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Study of Reactivity of a Chain-Bound Molecular Moiety by Intermolecular Exciplex Formation

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ABSTRACT

The effect of chain-binding on the reactivity of naphthyl groups towards intermolecular exciplex formation with triethylamine has been investigated. Polyamides of 2,6-bis(N-methyl methylamino)naphthalene with the diacid chlorides $\text{ClOC}(\text{CH}_2)_x\text{COCl}$ ($x = 2, 4, 6,$ and 8), designated P-2, P-4, P-6 and P-8, and 2,5-bis(n-methyl N-acetyl methylamino)naphthalene (MC) have been studied. Fluorescence spectra of dilute solutions of the polyamides and their model compound have been obtained in the presence of varying amounts of triethylamine (TEA) as a quencher. The variations of exciplex monomer fluorescence intensity ratio, I_E/I_M , with quencher concentration indicates the following reactivity order: $\text{MC} > \text{P-8} > \text{P-6} \approx \text{P-4} > \text{P-2}$, which reflects the relative diffusion rate and accessibility of the naphthalene moiety. This order also represents the relative chain flexibilities of the polyamides studied. Monomer fluorescence quenching is explained in terms of a scheme involving formation of an exciplex, and a nonfluorescent CT encounter complex. Stern-Volmer plots of monomer fluorescence quenching reveal an anomalous order where the monomer fluorescence

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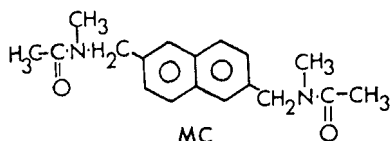
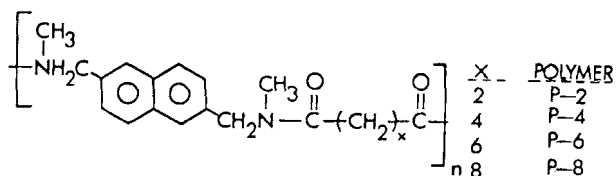
of the model compound is less effectively quenched. This may imply a slower dissociation rate constant of the nonfluorescent encounter complex in the case of the polymers.

INTRODUCTION

The binding of a chromophore in a polymer chain can lead to changes in its reactivity. Such changes, which may be termed "polymer effect," contrast the behavior of the moiety in a monomeric and a polymeric state. Reaction rates for small molecules have been accurately described in terms of collision theory and molecular dynamics. However when polymers are involved, the concept of "billiard ball" collisions between molecules of nearly the same size is no longer applicable. In solution in the molten state of a polymer, the random motion of free molecules is replaced by more restricted and coordinated motions caused by the steric restrictions of the chain. This is likely to affect the reactivity of that moiety.

Photophysical processes have proven potentially useful in studying the polymer effect on reactivity. Three types of studies have been reported in the literature: A study of the absorption characteristics of ground-state charge transfer (CT). Complexes of polymers are compared with those of model compounds [1-4]. Equilibrium constants and molecular extinction coefficients of the CT complexes are then used as a measure of reactivity. A study of the fluorescence quenching [5, 6] has been useful in this regard. Stern-Volmer (quenching) constants are determined and used as a measure of reactivity. A third approach [4] makes use of exciplex formation. Such interaction gives rise to exciplex fluorescence accompanied by monomer fluorescence quenching. Thus relative reactivities can be assessed both from the rate constant for monomer fluorescence quenching and that for exciplex formation as measured by enhancement of exciplex fluorescence. The specificity of an exciplex interaction which leads to the formation of a transiently stable and fluorescent complex, makes it a potentially reliable technique for studying the polymer effect on reactivity.

This report deals with the study of the reactivity of chain-bound naphthyl groups towards intermolecular exciplex formation with triethylamine. Using the polyamides and a model compound (MC), we will attempt to establish relative reactivity of "free" and "chain-bound" chromophores and dependence of such reactivity on polymer chain flexibility. This type of study can provide some useful guide in tailoring of functional (reactive) polymers used as drugs, catalysts, etc.



