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Some Photophysical Properties of Five New Carbazole-Containing Methacrylate Polymers

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ABSTRACT: Five new carbazole-containing polymers have been synthesized. With poly(*N*-vinylcarbazole) these form two series in which (a) the nitrogen atom of the chromophore is attached to the polymer backbone with an increasingly flexible linking moiety, PNVK, I, -II, -III, and (b) a series in which the backbone is attached to the 9-, 2- and 3-ring positions, I, IV, V. The molecular weights of the polymers have been characterized by membrane osmometry and gel permeation chromatography. These polymers are susceptible to photochemical degradation which causes both scission of the chain backbone and diminution of carbazole chromophore fluorescence. Sensitive viscosity measurements made on samples undergoing this main-chain scission have been used to obtain the intrinsic viscosity–molecular weight K, α values of the resulting fragments. Comparison of the absorption and emission spectra shows that appreciable excimer emission occurs only in the case of poly(*N*-vinylcarbazole) (PNVK) and poly[2-(9-ethyl)carbazolylmethyl methacrylate] (IV). Excimer emission from the latter is weakest in polar fluid solvents and strongest in a rigid glassy matrix. Luminescence decay measurements in the presence and absence of anthracene quencher suggest that down-chain energy migration is virtually absent in the sterically unhindered polymers I, II, III, and V, and this is confirmed by steady state analysis of collisional quenching. Collisional quenching of monomer excitation from IV indicates that the excitation is effectively immobilized in the region of not more than three neighboring chromophores. These results show that the flexibility of the linking group does not assist the adoption of the parallel overlap interchromophore geometry necessary (to different extents) for both excimer formation and resonance energy migration. However, geometrical constraints imposed by chain linking to the chromophore 2 position (polymer IV) do favor (relative to attachments at the 9- and 3-ring position) the adoption of a ground state interchromophore geometry permitting excimer formation with relatively minor conformational readjustment or monomer excitation energy migration.

The importance of electronic energy migration and transfer, and of excimer and exciplex formation, is now widely recognized in a variety of photochemical and photophysical phenomena. Polymeric materials in which neighboring chromophores are brought into proximity by the constraints of the chain backbone have considerable potential for exhibiting unique energy transfer characteristics. Thus previous studies have shown that it is possible to measure, quantitatively, down-chain energy migration coefficients in a variety of polymers,[1,2] that selected chromophores may be attached to the chain backbone with different geometries so giving different photophysical properties,[3,4] and that energy transfer and excimer formation are affected by external control of polymer chain conformations.[5,6]

The considerable technical and academic interest in the photoelectric properties of poly(*N*-vinylcarbazole) (PNVK) has led to many detailed studies of the excimer formation and singlet energy transfer properties of this polymer.[1,7-11] These studies have shown that in this polymer excimer formation (and therefore probably also energy migration) is affected by stereochemical configuration and by the adoption of a helical conformation.

The objective of this work was to study further the photoproperties of polymers containing the carbazole chromophore, and to determine how the properties are affected by the geometrical nature of the attachment of the chromophore to the chain backbone. To this end two series of polymers have been synthesized in which (a) the chain backbone is attached to the N atom at the 9 position by progressively larger and more flexible linking units and (b) the chain backbone is attached (via a methyl ester moiety) to the 9-, 2-, and 3-ring positions.

Experimental Section

1. Synthesis of Monomers. Five new carbazole-containing monomers (Ia–Va) were synthesized. Details of these reactions, and analytical data characterizing the novel reaction intermediates, will be published elsewhere. The syntheses produced good yields of crystalline monomers which were finally purified by column chromatography.

2. Synthesis and Characterization of Polymers (I–V) from Monomers (Ia–Va). The carbazole-containing poly(meth-

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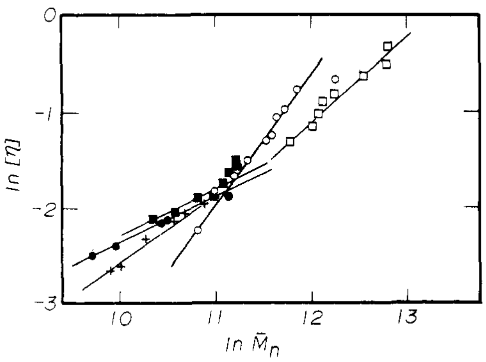


Figure 1. Intrinsic viscosity osmotic pressure molecular weight dependence of partly photodegraded samples of polymers I-V: +, I; ■, II; □, III; ●, IV; ○, V.

