

The Phosphorescence Spectrum and Photodegradation of Polystyrene Films

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Synopsis

Low-temperature polarized phosphorescence spectroscopy of polystyrene polymerized under different conditions is used to detect emission from phenyl alkyl ketone endgroups in addition to triplet excimer emission from phenyl groups. The carbonyl group concentration can only be lowered by vigorous chemical reduction; and from the phosphorescence excitation spectrum, these carbonyl groups are considered responsible for the initiation of polystyrene photodegradation by solar radiation.

INTRODUCTION

When polystyrene is subjected to outdoor weathering or similar photo-oxidative conditions, it undergoes rapid yellowing and, finally, embrittlement.¹ Many polymers such as polystyrene and the polyolefins show no electronic absorption bands down to the solar spectrum cut-off at 290 nm, and the identification of the absorption centres responsible for the initiation of photodegradation has been the subject of continued investigation.² Studies of the polyolefins have implicated catalyst residues,³ hydroperoxides, and carbonyl groups⁴ that are the result of synthesis and fabrication. The reaction path of the photo-oxidation of polystyrene has been studied,⁵ but the initial step of sunlight absorption by the polymer has not been elucidated.

Luminescence spectroscopy provides a sensitive method of determining both the polymer excited states and the impurities implicated in energy absorption.⁶ In particular, the phosphorescence from commercial polystyrene samples has been attributed to benzaldehyde⁷ and polymer carbonyl impurity groups⁸ and appears to be sample dependent. In this paper, the polarized delayed emission spectra, triplet lifetime, and excitation spectra of polystyrene films of varying purity are reported to identify the phosphorescent impurities present and their origin. The significance of these groups in photodegradation and the intrinsic emission from pure polystyrene films are discussed.

EXPERIMENTAL

Material

Samples A to F were polymerized by the methods indicated using B.D.H. styrene which was freed from inhibitor, prepolymerized, and vacuum distilled.

Sample A. Thermal polymerization under vacuum in a sealed ampoule at 80°C, after exhaustive freeze-thawing. Residual air pressure was lower than 10^{-4} torr.

Sample B. As for sample A but with azobisisobutyronitrile initiation at 60°C.

Sample C. As for sample A, but with a residual air pressure of 10^{-1} torr.

Sample D. As for sample B, but with a residual air pressure of 10^{-1} torr.

Sample E. Slow thermal polymerization at 25°C in the presence of air.

Sample F. Thermal polymerization under vacuum in a sealed ampoule at 80°C after rigorous oxygen removal by sealing distilled styrene in a grease-free vacuum manifold, freeze-thawing, and bulb-to-bulb distillation over freshly deposited sodium.

In all cases, polymerization was terminated at $\sim 40\%$ conversion and the polymers freed of residual monomer by repeated precipitation from toluene solution in methanol. Viscometry in toluene at 25°C gave \bar{M}_v ranging from 0.2×10^6 to 1.4×10^6 . The following samples were also studied:

Sample G. Two samples anionically polymerized with sodium in tetrahydrofuran under high-vacuum conditions. $\bar{M}_v = 2.0 \times 10^4$ and 5.8×10^4 . (We thank Dr. D. H. Richards of Explosives Research and Development Establishment, Waltham Abbey, England, for providing these samples.)

Sample H. A commercial sample (Styron 685, Dow Chemical Co. brand of polystyrene resin); $\bar{M}_v = 3.5 \times 10^5$.

Reduction Procedures

In attempts to reduce the carbonyl impurities identified (see Spectral Analysis) to the corresponding alcohol or alkane, the following standard reduction methods were employed: (a) A tetrahydrofuran solution of polystyrene was refluxed under nitrogen with excess lithium aluminium hydride for 12 hr and then hydrolyzed with dilute sulfuric acid. (b) A toluene solution of polystyrene, anhydrous hydrazine, and potassium *t*-butoxide was refluxed for 14 hr. (c) A diphenyl ether solution of polystyrene, hydrazine hydrate, and potassium hydroxide was refluxed and distilled for 6 hr.

In all cases, the polymer was twice precipitated after recovery.

