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The Mechanism of Light-induced Ageing and Light Stabilisation of Polymers

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This review deals with processes accompanying the light-induced ageing of polymers which are subjected simultaneously to the action of oxygen and ultraviolet and visible light, and also with the distinctive features of these processes and possible pathways for the stabilisation of polymeric materials. Under natural conditions, solar radiation leads to rapid mechanical breakdown of unstabilised polymeric materials. The light stabilisation of polymers is one of the most important problems, because of the wide application of these materials[1] in space engineering, national economy, and ordinary life.
The authors' aim was not to give the maximum cover of the available literature on this problem, which has become fairly extensive during the last 5–6 years; attention is mainly concentrated on the mechanisms of the processes occurring in light-induced ageing and the methods available for their investigation. The bibliography includes 122 references.

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1. CHANGE IN THE PRACTICAL PROPERTIES OF POLYMERS ON LIGHT-INDUCED AGEING

In most studies of light-induced ageing, the mechanical properties of polymers have been investigated as a function of the duration and conditions of irradiation[2-6]. This is quite reasonable, since the user is interested in the first place in the stability of such properties of the material as elasticity, strength, adhesion, constancy of dimensions, etc. However, most of the published work is of an unduly applied nature and reduces to simple statements of the magnitude of the changes occurring and the effect on these changes of various stabilisers against light.

Mechanical methods for testing polymers are most widely used. They are readily available and are highly sensitive. The changes in the ultimate strength and the relative elongation of polymer specimens as a function of the duration of irradiation are most frequently determined. The user obtains in this way virtually exhaustive data on the operational properties of the material, but, for a controlled increase of the stability of polymers with respect to light, it is necessary to know the internal mechanism of the observed changes.

Quantitative theory[7-9] relating the mechanical characteristics of the polymeric material to the chemical structure and the nature of the supermolecular structures is still in its development stage. A clear relation between the following changes in polymeric materials on light-induced ageing is by no means always clear: changes in chemical structure as a result of photochemical reactions, changes in supermolecular and hence crystalline structures as a result of the changes in chemical structure, and the changes in mechanical properties resulting from the changes in crystal structure. It is quite evident that, in studying the action of light on mechanical properties, it is necessary to follow the entire sequence of transformations. Only then can one hope to establish a quantitative relation between the first and last stages of the light-induced ageing process.

Instructive studies have been made by Baltenas[10,11] and by Ozawa and coworkers[5]. A number of polyethylene specimens differing in the number of local strains in the defects were investigated[10]: (1) a film (60μm) heat-treated in a vacuum above the melting point (this film is closest to equilibrium); (2) a film (60 μm) extruded under conditions of hot orientation and rapid cooling with high anisotropy of the mechanical properties, an irregular spherulitic structure, and local internal strains; (3) specimens obtained by cold drawing (neck) with breakdown into fibrils of the spherulitic structure and the maximum number of local strains. The specimens were irradiated with ultraviolet light from a PRK-2 lamp at 40°C in air over a period of 20 h.[13] On going from specimens (1) with a homogeneous spherulitic structure to specimens (2) and (3) with an increasingly defective structure, one observes an increase in the rate of accumulation of carbonyl groups (determined from infrared spectra), a more rapid decrease of mechanical strength, and an increase in the yellow colour of the specimens. These observations are consistent with the hypothesis[14] that the strength of the chemical bonds decreases with increasing mechanical strain in the specimen.

The study of the thermograms of the same specimens shows that, on light-induced ageing, the degree of crystallinity increases in all cases by 6–8%. Hence one may conclude that chemical bonds in the region of local strains are the first to dissociate in light-induced ageing, which may lead to the migration of units from the region of the defects to the crystal lattice. The so called destructive crystallisation takes place. The increase in the degree of crystallinity on ageing was noted also by other workers[5,15,16]. Thus the change in the properties of the polymeric material in light-induced ageing is determined mainly by the nature of the defects and not the structure of the crystal lattice[10].

The data quoted by Baltenas and Visciniene[12] are very instructive in this respect. The structure of the polyethylene coating of an aluminium foil is determined to a large extent by the method of its preparation. Fig. 1

presents the photomicrographs of sections of polyethylene coatings obtained by centrifugal deposition in a fluidised layer of polyethylene powder at 200°C. Slow cooling of the coating obtained in air results in a structure with large annular spherulites (Fig. 1*a*). On rapid cooling with water, smaller spherulites without visible rings are produced (Fig. 1*b*). Furthermore, in the latter case amorphous regions arise, particularly at the surface of the coating, without a visible spherulitic structure. It is found that the coating with a crystalline surface is more stable with respect to the action of ultraviolet light. Fig. 2 presents photomicrographs of the surface of the coating after irradiation for 30 h. On the coating with the crystalline surface (Fig. 2*a*), there are almost no cracks, while the coating with the amorphous surface (Fig. 2*b*) was virtually broken up as a result of the formation of a large number of cracks.

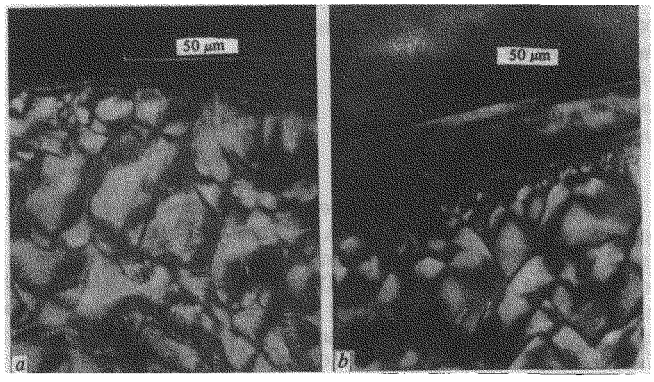


Figure 1. Spherulitic structure of a polyethylene coating in transverse section: *a*) obtained by centrifugal deposition with cooling in air; *b*) ditto with cooling in water.

The difference in the structures of the polymer is in turn determined by the chemical reactions occurring in the preparation of the coating. The formation of the structure with large spherulites on centrifugal deposition is probably caused by the thermal oxidation of polyethylene. In thermal oxidation in the melt, the macromolecules dissociate with formation of free radicals, whose reactions lead to the formation of oxygen-containing groups and to the cross-linking of the chains. It is suggested[17] that these chemical reactions appreciably alter the conditions for the formation of crystallisation nuclei (nucleation), as a result of which, the rate of their formation falls. There is a change in the relative rates of nucleation and crystallisation, which leads to the formation of large spherulites. The generation of amorphous regions on rapid cooling is due to the sharp decrease of the rate of nucleation. In the unoxidised polyethylene amorphous regions of this kind are absent. The increase of the rate of the light-induced ageing of the coating in the presence of amorphous regions may be caused by its higher permeability to oxygen.

The dependence of stability with respect to light on the dimensions of the crystalline regions and the degree of orientation of low-pressure polyethylene films has been investigated with irradiation, using a weatherometer, with light at a wavelength of 360–420 nm.[5]

The size of the crystallites and the molecular weight change little on irradiation. It is interesting to note that refusion of the specimens fully restores their mechanical properties. The authors' explanation is that amorphous regions of the polymel are the first to undergo polychemical oxidation, after which new crystalline regions appear, while large crystals break down under the action of high-energy quanta, giving rise to internal strains with weakened chemical bonds.

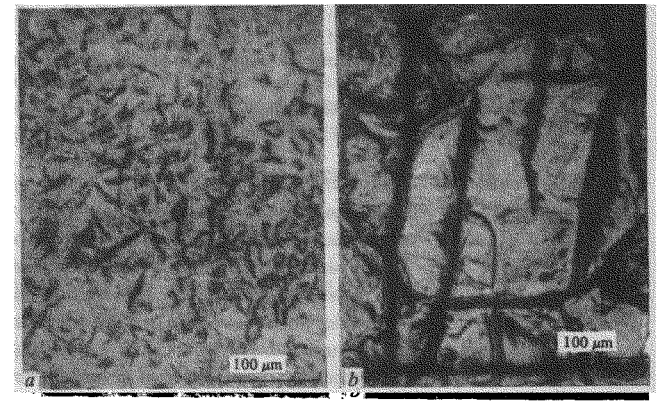


Figure 2. Photomicrographs of the surface of a polyethylene coating (viewed from above) after irradiation for 30 h with ultraviolet light: *a*) cooling in air; *b*) cooling with water.

The results obtained in the oxidation of polymers with different extents of branching provide an indirect indication of the relation between the light stability of the polymer and the structure of its macromolecules[18]. On irradiation with ultraviolet light (280 nm), polyolefins absorb oxygen at different rates depending on the degree of branching (Fig. 3).

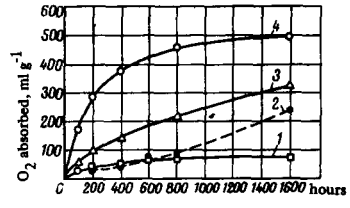


Figure 3. Variation of the extent of absorption of oxygen with the degree of branching of polyolefin specimens irradiated with ultraviolet light at a wavelength of 280 nm at 50°C: 1) linear polyethylene; 2) branched-polyethylene; 3) isotactic polypropylene; 4) poly-4-methylpent-1-ene.

Thus it is clear from the studies enumerated above that, although chemical reactions are important, they are by no means the sole factor determining the mechanical strength on light-induced ageing of polymeric materials and it is particularly important to take this into account in thermal processing of polymers.

The relation between the mechanical properties and chemical transformations in light-induced ageing of polymers has been investigated in greatest detail for the formation of cross-links on ultraviolet irradiation. The large number of studies on this problem has been stimulated by the cross-linking theory developed in detail for the ageing of polymers under the action of ionising radiation[19,20]. Although structure formation takes place under these conditions too, chemical reactions play a decisive role in this case, which makes it possible to establish certain quantitative relations between the number of cross-links and the mechanical properties.

2. KINETIC MECHANISM OF THE PHOTOCHEMICAL PROCESSES IN LIGHT-INDUCED AGEING

From the standpoint of the kinetics, the process of light-induced ageing of polymers can be divided into a number of stages, each of which is characterised by its own rate constant. These stages can occur both consecutively and simultaneously. In the latter case a number of competing reactions are observed, one of which may predominate, depending on the conditions.

Among the large number of studies dealing with the light-induced ageing of various polymers, there are only a few on the kinetic analysis of the results on the basis of a system of kinetic equations. This is fairly remarkable, because the studies on light-induced ageing are essentially kinetic, since the changes in a particular quantity are always investigated as a function of the duration of irradiation. The absence of kinetic analysis is due to the difficulties associated with the derivation and solution of an adequate system of kinetic equations and also with the complexity of the analysis of small amounts of products.

In this review an attempt is made to derive such a system and the solutions are analysed as far as possible.

