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Photoradical Ageing of Polymers

M. Ya. Mel'nikov^a; E. N. Seropegina^a

^a Department of Chemistry, Moscow State University, Russia

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Photoradical Ageing of Polymers

M. YA. MEL'NIKOV and E. N. SEROPEGINA

Moscow State University, Department of Chemistry, 119899, Russia

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1. INTRODUCTION

As was indicated earlier,¹ the major part in the process of ageing of polymeric materials is played by free radicals formed either on homolytical scission of the main chain or on homolytical detachment of side group atoms or radicals. In terms of the offered classification,¹ the ageing process includes, in the general case, three main stages: 1) initiation—the stage of formation of active centres; 2) development of ageing—the stage which determines the major changes in the properties of a polymeric material; 3) the stage of decay of the active centres of ageing.

Speaking of photoradical ageing, we select, among the whole set of data on photoageing of polymers under different conditions, those data which cover the relation between the ageing development stage and photochemical reactions of radicals. Of course, the initiation and decay of active centres of ageing may be due to different factors and follow different mechanisms.

The radicals whose formation can be expected in the processes of ageing of various carbon-chain and heterochain polymers should possess absorption spectra shifted towards the long-wave region as against the starting compounds and large extinction coefficients.^{2–4} Thus, polymers, due to the formation of radicals, become chromophorous beyond the intrinsic absorption region. In combination with rather high values of the quantum yields of their reactions³ often greatly exceeding the quantum yields of the homolytical scission of chains in a macromolecule,⁵ this makes the appearance of changes in macromolecules caused by photochemical reactions of macroradicals highly probable.

It is suggested, as a rule, that the invariability of the properties of a polymeric material is realized on condition that the number of elementary damages (chain scissions, destruction and formation of functional groups, formation of cross-links) is low as compared with the total number of units. The condition of the invariability of the properties of a polymer on ageing has the form¹:

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

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

$$\delta \ll 10^{-3}-10^{-4}.$$

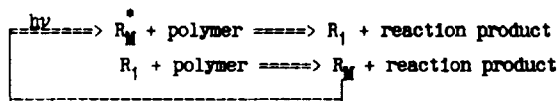
The situation may change radically if the action of light on a polymer is accompanied by such conditions under which each defect (macroradical) is capable of giving rise to a large number of transformations, thus changing the process over to the non-branching-chain reaction mode (chain length ν). In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

$$\delta = \Delta\nu \ll 10^{-3}-10^{-4}$$

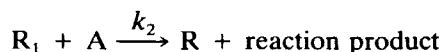
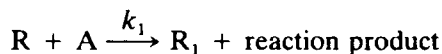
where Δ is the number of macroradicals per chemical bond in the main chain of the polymer, and ν is the chain length; for $\nu \approx 10-10^2$, $\Delta \ll 10^{-4}-10^{-7}$ which is consistent with their stationary concentration $\approx 10^{15}-10^{12} \text{ cm}^{-3}$.

The above-mentioned case of light-initiated repeated transformations of macroradicals with the accumulation of transformation products takes place in photoradical chain reactions first disclosed 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



and a nonbranching-chain reaction



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

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

where ε_R is extinction coefficient and Φ is quantum yield. This relationship holds under the condition that optical densities are low or, in other words, 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

$$k_{ef} = \epsilon_R \Phi I,$$

it became possible to find a quantitative criterion of the feasibility of such processes⁹:

$$\epsilon_R \Phi I \tau \gg 1.$$

For many macroradicals responsible for photoradical ageing of corresponding polymers discussed below, the values of ϵ_R and Φ fall between the $10-10^2 \text{ m}^2 \text{ mol}^{-1}$ 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_R , 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 of realization of 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).

Consider concrete data referring to the mechanism and efficiency of the reactions of electronically excited radicals in various carbon- and heterochain polymers.

2. PHOTORADICAL AGEING OF SOME CARBON- AND HETEROCHAIN POLYMERS

2.1. Polyolefins

Polyolefins are one of the classes of polymeric materials which are widely used for different purposes. Since pure polyolefins should absorb light in the wavelength 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 I lists reported data on the structure and ESR and UV absorption spectra of some of these species.

TABLE I

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
$\sim\text{CH}_2\dot{\text{C}}\text{HCH}_2\sim$	6	$a_{\text{H}}^{\alpha}=2,1$ $a_{\text{H}}^{\beta}=3,5$	radiolysis photolysis mechanical degradation	<200-300	$\lambda < 300$, $\epsilon_{215-250}^{\text{m}^2\text{mol}^{-1}}$ 150-180	(2,9-11)
$\sim\text{CH}_2\dot{\text{C}}\text{HCH}_3$	8	$a_{\text{H}}^{\alpha}=a_{\text{H}}^{\text{CH}_3}$ $a_{\text{H}}^{\beta_1}=2,3$ $a_{\text{H}}^{\beta_2}=4,3$	photolysis mechanical degradation	<120-140	$\lambda_{\text{max}} \approx 230$ - 240	(12, 13)
$\sim\text{CH}_2\dot{\text{C}}\text{H}_2$	8	$a_{\text{H}}^{\alpha}=2,2$ $a_{\text{H}}^{\beta_1}=5,4$ $a_{\text{H}}^{\beta_2}=1,7$	photolysis mechanical degradation	<120-140	-	(9-11)
$\sim\text{CH}=\dot{\text{C}}\text{HCHCH}_2\sim$	9	$a_{\text{H}}^{\alpha}=2,0$ $a_{\text{H}}^{\beta_1}=3,0$ $a_{\text{H}}^{\beta_2}=1,1$	radiolysis	<290-340	$\lambda_{\text{max}}=255$, $\epsilon_{255}^{\text{m}^2\text{mol}^{-1}}=730 \pm 150$	(9-11, 14)
$\sim(\text{CH}=\text{CH})_2\dot{\text{C}}\text{HCH}_2\sim$	1	$\Delta H_{1/2}=4$	radiolysis	-	$\lambda_{\text{max}}=285$, $\epsilon_{285}^{\text{m}^2\text{mol}^{-1}}=2900 \pm 600$	(9-11, 14)

On exposure to light in their absorption band,³ polyene radicals transform into appropriate alkyl and allyl macroradicals.²¹ It follows from the expression given in an earlier paper²²

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

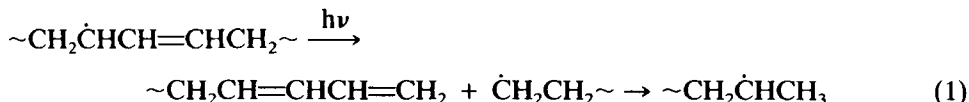
(where β is the exchange integral, N is the number of π -electrons) that as the length of the conjugated-chain grows, the difference of conjugation energies, ΔG , of the polyene radical and the corresponding molecule increases in its absolute value and at $N \geq 5$ the process of phototransformation of polyene radicals becomes energetically unfavourable. It was noted for lower N values that in polyethylene (PE)²³ and polypropylene (PP)¹⁶ dienyl and trienyl radicals form alkyl radicals on

TABLE I (Continued)

Radical	Number of lines in ESR spectrum	Parameters of ESR spectrum	Methods of radical generation	Range of thermal stability, K	Range of light sensitivity, nm	Literature stability
$\sim\text{CH}-\dot{\text{C}}\text{H}-\text{CH}\sim$ CH ₃ CH ₃	4	$a_{\text{H}}^{\alpha}=2,1$ $a_{\text{H}}^{\beta}=2,6$	photolysis radiolysis	<250-290	$\lambda_{\text{max}} < 230$, $\epsilon_{254} = 110 \pm 20$ $\text{m}^2 \text{mol}^{-1}$	[9-11, 15]
$\sim\text{CH}(\text{CH}_3)\dot{\text{C}}\text{H}_2$	4	$a_{\text{H}}^{\alpha} - a_{\text{H}}^{\beta} = 2,4$	photolysis	-	-	[16]
$\sim\text{CH}_2-\dot{\text{C}}-\text{CH}_2\sim$ CH ₃	6	$a_{\text{H}}^{\text{CH}_3} = 2,3$ $a_{\text{H}}^{\beta_1} = 3,0$ $a_{\text{H}}^{\beta_2} = 0,3$	photolysis radiolysis mechanical degradation	<120-140	-	[12, 17]
$\sim\text{CH}\dot{\text{C}}\text{H}\text{C}=\text{CH}\sim$ CH ₃ CH ₃	7	$a_{\text{H}}^{\alpha} = 1,5$ $a_{\text{H}}^{\beta} = 3,0$	radiolysis	-	$\lambda_{\text{max}} = 255$	[9-11, 18]
$\sim(\text{CH}=\text{CH})_2\dot{\text{C}}\text{H}_2\sim$ CH ₃ CH ₃	1	$\Delta H_{1/2} = 4$	radiolysis	-	$\lambda_{\text{max}} = 310$	[9-11, 18]
$\sim\text{C}(\text{CH}_3)_2\dot{\text{C}}\text{HC}(\text{CH}_3)_2\sim$	2	$a_{\text{H}}^{\alpha} = 2,1$	photolysis radiolysis mechanical degradation	<200-220	$\lambda_{\text{max}} < 230$, $\epsilon_{254} = 110 \pm 20$ $\text{m}^2 \text{mol}^{-1}$	[9-11, 15]
$\sim\text{CH}_2\dot{\text{C}}(\text{CH}_3)_2$	15	$a_{\text{H}}^{\text{CH}_3} =$ $a_{\text{H}}^{\beta_1} = 1,1$ $a_{\text{H}}^{\beta_2} = 1,3$	radiolysis photolysis mechanical degradation	<183	-	[9-11]
$\text{RO}_2^{\dot{}}$	1	$g_{\text{H}} = 2,042-2,045$ $g_1 = 2,005-2,009$	photolysis radiolysis mechanical degradation	<260-280 (PE) <250-290 (PP) <200-220 (PIB)	$\lambda_{\text{max}} = 250-280$ $\epsilon_{254} = 200 \pm 100$ $\text{m}^2 \text{mol}^{-1}$	[9-11, 20]

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 ($\lambda_{\text{max}} = 316 \text{ nm}$), revealed a dislocation process with the formation of H atoms^{24,25} whereas on photolysis in the long-wave D_0-D_1 transition ($\lambda_{\text{max}} = 559 \text{ nm}$) a photosubstitution reaction occurred.^{25,26}

It was noted that the exposure of allyl macroradicals in PE to light^{21,27} may lead to their dissociation with the formation of a diene and an allyl macroradical

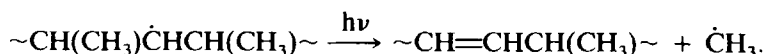


This conclusion was based^{21,27} on the ESR spectral data indicating the emergence, on exposure to light with $\lambda \geq 390$ nm, of a specific signal assigned to $\sim\text{CH}_2\text{CHCH}_3$ macroradicals and on a decrease in the viscosity-average molecular weight of the polymer to 2/3–1/4 of the initial value. It should be added, on the other hand, that the authors of one of the papers referred to above²⁷ 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 ($\approx 10^3$ m² mol⁻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 the maximum at 320 nm in PP¹⁸ whose photochemical reactions may also affect the molecular weight of the polymer. The transformations observed on photolysis of allyl radicals occur the π -orbital to the non-bonding 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 $\pi\pi^*$ transition band is the detachment of hydrogen atoms from the molecules of various organic compounds by an electronically excited radical.²⁸ 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 macro-radicals. 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; however, the lack of data necessary for making a judgement on the scale and efficiency of these processes should be emphasized once again.

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.^{2,3,29}

Quantum-chemical calculations for the ethyl radical³⁰ corroborate the possibility of its dissociation in an electronically excited state at C—C bond to afford a methyl radical and methylene in the ¹B₁ state.

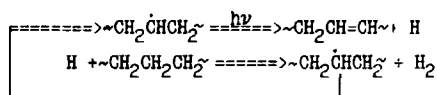
Studies of photochemical reactions in PP^{31–34} and polyisobutylene (PIB)³¹ revealed the formation of methyl radicals and methane ascribed to photodissociation of alkyl macroradicals



It was also noted³¹ 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 discussed

in Reference 2. Later on,³⁵ photodissociation reactions of alkyl macroradicals were detected. The reactions led to ruptures 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.³⁶ The same authors in their subsequent studies¹³ succeeded to show that such high values of the yields of certain stable products were due to photoradical chain reactions, such as



Given in Table II are the values of the quantum yields of the phototransformation reactions of allyl and alkyl radicals in polyolefins at 77 K.

It follows from Table II that 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^{31,34}).

