

Preliminary Note

The quenching of alkyl pyrene fluorescence by atactic and isotactic polystyrene

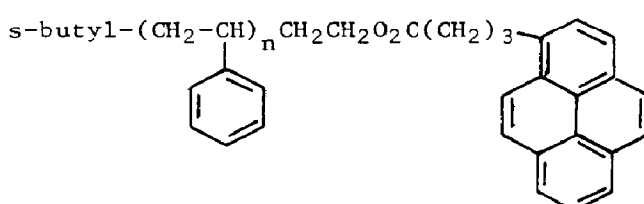
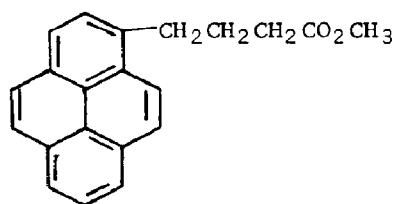
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1. Introduction

The fluorescence decay time of pyrene derivatives is shorter in toluene solution than in alkane solvents. While this difference is not large, it suggests that there are weak quenching interactions between the phenyl chromophore and the L_b lowest excited singlet state of pyrene and its derivatives. Our studies of pyrene-substituted polystyrene (PS) polymers [1] raised the possibility that the polymer might be a more effective quencher of pyrene fluorescence at similar chromophore concentrations. It became necessary for us to obtain reliable values for the lifetime of pyrene chromophores in the presence of high concentrations of polystyrene. Consequently we undertook a study of pyrene fluorescence quenching by polystyrene.



The kinetics of the fluorescence quenching of the two pyrene derivatives whose structures are shown above are described in this paper. Methyl-4-(1'-pyrene)-butyrate (1) was prepared from commercially available pyrenebutyric acid. The polymer 2 (PS 5900Py, $n \approx 50 - 60$) was prepared by initiating styrene polymerization in tetrahydrofuran (THF) at -78°C with *sec*-butyllithium followed by the addition of ethylene oxide and then acetic acid. This polymer was first purified and subsequently esterified with the acid chloride of pyrenebutyric acid. Details have been reported elsewhere [1, 2]. Its average molecular weight \bar{M}_n , as determined by gel permeation

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chromatography (GPC), is 5900, and $\bar{M}_w/\bar{M}_n = 1.2$. The fluorescence lifetimes of 1 and 2 are essentially identical in dilute solution in both cyclohexane ($\tau = 240$ ns) and toluene ($\tau = 193$ ns). This result suggests that intramolecular quenching by the polystyrene chain in 2 is of negligible importance.

2. Sample preparation

All samples were rigorously outgassed by five freeze-pump-thaw cycles and were sealed in cylindrical Pyrex cells. Tubing with outside diameters of both 7 mm and 13 mm were used, the former for samples containing large PS concentrations. The polymers were weighed directly into the sample tubes. A known volume (200 - 500 μ l) of a solution of 1 or 2 with a pyrene group concentration of 5×10^{-6} M was then added and the mixture was degassed on a vacuum line. Care had to be taken to prevent foaming since sealing the tubes tended to pyrolyze any polymer film on the inside of the tube and hence introduce quenchers into the final solution. After the tubes were sealed, they were annealed at 80 - 90 °C for 1 h to obtain uniform solutions. PS in cyclohexane precipitates at temperatures below 34 °C. The samples were warmed to 40 °C for 1 h before measurements were taken, and the tubes were inspected carefully to ensure that the solutions were homogeneous.

Fluorescence decay measurements were made by the time-correlated single-photon counting method. Samples in THF and toluene were run at room temperature (22 °C). Samples in cyclohexane were run at 35 °C. Toluene was distilled from sodium metal. Cyclohexane was stirred with successive portions of concentrated H_2SO_4 under nitrogen until the acid layer remained clear. It was washed with $NaHCO_3$ solution, dried and then distilled from sodium metal. A fresh bottle of THF (Caledon Laboratories, high pressure liquid chromatography grade) was opened and used immediately for the experiments in this solvent.

