In the process of selecting elongated structures with enthalpy changes less than 10 kcal/mol from the MOPAC optima, we have made an arbitrary choice about the accessibility of these states at 180 °C and ignored the associated reductions in entropy to attain them physically.

To put the arbitrary enthalpy limit of 10 kcal/mol in perspective, the difference between the chair and boat conformations in cyclohexane is ca. 6 kcal/mol.

Within the relatively narrow range of penetrant molecular weights examined (340-470), the molecular weight in various mathematical forms does not improve the model. It should be recognized that $\bar{M}_w^{-0.5}$, the molecular weight dependence used in eq 1, varies only about 15% over this range. The combination of this relative insensitivity to our molecular weight changes combined with some covariance with log(SABC) may explain our inability to detect a $\bar{M}_w^{-0.5}$ contribution. Given the relatively high temperature (180 °C), it is not surprising that potential H-bond donating by the dye to the polycarbonate also provides no detectable improvement to the model.

For the dyes examined, ignoring the entropy term (required to orient the molecule linearly) works fine. However, one suspects that this term may be sufficient to break down the correlation for higher molecular weight flexible molecules. It may be recalled that our working fluid, dimethyl–phenylmethyl siloxane (2100), does not significantly swell our polycarbonate membranes under the conditions of our measurements.

Conclusions/Summary

We have used a dimethyl–phenylmethyl (50–50) siloxane copolymer as a solvent for disperse type dyes in order to study dye diffusion through polycarbonate membranes. At temperatures (170–210 °C) above the polycarbonate T_g (ca. 150 °C) the fluid functions to maintain a known dye concentration at the surface (boundary) of the membrane without significantly swelling the polycarbonate. The technique is limited to temperatures where the rubbery membrane maintains physical integrity (ca. 20 °C below the flow point of our high $\bar{M}_w$ polycarbonate).

The precision for the determination of the dye I diffusion coefficient is about 1% cv over a short time frame where drifts of the temperature control devices are minimal. However, over an extended time frame (months) our ability to control the temperature (±0.1(5) °C) and the very strong temperature dependence of diffusion in the proximity of the polymer's T_g degrades the precision to ca. 5%.

The procedure requires the measurement of the equilibrium dye partitioning between polycarbonate and the silicone oil phase. Our spectral analyses accomplished by extracting dye from equilibrated membranes indicate a cv of about 1% for these determinations.

This novel procedure yields precise dye diffusion measurements at sufficiently low dye concentrations so as to avoid significant penetrant impact on the polymer T_g.

Consistent with laser-induced holographic grating relaxation (LIHGR) results in polycarbonate,[14] we find the very strong temperature dependence of the diffusion coefficients for dye I is well accommodated by the WLF temperature shift equation for diffusion.

Using this technique, we have successfully measured the diffusion coefficients for an array of 15 dyes of varying structural characteristics ($\bar{M}_w$, shape, flexibility, H-bond donating, etc.) in polycarbonate at 180.0 °C.

In an attempt to obtain a QSAR, we calculated the molecular structures using MOPAC software.[15] We were unable to obtain good correlations between calculated molecular properties for these structures and the measured diffusion coefficients.

However, if the MOPAC optimized structures were first "manually" elongated (or streamlined) prior to calculation of the molecular properties, an excellent correlation between the diffusion constant and the dye's shadow area projected down its long axis (SABC) was obtained. Using log(SABC) improves the model to a cross-validated R^2 of 0.96. No other suitable models were found.

The correlations are consistent with diffusion via molecular translations by dye (in an elongated state) along its long axis. Since the temperature dependence is consistent with the free volume theory for diffusion, we hypothesize that we are modeling the free volume fluctuation requirements to allow movement along the dye's long axis.

We observed no significant improvements to the log(SABC) model from parameters associated with either molecular weight or potential H-bonding between dye and polycarbonate. We believe this is a result of the narrow range of molecular weights examined and the relatively high temperature employed. Certainly, effects of H-bonding may become important at lower temperatures in other rubbery polymers.

Table V. Dye Spectral Properties

	in oil[a]	in acetone	
dye	λ_{max}	λ_{max}	$10^{-4}\epsilon$
I	539	544	5.71
II	541	549	5.57
III	544	549	5.90
IV	537	544	5.34
V	544	554	5.18
VI	539	549	4.77
VII	451	457	7.43
VIII	512	522	2.80
IX	562	552	4.34
X	441	447	5.37
XI	457	461	1.58
XII	535	542	1.57
XIII	387	381	6.09
XIV	606	609	2.71
XV	417	417	4.99

[a] Dimethyl–(phenylmethyl) siloxane used in the diffusion measurements.

Experimental Section

Materials. The silicone oil was dimethyl–phenylmethyl siloxane copolymer from Petrarch Systems (No. PS063). The high molecular weight (181 000 wt av) polycarbonate (MAKROLON 5705) was from Mobay.

HS400 Solvaperm Red Violet R (dye XII) was purchased from American Hoechst Corp.

