Photochemistry of Ketone Polymers. XI. Phosphorescence as a Probe of Subgroup Motion in Polymers at Low Temperatures

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ABSTRACT: The phosphorescence of a wide variety of polymer films containing ketone and/or naphthalene groups has been measured in the range 77–300°K. The emission decreased as the samples warmed up and Arrhenius curves for the temperature dependence show distinct linear regions with changes in slope at the temperatures corresponding to the onset of characteristic subgroup motion in the polymers. These specific relaxation processes, involving small segments and side groups of the polymer chains, are important in affecting the local accessibility of oxygen to quench the triplet state.

In recent years a large amount of work has been done on the photochemistry of ketone polymers in an effort to understand the effects of ultraviolet light on polymer systems. Much of the published work deals with reactions arising from electronically excited carbonyl groups. However, in ketone polymers at room temperature less than 10% of the absorbed energy leads to reaction or emission. Other nonradiative processes are responsible for the removal of most of the excitation energy. In this investigation we set out to study the effect of temperature on the luminescence intensity of a wide variety of polymer films in an attempt to understand the nature of these other modes of deactivation.

Luminescence has been monitored as a function of temperature in polymer films. In particular, polymer matrices have been used as hosts for the study of the effects of both temperature and pressure on the phosphorescence characteristics of aromatic guest molecules. The spin-forbidden $T_1 \rightarrow S_0$ radiative transition is a convenient probe for effects associated with the environment about a chromophore included in a parent polymer. The states are of lowest energy and the triplet state is long-lived. Poly(methyl methacrylate) (PMMA) remains an essentially amorphous solid up to about 100° and has been widely used for this purpose. Polyacrylonitrile and cellulose acetate have also been used. The guest is usually introduced as an added impurity and extensive degassing procedures are used to remove oxygen. Under these conditions the phosphorescence has been found to decrease by less than 50% in the range 77–300°K. The decrease has been attributed to a number of processes including intramolecular decay,[2a] phonon coupling,[2b] solvent shell quenching,[3] and triplet energy transfer.[4] In this investigation we have observed the emission from chromophores which were directly attached by chemical bonds to the polymer backbone and initially no degassing was carried out. Under these conditions the phosphorescence consistently decreased over several orders of magnitude in the range 77–300°K.

Experimental Section

Materials. A list of the polymers used is given in Table I. Unless otherwise stated the samples were synthesized and characterized in our laboratory. Most vinyl polymers were made by radical polymerizations in solution or in bulk using benzoyl peroxide or in aqueous suspension using ammonium persulfate. The polymers were reprecipitated three times into cool methanol and were often freeze-dried. Monomers were purified by fractional distillation before use.

Procedure. The polymer to be investigated was either pressed on a Carver Laboratory Press at 120° and 20,000 psi, or cast onto water from a benzene solution to give a film of approximately 0.1-mm thickness. The cast films were air-dried at room temperature for 2 days, then at 80° for 1 hr, and finally pumped under high vacuum ($<10^{-5}$ mm) for 2 weeks. This method was found to be efficient in removing even small amounts of solvent from the film. The films were then inserted between two quartz plates and placed in a brass cell holder into which one junction of an iron-constantan thermocouple was inserted. The cell holder was also equipped with a channel through which a cold stream of nitrogen could be passed to cool the sample. The coolant nitrogen gas was precooled by passing it through a brass coil immersed in liquid nitrogen. By varying the flow rate of the coolant gas by means of a needle valve, the temperature could be held at any desired value with a variation of not more than ±1°. The experiments were carried out by two different methods.

1. **Ballistic Warming.** The cell holder was immersed in liquid nitrogen until it cooled down, and then transferred into the phosphoroscope of the spectrometer (Perkin-Elmer MPF-2A fluorescence spectrophotometer equipped with a phosphorescence accessory). The cell was slowly warmed up by a stream of dry nitrogen which was also used to purge the surroundings of the cell to avoid condensation. The emission intensity was monitored on a strip-chart recorder, the temperature was simultaneously recorded on a digital printer connected to a digital millivoltmeter which monitored the emf of the thermocouple, one junction of which was in ice–water and the other in the sample holder. Temperature readings were taken at approximately 1–10-sec intervals. Every time the printer was activated, the print command signal was also fed through a condensor (0.02 μF) into the strip chart recorder. This signal, superimposed on the emission intensity signal, established a one-to-one correspondence between temperature and emission intensity. The excitation and observation wavelengths were held constant near the excitation and emission maxima, respectively. These peak maxima corresponded to the absorption maxima and phosphorescence maxima of low molecular weight analogs. The emission and excitation spectra observed for nominally pure homopolymers which would not otherwise show any emission, such as PMMA, PMAN, PAN, PVC, and PE (Table I), are of very low intensity but are distinctly characteristic of the carbonyl group. The excitation and emission maxima at 310 and 460 nm, respectively, have therefore been attributed to the presence of carbonyl groups introduced into the polymers by air oxidation during film formation. Slit widths were usually 5 mm (40-nm bandwidth), but other slit widths were found to give the same results. The chopper speed was set at its highest value, ~6500 rpm.

2. **Point by Point Determination.** The procedure was the same as above except that cooled N_2 was passed through the jacket of the cell holder, and by varying the flow rate of the cooled N_2 gas and the purging N_2 stream, constant temperatures were obtained. The samples were allowed to remain at a given temperature for approximately 1 min, and then the emission intensity and the temperature were recorded. The above methods give essentially the same results.

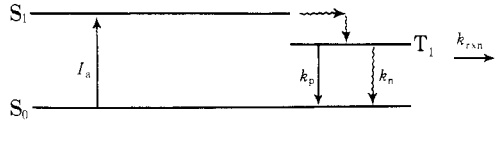
Results

Figure 1 shows a typical plot for the effect of temperature on the phosphorescence of copolymers of styrene, with methyl vinyl ketone, phenyl vinyl ketone, and with naphthyl methacrylate as minor components (5%). In particular, we have observed that the emission intensity from a wide variety of such polymer films containing either ketones or naphthalene groups decreased over more than four orders of magnitude as the samples warmed up from liquid nitrogen temperature. From the simplified Jablonskii diagram

Table I
Characteristics of Polymers

Monomers[a]	Polymer Abbrev	Synthesis	Mol Wt	Method	Remarks
Styrene[b]	PS	Anionic	200,000	Osmometry	Adventitious ketone
Styrene + MVK (5%)[c]	PS–MVK	Free-radical solution	32,250	Osmometry	
Styrene + MIPK (3%)	PS–MIPK	Free-radical solution	290,000	Viscosity	
Styrene + 5-hexen-2-one (1%)	PS–Hex	Free-radical solution	132,600	Osmometry	
Styrene + PVK (5%)	PS–PVK	Emulsion $(NH_4)_2S_2O_8$	735,000	Viscosity	
Styrene (added benzophenone)	PS + BzP				Benzophenone emission
Styrene + NMA (5%)	PS–NMA	Suspension			
Ethylene	PE[d]	Free radical	147,000	GPC (Dow)	Adventitious ketone
Ethylene + CO (0.5%)	PE–CO	Free radical	95,300	GPC (NBS)	
Ethylene + MVK (2%)	PE–MV	Free radical	41,400	GPC (waters)	
Ethylene + MIPK (2%)	PE–MIPK	Free radical	37,500	GPC (waters)	
Methyl methacrylate	PMMA[e]	Free-radical solution	47,500	Viscosity	Adventitious ketone
MMA + MVK	PMMA–MVK	Free-radical solution	47,500	Viscosity	Adventitious ketone
MMA (80%) + NMA (20%)[c]	PMMA–NMA	Free-radical solution			
PVK (10%) + NMA (10%) + MMA (80%)	PVK–NMA–MMA	Free-radical solution			
Vinyl chloride	PVC (1)	Emulsion	76,500	Viscosity	Adventitious ketone
Vinyl chloride	PVC (2)[f]	Free radical	39,000	Viscosity	
Vinyl chloride + MVK	PVC–MVK	Emulsion	69,200	Viscosity	
Vinyl chloride + MIPK	PVC–MIPK	Emulsion	70,700	Viscosity	
Acrylonitrile	PAN				Adventitious ketone
Acrylonitrile + MVK (7%)	PAN–MVK	Suspension	192,700	Viscosity	
Acrylonitrile + methyl-acrylate (20%) + MVK (5%)	PAN–MA–MVK	Solution	162,000	Viscosity	
Methacrylonitrile	PMAN				Adventitious ketone
Methacrylonitrile + MVK (7%)	PMAN–MVK	Bulk	165,000	Viscosity	
Methacrylonitrile (75%) + MMA (20%) + MVK (5%) MVK	PMAN–MMA–MVK	Solution			
MVK	PMVK	Free-radical solution	329,000	Viscosity	
Methyl isopropenyl ketone	PMIPK	Free-radical solution			
PVK	PPVK	Bulk	75,000	Osmometry	

