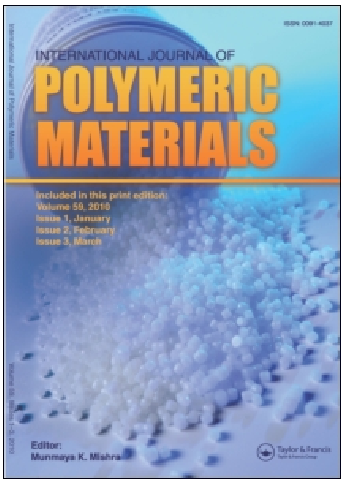

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Active Intermediates in Photoradical Ageing of Polymers

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The role of active intermediates in photoradical ageing of various carbon and heterochain polymers is reviewed. Guidelines are presented to influence the efficiency and direction of photochemical reactions allowing the control of structure and tailoring of properties for specific applications.

KEY WORDS Photochemical ageing, intermediates, polyolefins, polystyrene, halogen containing polymers, polyacrylates, polyvinyls, polyacrylates, polyamides, polyoxides, polyurethanes, reaction mechanism, reaction control.

1. INTRODUCTION

Free radicals play a major role in the ageing of polymeric materials and are formed either on homolytical scission of the main chain or on homolytical detachment of side group atoms or radicals.[1] In general the ageing process involves three stages: 1) initiation—formation of active centres; 2) development of ageing—changes in the properties of a material; 3) decay of the active centres of ageing.

Radicals and radical ions formed during the ageing process of various carbon and heterochain polymers should possess absorption spectra shifted towards the long-wave regions relative to the starting compounds and large extinction coefficients.[2–4] Polymers, due to the formation of radicals, become chromophorous, the quantum yields of the reactions[3] often exceeding that of the homolytical scission products.[5]

The condition stability of the properties of a polymer on ageing has the form[1]:

$$\delta \cdot (M/m) \cdot Z << 1 \quad \text{or} \quad \delta \cdot M << m/Z$$

where δ is the number of defects per chemical bond in the main chain of the polymer; M is the molecular weight of the polymer; m is the molecular weight of the base unit; Z is the number of bonds in the main chain of the polymer per base unit.

For most carbon- and heterochain polymers, (m/Z) lies in the $10–10^2$ range which at $M \simeq 10^5$ gives the following condition of the invariability of the properties of a polymeric material

$$\delta << 10^{-3}\text{–}10^{-4}.$$

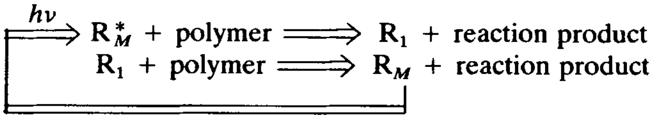
The situation may change radically if the action of light on a polymer is accompanied by such conditions under which each defect (macroradical) is capable of giving rise to a large number of transformations, thus changing the process over to the nonbranching-chain reaction mode (chain length ν). In this case the condition of the invariability of the properties of a polymeric material will have the form:

$$\delta = \Delta \cdot \nu << 10^{-3}\text{–}10^{-4}$$

where Δ is the number of macroradicals per chemical bond in the main chain of the polymer; for $\nu \simeq 10\text{–}10^2$, $\Delta << 10^{-4}\text{–}10^{-7}$ which is consistent with their stationary concentration $\simeq 10^{15}\text{–}10^{12}$ cm^{-3}.

The above case of light-initiated repeated transformations of macroradicals with the accumulation of transformation products takes place in photoradical chain reactions was first observed in low- and high-molecular compounds under different conditions.[6–8]

A comparison of the kinetic equations describing the course of a photoradical chain reaction



$$\xrightarrow{h\nu} R_M^* + \text{polymer} \Longrightarrow R_1 + \text{reaction product}$$
$$R_1 + \text{polymer} \Longrightarrow R_M + \text{reaction product}$$

and a nonbranching-chain reaction

$$R + A \xRightarrow{k_1} R_1 + \text{reaction product}$$

$$R_1 + A \xRightarrow{k_2} R + \text{reaction product}$$

indicates that they are identical provides optical radiation with intensity I is regarded as one of the "reagents," i.e.

$$k_1[A] = 2.3 \cdot \varepsilon_R \cdot \Phi \cdot I$$

under conditions that the optical densities are low or, the concentrations of radicals are comparatively small which is most frequently the case in processes of photoradical ageing of polymers.

Having characterized the efficiency of thermal reactions of radicals by lifetime

τ and using the following expression for the effective rate constant of the photoradical chain reaction

$$k_{ef} = 2.3 \cdot \varepsilon_R \cdot \Phi \cdot I,$$

it became possible to find a quantitative criterion for the feasibility of such processes[9]:

$$2.3 \cdot \varepsilon_R \cdot \Phi \cdot I \cdot \tau >> 1.$$

For many macroradicals responsible for photoradical ageing of corresponding polymers discussed below, the values of ε_R and Φ fall between the $10-10^2$ m^2mol^{-1} and $10^{-1}-10^{-2}$ limits, respectively. Since the intensity of sunlight at the Earth's surface is $10^{15}-10^{16}$ quanta/(s.cm^2) (depending on the spectral region), then the realization of photoradical chain reactions requires that

$$\tau \geq 10^3-10^5 \text{ s}.$$

Changes in ε, Φ and I in each specific case will bring about appropriate alterations in τ, too.

Thus, it can be seen that macroradicals, being present in a polymer in relatively low concentrations, may act as defects leading to changes in the properties of polymers on exposure to light. The requirements imposed by the condition for achieving chain photoradical reactions restrict photoradical ageing of polymers to the temperature range lying below their glass transition or melting temperatures, at relatively low initiation rates of the process of formation of macroradicals.

2. ACTIVE INTERMEDIATES IN PHOTORADICAL AGEING OF SOME CARBON- AND HETEROCHAIN POLYMERS

The formation of radical anions in different polymers takes place as a result of interaction between electrons produced by the influence of functional groups with a positive affinity to electrons.

The action of light on radical anions of different types (esters, acids, amides and disulphides) results in their conversion along two major pathways: dissociation and electron ejection.[10,11]

The processes of photoejection of electrons from radical anions (Table I) decrease the concentration of paramagnetic centres due to electron-hole recombination. The formation of excited states resulting from this process is not affect to any extent by the structure and functional composition of polymers, mainly because of the low probabilities of homolytic decomposition and stabilization of radicals in solid phase.[12]

The reactions of electronically excited radical anions cannot produce any significant molecular mass change except for aliphatic polyurethanes (PU) and this is indeed confirmed experimentally (Table II).

For aliphatic polyurethanes comparison of turbidimetric curves obtained[10] before

TABLE I

Quantum yields (Φ) of reactions of electron ejection and dissociation for some radical anions at 77 K[10,11]

Reaction	Φ·10²			
	313 nm	365 nm	405 nm	436 nm
$\sim CH_2CH(O\dot{C}O^-CH_3)CH_2\sim$				
$\Longrightarrow e^- + \sim CH_2CH(COOCH_3)CH_2\sim$	—	—	1.0 ± 0.3	0.6 ± 0.2
$\Longrightarrow \sim CH_2CHO^-CH_2\sim + CH_3\dot{C}O$	3	1.5	—	—
$\Longrightarrow \sim CH_2\dot{C}HCH_2\sim + CH_3COO^-$	2	0.8	—	—
$\sim CH_2CH(\dot{C}O^-OH)CH_2\sim$				
$\Longrightarrow e^- + \sim CH_2CH(COOH)CH_2\sim$	—	—	3	2
$\sim CH_2CH(\dot{C}O^-NH_2)CH_2\sim$				
$\Longrightarrow e^- + \sim CH_2CH(CONH_2)CH_2\sim$	—	—	2.5	1.5
$rCH_2SS^-CH_2r$				
$\Longrightarrow e^- + rCH_2SSCH_2r$	—	0.1	$5 \cdot 10^{-2}$	$2 \cdot 10^{-3}$
$\Longrightarrow rCH_2\dot{S} + rCH_2S^-$	—	$1 \cdot 10^{-2}$	$8 \cdot 10^{-4}$	$2 \cdot 10^{-5}$

TABLE II

The influence of photochemical reactions of radical anions on molecular mass change for some polymers[10]

Polymer	Type of reaction	Gel fraction (%)	Molecular mass
Polyacrylic acid	γ-radiolysis at 77 K + warming to room temperature	20.9	$M_w = 2.9 \cdot 10^5$
	γ-radiolysis at 77 K + photolysis of radical anions at 77 K + warming to room temperature	19.6	$M_w = 2.8 \cdot 10^5$
Polyvinyl butyral	γ-radiolysis at 77 K + warming to room temperature	—	$M_n = 1.6 \cdot 10^4$
	γ-radiolysis at 77 K + photolysis of radical anions at 77 K + warming to room temperature	—	$M_n = 1.6 \cdot 10^4$

and after the photolysis of radical anions did not show any noticeable changes in molecular mass of polymers which could be ascribed to the reactions of electronically excited radical anions. This is possibly due to the low concentration of radical anions compared with other paramagnetic species (<3% at the doses of γ-radiation—10–50 kGr).

It may be definitely stated that the reaction of electronically excited radical anions do not affect on processes of photoradical ageing.

Radical cations are produced under ionizing radiation action on substances at the same time with electrons and excited molecules. For nonpolar and polar media molecular cations and electrons produce in their reactions all spectrum of intermediates and final radiolysis products. Usually the study of radical cations in condensed phase is complicated by absence of selective absorption regions in their visible and UV-spectra and small lifetimes of radical cations even in solids because of geminate recombination, fragmentation and ion-molecular reactions.[13]

In γ-irradiated polystyrene a few types of radical cations stabilized on aromatic ring or in main chain and oxygen containing groups may be seen.[14] Radical cations stabilized in main polymer chain and oxygen containing groups dissociate under light with $\lambda \leq 540$ nm action and give hydrogen atoms

$$RH^{+} \Rightarrow R^{+} + H$$

that react with polymer forming cyclohexadienyl radicals. The action of light with $\lambda \leq 480$ nm on radical cations stabilized on aromatic ring reduce the yield of macroradicals.[15]

However well studied phototransformation of polymer radical cations did not show any noticeable changes in the structure and properties of polymers.

Thus, it is possible speak with confidence that the active intermediates playing important role in photoageing of different polymers are free radicals.

2.1 Polyolefins

Pure polyolefins should absorb light in the region shorter than 200 nm, the origination of radicals in them on exposure to light is possible if impurity groups (carbonyl, peroxide, hydroperoxide groups, etc.) or molecules (catalyst residues, various aromatic compounds, etc.) formed in the polymer or entering into it in the course of synthesis, processing and use and acting as initiators or sensitizers are excited. The formation of radical species in polyolefins also occurs under the action of ionizing radiation, mechanical loads and other energetic factors, several types of macroradicals (alkyl, allyl, polyene, peroxide, acyl, etc.) being formed in polyolefins of different chemical structures. Table III lists reported data on the structure and ESR and UV absorption spectra of some of these species.

On exposure to light in their absorption band,[3] polyene radicals transform into appropriate alkyl and allyl macroradicals.[27,28] It follows that

$$\Delta G = 2\beta \cdot [(\sin \pi/2N)^{-1} - \operatorname{ctg} \pi/(2N + 1) - 0.5]$$

where β is the exchange integral, N is the number of π-electrons) that as the length of the conjugated chain grows, the difference of conjugation energies, ΔG, of the polyene radical and the corresponding molecule increases in its absolute value and at $N \geq 5$ the process of phototransformation of polyene radicals becomes energetically unfavourable. It was noted for lower N values that in polyethylene (PE)[29] and polypropylene (PP)[22] dienyl and trienyl radicals form alkyl radicals on excitation with light. The mechanism of phototransformations of polyenyl radicals with $N < 5$ has not been clarified until now. It can only be remarked that cyclohexadienyl radicals, on their excitation in the D_0-D_2 electron transition ($\lambda_{max} = 316$ nm), revealed a dissociation process with the formation of H atoms[30,31] whereas on photolysis in the long-wave D_0-D_1 transition ($\lambda_{max} = 559$ nm) a photosubstitution reaction occurred.[31,32]

It was noted that the exposure of allyl macroradicals in PE to light[27,33] may lead to their dissociation with the formation of diene and an allyl macroradical

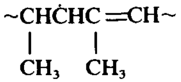
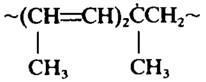
$$\sim CH_2\dot{C}HCL{=}CHCH_2\sim \xrightarrow{h\nu} \sim CH_2CH{=}CHCH{=}CH_2$$

$$+ \sim CH_2\dot{C}H_2 \Longrightarrow \sim CH_2\dot{C}HCH_3 \quad (1)$$

TABLE III

ESR spectral parameters and the thermal stability and light sensitivity ranges of radicals formed in some polyolefins

Radical	Number of lines in ESR spectrum	Parameters of ESR spectrum, mT	Methods of radicals generation	Range of thermal stability, K	Range of light sensitivity, nm	Literature
$\sim CH_2\dot{C}HCH_2\sim$	6	$a_H^\alpha = 2.1$ $a_H^\beta = 3.5$	Radiolysis Photolysis Mechanical Degradation	<200–300	$\lambda < 300, \varepsilon_{215-250} =$ 150–180 m^{2}mol^{-1}	2, 9, 16, 17
$\sim CH_2\dot{C}HCH_3$	8	$a_H^\alpha = a_H^{CH_3} =$ $a_H^{\beta_1} = 2.3$ $a_H^{\beta_2} = 4.3$	Photolysis Mechanical Degradation	<120–140	$\lambda_{max} \simeq 230-240$	18, 19
$\sim CH_2\dot{C}H_2$	8	$a_H^\alpha = 2.2$ $a_H^{\beta_1} = 5.4$ $a_H^{\beta_2} = 1.7$	Photolysis Mechanical Degradation	<120–140	—	9, 16, 17
$\sim CH{=}CH\dot{C}HCH_2\sim$	9	$a_H^\alpha = 2.0$ $a_H^{\beta_1} = 3.0$ $a_H^{\beta_2} = 1.1$	Radiolysis	<290–340	$\lambda_{max} = 255, \varepsilon_{255} = 730 \pm 150$ m^{2}mol^{-1}	9, 16, 17
$\sim(CH{=}CH)_2\dot{C}HCH_2\sim$	1	$\Delta H_{1/2} = 4$	Radiolysis	—	$\lambda_{max} = 285, \varepsilon_{285} = 2900 \pm 600$ m^{2}mol^{-1}	9, 16, 17, 20
$\sim\underset{CH_3}{\underset{\mid}{CH}}-\dot{C}H-\underset{CH_3}{\underset{\mid}{CH}}\sim$	4	$a_H^\alpha = 2.1$ $a_H^\beta = 2.6$	Photolysis Radiolysis	<250–290	$\lambda_{max} < 230, \varepsilon_{254} = 110 \pm 20$ m^{2}mol^{-1}	9, 16, 17
$\sim CH(CH_3)\dot{C}H_2$	4	$a_H^\alpha = a_H^\beta = 2.4$	Photolysis		—	22
$\sim CH_2-\underset{CH_3}{\underset{\mid}{\dot{C}}}-CH_2\sim$	6	$a_H^{CH_3} = 2.3$ $a_H^{\beta_1} = 3.0$ $a_H^{\beta_2} = 0.3$	Photolysis Radiolysis Mechanical Degradation	<120–140	—	18, 23

 $\sim\underset{CH_3}{\underset{\mid}{C}}H\dot{C}H\underset{CH_3}{\underset{\mid}{C}}{=}CH\sim$	7	$a_H^{\alpha} = 1.5$ $a_H^{\beta} = 3.0$	Radiolysis		$\lambda_{max} = 255$	9, 16, 17, 24
 $\sim(\underset{CH_3}{\underset{\mid}{C}}H{=}CH)_2\underset{CH_3}{\underset{\mid}{\dot{C}}}CH_2\sim$	1	$\Delta H_{1/2} = 4$	Radiolysis		$\lambda_{max} = 310$	9, 16, 17, 24
$\sim C(CH_3)_2\dot{C}HC(CH_3)_2\sim$	2	$a_H^{\alpha} = 2.1$	Photolysis Radiolysis Mechanical Degradation	<200–220	$\lambda_{max} < 230$, $\varepsilon_{254} = 110 + 20$ m^{2}mol^{-1}	9, 16, 17, 24
$\sim CH_2\dot{C}(CH_3)_2$	15	$a_H^{CH_3} = a_H^{\beta_1} = 1.1$ $a_H^{\beta_2} = 1.3$	Radiolysis Photolysis Mechanical Degradation	<183		9, 16, 17
$R\dot{O}_2$	1	$g_{\parallel} = 2.042–2.045$ $g_{\perp} = 2.005–2.009$	Photolysis Radiolysis Mechanical Degradation	<260–280 (PE) <250–290 (PP) <200–220 (PIB)	$\lambda_{max} = 250–280$ $\varepsilon_{254} = 200 \pm 100$ m^{2}mol^{-1}	9, 16, 17, 26

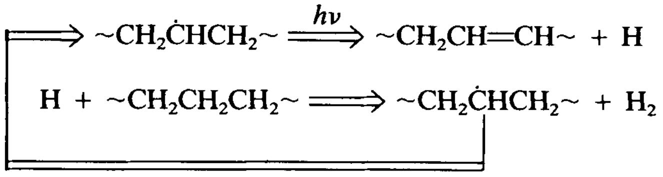
This conclusion was based[27,33] on the ESR spectral data indicating the emergence, on exposure to light with $\lambda \geq 390$ nm, of a specific signal assigned to $CH_2\dot{C}HCH_3$ macroradicals and on a decrease in the viscosity-average molecular weight of the polymer to 2/3–1/4 of the initial value. It should be added, on the other hand, that the authors of one of the papers referred to above[33] also studied the absorption spectra of γ-irradiated PE and, while observing a decrease in absorption (assigned to allyl radicals) on exposure to light, registered a decrease in optical density in the 220–230 nm region where one should have expected the appearance of intense absorption ($\approx 10^3$ m^2mol^{-1}) caused by the formation of diene groups. Besides, γ-irradiation of polyolefins may entail the formation of non-paramagnetic products (primarily, of the ionic nature) featuring absorption with a maximum at 320 nm in PP[24] whose photochemical reactions may also affect the molecular weight of the polymer. The transformations observed on photolysis of allyl radicals involves the π-orbital to the nonbonding orbital of the unpaired electron. There are no reported data on the reactions of low-molecular allyl radicals in this spectral region which might throw light on the feasibility of reaction (1). It can be noted that the only reliably established direction of the reaction of allyl radicals in the ππ* transition band is the detachment of hydrogen atoms from the molecules of various organic compounds by an electronically excited radical.[34] There are no direct data on the possible influence of such processes on the changes in the structure and functional composition of polyolefins although it is well known that the exposure of PP to light brings about a photostimulated recombination of allyl macroradicals. Since in this case the decay of radicals may be due both to the migration of a free valency along the polymer chain and to their spatial encounter, additional cross-linking of polyolefins should be observed.

The greatest influence on the change of the molecular weight of polyolefins, their structure and functional composition is exerted by the reactions of electronically excited alkyl radicals dissociating with the rupture of C—C bonds.[2,3,35] Quantum-chemical calculations for the ethyl radical[36] corroborate the possibility of its dissociation in an electronically excited state at C—C bond to afford a methyl radical and methylene in the $^1B_1$ state. Studies of photochemical reactions in PP[37–40] and polyisobutylene (PIB)[37] revealed the formation of methyl radicals and methane ascribed to photodissociation of alkyl macroradicals

$$\sim CH(CH_3)\dot{C}HCH(CH_3)\sim \xRightarrow{h\nu} \sim CH{=}CHCH(CH_3)\sim + \dot{C}H_3.$$

It was also noted[37] that phototransformations of radicals had no noticeable effect on the processes of destruction of the polymer's main chain. The occurrence of secondary photochemical reactions of alkyl radicals accounts for the numerous facts of formation of methyl radicals on PP exposure to light with $\lambda \leq 300$ nm Reference 2. Later on,[41] photodissociation reactions of alkyl macroradicals were detected. The reactions led to rupture in the main chain of the polyolefin but were characterized by low values of the quantum yield at 77 K.

