

The Mechanism of Photoprotection of Polystyrene Film by Some Ultraviolet Absorbers

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Synopsis

The efficiency of three commercial ultraviolet absorbers, a 2-hydroxy benzophenone, a 2-hydroxy benzotriazole, and a nickel chelate, in preventing the photo-oxidation of polystyrene films has been measured. When compared with the calculated screening and phosphorescence quenching efficiency, it is found that (i) the nickel chelate protects the substrate by UV screening alone and is a poor photoprotector, and (ii) the 2-hydroxy benzophenone and 2-hydroxy benzotriazole are more efficient photoprotectors and protect by triplet energy transfer from excited polymer carbonyl impurity groups in addition to UV screening.

INTRODUCTION

In the photoprotection of thin polymer films and fibers by commercial ultraviolet absorbers, the measured protective efficiency is often greater than the screening efficiency calculated from the preferential absorption of solar radiation by the additive.¹ This increased efficiency has been attributed to radiationless energy transfer from photoexcited centers, such as carbonyl groups, in the polymer to the UV absorber molecules.^{2,3} However, the only direct physical evidence for this process in a polymer-stabilizer system has been from the quenching of luminescence from chromophores that are of no significance in the initiation of polymer photodegradation.^{3,4} Recent photochemical studies of polypropylene and ketone model systems^{5,6} have contradicted these photophysical results and, in the polyolefins at least, it appears that hydroperoxide decomposition and free-radical scavenging may be more important than electronic energy transfer.

In this paper, a photochemical and photophysical study is presented of the protection of polystyrene films by the UV absorbers Cyasorb UV 9 (2-hydroxy-4-methoxybenzophenone; American Cyanamid Company), Tinuvin 327 [2-(3',5'-di-*t*-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole; Geigy Chemical Corporation], and Cyasorb UV 1084 [2,2'-thiobis(4-*t*-octylphenolato)*n*-butylamine nickel; American Cyanamid Company]. The photoprotective efficiency is compared with the calculated screening efficiency and the measured efficiency in quenching emission from the carbonyl units in the polystyrene films, to assess the importance of electronic energy transfer.

EXPERIMENTAL

Materials

The polystyrene used was either an extracted and precipitated commercial sample, Styron 685 (Dow Chemical Co. brand of polystyrene resin), or samples of distilled styrene polymerized either thermally or by free-radical initiation. The polymer was dissolved in toluene and precipitated in methanol to remove residual monomer. Thin films (15 μm) containing the additive were cast from benzene solution and evacuated. Additive concentration was obtained by UV absorption spectrophotometry. Cyasorb UV 9 and Tinuvin 327 were recrystallized before use; Cyasorb UV 1084 was used as obtained.

Photo-oxidation

Films were irradiated in air at 333°K with a 125-W medium-pressure mercury arc filtered by 3 mm of Schott Jena W G 295 glass. This removed the mercury lines at shorter wavelength than the solar radiation cut off at 290 nm. The light intensity at the samples was 8×10^{16} quanta/sec as determined by ferrioxalate actinometry. Photo-oxidation of the samples was followed by measuring the change in optical density at 240 and 340 nm in the UV absorption spectrum.

Phosphorescence Spectra

The delayed emission spectra from thin films were measured at 77°K. The output of a focused 200-W high-pressure mercury arc was filtered by 10 cm of aqueous NiSO_4 and CoSO_4 solution and a Wild KG1 filter to isolate exciting light from 290 nm to 350 nm. Phosphorescence from the back face of the film was isolated by a variable-speed phosphoroscope and measured by a 1.0 m Jarrell Ash Czerny Turner spectrometer. By using normal incidence and a reproducible sample position, the absolute emission intensities from solid films could be measured. The effect of reabsorption of the emitted phosphorescence by the UV absorber (i.e., an internal filter effect) was minimized by measuring the quenching of the second vibronic band at 430 nm where absorption by the additive was insignificant.

RESULTS AND DISCUSSION

Photo-oxidation

The photo-oxidation of polystyrene can be conveniently followed by the change in the UV absorption spectrum of the polymer at 340 nm.⁷ In this investigation, it was found that the change in optical density at 240 nm as a function of time of irradiation gave the same rate of photo-oxidation, and was more sensitive than measurements at 340 nm. This allowed the measurement of degradation at low exposure times and eliminated problems due to loss of additives on prolonged exposure.