[a] MVK, methyl vinyl ketone; MIPK, methyl isopropenyl ketone; NMA, 1-naphthyl methacrylate; CO, carbon monoxide; PVK, phenyl vinyl ketone. [b] Source, National Bureau of Standards (NBS), Washington, D. C. [c] Parts by weight. [d] Ethylene polymer series from Eastman Kodak. [e] Source, Fisher Scientific Co. Ltd. [f] Source, Pressure Chemical Co.



it is clear that the quantum yield (ϕ_p) of phosphorescence is given by the general expression

$$\phi_p = \phi_{isc}[k_p/(k_p + k_{rxn} + k_n)] \quad (1)$$

where ϕ_{isc} is the quantum yield for intersystem crossing, k_p is the rate constant for phosphorescence, k_{rxn} is the rate of chemical reaction, and k_n is the rate sum of all other nonradiative processes from the triplet state.

The intensity (I_p) of emission observed is directly proportional to the quantum yield

$$I_p \propto I_a\phi_p$$
$$I_p = AI_a\phi_{isc}[k_p/(k_p + k_{rxn} + k_n)] \quad (2)$$

where A is an instrumental factor and I_a is the intensity of light absorbed. For n,π^* states in ketones ϕ_{isc} is near unity and may be considered to be independent of temperature. For π,π^* states as in naphthalene, the intersystem crossing rate shows a small temperature dependence[5] but this effect is minimal relative to the overall temperature effect observed for the phosphorescence of the films containing naphthalene groups. In any case, the effect of temperature is to increase slightly the $S_1 \rightarrow T_1$ process to further populate the triplet level. This could not therefore account for a decrease in phosphorescence with temperature. The instrumental factor (A) as well as I_a and k_p are assumed to be constant over the temperature range, since the only possible changes in light scattering and refractive index may be ignored in our films where the path length is much less than 1 mm.

The decrease in phosphorescence must therefore be attributed to the discontinuous increase of some nonradiative process included in the k_n term. The term (k_n) may be divided into a temperature-independent part (k_0) and a temperature-dependent term which presumably has an Arrhenius form $k \exp(-E/RT)$. With these basic assumptions we can write

$$1/I_p - 1/I_0 = C\exp(-E/RT) \quad (3)$$

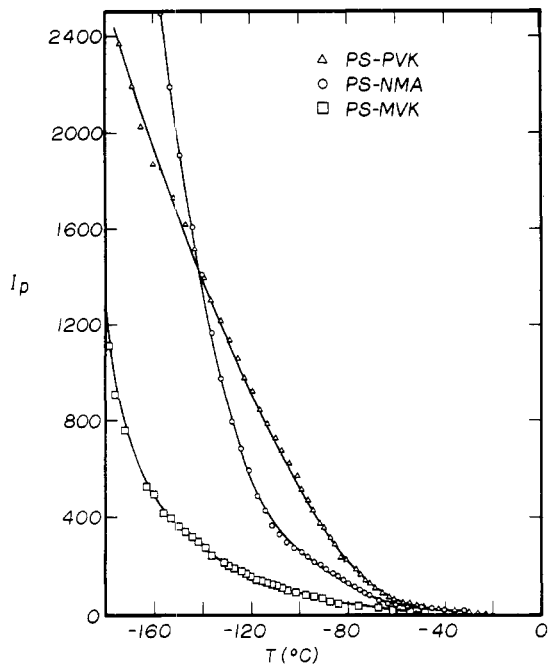


Figure 1. Phosphorescence intensity as a function of temperature in styrene copolymers.

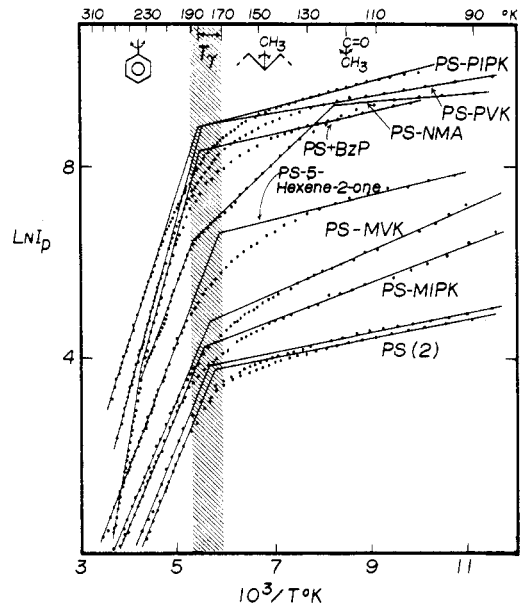


Figure 2. Arrhenius curves for polystyrene phosphorescence.

where I_0 is the intensity at absolute zero and C is a dimensionless constant. Extrapolation of I_p to low temperature shows that ignoring the term $1/I_0$ is justified so that

$$\ln I_p = C' \exp(E/RT) \qquad (4)$$

Arrhenius plots of $\ln I_p$ *vs.* $1/T$ should therefore give a straight line of slope E/R.

Figure 2 shows such Arrhenius plots for the experimental observations on polystyrene copolymers. It is clear that the curves show distinct linear portions with at least one common discontinuity in the slope within a narrow temperature region. The results for the many amorphous and semicrystalline polymers studied show similar abrupt changes in the Arrhenius behavior which appear characteristic for polymer types and which can be understood if different activation processes are involved for the phosphorescence quenching mechanism in different temperature regions.

Polymeric Transition Temperatures. The experimental results for a number of copolymer families were obtained by the ballistic warming method and plotted as suggested from eq 4. The extrapolated intercept regions were found to correspond to analogous transition temperatures observed for the various polymer families by mechanical, dielectric, and nmr methods. These other methods are known to detect local relaxations in the polymers at these temperatures. We therefore assume that the intrusion of the same low-temperature relaxations are somehow directly related to the phosphorescence decrease above the temperature regions of discontinuity.

We may broadly categorize the types of relaxations which take place in amorphous polymers in the temperature range of interest here into three classes. (a) Primary main-chain motions involving segments containing up to 20–40 monomer units in hindered dynamic fluctuation, alternately creating and filling free-volume spaces in the polymer matrix. In the narrow temperature range (T_g) in which this motion sets in, marked discontinuities are observed in the temperature derivatives of many bulk physical properties of the polymer. (b) Secondary main-chain motions involve the cooperative but restricted motions of segments of a few contiguous monomer units. (c) Side-chain motions involving rotation of small groups such as alkyl or aryl groups analogous to the behavior in small molecules. There is often an observed correlation between the activation energies for similar motion in small molecules.

It is useful to classify these processes by the temperature regions in which they are usually observed at low frequencies. The main rubber–glass transition at T_g is termed the α process. Below this temperature, the β process (secondary main chain) occurs often in the region 200–300°K; the other processes are designated γ, δ, ϵ, ⋯ with decreasing temperature. The classification is sometimes ambiguous since overlap arises because the region of observation of a particular transition may shift very significantly by varying the frequency of measurement. The transition temperatures are further influenced by a variety of factors such as the structure of the repeating unit, crystallinity, cross-linking, and the presence of diluents or plasticizers.[5]

The assignment of any observed transition to a particular viscoelastic process is not simple since the observed temperature for the transition depends on the frequency of the method used to detect it. Ketones have a triplet lifetime at low temperatures in the millisecond range. Since the emission does not change significantly before the principal transition point, it is reasonable to suppose that the lifetime does not change appreciably either. Therefore if the phosphorescence is to be quenched by some process related to the relaxation, that process must take place within the millisecond lifetime of the triplet. As a consequence, we would anticipate a correlation with other methods which use a frequency in the range of 10^2–10^4 Hz. Naphthalene triplets have a longer lifetime (~sec) so that the correlation with other results in the region of 1 Hz would be more appropriate in this case.

