Effect of Varying Polymer Matrices and Gases on the Singlet and Triplet Behavior of 2-Piperidinoanthraquinone

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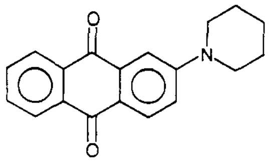
ABSTRACT: The photophysical behavior of 2-piperidinoanthraquinone (2-PAQ) was studied by embedding the solute dye in a variety of polymer matrices like poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), polycarbonates (Lexan), polystyrene (PS), and epoxy resins all at room temperature. Polymers containing the dye were cast in the form of blocks and also as very thin (1 mil = 25 μm) films. A simple experimental technique for preparing the polymer blocks containing the dyes in the shape of 5- or 10-mm thick blocks is described. Employing radiation of high input laser energy (λ = 532 nm, 450 mJ/cm^2), we have demonstrated the occurrence of cavitation in fluid solvents like benzene or toluene whereas in thin (1 mil) polymer films such a cavitation did not occur and only smooth triplet decay curves were seen. The exponentiality of the triplet decay in thin film was energy dependent; only single exponential decay was observed at low laser energies. The singlet, fluorescence, lifetimes in thin films were not affected by the gaseous environment whereas triplet lifetimes decreased in air or in oxygen compared to nitrogen. The singlet lifetimes in nitrogen-saturated films or blocks were comparable to those reported in ethanol glass at 77 K. The fluorescence lifetimes in nitrogen-saturated polymer blocks were the same as that observed in nitrogen-saturated thin films. The triplet decays in nitrogen-saturated blocks were single exponential irrespective of the input laser energies. In oxygen-saturated polymer blocks, both the singlet and triplet decays showed biexponential behavior. No evidence of hydrogen abstraction by the triplets formed was seen in films or blocks. Our studies (on microsecond time scales) in blocks did not indicate any diffusion of the triplet in the polymer matrices (laser input energy ~450 mJ/cm^2) as evidenced by the absence of triplet–triplet annihilation. We have shown on a short time scale (μs), based on the results of singlet and triplet decay of 2-PAQ, that vinyl polymers could provide a glassy, rigid environment for convenient study of photophysics of organic molecules by laser flash photolysis at room temperature. On the other hand, our studies also indicate that epoxy resins are not useful for photophysical studies. The nature of the decay kinetics can be used as a probe of the magnitude and variability of the microviscosity of vinyl polymers.

Introduction

In recent years, the study of photophysics and photochemistry of organic molecules dissolved in polymer matrices has gained importance.[1,2] Polymer glasses are convenient matrices for studies of the excited state of both singlet and triplet states of organic molecules over wide temperature ranges. Studies[3,4] of excited states of small "guest" molecules have provided the opportunity to probe the structure of the "host" polymeric matrices. For example, the physical transitions connected with changes in the mobility of certain structural units such as the temperature-dependent rotation of methyl groups or ester side groups in PMMA have been probed by observing the phosphorescence decay of benzophenone in solid PMMA matrices over the range of temperatures 80–433 K.[3,4] The clarity and macroscopic ridigity of most common polymers such as polystyrene and PMMA at room temperature make them comparable to those of organic EPA (ether–isopentane–ethanol) at 77 K and inorganic borate glasses. PMMA is the most widely used polymer owing to the relative ease of preparing solid solutions of organic solutes at room temperature (RT), its high transparency, and its insensitivity to moisture.

Despite the foregoing, the use of polymer matrices has some disadvantages. They have much greater free volume at RT than do conventional organic glasses, permit a significant degree of molecular motion of the dissolved dyes, and can be considered rigid only on a very short time scale. At temperatures above RT, there could be specific interactions (for example, H abstraction) between the small solute molecule and the host polymer. Also highly polar organic molecules often do not dissolve in PMMA and vinyl polymers like polyethylene or polypropylene, certain vinyl polymers also have high permeability to oxygen which could lead to the quenching of the excited states of organic solute molecules. Most of the studies reported in polymer matrices are concerned with the phosphorescence decay of the organic solutes as the rigid polymer matrices are convenient to observe phosphorescence at RT.[5] Examples of other photoprocesses studied in polymer matrices are photo-cis–trans isomerization (stilbene),[6] photochromic behavior (spiropyrans),[7] exciplex emission,[8] fluorescence,[9] and others.

A survey of literature on the subject of laser flash photolysis study of both singlet and triplet–triplet absorption of organic solutes in polymer matrices revealed that only very few reports are available.[1] In the present work, we have attempted a systematic study of the effect of varying (1) the nature of the polymer in thin (1 mil) films and also in polymer blocks (5 or 10 mm thick), (2) the gaseous environment of the polymers, (3) the molecular weight of the polymers, and (4) the input laser energy (532 nm) on the singlet and triplet excited states of 2-PAQ (1). The ready solubility in different polymers, thermal stability, and well-characterized excited states of 2-PAQ in fluid solvents[10-12] make 2-PAQ a good candidate for the present study.



