

THE ROLE OF ENERGY TRANSFER IN THE STABILIZATION OF POLYMERS

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ABSTRACT

Energy transfer processes can, in principle, represent a powerful new mechanism for the stabilization of polymers against degradation by ultra-violet light. The mechanism involves the transfer of electronic excitation from an absorbing group in the polymer to a 'quenching' group by either an intra- or intermolecular process. The efficiency of such processes depends in a complex way on the nature of the excited states of the donor and acceptor groups, and on the mobility of the polymer chain in the solid state. Studies are reported on the quenching of the photodegradation of polymers containing ketone and aromatic groups by various stabilizers.

INTRODUCTION

The phenomenon of 'weathering' of plastic materials usually consists of a complex sequence of chemical reactions, often initiated by the u.v. radiation of the sun. Solar radiation consists of a nearly Boltzmann distribution of energy with wavelengths extending from about 300 nm in the ultra-violet up to the infra-red region of the spectrum. There is a rather sharp cut-off at about 300 nm because the ozone layer of the atmosphere filters out the short wavelength radiation.

Figure 1 shows such a distribution curve in which the wavelength of the light has been converted to the energy per quantum in kilocalories per mole. The bond strengths of different kinds of chemical bonds that one might expect to find in polymers is also included. Only a very small amount of the total radiation is sufficiently energetic to break strong bonds such as NH and CH, but about ten per cent is sufficiently energetic to break a carbon-carbon bond. However, there is plenty of radiation in the sun's spectrum of sufficient energy to break the weak bonds, such as O—O, N—N and C—Cl. In simple terms this means that if you want to have a stable polymer, you should introduce into the polymer only stable bonds which will reduce the probability of degradative processes occurring on the absorption of light.

POLYMER PHOTOCHEMISTRY

Most commercial polymers when pure do not usually absorb in the spectral region above 300 nm and hence should not degrade in the ultra-

violet light of the sun. The first law of photochemistry states that there cannot be a photochemical reaction if there is no absorption. However, processed polymers do in fact have a slight absorption which extends up into the region above 300 nm. The usual mechanism for nearly all polymers which degrade in ultra-violet light is a sensitized photo-oxidation which is induced by small amounts of groups which absorb in this region of the spectrum. In our studies of photochemistry we have attempted to introduce into ordinary polymers such as poly(styrene) and poly(methyl methacrylate) controlled amounts of chemical groups absorbing in this region of the spectrum to study their photochemical reactions. The most common group which exists in polymers and which causes such photochemical reactions is the ketone group.

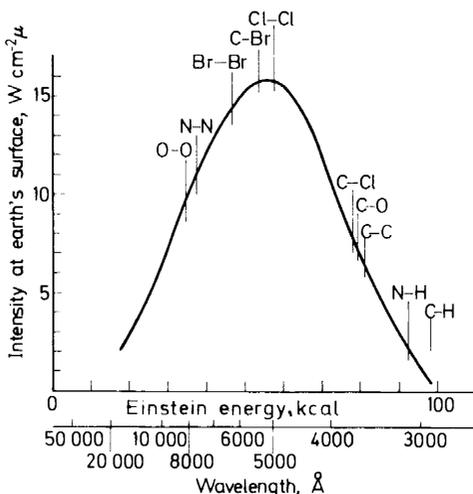


Figure 1. Distribution of solar energy.

In any photochemical reaction, the ways in which the energy of an absorbed photon is dissipated can be classified into photophysical processes and photochemical processes. The photophysical processes include fluorescence, which is simply re-emission of a quantum of light after absorption; phosphorescence, which is emission at a slightly longer wavelength and a slightly greater time interval; conversion to thermal energy; and energy transfer. The alternatives to these photophysical processes, the processes which compete with them for the energy of the quantum absorbed, are photochemical reactions such as the formation of free radicals, intermolecular rearrangements, cyclization, photoelimination and photoionization. Nearly all of these chemical processes will ultimately cause a deterioration in the physical properties of a plastic. It is true that if a plastic is cross-linked, in some cases initial improvement of its properties will occur. But if this process continues extensively, degradation will ultimately take place. When stabilizing a polymer, it is therefore desirable to eliminate the photochemical reactions, i.e. to maximize the photophysical processes, particularly

STABILIZATION OF POLYMERS AGAINST LIGHT

the conversion to thermal energy, and to minimize the photochemical processes. If one can increase the efficiency of this process, a much more stable polymer will result.