Several PS samples were used. PS 17 500 and PS 860 000 were narrow molecular weight standards from the Pressure Chemical Co. The sample of HO-PS8700-OH was prepared by us using potassium naphthalene as an initiator and was end capped with ethylene oxide. The numbers 17 500, 860 000 and 8700 refer to the \bar{M}_n values of the polymers. Our sample of isotactic PS was a gift from Dr. D. Vanderhart at the National Bureau of Standards. GPC determination showed $\bar{M}_n = 900\,000$ with a broad molecular weight distribution. ^{13}C nuclear magnetic resonance (NMR) investigation (solvent, $CDCl_3$; 23 °C) showed that it was more than 99% isotactic. NMR measurements (^{13}C ; $CDCl_3$; 23 °C) showed no impurities at the 1% level in any of the polymer samples.

All the PS samples not containing a pyrene chromophore showed a weak impurity fluorescence. This fluorescence was red shifted from the normal PS excimer fluorescence. It could be excited by irradiation at 335 - 345 nm and had a fluorescence decay time of 10 ns. This impurity could only be observed in solutions of PS containing at least 15 - 20 wt.% polymer. Since it was present in similar amounts in all PS samples whether prepared

by organometallic catalysts or by initiation with *sec*-butyllithium or potassium naphthalene, we attribute this impurity to the subsequent oxidation of the PS upon storage. UV measurements of polymer samples containing 200 mg of polymer in a total volume of 1 ml solution showed a long weak tail in the absorption spectrum extending out past 400 nm. The absorbance of this sample at 350 nm in a 1.0 cm cell was 0.02.

3. Results and discussion

Pyrene fluorescence decays were exponential over two decades of the emission decay except for samples containing more than 150 - 200 mg PS ml⁻¹. In these cases a weak short component ($\tau \approx 10$ ns) was detected in the initial decay channels (see above). The decay times τ were obtained by fitting the major component of the decay to a single-exponential form. The data were plotted according to the Stern-Volmer equation

$$\frac{1}{\tau} = \frac{1}{\tau^0} + k_Q[\text{PS}] \quad (1)$$

where τ is the fluorescence decay time for a given sample, τ^0 is the decay time at zero PS concentration in the appropriate solvent and k_Q is a phenomenological quenching constant. [PS] represents the concentration of monomer units (phenyl groups). Hence k_Q has units of litres reciprocal mole seconds per monomer.

Figure 1 shows a plot of $1/\tau$ versus [PS] for cyclohexane solutions containing atactic PS samples. This plot indicates that τ depends on the monomer group concentration but not on the molecular weight of PS. The value of k_Q determined from this plot is $1.81 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ monomer}^{-1}$. This

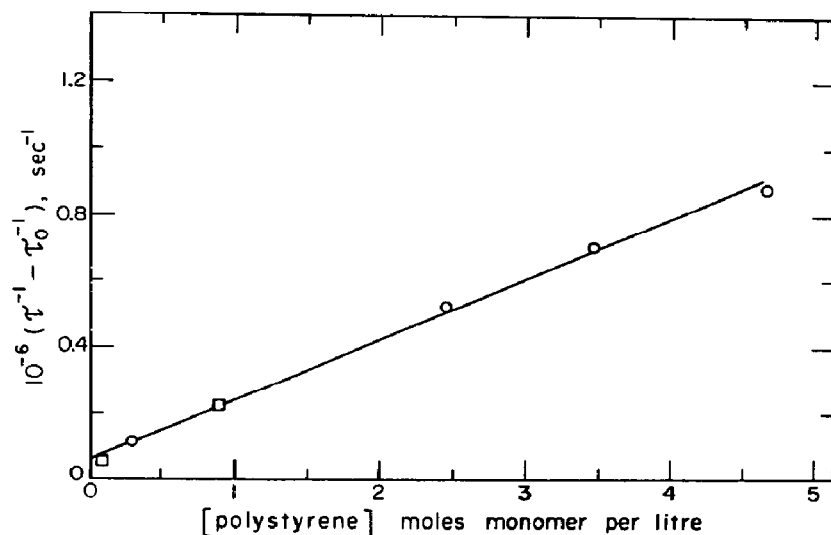


Fig. 1. Plot of $1/\tau - 1/\tau^0$ vs. [PS] in moles of monomer per litre for PS 5900Py (2) in cyclohexane at 35 °C in the presence of unlabelled polystyrene: ○, $\bar{M}_n = 17\,500$; □, $\bar{M}_n = 860\,000$. k_Q is determined to be $1.81 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ monomer}^{-1}$.

value is not very different from that for the toluene quenching of 1 or 2 obtained by comparing $1/\tau^0$ values in the two solvents and dividing by the molar volume of toluene. This manipulation gives $k_Q(\text{C}_6\text{H}_5\text{CH}_3) = 1.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ monomer}^{-1}$.

