Photophysics of Carbazole-Containing Systems. 3 Fluorescence of Carbazole-Containing Oligoethers in Dilute Solution

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ABSTRACT: Fluorescence techniques, including quenching and anisotropy measurements, have been used to study the photophysical behavior of the carbazole-based oligoethers poly{9-(2,3-epoxypropyl)-carbazole}, PEPCz, and poly{1,2-epoxy-6-(9-carbazolyl)-4-oxahexane}, PECzOH, and their model compounds, in dilute fluid solutions in THF. These compounds show no evidence of excimer formation under these conditions and their fluorescences exhibit first-order decay behavior regardless of the degree of polymerization of the oligomer. Both steady-state and time-resolved anisotropy measurements upon dilute, glassy solutions show that intramolecular energy migration occurs in the oligomers. Fluorescence quenching experiments, using both dimethylterephthalate and oxygen as quenchers, produced evidence which supports the supposition that in the absence of excimer trapping sites, intramolecular energy migration will be encouraged in dilute fluid solutions of the oligoethers. Unfortunately, the fluorescence quenching data did not permit evaluation of the extents of energy migration in the various polymers or the relative efficiencies with which migration occurs in the two different types of oligoether. This limitation would appear to be a general feature of fluorescence quenching measurements, despite their frequent adoption, in the past, in studies of energy migration in polymers.

Introduction

The photoconductive properties of poly(*N*-vinylcarbazole) PNVCz[1,2] have promoted many investigations of its photophysical behavior, both in solution (see, for example, refs 2−9) and in the bulk solid state.[10−15]

The photophysical behavior of PNVCz is intriguing since its fluorescence is dominated by emissions from two excimer species: emission centered at ca. 420 nm originates from a conventional "sandwich like" excited-state dimer[1,6,7] whereas that peaking at ca. 370 nm has been attributed to luminescence from a partially overlapped, "second" excimer.[6,7]

From the viewpoint of photoconduction, excimer formation is undesirable: it is generally believed that the trapping of migrating energy at excimer-forming sites decreases the efficiency of carrier generation.[16−19] Furthermore, there is strong evidence[20,21] that charge carrier trapping in amorphous photoconductive polymers is linked to the occurrence of excimer-forming sites. For example, it was found[21] that the hole mobility in a polycarbonate film doped with *trans*-1,2-biscarbazolylcyclobutane exceeded that of PNVCz by a factor of about 10. This observation was explained in terms of the low activation energy for hole transport in the doped film which resulted from the absence of excimer-forming sites.[21]

Since excimer formation constitutes a loss mechanism in photoconduction, attention has been focused on polymers lacking this characteristic, as potential photoconductors: examples of systems which have been developed and studied from this aspect of their behavior include poly{2-(9-carbazolyl)ethyl methacrylate},[17] poly{2-(9-carbazolyl)ethyl acrylate},[22] carbazole-substituted, N-acylated, linear poly(ethyleneimine) and dehydroaniline main chain polymers[23] and polymers containing *trans*-1,2-biscarbazolylcyclobutane in the main chain or as a pendant substituent.[24] Carbazole-containing oligoethers such as poly{9-(2,3-epoxypropyl)carbazole}, PEPCz, and poly{1,2-epoxy-6-(9-carbazolyl)-4-oxahexane}, PECzOH, as studied in the current work, are also representative of this class of material.

PEPCz has been produced on an industrial scale and was the most widely used polymeric photoconductor in the former Soviet Union. Despite having a lesser concentration of chromophores along its backbone, PEPCz is in no way inferior to PNVCz in its photoconductivity and exhibits superior mechanical and film-forming properties. (The presence of the ether links in the main chain and the oligomeric nature of the PEPCz combine to induce both good film-forming characteristics and a low T_g, relative to those of PNVCz.)

As a photoconductor, PECzOH is inferior to PEPCz. However, the presence of ether linkages in the side chain, in addition to those in the backbone, confers good film-forming properties upon PECzOH over a broad range of molar masses, in contrast to PEPCz which exhibits satisfactory mechanical properties only when its molar mass is less than ca. 1500.

In this report we compare the photophysical behaviors of PEPCz and PECzOH to those of 9-ethylcarbazole, EtCz, 9-(2,3-epoxypropyl)carbazole, EPCz, and 1,2-epoxy-6-(9-carbazolyl)-4-oxahexane, ECzOH, the latter two compounds being models for PEPCz and PECzOH, respectively. The structures of the model compounds and oligomers and/or polymers characterized in this work, are shown in Chart 1.

Experimental Section

(i) Materials. Dimethylterephthalate, DMT (Aldrich) and EtCz (Aldrich) were recrystallized twice from ethyl alcohol. {Mp DMT, 140−142 °C; EtCz, 67−68 °C.}

EPCz (Biolar, Latvia) was recrystallized five times from toluene {mp 110−111 °C}.

