Notes

Phosphorescence Quenching of Benzil by Polystyrene in Dilute and Semidilute Solutions

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Introduction

A number of recent studies have reported on phosphorescence quenching of small excited-state molecules by macromolecules in solution.[2-14] Horie and Mita[2-4] have published results concerning energy transfer from a benzil triplet to an anthracene moiety located either at the terminus or the center of a polystyrene chain while other studies have been reported concerning interactions between benzil triplets and anthracene moieties labeled randomly along a polystyrene chain backbone.[5] Another class of studies[6-14] concerned the interaction of small molecules with polymers which have many reactive sites along their backbones; these studies have included two investigations of phosphorescence quenching of benzil by polystyrene in benzene or other solvents.[6,7]

In the case of benzil phosphorescence quenching by polystyrene, the interaction is a non-diffusion-controlled process,[7] i.e., the polymer and benzil molecules may encounter each other many times before quenching occurs. A charge-transfer interaction has been proposed[7] as being responsible for the quenching although this is still uncertain. For this system, Stern–Volmer kinetics have been applied[6,7] to obtain the bimolecular quenching rate constant, k_q, by using the following relationship:

$$I_0/I = 1 + k_q\tau_0[Q] \quad (1)$$

where I_0 and I are the benzil phosphorescence intensities in the absence and presence of the quencher (polystyrene), respectively, τ_0 is the benzil phosphorescence lifetime in the absence of polystyrene, and [Q] is the concentration of polystyrene. Determinations of k_q made for the benzil–polystyrene/benzene system are inconsistent with each other, with the result obtained by Olea et al.[7] [1.3×10^4 L/(base mol) s] being almost an order of magnitude greater than that obtained by Horie and Mita[6] [1.9×10^3 L/(base mol) s]. This is not necessarily surprising as quenching studies with low k_q values are difficult to interpret, and accurate measurements are not trivial. In this study, we have investigated the quenching of benzil phosphorescence by polystyrene in dilute and semidilute solutions, this time employing cyclohexane and toluene as solvents; the applicability of eq 1 for evaluation of k_q in this system will be discussed.

Experimental Section

Sample solutions containing 1.0×10^{-3} M benzil and various polystyrene concentrations were prepared and shaken for 1 day prior to use. Benzil and spectrophotometric quality solvents were obtained from Aldrich, and nearly monodisperse polystyrene was obtained from Pressure Chemical Co. Polystyrene was purified by dissolving in toluene, precipitating in methonal several times, and drying in a vacuum oven at 60–70 °C for several days. The results obtained with purified polystyrene were compared with those with unpurified polystyrene and showed no significant difference. All samples were subjected to seven freeze–pump–thaw cycles in order to remove dissolved oxygen as completely as possible. Benzil phosphorescence intensities and lifetimes were measured with a SPEX system described previously.[15] The excitation and emission wavelengths were 400 and 560 nm, respectively.

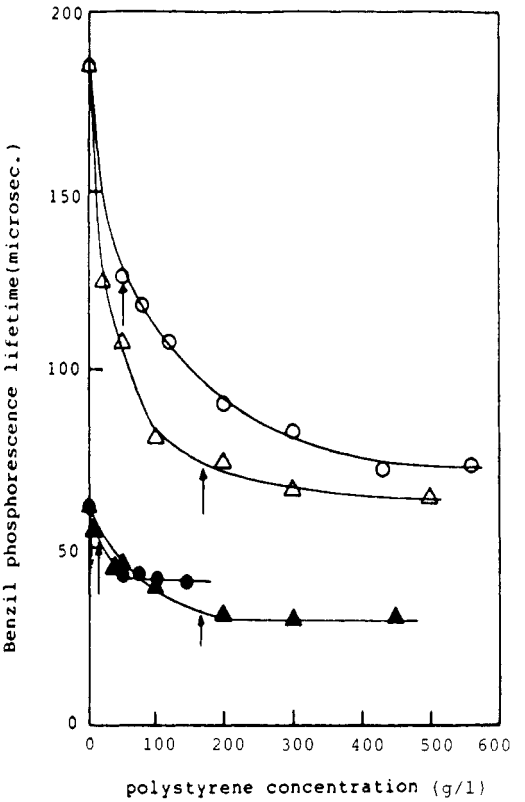

Figure 1. Benzil phosphorescence quenching in polystyrene solutions (arrows designate $c = 1/[\eta]$ for the cyclohexane and toluene solutions); τ versus concentration. Polymer solutions: (○) PS with MW 47 500 in cyclohexane; (△) PS with MW 4000 in cyclohexane; (●) PS with MW 670 000 in toluene; (▲) PS with MW 4000 in toluene.