It was found that successive exposure of PE to γ-radiation and UV light at 77 K raised the yield of the gel fraction about 2.5 times, that of hydrogen ~14 times and that of trans vinylene double bonds ~23 times.[42] The same authors[19] succeeded in showing that such high values of the yields of certain stable products were due to photoradical chain reactions, such as



$$\begin{aligned} &\Longrightarrow \sim CH_2\dot{C}HCH_2\sim \xRightarrow{h\nu} \sim CH_2CH{=}CH\sim + H \\ &H + \sim CH_2CH_2CH_2\sim \Longrightarrow \sim CH_2\dot{C}HCH_2\sim + H_2 \end{aligned}$$

In Table IV are the values of the quantum yields of the phototransformation reactions of allyl and alkyl radicals in polyolefins at 77 K. The destruction of the main chain features quantum yields ranging from 10^{-2} in PE to 10^{-5} in PIB (low efficiency of these reactions prevented their detection in PP and PIB).[37,40]

In order to explain the formation of cross-links in PE in an amount exceeding many times the starting number of paramagnetic species in the specimens, a suggestion about the breakage of C—H bonds "photosensitized" by alkyl radicals was put forward[42]

$$R_1^* + R_2H \Longrightarrow [R_1 \cdots H \cdots R_2] \Longrightarrow H + [R_1 + R_2].$$

The further trend of the process is determined by the behaviour of radicals R_1 and R_2 in the "cage"; H atoms interact with the molecules of the polymer thus reducing alkyl macroradicals. The proposed mechanism has not received sufficient experimental support since for methyl radicals the reaction of their photodissociation with the formation of methylene and a hydrogen atom has been

TABLE IV

Quantum yields of photochemical reactions of radicals in polyolefins

Polymer	Reactions	λ, nm	Quantum yield	Literature
PE	$\sim CH_2\dot{C}HCH_2\sim \Longrightarrow H + \sim CH_2CH{=}CH\sim$	>200	0.2	19
	$\Longrightarrow \sim CH{=}CH_2 + \sim CH_2\dot{C}HCH_3$	>200	$8\cdot10^{-3}$	19
	$\Longrightarrow \sim CH{=}CH_2 + R_X$	254	$(4 \pm 2)\cdot10^{-2}$	43*
	$\sim CH_2\dot{C}HCH_3 \Longrightarrow \dot{C}H_3 + \sim CH{=}CH_2$	>200	$4\cdot10^{-3}$	19
	$\Longrightarrow C_2H_4 + \sim CH_2\dot{C}HCH_3$	>200	10^{-3}	19
	$\sim\dot{C}HCH{=}CH\sim \Longrightarrow \sim CH_2\dot{C}HCH_2\sim$	254	$(8 \pm 3)\cdot10^{-2}$	44
		254	0.1	45
PP	$\sim CH(CH_3)\dot{C}HCH(CH_3)\sim \Longrightarrow \dot{C}H_3$ $+ \sim CH{=}CHCH(CH_3)\sim$	254	$(2.1 \pm 0.3)\cdot10^{-4}$	3
	$R_{all} \Longrightarrow R_{alk}$	254	$(13 \pm 3)\cdot10^{-3}$	44
PIB	$\sim C(CH_3)_2\dot{C}HC(CH_3)_2\sim \Longrightarrow \dot{C}H_3 +$ $\sim C(CH_3){=}CHC(CH_3)_2\sim$	254	$(1.5 \pm 0.3)\cdot10^{-4}$	41
	$\Longrightarrow \sim CH{=}C(CH_3)_2 + \dot{C}H_2C(CH_3)_2\sim$	254	$\leq10^{-5}$	

*Reaction of alkyl radicals in polyvinyl butyral.

reliably established, the reaction having a quantum yield about 0.1 at 4 K (which is comparable with the yield measured in PE) and giving the same end products.[46]

$$R_1 \xrightarrow{h\nu} R_1{:} + H$$

$$R_1{:} + R_2H \longrightarrow [R_1 + R_2]$$

This direction of photodissociation of alkyl macroradicals agrees with the results of a quantum-chemical calculation of the fragmentation of the methyl radical indicating that the first excited 1^2A state of $\dot{C}H_3$ with energy 5.73 eV should predissociate with the rupture of C—H bond.[47]

Studies of the mechanism of reactions of electronically excited peroxide radicals are of importance since radicals of this type are formed as intermediate species in processes of photochemical oxidation of polyolefins.

The maxima in the absorption spectra of peroxide radicals are found in the 230–280 nm region, the extinction coefficients being $\lambda_{max} = (0.8-3.2)\cdot 10^2\ m^2mol^{-1}$.[2] On the other hand, attempts at detecting optical absorption of peroxide radicals in PE and PP failed[44,48] although their formation in fairly large concentrations has been revealed in ESR spectra. Optical absorption of peroxide radicals in PIB ($\varepsilon_{254} = (2 \pm 1)\cdot 10^2\ m^2mol^{-1}$) has been found only recently.[26]

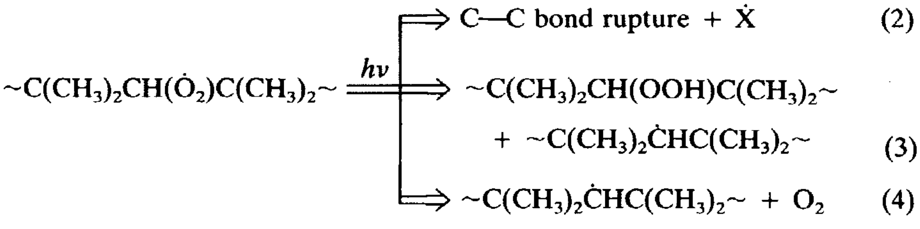
It has been thought for a long time[9,47,48] that excited peroxide radicals in polyolefins undergo substitution reactions giving hydroperoxides. Exposure to light in the spectral range covering the absorption bands of peroxides leads to their subsequent photochemical degradation

$$R\dot{O}_2 + RH \xrightarrow{h\nu} ROOH + R$$

$$ROOH \xrightarrow{h\nu} R\dot{O} + \dot{O}H$$

Studies of photochemical reactions of model low-molecular alkyl peroxide radicals indicated that the main direction of their reactions is dissociation with the formation of appropriate alkyl radicals and oxygen[43,48] and other dissociation products.[46]

It was found[26] that photolysis of peroxide radicals in PIB at 77 K leads to a decrease in the number-average molecular weight of the polymer, i.e. involves ruptures of C—C bond in the main chain of the polymer. Simulation of the kinetics of the process occurring in PIB showed (Figure 1) that satisfactory agreement between the calculated and experimental data existed for the 2:1:1 proportion between the quantum yields of reactions (2–4) which means that the degradation of the polymer chain is the key process



$$\sim C(CH_3)_2CH(\dot{O}_2)C(CH_3)_2\sim \xrightarrow{h\nu} \text{C—C bond rupture} + \dot{X} \qquad (2)$$

$$\sim C(CH_3)_2CH(\dot{O}_2)C(CH_3)_2\sim \xrightarrow{h\nu} \sim C(CH_3)_2CH(OOH)C(CH_3)_2\sim + \sim C(CH_3)_2\dot{C}HC(CH_3)_2\sim \qquad (3)$$

$$\sim C(CH_3)_2CH(\dot{O}_2)C(CH_3)_2\sim \xrightarrow{h\nu} \sim C(CH_3)_2\dot{C}HC(CH_3)_2\sim + O_2 \qquad (4)$$

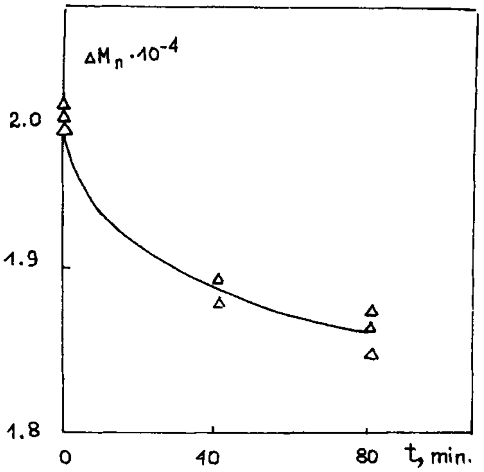
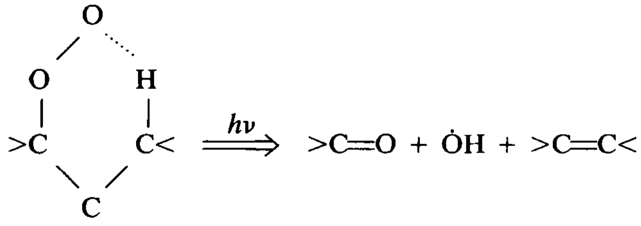


FIGURE 1 The kinetics of change of PIB number average molecular mass upon the photolysis of peroxide radicals at 77 K (points—experimental values, curve—calculated values).[26]

The mechanism of the process is believed[26] to be similar to that proposed earlier[49] for the thermal decomposition reactions of peroxide radicals



The proposed mechanism of the process and the experimentally found proportion of quantum yields are responsible for the earlier observed isotope effect in the reaction[49] and the low yields of hydroperoxides in photochemical reactions of peroxide radicals.[53]

The dissociation reaction of peroxide radicals involving C—C bond scission plays, to all appearances, an essential part in photooxidative degradation of various carbon- and heterochain polymers in a broad temperature range. This conclusion is based on the experimental findings[44] indicating that the quantum yield of consumption of peroxide radicals in deuteropolyethylene and deuteropolypropylene increased, in going from 77 K to 300 K, from 0.2 to 1 and from $4 \cdot 10^{-2}$ to 0.7, respectively.

On the other hand, a different interpretation of the above-mentioned experimental evidence is possible. Studies of photolysis (λ = 248 nm) of $H\dot{O}_2$ radicals in the gas phase[54] showed that the main photochemical process is dissociation at O—O bond

$$H\dot{O}_2 \xrightarrow{h\nu} H\dot{O}(X^2\Pi) + O(^1D)$$

A theoretical analysis of this process[55] indicates that more probable is the formation of 0 atoms in the ground ^3P state rather than in the excited (^1D) state. An identical pathway of photodegradation, by analogy with $H\dot{O}_2$ radical, is also proposed for some other alkyl peroxide radicals, such as $CH_3\dot{O}_2$, with the formation of a vibrationally excited methoxy radical[55]

$$CH_3\dot{O}_2(^2A) \xrightarrow{h\nu} CH_3\dot{O}(X^2E) + O(^1D)$$

This possibility has found experimental support,[56] the quantum yield of the formation of $CH_3\dot{O}$ (X^2E) radicals being 0.2 ± 0.1. Although no direct experimental evidence of the formation of alkoxy radicals has been found in studies of photochemical reactions using IR spectroscopy at 12 K in argon-oxygen matrices,[57–60] this is not surprising since photolysis, e.g. of $CH_3\dot{O}_2$, gives rise to a "hot" pair $[CH_3\dot{O} + O]$ for which several reaction pathways are possible: 1) Detachment of a hydrogen atom from $CH_3\dot{O}$ radical by O atom in the ^1D state and stabilization of the reaction products $[CH_2O + \dot{O}H]$ in the matrix cage, 2) Fast oxidation of the "hot" pair $[CH_3\dot{O} + O]$ by an oxygen molecule with the formation of H_2O, CO_2 and/or CO, $H\dot{O}_2$ and $\dot{O}H$.[61]

The idea of dissociation of electronically excited peroxide radicals at O—O bond, as the main direction of their reactions, is also supported by the results of studies of photodissociation of various types of peroxide radicals (alkyl, allyl, vinyl, cyclohexadienyl) grafted to a chemically activated SiO_2 surface.[62,63]

These data on photodissociation of peroxide radicals at O—O bond form basis of the following explanation of the formation of dissociation products of peroxide radicals at C—O bond. The reverse "cage" reaction between alkoxy radicals and oxygen atoms is accompanied by liberation of energy (the heat of reaction is ≃ 250 kJ/mol[64]) greatly exceeding the energy of C—O bond in peroxide radicals (e.g., in $CH_3\dot{O}_2$ it is equal to about 130 kJ/mol[65]) which may bring about their thermal degradation.

In the general case, the following transformation scheme can be offered for peroxide radicals in polyolefins:

$$R\dot{O}_2 \xrightarrow{h\nu} [R\dot{O} + O]$$

$$[R\dot{O} + O] \Longrightarrow [R + O_2] \Longrightarrow \left[\begin{array}{l} \Longrightarrow R + O_2 \\ \Longrightarrow R\dot{O}_2 \end{array}\right.$$

$$[R\dot{O} + O] \Longrightarrow [R'CHO + \dot{O}H]$$

$$[R'CHO + \dot{O}H] \Longrightarrow [R'CO + H_2O]$$

$$[R'CHO + \dot{O}H] + RH \Longrightarrow R'CHO + H_2O + R$$

$$[R\dot{O} + O] \Longrightarrow [R'' + CH_2O + O] \quad R - \text{primary}$$

$$[R\dot{O} + O] \Longrightarrow [{>}C{=}O + R_m + O] \quad R - \text{secondary, tertiary}$$

Alkoxy radicals RO formed in the course of the process can both react with the polymer molecules and undergo β-decomposition. Since the nature of R, the polymer matrix, may strongly affect the direction of the secondary reactions, it should be expected that photochemical transformations of peroxide radicals in various polymers can give rise to similar products but in greatly differing amounts.

2.2 Polystyrene

Polystyrene (PS) and styrene copolymers find application as structural materials, films, etc. The macromolecule of PS contains, apart from its own chromophore responsible for absorption in the wavelength region less than 300 nm, small amounts of carbonyl and peroxide groups, double bonds, monomer and benzaldehyde residues. PS ageing processes are accompanied by changes in molecular weight distribution (MWD), polymer fogging and yellowing embrittlement, etc.

Studies of PS ageing and of the effect of various factors on PS revealed different types of macroradicals, Table V.

The mechanism of photochemical reactions of macroradicals in PS has been studied insufficiently well. It can only be noted that photochemical reactions of macroradicals of the cyclohexadienyl type, R_5, are accompanied by the formation of R_1, R_4 and R_6 macroradicals, the quantum yield of phototransformation of R_5 at 77 K being $3 \cdot 10^{-2}$.[67] These data agree with information[2,35] indicating that radicals with the $\pi\pi^*$ excitation should participate in photosubstitution reactions whose quantum yields must be close to 10^{-1}–10^{-2}.[69] The transformations of radicals R_5 on exposure to light should not affect polymer degradation but promote it indirectly giving rise to radicals with an unpaired electron in the polymer's main chain.

Photoradical ageing of PS was studied most thoroughly under photooxidative ageing conditions where peroxide macroradicals R_9 of different structures act as active centres of ageing.[67,70–72] The decisive role of radical reactions is also witnessed by the data[73] indicating that the depth of photochemical transformation of PS and the scale of changes in its mechanical properties are determined by the rate of formation of free radicals rather than by reactions of singlet oxygen formed by photosensitizers.

The measured values of the quantum yields of the reaction of formation of free radicals in PS[67,74] Table VI, fall within 10^{-3}–10^{-5} range, undergo minor alterations with photon energy changing and grow with photolysis temperature.

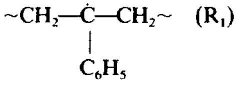
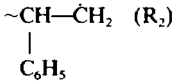
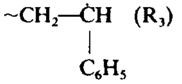
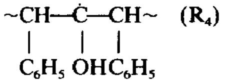
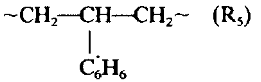
At the same time the values of the quantum yield of oxygen absorption on PS photolysis at room temperature under different oxygen pressures (150–400 Torr) lie within the 0.3–1.0 range thus pointing to the chain character of the processes involved.[74]

The measured quantum yields of the main reaction products Table VII. The data testify to a virtually full consumption of oxygen in the formation of deep oxidation products which is a kind of photochain "combustion" of the polymer. Based on experimental results obtained on polyolefins and model low-molecular compounds[26,51,67,70–72] the PS photooxidation reaction follows the scheme

$$R + O_2 \Longrightarrow R\dot{O}_2 \overset{h\nu}{=\!=\!=} R + \text{products } (H_2O,\ CO_2) \Longrightarrow R\dot{O}_2$$

TABLE V

ESR spectral parameters and the thermal stability and light sensitivity ranges of radicals formed in PS

Radical	Number of lines in ESR spectrum	Parameters of ESR spectrum, mT	Methods of radicals generation	Range of thermal stability, K	Range of light sensitivity, nm	Literature
 $\sim CH_2-\underset{C_6H_5}{\overset{\cdot}{C}}-CH_2\sim$ (R_1)	3	$a_H^{\beta_1} = 2.0$ $a_H^{C_6H_5} \simeq 0.5$	Radiolysis	<235	λ_{max} = 450, 305–318, 250–258	16, 17, 66–68
	5	$a_H^{\beta_1} = a_H^{\beta_2} \approx 2.0$ $a_H^{C_6H_5} \simeq 0.5$	Photolysis		$\varepsilon_{450} \simeq 3-7$, $\varepsilon_{305-318} = 100-1200$, $\varepsilon_{250-258} = 190-1400$ m^2mol^{-1}	
	7	$a_H^{\beta_1} \simeq 1.8$ $a_H^{\beta_2} \simeq 5.4$	Photolysis Radiolysis			
 $\sim \underset{C_6H_5}{CH}-\dot{C}H_2$ (R_2)		$a_H^{\alpha} = 2.2$ $a_H^{\beta} = 3.3$	Mechanical Degradation	<120–140	—	16
 $\sim CH_2-\underset{C_6H_5}{\dot{C}H}$ (R_3)	3	$a_H^{\alpha} = 1.5$ $a_H^{\beta_1} = 2.1$ $a_H^{\beta_2} = 0.2$	Mechanical Degradation Plasma irradiation	<330–350	Spectral properties analogous to radicals R_1	16, 76
 $\sim \underset{C_6H_5}{CH}-\underset{OH}{\overset{\cdot}{C}}-\underset{C_6H_5}{CH}\sim$ (R_4)	3	$a_H^{\beta} = 1.8$	Photolysis	—	Spectral properties analogous to α-hydroxyalkyl radicals	67
 $\sim CH_2-\underset{\dot{C}_6H_6}{CH}-CH_2\sim$ (R_5)	12	$a_H^{\beta} = 0.75$ $a^{o-H} = a^{p-H} = 0.1$ $a^{m-H} = 0.25$	Radiolysis Plasma irradiation		λ_{max} = 316, 559 $\varepsilon_{316} = 317 \pm 27$, $\varepsilon_{559} = 4.5 \pm 0.3$ m^2mol^{-1}	9, 16, 17, 31, 67, 76

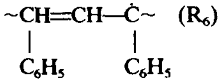
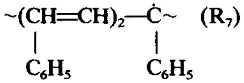
 $\sim \underset{C_6H_5}{CH}{=}CH{-}\underset{C_6H_5}{\dot{C}}\sim$ (R_6)	1	$\Delta H_{1/2} \simeq 2.0$	Photolysis	<370	—	17, 66, 67
 $\sim(\underset{C_6H_5}{CH}{=}CH)_2{-}\underset{C_6H_5}{\dot{C}}\sim$ (R_7)	1	$\Delta H_{1/2} \simeq 1.4$	Photolysis		—	67
Polyenyl radical (R_8)	1	$\Delta H_{1/2} \simeq 0.6$	Photolysis		—	66, 67
$R\dot{O}_2$ (R_9)	1	$\Delta H_{1/2} \simeq 1.6$	Photolysis Radiolysis Mechanical Degradation		$\lambda < 550$	17, 66, 67

TABLE VI

Quantum yields of the formation of radicals in PS[67,74]

Sample of PS	Conditions of photolysis	λ, nm	Quantum yield
Film, 1 = 2 mm	Vacuum, 77 K	≥236	$3\cdot10^{-5}$
	Vacuum, 300 K	≥236	$1.5\cdot10^{-4}$
	Vacuum, 300 K	≥300	$1.5\cdot10^{-4}$
	Vacuum, 77 K	≥236	$5\cdot10^{-5}$
	Air, 77 K	253.7	$5\cdot10^{-5}$
	Air, 77 K	≥360	$1.5\cdot10^{-5}$
	Air, 315 K	≥236	10^{-3}
Photooxidated	Air, 315 K	≥236	$2\cdot10^{-3}$
PS + 5% benzophenone	Air, 315 K	≥360	10^{-3}

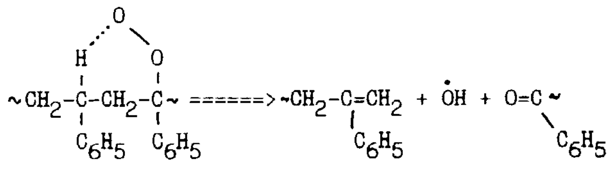
TABLE VII

Quantum yields of formation of main intermediate and final products on PS photooxidation[74]

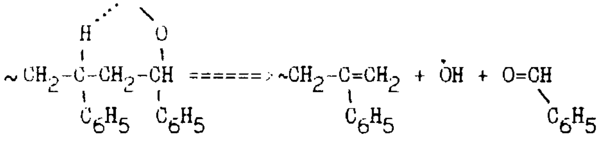
Process	Conditions of photolysis	λ, nm	*I*, quant/ (sm²s)	Quantum yield
Absorption of O_2	150 torr O_2, 300 K	253.7	$2\cdot10^{16}$	0.33
	200–400 torr O_2, 300 K	253.7	10^{16}	1.0
Formation of ROOH	Air 760 torr, 300 K	253.7	10^{16}	10^{-3}
Formation of >C=O	Air 760 torr, 300 K	253.7	10^{16}	10^{-3}
Chain scission	600 torr O_2, 300 K	253.7	10^{14}	10^{-3}
Formation of polyenyl radicals	Air 760 torr, 330 K	253.7	$2\cdot10^{16}$	$5\cdot10^{-6}$
Formation of CO_2 and H_2O	150 torr O_2, 300 K	253.7	$2\cdot10^{16}$	0.28
	400 torr O_2, 300 K	253.7	10^{16}	1.0

Phototransformation of peroxide radicals seems to be, in effect, photodissociation of electronically excited radicals; excitation of the radicals may, to all appearances, occur both by direct light absorption by radicals (for peroxide macroradicals in PS $\varepsilon_{330} = 4\cdot10^2$ m²mol^{-1} [74]) and by energy transfer from other chromophores.

