2–2 for $\sin^2(\theta/2) > 0.7$ all have slopes practically equal to that of the true asymptote. Also, the slope of a straight line approximating $P^{-1}(\theta, z)$ for $\sin^2(\theta/2) > 0.7$ is nearly equal to that of the asymptote in this case. If one first ascertains that the experimental $(Kc/I_\theta)_{c=0}{}^{\text{obsd}}$ lie near the asymptote, the slope of $P^{-1}(\theta, z)$ in that region may be used to obtain a value of $\overline{R^2}/\bar{M}$.

Conclusions

In conclusion, it is advisable to be very cautious in using the extrapolated asymptote to obtain $\bar{M}_n$. For distributions having $\bar{M}_n$ differing from $0.5\bar{M}_w$ and $P^{-1}(\theta, z)$ less than 4 at $\sin^2(\theta/2) = 1$ the experimentally observed $(Kc/I_\theta)_{c=0}$ lie appreciably off the asymptote. If $P^{-1}(\theta, z)$ considerably exceeds 4 in the region studied, the experimental points will lie near the asymptote, but the large slope of the asymptote under such conditions will make the long extrapolation to $\sin^2(\theta/2) = 0$ somewhat precarious. When large Gaussian chains are studied with light of short wavelength leading to $P^{-1}(\theta, z)$ values of approximately 3 or greater, a straight line approximating $P^{-1}(\theta, z)$ in this region (*i.e.*, $P^{-1}(\theta, z) \geq 3$) will have a slope nearly equal to the asymptotic slope. Such a line may then be used to calculate the ratio $\overline{R^2}/\bar{M}$ which will be independent of the molecular weight distribution except for corrections arising from the molecular weight dependence of R^2/M due to osmotic expansion of the coils.

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Photophysical Processes in Polymers. II. Intramolecular Triplet Energy Transfer in Styrene–1-Vinylnaphthalene Copolymers[1]

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ABSTRACT: Electronic energy transfer in copolymers of styrene and 1-vinylnaphthalene has been studied by means of delayed emission spectra run in a rigid glass at 77°K. Relative to the equivalent mixtures of polystyrene and poly(1-vinylnaphthalene), the copolymers excited by light absorbed by polystyrene show quenching of phosphorescence from the styrene-derived segments and sensitization of phosphorescence from the 1-vinylnaphthalene-derived segments. It is concluded that triplet energy has been transferred intramolecularly from the styrene- to the 1-vinylnaphthalene-derived portions of the chain. In effect, the 1-vinylnaphthalene segments not only act as detectors of intermolecular energy transfer in polystyrene, but play the role of "energy sinks" in the copolymer, thereby behaving as inhibitors to photodegradation of the copolymer. From the ratios of delayed fluorescence to phosphorescence from the 1-vinylnaphthalene-derived segments, it is concluded that these segments are distributed randomly rather than as blocks in the copolymer chains.

Polymers subjected to degrading ultraviolet light are generally protected by the incorporation of additives which act as absorbers of the offending radiation. The effect is to prevent, by optical filtering, absorption of the radiation by the polymer. In practice, however, part of the light is absorbed by the polymer, and in time the additives may themselves become ineffective through photolysis. In addition, a portion of the energy absorbed by the additives may in certain cases be transferred intermolecularly to the polymer.[2] The net effect is that the polymer is still subject to photodegradation, and its mechanism, both in the presence and in the absence of protective agents, will remain a subject of interest.

Once a bond has been broken at any point in a polymer molecule, overt degradation has begun. Methods of inhibition based on the control of subsequent processes are likely to be inefficient at best. On the other hand, if the energy of the absorbed photon can be dissipated before bond dissociation occurs, inhibition of the photodegradation process will have been effected. This necessitates a knowledge of the photophysical processes which take place between the event of photon absorption and bond dissociation.

