flect interpolation between the respective regimes.

The T dependence of ξ_p at the three concentrations is plotted in Figure 2. These data are T independent at the highest concentration as expected from both models. At the lowest concentration the data follow a power law that is close to the SJP entry in the table but differs by a factor of 2 from the DJ prediction.

The data at the intermediate concentration show an exponent consistent with the scaling prediction for region II, but it is clear that this result is due to crossover and is not evidence for scaling laws.

The data presented demonstrate that scaling behavior is not found in the region of the T–C diagram usually studied by experimentalists. In addition, a reasonable explanation is provided for the observation of "apparent" scaling exponents in the crossover near $\phi^\dagger$, which separates the marginal and Θ regimes.

Registry No. Polystyrene, 9003-53-6; cyclopentane, 287-92-3.

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Singlet Energy Migration of Anthracene Polymers in Polystyrene

Effective transformation of light into chemical energy is a subject that has received much attention of late.[1] One of the problems encountered in such work is the necessity for efficient collection of photonic energy at a site where complex chemistry can take place. For this to occur, photon harvesters, or "antennas", must be designed to facilitate energy transfer to the reaction center, which, on a molecular level, may be far removed from the original point of light absorption.[2]

Recently, Faulkner and Renschler[3] have estimated the degree to which singlet excitation energy may migrate between diphenylanthracene (DPA) sites when these are dispersed in a film of polystyrene (PS) and tetrabromo-*o*-quinone (TBBQ) is used as an acceptor. Values of up to 55 Å for the diffusion length of excitation energy (D), through hopping from one DPA site to another by a Förster energy-transfer mechanism, were obtained.[4] Since the rate of such transfer increases dramatically with decreasing distance between the sites,[5] it might be feasible to increase the extent of diffusion by chromophore polymerization rather than by increasing the small-molecule concentration. Polymer-bound chromophores may also be more compatible with a host film. Furthermore, the problem of site loss from the film, because of leaching, would then be severely curtailed. Energy migration in dilute polymer solutions has been invoked to explain various characteristics of macromolecular photophysics.[6]

Table I
Characteristics of the Polymers

polymer[a] (PPA-*co*-PS)	mole fraction[b]	τ,[c] ns
1	0.016	6.9
2	0.021	6.2
3	0.039	5.3
4	0.051	5.2

[a] Molecular weight (M_w) of each copolymer is 13 500 (PD = 1.5). [b] Mole fraction of phenylanthracene units in the copolymers (calculated from visible absorption spectroscopy). [c] Fluorescence lifetimes of neat films.

We have synthesized (10-phenyl-9-anthryl)methyl methacrylate[7] and copolymerized it with varying amounts of styrene (copolymers PPA-*co*-PS, 1–4). Table I lists the essential features of these polymers. Polystyrene films containing one of the copolymers, or the saturated monomer equivalent (PA), with or without quencher (TBBQ), were cast by dropping a benzene solution of the components onto a glass slide rotating at approximately 6000 rpm on a Headway Research Inc. (Model EC101) spin-casting apparatus. Mole ratios of the components in solution were retained on the slide. Films cast by allowing the solvent to evaporate slowly were not used in this study because visible inspection of the films, facilitated by the red color of the quencher, showed nonhomogeneity. Fluorescence decay curves, obtained by excitation of the phenylanthracene chromophore at 355 nm using a Nd:YAG laser, were digitized on a fast transient recorder (Tektronix Model 7912). The decay curves of the films could be fit satisfactorily to a single exponential over the time range t = 1.5 ns to t = 10 ns, over which time the emission had decreased about sevenfold. t = 0 was taken as the maximum of the decay curve. Mirroring Faulkner's work,[3] we then estimated the extent of singlet energy migration that occurs on irradiation when these copolymers are either dispersed in polystyrene or utilized as neat films and compared the results with those of the saturated monomer (PA) under identical conditions.

The occurrence of energy migration between PA sites in a polystyrene matrix is demonstrated by the dependence of γ, the Förster quenching parameter,[5] on fluorophore concentration. Extrapolation of a plot of γ vs. [PA] to zero fluorophore concentration yields a value of 0.43 for γ. From this value, R_0, the critical transfer distance between PA and TBBQ sites, is estimated to be ~25 Å. Faulkner cites a value of 28 Å for DPA–TBBQ pairs using this method, which agrees well with the value of R_0 obtained from theoretical considerations.[3]

The Yokota–Tanimoto theory[8] has been widely cited and used as a means of measuring D in those systems in which energy diffusion plays a significant part. Figure 1