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 forward³⁶



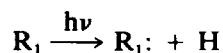
The further trend of the process is determined by the behaviour of radicals R_1 and

TABLE II
Quantum yields of photochemical reactions of radicals in polyolefins

Polymer	Reactions	λ , nm	Quantum yield	Literature
PE	$\sim \text{CH}_2 \dot{\text{C}}\text{HCH}_2 \sim \Rightarrow \text{H} + \sim \text{CH}_2 \text{CH}=\text{CH} \sim$	>200	0,2	[13]
	$\Rightarrow \sim \text{CH}=\text{CH}_2 + \sim \text{CH}_2 \dot{\text{C}}\text{HCH}_3$	>200	$8 \cdot 10^{-3}$	[13]
	$\Rightarrow \sim \text{CH}=\text{CH}_2 + R_x$	254	$(4 \pm 2) \cdot 10^{-2}$	[37]*
	$\sim \text{CH}_2 \dot{\text{C}}\text{HCH}_3 \Rightarrow \dot{\text{C}}\text{H}_3 + \sim \text{CH}=\text{CH}_2$	>200	$4 \cdot 10^{-3}$	[13]
	$\Rightarrow \text{C}_2\text{H}_4 + \sim \text{CH}_2 \dot{\text{C}}\text{HCH}_3$	>200	$1 \cdot 10^{-3}$	[13]
	$\sim \dot{\text{C}}\text{HCH}=\text{CH} \sim \Rightarrow \sim \text{CH}_2 \dot{\text{C}}\text{HCH}_2 \sim$	254	$(8 \pm 3) \cdot 10^{-2}$	[38]
PP	$\sim \text{CH}(\text{CH}_3) \dot{\text{C}}\text{HCH}(\text{CH}_3) \sim \Rightarrow \dot{\text{C}}\text{H}_3 +$	254	$(2,1 \pm 0,3) \cdot 10^{-4}$	[3]
	$\sim \text{CH}=\text{CHCH}(\text{CH}_3) \sim$			
	$R_{\text{all}} \Rightarrow R_{\text{alk}}$	254	$(13 \pm 3) \cdot 10^{-3}$	[38]
PIB	$\sim \text{C}(\text{CH}_3)_2 \dot{\text{C}}\text{HC}(\text{CH}_3)_2 \sim \Rightarrow \dot{\text{C}}\text{H}_3 +$	254	$(1,5 \pm 0,3) \cdot 10^{-4}$	[35]
	$\sim \text{C}(\text{CH}_3)=\text{CHC}(\text{CH}_3)_2 \sim$			
	$\Rightarrow \sim \text{CH}=\text{C}(\text{CH}_3)_2 +$	254	$\leq 10^{-5}$	
	$\dot{\text{C}}\text{H}_2\text{C}(\text{CH}_3)_2 \sim$			

* - reaction of alkyl radicals in polyvinyl butiral

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 had been reliably established; the reaction has a quantum yield about 0.1 at 4 K (which is comparable with the yield measured in PE) and gives the same end products.⁴⁰

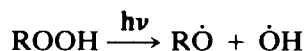
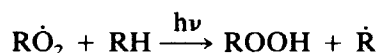


This direction of photodissociation of alkyl macroradicals agrees with the results of a quantum-chemical calculation of the fragmentation of the methyl radical indicating that the first excited 1^2A state of CH_3 with energy 5.73 eV should predissociate with the rupture of C—H bond.⁴¹

Studies of the mechanism of reactions of electronically excited peroxide radicals are of much 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 $\epsilon_{\lambda_{\max}} = (0.8-3.2) \times 10^2 \text{ m}^2 \text{ mol}^{-1}$.² On the other hand, attempts at detecting optical absorption of peroxide radicals in PE and PP failed^{37,42} although their formation in fairly large concentrations has been revealed in ESR spectra. Optical absorption of peroxide radicals in PIB ($\epsilon_{254} = (2 \pm 1) \times 10^2 \text{ m}^2 \text{ mol}^{-1}$) has been found only recently.²⁰

It has been thought for a long time^{9,43,44} 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



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^{40,45} and other dissociation products.⁴⁰

It was found²⁰ 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 meant that the degradation of the polymer chain is the key process.

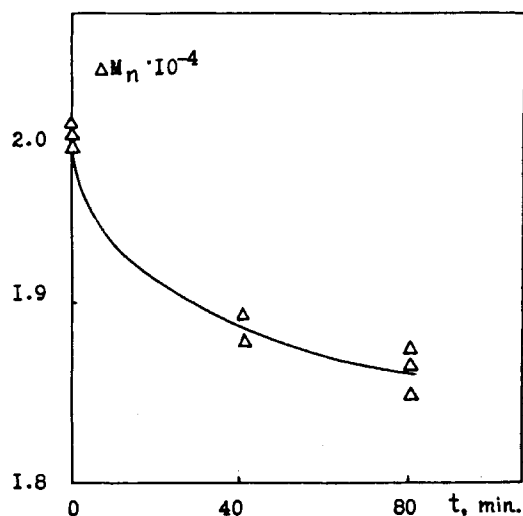
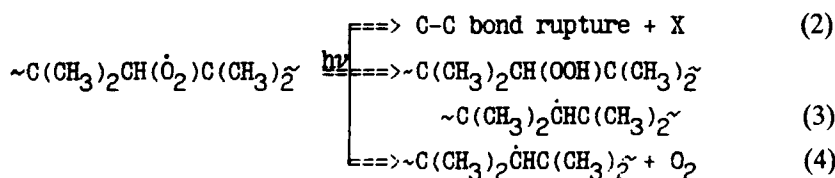
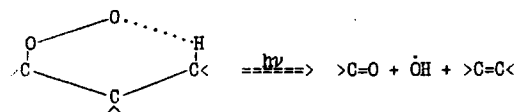


FIGURE 1 The kinetics of change of PIB number average molecular mass upon the photolysis of peroxide radicals at 77 K (points—experimental values, curve—calculated values).²⁰



The mechanism of the process is believed²⁰ to be similar to that proposed earlier⁴⁶ 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 reaction⁴³ and the low yields of hydroperoxides in photochemical reactions of peroxide radicals.⁴⁷



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 in the first place based on the experimental findings³⁸ 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 4×10^{-2} to 0.7, respectively.

On the other hand, a different interpretation of the above-mentioned experimental evidence is possible.

Studies of photolysis ($\lambda = 248 \text{ nm}$) of HO₂ radicals in the gas phase⁴⁸ showed that the main photochemical process was dissociation at O—O bond



A theoretical analysis of this process⁴⁹ indicates that more probable is the formation of O atoms in the ground ³P state rather than in the excited (¹D) state.

An identical pathway of photodegradation, by analogy with HO₂ radical, is also proposed for some other alkyl peroxide radicals, such as CH₃O₂, with the formation of a vibrationally excited methoxy radical⁴⁹

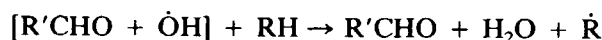
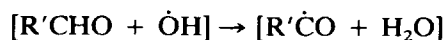
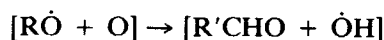
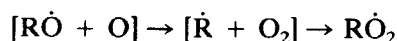
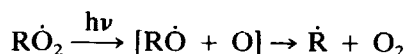


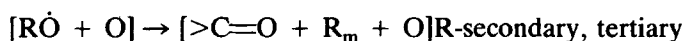
This possibility has found experimental support,⁵⁰ the quantum yield of the formation of CH₃O(X₂E) radicals is 0.2 ± 0.1. Although no direct experimental evidence of the formation of alkoxy radicals has been found in studies of photochemical reactions using IR spectroscopy at 12 K in argon-oxygen matrices,⁵¹⁻⁵⁴ this is not surprising since photolysis, e.g. of CH₃O₂, gives rise to a "hot" pair [CH₃O + O] for which several reaction pathways are possible: 1) Detachment of hydrogen atom from CH₃O radical by O atom in the ¹D state and stabilization of the reaction products [CH₂O + OH] in the matrix cage; 2) Fast oxidation of the "hot" pair [CH₃O + O] by an oxygen molecule with the formation of H₂O, CO₂ and/or CO, HO₂ and OH.⁵⁵

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 SiO₂ surface.^{56,57}

These data on photodissociation of peroxide radicals at O—O bond (which seems to be the principal reaction) 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/mol⁵⁸) greatly exceeding the energy of C—O bond in peroxide radicals (e.g., in CH₃O₂ it is equal to about 130 kJ/mol⁵⁹) which may bring about their thermal degradation.

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





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 information on which is presented in Table III.

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 is 3×10^{-2} .⁶¹ These data agree with information^{2,29} indicating that radicals with the $\pi\pi^*$ excitation should participate in photosubstitution reactions whose quantum yields must be close to 10^{-1} – 10^{-2} .⁶³ 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 acted as active centres of ageing.^{61,64–66} The decisive role of radical reactions is also witnessed by the data⁶⁷ 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^{61,68} given in Table IV fall within the 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.⁶⁸

The measured quantum yields of the main reaction products are listed in Table V. The data presented in Table V testify to a virtually full consumption of oxygen

TABLE III
ESR spectral parameters, 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
$\sim\text{CH}_2-\overset{\cdot}{\underset{\text{C}_6\text{H}_5}{\text{C}}}-\text{CH}_2\sim$ (R_1)	3	$a_H^{\beta_1} \approx 2,0$	radiolysis	< 235	$\lambda_{\text{max}} = 450,$ 305-318,	[10, 11, 60-62]
		$a_H^{\text{C}_6\text{H}_5} \approx 0,5$			250-258 $\epsilon_{450} \approx 3-7,$	
	5	$a_H^{\beta_1} = a_H^{\beta_2} \approx 2,0$ $a_H^{\text{C}_6\text{H}_5} \approx 0,5$	photolysis		$\epsilon_{305-318} =$ 100-1200, $\epsilon_{250-258} =$ 190-1400	
	7	$a_H^{\beta_1} \approx 1,8$	photolysis		$\text{m}^2\text{mol}^{-1}$	
		$a_H^{\beta_2} \approx 5,4$	radiolysis			
$\sim\text{CH}-\overset{\cdot}{\underset{\text{C}_6\text{H}_5}{\text{C}}}-\text{CH}_2$ (R_2)	6	$a_H^{\alpha} \approx 2,2$ $a_H^{\beta} \approx 3,3$	mechanical degradation	< 120-140	-	[10]
$\sim\text{CH}_2-\overset{\cdot}{\underset{\text{C}_6\text{H}_5}{\text{C}}}-\text{CH}$ (R_3)	3	$a_H^{\alpha} \approx 1,5$ $a_H^{\beta_1} \approx 2,1$ $a_H^{\beta_2} \approx 0,2$	mechanical degradation	< 330-350	spectral properties analogous to radicals R_1	[10]
$\sim\text{CH}-\overset{\cdot}{\underset{\text{C}_6\text{H}_5}{\text{C}}}-\underset{\text{OH}}{\text{C}}-\text{CH}\sim$ (R_4)	3	$a_H^{\alpha} \approx 1,8$	photolysis	-	spectral properties analogous to α -hydroxy-alkyl radicals	[61]
$\sim\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}}-\overset{\cdot}{\text{C}}-\text{CH}_2\sim$ (R_5)	12	$a_H^{\beta} \approx 0,75$ $a^{\text{O-H}} = a^{\text{P-H}} = 0,1$ $a^{\text{m-H}} \approx 0,25$	radiolysis		$\lambda_{\text{max}} \approx 316,$ (9-11, 559) $\epsilon_{316} \approx 317 \pm 27,$ $\epsilon_{559} = 4,5 \pm 0,3$ $\text{m}^2\text{mol}^{-1}$	[11, 60, 61]
$\sim\text{CH}=\underset{\text{C}_6\text{H}_5}{\text{C}}-\overset{\cdot}{\underset{\text{C}_6\text{H}_5}{\text{C}}}\sim$ (R_6)	1	$\Delta H_{1/2} \approx 2,0$	photolysis	< 370	-	[11, 60, 61]
$\sim(\text{CH}=\text{CH})_2-\overset{\cdot}{\underset{\text{C}_6\text{H}_5}{\text{C}}}\sim$ (R_7)	1	$\Delta H_{1/2} \approx 1,4$	photolysis		-	[61]
Polyenyl radical (R_8)	1	$\Delta H_{1/2} \approx 0,6$	photolysis		-	[60, 61]
RC_2^{\cdot} (R_9)	1	$\Delta H_{1/2} \approx 1,6$	photolysis radiolysis mechanical degradation		$\lambda < 550$	[11, 60, 61]

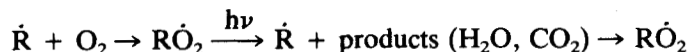
TABLE IV
Quantum yields of the formation of radicals in PS^{61,68}

Sample of PS	Conditions of photolysis	λ , nm	Quantum yield
film, 1-2 mm	vacuum, 77 K	≥ 236	$3 \cdot 10^{-5}$
	vacuum, 300 K	≥ 236	$1,5 \cdot 10^{-4}$
	vacuum, 300 K	≥ 300	$1,5 \cdot 10^{-4}$
	vacuum, 77 K	≥ 236	$5 \cdot 10^{-5}$
	air, 77 K	253,7	$5 \cdot 10^{-5}$
	air, 77 K	≥ 360	$1,5 \cdot 10^{-5}$
	air, 315 K	≥ 236	10^{-3}
	photooxidated	air, 315 K	≥ 236
PS+5% benzophenone	air, 315 K	≥ 360	10^{-3}