Table I
Polymer Molecular Weight Data

polymer	$M_n \times 10^{-3}$	M_w/M_n	$K(n)$, dL g^{-1}	α
I	63	2.6	4.0×10^{-5}	0.75
II	76	3.2	6.7×10^{-4}	0.50
III	334	2.3	5.6×10^{-6}	0.92
IV	71	2.5	6.3×10^{-4}	0.50
V	208	1.7	3.8×10^{-8}	1.37

acrylates) were all prepared by conventional AIBN-initiated free-radical addition polymerization of the methacrylate monomers in benzene at 60 °C. Polymerizations were carried to low conversions and the polymers were recovered and purified by reprecipitation from cold methanol. In order to obtain sufficient material for all laboratories the polymerizations were repeated under identical conditions.

Basic molecular weight characterization was effected by combining membrane osmotic pressure measurement with gel permeation chromatography (GPC). In all cases except III, the polymers had a single peak in molecular weight distribution. Polymer III exhibited an additional peak at very high molecular weights (10^6 to 10^7) beyond effective resolution of the GPC apparatus. Molecular weights obtained by GPC are only approximate unless the intrinsic viscosities or the Mark-Houwink K, α values, of the eluted fractions, are known. For new polymeric materials it is difficult to obtain sufficient material in a fraction for further characterization at a variety of concentrations, and so a procedure[12,13] employing single point viscosity and osmotic pressure determinations of samples undergoing photodegradation was used. This employs an ultrasensitive automatic viscometer, and is based on the assumption that photodegradation occurs at random along the polymer chain, so that partially degraded material formed by chain scission has a distribution M_w/M_n of 2. Additionally it is assumed that the resulting chain fragments effectively have the same structure as the parent polymer.

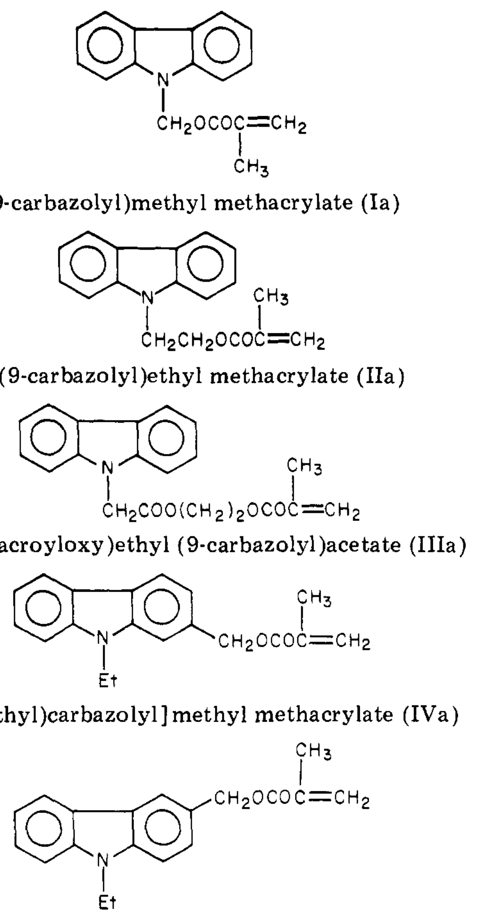
The changes in number average molecular weight and intrinsic viscosity occurring during photodegradation are illustrated in Figure 1. The osmotic pressure number average molecular weights of the whole samples, the distribution parameters obtained from GPC, and the K (number average), α values obtained from the degraded samples are listed in Table I.

3. Apparatus. The steady state absorption and emission spectra were obtained using a Perkin-Elmer 402 absorption spectrophotometer and a Perkin Elmer MPF-44 spectrofluorimeter.

Luminescence decay curves were observed using two Ortec-Applied Photophysics nanosecond spectrometers (Model SP2) and the spectrometer described by Birch and Imhof.[14] An SP2 connected on line to a PDP 11 computer was used for preliminary decay measurements and data analysis, and the more sensitive Birch-Imhof instrument was used for the lifetime quenching studies.

The second SP2 spectrometer was modified by placing monochromators in both excitation and emission beams and by linking the drive of the emission monochromator to the multichannel analyzer. In this way time-resolved spectra could be obtained, albeit of rather poor resolution and of arbitrary intensity.

