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Diffusion-Limited Photophysical Interactions as *in Situ* Probes of Conversion in Free Radical Polymerization: Quantitative Analysis with Predictive Free-Volume Theory

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Introduction. Several classes of photophysical probes, including molecular rotors,[1,2] excimers,[2-5] twisted intramolecular charge-transfer probes,[6-8] and reactive dye labels,[2,9,10] have been tested for monitoring polymerizations. However, these techniques may suffer from limitations. For example, in free radical polymerizations, rotor probes are sensitive only during the later stages of the gel effect and/or vitrification, yielding no information on conversion at earlier stages of the polymerization.[2] While other probe approaches may allow for sensitivity at low conversion, the relationship between photophysical measurables and conversion has usually been *correlative* at best. Here we report the first use of diffusion-limited luminescence quenching interactions in conjunction with a *predictive* free-volume theory[11] (a modification of the correlative theory by Vrentas and Duda[12,13]) which may allow conversion to be related *a priori* to changes in luminescence lifetimes or intensities. This theory adequately models the polymer concentration dependence of self-diffusion coefficients of solvent and ternary probe molecules[11-16] as well as diffusion-limited phosphorescence quenching rate constants involving small molecules[17-19] in polymer solutions. In free radical polymerizations, small-molecule interactions related to the glass and cage effects have also been modeled using this theory.[20]

We take advantage of the diffusion-limited nature of small molecule–small molecule luminescence quenching interactions which obey the Stern–Volmer equation:[21]

$$1/\tau = 1/\tau_0 + k_q[\mathrm{Q}] \qquad (1)$$

where τ (τ_0) is the excited-state lifetime of the chromophore in the presence (absence) of the quencher, k_q is the diffusion-limited quenching rate constant, and [Q] is the quencher concentration. (For quenching by dynamic interactions only, lifetime may be replaced by intensity.) k_q is related to the self-diffusion coefficients of the chromophore, D_c, and quencher, D_q, by the modified Smoluchowski equation:[21]

$$k_q = 4\pi b D_p N_A \qquad (2)$$

where b is the capture radius between the chromophore and quencher, $D_p = D_c + D_q$, and N_A is Avogadro's number. As the polymer concentration dependence of D_p is describable by the Vrentas–Duda free-volume theory,[11-13] the conversion dependence of τ (or, for strictly dynamic interactions, intensity) may be predicted. We demonstrate this here with phosphorescence quenching of biacetyl by anthracene; by adjusting the quencher concentration, this method can be generalized to diffusion-limited fluorescence quenching interactions.

Experimental Section. Biacetyl (2,3-butanedione), anthracene, benzoyl peroxide, and HPLC-grade chloroform were purchased from Aldrich and used as received. Methyl methacrylate (MMA), also from Aldrich, was treated with methylhydroquinone inhibitor remover and distilled from calcium hydride before use. Solutions contained 60 vol % MMA in chloroform with 0.039 M benzoyl peroxide. Biacetyl (1.0×10^{-3} M) was used as the chromophore and, for samples containing quencher, anthracene was present at 3.5×10^{-6} M.[22] Solutions were placed in polymerization tubes (11-mm-o.d., thick-walled borosilicate glass) jointed with high-vacuum stopcocks and septum ports through which thermocouples were threaded. As oxygen quenches biacetyl phosphorescence, samples were degassed through seven freeze–pump–thaw cycles.

Phosphorescence spectra and emission decays were measured with a SPEX Fluorolog-2 spectrophotometer with a phosphorescence attachment. Biacetyl was excited by a xenon lamp at 425 nm, and emission was monitored at 520 nm in right-angle mode as a function of polymerization time. Lifetimes were obtained by fitting the emission decays to single-exponential decays.[23] The temperature of the sample holder was controlled with a circulating water bath, and the temperature of the sample was monitored *in situ* via a thermocouple. Conversion was determined as a function of time by performing polymerizations separately on a number of samples under the same conditions used during the phosphorescence monitoring, stopping the reaction by precipitating the polymer in methanol, and weighing the sample after drying it in a heated vacuum oven.