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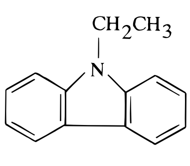
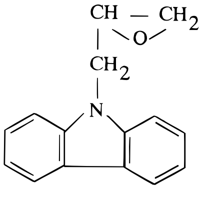
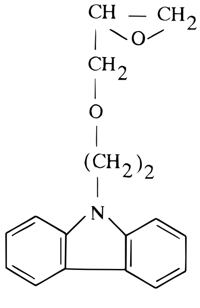
Chart 1



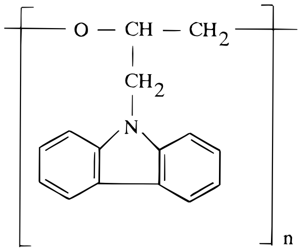
EtCz



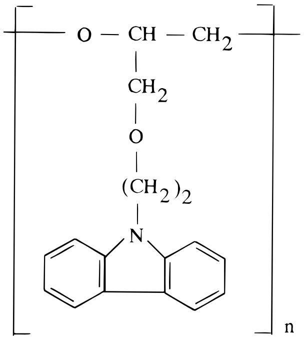
EPCz



ECzOH



PEPCz



PECzOH

ECzOH, kindly donated by Dr. A. Stanisauskaite (Kaunas Technical University) had been prepared by condensation of 9-(2-oxyethyl)carbazole and epichlorhydrin in the presence of KOH and was recrystallized several times from ether until no trace of anthracene could be detected, using fluorescence {mp 59−60 °C}.

Tetrahydrofuran, THF, and 2-methyltetrahydrofuran, MeTHF, were treated with CuCl and then fractionally distilled followed by reflux over CaH_2 and repeated fractional distillation (under nitrogen).

Oligomers of EPCz were prepared by polymerization of the monomer using both anionic (KOH) and cationic ($BF_3 \cdot Et_2O$) catalysts, producing products PEPCz-1 and PEPCz-2, respectively.

PECzOH oligomers were synthesized using different catalysts: PECzOH-1 was obtained by polymerization of ECzOH, in bulk, under the action of KOH. PECzOH-2 was obtained by polymerization of ECzOH using $SnCl_4$ in 1,2-dichloroethane solution. PECOH-3 was obtained by anionic polymerization of ECzOH using *N*,*N*-dimethylcyclohexylamine as catalyst.

All polymerizations were performed in the dark under an atmosphere of oxygen-free nitrogen to avoid photooxidation of the carbazole-containing species.

Molecular weights of oligomers were estimated by gel permeation (size exclusion) chromatography (PEPCz-1 and -2; PECzOH-2 and -3) and osmometry (PECzOH-1) as previously described.[25]

(ii) Instrumentation and Techniques. Steady-state fluorescence spectra were recorded on Perkin-Elmer LS50 and LS5 spectrometers. Solutions for spectroscopy were 10^{-5} M in chromophore. Deoxygenation, where appropriate, was effected by purging with oxygen-free nitrogen in sealable degassing cells.

Table 1. Values of Number Average Molar Mass ($\bar{M}_n$), Polydispersity (*D*), and Number Average Degree of Polymerization ($\overline{DP}$) of PECOH and PEPC Oligoethers

sample	($\bar{M}_n$)	*D*	($\overline{DP}$)
PEPCz-1	1120	1.1	5.0
PEPCz-2	1200	1.1	5.4
PECzOH-1	10000		37.5
PECzOH-2	2260	2.6	8.5
PECzOH-3	1040	1.1	3.9

Steady-state fluorescence anisotropy measurements were made on a Hitachi-Perkin-Elmer MPF 3L spectrometer. Samples, consisting of dilute, glassy solutions in MTHF at 77 K were placed in quartz sample tubes (3 mm diameter) located in liquid nitrogen in an optical (quartz) Dewar. The carbazolyl chromophores were excited using vertically polarized excitation and the intensities of emission passing through a polarizer, oriented in planes parallel and perpendicular to that of the incident excitation, respectively, were measured. The fluorescence anisotropy, r, was calculated using eq 1, where I =

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} - GI_{VH}} = \frac{D}{S} \tag{1}$$

fluorescence intensity and the subscripts denote the relative orientations, vertical (V) and horizontal (H) of the polarizing filters placed in the excitation and analyzing channels, respectively. *G* is a factor[26] which corrects for differences in both the transmission efficiencies and detection sensitivities in the analyzer channel of the apparatus.

Fluorescence decay curves were recorded on an Edinburgh Instruments 199 spectrometer operating on the time-correlated single photon counting principle.

Time-resolved fluorescence anisotropy measurements were recorded on an Edinburgh Instruments 199 spectrometer, fitted with a specially designed "toggling" unit in which the orientation of the analyzing polarizer is alternated (between planes aligned vertically and horizontally, respectively, to that of the excitation incident upon the sample). Under computer control and synchronized to the toggling, memories within the multichannel analyzer recording the time-resolved emission intensities, $I_{VV}(t)$ and $I_{VH}(t)$, are switched, through a series of data collection cycles. The time-dependent anisotropy, *r*(*t*), was constructed from the resultant difference, *D*(*t*), and sum, *S*(*t*), functions, according to eq 1.

Results and Discussion

(i) Characterization of the Oligoethers. Molar mass data for the various oligoethers synthesized in this work are summarized in Table 1.