In addition, the appearance of the transition could depend on morphological difference in samples prepared by a variety of techniques under different conditions. The results reported here include measurements for films cast from solution or molded, but consistency is still observed. The results were reproducible when the samples were allowed to stand at room temperature for a few hours. When the experiments were repeated immediately on the same

sample the transition temperature was often observed about 20–40° higher.

1. Styrene Polymers. Figure 2 shows the results for styrene copolymers with a wide selection of simple ketones. It also includes a sample of the National Bureau of Standards homopolymer (a molecular weight standard sample) which gives a similar but weaker emission, probably due to adventitious ketone groups incorporated at some stage of preparation or by air oxidation. The transition at 180°K ± 10°K is common to all the styrene polymers, independent of the particular probe. The transition is also observed when the emission of naphthalene is monitored in the copolymer of styrene and naphthyl methacrylate (NMA). The only significant difference is the appearance of a new transition at 120°K which we tentatively assign to the rotation of the α-methyl group of the NMA component. The transition is again observed in a commercial sample of polystyrene containing benzophenone as an additive. In this case the probe emitter is not chemically attached to the chain but is simply dissolved in the film. This main transition in polystyrene has been characterized more recently by Yano and Wada.[6] They observed a γ peak at 180°K (at 10^4 Hz) by dynamic mechanical methods. Previously Schmieder and Wolf[7] measured a γ peak at 133°K (at 11.3 Hz) and Illers and Jenckel[8] similarly at 132°K (at 1 Hz). A peak at 199°K was observed very recently by Ranicar and Fleming in the thermally stimulated conductivity (tsc) glow curve.[9] The observation of a γ transition for the NBS anionically polymerized samples negates the suggestion[8] that the transition is due to methylene sequences formed by head-to-head and tail-to-tail coupling. Our results are in very good agreement with Yano and Wada who attributed the transition they observed to the rotation of phenyl groups around the bond to the backbone chain. This is consistent with the absence of the γ-peak in dielectric loss measurements. No other transitions are anticipated in the temperature range studied since the γ' transition which has been reported (100°K at 10^4 Hz) seems to originate from polar groups introduced into molecules during bulk polymerization,[6] whereas the thermoluminescence (tl) peak at 150°K[9] was associated with impurities.

2. Ethylene Polymers. Figure 3 shows the results for ethylene copolymers. The transition at 163°K is common to all these polymers and appears to be characteristic for our polyethylene. The temperature dependence of impurity phosphorescence in polyethylene has been studied by Charlesby and Partridge[10] and more recently by Boustead[11] who observed a transition at about 185°K. Other workers had detected a similar transition much earlier by dynamic methods (188°K at 10^3 Hz, 193°K at 10^4 Hz). Both the thermoluminescence and tsc glow curves showed a peak at 135°K assigned to the γ relaxation.[9] Wada[12] observed a mechanical loss peak for polyethylene at 140°K similar to that noted by McCrum *et al.*[13] Our transition temperature is in particular agreement with the recent dielectric measurements of the γ peak by Phillips *et al.*[14] on some PE–CO samples of the same origin (*e.g.*, 175°K at 10^4 Hz for 1.0% PE–CO). Some differences are to be expected since polyethylene samples differ appreciably in their structure (degree of branching) and their relative crystalline and amorphous content depending on their conditions of preparation. The γ transition in this general region (130–200°K) has been assigned to the initiation of crankshaft-type motion postulated by Schatzki.[15] Boustead also reported transitions at 110°K and 243°K. In the higher temperature region where the intensity is small we observe a discontinuity in the Arrhenius plot for the homopolymer, indicating that some change has probably

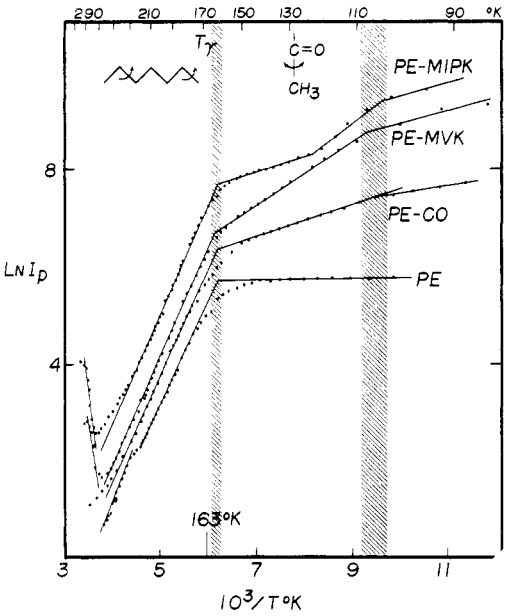


Figure 3. Arrhenius curves for polyethylene phosphorescence.

taken place although the transition is certainly not clear. This transition has been associated with the branch points in polyethylene, but the emission is too weak at these temperatures to conclude much from the results obtained here. However, a clear transition is also observed at 105 ± 5°K for PE–MVK and PE–MIPK film samples. Sinnott[16] noted a transition in the same temperature region for single crystals of polyethylene (111°K at 1 Hz) but no assignment was made for the observation. Small rotational chain oscillations could be responsible, but in these experiments a further possibility exists. The transition seems to depend on the ketone present and could be associated with the onset of rotation of the methyl group adjacent to the ketone. The comparative slopes for the PS–MVK and PS–MIPK curves below the temperature of the γ transition in PS are very similar to those for PE–MVK and PE–MIPK. Furthermore the slopes are markedly reduced in the other styrene copolymers where no methyl group is adjacent to the carbonyl group. Later we will refer to other polymers which did show a similar effect. In polyethylene the Arrhenius curve levels off at low temperature since no side groups are present and motion is restricted. In PE–CO, however, the motion below the γ transition is not frozen out as in PE, showing either that the introduction of a significant number of carbonyl groups affects the morphology of the polymer at these low temperatures, or alternatively, that the adventitious ketone in PE is in a different structural environment compared to copolymerized PE–CO. For example, it is possible that in PE–CO the ketone groups are more in amorphous regions or even in branches off the main chain, whereas in neat PE the CO is adventitiously incorporated more in crystalline regions where the matrix is rigid.

3. Methacrylate Polymers. Figure 4 shows the results for methyl methacrylate copolymers. The γ transition observed at about 155°K in commercial PMMA is the principal transition in this case. The introduction of methyl vinyl ketone increases the emission intensity so that a further β transition is observed at 248°K. The MMA–MVK curve also shows a lower temperature transition at 110°K similar to PE–MVK or PE–MIPK associated with the ketone methyl group rotation. The introduction of the naphthalene chromophore by copolymerization with naphthyl methacrylate shifts the γ transition up to 190°K, removes the possible low temperature one, but leaves the β transi-

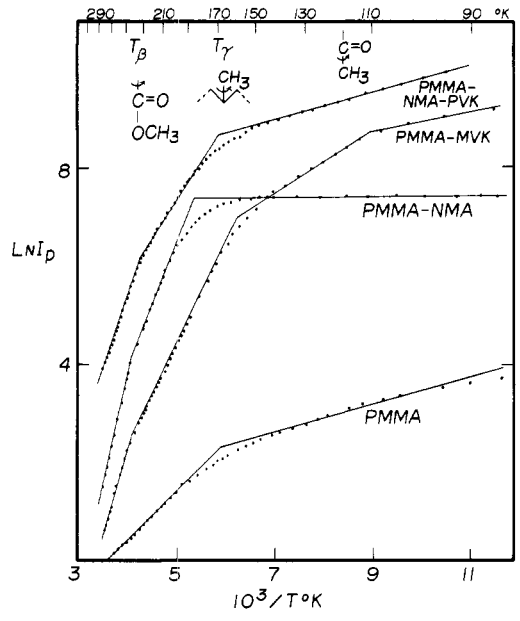


Figure 4. Arrhenius curves for poly(methyl methacrylate) phosphorescence.