Results and Discussion. Figure 1 shows how, in the absence of quencher, biacetyl phosphorescence intensity and lifetime, τ_0, vary during the polymerization of 60 vol % MMA in chloroform. The sigmoidal shapes of the data, with phosphorescence being insensitive to conversion up to the onset of the gel effect, are readily apparent. (The onset of the gel effect is characterized by the sudden increase in temperature[2,24] at about 650 min.) A similar sensitivity to conversion in bulk MMA polymerization has been observed with rotor[1,2] and fluorene[2] probe fluorescence. The agreement in the phosphorescence intensity and lifetime data suggests that the limited quenching, apparently from MMA, is dynamic for this system. In contrast, studies of benzil phosphoresence in bulk and solution polymerizations of MMA revealed that intensity was affected more than lifetime by conversion.[17,25]

While the inherent sensitivity of biacetyl phosphorescence to high conversion is of interest, sensitivity to low conversion can be achieved by investigating how diffusion-limited quenching interactions affect phosphorescence lifetime or intensity. In Figure 2, τ, the phosphorescence lifetime of biacetyl in the presence of 3.5×10^{-6} M anthracene, is plotted as a function of reaction time for the same conditions as in Figure 1. For comparison, τ_0 is also given. While the reaction time dependencies of τ and τ_0 have some similar features, there are differences. First, τ values are substantially lower than those of τ_0. Second, τ shows both significant sensitivity prior to the onset of the gel effect, increasing from 27 to 46 μs in the first 650 min, and enhanced sensitivity as compared to τ_0 throughout the gel effect; these features are due to the reduction in small-molecule diffusion with increasing conversion. The diffusion-limited nature of this interaction is substantiated by the fact that at the beginning of the polymerization $k_q = 7.9 \times 10^9$ M^{-1} s^{-1}, while after 900 min $k_q = 1.0 \times 10^9$ M^{-1} s^{-1}.

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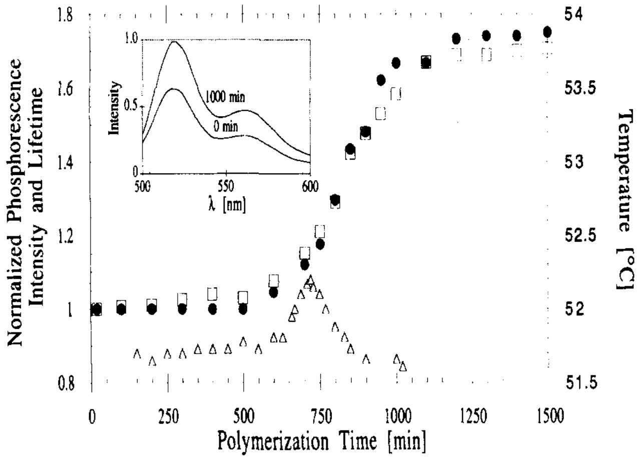

Figure 1. Emission intensity of biacetyl normalized to that at zero conversion (□), phosphorescence lifetime of biacetyl normalized to that at zero conversion (●), and the corresponding temperature profile (△) during the solution polymerization of MMA (60 vol % in chloroform) with benzoyl peroxide at 50 °C. Inset: Steady-state phosphorescence emission (λ_{ex} = 425 nm) spectra during the polymerization.

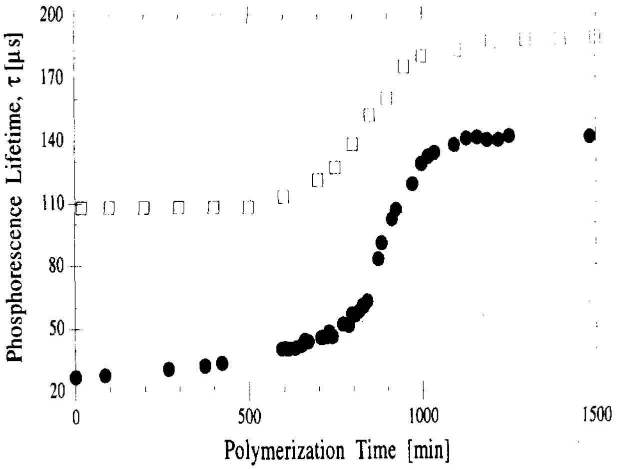

Figure 2. Biacetyl phosphorescence lifetime during the solution polymerization of MMA without anthracene, τ_0 (□), and with 3.5 × 10^{-6} M anthracene, τ (●).