Results and Discussion

Figure 1 shows benzil phosphorescence lifetime as a function of polystyrene concentration for several molecular weights of polystyrene both in cyclohexane and in toluene solutions. The lifetime is seen to drop dramatically with increasing polymer concentration in the dilute concentration regime and approaches a plateau at higher concentrations. Both the rate at which the phosphorescence lifetimes decrease with increasing polymer concentration at low polymer concentrations and the plateau lifetimes are functions of polymer molecular weight. As benzil phosphorescence is sensitive to even very small quantities of quencher, this may suggest the presence of some impurity bound to the polystyrene chain itself which may participate in quenching and is present in different quantities in the different molecular weight samples of polystyrene. Such an impurity cannot be removed by purifying the polymer, and this may explain why k_q varies

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Table I
I_0/I and τ_0/τ of Benzil Phosphorescence in Polystyrene (4000 MW)/Toluene Solutions

[PS], g/L	I_0/I	τ_0/τ	[PS], g/L	I_0/I	τ_0/τ
0	1	1	100	3.42	1.57
50	1.59	1.32	300	4.48	2.32

with polymer molecular weight but is insensitive to repeated purification. It is interesting to note that the concentrations at which the plateau in benzil phosphorescence lifetime is achieved are in the semidilute regime ($>[\eta]^{-1}$) for all polymer solutions. However, this "saturation" in quenching is not a good predictor of c^*, as the plateau concentration is at least as great for the 47 500 MW PS/cyclohexane solution as for the 4000 MW PS/cyclohexane solution.

A similar phenomenological behavior has been found by Winnik et al.[16] for pyrene fluorescence quenching in polystyrene–toluene solutions; in their study the pyrene lifetime decreased as polymer concentration increased and became a constant when the polymer concentration was above 100 g/L. However, as shown in Figure 2, in the present study there is no break in $1/\tau$ as polymer concentration increases as found in the system studied by Winnik et al.[16] Instead, a rather smooth increase to an eventual plateau in $1/\tau$ is observed with increasing concentration.

In addition to measuring phosphorescence lifetimes as a function of polymer concentration, phosphorescence intensities were also measured. A comparison of values of I_0/I and τ_0/τ, given in Table I, clearly shows that they are not equivalent. The higher values of I_0/I indicate that significant static quenching is present in addition to dynamic quenching. In the presence of static quenching, the proper form of the Stern–Volmer equation for evaluating interactions of the excited-state benzil with PS is the following:

$$\tau_0/\tau = 1 + k_q\tau_0[Q] \qquad (2)$$

As the lifetimes are unaffected by possible ground-state complex formation by benzil while measured intensities are strongly affected, k_q should be determined by measurements of excited-state lifetimes and not by measurements of intensities as was done by Horie and Mita[6] and Olea et al.[7]

In any case, it is clear that neither eq 1 nor eq 2 is seen to hold over the entire polymer concentration range under investigation in this study. This is in sharp contrast with results by Horie and Mita[2] which seem to follow eq 1 for polystyrene concentrations up to 400 g/L in benzene. Their results are surprising in that at concentrations well below 400 g/L the polymer should be substantially interpenetrated[17,18] so that the effects of additional polystyrene at high concentration would be minimal at best.

Assuming that Stern–Volmer kinetics in the form of eq 2 hold at low polystyrene concentrations (≤40 g/L) as shown in Figure 2, we found that for 4000 MW PS in toluene k_q was approximately 1.8×10^4 L/(base mol) s. This is of the same order of magnitude (within 40%) as found by Olea et al.[7] for polystyrene/benzene solutions. As solvent polarity plays a significant factor in charge-transfer interactions,[7] one might argue that the near equivalence of these results could be expected based on the similarity in dielectric constant of benzene and toluene. However, given the evidence concerning the presence of static quenching in these systems, the relatively close agreement between the results obtained in our study, in which k_q's were calculated with ratios of lifetimes, and those obtained by Olea et al.[7] may be fortuitous.

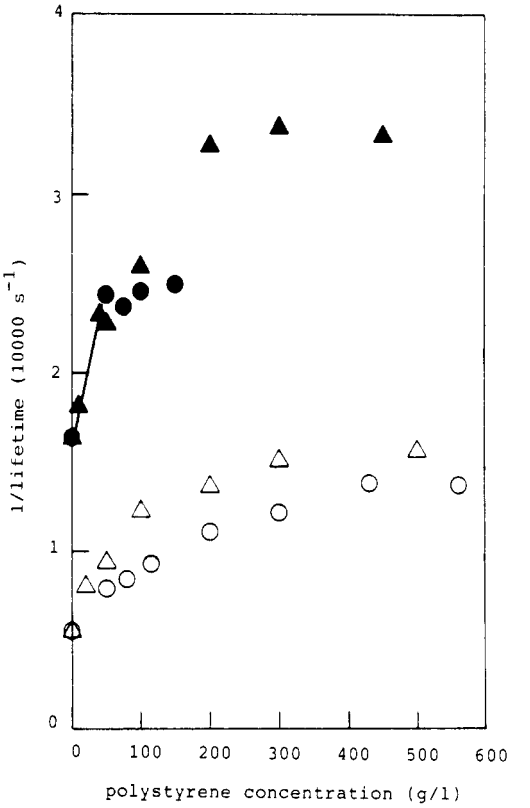

Figure 2. Benzil phosphorescence quenching in polystyrene solutions; $1/\tau$ versus concentration. Polymer solutions: (○) PS with MW 47 500 in cyclohexane; (△) PS with MW 4000 in cyclohexane; (●) PS with MW 670 000 in toluene; (▲) PS with MW 4000 in toluene; The straight line indicates the low polymer concentration Stern–Volmer relationship in the 4000 MW polystyrene/toluene system.

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Registry No. Benzil, 134-81-6; polystyrene, 9003-53-6.

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