Let us estimate the values of d_c/R_B which can be expected for real polymers. Using eq 15, 5, 3, and 6, we get for PI-PS block-copolymers for $f \sim 0.1$:

$$d_c/R_B = 2^{1/2}(\ln M)^{1/2} \qquad (16)$$

where M is the total molecular weight of a copolymer. The range $M = 10^4$–10^6 corresponds to $d_c/R_B = 4.3$–5.2. Taking into account Figure 2, we thus predict the following most probable picture of the ordering and structural transitions as a function of τ in the PI-PS melt: the gas of micelles–fcc structure–hex structure–bcc structure.

Registry No. (I)(S) (block copolymer), 105729-79-1.

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(5) An analogous problem for a slightly different system (for a mixture of a copolymer A-B and homopolymer) was considered in ref 6. Note that the type of a particular ordered structure formed by micelles was not predicted in this paper (and cannot be predicted since rather crude assumptions concerning the interactions of micelles were used there).
(6) Leibler, L.; Pincus, P. A. *Macromolecules* **1984**, *17* 2922.
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(8) The form (eq 7) of the ideal-gas term is used instead of the canonical form, $F_{id} = \mathcal{N}T \ln (c/e)$, since the argument of the logarithm should be dimensionless. The length, R_B, in eq 7 can be substituted by any other length: this substitution can be apparently compensated by the corresponding change of χ_c. Note that substitution of R_B by, say, R_A would produce an extremely small change of χ_c: $\chi_c \to \chi_c + \Delta\chi$, $\Delta\chi = 3Q^{-1}N_A^{-1} \ln (R_B/R_A) \ll \chi_c$.
(9) Note that, as was shown in ref 3, the interaction between micelles is a pair (two-body) interaction (provided that the distance between the nearest neighbors is larger than the radius of the core).
(10) The quantity U^*/T is equal to the product of the large parameter $\upsilon N_B Q^2/8\pi R_B^3 \sim N_B^{1/2}a^3/\upsilon$ and the small numerical factor φ^* so that both situations $U^*/T \gg 1$ and $U^*/T \ll 1$ are possible in principle. For real block–copolymer systems, the parameter U^*/T is always small. Nevertheless, the case $U^*/T \gg 1$ is considered here in order to obtain a complete picture of structural transitions.
(11) The ideal-gas term can be neglected since $U^* \gg T$.
(12) The concentration change at the transition point is expected to be rather small. Therefore, this ordering transition is in some sense analogous to a liquid-crystal phase transition.

On the Limitation of Comparative Quenching as a Measure of Electronic Energy Transfer in Polymers

YOSHIHIRO ITOH,[†] KEIKO KAMIOKA, and
S. E. WEBBER*

Department of Chemistry and Center for Polymer Research, University of Texas at Austin, Austin, Texas 78712.
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In some of the earliest work on electronic energy transfer (EET) in polymers by Fox et al.[1] and David et al.[2] it was noted that one manifestation of this phenomenon is that the polymeric excited state may be more easily quenched than the corresponding monomeric model compound. This is especially striking in low-temperature glasses in which no diffusion can occur. The physical idea is straightforward: if EET occurs, the excitation travels over a large volume, hence increasing the probability that a quencher species is encountered.

Table I
Comparison of the Fluorescence Quenching Parameters

(A) CCl_4

polymer	$\langle\tau\rangle$[g], ns	k_q, M^{-1} s^{-1}	Λ_E/D_{CCl_4}	R_0,[a] Å
r-MPh(42)$_{est}$[b]	32.9	2.2×10^8	0.50	8.8 (Phen)
PVPh[b]	17.0	5.4×10^8	2.64	
a-MPh$_{est}$[b]	42.5	2.6×10^8	0.78	
P(2VN-*co*-MMA)[c]	14.3	2.3×10^9	0.51	12 (2-MeNp)
P2VN-M[d]	7.4	1.2×10^9	0	
P(2VN-*alt*-MMA)[c]	43.4	3.0×10^9	0.97	
PVCz-M[d]	2.45	2.0×10^{10}	1.4–1.7	21 (MeCz)
PDPA-*co*-PS[e]	6.5	1.1×10^9	0	27 (DPA)
PDPA[e]	7.2	0.96×10^9	0	

