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# Photostabilization of Polymeric Materials

K. P. Ghiggino[a]
[a] Department of Chemistry, University of Melbourne, Victoria, Australia

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# PHOTOSTABILIZATION OF POLYMERIC MATERIALS

K. P. GHIGGINO

Department of Chemistry
University of Melbourne
Victoria 3052, Australia

Key Words: UV absorbers; Photostabilization; Polymer photochemistry

## ABSTRACT

Recent advances in our understanding of natural photoprotection mechanisms and the photophysical processes occurring in synthetic macromolecules and ultraviolet absorbing additives are reviewed. The application of photophysical measurements and ultrafast laser spectroscopy demonstrate that energy dissipation pathways in intramolecularly hydrogen-bonded UV absorbers are sensitive to the stabilizer structure and the surrounding polymer and solvent environment. The mechanisms of transport, trapping, and dissipation of absorbed light energy in macromolecules are described, and the factors important in determining the efficiency of these processes outlined. The implications of these studies for improving the design of photoprotecting additives and the development of new synthetic polymer materials with improved light stability are discussed.

## INTRODUCTION

In Nature, protection from the harmful effects of solar radiation is achieved by many methods. In addition to the well-documented antenna function of carotenoid pigments in plants, it is known [1] that such pigments are required for photosynthetic organisms to grow in oxygen-containing atmospheres. This photoprotective role of carotenoid pigments was initially attributed to their ability to efficiently scavenge singlet-excited oxygen [2] formed following light absorption by chlorophyll. Singlet oxygen is a highly reactive species which can lethally damage cell components. However, more recent work [3] using model porphyrin-carotenoid compounds suggests that efficient triplet–triplet energy transfer can occur from photoexcited chlorophyll pigments to carotenoids on a nanosecond time scale. This mechanism requires $\pi$-orbital overlap of the interacting chlorophyll and carotenoid and results in the efficient deactivation of chlorophyll triplet states before the sensitized formation of singlet oxygen can occur. Thus there is likely to be a complex interplay between the antenna function of carotenoids and their photoprotective role by quenching and scavenging mechanisms. The remarkable evolution of protein-pigment structures, which has led to the specific arrangements of photosynthetic pigments necessary to achieve these various roles, has recently been discussed [3].

Plants and organisms produce other pigments which act as natural sunscreens. Naturally occurring melanin in pigmented skin efficiently absorbs damaging ultraviolet solar radiation and dissipates this energy harmlessly [4]. Melanin formation in response to sun exposure is well known and acts as an active solar photoprotection mechanism. A number of UV screening agents, including mycosporine amino acids in corals, have also been identified in marine organisms [5, 6]. A particularly efficient absorbed light energy dissipation mechanism is observed in some flower pigments. The plant pigments quercetin (3,3′,4′,5,7-pentahydroxy flavone) and fisetin (3,3′,4′,7-tetrahydroxyflavone) emit fluorescence which is considerably red-shifted compared to the normal absorption [7]. This large red-shift of the emission has been attributed to the rapid formation ($<10$ ps) of a hydroxy-pyrilium structure following excited state proton transfer in the intramolecularly hydrogen-bonded hydroxyflavone structure. This transformation is illustrated in Fig. 1 for the related 3-hydroxyflavone molecule.

The transformation from the initial ground state molecule through the excited states of the normal and proton transferred species and final return to the initial state occurs on an ultrafast time-scale ($<40$ ps), providing an efficient deactivation pathway for absorbed light energy and resulting in a highly photostable light-absorbing molecule. This phenomenon has been used in the development of a novel proton transfer laser [7], and this efficient excitation energy depletion mechanism may possibly confer some photoprotection to the cellular environment of plants containing such pigments.