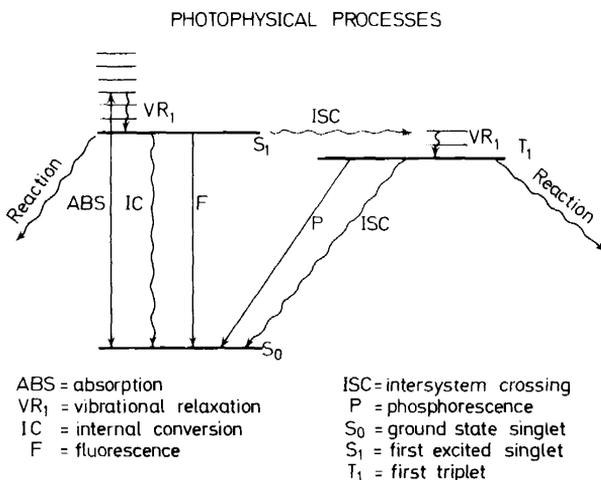


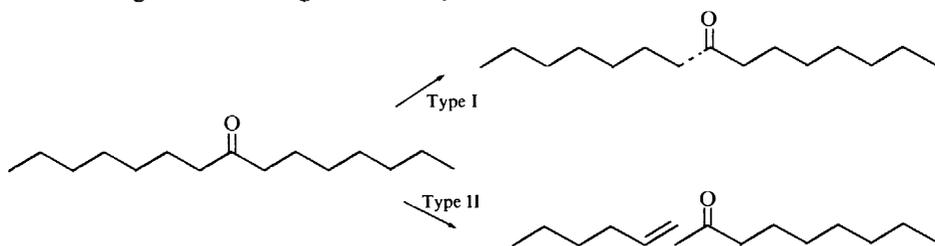
Figure 2. Modified Jablonski diagram.

Figure 2 shows an energy diagram which describes the kinds of processes which are possible. When a quantum of light is absorbed, a particular group is raised to some excited state, and since most groups will be in a singlet ground state, they will be excited to a vibrationally excited singlet state. In the solid phase there will be a rapid degradation of the vibrational energy down to the lowest vibrational level of the electronically excited singlet state, indicated as S_1 . From this S_1 excited state, all the processes that we are concerned with will occur. The simplest is fluorescence, that is emitting by dropping down to the ground state singlet. The second is internal conversion, that is conversion of that electronic energy into thermal energy. It is a spectroscopically forbidden process but there are various means by which it can occur and in many polymers it is the major process. The spin of the excited electron can also be inverted to give the triplet state, by intersystem crossing to a vibrationally excited triplet and dropping down to the lowest vibrational state, T_1 , of the triplet. Chemical reaction can occur from either the singlet or the triplet excited state. Similarly, by intersystem crossing one can convert the triplet energy to thermal energy, or a quantum of light can be emitted by phosphorescence.

KETONE PHOTOCHEMISTRY

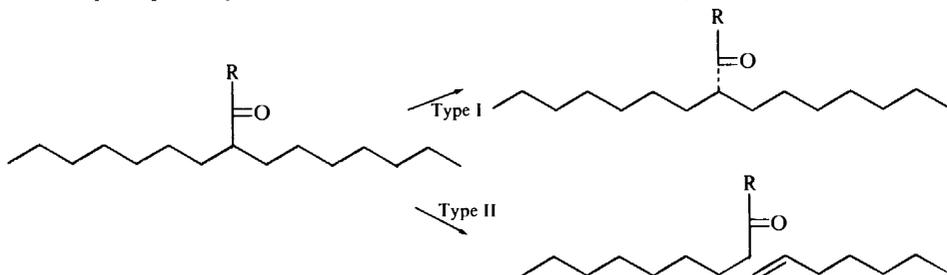
In our laboratory we have studied these processes involving ketones included either in the backbone or the sidechain of a polymer. These ketone groups are important because they are among the few functional groups

which do absorb in this region above 300 nm and they are byproducts of the photo-oxidation of polymers. They seem to be the photosensitive groups involved in the fundamental degradation processes in many polymer systems. If a ketone is incorporated in the backbone of the polymer (such as by copolymerizing ethylene and carbon monoxide, for example, or by making a polyester which contains a group which will give such a structure), there are two major reactions which occur on the absorption of light^{1, 2}. (There are in fact three more which do not alter the molecular weight.) The two major ones are type I which gives two free radicals and type II molecular rearrangement which gives a methyl ketone and a double bond and results



in breaking the chain. In both cases the chain breaks and this ultimately leads to a lowering of the molecular weight and an ultimate degradation in the physical properties.