The mechanism of photodissociation of peroxide macroradicals in PS has not been elucidated. It can be suggested that it resembles the mechanism of thermal degradation of peroxide macroradicals in PS[75]:



$$\sim CH_2-\underset{C_6H_5}{\overset{H\cdots O-O}{C}}-CH_2-\underset{C_6H_5}{C}\sim \Longrightarrow \sim CH_2-\underset{C_6H_5}{C}=CH_2+\dot{O}H+O=\underset{C_6H_5}{C}\sim$$



$$\sim CH_2-\underset{C_6H_5}{\overset{H\cdots O-O}{C}}-CH_2-\underset{C_6H_5}{CH} \Longrightarrow \sim CH_2-\underset{C_6H_5}{C}=CH_2+\dot{O}H+O=\underset{C_6H_5}{CH}$$

The formation of low-molecular OH radicals ensures high rates of migration of the free valency in PS undergoing oxidation.

The length of the photoradical PS oxidation chain evaluated from the quantum yield values given in Tables II and III is $3 \cdot 10^2 - 4 \cdot 10^3$. It should be added that in a thermal PS oxidation process occurring in dark the length of the reaction chain

$$R + O_2 \Longrightarrow R\dot{O}_2 \Longrightarrow R$$

is 10.[70]

Photoradical oxidation of PS leads to great changes in polymer's macrocharacteristics. Within a period of 260 hours of exposure ($\lambda = 253.7$ nm, $I = 10^{16}$ quanta/(cm^{2}s)), the weight and thickness of PS films decreased by 60 and 40%, respectively. Of particular importance is the fact that PS oxidation following the photoradical chain mechanism occurs on exposure to natural sunlight.

2.3 Fluorine- and Chlorine-Containing Polymers

In fact, there can be found almost no data on photochemical reactions of fluoroalkyl macroradicals with maxima in their absorption spectra located in the 215–265 nm region ($\varepsilon \simeq 60-100$ m^{2}mol^{-1}).[77–79] It is known that in a copolymer of tetrafluoroethylene with hexafluoropropylene $\sim CF_2\dot{C}(CF_3)CF_2\sim$ macroradicals, on exposure to light at 77 K, transform into $\sim CF_2CF(\dot{C}F_2)CF_2\sim$ radicals featuring a specific ESR spectrum.[80] On the other hand, $[(CF_3)_2CF]_2\dot{C}C_2F_5$ radicals ($\lambda_{max} < 220$ nm) formed on radiolysis of hexafluoropropylene trimer (HFPT) decay on photolysis with 300 nm light both at 300 and 77 K. It was shown[81,82] that photodegradation involves the formation of trifluoromethyl radical

$$[(CF_3)_2CF]_2\dot{C}C_2F_5 \xRightarrow{h\nu} (CF_3)_2CFC{=}CF(CF_3)C_2F_5 + \dot{C}F_3$$

At 300 K the $\dot{C}F_3$ radical formed adds to the double bond in HFPT to form a long-lived $[(CF_3)CF]_3\dot{C}$ radical. At 77 K this process is not observed, and in the course of specimen thawing $\dot{C}F_3$ radicals decay in the 100–150 K range.

Electronically excited fluoroalkyl radicals undergo dissociation at the β-bond. It would be natural to expect photodissociation of fluoroalkyl radicals at the C—F bond, but it is difficult to record this process by virtue of the high reactivity of F atoms. It is anticipated that fluorine atoms in perfluorinated polymers will interact primarily with double bonds, impurities of various organic compounds or recombine. There are no data concerning the effect of such processes on the changes in macrocharacteristics of fluorine-containing polymers.

The mechanism of photochemical reactions of peroxide macroradicals having the absorption maximum at $\simeq 240$ nm, $\varepsilon_{240} \simeq 70$ m^{2}mol^{-1} has been studied in much more detail.[77] It was also found[82,83] that exposure to light with $\lambda \leq 280$ nm transforms $\sim CF_2CF(O\dot{O})CF_2\sim$ radicals into terminal fluoroalkyl radicals; mass and IR spectrometry revealed CF_2O and CO among the reaction products.[84,85] It was assumed[84] that the reaction runs as follows

$$\sim CF_2CF(O\dot{O})CF_2\sim \xRightarrow{h\nu} \sim CF_2\dot{C}F_2 + CF_2O + CO + CF_3CF_2\sim$$

It seems that the mechanism of this photochemical reaction is identical with that of the thermal degradation of peroxide radicals in polytetrafluoroethylene.[86,87] The use of $\sim CF_2CF(^{18}O^{18}\dot{O})CF_2\sim$ peroxide radicals labelled with ^{18}O isotope made it possible to reveal[87] the formation of large amounts of $C^{18}OO$ and $C^{18}O$ in the course of the process which was assumed to be due to the following reactions

$$\sim CF_2CF(^{18}O^{18}\dot{O})CF_2\sim \Longrightarrow [\sim CF_2CF^{18}O^{18}OCF_2\sim] \Longrightarrow \sim CF_2CF^{18}\dot{O} + {}^{18}\dot{O}CF_2\sim$$

$$^{18}\dot{O}CF_2\sim \Longrightarrow CF_2{}^{18}O + \dot{C}F_2CF_2\sim$$

$$CF_2{}^{18}O + H_2O \Longrightarrow HF + C^{18}OO$$

The decay of the middle peroxide radicals leads to decrease in the molecular weight of the polymer.

The action of light on the peroxide end radicals in polytetrafluoroethylene at temperatures below 170 K leads to the formation of fluoroalkyl end radicals and oxygen[83]

$$\sim CF_2CF_2\dot{O}_2 \xrightarrow{h\nu} \sim CF_2\dot{C}F_2 + O_2$$

whereas at temperatures exceeding 170 K photodissociation of peroxide end radicals runs by the following reaction

$$\sim CF_2CF_2\dot{O}_2 \xrightarrow{h\nu} \sim CF_2\dot{C}F_2 + 2\ CF_2O$$

Determinations of the number of fluorine ions obtained on hydrolysis of fluorophosgene evolved during photolysis showed[7,88] that from 50 to 90 fluorine ions are formed per radical decayed as a result of photorecombination occurring in this case which means that a photoradical chain process takes place. The quantum yields of consumption of peroxide radicals in polytetrafluoroethylene are $(1.5 \pm 0.5) \cdot 10^{-2}$ at 77 K and 0.1 ± 0.03 at 300 K.[41]

The dissimilarity in the behaviour of peroxide end macro radicals in polytetrafluoroethylene at different temperatures remains unclear. It is possible that its conformation may be of great importance since the frequency of rotation of the radical grows with temperature, the potential barrier of rotation of the radical about C—O bond is 1.1 kJ/mol.

It was found in experiments on photochemical dehydrochlorination of poly(vinyl chloride) in vacuum[89-91] that the accumulation kinetics of polyenes has a number of specific features related to the existence of an induction period after the end of which dehydrochlorination goes on at an almost constant rate. The conservation of an invariable length distribution of polyenes depends on the spectral composition of light and to the existence of a strong dependence of the quantum yields of dehydrochlorination on the wavelength of the acting light. Synergistic effects of long-wave light with $\lambda > 290$ nm in combination with $\lambda = 254$ nm light manifesting itself not only on simultaneous but also on sequential exposure and leads to a reduction in the dehydrochlorination rate on introduction of a plasticizer. These facts point to the existence of a relatively long-lived intermediate product responsible for photochemical dehydrochlorination of poly(vinyl chloride).

Investigations of the kinetics of formation, mutual transformation and consumption of alkyl and polyenyl radicals made it possible to conclude that these species are the intermediate products of photochemical dehydrochlorination of the polymer. This conclusion is supported by the following facts:

—The quasi-stationary concentration of the radicals is established at a quasi-stationary dehydrochlorination rate;
—the radicals are thermally stable in vacuum at room temperature;
—the absorption spectrum of polyenyl radicals with a short conjugation chain matches the action spectrum of long-wave light;
—the introduction of a plasticizer results in a simultaneous decrease in the stationary concentration of the radicals and in the dehydrochlorination rate;
—exposure to long-wave light leads to a slight narrowing of the ESR spectrum of polyenyl radicals which indicates that the conjugation length in radicals changes.

An evaluation of the quantum yield of the reaction on exposure to light with $\lambda = 254$ nm on assumption that the ε value for radicals is $\approx 10^3$ m^2mol^{-1} and $I_0 =$ 1.4 Einstein/h gives $\phi \sim 0.7$.

2.4 Polyacrylates

The most widely used member of this class of polymers is poly(methyl methacrylate) (PMMA). The formation of radicals in pure PMMA containing no additives may occur not only on exposure to ionizing radiation and mechanical degradation but also on the action of light with a long-wave bondary of 250–280 nm (the extinction coefficient of the polymer at $\lambda = 254$ nm is 0.037 m^2mol^{-1}).[92] The quantum yields of formation of various radical products of PMMA photolysis at 77 K with light at $\lambda = 253.7$ nm are in Table VIII.[93]

The formation of radicals sensitized or initiated by various additives on exposure to light with larger wavelengths is also possible.[94,95]

The process of PMMA ageing involves degradation of the main chain of the polymer, liberation of volatile products, formation of unsaturated groups in the structure of the macromolecules.

Investigations of PMMA ageing under various conditions points to the formation

TABLE VIII

Quantum yields of formation of radical products of PMMA photolysis

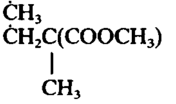
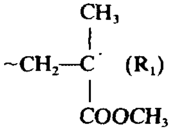
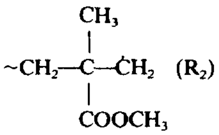
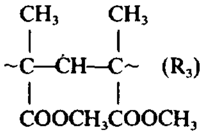
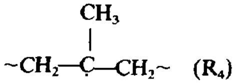
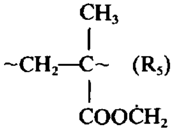
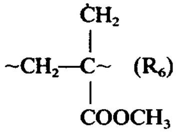
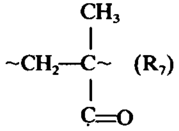
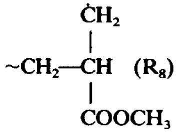
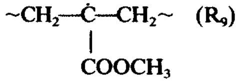
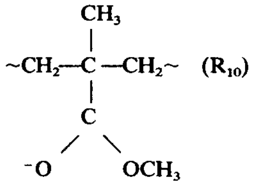
Radical	Quantum yield · 10^2
$\dot{C}H_3$	8.3
 $\dot{C}H_2C(COOCH_3)(CH_3)$	4.8 1.4 (300 K)
$CH_3O\dot{C}O$	7.0
$H\dot{C}O$	1.2
$CH_3\dot{C}O$	4.4

TABLE IX

ESR spectral parameters and thermal stability and light sensitivity ranges of radicals formed in PMMA

Radical	Number of lines in ESR spectrum	Parameters of ESR spectrum, mT	Methods of radicals generation	Range of thermal stability, K	Range of light sensitivity, nm	Literature
 $\sim CH_2{-}\overset{CH_3}{\underset{COOCH_3}{C^{\cdot}}}$ (R_1)	9	$a_H^{CH_3} = 2.2 \pm 0.1$ $a_H^{\beta_1} = 1.3 \pm 0.1$ $a_H^{\beta_2} = 1.1 \pm 0.1$ $g = 2.0033$	Photolysis (77–293 K) Radiolysis (293 K) Mechanical Degradation (77–293 K) Plasma irradiation	≤350	$\lambda_{max} = 420$, $\varepsilon_{420} = 4 \pm 1$ m^2mol^{-1}	4, 9, 16, 17, 97–101
 $\sim CH_2{-}\overset{CH_3}{\underset{COOCH_3}{C}}{-}\dot{C}H_2$ (R_2)	3	$a_H^{\alpha} = 2.2 \pm 0.1$	Photolysis Radiolysis Mechanical Degradation of dilute solution PMMA (93 K)		Spectral properties of alkyl radicals	9, 16, 96, 100–104
 $\sim\overset{CH_3}{\underset{COOCH_3}{C}}{-}\dot{C}H{-}\overset{CH_3}{\underset{COOCH_3}{C}}\sim$ (R_3)	2	$a_H^{\alpha} = 2.4$ $(1.9) \pm 0.1$ $g = 2.0025$ $(2.0034) \pm 0.0004$	Photolysis (77 K) Mechanical Degradation Plasma irradiation	<240–260	$\lambda_{max} < 300$, $\varepsilon_{254} = 120 \pm 30$ m^2mol^{-1}	9, 16, 95, 96, 101, 105–107
 $\sim CH_2{-}\overset{CH_3}{\underset{\cdot}{C}}{-}CH_2\sim$ (R_4)	24	$a_H^{CH_3} = 2.1 \pm 0.1$ $a_H^{\beta_1} = 4.2 \pm 0.1$ $a_H^{\beta_2} = 0.62 \pm 0.1$	Photolysis (77 K)	<175	Spectral properties of alkyl radicals	9, 16, 95, 96, 98, 104
 $\sim CH_2{-}\overset{CH_3}{\underset{COO\dot{C}H_2}{C}}\sim$ (R_5)	3	$a_H^{\alpha} = 2.2$ $(1.58) \pm 0.1$ $g = 2.0036$ $(2.0045) \pm 0.0001$	Photolysis Radiolysis	<188	$\lambda_{max} = 370$, $\varepsilon_{313} = 60 \pm 20$ m^2mol^{-1}	2, 3, 9, 16, 17, 95, 96, 99, 107, 109

 $\dot{C}H_2$–C(~CH$_2$~)(COOCH$_3$) (R_6)	3	$a_H^\alpha = 2.2$ $(3.0) \pm 0.1$ $g = 2.0036 \pm 0.0001$	Photolysis Radiolysis	<188	Spectral properties of alkyl radicals	9, 16, 17, 95, 96, 99, 107, 109
 $\sim CH_2-C(CH_3)(\dot{C}{=}O)\sim$ (R_7)	1	$\Delta H_{1/2} = 1.3 \pm 0.1$ $g = 2.0010 \pm 0.0006$	Photolysis	<188	$\lambda < 650$, $\varepsilon_{540} \sim 5-6$, $\varepsilon_{254} \sim 100\ m^2mol^{-1}$	3, 9, 16, 17, 95, 110
 $\sim CH_2-CH(\dot{C}H_2)(COOCH_3)$ (R_8)	4	$a_H^\alpha \simeq 2.2$ $a_H^\beta \simeq 4.0$	Mechanical Degradation		Spectral properties of alkyl radicals	111
 $\sim CH_2-\dot{C}(COOCH_3)-CH_2\sim$ (R_9)	8	$a_H^{\beta_1} = 4.8 \pm 0.1$ $a_H^{\beta_2} = 2.4 \pm 0.1$ $a_H^{\beta_3} = 1.2 \pm 0.1$ $a_H^{\beta_4} = 0.1 \pm 0.03$	Radiolysis		—	18
 $\sim CH_2-C(CH_3)(C(^{-}O)OCH_3)-CH_2\sim$ (R_{10})	1	$\Delta H_{1/2} = 1.3 \pm 0.1$	Radiolysis		$\lambda_{max} = 320$, $\varepsilon_{320} = 200 \pm 70\ m^2mol^{-1}$	3, 9, 16, 17, 112
$R\dot{O}_2$ (R_{11})	1	$g_N = 2.042-2.045$ $g_\perp = 2.005-2.009$	Radiolysis Photolysis Mechanical Degradation	<260–280		9, 16, 17

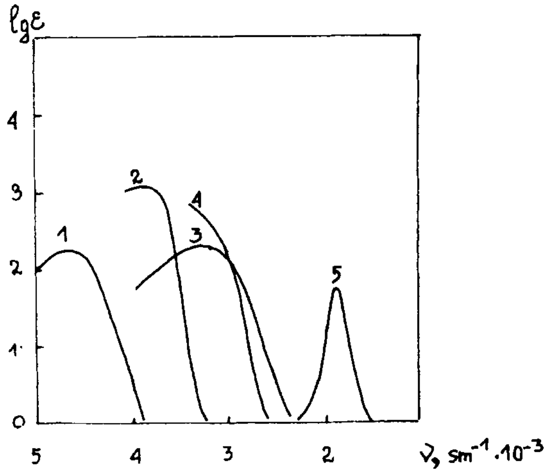
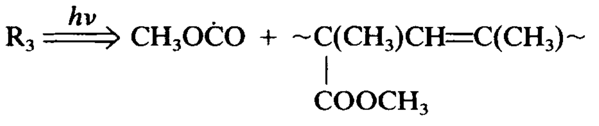


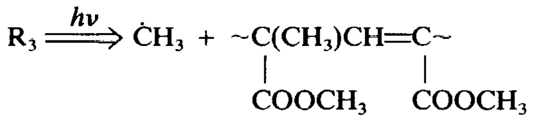
FIGURE 2 Absorption spectra of PMMA (1) and relevant radicals: 2—R_3, 3—$RO\dot{C}O$, 4—R_5, 5—$R\dot{C}O$.

of all types of macro- and low-molecular radicals possible for this polymer, except $CH_3\dot{O}$ radicals highly reactive even at 77 K and H atoms, Table IX.

