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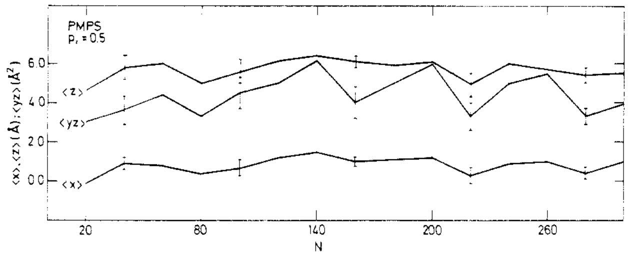

Figure 4. Variation of some components of $\langle \mathbf{R} \rangle$ and $\langle \mathbf{RR}^T \rangle$ with N; $\delta\varphi = 15°$, $p_r = 0.5$. Illustrative errors bars are included.

tributed to the high influence of the stereochemical definition of the first diads on those asymmetry effects. This way, a Monte Carlo sample of stereochemical sequences which gives excellent reproduction of even moments $\langle R^{2p} \rangle$ may yield a less satisfactory description of spherically asymmetric averages. Though these oscillations are only slighly higher than the statistical errors associated to our averages, they are significant enough to preclude an asymptotically well-defined diagonalization of $\langle \mathbf{RR}^T \rangle$ for the longest chains, diagonalization which was customarily used to define the three principal axes in other polymers.[6,9,10]

As a concluding remark, we can state that the quasi-analytical scheme to obtain moments and distribution functions of **R** established in previous work for simpler chains is also useful to obtain these quantities in the case of chains with nonregular stereochemical structures. Consequently, we have been able to perform such calculations for atactic PMPS chains with different replication probabilities. Though some subtle characteristics related with the asymmetry of **R** may require wider Monte Carlo samples of stereochemical sequences, most of the conformational properties of these chains can be successfully calculated with this numerically efficient scheme. A dramatic increase of the cyclization probability and non-Gaussian effects for chains close to the isotactic limit is the main prediction of our calculations. The lack of extensive experimental work on conformational properties of PMPS chains with well-known tacticity precludes, however, a direct comparison of these calculations with experimental data.

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Coil Dimensions of Poly(2-vinylnaphthalene) in Solution and Their Influence on Triplet Photophysics

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ABSTRACT: A quantitative determination of the coil dimensions of poly(2-vinylnaphthalene) (P2VN) in different solvents and solvent mixtures has been made by using disymmetry coefficients determined from measurements of Rayleigh light scattering. The polymers were prepared by using standard methods of anionic polymerization. Triplet luminescence spectra were recorded in these different solvents at 77 K and ambient temperatures. Pulse-probe methods were used to determine concentrations of transient triplets as a function of time following laser excitation. The specific rate constants for triplet–triplet annihilation were evaluated by assuming exclusively intramolecular processes and were found to increase regularly with decreasing coil radius. Ratios of the intensities of delayed fluorescence to phosphorescence in these solvents were also consistent with the conclusion that triplet–triplet annihilation increases in rate as the effective coil volume decreases. It is concluded that triplet exciton migration does not occur exclusively along the chain contour and that nonneighbor processes make a significant contribution.

Introduction

The focal point of this particular study is upon average interchromophore separation distances in poly(2-vinylnaphthalene) in good and poor solvents and the effect which a variation in these distances might have upon the photophysics of triplet states of the naphthalene chromophore produced by laser photoexcitation. It is well-known that an important component of the triplet state photophysics of vinyl aromatic polymers is that of energy migration, often described as random exciton hopping.[1] It seems important to sharpen the image of this process and try to learn whether or not the steric constraints imposed by the presence of the aromatic chromophore on every third backbone carbon atom moderate, in any way, the randomness of the migratory process.

The basic question that the study is intended to address is whether the migration process most closely resembles a one-dimensional neighbor-to-neighbor process or a three-dimensional randomly oriented process. These, of course, are the extremes of behavior which are to be expected. In any real system one must be prepared to deal with intermediate cases. To approach this question a decision was made to test the effect of altering average interchromophore separation distances in isolated polymer molecules by the use of good and poor solvents for P2VN. To a first approximation, one expects the average neighbor-neighbor distance to be unaffected by a variation in average coil radius. That is, these distances would be

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expected to be essentially the same whether the chain is fully stretched out or tightly coiled. On the other hand, a net average decrease in interchromophore separation distance would be expected as a result of tighter coiling of the macromolecule in relatively poor solvents as nonnear neighbors are forced into a more confined volume. With this picture in mind, the rate of energy migration of a strictly neighbor-to-neighbor process should depend little, if at all, upon the overall coil dimension. Conversely, a three-dimensional random hopping process should reflect, in its rate, a strong dependence upon coil radius. The necessary components of such a study include a reliable method to determine changes in polymer coil dimensions in the various solvents employed. In addition, a trustworthy evaluation of rates of triplet energy migration must also be employed.