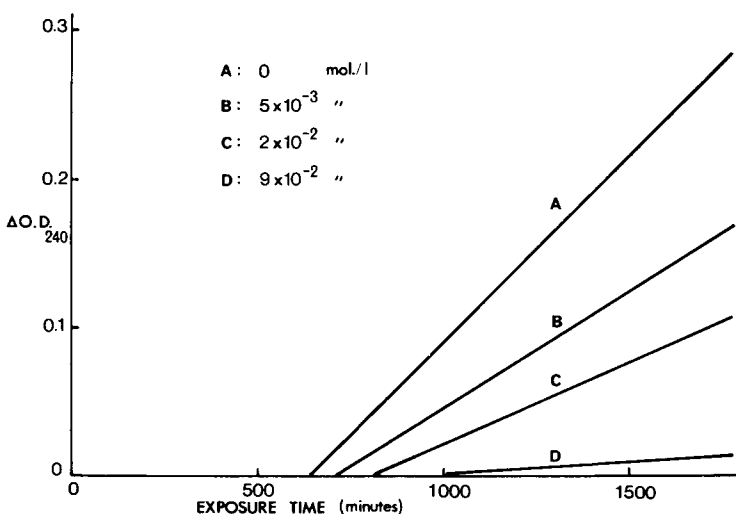


Fig. 1. Ultraviolet exposure of $15 \mu\text{m}$ polystyrene films at 333°K . Change in sample optical density at 240 nm as a function of exposure, for samples containing the indicated concentrations of Cyasorb UV 9.

Figure 1 shows the change in optical density at 240 nm ($\Delta\text{O.D.}_{240}$) as a function of exposure time for films with increasing concentration of Cyasorb UV 9. Similar curves were obtained for polystyrene containing the other additives studied. It is seen that there is an induction period before the onset of degradation that depends on the additive concentration. The rate of photo-oxidation following this induction period decreased with increasing additive concentration. The protective efficiency of a UV absorber at a given concentration, R/R_0 , is defined as the ratio of the rate of degradation in the presence of the additive to that of the pure film. In Figure 2, the photoprotective efficiency of the UV absorbers studied is plotted as a function of concentration. The results presented in Figures 1 and 2 were obtained for a single batch of thermally polymerized polystyrene. Studies of the other polystyrene samples (see previous section) gave identical UV absorber performance.

Calculated Protective Efficiency

From the known extinction coefficients of the UV absorber and the sensitizing unit in the polymer, the light absorbed by the film was calculated. If the optical density of the photosensitive center is low compared with that of the UV absorber, the calculated protective efficiency, R/R_0 is given by

$$R/R_0 = 0.4343 \left(\frac{1 - 10^{-D_{scr}}}{D_{scr}} \right)$$

where D_{scr} is the optical density of the UV absorber.⁸ This gives the protective efficiency of the additive as a UV screener alone.

The calculated values of R/R_0 as a function of UV absorber concentration are given in Figure 2 for a sample thickness of $15 \mu\text{m}$.