Photophysical processes in small molecules have been under intensive investigation.[3] In polymer molecules the same processes undoubtedly take place, but an additional degree of freedom is provided by the chain itself. An analogy might be drawn to crystals in which exciton migration along chains of small molecules or atoms can occur.[4,5] From the standpoint of polymer photolysis, it is of particular interest to know whether energy is delocalized along a polymer chain.

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(1) Paper I: R. F. Cozzens and R. B. Fox, *J. Chem. Phys.*, in press. These papers were presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, and the 157th National Meeting, Minneapolis, Minn., April 1969.

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(3) See, for example, J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966.

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If it is, a chain break may occur at a photochemically labile point or, conversely, the energy may be dissipated through transfer to an "energy sink" in the chain.

Intramolecular electronic energy transfer has been shown to occur in a few polymers.[6,7] We[1] have shown by delayed fluorescence and quenching studies that in poly(1-vinylnaphthalene) such transfer of triplet energy takes place and that it is influenced by chain end groups. This investigation has now been extended to a series of copolymers of styrene and 1-vinylnaphthalene, in which the groups derived from the latter monomer effectively act as "energy sinks" with respect to the segments derived from styrene.

Experimental Section

Reagent grade solvents were used; methylene chloride and methanol were batches selected for their low fluorescence. All phosphorescence measurements at 77°K were carried out in a 1:1 diethyl ether–tetrahydrofuran glass;[7] both solvents were distilled, the tetrahydrofuran from lithium aluminum hydride.

Homopolymers and copolymers were prepared in the absence of air and light in bulk at 70° from appropriate degassed mixtures of the freshly distilled monomers and 0.5% by weight of azobisisobutyronitrile. Conversions in excess of 50% were obtained. All polymers were purified by three to four reprecipitations from methylene chloride or tetrahydrofuran solutions with methanol; the final samples were dried under vacuum at room temperature. Intrinsic viscosities were determined in benzene solutions at 25°. Copolymer compositions were determined from their absorptivity at 286 nm in the case of materials containing less than about 50% 1-vinylnaphthalene-derived units; for high naphthalene contents, the composition data of Loshaek and coworkers[8] were used. The polymers are described in Table I.

Table I

Polymers and Copolymers of Styrene and 1-Vinylnaphthalene (VN)

Wt % VN in monomer feed	$[\eta]$, g dl^{-1}	Mol % VN in polymer
0.44		1.02
1.7	0.63	1.40
4.2		3.40
5.8		4.84
10	0.32	8.33
36	0.17	34.4
69	0.11	63
92	0.087	90
99	0.074	99
100	0.085	100

Emission spectra were measured at 77°K in an Aminco–Bowman spectrophotophosphorimeter having a mercury–xenon arc source and a 1P28 detector tube; no corrections were made for detector response or source output. Reproducibility of phosphorescence intensities was about 10% for a series of solutions of a given polymer at one concentration. Intensities were measured as peak heights.

Typical delayed emission spectra are shown in Figure 1. All solutions were 10^{-3} M in naphthyl-containing groups; for each copolymer solution, a corresponding solution was made by weighing polystyrene and poly(1-vinylnaphthalene). Thus, while naphthyl group concentration was constant throughout this work, phenyl group concentration varied. Sensitization and quenching data were obtained from the raw emission spectra by a normalization procedure to compensate for lamp output and cell alignment variations. Delayed emission spectra excited by 290-nm radiation, which is not absorbed by the polymer segments derived from styrene, and by 260-nm radiation, which is absorbed by the styrene-derived segments, were run concomitantly. For each copolymer–mixture pair, the ratio of copolymer phosphorescence intensity, P_c, to the phosphorescence intensity of the mixture, P_m, was observed. With λ_{ex} = 290 nm the phosphorescence at 520–530 nm can only be due to the direct excitation of the naphthyl chromophores. If the absorption coefficients and quantum yields for emission are the same for a given chromophore in homopolymer or copolymer form, the P_c/P_m for λ_p = 520–530 nm and λ_{ex} = 290 nm should apply as a normalization factor, k, throughout the spectrum. Thus, for λ_{ex} = 260 nm, the observed phosphorescence intensity from the mixed polymers multiplied by k will yield a P_m normalized to the corresponding P_c data from the copolymer.