To evaluate the dimensions of polymer coils, it was noted that Rayleigh light scattering has been used for many years as an accepted technique to probe the behavior of polymer chains in solution.[2] Solute–solvent interactions, as reflected in the second virial coefficients, as well as root-mean-square end-to-end distances and radii of gyration are among the properties which this method are able to provide. It was decided, therefore, to use this method in the present work in order to evaluate coil dimensions in the various solvents and solvent mixtures employed.

In order to monitor relative rates of triplet energy migration, it is convenient to use the process of triplet-triplet annihilation, which leads to delayed fluorescence (DF). The rate-controlling step in T–T annihilation is translational motion: either energy transfer of else bulk diffusion of the chromophores.[3] Since phosphorescence is a first-order process and independent of interchromophore separation distance, one useful measure of relative translational rates is the ratio of DF intensity to phosphorescence intensity. A more direct evaluation of the rate of DF is the determination of the second-order rate constant associated with this process. Both of these methods are employed in the present work.

Experimental Section

1. Monomer Purification. Commercially available (Aldrich Chemical Co.) 2-vinylnaphthalene (2VN) was recrystallized from 95% ethanol. It was next eluted with 70/30 benzene/cyclohexane (volume/volume) through a 60–200 mesh silica gel column, with the first four 12-mL fractions recovered. The solvent was stripped from the monomer and then placed in a vacuum oven to remove any remaining solvent. The monomer was further purified by two vacuum sublimations.

2. Anionic Polymerization. Two polymers were synthesized by anionic polymerization using *n*-butyllithium (*n*-BuLi) initiator.[4] Using an oxygen-free environment in a glovebox, 2 g of 2VN monomer in 10 mL of dry tetrahydrofuran (THF) was purged with dry nitrogen gas in order to remove any absorbed oxygen. In a separate container, 2 mL of this monomer solution was combined with 0.25 mL of tetramethylethylenediamine (TMEDA). To this solution was added 1 mL of *n*-BuLi (1.6 M in hexanes) by syringe. The solution took on a deep red-brown as the anions were formed. The remainder of the monomer solution was added by pipet. When the reaction was complete, purified methanol was added to ensure total quenching of the anions.

In the case of the first polymerization, 1 mL of *n*-BuLi was added. For the second polymer synthesis, 0.20 mL of initiator was used with approximately 3 g of monomer in solution. In the discussion below, these polymers are referred to as P2VN#1 and P2VN#2, with respect to their order of synthesis.

The polymers were purified by two reprecipitations of their benzene solutions from methanol. Approximately 0.83 and 1.4 g of P2VN#1 and P2VN#2, respectively, were recovered.

3. Characterization of Synthesized Polymers. The two polymers were characterized for molecular weight by means of light scattering[5] measurements in benzene solution. Light scattering measurements were made by using a Brice-Phoenix light scattering photometer[6] modified for use with a Tektronix DM-44 digital voltmeter as a voltage measurement device. Instrument calibration was done by using a polystyrene standard[7] with a reported weight-average molecular weight of 110 000 g/mol as determined by viscosity. Optical grade benzene solvent was clarified by centrifugation for 20 min at 10 000 rpm in a Sorvall centrifuge. Solutions made up in this centrifuged solvent were then filtered through a 0.2-μm filter (Millipore GVWP02500) directly into the sample cell. Specific refractive index measurements available in the literature[8] were used to calculate the weight-average molecular weight of the polymer. The molecular weights determined by this method are 1.34×10^4 and 1.29×10^6 g/mol for P2VN#1 and P2VN#2, respectively.

Light scattering was also used to evaluate polymer coil dimensions in the various solvents and solvent mixtures. For the 2-methyltetrahydrofuran solutions and the mixed solvents, a Brice-Phoenix differential refractometer was used to measure the refractive index increments. Turbidity measurements were made at various angles and extrapolated to 0° by using the method of Zimm[9] in order to account for nonisotropic light scattering at 90° due to the large molecular size in comparison to the wavelength of the incident light.[10]

4. Solvents and Solvent Mixtures. Solvents were chosen for their glass-forming ability at 77 K and for their varying solubility properties. Mixtures of 2-methyltetrahydrofuran/isopentane were found to be glass-forming and capable of dissolving the polymers up to 40% (by volume) of isopentane. The various solvents used were purified as follows.