(ii) Steady-State Fluorescence Spectra. Fluorescence excitation and emission spectra of dilute solutions of ECzOH and PECzOH-2 are shown in Figure 1. The spectral profiles of the PECzOH oligoethers were found to be invariant with mode of synthesis, molar mass, excitation wavelength (for emission spectra), and emission wavelength (for excitation spectra) and to be very similar (except for a slight red-shift in those of the oligomeric species) to that of the low molar mass analogue, ECzOH. Similar observations apply to the fluorescence of PEPCz oligomers in relation to that of their model compound, EPCz. The independence of the excitation and emission profiles of choice of emission and excitation wavelengths, respectively, suggests that emissive intercarbazolyl complexes do not form in the oligoethers. In particular, the fact that the emission spectral shape follows precisely (apart from the slight

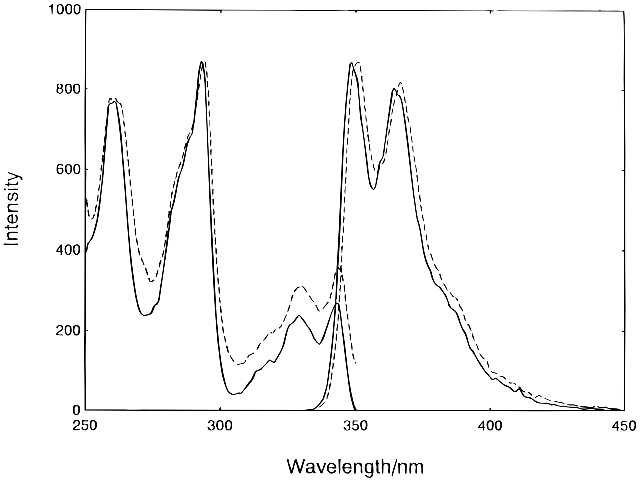


Figure 1. Fluorescence excitation and emission spectra of ECzOH (—) and PECzOH-2 (– –) in dilute (10^{-5} M) deoxygenated solution in THF at 298 K.

red shift) that of the appropriate low molar mass analogue is convincing evidence that fluorescent, intramolecular excimers are not formed to any significant extent in either class of oligoether.

(iii) Fluorescence Decay Measurements. Steady-state fluorescence spectroscopy, suggests that neither the PEPCz nor PECzOH oligoethers form fluorescent excimers. However, the shapes of the spectra would *not* be sensitive to formation of a nonfluorescent complex. Time-resolved fluorescence techniques, on the other hand, offer very sensitive means of examining the behavior of a population of excited-state chromophores: excimer formation in the oligoethers would be accompanied by a reduction in the average lifetime of the carbazolyl excited states (whether, or not, the excimer itself was fluorescent).

The time-resolved fluorescence decays of each oligoether system could be described adequately by a single-exponential model function of the form

$$i(t) = A \exp(-t/\tau) + B \qquad (2)$$

where $i(t)$ is the emission intensity, t = time, and τ is the excited-state lifetime. A typical decay, single-exponential fit and distribution of residuals is shown in Figure 2. Fluorescence lifetimes resultant from such fits are listed in Table 2. Reference to these data reveals that little, if any, quenching of the carbazolyl excited state occurs upon incorporation into an oligoether. At 13.4 ± 0.7 ns the lifetimes are typical of those reported[27-29] for "isolated" carbazoles in degassed, relatively nonpolar media. Furthermore, the lifetime estimates are unaffected, within experimental error, by the wavelength of analysis of the fluorescence. These observations, combined with those from steady-state spectroscopy, offer convincing evidence that excimer formation is absent from these systems.

The absence of intrinsic intramolecular energy traps in these oligoethers should encourage energy migration, important to the process of charge carrier generation, in these species. In the following sections, we describe our attempts to detect and characterize intramolecular energy migration in these oligomers, by photophysical means.

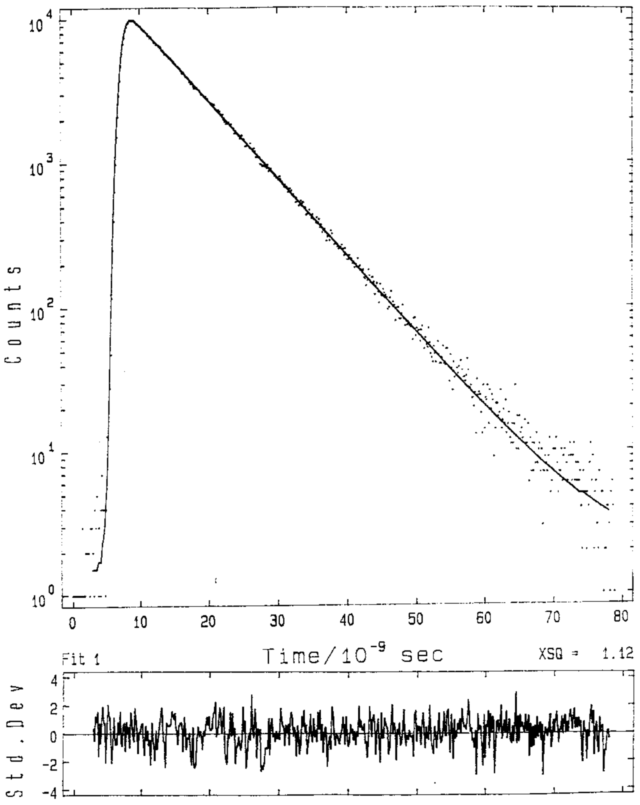


Figure 2. Fluorescence decay curve, best fit to a single-exponential model function and distribution of resultant residuals, for PECzOH-1 (10^{-5} M) in THF (air-saturated) at 298 K. (λ_{ex} = 310 nm; λ_a = 390 nm).