Scheme I



(9-carbazolyl)methyl methacrylate (Ia)

2-(9-carbazolyl)ethyl methacrylate (IIa)

2-(methacroyloxy)ethyl (9-carbazolyl)acetate (IIIa)

[2-(9-ethyl)carbazolyl]methyl methacrylate (IVa)

[3-(9-ethyl)carbazolyl]methyl methacrylate (Va)

Results and Discussion

1. Photochemical Stability. Although it might be expected that the carbazole chromophore should confer stability by masking any ultraviolet initiated ester decomposition[15] or resulting chain scission of the poly(methacrylate) unit, the osmotic pressure measurements illustrated in Figure 1 unambiguously show that all the polymers suffer a reduction in molecular weight of at least a factor of 10. Such a diminution is only possible by chain scission. In the case of polymer V most susceptible to photochemical scission it has been possible to measure a scission quantum efficiency, and this was 4.6×10^{-3} at λ_{ex} 313 nm in tetrahydrofuran. This quantum yield is perhaps surprisingly high, but being calculated from the fragment number average chain lengths and the actual quanta absorbed it is unlikely to be wrong by an order of magnitude and is indicative of the efficient photochemical step.

Since the end groups of the chain fragments are present in small concentration, it has not yet proved possible to carry out the chemical analysis necessary to elucidate the degradation mechanism. Hypotheses as to the exact mechanism can be no more than mere speculation at this juncture, although photolytic cleavage of amino-substituted esters is well established and is thought to arise via intramolecular electron transfer processes.[16] Furthermore carbazole is well known[17,18] for its ability to function as an electron donor in both ground and excited states and hence comparable photoinduced cleavage of carbazole substituted esters must be anticipated.

The photochemical instability, as well as causing a detectable diminution in carbazole fluorescence emission,

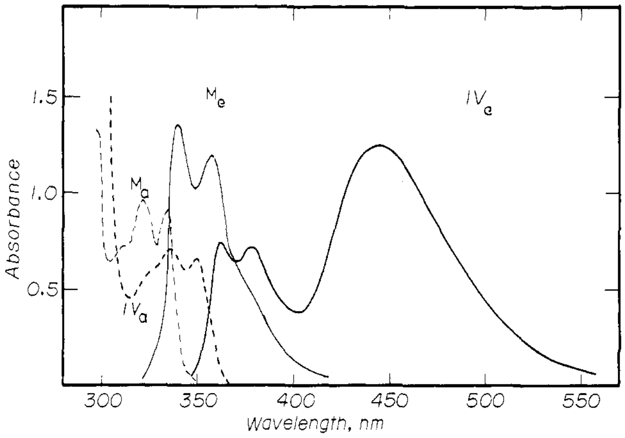


Figure 2. Absorption (---) and fluorescence (—) (arbitrary units) spectra of model compound, M, and polymer IV, in CH_2Cl_2. Absorption concentration of monomer units, [M] = 1.83×10^{-4} M, [IV] = 2.05×10^{-4} M.

gives rise to a small tail in the absorption spectrum between 380 and 420 nm. Irradiation sufficient to cause a tenfold diminution in number average chain length gives rise to extinction coefficients (per mole of initial monomer residue) of 50 at 380 nm dropping to 14 at 420 nm (all from zero before irradiation except in IV which showed some evidence of photodegradation before examination).

2. The *K*, α Parameters. The use of photoinitiated chain scission for the evaluation of viscosity K, α parameters requires the assumption that the scission can occur at points randomly selected on the chain (so that the fragments have the statistical size distribution, $M_w/M_n = 2$). In addition it is assumed that any chemical change on side groups as a result of the photoscission occurs only at the ends of the resulting fragments and so does not alter the general hydrodynamic properties of the broken chain. The second assumption will not be valid if only a very minor proportion of photochemical reactions result in scission. If this should be the case, and if the hydrodynamic properties of the photochemically modified chains differed markedly from the original poly(methacrylate), the plots of Figure 1 would be expected to show pronounced curvature (points at low $[\eta]$ and M_n representing extensively modified polymers). In view of the linearity (within experimental error) of the plots for each polymer, we believe that this assumption is reasonable for the polymers and the extents of photodegradation involved.

The linearity of the plots in Figure 1 implies also that after some initial degradation, further scission produces samples of constant M_w/M_n ratio. While other degradation mechanisms for which this may not be 2 are possible, the maximum effect is an error of ×2 in K and no change in α. However, the unambiguous osmotic pressure evidence of chain scission, continuing under prolonged irradiation, does indicate that the assumption of random scission is reasonable.