The ketone groups may also be contained in sidechains of the polymer^{3, 4}. Upon photolysis, the sidechain ketones indicated by this structure also



undergo the type I and type II reactions. Type I in this case does not give an actual break in the main chain. Type II is the only reaction in this case where the molecular weight of the polymer is reduced and consequently with sidechain ketones this is the mechanism by which the reduction in molecular weight takes place. Since most of the oxidation processes by which ketone structures are introduced into polymers will give sidechain ketones, this appears to be a very important reaction in the photodegradation of polymer systems.

Usually an u.v. absorber is added to the polymer to stabilize such systems. Additives, such as substituted 2-hydroxy benzophenones, have molar extinction coefficients about a thousand times greater than that of the ketone group in the polymer. Consequently a very small amount of this material added will absorb 90 or 95 per cent of the light and prevent the light from being absorbed by the ketone carbonyl. This is a simple but very effective mechanism for stabilization, and it is the major mechanism by which stabilization

of polymers has been achieved in the past. The only alternative to this kind of stabilization mechanism is to remove the energy absorbed before chemical reaction can occur. The most effective mechanism for doing this is to transfer the energy from the site at which it has been absorbed in the polymer to some other location. This process we call 'energy transfer'.

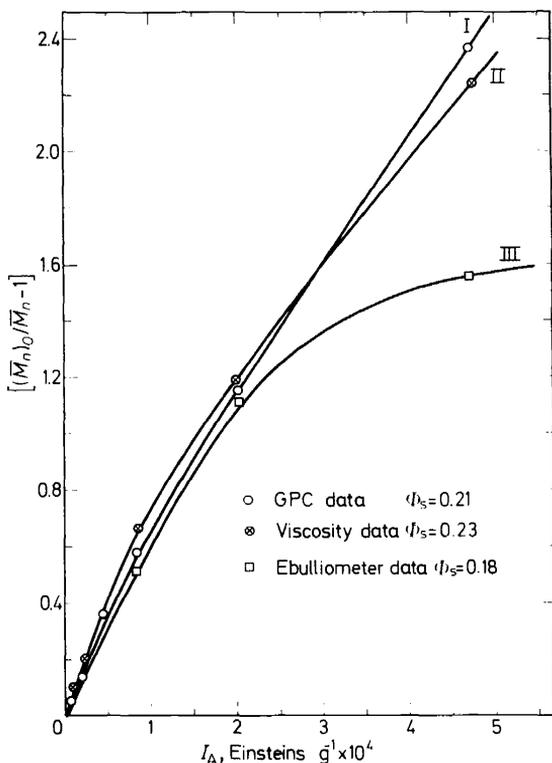


Figure 3. Photodegradation rate of MMA-MVK copolymer (3% MVK) determined by gel permeation chromatography, intrinsic viscosity, and ebulliometric methods. The copolymer was irradiated in benzene solution at 25°C, 313 nm.

The efficiency of a photolytic process is defined in terms of the quantum yield. The quantum yield for scission, Φ_s , is measured simply by measuring the molecular weight of the polymer by various means, and plotting

$$\left(\frac{\bar{M}_n}{\bar{M}_n}_0 - 1\right)$$

as a function of the light absorbed. Such a graph is shown in Figure 3 using three different molecular weight measurements: gel permeation chromatography, viscosity, and ebulliometry. The initial slope of these curves is identical in the three cases and the chain scission quantum yield here is about 0.20 for a methyl vinyl ketone-methyl methacrylate copolymer in solution. This quantum yield means that 20 per cent of the quanta absorbed

by the polymer result in an actual break in the polymer chain. If the process were perfectly efficient, the quantum yield would be equal to one.

LUMINESCENCE OF POLYMER SYSTEMS

If one looks at the luminescence of a polymer system as a function of temperature, it can be seen that first of all at very low temperatures we find that only luminescence occurs when a polymer is irradiated. Degradation processes are negligibly slow at liquid nitrogen temperatures⁵. At -180°C phosphorescence is the major process which occurs when we irradiate a ketone-containing polymer such as a styrene-methyl vinyl ketone copolymer.