TABLE V
Quantum yields of formation of main intermediate and final products on PS photooxidation⁶⁸

Process	Conditions of photolysis	λ , nm	I, quant/ ($\text{sm}^2 \cdot \text{s}$)	Quantum yield
absorption of O_2	150 tor O_2 , 300 K	253,7	$2 \cdot 10^{16}$	0,33
	200-400 tor O_2 , 300 K	253,7	10^{16}	1,0
formation of ROOH	air 760 tor, 300 K	253,7	10^{16}	10^{-3}
formation of $>\text{C}=\text{O}$	air 760 tor, 300 K	253,7	10^{16}	10^{-3}
chain scission	600 tor O_2 , 300 K	253,7	10^{14}	10^{-3}
formation of poly-enyl radicals	air 760 tor, 330 K	253,7	$2 \cdot 10^{16}$	$5 \cdot 10^{-6}$
formatin of CO_2 and H_2O	150 tor O_2 , 300 K	253,7	$2 \cdot 10^{16}$	0,28
	400 tor O_2 , 300 K	253,7	10^{16}	1,0

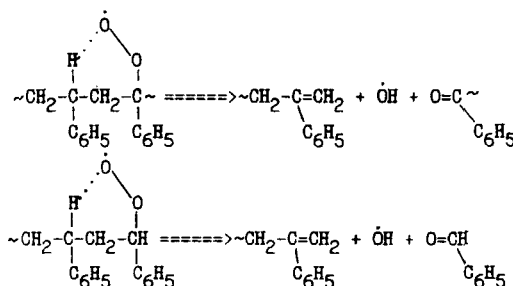
in the formation of deep oxidation products which is, in fact, a kind of photochain "combustion" of the polymer. An opinion based on the experimental results obtained on polyolefins and model low-molecular compounds^{20,45} was expressed^{61,64-66} that the PS photooxidation reaction followed the scheme



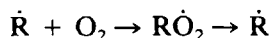
Phototransformation of peroxide radicals seems to be, in effect, photodissociation of electronically excited radicals; excitation of the radicals may, to all appearances, occur both by direct light absorption by radicals (for peroxide macroradicals in PS $\epsilon_{330} = 4 \times 10^2 \text{ m}^2 \text{ mol}^{-1}$ ⁶⁸) and by energy transfer from other chromophores.

The mechanism of photodissociation of peroxide macroradicals in PS has not been elucidated. It can only be suggested that it resembles the mechanism of thermal degradation of peroxide macroradicals in PS.⁶⁹ 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 $3 \times 10^2 - 4 \times 10^3$. It should be added that in a thermal PS oxidation process occurring in dark the length of the reaction chain

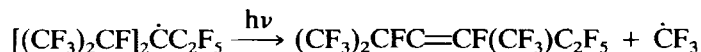


is 10.⁶⁴

Photoradical oxidation of PS leads to great changes in polymer's macrocharacteristics. Thus, within a period of 260 hours of exposure ($\lambda = 253.7 \text{ nm}$, $I = 10^{16} \text{ quanta}/(\text{cm}^2 \text{ s})$), 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 215–245 nm region.⁷⁰ It is only known that in a copolymer of tetrafluoroethylene with hexafluoropropylene $\sim\text{CF}_2\text{C}(\text{CF}_3)\text{CF}_2\sim$ macroradicals, on exposure to light at 77 K, transform into $\sim\text{CF}_2\text{CF}(\text{CF}_2)\text{CF}_2\sim$ radicals featuring a specific ESR spectrum.⁷¹ On the other hand, $[(\text{CF}_3)_2\text{CF}]_2\text{CC}_2\text{F}_5$ radicals ($\lambda_{\text{max}} < 220 \text{ nm}$) formed on radiolysis of hexafluoropropylene trimer (HFPT) decay on photolysis with 300 nm light both at 300 and 77 K. It was shown^{72,73} that photodegradation involved the formation of trifluoromethyl radical



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

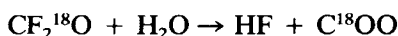
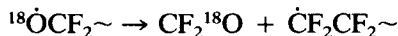
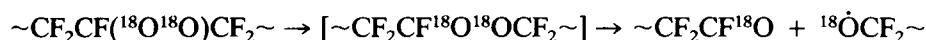
Thus, electronically excited fluoroalkyl radicals undergo dissociation at β -bond. It would be natural to expect photodissociation of fluoroalkyl radicals at C—F bond too but it is difficult to record this process by virtue of high reactivity of F atoms. It is anticipated that fluorine atoms in perfluorinated 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 ≈ 240 nm, $\epsilon_{240} \approx 70 \text{ m}^2 \text{ mol}^{-1}$ has been studied in much more detail.⁷⁰ It was also found^{73,74} that exposure to light with $\lambda \leq 280$ nm transformed $\text{CF}_2\text{CF}(\text{OO})\text{CF}_2$ radicals into terminal fluoroalkyl radicals; mass and IR spectrometry revealed CF_2O and CO among the reaction products.^{75,76} It was assumed⁷⁵ that the reaction run as follows

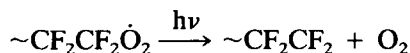


It seems that the mechanism of this photochemical reaction is identical with that of the thermal degradation of peroxide radicals in polytetrafluoroethylene discussed in detail earlier.^{77,78} The use of $\sim\text{CF}_2\text{CF}(^{18}\text{O}^{18}\text{O})\text{CF}_2\sim$ peroxide radicals labelled with ^{18}O isotope made it possible to reveal⁷⁸ 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

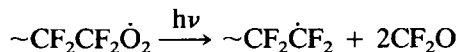


The decay of the middle peroxide radicals leads to an essential decrease in the molecular weight of the polymer.

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 oxygen⁷⁴



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



Determinations of the number of fluorine ions obtained on hydrolysis of fluorophosgene evolved during photolysis showed^{7,79} that from 50 to 90 fluorine ions were formed per radical decayed as a result of photorecombination occurring in this case which meant that a photoradical chain process took place. The quantum

yields of consumption of peroxide radicals in polytetrafluoroethylene are $(1.5 \pm 0.5) \times 10^{-2}$ at 77 K and 0.1 ± 0.03 at 300 K.³⁸

The dissimilarity in the behaviour of peroxide end macroradicals 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 vacuum⁸⁰⁻⁸² that the accumulation kinetics of polyenes had a number of specific features related to the existence of an induction period after the end of which dehydrochlorination went on at an almost constant rate; the conservation of an invariable length distribution of polyenes up to large conversions depending, however, on the spectral composition of light; to the existence of a strong dependence of the quantum yields of dehydrochlorination on the wavelength of the acting light; to the synergistic effect 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; to the 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 were 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 $\approx 10^3$ m² mol⁻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 boundary of 250–280 nm (the extinction coefficient of the polymer at $\lambda = 254$ nm is 0.037 m² mol⁻¹).⁸³

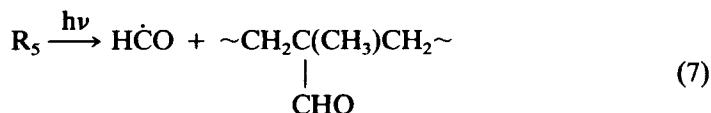
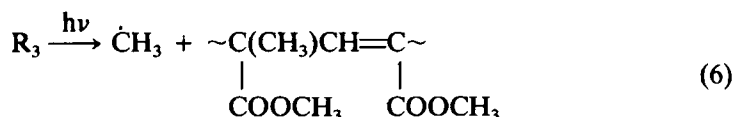
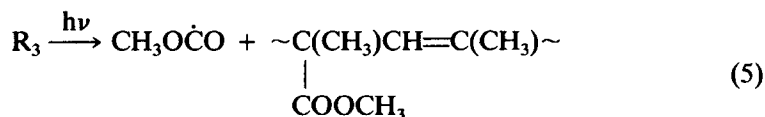
Given in Table VI are the quantum yields of formation of various radical products of PMMA photolysis at 77 K with light at $\lambda = 253.7 \text{ nm}$.⁸⁴

The formation of radicals sensitized or initiated by various additives on exposure to light with larger wavelengths is also possible.^{85,86}

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 pointed to the formation of all types of macro- and low-molecular radicals possible for this polymer, except CH_3O radicals highly reactive even at 77 K and H atoms (Table VII).

It follows from Table VII 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^{102,103} 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^{87,97,104-109}; it was found that in PMMA macroradicals R_3 and R_5 were engaged in the following photochemical reactions:



The quantum yields of reactions (5-7) at 77 K are presented in Table VIII.^{3,109}

TABLE VI

Quantum yields of formation of radical products of PMMA photolysis	
Radical	Quantum yield $\cdot 10^2$
$\dot{\text{C}}\text{H}_3$	8.3
$\dot{\text{C}}\text{H}_2\underset{\substack{ \\ \text{COOCH}_3}}{\text{C}}(\text{COOCH}_3)$	4.8
$\underset{\substack{ \\ \text{CH}_3}}{\text{CH}_2}\text{O}\dot{\text{C}}\text{O}$	1.4 (300 K)
$\text{CH}_3\text{O}\dot{\text{C}}\text{O}$	7.0
$\text{H}\dot{\text{C}}\text{O}$	1.2
$\text{CH}_3\dot{\text{C}}\text{O}$	4.4

TABLE VII

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, mf	Methods of radicals generation	Range of thermal stability, K	Range of light sensitivity, nm	Literature
$\sim \text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{COOCH}_3}{\text{C}}} \cdot \quad (\text{R}_1)$	9	$a_{\text{H}}^{\text{CH}_3} = 2,2 \pm 0,1$ $\beta_{\text{H}}^{\text{I}} = 1,3 \pm 0,1$ $\beta_{\text{H}}^{\text{II}} = 1,1 \pm 0,1$ $g = 2,0033$	photolysis (77-293 K) radiolysis (293 K) mechanical degradation (77-293 K)	<350	$\lambda_{\text{max}} = 420$, $\epsilon_{420} = 4 \pm 1$ $\text{m}^2 \text{mol}^{-1}$	[4,9-11,88-91]
$\sim \text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{COOCH}_3}{\text{C}}} - \text{CH}_2 \cdot \quad (\text{R}_2)$	3	$a_{\text{H}}^{\alpha} = 2,2 \pm 0,1$	photolysis radiolysis mechanical degradation of dilute solution PMMA (93 K)		spectral properties of alkyl radicals	[9,10,87,91]
$\sim \overset{\text{CH}_3}{\underset{\text{COOCH}_3}{\text{C}}} - \text{CH} - \overset{\text{CH}_3}{\underset{\text{COOCH}_3}{\text{C}}} \cdot \quad (\text{R}_3)$	2	$a_{\text{H}}^{\alpha} = 2,4 (1,9) \pm 0,1$ $g = 2,0025 (2,0034) \pm 0,0004$	photolysis (77 K) mechanical degradation	<240-260	$\lambda_{\text{max}} < 300$, $\epsilon_{254} = 120 \pm 30$ $\text{m}^2 \text{mol}^{-1}$	[9,10,86,87,95-97]
$\sim \text{CH}_2 - \overset{\text{CH}_3}{\underset{\cdot}{\text{C}}} - \text{CH}_2 \cdot \quad (\text{R}_4)$	24	$a_{\text{H}}^{\text{CH}_3} = 2,1 \pm 0,1$ $\beta_{\text{H}}^{\text{I}} = 4,2 \pm 0,1$	photolysis (77 K)	<175	spectral properties of alkyl radicals	[9,10,86,87,89,94]

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 believed⁹¹ to be accompanied 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.¹¹⁰ Similar processes of photodissociation of radicals of the growing chain were detected in poly(acrylic acid)¹¹¹; 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,¹¹² the quantum yields of reactions (8, 9) of dissociation of radicals R_1

TABLE VII (Continued)