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Experimental Section

2-PAQ was synthesized by refluxing 2-chloroanthraquinone with a large excess of piperidine for several hours.[11,12] Purification was done by recrystallizing the crude product from ethanol then chromatographing on alkaline alumina from CCl$_4$ and eluting with a 1:1 mixture of (by volume) of acetone and CCl$_4$. After a further recrystallization from ethanol, the compound had mp 165 °C.

PMMA blocks of 2-PAQ (5 or 10 mm thick) were made by polymerizing a syrup made up of the monomer free from the inhibitor in which PMMA (MW 70 000, Polysciences) was dis-

Table I
Photophysical Parameters of 2-PAQ in Polymer Blocks[a]

polymer block	absorptn[c] max	fluoresc max	fluoresc lifetime, ns	T–T[d] absorptn max, nm	triplet[e] lifetime, μs
benzene	455	570	7.7	400, 580	18
PMMA(N_2)	462	582	14	400, 580	130
PMMA(O_2)	460	595	5.6, 14	420, 560	9, 40
PEMA(N_2)	463	588	15	400, 580	160
PMMA[b] + PBMA(N_2) (copolymer)	463	575	15.5	400, 580	175
PEMA[b] + PBMA(N_2) (copolymer)	464	580	16.5	400, 580	180
epoxy resin (N_2)	475	612	4.1, 15	410, 540	83, 490

[a] The polymer blocks were 5 or 10 mm thick. [b] PBMA refers to poly(butyl methacrylate) and PEMA to poly(ethyl methacrylate). [c] The concentration of 2-PAQ in polymer blocks was ~5 × 10^{-4} M. [d] The laser flash photolysis was carried out with λ = 532 nm. [e] The input laser energy was on the order of 430 mJ/cm^2.

solved (15% by weight) along with 0.1% of azoisobutyronitrile (AIBN). AIBN is the free radical initiator. 2-PAQ of desired concentration was then dissolved in the above syrup. The syrupy liquid was then degassed in vacuum and transferred into glass cuvettes (the cuvettes of 10 or 5 mm path length had rounded corners) which were precoated with a saturated solution of cellulose acetate in ether. The transfer of the syrup into the cuvette was done inside a glovebag filled with N_2. A thin steel wire was inserted into the syrup. The cuvette was closed with a stopper and transferred into a tube. This entire operation was also done inside the N_2 glovebag. The tube containing the cuvette was placed in the oven (40–45 °C) for 2 days. The polymer block formed was then released by cooling the cuvette in ice or dipping in liquid nitrogen. The polymer block was kept in N_2 atmosphere to prevent any surface oxidation. The polymer formed as a block was analyzed (Texstar Plastics Co.) by gel permeation chromatography and the molecular weight (number average) was in the range of 307 000. The copolymer blocks of poly(methyl methacrylate) (PMMA) + poly(butyl methacrylate) (PBMA) and poly(ethyl methacrylate) (PEMA) + poly(butyl methacrylate) were made by polymerizing the mixture of monomers (1:1 by volume). The initiator used was 0.1% AIBN. The procedure is the same as described for PMMA block preparation. Our method of preparing the polymer blocks for spectroscopic studies differs from those reported in the literature. Often the polymer block was prepared by polymerizing the monomer in presence of the dye (80 °C) in a Pyrex tube and the tube was then broken, and the polymer was cut and polished. We found the optical clarity of the polymer blocks prepared this way was of inferior quality.

For oxygen-saturated polymer samples in the form of blocks, the same procedure as described above was adopted except that the glovebag was filled with oxygen instead of nitrogen. The curing time of the oxygen-saturated polymer samples lasted more than a week.

Polymer blocks of epoxy resin (5 or 10 mm thick) were made by mixing the commercially available epoxy solutions A and B where B is the hardener (Epoxy Technology Inc, MA). The epoxide functions were based on the bisphenol A–polyglycidyl ether unit. The hardners were aliphatic amines containing primary and seconcary amine functions, for example, diethylenetriamine ($H_2N(CH_2)_2NH(CH_2)_2NH_2$). Amine and epoxide concentrations were fixed in stoichiometric ratio. The curing time at RT was about 24 h. The extent of curing at this condition was about 80%. If 100% curing was desired, the sample was heated after the above treatment for 1 h at 65 °C. Solution containing A and B in the ratio of 3:1 by volume with desired amount of 2-PAQ was degassed and transferred to the cuvette with rounded corners inside a nitrogen-filled glovebag. The cuvette was precoated with a silicon releasing agent (Dow Corning 20, release agent) and dried.