Ultraviolet absorbers, quenching agents, and scavenging agents have also been employed extensively in the photostabilization of synthetic polymer materials. In

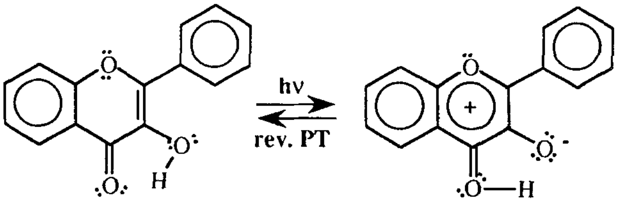

FIG. 1. Light-induced intramolecular proton transfer process in 3-hydroxyflavone molecule.

many cases their mechanisms of photoprotection closely follow those observed in natural systems. In this review, developments in our understanding of the mode of action of ultraviolet absorbers and photostabilizers based on intramolecularly hydrogen-bonded molecular structures will be particularly addressed with emphasis on recent results from ultrafast laser-based photophysical measurements. The possibilities for improving photostabilizer performance in view of our understanding of photochemistry in natural and synthetic macromolecules will be discussed.

## PHOTOPHYSICAL PROCESSES IN ULTRAVIOLET (UV) ABSORBERS

UV absorbers operate by preferentially absorbing the UV component of radiation incident on a polymeric material and dissipating the absorbed energy harmlessly by various radiative and nonradiative processes. The UV absorber molecule should not only be highly photostable but should also have a large extinction coefficient in the wavelength range in which the material to be protected is most susceptible to photodegradation. Ultraviolet stabilizers should be compatible with the polymer substrate, be capable of surviving the processing conditions, and should not be readily exuded or leached from the polymer.

Many different classes of compounds have been investigated as potential UV absorbers for polymeric substrates with the *o*-hydroxybenzophenones, *o*-hydroxyphenylbenzotriazoles, and derivatives of phenyl salicylate being widely used [8-13]. The first two classes of compounds dissipate their absorbed energy through a mechanism involving a rapid excited state rearrangement of an intramolecularly hydrogen-bonded structure. As a result, the absorbed light energy is lost rapidly, usually as heat, the molecule remains chemically unchanged and is able to undergo a large number of these excitation-deexcitation cycles. The mechanism of stabilization through which the aromatic salicylates function is slightly different in that they are photolyzed into highly stable intramolecularly hydrogen-bonded products with strong absorbance in the near-UV wavelength region via a photo-Fries rearrangement. The excited-state processes in these molecules are presented in Fig. 2.

Ultrafast laser spectroscopy techniques and photophysical measurements have been applied to study the mechanisms of excitation energy dissipation in photostabilizers such as the *o*-hydroxyphenyl-*s*-triazines [14, 15], *o*-hydroxybenzophenones [16, 17], and *o*-hydroxyphenylbenzotriazoles [18-30]. The effectiveness of these compounds varies markedly depending on the nature of the substrate and structural variations in the stabilizer. This is illustrated in Fig. 3 where the photodegradation of two structurally related hydroxybenzophenone stabilizers are reported in an acrylic polymer coating. While the light-absorbing chromophore is quite similar for the two compounds, the difference in photostability of the additives has been attributed to the hydrophobic side-chain influencing the polymer environment occupied by the stabilizer molecules [31].

Recent studies indicate that the photophysics of the compounds is strongly affected by the immediate molecular environment of the photostabilizer [21, 23-26, 30]. Hydroxyphenylbenzotriazole derivatives, for example, are capable of forming intramolecular hydrogen bonds between a nitrogen atom on the triazole ring and the phenolic proton, resulting in a coplanar arrangement of the aromatic rings. Schematic ground state and excited state energy surfaces describing the fate of