PS also quenches pyrene fluorescence in toluene solution. Stern-Volmer behaviour is only apparent at low concentrations. At PS concentrations above 1 M (10 g per 100 ml) the pyrene lifetime becomes independent of polymer concentration (Fig. 2). Although the data show considerable scatter, the slope at low concentrations is approximately $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ monomer}^{-1}$. Another feature that makes these results unusual is that the actual data differ somewhat for 1 and 2 and that the plots show further variations in the initial slopes and limiting τ values when PS 17 500 is used as the quencher. These observations were unexpected and are difficult to explain.

We had originally anticipated that toluene and the PS repeat unit would be comparable quenchers of pyrene fluorescence. Consequently we predicted that τ in toluene would be independent of [PS]. This is observed only at [PS] > 1 M. If trace impurities in the PS samples (see above) were responsible for quenching pyrene fluorescence, increasing the concentration of PS in toluene would lead to increased quenching of pyrene by PS (see eqn. (1)) since impurity concentration would necessarily increase with PS concentration. The constancy of τ at high PS concentrations in toluene is evidence that the other observations reported here are not due to impurity quenching. (An impurity present at the 0.1% per monomer level would be undetected by NMR and could explain the fluorescence quenching in cyclohexane and THF solutions. However, it could not explain the quenching behaviour in toluene (Fig. 2).)

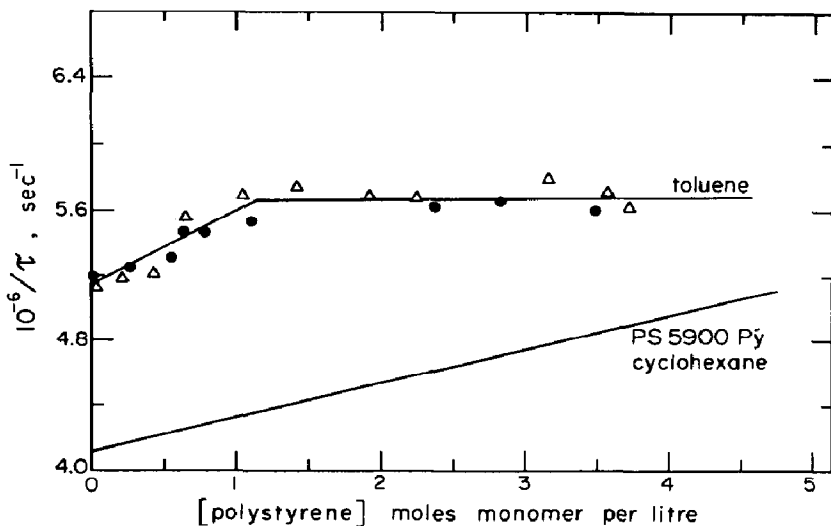


Fig. 2. Plot of $1/\tau$ vs. [PS]: lower curve, replot of the data from Fig. 1 in cyclohexane; upper curve, PS 5900Py (2) (●) and $\text{Py}(\text{CH}_2)_3\text{CO}_2\text{CH}_3$ (1) (Δ) in toluene in the presence of HO-PS8700-OH. [PS] is in units of moles of monomer per litre.

One clue to a possible explanation of the quenching results in toluene solution is shown in Fig. 2. Extrapolating the $1/\tau$ plot for the data in cyclohexane to high concentrations suggests that this line will intercept the $1/\tau$ line in toluene for [PS] in the range 9 - 10 M. This behaviour is not unreasonable since 10 M PS is essentially pure polymer. This leads us to suspect that the role of PS at low concentrations is to modify the ability of the toluene solvent to act as a quencher for pyrene fluorescence.