Polymer films (1 mil thick) containing 2-PAQ were prepared by dissolving the polymers (PEMA, PMMA, PS, or Lexan) and the dye in toluene or chloroform and spreading the viscous solutions over a glass plate. A mechanical spreader (Gardner Instruments, Bethesda, MD) was used to make films of 1 mil thick. The dried films were cut to 2 cm × 2 cm pieces placed in a tube and degassed (10^{-3} Torr) for 2 days to remove any traces of solvent. The tubes containing films were then filled with N_2, air, or O_2 for the laser photolysis study. The molecular weight of the PMMA, PEMA, or PS used for making films varied from 70 000 to ~500 000 (Polysciences Inc).

The microsecond laser flash experiments were carried out by using a Q-switched Nd:YAG laser (11-ns pulse width). The excitation source was the 532-nm second harmonic. The kinetic absorption spectrophotometer used to detect ΔOD changes has been described by us previously.[13] The detection limit of the kinetic system was ~200 ns. The laser pulse was incident on the polymer block at 90° to that of the monitoring light.

For laser flash experiments on films, in general, the films were mounted on a frame to hold the corners and placed 45° to the laser pulse and the monitoring light. It is worth mentioning here that in practically all the previous studies in which polymer films were used, the polymer films were sealed in quartz plates and degassed for laser irradiation. We generally have chosen not to follow this technique to avoid refractive index differences between the glass and the polymer film; however, we have provided further discussion on this point.

The fluorescence lifetimes were measured by a single photon counting technique. The excitation was done by a Nd:YAG mode-locked laser pumping at 532 nm (60-ps pulse) a dye laser. The excitation wavelength tuned was 710 nm and this was frequency doubled (average power about 1 μW). The response time of the photon-counting detection system was 300 ps fwhm. The fluorescence spectra were recorded in a Perkin-Elmer spectrofluorometer.

Results and Discussion

2-PAQ when excited with laser flash (λ = 532 or 355 nm) in N_2-saturated solutions of benzene or toluene produced a triplet with the difference absorption (ΔOD) spectrum having maxima at 400 and 580 nm (Figure 1). First-order decay (kinetics) was observed for the triplet with a lifetime of 18 μs. The triplet was quenched by oxygen with a bimolecular quenching rate constant of $2 \times 10^9\ m^{-1}\ s^{-1}$. In solvents like benzene, toluene, or isopropyl alcohol, the 2-PAQ triplet did not abstract hydrogen, indicating that the configurational nature of the lowest triplet must be π,π^* and not n,π^*. This is consistent with the earlier reports[10-12] that the triplet reacts by electron transfer rather than H-abstraction. Shifts in both absorption and emission spectra observed with increasing solvent polarity showed that the first excited state of 2-PAQ is considerably more polar than the ground state.[11a]

Table I gives the photophysical data on the behavior of 2-PAQ in polymer blocks. The ground-state absorption maxima in vinyl polymer blocks were slightly red shifted relative to that in benzene. Similar red shifts were observed in the emission maxima also. The red shifts may be due to the slight polarity of vinyl monomers as the singlet excited state of 2-PAQ is sensitive to polarity.[11a] It is striking that in nitrogen-saturated blocks of PMMA, PEMA, PMMA–PBMA, and PEMA–PBMA, the singlet lifetimes were almost the same and equal to that reported in ethanol glass at 77 K.[14] This suggests that the above solid polymer matrices are glassy and rigid at RT, and that all collisional nonradiative processes which could reduce

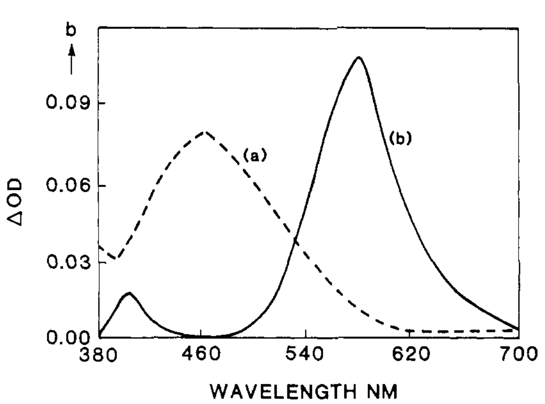

Figure 1. (a) Ground-state absorption spectrum of 2-PAQ in PMMA block (5 mm thick, N_2 saturated); (b) difference absorption spectrum (ΔOD) of 2-PAQ in PMMA block (5 mm thick, N_2 saturated) observed with laser flash (λ = 532 nm; laser input energy = 450 mJ/cm^2). The shape of the ΔOD spectrum in benzene was the same as that of the PMMA block.

the fluorescence lifetimes are almost nonexistent. We have to mention here that the optical clarity and transparency of the higher homologue blocks PEMA, PMMA–PBMA, and PEMA–PBMA were inferior to those of PMMA.