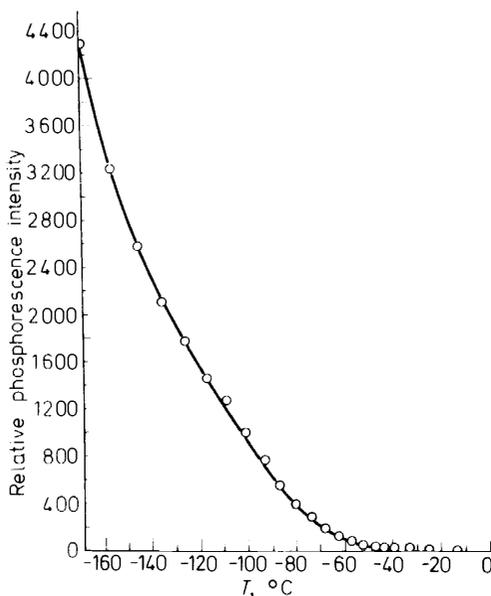


Figure 4. Phosphorescence intensity as a function of temperature, PS-MVK film.

(See Figure 4.) The yield of phosphorescence drops off drastically as the temperature increases towards room temperature. At room temperature there is practically no visible phosphorescence. Chemical reaction in all cases requires the movement of atoms and molecular groups within the polymer structure. At very low temperatures the rigidity of the structure is such that these movements cannot occur. As a result, the photophysical processes are nearly 100 per cent efficient. The energy that is absorbed originally as the singlet is converted to the triplet and the triplet emits a quantum of light which we call phosphorescence.

Fluorescence, on the other hand, is almost independent of temperature, as shown in Figure 5. The yield is much lower than the phosphorescence at all temperatures and nearly constant with temperature. For polymers at very low temperatures the major process involved will be the conversion of

STABILIZATION OF POLYMERS AGAINST LIGHT

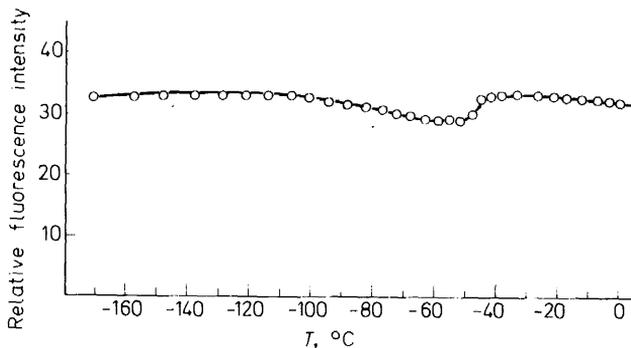


Figure 5. Fluorescence intensity as a function of temperature, PE-CO film.

energy, first of all from the singlet to the triplet by intersystem crossing, and from the triplet to the ground state by phosphorescence. As the temperature is increased, the mobility of the polymer becomes much greater and the phosphorescence decreases so that more of the energy is converted either into thermal energy or into chemical reactions.

At temperatures less than -100°C we can expect that nearly all the energy will go into luminescence⁶. If there is an easy conversion into a triplet, phosphorescence is the favoured process. In the range -100°C up to the glass transition temperature, the major process involved will be the conversion of electronic excitation energy into thermal energy, and at temperatures greater than T_g (the melting point of the polymer) there are two important processes, photochemical reactions and thermal conversion. Below T_g or T_m the photochemical quantum yields are quite small, but still sufficiently large to cause degradation over a long period of time.

PHOTOCHEMISTRY IN THE SOLID STATE

One of the easiest ways to study polymers is to put them in solution and study them in the liquid state. However, since most plastics are used in the solid state, one wants to know what happens under these conditions. It was shown some years ago¹ that in poly(ethylene-CO) the quantum yields for various processes varied with temperature in solution. The type I quantum yield, which is quite small at ordinary temperatures, increases to the equivalent of the type II at 90°C . The quantum yield for luminescence is extremely small at both these temperatures, and the quantum yield for conversion of the electronic energy to thermal energy is quite large in both cases, namely 0.97 and 0.95. For poly(ethylene) at ambient temperatures the major process is still conversion to thermal energy. Only a very small portion of the total energy ends up in the degradation process. However, it is this small portion that we would like to get rid of because these polymers in fact degrade very rapidly in ultra-violet light. There is a very large u.v. component in the sun's radiation and a process which is only two per cent efficient can still cause a great deal of degradation.