1. Initation:

$$S + h\nu \xrightarrow{k_1} S^*, \qquad (1)$$

where S is a macromolecule containing an absorbing group in the ground singlet state and S^* the same macromolecule with the absorbing group in an excited singlet state.

2. Return to the initial state by light emission (fluorescence):

$$S^* \xrightarrow{k_2} S + h\nu'. \qquad (2)$$

3. Transition to an excited triplet state and a radiationless transition unaccompanied by dissociation:

$$S^* \xrightarrow{k_3} T; \quad S^* \xrightarrow{k_4} \tilde{S}, \qquad (3)$$

where $\tilde{S}$ is a molecule with excited vibrational states.

4. Return to the initial state by a singlet–singlet energy transfer (quenching of fluorescence):

$$S^* + A \xrightarrow{k_5} S + A^*, \qquad (4)$$

where A is an acceptor molecule.

5. Transformation of the triplet state:

$$T \xrightarrow{k_6} . \qquad (5)$$

6. Photodissociation:

$$S^* \xrightarrow{k_7} 2R. \qquad (6)$$

7. Formation of photolytic products:

$$M{-}M + R^{\cdot} \xrightarrow{k_8} R + P_l, \qquad (7)$$

where M–M is a section of the macromolecule without an absorbing centre.

8. Cross-linking (chain termination) and diffusion of microradicals from the polymer matrix (linear termination):

$$2R \xrightarrow{k_9} C: \ R \ \text{(condensed phase)} \xrightarrow{k_9'} R \ \text{(gas)}. \qquad (8)$$

9. Oxidative processes:

$$R + O_2 \xrightarrow{k_{10}} P_0 + R, \qquad (9)$$

where P_0 are products obtained via a peroxy-radical; k_1–k_9 are the rate constants for the processes, ν is the frequency of the active light, and ν' the frequency of the light emitted in fluorescence (in the general case $\nu \neq \nu'$). The reversal of stage (4) results in sensitisation via impurities.

Despite the large number of stages quoted above, the mechanism is to a large extent simplified—in particular it is assumed that light-induced ageing takes place mainly via singlet states, the complex stages (7) and (9) are described by overall constants, quenching by oxygen is not taken into account, and it is assumed that various radicals have the same reactivity (the one-centre approximation). Stages (1)–(8) determine the kinetics of light-induced ageing in the absence of oxygen, i.e. in photolysis. The entire set of stages (1)–(9) describes oxidative ageing. Since all the photolytic processes can take place in oxidative light-induced ageing, the large number of studies dealing with the photolysis of various polymers is not surprising. The determination of the kinetic parameters for the photolytic breakdown of polymers is simpler than for oxidative ageing and yields important information about the initiation of photochemical processes. Usually[21–24] the first four stages of the mechanism, describing the physical photoactivation and deactivation processes, are not treated in detail and are combined in a single initiation stage. For example, the initiation stage in the photochemical oxidation of polyethylene[21,25] and polystyrene[26] is described as follows:

$$\ldots CH_2{-}CH_2{-}CH_2{-}CH_2\ldots \xrightarrow{h\nu\ O_2} \ldots CH_2{-}CH_2{-}\underset{\displaystyle OOH}{CH}{-}CH_2\ldots,$$

$$\ldots CH_2{-}\underset{\displaystyle C_6H_5}{CH}{-}CH_2\ldots \xrightarrow{h\nu\ O_2} \ldots CH_2{-}\underset{\displaystyle C_6H_5}{\overset{\displaystyle OOH}{C}}{-}CH_2\ldots.$$

Undoubtedly mechanisms of this kind make it very difficult to understand the most important stage in light-induced ageing, namely initiation, and in photolysis by sunlight (λ = 290 nm) the nature of the light-absorption centres is completely obscure, since pure saturated hydrocarbons, for example, are transparent in this wavelength range.

3. THE MECHANISM OF INITIATION IN LIGHT-INDUCED AGEING. EXCITED STATES

The principal difference between photochemical and dark reactions is due to the nature of initiation of the process as a whole. In a dark reaction the energy required to overcome the activation barrier is drawn from the internal energy of the system and the rate and mechanism of the process under these conditions are determined by the temperature of the system. In a photochemical reaction the energy is provided from outside in the form of quanta of electromagnetic radiation and at a given temperature of the system the rate and mechanism of the process are determined by the intensity of the initiating radiation and its spectral distribution.

Usually[27,28] the primary photochemical step is regarded as the chemical reaction of the molecule excited by light absorption with formation of one or several primary photochemical products. However, the light absorption itself is essentially a chemical reaction of the molecule.

Indeed the chemical properties of the molecule are determined by the structure of its electron shell, which changes considerably on absorption of light; the chemical properties of the excited molecule, in particular its reactivity, may differ sharply from those of the molecule in the normal state[29,30].

Evidently, for a theoretical prediction of the nature of the excitation of the polymer molecule and hence of the entire light-induced ageing process as a function of the intensity of the incident radiation and its spectral distribution, it is necessary to have a clear idea about the nature of the absorbing groups and their electronic states.

The principal component of solar radiation at sea level consists of the long-wavelength region above 300 mn and only a small part of it is radiation at a wavelength less than 300 nm. The absorption spectra of the commonest polymers—poly(vinyl chloride) poly(methyl methacrylate), polystyrene, polyethylene, polypropylene, cellulose, polyamides, etc. —do not contain absorption bands in the region above 300 nm and therefore it would appear they should not undergo light-induced ageing. However, these polymers break down rapidly in sunlight. Hence it follows that it is precisely the small component of the short-wavelength solar radiation in the region of 300 nm that initiates the secondary photochemical processes leading to the light-induced ageing of polymers. The wings of the absorption bands attributed to carbonyl groups and polyene conjugated structures enter this region (the long-wavelength band of acetone is in the region of $\lambda_{max} = 280$ nm [31] and the band of $CH_3-(CH=CH)_4-CH_3$ is in the region of $\lambda_{max} = 290$ nm [32]). These groups and structures may be regarded as initiation centres for light-induced ageing in polymers whose monomer units do not contain absorbing groups†. The carbonyl group may form part of a monomer unit of the polymer, for example in polyamides, polymethacrylates, etc. In carbon chain polymers such as polyethylene, polypropylene, and polystyrene carbonyl groups and double bonds arise by thermal oxidation in the polymerisation and processing of the polymers.

An indirect demonstration of the role of C=O groups in light-induced ageing processes of polymers is provided by data on the photochemical degradation of poly(vinyl chloride) (with light at 300 nm). The photochemical degradation was appreciably accelerated on addition of acetone to the polymer[33,34].

The apparent absence of the corresponding bands in the absorption spectra of the polymers is due to the low concentration of the initiating groups and frequently the fact that such bands are masked by the intense bands associated with the chemical groups forming part of the monomer units of the polymer. For example, the spectrum of polystyrene is determined mainly by the absorption of the phenyl rings. Because of the difficulties of the direct spectroscopic determination of the absorbing groups of the above type, investigators resort to indirect methods (for example the measurement of the activation spectrum—the dependence of the quantum yields of the photochemical processes on the wavelength of the initiating radiation[35,36]) (Fig. 4).

It was also shown[37] that the maximum luminescence of polypropylene is observed on excitation with light at 280 nm, although in this region there is no detectable absorption maximum. Since the luminescence intensity is approximately proportional to the number of excited molecules, one may propose that, on irradiation with light at this wavelength, the most intense breakdown of the polymer will occur.

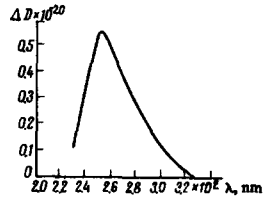


Figure 4. Variation of the optical density of poly(vinyl chloride) with the wavelength of ultraviolet radiation per incident quantum.

In view of the special role of carbonyl groups in light-induced ageing of various polymers, we shall consider in greater detail (as a model) the electronic structure of complex carbonyl-containing molecules[30,38]. It must be noted that the ultraviolet spectra and hence also the electronic structure of the carbonyl compounds of the polymers have been scarcely investigated and therefore the data quoted are suitable only for an approximate prediction of the course of photochemical processes in polymers.

The electronic structure of the carbonyl-containing compound in the region of the C=O group is determined by the presence of three groups of electrons:

(1) The non-bonding n electrons in the valence shell of the oxygen atom which do not enter into a chemical bond; (2) the bonding π electrons, the wave function of which is antisymmetric relative to the plane passing through the C=O bond; (3) the bonding σ electrons, the wave function of which is symmetrical relative to the axis of the C=O bond. The π electrons are usually delocalised in the region of the C=O group and the σ electrons are localised at the atoms which they bind together.

In a one-electron scheme these three groups of electrons correspond to three groups of levels (Fig. 5). The ground state of the molecule corresponds to the population of the one-electron states which ensures the minimum total energy of the molecule.

An excited state of the molecule arises as a result of the transition of one of the n, π, or σ electrons to an antibonding π^* or σ^* level. Depending on the nature of the transition, the excited states are denoted as follows: an $S_{n\pi^*}$ (singlet $n\pi^*$) state of the molecule arising by transition of a $2p$ electron from the n orbital to an antibonding π^* orbital, a $T_{n\pi^*}$ (triplet $n\pi^*$) state—a similar transition but with a change in the resultant spin of the system, etc.

The electronic absorption bands attributed to the carbonyl group are due to the corresponding transitions. The short-wavelength band with $\lambda_{max} = 150$ nm (8.3 eV) is due to the $\pi \rightarrow \pi^*$ transition, the middle band with $\lambda_{max} = 190$ nm (6.5 eV) corresponds to the $n \rightarrow \sigma^*$ transition, and the long-wavelength band with $\lambda_{max} = 280$ nm (4.4 eV), which is the most interesting from the standpoint of light-induced ageing, is caused by the $n \rightarrow \pi^*$ transition. In the region of the long-wavelength boundary of this band at

†The initiation can of course take place also via impurity molecules.

340 nm (3.6 eV) a vibrational structure is observed. In this transition both $S_{n\pi^*}$ and $T_{n\pi^*}$ excited states may be populated. Precisely these are the initial states in photochemical reactions undergone by various polymers with a carbonyl group in light-induced ageing and the concentration of these states must appear in the kinetic equations describing the light-induced ageing of a particular polymer.

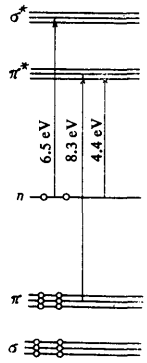


Figure 5. Schematic representation of one-electron levels in a molecule containing a carbonyl group.