(B) O_2

polymer	$\langle\tau\rangle$[g], ns	k_q, atm^{-1} s^{-1}	Λ_E/D_{O_2}	R_0, Å
r-MPh(42)$_{est}$[b]	32.9	7.4×10^7	0	8.8 (Phen)
PVPh[b]	17.0	7.9×10^7	0.03	
a-MPh$_{est}$[b]	42.5	7.8×10^7	0.01	
PDPA-*co*-PS[f]	6.8	1.7×10^8	0.09	27 (DPA)
PDPA[f]	7.1	1.5×10^8	0	

[a] Reference 8. Phen, phenanthrene; 2-MeNp, 2-methylnaphthalene; MeCz, *N*-methylcarbazole; DPA, 9,10-diphenylanthracene. [b] Reference 6. [c] Reference 3b. [d] Reference 3c. [e] Reference 7a. [f] Unpublished data. [g] $\langle\tau\rangle = \sum a_i\tau_i^2/\sum a_i\tau_i$ for multiexponential fluorescence decay.

In some of these papers and our own publications[3] this idea was applied by using the extension by Voltz et al.[4] of the Smoluchowski–Einstein equation:

$$k_q = 4\pi(D_Q + D_{seg} + \Lambda_E)R_QP_Q \qquad (1)$$

where k_q = quenching rate constant, R_QP_Q = product of interaction radius and probability of quenching per encounter, D_Q = the diffusion constant of the quencher, D_{seg} = the segmental diffusion constant of the chromophore bound to a polymer chain, and Λ_E = down-chain EET rate, expressed as a diffusion constant.

In our work we have determined k_q for a model polymer (k_q^{model}) in which there is a very low loading of chromophore[5] and for which it is assumed that $\Lambda_E \cong 0$. The quenching constant is then determined for a polymer in which it is assumed that $\Lambda_E > 0$ is possible (k_q^{polym}). It is further assumed that $D_{seg} \cong 0$ for both cases and that $R_Q^{model}P_Q^{model} \cong R_Q^{polym}P_Q^{polym}$. With these assumptions

$$(k_q^{polym} - k_q^{model})/k_q^{model} = \Lambda_E/D_Q \qquad (2)$$

While all the assumptions that lead to eq 2 may be questioned, the underlying concept is simple: The faster the excitation moves along the coil (and hence the larger the volume swept out per unit time), the more efficiently the excited state is quenched. We wish to point out here that this is not always correct and that the use of eq 2 may lead to an underestimate of Λ_E.

We were led to reconsider the use of eq 1 and 2 because the Λ_E values for several different polymers were strikingly different using CCl_4 and O_2 as quenchers.[6,7] These data are summarized in Table I along with the Forster R_0 values for self-transfer.[8] These data illustrate the following: (1) for the phenanthrene polymers $\Lambda_E > 0$ is obtained for CCl_4

[†] Permanent address: Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, Japan.

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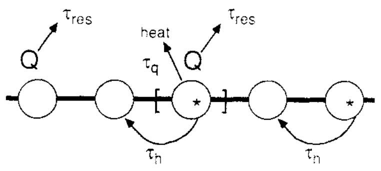

Figure 1.

quenching, but for O_2 quenching $\Lambda_E \cong 0$; (2) for the diphenylanthracene polymers $\Lambda_E \cong 0$ was estimated for both quenchers even though $R_0 \cong 2.7$ nm and no excimer fluorescence is observed (i.e., self-trapping does not seem to occur). It is very hard to understand why EET should not occur for this polymer.

Upon reflection we question the naive use of the Smoluchowski–Einstein equation for these problems. What we believe is a more valid physical picture is illustrated in Figure 1. We think of EET as occurring essentially one-dimensionally along the polymer chain, and the quenchers (Q) can diffuse onto and away from this chain with an average "residence time" τ_{res}. We define an average "hopping time" for the motion of the excitation between sites as τ_h and a "quenching time" for sites adjacent to a quencher as τ_q. We may distinguish three cases:

(1) $\tau_{res} \gg \tau_q \gg \tau_h$: In this case the quencher may be considered as residing permanently on the polymer (this would be especially suitable for low-temperature glasses), and the quenching is slow compared to the EET. In this case EET can remove the excitation from the vicinity of Q before quenching occurs and hence does not serve to enhance the quenching (this is demonstrated more quantitatively below).