Table 2. Fluorescence Lifetimes of Carbazole-Containing Oligoethers, Their Monomeric Model Compounds and EtCz in Dilute (10^{-5} M) Deoxygenated THF at 298 K (λ_{ex} = 290 nm)

compound	τ/ns (±0.1)[a]	compound	τ/ns (±0.1)[a]
EtCz	13.9	PEPCz-2	13.0
EPCz	13.8	PECzOH-1	13.4
ECzOH	13.6	PECzOH-2	13.3
PEPCz-1	12.7	PECzOH-3	13.3

[a] Fluorescence was analyzed at various wavelengths between 350 and 400 nm. Figures quoted are lifetime estimates (and variance) over this range.

Table 3. Fluorescence Isotropies (r^{-1}) of Carbazole-Containing Systems in MeTHF Glasses (10^{-5} M; 77 K; λ_e = 330 nm; λ_a = 350 nm)

compound	r^{-1}	compound	r^{-1}
EtCz	17.8 (± 2)	PEPCz-2	67 (± 10)
EPCz	17.7 (± 2)	PECzOH-1	∞
PEPCz-1	54 (± 10)		

(iv) Emission Anisotropy Measurements. Energy migration between a set of imperfectly aligned chromophores serves to depolarize the radiation emitted by the system, to a degree dependent upon the extent of migration. Table 3 lists values of the "isotropy", r^{-1}, of the fluorescence emitted by selected PEPCz and PECzOH species and monochromophoric model compounds dispersed (10^{-5} M) in MeTHF at 77 K. At the low concentrations of chromophore employed, intermolecular energy transfers are absent: the fluorescence isotropies exhibited by the model compounds EtCz and EPCz are, over a limited range, independent of concentration. At higher concentrations, the emission from these samples becomes increasingly depolarized, consequent upon intermolecular energy migration between the carbazolyl species dispersed in the rigid matrix. These observations are consistent with those of Johnson[30] who demonstrated {via fluorescence quenching experi-

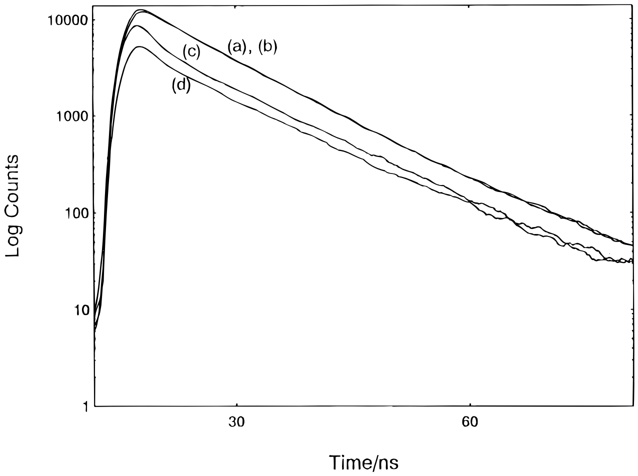


Figure 3. Time-resolved fluorescence anisotropy data for PEPCz-1 (curves a and b) and EtCz (curves c and d) in dilute (10^{-5} M in chromophore) glassy solutions in MTHF at 77 K ($\lambda_e = 320$ nm; $\lambda_a = 360$ nm).

ments, as discussed in part v} that *N*-isopropylcarbazole exhibits intermolecular energy migration in rigid polystyrene films (at 298 K).

The fluorescence anisotropies of EtCz and EPCz are (as a consequence of the experimental conditions) representative of the intrinsic anisotropies of the carbazole chromophore in these molecules. The excellent agreement obtained between the steady-state fluorescence anisotropies of EtCz and EPCz both inspires faith in the reliability of the data and indicates that the electronic properties of the chromophore are little affected by the differences in the substituents (Et and EP) attached to the chromophore at its 9-position. If allowance is made for the relatively low wavelength resolution employed in the current work, the r_o data obtained for EtCz and EPCz are in good agreement with those previously reported for EtCz and *N*-isopropylcarbazole.[30]

The data presented in Table 3 offer clear evidence of intramolecular energy migration in the PEPCz oligomers and the PECzOH-1 polymer: the fluorescence of the oligomers exhibits less anisotropy than either of the model compounds, and that of the high molar mass PECzOH polymer is completely depolarized. However, steady-state anisotropy measurements upon solutions of chromophores in low-temperature glasses (and solid solutions in general) are fraught with potential difficulties in obtaining appropriate corrections to the data by employing suitable “blanks” to compensate for background scattering effects induced (particularly) by polymeric solutes. Consequently, we have used time-resolved fluorescence measurements to demonstrate, unequivocally, that intramolecular energy migration does indeed occur in the PEPCz and PECzOH species. Typical data are shown in Figure 3.

In the case of EtCz, $I_{VV}(t)$ and $I_{VH}(t)${curves c and d, respectively, in Figure 3} converge slowly across the entire time span in which fluorescence is evident. Clearly, there is little (if any) loss in anisotropy of the fluorescence with time. {In this instance, the rate of convergence of $I_{VV}(t)$ and $I_{VH}(t)$, i.e., the decay of $D(t)$, eq 1, is determined solely by the lifetime of fluorescence}. In contrast, the corresponding intensity components {curves a and b} in the fluorescence of PEPCz-1 are coincident at all but the shortest times following excitation, as a consequence of the randomizing influence of the migration of energy, evident in the oligomer.