Since under the usual experimental conditions absorption in the region of about 300 nm plays the main role, in the treatment below S^* must be understood as the $S_{n\pi^*}$ state. Eqns. (2)–(6) of the kinetic mechanism of light-induced ageing describe the processes involved in the degradation of the electronic excitation energy absorbed in the primary step (1). The relation between the rates of these processes ultimately determines the rate of light-induced ageing. Thus, for example, the number of breaks in the macromolecular chain (degradation), which has a destructive effect on the mechanical properties of the polymer, is determined (see below) by the relation $D = k_6 \int_0^t (S^*)dt = k_6(\bar{S}^*)t$, where $(\bar{S}^*)$ is the average concentration of excited states during the time of exposure t, i.e. with increasing (S^*), the rate of degradation of the polymer rises. However, if the rates of processes (2)–(5) are high, the concentration of excited states and hence also the rate of degradation are insignificant. The data for the constants k_2–k_5 may be obtained by spectroscopic luminescence techniques.

Many polymers in the solid state and in solution exhibit bright luminescence. Polymers with a wide variety of chemical structures, including biopolymers, have been investigated qualitatively[39]. The luminescence spectra‡ of all the polymers investigated extend as a continuum over the region 300–700 nm (when an ISP-51 glass spectrograph is used). This luminescence is not characteristic. It consists of maxima with fixed positions in the red part of the spectrum and the adjacent broad diffuse maximum in the blue-violet part. The latter maximum changes its position from compound to compound and with molecular weight in the same homologous series.

‡The observed glow has been referred to as fluorescence[39] without the appropriate evidence being adduced (see below).

Gachkovskii[39] did not explain the changes in the luminescence spectrum and their origin. It may be supposed that the observed glow is caused by the presence in the polymer of impurity groups, for example terminal groups, which consist of part of the initiator molecule. The relative content of these groups and therefore also the luminescence yield must fall with increasing molecular weight.

A more careful study of the luminescence of various polymers was carried out by Charlesby and Partridge[40,41]. The main aim of these investigations was to establish the nature of the centres responsible for the thermoluminescence observed when raising the temperature of the polymer specimens subjected to the action of γ-radiation or ultraviolet light at 77°K; the luminescence of the same polymers at room temperature, excited by ultraviolet light of different wavelengths, was studied simultaneously. The luminescence spectra of polyethylene, polypropylene, polystyrene, and polytetrafluoroethylene are produced by the superposition of the fluorescence spectra in the region of 300–400 nm and phosphorescence spectra in the region of 400–600 nm. The thermoluminescence spectra of these polymers are in the main analogous to their luminescence spectra.

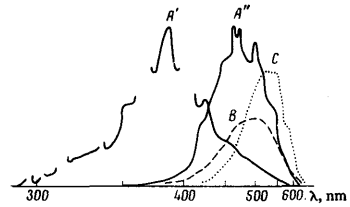


Figure 6. Luminescence spectrum of polyethylene: *A'*) and *A''*) complete luminescence spectrum; *B*) phosphorescence spectrum obtained on irradiation of polyethylene through a glass filter; *C*) phosphorescence spectrum obtained on irradiation of polyethylene through a filter transmitting light at wavelengths greater than 350 nm; the spectra are presented with different intensity scales.

Fig. 6 shows the luminescence spectrum of polyethylene resolved into the ultraviolet (*A'*) and visible (*A''*) components. The luminescence spectra of low- and high-density polyethylene are produced by the superposition of at least four spectra, which differ in structure and the limiting excitation wavelength. The complete phosphorescence spectrum (*A''*) of polyethylene consists of a series of sharp vibrational peaks against the background of a broad spectral band. Spectrum *B* is obtained when a glass filter, transmitting light at wavelengths greater than 300 nm, is interposed in the path of the exciting beam. Spectrum *C* is obtained with a filter transmitting light at a wavelength greater than 350 nm. The difference between spectrum *A''* and the sum of spectra *B* and *C* may be due to the presence of an undetected spectrum *D*. At a wavelength greater than 420 nm phosphorescence is not excited.

The phosphorescence spectrum of polystyrene is very similar to those of acetophenone and benzophenone, investigated by Kasha[42]. Kasha attributes the phosphorescence of benzophenone and acetophenone to the $n \rightarrow \pi^*$ transition of the carbonyl group. The distance between the distinct bands in the vibrational structure corresponding to the

stretching vibrations of the carbonyl group is 1665 cm^{-1} for benzophenone and 1690 cm^{-1} for acetophenone. In the phosphorescence spectrum of polystyrene this interval is 1600 ± 150 cm^{-1}. The great similarity of the phosphorescence spectrum of polystyrene to those of benzophenone and acetophenone can be hardly attributed to isolated admixtures of the latter. It is most likely that the phosphorescence of polystyrene is due to the presence of small amounts of carbonyl groups produced in the polymer during its preparation. Three types of carbonyl groups, two terminal and one distributed at random, are possible:

$$\underset{\underset{C_6H_5}{|}}{R-C=O}\ (I), \qquad \underset{\underset{H}{|}}{R-C=O}\ (II), \qquad \underset{\underset{O}{\|}}{R-C-R}\ (III).$$

The presence of these groups may explain the observed features of the phosphorescence spectra. Groups of type (I) give rise to a spectrum analogous to that of acetophenone but displaced towards the red region due to the presence of a heavy alkyl substituent—the polystyrene chain, as is observed for alkyl-substituted methyl ketones[43]. Spectra of groups (II) and (III) should be similar to those of aliphatic aldehydes and ketones and also polyethylene if the phosphorescence spectrum of the latter is due to carbonyl groups. These hypotheses are confirmed by experimental data. In particular, the fluorescence spectrum of polystyrene may be attributed to emission by carbonyl groups.

It is quite evident that the luminescence of polystyrene is not associated with the phosphorescence and fluorescence spectra of toluene (which should be the case if the isolated phenyl groups of the macrochain were responsible for the major part of the emission), since the 0,0 bands of toluene are in the region of 270 and 347 nm.[44] Nor can they be attributed to terminal groups, since the polystyrene was obtained by thermal polymerisation.

The luminescence of polyethylene cannot be due to the properties of the polyethylene chains, since saturated hydrocarbons do not luminesce. In this connection it is interesting to note that the entire luminescence spectrum is observed even in comparatively pure saturated hydrocarbons, such as, for example, pentatriacontane deposited in a thin layer on a quartz support.

It may be supposed that the luminescence of polyethylene is caused by the presence of double bonds in the chain. Evans[45] showed that the triplet 0,0 absorption bands of ethylenes lie in the region of 350 nm and Wilkinson and Mulliken[46] observed a singlet 0,0 band near 250 nm. Bearing in mind the presence of an "infinitely long" alkyl substituent in polyethylene, one may postulate the possibility of a corresponding shift of these bands towards the longest wavelengths observed in the phosphorescence spectra of polyethylene as 380 and 295 nm respectively. However, so far it has proved impossible to obtain reliable phosphorescence spectra of ethylene or its substituted derivatives. According to Potts[47], this may be caused by the capacity of the molecules of the ethylene type to rotate rapidly about the C=C bond after undergoing a transition to the triplet state. This entails an energy loss, the molecule reaches the point of intersection of the singlet and triplet terms and can undergo a radiationless transition to the ground state.

However, the majority of available facts are consistent with the hypothesis that carbonyl groups are the luminescence centres in polyethylene and polystyrene. This is suggested by the decrease of the luminescence yield on γ-radiolysis of the polymers (the number of double bonds then increases) and the increase of the luminescence yield on heating the polymer in air (the number of carbonyl groups increases).

Charlesby and coworkers[40,41] encountered considerable difficulties due to the inadequate sensitivity of the apparatus and the non-monochromatic nature of the exciting radiation. For example, the visual fluorescence observed for polytetrafluoroethylene could not be recorded with a spectrograph, which of course hinders a quantitative assessment of the observed phenomena.

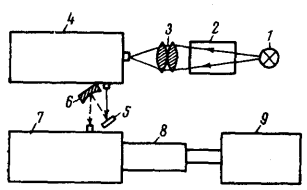


Figure 7. Diagram of apparatus for the recording of luminescence spectra: 1) DRL-500 mercury lamp; 2) water filter for the absorption of heat; 3) quartz condenser; 4) EMR-3 mirror monochromator; 5) specimen; 6) parabolic mirror; 7) SFD-2 monochromator; 8) FEU-19M photomultiplier; 9) U2-4 amplifier.

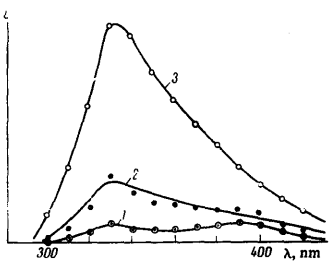


Figure 8. Effect of Tinuvine P (0.01 mole kg^{-1}) on the luminescence of polypropylene: 1) observed luminescence spectrum of the polymer with Tinuvine P; 2) luminescence spectrum of the polymer with Tinuvine P corrected for reabsorption and screening; 3) observed luminescence spectrum of the polymer without added Tinuvine P; L—luminescence intensity in relative units; the wavelength of the exciting light was 280.4 nm.

These difficulties were overcome after the construction from standard equipment of an apparatus (Fig. 7) for the investigation of low intensity luminescence with monochromatic excitation[37]. Fig. 8 shows a luminescence spectrum of atactic polypropylene obtained on this apparatus (Fig. 8, curve *3*). The spectrum of isotactic polypropylene is similar. These spectra make it possible to investigate quantitatively the form of the spectrum and the luminescence yield (see below).

It follows from the data quoted above that the fluorescence (reaction (2)] and phosphorescence [reactions (3) and (5)] processes may compete to a considerable degree with the photodissociation process (6), which is confirmed[40]

by the very low quantum yields of the radicals. We shall not consider here the role of the triplet states, because at room temperatures they are probably important only at very high light intensities (two-quantum processes[48]). The migration of energy [reaction (4)] will be examined below and now we shall consider the more important photodissociation reaction (6), which determines the nature of the radicals responsible for numerous secondary photochemical processes in light-induced ageing of polymers.

4. THE NATURE OF RADICALS FORMED ON ULTRAVIOLET IRRADIATION OF POLYMERS

The method most widely used at present to investigate the radicals formed on ultraviolet irradiation of polymers is electron spin resonance. As a rule these radicals are very reactive and they must be stabilised by a rigid polymeric matrix at low temperatures. Quantitative data concerning the accumulation of these radicals, their lifetimes, etc. at low temperatures cannot of course be used directly for kinetic calculations at room temperatures. However, these data are important for the understanding of the mechanism of light-induced ageing processes.

The processes involved in the formation of radicals in low-temperature photolysis (77°K) of polyethylene[41,49-51], polypropylene[49-54], poly(methyl methacrylate)[55], polystyrene, a number of polyolefins[49], and polyphenylmethylsiloxan[56] have been investigated in greatest detail.

