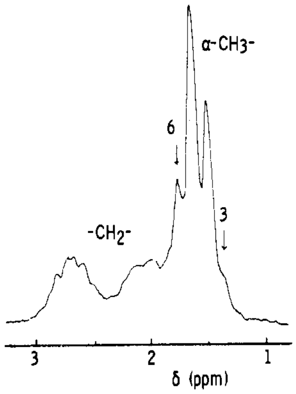

Figure 6. ^{1}H NMR spectrum of poly(MAA-*co*-MMA) derived from poly(MBMA-*co*-MMA) (100 MHz, 100 °C, pyridine-d_5, HMDS).

important role in determining the stereoelection of the polymerization.

The distribution of the monomers in poly(MBMA-*co*-MMA) was investigated from the ^{1}H NMR spectrum (Figure 6) of the methacrylic acid (MAA)-MMA copolymer which had been derived from the copolymer by treating with hydrogen bromide. The ^{1}H NMR spectrum indicates that the contents of MAA-MAA-MAA (peak 6) and MMA-MMA-MMA (peak 3) triads were very low.[7] Therefore, the copolymer must consist of rather many alternating sequences of MBMA and MMA connected in isotactic manner. The optical purity (46.1%) of the unreacted MBMA was about a half of the purity expected from the data at 56.6% polymer yield in Figure 1. This lower asymmetric selectivity may be due to the fact that both (*S*)- and (*R*)-elective centers were formed by the initiation reaction of the c-HexMgCl-(−)-sparteine system with MMA in addition to the preferential formation of the (*S*)-elective center from the catalyst system and (*S*)-MBMA. The (*S*)- and (*R*)-elective centers probably have the same structure as in the homopolymerization of (*RS*)-MBMA and might form a mixture of an (*S*)-MBMA-MMA copolymer and an (*R*)-MBMA-MMA copolymer of highly isotacticity. Of course, we cannot exclude the possibility that the existence of MMA lowers the selectivity of (*S*)-elective center so that (*R*)-MBMA is incorporated into a polymer chain more easily. In the copolymerization of methacrylates, the interaction between the ester groups is complicated relative to the homopolymerization of methacrylates and hence the preparation of highly stereoregular copolymers was usually difficult.[8] It is therefore an interesting result that a highly isotactic copolymer was formed in the present copolymerization.

As shown in Figures 1 and 2, c-HexMgCl- and c-HexMgBr-(−)-sparteine systems brought about similar results. Using these systems, optically pure (*R*)-MBMA will be obtained in about 35% yield.

Conclusion

c-HexMgCl- and c-HexMgBr-(−)-sparteine systems were highly asymmetric-selective catalysts for the polymerization of (*RS*)-MBMA. This high selectivity was ascribed to the fact that an (*S*)-elective center having a high selectivity was formed preferentially in the initiation reaction and (*R*)-elective center was formed after more than 80% (*S*)-MBMA had been consumed. Each of the (*S*)- and (*R*)-elective centers yielded different polymer chains. In the copolymerization of MBMA with α,α-dimethylbenzyl methacrylate, these centers gave the homopolymer of MBMA having the same optical purity and isotacticity as the above polymerization. However, these centers copolymerized rather alternatingly MBMA with MMA to form an optically active isotactic copolymer.

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The Effect of Molecular Weight on Triplet Exciton Processes. 2. Poly(2-naphthyl methacrylate)

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ABSTRACT: Delayed fluorescence and phosphorescence of different molecular weight samples of poly(2-naphthyl methacrylate) in matrices of 2-methyltetrahydrofuran at 77 K are reported. The intensity of delayed fluorescence, arising from triplet excitation annihilation, increases with molecular weight, while the phosphorescence intensity and lifetime decrease. The phosphorescence decay is much slower than the delayed fluorescence and neither decay is exponential. The general characteristics of triplet exciton processes on polymers are briefly discussed.

I. Introduction

In this paper is described the results of studies of the effect of molecular weight on delayed emission for poly(2-naphthyl methacrylate). We will also briefly discuss what seem to be some of the general results of studies of triplet excitons in aryl polymers.

The pioneering work of Fox and Cozzens[1] on poly(1-vinylnaphthalene) (P1VN) demonstrated triplet-triplet annihilation in polymer systems leading to delayed fluorescence. They observed no systematic change of emission with molecular weight and attributed the differences in emission intensity for different molecular weight samples to "end group effects". The molecular weights they reported were very low, corresponding to a degree of polymerization from 16 to 25. Guillet and Somersall[2] prepared 2-naphthyl methacrylate (P2NMA) polymers and observed triplet-triplet annihilation

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leading to delayed fluorescence. They did not study the molecular weight dependence of delayed emission. Following the work of Fox and Cozzens,[1] Somersall and Guillet[2] determined the apparent triplet transfer rate along P2NMA by the use of extrinsic triplet quenchers. This transfer rate was estimated to be 1.5 times greater than for P1VN.