Radical	Number of lines in ESR spectrum	Parameters of ESR spectrum	Methods of radical generation	Range of thermal stability, K	Range of light sensitivity, m μ	Literature reference
		$\beta_2 = 0.62 \pm 0.1$				
$\sim \text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{COOCH}_2}{\text{C}}} \sim (R_5)$	3	$a_H^\alpha = 2.2$ (1.58) \pm 0.1 $g = 2.0036$ (2.0045) \pm 0.0001	photolysis radiolysis	<188	$\lambda_{\text{max}} = 370$, $\epsilon_{313} = 60 \pm 20$ m 2 mol $^{-1}$	(2.3, 9-II, 86,87, 90,97, 99)
$\sim \text{CH}_2 - \overset{\dot{\text{C}}\text{H}_2}{\underset{\text{COOCH}_3}{\text{C}}} \sim (R_6)$	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-II, 86,87, 90,97, 99)
$\sim \text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{C}=\text{O}}{\text{C}}} \sim (R_7)$	1	$\Delta H_{I/2} = 1.3 \pm 0.1$ $g = 2.0010 \pm$ 0.0006	photolysis	<188	$\lambda < 650$, $\epsilon_{540} \approx 5-6$ $\epsilon_{254} \approx 100$ m 2 mol $^{-1}$	(3,9-II, 86,100)
$\sim \text{CH}_2 - \overset{\dot{\text{C}}\text{H}_2}{\underset{\text{COOCH}_3}{\text{C}}} \sim (R_8)$	4	$a_H^\alpha \approx 2.2$ $a_H^\beta \approx 4.0$	mechanical degradation		spectral properties of alkyl radicals	(101)
$\sim \text{CH}_2 - \text{C}(\text{COOCH}_3) - \text{CH}_2 \sim (R_9)$	8	$\beta_1 = 4.8 \pm 0.1$ $a_H^2 = 2.4 \pm 0.1$ $\beta_3 = 1.2 \pm 0.1$ $a_H^4 = 0.1 \pm 0.03$	radiolysis		-	(12)
$\sim \text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{O}-\text{C}-\text{OCH}_3}{\text{C}}} - \text{CH}_2 \sim (R_{10})$	1	$\Delta H_{I/2} = 1.3 \pm 0.1$	radiolysis		$\lambda_{\text{max}} \approx 320$, $\epsilon_{320} = 200 \pm 70$ m 2 mol $^{-1}$	(3,9- 11, 102)
$\text{RO}_2 (R_{11})$	1	$g_1 = 2.042-2.045$ $g_1 = 2.005-2.009$	radiolysis photolysis mechanical degradation	<260-280		(9-II)

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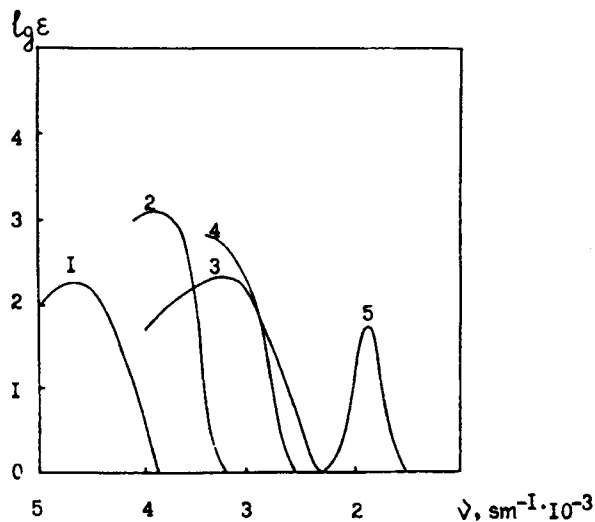
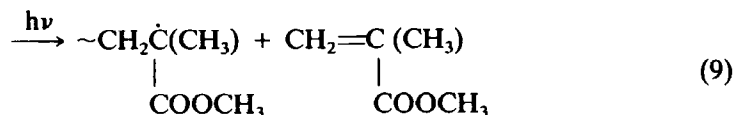
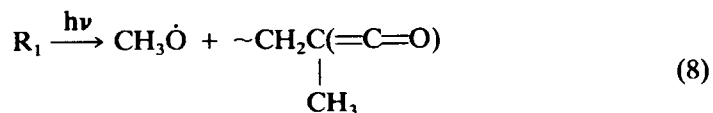


FIGURE 2 Absorption spectra of PMMA (1) and relevant radicals: 2— R_3 , 3— $ROCO$, 4— R_5 , 5— RCO .

TABLE VIII

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

Radical	Quantum yield 10^2			λ , nm
	(5)	(6)	(7)	
R_3	$0,10 \pm 0,05$	$0,4 \pm 0,2$	-	254
R_5	-	-	8 ± 4	313



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

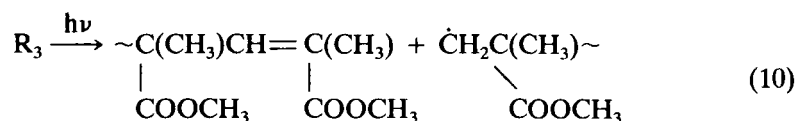
consumption of radicals R_1 in PMMA in the band of the so-called "forbidden" transition ($\lambda = 400 \text{ nm}$) is $(1.9 \pm 0.3) \times 10^{-5}$ for the initial portion of the kinetic curve⁹¹ which makes the value of Φ_9 (determined from the relationship given above) immeasurably low.

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 determine¹¹³ the quantum yield of formation of additional ruptures in the main chain of the polymers (≈ 0.1) and the characteristic diffusion step (2 nm which is close to Kuhn's size of the kinetic segment for PMMA).¹¹⁴ Since mostly R_1 radicals are stabilized in PMMA at room temperature, the value of the measured quantum yield¹¹³ 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 $\Phi_9 = 0.4\text{--}0.5$.

Photochemical reactions of acyl radicals R_7 in PMMA lead, as in 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



Assuming that reaction (10) requires free volume $v \approx 0.045\text{--}0.05 \text{ nm}^3$ (free volume necessary for the emergence of the end radical from the "cage"¹¹⁵) and knowing the quantum yields of reactions (5, 6), one can evaluate the maximum value of the quantum yield of reaction (10) which is $5 \times 10^{-4}\text{--}10^{-3}$.

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 IX, 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, as is seen from Table X, are characterized by a certain indefiniteness in the assignment of the ESR and optical absorption spectra of these species.

By analogy with well studied photochemical reactions of radical anions of low-molecular esters,² PMMA radical anions should dissociate with quantum yields close to 10^{-2} at 77 K

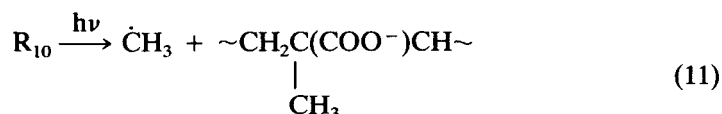


TABLE IX

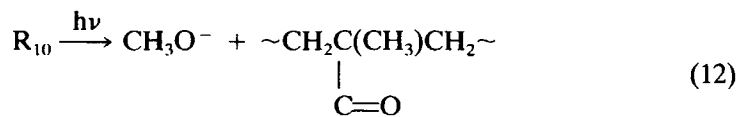
Quantum yields of degradation and decomposition of ester groups on direct photolysis of PMMA

Quantum yield of degradation · 10 ³			Quantum yield of ester groups decomposition	Literature
air	inert atmosphere	vacuum	vacuum	
2,3	-	-	-	[116]
13-18	-	22-40	-	[117]
8,7	4,8	-	I	[118]
9,3	9,3	-	-	[119]
3,2	5	-	-	[120, 121]
-	-	-	0,5	[108]
-	-	50	I	[84]

TABLE X

Parameters of ESR and optical absorption spectra of PMMA radical anions

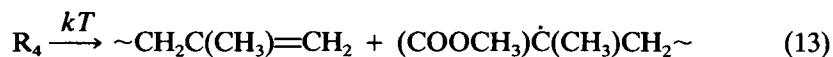
Number lines in ESR spectrum	Parameters of ESR spectrum	λ_{max} , nm	Literature
3	$a_H = 1,1 \text{ mT}$	305, 320	[122]
I	$\Delta H_{I/2} = 1,3 \text{ mT}$	320	[123]
3	$a_H = 1,1 \text{ mT}$	420	[124]
I	$\Delta H_{I/2} = 0,5 \text{ mT}$	440	[125]
-	-	365, 410, 1050	[126]
I	-	725	[127]



Thus, photochemical reactions of radical anions on exposure to long-wave ($\lambda \leq 600 \text{ nm}$) 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, for instance, additional polymerization of the latter.¹²⁸

An analysis of the kinetics of accumulation of radicals and of changes in the viscosity-average molecular weight of PMMA on photolysis sensitized by aromatic compounds¹²⁹ 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 concluded¹⁰⁷ that the rup-

tures in the main chain were caused by thermal decomposition of radicals R_4 formed on photolysis of radicals R_7



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 believed¹³⁰ to be due to thermal decomposition of radicals R_3 by reaction (10). Without arguing the validity of the main conclusions referred to above,¹⁰⁷ it should be noted that spin trap studies of the nature of radicals formed on PMMA degradation in the liquid phase^{92,131,132} showed 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 the authors' opinion, 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 emphasized¹³¹ 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.^{94,132}

Later on,¹³³ 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 found¹³⁴ that the primary act of direct PMMA photolysis with the quantum yield close to 0.5 resulted in the formation of isolated vinylidene bonds which, together with isolated double bonds formed in the course of thermal and photochemical reactions of radicals, could accept efficiently various low-molecular

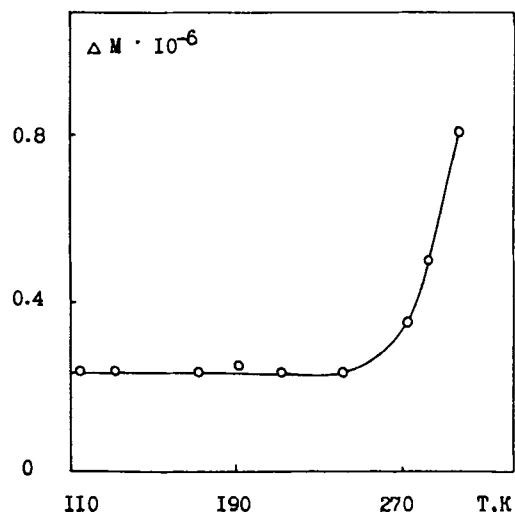


FIGURE 3 Change of PMMA molecular mass upon the photolysis at different temperatures.¹³¹

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,¹³⁵ there was disclosed the reaction of photodissociation of such radicals in PMMA leading to the formation of molecular oxygen.¹³⁶ By analogy with photochemical reactions of peroxy radicals in polyolefins¹³⁵ and polystyrene,⁶⁴ 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)¹⁰³ and poly(ethyl acrylate)¹³⁷ 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)

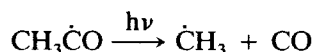
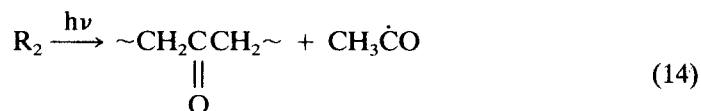
Table XI lists the data referring to ESR spectral parameters, thermal stability and light sensitivity of radicals formed in poly(vinyl acetate) (PVAc), poly(vinyl alcohol) (PVA) and one of its acetals, poly(vinyl butyral) (PVB), on various exposures. By virtue of the fact that polyacetals also contain 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 .¹⁴¹ Such processes were earlier suggested for ketyl radical anions.¹⁴⁵ The character of the ESR spectra of PVAc excludes the possibility of the earlier assumed¹⁴⁶ dark protonation of R_1 with the formation of RC(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.^{37,147}

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



and the formation of CH_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

TABLE XI

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	Life-time
$\sim \text{CH}_2\overset{\cdot}{\text{C}}\text{HCH}_2\sim (\text{R}_1)$ OCOCH ₃	2	$a_{\text{H}}^{\text{CH}_3}=2,3$	radiolysis PVA	-	$\lambda_{\text{max}}=320,$ $\epsilon_{320}=220\pm 80$ $\text{m}^2\text{mol}^{-1}$	[138]
	2	$a_{\text{H}}^{\text{CH}_3}=2,8$	radiolysis PVA1	-	$\lambda_{\text{max}}=290-300,$ $\epsilon_{300}=250\pm 100$ $\text{m}^2\text{mol}^{-1}$	[139]
	2	$a_{\text{H}}^{\text{CH}_3}=2,6$	radiolysis PVB	< 160	$\lambda_{\text{max}}=320,$ $\epsilon_{320}=350\pm 110$ $\text{m}^2\text{mol}^{-1}$	[15, 140]
$\sim \text{CH}_2\overset{\cdot}{\text{C}}\text{HCH}_2\sim (\text{R}_2)$ OCOCH ₃	3	$a_{\text{H}}^{\beta_1}=2,1$ $a_{\text{H}}^{\beta_2}=0,3$	radiolysis photolysis	-	$\lambda_{\text{max}} < 300,$ $\epsilon_{365}=40\pm 10$ $\text{m}^2\text{mol}^{-1}$	[102, 139, 141]
$\sim \overset{\cdot}{\text{C}}\text{HCH}_2$ OCOCH ₃	3		radiolysis mechanical degradation	-	spectral (3,138) properties of alkyl radicals	
$\sim \text{CH}_2\overset{\cdot}{\text{C}}\text{HCH}_2\sim (\text{R}_4)$ OCOCH ₂	3	$a_{\text{H}}^{\alpha}=2,1$	photolysis	-	$\lambda_{\text{max}}=320^*$ $\epsilon_{320}=80$ $\text{m}^2\text{mol}^{-1}$	[141, 142]
$\sim \text{CH}-\overset{\cdot}{\text{C}}\text{H}-\text{CH}\sim (\text{R}_5)$ OCOCH ₃ OCOCH ₃	4	$a_{\text{H}}^{\alpha}=a_{\text{H}}^{\beta}=2,5$	photolysis	-	spectral properties of alkyl radicals	[102]
$\sim \text{CH}_2\overset{\cdot}{\text{C}}\text{H} (\text{R}_6)$ OCOCH ₃	5	$a_{\text{H}}^{\alpha}=a_{\text{H}}^{\beta_1}=2,1$ $a_{\text{H}}^{\beta_2}=4,2$	radiolysis**	-	spectral properties of radical R ₂	[141, 143]
$\sim \text{CH}_2\overset{\cdot}{\text{C}}\text{HCH}_2\sim (\text{R}_7)$ OH	3	$a_{\text{H}}^{\beta_1}=3,4$ $a_{\text{H}}^{\beta_2}=0,5$	radiolysis	<330-360	$\lambda_{\text{max}}=225-235,$ $\epsilon_{230}=170\pm 50$	[139]

specimens) among gaseous reaction products was noted.¹⁴¹ The quantum yield of reaction (14) measured at 77 K was 0.13 ± 0.04 .¹⁴⁷