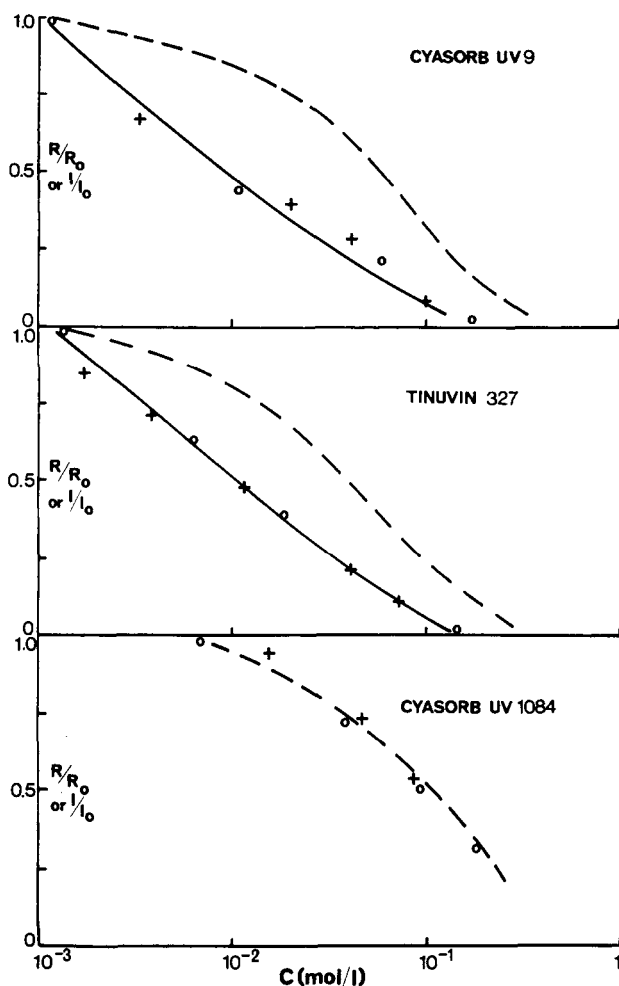


Fig. 2. Protective efficiency of UV absorbers in $15 \mu\text{m}$ polystyrene films as a function of UV absorber concentration: (+) measured photo-oxidative protective efficiency, R/R_0 ; (o) measured phosphorescence quenching efficiency, I/I_0 ; (—) calculated screening efficiency, R/R_0 .

Phosphorescence Quenching

When excited with UV light in the wavelength range of 290–350 nm, i.e., with energy lower than that of the first $S_1 \leftarrow S_0$ transition, polystyrene shows a structured phosphorescence spectrum from 390 nm to 580 nm that is attributed to triplet state emission from phenyl alkyl ketone units on the polymer chain.^{9,10} These aromatic carbonyl units have been implicated in the initiation of photo-oxidation,^{8,10} which, from studies of model systems such as butyrophenone, occurs through the excited triplet state.

When the commercial UV absorbers are incorporated in the polymer films, the phosphorescence intensity is decreased. The phosphorescence

quenching efficiency I/I_0 is the ratio of the emission intensity in the presence of the absorber to that of the pure film. The dependence of I/I_0 at 430 nm on the UV absorber concentration is plotted in Figure 2.

The decrease in phosphorescence intensity with increased additive concentration can arise either from competitive absorption of incident UV radiation by the absorber, i.e., a screening effect, or radiationless energy transfer from the excited carbonyl units, in addition to screening. If screening alone is occurring, then the phosphorescence quenching curves should agree with the calculated protective efficiency curves. If energy transfer is occurring in addition to screening, the phosphorescence will be quenched at much lower additive concentrations, depending on the energy transfer efficiency.

The data plotted in Figure 2 demonstrate the following:

(i) There is close agreement between the measured photo-oxidative protective efficiency and phosphorescence quenching efficiency for all three additives. This supports the premise that the phosphorescent polystyrene carbonyl units are important in photodegradation. Thus, if an additive can reduce the steady-state triplet carbonyl concentration, it should retard photodegradation.

(ii) Samples containing Cyasorb UV 9 and Tinuvin 327 show photo-oxidation and phosphorescence quenching efficiencies greater by a factor of about 2 than the calculated protective efficiency over the concentration range of additive usually employed in commercial samples (i.e., from 0.1 wt-% to 1.5 wt-% additive, or about 5×10^{-3} mole/l to 10^{-1} mole/l.).

(iii) Samples containing Cyasorb UV 1084 show close agreement between the experimental and calculated curves. In addition, Cyasorb UV 1084 appears to be a poor photoprotector of polystyrene, quite high concentrations being required to inhibit photo-oxidation.

It seems clear that the photoprotective ability of the nickel chelate, Cyasorb UV 1084, in thin polystyrene films can be ascribed solely to competitive absorption of UV radiation. This is in contrast to the results for Cyasorb UV 9 (a hydroxy benzophenone) and Tinuvin 327 (a hydroxy benzotriazole), for which UV absorption alone cannot explain the protective efficiency. In view of the coincidence of the data for phosphorescence quenching and photo-oxidation quenching for samples containing the last two additives, the increased protective efficiency most probably arises through radiationless energy transfer from the excited polystyrene carbonyl units to the additive molecules. If this is correct, it is important to determine why energy transfer to the Cyasorb UV 1084 molecules is not occurring, since nickel(II) chelates have been postulated as efficient quenchers of excited states in polypropylene.^{2,4}

Mechanisms of Energy Transfer

Long-range, single-step radiationless energy transfer can occur from the excited singlet or triplet state of a donor molecule to the singlet or triplet state of an acceptor molecule.¹¹ The distance over which transfer can

occur is determined largely by the interaction energy between the donor and acceptor molecules. This is typically 20 to 60 Å for singlet-singlet transfer (dipole-dipole interaction) and 10 to 20 Å for triplet-triplet energy transfer (exchange interaction). For efficient transfer to occur, the acceptor must have the appropriate electronic energy level at a lower energy than the donor energy level. To minimize back transfer, this energy separation should be greater than thermal energies.