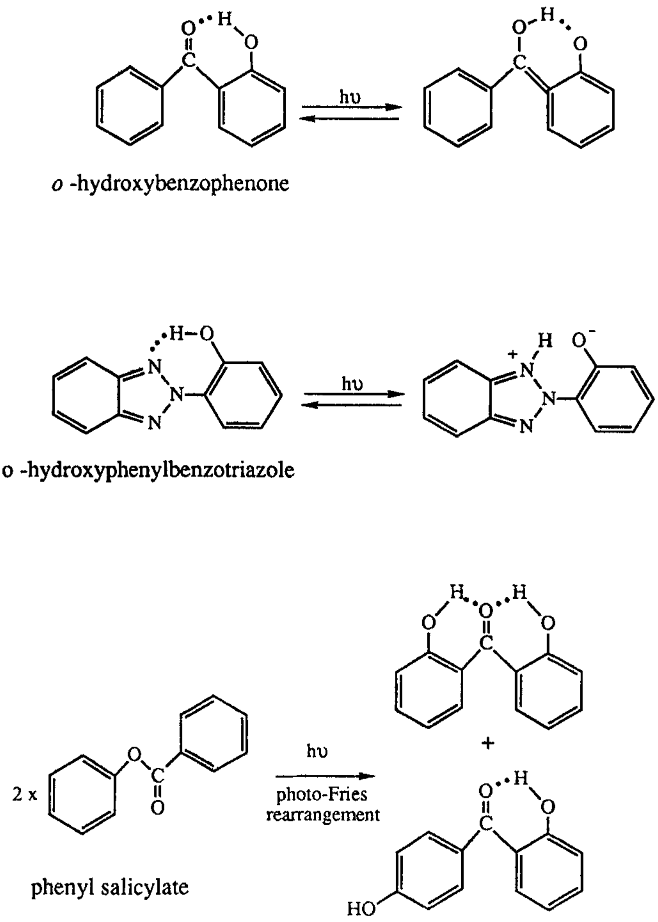

FIG. 2. Excited state molecular rearrangements in *o*-hydroxybenzophenone, *o*-hydroxyphenylbenzotriazole, and phenyl salicylate.

excitation energy in this planar intramolecularly hydrogen-bonded arrangement are illustrated in Fig. 4. Following the initial excitation (process 1) of the stabilizer from its ground state ($S_0$) to the first excited singlet state ($S_1$), the hydrogen bond facilitates the occurrence of a very rapid excited-state intramolecular proton transfer (ESIPT) process (process 2). Due to electronic rearrangements following excitation, the triazole becomes more basic while the phenol is more acidic. The resulting proton-transferred form of the molecule is believed to dissipate the excitation energy rapidly, mainly by internal conversion (processes 3 and 4), to reform the original ground state molecule. This rapid radiationless and nondegradative deactivation pathway gives rise to the high degree of photostability of these molecules. The short excited-state lifetimes ($<1$ ps) also decrease the likelihood of initiating degradative processes in the substrate, and this factor, combined with their high extinction coefficients, makes them suitable as UV absorbers.

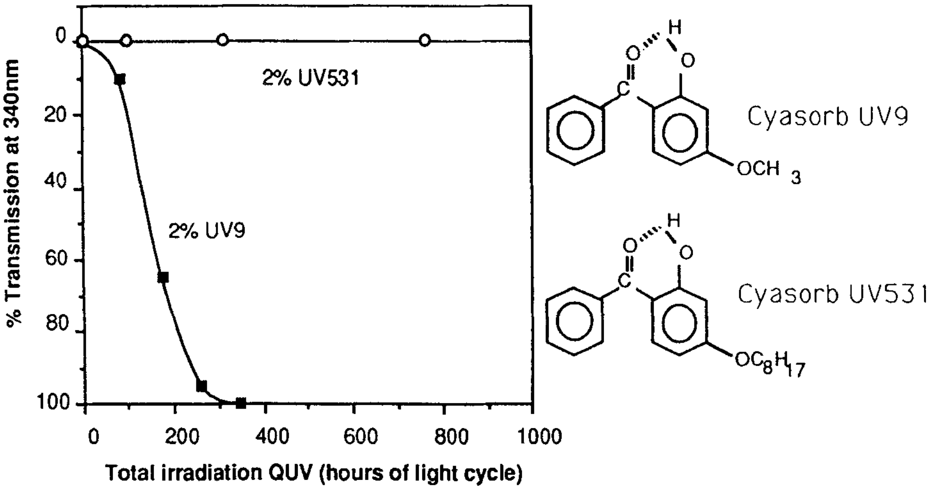

FIG. 3. Photostability of Cyasorb UV9 and Cyasorb UV531 in a commercial acrylic polymer latex following irradiation in a QUV cabinet. Increase in film transmission indicates loss of UV absorber.