3. Luminescence Spectra and Excimer Formation. The absorption and emission spectra of 9-(hydroxymethyl)carbazole (M), and of poly([2-(9-ethyl)carbazolyl]methyl methacrylate) (IV) in methylene chloride are illustrated. Only in the case of IV is there appreciable excimer formation. Generally the fluorescence emission is the mirror image of the $^1L_b \leftarrow {}^1A$ absorption band, as expected for "monomer" emission from the singlet state of an excited carbazolyl chromophore *not* in strong interaction with a neighbor.

The spectroscopic data of all the polymers are summarized in Table II, together with comparative data for poly(*N*-vinylcarbazole) (PNVK). These wavelengths were not affected by traces of dissolved oxygen.

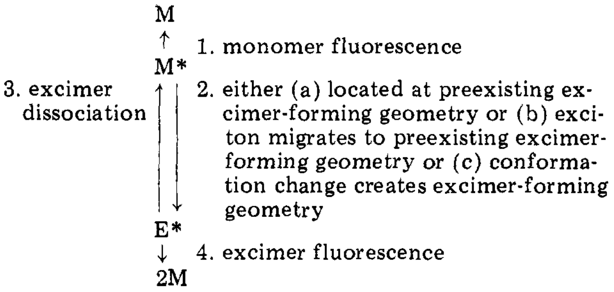
Table II
Spectral Data of Monomer and Polymers in Methylene Chloride

	absorption peaks, nm		monomer emission peaks, nm		excimer emission peak(s)
compd	λ_1	λ_2	λ_3	λ_4	λ_5
M	321	335	341	356	
I	318	330	336	350	
II	329	343	348	365	
III	325	338	347	362	
IV	336	350	362	377	425
V	334	349	358	374	
PNVK	331	344			380, 430

Table III
Spectral Properties of Polymer IV in Different Solvents

solvent	λ_{max} excimer	I_E/I_M
C_6H_6	418	3.3
CH_2Cl_2	440	2.7
$CHCl_3$	435	2.0
C_4H_8O	425	2.1
$CH_3COOC_2H_5$		1.0
CH_3CN		1.0
PMMA film	440	100

Scheme II



The fluorescence of a dilute solution of IV in a poly(methyl methacrylate) film was characterized by similar excimer and monomer emission peaks. However, the intensity ratio I_E/I_M was much larger than in fluid solution in polar or nonpolar solvents, as illustrated in Table III.

Since excimer formation is a stepwise process in which a "monomeric" chromophore absorbs a photon, followed by interaction with a neighboring ground state chromophore, it is relevant to ask how the preexisting ground state geometry or conformational change during the excited state lifetime permit excimer formation. In this context it is important to remember that a flexible polymer chain in fluid solution undergoes dynamic conformational fluctuations such that at any instant of time a fraction of chain segments may exist in unfavorable high-energy conformations, or any segment may in a finite time "hunt" through a number of conformations of different energy. In addition conformation change can lead to "thermal" excimer dissociation.

The principal processes involved in excimer formation are illustrated in Scheme II.

The high excimer ratios in the glassy solvent and the very rapid excimer emission rise time (see below) indicate that *large scale* conformational rearrangement, 2(c), is *not* a necessary prerequisite for excimer formation, so that a certain number of ground state chromophore pairs must preexist in a geometry permitting excimer formation on very *small scale* group adjustments when one of the

Table IV
Energy Transfer Data of Monomer and Polymer in CH_2Cl_2

compd	lifetime ± 0.1 ns (not degassed)	calcd Förster R_0 (anthracene), nm	Yokota-Tanimoto D_{E-Q}, m^2 s^{-1} × 10^{-9}
M	7.0	2.8	1.25
I	7.7	2.7	1.8
II	7.8	2.7	1.7
III	5.4	2.7	1.0
IV	3.0_M, 8.4_E	*a*	*a*
V	7.1	2.7	1.1
PNVK[1,19]	14_{M-E}	1.4_{M-E}	11.0

[a] Not applicable.

chromophores becomes electronically excited. The monomer and excimer lifetimes are both virtually unchanged in glassy, polar, and nonpolar fluid environments, so the dissociation process, 3, is either unimportant in competition with the radiative processes 1 and 4, or again the reversible processes 2 and 3 are both independent of large scale chromophore movement. The former possibility would be expected for an excimer functioning as a "deep trap", and in this context we note that the monomer–excimer band center wavelength difference is equivalent to about 15 kT.

