1752 *Macromolecules* 1981, *14*, 1752–1757

Excimer Fluorescence as a Probe into the Solution Behavior of a Polyester of *p*-Phenylenediacrylic Acid

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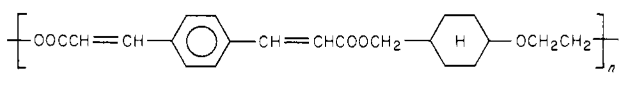
ABSTRACT: A polyester of *p*-phenylenediacrylic acid (PPDA) and the small-molecule model diethyl *p*-phenylenediacrylate (Et$_2$PDA) show monomer and excimer fluorescence in solution. The kinetics of fluorescence decay indicate ground-state interaction between PDA groups in both systems. Excimers arise here not via the usual bimolecular quenching mechanism but by the excitation of preformed chromophore pairs. As a consequence, in solutions of PPDA, the quantum yield of excimer fluorescence measures directly and in absolute terms the number of intersegmental contacts of the polymer chain. In the isolated PPDA molecule on average every fourth chromophore takes part in an intermolecular contact; with increasing polymer concentration the contact frequency increases and intramolecular contacts are replaced by intermolecular ones. In that way, the state of aggregation which is responsible for the photochemical, and the photographic, behavior of the solid matrix is preformed in solution, in response to a weak ground-state interaction between PDA groups.

In an earlier paper[1] one of us reported on the photochemistry of a polyester of *p*-phenylenediacrylic acid (PPDA), the structure of which is



PPDA

It was found that irradiation of a solid film of PPDA led to the formation of cyclobutane rings between the ethylenic double bonds of the *p*-phenylenediacrylate (PDA) chromophores in adjacent polymer chains. The unusually high chemical yield of the process (up to 85%) and the predominance of one particular isomer (β-truxinate) in the photoproducts seemed incompatible with a purely random arrangement of chromophores in the matrix, yet X-ray diffraction experiments failed to show any signs of crystallinity either in the coated films or in the powdered material. It was therefore suggested that in the amorphous matrix the PDA groups aggregate in a way reminiscent of the organization of liquid crystals. Since the polymer films were prepared from solution, it was thought that the state of aggregation assumed to exist in the matrix would manifest itself in the fluid phase at some stage prior to solidification. The present work is an attempt to detect interchromophore correlation in solutions of the polymer PPDA and in solutions of a small-molecule model, diethyl *p*-phenylenediacrylate (Et$_2$PDA).

Esters of PDA are known to form excimers.[1,2] This makes it possible to monitor chromophore interactions in solution by fluorescence spectroscopy. Accordingly, we have (a) determined the quantum yield of monomer and of excimer fluorescence over a wide concentration range in 1,2-dichloroethane solutions of PPDA and of Et$_2$PDA and (b) investigated the kinetics of fluorescence decay by laser flash spectroscopy.

The key result of these experiments is the finding that the decay time of monomer fluorescence in solution is independent of concentration. This means that PDA excimers are not formed by the usual process of dynamic quenching of an excited chromophore[3] but rather by the excitation of a chromophore pair which had been formed prior to excitation. This result clearly indicates ground-state interaction between PDA groups and implies the establishment of a ground-state equilibrium between single chromophores and chromophore pairs in solutions of Et$_2$PDA. (In this situation the excited species is, strictly speaking, an excited pair complex. However, for the sake of brevity the term excimer will be used in this paper.) The effect is even more significant in PPDA, where it determines the configuration of the polymer chain in solution and ultimately the micromorphology of the solid matrix.

Experimental Section

Materials. The diethyl ester of *p*-phenylenediacrylic acid (Et$_2$PDA) and the polyester PPDA were supplied by the Eastman Kodak Research Laboratories and were used as received. The molecular weight of PPDA was 1.5×10^5 (M_w). Solutions were prepared by weight in 1,2-dichloroethane (analytical grade) and care was taken to disperse the polymer by stirring the solution for 24 h.

Fluorescence spectra were recorded with a fluorimeter described earlier.[4] The instrument was used with oblique frontal irradiation of the samples in order to measure fluorescence yields in concentrated solutions. The exciting light source was a 150-W stabilized xenon arc (Wotan) coupled to a Bausch and Lomb high-intensity monochromator. Irradiation was at 290 nm, with slit settings corresponding to a spectral bandwidth of 3.5 nm. The spectral sensitivity of the detector was calibrated by the method of Melhuish[5] using a rhodamine G quantum counter. The calibration was checked against published data.[6]

Absolute quantum yields were determined on air-saturated solutions by the method of Parker and Rees:[7] the corrected emission spectra, in wavenumber presentation, were integrated and compared with 4,4′-dibenzoxazolylbiphenyl ($\phi_F = 1.00$ in DCE)[4] as standard. The fluorescence spectrum of a 10^{-3} M solution of Et$_2$PDA was used as a secondary reference.