However, in hydrogen-bonding solvents and in some polymer substrates the intramolecular hydrogen bonding can be disrupted, resulting in a nonplanar arrangement of the triazole and phenolic rings. This results in a change in the absorption spectrum and, since the ESIPT process is prevented, an increase in excited state lifetimes of the stabilizer with the potential to initiate photodegradative processes (cf. Fig. 4).

Recently, the photophysics of the widely used UV absorber 2-(2′-hydroxy-5′-methylphenyl)-2*H*-benzotriazole (TIN) and its sulfonated derivative, sodium 2-(2′-hydroxy-5′-methylphenyl)-2*H*-benzotriazole-3′-sulfonate (TINS), were studied in solution and polymer substrates [21, 24, 30]. Evidence was found that the ground-state conformation adopted by each of these molecules is sensitive to the molecular environment. In nonpolar solvents TIN exists mainly in an intramolecularly hydrogen-bonded form which is nonfluorescent at room temperature. In polar, hydrogen-bonding solvents and polymers, fluorescence at 400 nm is observed which is attributed to those molecules which are intermolecularly hydrogen-bonded to the solvent/substrate and which do not undergo ESIPT. Picosecond spectroscopy has given further insight into these processes and shown that in hydroxylic solvents the intramolecular proton transfer process can occur through a solute–solvent complex [21, 24]. The ESIPT process in a range of intramolecularly hydrogen-bonded molecular systems has recently been reviewed [32].

Analysis of the absorption spectra, fluorescence yields, and lifetimes has allowed the proportion of the planar and nonplanar forms of TINS to be evaluated in a range of polymer substrates [24]. The results, presented in Table 1, dramatically demonstrate the sensitivity of the stabilizer conformation to the polymer environment.