Reagent benzene was shaken with equal volume of H_2SO_4 to remove any dissolved thiophene. It was then washed with dilute NaOH and then twice with H_2O. It was dried over anhydrous sodium sulfate and then distilled from P_2O_5. A final reflux over CaH_2 was performed for 2 h, and then the distillate was stored over molecular sieves.

Reagent grade 2-methyltetrahydrofuran was first run through an activated alumina column to remove any peroxides and inhibitors. It was then distilled from lithium aluminum hydride.

Reagent grade methanol was refluxed for 2 h with $CuSO_4$ and then distilled with the first and last 10% fractions discarded. It was then refluxed with Ca metal for 2 h and then distilled. A final 2-h reflux was done with $AgNO_3$ followed by distillation. Again, the first and last fractions were discarded.

Tetrahydrofuran used in the polymer syntheses was first run through an activated alumina column to remove any inhibitor. It was then refluxed with a Na–K amalgam and benzophenone, which imparted a deep blue color to the solution as an indication of dryness. This solvent was collected by distillation as needed.

Methylcyclohexane and isopentane (2-methylbutane) were both spectral grade and were used without any further purification.

5. Sample Preparation. Solutions were made up in 25-mL volumetric flasks at a concentration of approximately 10^{-3} M, with freshly distilled solvent. They were transferred by using a Pasteur pipet into 40-mm o.d. quartz tubes. Spectral and kinetic analyses of frozen solutions took place in an optical (quartz-walled) Dewar flask filled with liquid nitrogen to maintain the sample temperature at 77 K. Triplet–triplet absorption experiments at 77 K were carried out with samples sealed in 1-cm diameter cylindrical cells with quartz windows. These cells have a 1-mm path length. Fresh solution was added to a clean cell attached to a ground-glass joint that allowed the cell apparatus to be attached to a high vacuum system. The solution was degassed by multiple freeze–pump–thaw cycles and was then sealed off under vacuum by using a hand torch.

Ambient temperature measurements utilized a similar quartz cylindrical cell, but having a 10-mm path length. This cell was attached to a reservoir and a standard taper joint in a T fashion. The sample solution (approximately 20 mL) was introduced into the reservoir, and the apparatus was then attached to the vacuum system. Again, multiple freeze–pump–thaw cycles were used to degas the solution, and then the cell configuration was sealed off under vacuum by using a hand torch. The sample was transferred to the cell for analysis by tipping the thawed solution from the reservoir into the cell.

6. Instrumentation for Luminescence Measurements. Two different instruments were used for luminescence mea-

Table I
Polymer Coil Dimensions Determined from Z_{45} for P2VN#2 at Ambient Temperature

solv	Z_{45}	$10^6 R_e$, cm
benzene	5.45	9.24
MTHF	1.397	4.68
30/70 IP/MTHF	1.057	1.96

surements. One employed a constant-beam source and has been described before in the literature.[11] This phosphorimeter was of conventional design, and its essential features are the following. A 1000-W Hg–Xe source was used for excitation. Mechanical choppers driven by synchronous motors were used to chop the excitation and emission beams and were phased so that excitation light could not leak past the blades of the emission chopper. The emission beam was directed to the slits of a monochromator and, after traversing the monochromator, was detected by an end window photomultiplier. The other system employed pulsed laser excitation and has also been described in earlier publications from this laboratory.[12] It employs a XeCl excimer laser (Tachisto model 401XR) as an excitation source. The pulse width of this laser, 20 ns, provided the capability for measurement at very short delay times. In this system luminescence was monitored by using a SPEX monochromator (Model 1135) and a Thorn-EMI Gencom photomultiplier (Model RFI/B289). The photomultiplier high voltage was provided by a Butler Designs Pacific (Model HV-1565) power supply. The output was amplified and inverted by using an operational amplifier assembly before being collected with a Nicolet LAS 12/70 signal averager.

Data from both instruments were collected digitally by using signal averaging computers and were then transferred to a mainframe computer for analysis. The exception to this method was for the ambient temperature triplet–triplet absorption experiments, where voltage measurements were made from oscilloscope traces, and the data were manipulated manually.

In both systems a portion of the excitation beam was sampled to supply a trigger pulse to an oscilloscope (Tektronix Model 465) which in turn, after an established delay time, supplied a secondary trigger pulse to the signal averager. Data acquired in the signal averager were transferred by RS232C serial output to a buffered Tektronix 4025 terminal and then transferred to the University's CDC Cyber 830 computer for analysis. Data were also stored on an IBM System 9000 benchtop computer by RS232C serial output.