These time-resolved data constitute indisputable evidence for energy migration in the PEPCz and PECzOH oligomers. Time-resolved anisotropy measurements have been used previously to detect and quantify energy migration in polymers.[31-33] However, this is the first instance, to our knowledge, of its application to carbazole-based systems.

If the anisotropy function, $r(t)$, is assumed to decay exponentially, i.e.

$$r(t) = r_o \exp(-t/\tau_r) \tag{3}$$

where r_o is the intrinsic anisotropy of the chromophore, a number of approaches can be adopted in attempting to evaluate the relaxation time, τ_r, from the observed, orthogonally disposed intensities, $I_{VV}(t)$ and $I_{VH}(t)$. (See for example, ref 34 and references therein.) Applying the impulse reconvolution[35,36] method in analysis of the PEPCz-1 data shown in Figure 3 resulted in an estimate of 2.1 ns for τ_r. This result can be used to check whether, or not, the steady-state fluorescence isotropy data, presented in Table 3, are reasonable, as discussed below.

In addition, the impulse reconvolution analysis, using a function of the form shown in eq 3 to model $r(t)$, produced an estimate of r_o of 0.03. This is a much reduced value for the intrinsic anisotropy of carbazole derivatives compared to that expected on the basis of either literature reports[30] or our steady-state isotropy estimates from model compounds as recorded in Table 3 which correspond to an r_o value on the order of 0.06. We believe that the discrepancy between the value for r_o estimated from time-resolved anisotropy measurements upon PEPCz and either EtCz or EPCz as model compounds originates, in part, from the influence of energy migrative processes which occur on time scales below the resolution of the current TRAMS, as discussed below. However, fluorescence anisotropy measurements upon model compounds in frozen matrixes do not always furnish estimates of r_o which are representative of that for a polymer-bound chromophore. In this context, we wish to note that TRAMS studies upon the segmental mobilities of hydrophobically modified poly(methacrylic acid) in aqueous media, using trace quantities of copolymerized NVCz as a fluorescent label, indicate[37] that the value of r_o for the polymer-bound chromophore exceeds (by a significant margin) that estimated, here, for EtCz. Since EtCz might otherwise be considered as a suitable model for the copolymerized NVCz label, these observations promote both caution and concern, regarding anisotropy experiments which rely upon the use of low molar mass model compounds for the determination of r_o of a chromophore incorporated into a polymer.

Bearing these reservations in mind, we can proceed as follows. In the fluorescence steady-state, r^{-1}, is related to τ_r *via*

$$r^{-1} = r_o^{-1} [1 + (\tau_f / \tau_r)] \tag{4}$$

Considering the PEPCz-1 system, with $\tau_f = 13$ ns (Table 2) and r_o^{-1} taken as that (17.7) for the model compound, EPCz (Table 3), eq 4 yields an estimate for r^{-1} of ca. 127 which would correspond, effectively, to complete depolarization of the emission, within the limits of accuracy of the steady-state experiment. Given (Table 3) that the steady-state isotropy measurements were more reproducible than implied by the above calculation, it would appear that the model compounds EtCz and EPCz do not provide an adequate estimate of r_0 for the oligomer-bound chromophore. If the value of r_0 were 0.11, for example, the resultant estimate from eq 4 for r^{-1} would (at 65) be of the order observed for the two PEPCz oligomers. Such a value of r_0 would not be exceptionally high for a carbazole substituent of a polymer.[37]

Returning to the TRAMS data for the PEPCz-1 oligomer, it can be noted that, of necessity (using flashlamp excitation at kilohertz frequencies), these are of a quality which is poorer (in terms of both time resolution and signal-to-noise ratio) than would be desirable for rigorous quantitative analysis. The main function of these data, in this study, is to illustrate the existence of energy migration in the oligomers. Nevertheless, it is clear, from Figure 3, that the fluorescence from PEPCz-1 contains very little anisotropy even at the shortest times. Impulse reconvolution analysis[35,36] of the decay curves reinforces this impression (yielding an estimate of r_0 of only 0.03). This rather qualitative observation would suggest that some components of the energy migration occurring in these oligomers operate on shorter time scales than the nanosecond ranges accessed in the current work. This would appear to be a plausible supposition: Ghiggino and co-workers have observed, through a variety of approaches, that migration in polymers containing naphthyl chromophores occurs more rapidly than would be expected on the basis of a series of "Förster hops". (See, for example, refs 33 and 38 and references therein.)

(v) Fluorescence Quenching Measurements. Emission anisotropy measurements, as described in part *iii* above, can detect the presence of energy diffusion involving a relatively small number of migrative hops. On the other hand and in principle, fluorescence quenching measurements can be used to measure migration distances which result from many energy transfers between like chromophores. This approach was adopted, to great effect, by Johnson[30] in studying energy migration between

N-Isopropylcarbazole molecules dispersed in solid solutions in polystyrene. More commonly, however, in polymer science, the quenching tehcnique has been used to try to quantify intramolecular energy migration in macromolecules dispersed in dilute fluid solutions. (The literature is rather extensive: for an overview of earlier investigations involving fluorescence quenching, see ref 23 and references therein.)