Biexponential decay of 2-PAQ fluorescence with lifetimes 5.6 and 14 ns was observed in oxygen-saturated PMMA block. The short lifetime (5.6 ns) suggests that there are regions in the polymer structure where the trapped oxygen is in close proximity with an excited 2-PAQ molecule resulting in some static quenching (diffusion of oxygen may be extremely slow, the diffusion coefficient of O_2 in PMMA at 20 °C is 3.8×10^{-7} cm^2 s^{-1}.[15] The significant red shift in the fluorescence maximum indicates there could be some bonding interactions of 2-PAQ with O_2 in close proximity. The large spectral shifts of the maximum to lower frequency observed for both absorption and emission of 2-PAQ in epoxy resin blocks were indicative of some kind of complex formation in the ground state between the hardener aliphatic amine which contains both primary and secondary amine functions. We believe the interaction would take place between the uncured hardner and PAQ. Under our experimental conditions the curing was only ~80%. Also, complex-forming interactions with the OH groups and the aromatic ring system in the epoxide function (Bisphenol A polyglycidyl ether unit) may be possible. The addition of an amine to 2-PAQ in cyclohexane was shown to quench the fluorescence by electron transfer.[11] Similar ground-state complex-forming interactions were observed in alcohols also. Hence, the short lifetime of 4.1 ns may be attributed to the above complex-forming interactions and the long-lived component (14 ns) may reflect the free 2-PAQ lifetime similar to those observed in vinyl polymer blocks.

Figure 1 is the ΔOD spectrum of 2-PAQ (~5×10^{-4} M) observed in PMMA block (nitrogen saturated) for laser (532 nm) excitation. The transient spectrum is the same as that observed in benzene. We measured a quantum yield of ~0.5 for the 2-PAQ triplet in benzene by using benzophenone actinometry with laser flash excitation at 355 nm. The triplet lifetime in PMMA was 7 times longer than that observed in N_2-saturated benzene, suggesting that collisional deactivation of the triplet by the solvent molecules as observed in benzene was absent. Another striking feature was the observation of strict first-order fits for the triplet and only one first-order decay on a 400-μs time scale at all input laser energies. Absence of mixed-(first and second) order kinetics and the presence of only one first-order decay suggests that the PMMA block is devoid of regions of low microviscosity which could facilitate triplet–triplet annihilation and is devoid of regions of varying microviscosity (which would result in more than one first-order decay). There is no experimental evidence of diffusion of the 2-PAQ triplet, at least in our time scale. In polymer blocks made up of the higher homologues of PMMA, namely, PEMA(N_2), PMMA + PBMA(N_2), and PEMA + PBMA(N_2), an increasing trend in the triplet lifetimes was seen (Table I). This lengthening of triplet lifetime is suggestive of higher melt viscosity of the polymer in the homologue series of acrylate polymers. Determination of molecular weights of the above polymers would be needed to confirm this. Figure 2 shows the ΔOD spectrum in an oxygen-saturated PMMA block was not identical with that in nitrogen-saturated blocks. The biexponential decay with shortened lifetimes may indicate quenching of some of the 2-PAQ triplets by trapped oxygen in close contact with 2-PAQ. Diffusion of oxygen in the polymer block would be very slow (see discussion earlier). Both singlet and triplet studies show that the distribution of oxygen relative to solute molecules in the polymer block is not homogeneous as evidenced by nonexponential decay (the decay analyzes for two first-order processes). We also noticed that oxygen or air did not easily diffuse through the PMMA blocks. The PMMA(N_2) block exposed to air for few days did not have shortened triplet lifetime.

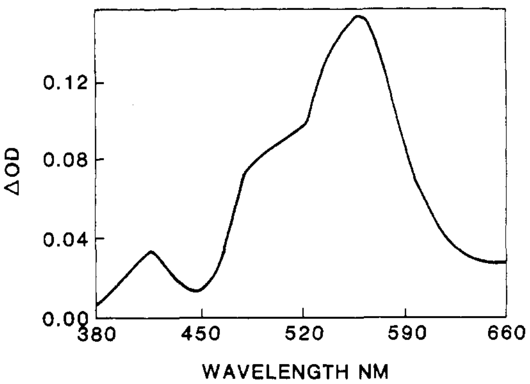

Figure 2. Difference absorption spectrum (ΔOD) of 2-PAQ in a PMMA block (5 mm), oxygen saturated, observed with laser flash (λ = 532 nm). The delay time is 1 μs.