EXPERIMENTAL

Materials

Acceptors. Syntheses of P-2, P-4, P-6, P-8, and MC have been described elsewhere [7]. The concentration of the polymer is based on the repeating units.

Donor (Quencher). Triethylamine (TEA) was purified by vacuum distillation.

Solvent. Methylene chloride was a spectral quality grade from Mallinckrodt Chemical Works.

Fluorescence Spectra and Lifetime Measurements

The fluorescence spectra were obtained by transmission by use of an Aminco-Bowman spectrofluorimeter. Fluorescence lifetimes were obtained by a single photon counting technique with a nanosecond time-resolved fluorimeter.

RESULTS

The fluorescence spectra of dilute solutions (1×10^{-4} M) of P-4 containing varying amounts of TEA are shown in Figs. 1 and 2. Similar fluorescence spectra were obtained for solutions of TEA with the other polymers and the monomer model compound. A gradual quenching of the naphthalene monomer fluorescence at ~ 360 nm is accompanied by the appearance of a broad band at ~ 500 nm. The long-wavelength band is attributed to the known intermolecular exciplex fluorescence, when TEA acts as donor and naphthalene acts as acceptor. As the concentration of TEA is increased, the intensity

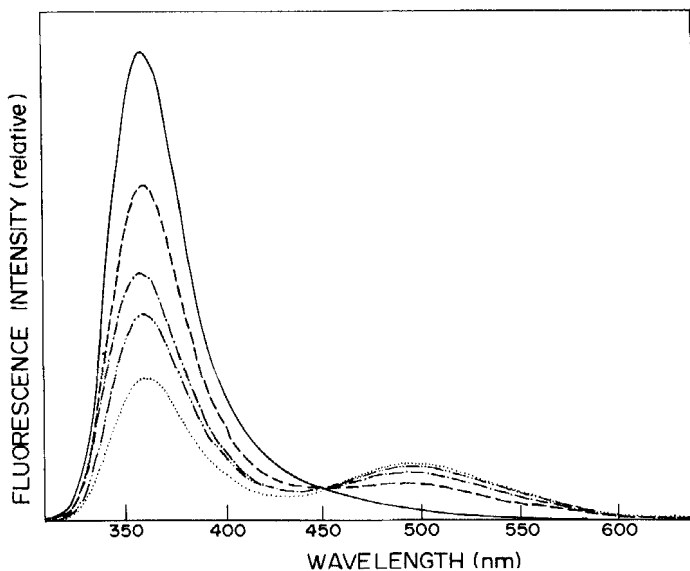


FIG. 1. Room temperature fluorescence spectrum of P-4 (1×10^{-4} M) containing various concentrations of TEA as donor [TEA]: (—) 0.0 M; (---) 0.01 M; (- · -) 0.02 M; (- · ·) 0.04 M; (· · ·) 0.06 M; λ_{ex} , 290 nm; solvent, CH_2Cl_2 .

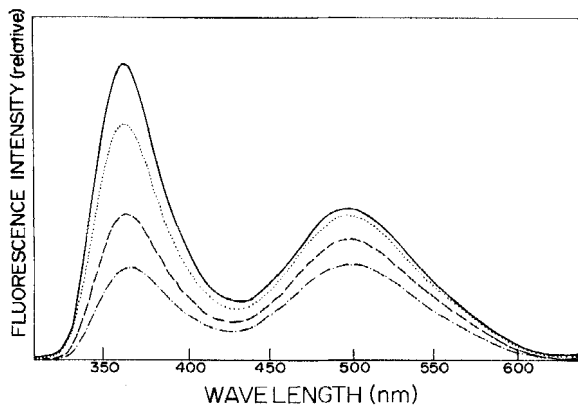


FIG. 2. Room temperature fluorescence spectra of P-4 (1×10^{-4} M) containing various concentrations of TEA as donor [TEA]: (—) 0.09 M; (· · ·) 0.11 M; (---) 0.19 M; (- · -) 0.31 M.