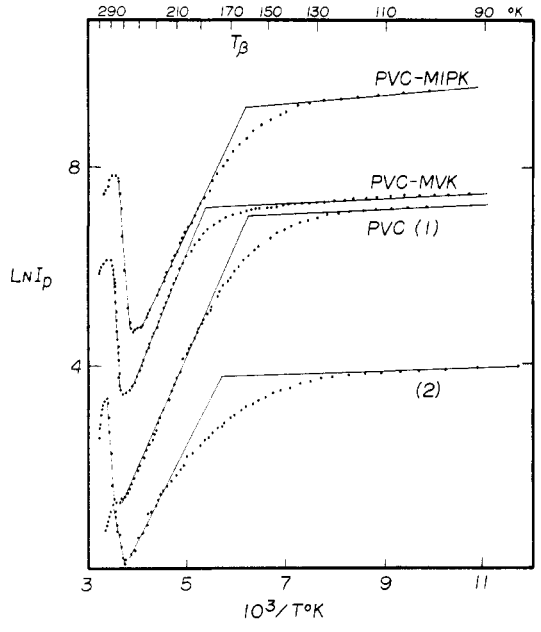


Figure 5. Arrhenius curves for poly(vinyl chloride) phosphorescence.

tion virtually unchanged. This polymer is very rigid and the Arrhenius curve levels off at lower temperature as in polyethylene. Copolymerization with both phenyl vinyl ketone and the naphthyl methacrylate shifts the β transition to 235 ± 3°K and the γ transition to an intermediate value (~175°K). Other workers observed a γ transition by mechanical methods (100°K at 1 Hz),[17] nmr (165°K),[18] and light scattering (152°K),[19] but the assignment is not yet unambiguous. The observation of the transition (145–165°K) in PMMA, poly(α-methylstyrene) and poly(methacrylic acid) which each have an α-methyl group and the absence of the transition in poly(methylacrylate) has encouraged most workers to favor the rotation of the α-methyl group as being responsible for the γ transition.[20] The ester methyl group is considered to be responsible for the non-zero slope at low temperatures. The higher temperature β transition has also been observed by other techniques[20] and in particular, by light scattering (253°K).[19] This latter transition has been assigned to the rotation of the entire ester group.

4. Vinyl Chloride Polymers. Figure 5 shows the results for polymers of vinyl chloride. The transition observed in our films in the region of 160–185°K is shifted on the temperature scale as much as 50–60°K lower than the observed mechanical loss peak (210–230°K, at 1–10 Hz).[21] The β relaxation in PVC has been well studied but the exact nature of the transition is not clear. Pezzin *et al.*[21] observed the dynamic-mechanical properties of PVC and demonstrated that the shape, intensity and position of the β process is not affected by free volume, crystallinity or local changes in the distribution of chlorine atoms. Small quantities of plasticizer reduced the loss peak and shifted it to lower temperature. Similar effects have been shown to result from residual solvent left in the polymer films when cast from solution. The shift to lower temperature which we have observed in our method could be attributed in part to the plasticizing effect of residual solvent trapped in the films cast from H_4furan solution. However, it should also be noted that the β peak is known to be considerably broad (spread over 150° at 1 Hz).[21] This has been described as a consequence of the continuous distribution of the activation energy associated with the β-relaxation process. All the measurements to date have been explained either by the crank-shaft rotation of four carbon chain sections or by the process of loosening intermolecular cohesive forces between dipolar bonds. The PVC polymers show a novel and interesting feature in their emission-temperature behavior. The phosphorescence intensity clearly goes through a minimum and then rises under continuous irradiation within less than 10 min on the spectrometer. The emission then levels off and finally begins to fall off again very slowly. The effect is more marked in the PVK–ketone copolymers than in the formal PVC homopolymers. The recovery of emission is also observed as a minor effect in the ethylene polymers. An interpretation of these observations is given later.

5. Acrylonitrile Copolymers. Figures 6 and 7 show the results for several nitrile-based copolymers. The homopolymers (PAN and PMAN) show adventitious ketone emission which follow Arrhenius curves analogous to PE. These curves (also included in Figure 7) clearly level off at low temperatures up to the single transition region (PAN at 216°K and PMAN at 234°K). The introduction of phenyl vinyl ketone in a PAN copolymer shifts the transition to higher temperature (235°K) but shows no other effect. In contrast, the introduction of methyl vinyl ketone introduces a lower temperature transition (107–125°K). The transition is marked and has an unusually high slope for that region. We have therefore tentatively assigned it to the rotation of the entire acetyl group in the PAN-MVK copolymer. A similar transition will be noted in the homopolymer PMVK itself. In PMAN, on the other hand, the methyl vinyl ketone introduces a smaller slope in the same region. In this case we assign the effect to the rotation of the smaller methyl group above the lower temperature transition. We have already noted this same transition in PS, PMMA, and PE when the methyl vinyl ketone is the emitting monomer. The addition of an ester as a major third component (20%) in the copolymers of PAN and PMAN shows no marked effects in the Arrhenius curves (Figures 6 and 7). Semicrystalline polymers usually exhibit crystalline, primary and local mode relaxations. Hayakawa *et al.*[22] studied the dielectric relaxation of PAN in the paracrystalline phase and identified a transition at 358°K which they attributed to bending vibrations of chains resulting in a relaxation from rotational vibration. Schmieder and Wolf[7] used a mechanical method to observe four transitions at 168, 268, 378, and 413°K when

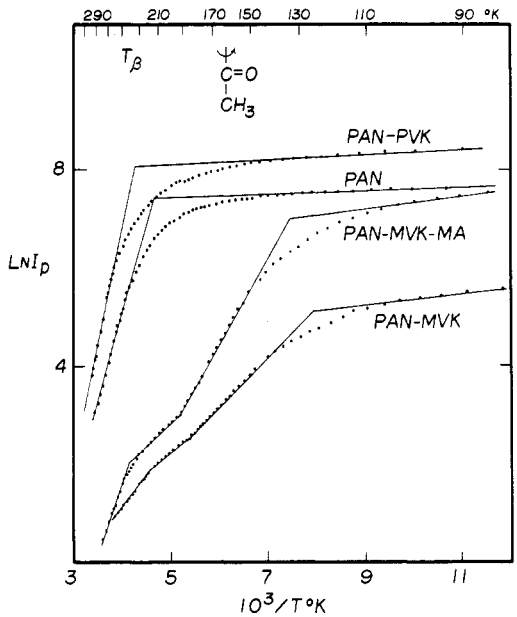


Figure 6. Arrhenius curves for poly(acrylonitrile) phosphorescence.

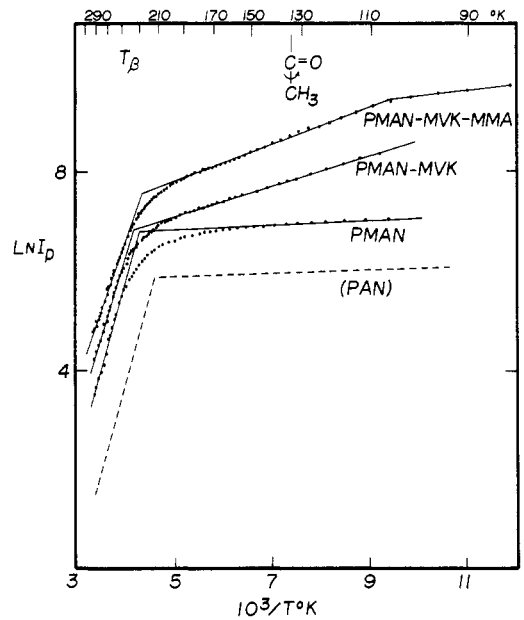


Figure 7. Arrhenius curves for poly(methacrylonitrile) phosphorescence.

measured at 4–10 Hz. The dielectric loss peak observed by Van Beek[23] at 293°K (at 70 Hz) corresponds to the γ peak due to coordinated motions of nitrile groups. The transitions we observed for PAN and PMAN in the 215–240°K region is shifted again 50–60°K lower than the mechanical and dielectric loss maxima for the γ peak (as we have noted also for PVC). It appears that this type of transition in polar polymers is generally extended over a broad temperature range in such cases. The absence of any transition for α-methyl rotation in PMAN is most likely a consequence of extended hydrogen bonding to the very polar cyanide groups.