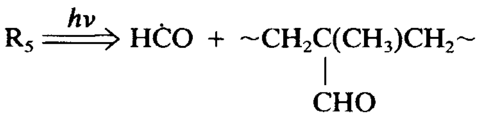
It follows, Table IX and Figure 2, that the absorption spectra of macroradicals R_2, R_4, R_6 and R_8 should strongly overlap with the intrinsic absorption spectrum of PMMA and that their photochemical reactions under direct polymer photolysis conditions are hardly probable. The transformations of radicals in γ-irradiated PMMA at 77 K observed on subsequent exposure to light[112,113] were misinterpreted because of erroneous identification of some ESR spectra. The most comprehensive analysis of the mechanism of photoradical processes in PMMA was made using ESR spectra[96,107,114–119]; it was found that in PMMA macroradicals R_3 and R_5 are engaged in the following photochemical reactions:



$$R_3 \xrightarrow{h\nu} CH_3O\dot{C}O + {\sim}\underset{\displaystyle COOCH_3}{C}(CH_3)CH{=}C(CH_3){\sim} \qquad (5)$$



$$R_3 \xrightarrow{h\nu} \dot{C}H_3 + {\sim}\underset{\displaystyle COOCH_3}{C}(CH_3)CH{=}\underset{\displaystyle COOCH_3}{C}{\sim} \qquad (6)$$



$$R_5 \xrightarrow{h\nu} H\dot{C}O + {\sim}CH_2\underset{\displaystyle CHO}{C}(CH_3)CH_2{\sim} \qquad (7)$$

The quantum yields of reactions (5–7) at 77 K are presented in Table X.[3,119]

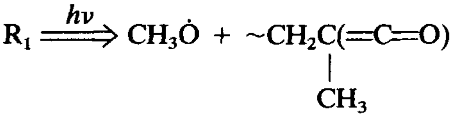
The photochemical reactions of the radicals of the growing chain, R_1, on exposure to light in a wavelength range of 305–370 nm at 77 K are believed[100] to be accom-

TABLE X

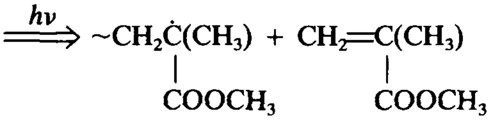
Quantum yields of photochemical reactions of radicals in PMMA at 77 K

Radical	Quantum yield · 10^2			λ, nm
	(5)	(6)	(7)	
R_3	0.10 ± 0.05	0.4 ± 0.2	—	254
R_5	—	—	8 ± 4	313

panied by the formation of methoxy radicals interacting with the polymer to give radicals R_3, R_5, R_6. The feasibility of such R_1 dissociation reaction was discussed earlier.[120] Similar processes of photodissociation of radicals of the growing chain were detected in poly(acrylic acid)[121]; in this case dissociation followed two channels leading to the formation of hydroxy radicals and ketenes and to scissions in the main chain of the polymer. According to the concepts of the free volume model featuring good agreement between the experimentally determined and calculated efficiency of the processes of photodissociation of radicals in the solid phase,[122] the quantum yields of reactions (8, 9) of dissociation of radicals R_1



$$R_1 \xrightarrow{h\nu} CH_3\dot{O} + {\sim}CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}(=C=O) \qquad (8)$$



$$\xrightarrow{h\nu} {\sim}CH_2\underset{\displaystyle COOCH_3}{\underset{|}{\dot{C}}}(CH_3) + CH_2{=}\underset{\displaystyle COOCH_3}{\underset{|}{C}}(CH_3) \qquad (9)$$

are connected by the relationship

$$\Phi_9 = \Phi_8^{V_9/V_8}$$

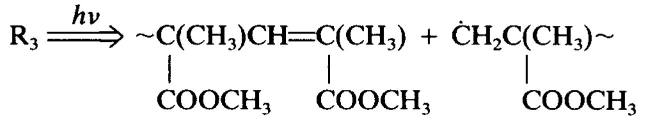
where V_8, V_9 are the van der Waals volumes of the methoxy radical and methyl methacrylate molecule. The quantum yield of reaction (8) measured from the consumption of radicals R_1 in PMMA in the band of the so-called "forbidden" transition (λ = 400 nm) is $(1.9 \pm 0.3)\cdot 10^{-5}$ for the initial portion of the kinetic curve[100] which makes the value of Φ_9 (determined from the relationship given above) immeasurably low.

Measurements of the changes in the total concentration of radicals on the exposure of X-ray irradiated PMMA to 300–380 nm light at room temperature made it possible to determine[123] the quantum yield of formation of additional ruptures in the main chain of the polymers ($\simeq$0.1) and the characteristic diffusion step (2 nm which is close to Kuhn's size of the kinetic segment for PMMA[124]). Since mostly R_1 radicals are stabilized in PMMA at room temperature, the value of the measured quantum yield[123] may be used in evaluating the lower efficiency boundary of reaction (4). In this case the quantum efficiency of reaction (5) determined from the relationship given above is Φ_9 = 0.4–0.5.

Photochemical reactions of acyl radicals R_7 in PMMA lead, as is the case with other systems,[2] to their dissociation and the formation of alkyl radicals R_4.

It follows from the data presented above that photoradical processes in PMMA lead to the degradation of ester groups, formation of low-molecular products (CO, CO_2, CH_4, methyl methacrylate), accumulation of isolated double bonds but do not affect directly the main chain of the polymer.

In principle, ruptures of the main chain of PMMA may result from photochemical reactions of radicals



$$R_3 \xrightarrow{h\nu} \sim\underset{\displaystyle COOCH_3}{C}(CH_3)CH{=}\underset{\displaystyle COOCH_3}{C}(CH_3) + \dot{C}H_2\underset{\displaystyle COOCH_3}{C}(CH_3)\sim \qquad (10)$$

Assuming that reaction (10) requires free volume $V \simeq 0.045-0.05\ nm^3$ (free volume necessary for the emergence of the end radical from the "cage"[125]) and knowing the quantum yields of reactions (5, 6), one can evaluate the maximum value of the quantum yield of reaction (10) which is $5 \cdot 10^{-4}-10^{-3}$.

Comparing the quantum yields of photochemical reactions of radicals in PMMA with those of degradation and decomposition of ester groups on direct photolysis listed in Table XI, it can be noted that they have similar values; however, photochemical reactions of radicals may occur on exposure to longer-wave light.

A special place in photochemical reactions of active intermediate species in PMMA is occupied by transformations of radical anions R_{10}. The reported data, Table XII, are characterized by a certain indefiniteness in the assignment of the ESR and optical absorption spectra of these species. This indefiniteness could be take off by the data of a recent study,[139] where ab initio molecular orbital calculations indicated that a strong absorption band at $\lambda < 320$ nm and a weak one at 440 nm were attributed to $\pi\pi^*$ and $n\pi^*$ transitions of R_{10}, respectively.

By analogy with well studied photochemical reactions of radical anions of low-

TABLE XI

Quantum yields of degradation and decomposition of ester groups on direct photolysis of PMMA

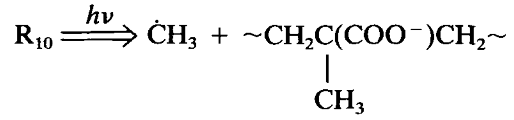
Quantum yield of degradation $\cdot 10^3$			Quantum yield of ester groups decomposition vacuum	Literature
Air	Inert atmosphere	Vacuum		
2.3	—	—	—	126
13–18	—	22–40	—	127
8.7	4.8	—	—	128
9.3	9.3	—	—	129
3.2	5	—	—	130, 131
—	—	—	0.5	118
—	—	50	1	93
0.21–0.41	—	—	—	132

TABLE XII

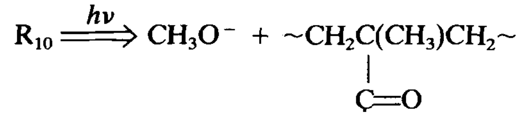
Parameters of ESR and optical absorption spectra of PMMA radical anions

Number of lines in ESR spectrum	Parameters of ESR spectrum	λ_{max}, nm	Literature
3	a_H = 1.1 mT	305, 320	133
1	$\Delta H_{1/2}$ = 1.3 mT	320	134
3	a_H = 1.1 mT	420	135
1	$\Delta H_{1/2}$ = 0.5 mT	440	136
—	—	365, 410, 1050	137
1	—	725	138

molecular esters,[2] PMMA radical anions should dissociate with quantum yields close to 10^{-2} at 77 K



$$R_{10} \xRightarrow{h\nu} \dot{C}H_3 + {\sim}CH_2\underset{\substack{|\\ CH_3}}{C}(COO^-)CH_2{\sim} \tag{11}$$



$$R_{10} \xRightarrow{h\nu} CH_3O^- + {\sim}CH_2\underset{\substack{|\\ C{=}O}}{C}(CH_3)CH_2{\sim} \tag{12}$$

Thus, photochemical reactions of radical anions on exposure to long-wave ($\lambda \leq$ 600 nm) light may lead to the decomposition of ester groups, thus being a source of low-molecular radicals capable of reacting with the polymer and traces of the monomer in a broad temperature range which brings about additional polymerization of the latter.[140]

Analysis of the kinetics of accumulation of radicals and of changes in the viscosity-average molecular weight of PMMA on photolysis sensitized by aromatic compounds[141] disclosed a similar course of these processes although it did not exclude unambiguously the effect of photoradical processes on degradation of the polymer's main chain. On the basis of examination of changes in the molecular weight of PMMA on the warming-up of polymer specimens irradiated at 77 K, the specimens differing in their radical composition, it was concluded[117] that the ruptures in the main chain are caused by thermal decomposition of radicals R_4 formed on photolysis of radicals R_7

$$R_4 \xRightarrow{h\nu} {\sim}CH_2C(CH_3){=}CH_2 + (COOCH_3)\dot{C}(CH_3)CH_2{\sim} \tag{13}$$

On the other hand, an abrupt decrease in the molecular weight of PMMA (photolyzed at different temperatures) at temperatures exceeding 250 K (Figure 3) is believed[142] to be due to thermal decomposition of radicals R_3 by reaction (10). Without arguing the validity of the main conclusions referred to above,[117] it should be noted that spin trap studies of the nature of radicals formed on PMMA deg-

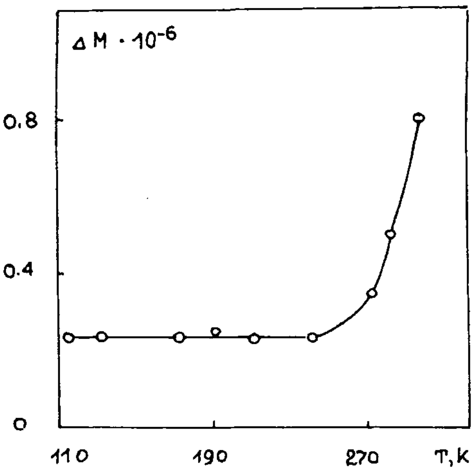


FIGURE 3 Change of PMMA molecular mass upon the photolysis at different temperatures.[143]

radation in the liquid phase[102,143,144] shows the formation of adducts of spin traps (2,6 dichloro-nitrosobenzene, 2,4,6-tri-*tert*.butylnitroso-benzene, pentamethyl-nitrosobenzene) with radicals R_2 formed, in reaction (10). The inconclusiveness of the interpretation of the ESR spectrum of the spin adduct was excluded by using PMMA fully deuterated in the methyl and ester groups. It was emphasized[143] that attempts at detecting the formation of adducts with radicals R_4 failed which spoke of their absence or a very low concentration under experimental conditions. The occurrence of reaction (10) at 273 K leading to a reduction in the molecular weight of PMMA was corroborated on an example of specimens of the polymer subjected to mechanical degradation at 77 K.[104,144]

Later on,[145] it was found that the appearance of ruptures of macromolecules in PMMA at 293 K was caused by thermal degradation both of radicals R_3 and R_4 formed on addition of low-molecular radicals to isolated double bonds. R_4 radicals are also formed in photochemical reactions of radicals R_5, R_7 and radical anions R_{10}. Besides, it was found[146] that the primary act of direct PMMA photolysis with the quantum yield close to 0.5 results in the formation of isolated vinylidene bonds which, together with isolated double bonds formed in the course of thermal and photochemical reactions of radicals, can accept efficiently various low-molecular radicals to give radicals R_4, thus accelerating indirectly the degradation of the PMMA chain. In the case of mechanochemical degradation or low photolysis depths the major particle leading to PMMA chain degradation is radical R_3.

The influence of photochemical reactions of peroxy radicals R_{11} on PMMA ageing processes has not been the subject of special studies. It can only be remarked that just as in the case of peroxy radicals in polyolefins,[147] there was disclosed the reaction of photodissociation of such radicals in PMMA leading to the formation of molecular oxygen.[148] By analogy with photochemical reactions of peroxy radicals in polyolefins[147] and polystyrene,[70] it can be assumed that in the case of PMMA these processes will also result in the ruptures of C—C bonds.

Observed in poly(methyl acrylate)[113] and poly(ethyl acrylate)[149] were ESR spectral changes ascribed to photochemical reactions of radicals. It can be expected that the direction and efficiency of photoradical reactions in these polymers will be similar to those observed in PMMA.

2.5 Poly(Vinyl Acetate), Poly(Vinyl Alcohol), Poly(Vinyl Acetals), Poly(Vinylene Carbonate)

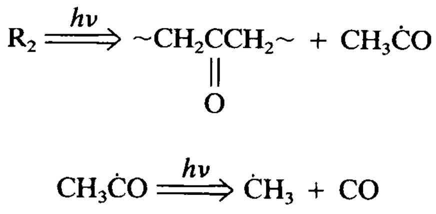
Table XIII lists the data referring to ESR spectral parameters, thermal stability and light sensitivity of radicals formed in poly(vinyl acetate) (PVAc), poly(vinyl alcohol) (PVA) and one of its acetals, poly(vinyl butyral) (PVB), on various exposures. By virtue of the fact that polyacetals also contain acetate and hydroxy groups, radicals similar to those recorded in PVAc and PVA can form in these polymers and photoradical processes similar in their mechanism and consequences can develop.

Poly(Vinyl Acetate)

Radical anions R_1 formed on PVAc exposure to ionizing radiation at 77 K interact in the dark with the molecules of the polymer to give radicals R_2 and R_4.[153] Such processes were earlier suggested for ketyl radical anions.[157] The character of the ESR spectra of PVAc excludes the possibility of the earlier assumed[158] dark protonation of R_1 with the formation of $R\dot{C}(OH)OR$ type radicals.

Exposure to light brings about R_1 dissociation with the formation of appropriate alkyl and acyl radicals with quantum yields close to 10^{-2} at 77 K and does not affect directly the MWD of the polymer.[10,43]

The action of light on radicals R_2 causes their dissociation by reaction (14)



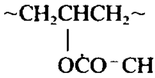
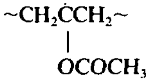
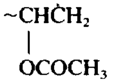
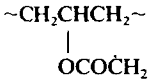
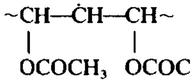
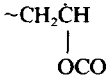
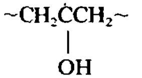
$$\begin{gathered} R_2 \xrightarrow{h\nu} {\sim}CH_2\underset{\underset{O}{\|}}{C}CH_2{\sim} + CH_3\dot{C}O \\ CH_3\dot{C}O \xrightarrow{h\nu} \dot{C}H_3 + CO \end{gathered} \tag{14}$$

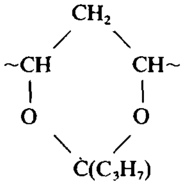
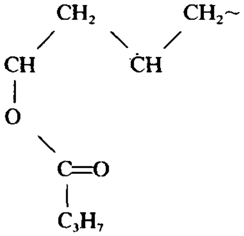
and the formation of $\dot{C}H_3$ radicals active under photolysis conditions and of carbonyl groups in the main chain of the polymer. PVAc molecular weight measurements in the course of reaction (14) showed that the reaction did not bring about degradation of the main chain of the polymer although efficient formation of methane and carbon monoxide (in amounts exceeding the quantity of radicals R_2 in the specimens) among gaseous reaction products was noted.[153] The quantum yield of reaction (14) measured at 77 K was 0.13 ± 0.04.[10]

Photochemical reactions of radicals R_3, R_4 and R_5 in PVAc have not been studied. It can only be noted that the very fact of the formation of radicals R_5 in PVA raises strong doubts since their assignment was made[112,160] on the basis of an erroneous,[153,160] idea of photoisomerization of radicals R_2. Photochemical reactions of

TABLE XIII

ESR spectral parameters and thermal stability and light sensitivity ranges of radicals, formed in PVAc, PVA and PVB

Radical	Number of lines in ESR spectrum	Parameters of ESR spectrum, mT	Methods of radicals generation	Range of thermal stability, K	Range of light sensitivity, nm	Literature
 $\sim CH_2\underset{\substack{\vert \\ O\dot{C}O{-}CH_3}}{C}HCH_2\sim$ (R_1)	2	$a_H^{CH_3} = 2.3$	Radiolysis PVA	—	$\lambda_{max} = 320$, $\varepsilon_{320} = 220 \pm 80$ m^2mol^{-1}	150
	2	$a_H^{CH_3} = 2.8$	Radiolysis PVA1	—	$\lambda_{max} = 290-300$, $\varepsilon_{300} = 250 \pm 100$ m^2mol^{-1}	151
	2	$a_H^{CH_3} = 2.6$	Radiolysis PVB	<160	$\lambda_{max} = 320$, $\varepsilon_{320} = 350 \pm 110$ m^2mol^{-1}	21, 152
 $\sim CH_2\underset{\substack{\vert \\ OCOCH_3}}{\dot{C}}CH_2\sim$ (R_2)	3	$a_H^{\beta_1} = 2.1$ $a_H^{\beta_2} = 0.3$	Radiolysis Photolysis	—	$\lambda_{max} < 300$, $\varepsilon_{365} = 40 \pm 10$ m^2mol^{-1}	111, 151, 153
 $\sim \underset{\substack{\vert \\ OCOCH_3}}{C}H\dot{C}H_2$ (R_3)	3		Radiolysis Mechanical Degradation	—	Spectral properties of alkyl radicals	3,150
 $\sim CH_2\underset{\substack{\vert \\ OCO\dot{C}H_2}}{C}HCH_2\sim$ (R_4)	3	$a_H^{\alpha} = 2.1$	Photolysis	—	$\lambda_{max} = 320^*$, $\varepsilon_{320} = 80$ m^2mol^{-1}	153, 154
 $\sim \underset{\substack{\vert \\ OCOCH_3}}{CH}{-}\dot{C}H{-}\underset{\substack{\vert \\ OCOCH_3}}{CH}\sim$ (R_5)	4	$a_H^{\alpha} = a_H^{\alpha} = 2.5$	Photolysis	—	Spectral properties of alkyl radicals	112
 $\sim CH_2\underset{\substack{\vert \\ OCOCH_3}}{\dot{C}}H$ (R_6)	5	$a_H^{\alpha} = a_H^{\beta_1} = 2.1$ $a_H^{\beta_2} = 4.2$	Radiolysis†	—	Spectral properties of radical R_2	153, 155
 $\sim CH_2\underset{\substack{\vert \\ OH}}{\dot{C}}CH_2\sim$ (R_7)	3	$a_H^{\beta_1} = 3.4$ $a_H^{\beta_2} = 0.5$	Radiolysis	<330–360	$\lambda_{max} = 225-235$, $\varepsilon_{230} = 170 \pm 50$ m^2mol^{-1}	151

~$CH_2\dot{C}H(OH)$ (R_8)	3	$a_H^{\alpha} = a_H^{\beta_1} = 2.3$	Mechanical Degradation of water solutions, 77 K	<170	Spectral properties of radical R_7	103
~$CH(OH)\dot{C}H_2$ (R_9)	4	$a_H^{\alpha} = 2.2$ $a_H^{\beta_1} = 3.7$	Mechanical Degradation of water solutions, 77 K	<170	Spectral properties of alkyl radicals	103
~$(CH{=}CH)_n\dot{C}{=}O$ (R_{10})	1	$\Delta H_{1/2} = 1.7$	Radiolysis	<150	λ_{max} = 375, 400, 500	156
 (R_{11})	3	$a_H^{\beta} = 3.1$	Radiolysis	<190–200	$\lambda_{max} \leq 250$, $\varepsilon_{254} = 230 \pm 70$ m^2mol^{-1}	43, 152
 (R_{12})	6	$a_H^{\alpha} = 2.1$ $a_H^{\beta} = 3.5$	Radiolysis	<200	$\lambda_{max} \leq 250$ $\varepsilon_{254} = 230 \pm 70$ m^2mol^{-1}	43, 152

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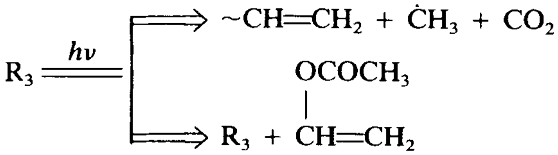
*Spectral properties of corresponding low molecular radicals.