We also observed the absence of H-abstraction from the "host" polymer matrix by 2-PAQ triplets whether in block or thin films of vinyl polymers and Lexan. The long-lived 2-PAQH would be expected to have a maximum around 380 nm.[16] The absence of H atom abstraction is in agreement with the solution studies where the triplet being of π,π^* nature did not abstract hydrogen even in isopropyl alcohol[11]—contrary to that observed for benzophenone in PMMA films where H abstraction by the triplet occurred.[17] The benzophenone triplet being of n,π^* origin is known to abstract H from H-donor solvents.

Epoxy resin provided a different environment for 2-PAQ compared to PMMA. The ΔOD spectrum had maxima at 410 and 540 nm with a shoulder around 480 nm. Biexponential decays of 83 and 490 μs were observed. The unusually long lifetime indicates the presence of another species in addition to the triplet. The shorter decay component (83 μs) may correspond to that of 2-PAQ triplet.

As mentioned earlier, the epoxy is not 100% cured in our preparations and therefore it is possible that electron transfer may occur between the hardener amine, for example, diethylenetetramine and 2-PAQ, in the excited state leading to the formation of semiquinone-free radicals (2PAQ$^{\bullet}$H or 2PAQ$^{\bullet-}$) in addition to the triplet of 2PAQ. Electron transfer from the tertiary amine of the cured resin is unlikely. Allen et al.[10] showed electron transfer between

Table II
Effect of Varying the Gaseous Environment of the Polymer Films on the Singlet and Triplet Decays of 2-PAQ[a,b]

polymer	*P*,[c] *Zn* N_2	*P*,[c] *Zn* O_2	singlet[d] lifetimes, ns	triplet lifetimes, µs N_2	triplet lifetimes, µs air	triplet lifetimes, µs O_2
polycarbonate (Lexan)	0.3	1.4	13	47	37	30
polystyrene	0.79	2.63	13.5	62	39	20
PMMA[e]	0.22	1.15	14	34	31	26

[a] The films had thicknesses of 1 mil (=25 µm). [b] λ excitation = 532 nm, input laser energy = 80 mJ/cm^2. [c] *P*, the permeability coefficient, is the product of the diffusion coefficient and the solubility coefficient. These values are taken from ref 21b. Values in [cm^3/(STP) cm cm^{-2} s^{-1} (cmHg)$^{-1}$] × 10^{10}. [d] The singlet lifetimes were the same in N_2, air, or O_2 (±10%). [e] The values of PEMA are taken as approximate values for PMMA.[15b]

Table III
Effect of Varying Molecular Weight of PMMA in Films on the Photophysical Parameters of 2-PAQ[a]

molecular wt	fluoresc lifetime, ns	triplet[b] lifetime, µs
75 000	14	30
200 000	14.2	43
443 000	14	43

[a] The films after drying were kept in air; the thickness of the film is ~25 µm. [b] The laser flash excitation was 532 nm, the input laser energy = 32 mJ/cm^2.

2PAQ and the hardner polymeric amines like polyoxypropylenetriamine in toluene solution. Quinones are known to be good acceptors in electron transfer reactions. The production of these free radicals may occur within the lifetime of the laser flash. It is likely that the free radicals are probably in the radical anion form, 2-PAQ^{-}.[10,11,16] Earlier studies by pulse radiolysis and laser flash photolysis in fluid solvents have shown that the semiquinone radical anion spectrum had a maximum around 480 nm.[10,11,16] Both singlet and triplet studies of 2-PAQ in epoxy resin block indicate that although an epoxy forms a clear glass, it is far from ideal for photophysical studies because of possible chemical interactions with the solute.

Tables II and III summarize the photophysical data on the singlet and triplet states of 2-PAQ in polymer films. The polymer films were saturated in air, O_2, or N_2 and directly subjected to laser flash photolysis unlike in literature reports[17] where the films were sealed in glass plates under vacuum. We used very thin films of ~25 µm thickness (1 mil) to examine their ability to withstand high-energy laser pulses and evaluate any effects on the dissolved 2-PAQ solute. A striking observation was made during our studies. Whereas cavitation occurred when 2-PAQ in benzene or toluene was subjected to a laser pulse (λ = 532 nm) which was of the order of 450 mJ/cm^2, Figure 3, no such cavitation resulted in 2-PAQ containing thin films (25 µm) of PS, PMMA, PEMA, or Lexan and only a smooth decay curve was seen. Cavitation is a consequence of the local heating of the fluid solvent resulting in formation of thermal bubbles due to the release of thermal energy from the solute dye through nonradiative decay processes to the solvent. The profile of the decay trace in benzene reflects the scattering of light by the thermal bubbles so formed, Figure 3. The "rigid" solid polymer matrix in the form of thin film seems to withstand such heating effects. Also, no cracking or any other damage was noted on the surface of the film.