Photochemical reactions of radicals R₃, R₄ and R₅ in PVAc have not been studied. It can only be noted that the very fact of the formation of radicals R₅ in PVA raises strong doubts since their assignment was made^{102,149} on the basis of an erroneous, as has been shown,^{141,149} idea of photoisomerization of radicals R₂. Photochemical reactions of terminal radicals R₃ 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

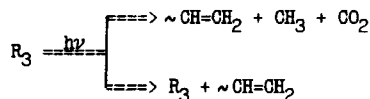
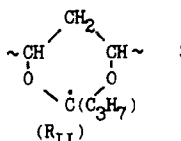
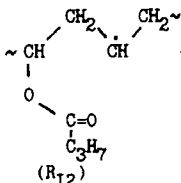


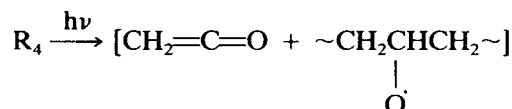
TABLE XI (Continued)

Radical	Number of lines in ESR spectrum	Parameters of ESR spectrum, $m\Gamma$	Methods of radicals generation	Range of thermal stability, K	Range of light sensitivity, nm	Literature
$\sim\text{CH}_2\dot{\text{C}}\text{H}(\text{OH})$ (R_3)	3	$a_{\text{H}}^\alpha = a_{\text{H}}^\beta = 2,3$	mechanical degradation of water solutions, 77 K	< 170	spectral properties of radical R_7	[98]
$\sim\text{CH}(\text{OH})\dot{\text{C}}\text{H}_2$ (R_9)	4	$a_{\text{H}}^\alpha = 2,2$ $a_{\text{H}}^\beta = 3,7$	mechanical degradation of water solutions, 77 K	< 170	spectral properties of alkyl radicals	[93]
$\sim(\text{CH}=\text{CH})_n\dot{\text{C}}=\text{O}$ (R_{10})	1	$\Delta H_{1/2} = 1,7$	radiolysis	< 150	$\lambda_{\text{max}} = 375, 400, 500$	[144]
	3	$a_{\text{H}}^\beta = 3,1$	radiolysis	< 190-200	$\lambda_{\text{max}} \approx 250, \epsilon_{254} = 230 \pm 70$	[37, 140]
	6	$a_{\text{H}}^\alpha = 2,1$ $a_{\text{H}}^\beta = 3,5$	radiolysis	< 200	$\lambda_{\text{max}} \approx 250, \epsilon_{254} = 230 \pm 70$	[37, 140]

* - spectral properties of corresponding low molecular radicals.

** - radiolysis of vinylacetate

the free valency 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: $0.5-0.6^{142}$



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.

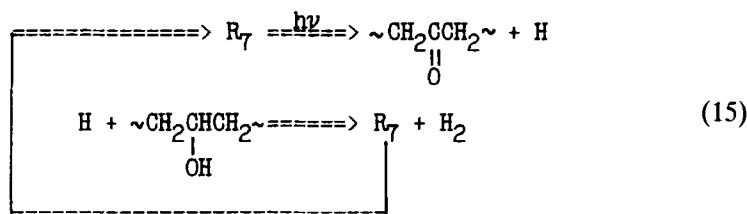
Thus, photochemical reactions of radicals in PVAc leading to the decomposition of ester groups and the formation of carbonyl groups in the main chain of the polymer are not a direct cause of ruptures in its main chain.

A comparison of the kinetics of accumulation of radicals and of molecular weight changes in PVAc on photolysis sensitized by aromatic compounds showed¹²⁹ that the degradation of the main chain occurred 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 attributed¹⁰⁹ to the formation and subsequent reactions of carbonyl groups formed in the main chain.

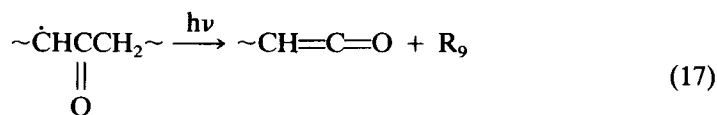
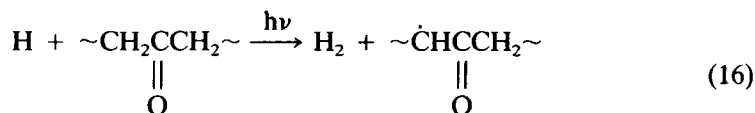
Poly(vinyl alcohol)

R₇, the most thermally stable radicals in PVA, undergo dissociation on exposure to light with 300 < λ < 400 nm^{139,150} by reaction (15) peculiar to α-hydroxyalkyl radicals.¹⁵¹



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—[H₂]_{*t*}/∫ R dt—reached high values after 4 h of photolysis—17, 42 and 103—for different photolysis temperatures—98, 188 and 273 K, respectively.¹⁵⁰

Ruptures in the main chain of PVA macromolecules can result from the reactions 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 R₇ was attributed to reaction (16, 17)¹⁵⁰



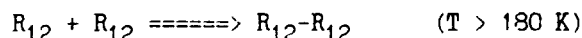
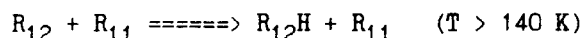
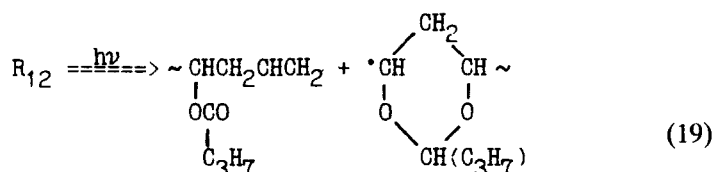
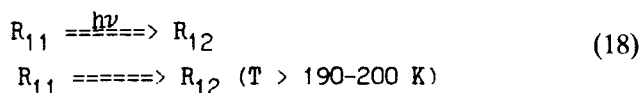
similar to the well known reactions of radicals formed in low-molecular aldehydes and ketones.^{152,153}

A conclusion was made¹⁵⁰ that the decrease in the molecular weight of PVA, with other conditions being equal, was 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 R₈–R₁₀ in PVA have not been studied. It can be remarked that photolysis of radicals R₈ should proceed similarly to reaction (15) and that of radicals R₁₀ to processes of photodissociation of acyl radicals.¹⁵⁴

Poly(vinyl acetals)

Photoradical processes in poly(vinyl acetals) have been studied most comprehensively on an example of 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 reaction¹⁵⁵) 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} .



The quantum yields of reactions (18, 19) measured on exposure to light with $\lambda = 254$ nm at 77 K were about $(4 \pm 2) \times 10^{-2}$.^{37,140} 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.³⁷

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.

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 XII) 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 ascribed¹⁵⁹ to radicals R_4 is due¹⁶⁰ to the formation of $\text{CH}_3\text{CHCONH}_2$ radicals on radiolysis of PAAm containing large amounts of the monomer.¹⁶³ The warming-up of PAA and PAAm (irradiated at 77 K) to 300 K 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.¹²

TABLE XII

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
$\sim\text{CH}_2\dot{\text{C}}\text{HCH}_2\sim$ CO ⁻ OH	(R ₁)	1 $\Delta H_{1/2}=1.4$ $g=2.003$	radiolysis	< 140	$\lambda < 450$, $\epsilon_{320} = 120 \times 10^2$ $\text{m}^2 \text{mol}^{-1}$	[9, 111]
$\sim\text{CH}_2\dot{\text{C}}\text{HCH}_2\sim$ CO ⁻ NH ₂	(R ₂)	1 $\Delta H_{1/2}=2.1$ $g=2.003$	radiolysis	< 150	$\lambda < 450$, $\epsilon_{330} = 150 \times 10^2$ $\text{m}^2 \text{mol}^{-1}$	[156, 157]
$\sim\text{CH}_2\dot{\text{C}}\text{HCH}_2\sim$ COOH	(R ₃)	3 $\beta_{\text{H}}^{\text{I}}=2.6$ $a_{\text{H}}^{\text{I}}=2.6$	radiolysis	< 180-210	$\lambda < 350$, $\epsilon_{270} = 40 \times 10^2$ $\text{m}^2 \text{mol}^{-1}$	[111, 158]
$\sim\text{CH}_2\dot{\text{C}}\text{HCH}_2\sim$ CONH ₂	(R ₄)	3 $\beta_{\text{H}}^{\text{I}}=2.5$ $a_{\text{H}}^{\text{I}}=2.2$	radiolysis photolysis	< 200	$\lambda < 350$, $\epsilon_{290} = 200 \times 10^2$ $\text{m}^2 \text{mol}^{-1}$	[157, 159, 160]
$\sim\text{CH}_2\dot{\text{C}}\text{H}$ COOH	(R ₅)	3 $a_{\text{H}}^{\alpha}=2.0$ $\beta_{\text{H}}^{\text{I}}=2.5$ $a_{\text{H}}^{\text{I}}=2.5$	radiolysis mechanical degradation	< 330	spectral properties of radical R ₃	[111, 161, 162]
$\sim\text{CH}_2\dot{\text{C}}\text{H}$ CONH ₂	(R ₆)	3 $a_{\text{H}}^{\alpha}=2.0$ $\beta_{\text{H}}^{\text{I}}=2.5$ $a_{\text{H}}^{\text{I}}=2.5$	radiolysis	< 350	spectral properties of radical R ₄	[157]

Studies of photochemical reactions of radical anions R₁ and R₂ in PAA and PAAM showed^{111,159,160} that photolysis led to their disappearance and to a reduction in the total concentration of paramagnetic centres which was believed to be associated with electron photoejection processes.



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 these polymers.¹⁴⁷

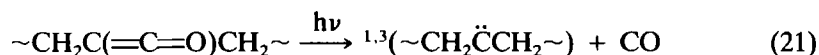
A detailed analysis of the mechanism of photolysis of radicals R₃ and R₄,^{111,159,160} with invoking relevant data for model low-molecular compounds,^{109,164} made it possible to assert that the main direction of these processes is dissociation



rather than isomerization, as was suggested earlier.^{157,165}

The formation of ketene on photodegradation of radicals R₃ and R₄ was cor-

robored spectroscopically in the solid phase (from the appearance of a characteristic absorption band with the maximum in the 365 nm region¹⁶⁶) and by mass spectroscopic determinations of carbon monoxide among its photolysis products



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.¹⁶⁰ 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^{111,159,160} 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^{111,159,160} quantum yields of the elementary stages (20, 21) and effective recombination constants of radicals were employed in mathematical simulation of the process kinetics (Figure 4); 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^{159,160} that at short photolysis times the MWD curves moved

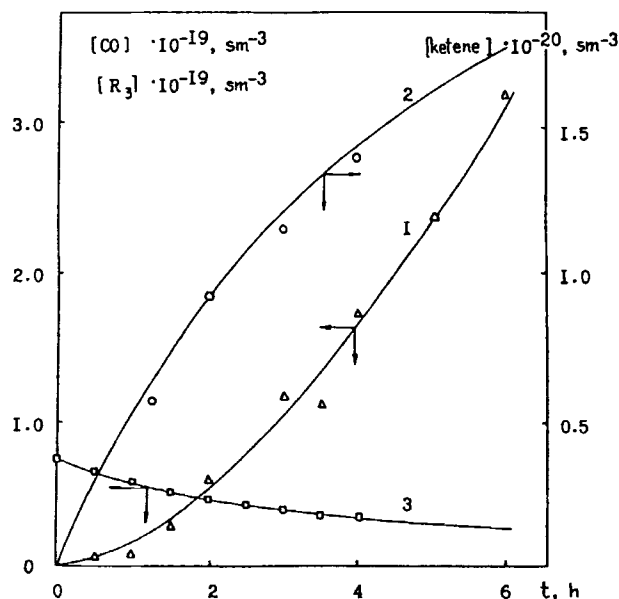
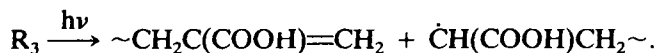


FIGURE 4 Kinetic curves for accumulation of carbon monoxide (1) and ketene (2), and consumption of radicals R_3 (3) upon the photolysis $\lambda \geq 280$ nm of PAA at 77 K.¹⁵⁹

towards lower molecular weights which attested to the occurrence of photochemical reactions of radicals R_3 leading to ruptures in the main chain



An evaluation of the quantum yield of the reaction gives $\approx 1.5 \times 10^{-2}$ which is much lower than the quantum yields of reaction (20) being as large as 0.1–0.2 in PAA and PAAM.^{111,159,160}

At large photolysis times, effective cross-linking in the polymer ascribed^{111,159,160} to the reactions of carbenes formed in process (21) is observed.