Photo-oxidations

Thin films (10 to 20 μm) were cast from chloroform or benzene solution on either mercury or a silica plate. Films were mounted, evacuated to 10^{-4} torr to remove residual solvent, and photo-oxidized in air at 60°C with an Osram 125-W medium-pressure mercury arc. The course of oxidation was

followed by the change in the UV absorption spectrum at 340 nm and the growth of the 1685 cm^{-1} carbonyl band in the infrared.⁹

Preparation of 1,3-Diphenylpropan-1-one

This model ketone was synthesized by catalytic hydrogenation of benzalacetophenone.¹⁰ The product was recrystallized from petroleum ether and zone refined to a melting point of 71.5°C .

Emission Spectra

Thin polystyrene films were totally immersed in liquid nitrogen in a partially silvered synthetic silica Dewar flask. Luminescence was excited by a broad band of UV from 250 nm to 350 nm filtered from the focussed output of a 900-W Xenon arc or a 200-W high-pressure mercury arc by an aqueous solution of NiSO_4 and CoSO_4 and a Chance-Pilkington OX7 filter. Delayed emission was separated from fluorescence by a variable-frequency (10 to 80 Hz), single-shutter rotating can phosphoroscope, focussed on the entrance slit of a 1.0-m Czerny Turner monochromator ($f/9$, dispersion $16\text{ \AA}/\text{mm}$), and detected by an EMI 9558 photomultiplier. Phosphorescence decay curves were recorded on a Tektronix 549 storage oscilloscope. Phosphorescence excitation spectra were obtained with the Xenon arc and an $f/3.5$, 0.25-m Bausch and Lomb high-intensity monochromator for excitation and monitoring a broad band of emitted light isolated by filters. The excitation spectra were corrected for the variation of light source intensity and monochromator transmission.¹¹ Polaroid HNP'B sheet having a UV cut off at 270 nm was used as a polarizer.

RESULTS AND DISCUSSION

Spectral Analysis

In a frozen solution at 77°K , atactic polystyrene is reported to show a highly structured delayed emission, commencing from 350 nm, identical to the phosphorescence of ethylbenzene,¹² i.e., emission is occurring from isolated phenyl units. In contrast, in the solid state, the phosphorescence spectrum commences around 390 nm and consists of a number of poorly resolved bands superimposed on a broad background (Fig. 1). By altering the delay period between the excitation and observation of phosphorescence from 2 ms (i) to 75 ms (ii), two distinct spectra are obtained with different polarization properties. The structured, short-lived component (i) and the broad, long-lived component (ii) of the phosphorescence spectrum of Figure 1 will be considered separately.

(i) Short-Lived Emission

The structured bands of the polystyrene phosphorescence spectrum have been analyzed in Figure 1 as two vibrational progressions of $\approx 1650\text{ cm}^{-1}$ with electronic origins at 386 nm (weak) and 398 nm (strong). Recent studies of emission spectra of the phenyl alkyl ketones such as butyrophe- none show that the phosphorescence consists of two vibrational progressions of 1650 cm^{-1} with origins at 384 nm and 397 nm.^{13,14} The relative in-

TABLE I
Degree of Polarization P of Polystyrene Phosphorescence from Sample C at Delay Times
of (i) 2 ms and (ii) 75 ms

Wavelength (nm)	$P(\pm 0.02)^a$	
	(i)	(ii)
400	+0.3	0
430	+0.12	0
460	+0.13	0
490	+0.12	0

^a P is defined as $(I_{11} - I_1)/(I_{11} + I_1)$, where I_{11} and I_1 represent emission intensities parallel and perpendicular to the polarization direction of the exciting light.