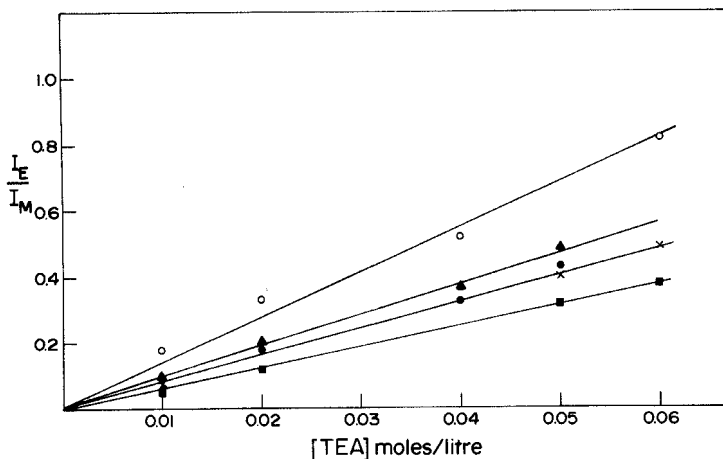


FIG. 3. Ratio of exciplex to monomer fluorescence intensity as a function of donor (TEA) concentration with various acceptors: (○) MC; (■) P-2; (×) P-4; (●) P-6; (▲) P-8. The acceptor concentration is 1×10^{-4} M.

of exciplex fluorescence increases, reaching a maximum value at ~ 0.09 M (see Fig. 2). Above this value, quenching of exciplex as well as monomer emission occurs. The isoemissive point observed in Fig. 1 is lost at higher concentrations of TEA, as shown in Fig. 2.

Plots of intensity ratios of exciplex and monomer fluorescence, I_E/I_M , as a function of donor concentration [TEA] are shown in Fig. 3. The slopes of these lines ξ are given in Table 1. If the I_E/I_M ratio represents the extent of exciplex formation, then our results show that the model compound MC is more reactive than naphthalene groups in the polymers, and among the polymers, the order of reacting is as follows: P-8 > P-6 \approx P-4 > P-2. Stern-Volmer plots (Fig. 4) show deviations from linearity for all the compounds at high donor concentrations. However, from the initial slopes at low donor concentrations, quenching constants, K, are obtained. The quenching constants are larger for the polymers than for the MC (Table 1). Plots for P-2, P-4, and P-6 show approximately the same initial slopes, but that of P-8 is higher.

Fluorescence decay times, τ_M and τ_E , for monomer (in absence of quencher) and exciplex, respectively, are given in Table 1. Our results show that the decay times for polymer exciplexes with TEA are of the same order of magnitude; however, that of the model compound is slightly lower. The decay times τ_M of the naphthalene monomers are similar and thus appear insensitive to chain binding.

TABLE 1. Photophysical Parameters for Exciplex Formation

Compound	τ_M (nsec)	$k_M \times 10^7$ (sec^{-1})	τ_E (nsec)	$k_E \times 10^7$ (sec^{-1})	K	ξ
MC	19.6	5.1	11.9	8.4	25	14
P-2	19.2	5.2	14.2	7.0	~43	6.6
P-4	19.7	5.1	12.7	7.9	~43	~ 8.3
P-6	20.2	5.0	14.2	7.1	~43	~ 8.3
P-8	19.8	5.1	13.4	7.5	50	9.6