There are many possible mechanisms for this fluorescence quenching. These include donor-acceptor interactions, electron transfer and electronic energy transfer. It is normally difficult to ascribe specific mechanisms to the kind of weak quenching observed here. We have to be satisfied by rejecting some possibilities and focusing attention on specific aspects of the phenomenon. For example, since the quenching is inefficient neither solvent nor bulk viscosity would be expected to play a role, in accord with our observations. Index of refraction changes in the solution as a function of PS concentration would affect the radiative rate of the pyrene groups. Since the fluorescence quantum yields of 1 and 2 are less than unity, this is only one factor contributing to the magnitude of τ^0 in eqn. (1).

In order to explore the role of tacticity in the quenching process, we examined a sample of isotactic PS (it-PS) as a quencher. For reasons of solubility, these experiments were carried out in THF solution. Experiments with atactic PS showed that a change of solvent had no effect on the quenching of 1^* by PS 860 000 ($k_Q = 1.75 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ monomer}^{-1}$). Quenching of 1^* by it-PS 900 000 is a factor of 2.8 larger ($k_Q = 4.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ monomer}^{-1}$) than that by atactic PS (Fig. 3). This result indicates that local conformational effects play a small but significant role in the quenching process.

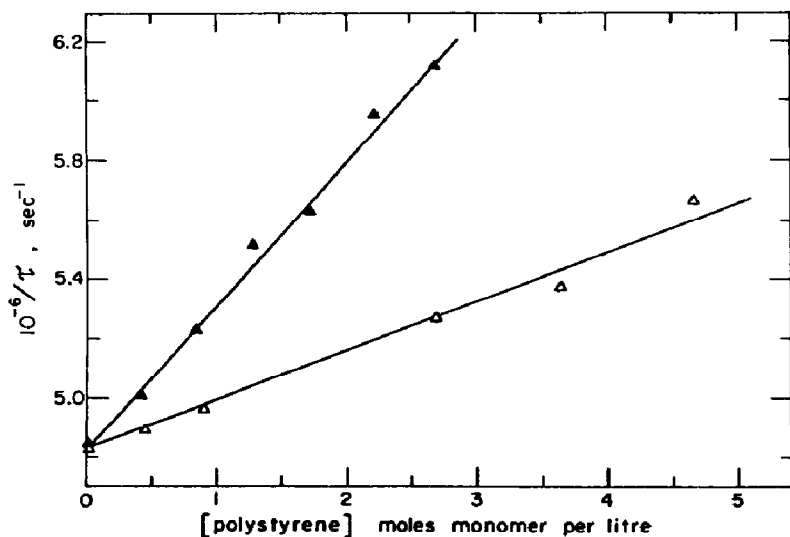


Fig. 3. Plot of $1/\tau$ vs. [PS] for $\text{Py}(\text{CH}_2)_3\text{CO}_2\text{CH}_3$ (1) plus atactic (Δ) and isotactic (\blacktriangle) PS in THF solution. The values of k_Q are $4.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ monomer}^{-1}$ for isotactic PS and $1.75 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ monomer}^{-1}$ for atactic PS.

4. Conclusions

Both toluene and atactic PS are weak quenchers of alkyl-substituted pyrene fluorescence. The former gives $k_Q = 1.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ monomer}^{-1}$ and the latter gives $k_Q = 1.81 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ monomer}^{-1}$ in THF and cyclohexane. These values are independent of the molecular weight of the PS. Isotactic PS is a significantly better quencher, with $k_Q = 4.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ monomer}^{-1}$. The mechanism of this quenching is unknown. Impurity quenching and energy transfer to "preformed excimer sites" in the PS have been ruled out as significant contributors to the quenching process.

A very unusual phenomenon is observed in toluene solution. For PS concentrations above 1 M, the lifetime of alkyl pyrene derivatives is independent of [PS]. Below 1 M, the pyrene lifetime increases with decreasing [PS] consistent with an effective rate constant of quenching of $3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \text{ monomer}^{-1}$.

1 A. E. C. Redpath and M. A. Winnik, *Ann. N.Y. Acad. Sci.*, **366** (1981) 75 - 92.

2 M. A. Winnik, A. E. C. Redpath and D. H. Richards, *Macromolecules*, **13** (1980) 328 - 335.