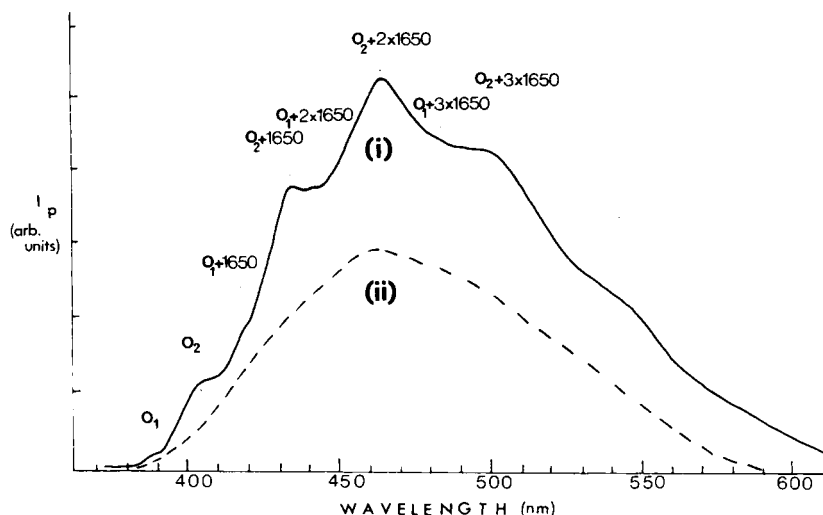


Fig. 1. Phosphorescence spectrum of a thin film of polystyrene at 77°K. The vibrational analysis is shown with electronic origins O_1 and O_2 at 386 nm and 398 nm. Spectra (i) and (ii) were obtained after delay periods of 2 ms and 75 ms, respectively, between excitation and emission.

tensity of these two progressions is matrix dependent and is believed to arise from two possible conformations of the carbonyl group.¹⁴ The close similarity of this emission to the polystyrene phosphorescence strongly suggests the presence of a phenyl alkyl ketone analog in the polymer. The decay of the polystyrene phosphorescence was found to be nonexponential, and the short-lived component was analyzed in terms of two first-order rate constants $k_1 = 330 \text{ s}^{-1}$ and $k_2 = 12.5 \text{ s}^{-1}$ ($\tau_p = 0.003 \text{ s}$ and 0.08 s). This nonexponential phosphorescence decay has also been observed from phenyl alkyl ketones and has been assigned to perturbation between closely lying ${}^3n\pi^*$ and ${}^3\pi\pi^*$ states leading, for example, to triplet lifetimes for butyrophenone of 0.005 s and 0.10 s.¹⁴ The assignment of the structured polystyrene phosphorescence as emission from the ${}^3n\pi^*$ state of a phenyl alkyl ketone unit is further supported by the polarization data presented in Table I. Emission from a ${}^3n\pi^*$ state is polarized predominantly in-plane, giving a positive value of P , the degree of polarization, up to a limit of $+0.5$ ¹⁵ Allowing for experimental depolarization effects, a positive value

of P is alone strong evidence for a ${}^3n\pi^*$ state. The possible origin of this phenyl alkyl ketone unit in the polymer is considered later on.

(ii) *Long-Lived Emission*

The broad, underlying spectrum (ii) of Figure 1 is associated with an excited state having a lifetime of 1.5 s as well as a small amount of the structured emission that is not quite removed by the 75 ms delay period. The emission was depolarized (Table I). The long triplet lifetime suggests that emission arises from the ${}^3\pi\pi^*$ state of an aromatic hydrocarbon. This is either present as an impurity or is intrinsic to the polystyrene. The structureless spectrum and the zero polarization suggest it is not an aromatic impurity. Such impurities as residual monomer were further discounted as the spectrum was unchanged after successive precipitations and after evacuation to 10^{-4} torr for several hours at the polymer softening point.¹⁶ It is suggested that the emission arises from triplet state excimers formed between adjacent phenyl groups, one of which is in an excited triplet state.

Formation of excimers in polystyrene has previously been reported only in the singlet state; the fluorescence spectrum from thin films at 295°K being broad and structureless and the observed separation between the singlet state absorption origin and the broad band maximum being 6900 cm^{-1} .¹⁶ Theoretical calculations suggest that stable triplet excimers can also be formed in substituted benzenes such as polystyrene,^{17,18} and such emission has been observed from the halogenated benzenes¹⁹ and alkyl benzenes.²⁰ The measured separation between the maximum of spectrum (ii) and the reported triplet-state origin¹² is 6600 cm^{-1} . This is in close agreement with calculations for benzene-like triplet excimers and the experimental observations of the model dimer system (2,2')-paracyclophane.¹⁸