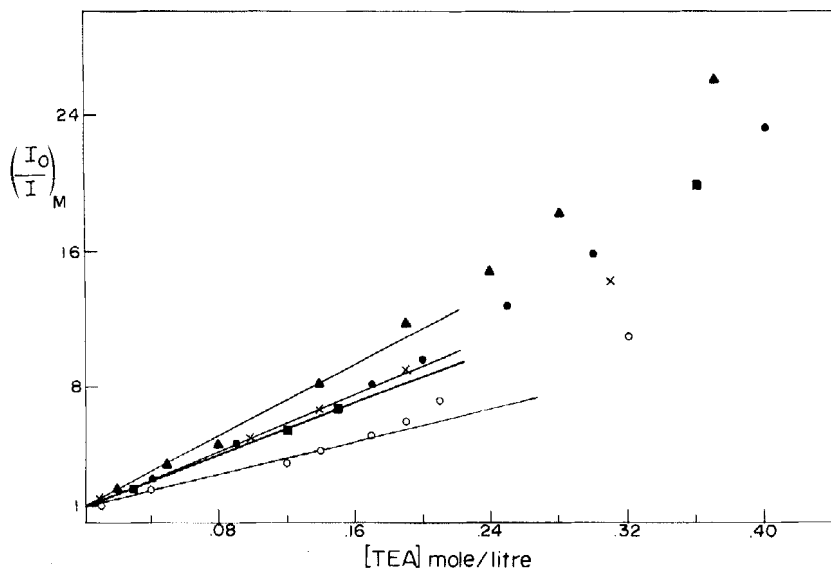
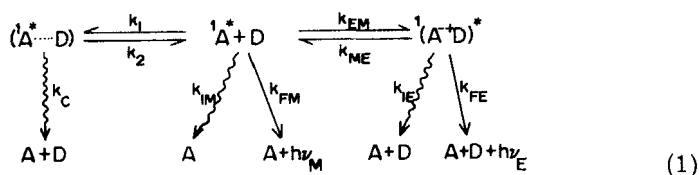


FIG. 4. Ratio of monomer fluorescence intensity in the absence (I_0) and in the presence (I) of the donor at varying concentrations with various acceptors: (\circ) MC; (\blacksquare) P-2; (\times) P-4, (\bullet) P-6; (\blacktriangle) P-8. The acceptor concentration is 1×10^{-4} M.

DISCUSSION

The preceding results may be explained by considering the kinetics of intermolecular fluorescence quenching due to exciplex formation. It has been shown recently [8] that exciplex formation alone cannot account for monomer-fluorescence quenching in exciplex-forming systems. The observed continued increase in I_E/I_M ratio beyond an optimum quencher concentration that gives maximum exciplex intensity suggests the involvement of an additional process. To account for the observed results the mechanism (1) is proposed.



Where A and D represent the acceptor (naphthyl group) and donor (amino group) respectively. $\text{A}^+ \text{D}^-$ is an intermolecular exciplex, and $\text{A}^* \cdots \text{D}$ is a transitory nonfluorescent (encounter) CT complex. In the scheme, radiative and nonradiative processes are denoted by solid and wavy lines respectively. For simplification we define the following parameters:

$$k_M = k_{FM} + k_{IM}$$

and

$$k_E = k_{FE} + k_{IE}$$

Assuming photostationary conditions, it can be shown that:

$$I_M = \frac{k_{FM} I_a}{X - (Y + Z)[D]} \quad (2)$$

and

$$I_E = \frac{k_{FE} k_{EM} I_a [D]}{(k_{ME} + k_E) \{X - (Y + Z)[D]\}} \quad (3)$$

where $Y = k_1 k_2 / k_2 + k_c$

$$Z = k_{EM} k_{ME} / k_{ME} + k_E$$

and

$$X = \{ (k_1 + k_{EM}) [D] + k_M \}$$

Then

$$\begin{aligned} I_E / I_M &= k_{FE} k_{EM} [D] / [k_{FM} (k_{ME} + k_E)] \\ &= \xi [D] \end{aligned} \quad (4)$$

Also

$$\begin{aligned} \frac{I_0}{I_M} &= 1 + \frac{[k_1 k_c (k_{ME} + k_E) + k_{EM} k_E (k_2 + k_c)] [D]}{k_M (k_2 + k_c) (k_{ME} + k_E)} \\ &= 1 + K [D] \end{aligned} \quad (5)$$