When polyethylene was irradiated in air at room temperature, an ESR signal was not recorded[49]. At 77°K free radicals of two types were detected[51]: $\ldots CH_2-\dot{C}H-CH_2\ldots$, whose spectrum is the same as that of polyethylene subjected to ionising radiation and described in a number of studies[57-61], and the radical $\ldots CH_2-\dot{C}H_2$, arising on dissociation of the C–C bond of the polymer chain, which is not observed in the radiolysis of polyethylene. These two types of radicals are formed with approximately equal yields. Heating to 178°K transforms the initial ESR spectrum into a singlet, which has been tentatively attributed to a free radical of the allyl type produced from the radical $\ldots CH_2-\dot{C}H_2$ on dehydrogenation with the migration of the free valency along the polymer chain.

The results from the study of the ESR spectra of polypropylene irradiated with ultraviolet light differ from those obtained in the radiolysis of this polymer. The action of ionising radiation of polypropylene at a low temperature leads to the formation of the alkyl radical[62-69] $\ldots CH_2-\dot{C}(CH_3)-CH_2$. When the system is heated to room temperature, the eight-line spectrum of this radical is converted into a nine-line spectrum attributed to the allyl radical[64,66,67] $\ldots CH_2-\dot{C}(CH_3)-CH=C(CH)_3-CH_2\ldots$

γ-Irradiation of polypropylene at room temperature leads to the formation of a 17-line spectrum, attributed[66,67] to radicals of the allyl type. On the basis of new data, it is suggested that[70] this spectrum is due to an alkyl radical.

It follows from the results quoted above that, as a result of the action of ionising radiation on polypropylene, dissociation of C–H bonds predominates. The action of ultraviolet light on polypropylene at 77°K leads to the formation of a number of alkyl radicals.

Typical radical accumulation curves are presented in Fig. 9. The interpretation of the ESR spectra led to the discovery of the presence of the methyl radical[49,51,54] $\dot{C}H_3$ and the macroradicals $\ldots CH_2-\dot{C}H-CH_2\ldots$ and $\ldots CH(CH_3)-\dot{C}H-CH(CH_3)\ldots$ and also radicals with a free valence at the terminal CH_2 group, which are formed on dissociation of the C–C bond of the polymer chain: $\ldots CH_2-CH(CH_3)-\dot{C}H_2$.

The presence of the last named radical is most likely, since heating to 178°K converts the initial spectrum into a singlet, which, by analogy with polyethylene irradiation with ultraviolet light, was also attributed to an allylic radical arising on dehydrogenation of $\ldots CH_2-CH(CH_3)-\dot{C}H_2$.[51] The energy of ultraviolet light at a wavelength of 344.5 nm, consumed in the formation of a single free radical stable at 77°K, is 1.1×10^5 eV for polyethylene and 0.17×10^5 eV for polypropylene[51].

It is suggested[49,54,56] that the $\dot{C}H_3$ radicals can rotate rapidly in the polymer matrix even at liquid nitrogen temperature. This averages out the anisotropic broadening and yields the fairly well resolved ESR spectrum of polypropylene irradiated with ultraviolet light. The rotation frequency of $\dot{C}H_3$ in the polymer matrix is somewhat reduced (to about 30 MHz), and this accounts for the stabilisation of these radicals[51], which can exist for a week at 77°K.[49]

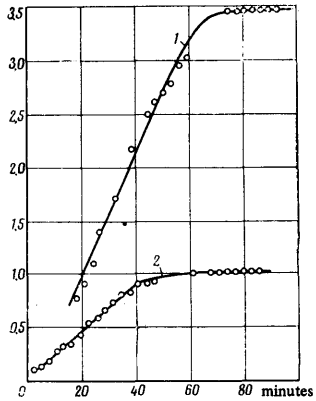


Figure 9. Curves for the accumulation of radicals in the photolysis of thermally oxidised atactic polypropylene: 1) irradiation in a quartz tube; 2) irradiation in a Pyrex tube (1 unit on the ordinate scale corresponds to 10^{16} particles).

When polypropylene was exposed to ionising radiation, the methyl radical was not detected. However, its intermediate existence is indicated by the presence of methane in the radiolysis products[71].

The irradiation of polyolefins containing short side chains results in the formation of free radicals of the corresponding side groups or methyl radicals if the side group contains a methyl[49]. Thus ethyl radicals $\dot{C}_2H_5$ and the macroradicals $\ldots CH_2-\dot{C}H-CH_2\ldots$ are formed in polybut-1-ene on irradiation with ultraviolet light; irradiation of poly-4-methylpent-1-ene leads to the formation of the same radicals as in polypropylene, while radicals similar to those in irradiated polyethylene are formed in polydodec-1-ene and polypent-1-ene.

In the low-temperature photolysis of poly(methyl methacrylate) (irradiation with the light of the DRSh-500 lamp) free radicals of two types were observed[55]: $\ldots CH_2-\dot{C}(CH_3)(COOCH_3)\ldots$, formed on dissociation of the main chain and long-lived only at the temperature of liquid nitrogen, and the radicals $\ldots CH_2-\underset{\displaystyle COOCH_3}{\overset{\displaystyle |}{\dot{C}}}H(CH_2)$, which persist at

room and higher (340°K) temperatures for several months. The authors believe that the radicals of the second type are produced from the radicals of the first type by the capture of a hydrogen atom from the methyl group by the free valence of the carbon atom in the polymer chain.

On ultraviolet irradiation of polystyrene, a broad singlet, tentatively attributed to phenyl radicals, was observed[49]. Free radicals of two types were identified by the ESR method in the low-temperature photolysis of polyphenylmethylsiloxan[56]: $\dot{C}H_3$ and $R-\dot{C}H_2$. The study of the kinetics of the accumulation of these radicals as a function of light intensity established that the relation between the rate of accumulation of the $\dot{C}H_3$ radicals and the intensity I_0 is $W_{CH_3} \propto I_0^2$ for low values of I_0 and $W_{CH_3} \propto I_0$ at high values of I_0, i.e. the relation becomes linear. For R = $\dot{C}H_2$, the rate of formation varies linearly with I_0 over the entire range of intensities investigated.

On the basis of these results, it was also concluded that the formation of the $\dot{C}H_3$ radical, requiring the dissociation of the Si–C bond, involves two quanta and the formation of $R-\dot{C}H_2$, requiring the dissociation of the C–H bond, involve one quantum. The authors assume that the absorption of the first quantum causes the transition of the molecule to an excited state in which the Si–C bond dissociates in such a way that the $\dot{C}H_3$ radical remains within the cage (one quantum at 300 nm is sufficient to dissociate the Si–C bond). This state of the radical in the cage presupposes a strong interaction with the residue of the molecule. Only the absorption of the second quantum enables the $\dot{C}H_3$ radical to leave the cage.

Strictly speaking a two-quantum process in photochemistry is thought to be one in which the absorption of the second quantum takes place from a photo-excited molecular level[48]. The quadratic relation between the rate of accumulation of radicals and light intensity can also be obtained when a molecule adsorbes two light quanta (a two-quantum mechanism), as in the case where the formation of radicals takes place via an intermediate compound (complex) produced under the action of the first light quantum followed by the absorption of a second quantum. In the latter case there is a two-stage mechanism. Therefore it is more correct to suppose that in the photolysis of polyphenylmethylsiloxan the generation of $\dot{C}H_3$ radicals involves a two-stage mechanism.

A two-quantum process is possible in photoinitiation via the CO group[32,41]. Thus thermoluminescence of polyethylene produced by ultraviolet light at 365 nm has been observed. This corresponds to a photon energy of 3.4 eV, which is insufficient for the ionisation of the carbonyl group. However, when the triplet state generated by the absorption of the first photon is long-lived (about 2 s), there is a possibility of absorption of a second photon before the molecule returns to the initial state by emitting a phosphorescence photon. The second photon raises the energy of the molecule above the ionisation limit and the CO group ionises.

As already mentioned above, in the group of polymers examined, the most probable centres absorbing ultraviolet light (at 300 nm) are impurity carbonyl groups in polyethylene, polypropylene, and other polyolefins, CO groups forming part of the monomer unit in poly(methyl methacrylate), and the phenyl rings in polymers such as polystyrene and polyphenylmethylsiloxan ($\lambda < 300$ nm).

Since the appropriate data are not available for the polymers, it is useful to employ data on the photodissociation of low-molecular compounds to elucidate the mechanism of the formation of radicals on ultraviolet irradiation of polymeric molecules in which the absorption centres consist of CO groups and benzene rings.

It may be assumed[30] that in the excited state the molecule has an additional valency compared with the ground state. In the $n\pi^*$ state (the $n \rightarrow \pi^*$ transition in the CO group) the molecule has an atomic valence and in the $\pi\pi^*$ state (the $\pi \rightarrow \pi^*$ transition in the benzene ring) the valence is delocalised over the entire molecule. The mechanisms of the reactions of molecules in these two states are different. In consequence of the delocalisation of the valence in the excited $\pi\pi^*$ state and in the absence of $\sigma-\pi$ conjugation, the utilisation of the valence is difficult and the molecules may break down simply due to the conversion of electronic energy into vibrational energy of a bond in the molecule. Then there may be two pathways for the conversion of the excitation energy into bond vibrational energy: the "direct" pathway when the electronic energy of the molecule is converted into the vibrational energy of the bond, the electron density of which changes at the instant of the transition (for example in the C–R bond of substituted benzene); the "indirect" pathway when the excitation energy is converted into the vibrational energy of the bond, but the electron density of the latter remains unchanged. The second pathway presupposes a pre-dissociation mechanism of the decomposition.

The mechanism of the photochemical decomposition of molecules in $n\pi^*$ states differs from the mechanism of the breakdown of molecules in $\pi\pi^*$ states. The presence of an atomic valence in the excited state leads to the possibility of intermolecular and intramolecular chemical reactions. In the intramolecular mechanism utilising the valence of the $n\pi^*$ state of the molecule the chemical bond linking atoms located in the same plane as the symmetry axis of the wave function of the n electron will dissociate. Thus in acetaldehyde in the $n\pi^*$ state the C–H bond will dissociate, in acetone the $C-CH_3$ bond, and in benzaldehyde the C–H or C–Ph bond.