Recent work by the present authors[3] on poly(2-vinylnaphthalene) (P2VN) and Yokoyama et al.[4] and Klöpffer et al.[5] on poly(*N*-vinylcarbazole) (PNVC) have demonstrated the dependence of the delayed emission of the respective polymers on the molecular weight over substantial molecular weight ranges. These studies have shown substantial differences in the molecular weight dependence of the delayed emission for the two polymers (as is to be expected) but the qualitative aspects of the behavior were undeniably similar.

Methacrylate polymers were investigated for a combination of structural and synthetic reasons. The effect of the side-chain structure on the triplet energy transfer properties was not obvious. On the one hand, regular uncrowded stacking of side groups, which is expected in P2NMA, would be expected to enhance triplet energy transfer, but the crowding of the side groups in vinyl polymers also could enhance triplet energy transfer. Methacrylate monomer undergoes facile coupling to a variety of photochemically interesting side groups and the products, often sublimable solids, are readily purified. Štolka[6] has shown that anthracene, which is traditionally a difficult moiety in polymer syntheses, can be incorporated into polymers of arbitrary molecular weight and copolymers of chosen composition. Further enhancing the broad utility of this scheme is the fact that there are a number of completely different syntheses of monomers starting most often from the readily available precursor methacryloyl chloride. A variety of polymerization methods can give controllable molecular weights, narrow polydispersities, and/or stereoregular polymers with a variety of interesting chromophores. Also, the methacrylate system has broad practical appeal because of the widespread commercial use of related polymers. On the negative side, many methacrylates may not be stable in room temperature solution for periods longer than a few weeks (vide infra) such that suitable storage conditions are mandatory.[7]

In this paper we will show that the molecular weight dependence of the delayed emission of P2NMA is qualitatively similar to P2VN and PNVC. There are quantitative differences and similarities between P2VN and P2NMA that do not admit of a simple analysis in terms of the difference in side group structure. Our observations may be summarized as follows:

(1) The intensity of delayed fluorescence (DF) increases with molecular weight, accompanied by a slight decrease in phosphorescence (Ph) intensity. At higher molecular weights these intensities tend to become constant (i.e., the molecular weight effect "saturates"). The overall magnitude of the former effect is slightly smaller than observed for P2VN[3] and much smaller than Klöpffer et al.[5] report for PNVC.

(2) The phosphorescence decay at long times is exponential but the lifetime depends on molecular weight. Since the intensity of DF has fallen to approximately zero ($<10^{-3}$ of the intensity at short times), this molecular weight dependence cannot be ascirbed to biexcitonic annihilation. While some molecular weight dependent "structural" effect is possible, it seems likely to us that mobility of triplet excitons persists at long times and the molecular weight dependence arises from the enhanced susceptability of excitons to residual triplet quenchers (e.g., O_2) in the 77 K matrix.[8]

(3) The rate of decay of DF for short time intervals (~2.4 ms) increases with decreasing molecular weight. The magnitude of this effect is smaller than the corresponding results for P2VN but qualitatively similar.

(4) At longer times the rate of decay of DF and Ph is much less molecular weight dependent than was found for P2VN. In addition the rate of decay of DF in P2NMA is much slower than P2VN. The degree of nonexponentiality of Ph decay increases somewhat with molecular weight, but less dramatically than for P2VN.

II. Experimental Section

A. Synthesis. The synthesis of 2-naphthyl methacrylate was carried out using a Schotten-Baumann technique. 2-Naphthol (99%) from Aldrich was recrystallized twice from hot water and then sublimed three times to obtain a white crystalline material with a sharp literature value melting point (122 °C).[9] One gram of this material was dissolved in 20–25 mL of 3 M KOH (aq) and the colorless solution was cooled with ice. Two milliliters of methacryloyl chloride were added to this solution in 0.5-mL portions, accompanied by vigorous shaking. The solution was cooled with ice throughout the addition. The monomer is spontaneously precipitated from the solution as small (~1-mm diameter) beads which are then isolated and washed with 200 mL of cold water. The beads are either recrystallized from methanol and dried overnight under vacuum or simply dried, and in either case the material is sublimed three times, including one sublimation immediately before use. Since recrystallization did not seem to make any difference to the product if the sublimations were done slowly enough, it was not regularly used. Monomer was stored in a freezer under N_2.

Polymers were prepared in tetrahydrofuran (THF) which had been refluxed over lithium aluminum hydride for at least 3 days and then distilled. The 10% solutions of 2NMA monomer in THF were initiated using azobis(isobutylnitrile) (AIBN) in concentrations from 1 to 0.01%. One polymer was prepared in bulk using 0.1% AIBN. This material gave the highest molecular weight found. All solutions were placed in a 60 °C oven for 12 to 24 h and the polymer was thereafter promptly precipitated three times into methanol. The typical yield for this reaction was 25–50% polymer. The white polymer powders were stored under N_2 in a freezer until used to make samples. The possibility of decomposition of the dry polymer was taken seriously, but under our storage conditions no perceptible decomposition occurred as witnessed by identical delayed emission spectra of the same polymer for solutions prepared 9 months apart.