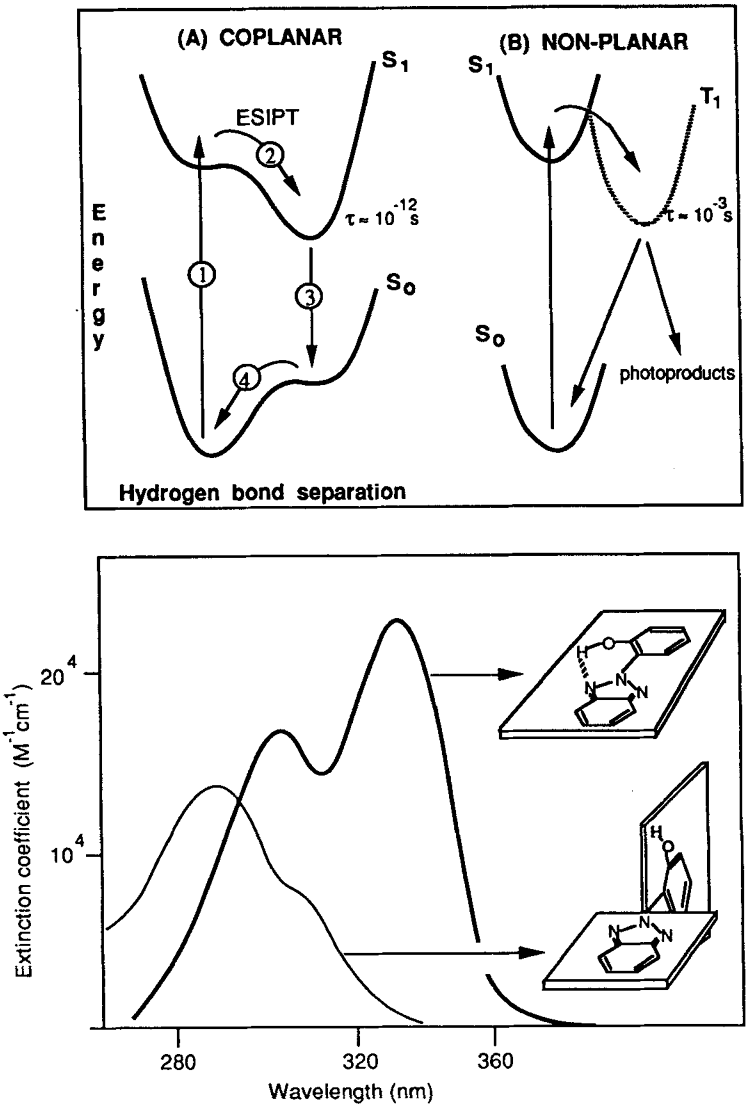

FIG. 4. Upper diagram: Schematic energy surfaces as a function of intramolecular hydrogen-oxygen separation for planar and nonplanar forms of *o*-hydroxyphenylbenzotriazole. Lower diagram: Absorption spectra for planar and nonplanar forms of *o*-hydroxyphenylbenzotriazole.

The mechanism of the photoprotective action of TINS in wool has also been investigated in some detail [33]. The absorber is much less effective than would be expected on the basis of its UV screening action. Intermolecular hydrogen-bonding interactions between the absorber molecules and the polar side-chains in wool, which disrupt the intramolecular proton transfer process, are believed to be responsible for the reduction in photoprotective effectiveness.

TABLE 1. Photophysical Parameters of TINS in Synthetic Polymer and Protein Substrates. Fluorescence Quantum Yield Values Were Obtained Using an Excitation Wavelength of 300 nm Unless Otherwise Indicated

| Substrate | $\phi_f$ | $\phi_f^{corr}$ | $\tau$ (ns) | Mol% nonplanar |
|---|---|---|---|---|
| PVA | 0.019 ± 0.003 | 0.24 ± 0.02 | 1.3 ± 0.1 | 11 |
| | 0.007 ± 0.002[b] | 0.24 ± 0.02 | 1.3 ± 0.1 | 11 |
| PVP | 0.16 ± 0.02 | 0.20 ± 0.02 | 1.14 ± 0.04 | 86 |
| Lysozyme | 0.035 ± 0.004[a] | 0.20 ± 0.02 | 1.10 ± 0.05 | 35 |
| Gelatin | 0.057 ± 0.006 | 0.19 ± 0.02 | 1.1 ± 0.1 | 41 |
| Wool | 0.050 ± 0.006 | (0.20) | (1.1) | 33 |
| | 0.014 ± 0.004[b] | (0.20) | (1.1) | 20 |

[a] $\lambda_{exc}$ = 315 nm.
[b] $\lambda_{exc}$ = 340 nm.

Structural modifications of UV absorbers of this type which favor and/or protect intramolecular hydrogen bonding should lead to improvements in photostability [30].

## POLYMERIZABLE UV ABSORBERS

Low molecular weight stabilizers, such as those discussed above, have significant shortcomings in that it is possible for them to diffuse through the polymer matrix, resulting in nonuniform protection, and they can be incompatible with the polymer, leading to exudation and leaching from the substrate [34-36]. The loss of stabilizers through such processes is predominantly a surface phenomenon, making this region the most susceptible to degradation. Reduction of stabilizer content may also occur during processing of the polymer due to the high volatility of these low molecular weight molecules [34, 37].

