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M. Ya. Mel'nikov^a

^a Department of Chemistry, Moscow State University, Moscow, Russia

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Photoradical Ageing of Polymers

M. YA. MEL'NIKOV

Department of Chemistry, Moscow State University, 119899 Moscow, Russia

New data referring to the mechanism and quantum efficiency of electronically excited macroradicals and radical anion reactions in various carbon- and heterochain polymers at temperatures below their glass transition or melting points are presented and discussed. Basic mechanisms of the photochemical reactions, including new data on the mechanism of the photochemical reactions of peroxide radicals, the effect of various factors (photon energy, free volume, molecular organization of the medium) on the direction and efficiency of reactions of electronically excited macroradicals are considered. The important role of photochemical chain reactions in photoageing, including photooxidation of polymers, is demonstrated. It was found that by varying photon energy, temperature, photolysis time and by taking advantage of the competition between thermal and photochemical reactions, it is possible to change the functional composition and molecular mass distribution of polymers in some desired direction.

KEY WORDS Polymers, photoradical ageing

RESULTS AND DISCUSSION

When speaking about the processes of photoradical ageing of polymers, one means the contribution of secondary photochemical reactions of intermediates (radicals, radical ions) produced in polymeric materials by the action of different sources (ionizing radiation, light, mechanical loading, etc.). At temperatures below the melting point of a polymer or these intermediates may reach high stationary concentrations. In many cases that is enough to allow secondary photochemical reactions of these intermediates.

The first question we must answer is: "What is the nature of the intermediates, which reactions have the maximum influence on changes in the physico chemical properties of the polymers during photoageing? Are they radicals, radical anions or radical cations?"

Figures 1 and 2 present data on the spectral distribution of sun light at the Earth's surface, the electronic spectra of the chromophors that cause photoageing of some polymers, various intermediates produced in polymers and low molecular weight model compounds. From this data it follows that the formation of these intermediates expands considerably the region of spectral sensitivity of these polymers.

The formation of radical anions in various polymers takes place as a result of the interaction of electrons produced by the same energy sources, with functional groups having a positive affinity for electrons. The action of light on radical anions of different types (esters, acids, amides and disulphides) results in their conversion via two major pathways: dissociation and electron ejection.

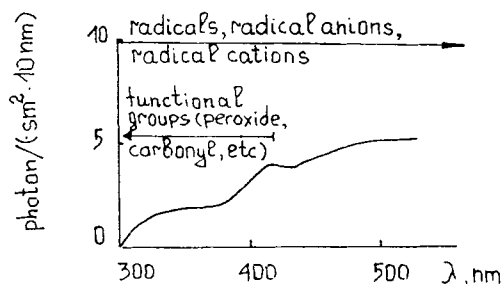


FIGURE 1 Spectral distribution of Sun light on the Earth surface and the data on electronic spectra of chromophorus groups causing photoageing and various intermediates produced in some polymers.

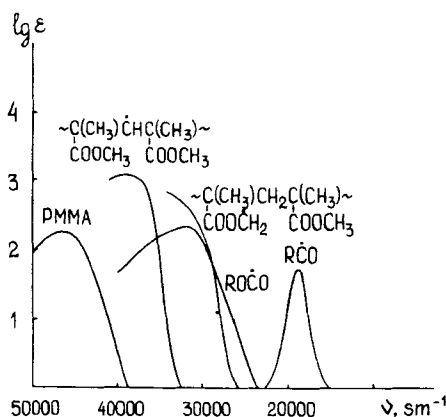


FIGURE 2 Absorption spectra of polymethyl methacrylate (PMMA) (1) and relevant macroradicals.

The processes of electron photoejection from radical anions (see Table I for their quantum yields) decrease the concentration of paramagnetic center due to electron-hole recombination. The formation of excited states resulting from this process does not affect, to any considerable extent, the structure and functional composition of polymers, mainly because of the low probabilities of homolytic decomposition and stabilization of radicals in the solid phase. The reactions of electronically excited radical anions cannot produce any considerable change in the molecular mass of polymers, except for aliphatic polyurethanes (PU). This has indeed been confirmed experimentally (Table II).

For PU, the comparison of turbidimetric curves obtained before and after the photolysis of radical anions also did not show any noticeable changes in the molecular weight of the polymers, which could be ascribed to the reactions of electronically excited radical anions. This is possibly due to the low concentration of radical anions compared with other paramagnetic species (<3% at a dose of γ -radiation from 10–50 kGr).¹

Thus, it may definitely be stated that the reaction of electronically excited radical anions in polymers do not noticeably affect the processes of photoradical ageing.

Radical cations (molecular cations) are produced as primary products ionizing radiation acting on substances at the same time as electrons and excited molecules.