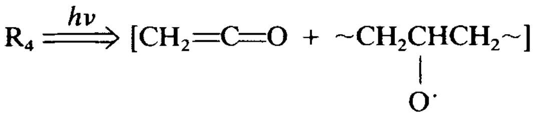
†Radiolysis of vinylacetate.

terminal radicals R_3 should occur on exposure to light with $\lambda < 300$ nm and involve the rupture of C—O or C—C bonds in β-position with respect to the free valency



$$R_3 \xrightarrow{h\nu} \begin{cases} \sim CH{=}CH_2 + \dot{C}H_3 + CO_2 \\ R_3 + \underset{\displaystyle OCOCH_3}{CH}{=}CH_2 \end{cases}$$

without rupturing, to any noticeable extent, the main chain of the polymer. Photochemical reactions of radicals R_4, by analogy with low-molecular analogues, will involve the splitting of C—O bond with sufficiently high values of quantum yields: 0.5–0.6[154]



$$R_4 \xrightarrow{h\nu} [CH_2{=}C{=}O + \sim CH_2\underset{\displaystyle O^{\cdot}}{CH}CH_2\sim]$$

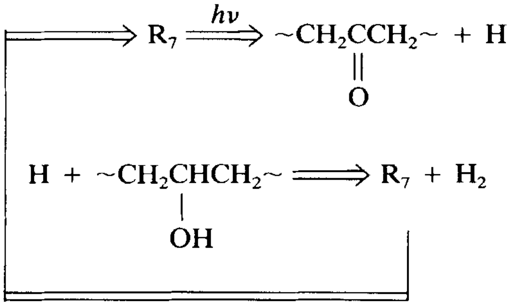
The final composition of the products will be determined by the competition between the intracage reactions of the formed intermediate products and the processes accompanied by their emergence beyond the cage bounds.

Thus, photochemical reactions of radicals in PVAc leading to the decomposition of ester groups and the formation of carbonyl groups in the main chain of the polymer are not a direct cause of ruptures in its main chain.

A comparison of the kinetics of accumulation of radicals and of molecular weight changes in PVAc on photolysis sensitized by aromatic compounds showed[141] that the degradation of the main chain occurs in thermal reactions of radicals (presumably R_2) taking place in warming the polymer up from low to room temperature. In the course of repeated "photolysis—warming-up" cycles the light stability of PVA goes down which is attributed[119] to the formation and subsequent reactions of carbonyl groups formed in the main chain.

Poly(Vinyl Alcohol)

R_7, the most thermally stable radicals in PVA, undergo dissociation on exposure to light with $300 < \lambda < 400$ nm[151,161] by reaction (15) peculiar to α-hydroxyalkyl radicals[151]

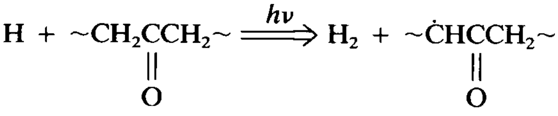


$$R_7 \xrightarrow{h\nu} \sim CH_2\underset{\displaystyle \overset{\|}{O}}{C}CH_2\sim + H$$

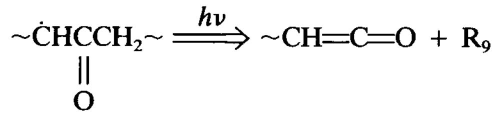
$$H + \sim CH_2\underset{\displaystyle OH}{CH}CH_2\sim \Longrightarrow R_7 + H_2 \qquad (15)$$

Photolysis results in the formation of carbonyl groups and hydrogen in amounts exceeding many times the starting amount of radicals which testifies to the occurrence of a photoradical chain reaction. The chain length characterized in PVA by the number of hydrogen molecules formed within time *t* per radical participating in the photochemical reaction—$[H_2]_t/\int R\,dt$—reached high values after 4 h of photolysis—17, 42 and 103—for different photolysis temperatures—98, 188 and 273 K, respectively.[161]

Rupture in the main chain of PVA macromolecules can result from the reaction of photodecomposition and thermal decomposition of radicals and from photochemical reactions involving carbonyl groups in the main chain. A reduction in the molecular weight of PVA caused by photochemical reactions of radicals R_7 was attributed to reactions (16, 17)[161]



$$H + {\sim}CH_2\underset{\underset{\displaystyle O}{\|}}{C}CH_2{\sim} \xrightarrow{h\nu} H_2 + {\sim}\dot{C}H\underset{\underset{\displaystyle O}{\|}}{C}CH_2{\sim} \qquad (16)$$



$$ {\sim}\dot{C}H\underset{\underset{\displaystyle O}{\|}}{C}CH_2{\sim} \xrightarrow{h\nu} {\sim}CH{=}C{=}O + R_9 \qquad (17)$$

similar to the well known reactions of radicals formed in low-molecular aldehydes and ketones.[163,164]

It was concluded[161] that the decrease in the molecular weight of PVA, with other conditions being equal, is the stronger the higher the initial concentration of radicals and the photolysis temperature which was thought to be due to the growth of the efficiency of reactions (16, 17) under these conditions.

Photochemical reactions of radicals R_8–R_{10} in PVA have not been studied. Photolysis of radicals R_8 should proceed similarly to reaction (15) and that of radicals R_{10} to processes of photodissociation of acyl radicals.[165]

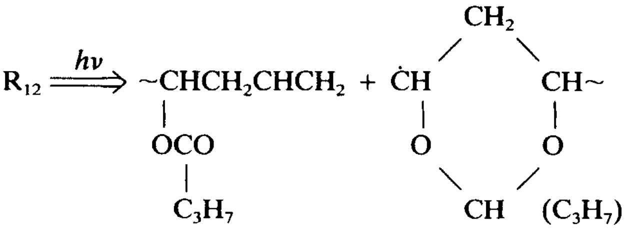
Poly(Vinyl Acetals)

Photoradical processes in poly(vinyl acetals) have been studied most comprehensively on PVB. R_1 radicals undergoing stabilization in PVB take part in dissociation reactions discussed above. For radical anions in poly(vinyl ethylal), another channel of their consumption was disclosed, the channel (electron photoejection reaction[166]) leading to the decay of paramagnetic centres with the efficiency close to that of photodissociation processes, $\approx 10^{-2}$.

The initiation stage of photoradical degradation of PVB on exposure to ionizing radiation or light is the formation of radicals R_{11} which at $T > 190$–200 K undergo photochemical or thermal decomposition with the formation of alkyl type radicals R_{12}

$$R_{11} \xrightarrow{h\nu} R_{12} \tag{18}$$

$$R_{11} \Longrightarrow R_{12}\ (T > 190\text{–}200\ \mathrm{K})$$



(19)

$$R_{12} + R_{11} \Longrightarrow R_{12}H + R_{11} \qquad (T > 140\ \mathrm{K})$$

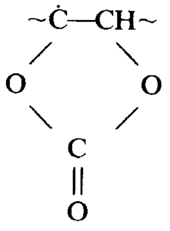
$$R_{12} + R_{12} \Longrightarrow R_{12} - R_{12} \qquad (T > 180\ \mathrm{K})$$

The quantum yields of reactions (18, 19) measured on exposure to light with $\lambda = 254$ nm at 77 K were about $(4 \pm 2)\cdot 10^{-2}$.[43,152] Radicals R_{12} at $T > 140$ K, on interacting with the polymer molecules, reduce radicals R_{11}. On exposure to light with $\lambda < 300$ nm at low temperatures (below 180 K), reaction (19) leading to ruptures in the main chain of PVB occurs. At higher temperatures the decay of R_{12} may give rise to cross-linking. The suggested mechanism was corroborated by the results of studies of MWD changes in PVB on photolysis in various temperature regions sensitized by aromatic compounds.[43]

Thus, in PVB cross-linking of polymer chains is the result of recombination of radicals R_{12} whose photochemical reactions lead to the degradation of the main chain of the polymer. The relative contribution of any certain process to the ageing mechanism is determined by the spectral composition of the light used and by photolysis temperature.

Poly(Vinylene Carbonate)

Figure 4a,g presents the ESR and UV spectra of middle macroradicals



stabilized in poly(vinylene carbonate) at 77 K. These radicals produce in the ESR

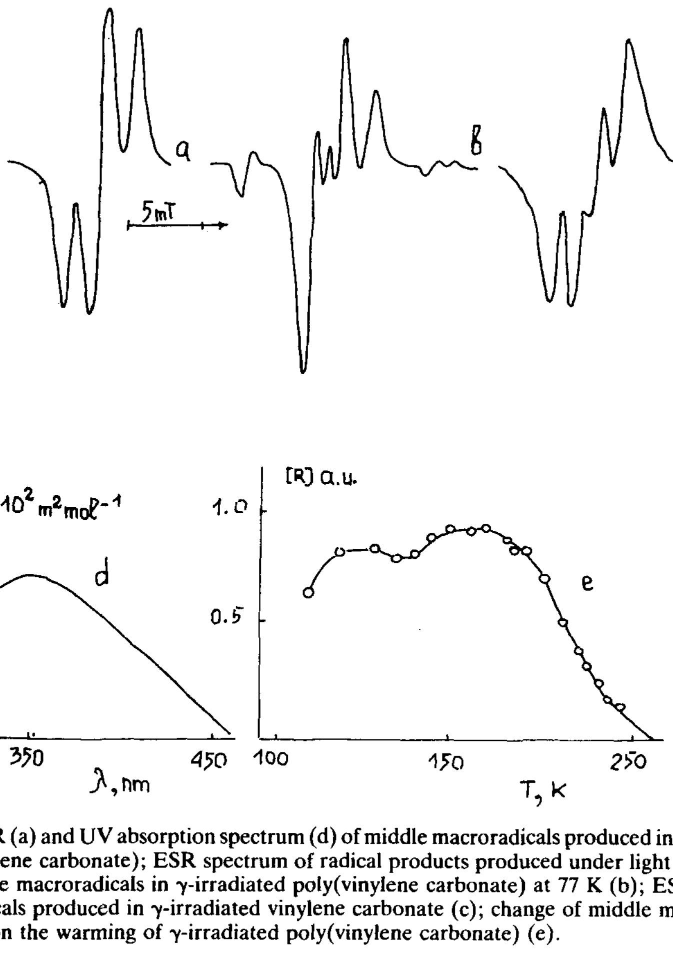
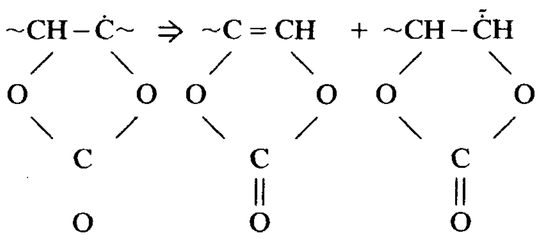


FIGURE 4 ESR (a) and UV absorption spectrum (d) of middle macroradicals produced in γ-irradiated at 77 K poly(vinylene carbonate); ESR spectrum of radical products produced under light action (λ = 313 nm) on middle macroradicals in γ-irradiated poly(vinylene carbonate) at 77 K (b); ESR spectrum of end macroradicals produced in γ-irradiated vinylene carbonate (c); change of middle macroradicals concentration upon the warming of γ-irradiated poly(vinylene carbonate) (e).

spectrum a signal consisting of three lines with splitting of ≃1.9 mT and in UV spectrum-absorption band with $\lambda_{max} = 350$ nm and $\varepsilon_{350} = 120 \pm 30$ m²mol⁻¹. The middle macroradicals are stable below 180 K and at temperatures higher 260 K they cannot stabilized in poly(vinylene carbonate).[167] The study of the nature of macroradicals, produced at mechanodegradation of poly(vinylene carbonate) has been show that the middle macroradicals in this case produce in the ESR spectrum a signal consisting of two lines with splitting ≃3.2 mT.[168] The distinction between the data[167,168] can be connected with the procedure of analysis ESR spectra in the last case.

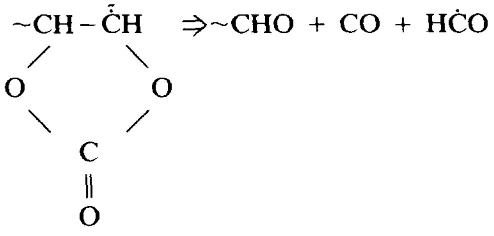
The action of light (λ < 450 nm) on the middle macroradicals in poly(vinylene carbonate) at 77 K causes their disappearance and formation of formyl radicals HCO. The action of light (λ < 350 nm) on the γ-irradiated polymer at 77 K causes formation of formyl radicals and radical anions $CO_3^{\overline{\cdot}}$ [169] (Figure 4b).

The photochemical reactions of middle macroradicals in poly(vinylene carbonate) seem to be similar to the earlier observed in propylene carbonate[170]:



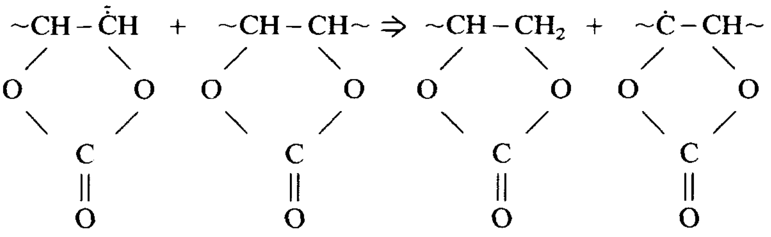
(20)

However under photolysis of middle macroradicals in poly(vinylene carbonate) the authors[167] cannot observed the formation of the end macroradicals. So far as at the mechanodegradation of poly(vinylene carbonate), γ-irradiation of vinylene carbonate[167] the end macroradicals are observed at the temperature below 220 K (these radicals produce in the ESR spectrum four lines with a_{α}^{H} = 1.4 mT, a_{β}^{H} = 3.5 mT) (Figure 4c). The authors[167] are assumed that these radicals produce in reaction (20) in vibrationally excited states. The vibrationally excited end macroradicals dissociate with formation of formyl radicals



(21)

or react with polymer and reduce the middle macroradicals



(22)

The quantum yields of reactions (20, 21) are presented in Table XIV.

The possibility of decomposition of vibrationally excited radicals has been ex-

TABLE XIV

Quantum yields of photochemical reactions of middle macroradicals in poly(vinylene carbonate) under light action with different photon energy[167]

λ, HM	$\Phi_{20} \cdot 10^2$	$\Phi_{21} \cdot 10^2$
254	1.4 ± 0.3	1.1 ± 0.2
313	1.1 ± 0.2	0.5 ± 0.3
365	0.6 ± 0.1	0.3 ± 0.1

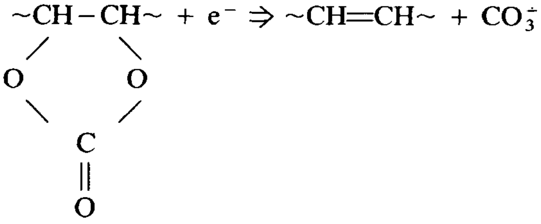
TABLE XV

Molecular mass change of poly(vinylene carbonate) under different action[119]

Sample of poly(vinylene carbonate)	$M_n \cdot 10^{-4}$	Dose of light absorbed by middle macroradicals, 10^{19} quanta
Initial polymer	17.5	—
γ-irradiated (20 kGr) polymer	9.3	—
γ-irradiated (20 kGr) and photolyzed polymer:		
λ = 254 nm	7.6	0.41
λ = 313 nm	5.0	2.43
λ = 365 nm	5.9	1.05

aminating at the study of mechanodegradation of polyorganosiloxanes.[171] The fact that reaction (21) take place has been confirming by decreasing polymer molecular mass under light action ($\lambda < 400$ nm) on γ-irradiated at 77 K poly(vinylene carbonate)[119] (Table XV).

In γ-irradiated propylene carbonate the generation of radical anions $CO_3^{\overline{\cdot}}$ is a result of dissociate addition of electrons produced under light excitation of ionic radiolysis products to propylene carbonate molecules.[170] The formation of radical anions $CO_3^{\overline{\cdot}}$ in poly(propylene carbonate) under light action ($\lambda < 350$ nm) seem to be similar to the observed reaction in propylene carbonate.[170]



The stabilization of ionic products of radiolysis poly(vinylene carbonate) at 77 K has been confirming the existence on the warm curves the regions of increasing the concentration of middle macroradicals produced in recombination reactions of ionic particles (Figure 4d).

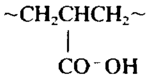
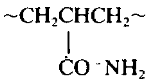
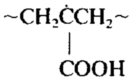
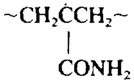
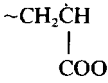
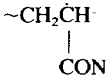
Thus, photochemical reactions of macroradicals in poly(vinylene carbonate) lead to both effective main chain scission and degradation of polymer groups at the temperature below 260 K, i.e. in the region of thermal stability of middle macroradicals.