The fluorescence decays were strikingly single exponential in thin films of different polymers with a rate constant of the order of 1 × 10^8 s^{-1} and were not affected by O_2 or air (Table II). The fluorescence lifetimes were the same as that observed in PMMA or PEMA blocks. The insensitivity to O_2 or air in thin films is not surprising as even in fluid solvents, oxygen did not cause any significant quenching effect on the fluorescence lifetime of 2-PAQ, consistent with the diffusion-limited bimolecular quenching rate constant for O_2 (~10^{10} M^{-1} s^{-1}).[11a] Considering the permeability coefficients of oxygen in polymer films[15] (Table II) and the lifetimes of 2-PAQ fluorescence of the order of nanoseconds, dynamic quenching by oxygen would not be expected.

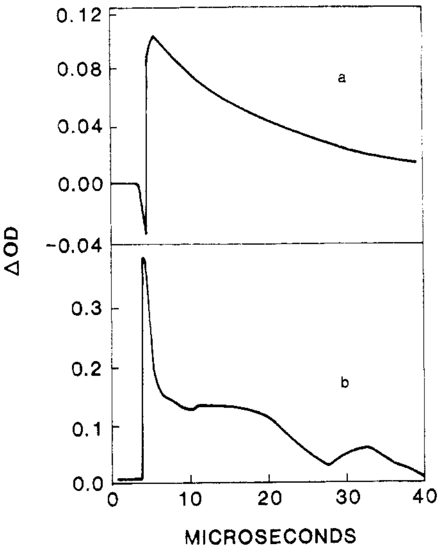

Figure 3. Effect of high laser (λ =532 nm) energy on the triplet decay. (a) The triplet decay of 2-PAQ in a PMMA film (1 mil thick, MW 200 000), input laser energy 450 mJ/cm^2, monitoring wavelength = 540 nm. (b) The triplet decay of 2-PAQ in toluene (N_2) observed at λ = 540 nm, input laser energy = 450 mJ/cm^2.

Aminoanthraquinones were shown to aggregate (~10^{-2} M) in solvents like benzene in the ground state.[18] Similar aggregation may also occur for 2-PAQ. We maintained the concentration of 2-PAQ in polymer blocks and films to be on the order of ~10^{-3}–10^{-4} M to avoid complications arising from aggregate formation. When dissolving a high concentraion of 2-PAQ (~10^{-1} M) in PMMA or polystyrene film (25 mm thick), we observed a reduction in the singlet lifetime from 14 to 8 ns, indicating the possible aggregation of 2-PAQ. A similar effect was seen in toluene also.

The ΔOD (transient) spectra obtained in nitrogen-saturated thin films of PMMA, PS, and Lexan were the same as that observed in N_2-saturated PMMA blocks and identical with that observed in benzene with nitrogen saturation. The triplet lifetimes (Table II) of 2-PAQ in thin films in N_2 for different polymers were about 2–3 times longer than in benzene, whereas in PMMA blocks they were 6 times longer). This is rather difficult to explain, assuming in thin films or blocks the polymer really provides a rigid glassy matrix. The films were cast from solutions of the polymers in toluene, $CHCl_3$, or CH_2Cl_2. It was hoped that the pumping on the "dry" films for a few days would be enough to remove any traces of trapped solvent molecules, but in general, the complete absence of solvent cannot be proved.[2a] The presence of even traces of solvent molecules in the film could shorten the triplet lifetimes if the 2-PAQ were in local pockets. In addition to the foregoing consideration, we conducted an experiment where we pumped on a film of originally granular PMMA (MW 100 000) for 2 days (10^{-3} Torr), opened up the container in a nitrogen-filled glovebox, and finally sealed the film between two glass plates (in the nitrogen-

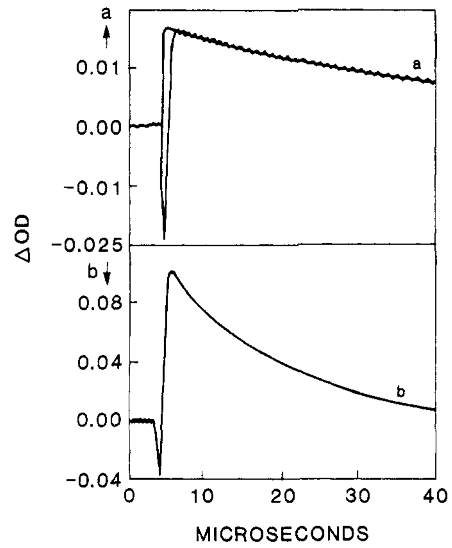

Figure 4. Effect of varying laser energy on the triplet decay of 2-PAQ. The combined plot of the decay of the 2-PAQ triplet in PMMA film (air saturated, 1 mil thick, MW 200 000): (a) laser energy 30 mJ/cm^2; (b) laser energy 450 mJ/cm^2.