On this basis the different excimer intensities observed in the different solvents must reflect the different populations of preexisting excimer-forming geometries which become excited by processes 2(a) and/or 2(b), the population of such high-energy ground-state conformations being greatest in the poorest solvents.

Comparison of polymers I, II, III, and PNVK indicates that the geometrical constraints imposed by the N-substituted vinyl backbone are no barrier to the adoption of the appropriate interchromophore geometry, but that the intervention of even a three-atom link does not allow adjustment of any ground-state geometry equally or more favorable for excimer formation. In view of the fact that adjustment of the flexible linking group to the repulsive ground state approach necessary for excimer formation is likely to be endothermic and exoentropic, the rate of achievement of such a state in fluid solution is likely to be small compared with the rate of monomer excited state decay or of excimer dissociation. Alternatively, for similar reasons, the equilibrium concentration of such geometries would be low in any rigid environment.

Comparison of the 9-, 2- and 3-substituted chromophores (polymers I, IV, and V) shows excimer formation only in structure IV, suggesting that favorable steric constraints are greatest when the backbone is linked to the 2 position. Rigorous purification and dilution studies have confirmed that this unstructured long-wavelength emission is caused by a true intramolecular excimer, and is not caused by impurity of intermolecular effects.

4. **Energy Migration and Transfer.** The luminescence decay curves for monomer emission from polymers in dilute solution (in methylene chloride) all fitted exponential functions, and the observed lifetimes are listed in Table IV. Fitting was performed using the nonlinear least-squares convolution technique with a χ^2 "goodness of fit" criterion.[14] Slight oxygen quenching was observed in nondegassed samples. Nevertheless the significant features exhibited in both normal and deoxygenated solutions are the uniformity of the lifetimes in the model compound and polymers I, II, and V, the much reduced monomer lifetime in IV, and the long excimer lifetime in PNVK.

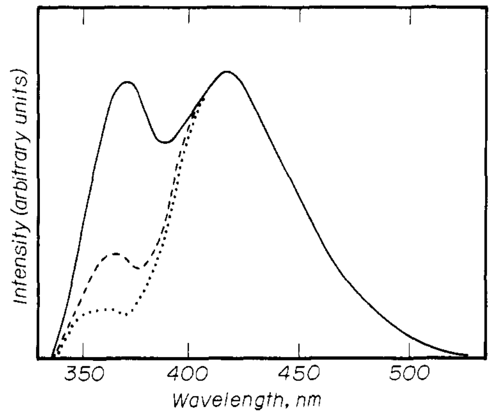


Figure 3. Time-resolved fluorescence spectrum of IV in methylene chloride: —, 0 to 0.23 ns: - - -, 8.0 to 9.4 ns; ···, 19 to 24 ns. All arbitrary units fitted to the excimer emission peak.

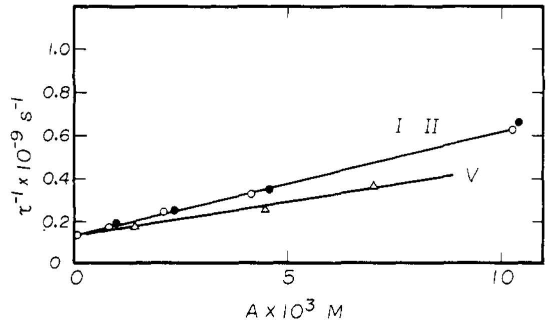


Figure 4. Inverse lifetimes of fluorescence of polymers I, II, and V quenched by anthracene.

The short monomer lifetime in IV is in line with formation of excimer from excited monomer either by rapid energy migration to sites of preformed favorable geometry or by conformational change during the excited state lifetimes. The excimer emission rise time was not measurably (±0.5 ns) different from the monomer emission rise time, indicating that slow energy migration to an excimer site, or slow conformational change, are not involved in excimer formation. Time-resolved spectra of IV were obtained and are illustrated in Figure 3, where arbitrary intensities are normalized to constant excimer emission. The relative intensities of monomer and excimer emission are consistent with the different lifetimes of monomer and rapidly formed excimer states which do not rapidly redissociate to monomer, but do not, of themselves, rule out time-dependent conversion of energy from the monomer excited state to the excimer.