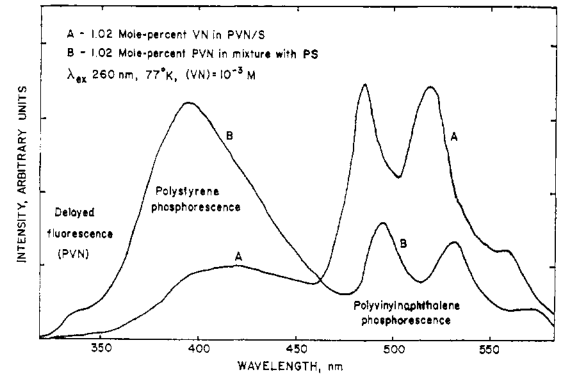

Figure 1. Delayed emission spectra for a mixture of polystyrene (PS) and poly(1-vinylnaphthalene) (PVN) and the corresponding copolymer (PVN/S).

Results and Discussion

Polystyrene phosphorescence is characterized by a single broad band centered at about 400 nm.[9] It is excited by 260-nm radiation, near the polystyrene absorption maximum, but not by 290-nm radiation. Delayed emission from poly(1-vinylnaphthalene) consists of a group of phosphorescence bands in the 500-nm region and delayed fluorescence at 346 nm (Figure 1). The intensity of the emission is at a maximum with 290 nm excitation. In Figure 1, spectrum B, is shown the delayed emission from a mixture of these two polymers containing 1 mol % poly(1-vinylnaphthalene). Emission from both polymers with λ_{ex} = 260

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(6) G. I. Lashkov and V. L. Ermolaev, *Opt. Spectry.*, **22**, 462 (1967).

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(9) The phosphorescence of our polystyrene is displaced to somewhat longer wavelengths relative to that of toluene. While sensitized phosphorescence from a solvent impurity is thereby eliminated, phosphorescence from an impurity in the polymer is not. The presence of such an impurity in the polymer would not alter our conclusions. It is reasonable to expect the normal emission of polystyrene to resemble that of toluene, since normal phosphorescence and fluorescence of ethylbenzene and polystyrene are in similar regions.[7]

nm is apparent; with λ_{ex} = 290 nm, the 400-nm emission was not observed.

Spectrum A in Figure 1 is that from a styrene–1-vinylnaphthalene copolymer containing 1 mol % 1-vinylnaphthalene-derived groups under conditions identical with those for spectrum B. Relative to spectrum B, four differences in the spectrum of the copolymer are evident: (1) the intensity of the styrene-derived phosphorescence has decreased; (2) the intensity of the 1-vinylnaphthalene-derived phosphorescence has increased; (3) in spite of the latter increase, no delayed fluorescence is observed; and (4) the bands in the 500-nm region are shifted about 10 nm to lower wavelengths.

The first two observations are amplified in Figures 2 and 3. In Figure 2, the quenching of styrene-derived phosphorescence as indicated by the ratio of the phosphorescence intensity at 400 nm for the copolymer, P_c, relative to the corresponding mixture, P_m, becomes more complete as the proportion of naphthyl groups in the copolymer increases. Above about 4 mol % naphthyl-containing mers in the copolymer, styrene-derived phosphorescence was almost completely quenched. Sensitization of the naphthyl-group phosphorescence as a function of copolymer composition is shown in Figure 3. The sensitization became immeasurably small beyond about 4 mol % naphthyl-containing mers in the copolymer.

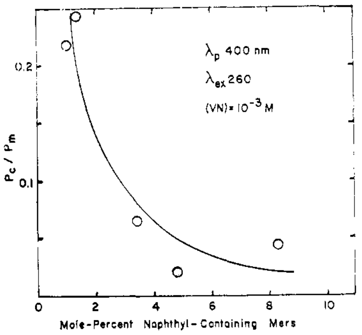

Figure 2. Quenching of phenyl group phosphorescence by naphthyl groups in styrene–1-vinylnaphthalene copolymers.