7. Triplet–Triplet Absorption Measurements. Triplet–triplet absorption measurements were made by using the laser system with the following modifications. A tungsten lamp connected to a d.c. power source (a 12-V automotive battery) was used to probe the sample along the same axis as the laser excitation. A square quartz window was placed directly in the path of the laser beam in front of the sample holder. It was oriented so that its top edge was parallel to the table top and makes an angle of 45° with the laser beam path. The probe beam makes an angle of 90° with the laser beam path and is directed to reflect off the center of the quartz window. Thus, the reflected portion of the probe beam and laser beam travel the same path from the quartz window to the sample. Of course, only a portion of the probe beam was reflected, but it was of adequate intensity to provide sufficient illumination of the sample. A portion of the laser excitation was also reflected by this quartz plate, but it was a high intensity beam and the loss due to reflection was negligible. A rectangular slit of dimensions 10 mm by 5 mm used with the long axis vertical was placed adjacent to the cell. The probe beam was focused by using quartz lenses such that the entire area within the slit was illuminated. The laser excitation beam was focused by using quartz lenses in order to uniformly illuminate the area within the slit. This method assured that all of the luminescence seen by the detection system was from a sample that had been uniformly illuminated by both the probe and the laser excitation beams. Absorption of the constant-intensity probe beam by triplet species after laser excitation was monitored at 425 nm, where an extinction coefficient of 12 000 M cm^{-1} been determined.[13]

Results and Discussion

Values of the root-mean-square radius of gyration, R_e, for P2VN#2 were determined from the disymmetry coefficients,[14] Z_{45}, and are found in Table I. The value of Z_{45} was determined from the ratio of the intensity of scattered light at 45° versus 135°. The R_e values were then determined from scattering functions[5] for random coil polymer molecules. Both benzene and MTHF are ordinarily thought of as good solvents for P2VN; however, these results indicate that benzene is definitely the better solvent of the two. Of course, the addition of a nonsolvent, isopentane, accomplishes the expected result of decreasing, even further, the coil dimension of the polymer. An attempt was made to use a 50/50 mixture of isopentane and MTHF, but the solubility of P2VN#2 was marginal in this mixture and it was not possible to be certain that a homogeneous solution formed. In any event, a nearly 5-fold change in R_e is found here which produces a change in coil volume of greater than one-hundred-fold. The results obtained by using light scattering are also reflected in differences in intrinsic viscosities determined for P2VN#1 in these same solvents. In units of cm^3/g, intrinsic viscosities of 48.0, 34.8, and 14.1 were determined for benzene, MTHF, and the 30/70 IP/MTHF mixture, respectively. Unlike its higher molecular weight counterpart, the P2VN#1 sample was found to be soluble in a 50/50 mixture of IP/MTHF. Viscosity measurements were not attempted in this mixture, however, because of the rather rapid evaporation of isopentane that produced significant uncertainties in the solvent composition upon extended exposure in the open laboratory. It was, however, possible to obtain emission spectra from these solutions at 77 K as will be seen below.

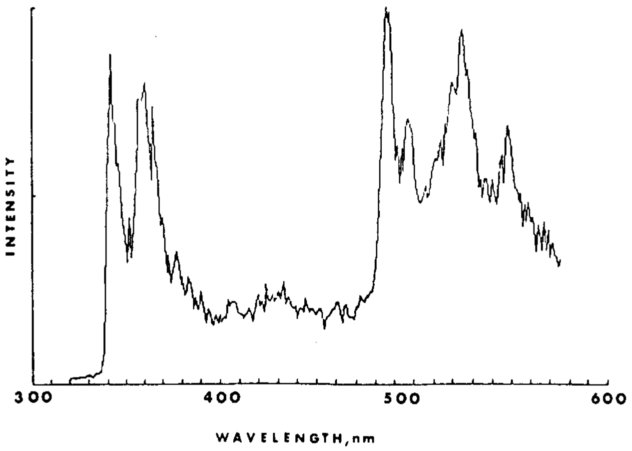

Figure 1. Delayed luminescence spectrum of P2VN#2 in MTHF at 77 K. Chromophore concentration is 1.5 × 10^{-3} M, and the delay time is 10 ms.