6. Polyketones. Figure 8 shows the results for three homopolymers. Mikhailov and Krasner[24] reported a transition at 213°K (at 10^4 Hz) from dielectric measurements on PMVK but made no assignment to any particular subgroup motion. Comparison of the Arrhenius slopes and transition regions for the other polymers studied encourage us to suggest which transitions are involved in these polyketones. The lower transition (145°K) in PMVK can be assigned to the oscillation of the entire acetyl group since the slope (activation energy) above T_{trans} is comparatively large, whereas the non-zero slope below T_{trans} is attributed to the residual oscillation of the methyl group. The effect of introducing MVK in PAN produced a similar transition in the region near 120°K. The higher transition in PMVK at 230°K is assigned to the onset of main chain motion by comparison with the β transition of other polymers. The introduction of α-methyl groups in PMIPK reduces both the mobility of the larger acetyl group and the flexibility of the main chain. The transition at 145°K is thereby eliminated but the curve is otherwise similar to PMVK. The higher temperature transition at 234°K is assigned to analogous motion of the main chain in this polymer. However, the rotation of the α-methyl group (or even the acetyl group) could also be invoked. In the case of PPVK the methyl groups are absent and the transition at 196°K is assigned to the rotation of the benzene ring (by comparison with PS). The planar conjugation could lead to the preferred oscillation of the entire benzoyl group in this case. The reason for the reproducible upward curvature at lower temperatures in this polymer remains obscure but may be related to the efficiency of intramolecular triplet energy migration observed in PPVK[25] which is dependent on the accessibility of some preferred chain configuration.

Discussion

These observations clearly demonstrate the discontinuous behavior of phosphorescence as a function of temperature in a wide variety of polymer films. The consistent correlation of the temperature regions of the discontinuities in the Arrhenius behavior with the observations of relaxational processes by other methods, leaves no doubt that the effects on phosphorescence are directly related in some way to the local relaxations in the polymers.

We have argued earlier that it is the conglomerate term k_n in eq 2 which has a direct temperature dependence and leads to a decrease in the competitive phosphorescence yield as the polymer films warm up from liquid nitrogen temperature. This term k_n is actually a rate sum of all the physical radiationless processes taking place from the lowest triplet state. In principle the sum could include three different components for the rates of: (i) intramolecular decay, (ii) intermolecular (collisional) deactivation, and (iii) bimolecular quenching processes. Each of these terms is a prospective candidate for Arrhenius behavior and will be discussed in turn.

The general nature of radiationless processes and the mechanism by which discrete compound states can decay by coupling into a dense continuum manifold in a truly intramolecular process has been much discussed in the literature. Experimental approaches to the problem of temperature effects on excited state processes have previously been made on organic molecules dissolved in polymers. In this investigation we have observed the emission from chromophores which were directly attached by chemical bonds to the polymer backbone. However, since a "temperature effect" on triplet state lifetimes in solid *solution* has already been observed, there have been several attempts to explain these effects in terms of intrinsic properties of the guest molecules. The experimental conditions have warranted the basic assumption that the host plastic was an essentially inert matrix which provided only steric constraints on the embedded aromatic molecules. In particular, extensive degassing procedures were used to remove not only oxygen, but also peroxides and trace quantities of solvent which tend to plasticize or soft-

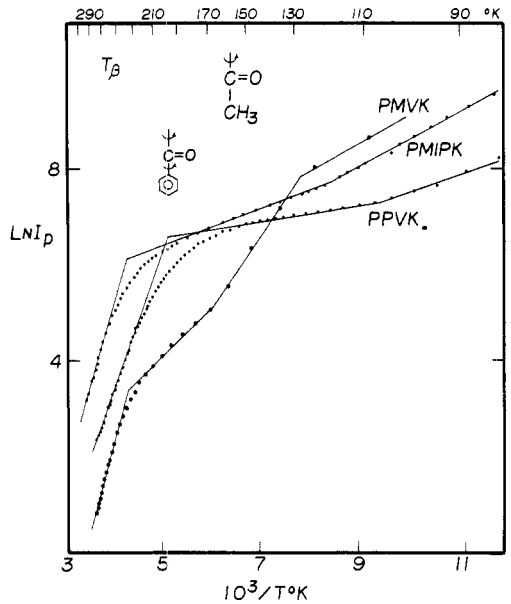


Figure 8. Arrhenius curves for poly(vinyl ketone) phosphorescence.

en the polymer. Acute temperature dependences are then conspicuously absent. In such cases the temperature effect is small but real. The activation energies are usually less than 1 kcal/mol and of the order of molecular vibrational energies. In our experiments we found entirely different results when no degassing was done in preparing the polymer films. The change in phosphorescence intensity is very marked and the activation energies at temperatures just below or near the transition temperatures are very much larger in this case. These results are therefore subject to an entirely different interpretation.

1. Intramolecular Decay. To account for the observed behavior for small molecules dissolved in polymers, Kellogg and Schwenker[2b] favored the involvement of phonon modes which become thermally activated and so enhance the radiationless $T_1 \longrightarrow S_0$ transition. Jones and Siegel[2a] attributed the observed activation energy (500 cm^{-1}) to lower frequency intramolecular vibrations (out-of-plane bending modes). They were careful not to rule out the possibility that the matrix was applying constraints on the nuclear conformations of the triplet state molecules which were removed somewhat as the matrix relaxed in the region of higher second-order transition temperatures. Baldwin[26] carried out an empirical calculation for naphthalene-d_8 molecules with a Boltzmann distribution among the lowest six ground vibrational frequencies and obtained a reasonable fit with the triplet lifetime data at different temperatures. He therefore favored the early suggestion of Moodie and Reid[27] that distortion of the π-electron density, such as one might find for bending of the molecular plane, allows coupling terms which were previously zero in the Hamiltonian to become non-zero. The failure to observe a deuterium effect was then to be anticipated for an effect due only to such structural distortion rather than to stretching modes.

Benzene in particular is exceptional among aromatics with regard to its high sensitivity to both environmental and temperature effects on the phosphorescence lifetime. Rabalais *et al.*[28] consider this as evidence for effects related to both the "nakedness" of benzene (absence of appropriate coupling vibrations) and the small size of the space available to its π-electron density, which both make it sensitive to solvent-assisted distortion. The results for benzene in frozen glasses have been interpreted in terms of simple thermal activation of modes which couple the different state manifolds and which are weakly influenced by the host environment.[29] Other authors[30] have insisted that glass relaxation is a necessary and perhaps controlling process. Jones and Calloway[31] observed the fast nonexponential decay of naphthalene-d_8 in polystyrene and maintained that benzene was not indeed "anomalous" since these results could be explained if the softer PS matrix at 300°K, the nuclear conformations of naphthalene-d_8 are no longer constrained by the matrix and the conformation for effective promoting modes then becomes accessible.

None of the above mechanisms of matrix constraint is adequate to explain the pronounced temperature effect we have observed above the "onset" temperatures in this work. The observed changes in phosphorescence yields are much too large. They span over four orders of magnitude. The interpretation of the small temperature effect on guest aromatics in truly inert hosts may indeed be attributed to intramolecular decay events, but is certainly not applicable for the large, common effect observed in our polymers. These observations are common for a small chromophore such as the carbonyl group, which could be a case of Jortner's resonance limit, on the one hand, as well as for a large chromophore such as the naphthalene moiety which certainly belongs to the statistical limit on the other extreme.[32] Further, both n,π^* (high energy) triplets and π,π^* (lower energy) triplets show the marked temperature effects on phosphorescence yield. All polymers investigated show the effect and the unusual case of PVC would be unaccounted for by any such intramolecular decay mechanism.

2. Intermolecular (Collisional) Deactivation. The second term in the rate sum of nonradiative processes from the triplet state above refers to possible intermolecular (collisional) deactivation processes. It has been invoked to account for the temperature dependence of impurity phosphorescence in polyethylene under uv excitation.[11] This qualitative mechanism of Boustead attributes the decrease in phosphorescence with temperature primarily to mechanical relaxations caused by the collisional deactivation associated with molecular motions in the amorphous regions of the polymer. A similar mechanism is hinted at by Rodriquez and Offen[3] to account for the *T,p* effects on some fused-ring aromatics in PMMA. In more obscure qualitative terms they proposed a mechanism of solvent shell quenching in which intramolecular, radiationless processes are "sensitive to electrostatic and repulsive interactions and orientational dynamics." The molecular motion (perhaps the β process) near the solute induces stronger mixing of the solute with solvent states in this case.

The current theories of radiationless processes have refined the essential ideas of Robinson and Frosch[33] but there is still no mechanism by which the radiationless decay could be enhanced by environmental perturbations such as Brownian motion, of magnitude $kT \ll \Delta E$, where ΔE is the quantum of electronic energy to be given up to the environment. Collisional perturbations will be effective only if (i) $kT \sim \Delta E$; (ii) the solvent matrix furnishes a specific perturbation greater than that mixing states in the free molecule, such as an external heavy-atom effect; or (iii) there is a specific solvent–solute interaction strong enough to change the essential character of the molecule in solution, such as by hydrogen bonding. None of these special situations are realized in our polymer systems and intermolecular mechanical relaxation is not to be expected.