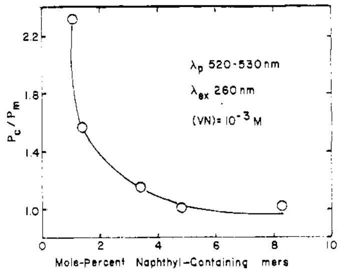

Figure 3. Sensitization of naphthyl group phosphorescence by phenyl groups in styrene–1-vinylnaphthalene copolymers.

Since we are dealing with emission from triplet levels, these results clearly point to triplet energy transfer from styrene-derived segments to 1-vinylnaphthalene-derived segments in the copolymer. The transfer must be intramolecular at least to the extent that it has been observed, since any intermolecular energy transfer should occur as well in the mixed polymers as in the copolymers. In absolute terms, the phosphorescence intensities from polystyrene alone and polystyrene containing about 1 mol % poly(1-vinylnaphthalene) were very similar, which suggests that little intermolecular quenching takes place under these conditions.

The observation of delayed fluorescence resulting from triplet–triplet annihilation in poly(1-vinylnaphthalene)[1] allows some insight into the chain structure of the styrene–1-vinylnaphthalene copolymers. Sequence lengths for each repeating unit in a copolymer can be calculated on a statistical basis from reactivity ratios, but direct measures of the distribution or arrangement of repeating units are not ordinarily available. In our earlier work[1] with a few methyl methacrylate–1-vinylnaphthalene copolymers, it appeared that, statistically at least, some minimum poly(1-vinylnaphthalene) chain length was required before delayed fluorescence became experimentally detectable. A similar situation obtains with styrene–1-vinylnaphthalene copolymers. At one extreme, if all naphthyl-containing mers were gathered together in a block, it would be expected that the ratio of phosphorescence to delayed fluorescence intensities, P_c/DF_c, would be much as it is in pure poly(1-vinylnaphthalene) except where the naphthyl-containing sequence drops below about 15 units in length. At perfect alternation, no two naphthyl-containing mers could be adjacent at mole percentages of less than 50, and no delayed fluorescence would be observed.

In Figure 4 is shown a plot of P_c/DF_c against copolymer composition for λ_{ex} = 290 nm. For 5–100 mol % naphthyl-containing mers, P_c/DF_c was found to be essentially unity. Below 5 mol %, P_c/DF_c begins to increase as the result of a decrease in delayed fluorescence. Evidently in this region, the naphthyl-containing sequences have become too short to allow triplet–triplet annihilation to take place. A precise determination of over-all chain length would allow an estimate of the actual lengths of the naphthyl sequences. A plot similar to Figure 4 was also obtained from data derived from 260-nm excitation. This means that triplet–triplet annihilation will result whether the naphthyl-containing segments absorb photons directly or receive energy by transfer from a styrene-derived segment.

A comment was made above that the phosphorescence peaks for the copolymer were shifted to shorter wavelengths relative to the mixed polymers. This was true for copolymers having at least up to about 50

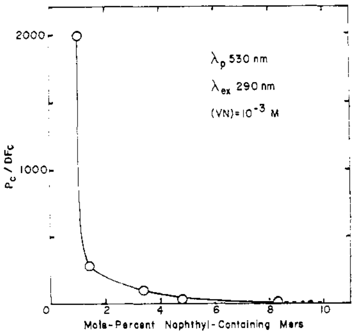

Figure 4. Naphthyl-containing segment size and triplet–triplet annihilation in styrene–1-vinylnaphthalene copolymers.

mol % naphthyl-containing segments. A major difference between poly(1-vinylnaphthalene) and its copolymers would, of course, be in the nature of the end groups and in the type of chain coiling since the copolymer chains are undoubtedly longer than the homopolymer chains. If the event of phosphorescence occurs at the chain ends in a delocalizing system such as this, then the shift may be accounted for, but at present such explanations are not satisfactory.