B. Sample Preparation. Samples for spectroscopic analysis were prepared as described in our previous paper on P2VN,[3] but one major change was necessary. Previously we had used a 1:1 (by volume) mixture of THF and diethyl ether (Et_2O) as our solvent. Based on the article by Somersall and Guillet[2] we assumed that we could continue to do so. Our first four polymers of P2NMA with molecular weights of from 30 000 to 90 000 indicated that THF–Et_2O was a very poor solvent for P2NMA for molecular weights greater than ~40 000. Solutions 1×10^{-3} M in naphthyl side groups were obviously turbid, unlike previous naphthalenic polymer samples we have studied. These solutions were unsuitable for the present experiments.[10]

Pure 2-methyltetrahydrofuran (MTHF) was found to be a suitable solvent after the following treatment. It is first passed through a dry column of highly activated alumina.[11] It is then refluxed over lithium aluminum hydride for 2 days under a N_2 atmosphere. The freshly distilled solvent is free of all delayed emission impurities and will remain so for some weeks.[12] It is an excellent solvent for P2NMA of the highest molecular weights encountered in this work. All spectroscopic samples were prepared at 1×10^{-3} M in naphthyl side groups.

Samples from our first series of polymers were prepared and their spectra were recorded. After a delay of 3 months the second series of polymers were completed and samples of them and the original samples were examined. Substantial differences were noted between the spectra of the original samples when new and after 3 months. The spectra of the newest polymers agreed very well with the spectra previously recorded for the first set of samples when fresh. The first set of samples had been stored at room temperature with no special protection from room lights since in our experience with P2VN no such treatment was required. Agreement among freshly prepared solutions from the old and new polymers was, we felt, absolutely necessary to show a lack of decomposition of the polymers stored as a powder, in the dark, and at freezer temperatures. The agreement was forthcoming, with old and new polymer batches fitting on the same smooth curves of photophysical behavior. The recent article by Li and Guillet[7] may give some insight into the nature of the decomposition reaction.

C. Sample Excitation, Observation Conditions. The methods were as previously reported for P2VN.[3] A homemade phosphorimeter

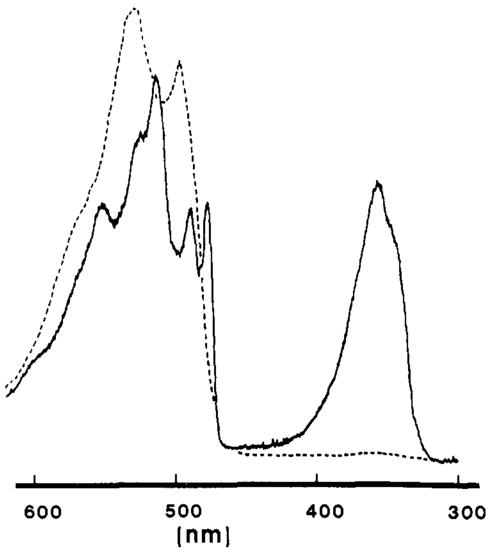

Figure 1. A typical delayed emission spectrum for P2NMA (mol wt = 79 000) for a fresh sample (solid line) and a sample that has developed the impurity emission (dashed line). The latter spectrum is approximately 10× more intense than the former. The concentration of naphthalene moieties is 1.0 (± 0.05) × 10^{-3} for all solutions.

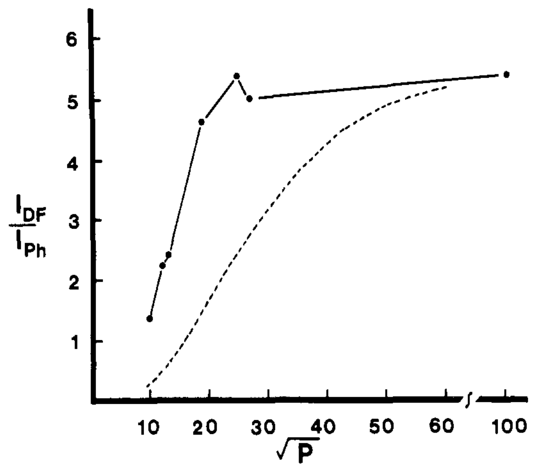

Figure 2. The ratio I_{DF}/I_{Ph} for P2NMA vs. $\bar{P}^{1/2}$ (●). For comparison the similar plot of data for P2VN is presented (dashed line), scaled down by a factor of approximately eight (DF is more intense and Ph less intense for P2VN).