In order to overcome these deficiencies, the synthesis of several classes of polymerizable UV absorbers has been reported. These include vinyl derivatives of *o*-hydroxybenzophenone [38, 39], *o*-hydroxyphenylbenzotriazole [40-44], methylsalicylate [45-47], and *a*-cyano-*b*-phenylcinnamate [48, 49] as well as acryloyl and methacryloyl derivatives of *o*-hydroxybenzophenone [50] and *o*-hydroxyphenylbenzotriazole [51]. It has been shown, for example, that in contrast to lower molecular weight analogues, a polymerizable *o*-hydroxyphenylbenzotriazole derivative incorporated covalently into a film of polyester resin is retained at the polymer surface following irradiation, suggesting they are more suitable for use in the long-term photostabilization of polymers [35].

Recent studies on the temperature dependence of fluorescence and photolability of copolymer films of 2(2′-hydroxy-4′-methacryloxyphenyl)-2*H*-benzotriazole and methyl methacrylate (HMPB-*co*-MMA) over a wide temperature range (10-300

K) have given an insight into the excited relaxation mechanisms occurring in the polymer-bound HMPB stabilizer [52]. The temperature dependence of fluorescence from these polymer films is illustrated in Fig. 5.

The temperature-insensitive short wavelength band with a maximum at 390 nm is assigned to emission from a small amount of nonplanar HMPB chromophores in which the intramolecular hydrogen bond is disrupted while the highly temperature-sensitive red-shifted emission at 550 nm arises from fluorescence from the proton-transferred HMPB tautomer. The room temperature fluorescence lifetimes of the 550 and 390 nm bands have been measured by picosecond spectroscopy to be 40 and 895 ps, respectively. Analysis of the temperature-dependent behavior [52] demonstrates that the rapid nonradiative process depleting the proton-transferred tautomer and responsible for the photostability displays non-Arrhenius behavior assigned to two competing radiationless processes of low activation energy or quantum mechanical tunneling. Continuous irradiation of the HMPB-*co*-MMA copolymer films (Fig. 6) leads to a decrease in intensity of the 390-nm band consistent with photodegradation of the nonplanar HMPB chromophores while the 550-nm emission is unaffected. These findings confirm that it is the planar intramolecular hydrogen-bonded form of polymer-bound HMPB which is the most photostable and thus more efficient in protecting against photodegradation of polymers.

## ENERGY TRAPPING AND PHOTOSTABILIZATION IN VINYL AROMATIC POLYMERS

The high local concentration of chromophores within a vinyl aromatic polymer chain is conducive to the migration of excitation energy between aromatic moieties and energy trapping at either excimer (excited state dimer) sites or other

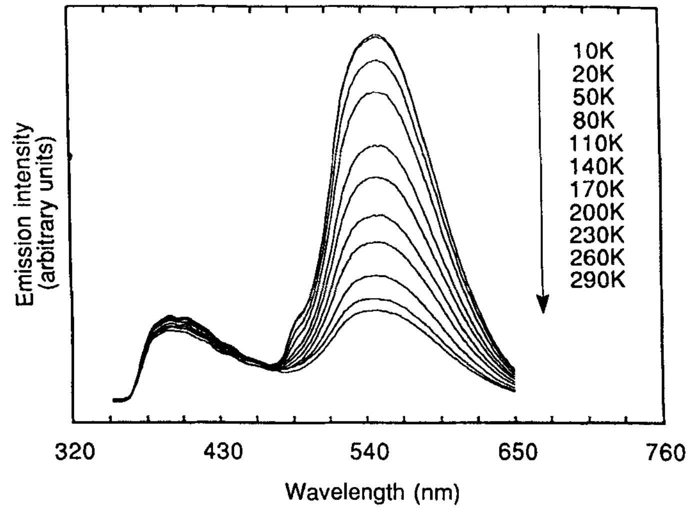

FIG. 5. Temperature dependence of fluorescence for a HMPB (1%)-*co*-MMA film (excitation wavelength 340 nm).