Dyes I-VI were prepared by procedures analogous to those used for dye III.[18] Several other dyes were prepared according to literature preparations (VIII,[19] IX,[20] X,[21] and XIII[23]).

Preparation of Dye VII. A slurry of 1,3,3-trimethyl-2-(acetanilidovinyl)indolium iodide quaternary salt (2.2 g) was prepared in 50 mL of ethanol. Then 1-phenyl-3-(dimethylamino)-pyrazolin-5-one (2 g) and triethylamine (1 g) were added. The mixture was gently refluxed for 15 min. The mixture was cooled, and 100 mL of water was added. The oil solidified and was collected by filtration. The dye was redissolved with ether and passed through a pad of silica (ethyl acetate:methylene chloride, 1:2). Evaporation yielded 1.4 g of metallic blue-red crystals.

Preparation of Dye XIV. 2-Butyramidophenol (0.45 g) and 4-(diethylamino)aniline hydrochloride (0.50 g) were added to 30 mL of methanol, 10 mL of water, and 1.5 mL of ammonium hydroxide. A solution of 4.12 g of potassium ferricyanide in 20 mL of water was added dropwise. The mixture was stirred for 1 h, diluted with 80 mL of water, filtered, washed with water, and dried. Sample was recrystallized from methanol/methylene chloride to yield metallic bronze needles (0.7 g).

Preparation of Dye XV. Phosphorus oxychloride (16 g) was added slowly to a cooled solution of dimethylformamide over a period of 10 min. Dibutylaniline (20.5 g) was slowly added while cool, and then the reaction mixture was heated for 1 h. After the solution was cooled and diluted with ethanol, *N*-benzylcyanoacetamide (18 g) was added together with sodium acetate (25 g). The flask was returned to the steam bath and heated for an additional 3 h. The product was isolated by dilution with water whereupon it oiled out. Upon chilling and scratching, the dye crystallized. After filtration and drying, the yield of crude greenish crystals was 33 g. Recrystallization from 2-propanol yielded 28 g (72%) of yellow crystals, which showed no impurities by TLC and NMR.

Table V includes the wavelengths and molar extinction coefficients of the dyes in acetone. Also included are the wavelengths used in the spectral monitoring of the dyes in oil.

Methods. Membrane Preparation. Polycarbonate in dichloromethane was coated on 7-mil polyester support with an extrusion hopper to yield 22 g/m^2 dry coverage. The membrane may be handled on the support and peeled off when ready for use. Coating uniformity as evidenced by gravimetric comparison of 1-cm^2 punches and by 200 micrometer measurements across sections of the membranes is about 2% cv. The thicknesses of the membranes are calculated from the weight and density[12] of the 3-in.^{2} punches. The thickness increases about 2% upon raising the temperature to 200 °C.

Temperature Control and Standardization. The temperature controllers and associated thermocouples were periodically recalibrated against a Cole Parmer platinum RTD thermometer. The platinum RTD thermometer is a secondary standard, which was calibrated at 179.713 °C by Henry Staab (Eastman Kodak Co. Corporate Metrology) using NIST calibrated equipment and procedures.

Check for Polymer Swell by Silicone Oil. A dozen punches of membrane (1 cm^2) were weighed before and after being dipped in silicone oil and thoroughly blotted. The samples were then incubated 3 h at 180 °C in the oil, thoroughly blotted, and reweighed. The residual oil 20 ± 8 μg adhering to the 10-mg samples upon wetting at room temperature was essentially identical to the 25 ± 13 μg weight increase noted after incubation.

Partition Constant Measurements (K_p). Dye in silicone oil (ca. 2×10^{-3} M) at a temperature of interest is equilibrated with a polymer membrane (known weight) for a fixed time. The membrane is (a) removed and thoroughly blotted, (b) reweighed to check for swell or incomplete blotting, and (c) quantitatively extracted with acetone. From the spectral analysis, the weight of the membrane, and its density at the temperature of the experiment, the concentration of dye in the polymer is calculated. An aliquot (gravimetric) of oil is diluted with acetone and similar spectral analysis yields the concentration of dye in the bath and the dye in polymer:oil ratio is calculated. For the purposes here, no correction for oil expansion is necessary. A time series establishes the completion of equilibration and yields the K_p.

Diffusion Coefficient Measurements (D_{SS}). A section of membrane is punched (1.5 × 2 in.), weighed, and mounted vertically between supports separating donor and receiver baths. The supports contain 5 matching horizontal slots (ca. 4 × 44 mm), which allow exposure of the membrane (8.75 cm^2) to donor and receiver baths.

The apparatus is placed within a constant temperature oil bath to minimize thermal losses. This external bath consists of an Ace Glass INSTATHERM oil bath with a Cole Parmer DIGISENSE temperature controller. After installation of the diffusion apparatus, the bath is further insulated with fiberglass insulating pads. The entire apparatus is maintained in a polycarbonate enclosure for safety and to minimize drafts.

The apparatus is charged carefully with silicone oil to minimize hydrostatic pressure imbalances across the membrane. In our apparatus, the dye donor reservoir, the outer bath, contains 191 g of oil, which includes 17 g containing dye initially isolated in a test tube. The receiver bath, inner reservoir, contains 46 g of oil. The baths are circulated with mechanically driven centrifugal pumps. The rpms are monitored when necessary with a phototachometer.