The energies of the singlet and triplet states of the polystyrene carbonyl unit (donor) and the three UV absorbers (acceptors) relative to the ground state are shown in Table I. It is seen that the triplet energies of both the hydroxy benzophenone and the hydroxy benzotriazole molecules are less than the carbonyl triplet energy by at least 1500 cm^{-1} , whereas the phenolato ligand of the nickel chelate has a triplet energy some 1700 cm^{-1} greater than that of the polystyrene carbonyl. Consequently, the efficiency of triplet energy transfer from the polystyrene carbonyl to Cyasorb UV 9 and Tinuvin 327 will be much greater than to Cyasorb UV 1084.

TABLE I
Singlet- and Triplet-State Energies of Commercial UV
Absorbers and Polymer Carbonyl Groups

	S_1 , cm^{-1a}	T_1 , cm^{-1}
Polystyrene carbonyl	29,000	25,300 ^b
Tinuvin 327	28,200	<23,000 ^c
Cyasorb UV 9	30,500	23,800 ^d
Cyasorb UV 1084	29,000	27,000 ^e
Polypropylene carbonyl	33,000	29,500 ^e

^a Singlet-stage energies obtained from absorption spectra.

^b References 9 and 10.

^c Reference 13.

^d Reference 14.

^e Reference 15.

An estimate of the efficiency of this energy transfer process is given by the critical interaction radius for quenching the carbonyl triplet state. When the measured phosphorescence quenching curve for Tinuvin 327 (Fig. 2) is corrected for the contribution due to screening, a half-quenching concentration of 0.036 mole/l. is obtained. Applying Perrin's formula for triplet-triplet transfer in rigid solution,¹¹ a critical radius of 15 Å is obtained. This is similar to values for energy transfer between small molecules in rigid media.

In considering the energy levels of the nickel chelate, only the ligand electronic transitions have been considered important for energy transfer. While direct energy transfer to the metal ion can also occur, the efficiency of this process depends on the extent of delocalization of the metal *d*-orbitals over the ligand orbitals and is in general much lower than energy transfer to the ligand.¹²

CONCLUSIONS

The results of this investigation suggest that the chemical nature of both the UV stabilizer and the polymer will determine the mechanism and efficiency of photoprotection of a polymer film. The route by which photodegradation occurs and the importance of impurities remaining after either synthesis or processing have to be known to determine the most efficient method of stabilization. The detailed studies of Wiles⁵ showed that polymer hydroperoxide decomposition was the dominant initiation route in polypropylene photo-oxidation, and those UV stabilizers such as the nickel chelates that showed some antioxidant ability were the more efficient photoprotectors. However, direct carbonyl chromophore excitation is most probably the significant initiating route in polystyrene,^{8,10} and the coincidence of the photophysical and photochemical data reported here support this. Energy transfer from the excited triplet state of polystyrene carbonyl groups to the UV stabilizer is thus a significant photoprotective mechanism and explains the increased efficiency of those organic additives having low-lying triplet energy levels over the less efficient nickel chelate. It is noted that in polypropylene, the aliphatic carbonyl impurity energy levels will occur¹⁵ near $33,000\text{ cm}^{-1}$ (S_1) and $29,500\text{ cm}^{-1}$ (T_1) so that, from Table I, the nickel chelate can in this case also protect by energy transfer, if initiation through carbonyl groups occurs in addition to hydroperoxide decomposition.

It is emphasized that this investigation of the mechanism of photoprotection has minimized other factors that can affect real polymer performance, such as the actual photolytic stability of the additive, the compatibility of the additive with the polymer (and thus the rate of additive loss during weathering), and the uniformity of additive distribution in the matrix. In semicrystalline polypropylene, the last consideration is much more important than in amorphous polystyrene.

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