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Solvent dependence of magnetic-field effect in a polymer-linked exciplex system

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The response of pyrene–polystyrene–dimethylaniline (Py–PS–DMA) polymer ($M_n = 4770$) to an externally applied magnetic field has been examined in different solvents. Although the dielectric-constant (ϵ) effect is similar to that for the unlinked system, a closer look shows an interesting dependence on the nature of the solvent mixture. In pure acetone $\Delta\phi/\phi$ is higher than that in a mixed solvent (tetrahydrofuran/dimethylformamide) of the same ϵ. The results have been explained on the basis of the fact that the influences of coil extension on the magnetic-field effect and the dielectric-constant effect compete with each other, resulting in different behaviours depending on the nature of the solvent mixture.

(Keywords: polymer-linked exciplex; magnetic-field effect; solvent dependence)

INTRODUCTION

The importance of micelles in connection with the observation of magnetokinetic phenomena was first realized by Turro *et al.*[1,2]. They have shown that considerable enhancement of the magnetic-field effect (MFE) is possible if triplet-born neutral radical pairs (RPs) are encaged in micelles[3]. But when one is interested in observing MFE on charged singlet RPs by monitoring their luminescence (resulting from recombination), micellar encagement has not produced any significant results. This is primarily because of the fact that the magnitude of MFE on radical ion-pair (RIP) recombination largely depends on the dielectric constant (ϵ) of the medium; since the exciplex resides in the interface region where the average dielectric constant is high, MFE on exciplex luminescence can hardly be observed[4].

These limitations of micelles as a means of restricting the free diffusion of the RP partners may be bypassed in another way, namely by attaching 'magnetically insensitive' spacers. The spacer chains normally consist of methylene groups $-(CH_2)-$, which may be considered to be 'magnetically inactive' as the hyperfine coupling constants of methylene protons are very small[5] (of the order of 0.03 G). As a result of such linking, the MFE, which results from a complicated intermingling of diffusion and spin dynamics, gets modified through convolution with chain dynamics. Extensive studies have been carried out in short-methylene-chain-linked systems by Weller *et al.*[6–8] and later by Tanimoto *et al.*[9–12]. In the above studies, apart from the work of Tanimoto *et al.*[9], we find that very little attention has been paid to radicals joined by a regular polymer chain; the latter is expected to give them more freedom of movement than when they are joined by short-chain methylene groups.

Dilute polymer solutions may in a sense be considered as 'inhomogeneous', as they experience an environment which is different from that in bulk. Recently, Winnik *et al.*[13–16] have shown that an elegant method to probe the solvent environment inside the coil is to attach exciplex-forming groups at the ends of the polymer chain. Since exciplex fluorescence responds fairly well to solvent polarity[17,18], such types of modified polymers may give reliable information on the environment experienced by the end-groups in cyclized conformations of the chain. Although the above aspect of the dependence of exciplex luminescence on chain conformation is a fairly well explored region, the dependence of the spin rephasing process of the RPs on chain dynamics is still an open question. Intrigued by the investigations on the solvent dependence of linked exciplex luminescence, we thought it worth while to extend our MFE studies to such types of polymer-chain-linked exciplex systems. The polymer we have chosen is a polystyrene-linked (PS) pyrene–dimethylaniline (Py–DMA) system. We have found that, in pure acetone, the magnetic-field-modulated luminescence ratio ($\Delta\phi/\phi$) is higher than that in a mixed solvent (tetrahydrofuran/dimethylformamide, THF/DMF) of the same ϵ. The $\Delta\phi/\phi$ drops considerably on adding a small amount of cyclohexane or benzene to pure acetone. The $\Delta\phi$ vs. ϵ curve was found to depend on the nature of the molecules used to prepare the solvent mixture. This observation is strikingly different from that observed in the case of the unlinked Py–DMA system, where $\Delta\phi/\phi$ peaks around $\epsilon \approx 16$, irrespective of the