Fluorescence Decay Kinetics. Fluorescence decay profiles were recorded with a high-resolution time-resolved fluorescence spectrometer, the operation of which has been described in full elsewhere.[8] Sample excitation, at 295 nm, was achieved with a frequency-doubled, cavity-dumped, synchronously pumped, mode-locked dye laser (Spectra-Physics). The fluorescence was monitored through a monochromator (Hilger and Watts D330) with a spectral resolution of 2 nm. Conventional single-photon-counting detection methods were employed,[9] and the data were analyzed on a Perkin-Elmer Interdata 7/32 computer using procedures discussed elsewhere.[10,11]

The above system was unable to resolve accurately decay times of less than 100 ps. For shorter fluorescence lifetimes decay measurements were performed with a spectrometer with single-shot excitation and streak camera detection.[12,13] A single pulse from a frequency-trebled mode-locked neodymium(III) glass rod laser was used for sample excitation at 354 nm. The fluorescence was monitored with an S20 Imacon 600 streak camera (John Hadland (P.I.) Ltd.).

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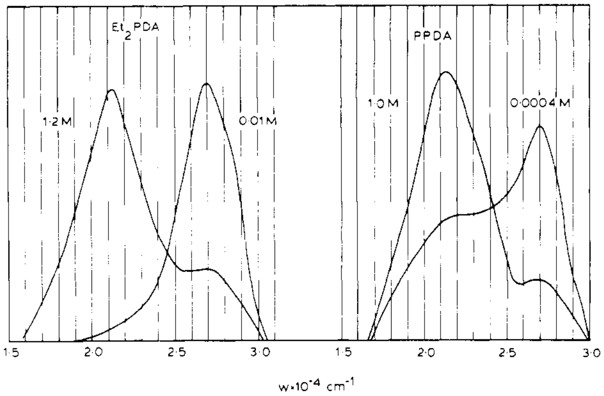


Figure 1. Fluorescence spectra of dilute and of concentrated solutions of Et$_2$PDA and of PPDA in 1,2-dichloroethane.

Ancillary Measurements. Gel permeation chromatography was carried out on an AR gel column of pore sizes 0.3 × 10^3, 1 × 10^3, and 3 × 10^3 nm with THF as eluent. The column was calibrated with a set of narrow polystyrene fractions (Waters); molecular weights were calculated as polystyrene equivalents.

A Sofica 42000 goniophotometer was used for the light scattering experiments. The refractive index increment was determined with a Brice-Phenix differential refractometer. Molecular weights and radii of gyration were obtained from computer-generated Zimm plots.

Results

Fluorescence Quantum Yields. Because of the photoreactivity of the PDA group, all measurements were made on fresh solutions. Two types of emissions were observed: one, with a maximum at 370 nm, was identified as monomer fluorescence;[1,14] the other, centered around 470 nm (corrected spectra), is associated with an excimer.[2] Figure 1 shows the corrected fluorescence spectra of Et$_2$PDA and of PPDA at a low and a high concentration in 1,2-dichloroethane.

The quantum efficiency of the monomer fluorescence was determined on a 10^{-3} M solution of Et$_2$PDA where the excimer emission is negligible. The quantum efficiency of the excimer fluorescence was derived by numerical resolution from the emission spectrum of a 0.1 M solution. The values obtained in this way are

$$q_{FM} = 0.023 \qquad q_{FD} = 0.039$$

leading to the efficiency ratio

$$Q = q_{FD}/q_{FM} = 1.70$$

It was assumed that this value of the quantum efficiency ratio applies equally to solutions of PPDA since monomer as well as excimer fluorescence lifetimes (vide infra) were found to be nearly identical in both systems.

The fluorescence data for solutions of Et$_2$PDA and of PPDA are summarized in Figure 2, where the excimer-to-monomer fluorescence ratio $R = \phi_{FD}/\phi_{FM}$ is plotted logarithmically as a function of chromophore concentration.

Fluorescence Decay Times. The time decay of fluorescence was monitored at 370 and 470 nm. The fluorescence emission at 370 nm is very short-lived; its lifetime was found to be about 20 ps. The experimental data are collected in Table I, where it can be seen that the lifetime of the excited monomer is entirely independent of concentration.