(2) $\tau_{res} \ll \tau_h$: Quencher contacts at a given site are made and broken quickly on the time scale of EET, and quencher contacts occur randomly along the polymer chain. In this limit an excitation experiences many collisions during the time τ_h required to move to a nearby chromophore. This also includes the case that $\Lambda_E \cong 0$ (i.e., $\tau_h \cong \infty$). We are not aware of a quantitative theory that deals with this case except in the limit $\tau_h \cong \infty$, in which case the classical Smoluchowski–Einstein equation should obtain. For this case τ_q is not relevent because the polymer and the model compound are affected equally by efficient or inefficient quenching.

(3) $\tau_{res} \gg \tau_h \gg \tau_q$: The quenching rate constant is so high that any excitation that reaches a quencher site is immediately quenched. In this case EET to the quenching site greatly improves the quenching efficiency (see Figure 1).

Case 1 and 3 can be explored by using the 1-D lattice model of Lakatos-Lindenberg et al.[9] This model is like that illustrated in Figure 1 and is comprised of an infinite 1-D lattice with a fraction c of lattice sites with adjacent quencher. The quenchers are stationary, and for the purposes of this discussion we assume that only the site adjacent to Q is quenched. The two important rate constants in this model are F $(=1/\tau_h)$ and S $(=1/\tau_q)$. A closed expression for the zeroth moment of the total excitation function is obtained by Lakatos-Lindenberg et al.:[9]

$$M_0^{\infty}(c) = \frac{(4/F)[2 + Q(1 - c)]}{Q\{8c + (1 - c^2)Q - (1 - c)Q^{1/2}[16c + Q(1 + c)^2]^{1/2}\}} \tag{3}$$

where Q = S/F and c was defined above. $M_0^{\infty}(c)$ represents the steady-state fluorescence intensity of the excited chromophore for infinite intrinsic lifetime of the excited state. These workers suggest the following approximation for finite lifetime τ:

$$1/M_0(c) = 1/M_0^{\infty}(c) + 1/\tau \tag{4}$$

While eq 3 is unwieldy, its limiting behavior is simple. If we assume $c \ll 1$ and the validity of eq 4, then

$$\lim_{Q \to 0} M_0(0)/M_0(c) = 1 + S\tau c \quad \text{(case 1)} \tag{5a}$$

$$\lim_{Q \to \infty} M_0(0)/M_0(c) = 1 + 2F\tau c \quad \text{(case 3)} \tag{5b}$$

These two equations are analogous to the classical Stern–Volmer quenching expressions in which S and F play the role of k_q. The $Q \approx 0$ limit corresponds to a small quenching rate constant relative to the EET rate constant, and the steady-state intensity is not affected by the value of F. Hence in this limit $\Lambda_E \approx 0$ would be incorrectly estimated. We believe this is the case for the DPA polymers (Table I). On the other hand, if the quencher is very effective (i.e., a so-called "disruptive quencher"), then the steady-state quenching depends strongly on F and a physically realistic estimate of Λ_E via eq 2 may be anticipated.

What we wish to point out with these comments is that the method of comparative quenching may produce a valid estimate of Λ_E under the limited condition referred to as case 3 above. For the other cases Λ_E will always be underestimated. This implies that in using this method the experimentalist should attempt to compare a number of quenchers with different intrinsic quenching rate constants. We do not see any simple way to vary the residence time of a quencher on a polymer chain. It would seem most reasonable to use quenchers with similar diffusion constants and to avoid quenchers with specific polymer interactions.[10] In general it would be best to use quenchers that are covalently bound to the polymer, but this is experimentally inconvenient.

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(10) Conversely, strong adsorption onto a polymer chain would increase τ_{res} and permit use of analytical solutions like eq 3. However, there would exist the difficulty of estimating the local concentration of the quencher on the polymer.