After the device is covered with a couple 0.25-in.-thick borosilicate glass plates to further reduce thermal losses, a fiber optic probe from a Model 200 guided wave spectrophotometer is placed in the receiver bath. The data are collected with a personal computer.

The INSTATHERM bath is brought up to temperature, and the unit is allowed to equilibrate. Both the donor and receiver baths contain supplemental 100-W quartz immersion heaters with individual DIGISENSE temperature controllers (bare type J (iron/constantan) thermocouples).

When the temperature stabilized, the run was initiated by breaking the test tube, which was isolating the dye, and beginning the spectral data collection. Near the completion of the run the optical density in the receiver bath is noted and quantitative (gravimetric) samples are removed from both the receiver and donor baths. After dilution in acetone, spectral analysis yields the bath concentrations and a calibration for the fiber optic spectral measurements.

Spectral Analyses of the Photochromic Dye, Dye XV. A solution of dye XV was prepared at 0.02 g/L in HPLC grade acetone. The solution was maintained in the dark and the absorption spectrum was recorded. Then the optical cell containing the dye solution was irradiated with a 500-W slide projector using a Corning 3-75 glass filter to screen out the UV light. By screening out the UV and irradiating with blue light the photostationary state is shifted toward the hypsochromically absorbing entity. After photolysis the hypsochromically shifted spectrum was recorded. Assuming the known total concentration of dye XV has not changed significantly, multiple regression curve fitting of the "unknown" curve completed the analysis.

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References and Notes

(1) (a) Zhang, X.; Wang, C. *Macromolecules* **1990**, *23*, 1218. (b) Wang, C.; Xia, J. *J. Chem. Phys.* **1990**, *92*, 2603.

(2) (a) von Meerwall, E. *Rubber Chem. Technol.* **1985**, *58*, 527. (b) von Meerwall, E.; Skowronski, D.; Hariharan, A. *Macromolecules* **1991**, *24*, 2441.

(3) (a) Mauritz, K.; Storey, R.; George, S. *Macromolecules* **1990**, *23*, 441. (b) Mauritz, K.; Storey, R. *Ibid.* **1990**, *23*, 2033. (c) Coughlin, C.; Mauritz, K.; Storey, R. *Ibid.* **1990**, *23*, 3187. (d) Coughlin, C.; Mauritz, K.; Storey, R. *Ibid.* **1991**, *24*, 1526. (e) Coughlin, C.; Mauritz, K.; Storey, R. *Ibid.* **1991**, *24*, 2113.

(4) (a) Vaz, R.; von Meerwall, E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 637. (b) Vaz, R.; von Meerwall, E. Unpublished preprint, 1992.

(5) Blyholder, G.; Prager, S. *J. Phys. Chem.* **1960**, *64*, 702.

(6) Gupta, V.; Gupta, A.; Rajan, V.; Kasturia, N. *Text. Res. J.* **1984**, 54.

(7) Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford Press: Oxford, U.K., 1986; p 44.

(8) Daynes, H. *Proc. R. Soc. London* **1920**, *97A*, 286.

(9) Wang, C.; Xia, J. *Macromolecules* **1988**, *21*, 3519.

(10) Ferry, J. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980; p 303.

(11) Vrentas, J.; Duda, J.; Hou, A. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 2739.

(12) Ishida, Y.; Matsuoka, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1965**, *6*, 795.

(13) Vrentas, J.; Duda, J. *J. Appl. Polym. Sci.* **1977**, *21*, 1715.

(14) Vrentas, J.; Vrentas, C. *J. Polym. Sci., Part C: Polym. Lett.* **1990**, *28*, 379.

(15) Ehlich, D.; Sillescu, H. *Macromolecules* **1990**, *23*, 1600.

(16) Frank J. MOPAC Consultant, Seiler Research Lab, U.S. Air Force Academy, CO 80840-6528.

(17) (a) Rohrbaugh, R.; Jurs, P. *Anal. Chem.* **1987**, *59*, 1048. (b) Stouch, T.; Jurs, P. *J. Chem. Inf. Comput. Sci.* **1986**, *26*, 4.

(18) (a) Weaver, M.; Fleischer, J. U.S. Pat. 4,374,767, 1983. (b) Fleischer, J.; Clark, G.; Maner, R. U.S. Pat. 4,374,768, 1983.

(19) Stolle, R.; Bach, G.; Hirsch, B. *J. Signalaufzeichnungsmater.* **1981**, *9*, 31.

(20) Chapman, D.; Evans, S. U.S. Pat. 5,079,213, 1992.

(21) Weaver, M.; Wallace, D.; Straley, J. U.S. Pat. 3,247,211, 1966.

(22) Kazankov, M.; Ufimtsev, V. *Khim. Geterotsikl. Soedin.* **1972**, 373.

(23) Ruggli, P.; Petitjean, C. *Helv. Chim. Acta* **1938**, *21*, 711.