The emission at 470 nm decays more slowly. A typical decay curve is shown in Figure 3. It is described by a two-component decay function of the form

$$i(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

Here τ_1 is a short-lived signal identified as monomer fluorescence and τ_2 is the decay time of the excimer. It can ben seen in Table I that τ_2 decreases with increasing concentration of PDA groups, which indicates bimolecular quenching of the excimer by the monomeric species.

The emission of PPDA in 1,2-dichloroethane was monitored over a wide concentration range. The monomer

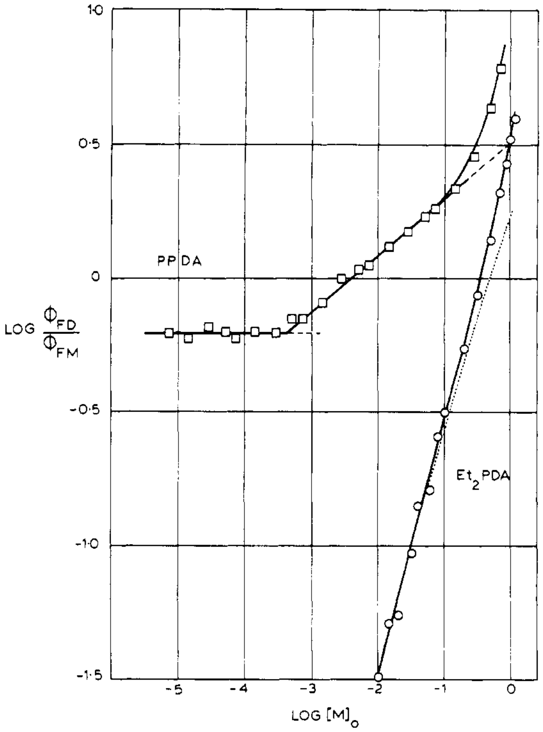


Figure 2. Ratio of excimer-to-monomer fluorescence as a function of chromophore concentration for Et$_2$PDA and for PPDA in 1,2-dichloroethane (logarithmic presentation).

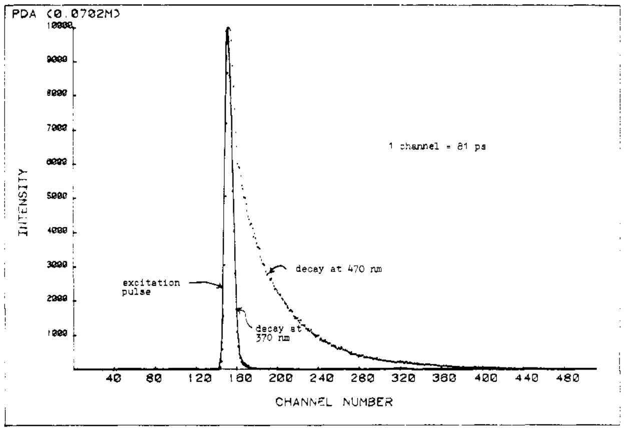


Figure 3. Time decay of excimer fluorescence in a 0.07 M solution of Et$_2$PDA in 1,2-dichloroethane.

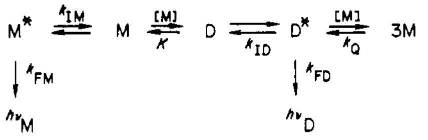
Table I

Fluorescence Decay Times at 470 nm (Excimer) and at 370 nm (Monomer) in Solutions of Et$_2$PDA and PPDA

chromophore concn, mol dm^{-3}	Et$_2$PDA 470 nm τ_D,[a] ns	Et$_2$PDA 370 nm τ_M,[b] ps	PPDA 470 nm τ_D,[c] ns	PPDA 370 nm τ_M,[d] ps
0.012	4.32	20.5	5.5	68
0.035	4.27	29.8	5.0	81
0.070	3.80	13.8	5.0	39
0.118	3.21	20.6	5.1	49
0.352	2.12	24.2	4.6	87

[a] ±0.1 ns. [b] ±10 ps. [c] ±0.3 ns. [d] ±20 ps.

Scheme I



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

$$k_{FD} + k_{ID} = k_D$$

decay time is again shorter than 80 ps at all concentrations. Excimer decay times are also listed in Table I. They are nearly identical with the excimer decay times found in dilute solutions of Et_2PDA.