Table 1. Vrentas/Duda Model Parameters[a]

component *i*	1. chloroform	2. MMA	3. PMMA
K_{1i}/γ (10^{-4} cm^3/g K)	6.52	7.0	3.05
$K_{2i} - T_{gi}$ (K)	−37.9	−32.07	−301
M_{ij}	119.39	100.12	187.81
$\hat{V}_i^*$ (cm^3/g)	0.510	0.872	0.788

[a] Parameters for chloroform and PMMA were taken from ref 11, while parameters for MMA were calculated based on a fit of the theory to MMA self-diffusion measurements in MMA/PMMA.[16]

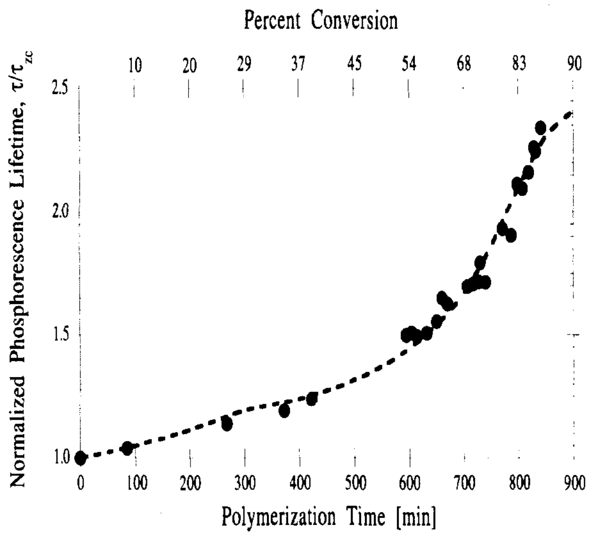

Figure 3. Normalized biacetyl phosphorescence lifetime in the presence of 3.5 × 10^{-6} M anthracene, τ/τ_{zc}, during the solution polymerization of MMA (●), and prediction of normalized phosphorescence lifetime (dashed line) based on experimental values of τ_0/τ_{zc} and values of k_q/k_{qzc} predicted by Vrentas–Duda theory. See text for explanation.

The conversion dependence of τ can be explained using the Vrentas–Duda theory. From eq 2 it is apparent that k_q at a given conversion normalized to its value at zero conversion, k_{qzc}, is equivalent to D_p/D_{pzc}, where D_{pzc} is the sum of the ternary probe diffusion coefficients at zero conversion. The polymer concentration dependence of D_p can be related to that of the solvent self-diffusion coefficient, D_s, in a polymer–solvent–probe system:[12,17-19,26]

$$\ln(D_p/D_{pzc}) = \xi_{ps} \ln(D_s/D_{szc}) \qquad (3)$$

with

$$\xi_{ps} = (\hat{V}_p^* M_{jp}/\hat{V}_s^* M_{js}) \qquad (4)$$

where ξ_{ps} is the ratio of the jumping unit size of the probe to solvent (see ref 26). $\hat{V}_p^*$ and $\hat{V}_s^*$ are the specific hole free volumes of the probe and solvent required for a jump, respectively, and M_{jp} and M_{js} are the corresponding molecular weights of a jumping unit. For the biacetyl–anthracene system, we assume that ξ_{ps} = 1.0, i.e., D_p/D_{pzc} = D_s/D_{szc}. This is justified given that ξ_{ps} was found to equal 1 for the benzil–anthracene system[27] with several polymer–solvent systems.[17-19] As we have two "solvent" molecules present, chloroform and MMA, we have assumed that biacetyl and anthracene have jumping unit sizes similar to that of chloroform.[28] With this assumption, $k_q/k_{qzc} = D_p/D_{pzc} = D_1/D_{1zc}$, the polymer concentration dependence of the self-diffusion coefficient of chloroform (component 1).