Peters[38] calculated theoretically the electron densities of the bonds in formaldehyde for different electron transitions in the CO group. It follows from these data that the photolysis of low-molecular carbonyl compounds takes place via a stage involving the homolytic dissociation of one of the C–C or C–H σ bonds adjacent to the carbonyl group. Jellinek[23] points out that in the photolysis of low-molecular ketones caused by the absorption of light by the CO group two types of reactions may occur: (1) reactions with formation of free radicals with dissociation of the σ bond adjacent to the CO group:

$$R-CO-R_1 \xrightarrow{h\nu} \dot{R} + R_1\dot{C}O \rightarrow \dot{R} + \dot{R_1} + CO;$$

(2) reactions accompanied by the dissociation of the C–C bond in the $\alpha-\beta$-position relative to the CO group; in this case radicals are not formed:

$$R-CH_2-CH_2-CH_2-CO-R_1 \xrightarrow{h\nu} RCH=CH_2+CH_2COR_1.$$

The formation of free radicals in the photolysis of monosubstituted benzenes and low-molecular carbonyl compounds has been confirmed experimentally by a tracer method[30]. Methyl radicals $\dot{C}H_3$ have been detected by the ESR method in the low-temperature photolysis of acetone and its aqueous solution[72]. However, the similarity to the photolysis of low-molecular compounds also fails to provide an unambiguous answer to the question of the site of bond dissociation in a polymer molecule on formation of free radicals. Among the polymers examined, polystyrene and polyphenylmethylsiloxan contain a benzene ring in the

monomer unit. According to the photodissociation mechanism of monosubstituted benzenes, it would appear that in the photolysis of polystyrene and polyphenylmethylsiloxan one might expect the photodissociation of the C–R bond of the benzene ring with formation of a phenyl radical and the counter-radical of the polymer molecule. The photolysis products should contain benzene or its derivatives. As already mentioned[49,50] the broad singlet in the ESR spectrum observed in the photolysis of polystyrene was tentatively assigned to the phenyl radical. The gaseous photolysis products at 77°K were not analysed.

However, in most studies on the photochemical degradation of polystyrene[26,73–75] it is suggested that the light-induced ageing of the polymer begins with the dissociation of a C–H bond at a tertiary carbon atom. As stated above, in the low-temperature photolysis of polyphenylmethylsiloxan the radicals $\dot{C}H_3$ and $R-\dot{C}H_2$ were detected, while the phenyl radical was not.

Possibly in the photolysis of polymers the excitation energy is transmitted from the benzene ring over larger distances than in monosubstituted benzenes causing the dissociation of remote bonds: C–H in polystyrene and $C-CH_3$ and CH_2-H in polyphenylmethylsiloxan.

In the photolysis of polymers with a C=O chromophoric group in the monomer unit one may expect, using the same analogy with the photolysis of low-molecular carbonyl compounds, the formation of radicals on dissociation of a bond adjacent to the CO group or in the α–β-position relative to this group[23,30]. In the first case photolysis should be accompanied by the evolution of gaseous carbon monoxide.

In their study of the photolysis of polyamides at room temperature in a vacuum, Stephenson et al.[76] detected carbon monoxide among the gaseous photolysis products. In the photolysis of polyurethane, carbon monoxide was detected mass-spectrometrically[77]. Unfortunately the ESR spectra of the free radicals were not investigated in the first of these studies[76], while in the second[77] an ESR signal was observed but the radicals were not identified.

Evidently one may justifiably assume that in all these polymers the dissociation of the main chain takes place at bonds adjacent to the carbonyl group. In polyethylene, polypropylene, and other polyolefins the impurity carbonyl groups enter into the composition of the molecule, being located most probably in the main polymer chain: $\ldots CH_2-CO-CH_2-CH_2\ldots$ (polyethylene) and $\ldots CH_2-CH(CH_3)-CO-CH(CH_3)-CH_2\ldots$ and $\ldots CH_2-CO-CH_2-CH(CH_3)-CH_2\ldots$ (polypropylene).

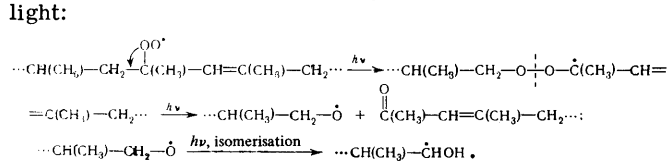
It has been suggested[51] that free radicals arising as a result of the dissociation of the main chain and with a free valence at the CH_2 group are produced in the photolysis of polyethylene and polypropylene: $\ldots CH_2-\dot{C}H_2$ for polyethylene and $\ldots CH(CH_3)-\dot{C}H_2$ for polypropylene. It may be supposed that in this case the C–C σ bond adjacent to the CO group dissociates. This photodissociation should be accompanied by the evolution of gaseous carbon monoxide. The gaseous products of the low-temperature photolysis of polyethylene and polypropylene were not analysed. At room temperature the photolysis of polyethylene in a vacuum and in a nitrogen atmosphere is accompanied by the evolution of hydrogen and methane[76]. Possibly, since the CO groups are present as impurities in the polymers investigated, carbon monoxide is difficult to detect experimentally because of its small amount.

However, the formation of the macroradicals $\ldots CH_2-\dot{C}H-CH_2\ldots$ in the photolysis of polyethylene and the radicals $\ldots CH_2-\dot{C}H-\dot{C}H_2\ldots$ and $\ldots CH-(CH_3)-\dot{C}H-CH(CH_3)\ldots$ in the photolysis of polypropylene, and also data on the formation of radicals in polyolefins subjected to ultraviolet irradiation, when the side groups, or the methyls entering into the composition of the side group, mainly dissociate[49,50], suggest that in this case the photodissociation of polymers is not consistent with the mechanism of the photolysis of low-molecular carbonyl compounds. Possibly the excitation energy is transmitted over greater distances in the polymer molecule or the free valence migrates readily under the action of light.

Free radicals can change under the action of light and heat. In their study of the behaviour of radicals (generated by the γ-irradiation of a number of polymers at 77°K) under the action of the unfiltered light of a DRSh-250 lamp and heat, Milinchuk and Pshezhetskii[67,78,79] found that in many cases the radicals are destroyed and also that the ESR spectra of the radicals may change without a decrease in their concentration. In this case the destruction takes place at liquid nitrogen temperature where the possibility of mobility of different segments of the macromolecule may be virtually excluded.

The alkyl radical $\ldots CH_2-\dot{C}(CH_3)-CH_2\ldots$ formed initially in polypropylene at 77°K was converted on heating into the allyl type radical $\ldots CH_2-C(CH_3)-CH=C(CH_3)-CH_2\ldots$ and into the polyene radical $\ldots CH_2-\dot{C}(CH_3)-[CH=C(CH_3)]_n-CH_2\ldots$ The irradiation of allyl radicals with unfiltered light of a DRSh-250 lamp caused the reversion of the allyl radical to the alkyl radical. All the transformations of the radicals were deduced from changes in the hyperfine structure of the ESR spectra. The authors suggest that the mechanism of the formation of allyl and polyene radicals consists in the migration of the free valence of the alkyl radical along the polymer chain to a carbon atom adjacent to a double or conjugated bond. The migration is facilitated by the absorbed energy of the photon, which lowers the potential barrier to the migration of hydrogen atoms and the absorption is not necessarily associated solely with the chromophoric groups. Possibly the free radicals themselves absorb light. The mechanism of the migration of free valence in the macromolecule under the action of light and heat can explain the radical destruction processes at 77°K, the cross-linking and dissociation of the chain, the formation of double bonds, and the occurrence of conjugation.

Under the action of ultraviolet light, the peroxy-radicals derived from polypropylene are capable of isomerising to alkyl radicals[67]. The oxygen molecule is then incorporated in the polymer chain with formation of an –O–O– bond which is split by ultraviolet light with formation of a hydroxy-radical and a carbonyl group. Peroxy-radicals were accumulated by the oxidation of the alkyl radicals from polypropylene formed by γ-irradiation. The peroxy-radicals isomerised under the action of ultraviolet light with a maximum efficiency at 310–320 nm. The authors suggested that the peroxy-radical itself absorbs light:



Taking into account the possibility of the isomerisation of peroxy-radicals under the action of ultraviolet quanta from sunlight ($\lambda \simeq 300$ nm), one should note that the classical mechanism of oxidation via a stage involving the formation of hydroperoxide may not obtain in the photochemical oxidation of polypropylene, since the isomerisation is faster than the reaction $R\dot{O}_2 + RH \rightarrow$, which requires a favourable

encounter between the peroxy-radical and the hydrogen atom. Two mechanisms are possible for the reaction of $\dot{RO}_2$: isomerisation and the formation of hydroperoxide. This hypothesis requires experimental test.

Alkyl radicals obtained in the low-temperature photolysis or radiolysis of polymers are oxidised to peroxy-radicals on heating in an atmosphere of oxygen. The temperature of the oxidation of $\dot{R}$ to $\dot{RO}_2$ is 150° ± 10°K for polyethylene, natural rubber, and a number of saturated hydrocarbons, the recombination temperature being 210° ± 10°K.[80] The oxidation temperature of alkyl radicals was established on the basis of thermoluminescence data obtained on heating specimens irradiated with fast electrons. The thermoluminescence curves in the region of the phase transition temperatures show sharp rises, which are usually attributed to the lowering of the concentration of free radicals. The sharp rise ("flash") of thermoluminescence at temperatures 50–90 deg below the glass point, at which the concentration of radicals does not change, was attributed to the reaction of alkyl radicals with the oxygen dissolved in the specimen. Specimens subjected to preliminary evacuation did not show a rise of this kind in the thermoluminescence curve.

Since the temperature of the oxidation of alkyl radicals proved to be the same for polyethylene, natural rubber, and saturated hydrocarbons, it may be suggested that the reactivity of macroradicals is approximately the same and the temperature variation of the rate of oxidation of radicals is determined primarily by the increased mobility of segments of the chain and the penetration of oxygen to the site of the free valence.

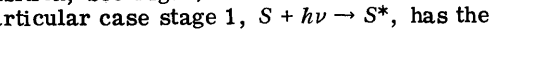
5. KINETICS OF THE FORMATION OF THE PRODUCTS OF LIGHT-INDUCED AGEING

To obtain the theoretical relation between the accumulation of any one product and the duration of exposure to light, it is necessary to set up a system of kinetic equations in accordance with the mechanism. The variation of the concentrations of the reactants and products depends on the nature of the photoinitiation and destruction of radicals and therefore the kinetic equations will be different for different polymers.

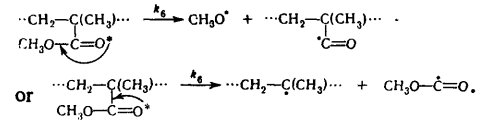
Poly(methyl methacrylate) (PMMA) and polystyrene (PS) constitute a group of polymers in which the absorption of light (stage 1) can take place in any monomer unit and in early stages of the reaction the number of absorbing centres may be regarded as almost constant. The absorbing centres in PMMA are ester carbonyl groups and in polystyrene phenyl rings if the wave-length of the initiating radiation is less than 300 nm. The nature of these groups and their positions determine the mechanism of the degradation of the absorbed energy.

In view of the large number of studies dealing with the light-induced ageing of PMMA,[23,55,81-88] the mechanism of the reactions occurring in this polymer may be regarded as sufficiently well established. We shall consider initially the photolysis of PMMA at a wavelength of 254 nm. The absorption of a photon is accompanied by the transition of a p electron of the carbonyl group from the non-bonding orbital of the oxygen atom to the anti-bonding orbital ($n \rightarrow \pi^*$ transition, see Fig. 6).