The delayed emission spectrum at 77 K of P2VN#2 is illustrated in Figure 1. The phosphorescence band begins at 484 nm, and the onset of delayed fluorescence occurs at 338 nm. The solution concentration was 1.5 × 10^{-3} M, and the solvent is MTHF. This spectrum is recorded at a delay time of 10 ms after the excitation pulse. In every case where direct comparisons were made between delayed emission spectra of P2VN#1 and P2VN#2 the ratio of intensities of delayed fluorescence to phosphorescence was greater for the higher molecular weight compound in agreement with earlier observations of this interesting effect.[15]

There is very little effect upon emission spectra of a change in solvent apart from changes in the ratio of DF intensity to phosphorescence intensity. It is a basic assumption in this work that differences in solvent quality measured at ambient temperature will also hold true, at least in a relative sense, at 77 K. Thus, it seems very likely that a decrease in R_e which is found in going from pure

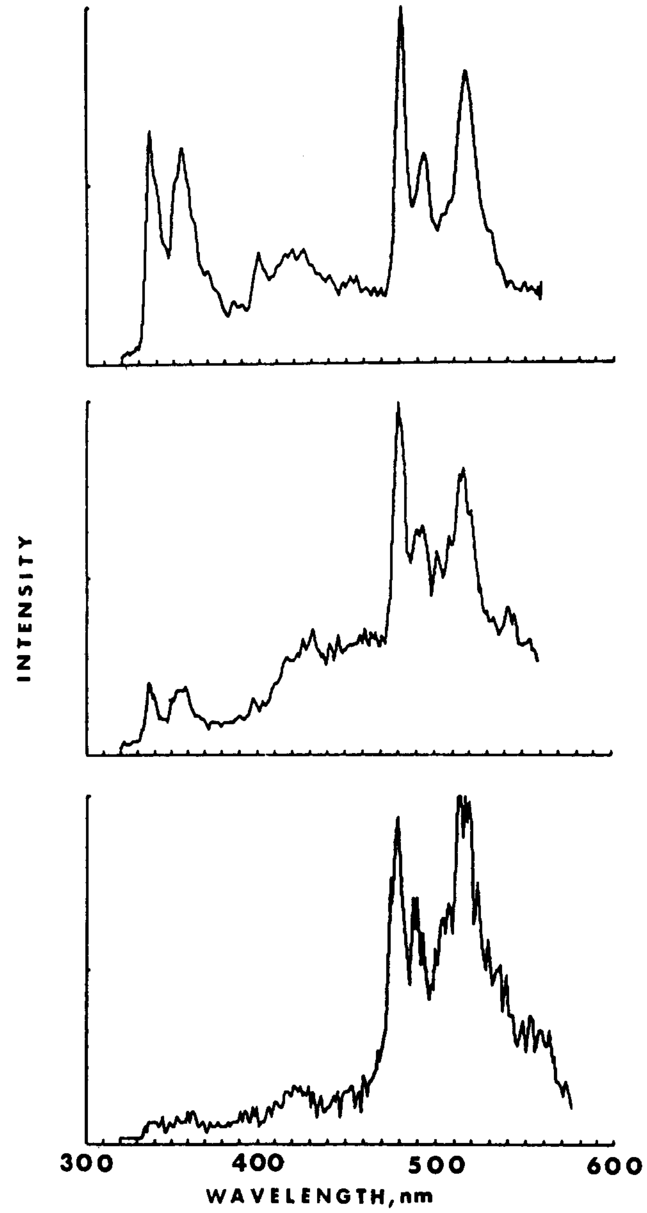

Figure 2. Delayed luminescence spectra for P2VN#1 at 77 K and a delay of 10 ms after excitation. Top is in pure MTHF, middle is in 30/70 isopentane/MTHF, and bottom is in 50/50 isopentane/MTHF.

MTHF to 30/70 IP/MTHF at ambient temperature would also be found at 77 K. In fact, from equilibrium thermodynamics, one expects that any differences observed at 298 K would be even more pronounced at 77 K. This view is further reinforced by experiments of Jackowicz and Morawetz,[16] who found that the degree of polymer interpenetration which occurred upon freezedrying polymer solutions depended upon the concentrations of the initial fluid solutions.