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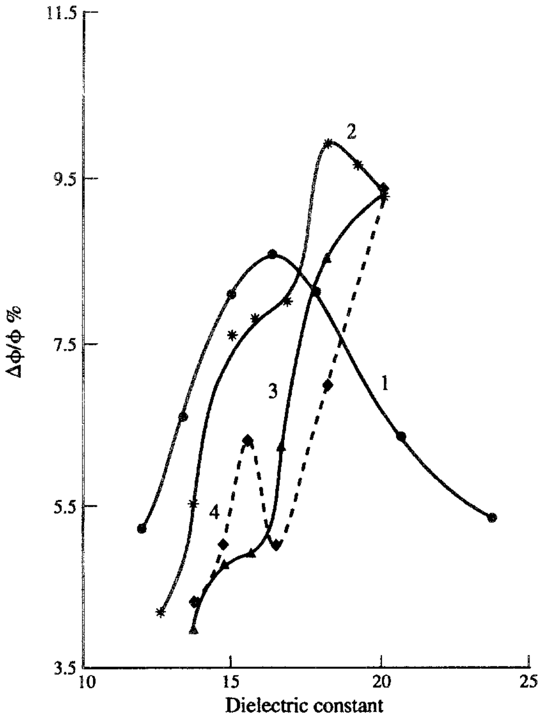

Figure 1 Dependence of $\Delta\phi/\phi$ on dielectric constant (ϵ) in different solvent mixtures: (1) THF/DMF mixture; (2) THF/acetone mixture; (3) benzene/acetone mixture; (4) cyclohexane/acetone mixture

choice of solvent mixture. The results clearly reflect the effect of polymer conformation on RIP spin evolution and diffusion. We have also attempted a time resolution of the MFE for more detailed dynamic information, and have offered some qualitative explanation regarding the intriguing behaviour of pyrene lifetimes in different solvent mixtures.

EXPERIMENTAL

The steady-state magnetic-field effect studies have been carried out with a phase-sensitive detection system fabricated in this laboratory and which has been described in detail in our earlier communications[19,20]. The time-resolved studies have been carried out in a nanosecond fluorimeter (Applied Photophysics) based on the time-correlated single-photon-counting technique. The experimental details have been published elsewhere[21].

The polymer Py–PS–DMA was prepared by anionic polymerization (by G. Beinert[22] in Strasbourg) with the pyrene group attached by the Toronto group. The synthesis and characterization of these polymers have been fully described[22]. The sample examined here ($M_n = 4770$, $M_w/M_n = 1.100$) has been shown to have 1.0 DMA and 0.85 Py groups per chain.

Dried and redistilled spectroscopic-grade solvents have been used. Each sample has been made free from oxygen by bubbling N_2 gas for about 40 min.

RESULTS AND DISCUSSION

Steady-state studies

Figure 1 shows the percentage magnetic-field effect ($\Delta\phi/\phi$ %) as a function of dielectric constant (ϵ) of the solvent in different solvent mixtures; ϕ is the quantum yield of exciplex fluorescence and $\Delta\phi$ is the corresponding change in the presence of an externally applied magnetic field. Interestingly, in THF/DMF solvent mixture, $\Delta\phi/\phi$ is the same as that in the case of unlinked Py–DMA system, peaking around $\epsilon \approx 16$. Restricted diffusional excursion of the radical partners is expected to increase the MFE, as observed by Weller *et al.*[6–8]. They reported an extremely large increase in MFE (up to $\approx 50\%$) in the case of Py–$(CH_2)_n$–DMA, where $n = 16$. Our results, and those obtained by Basu *et al.*[23], show that in long-chain polymers the diffusion is not as restricted as one would expect and the RPs behave as if they were free. This unrestricted motion in the region where $J = 0$ is further facilitated by the extended conformation taken up by the polymer in a mixture of 'good' solvents such as THF and DMF.

Figure 1 also reveals the unique behaviour of acetone ($\epsilon \approx 20$)*, in which the highest $\Delta\phi/\phi$ ($\approx 9.5\%$) has been obtained. In unlinked Py–DMA system, $\Delta\phi/\phi$ in pure acetone is around 6%. This points to the fact that the intervening polystyrene chain must have a role to play in this enhancement of MFE. Acetone is known to be a bad solvent for polystyrene[4], so that the polymer is forced to take up a coiled conformation. The coiled structure may in turn serve as a reflection boundary for the RIPs, thus imposing a further restriction on their diffusion. In other words, the effect is similar to the micellar supercage effect. An alternative explanation could be as follows: keeping in mind that dilute polymer solutions may be regarded as 'inhomogeneous' as far as viscosity and polarity of the medium is concerned, the MFE would depend on the average polarity sensed by the RIP when they undergo cyclization. Owing to the coiled conformation in acetone solvent, the effective ϵ may become less than 20, somewhere around the ϵ_{max} for free Py–DMA, and thus the $\Delta\phi/\phi$ increases. But the ratio of the exciplex lifetime in acetone and isodielectric THF/DMF mixture (where the polymer is supposed to have extended conformation) is around 2:3, so the explanation that the average local ϵ is less in acetone than in the THF/DMF is not tenable. We therefore suppose that the coiled conformation of the polymer restricts the relative separation of the RIP, and it is this factor, rather than any 'dielectric enrichment' effect, which plays the key role in enhancement of MFE in acetone.