In this particular case stage 1, $S + h\nu \rightarrow S^*$, has the form



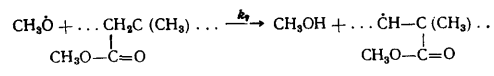
Then the excitation energy is transmitted by an intramolecular transition without emission to an ester C–O bond or a C–C bond, which leads to the photodissociation of the bond (stage 6 in the general mechanism, p. (149):



If each photon absorption step resulted in photodissociation the quantum yield φ of the photochemical reaction in light-induced ageing would be of the order of unity or even more than unity for a chain mechanism. However, at room temperature φ for a wide variety of polymers is of the order of 0.01 and frequently smaller by 2–3 powers of ten[23].

The mechanism which we propose for light-induced ageing clearly reveals the competing processes involving the degradation of electron excitation energy [reactions (2)–(6)] and permits a theoretical prediction of the quantum yield, provided that the corresponding rate constants are known.

The main products of the photolysis of PMMA are carbon monoxide, methanol, and methyl formate (see Fig. 10). Methanol is formed as a result of the secondary reaction



(stage 7 in the general mechanism, $P_f = CH_3OH$).

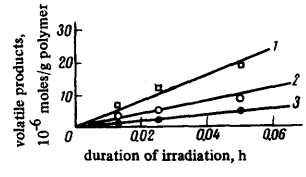


Figure 10. Amount of volatile products per gramme of PMMA as a function of the duration of irradiation at 30°C: 1) carbon monoxide; 2) methanol; 3) methyl formate.

The accumulation of methanol as a function of time is determined by the following set of equations

$$\frac{d(P_f)}{dt} = k_7(\text{M—M})(\text{R}), \tag{10}$$

$$\frac{d(\text{R})}{dt} = 2k_6(S^*) - k_8(\text{R})^2, \tag{11}$$

$$\frac{d(S^*)}{dt} = k_1 I_0(S) - [k_2 + k_3 + k_6](S^*). \tag{12}$$

Here round brackets denote the concentration of the corresponding reactant in cm^{-3}: (M–M), the concentration of hydrogen atoms combined with secondary carbon atoms, is almost constant and therefore $k_7(\text{M–M}) = \text{const.} = k'_7$; (S), the concentration of ester carbonyl groups is also almost constant, i.e. $k_1(S) = \text{const.} = k'_1$. Further, assuming that

the concentration of S^* corresponds to the steady state§, i.e. $d(S')/dt = 0$, we have from Eqn. (12)

$$(S^*)_{st} = \frac{k_1(S)I_0}{k_q}, \qquad (12a)$$

where $k_q = k_2 + k_3 + k_6$.

Similarly at the steady state¶ concentration (R), i.e. with $d(R)/dt = 0$, we have

$$(R)_{st} = \left(\frac{2k_6k_1}{k_qk_8}\right)^{\frac{1}{2}} I_0^{\frac{1}{2}} \sqrt{(S)}. \qquad (12b)$$

The accumulation of methanol is then determined from the equation

$$(P_f) = \int_0^t k_7(M-M)(R)\,dt = t\left(\frac{2k_6k_1}{k_qk_8}\right)^{\frac{1}{2}} k_7(M-M)I_0^{\frac{1}{2}}\sqrt{(S)}, \qquad (13)$$

i.e. the amount of methanol is proportional to the duration of exposure t, in agreement with Fig. 10.

The quantum yield of methanol is

$$\varphi_{CH_3OH} = \frac{(P_f)}{\Delta N}, \qquad (14)$$

where ΔN is the number of photons absorbed during time t. Assuming that radiation is only slightly absorbed in a layer ΔX, we have

$$\Delta N = I_0 t \cdot \kappa_1(S)\Delta X. \qquad (15)$$

Consequently

$$\varphi_{CH_3OH} = \left(\frac{2k_6k_1}{k_qk_8}\right)^{\frac{1}{2}} \cdot \frac{k_7\sqrt{(S)}}{I_0^{\frac{1}{2}}D}(M-M), \qquad (16)$$

where $D = k_1(S)\Delta X$ is the optical density of this layer.

It follows from the expressions obtained that, for a theoretical calculation of the rate of accumulation of the product and of the quantum yield with respect to this product, it is necessary to know a number of constants, which are not as a rule available. The data on the quenching constant k_q are particularly scarce and therefore it is difficult to assess the validity of the hypotheses concerning the mechanism of photolysis in this and other cases. However, the relations obtained make it possible to assess the nature of the process as a function of the given conditions. In particular, when account is taken of the quenching processes (2)–(6), the correct value of φ can be obtained with the aid of the constant k_q on substituting reasonable values of the constants. Unless k_q is taken into account, the discrepancy can amount to ten powers of ten.

It follows from Eqns. (13) and (16) that very important data on the mechanism of light-induced ageing can be secured by studying the kinetics of light-induced ageing at various intensities I_0 of the incident light.

In the case considered, the rate of accumulation of the photolysis products is directly proportional and the quantum yield inversely proportional to the square root of the intensity of the incident light. Experimental confirmation of this relation implies that the destruction of radicals takes place when two radicals meet (quadratic termination). However, such a mechanism of destruction in light-induced ageing of polymers is not the only one possible.

In the light-induced ageing of polystyrene, investigated in detail by Grassie[73,75] and other workers[26,74,89,90], a linear relation between the rate of formation of volatile and other products and the intensity I_0 of the incident light is observed both in photolysis and in photochemical oxidation. Precisely this fact is reflected in stage (8) of the general mechanism. Usually the destruction of radicals without collision with another radical (linear termination) in the condensed phase is disregarded. However, if account is taken of the fact that photochemical processes take place in a very thin surface layer, then, in view of the high mobility of hydrogen atoms and light $\dot{C}H_3$ radicals and the considerable inertia of macroradicals, it is quite possible that the light radical diffuses to the gas phase and therefore escapes from the reaction. The data quoted by Pudov and Taitarenko[91] indicate the occurrence of processes of this type.

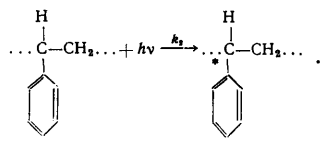
Grassie and Weir[75] investigated the photochemical oxidation of polystyrene films under the action of ultraviolet light (at 254 nm) at oxygen pressures up to 600 mmHg and temperatures of 28–57°C. Only water and carbon dioxide are formed in appreciable amounts from the gaseous products. At an oxygen pressure below 20 mmHg the rate measured from the absorption of oxygen is independent of the intensity I_0 of the incident light and at higher pressures it is proportional to I_0.

In accordance with the general mechanism of light-induced ageing the absorption of oxygen takes place in stage (9):

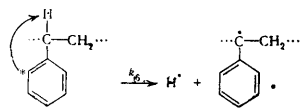
$$\frac{d(O_2)}{dt} = -k_9(O_2)(R), \qquad (17)$$

$$\frac{d(R)}{dt} = k_6(S)^* - k_8'(R), \qquad (18)$$

where (S^*) represents, as for PMMA, the steady-state concentration of excited states, with the difference that in polystyrene the absorbing centres are benzene rings:



As pointed out above, the electronic excitation energy during its dissipation is transmitted to the C–H bond of a tertiary carbon atom, which leads to the elimination of a hydrogen atom:



It is interesting that in the photochemical oxidation of polystyrene hydrogen is absent from the gaseous products, which is probably due to the rapid reaction $\dot{H} + O_2 \rightarrow H\dot{O}_2$.

As in PMMA, the steady-state concentration $(S^*)_{st}$ is determined from Eqn. (12):

$$(S^*)_{st} = \frac{k_1(S)I_0}{k_q}.$$

The steady-state concentration of the radicals $[d(R)/dt = 0]$ is determined from Eqn. (18):

$$(R)_{st} = \frac{k_6k_1(S)}{k_8'k_q} \cdot I_0.$$

Then, in accordance with Eqn. (17), the consumption of oxygen is determined by the equation

$$-\Delta(O_2) = \int_0^t k_9(O_2)(R)\,dt = \frac{k_9k_6k_1(S)}{k_8'k_q} \cdot (O_2)\ I_0t,$$

---

§The exact solution is $(S^*) = k_1(S)I_0(1-e^{-k_2t})/k_q$, i.e. $k \simeq 10^8\ s^{-1}$. To a high degree of accuracy after only one 1 s, $(S^*) = k_1(S)I_0/k_q$, i.e. (S^*) depends only on (S).

¶The exact solution is $(R) = (R)_{st}\tanh bt$.

i.e. in agreement with the experimental data at high pressures, the amount of oxygen absorbed is proportional to the concentration of O_2 and the light intensity I_0. In reality the situation is more complex and radical diffusion and gas diffusion processes play a considerable role. In particular, the solubility of oxygen in the polymer is low and proportional to its pressure[92]. Therefore at oxygen pressures below 20 mmHg the rate of absorption of O_2 is fully determined by the rate of diffusion and is independent of the light intensity. It is noteworthy that, depending on the conditions and the properties of the polymer, both linear and quadratic termination can occur in the system simultaneously and the variation of the rate of the process with intensity may be, generally speaking, of any kind.

Kinetic analysis of light-induced ageing is more complex for polymers where initiation takes place via absorbing groups of impurities, for example carbonyl groups. As already mentioned, polyethylene, polypropylene, and poly(vinyl chloride) belong to polymers of this type. In a number of studies[93-98] dealing with the light-induced ageing of polyethylene and polypropylene it has been shown that ultraviolet irradiation of such polymers is accompanied by the absorption of oxygen and the accumulation of oxygen-containing groups: carbonyl groups, hydroxy-groups, and others. The rate of absorption of O_2 by polyethylene is proportional to the square root of the intensity, i.e. quadratic chain termination takes place.

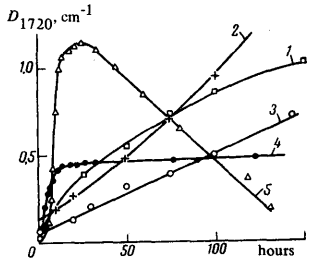


Figure 11. Kinetics of the accumulation of CO groups in the light-induced ageing of various polymers: 1) low-pressure polyethylene; 2) high-pressure polyethylene; 3) high-pressure polyethylene with a stabiliser (phenyl-α-naphthylamine + diphenylphenylenediamine + carbon black); 4) poly(vinyl chloride); 5) polyvinylbutyraldehyde.

The accumulation of CO groups is a complex function of time (Fig. 11, curves *1* and *2* for polyethylene) and depends on the properties of the polymer. In high-pressure polyethylene the number of CO groups rapidly increases with acceleration, while in low-pressure polyethylene the rate of accumulation of CO groups falls and after a certain time their accumulation is strongly retarded[96].

The difference between the nature of the ageing of high- and low-pressure polyethylene may be accounted for by their different degrees of crystallinity. It has been shown[18] that the rate of photochemical oxidation, determined from the absorption of O_2, is higher for crystalline polyethylene than for the pressed material, which is to a large extent amorphous. There is no doubt that this finding is related to the change in the rate of diffusion and solubility of oxygen on increasing the crystallinity of the polymer[92].