As long as coupling can occur between aromatic rings along a polymer chain, it would appear that intramolecular energy transfer is possible. Triplet energy transfer has been demonstrated here; singlet transfer has not been excluded. Since energy can be transferred from one type of copolymer segment to another and, at least in the present instances, the accepting segment can eliminate the energy radiatively, it may be possible to photostabilize certain polymers by incorporating energy acceptors into the chain. A knowledge of energy levels is necessary; the lowest triplet energy levels for alkylbenzenes and 1-alkylnaphthalenes are about 29 and 21 kK, respectively, and the transfer of energy is in the direction predicted by these values. In effect, polystyrene should be stabilized in regard to absorbed energy by the substitution of a small number of naphthyl groups for phenyl groups along the chain.

Conclusions

Intramolecular triplet energy transfer has been shown to take place in polystyrene in a rigid matrix. In copolymers of styrene and 1-vinylnaphthalene, intramolecular triplet energy transfer occurs from styrene-derived segments to 1-vinylnaphthalene-derived segments. A radiatively emitting copolymer segment or, by implication, homopolymer end group can be utilized as the detector of intramolecular energy transfer. Intramolecular energy transfer can be utilized in certain cases to obtain direct evidence of copolymer chain sequence distribution.

Structure of Poly(ethylene oxide) Complexes. III. Poly(ethylene oxide)–Mercuric Chloride Complex. Type II

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ABSTRACT: The structure of the crystalline complex of poly(ethylene oxide)–mercuric chloride type II has been determined by X-ray diffraction and infrared absorption methods. The unit cell is orthorhombic with the lattice constants, a = 7.75 Å, b = 12.09 Å, c (fiber axis) = 5.88 Å, and the unit cell contains four $HgCl_2$ molecules and four CH_2CH_2O units. Two poly(ethylene oxide) chains pass through the lattice. The space group consistent with the systematic absences is Pncm-$D_{2h}{}^7$ or Pnc2-$C_{2v}{}^6$. The positions of the Hg and Cl atoms can be determined by X-ray diffraction method. The molecular structure of poly(ethylene oxide) has been deduced by means of far-infrared absorption and normal coordinate treatments. The conformation of poly(ethylene oxide) in the complex of type II has been found to be the form near to $TG_2T\overline{G}_2$; that is

$$-CH_2-(\underset{167^\circ}{-}O\underset{81^\circ}{-}CH_2\underset{73^\circ}{-}CH_2\underset{-167^\circ}{-}O\underset{-81^\circ}{-}CH_2\underset{-73^\circ}{-}CH_2-)_n-$$

This molecular structure has been confirmed by the improvement of the agreement between the observed and calculated structure factors, and by the reasonable entry of this model into the interstice of the unit cell between $HgCl_2$ molecules.

In a previous paper[2a] it has been reported that poly(ethylene oxide) (PEO)[2b,3] forms two kinds of crystalline complexes with mercuric chloride, one of which consists of mole ratio of $4CH_2CH_2O:1HgCl_2$ and the other consists of mole ratio of $1CH_2CH_2O:1HgCl_2$. The structure of the former crystalline complex, denoted as type I, was determined by X-ray analysis, and the conformation of PEO in type I was found to be the $T_5GT_5\overline{G}$ form.

In the present work we have studied the crystal structure of the latter crystalline complex, denoted as type II, by use of X-ray diffraction and infrared absorption methods. On the analysis of type II, it is very difficult to determine the molecular structure of PEO by X-ray diffraction alone, because the contribution of heavy atoms (Hg, atomic number 80; Cl, 17) to the structure factors in type II is much larger than that in type I. In such a case the far-infrared absorption method is very useful, where some bands are strongly sensitive to the molecular conformation of PEO. The molecular conformation of PEO can be deduced by comparison of the observed data with the calculated frequencies by the normal coordinate treatment for a suitable model. The PEO model thus obtained will be confirmed by the reasonable entry into the interstice of the unit cell between $HgCl_2$ molecules. It seems

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