A comparison between emission spectra obtained at 77 K for solutions of P2VN#1 in MTHF, 30/70 IP/MTHF, and 50/50 IP/MTHF is presented in Figure 2. In each of these spectra the delay time after excitation is the same at 10 ms. A significant point to notice is that the intensity ratios of DF to phosphorescence decrease monotonically as the solvent quality decreases. In fact, for the 50/50 mixture there remains only a suggestion of delayed fluorescence emission at 10 ms after the excitation pulse. These data suggest that the DF signal is decaying away more rapidly as the coil dimension decreases. This may mean that the annihilative process is occurring at a faster rate as the effective local concentration of chromophores within a given polymer coil increases. If the triplet–triplet annihilation rate is enhanced with decreasing coil size, then the singlet–singlet annihilation rate may be similarly enhanced.[17] Masuhara and co-workers[18] have effectively demonstrated the importance of these singlet–singlet processes especially in polymeric systems. Thus, it is necessary to use an experimental approach directly related to triplet state processes in order to determine the effect of coil size on rates of intramolecular triplet migration. We will now explore these effects further by an examination of rates of delayed fluorescence decay in different solvents.

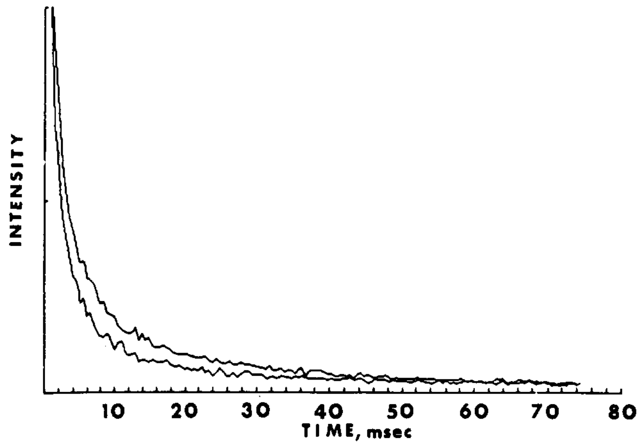

Figure 3. Decay of delayed fluorescence intensity of P2VN#2 at 77 K. The upper curve is for pure MTHF, and the lower is for a 40/60 mixture of isopentane/MTHF.

Since the rate of DF decay at any time after the excitation pulse depends upon the absolute value of the triplet concentration, these comparison experiments had to be done as a pair to be certain that the intensity of the excitation pulse was the same for each sample. Experience has shown that a gradual decrease in pulse intensity occurs after each fresh refill of the active gases in the excimer laser. The chromophore concentrations should be comparable as well, but, in this experiment, the concentration in pure MTHF was actually twice that in the mixed-solvent system. This difference does not, however, compromise the conclusions as will be seen below.

The DF decay monitored at 345 nm for P2VN#2 in pure MTHF and in a 40/60 mixture of isopentane/MTHF is illustrated in Figure 3. The detector sensitivity was adjusted to provide, as nearly as possible, the same zero time luminescence intensity for each sample. It is clear that the rate of DF decay is more rapid in the mixed solvent especially during the early stages of the decay period. This is true in spite of the fact that the beginning triplet concentration in MTHF is definitely larger than in the mixed solvent due to the larger chromophore concentration in the case of pure MTHF. Of course, this disparity in triplet concentration would be relevant only if intermolecular processes were occurring concurrent with intramolecular ones. These results, therefore, provide a further indication that a decrease in coil dimension produces a more rapid rate of triplet exciton migration. Let us now turn to a third experimental approach to test this conclusion involving a determination of the specific rate constant for triplet–triplet annihilation.

The energy gap between the first excited triplet state of the naphthalene chromophore and the first excited singlet state is too large to accommodate a delayed fluorescence mechanism based upon thermally assisted reverse intersystem crossing from T_1 to S_1, the so-called "E-type" process. It would seem, therefore, that an an-

Table II
Specific Rate Constants for T-T Annihilation for P2VN#1 in Different Solvents at 77 K

solv	$10^{-5}k_2$, M^{-1} s^{-1}
MTHF	1.0 ± 0.1
30/70 IP/MTHF	1.3 ± 0.1
50/50 IP/MTHF	1.9 ± 0.2

nihilative mechanism for delayed fluorescence, the "P-type" process, should be accepted by default. Nevertheless a positive indication of the existence of the annihilative mechanism was sought by earlier investigators of the triplet photophysics of P1VN by monitoring the effect of excitation intensity upon the intensity of DF.[19] At sufficiently low values of the intensity of absorbed radiation, it is predicted and found that the DF intensity should depend upon the square of the excitation intensity. This dependence was again tested in the present investigation and, as found in earlier work, the square law dependence is obeyed.