2.7. Polyoxides

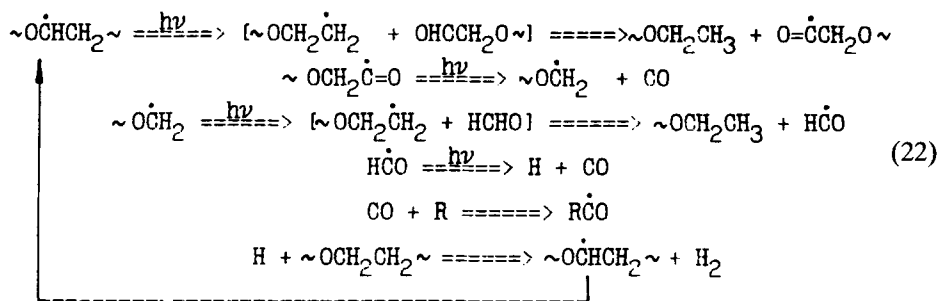
In the course of photolysis (initiated and sensitized by aromatic compounds^{2,173,174}) of polyoxides subjected to the action of ionizing radiation^{167–170} and mechanical loads,^{12,171} middle and end macroradicals and paramagnetic particles having a singlet ESR spectrum undergo stabilization (Table XIII).

Also, the exposure of polyoxides to light leads to the formation of such low-molecular radicals as HCO, CH₃ which points to the occurrence of secondary photochemical reactions of intermediate products.^{173,174} Temperature rise from 77–100 K stabilizes mostly middle radicals in polyoxides.

It follows from Table XIII 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 schemes¹⁷² of photochemical and some dark reactions of radicals in polyoxides do not stand up to criticism for they were based on a mis-interpretation 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^{109,175} 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:



The kinetic curves of the accumulation of acyl and formyl radicals on photolysis of middle $\sim OCHCH_2\sim$ and end $\sim OCH_2$ radicals in poly(ethylene oxide) displayed in Figure 5 speak in favour of the processes given in the scheme.

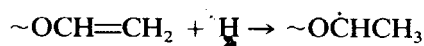
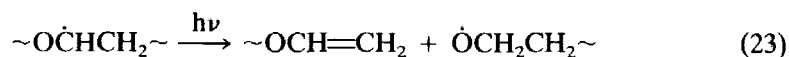
TABLE XIII

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

Radical	Number of lines in ESR spectra	Parameters of ESR spectrum, mT	Methods of radicals generation	Range of thermal stability	Range of light sensitivity, nm	Literature
$\sim\dot{\text{O}}\text{CH}_2$	3	$a_{\text{H}}^{\alpha}=1,8-2,5$	radiolysis photolysis mechanical degradation	<250-270	$\lambda < 360$, $\epsilon_{260} = 190 \pm 60$ $\text{m}^2\text{mol}^{-1}$	[9,12, 109]
$\sim\dot{\text{O}}\text{CHO}\sim$	2	$a_{\text{H}}^{\alpha}=1,1-1,6$ $g=2,0039-2,0054$	radiolysis mechanical degradation	<350-370	spectral	[9,12] properties analogous to radicals OCH_2
$\sim\text{CH}_2\dot{\text{O}}^*$	1	$\Delta H_{1/2} = 1,7-2,2$	radiolysis photolysis mechanical degradation			[9]
$\sim\dot{\text{O}}\text{CHCH}_2\sim$	3	$a_{\text{H}}^{\alpha}=a_{\text{H}}^{\beta_1}=1,5-2,1$ $a_{\text{H}}^{\beta_2} < 0,5$	photolysis radiolysis mechanical degradation	-	$\epsilon_{235} = 150 \pm 10$	[2,12]
$\sim\dot{\text{O}}\text{CHCH}_3$	5	$a_{\text{H}}^{\alpha}=a_{\text{H}}^{\text{CH}_3}=1,9$	photolysis	-	spectral	[109] properties analogous to radicals OCHCH_2
$\sim\text{OCH}_2\dot{\text{C}}\text{H}_2$	6	$a_{\text{H}}^{\alpha}=2,2$ $a_{\text{H}}^{\beta_1}=5,0$ $a_{\text{H}}^{\beta_2}=2,1$	mechanical degradation of water solutions, 77 K	-	spectral	[109] properties of alkyl radicals

* - ESR spectrum belong to acyl radicals $\text{RCO}\cdot$.

The possibility of a different course of reaction (22) is indicated by the formation of radicals $\sim\text{OCHCH}_3$ 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



It is to be noted that the mechanisms of photochemical reactions of radicals in polyoxides given above are corroborated by the results of investigations of reactions of electronically excited radicals in low-molecular ethers.^{109,151}

As follows from an analysis of the data pertaining to the mechanism of photo-

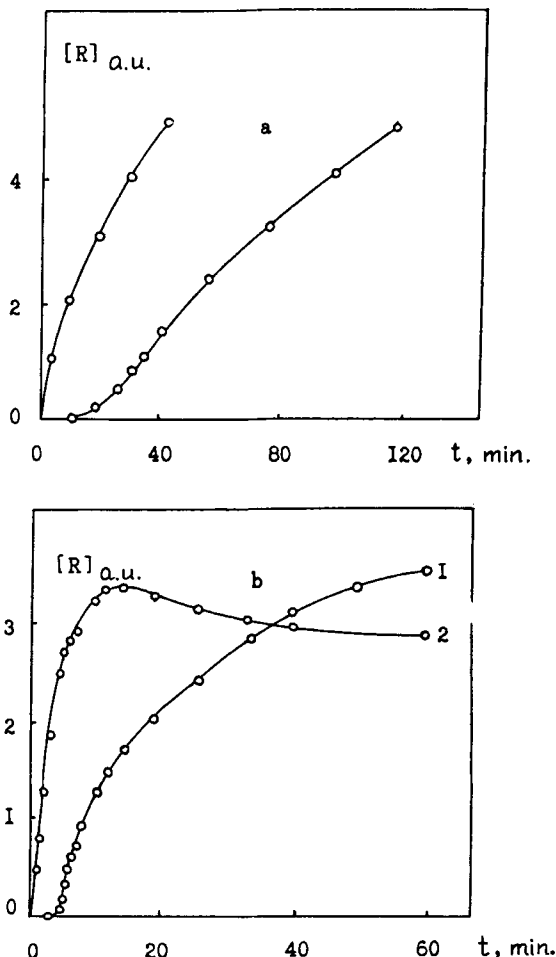


FIGURE 5 Kinetic curves for accumulation of acyl RCO (1) and formyl HCO (2) radicals upon the photolysis of radicals $\sim\text{OCHCH}_2\sim$ (a) and $\sim\text{OCH}_2$ (b) at 77 K.¹⁷⁵

radical reactions in polyoxides, chain photoradical reactions involving stages (22, 23) and leading to the degradation of the main chain and an experimentally determined reduction in the molecular weight¹⁰⁹ 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 $\approx 8 \times 10^{-3}$ (exposure to light with $\lambda = 313$ nm).

2.8. Polyamides and Aliphatic Polyurethanes

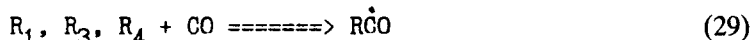
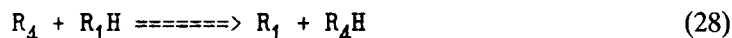
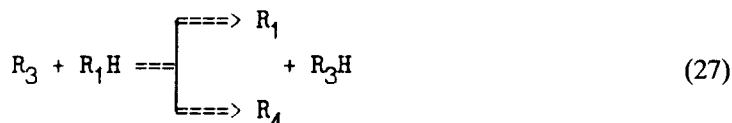
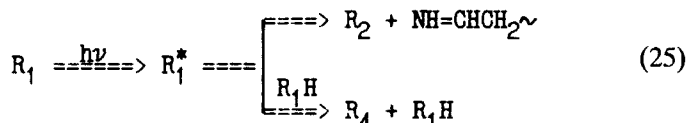
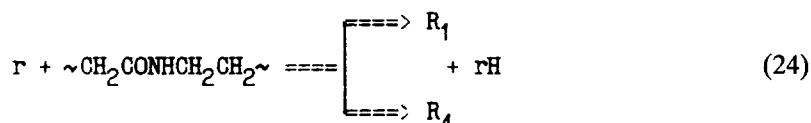
Polyamides (PS) and aliphatic polyurethanes (PU) find extensive application for different purposes; on the other hand, they alter rather strongly their service properties as a result of light and photooxidative ageing.

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 ($\epsilon < 10 \text{ m}^2 \text{ mol}^{-1}$) at its absorption maximum (210–240 nm). It was also reported that at $\lambda \approx 300 \text{ nm}$ the ϵ value for pure amides was $2 \times 10^{-3} \text{ m}^2 \text{ mol}^{-1}$.¹⁷⁶

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.^{177–179} 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.¹⁸⁰ 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.^{181,182} Table XIV 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^{181,182}:



Phototransformations of R_1 type radicals were observed in low-molecular amides and polyamides.^{181–186} It is noteworthy that radicals of this type are formed in amides and polyamides on their sensitized and initiated photolysis,^{181–183,187} exposure to ionizing radiation,¹⁸⁰ mechanical degradation,¹² 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 polycaproyamide.^{180,183} It is safe to say that the absorption 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 $\text{m}^2 \text{ mol}^{-1}$, respectively⁴).

Reaction (25) was taken into consideration^{181,182} only on the basis of the earlier data¹⁸⁰ since the researchers were unable to obtain any information supporting its

TABLE XIV

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

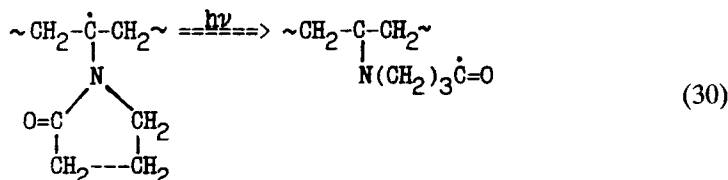
Radical	$\theta = 0$		$\theta = 90^\circ$		Thermal stability, $^\circ\text{K}$	Note
	Number of lines in ESR spectra	Parameters of ESR spectra	Number of lines in ESR spectra	Parameters of ESR spectra		
$\sim\text{CH}_2\text{CONH}\dot{\text{C}}\text{HCH}_2\sim$ (R_1)	4	$2.8 \pm 0.1 \text{ mT}$	5	7.2 mT	<293	sensitive to the light $\lambda=365 \text{ nm}$ action
$\sim\text{CH}_2\dot{\text{C}}\text{O}$ (R_2)	1	$g=2.0010 \pm 0.0004$ $\Delta H_{1/2} = 1.55 \pm 0.1 \text{ mT}$	1	$g=2.0010 \pm 0.0004$ $\Delta H_{1/2} = 1.55 \pm 0.1 \text{ mT}$	<273	sensitive to the light $\lambda > 445 \text{ nm}$ action
$\sim\text{CH}_2\dot{\text{C}}\text{H}_2$ (R_3)	6	$2.2 \pm 0.1 \text{ mT}$	6	$2.2 \pm 0.1 \text{ mT}$	<117	-
$\sim\text{CH}_2\text{CH}\dot{\text{C}}\text{H}_2\sim$ (R_4)	4	$2.8 \pm 0.1 \text{ mT}$	10	$1.6 \pm 0.1 \text{ mT}$	<156	-

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

occurrence in the polymer. The scheme of reactions presented above is fully consistent with the results obtained in studies of phototransformations of radicals in low-molecular amides.¹⁸³⁻¹⁸⁶ Of the greatest significance in this scheme are reactions (24, 26-29) 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 CHRCONHCHR 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.^{188,189}

Photochemical reactions of poly(vinyl pyrrolidone) middle radicals similar in their structure to amide radicals lead, on exposure to light with $\lambda = 313 \text{ nm}$ at 77 K, to the formation of acyl radicals caused by the pyrrolidone ring opening.¹⁹⁰ 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.