When $k_E \gg k_{ME}$ and $k_c \gg k_2$, then Eq. (5) reduces to

$$I_0 / I_M = 1 + (k_1 k_{EM} [D] / k_M) \quad (6)$$

Equation (6) is a Stern-Volmer type relation which contains an additional rate constant k_1 to account for quenching of monomer fluorescence due to formation of non-fluorescent CT complex. The relative slopes of the lines in Fig. 3 may be explained in terms of Eq. (4). The value of k_{FM} for the polymers and the model compound are similar (see τ_M values Table 1). Assuming $k_E \gg k_{ME}$ and that k_{FE} and k_{IE} remain the same, a larger ratio of I_E / I_M implies a larger rate constant for exciplex formation, k_{EM} , for the model compound compared to that for the polymers. This greater reactivity of the model compound towards intermolecular exciplex formation may be attributed to a smaller diffusion constant of the polymer and to a steric factor. Since exciplex formation is a diffusion-controlled process, we may approximate k_{EM} , the rate constant for exciplex formation by [6]:

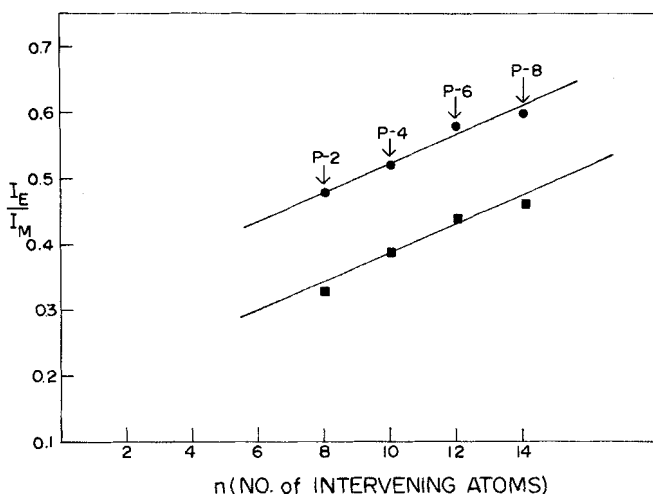


FIG. 5. Ratio of exciplex to monomer fluorescence intensity as a function of chain length at various [TEA]: (■) 0.06 M, (●) 0.09 M.

$$k_{EM} \sim 4\pi ND(\gamma R_0) \times 10^3$$

where γR_0 is the effective action diameter, D is the sum of diffusion constants for acceptor and donor molecules, and N is Avogadro's number. The slow motion of polymer molecules would lead to a comparatively lower D value. The steric strain of the polymer chain would restrict the ability of the naphthalene moiety to assume an optimum configuration for exciplex interaction. Such restrictions are absent for the model compound.

Among the polymers, we noted that the order of reactivity for exciplex formation is $P-8 > P-6 \approx P-4 > P-2$, which is parallel to an increase in the length of the methylene chain in the polymer backbone, i. e., an increase in chain flexibility. Thus it appears that steric restrictions on the motion of chain naphthalene moieties increase in the same order, $P-8 > P-6 > P-4 > P-2$, leading to the order of reactivity stated above and depicted in Fig. 5.

The indication from the initial slopes of the Stern-Volmer plots (Fig. 4) that the quenching constant (K) for the model compound is smaller than those for the polymers, appears anomalous, on the basis of a more reactive model compound. However, our kinetic analysis shows that the quenching constant K is a complex term, involving many rate constants [Eq. (5)]. Without knowing the values of k_{ME} , k_1 , and k_2 for the model compound as well as the polymers it is difficult to

explain the observed anomaly. It is possible that the rate constant for the dissociation of the encounter complex k_2 is smaller for the polymers compared to that of the model compound giving rise to a more efficient quenching of monomer fluorescence for the polymers. The observed deviations from linear Stern-Volmer plots at high donor concentrations may indicate a complex interaction involving more than one donor molecule.

In conclusion, intermolecular exciplex formation appears to be an effective method for establishing the extent to which the reactivity of a chemical moiety can be affected as a result of binding in a polymer chain. Also, intermolecular exciplex interaction involving a chain-bound reactive group appears sensitive to the flexibility of the intervening chain.

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