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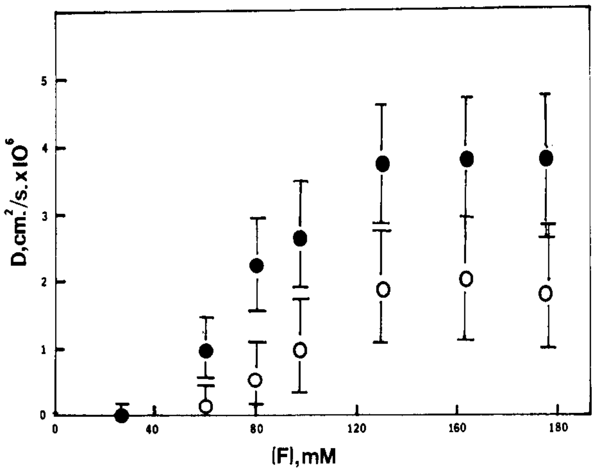

Figure 1. Dependence of D on fluorophore concentration. PA in PS (open circles); PPA-*co*-PS in PS (closed circles). Each closed circle represents an averaged value of D from each of the copolymers. Films contained 12.0 mM TBBQ as acceptor.

shows a plot of D, obtained with this theory, as a function of [F], the fluorophore concentration, for the monomeric or polymeric species. At a sufficiently high fluorophore concentration singlet energy migration between phenylanthracene sites can compete with transfer to the TBBQ quencher by a single-step Förster transition or other dissipation mechanisms.

For PA this corresponds to a [F] of about 60 mM, at which the mean nearest-neighbor distance, l, is ~17 Å. A value of R_0 = 22 Å has been given as the critical transfer distance between 9-phenylanthracene sites.[10] At [F] ≥ 60 mM the migration distance appears to increase rapidly but then tails off at [F] ~120 mM (l = 13 Å), at which the value of D is approximately 2×10^{-6} cm^2 s^{-1}, a rate that corresponds to a root-mean-square diffusion length[11] of 32 Å. This is about 15 Å lower than the estimate of energy migration distances between DPA–DPA sites[3] and reflects the decrease in the resonance transfer efficiency, and hence of self-transfer, of our system.

Figure 1 also shows values of D obtained for (PA-*co*-PS) copolymers dissolved in polystyrene. Within the errors of our experiment there are two differences for this system when compared to that of PA in PS. First, the singlet energy migration appears to gain significance at a lower site concentration. Second, for the same chromophore doping, the coefficients of diffusion are about twice as high for the copolymer than for the monomer. This could signify that polymer chains containing anthracene units give rise to domains within the polystyrene matrix across which energy migration is very efficient. The limiting factor influencing the magnitude of D would then be the interdomain spacing. For copolymers PPA-*co*-PS 1 and 4 in polystyrene at [F] ~ 50 mM (the concentration at which energy migration becomes significant) it can be estimated that these domains are approximately 12 and 35 Å apart, respectively, assuming that the density of the copolymer is the same as that of PS (1.04 g/cm^3). Each domain has an average radius of ~17 Å for a polymer of molecular weight 13 500 and contains approximately 2 and 5 fluorophore units for PPS-*co*-PS 1 and 4, respectively. In each polymer coil, therefore, the anthracene units are spaced much closer together than R_0. But these domains are also within striking distance of each other (assuming homogeneous mixing and even distribution) even for the highest doped copolymer where the domains are spaced farthest apart for any given concentration of fluorophore. It is of interest to note that within the error of our results, we could find no increase in D with increase of fluorophore mole fraction in the copolymers. Furthermore, neat films of the copolymers showed no large increase in D even for [F] ~ 450 mM, for which $D \sim 4 \times 10^{-6}$ cm^2 s^{-1} for PPA-*co*-PS4 film (omitted from Figure 1 for the sake of clarity). Hence the migration distance is zero until a certain site concentration, at which point it rapidly increases but then soon levels out to a constant value. The maximum root-mean-square diffusion length corresponding to this value of D is ~ 43 Å for our system (cf. 32 Å for monomeric PA). Copolymerization, therefore, appears to enhance energy migration with respect to a small molecule. It also appears to be possible to optimize the films in terms of fluorophore concentration.

It is surprising at first that D does not increase to higher values as [F] increases. One contributing factor is that as [F] increases there is a concomitant decrease in the fluorescence lifetime (τ_f). This is minimal for the monomer but is significant for the polymers, especially at high loading. For instance, τ_f for a PPA-*co*-PS4 neat film is only 5.2 ns while that of isolated monomer in PS is 8.8 ns. Aggregation, which induces self-quenching, may be the origin of this phenomenon although there is very little difference between the fluorescence emission from a copolymer in film or in fluid solution over the range of [F] used in this study. There is no fluorescence spectrum perturbation observed for the monomer. However, the fluorescence from homopolymer poly(phenylanthracene) (PPA) loses some of its structure when dissolved in PS and is both broad and red-shifted when in powder form.[12] These changes must be considered as alternative deactivation pathways for the excited state and as such will reduce the possibility of energy migration.

A more detailed description of the experimental procedures and results will be published elsewhere.[12]

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Registry No. PS, 9003-53-6; PPA-*co*-PS, 85702-20-1.

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