Upon addition of a mobile species, acting as a purely dynamic quencher for a fluor, fluorescence quenching should be described by the Stern−Volmer equation:

$$\frac{I^\circ}{I} = \frac{\tau^\circ}{\tau} = 1 + k_q\tau^\circ[\mathrm{Q}] \qquad (5)$$

F° and F are the values of the relevant fluorescence parameter (intensity, I, or lifetime, τ) in the absence and presence of a given concentration of quencher, [Q], respectively. k_q is the bimolecular rate constant governing the collisional quenching of the chromophore's excited state by Q. Assessment of the effects of the migration of energy toward the mobile, diffusing quencher involves comparison of the value of k_q obtained in quenching of the fluorescence of the macromolecule with that governing the quenching of an appropriate model compound.

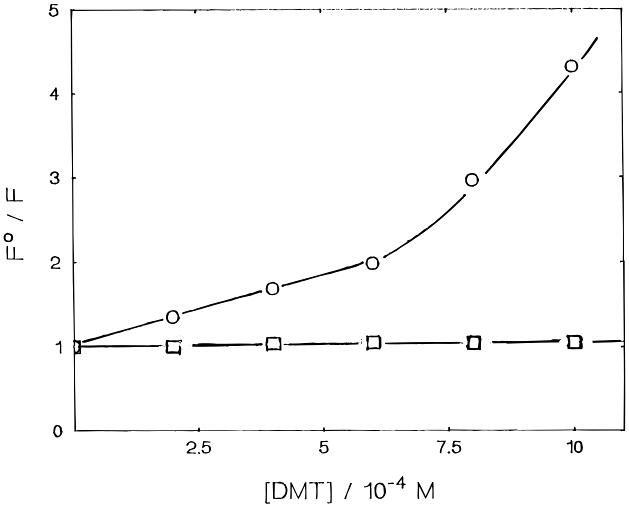


Figure 4. Plots of fluorescence quenching ratio, F°/F, against [DMT]. (●) F = intensity (□) F = lifetime.

Table 4. Rate Constants for the Dynamic Quenching of Fluorescence from Selected Carbazole Derivatives in THF at 298 K

compound	$k_q/10^{10}$ M^{-1} s^{-1}	compound	$k_q/10^{10}$ M^{-1} s^{-1}
EPCz	1.3	ECzOH	1.2
PEPCz-1	0.72	PECzOH-1	1.0

In the context of carbazole-containing polymers, fluorescence quenching has been used to demonstrate the existence of energy migration in PNVCz,[39] copolymers of NVCz (with acenaphthylene)[40] and carbazole-substituted N-acylated polethyleneimine and N-acylated dehydroalanine main-chain polymers.[23] With this in view, we attempted to use fluorescence quenching to examine the dependence of intramolecular energy migration in the various carbazole-containing oligoethers. Dimethyl terephthalate, DMT, was chosen as quencher since long-range (Förster) resonant energy transfer from carbazole to DMT is precluded since (a) the overlap integral governing DMT absorbance and carbazole fluorescence is zero[41] (b) DMT is reported[30] to quench *N*-isopropylcarbazole fluorescence, in fluid solution, at a rate corresponding to the diffusion limit through a charge transfer interaction involving the electronically excited carbazole derivative and ground-state DMT, and (c) DMT has been used, previously, to study energy migration in carbazole-substituted polymers.[23]

Representative fluorescence quenching data are shown in Figure 4. The quenching behavior is typical of that exhibited by all of the systems studied: the lifetime data are linear (and remain so over more extensive ranges in [DMT] than are shown in Figure 4) whereas the intensity data are markedly curved, concave to the ordinate. As expected, the lifetime data, reflecting dynamic quenching of the carbazole excited state, obey the Stern−Volmer equation. k_q values obtained from the slope of the lifetime-based quenching plots are listed in Table 4. Deviations from Stern−Volmer behavior in intensity-based measurements of quenching are not uncommon and often reflect the presence of "static quenching" wherein the quencher associates, in the ground state, with the fluorescent energy donor. However, the dependence of the intensity data upon quencher concentration could not be described (for oligoethers or model compounds) by a function which assumed that ground-state complexes of DMT and Cz species exist in equilibrium with free quencher and fluor and enhance the effects of the dynamic component of the quenching. At the present time, the origins of the deviations (which were of a similar magnitude in model compound, oligomers, and polymer alike) remain unclear.

Considering the dynamic quenching data presented in Table 4, it is apparent that the model compounds, EPCz and ECzOH, are quenched at a rate corresponding to the diffusion limit expected for THF at 298 K. In the case of both the oligoether, PEPCz-1, and the polymer, PECzOH-1, the values of k_q are reduced relative to those obtained for the corresponding model compounds, EPCz and ECzOH, respectively. This observation contrasts with the experience of Arora et al.[23] who reported an enhancement (by a factor of 1.35) in the quenching of their carbazole-substituted *N*-acetylated dehyroalanine polymer over that of its corresponding low molar mass analogue. In their case, the quenching experiment would seem to offer good evidence of intramolecular energy migration between the polymer-bound carbazole substituents. By a similar token, it would be tempting to assume that the current data show that energy migration does not occur to any significant extent in the oligoethers studied in the current work. However, the situation is far from clear. It could be argued (as discussed below) that our data indicate that energy migration *does* occur in the systems currently under investigation. Indeed, the only meaningful conclusion that might emerge from our quenching studies is that the quenching approach can produce data which can be taken as constituting unambiguous evidence of intramolecular energy transport *only* in instances where k_q for the polymer system significantly exceeds that of the model compound.