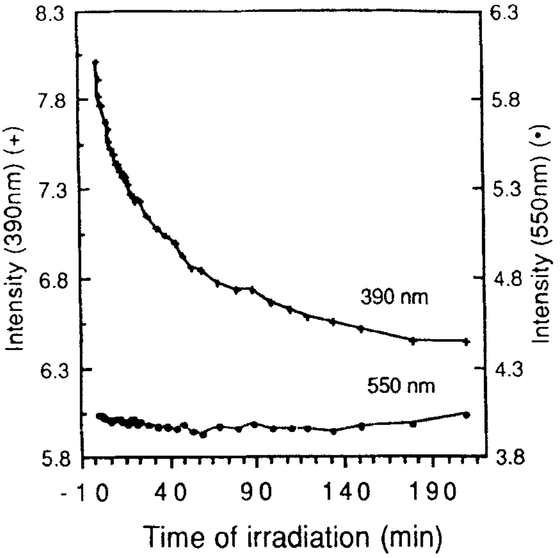

FIG. 6. Fluorescence intensity of 390 and 550 nm bands during continuous irradiation at 300 nm of a HMPB-*co*-MMA film at 10 K.

lower energy groups incorporated in the chain. These excited state processes are shown schematically in Fig. 7.

Fluorescence techniques [53–55] provide a convenient means for following these processes which occur on nanosecond and picosecond time-scales. Fluorescence can occur either from excited aromatic chromophores of the polymer ("monomer" fluorescence), from excimers formed between two aromatic groups on the chain (or on different chains at high polymer concentrations and in solid films),

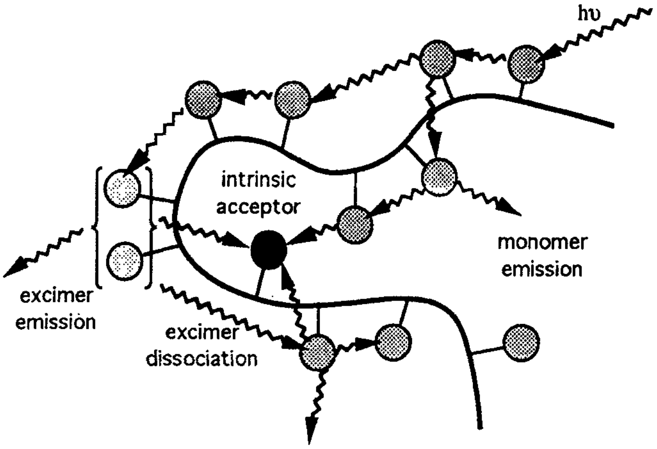

FIG. 7. Photophysical processes occurring in a vinyl aromatic polymer chain following photoexcitation.

or from lower energy trap chromophores which have been introduced into the polymer chain.

The mechanisms of the energy transport processes occurring in such polymers have recently been discussed [56, 57]. Hopping of excitation energy between adjacent chromophores by a coulombic dipole-dipole interaction was thought to be the major mechanism responsible for the delocalization of energy away from the initial site of light absorption. However, recent picosecond fluorescence measurements on acenaphthylene polymers [56] have detected far greater rates of energy transport and trapping than can be accounted for by this mechanism alone. It now seems likely that the involvement of orbital-overlap-dependent energy transfer mechanisms occurring between adjacent chromophores and mediated by "superexchange" processes through the bonds of the polymer backbone can enhance the efficiency and rate of excitation energy relocation in macromolecules above that expected for nonlinked chromophores [57].

Since energy trapping can be so efficient in polymers, the possibility of using this process to photostabilize aromatic polymer systems has been explored [58]. The fluorescence spectra of dilute solutions of a series of copolymers of 2-naphthyl methacrylate and 2(2′-hydroxy-4′-methacryloxyphenyl)-2*H*-benzotriazole (2NMA-*co*-HMPB) are illustrated in Fig. 8. The spectrum of the 2NMA homopolymer displays a structured fluorescence at 330 nm from the monomeric 2-naphthyl chromophores together with a broad structureless excimer emission with a maximum at 400 nm. Both emissions are quenched with increasing concentrations of the HMPB