The quantum yields for types I and II processes in poly(ethylene-CO) at room temperature are almost identical in the solid and the liquid state. This is because poly(ethylene) at this temperature is well above its glass transition ($T_g - 100^\circ\text{C}$) and thus the molecules in poly(ethylene) are sufficiently mobile so that all of the photochemical processes (i.e. all the rearrangements of the molecular structure which are necessary to carry out the reaction) can take place.

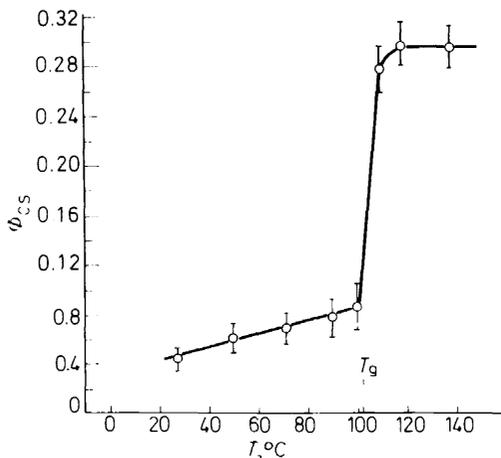


Figure 6. Quantum yield of chain scission as a function of temperature, PS-PVK film.

In polymers such as poly(styrene) which have glass transitions in the region of interest, there is a strong effect of the glass transition on quantum yields. For example, in (styrene-phenyl vinyl ketone) the quantum yield for chain scission increases slightly with temperature up to the glass transition⁵ (Figure 6). Below T_g , Φ_s is still fairly low, 0.04 to 0.08, but there is a sudden drastic increase at the glass transition, going up to about 0.3, which is exactly the quantum yield for the same process in the liquid state.

When the phosphorescence of such a copolymer is studied as a function of temperature, one will see the effect of molecular mobility. If one plots the logarithm of the intensity of phosphorescence as a function of $1/T$, one finds that two straight lines are obtained. For a methyl methacrylate copolymer containing a small amount of methyl vinyl ketone two lines are obtained corresponding to two activation energies. The transition at -140°C corresponds to a well-known transition at which motion of the α -methyl group occurs. Rotation of these groups increases the probability of energy transfer and of conversion of electronic excitation into thermal energy. This then represents a more fundamental aspect of photochemistry. If one wishes to convert more energy to thermal energy, that is to stabilize the polymer, it is necessary to have molecular motion of the pendant groups in the polymer.

In poly(methyl methacrylate) the α -methyl group rotates at -140°C , and the ester methyl group at -220°C . The whole ester group rotates at -20°C and of course the glass transition corresponds to the motion of long segments of the chain at $+100^\circ\text{C}$. Photochemical evidence for all of these processes can be found. All of these various forms of motion of the polymer will affect the efficiency of the photochemical process.

ENERGY TRANSFER

Energy is transferred in a number of ways in a ketone system. The initial excitation occurs in the carbonyl group, but reaction actually takes place at either the α - β or β - γ C—C bonds, so that there must be even in photochemical reaction a transfer of the energy from one bond system to another. That is a very simple case of energy transfer. However, the more practical cases are those in which we can introduce groups into the polymer itself, either as part of the polymer chain or as an additive which will remove the energy of the absorbed quantum during the lifetime of the excited state of such a molecule. There are various kinds of energy transfer processes. The so-called 'Förster' mechanism involves the long range transfer of energy across quite long distances in the polymer, up to 100 \AA due to dipole-dipole interactions. Short range transfer involves the so-called 'exchange mechanism' which is simply a transfer of electronic excitation between an excited molecule and a non-excited molecule during a collision, due to overlap of electronic charge clouds. In addition, there are exciton mechanisms which occur in crystals and also in polymers, and cause delocalization of energy over a large distance and this results in a transfer of energy from one position to another.