Discussion

Mechanism of Excimer Formation. The mechanism of excimer formation in solutions of Et_2PDA and of PPDA may be inferred from the kinetics of fluorescence decay. The monomer lifetime in both systems is short and independent of chromophore concentration. As a consequence, PDA excimers cannot be formed by the usual bimolecular quenching mechanism but must arise through the excitation of chromophore pairs formed in solution prior to excitation.

The absence of a long-lived component in the monomer fluorescence at 370 nm (see Figure 3) shows that dissociation of the excimer into an excited- and a ground-state monomer does not occur. Finally, the gradual decrease of the excimer lifetime with increasing Et_2PDA concentration indicates that the PDA excimer can be quenched in a bimolecular encounter with the ground state of the chromophore.

These observations are summarized in Scheme I, where M stands for the monomeric chromophore and D represents the chromophore pair which, on excitation, gives rise to the excimer D*. The excited monomer M* can either emit fluorescence ($h\nu_M$) or decay to the ground state by a first-order process (k_{IM}). The excimer may either emit ($h\nu_D$), decay spontaneously to the ground state (k_{ID}), or be quenched by a third ground-state chromophore in a bimolecular encounter (k_Q). The rate constants of the combined decay processes follow directly from the fluorescence lifetimes.

$$\tau_1^{-1} = k_M$$

$$\tau_2^{-1} = k_D + k_Q[M]$$

Their values are

$$k_M = (5 \pm 1) \times 10^{10}\ s^{-1}$$

$$k_D = (2.2 \pm 0.1) \times 10^8\ s^{-1}$$

$$k_Q = (7.3 \pm 0.3) \times 10^8\ s^{-1}\ mol^{-1}\ dm^3$$

The overall rate constant for excimer decay in solutions of PPDA is

$$k_D = (2.4 \pm 0.1) \times 10^8\ s^{-1}$$

The very fast decay of the excited monomer (k_M) is thought to be associated with the "perpendicular" geometry of the excited ethylenic double bond.[15] In this geometry the energy levels of ground and excited states approach each other, thus promoting internal conversion. The rate constant of the radiative process $S^* \rightarrow S + h\nu$, which follows from k_M and q_{FM}, has a value of

$$k_{FM} = q_{FM}k_M = 1.1 \times 10^9\ s^{-1}$$

which is normal for an allowed transition in an aromatic system.[11] The lifetime of the PDA excimer is comparatively long. Excimer stabilization which is derived from the overlap between π and π^* orbitals will oppose an out-of-plane change of geometry and will in this way inhibit the decay channel responsible for the short lifetime of the excited monomer. The emission maxima of monomer and excimer fluorescence are 5750 cm^{-1} apart. This corresponds to an excimer binding energy of about 9 kcal mol^{-1}, comparable to the binding energy of the pyrene excimer.[16] The rate of the radiative deactivation of the excimer, $k_{FD} = 10^7\ s^{-1}$, is also close to that of the pyrene excimer and to that of other excimers reported in the literature.[3]

The rate constant of the bimolecular quenching process (k_Q) is more than an order of magnitude smaller than the diffusion-controlled rate in dichloroethane.[17] This process is therefore only of minor importance.

Equilibrium between Single Chromophores and Chromophore Pairs in Et_2PDA. Fluorescence decay measurements suggest the existence of a ground-state equilibrium between single chromophores and chromophore pairs in solutions of Et_2PDA.

$$M + M \rightleftarrows D \qquad (1)$$

(Ground-state interaction between PDA groups is also indicated by a slight but significant broadening of the absorption spectrum of the chromophore in going from Et_2PDA to PPDA in solution and to the solid PPDA film.) In these conditions the quantum yield of monomer fluorescence in solution is determined by the fraction of incident quanta absorbed by single chromophores

$$\phi_{FM} = q_{FM}\frac{\epsilon_M[M]}{\epsilon_M[M] + \epsilon_D[D]} \qquad (2)$$

Here ϵ_M and ϵ_D are the molar extinction coefficents of single chromophores and of chromophore pairs and [M] and [D] stand for the molar concentrations of the two species. If the ground-state equilibrium in solution is characterized by an equilibrium constant

$$K = [D]/[M]^2 \qquad (3)$$

eq 2 may be written in the form

$$q_{FM}/\phi_{FM} = 1 + 2K[M] \qquad (4)$$

where the factor 2 appears because $\epsilon_D = 2\epsilon_M$. Equation 4 resembles the Stern–Volmer law,[18] but K has now a different significance and [M] is the concentration of the monomeric component only. In terms of the overall chromophore concentration