The coiled conformation of the polymer in acetone is further corroborated by Py lifetime studies. The Py lifetime will be dependent on the distribution of the initial Py–DMA distance, the relationship of the electron-capture cross-section with the Py–DMA distance, and the tortuous path of beam folding. All three are expected to be dependent on polymer–solvent interaction. The relatively short Py lifetime in acetone (≈ 32 ns), compared to other pure 'good' solvents such as THF (≈ 77 ns), benzene (≈ 73 ns) and DMF (≈ 62 ns) is indicative of the fact that the initial coiled-up conformation in acetone evolves into the exciplex-forming conformation via a short direct route.

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*This value is higher than the previous one reported from this laboratory[23]. This is because the previous experiments were carried out with freshly prepared solution, while we have soaked the polymer in solvents for 12 h in order to ensure complete dissolution in 'θ' or 'bad' solvents. We have verified that no degradation occurred with time

Interesting changes occur when the coiled structure is allowed to uncoil sufficiently, such as in solvent mixtures that show a co-solvency effect[25,26] towards polystyrene. We have added different types of solvent to acetone, such as cyclohexane, which is a 'theta'-solvent for polystyrene[24], and THF, DMF and benzene, which are 'good' solvents[24]. It is here that the situation gets complicated. It is a well known fact that one of the necessary criteria for spin evolution of the RPs to take place is that the RIPs must be separated by a certain distance (> 10 Å) and the re-encounter probability must be high. In solutions of low ϵ, the solvent-separated ion pairs (SSIPs) tend to come closer than this distance so that $\Delta\phi/\phi$ is small. On the other hand, in a solution of high ϵ, the probability of re-encounter of the SSIPs becomes less, which again leads to a decrease in $\Delta\phi/\phi$. Qualitatively at least, one can easily understand why $\Delta\phi/\phi$ peaks at an intermediate ϵ and why the occurrence of significant MFE needs a careful tuning of inter-radical separation. Preferential solvation of the spacer chain would affect the inter-radical distance, and the extent to which this occurs is very well revealed in *Figure 1*. Unfortunately, with the present state of our knowledge of polymer–solvent interaction, it is very difficult to explain the nature of the curves (of *Figure 1*) individually, but the general conclusion that can be drawn unambiguously is that addition of a 'good' or 'theta' solvent to a bad solvent initiates a co-solvency effect, which results in uncoiling of the polymer chain.

In addition to a co-solvency effect, a very subtle 'correlation hole' effect may have an important role to play in our experiments[7]. This effect arises from the concept of the excluded-volume effect. Because of the correlation hole, the two chain ends have a much lower probability of coming together when the polymer is in a good solvent than when it is in a poor solvent. Thus, in acetone the end-group re-encounter probability is high, resulting in enhanced MFE. Addition of a good solvent decreases this probability (resulting in a lowering of $\Delta\phi/\phi$), although the mean end-to-end distance remains basically unaltered. In fact excluded-volume effects (a factor of ca. 9 on the cyclization of PS= 5000) may play a more significant role in short-chain polymers[28]. Thus there are two factors that modify the inter-radical separation: (a) dielectric constant (ϵ) of the medium and (b) solvation of the polymer backbone. The three curves in *Figure 1* reflect the competition between these two processes.

The phenomenon may be looked upon from another more-or-less equivalent angle. Petrov *et al.*[29] have recently advanced arguments to explain that MFE on exciplex luminescence is largest in a polar–non-polar mixed medium (of permittivity 15–20) than in a homogeneous medium. Their model, based on the microscopic heterogeneity of polar–non-polar mixed solvent, is as follows: The polar solvent specifically solvates the D^+ and A^- species, while the non-polar solvent lowers the average ϵ, so as not to allow the solvated ions to separate too far. The ionic radicals are separated optimally where spin evolution and recombination occur. In the present case of solution of the polymer in acetone, the latter may be considered as the polar component and the polymer hydrocarbon component as the microscopically immiscible non-polar component of the mixture. The polymer hydrocarbon backbone makes the system microscopically heterogeneous and restricts the separation of D^+ and A^- possibly more due to the coiling effect than due to lowering of average permittivity. When a third component is added, it helps miscibility of the polymer backbone and acetone, and this decrease in microscopic heterogeneity generally decreases the MFE.