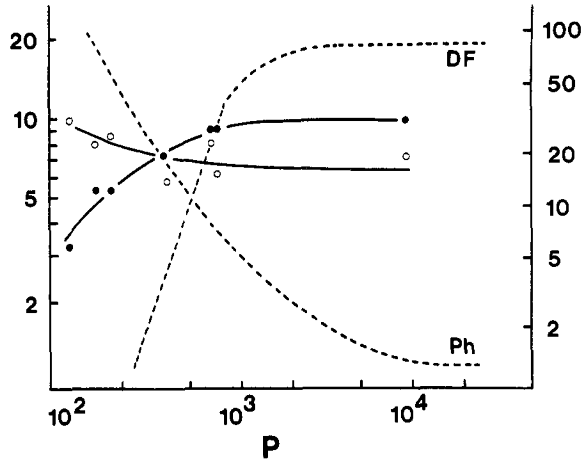

Figure 3. A fully logrithmic plot of I^0_{DF} (●), I^0_{Ph} (○) vs. $\bar{P}$ for P2NMA (left ordinant). Similar data for PNVC from Klopffer et al.[5] are indicated by the dashed line (right ordinant). Note the different log scale used for the PNVC data.

was used in two modes: (1) standard chopper arrangement with ~2.4 ms observation, excitation periods with approximately 0.1 ms dark period between the cessation of excitation and the beginning of the observation; and (2) two slaved shutters (Uniblitz type 26-B, Vincent Associates) that could shut off excitation and open up the observation side with a time step of ~0.2 ms, allowing for variable excitation and observation periods. The first configuration is used for delayed emission spectra and measuring the decay of delayed emission at early times, and the second configuration is used to measure delayed emission decay at long times. All decay curves are obtained by extensive signal averaging.

Excitation is usually effected by a 200-W high-pressure Hg lamp through a Corning 7-54 filter. The same spectrum is observed if a 3130-Å interference filter is used in conjunction with the 7-54 UV filter, but the DF is weakened significantly (DF depends approximately on the square of the excitation intensity).

In some experiments the relative intensity of DF and Ph at $\lambda_{\max}$ for each emission is obtained as follows: (1) the observation monochromator is set at $\lambda_{\max}$ to obtain the waveform of the signal, which reflects the observation period (~2.4 ms) and the amount of decay of the delayed emission (negligible for Ph), (2) the waveform is signal averaged for 512–2048 cycles, with different input sensitivities, (3) the height of the signal at the beginning of the waveform is taken as the intensity, I^0_{DF} or I^0_{Ph}, since no significant decay of the delayed emission is presumed to have occurred during the ~0.1 ms between the excitation and observation period. The day-to-day reproducibility of this arrangement is better than 5%.

All measurements were at 77 K using liquid nitrogen as a coolant.

III. Observations

Figure 1 presents the delayed emission spectra for P2NMA as recorded in our lab. The region around 3400 Å corresponds to the delayed fluorescence of P2NMA. The emission around 5200 Å corresponds to typical naphthalenic phosphorescence. It should be noted that our spectra do not agree in detail with that of Somersall and Guillet.[2] We ascribe the differences to two major causes: (1) in our work with P2VN we found that the use of benzoyl peroxide as an initiator (used by Somersall and Guillet for their P2NMA sample) consistently gave polymers whose phosphorescence spectra were not naphthalenic; and (2) at room temperature and in room light we have observed that solutions of P2NMA, even those thoroughly outgassed and sealed under vacuum, have a shelf life of 3 weeks or less before substantial increases in the phosphorescent emission intensity, a shift in $\lambda_{\max}$(Ph), a loss of structure in the phosphorescence, a change in phosphorescence lifetime, and a slight (20–30%) decrease in delayed fluorescence intensity are observed. An example of this impurity spectrum is also presented in Figure 1. All of these observations indicate that a decomposition product with a substantial emission yield is present. The behavior of this polymer may be contrasted to that of P2VN where in similar solvents no significant decomposition has been observed over a period well in excess of 2 years.

A plot of the intensity of delayed fluorescence at $\lambda_{\max}$DF divided by the intensity of the phosphorescence at $\lambda_{\max}$Ph vs. the square root of the degree of polymerization ($\bar{P}$) is presented in Figure 2 (see footnote *a*, Table I). This plot is presented since it is by far the easiest and most direct data to obtain, being taken directly from the delayed emission spectrum.[13] The qualitative behavior of this plot, i.e., a toe region at low $\bar{P}$, leading to an essentially linear upward sloping section, thus to saturation at sufficiently high $\bar{P}$, is a constant feature of all polymers thus far studied. A log–log plot of the relative intensities of delayed fluorescence (I^0_{DF}) and phosphorescence (I^0_{Ph}) vs. $\bar{P}$ is presented in Figure 3. These intensities were taken from signal averaged chopper waveforms as discussed in the Experimental Section. In Figure 3 the data of Klöpffer et al.[5] for PNVC are indicated for comparison. The qualitative behavior of the two polymers is again clearly similar although it should be noted that the data of Klöpffer

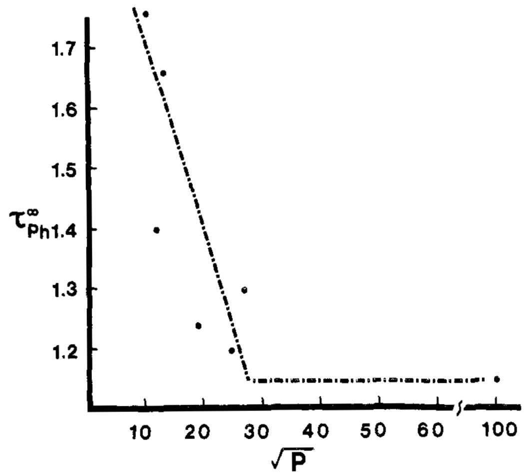

Figure 4. Plot of τ^{∞}_{Ph} (long time phosphorescence lifetime) vs. $\bar{P}^{1/2}$ for P2NMA.