In view of this result it is clear that triplet state chromophores may disappear by the concurrent processes

$$T \rightarrow {}^1S_0 + h\nu_{\text{phos}} \qquad (1)$$

and

$$T + T \rightarrow {}^1S^* + {}^1S_0 \qquad (2)$$

We assume that, in all of these results, the solutions are sufficiently dilute so that the observed phenomena are intramolecular in character. If, as the spectroscopic results suggest, triplet exciton migration occurs between nonneighbors as well as neighboring chromophores, it may be reasonable to view this intramolecular migration as a random hopping process. In this case each polymer coil could be viewed as a separate, very small, reaction vessel and the rate equation which would apply, on average, to each of these coils is

$$-\mathrm{d}T/\mathrm{d}t = k_1T + k_2T^2 \qquad (3)$$

where T is the triplet concentration and k_1 and k_2 refer to rate constants for steps 1 and 2, respectively. The solution to this equation is straightforward and has been used in recent publications from this laboratory to evaluate the rate constants, k_2, from triplet decay data.[12] The results of such an analysis are presented in Table II. For these experiments the polymer sample used was P2VN#1 since it formed homogeneous solutions in a wider range of solvent compositions.

The major observation here is that the specific rate constant for triplet–triplet annihilation increases monotonically as greater proportions of the nonsolvent are present in the solvent mixture. It is clear that these results are consistent with the observed intensity ratios of DF to phosphorescence found in the emission spectra recorded in different solvents and also consistent with the more rapid rate of DF decay for a solvent mixture compared with pure MTHF. This tends to reinforce the view proposed earlier that triplet exciton migration is not strictly a one-dimensional process involving hopping events along the contour of the polymer chain and may, in fact, approach a three-dimensional random flight model.

At ambient temperature the rate of triplet–triplet annihilation is expected to be controlled by a combination of exciton migration and intramolecular bulk translational diffusion of polymer segments. A random flight model is, therefore, to be expected in this case. In Table III a summary is given of k_2 values for T–T annihilation at these elevated temperatures in the various solvent systems.

Table III
Values of the Rate Constant for Triplet-Triplet Annihilation Obtained at Ambient Temperature for Two Samples of P2VN

solv	$10^{-8}k_2$, M^{-1} s^{-1}	solv	$10^{-8}k_2$, M^{-1} s^{-1}
P2VN#1		P2VN#2	
benzene	4.8 ± 0.02	benzene	2.9 ± 0.4
MTHF	5.8 ± 0.2	MTHF	3.6 ± 0.2
30/70 IP/MTHF	4.5 ± 0.5	30/70 IP/MTHF	4.2 ± 0.3

At ambient temperature the observed rate constants are over 3 orders of magnitude larger than at 77 K. It is interesting that, in general, the rate constants are somewhat smaller for the larger molecular weight compound, P2VN#2. Furthermore, there seems to be a trend toward larger values of k_2 with decreasing solvent quality for P2VN#2 but no trend is found for P2VN#1. Further experimental work will be needed to establish the relative contributions of energy transfer and translational diffusion to the overall rate of triplet–triplet annihilation in polymeric systems dissolved in fluid media.

Conclusions

The coil dimensions of P2VN vary in the expected way with changes in solvent quality as determined by light scattering experiments. In particular, the addition of a nonsolvent, isopentane, to the solvent, MTHF, produces a significant contraction of coil volume. The rate of triplet decay, as determined by an evaluation of specific rate constants for triplet–triplet annihilation at 77 K, shows a definite increase as the polymer coil decreases in volume. The ratio of delayed fluorescence to phosphorescence intensity at a fixed delay time after the excitation pulse decreases with a decrease in coil volume. It is concluded that the rate of energy transfer in isolated polymer molecules depends upon the effective coil volume, increasing in size as the coil volume decreases. Since this type of behavior would not be expected for a purely neighbor-to-neighbor mechanism for energy migration, it is concluded that nonneighbor energy migration events occur to a significant extent in P2VN.

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Registry No. P2VN, 28406-56-6.

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Aggregation of Amylose in Aqueous Systems: The Effect of Chain Length on Phase Behavior and Aggregation Kinetics

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ABSTRACT: Nearly monodisperse amyloses having a wide range of chain lengths have been enzymically synthesized in vitro. The rate of aggregation from aqueous 0.2–5.0% solution and the physical form of extensively aggregated material have been studied as a function of chain length. Aggregation (monitored by turbidity) is found to be most rapid for chain lengths of ~100 residues in agreement with previous results (Pfannemüller, B.; Mayerhöfer, H.; Schulz, R. C. *Biopolymers* **1971,** *10,* 243–261) for initial aggregation rates in 0.1% solution. Amyloses having chain lengths of <110 residues are found to precipitate from aqueous solution. Both precipitation and gelation occur for chain lengths of 250–660 residues. For longer chains (>1100 residues) gelation is found to predominate over precipitation. The variation of phase behavior and aggregation rate with chain length is rationalized on the basis of ordered polymer–polymer associations involving chain segments of typically less than 100 residues.