$$[M]_0 = [M] + 2[D] \qquad (5)$$

eq 4 takes the form

$$q_{FM}/\phi_{FM} = 1 + \tfrac{1}{2}\{\sqrt{1 + 8K[M]_0} - 1\} \qquad (6)$$

In Figure 4 the ratio q_{FM}/ϕ_{FM} is plotted logarithmically as a function of $[M]_0$. The experimental data show a reasonable fit with eq 6 for a value of $K = 1.0$. Only at high concentrations ($[M]_0 > 0.3$ M) do the experimental points deviate seriously from eq 6, and here the monomer fluorescence is lower than predicted for the equilibrium. We believe this effect is caused by energy transfer from excited monomer to chromophore pairs. A similar behavior is observed in concentrated solutions of PPDA.

The ratio of excimer-to-monomer fluorescence, $R = \phi_{FD}/\phi_{FM}$, can be treated similarly. In a mixture of single and of paired chromophores, R is determined by the ratio of the incident radiation quanta absorbed by either species.

$$R = \frac{q_{FD}}{q_{FM}}\frac{\epsilon_D[D]}{\epsilon_M[M]} = 2\frac{q_{FD}}{q_{FM}}K[M] \qquad (7)$$

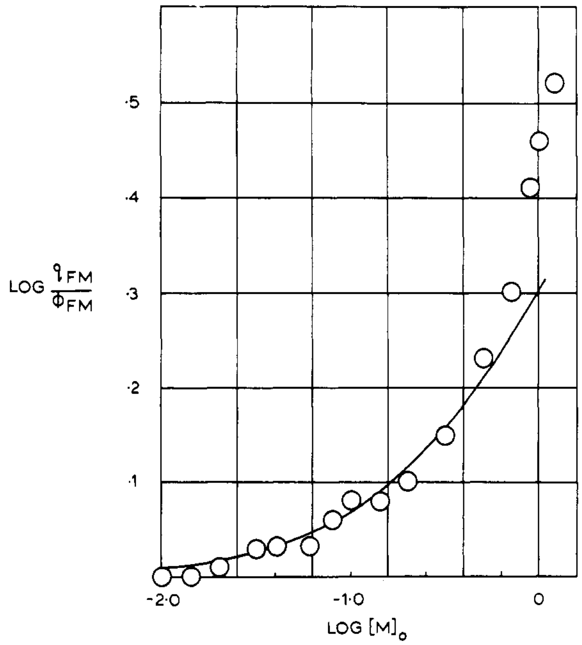


Figure 4. Concentration quenching of the monomer fluorescence in solutions of Et_2PDA in 1,2-dichloroethane. The solid line corresponds to eq 6 for a value of the equilibrium constant K = 1.0.

In terms of the overall chromophore concentration eq 7 takes the form

$$R = \frac{\phi_{FD}}{\phi_{FM}} = \frac{1}{2}\frac{q_{FD}}{q_{FM}}\{\sqrt{1 + 8K[M]_0} - 1\} \tag{8}$$

In Figure 2 the experimental data are compared with eq 8 for a value of $K = 1.0$ and are seen to be in reasonable agreement with the equilibrium prediction, up to a concentration of about 0.3 M. Above that concentration excimer fluorescence is favored at the expense of monomer fluorescence because of energy transfer from the excited monomer to a chromophore pair.

In summary, the fluorescence of Et_2PDA solutions is well described in terms of a ground-state equilibrium between single molecules and molecular pairs. The equilibrium constant $K = 1.0$, equivalent to a standard free energy change of $\Delta G^\circ = 0$, indicates a weak ground-state interaction between the PDA chromophores.

The correlation between excimer fluorescence and the ground-state association of PDA groups, established on the model of Et_2PDA, will now be used to probe chromophore interactions in the photoreactive polymer PPDA.

Chromophore Correlation in Solutions of PPDA. It will be recalled that in PPDA the chromophores are part of the polymer backbone. Excimers cannot, therefore, be formed between nearest neighbors in the chain but must arise through contacts between different macromolecules or between distant parts of the same chain. In this respect PPDA differs from most excimer-forming polymers reported in the literature,[19] where the active chromophores are located in side chains and where nearest-neighbor interaction is the dominant factor.[20]

Another point of difference between PPDA and, for example, polystyrene[22] or poly(vinylnaphthalene)[23] is the absence of down-chain energy migration.[19] In PPDA neighboring chromophores do not easily adopt a parallel orientation; also, they are separated by at least 15 Å, which is just beyond the critical distance for Förster transfer between identical chromophores.[18] As a result, *every quantum of excimer emission in PPDA must be associated with a radiation quantum absorbed by a chromophore pair. Excimer fluorescence monitors therefore directly and in absolute terms the intramolecular and intermolecular contacts of the polymer chain.* The fraction of PDA units which take part in such contacts is defined as