filled glovebox). The triplet lifetime in this case was ~110 μs, which was close to that obtained in nitrogen-saturated PMMA blocks. The difference between this number and the ~60 μs found for the same nitrogen-saturated film that was exposed to the air for ~5 min (in this case, the film was not sealed in glass plates) while mounting for laser experiment is notable. This suggests it may be possible for air to displace nitrogen in a relatively short time by permeation of the film, resulting in some quenching by oxygen.

The triplet quenching by O_2 saturation in films was more pronounced in PS than in other films; PMMA shows a less significant effect (Table II). The magnitude of quenching seems to relate in a qualitative way to the permeability coefficient of O_2 in the film, bearing in mind the values for solvent cast films may not be quite the same. The variation of molecular weight of PMMA films kept in air did not affect the triplet lifetimes except in the case of lower molecular weight (75 000) where it was shorter, Table III. Table III also shows the fluorescence decays of 2-PAQ were insensitive to molecular weight.

The variation of laser input energy on the triplet decay kinetics of 2-PAQ in thin films (Figure 4) showed that at energies up to 100 mJ/cm^2, only strict first-order decay was evident, whereas at higher laser energies, the decay was multiexponential composed of first-order and second-order decays. At high laser energies (450 mJ/cm^2), the number of triplets formed may be very high, considering that the concentration of 2-PAQ in films is on the order of 10^{-2}–10^{-3} M in 1 mil. With such high concentration of triplets, it is possible to imagine situations wherein the triplet molecules are in close proximity to each other, resulting in static quenching. Also, even slow diffusion could lead to triplet–triplet annihilation, resulting in a mixed-order kinetics consisting of a fast triplet decay and a slower second-order decay due to triplet–triplet annihilation. On a longer time scale, similar observation was made for benzophenone decay in PMMA film.[17,19] The possibility of slow diffusion of the solute 2-PAQ molecules implies the presence of regions of different microviscosity in the polymer films.

Conclusion

The results of laser flash photolysis and fluorescence studies in polymer blocks and thin polymer films show that vinyl polymers provide a convenient "rigid" glassy matrix to observe the singlet and triplet excited states of 2-PAQ at room temperature. The results of fluorescence are comparable to that reported in ethanol glass at 77 K.

When viewed with the literature reports on the subject of using PMMA film as a host matrix, our work has shown that on a short time scale (microsecond) at low laser energies complications like nonexponential decay at RT for singlet and triplet excited states attributed to the inhomogeneous distribution of free volume in the polymer films are nonobservable.

The lack of observation of triplet–triplet annihilation and also the lack of dynamic oxygen quenching in polymer blocks on the microsecond time scale in the present work lead to the suggestion that the distribution of the free volume in the polymer may indeed be homogeneous and regions of low microviscosity are absent in our preparations. However, the literature reports on this subject have shown that very slow diffusion of oxygen and dye in uniform high viscosity/molecular weight polymers does occur and when the lifetime of the excited state is long (seconds or upper milliseconds, as in the case of phosphoresence), effective quenching by oxygen does occur.[1] Also, the absence of mixed-order kinetics and the presence of only one first-order decay indicate the absence of low microviscosity and varying microviscosity, respectively. Our work also has shown that thin films can withstand energies on the order of 500 mJ/cm^2 without cracking and no cavitation as seen in fluid solvents is observed. The present work had shown that epoxy resins provide a clear transparent rigid matrix but interaction of the resin or an unreacted component with the solute renders them nonideal for photophysical studies.

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Registry No. 2-PAQ, 6345-74-0; PMMA, 9011-14-7; PEMA, 9003-42-3; PS, 9003-53-6; (BMA)(MMA) (copolymer), 25608-33-7; (EMA)(BMA) (copolymer), 52496-45-4; O_2, 7782-44-7; N_2, 7727-37-9.