There are two models which are of particular interest in stabilizing polymers. The first is the so-called Stern-Volmer model which involves a dynamic process similar to diffusion. The equation for this is

$$\Phi_0/\Phi = 1 + k_q\tau[Q]$$

where $[Q]$ is the concentration of the quenching molecule, k_q is the rate constant for collision, and τ is the lifetime of the excited state. In many cases we can equate k_q , the collisional rate constant, with k_d , the rate constant for diffusion. In some cases, if we are dealing with a rigid polymer system, in particular with polymer glasses at low temperatures, we will use the so-called Perrin model. This model implies that quenching will occur if a quencher is within a certain distance of the excited molecule. This gives an exponential concentration term in the quencher of this form

$$\Phi^0/\Phi = \exp(-vN[Q])$$

where $v = \frac{4}{3}\pi R_0^3$ and N is Avogadro's number. *Figure 7* shows an experimental plot of a Stern-Volmer equation for a poly(ethylene)-carbon monoxide copolymer containing ketone groups, with cyclo-octadiene which is a quencher which does not absorb any light of the wavelength used⁷. Instead of getting a straight line as predicted from the Stern-Volmer equation, the line is originally straight and then curves over. This is because the cyclo-octadiene quenches only the triplet state, whereas reaction out of the singlet

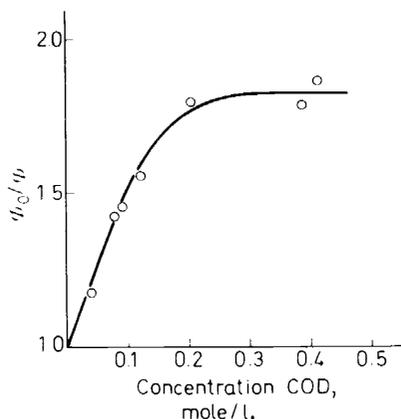


Figure 7. Quenching of chain scission in poly(ethylene-CO) by 1-3 cyclo-octadiene.

groups, poly(phenyl vinyl ketone) in this case (Figure 8), the line is quite not quenched. From such a curve one can determine the portion of the reaction which comes from the singlet and the portion which comes from the triplet. With aliphatic ketones, both the singlet and the triplet reactions are important. On the other hand, when dealing with aromatic ketone groups, poly(phenyl vinyl ketone) in this case (Figure 8), the line is quite

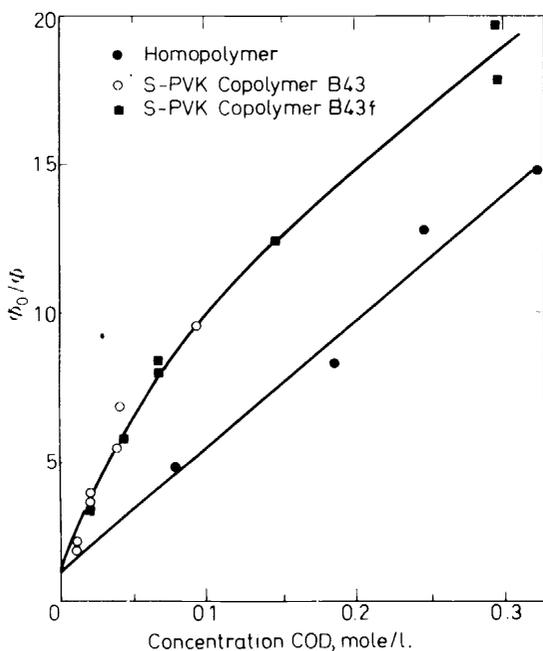


Figure 8. Stern-Volmer plot for quenching of photoscission in poly(PVK) and S-PVK copolymers by COD in benzene solution.

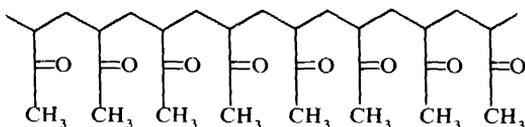
STABILIZATION OF POLYMERS AGAINST LIGHT

straight, right up to the highest concentrations and, in fact, the cyclo-octadiene will inhibit at least 99 per cent of the total reaction. With an aromatic ketone we know that internal conversion is almost complete in these systems. Almost all of the reaction comes out of the triplet state and the triplet quencher will be almost totally effective in removing the excited state energy before reaction can take place. In the copolymer there is a curvature which is due to the fact that two kinds of ketone groups are present in the copolymer: isolated ketone groups (i.e. ketones surrounded by styrene units) and sequences of ketone groups. These have different lifetimes and quantum yields as shown in *Table 1*.