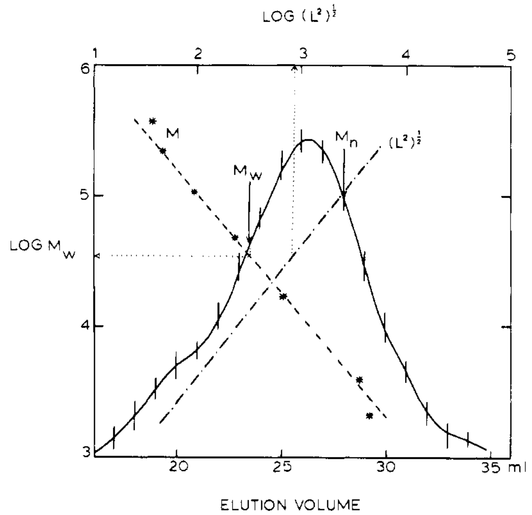


Figure 5. GPC elution curve of PPDA in THF solution. The correlation line M relates to the molecular weight calibration with narrow polystyrene fractions (experimental points indicated by asterisks); the correlation line $(L^2)^{1/2}$ refers to the corresponding mean-square end-to-end distances.

$$f_D = 2[D]/[M]_0 \tag{9}$$

It follows from eq 5 and 7 that f_D is related to the fluorescence ratio by the expression

$$f_D = R/(R + Q) \tag{10}$$

With these preliminaries the fluorescence behavior of PPDA in solution can now be discussed. The experimental results are summarized in the upper part of Figure 2. Three branches of the R vs. $[M]_0$ curve can be clearly distinguished:

(i) At concentrations below 5×10^{-4} M the fluorescence ratio is independent of the chromophore concentration.

(ii) Between 5×10^{-4} and 0.2 M log R is a linear function of log $[M]_0$ and increases with a slope of about 0.2.

(iii) Above 0.2 M the fluorescence ratio increases steeply with concentration. This branch of the curve reflects the onset of energy transfer from isolated to paired chromophores.

Branches i and ii correspond to the dilute and semidilute regimes in polymer solutions.[24] At concentrations below 5×10^{-4} M the macromolecules are presumed to form isolated coils. In this region all excimers must be the result of intramolecular contacts. It can be seen from Figure 2 that here R has a value of 0.6 which, together with Q = 1.70 leads to f_D = 0.26.

This is a remarkable result. It means that in the isolated PPDA molecule on average every fourth chromophore takes part in an intramolecular contact. Such a high contact frequency implies a more compact arrangement of chromophores than would be encountered in a polymer chain of noninteractive segments. This inference is supported by the combined results of gel permeation chromatography and light scattering. Elution of PPDA with THF in a GPC column calibrated with narrow polystyrene fractions indicates a log normal distribution of molecular weight characterized by the ratio M_w/M_n = 7.7, an apparent weight-average molecular weight of 33 000, and a mean-square end-to-end distance of 800 Å, corresponding to a radius of gyration of 330 Å (see Figure 5). Light scattering in dichloroethane gives a radius of gyration of

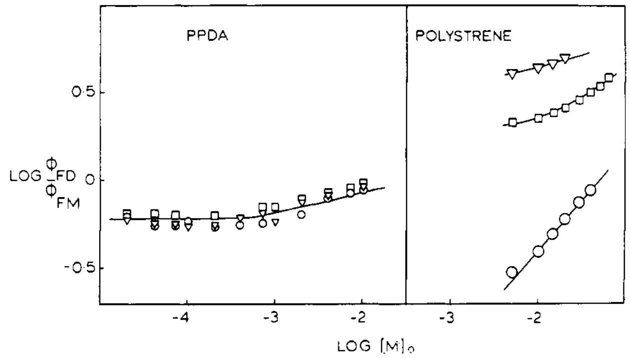


Figure 6. Effect of solvent on the excimer-to-monomer fluorescence ratio for PPDA and for polystyrene. Solvents: (▽) dioxane; (□) 1,2-dichloroethane; (○) chloroform.

350 Å and a weight-average molecular weight of (1.55 ± 0.05) × 10^5. With this molecular weight, PPDA occupies in dilute solution the same molar volume as polystyrene of molecular weight 0.33 × 10^5; evidently, the PPDA molecule is about 5 times more compact than polystyrene.