The rate constant, k_q, governing bimolecular quenching involving mobile fluorescent and quencher species, might be modeled, in a simple approach, by eq 6 in

$$k_q = 4\pi\sigma N_A\,(D_f + D_q)\gamma \tag{6}$$

which σ is the encounter distance and D_f and D_q are the diffusion coefficients of fluor and quencher, respectively. γ is an efficiency factor reflecting steric (and other) constraints upon the collisional encounter producing a productive interaction between the two species. When the fluor is attached to a macromolecule, its translational diffusion is reduced to negligible proportions compared to that of the quencher. In the absence of energy migration, D_f is effectively reduced to zero and k_q will, to a first approximation, be halved. On this basis, Webber et al.[39,42,43] Abuin et al.[44] and Ishii et al.[45] have compared k_q for the polychromophoric species with $^1/_2\ k_q$ for an "equivalent" low molar mass fluorescent model, in the same solvent, to obtain a value for the apparent singlet energy migration constant relative to that for mean mutual diffusion of donor and quencher.

In the case of the oligomer PEPCz-1, k_q is reduced (cf. Table 4) to ca. 0.55 of that determined for its low molar mass model, EPCz. This could be interpreted as good supportive evidence that, as indicated by fluorescence anisotropy, a limited degree of energy migration occurs within the oligomer. In the case of the polymeric species PECzOH-1 energy (provided migration is efficient) will be free to diffuse over much greater distances per unit time than in the relatively short-chain oligomers. The data presented in Table 4 appear to support this line of reasoning. k_q for the polymer is reduced only to 83% of that of its low molar mass analogue, ECzOH.

Table 5. Rate Constants for Quenching, by CCl_4, of the Fluorescence of Labeled Polymers and Low Molar Mass Analogs [Data Reduced to a Common Solvent Viscosity of 0.552 cps]

label or model compound[a]	polymer[b]	$k_q^{\,p}/M^{-1}{}_{ns}$	$k_q^{\,m}/M^{-1}{}_{ns}$	$k_q^{\,p}/k_q^{\,m}$
ACEN			11.5[c]	
ACE	PMMA	3.9[c]	(11.5)	0.34
ACE(T)	PMMA	5.8[c]	(11.5)	0.50
1-MN			7.3[c]	
1-VN	PMMA	2.4[c]	(7.3)	0.33
2-EN			3.9[d]	
2-VN	PMMA	2.2[c]	(3.9)	0.56
2-VN	PMMA	1.27[d]	(3.9)	0.33
9-MA			6.3	
9-MA(T)	PS	4.1[e]	(6.3)	0.65
9-VA	PS	2.1[e]	(6.3)	0.33

[a] ACEN = acenaphthene; 1-MN = 1-methylnaphthalene; 2-ET = 2-ethylnaphthalene; 9-MA = 9-methylanthracene. ACE, 1-VN, and 9-VA represent labels integrated into the host polymer chain by copolymerization of small amounts of acenaphthylene,[46] 1-vinylnaphthalene[46] and 9-vinylanthracene,[47] respectively. ACE(T) and 9-MA(T) represent labels located at polymer chain termini through chain transfer, during radical polymerization, to acenaphthene[46] and 9-methylanthracene,[47] respectively. [b] PMMA = poly(methyl methacrylate); PS = polystyrene. [c] Data taken from ref 46. [d] Data taken from ref 49 and reduced to $\eta = 0.552$ cps. [e] Data taken from ref 47.

Using the equation

$$\Lambda = \left(\frac{k_q^{\,p}}{0.5k_q^{\,m}} - 1\right)\bar{D} \tag{7}$$

we obtain

$$\Lambda = 0.67\bar{D} \tag{8}$$

where $\bar{D} = {}^1/_2(D_f + D_q) = {}^1/_2 D_q$ assuming that $D_f = 0$. This would appear to indicate that energy migration makes a significant contribution to the observed quenching efficiency. However, there are a number of flaws inherent in such an analysis, despite the fact that the greatest obstacle that normally besets the quenching approach (namely that the fluorescence from the polymer is usually not a simple exponential function of time) is not encountered in these systems.

(a) The method assumes that the quenching probability per collision, embodied in γ in eq 6, is the same for the polymer as it is for the model compound. This would appear to be a somewhat rash assumption: intuitively, one might feel that interactions with neighboring substituents could influence the productivity of collisions in effecting quenching of an excited-state appended to a polymer. Intuition is borne out by observation as revealed by reference to Table 5.

We can gain some insight into the effects that steric interactions with the polymer chain and neighboring substituents might have upon γ if we examine the quenching of fluorescent labels (i.e. chromophores bound to polymers at such low concentrations as to preclude energy migration). The quenching data presented (Table 5) for a series of fluorescent labels and plausible model compounds show that the premise that $k_q^{\,p}/k_q^{\,m} = 0.5$, as applied in eq 7 is seldom justified. The k_q data, reduced to a common viscosity, reveal some of the problems inherent in attempting to use $k_q^{\,p}/k_q^{\,m}$ values to estimate extents of intramolecular energy migration in macromolecules (or even simply to infer its presence).