The amount of oxygen absorbed varies with time as a function of the crystallinity as well as the number of carbonyl groups.

The experimental data presented here are satisfactorily consistent with the general mechanism of light-induced ageing proposed above. Since the number of carbonyl groups is proportional to the amount of oxygen absorbed, it follows that $d(O_2)/dt = (P_0)/dt$, where (P_0) denotes in this case the concentration of initiating carbonyl groups. Since the carbonyl groups formed here behave at the same time as absorption centres, it follows that $(S) = (S_0) + (P_0)$, where (S_0) is the concentration of S at the initial instant of illumination at $t = 0$. Consequently $d(P_0)/dt = d(S)/dt$, i.e. the accumulation of P_0 is determined by the accumulation of S. In accordance with the general mechanism,

$$\frac{d(S)}{dt} = -k_1 I_0 (S) + k_2 (S^*_{st}) + k_9 (O_2)(R). \qquad (19)$$

As for PMMA, the steady-state concentrations $(S^*)_{st}$ and $(R)_{st}$ are determined by Eqns. (12a) and (12b) respectively. After substitution of $(S^*)_{st}$ and $(R)_{st}$ in Eqn. (19), we obtain

$$\frac{d(S)}{dt} = -k_1 I_0 \left(1 - \frac{k_2}{k_q}\right)(S) + k_9 \left(\frac{2k_6 \cdot k_1}{k_q\, k_8}\right)^{1/2} I_0^{1/2} (S)^{1/2}.$$

The differential equation obtained is a Bernoulli equation and can be solved analytically:

$$(S) = e^{-2p' I_0 t}\left[(S_\infty)^{1/2} e^{p' I_0 t} + (S_0)^{1/2} - (S_\infty)^{1/2}\right]^2, \qquad (20)$$

where $p' = (k_1/2)\,(1 - k_2/k_q)$ and (S_∞) is the limiting concentration of carbonyl groups at irradiation time $t \to \infty$:

$$S_\infty = \frac{2k_9^2}{k_1}\,\frac{k_6}{(k_q - k_2)}\,\frac{k_q}{}\cdot\frac{(O_2)^2}{I_0}. \qquad (21)$$

According to solution (20), the concentration of CO groups increases steadily with time if $(S_0) < (S_\infty)$ and reaches a constant value (S_∞), which is in fact observed experimentally[96]. The time required for the attainment of the limiting concentration falls very rapidly (exponentially) with increasing intensity and strongly depends on the absorption (k_1) and quenching (k_2 and k_q) constants. The limiting concentration (S_∞) increases in direct proportion to the square of the concentration of oxygen and in inverse proportion to the intensity I_0.

The variation of (S_∞) with I_0 is particularly interesting It follows from Eqn. (20) that, when $(S_0) > (S_\infty)$, the concentration of CO groups must decrease with time during the initial period of the reaction until the limiting value (S_∞) is attained. Consequently if I_0 is small and (S_∞) large, carbonyl and other oxygen-containing groups will accumulate in light-induced ageing. Conversely, if I_0 is large, then S_∞ is small, and in the initial period the concentration of oxygen-containing groups should fall. This behaviour was confirmed experimentally in a number of studies[98,99] for the carbonyl groups of oxidised polyethylene (by infrared spectroscopy) and the hydroperoxy-groups of oxidised polypropylene (iodometrically). It is also interesting to note that, according to Eqn. (20), the rate of decomposition of oxygen-containing groups decreases with increasing oxygen pressure.

The conclusions based on the kinetic analysis of light-induced ageing of polyolefins are in general valid also for poly(vinyl chloride). It must be pointed out that a fairly large number of studies[100-106] dealing with this polymer are frequently contradictory, particularly as regards the composition of gaseous photochemical degradation products.

The paper by Reinisch[36], in which a general account is given of preceding studies and the experimental part was

carried out very carefully, must be regarded as the most reliable. Not even traces of water, carbon monoxide, and carbon dioxide, the formation of which was indicated, for example by Wilson[100] and others, were observed in the photolysis of poly(vinyl chloride). These products, together with hydrogen chloride, are characteristic of the photochemical oxidation of poly(vinyl chloride). The initiating centres are impurity CO groups both in the photochemical oxidation and in the photolysis of oxidised poly(vinyl chloride) (this in fact accounts for the evolution of the products enumerated above). In extensive oxidation and in the photolysis of non-oxidised poly(vinyl chloride) the absorbing centres are polyene structures.

6. THE MECHANISM OF THE SENSITISATION AND STABILISATION OF POLYMERS AGAINST LIGHT

Most of the studies on the light-induced ageing of polymers involve the search for effective additives, called light stabilisers, which inhibit the light-induced ageing and protect the polymer from the destructive effect of sunlight. However, so far there is no single point of view on the mechanism of light stabilisation, which hinders to a great extent the search for substances with protective activity and also the selection of light stabilisers for new polymers.

The most widely held is the view that the mechanism of light stabilisation reduces to the screening effect of the additive[4,85,107-109], i.e. it is suggested that the light stabiliser acts as a filter weakening the flux of ultraviolet radiation incident on the polymer. Attempts are then made[110] to establish a correlation between the absorption spectrum and the efficiency of the light stabiliser. If the absorption spectrum of the light stabiliser is known, it is not difficult to determine, in accordance with the Beer–Lambert law, the energy absorbed by a planar polymer specimen without an additive:

$$\Delta\epsilon_0 = Ft\sum_{\lambda_1}^{\lambda_2} I_{0\lambda}(1-e^{-\epsilon_{p\lambda}c_p d}), \qquad (21a)$$

and the energy absorbed by the same specimen with added light stabiliser (on the assumption that the absorbing centres are independent):

$$\Delta\epsilon_s = Ft\sum_{\lambda_1}^{\lambda_2} I_{0\lambda}(1-e^{-(\epsilon_{p\lambda}c_p+\epsilon_{s\lambda}C_s)d})\frac{\epsilon_{p\lambda}C_p}{\epsilon_{p\lambda}C_p+\epsilon_{s\lambda}C_s}. \qquad (21b)$$

Then the protective effect of the light stabiliser may be determined from the relation[111]

$$PE = \frac{\Delta\epsilon_0}{\Delta\epsilon_s} = \frac{\sum_{\lambda_1}^{\lambda_2} I_{0\lambda}(1-e^{-\epsilon_{p\lambda}C_p d})}{\sum_{\lambda_1}^{\lambda_2} I_{0\lambda}(1-e^{-(\epsilon_{p\lambda}C_p+\epsilon_{c\lambda}C_s)d})\frac{\epsilon_{p\lambda}C_p}{\epsilon_{p\lambda}C_p+\epsilon_{s\lambda}C_s}}. \qquad (21c)$$

Here $I_{0\lambda}$ is the intensity of incident light at a given wavelength λ, $\epsilon_{p\lambda}$ the molar extinction coefficient of the initiating groups of the polymer† (cm^2), C_p the concentration of these groups (cm^3), $\epsilon_{s\lambda}$ and C_s the corresponding values for the light stabiliser, F the surface area of the specimen, d its thickness, and t the duration of irradiation. Each term of the sums in the numerator and denominator represents the energy absorbed by the polymer at a given wavelength and the sums themselves define the energy absorbed in the wavelength range from λ_1 to λ_2. The functions $\epsilon_{p\lambda}C_p d = D_p$ and $\epsilon_{s\lambda}C_s d = D_s$ represent the optical densities of the polymer and the light stabiliser and may be determined experimentally by spectrophotometric measurements. The summation can be performed graphically.

It follows from Eqn. (21c) that, since $\Delta\epsilon_s$ is always less than $\Delta\epsilon_0$, PE is always greater than unity, i.e. almost any substance absorbing ultraviolet light at a given wavelength λ should exhibit a stabilising effect in irradiation with light having this wavelength.

Experimental tests[105,110] showed that this is not so. In general there is no correlation between the ultraviolet spectra of light stabilisers and their stabilising effect. For example, Schlimper[105] points out that, despite the broad and intense absorption band in the region of 300–400 nm, azo-compounds exhibit poor stabilising properties in relation to poly(vinyl chloride) and polyamides.

Direct comparison of the calculated value of the protective effect PE with experimental data on the light-induced ageing of different polymers shows[95,111] that the effect of additives cannot be explained merely by screening. Furthermore, benzophenone, which absorbs in the ultraviolet region, not only does not stabilise polyethylene film but actually accelerates its light-induced ageing[112], i.e. behaves as a sensitiser.

The attempt to eliminate completely the observed inconsistency between the absorbance of the light stabiliser and its protective effect on the hypothesis of photochemical reactions of the additive and its chemical interaction with the polymer[107-109,112] was also unsuccessful[95].

Recently a mechanism has been developed[37], according to which the protective effect or, conversely, the sensitising effect of the additive depends not only on the absorbance or photochemical reactions but also on the capacity of the given additive to participate in non-radiative transfer of electron energy as an acceptor or a donor. The derivation of Eqn. (21c) itself contains the assumption of the independence of the absorption by different centres, i.e. the possibility of the interaction of these centres is thereby assumed in principle.

The postulate of non-radiative energy transfer between molecules and photochemical processes is itself not new and has been elucidated in detail both theoretically and experimentally. In particular the work of the school of Vavilov and Terenin in this field should be mentioned[113-115].

The hypothesis of the occurrence of such processes in the light-induced ageing of polymers has been put forward by various workers, in particular by Schmitt and Hirt[111], but these questions have not been adequately elucidated in respect of light stabilisers. Probably this is due not only to the experimental difficulties but also to the deep-rooted concept of the screening mechanism for the effect of light stabilisers.

It has been suggested[37] that the protective effect of the light stabiliser, caused by the non-radiative energy transfer from the excited centre of the polymer molecule to the light stabiliser molecule, can be estimated from the efficiency of the quenching of the luminescence of the polymer by the given light stabiliser (in this case the additive behaves as an energy acceptor, denoted in the general kinetic mechanism by A). Indeed, since the luminescence intensity is proportional to the number of excited polymer molecules, the decrease of the intensity can characterise in principle the decrease in the number of molecules tending to decompose (stage 6), and therefore also the efficiency of the light stabiliser. Quenching may of course not be due solely to energy transfer and therefore the proposed characterisation of the protective effect may

†It is assumed that the absorption by other groups is low.

prove to be incomplete, like the characterisation based solely on the screening effect. The above hypotheses have been tested for common light stabilisers added to polypropylene[37].

Curve 3 in Fig. 8 represents the luminescence spectrum of polypropylene without additive excited by light at 280.4 nm. On addition of 0.01 mole kg^{-1} of 2-hydroxy-5-methylphenylbenzotriazole (Tinuvine P), an effective light stabiliser for polypropylene, the luminescence intensity L falls sharply (curve 1). It has been shown experimentally that L is proportional to the amount of light absorbed by the polymer.