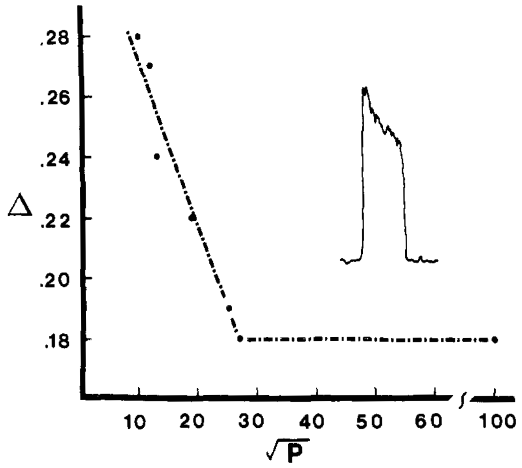

Figure 5. Plot of Δ (see eq 1 of text) vs. $\bar{P}^{1/2}$ for P2NMA. The insert shows a typical signal averaged waveform (width ~2.4 ms) which is used to compute Δ.

et al. have been scaled down relative to that of P2NMA. The high molecular weight sample of P2NMA indicates that I^0_{Ph} reaches saturation at a $\bar{P} \sim 1000$. If one assumes that the triplet radiative rate is not changing with $\bar{P}$ for these materials, then the clear implication of Figure 3 is that the concentration of triplets at $t = 0$ is decreasing with increasing $\bar{P}$; this effect is particularly dramatic for PNVC. Two plausible explanations may be tendered: (1) the triplet lifetime decreases with increasing $\bar{P}$ (vide infra), such that the steady state concentration decreases with $\bar{P}$, (2) similarly, the importance of bimolecular processes increases with $\bar{P}$ such that increasing $\bar{P}$ decreases the steady state concentration of triplets. I^0_{DF} for P2NMA varies with $\bar{P}$ more slowly than the I^0_{DF} for PNVC (and P2VN).[14] It is tempting to interpret the leveling off of I^0_{DF} as expressing some simple measure of the triplet transfer distance in one triplet lifetime. The exciton transfer rate implied by this idea is not in good agreement with that obtained from quenching studies (vide infra).

Figure 4 is a plot of the lifetime of the phosphorescence measured at long times (τ^{∞}_{Ph}) vs. $\bar{P}$. The decay curves used to obtain τ^{∞}_{Ph} covered the period between 1 and 4 lifetimes and intentionally excluded the decay occurring in less than 1 lifetime because of the nonexponentiality in this time region. Since our phosphorimeter is capable of outputing these curves logarithmically, the "straightness" of the decay curve can be double checked and is confirmed for each curve taken. It also should be stressed that in the longer time region the intensity of delayed fluorescence is two to three orders of magnitude lower than the phosphorescence intensity. Since at these long times the triplet annihilation is negligible, a possible explanation for this molecular weight effect is that triplets on each polymer chain continue to transfer even at long times until they encounter an extrinsic quencher (e.g., residual oxygen). Triplets on high molecular weight chains will be able to sweep out more volume in the matrix and thus be more likely to interact with quenchers. It has been previously mentioned that the P2NMA samples of molecular weight greater than 40 000 ($\bar{P} \cong 190$) formed turbid solutions in THF–Et_2O solutions. When these samples were examined for τ^{∞}_{Ph} vs. $\bar{P}$ a curve parallel to and displaced to longer lifetimes by 30% relative to the MTHF samples was obtained. While the difference in solvent may have some effect on the τ^{∞}_{Ph}, it is not difficult to imagine that the tightly coiled polymer molecules (presumably in aggregates) are in contact with a lesser volume of solvent than in 2MTHF and thus there is less quenching.

Figure 5 is a plot of a quantity Δ defined as[15]

$$\Delta = \frac{I_{DF}(0) - I_{DF}(2.4\ \mathrm{ms})}{I_{DF}(0)} \qquad (1)$$

vs. $\bar{P}$. The initial decay rate of the delayed fluorescence is clearly related to $\bar{P}$. For P2VN the plot of Δ vs. $\bar{P}$ had a range of Δ approximately twice that recorded here although the average value of Δ is approximately the same for both polymers. The implications of this curve are that there is a lower rate of triplet–triplet annihilation at high molecular weights, that there is a "saturation" of the molecular weight dependence of Δ, and that significant amounts of DF decay occur in a short period of time. The lower decay rate of DF for large $\bar{P}$ is not completely unexpected since the absolute magnitude of the triplet concentration (as reflected by the value of I^0_{Ph}) is decreasing with $\bar{P}$. The initial rate of decay of DF also must be related to the distribution of "nearest neighbor" exciton–exciton separations and the average rate of exciton migration along the chain. The decrease in Δ with molecular weight implies that the average exciton separation is a significant fraction of the chain length for the lower molecular weight polymers, if one assumes that the molecular weight does not affect the transfer rate. We will come back to this point later. We have collected all relevant data for our polymer samples in Table I.