Table 1. Comparison of copolymer and homopolymer

Type	Φ_0	$k_q\tau$	τ (sec $\times 10^8$)
Homopolymer	0.245	43	1.7
Copolymer	0.176	120	4.8

Synthetic polymers are chemically unique because in general they consist of a carbon backbone with chromophoric or other groups regularly spaced along the sidechain of the polymer. Poly(methyl vinyl ketone), for example, has a structure of this kind



This means that there is a sequence of chromophores which are closely held at a similar distance from each other. In fact one can almost think of this as being a linear crystal—a one-dimensional crystal in which there is a fixed relationship between the distances of these carbonyl groups from each other. No matter how one dilutes a polymer or stretches it, this relationship will hold. If light is absorbed in such a molecule, the excitation may be delocalized over several of these groups. In fact there is now very good evidence that in some cases excited state energy can hop from one of these to another along the chain. This has a number of effects on various photochemical processes. For example, in poly(methyl vinyl ketone) the quantum yield for degradation is lower by a factor of ten than if the ketone groups are isolated as in a copolymer, possibly because of the delocalization of the excitation energy⁴.

Figure 9 shows the absorption and fluorescence spectrum of poly(methyl isopropenyl ketone) and poly(methyl vinyl ketone) as compared with acetone and heptanone⁸. In absorption, the absorbance of the polymeric ketones is greater and the increase in molar extinction coefficient is an indication of the interaction of the ketone chromophore groups along the chain. In addition, the fluorescence wavelengths are shifted, as is the peak maximum for the absorption.

If ketones are used to quench naphthalene fluorescence, one finds that the polymeric ketones are much less efficient than heptanone or acetone. If, on

the other hand, the luminescence from the ketone is quenched by, say, biacetyl, one finds quite the opposite effect, that is the efficiency factor for the small molecules is considerably less than it is for the large polymeric molecules. Thus a polymeric molecule exhibits a low efficiency for the quenching of naphthalene but a high efficiency for the molecule being quenched itself. This is evidence for the delocalization of the energy across the long polymer chain.

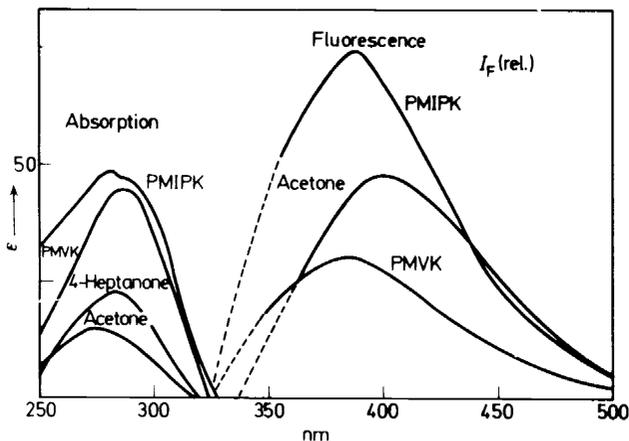


Figure 9. Absorption and emission spectra of various ketones in solution.

There is one other mechanism of energy transfer, the transfer of triplet energy in naphthalene groups. This was shown by Fox and Cozzens⁹ with poly(vinyl naphthalene) at cryogenic temperatures and is a process whereby because of the long lifetime of the naphthalene triplet, absorption of two photons in a polymer takes place during the lifetime of one of the excited states. There is a finite probability of having two excited states on the same polymer molecule at the same time. These excited states can migrate by an energy transfer process, either by hopping or by a long range process, and when the two triplets meet, delayed fluorescence results. That is, the two triplets combine to give a singlet excited state which fluoresces and a ground state molecule. This gives emission at fluorescence wavelengths, but with the lifetime of phosphorescence.

We have carried out similar studies with poly(naphthyl methacrylate)¹⁰ and the absorption spectra for normal fluorescence, delayed fluorescence and phosphorescence were observed (Figure 10). The delayed fluorescence has the same lifetime as phosphorescence and can be observed in a phosphorescence accessory. The intensity of delayed fluorescence plotted versus that of the phosphorescence gives a straight line with a slope of two, which is precisely the kinetics one would predict in order to have a bimolecular quenching process.