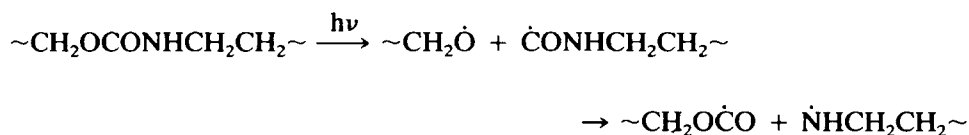


Similar reactions were observed in radicals stabilized in γ -irradiated β -chloroethylpyrrolidone-2 at 77 K on exposure to light.¹⁰⁹

It took a comparatively long time¹⁹¹ to succeed in recording the formation of

peroxide radicals R_1O_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^{192,193} not only disclosed the formation of R_1O_2 radicals on PA photooxidation but also demonstrated that their decay on exposure to light follows the bimolecular law, the effective rate constant was 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^{194–197}



It is assumed in this case that primary radicals are not stabilized but undergo further transformations. It was possible to demonstrate,¹⁹⁸ 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 could only be obtained on the assumption that C—O bond scission in the urethane group was the major event in the primary act (Figure 6). 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.¹⁹⁹

Primary radicals formed on PU photolysis, mechanical degradation or exposure to ionizing radiation^{200,201} give rise to rather stable radicals of the $\sim\text{CH}_2\text{OCONH}\dot{\text{C}}\text{HCH}_2\sim$ type. The possibility of photochemical reactions of radicals of this kind was indicated by the results of initiated photolysis experiments¹⁹⁴ in which the estimated stationary concentration of the radicals was independent of light intensity. The proposed mechanism of the reaction of dissociation of these radicals¹⁹⁴ is similar to that discussed above for PA



Detailed investigations of the mechanism of photochemical reactions in PU demonstrated^{109,200,201} that the action of light with $\lambda = 365$ nm on $\sim\text{CH}_2\text{OCONH}\dot{\text{C}}\text{HCH}_2\sim$ radicals formed on γ -irradiation of PU led, at small photolysis times, to the formation of $\text{RO}\dot{\text{C}}\text{O}$ radicals (a singlet line in ESR spectra with a half-width of $\approx 0.9mT$ and $g = 2.002$) and to a fast establishment of their stationary concentration and at large photolysis times, to the formation of acyl radicals $\text{R}\dot{\text{C}}\text{O}$ 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

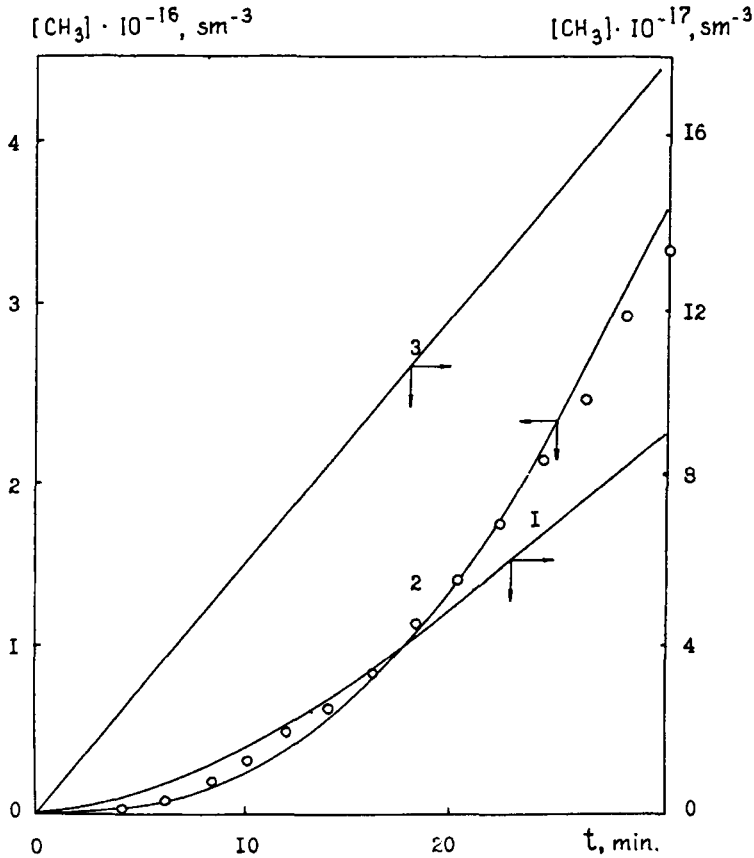
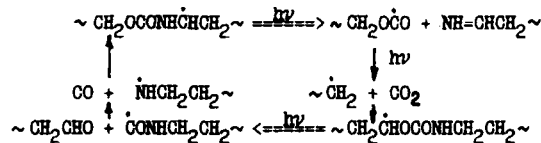


FIGURE 6 The kinetics of accumulation of methyl radicals upon the photolysis of methyl-*N*-ethyl-carbamate at 77 K (points—experimental values, curves—calculated values at different mechanisms of primary act: 1—C(=O)—N bond rupture, 2—C(=O)—O bond rupture, 3—C(=O)O—C bond rupture).¹⁹⁸

action of light on $\sim\text{CH}_2\text{OCONHCHCH}_2\sim$ radicals which is attributed to the interaction of CO with alkyl end radicals $\sim\text{CH}_2$ formed in the course of photochemical reactions of radicals.^{109,200,201}

The orderliness of the structure of PU²⁰² enables complex photoradical reactions in them^{109,200,201}; the mechanism of such reaction is shown in the scheme:



Changes in the composition of gaseous products and in the molecular weight distribution of PU in the course of photolysis^{109,200,201} and the formation of new functional groups²⁰³ speak in favour of this scheme. Exposure to light in the absorption band of $\text{CH}_2\text{OCONHCHCH}_2$ radicals at room temperature in PU pro-

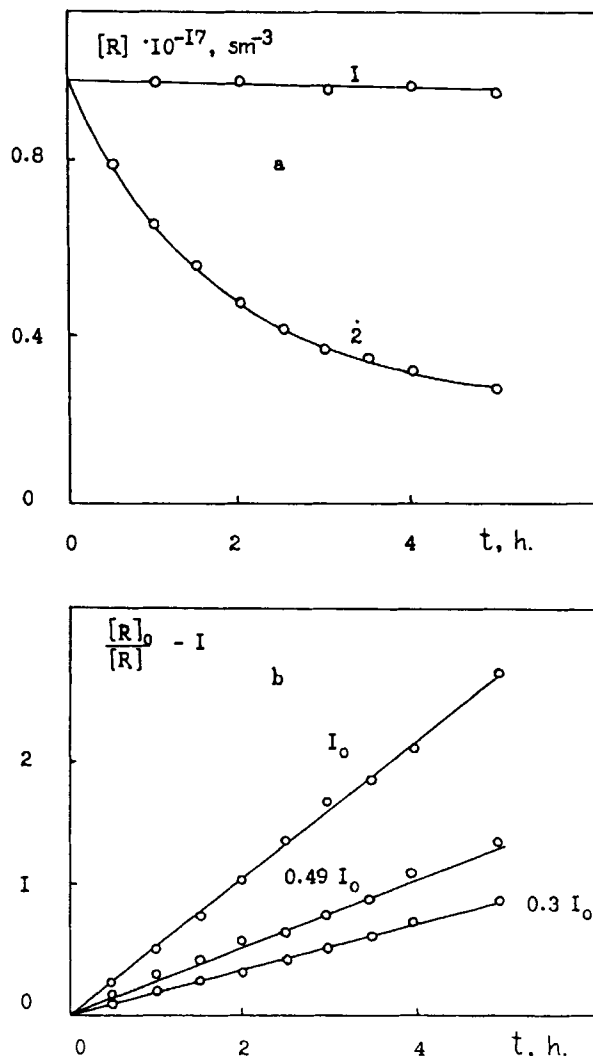


FIGURE 7 The kinetics of change of radicals $\sim\text{CH}_2\text{OCONHCHCH}_2\sim$ concentration in 4,6-polyurethane (a) at 293 K in the dark (1) and under the action of 365 nm light (2) and linear anamorphoses (b) of kinetic curves for photorecombination of $\sim\text{CH}_2\text{OCONHCHCH}_2\sim$ radicals at different light intensity.¹⁰⁹

duced 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 intensity¹⁰⁹ (Figure 7). 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.²⁰²

Photochemical reactions of radical anions (singlet lines in ESR spectra with $\Delta H_{1/2} \approx 1.0\text{--}1.6\text{mT}$ and $g \approx 2.003$) formed in low concentrations upon exposure of PA, PU and their low-molecular analogues to ionizing radiation at low

TABLE XV

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
$\sim\text{CH}_2\text{CONH}\dot{\text{C}}\text{HCH}_2\sim$	(I)	365	2,7±0,7	n-butyl-acetamide	[205]
$\sim\text{CH}_2\text{OCONH}\dot{\text{C}}\text{RCH}_2\sim$	(8)	365	1,0±0,5	methyl-N-ethylcarbamate	[200,201]
	(8)	365	~ 1	ethyl-N-isopropyl-carbamate	[200,201]
$\sim\text{CH}_2-\overset{\text{O}=\text{C}}{\underset{\text{CH}_2}{\text{N}}}-\text{CH}_2\sim$	(30)	313	20±10	polyvinyl-pyrrolidone	[190]

temperatures^{186,200,201,204} result mostly in the ejection of an electron with quantum yields close to 10^{-2} ¹⁵⁵ and have no essential effect on the molecular weight distribution of the polymers.¹⁴⁷

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 and listed in Table XV.

3. Photoreaction Chain Reactions

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

The most characteristic features of photoreaction 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 reactions²⁰⁶; in polystyrene, the oxygen absorption rate in a photooxidative ageing process exceeds the consumption rate of radicals almost by a factor of 10^3 .⁶⁵

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 dependence⁹:

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

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 concrete mechanism of photoreaction chain reactions, this

expression is valid for processes of photorecombination of radicals in polyolefins,²⁰⁷ polytetrafluoroethylene,²⁰⁶ polyurethanes¹⁰⁹ and polyamides,¹⁹³ poly(acrylic acid) and poly(acryl amide),^{111,159} 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 8). The maximum chain length in photoradical chain processes studied by now in polymers exceeds 103.⁶⁶

4. Specific Features of the 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.²⁰⁸ 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.²⁰⁹

The unusual character of the kinetic curves of accumulation of the products of photochemical reactions of radicals was first revealed in poly(vinylene carbonate).³⁷ The kinetic curve of accumulation of formyl radicals HCO formed on photodissociation of middle macroradicals has two clearly discernible linear sections (Figure 9). The observed dependences can be easily explained on the assumption of a bimodal distribution of middle macroradicals in reactivity; however, the values of the thus obtained parameters (quantum yield, the proportion of radicals with high

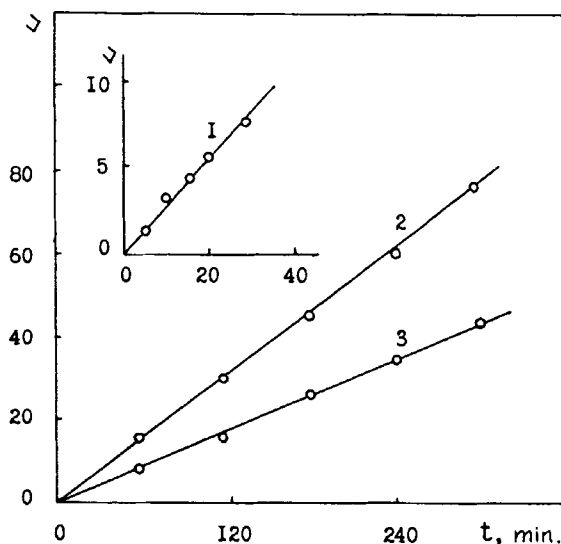


FIGURE 8 Relationship between photoradical reaction chain length and duration of photolysis at 77 K for different polymers: 1—PVA, 2—PAAm, 3—PAA.