In Figure 6 is presented the decay of DF (two-cycle semilogrithmic) and Ph (one-cycle semilogrithmic) over a 1-s period for a typical polymer. If the relation $I_{DF}(t) \propto I_{Ph}(t)^2$ held, as would be expected for homogeneous solutions, these decay curves should be superimposible, which is clearly not the case. Such a deviation from "normal" kinetic behavior is typical of all polymers studied to date.[16] We have also included a representation of the decay of DF for P2VN for a polymer of comparable $\bar{P}$. As can be seen, the DF decays much faster for this latter polymer. In fact, one of the most striking differences between P2NMA and P2VN is that the latter showed a very systematic decrease in the decay rate of DF with increasing molecular weight for all time ranges. There is virtually no difference in the DF decay rate from 0.01 to ~1 s as molecular weight of the P2NMA is varied. The decay of DF at longer times yields an average $\tau_{DF} \sim 390 \pm 20$ ms. We do not have a satisfactory explanation for this difference between these two polymers.

IV. Discussion

Many of the observations concerning P2NMA are quite similar to our earlier studies on P2VN.[3] If one compares the molecular weight dependence of I^0_{DF} and I^0_{Ph} for these two polymers and PNVC[5] they appear to form a series P2NMA < P2VN ≪ PNVC, where the inequality refers to the dynamic range of the molecular weight effect (see Figure 3 where

Table I
P2NMA Polymers Used in this Study and Their Properties

Mol wt	$[\eta]^a$	$I^0{}_{PH}{}^b$	$I^0{}_{DF}{}^b$	$\tau^\infty{}_{PH}$, s	Δ
20 450	6.39	1.0	0.33	1.76	0.28
29 800	7.86	0.80	0.54	1.40	0.27
37 400	8.91	0.87	0.54	1.66	0.24
79 000	13.48	0.58	0.72	1.24	0.22
148 000	19.02	0.81	0.93	1.20	0.19
159 800	19.8	0.61	0.91	1.30	0.18
$>2 \times 10^6$	276.2	0.71	1.0	1.15	0.18

[a] Using the relation $[\eta]_0 = 2.72 \times 10^{-2} M^{0.55}$ in benzene at 20 °C (J. Niezette, N. Hadjichristidis, and V. Desreux, *Eur. Polym. J.*, **13,** 41 (1977)). Note that $\bar{P}$ is derived from $\bar{M}_v$ (viscosity molecular weight) which will tend to overestimate P since $\bar{M}_n < \bar{M}_V$/
[B] Relative values, scaled to unity for most intense emission.

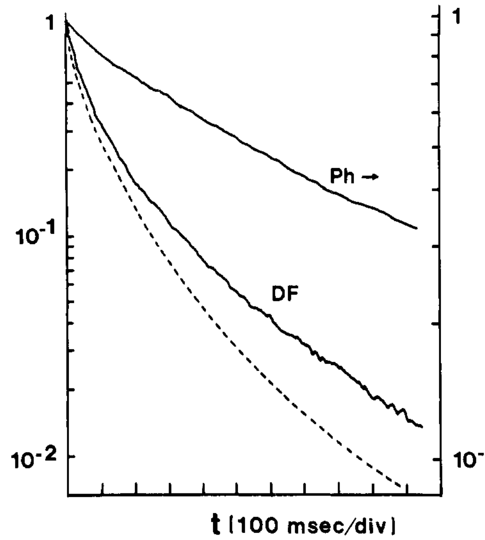

Figure 6. Semilogrithmic plot of decay of DF (2 cycle) and Ph (1 cycle) for P2NMA sample with a molecular weight of 148 000 (solid lines). For comparison the decay of DF for P2VN (of comparable degree of polymerization) is presented (dashed line).

P2NMA and PNVC are compared directly). The same inequality holds with respect to the overall rate of decay of DF[17] and long time phosphorescence lifetime. We have also observed that all emission parameters ($I^0{}_{DF}/I^0{}_{Ph}$, $\tau^\infty{}_{Ph}$, Δ) tend to "saturate" at the same molecular weight, implying a common origin for the molecular weight effect. The most significant difference between P2NMA and P2VN is the near absence of a molecular weight effect on the longer time decay of DF in the former. It is also true that the absolute intensity of DF in P2VN is approximately twice that of P2NMA, and the absolute intensity of Ph in P2NMA is approximately twice that of P2VN, under conditions of essentially equal excitation. This effect does not appear to arise solely from emission quantum yield differences of a 2-ethylnaphthalene moiety vs. a 2-naphyl ester moiety.[18]

As mentioned in section III there are some differences in the spectral properties of P2NMA observed by us and the earlier work of Somersall and Guillet.[2] In particular our delayed emission spectra of fresh samples (Figure 1) are more structured in the phosphorescence region, and our phosphorescence lifetimes at long times are approximately twice as long. We have already noted the solubility differences, which could be rationalized entirely on the basis of molecular weight differences. The difference in our solvent (MTHF) and that of Somersall and Guillet (1:1 THF–Et_2O) does not seem to be the cause of the spectral differences because we also studied our lower molecular weight polymers in a THF–Et_2O glass with results essentially identical to the MTHF glass. Possibly some decomposition of the samples of Somersall and Guillet occurred before spectral data were taken.