(i) $k_q{}^p/k_q{}^m$ values for labels of internal segments of PMMA (ACE, 1-VN, and, in one instance,[50] 2-VN) and PS (9-VA) are remarkably similar but considerably less than the value of 0.5 generally assumed in quenching estimates of energy migration[39,42–45].

(ii) $k_q{}^p/k_q{}^m$ values for labels located at the termini of PMMA[46] or PS[47] are significantly larger than those for analogous structures attached to internal segments of the polymer chain. (This may reflect the lesser "steric crowding" to which a terminal label is subjected and/or the greater relaxational freedom[46–48] enjoyed by a terminal, compared to an internal, segment).

(iii) In two of the cases examined $k_q{}^p/k_q{}^m$ values greater than 0.5 were obtained.

Webber et al.[49] recognized the potential difficulties associated with the use of small molecule models and adopted a low content 2-VN/MMA copolymer as model in their studies of energy migration in 2-VN/MMA copolymers and P2-VN itself. In this study the authors noted the considerable difference in estimates of Λ which occurred if a small molecule (2-EN) was adopted as the model compound. [This discrepancy is reflected in the $k_q{}^p/k_q{}^m$ value of 0.33 recorded in Table 5 for this label/model pair].

The use of a labeled polymer as a model system in the absence of migration seems reasonable when studying (as were Webber et al.[49]) energy migration in alternating copolymers: the nearest neighbors of the chromophore are the same in each instance. Greater problems attend the choice of an appropriate model when, as in the current work, information is sought on energy migration in homooligomeric and homopolymeric species.

(b) The approach assumes that the quencher is uniformly dispersed throughout the system It is the bulk concentration of quencher which is used to calculate k_q. In reality, the quencher will be partitioned between the bulk solvent and the solvent swollen polymer coil. Hence the local quencher concentration which controls the quenching of a polymer-bound fluor, is unknown. (This may be a factor of some importance in *producing* the observed discrepancies in the apparent value of $k_q{}^p$ compared to $k_q{}^m$). An extreme case of systems in which such partitioning effects are of paramount importance concerns fluorescence quenching studies upon labels located within hydrophobic domains formed in aqueous solutions of certain hydrophobically modified copolymers. (See, for example, ref 50 and references therein).

(c) The technique would require that specific interactions between polymer and quencher are absent. In the current case, quenching efficiencies based upon fluorescence intensity measurements are markedly different from those based upon lifetime data. It is solely the *dynamic* process within the overall mechanism that we have examined in estimating k_q. Nevertheless the (unknown) nature of the considerable static component of the quenching of the oligocarbazole fluorescences by DMT would bring the reliability of estimates of rates of energy migration into question even if the major reservations regarding the viability of the method (as discussed earlier) could be proved groundless. It would appear that, despite its previous use in the study of energy migration in carbazole-based polymers[23] which appeared not to be complicated by the effects of static interactions, DMT was not the best choice of quencher for studying the effect in our carbazole-containing oligoethers, as discussed above.

The problems associated with choice of an appropriate model compound and quencher may be placed further in context by considering the influence of the structure of the *quencher* upon the probability of quenching per collision. Abuin et al.[51] investigated the effects of quencher structure (for oxygen and a series of ketones as quenchers) upon the quenching of fluorescence of poly(2-phenylethyl methacrylate) and 2-phenylethyl acetate. It was shown that $k_q{}^p/k_q{}^m$ decreased as the steric bulk of the quencher increased: this is clear evidence that it can *not* be assumed that γ is equal for a substituent bound to a particular polymer and a model compound (even if also bound to a polymer). In the case of a bulky quencher, such as DMT, the assumption that γ is the same for EPCz and PEPCz or for ECzOH and PECzOH would be particularly open to question.

We have, in studying both degassed and air-saturated solutions, employed another, less sterically hindered quencher, oxygen. In the absence of knowledge of the Henry's law constant for the oxygen/THF system, the concentration of dissolved oxygen at a partial pressure of 0.2 atm is unknown. Consequently, it is not possible to estimate $k_q{}^p$ and $k_q{}^m$ from the lifetime data. However, the ratio $k_q{}^p/k_q{}^m$ may be readily derived. For the PEPCz/EPCz system a value of 1.04 results, whereas for PECzOH/EPCz, $k_q{}^p/k_q{}^m$ is estimated as 1.0. These data would support a proposal that energy migration (as revealed by emission depolarization) occurs to some extent in PEPCz and PECzOH. However, the many assumptions involved in the quenching approach (even with a quencher of small dimensions, as in the case of oxygen) preclude evaluation of the actual extent of the migration (or, indeed, of quantifying the relative migration lengths in polymer and oligomer, respectively).

Conclusions

1. There is no evidence from either fluorescence spectroscopy or decay data for excimer formation in PEPCz or PECzOH oligomers.

2. Fluorescence anisotropy measurements have shown, unambiguously, that intramolecular energy migration occurs in PEPCz and PECzOH species, immobilized in dilute, glassy (MTHF) solutions.

3. Fluorescence quenching data suggest that intramolecular energy migration occurs in PEPCz and PECzOH oligomers in dilute, fluid (THF) solutions. The quenching data do not allow the extents to which energy migrates in these systems to be quantified. It is concluded that fluorescence quenching experiments have limited potential for estimating migrative path lengths for diffusion of polymer-borne energy in mobile, fluid media except under rather special circumstances (e.g., for alternating copolymers).

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