In order to examine further the possibilities of exciton energy migration in polymers I, II, III, and V observation has been made (Figure 4) of fluorescence decay curves in the presence and absence of anthracene, which quenches the polymer emission by accepting energy via long-range resonance transfer. Since in fluids both molecular and exciton diffusion must be considered, the quenched decays have been fitted to the Yokota–Tanimoto[20] solution of the diffusion equation. In this case the parameter obtained was the total "diffusion coefficient" (i.e., molecular plus exciton, $D_{E-Q} = D_{MOL} + D_{EXC}$). The fitted "diffusion coefficient" and R_0 values obtained from spectral overlap calculations are given in Table IV. These "diffusion coefficients" all span the value, D_{MOL}, expected for anthracene in dichloromethane and exhibited by the model compound, $D_{ANTH} + D_{MODEL}$, indicating that exciton diffusion, D_{EXC}, is insignificant in these polymers. Where exciton mobility does occur (PNVK) the D_{E-Q} value is clearly much larger than D_{MOL}.

Table V
Collisional Quenching Parameters

polymer	quencher	quenching rate constant × 10^{11}, cm^3 $molecule^{-1}$ s^{-1}	collision radius, nm
M	DMT	1.6	0.6
I	DMT	1.4	0.5
II	DMT	2.4	0.8
IV	DMT	1.05 (monomer)	0.4
V	DMT	1.5	0.5
M	HCX	1.1	0.4
II	HCX	2.5	0.9
IV	HCX	2.4 (monomer)	0.8
V	HCX	2.0	0.7

Two of the difficulties in reaching such a conclusion are that (a) in calculating the spectroscopic Förster critical distance, R_0, it is necessary to include the quantum efficiency for donor fluorescence (all assumed equal to 0.40 in these polymers) and the refractive index of the medium between exciton and quencher (assumed to be that of solvent) and (b) in calculating quenching efficiencies the concentration of quencher in the proximity of the exciton, i.e., within the swollen polymer coil, is assumed equal to that in the bulk of the solution. In this case apparent absence of exciton migration, manifested as somewhat inefficient quenching, might result from a lower than statistical concentration of anthracene in the dissolved macromolecular coil. Any thermodynamic attraction or repulsion between polymer and the three acceptors, anthracene, dimethyl terephthalate, and hexachloroxylene, would be most unlikely to lead to identical perturbations of concentration. Furthermore, the absence of spectral overlap between carbazole and the collisional quenchers meant that continuous irradiation intensity measurements could be made without complications due to radiative emission and reabsorption or primary absorption by acceptor.

Stern–Volmer plots of the quenched intensities were straight lines (six points on each). Quenching of fluorescence from the model compound, M, from polymers I, II, IV, and V by dimethyl terephthalate, and from polymers II, IV, and V and the model compound by hexachloroxylene yielded the quenching rate constants and reaction radii summarized in Table V. In all cases the reaction distances are of the order of the separation of neighboring chain chromophores. When monomer excitation energy can migrate over several chromophores during the excited state lifetime (when the time required for exciton jump is considerably less than the time for diffusive approach of quencher to a specific exciton site), the *effective* reaction radius always appears greater than either the interchromophore distance[1,2] or a chromophore–quencher intermolecular distance. Consequently these results indicate that the initial monomer excitation is constrained within a distance encompassing three chromophore units (one on each side of the initially excited group) over the time scale of the diffusion-controlled approach of quencher.

The absence of extensive (over more than 2–3 chromophore units) energy migration in polymers I, II, III, and V together with the absence of excimer emission are in line with a ground-state chain geometry in which neighboring carbazole units do not adopt the parallel overlap arrangement required.[10,19,21]

The absence of extensive migration in IV (as determined from the limited effective collision radii) but the presence of rapid conversion of monomer to excimer energy indicate that the chain must contain a large number of sites of preformed geometry suitable for excimer formation, such that any site must be within one or two chromophoric groups of the site of energy absorption. This conclusion is supported by the extreme excimer emission observed when the chain is immobilized in the rigid matrix.

The overall conclusion is that in polymers I, II, III, and V the chain conformations are such that excimer forming geometries neither preexist to any observable extent nor are formed during the monomeric excited state lifetime. Furthermore the chromophore excited state energy is immobilized on between one and three chromophore units on the chain. In polymer IV excimer formation is possible. Since the monomer excitation energy does not migrate over large effective distances (as in PNVK), and since excimer emission is most efficient in a rigid medium, the ground state chain conformation must contain a large number of units in a "preformed" geometry allowing excimer formation with relatively minor adjustments to the interchromophore separation.

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