Somersall and Guillet[2] also measured the quenching rate of DF and Ph by extrinsic quenchers and estimated the exciton transfer rate (ω_t) as 300 s^{-1} using the formulation of David et al.[19] If our value of $\tau^\infty{}_{Ph}$ is used, a transfer rate on the order of 150 s^{-1} is obtained.[20] We have observed Δ values of ~0.25 for an observation time (t_{obsd}) of ~2.4 ms (see Figure 5) which implies that approximately one fourth of all exciton pairs that can annihilate do so within 2.4 ms. During a time interval t_{obsd} a pair of excitons can annihilate with good probability if they are separated by $(t_{obsd}\omega_t)^{1/2}$ chromophores. Using either $\omega_t = 150$ or 300 s^{-1} and $t_{obsd} = 2.4$ ms, we obtain the results that excitons separated by no more than approximately one to three chromophores would annihilate during a 2.4-ms period. Obviously it is not true that 25% of the exciton pairs are separated by one to three chromophores.[21] We believe that the use of Stern–Volmer quenching rates to derive exciton transfer rates is at the heart of the problem with respect to this calculation. The difficulty is very likely in estimating the number of quencher–chromophore contacts from the quencher concentration. Because the space around the polymer chromophore is relatively crowded, the probability of a quencher contact is significantly decreased relative to a monomeric chromophore.

It is unfortunate that our experimental arrangement does not allow a more accurate estimate of the average number of triplets on a chain. Likewise a direct method for estimating the rate of triplet energy transfer between chromophores is badly needed. The plausible range of transfer rates is rather large based on present experimental evidence. For example, suppose we assume that the "saturation" of the molecular weight dependent properties described in the previous section occurs when $\bar{P} \sim (\omega_t \tau^\infty{}_{Ph})^{1/2}$. Since saturation occurs for $\bar{P} \sim$ 600–700 for P2NMA and $\tau^\infty{}_{Ph} \sim 1.6$ s, we obtain an estimate of ω_t in the range 2–3 × 10^5 s^{-1}, which is three orders of magnitude larger than estimated from quenching rates.[22] This estimate of ω_t would allow excitons separated by ~25 chromophores to annihilate in 2.4 ms, which in our opinion is much more reasonable under our excitation conditions. All of these estimates beg the question of the role of intrinsic energy traps (chemical or structural) and "end effects" (which may be equivalent to the aforementioned intrinsic traps).

What can one conclude is the cause of the observed molecular weight effects in P2NMA and the previously studied polymers? Certainly it must be true that as $\bar{P}$ increases the probability of multiple excitation of the same polymer chain increases, thereby increasing the probability of annihilation. Since the annihilation channel is more important for high $\bar{P}$, the average triplet lifetime decreases with $\bar{P}$, such that the steady state concentration of triplets decreases. This mechanism can account for the decrease in $I^0{}_{Ph}$ with molecular weight that is observed.[23] When $\bar{P}$ is much less than L_D (the exciton diffusion length) the rate at which all pairs of excitons annihilate is increased, such that the initial rate of DF decay is expected to increase as $\bar{P}$ decreases.[24] This follows the observed dependence of the initial rate of DF decay. One can also reasonably argue that the $\bar{P}$ dependence of the DF decay rates arises from the average time for migration to an "end group trap", and the now immobilized exciton can no longer efficiently contribute to the DF (however, "heterogeneous" annihilation between this trapped triplet and residual excitons is a possibility). From this model, or any trapping model, one would conclude that the long-time phosphorescence originates entirely from traps, presumably with the same lifetimes. Our observations of the molecular weight dependence of $\tau^\infty{}_{Ph}$ argues against this model for P2NMA (and P2VN). On the other hand, Klöpffer et al.[5] did not report a similar decrease of $\tau^{\infty}_{\mathrm{Ph}}$ with molecular weight for PNVC.

The fact that $I_{\mathrm{DF}}(t)$ is not proportional to $I_{\mathrm{Ph}}(t)^2$ (see Figure 6) illustrates that the triplets that yield these two emissions are not part of a homogeneous population. Among other possibilities, this excludes a thermal detrapping model in which an exciton, once formed via detrapping, moves rapidly until retrapped or annihilation occurs. We cannot exclude a model in which: (1) both trapped and mobile triplets are present, with thermal detrapping of the former and relatively slow transfer rates for mobile triplets (such that the rate-determining step in annihilation is not only detrapping but also the "collision time" plays a significant role in determining the decay rate); (2) our ensemble of polymers is very inhomogeneous with respect to the number of excitons (following, for example, a Poisson distribution). In addition the distribution of exciton separations could be quite variable. This model can account for our observations, at least qualitatively,[23] so long as the average exciton occupation number is fairly small for small $\overline{P}$.