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Compositional Variation of the Structure and Solid-State Transformations of Vinylidene Fluoride/Tetrafluoroethylene Copolymers

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ABSTRACT: Random copolymers of vinylidene fluoride (VF$_2$) with tetrafluoroethylene (F$_4$E) have been synthesized over the full compositional range, and their crystalline structures have been studied at ambient temperature, as well as during heating to the melting point and subsequent cooling. The room-temperature structure changes from α-PVF$_2$ (for compositions with $\geq \sim 93$ mol % VF$_2$) to β-PVF$_2$ (for ~92–71 mol % VF$_2$), to β-PVF$_2$ and PTFE-like (for ~71–35 mol % VF$_2$), and eventually to PTFE (for ≤ 34 mol % VF$_2$). The interchain lattices expand as more F$_4$E units are incorporated into the molecules; the β-PVF$_2$ lattice does so at a rate ~6 times that of the PTFE-like structure. Thermal cycling of copolymers containing ≥ 83 mol % VF$_2$ between room temperature and the melting point shows no solid-state transformations. However, between ~82 and 72 mol % VF$_2$, discrete and reversible Curie transitions are obtained, of the same type as found earlier in VF$_2$ copolymers with *tri*fluoroethylene. When the VF$_2$ content is reduced to 71–35 mol %, such transformations are smeared out, with both phases coexisting over increasingly broader temperature ranges. These effects are explained by the influence of tetrafluoroethylene units in expanding the interchain packing, introducing random deviations from the all-trans conformation of the ferroelectric phase, and facilitating adoption of the disordered conformation of the paraelectric phase.

Introduction

Copolymers of vinylidene fluoride with tetrafluoroethylene (VF$_2$/F$_4$E) have been receiving increasing attention, particularly since the first report in 1983 of Curie transitions in these ferroelectric materials.[1] Such copolymers were shown by Lando and Doll[2] to be capable of crystallizing from the melt with the unit cell of the ferroelectric β phase, provided they contain at least 7 mol % of tetrafluoroethylene. Piezoelectricity and pyroelectricity in some VF$_2$/F$_4$E copolymers were investigated by a number of authors,[3-6] who demonstrated the attendant dipolar rotation[4] and the nonuniformity of the resulting polarization.[6]

Our initial reports[1,7] of a Curie transition in VF$_2$/F$_4$E copolymers were from specimens containing 81 mol % VF$_2$. Subsequent studies of copolymers in similar compositional ranges indicated the presence[8,9] or absence[10-12] of such a transition. Clearly, therefore, the *compositional dependence* of phase transformations in VF$_2$/F$_4$E over the full range (from PVF$_2$ to PTFE) ought to be examined. In addition, the crystalline structure of these copolymers as a function of composition also requires examination because of the lack of extensive data in the literature. The earliest such data are those of Leshchenko and co-workers,[13] who provided electron diffraction patterns of the compositional range 59–84 mol % VF$_2$. They interpreted their patterns as indicating essentially the same unit cell dimensions for all of these compositions, corresponding to a slightly expanded β-PVF$_2$ structure. Lando and Doll[2] subsequently showed that a copolymer containing 93 mol % VF$_2$ also crystallizes from the melt with a somewhat expanded β cell. More recently, Moggi et al.[14] obtained X-ray diffraction patterns of such copolymers, which indicated a structural change from β-PVF$_2$ to PTFE with decreasing VF$_2$ content.

We have prepared VF$_2$/F$_4$E copolymers over a wide range of composition, and we report here both their ambient-temperature structures and their phase transformations upon heating and cooling.

Experimental Section

The VF$_2$/F$_4$E copolymers were synthesized by emulsion polymerization at 60 °C as described previously.[15] Their molecular structures were determined by use of a variety of solution NMR techniques: ^{1}H NMR at 500 MHz, ^{19}F NMR at 470.7 MHz, and ^{13}C NMR at 50.3 MHz. Full regiosequence assignments through the heptad level indicated random addition with no blockiness, in agreement with a first-order Markov copolymerization model. For purposes of comparison with the literature, the ^{19}F NMR spectra of two commercial samples used in previous work,[5-7,10-12] were also examined together with that of one synthesized here and having the same nominal composition. The three spectra are seen in Figure 1 to be virtually identical, indicating no systematic differences among the samples in the literature.

For X-ray diffractometric studies, the copolymers were molded into thin films in a heated press and then rapidly cooled to ambient temperature. They were then placed on a resistive diffractometer heater whose temperature and uniformity had been calibrated by melting point standards to ±1 °C and scanned in the reflection mode at 0.5–2.0° 2θ/min, using nickel-filtered Cu Kα radiation. For transmission fiber patterns, the specimens were oriented manually at room temperature because of the small quantities of material available.

Results and Discussion

1. Room-Temperature Structure. X-ray diffraction patterns of our VF$_2$/F$_4$E copolymers at ambient temperature are seen in Figure 2. The reciprocal-space region depicted here is deliberately restricted between 15° and 25° 2θ because we want to discuss the fine features of the major intermolecular peak, which have eluded previous investigations;[13,14] the region beyond ~25° 2θ is as pres-

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