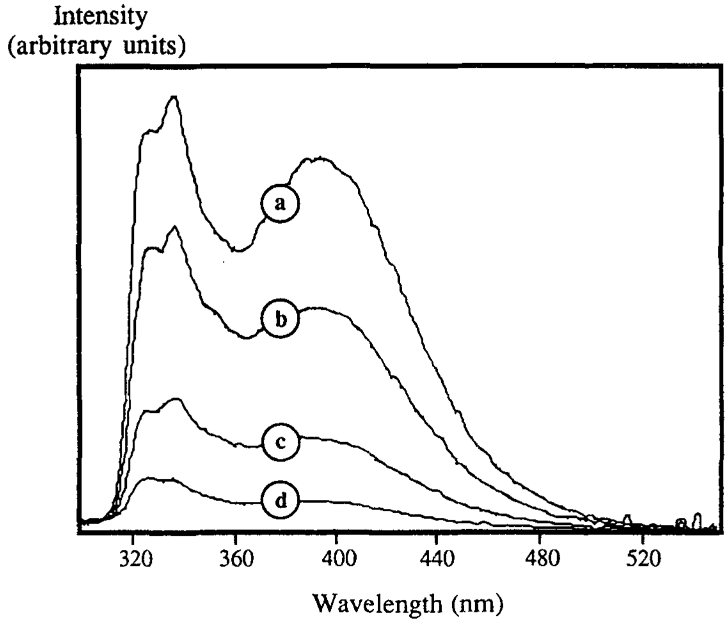

FIG. 8. Fluorescence emission spectra in dilute degassed benzene solution of poly(2-naphthyl methacrylate) (a) and copolymers of 2NMA and HMPB with mol% HMPB concentrations of 1.1% (b), 3.2% (c), and 6.2% (d). Excitation wavelength 285 nm.

chromophore incorporated in the polymer. The average number of HMPB chromophores in each polymer chain at the highest concentration is about two.

Time-resolved fluorescence experiments confirm that quenching of the emission is accompanied by a marked decrease in the fluorescence lifetime of the 2NMA monomer and excimer states due to the transfer of light energy initially absorbed by the 2NMA chromophores to the HMPB energy traps [58]. The photostability of the polymers has also been examined. Poly(2-naphthyl methacrylate) is photochemically unstable due to efficient photo-Fries rearrangements, and its degradation can be monitored readily by increasing optical absorption of the photoproducts. The 2NMA-*co*-HMPB copolymers in solution were found to be considerably more photostable than could be accounted for by any UV screening effect [58]. In this case the HMPB is acting as a photostable acceptor of excitation energy from the initially excited naphthyl chromophores. Degradative processes are now no longer able to compete with the reduced excited state lifetimes of the polymer, resulting in enhanced photostability. Incorporation of 2-hydroxyphenylbenzotriazole stabilizers in solid films of poly(2-naphthyl methacrylate) has also been shown to lead to quenching of excimer site fluorescence lifetimes and a corresponding decrease in polymer photodegradation [59].

## CONCLUSIONS

Natural systems employ a variety of light screening compounds, scavenging and energy trapping mechanisms to protect biological functions from the damaging effects of solar radiation. The diversity of natural photoprotective agents is yet to be fully elucidated, but there is considerable potential for new light stabilizing additives for polymer materials to be developed based on natural sunscreen compounds. The understanding of energy dissipation pathways occurring in UV stabilizers and polymers gained particularly from photophysical studies and ultrafast laser spectroscopy measurements has indicated some ways that photostabilizer performance can be enhanced by structural modifications and judicious choice of polymer/stabilizer formulations. In particular, recent studies have given considerable insight into the mechanisms of relocation of absorbed light energy in polymer systems and demonstrated the importance of energy trapping as a photostabilizing mechanism. Such mechanisms are closely related to those proposed to occur in photosynthetic systems and emphasize the importance an understanding of biological photoprotection might have in the future development of photostable polymeric materials.

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