For a ternary solution consisting of solvent 1 (chloroform), solvent 2 (MMA), and polymer 3 [poly(methyl methacrylate)], the Vrentas–Duda free-volume theory[12] predicts the following polymer concentration dependence of $\ln(D_1/D_{1zc})$:

$$\ln\left(\frac{D_1}{D_{1zc}}\right) = \left[-\frac{\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi_{12} \hat{V}_2^* + \omega_3 \xi_{13} \hat{V}_3^*)}{\hat{V}_{FH}}\right] \qquad (5)$$

where ω_i is the weight fraction of component *i*, $\hat{V}_{FH}$ is the average hole free volume per gram of solution, γ is an overlap factor, introduced because the same free volume is available to more than one molecule, and ξ_{ij} is the ratio of jumping unit size of component *i* to component *j*. The specific hole free volume may be expressed as[29]

$$\frac{\hat{V}_{FH}}{\gamma} = \frac{K_{11}}{\gamma}\omega_1(T - T_{g1} + K_{21}) + \frac{K_{12}}{\gamma}\omega_2(T - T_{g2} + K_{22}) + \frac{K_{13}}{\gamma}\omega_3(T - T_{g3} + K_{23}) \qquad (6)$$

where K_{1i} and K_{2i} are free-volume parameters for component *i*, and T_{gi} is its glass transition temperature. Table 1 lists the parameters used in this study.

The conversion dependence[30] of τ can be predicted using a combination of eqs 1 and 5 and measured values of τ_0 as a function of conversion.[31] Figure 3 demonstrates the success of this approach, exhibiting excellent correspondence between the experimental values of τ normalized to that at zero conversion, τ_{zc}, and those calculated using the predictive Vrentas–Duda theory. The 65% increase in τ/τ_{zc} up to the onset of the gel effect in this solution MMA polymerization compares favorably with the sensitivity of *in situ* excimer probe or reactive dye label studies[2] of bulk MMA polymerization and is vastly superior to the use of rotor probes[1,2] or free fluorene probe[2] fluorescence. The sensitivity of τ/τ_{zc} to conversion could be enhanced further if the chromophore and quencher had ξ_{ps} values larger than 1.0. For conditions identical to those employed here but with $\xi_{ps} = 2.0$, the increase in τ/τ_{zc} up to the onset of the gel effect is predicted to be 90%. This would allow for more accurate determinations of conversion from phosphorescence measurements.

The success of this approach is not limited to the use of phosphorescence quenching. Rather, the example illustrated here is one of a class of diffusion-limited interactions, including diffusion-limited fluorescence quenching, which exhibits sensitivity to conversion. This study has provided a quantitative means not only to interpret but in some cases predict the sensitivity of these interactions to conversion. The application of this free-volume approach to diffusion-limited intermolecular excimer and fluorescence nonradiative energy transfer probe studies, which can be done in the presence of oxygen, is underway.

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(23) Since the SPEX Fluorolog-2 does not measure emission decays directly, a BASIC program was written for the SPEX that allows for measurement of emission intensities at various times after triggering the lamp. In this way, a decay profile is obtained at each polymerization time. An IBM-compatible computer, interfaced through an RS232 port, was utilized to trigger the SPEX program at each polymerization time and to download the data for further analysis. Non-single-exponential decay behavior was observed during bulk polymerization, especially in the region of the gel effect where conversion increases rapidly during the measurement time (in most cases less than 90 s). However, due to the slower kinetics of the solution polymerizations, measurements were not biased by polymerization occurring during the measurement time, and emission decays could be fit to single-exponential decays with $r^2 > 0.999$.

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(27) As biacetyl is smaller than benzil, it is not expected that biacetyl will have a larger jumping unit than benzil. Further, the probe jumping unit sizes are not expected to be smaller than that of the solvent molecule.

(28) The jumping unit of biacetyl is expected to be similar to that of chloroform as the molar volume of biacetyl is close to that of chloroform (and smaller than that of methyl methacrylate). Although the volume of anthracene is larger than that of chloroform, the jumping unit is expected to be a fraction of that size—resulting in a jumping unit similar to that of chloroform. This is consistent with experimental evidence that the concentration dependence of D_p/D_{pzc} is in better agreement with the predicted concentration dependence of the chloroform self-diffusion, D_1/D_{1zc}, than that for MMA, D_2/D_{2zc}.

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(31) Note, if τ_0 is not a function of conversion, measurements are not needed.