2.6 Poly(Acrylic Acid), Poly(Acryl Amide)

The compositions of the radical species formed in poly(acrylic acid) (PAA) and poly(acryl amide) (PAAm) on low-temperature radiolysis (Table XVI) are identical: radicals R_3 and R_4 and radical anions R_1 and R_2. The five-line ESR spectrum with the 2.2 mT splitting ascribed[175] to radicals R_4 is due[176] to the formation of $CH_3\dot{C}HCONH_2$ radicals on radiolysis of PAAm containing large amounts of the monomer.[179] The warming-up of PAA and PAAm (irradiated at 77 K) to 300 K

TABLE XVI

ESR spectral parameters and thermal stability and light sensitivity ranges of radicals, formed in PAA and PAAm

Radical	Number of lines in ESR spectrum	Parameters of ESR spectrum, mT	Methods of radicals generation	Range of thermal stability, K	Range of light sensitivity, nm	Literature
 $\sim CH_2\underset{\substack{\vert\\ CO\text{-}OH}}{CH}CH_2\sim$ (R_1)	1	$\Delta H_{1/2} = 1.4$ $g = 2.003$	Radiolysis	<140	$\lambda < 450$, $\varepsilon_{320} = 120 \pm 40$ m^2mol^{-1}	9, 121
 $\sim CH_2\underset{\substack{\vert\\ \dot{C}O\text{-}NH_2}}{CH}CH_2\sim$ (R_2)	1	$\Delta H_{1/2} = 2.1$ $g = 2.003$	Radiolysis	<150	$\lambda < 450$, $\varepsilon_{330} = 150 \pm 40$ m^2mol^{-1}	172, 173
 $\sim CH_2\underset{\substack{\vert\\ COOH}}{\dot{C}}CH_2\sim$ (R_3)	3	$a_H^{\beta_1} = 2.6$	Radiolysis	$<180-210$	$\lambda < 350$, $\varepsilon_{270} = 40 \pm 10$ m^2mol^{-1}	121, 174
 $\sim CH_2\underset{\substack{\vert\\ CONH_2}}{\dot{C}}CH_2\sim$ (R_4)	3 5	$a_H^{\beta_1} = 2.5$ $a_H^{\beta} = 2.2$	Radiolysis Photolysis	<200	$\lambda < 350$, $\varepsilon_{290} = 200 \pm 70$ m^2mol^{-1}	173, 175 173, 175, 176
 $\sim CH_2\underset{\substack{\vert\\ COOH}}{\dot{C}H}$ (R_5)	3	$a_H^{\alpha} = 2.0$ $a_H^{\beta_1} = 2.5$	Radiolysis Mechanical Degradation	<330	Spectral properties of radical R_3	121, 177, 178
 $\sim CH_2\underset{\substack{\vert\\ CONH_2}}{\dot{C}H}$ (R_6)	3	$a_H^{\alpha} = 2.0$ $a_H^{\beta_1} = 2.5$	Radiolysis	<350	Spectral properties of radical R_4	173

or their irradiation at room temperature leads to the stabilization only of R_5 and R_6 formed in the growing chain in the course of interactions of the radicals with the monomer.[18]

Studies of photochemical reactions of radical anions R_1 and R_2 in PAA and PAAm showed[10,121,176] that photolysis leads to their disappearance and to a reduction in the total concentration of paramagnetic centres which is believed to be associated with electron photoejection processes.

$$R_1 \xRightarrow{h\nu} e^- + {\sim}CH_2CH(COX)CH_2{\sim}, \text{ where } X = OH, NH_2.$$

The efficiency of the process increases from a relatively low value ($\approx 10^{-2}$) by a factor of 1.5–2 with the growth of the photon energy. Photochemical reactions of radical anions in PAA and PAAm do not give rise either to any other radical species or to chemical transformations of macromolecules and therefore do not exert any noticeable influence on the progress of ageing of the polymers.[159]

A detailed analysis of the mechanism of photolysis of radicals R_3 and R_4,[121,175,176] with invoking relevant data for model low-molecular compounds,[119,180] made it possible to assert that the main direction of these processes is dissociation

$$R_3(R_4) \xRightarrow{h\nu} {\sim}CH_2C({=}C{=}O)CH_2{\sim} + \dot{X}. \qquad (23)$$

rather than isomerization, as was suggested earlier.[173,181]

The formation of ketene on photodegradation of radicals R_3 and R_4 was corroborated spectroscopically in the solid phase (from the appearance of a characteristic absorption band with the maximum in the 365 nm region[182]) and by mass spectroscopic determinations of carbon monoxide among its photolysis products

$${\sim}CH_2C({=}C{=}O)CH_2{\sim} \xRightarrow{h\nu} 1.3({\sim}CH_2\ddot{C}CH_2{\sim}) + CO \qquad (24)$$

Photolysis of radicals R_3 and R_4 is accompanied by their decay obeying the second order kinetic law with the effective rate constant linearly dependent on light intensity.[176] The occurrence of reactions involving free valency migration leads to the development of degradation processes throughout the whole volume of PAA or PAAm.

Radicals R_5 and R_6 in the growing chain take part in photochemical reactions similar to those discussed above.

The formation of ketenes and carbon monoxide in amounts exceeding many times the initial amount of macroradicals in PAA and PAAm testifies[121,175,176] to the occurrence of photoradical chain reactions. The chain length determined as the ratio of the amount of the formed products (ketene and carbon monoxide) to the amount of recombined radicals grows with photolysis time and approaches 40 under experimental conditions.

The measured[121,176] quantum yields of the elementary stages (23, 24) and effective recombination constants of radicals were employed in mathematical simulation of

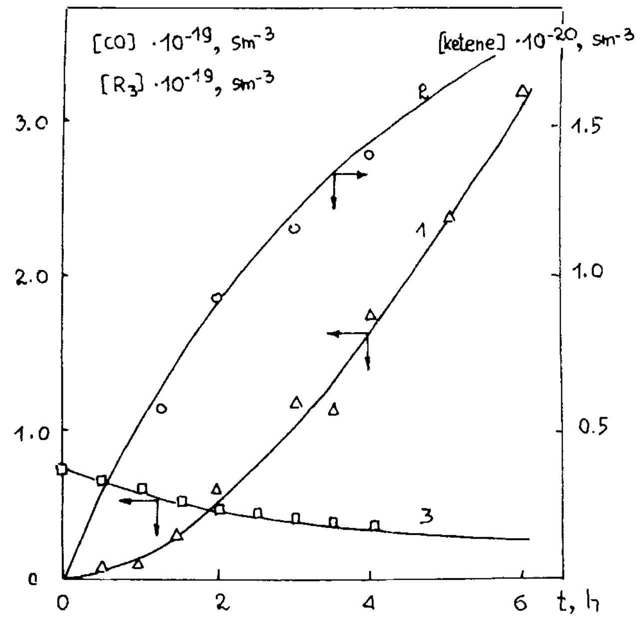


FIGURE 5 Kinetic curves for accumulation of carbon monooxide (1) and ketene (2), and consumption of radicals R_3 (3) upon the photolysis $\lambda \geq 280$ nm of PAA at 77 K.[175]

the process kinetics (Figure 5); the results of simulation showed good agreement between calculated and experimental data.

MWD determinations of PAA in the course of photochemical reactions of radicals R_3 demonstrated[175,176] that at short photolysis times the MWD curves move towards lower molecular weights which attested to the occurrence of photochemical reactions of radicals R_3 leading to ruptures in the main chain

$$R_3 \xrightarrow{h\nu} \sim CH_2C(COOH){=}CH_2 + \dot{C}H(COOH)CH_2\sim.$$

An evaluation of the quantum yield of the reaction gives $\approx 1.5 \cdot 10^{-2}$ which is much lower than the quantum yields of reaction (23) being as large as 0.1–0.2 in PAA and PAAm.[121,175,176]

At large photolysis times, effective cross-linking in the polymer ascribed[121,175,176] to the reactions of carbenes formed in process (24) is observed.

2.7 Polyoxides

In the course of photolysis (initiated and sensitized by aromatic compounds[2,189,190]) of polyoxides subjected to the action of ionizing radiation[183–186] and mechanical loads,[18,187] middle and end macroradicals and paramagnetic particles having a singlet ESR spectrum undergo stabilization (Table XVII).

The exposure of polyoxides to light leads to the formation of such low-molecular radicals as $H\dot{C}O$, $\dot{C}H_3$ which points to the occurrence of secondary photochemical

TABLE XVII

ESR spectral parameters and the thermal stability and light sensitivity ranges of radicals, formed in some polyoxides

Radical	Number lines in ESR spectrum	Parameters of ESR spectrum, mT	Methods of radicals generation	Range of thermal stability, K	Range of light sensitivity, nm	Literature
$\sim O\dot{C}H_2$	3	$a_H^{\alpha} = 1.8–2.5$	Radiolysis Photolysis Mechanical Degradation	<250–270	$\lambda < 360$, $\varepsilon_{260} = 190 \pm 60$ m^2mol^{-1}	9, 18, 119
$\sim O\dot{C}HO\sim$	2	$a_H^{\alpha} = 1.1–1.6$ $g = 2.0039–2.0054$	Radiolysis Mechanical Degradation	<350–370	Spectral properties analogous to radicals $O\dot{C}H_2$	9, 18
$\sim CH_2\dot{O}$*	1	$\Delta H_{1/2} = 1.7–2.2$	Radiolysis Photolysis Mechanical Degradation		—	9
$\sim O\dot{C}HCH_2\sim$	3	$a_H^{\alpha} = a_H^{\beta_1} =$ 1.5–2.1 $a_H^{\beta_2} < 0.5$	Photolysis Radiolysis Mechanical Degradation	—	$\varepsilon_{235} = 150 \pm 10$	2, 18
$\sim O\dot{C}HCH_3$	5	$a_H^{\alpha} = a_H^{CH_3} = 1.9$	Photolysis	—	Spectral properties analogous to radicals $\sim O\dot{C}HCH_2\sim$	119
$\sim OCH_2\dot{C}H_2$	6	$a_H^{\alpha} = 2.2$ $a_H^{\beta_1} = 5.0$ $a_H^{\beta_2} = 2.1$	Mechanical Degradation of water solutions, 77 K	—	Spectral properties of alkyl radicals	119

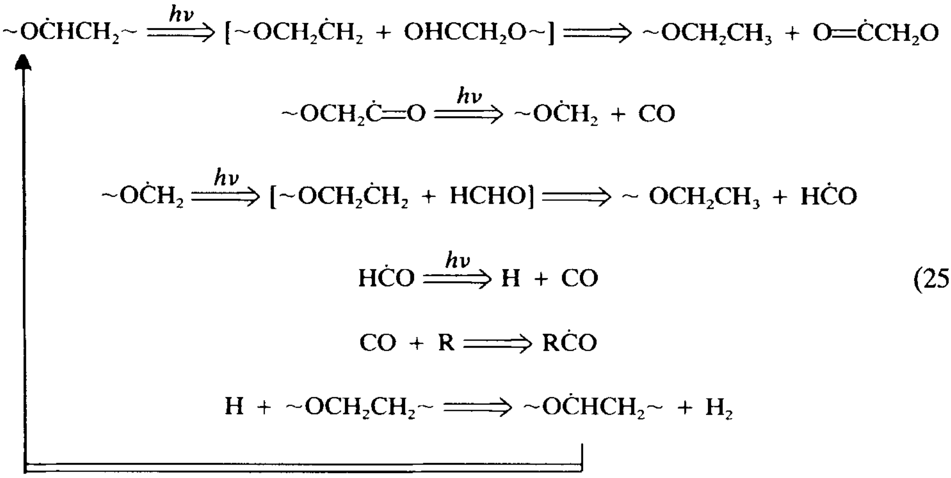
*ESR spectrum belongs to acyl radicals $R\dot{C}O$.

reactions of intermediate products.[189,190] Temperature rise from 77–100 K stabilizes mostly middle radicals in polyoxides.

It follows from Table XVII that the optical characteristics of radicals formed in polyoxides are close to those determined in the case of radicals in low-molecular analogues of polyoxides.[2]

The earlier proposed schemes[188] of photochemical and some dark reactions of radicals in polyoxides do not stand up to criticism for they were based on a misinterpretation of the singlet ESR spectra belonging, in reality, to acyl rather than alkoxy radicals.

Investigations of the kinetics and mechanism of the transformation of radicals formed in polyoxides on their sensitized and initiated photolysis, γ-irradiation and mechanical degradation made it possible to present[119,191] the most precise and comprehensive picture of the reactions involved. Thus, for poly(ethylene oxide) the scheme of photochemical and thermal reactions of radicals can be depicted as follows:



$$
\begin{gathered}
\sim\!O\dot{C}HCH_2\!\sim\; \xrightarrow{h\nu} [\sim\!OCH_2\dot{C}H_2 + OHCCH_2O\!\sim] \Longrightarrow \sim\!OCH_2CH_3 + O{=}\dot{C}CH_2O \\
\sim\!OCH_2\dot{C}{=}O \xrightarrow{h\nu} \sim\!O\dot{C}H_2 + CO \\
\sim\!O\dot{C}H_2 \xrightarrow{h\nu} [\sim\!OCH_2\dot{C}H_2 + HCHO] \Longrightarrow \sim OCH_2CH_3 + H\dot{C}O \\
H\dot{C}O \xrightarrow{h\nu} H + CO \\
CO + R \Longrightarrow R\dot{C}O \\
H + \sim\!OCH_2CH_2\!\sim\; \Longrightarrow \sim\!O\dot{C}HCH_2\!\sim + H_2
\end{gathered}
\tag{25}
$$

The kinetic curves of the accumulation of acyl and formyl radicals on photolysis of middle $\sim\!O\dot{C}HCH_2\!\sim$ and end $\sim\!O\dot{C}H_2$ radicals in poly(ethylene oxide) displayed in Figure 6 speak in favour of the processes given in the scheme.

The possibility of a different course of reaction (25) is indicated by the formation of radicals $\sim\!O\dot{C}HCH_3$ in a frozen poly(ethylene oxide) solution containing Fe^{2+} and H_2SO_4 additives, i.e. in a system which is an efficient photogenerator of hydrogen atoms

$$
\begin{gathered}
\sim\!O\dot{C}HCH_2\!\sim\; \xrightarrow{h\nu} \sim\!OCH{=}CH_2 + \dot{O}CH_2CH_2\!\sim \\
\sim\!OCH{=}CH_2 + H \Longrightarrow \sim\!O\dot{C}HCH_3
\end{gathered}
\tag{26}
$$

It is to be noted that the mechanisms of photochemical reactions of radicals in

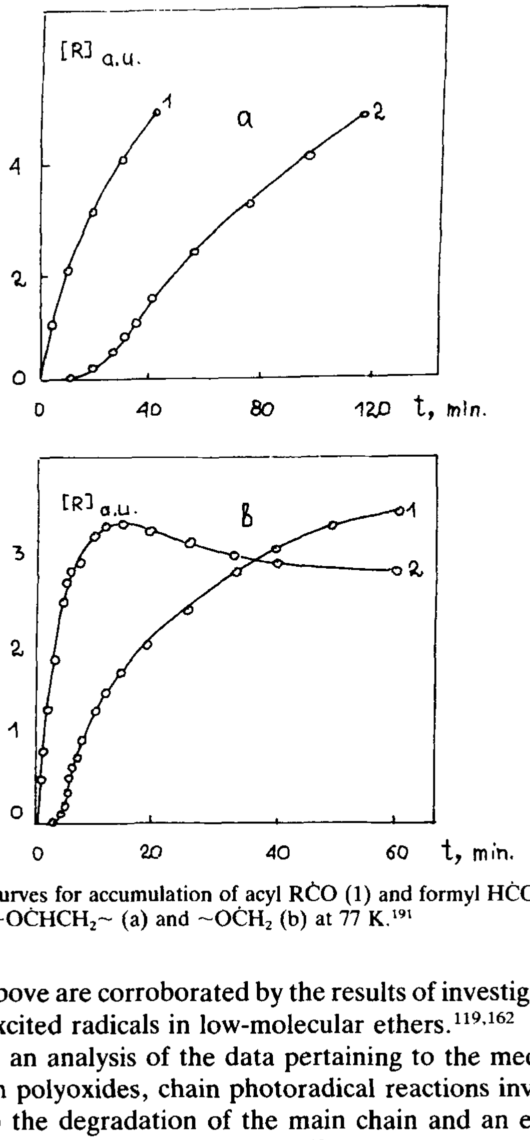


FIGURE 6 Kinetic curves for accumulation of acyl $R\dot{C}O$ (1) and formyl $H\dot{C}O$ (2) radicals upon the photolysis of radicals $\sim O\dot{C}HCH_2\sim$ (a) and $\sim O\dot{C}H_2$ (b) at 77 K.[191]

polyoxides given above are corroborated by the results of investigations of reactions of electronically excited radicals in low-molecular ethers.[119,162]

As follows from an analysis of the data pertaining to the mechanism of photoradical reactions in polyoxides, chain photoradical reactions involving stages (25, 26) and leading to the degradation of the main chain and an experimentally determined reduction in the molecular weight[119] occur in these polymers. An evaluation of the quantum yield of the chain rupture reaction in polyformaldehyde caused by photolysis of the middle macroradical gave at 77 K $\simeq 8 \cdot 10^{-3}$ (exposure to light with $\lambda = 313$ nm).

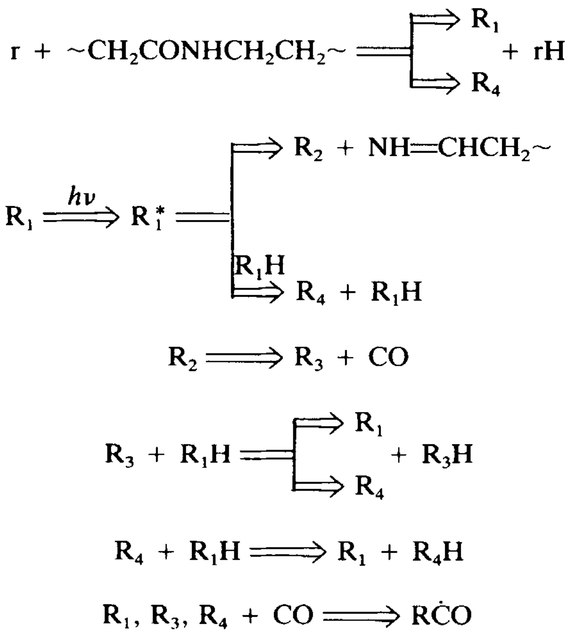
2.8 Polyamides and Aliphatic Polyurethanes

Polyamides (PA) and aliphatic polyurethanes (PU) find extensive application for different purposes; on the other hand, they alter strongly their service properties as a result of light and photooxidative ageing. The action of light on these polymers may involve both their direct photolysis and secondary photochemical reactions of various intermediate products appearing in the polymer as a result of energy effects differing in their nature.

Long-wave n,π^* absorption of the amide group is characterized by low values of the extinction coefficients ($\varepsilon < 10$ m^2 mol^{-1}) at its absorption maximum (210–240 nm). It was also reported that a $\lambda \simeq 300$ nm the ε value for pure amides is $2 \cdot 10^{-3}$ m^{2}mol^{-1} [192]

Some studies dedicated to the elucidation of the nature of radicals formed on PA exposure to light have not resulted in sufficiently unequivocal interpretations of the ESR data.[193-195] The assignment of the observed ESR signals to the radicals of a primary and secondary origin was complicated by the well known fact of light sensitivity of radicals in PA.[196] The nature of radicals and the mechanism of their mutual transformation in PA were investigated most thoroughly and reliably on an example of photolysis of oriented PA films initiated by $FeCl_3$ additives.[197,198] Table XVIII gives the data referring to the structure, ESR spectral parameters, thermal stability and light sensitivity of some radicals formed under these conditions.

The following scheme of reactions substantiated by the results of studies of the nature of the transforming radical centres and of the kinetics of their mutual transformations was proposed[197,198]:



$$r + {\sim}CH_2CONHCH_2CH_2{\sim} \Longrightarrow \left[\begin{array}{l} \Longrightarrow R_1 \\ \Longrightarrow R_4 \end{array}\right. + rH$$

$$R_1 \xrightarrow{h\nu} R_1^* \Longrightarrow \left[\begin{array}{ll} \Longrightarrow R_2 + NH{=}CHCH_2{\sim} & (27) \\ \xrightarrow{R_1H} R_4 + R_1H & (28) \end{array}\right.$$

$$R_2 \Longrightarrow R_3 + CO \tag{29}$$

$$R_3 + R_1H \Longrightarrow \left[\begin{array}{l} \Longrightarrow R_1 \\ \Longrightarrow R_4 \end{array}\right. + R_3H \tag{30}$$

$$R_4 + R_1H \Longrightarrow R_1 + R_4H \tag{31}$$

$$R_1, R_3, R_4 + CO \Longrightarrow R\dot{C}O \tag{32}$$

Phototransformations of R_1 type radicals were observed in low-molecular amides and polyamides.[197-202] It is noteworthy that radicals of this type are formed in amides and polyamides on their sensitized an initiated photolysis,[197-199,203] exposure to ionizing radiation,[196] mechanical degradation,[18] i.e. on the action of energetic factors differing in their nature. Absorption spectra of radicals R_1 with the maximum at 360–380 nm were recorded in irradiated polycaproamide.[196,199] It is safe to say that the absorption

TABLE XVIII

ESR spectral parameters and thermal stability and light sensitivity ranges of radicals in PA

	θ* = 0		θ = 90°			
Radical	Number of lines in ESR spectra	Parameters of ESR spectra	Number of lines in ESR spectra	Parameters of ESR spectra	Thermal stability, °K	Note
$\sim CH_2CONH\dot{C}HCH_2\sim$ (R_1)	4	2.8 ± 0.1 mT	5	7.2 mT	<293	Sensitive to the light $\lambda = 365$ nm action
$\sim CH_2\dot{C}O$ (R_2)	1	$g = 2.0010 \pm 0.0004$ $\Delta H_{1/2} = 1.55 \pm 0.1$ mT	1	$g = 2.0010 \pm 0.0004$ $\Delta H_{1/2} = 1.55 \pm 0.1$ mT	<273	Sensitive to the light $\lambda \geq 445$ nm action
$\sim CH_2\dot{C}H_2$ (R_3)	6	2.2 ± 0.1 mT	6	2.2 ± 0.1 mT	<117	—
$\sim CH_2\dot{C}HCH_2\sim$ (R_4)	4	2.8 ± 0.1 mT	10	1.6 ± 0.1 mT	<156	—

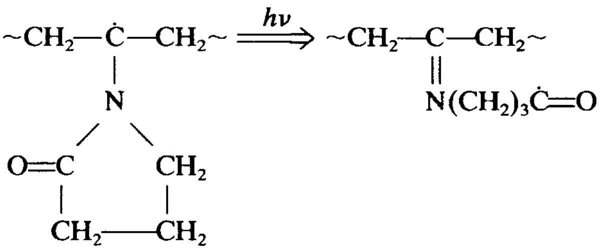
*θ = the angle between the magnetic field direction and the axis of films orientation.

spectra of these species are identical with those recorded in amides (absorption maxima at 235–265 and 350–380 nm with extinction coefficients being 500–700 and 160–200 m^{2}mol^{-1}, respectively[4]).