In a classic experiment, Tsai and Robinson[34] measured the phosphorescence lifetime of naphthalene in highly purified 3-methylpentane fluid solution at −45°C. By com-

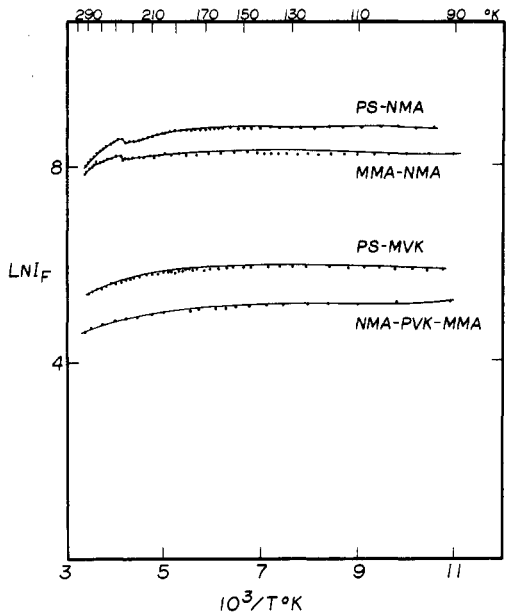


Figure 9. Arrhenius curves for polymer fluorescence.

parison with the lifetime in solid matrices it was demonstrated that the usual absence of phosphorescence in the liquid state is *not* due to bimolecular collisions with the solvent, but rather to quenching by impurities and bimolecular depopulation (T-T) processes. Moreover, Kropp and Dawson[35] found that the phosphorescence decay of coronene in both PMMA and DER-332 epoxy-resin (from Dow Chemicals) remained similar, even in the temperature range (80–120°C) where PMMA goes through a second order transition while DER-332 remains rigid. It follows that the mechanical motion of the host polymer did not significantly affect the phosphorescence. The marked discontinuous changes observed in the temperature effect on our polymer phosphorescence cannot be adequately accounted for by any such collisional relaxation.

3. Bimolecular Quenching. The final term in the sum of non-radiative processes depleting the triplet population involves energy transfer to some quenching species. Kropp and Dawson[35] compared the polymer system to mixed crystals and proposed an analogous intermolecular electronic energy transfer to the host plastic as the predominant process in the temperature-dependent deactivation of coronene in plastics. By adding the activation energies to the coronene triplet level they estimated the triplet levels of PMMA and DER-332 to be about 25,000 cm^{-1}. Similarly, Graves *et al.*[4] studied a variety of aromatics in PMMA matrices in the 77–400°K range. Assuming this thermally activated intermolecular electronic transfer to be the predominant process in the high-temperature region, they estimated a triplet energy for PMMA at 25,100 ± 500 cm^{-1}. The phosphorescence of pure PMMA and of MMA in EPA glass is consistent with this triplet assignment. Benzene was anomalous, presumably because its triplet level lies above that of the host polymer.

However, the results in this work do not bear this energy-transfer mechanistic interpretation since the variety of polymers and chromophores studied shows no correlation with triplet energy levels. For example, the σ,σ^* triplet level of polyethylene or PVC must certainly lie well above the ketone triplet and such thermal excitation leading to transfer to the main chain is not to be expected. On the other hand, in the polystyrene family there should be a range of activation energies necessary to promote from the triplet levels of naphthalene, aromatic ketones and aliphatic ketones. The observed values are not very different and are probably to be associated with a common activation process not significantly influenced by triplet energy levels.

West *et al.*[36] attributed the nonexponential phosphorescence decay behavior of aromatics in PMMA at higher temperatures outside the neighborhood of liquid nitrogen temperature to diffusion-controlled quenching by residual monomer in regions of varying, but relatively low, viscosity. Jones and Livingstone[37] had made similar measurements in viscous solvents and found at higher temperatures, a rapid rise in decay rates with increasing temperature which they attributed to adventitious quenchers, present in trace amounts even in highly purified solvents. Typically, phosphorescence from the long-lived triplet state is only observed when diffusion of such impurities is reduced such as in rigid matrices and at low temperatures.

The polymers studied in this work have been prepared by different methods but the discontinuous temperature effects are observed in all cases. The common procedure of extensive degassing (monomers and polymers) was *not* carried out as the films were prepared in air. Oxygen is known to be a ubiquitous quencher of phosphorescence and could be involved in some thermally activated process which quenched the triplet states in our polymers.

Very recently Merkel and Kearns[38] investigated oxygen quenching of excited singlet and triplet state carbonyl compounds in room temperature carbon tetrachloride solutions. They found that fluorescence intensities in nitrogen- and oxygen-saturated solutions were the same within experimental reproducibility. Singlet lifetimes were much less than 0.5 nsec (shortened by CCl_4 quenching), so that the rate of oxygen quenching was not competitive with emission. In contrast, the phosphorescence was quenched at a rate k_q which had a maximum value of $k_D/9$, where k_D is a bimolecular encounter rate constant. Aromatic hydrocarbon triplets are quenched even more efficiently than the carbonyl triplets, presumably because the electronic orbitals are more easily accessible to the molecular oxygen in the aromatic case.[38]

This oxygen quenching phenomenon is entirely consistent with the results obtained in our polymers. First, the short-lived fluorescence emission showed negligible dependence on temperature in the range 77–300°K (Figure 9). This is consistent with the failure of oxygen to quench fluorescence significantly. The contrast to long-lived phosphorescence is more than apparent. Oxygen is a *triplet* quencher. Secondly, in the terpolymer of MMA, NMA and PVK we observed that the lower temperature transition detected in the curves for direct or ketone-sensitized emission of naphthalene is distinctly and reproducibly absent in the residual emission of the ketone chromophore from the same polymer (Figure 10). This is consistent with the more facile oxygen quenching of the naphthalene chromophore which reveals the effect of the lower transition whereas the ketone does not. Similarly, the lower temperature α-CH_3 group rotation in NMA-PS is clearly obvious but the same transition is distinctly absent in the case of PIPK-PS or MIPK-PS, where only the probe is changed in this case. This is again consistent with the higher efficiency of naphthalene triplet quenching by oxygen.

The recovery of phosphorescence in the singular case of PVC is also easily understood with the oxygen-quenching mechanism. It is well known that in the photochemistry of PVC, the primary chemical step involves free-radical formation by the cleavage of C–H or a C–Cl bond.[39] A chain process of HCl elimination then follows leading to extended conjugation and coloring. Free-radical combination of polymer radicals leads to cross-linking and gela-

tion. Oxygen adds very rapidly to aliphatic free radicals to form peroxy radicals, which are subsequently converted to oxygen-containing compounds such as ketones. In this special case of PVC then, oxygen originally trapped in the film is consumed with time by this very efficient photooxidation reaction during the course of irradiation and warming up. Eventually, most of the molecular oxygen for quenching is removed by photochemical means and additional ketone groups are formed. The common effect is the retrieval of substantial ketone phosphorescence emission. Consistent with this, an increase in the carbonyl absorption in the infrared spectra of irradiated PVC films has also been observed. The recovery of phosphorescence is more marked in the PVC–ketone copolymers, presumably because the incorporation of ketone units provides more free radicals by the Norrish type I process and therefore gives a more efficient scavenging of oxygen.

We have attempted to degas a film of PE–CO in a convenient quartz cell fitted onto a vacuum line. After degassing for 1 week, the effect of temperature on the phosphorescence was unchanged. Routine physical degassing of the polymer films appeared inappropriate since only low partial pressure of oxygen ($<10^{-2}$ mm)[40] is necessary for effective quenching to take place. The recovery effect of phosphorescence intensity in PVC polymers was reduced when runs were repeated on the same sample due to the removal of oxygen by free-radical trapping. Under these conditions room temperature ketone phosphorescence could also be observed in the irradiated PVC–MVK films.

In an additional experiment, films of PVC–MVK or films doped with naphthalene have been irradiated on the spectrometer at room temperature as in a normal temperature-run measurement. When the nitrogen stream was turned on, the phosphorescence intensity increased from zero and levelled off. When the flow was stopped, the phosphorescence intensity decreased back to zero. This could be repeated many times. These observations are definitive for oxygen quenching as the mechanism for reduced phosphorescence in our technique.