It would appear that the decrease of luminescence intensity may be explained by the fact that, in consequence of the absorption of the initiating radiation by the light stabiliser, the energy absorbed by the polymer decreases by an amount

$$\Delta\epsilon = \Delta\epsilon_0 - \Delta\epsilon_s \qquad \text{[see Eqns.(21a) and (21b).]}$$

The additional decrease of L takes place as a result of reabsorption—the absorption of the light due to the luminescence by the light stabiliser. Consequently, when appropriate corrections are made for screening and reabsorption, curve *1* should coincide with curev *3*. However, these corrections yield only curve *2*, which lies much below curve 3. Hence it follows that in the presence of the light stabiliser some kind of quenching mechanism operates. In particular, such a mechanism may be energy transfer from polymeric molecules to light stabiliser molecules.

Thus in the study of light-induced ageing it is necessary to take into account both the screening effect of the light stabiliser and its protective acceptor effect. In the general mechanism of light-induced ageing the possibility of of the inhibiting effect of acceptor additives was taken into account in stage 4. Allowance for this effect is reflected in the appearance of yet another term, $k_4(A)$, in the denominator of the expression for the steady-state concentration of excited centres $(S^*)_{st}$ and the steady-state concentration of the radicals $(R)_{st}$, since the quenching constant is now defined by the equation $k_q' = k_2 + k_3 + k_6 + k_4(A)$. Since this quantity enters with a plus sign into the denominator, in the presence of a light stabiliser (acceptor A), $(S^*)_{st}$ and $(R)_{st}$ are smaller than in the polymer without additives. Correspondingly the rate of accumulation of oxygen-containing products will be lower, in agreement with experiment (Fig. 8, cf. curves *2* and *3*).

The screening effect of additives in the polymer was not taken into account the general mechanism, because in the preceding sections we did not deal with the problem of the effect of additives and in fact we assumed that the process takes place in a thin layer under the action of monochromatic light. Assuming that the incident light is *monochromatic* to simplify the treatment, we shall now introduce a correction for screening. In the presence of a light stabiliser of the acceptor type at a concentration (A) in a flat specimen of thickness d and with a surface area F, the number of excited states initiated during a time dt is, according to Eqn. (21b),

$$dS^* = I_0 F\, dt\,(1 - e^{-[\epsilon_S(S)+\epsilon_A(A)]d})\,\frac{\epsilon_S(S)}{\epsilon_S(S)+\epsilon_A(A)},$$

and the rate of initiation of excited states, expressed in $cm^3\ s^{-1}$, is defined by the following equation in the presence of A:

$$\Delta I_s = \frac{dS^*}{dF\,dt} = \frac{d(S^*)}{dt} = k_1' I_0(S), \qquad (22)$$

where

$$k_1' = \frac{\epsilon_S}{d[\epsilon_S(S)+\epsilon_A(A)]}\cdot(1 - e^{-[\epsilon_S(S)+\epsilon_A(A)]d}).$$

Here (S) and (A) are the concentrations of the absorbing centres of the polymer and acceptor respectively and ϵ_S and ϵ_A are their molar extinction coefficients, i.e. in the modification of Eqn. (21b) it was assumed that

$$C_p = (S),\ C_s = (A),\ \epsilon_{p\lambda} = \epsilon_S,\ \epsilon_{s\lambda} = \epsilon_A.$$

When $d \ll 1$, we obtain the following expression from Eqn. (22) on expanding the exponential term in series:

$$\Delta I_s = \epsilon_S\ \ I_0(S). \qquad (22a)$$

As was to be expected, for an infinitely thin specimen, we obtain the expression used earlier for the rate of initiation. To show that, it is sufficient to put $\epsilon_S = k_1$. The significance of the constant k_1 now becomes clear.

The general form of the kinetic equations does not change after the introduction of corrections for quenching and screening, but the constants have different values. For example, the accumulation of oxygen-containing products in initiation via impurity CO groups in the presence of a light stabiliser is defined by a relation analogous to Eqn. (20):

$$S = e^{-2p''I_0 t}\,(S_\infty^{1/2} e^{p''I_0 t} + S_0^{1/2} - S_\infty^{1/2})^2,$$

where the constants are

$$p'' = \frac{k_1'}{2}\left(1 - \frac{k_2'}{k_q'}\right) = \frac{1}{2}\frac{\epsilon_S}{[\epsilon_S(S)+\epsilon_A(A)]}(1 - e^{-[\epsilon_S(S)+\epsilon_A(A)]d})\left(1 - \frac{k_2 + K_4(A)}{k_q + k_4(A)}\right);$$

$$S_\infty' = \frac{2k_9^2\ \ k_6\ \ k_q'}{k_1'(k_q - k_2)}.$$

It is evident from the above expressions that, on introduction of additives into the polymer, the accumulation of products depends in a very complex manner on the concentration of the light stabiliser and the initiating centres and on the thickness of the specimen. Analysis of these relations may be greatly simplified for short time intervals.

This assumption is quite acceptable for the analysis of slow light-induced ageing processes. The relations obtained lead to the interesting finding that in very thin specimens the light stabiliser has no influence whatever if it exhibits only a screening effect. This conclusion is quite clear also on the basis of physical considerations; in a very thin layer the molecules of the light stabiliser cannot "eclipse" the absorbing centres of the polymer.

Furthermore, the additive may have a sensitising effect, i.e. may accelerate photochemical processes by the transfer of the energy absorbed by the additive to the polymer and can at the same time retard the light-induced ageing of thick specimens. A phenomenon of this kind was observed by Grassie[75] for the stabilisation of polystyrene by the widely known light stabiliser 2-hydroxy-4-methoxybenzophenone. In thin layers this light stabiliser accelerates the oxidation. In thick specimens the surface layer breaks down more rapidly on addition of the light stabiliser, but the main bulk of the polymer is protected from the action of light by the screening effect of the additive.

Thus, as a result of the interaction of two effects (screening and energy transfer) the same substance can exhibit stabilising and sensitising activity depending on the conditions. This has been clearly shown by Fox and Price[116]. It has been found that the characteristic features of the photolysis ($\lambda = 254$ nm) of PMMA and poly-α-methylstyrene dissolved in methylene chloride with

various additives can be accounted for by postulating the possibility of energy transfer between the additive and the polymer. The energy transfer can take place via both triplet and singlet levels. It has been observed that most additives, in particular the familiar light stabiliser 2,4-dihydroxybenzophenone, sensitise the photolysis of PMMA. The sensitisation, as for polystyrene films[75], is usually masked by the filtering effect of the additive. On the other hand, benzophenone has a stabilising effect because of the energy transfer from the PMMA molecule to the triplet level of benzophenone.

Two principles, on the basis of which light stabilisers can be selected for polymers, follow from the above findings. In the first place the light stabiliser must have an electron level which corresponds to a maximum in the absorption spectrum in the same region as the maximum in the luminescence spectrum of the polymer. This will ensure the greatest overlapping of the maxima and hence will give rise to the greatest possibility of energy transfer[113]. In the second place the light stabiliser must have an electron level which corresponds to a maximum in the absorption spectrum in the same region as the maximum in the absorption spectrum of the polymer.

In conclusion we may note that the laws governing the effect of light stabilisers are in the main valid also for the effect of dyes[5,6] on light-induced ageing of polymers.

7. METHODS FOR THE ACCELERATION OF LIGHT-INDUCED AGEING

In connection with the low rate of the light-induced ageing process under natural conditions (duration of tests up to 7.5 years[117]), methods of accelerated ageing have found wide application. For this purpose, a number of industrial and laboratory devices have been constructed.

In the development of apparatus for the artifical light-induced ageing the principal problem is of course the possibility of creating conditions resembling natural conditions to the maximum extent. In view of what has been said above, the difficulty of constructing such apparatus is quite evident. It consists in the fact that the requirements for rapid tests and for the maximum similarity to natural conditions are mutually exclusive. The point is that the creation of a source with a spectrum analogous to that of the sun does not by itself ensure that the data on light-induced ageing obtained with the aid of such a source can be applied under natural conditions, since the variation of the rates of various photochemical processes with intensity and hence the variation of the rate of the overall light-induced ageing process is frequently complex (see above).

For example, it has been shown by X-ray diffraction[18,119] that on ultraviolet irradiation the crystallinity of cellulose (cotton fibre) decreases steadily. It is then found that the decrease under the action of sunlight is smaller by a factor of only 3–5 than the decrease obtained by irradiation with the unfiltered light of a mercury lamp (200–800 nm), although the intensity in the latter case is higher by a factor of about 50 and a considerable part of the energy in the spectrum corresponds to the short-wavelength region.

If it is remembered that the emission intensity of artifical sources is frequently higher by a factor of hundreds and even thousands than that of solar radiation, it is quite evident that, for extrapolation to natural conditions, it is essential to have data on artificial light-induced ageing at different intensities and hence in the design of apparatus for accelerated ageing, provision must be made for the regulation of light intensity over a fairly wide range.

Another no less important requirement which must be taken into account in the design of apparatus for artificial light-induced ageing is the creation of a source with a spectral energy distribution resembling sunlight with sufficient precision particularly in the short-wavelength region. Only then can one transfer with adequate justification the results of artificial light-induced ageing to natural conditions. The presence of bands in the absorption spectra of polymers[73,77] by itself shows that the sensitivity of the polymer to radiation of different wavelengths (activation spectrum) will vary.

A particularly striking illustration of the dependence of the rate of light-induced ageing on the wavelength of ultraviolet radiation is provided by the data[36] in Fig. 4. The rate of change of the optical density (D) of poly(vinyl chloride), which is proportional to the amount of hydrogen chloride evolved, increases with increasing wavelength, passes through a maximum at 260 nm, and then falls to zero at 332 nm. The maximum is then found to coincide with the absorption maximum of polyene structures, which behave as activation centres for the light-induced ageing of poly(vinyl chloride).

It would appear that the problem of obtaining the required spectral distribution in the light source might be solved by studying the light-induced ageing under the action of monochromatic radiation at different wavelengths. The resulting rates of light-induced ageing might be adjusted to the solar spectrum by summing the rates of ageing at different wavelengths taking into account the intensity. However, in the general case such summation is not valid because of a kind of "synergism" of different wavelengths. For example, in the photolysis of poly(vinyl chloride) the number of photons required to obtain the same amount of hydrogen chloride with monochromatic irradiation is approximately 100 times greater than with polychromatic irradiation[35].

Apart from the conditions which must be satisfied by the emission, apparatus for artificial light-induced ageing must also make provision for the control of temperature and moisture content, which must correspond to the natural conditions. The available apparatus for artificial light-induced ageing as a rule only partially satisfies the conditions formulated above[77,98,118–122].

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