Reaction (28) was taken into consideration[197,198] only on the basis of the earlier data[196] since the researchers were unable to obtain any information supporting its occurrence in the polymer. The scheme of reactions presented above is fully consistent with the results obtained in studies of phototransformation of radicals in low-molecular amides.[199–202] Of greatest significance in this scheme are reactions (27, 29–32) since these particular reactions ensure the photoradical chain mode of the process leading to the efficient degradation of the polymer's main chain.

Photodissociation of $\sim$CHRCONH$\dot{C}$HR$\sim$ radicals giving rise to the splitting of the peptide bond was observed in silk fibroin (subjected to mechanical degradation at 77 K) on exposure to light in the 330–390 nm wavelength range.[204,205]

Photochemical reactions of poly(vinyl pyrrolidone) middle radicals similar in their structure to amide radicals lead, on exposure to light with $\lambda = 313$ nm at 77 K, to the formation of acyl radicals caused by the pyrrolidone ring opening[206]



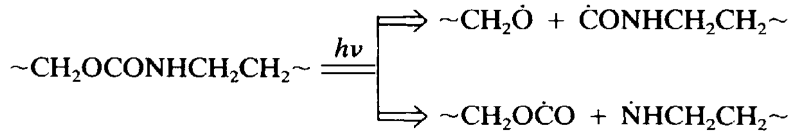
(33)

Measurements of the molecular weight distribution of the polymer in the course of this process indicated that ruptures in the main chain of the polymer did not appear.

Similar reactions were observed in radicals stabilized in γ-irradiated β-chloroethylpyrrolidone-2 at 77 K on exposure to light.[119]

It took a comparatively long time[207] to succeed in recording the formation of peroxide radicals $R_1\dot{O}_2$ on PA photooxidation regardless of the fact that these species had been convincingly detected on mechanical degradation and γ-irradiation of PA. Subsequent studies[208,209] not only disclosed the formation of $R_1\dot{O}_2$ radicals on PA photooxidation but also demonstrated that their decay on exposure to light follows the bimolecular law, the effective rate constant being proportional to the intensity of light. The mechanism of this process is unclear but high values of the effective rate constant point to the formation of low-molecular radicals—free valency carriers in the photostimulated recombination reaction.

The major primary photochemical processes taking place on PU exposure to light are the reactions of dissociation at C—N and C—O bonds in the urethane group[210–213]



$$\sim\mathrm{CH_2OCONHCH_2CH_2}\sim \xrightarrow{h\nu} \begin{cases} \sim\mathrm{CH_2\dot{O}} + \mathrm{\dot{C}ONHCH_2CH_2}\sim \\ \sim\mathrm{CH_2O\dot{C}O} + \mathrm{\dot{N}HCH_2CH_2}\sim \end{cases}$$

It is assumed in this case that primary radicals are not stabilized but undergo further transformations. It was possible to demonstrate,[214] on an example of the kinetics of accumulation of radicals on photolysis of a PU model compound—methyl-*N*-ethyl carbamate—that good agreement between the calculations and experimental results can only be obtained on the assumption that C—O bond scission in the urethane group is the major event in the primary act (Figure 7). Even in the case of poly(oxime urethane), a photodegradable polymer containing a weak N—O bond in its structure, are the experimental data referring to the composition of radical and gaseous low-temperature photolysis products explained by C—O bond scission in the primary act.[215]

Primary radicals formed on PU photolysis, mechanical degradation or exposure to ionizing radiation[216,217] give rise to rather stable radicals of the $\sim CH_2OCONH\dot{C}HCH_2\sim$ type. The possibility of photochemical reactions of radicals of this kind was indicated by the results of initiated photolysis experiments[210] in which the established stationary concentration of the radicals was independent of light intensity. The proposed mechanism of the reaction of dissociation of these radicals[210] is similar to that discussed above for PA

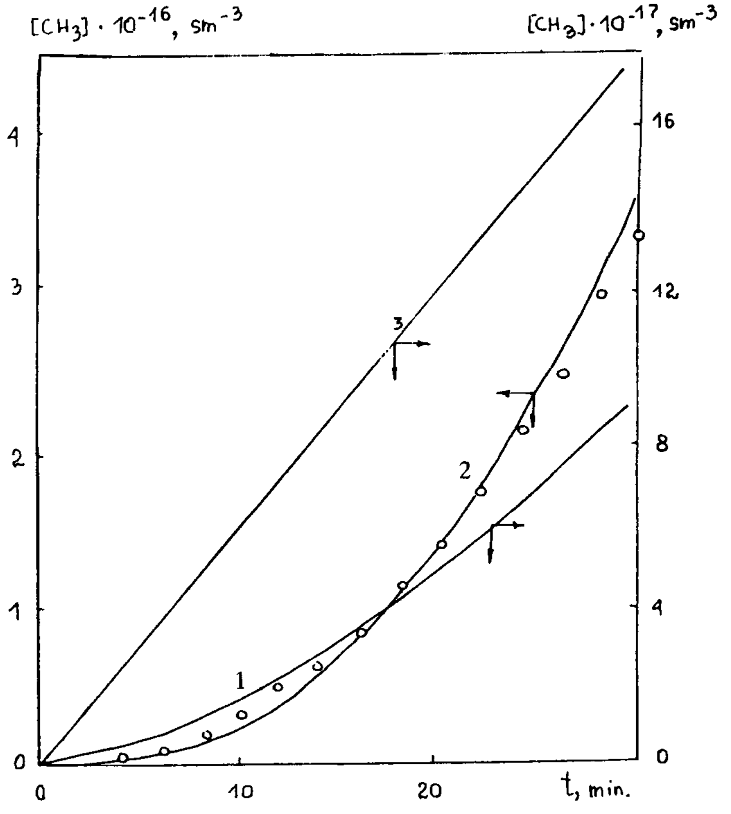
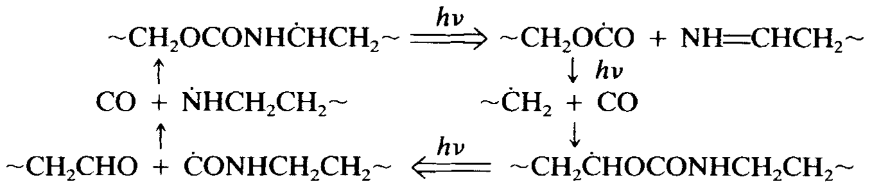


FIGURE 7 The kinetics of accumulation of methyl radicals upon the photolysis of methyl-*N*-ethylcarbamate at 77 K (points—experimental values, curves—calculated values at different mechanisms of primary act: 1—C(=O)—N bond rupture, 2—C(=O)—O bond rupture, 3—C(=O)O—C bond rupture).[214]

$$\sim CH_2OCONH\dot{C}HCH_2\sim \xrightarrow{h\nu} \sim CH_2O\dot{C}O + NH{=}CHCH_2\sim \tag{34}$$

Detailed investigations of the mechanism of photochemical reactions in PU demonstrated[119,216,217] that the action of light with $\lambda = 365$ nm on $\sim CH_2OCONH\dot{C}HCH_2\sim$ radicals formed on γ-irradiation of PU leads, at small photolysis times, to the formation of $RO\dot{C}O$ radicals (a singlet line in ESR spectra with a half-width of $\simeq 0.9$ mT and $g = 2.002$) and to a fast establishment of their stationary concentration and at large photolysis times, to the formation of acyl radicals $R\dot{C}O$ in considerable amounts. The formation of acyl radicals takes place, in spite of the production of carbon monoxide on PU γ-irradiation, only after the action of light on $\sim CH_2OCONH\dot{C}HCH_2\sim$ radicals which is attributed to the interaction of CO with alkyl end radicals $\sim \dot{C}H_2$ formed in the course of photochemical reactions of radicals.[119,216,217]

The orderliness of the structure of PU[218] enables complex photoradical reactions in them[119,216,217]; the mechanism of such reaction is shown in the scheme



$$\begin{tikzcd}
\sim CH_2OCONH\dot{C}HCH_2\sim \arrow[r, Rightarrow, "h\nu"] & \sim CH_2O\dot{C}O + NH{=}CHCH_2\sim \arrow[d, "h\nu"] \\
CO + \dot{N}HCH_2CH_2\sim \arrow[u] & \sim \dot{C}H_2 + CO \arrow[d] \\
\sim CH_2CHO + \dot{C}ONHCH_2CH_2\sim \arrow[u] & \sim CH_2\dot{C}HOCONHCH_2CH_2\sim \arrow[l, Rightarrow, "h\nu"']
\end{tikzcd}$$

Changes in the composition of gaseous products and in the molecular weight distribution of PU in the course of photolysis[119,216,217] and the formation of new functional groups[219] support this scheme. Exposure to light in the absorption band of $\sim CH_2OCONH\dot{C}HCH_2\sim$ radicals at room temperature in PU produced from hexamethylene diisocyanate and 1,4-butanediol and possessing stability in this temperature range leads to their decay following a bimolecular law with the rate constant proportional to light intensity[119] (Figure 8). The length of the free valency migration "step" evaluated from these dependences was found to be 0.7–0.8 nm which is in sufficiently reasonable agreement with the scheme of photochemical and dark reactions discussed above and taking account of the structure of PU.[218]

Photochemical reactions of radical anions (singlet lines in ESR spectra with $\Delta H_{1/2} \simeq 1.0$–$1.6$ mT and $g \simeq 2.003$) formed in low concentrations upon exposure of PA, PU and their low-molecular analogues to ionizing radiation at low temperatures[202,216,217,220] result mostly in the ejection of an electron with quantum yields close to 10^{-2} [166] and have no effect on the molecular weight distribution of the polymers.[10]

Unfortunately, data on the quantum yields of photochemical reactions in PA and PU are lacking. However, in order to evaluate the yields, one can make use of the figures obtained for low-molecular model compounds at 77 K, Table XIX.

3. PHOTORADICAL CHAIN REACTIONS

It has already been noted that the process of photoradical ageing of polymers can occur in the mode of a photoradical chain reaction.

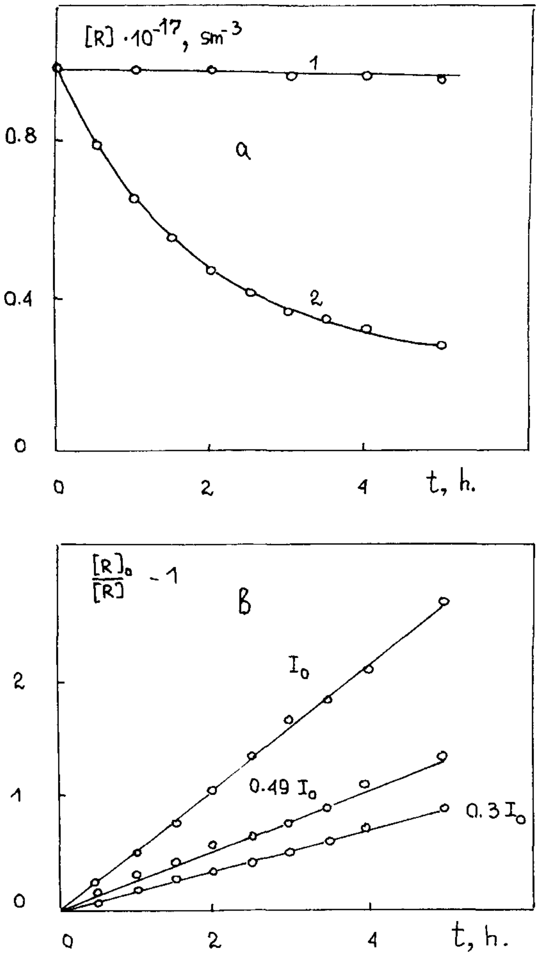


FIGURE 8 The kinetics of change of radicals ~$CH_2OCONH\dot{C}HCH_2$~ concentration in 4,6-polyurethane (a) at 293 K in the dark (1) and under the action of 365 nm light (2) and linear anamorphoses (b) of kinetic curves for photorecombination of ~$CH_2OCONHCHCH_2$~ radicals at different light intensity.[119]

The most characteristic features of photoradical chain reactions are:

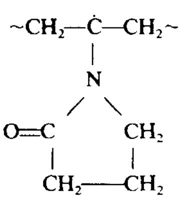
1. Anomalously high yields of stable products of transformation of radicals exceeding dozens and hundreds of times the stationary concentrations of radicals. Thus, in γ-irradiated polytetrafluoroethylene up to 45 molecules of fluorophosgene are formed per peroxide radical consumed in the course of photochemical reactions[222]; in polystyrene, the oxygen absorption rate in a photooxidative ageing process exceeds the consumption rate of radicals almost by a factor of 10^3.[71]

2. The occurrence of photorecombination of radicals in a temperature range ruling out their translational mobility in the dark. The change in the concentration of radicals in this case is expressed by the following dependence[9]:

$$[R]^{-1} = [R]_0^{-1} + \frac{2}{3}\pi\cdot\lambda^3\cdot\varepsilon\cdot\Phi\cdot I\cdot t$$

TABLE XIX

Quantum yields of photochemical reactions of radicals in some low and high molecular compounds

Type of radicals	Reaction	λ, nm	Quantum yield · 10^2	Compound	Literature
$\sim CH_2CONH\dot{C}HCH_2\sim$	(27)	365	2.7 ± 0.7	*n*-butyl-acetamide	221
$\sim CH_2OCONH\dot{C}RCH_2\sim$	(34) (34)	365 365	1.0 ± 0.5 ≈1	Methyl-*N*-ethylcarbamate Ethyl-*N*-isopropyl-carbamate	216, 217 216, 217
	(33)	313	20 ± 10	Polyvinyl-pyrrolidone	206

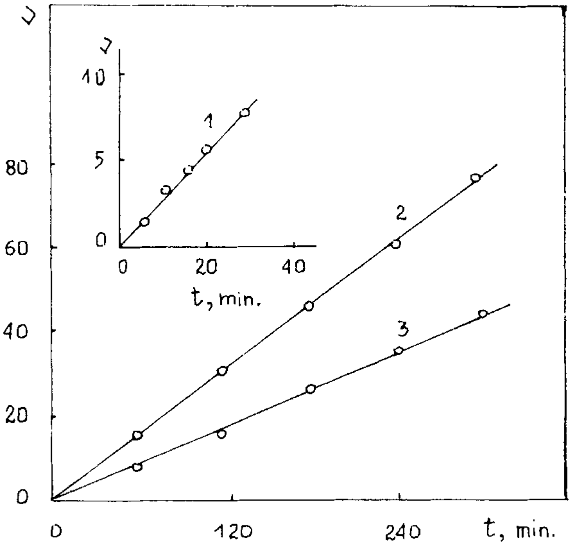


FIGURE 9 Relationship between photoradical reaction chain length and duration of photolysis at 77 K for different polymers: 1—PVA, 2—PAAm, 3—PAA.

where [R] and $[R]_0$ are the current and initial concentrations of the radicals, λ is the length of elementary movement per act.

Regardless of the mechanism of photoradical chain reactions, this expression is valid for processes of photorecombination of radicals in polyolefins,[223] polytetrafluoroethylene,[222] polyurethanes[119] and polyamides,[209] poly(acrylic acid) and poly(acryl amide),[121,175] etc.

3. *In the case that radicals are generated in the polymer prior to its exposure to light, linear growth of the chain of a photoradical chain reaction with the photolysis*

time, Figure 9. The maximum chain length in photoradical chain processes studied by now in polymers exceeds $\approx 10^3$.[72]

4. KINETICS OF PHOTORADICAL REACTIONS IN POLYMERS

The occurrence of a photoradical reaction in a polymer matrix involves different spatial motions of the interacting species and their transformation products and gives rise to changes in the location of the surrounding molecules, generates local stresses. In the solid phase, high energy barriers to the processes of spatial motion of species retard relaxation processes related to such motions and give rise to complex kinetic dependences between the reactions taking place in the solid phase, viz. kinetic non-equivalence.[224] The principle of this phenomenon is that the solid phase features a non-restorable (during the time of the experiment) distribution of chemically identical particles in reactivity. A detailed kinetic analysis of non-equivalence was made earlier.[225]

The unusual character of the kinetic curves of accumulation of the products of photochemical reactions of radicals was first revealed in poly(vinylene carbonate).[43] The kinetic curve of accumulation of formyl radicals HCO formed on photodissociation of middle macroradicals has two clearly discernible linear sections, Figure 10. The observed dependences can be easily explained on the assumption of bimodal distribution of middle macroradicals in reactivity; however, the values of the thus obtained parameters (quantum yield, the proportion of radicals with high and low reactivity) can hardly find an explanation and are, most probably, far from the real levels.[43] More accurate is the model[226] which assumes that the reaction involves not only the consumption of highly reactive species but also their restoration due to the reorganization of the surroundings on dissipation of the energy of photons absorbed in the medium. As a result, a new stationary distribution of species in reactivity is established. The dependences similar to those referred to

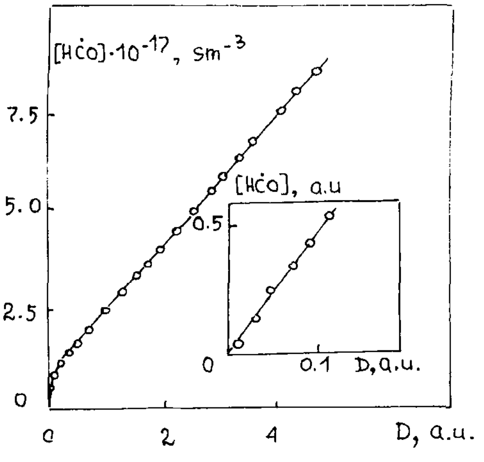


FIGURE 10 Dependence of accumulation HCO radicals at photolysis of middle radicals in PVCb at 77 K on dose of light absorbed.[43]

above,[43] were observed in our studies of various photochemical reactions of radicals in polymers, such as photolysis of peroxide radicals in PIB, middle radicals in PMMA, sulphonyl radicals in PP and in a copolymer of tetrafluoroethylene with hexafluoropropylene, etc.

In the case of photochemical reactions of sulphonyl macroradicals dissociating on exposure to light

$$R\dot{S}O_2 \xrightarrow{h\nu} \dot{R} + SO_2$$

it was possible to observe the effect of the energy of the photon within one electronic absorption band on kinetic non-equivalence, Figure 11, which indicated that the initial distribution of macroradicals in reactivity is determined, among other factors, by the energy of the photon.[227]

Occurring during the transition of a radical to a reactive excited state (within the interval between the absorption of a light quantum and the primary reaction) in the course of photochemical reactions, with the exception of processes starting in an unrelaxed state, is the liberation of a large proportion of the energy of the absorbed photon dissipating in the medium.