A decade ago Oster *et al.*[41] reported that oxygen quenched the phosphorescence of luminescent compounds in plastics. At room temperature, a luminescent plastic film which had been evacuated (10^{-5} mm for 0.5 hr) exhibited a progressive decrease in phosphorescence lifetime after oxygen was introduced. In certain cases, notably poly(vinyl alcohol), the phosphorescence of dyes could be observed without prior evacuation, presumably due to the lower diffusion of oxygen in the plastic. However, they attributed "the abrupt decrease in intensity of phosphorescence of the plastic in air at the transition temperature of poly(vinyl alcohol) in part to the marked increase of diffusivity of oxygen in the material above the temperature." Furthermore, samples which had been quenched with oxygen at room temperature nevertheless exhibited a strong phosphorescence at liquid nitrogen temperature in the presence of ambient oxygen. The quenching of oxygen was reduced at low temperatures. In all cases, lowering the temperature increased the phosphorescence lifetime, even of degassed samples. The results indicated that the lifetime of phosphorescence could be influenced not only by the "local viscosity" in the plastic (micro-Brownian movement of the polymer segments), but also by specific interaction of the compounds with the polymeric matrices.

The quenching of phosphorescence by oxygen was applied by Czarnecki and Kryszewski in an afterglow moving-boundary technique for the determination of diffusion coefficients of gases in polymers.[42] Photographs of the afterglow areas showed a decrease in size of the luminescent core of sample rods upon exposure to an oxygen environment with extended aging. A similar method due to Shaw[43] permitted correlation of the overall decrease in phosphorescence intensity with the size of the phosphorescent core. Jones[40] exposed very thin polymer films to an oxygen environment and measured the lifetime of additive phosphorescence as a function of oxygen pressure (0–40 μ) to find estimates of oxygen permeability.

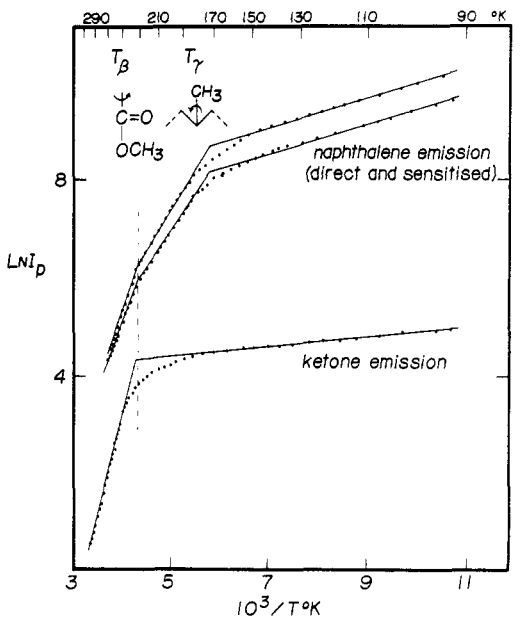


Figure 10. Arrhenius curves for phosphorescence of copolymer MMA–NMA–PVK (10:10:80).

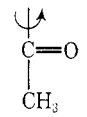
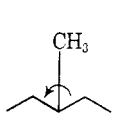
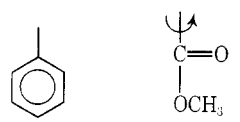
There is therefore abundant corroborative evidence for the interpretation of oxygen quenching as the dominant mechanism competing with phosphorescence from the polymer films above the transition temperatures. In the case of those polymers without side groups (polyethylene, PVC, polyacrylonitrile) the phosphorescence levels off at low temperatures. For polymers bearing mobile side groups (polystyrene, PMMA, poly(vinyl ketones)) the phosphorescence does not level off down to liquid nitrogen temperature because some thermal motion coupled to the radiationless decay processes is not completely frozen out. As the polymers warm up, additional motion sets in as specific group relaxations become accessible. Oxygen quenching thereby becomes more effective and phosphorescence drops off more rapidly.

In summary, we attribute the common discontinuous decrease in phosphorescence of polymer films with rising temperature to the increasing efficiency of oxygen quenching of the triplet states. More importantly, the regions of discontinuity are coincident with the onset temperatures for specific subgroup motions in the polymers. This therefore provides definitive evidence for the intuitive idea that the motion of gases such as oxygen in a plastic at low temperatures is directly associated with the micro-Brownian motion of small groups in the polymer.

Activation Energies. The results reported here afford activation energies which we suggest are directly attributable to the thermal relaxation of small groups and segments of the polymers and the concomitant increase of activated jumps of diffusing molecules. The activation energies from phosphorescence quenching and the related transition temperatures are summarized in Table II. We can now make a number of observations from this table.

(1) At low temperatures, *i.e.*, below any observed transition, there are three classes of phosphorescence behavior. (a) The homopolymers without polyatomic side

Table II
Transition Temperatures (T_{trans}(°K)) and Activation Energies (E_a(kcal/mol)), from Arrhenius Plots of Polymer Phosphorescence Intensity

Polymers	Low-Temperature[a] a	b	c							Chain Segment Rotation	
PS		x					178	5.2			
PS–PVK		x					182	7.0			
PS–PIPK		x					183	6.2			
PS–MVK			x				175	4.7			
PS–MIPK			x				183	4.9			
PS–5-hexen-2-one			x				175	5.4			
PS–NMA		x			120	2.0					
PE	x									163	4.3
PE–CO		x								163	4.5
PE–MVK		x								163	4.5
PE–MIPK		x								163	4.5
PMMA		x			~155	2.2					
PMMA–MVK		x			148	4.2			248	7.6	
PMMA–NMA	x				189	5.6			245	9.2	
PMMA–NMA–MVK (80:10:10)		x			173	3.0			236	6.0	
PVC (comm)	x									180	4.0
PVC (lab)	x									163	4.7
PVC–MVK	x									188	5.0
PVC–MIPK	x									163	4.2
PAN	x									~216	7.5
PAN–PVK	x									235	9.8
PAN–MVK		x		125	2.1					216	9.8
PAN–MA–MVK (75:20:5)		x		136	3.7					238	5.8
PMAN	x									234	7.6
PMAN–MVK		x								238	7.0
PMAN–MMA–MVK (75:20:5)		x	x							230	5.6
PMVK			x	145	5.8					230	12.2
PMIPK			x							233	7.2
PPVK			?				196	5.7			

[a] Classes a, b and c denoted by appropriate x marks correspond to: a, $E_a = 0$; b, $0 < E_a < 200$ cm^{-1}; c, $200 < E_a < 400$ cm^{-1}.

groups (PE, PVC, and PAN) and some copolymers which have α-methyl groups in the repeat unit (PMMA–NMA and PMAN), show Arrhenius curves which practically level off at low temperatures, where oxygen mobility is negligible. These polymers are more rigid (some paracrystalline) and there are no thermally activated processes to deplete the triplet-state population effectively below the first transition. (b) Most of the copolymers, and the homopolymer PS itself, do not level off above liquid nitrogen temperature, but reveal low activation energies of the same order as molecular rotations (≤200 cm^{-1}). Thermal motion of small side groups probably enhances radiationless decay by some intramolecular modes coupling with the matrix. (c) Some polymers, particularly those containing methyl ketone groups (PS–MVK, PS–MIPK, PS–5-hexen-2-one, PMVK and PMIPK), are exceptional. They reveal substantial positive slopes (200–400 cm.$^{-1}$) as low as liquid nitrogen temperature. The local methyl group rotation presumably is often not frozen out and this promotes radiationless decay which could be independent of oxygen quenching.

(2) The homopolymers, with the exception of the polymeric ketones, show generally a principal transition which we associate with the enhancement of oxygen quenching due to increased mobility of the gas molecules. Our values for the activation energies above the transition temperature are consistently lower than the values from the mechanical and dielectric methods, where these exist (as in PS, PE, and PVC). These second order transitions have a spectrum of activation energies dependent on the magnitude of segment of group rotations or oscillations and it would seem that for diffusion of the oxygen molecule (diameter 2.92 Å), only relatively small displacements are necessary, whereas for the loss peaks to be observed, the effects require more substantial group motion. Furthermore, the diffusion step could probably be enhanced in a kinetic sense by the presence of the mobile penetrant itself, since a more cooperative motion may be involved here than in the simple mechanical relaxation.