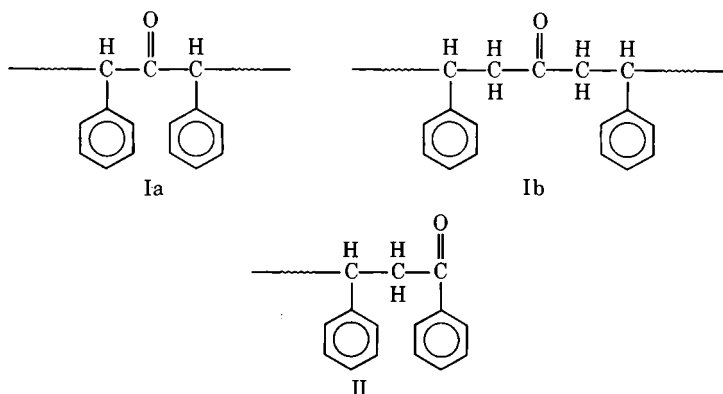
Excimer lifetimes are of the same order as the corresponding "free molecule" lifetimes. Allowing for increased radiationless quenching in the solid state, the measured value of 1.5 s is comparable with the triplet lifetime of 3 s reported for polystyrene in a frozen glass.²¹ The depolarized emission can also be explained by triplet excimer formation. Apart from experimental artifacts, one of the common explanations for phosphorescence depolarization is triplet energy transfer,²² i.e., energy is transferred from the site of absorption to the excimer forming site before emission occurs. The increased efficiency of this process in the solid state would explain the absence of the structured emission expected from isolated phenyl units, as was observed from frozen solutions of polystyrene.¹²

Sample Dependence of Carbonyl Emission Centers

The emission spectrum of Figure 1 is characteristic of samples C, D, and E, i.e., those polymers polymerized in the presence of oxygen. Samples A, B, and F, which were polymerized at low residual air pressure, show spectral features similar to Figure 1, but the structured emission is weaker and less well resolved (Fig. 2). The commercial sample, H, showed a similar spectrum. Sample G, which was anionically polymerized, shows

almost negligible structured emission, and the emission spectrum (Fig. 2) is equivalent to the broad underlying excimer emission of Figure 1(ii).

The emission from samples C, D, and E could be reduced to an intensity more comparable with that of the samples A, B, F, and H by the vigorous Wolf Kishner reduction (b) and (c) given above but not by the lithium aluminium hydride reduction (a). None of the chemical reductions employed could alter the emission spectrum of samples, A, B, F, G, or H. Soxhlet extraction or precipitation did not alter the emission from any of the samples. These results suggest that the carbonyl emissive centers are attached to the polymer chain and are formed during polymerization. The carbonyl groups can be formed either in-chain (Ia or b) or at the chain ends (II):



The carbonyl units Ia and Ib are unconjugated and will not show phenyl alkyl ketone-like emission. For example, the ketone model of Ia, 1,3-diphenylpropan-2-one, has a triplet state energy of 79 kcal/mole, so that emission would commence around 362 nm. The singlet absorption spectrum of this ketone shows features of a perturbed alkyl ketone rather than of an aromatic ketone.²³ The model for the carbonyl unit (II), 1,3-diphenylpropan-1-one, has been synthesized (see above) and its emission spectrum and lifetime measured. This showed the spectral features of phenyl alkyl ketone emission. The 3-phenyl substituent had not perturbed the lowest ${}^3n\pi^*$ state, and the triplet lifetime was analyzed as the sum of two components of 0.003 s and 0.1 s.