The problem of the mechanism of transfer of excessive energy concentrated on photoexcitation of macroradicals to the medium for its restructuring remains unclear. It can only be remarked that the rate constant of intramolecular vibrational relaxation measured for alkyl radicals is $(5-8)\cdot 10^{12}\ s^{-1}$ [228] which strongly restricts the time interval within which the excessive vibrational energy can dissipate in the medium. The suggestion that the dissipated photoexcitation energy can be conducive to an increase in mobility in the solid phase was used earlier[229] for explaining photoselection data. Also, some authors believe[230] that dissipation of vibrational energy can lead to a local microwarming of the medium in close vicinity of the species which has absorbed a light quantum. However, in the case of photochemical

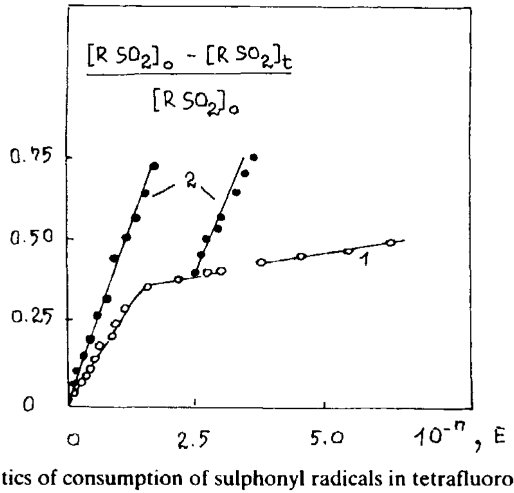


FIGURE 11 The kinetics of consumption of sulphonyl radicals in tetrafluoroethylene-hexafluoropropylene (TFE-HFP) copolymer in the photolysis at 365 nm (1; n = 6) and 313 nm (2; n = 5) at 77 K.[227] (D—absorbed dose, einstein).

reactions of macroradicals a qualitatively different explanation of the effects is possible. It was shown[231,232] that in one-dimensional molecular chains consisting of periodically repeating molecules the generation of specific collective excitations—solitons—is possible, the solitons propagating along the chain together with local deformation. Since the ultimate rate of motion of solitons is the velocity of sonic waves associated with longitudinal vibrations of the molecules, solitons, on their travel, do not irradiate phonons; in other words, their energy is not transformed into the thermal motion energy until a soliton reaches a structural defect where its energy will be released. This particular process is believed to give rise to an anomalous increase in the recombination rate constants of methyl radicals in PMMA and poly(dimethyl siloxane) under the action of light on impurity dye molecules.[233] The formation of solitons in only possible under the action of local excitations, the probability of excitation being the largest in the case where it occurs at the end of the molecular chain.[234]

In any case, "inactive" photons or photons possessing excessive energy favour the establishment of a spatial arrangement of reacting species which is optimal for a chemical reaction. This is also indicated by the growth of the quantum yields of the reactions of photodissociation of various macroradicals with photon energy increasing within one electronic absorption band.[10]

The kinetics of many chemical reactions in polymers is determined by the molecular dynamics of the polymer; one of the major parameters determining the kinetics of reactions in the polymer is its free volume. The concepts of the free volume model[235] can be successfully used in evaluating the dissociation quantum yields of different macroradicals in polymers,[10] just in the same manner as in the case of radicals in vitrified low-molecular organic compounds,[164] Figure 12.

There can be found some indirect indications[236] that the free volume is not the sole structural parameter determining the properties of the matrix, its mobility. Of utmost importance is the free volume distribution but until now these concepts have not been employed in describing photoradical processes in polymers.

The results presented above demonstrate that kinetic non-equivalence in reac-

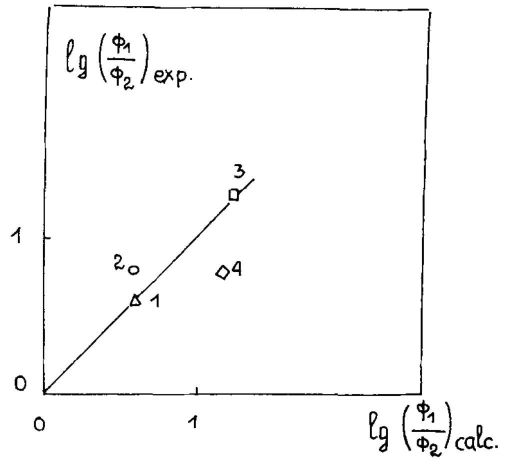


FIGURE 12 Calculated and experimental quantum yields for dissociation of electronically excited radicals at 77 K [10]: 1—PE, 2—PAA, 3—PIB, 4—PMMA.

tions of macroradicals in polymers can by no means be observed in all cases which is due, on the one hand, to the low proportion of relatively reactive species and, on the other hand, to the levelling effect of the energy of the photon or other factors (mechanical loads, temperature, etc.) restoring the distribution of species in reactivity.

5. POSSIBILITIES OF INFLUENCING THE EFFICIENCY AND DIRECTION OF PHOTORADICAL REACTIONS IN POLYMERS

It follows from the data presented above that photochemical reactions of macroradicals can affect photoradical ageing of polymers in the following manner:

1. Destruction of the functional groups of the polymer without affecting its main chain. New functional groups generated in the course of these processes may turn out to be chromophorous and lead to polymer degradation directly during light absorption or possess high reactivity in such chemical reactions as, for instance, oxidation.
2. Degradation of the main chain of the polymer greatly affecting physico-chemical properties of polymers.
3. Formation of radicals or intermediate products whose reactions lead to polymer cross-linking.

In this context, it is very important to consider the ways of influencing the direction and efficiency of photoradical reactions in polymers and reveal the factors determining any certain course of the process.

The quantum efficiency of photochemical reactions of radicals in polymers at 77 K is, as a rule, dependent on the energy of the photon within one electronic absorption band; it increases with the photon energy growing[10,122] (Figure 13). On the other

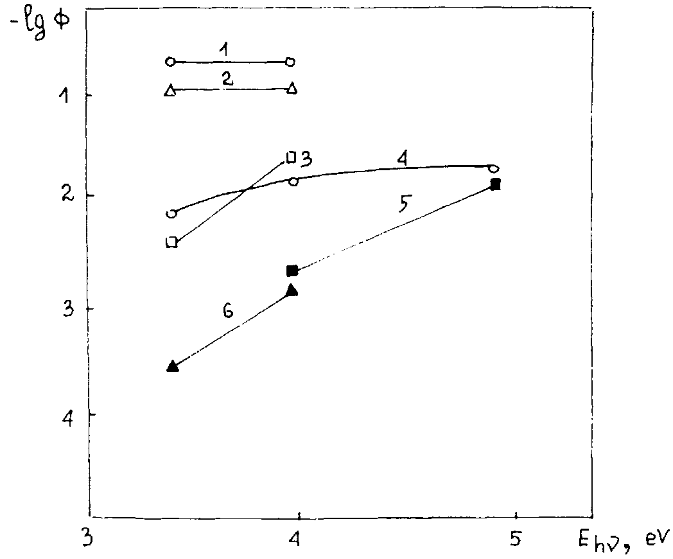
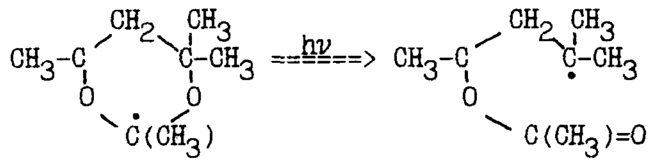
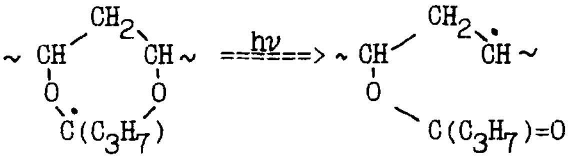


FIGURE 13 Dependence of quantum yields of dissociation of electronically excited radicals on photon energy at 77 K[10,122]: 1—polyvinyl pyrrolidone, 2—PVA, 3—$\mathrm{RS\dot{O}_2}$ in PP, 4—polyvinylene carbonate, 5—PVB, 6—$\mathrm{RS\dot{O}_2}$ in TFE-HFP copolymer.

hand, for quantum yields exceeding ≈0.1 this dependence disappears which indicates the governing, in many instances, role of processes of structural reorganization of the matrix controlling the effective value of the quantum yield. Of much interest is the fact that the quantum yields of photodissociation of low- and high-molecular radicals of the same type manifest cardinally different dependences on the energy of photon, as is the case with PVB and 2,4,4,6-tetramethyl-1,5-dioxane.[122] In terms of the free volume model, this means that for two processes featuring great similarity in their chemical mechanism (35 and 36) to occur, substantially different free volumes are required. It is most likely that small-scale rearrangements in the surroundings in the first case are replaced by larger-scale motions in the second case.

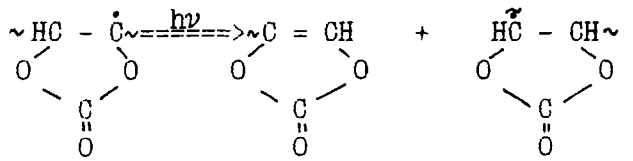


(35)

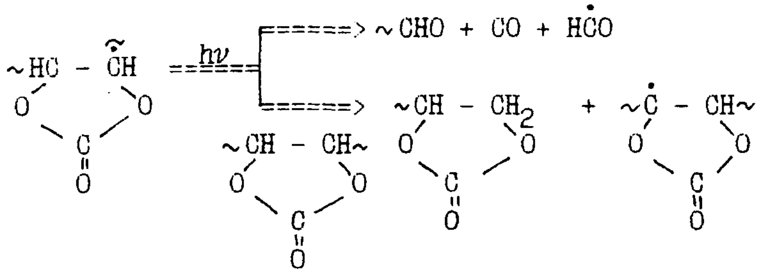


(36)

Changes in the energy of the photon within the limits of one electronic absorption band can affect the relative contribution of a certain pathway of decay of electronically excited radicals which, for instance was found in poly(vinylene cabonate)



(37)



(38)

(39)

An increase in the energy of the photon from 3.4 eV (λ = 365 nm) to 4 eV (λ = 313 nm) alters the ratio of the quantum yields of reactions (37–39) from 1:0.5:0.5 to 1:0.8:0.2.

While increasing the free volume, the temperature growth in the region of the temperature stability of macroradicals should bring about an increase in the quantum yields of the reactions on the strength of the well-known relationship[12]

$$\Phi = \exp(-\alpha \cdot \nu_r/\nu),$$

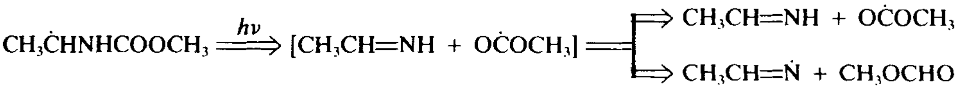
where Φ is quantum yield, α is proportionality factor, v is average thermodynamic volume per matrix molecule, v_r is the volume of an atom, radical or molecule leaving the cage. Indeed, the available reported data support this suggestion, Table XX.

The effect of pressure on the efficiency of photochemical reactions of radicals in polymers was not studied. However, remembering that the reactions of thermal decay of radicals have a positive activation volume which is, as a rule, smaller than that of corresponding molecules,[237] it should be expected that quantum yields will decrease with pressure. It is to be added that at the stage of transition of a radical to the excited state accompanied, as a rule, by a change in the geometry of the species, pressure increase will also alter the rate of radiationless processes.

For reactions of phototransformation of radicals taking several channels and characterized by different activation volumes, pressure change can be used for preferably running a reaction with a smaller activation volume.

A change in the energy of the photon and a switch from one electronic absorption band to another may alter not only the quantum efficiency of the process but also its direction. Thus, cyclohexadienyl radicals, on excitation in the D_0-D_2 electron transition band, dissociate to give hydrogen atoms[24,25] while in the D_0-D_1 transition band they detach in an excited state a hydrogen atom from the molecules of the medium,[31,32] quantum yield in PS matrix changing from 0.21 to 0.07.[31] Using this property of radicals, it is possible, for instance, by varying the wavelength of the ionizing light, to alter the mechanism of migration of a free valency in PS, with (or without) the participation of the hydrogen atom—free valency carrier.

A significant part in the process of dissociation of electronically excited radicals (in those cases where they are accompanied by the formation of particles which may leave the bounds of the "cage" and become stable or interact in the "cage" with the formation of new radicals) is played by the molecular organization of the system. This part is so important in some instances that radicals of the same sort give rise to dissimilar products in different matrices. Thus, exposure of radicals of N-alkyl carbamates to light results in the formation both of alkoxy in alkyl imine radicals



$$CH_3\dot{C}HNHCOOCH_3 \xrightarrow{h\nu} [CH_3CH{=}NH + \dot{O}COCH_3] \begin{cases} \Rightarrow CH_3CH{=}NH + \dot{O}COCH_3 \\ \Rightarrow CH_3CH{=}\dot{N} + CH_3OCHO \end{cases}$$

while photodissociation of similar radicals in aliphatic PU formed from hexamethylene diisocyanate and 1,4-butane- and 1,6 hexanediols gives only alkoxy carbonyl radicals

$$\sim CH_2\dot{C}HNHCOOCH_2\sim \xrightarrow{h\nu} \sim CH_2CH{=}NH + \dot{O}COCH_2\sim$$

This difference is ascribed[121] to rigid fixation of the segments of PU macromolecules by a system of hydrogen bonds ruling out the mobility of the fragments of the polymer chain required for the formation of alkyl imine radicals.

For a goal-oriented change of the properties of a polymeric material, it is con-

TABLE XX

Temperature dependence of quantum yields of electronically excited radicals reactions in polymers

Radical	Polymer	Quantum yield					Literature
		77 K	98 K	188 K	273 K	300 K	
$R\dot{O}_2$	DPE	0.2 ± 0.07	—	—	—	0.7 ± 0.3	156
	DPP	0.04 ± 0.01	—	—	—	0.7 ± 0.3	156
	PTFE	0.015 ± 0.005	—	—	—	0.1 ± 0.05	156
$\sim CH_2\underset{\underset{OH}{\vert}}{\dot{C}}CH_2\sim$	PVAl	—	Φ	2.5Φ	6Φ*	—	161

* The value determined from the chain length data, obtained at different temperatrures.

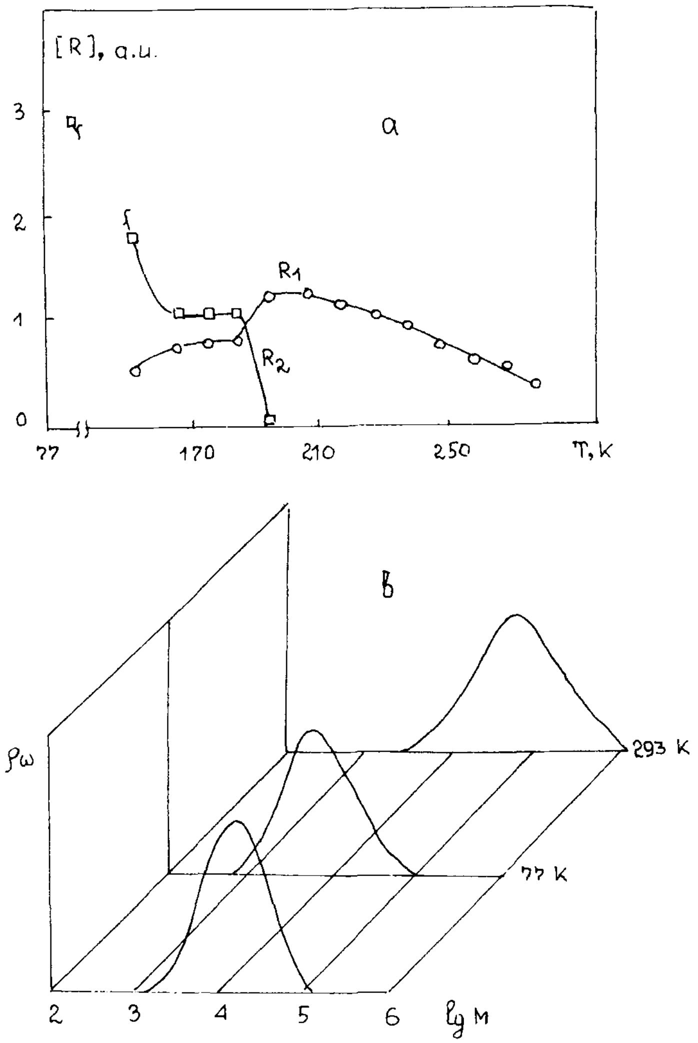


FIGURE 14 Change of radical concentration (a) and molecular mass distribution of PVB depending on temperature photoradical ageing.[10,122]

venient to make use of these rather numerous cases where thermal and photochemical reactions of macroradicals alter differently the properties of polymers. Thus, photochemical reactions of alkyl macroradicals R_{12} in PVB lead to destruction of the main chain whereas thermal reactions of the same radicals, to polymer cross-linking. By carrying out the process at temperatures below 180 K (thermal stability region of R_{12}) and using light with $\lambda \leq 300$ nm, one can succeed in polymer degradation; on the other hand, longer-wave light or higher temperatures will lead to its cross-linking, Figure 14.

Thus, the relative contributions of cross-linking and degradation processes to photoradical ageing can be determined by the spectral composition of light and the temperature of photolysis.

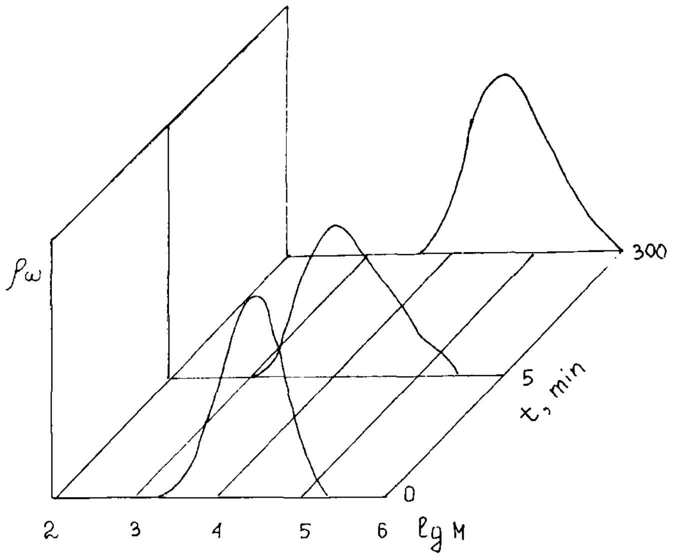


FIGURE 15 Change of molecular mass distribution in PAA depending on the time of photoradical ageing.

On the other hand, in the cases where modification of a polymeric material is due to photochemical reactions of the product formed in a photoradical chain reaction, the contributions of these processes can be controlled by varying such factors as the wavelength of light in photolysis (use of light effective in the absorption band of the intermediate product), photolysis time, temperature, introduction of additives entering into thermal chemical reactions with the intermediate product. This statement can be exemplified by the situation taking place on photoradical ageing of poly(acrylic acid) and poly(acryl amide) where photochemical reactions of middle macroradicals give rise to ruptures in the main chain and ketene accumulation and photochemical reactions of ketene to polymer cross-linking. As a result, the character of MWD change at the early and later stages of photolysis is different, Figure 15.

It follows from the data presented above that using photoradical chain reactions, it is possible to make goal-oriented changes in the functional composition and MWD of polymers. It should be emphasized that these changes in each particular class of polymers have their individual peculiarities. Nevertheless, there exist such common phenomena as photostimulated recombination of macroradicals which can be used in polymer cross-linking. In some instances this will make it possible to avoid undesirable heating of a material to temperatures ensuring necessary translational mobility of macroradicals and, employing. First of all, reactions of photosubstitution or formation of atoms and low-molecular radicals, to carry out cross-linking in the crystal phase where it is difficult to achieve the goal by other methods.

Of certain practical importance may be the effect of non-uniform distribution of the products of photoradical chain reactions in polymers exerting a strong influence on the service properties of polymers (growth of the glass transition temperature, reduction of deformation, increase in mechanical strength, etc.). The most promising ways of modifying different polymeric materials by per-forming photoradical chain reactions in them are: combination of the effects of ionizing radiation of different nature and of light; combination of mechanical actions imparting certain anisotropy to the material and of the effect of light.

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