(3) In the case of the PS transition involving a phenyl group motion, the activation energy above the transition (E_a ~ 4.7–7.0 kcal/mol) is smaller than the value (8.3 kcal/mol) for oxygen diffusion at ambient temperatures.[44] The difference is in the right direction by analogy with the decrease observed at T_g in Arrhenius curves for diffusion. Similarly, in the transition of PE involving chain segment motion, the activation energy above the transition (4.4 kcal/mol) is lower than to that for oxygen diffusion in low-density PE (9.6 kcal/mol).[44]

(4) The activation energy for methyl group rotation is known from microwave spectra E_a = 0.9 kcal)[45] and agrees very well with the values obtained for the lower temperature range in the polymers containing methyl ketones.

(5) The regions of temperature and the corresponding activation energies are similar for each particular subgroup in different polymers.

(6) The major transitions for all polymers in the same "family" and the corresponding activation energies also show good correlation.

The above observations support the consistency of the interpretations we have presented for the phosphorescence behavior over the temperature range.

Macroscopic Transport and Accessibility. It is tempting to consider whether the thermal activation of oxygen diffusion observed at a microscopic level by the phosphorescence probe is in some way different from the macroscopic diffusion process observed by normal permeation or sorption methods. In principle, the chromophore to be quenched could reside in low concentration in a cage-like environment which precludes (by steric hindrance) the interaction of oxygen without the relaxation of the obstructing groups which form the "cage." The temperature effect is then a manifestation of the relaxation directly associated with groups in the immediate vicinity of the chromophore. In this way we could formally distinguish the "accessibility" of the chromophore to oxygen from the macroscopic diffusion of the penetrant in the polymer.

In search of experimental evidence for this "accessibility" concept we can note a few observations.

(1) The localized transition due to rotation in the case of the methyl ketone chromophore at low concentration and which has been observed for a variety of polymers is unlikely to affect the macroscopic diffusion significantly. However, since the chromophore is itself the sensor or probe in the phosphorescence method, the immediate environment about the ketone group does become of crucial importance to the observed effect. Thus when MVK or MIPK is the sensor (*e.g.*, in PS, PE, PMMA, PAN, or PMAN, with ketone), a low-temperature transition is observed in the phosphorescence curves which can be attributed to the highly localized rotation of the methyl (and sometimes, acetyl) group. If the activation process in this low temperature region involves oxygen quenching, then the importance of macroscopic transport could be neglected here. Alternatively, the activation process may involve specific enhancement of the radiationless decay by vibronic coupling, as discussed earlier.

(2) Similarly, the presence of an α-methyl group only in the monomer containing the naphthalene chromophore in the PS–NMA copolymer confines this group to the neighborhood of the emitter. A transition attributable to the rotation of the α-methyl group is observed even though this localized relaxation is not expected to influence the overall diffusion of oxygen.

(3) Further, in the case of the terpolymer of MMA–NMA–PVK (80:10:10) the α-methyl transition is observed in the naphthalene emission curve with either direct excitation at 310 nm or by sensitization through triplet–triplet transfer from the ketone excited at 350 nm (Figure 10). Yet this transition is conspicuously absent from the curve for the residual ketone emission in the same polymer. This could be good evidence for a specific localized effect in which accessibility of the naphthalene group is influenced by the nearby α-methyl group, whereas the ketone is in a different environment. The more dominant effect of the ester methyl rotation is manifested in both cases. Alternatively, the difference may be related to the efficiency with which the π,π^* triplet of naphthalene and that of the n,π^* triplet ketone is quenched by oxygen, as has been referred to earlier.

(4) The introduction of a structurally similar third component such as MMA in the terpolymer MAN–MMA–MVK (75:20:5) or MA in AN–MA–MVK (75:20:5) gives the same Arrhenius behavior as the polymers containing only MAN–MVK (7%) and PAN–MVK (7%), respectively. This strongly suggests that the local environment of the ketone is essentially unaltered even though the macroscopic properties are different.

(5) The failure of common degassing in the solid state is not definitive but is consistent with slow macroscopic diffusion in and out of the plastic. The phosphorescence method of Shaw[43] demonstrates how slow this process can really be.

(6) As noted above, the regions of temperature and the corresponding activation energies are not very different for any particular subgroup motion in a wide variety of polymer types. This is certainly consistent with a localized relaxation process and is unreasonable for a macroscopic picture.

In summary, there is some experimental evidence to support the concept of localized "accessibility" as distinct from macroscopic transport in the interpretation of this phosphorescence method for probing these low-temperature relaxations by oxygen quenching of excited states in polymers. More widespread application of the technique could give further insight into the exact nature of these transport processes.

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Gas Chromatography on Polymers at Temperatures Close to the Glass Transition

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ABSTRACT: The effect of very slow penetrant diffusion rates on chromatographic peak broadening was calculated in an attempt to explain the peak shapes and retention volumes on polymeric stationary phases at temperatures close to the glass transition. It was assumed that slow bulk diffusion was the predominant cause of peak broadening, and that polymer-penetrant equilibrium was approached exponentially with time. As illustration, peak shapes for *n*-tetradecane on a polystyrene stationary phase were calculated using chromatographic data determined well above T_g, together with data predicted by a free volume theory for the temperature dependence of diffusion rates close to T_g. This approach predicted the observed broadening and skewing of peaks as the temperature approached T_g from above, but further elaboration is necessary close to T_g.

It has been shown that a gas chromatographic technique may be used to determine the glass transition temperature of polymers.[2a,b] The method involves measuring the retention volumes as a function of temperature for a suitable low molecular weight "probe" on the polymeric stationary phase. The normally linear plot relating the logarithm of the retention volume to the reciprocal absolute temperature shows a discontinuity in the region of the transition temperature. The shape of the retention diagram has been qualitatively explained[2a] by assuming that below T_g the probe interacts only with the surface of the glassy polymer because the rate of diffusion of the probe through the polymer is too slow to permit significant bulk interaction. Conversely, well above T_g, surface effects are negligible and the retention volume is a measure of the thermodynamic interaction of the probe with the bulk polymer. Close to T_g, it has been proposed that a combination of these two retention mechanisms leads to nonequilibrium sorption of the probe molecule; as the temperature rises the increasing penetrability of the polymer outweighs the effects of increasing probe vapor pressure, so that retention volumes increase in this region. In this paper, the factors which affect the gas chromatographic retention of low molecular weight probes on polymers close to their glass transition temperatures will be considered in some more detail.

Experimental Section

Peak shapes above T_g were determined using *n*-tetradecane (Qualkits, PolyScience Corp.) with a 100-cm column of 0.25-o.d. copper tubing containing 27.9 g of 40–60 mesh glass beads coated with 0.16 g of polystyrene (Pressure Chemical, std mol wt 51,000). Average polymer thickness, estimated from the surface-to-volume ratio of the coating, was about 0.8×10^{-6} m. The column was used in a Varian Aerograph Model 1720 gas chromatograph with helium carrier gas and a thermal conductivity detector. Other details were as previously published.[3]

The calculations of peak shapes were made using a simple APL computer program. The hyperbolic Bessel functions in eq 13 were evaluated using either an appropriate asymptotic series[4] or an exponential approximation,[5] depending on the value of the argument.

Kinetic Aspects of Chromatographic Peak Shape

As the temperature of the polymer–probe system is reduced through the glass transition temperature, a considerable decrease in the rate of diffusion of probe through the polymer is expected. This kinetic phenomenon affects the rate at which equilibrium is attained between vapor and polymer at every position along the gas chromatographic (gc) column, which in turn governs the width of the eluted gc peak. To attempt to quantify this effect, a brief review of some aspects of chromatographic peak broadening is required. The following summary follows the approach and terminology of Littlewood.[5] The starting point is the "first-order conservation equation" of chromatography[6] which expresses the conservation of mass within a chromatographic peak as it is carried through a column.

$$\partial c/\partial x + a(\partial c/\partial V) + m(\partial q/\partial V) = 0 \quad (1)$$

where V is the volume of gas passed through the column (cm^3), x is the distance from inlet end of column (cm), q is the vapor concentration in stationary phase (mol/g), c is the vapor concentration in gas phase (mol/cm^3), m is the mass of stationary phase per unit length of column (g/cm), and a is the volume of gas phase per unit length of column (cm^2). If the usual chromatographic condition of very small sample size is met, then the isotherm of interaction of the sample vapor between stationary and gas phase may be linear so that

$$q = \beta c \quad (2)$$

where β is the partition coefficient. If, however, interaction between the two phases is not instantaneous, it is necessary to replace eq 2 by

$$q = \beta c f(t) \quad (3)$$

where $f(t)$ is some function of time which approaches