The formation of the carbonyl unit (II) can occur in the course of polymerization. Growing polystyrenyl free radicals are readily scavenged by oxygen to form peroxy radicals and then a polystyrene peroxide.²⁴ Decomposition of isolated peroxide units will yield a phenyl-alkyl ketone endgroup and an hydroxyl endgroup.²⁵

Initiation of Photodegradation

Figure 3 shows the excitation spectrum of polystyrene phosphorescence in the tail of the polymer $S_1 \leftarrow S_0$ absorption band. Also shown in this figure is the band edge of the solar spectrum at the earth's surface²⁶ and the reported action spectrum for the degradation of polystyrene film.²⁷

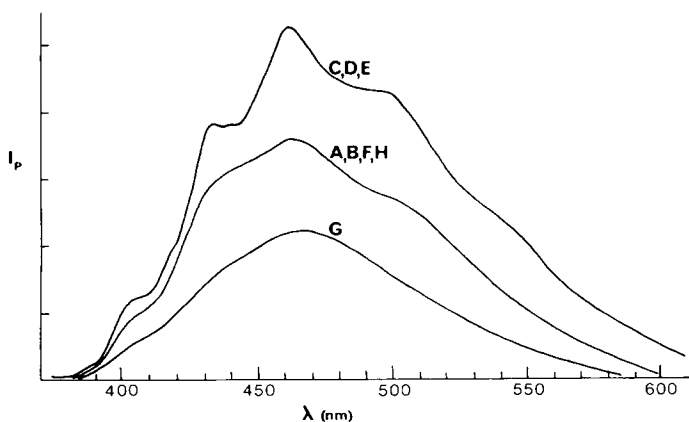


Fig. 2. The variation in the phosphorescence spectrum of cast films of polystyrene polymerized under different conditions: (a) samples C, D, and E; (b) samples A, B, F, and H; (c) sample G. Details of the samples are given in text.

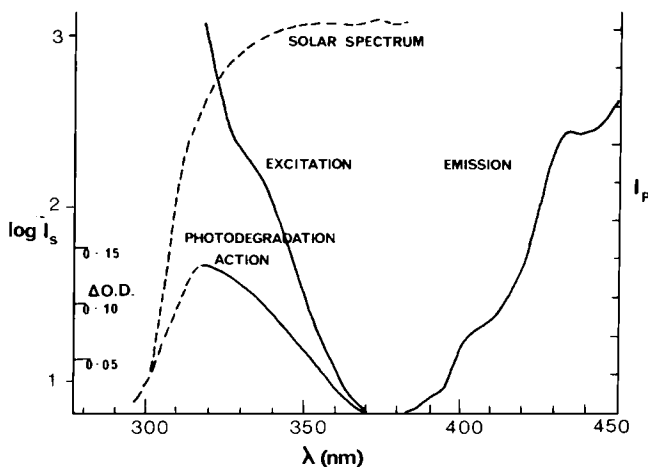


Fig. 3. The corrected excitation spectrum of polystyrene phosphorescence compared with the action spectrum of photodegradation (reference 27). The extent of degradation is given by $\Delta O.D.$, the change in sample optical density at 400 nm. The solar spectral intensity, given as $\log I_s$ ($nW/cm^2\text{\AA}$) is taken from reference 26.

While the rapid fall-off in the solar band edge and the variation of this with latitude²⁶ precludes an accurate analysis, it can be seen that if the excitation spectrum is multiplied by the solar spectrum, the action spectrum of degradation is generated. The excitation spectrum is similar to the absorption spectrum of a phenyl alkyl ketone such as butyrophenone so that the absorption of light in this region is due to the polymer carbonyl groups rather than direct absorption by the polystyrene. It follows that the photodegradation of polystyrene is most likely initiated by the aromatic carbonyl groups.

The quantum yield of free-radical formation by the scission of a phenyl alkyl ketone is less than 10^{-3} , so the formation of polymer hydroperoxides

to initiate autoxidation must occur as a secondary process.²⁸ Possible initiating sequences would be Norrish type II scission to give acetophenone and an unsaturated chain end followed by (i) singlet oxygen formation and attack on the unsaturation to form a hydroperoxide,²⁹ or (ii) hydrogen atom abstraction from the polystyrene by the excited acetophenone leading to hydroperoxide formation α to the phenyl group of the polymer.

The photoxidation of polystyrene films (see above) was accompanied by an increase in carbonyl absorption in the IR spectrum. However, the emission intensity from the samples decreased, although it would have been expected that auto-oxidation would lead to an increase in aromatic carbonyl concentration.^{5,9} It is possible that the formation of extended unsaturation on the polymer surface effectively screens the substrate and lowers the emission intensity.

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