Introduction

Amylose is an essentially linear polysaccharide composed of α-(1$\rightarrow$4)-linked D-glucose units. It occurs naturally in starch granules together with amylopectin, an α-(1$\rightarrow$4)-linked D-glucan which is highly branched through additional α-(1$\rightarrow$6) linkages. Starch granules contain densely packed polysaccharide and include regions of long-range ordering (crystallinity) which are thought to involve crystallization of amylopectin branches.[1,2] Amylose is considered to be present predominantly in the amorphous phase of starch granules.[1,2] Heating aqueous dispersions of starches causes granules to expand and amylose to be leached from the amorphous phase.[1,2] Subsequent aggregation of the amylose is thought to be responsible for the formation of viscoelastic pastes or, at higher concentrations, gels after cooling hot aqueous starch dispersions.[3,4]

The properties of amylose in aqueous solution have been widely studied.[1] Results from light-scattering experiments[1,5] show that amylose in aqueous solution has the properties of a non-free-draining coil with calculated unperturbed values of the characteristic ratio and persistence length of ~4.5 and 12.1 Å, respectively.[1,5] The aggregation of amylose in dilute (<0.5% w/v) aqueous solutions has been studied by a number of workers principally using light-scattering methods.[6-9] A major finding of such studies is that the rate of aggregation of amylose is strongly dependent on the chain length (degree of polymerization, DP). With increasing chain lengths, amylose aggregation is first slow (for DP < 50), increases rapidly to a maximum rate[9] (at DP ~ 80), and then becomes steadily slower until, for DP > 2000, only slow and limited aggregation is observed in dilute solution.[6,7] Explanations for this unusual behavior have invoked the presence of regions of rigid helical conformations (of ~80 residues[9] or 40–900 residues[8]) within chains, but there is no convincing experimental evidence for this assertion, and the relatively short (for polysaccharides[10]) persistence length of amylose in solution[1,5] would seem to preclude significant rigid helical segments.

In the present work we have extended these previous studies by examining the influence of amylose chain length on aggregation behavior in aqueous solutions of higher concentrations (0.5–5.0% w/v) than have hitherto been studied systematically. As the amylose content of starches is typically 20–25%, this concentration range corresponds to concentrations of starch (~2–20% w/v) which are used to form pastes or gels. Although amyloses from different botanical sources show molecular weight variations, they are all polydisperse (DP_w/DP_n = 1.3–3.4)[11,12] and are therefore unsuitable for detailed studies of chain length effects. Furthermore, many natural amyloses are not completely linear due to a small proportion of α-(1$\rightarrow$6) branching linkages.[1,13] However, it is possible to synthesize enzymatically strictly linear amyloses of very narrow molecular weight distribution in vitro by using the enzyme phosphorylase.[14]

In this report, we describe the phosphorylase-mediated synthesis of amyloses of narrow molecular weight distribution and their aggregation behavior in aqueous solutions. A preliminary account of part of this work has been reported.[15] In the following two reports, we describe rheological studies on amylose gels[16] and discuss the molecular mechanisms underlying amylose aggregation.[17]

Materials and Methods

Maltoheptaose was obtained from Boehringer and glucose 1-phosphate (dipotassium salt) from Sigma. Phosphorylase activity was assayed by the method of Lee,[18] amylase activity by the method of Fischer and Stein,[19,20] and phosphate according to Lowry and Lopez.[21]

Purification of Potato Phosphorylase.[22-24] Potatoes (6 kg) were scrubbed and sliced, soaked in 0.7% sodium dithionite/0.7% sodium citrate for 1 h,[23] washed with ice-cold water, suspended in minimum 0.1 M tris(hydroxymethyl)methylamine/citrate buffer (pH 7.0), and liquidized. The crude extract was kept at 329 ± 1 K for 10 min to destroy α-amylase activity[24] and then centrifuged (4200*g*, 1 h). The supernatant was made up to 100 g/L ammonium sulfate, the precipitate was removed, and the ammonium sulfate concentration was adjusted to 250 g/L to precipitate phosphorylase.[24,25] After dissolution in 20 mM imidazole (20 mL) and dialysis against 20 mM imidazole, the solution was centrifuged (13 000*g*, 30 min) and the supernatant applied to a DEAE Sepharose column (200 mL).[22] After a washing with 20 mM imidazole (800 mL), phosphorylase was eluted with a sodium chloride

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