The positive ground-state interaction responsible for the compactness of PPDA is also confirmed by the insensitivity of the excimer-to-monomer ratio to changes of solvent. The fluorescence ratio measured for PPDA in the three solvents dioxane, dichloroethane, and chloroform is plotted as a function of chromophore concentration in Figure 6 and can be seen to be hardly affected by the solvent change. By contrast, the fluoresence ratios of polystyrene in these solvents differ widely.[25]

The transition from the dilute to the semidilute solution regime occurs for PPDA at a concentration of 5 × 10^{-4} M. The theory of polymer solutions[26] connects this "critical" concentration with the molecular weight of the polymer

$$c^* = kM^{-0.8} \tag{11}$$

Although the preexponential factor remains undefined, recent work of Destor et al.[27] gives it a value of $k = 7 \times 10^3$ g dm^{-3} for poly(oxyethylene) in water and for poly(vinyl acetate) in acetonitrile. With this constant, the critical concentration of PPDA in dichloroethane would be expected at 1.3 × 10^{-3} M. Above c^*, a scaling law of the form

$$R \sim c^{5/4} \tag{12}$$

can be derived from the concentration dependence of R. In a recent series of papers de Gennes and others[24,28-30] have shown that in semidilute solution the average distance (ξ) between intermolecular chromophore contacts depends on the $-^3/_4$ power of concentration. As a result, the number of contacts in unit volume is proportional to $c^{9/4}$, and the fluorescence ratio which monitors the number of contacts per chain should be proportional to the product $c^{9/4}c^{-1} = c^{5/4}$. Roots and Nyström[31] have confirmed this scaling law in their recent work on polystyrene. PPDA solutions, however, behave quite differently and follow a scaling law with a much lower exponent of concentration, viz.

$$R \sim c^{1/5} \tag{13}$$

It is suggested that this is again a consequence of the ground-state interaction between chromophores. The point is illustrated in Figure 7, which shows the lattice diagram of a polyester chain of 100 chromophores in which 13 contact pairs (f_w = 0.26) have been distributed at random. Free flight statistics are evidently inappropriate for this model; chromophore interaction rather establishes a (three dimensional) network which restricts the choice of configurations available to most segments of the free chain. In this way the ability of the free segments to adapt to the orientation of an approaching partner, a precondition of pairing, is much reduced, and hence the weak response of the excimer count to an increase in the overall chromophore concentration.

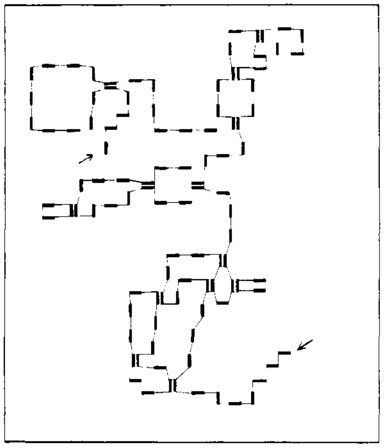


Figure 7. Lattice diagram of a polyester chain of 100 chromophores in which 13 contact pairs have been distributed at random.

The genesis of the matrix morphology which ultimately is responsible for the chemical and the photographic properties of the system may now be described as follows: in dilute solution ground-state interaction between the PDA groups of the polymer ensures a high frequency of intrachain contacts. Up to a chromophore concentration of about 10^{-3} M, on average every fourth PDA group takes part in a contact. As the solvent evaporates and the macromolecules start to overlap, intramolecular contacts are gradually replaced by intermolecular ones,[32] and the overall contact density of the system increases. At a concentration of 0.1 M a state is reached where half of all PDA groups are associated in pairs, and in the highly viscous 1 M solution, just prior to solidification, the fraction of paired chromophores rises to f_w = 0.6. This result agrees well with a chemical analysis of the irradiated matrix,[1] where it is found that about 50% of the products of irradiation are derivatives of β-truxinic acid, the product associated with the excimer. The concordance of all these data shows that the state of aggregation of chromophores in the solid matrix is indeed preformed in solution and arises there in response to a weak ground-state interaction between PDA groups.

It is finally of interest to note the profound effect of the polymer chain on the degree of chromophore correlation. In the isolated coil of a PPDA molecule the "local" concentration of PDA groups is of the order of 10^{-3} mol L^{-1}. If we compare the excimer-to-monomer ratio of a 10^{-3} M solution of Et$_2$PDA with that of the isolated PPDA coil (i.e., a PPDA solution with a nominal concentration of less than 7 × 10^{-4} M), it can be seen that at the same local chromophore concentration the intermolecular forces, which are hardly noticeable in the ensemble of free Et$_2$PDA groups ($R \sim 0.01$), produce in the polymer a high degree of chromophore correlation ($R \sim 0.6$). Thus, the observed behavior is not a concentration effect, but the result of a primitive mechanism of self-assembly, brought about by the cooperative influence of the polymer chain.