From this paper and the work of others certain generalizations concerning triplet energy transfer in polyvinylaryl materials have emerged: (1) DF and Ph decay at very different rates and do not follow the relationship $I_{\mathrm{DF}}(t) \propto I_{\mathrm{Ph}}(t)^2$, implying a heterogeneous population of triplets, (2) DF becomes progressively more important as molecular weight increases, which is almost certainly related to the statistics of chain excitation, but could in some cases arise from end-group quenching, (3) the Ph intensity tends to decrease with increasing molecular weight, probably as a consequence of opening the biexcitonic annihilation channel. Still unresolved by the work done to date are: (1) What is the average number of excitons on a polymer chain for a particular experiment? (2) What is the nature of the distribution of exciton transfer rates for a given polymer–solvent–temperature situation? (3) What fraction of triplets become immobilized under the conditions of present experiments and what is the effect of the immobilization on the observed delayed emission kinetics and relative intensities? New experimental approaches are required to answer these questions directly and to provide an opportunity for a theoretical model of these systems to be developed.

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References and Notes

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(8) We have found that there is a strong molecular weight effect in quenching of DF and Ph in P2VN (Part 3 of this series, following paper in this issue) by extrinsic quenchers (piperyline). This effect is consistent with this suggestion for P2NMA.

(9) Purification for 2-naphthol using zone refining techniques proved not to be feasible because of the differential expansion of the liquid and solid leading to catastrophic failure of the sample tube.

(10) Since Guillet and Somersall made no mention of this phenomena it can be inferred that the molecular weight of their polymer sample(s) was less than ~40 000.

(11) Activated alumina fresh out of the bottle is not always active enough for this procedure and must be heated to ~300 °C in a vacuum oven for 3–4 h.

(12) In ref 5 Klöpffer et al. report a phosphorescence impurity that builds up in MTHF. We have not observed this impurity in MTHF per se, although we do observe an identical impurity emission building up in P2NMA/MTHF or P2NMA/THF–Et_2O samples. We ascribe this impurity emission to a decomposition of P2NMA, since it does not depend on the solvents used and THF–Et_2O is known to be stable.

(13) For P2VN and P2NMA we have observed decreases in I^0_{DF} and I^0_{Ph} with irradiation time. These changes are not insignificant; for P2NMA they are on the order of 25% for I^0_{Ph} over a period of 30 min. The delayed emission spectra are taken in a systematic fashion and the ratios of $I^0_{\mathrm{DF}}/I^0_{\mathrm{Ph}}$ are reproducible to within 5%.

(14) The behavior of P2VN is rather similar to P2NMA on a plot like Figure 3 except that the dynamic range of DF is greater by approximately a factor of 3.

(15) Δ may be related to the 1/*e* lifetime of DF as follows: $\tau_{\mathrm{DF}} = 2.4/\Delta$ (in ms). Because of the highly nonexponential nature of the DF decay this 1/*e* lifetime is not very meaningful.

(16) Interestingly a number of workers have reported that $I_{\mathrm{DF}}(0) \propto I_{\mathrm{Ph}}(0)^2$ (where $t = 0$ implies a steady state value of the intensity).

(17) In ref 5 no details of the decay of DF are given except that τ_{DF} is on the order of 3–4 ms. No mention is made of any systematic variation of τ_{DF} with molecular weight. This value is roughly the same as observed for the lowest molecular weight samples of P2VN and substantially shorter than for high molecular weight P2VN or the P2NMA samples studied herein.

(18) The quantum efficiencies of fluorescence for 2-methoxynaphthalene, 2-naphthol, and 2-methylnaphthalene are 0.42, 0.27, and 0.27, respectively. J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, London, 1970, Tables 4.3 and 4.5.

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(20) The value of 150 s^{-1} is quite close to that obtained by David et al. (ref 19) for poly(1-vinylnaphthalene) and polyacenaphthylene and our work on P2VN (ref 8).

(21) We have estimated our excitation flux and absorption to be such that approximately 1% of the chromophores are excited.

(22) By this reasoning the transfer rate for P2VN would be $\sim 4 \times 10^5\ s^{-1}$ and for PNVC would be $\sim 8 \times 10^5\ s^{-1}$.

(23) In unpublished, preliminary calculations by one of us (S.E.W.) it has been found that the $\overline{P}$ dependence of I^0_{Ph} can be accounted for using these ideas if the average exciton occupation numbers for the smallest $\overline{P}$ values are fairly small ($\leqslant 1$). However, these same calculations tend to underestimate the dynamic range of I^0_{DF} such as observed by Klöpffer et al.[5]

(24) For small $\overline{P}$ a larger fraction of polymer chains is singly occupied; for those polymers that are multiply occupied (which are the only ones for which DF is observed) the average exciton separation will tend to be smaller than for multiply occupied chains with $\overline{P}$ large. In other words, for small $\overline{P}$ and small numbers of excitons the fluctuations around the mean density of excitons will be more significant than for large $\overline{P}$ and larger numbers of excitons.