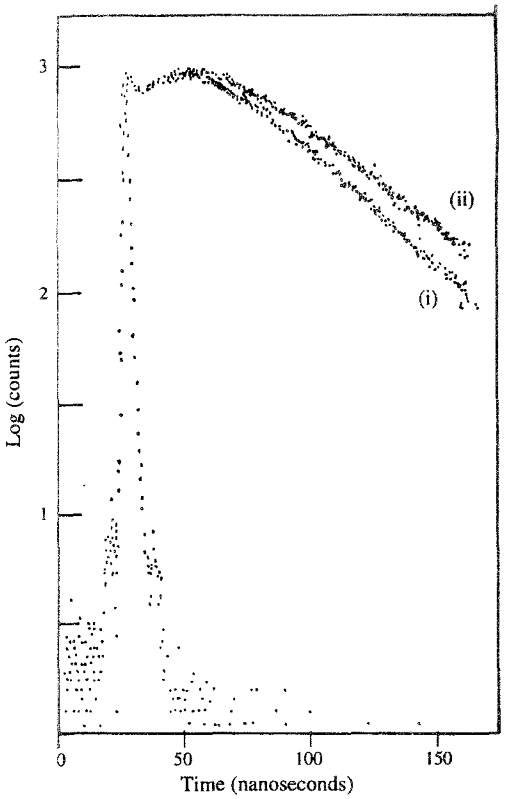

Figure 2 Single-photon-counting histograms of Py–PS–DMA at 550 nm showing exciplex decay at $\epsilon \approx 20$ in acetone: (i) without magnetic field (51 ns) and (ii) with an external magnetic field of 240 G ($\imath = 63$ ns)

Time-resolved studies

The time-resolved exciplex luminescence curve (*Figure 2*) has clearly two parts—a growth part and a decay part. The growth is slow and generally of the order of Py decays. Unfortunately, short-lived impurity emission complicates matters, so that a fully fledged analysis of the decay curves is not possible. Nevertheless, Basu *et al.*[23] have shown that the time-resolved curves in pure acetone in the presence and absence of a magnetic field can be reproduced by assuming reasonable values of the rate constants. We felt that a meaningful comparison of parameters in different solvents was not possible, and have not, therefore, considered it profitable to carry out an analysis of the curves in different solvents. Instead, we confine ourselves to making a few qualitative remarks regarding the solvent effect (and magnetic effect) on exciplex decays.

Since the growth time is much faster than the decay time (*Figure 2*) we have employed a single-exponential analysis (i.e. $I = I_0 e^{-t/\lambda}$) near the tail region of the curve, where any contamination from the growth part could be neglected. We could recover fairly reliable λ values (as indicated from the χ^2 and Durbin–Watson parameters), which may be expected to correspond roughly to the exciplex lifetime.

The dependence of the exciplex decay time on the

Table 1 Comparison of pyrene and exciplex lifetimes in different solvent mixtures

Solvent composition	Py lifetime, τ_{Py}(ns)	Exciplex lifetime, τ_{ex}(ns)
THF/DMF	90	87
THF/acetone	55	70
Benzene/acetone	40	60
Cyclohexane/acetone	27	51

solvent composition has been studied by preparing isodielectric solvent mixtures. This is shown in *Table 1*. The point to note is that there seems to be a rough parallelism of the variation in Py lifetime and exciplex decay time. The variation in Py decay is presumed to be due to variation in the cyclization rates of the end-groups; the variation in exciplex decay time may similarly be presumed to be due to re-dissociation of the exciplex or re-separation of the end-groups. The results therefore mean that those solvents which increase the folding rate of the polymer also increase the unfolding rate. This is understandable if only the activation barrier is influenced by the solvent. In some solvents the polymer segments may be more stiff than in others.

CONCLUDING REMARKS

The above investigation demonstrates the dependence of magnetic-field-modulated luminescence of a polymer on solvent composition. Although a detailed explanation of the variation of MFE of the polymer with the nature of the molecules of the solvent mixture or with the molecular weight of the polymer has not yet been possible, the unusual features in the $\Delta\phi/\phi$ vs. ϵ curves in different solvent mixtures do point out the importance of polymer conformation on inter-radical separation during cyclization and hence on spin evolution. We believe that the results throw a new, albeit qualitative, light on MFE in polymer-linked systems, and it would be worth while to extend such studies to polymers of varying chain lengths, and develop an appropriate theory taking all the factors into consideration.

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