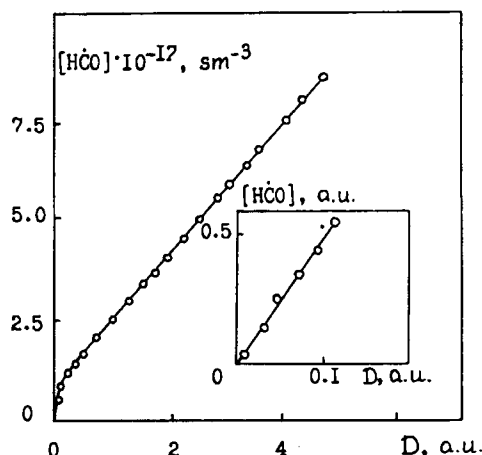
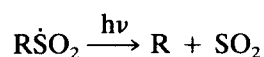


FIGURE 9 Dependence of accumulation HCO radicals at photolysis of middle radicals in PVCb at 77 K on dose of light absorbed.³⁷

and low reactivity) can hardly find an explanation and are, most probably, far from the real levels.³⁷ More accurate is the model²¹⁰ 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 above,³⁷ 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



it was possible to observe the effect of the energy of the photon within one electronic absorption band on kinetic non-equivalence (Figure 10) which indicated that the initial distribution of macroradicals in reactivity was determined, among other factors, by the energy of the photon.²¹¹

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 in $(5-8) \times 10^{12} \text{ s}^{-1}$ ²¹² which strongly restricts the time interval within which the excessive vibrational energy can dissipate in the

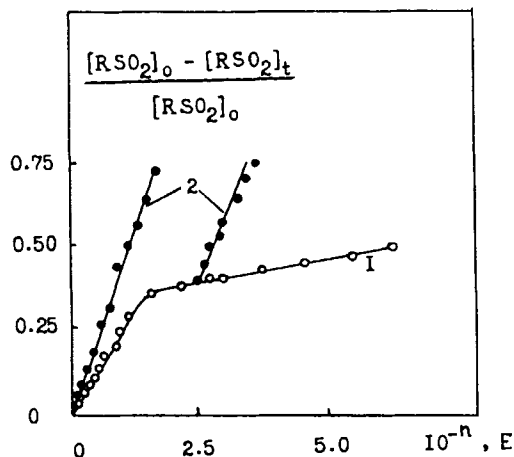


FIGURE 10 The kinetics of consumption of sulphonyl radicals in tetrafluoroethylene-hexafluoropropylene (TFE-HFP) copolymer in the photolysis at 365 nm (1; $n = 6$) and 313 nm (2; $n = 5$) at 77 K.²¹¹ (D—absorbed dose, einstein).

medium. The suggestion that the dissipated photoexcitation energy can be conducive to an increase in mobility in the solid phase was used earlier²¹³ for explaining photoselection data. Also, some authors believe²¹⁴ 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 reactions of macroradicals a qualitatively different explanation of the effects is possible. It was shown^{215,216} that in one-dimensional molecular chains consisting of periodically repeating molecules the generation of specific collective excitations—solitons—was possible, the solitons propagating along the chain together with the 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.²¹⁷ The formation of solitons is 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.²¹⁸

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.¹⁴⁷

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 model²¹⁹ can be successfully used in evaluating the dissociation quantum

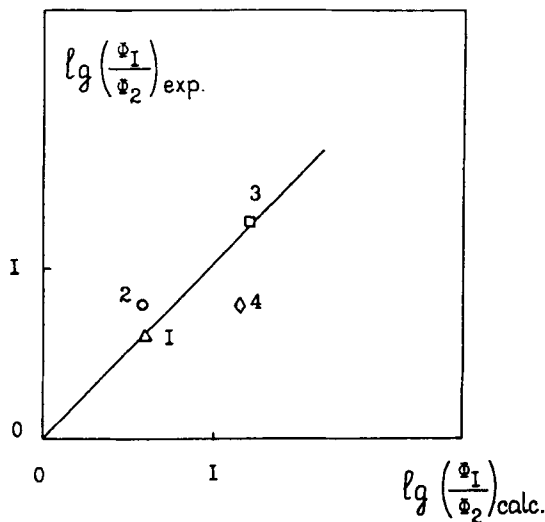


FIGURE 11 Calculated and experimental quantum yields for dissociation of electronically excited radicals at 77 K¹⁴⁷: 1—PE, 2—PAA, 3—PIB, 4—PMMA.

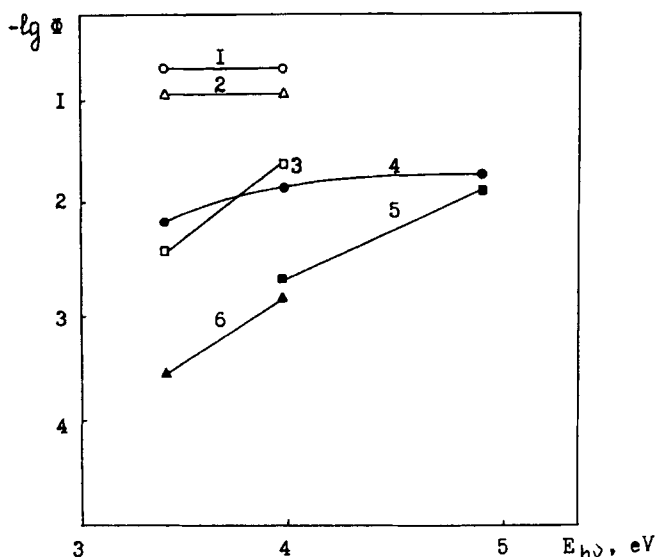


FIGURE 12 Dependence of quantum yields of dissociation of electronically excited radicals on photon energy at 77 K^{112,147}: 1—polyvinyl pyrrolidone, 2—PVA, 3—RSO₂ in PP, 4—polyvinylene carbonate, 5—PVB, 6—RSO₂ in TFE-HFP copolymer.

yields of different macroradicals in polymers,¹⁴⁷ just in the same manner as in the case of radicals in vitrified low-molecular organic compounds¹⁵³ (Figure 11).

There can be found some indirect indications²²⁰ 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 nonequivalence in reactions

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^{112,147} (Figure 12). On the other 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 cardinal different dependences on the energy of photon, as is the case with PVB and 2,4,4,6-tetramethyl-1,5-dioxane.¹¹² In terms of the free volume model, this means that for

TABLE XVI

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	
$\dot{R}O_2$	DPE	0,2±0,07	-	-	-	0,7±0,3	[144]
	DPP	0,04±0,01	-	-	-	0,7±0,3	[144]
	PTPE	0,015±0,005	-	-	-	0,1±0,05	[144]
$\sim CH_2\dot{C}CH_2 \sim$ OH	PVA1	-	0	2,50	60*	-	[150]

* - the value determined from the chain length data, obtained at different temperatures.

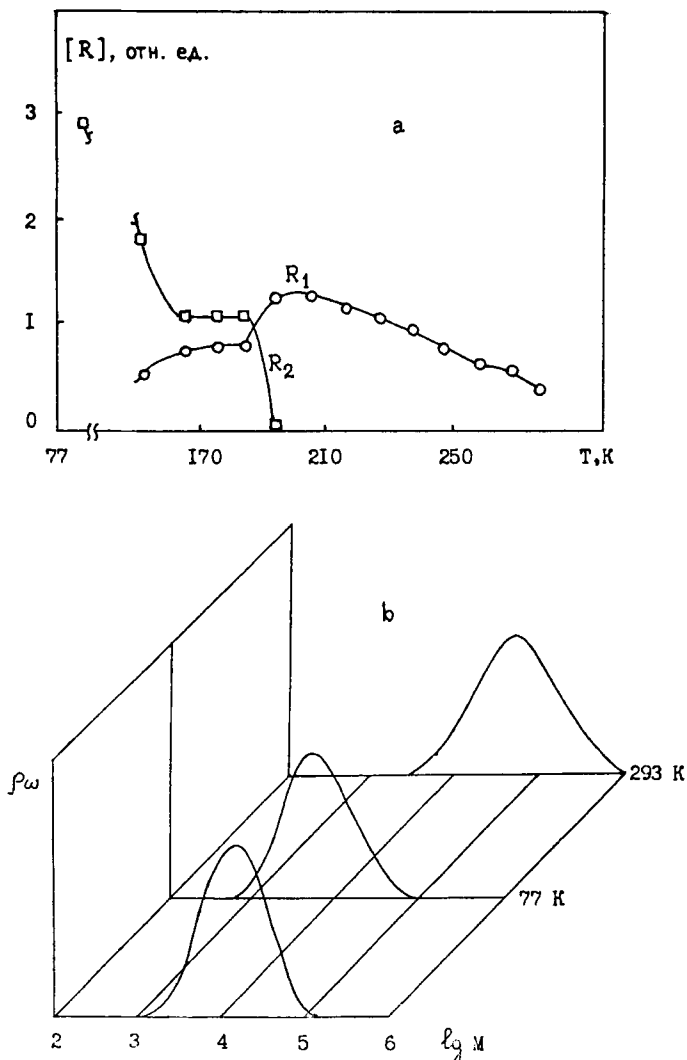
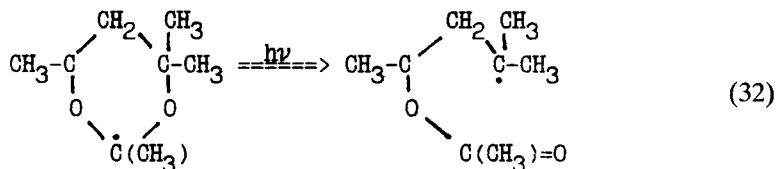


FIGURE 13 Change of radical concentration (a) and molecular mass distribution of PVB depending on temperature photoradical ageing.^{112,147}

two processes featuring great similarity in their chemical mechanism (32 and 33) 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.



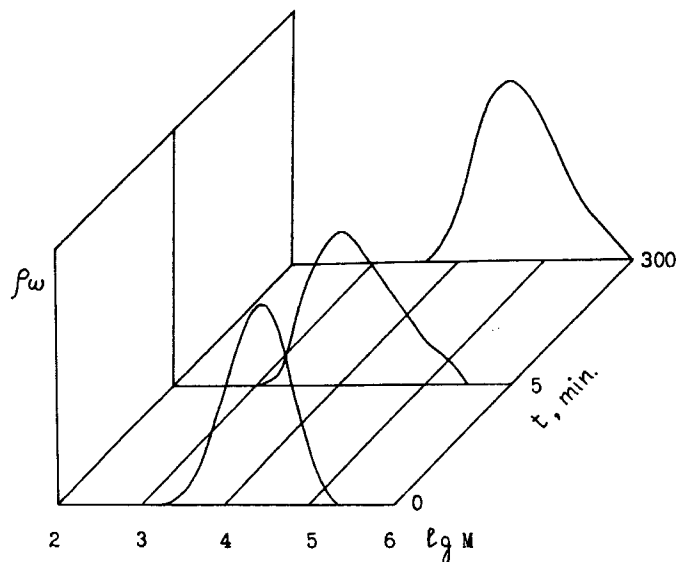
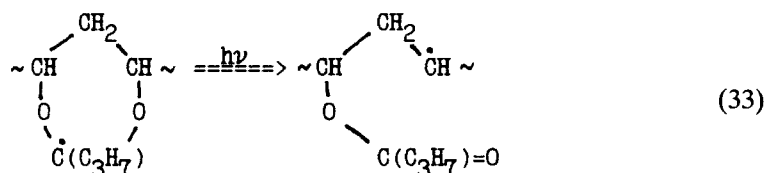
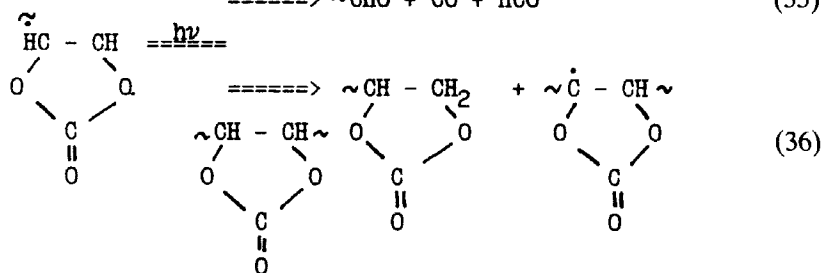
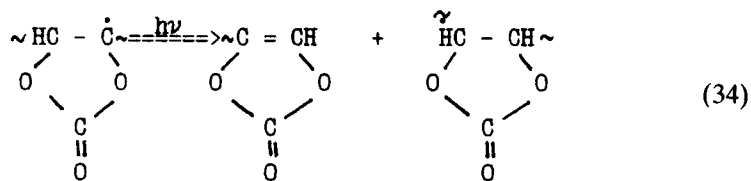


FIGURE 14 Change of molecular mass distribution in PAA depending on the time of photoradical ageing.



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 carbonate). An increase in the energy of the photon from 3.4 eV ($\lambda = 365$ nm) to 4 eV ($\lambda = 313$ nm) alters the ratio of the quantum yields of reactions (34–36) 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 relationship²²¹

$$\Phi = \exp(-\alpha \cdot v_r/v),$$

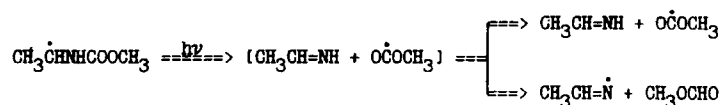
where Φ is quantum yield, α is proportionality factor, v is average thermodynamic volume per matrix molecule, v_r is the volume of an atom, radical or molecule leaving the cage. Indeed, the available reported data support this suggestion (Table XVI).

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,²²² 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.

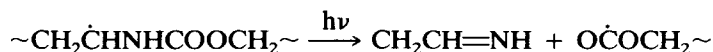
For reactions of phototransformation of radicals taking several channels and characterized by different activation volumes, pressure change can be used for preferably running a reaction with a smaller activation volume.

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,^{25,26} quantum yield in PS matrix change from 0.21 to 0.07.²⁵ 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 processes 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 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



This difference is ascribed¹¹¹ 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 convenient to make use of those 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 13).

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.

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 14).

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 performing 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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