At 25°C the fluorescence spectrum of poly(naphthyl methacrylate) depends on the solvent (Figure 11). In a good solvent such as chloroform, only normal

STABILIZATION OF POLYMERS AGAINST LIGHT

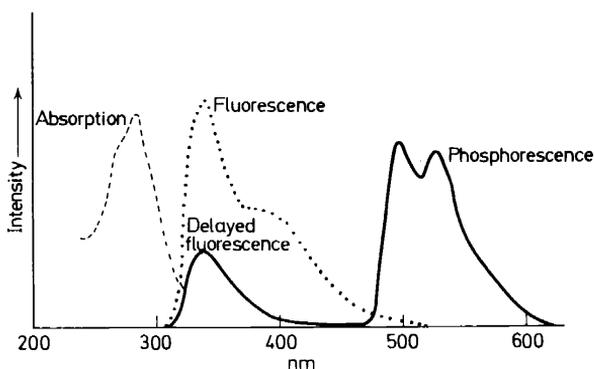


Figure 10. Absorption and emission spectra of poly(α -naphthyl methacrylate).

fluorescence occurs. A poor solvent gives excimer fluorescence which is caused by the interaction of one excited with one ground state naphthalene unit. In the bulk phase only the excimer fluorescence is observed. In mixed solvents, however, the spectrum is removed from the normal fluorescence to the excimer fluorescence. We can demonstrate that it is not possible to form the excimer between two adjacent naphthalene groups. Consequently the polymer molecule then must bend back on itself and form the excimer. In a good solvent the chain is expanded so the probability of forming the excimer is very small. On the other hand, in a poor solvent, the chains are tightly coiled up on each other just as they are in the bulk polymer and there is a very high probability of forming the excimer. In the bulk and in the poor solvent, the excimer is formed and fluoresces. In a good solvent, the excimer does not form to any appreciable extent and normal fluorescence occurs.

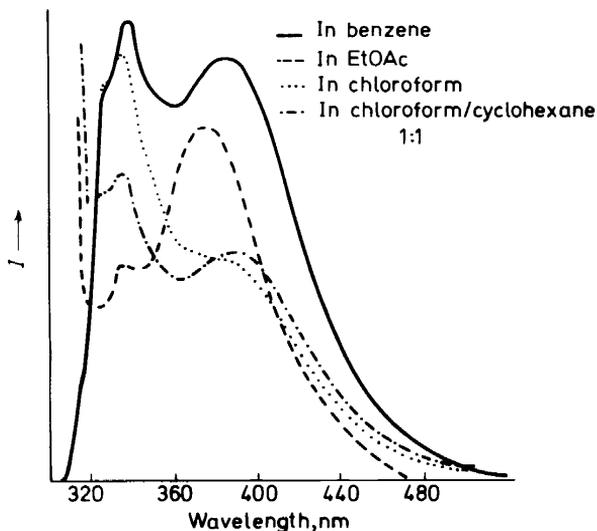


Figure 11. Fluorescence of poly(α -naphthyl methacrylate) in various solvents.

One other form of energy transfer which we have studied is the energy transfer from photochemically excited ketones to carbon tetrachloride¹¹. The importance of this form of energy transfer lies in the fact that when we put plasticizers and other molecules into polymer systems, quite different photochemistry can result. A ketone dissolved in carbon tetrachloride gives primarily the photochemical reaction products of CCl₄. The excited state

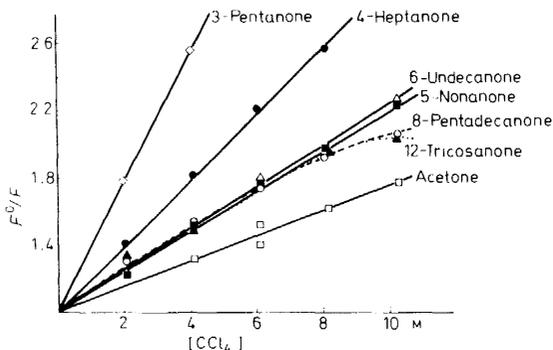


Figure 12. Quenching of ketone fluorescence by carbon tetrachloride.

of the ketone forms what is called an 'exciplex', a complex with carbon tetrachloride, and the carbon tetrachloride then becomes excited, the ketone becomes deactivated, and the decomposition products of carbon tetrachloride result, usually chlorine atoms and $\cdot\text{CCl}_3$ radicals. Figure 12 shows that CCl₄ quenches the fluorescence of the ketones added to it. As the fluorescence is quenched by the carbon tetrachloride the amount of chemical reaction is increased. This fourth kind of energy transfer process is due to an excited state charge transfer complex between the absorbing molecule (the ketone) and another molecule, in this case carbon tetrachloride.

In summary, many types of energy transfer processes, both inter- and intra-molecular can occur in polymer systems. A more thorough study of the mechanisms of these processes should assist in devising practical routes for the stabilization of macromolecules against weathering damage due to the absorption of ultra-violet light from the sun.

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