Acknowledgment. We thank Dr. A. D. Osbourne and Miss A. Winkworth for help with the streak camera measurements and Mrs. Sheila O'Keefe for the light scattering data.

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Vibrational Spectra and Disorder–Order Transition of Poly(vinylidene fluoride) Form III

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ABSTRACT: Infrared and Raman spectra of poly(vinylidene fluoride) crystal form III with $\mathrm{T_3GT_3\bar{G}}$ molecular conformation have been analyzed by factor group analysis and normal coordinate treatments. Vibrational bands characteristic of some kinds of conformational sequences have been identified: the bands at 299, 776, 811, 1115, and 1134 $\mathrm{cm^{-1}}$ for the $\mathrm{T_3G}$ sequence, the bands at 1385, 858, and 614 $\mathrm{cm^{-1}}$ for the TG sequence, and the bands at 350, 370, 432, 442, 512, 539, 748, 835, 1234, and 1330 $\mathrm{cm^{-1}}$ for the TT sequence. Annealing of the form III sample cast from dimethylacetamide solution results in increased intensities of the $\mathrm{T_3G}$ and TG infrared and Raman bands and decreased intensities of the trans bands. It also results in a high-temperature shift of the DSC melting point, in the sharpening of low-frequency infrared bands (including lattice modes), and in the intensification of X-ray diffraction spots. These experimental observations have been explained by the following disorder–order structural change induced by the heat-treatment process. The as-cast (unannealed) form III crystal consists of disordered chains containing to some extent long trans sequences within the basic repeat $\mathrm{T_3GT_3\bar{G}}$ units (...TTTGTTT$\mathrm{\bar{G}}$TTTTTTTTTGTTT$\mathrm{\bar{G}}$TT...). Annealing at a temperature close to the melting point induces an interchange between gauche and trans rotational isomers, and the molecular chains become much more ordered with regularly repeating $\mathrm{T_3GT_3\bar{G}}$ (...TTTGTTT$\mathrm{\bar{G}}$TTTGTTT$\mathrm{\bar{G}}$...) units.

It has been reported that poly(vinylidene fluoride) (PVDF) crystallizes into at least four types of crystal forms, namely, forms I, II, III, and polar form II ($\mathrm{II_p}$), depending on the crystallization temperature,[1,2] mechanical stress,[3-7] casting solvent,[4,8,9] electric field,[10-14] and other crystallization conditions. In a previous paper[9] we analyzed the vibrational spectra of crystal forms I, II, and III by normal coordinate treatments and confirmed that form III exists as a crystal phase independent of forms I and II. The infrared and Raman spectra of form III cast from a dimethylacetamide (DMA) solution could be explained approximately in terms of an all-trans conformation molecular model because these spectra of the "as-cast" form III are similar to those of form I over the entire 4000–30-$\mathrm{cm^{-1}}$ frequency region (Figure 1). For the high-frequency region of the infrared spectra, Cortili and Zerbi[8] also indicated the similarity of the spectra of form I and form III cast from a dimethyl sulfoxide ($\mathrm{Me_2SO}$) solution. In our previous paper,[9] however, there still remained some problems in interpreting the difference in some parts of the spectra between forms I and III.

Recently, Lando et al.[15] succeeded in obtaining X-ray fiber photographs of uniaxially oriented fiber specimens of crystalline form III that were obtained by stretching the cast film at a temperature immediately below the melting point and proposed that the molecular chain of form III may have one of several possible molecular models, $\mathrm{T_3GT_3\bar{G}}$, $\mathrm{TGT\bar{G}T\bar{G}TG}$, and so on, but not the planar-zigzag conformation of form I. Banik et al.[16-18] supported this suggestion by potential energy calculations. Bachmann et al.[19] obtained the "crystalline" infrared spectra (as they called it) of form III as a difference between the spectra measured before and after annealing of the as-cast form III by Fourier transform infrared spectroscopy. They stated that the weak infrared bands appearing in the spectra of crystalline form III correspond to the gauche bands of form II (molecular conformation $\mathrm{TGT\bar{G}}$) and supported the proposal made by Lando et al.,[15] although

0024-9297/81/2214-1757$01.25/0