TABLE I

Quantum yields (Φ) of reactions of electron ejection and dissociation for some radical anions at 77 K

Reaction	$\Phi \cdot 10^2$			
	313 nm	365 nm	405 nm	436 nm
$\sim\text{CH}_2\text{CH}(\overset{\cdot}{\text{O}}\text{CO}^-\text{CH}_3)\text{CH}_2\sim$				
$\implies e^- + \sim\text{CH}_2\text{CH}(\text{COOCH}_3)\text{CH}_2\sim$	-	-	1,0±0,3	0,6±0,2
$\implies \sim\text{CH}_2\text{CHO}^-\text{CH}_2\sim + \text{CH}_3\overset{\cdot}{\text{C}}\text{O}$	3	1,5	-	-
$\implies \sim\text{CH}_2\overset{\cdot}{\text{C}}\text{HCH}_2\sim + \text{CH}_3\text{COO}^-$	2	0,8	-	-
$\sim\text{CH}_2\text{CH}(\overset{\cdot}{\text{C}}\text{O}^-\text{OH})\text{CH}_2\sim$				
$\implies e^- + \sim\text{CH}_2\text{CH}(\text{COOH})\text{CH}_2\sim$	-	-	3	2
$\sim\text{CH}_2\text{CH}(\overset{\cdot}{\text{C}}\text{O}^-\text{NH}_2)\text{CH}_2\sim$				
$\implies e^- + \sim\text{CH}_2\text{CH}(\text{CONH}_2)\text{CH}_2\sim$	-	-	2,5	1,5
$\text{rCH}_2\text{SS}^-\text{CH}_2\text{r}$				
$\implies e^- + \text{rCH}_2\text{SSCH}_2\text{r}$	-	0,1	$5 \cdot 10^{-2}$	$2 \cdot 10^{-3}$
$\implies \text{rCH}_2\overset{\cdot}{\text{S}} + \text{rCH}_2\text{S}^-$	-	$1 \cdot 10^{-2}$	$8 \cdot 10^{-4}$	$2 \cdot 10^{-5}$

For slightly polar and polar media, the reactions of molecular cations and electrons produce a spectrum of intermediates and final radiolysis products. Usually the study of radical cations in the condensed phase is complicated by the absence of selective absorption regions in their visible and UV-spectra (Figure 1) and the short lifetimes of radical cations even in solids because of geminate recombination, fragmentation and ion-molecular reactions.²

Today we do not know of reliable data about any noticeable changes in the structure and properties of polymers during the photochemical reactions of polymer radical cations.

Thus, it may be definitely stated that the reaction of electronically excited radical anions and radical cations in the polymers studied can have a noticeable affect only under specific conditions, for instance, under the joint action of light and a powerful stream of ionizing radiation.

So, it is possible to say with confidence that the active intermediates playing an important role in the photoradical ageing of various polymers are free radicals.

In this connection we would like to provide information about the basic mechanisms of the reactions of electronically excited radicals, their efficiency, the major factors influencing their efficiency and the direction of these reactions.

The data we have obtained show that the type of photochemical reactions of macroradicals is photodissociation. These processes differently effect changes in the polymers:

1. Photochemical reactions of macroradicals result in degradation of the func-

TABLE II
The influence of photochemical reactions of radical anions on molecular mass change for some polymers

Polymer	Type of reaction	Gel fraction (%)	Molecular mass
polyacrylic acid	γ -radiolysis at 77 K + warming to room temperature	20,9	$M_w=2,9 \cdot 10^5$
	γ -radiolysis at 77 K + photolysis of radical anions at 77 K + warming to room temperature	19,6	$M_w=2,8 \cdot 10^5$
polyvinyl butyral (PVB)	γ -radiolysis at 77 K + warming to room temperature	-	$M_n=1,6 \cdot 10^4$
	γ -radiolysis at 77 K + photolysis of radical anions at 77 K + warming to room temperature	-	$M_n=1,6 \cdot 10^4$

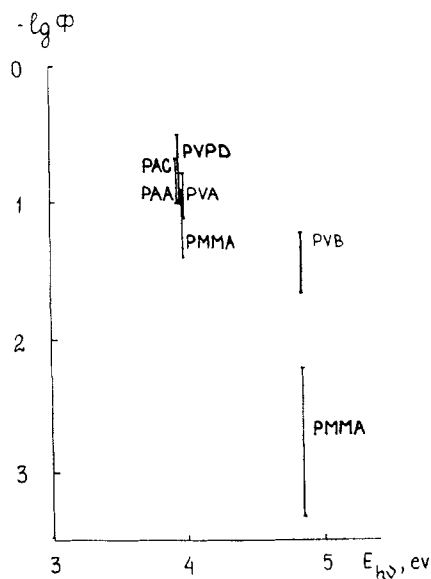


FIGURE 3 Quantum yields for the reaction of electronically excited macroradicals at 77 K.

tional groups of a polymer but do not affect its main chain. New functional groups emerging from these processes may turn out to be chromophors, for example, carbonyl groups and, hence, to cause polymer ageing due to their direct absorption of light; or as double bonds they may be more reactive in chemical reactions: especially in processes of oxidation. The efficiency of these kinds of photochemical reactions of macroradicals are illustrated in Figure 3.

2. Photochemical reactions of macroradicals may cause degradation of the main chain of the polymer and thus may produce significant changes in the physicochemical properties of polymers during the process of their photoageing. Data presented in Figure 4 show that the quantum yields of these reactions at 77°K are comparable with or exceed those of bond scission in polymer photolysis but they can be achieved with light of longer wavelengths.

3. Photochemical reactions of macroradicals produce secondary radicals or intermediate species, resulting in polymer cross-linking due to their reactions. These processes, which occur in some polymers, will be considered later, using specific cases as examples.

Let us consider some new data about the mechanisms of the photochemical reactions of macroradicals. The first group of results deals with the photochemistry of peroxide radicals—the main intermediates in processes of photooxidative ageing of polymers. The data obtained (Table III) for photochemical reactions of different peroxide radicals on a chemically activated SiO_2 surface show that the primary chemical act is the dissociation of the O—O bond. The various behaviors of the pair $[\text{RO} + \text{O}(^3\text{P})]$ produced in these processes defines further the direction of chemical their reactions in different polymers and model compounds. These various

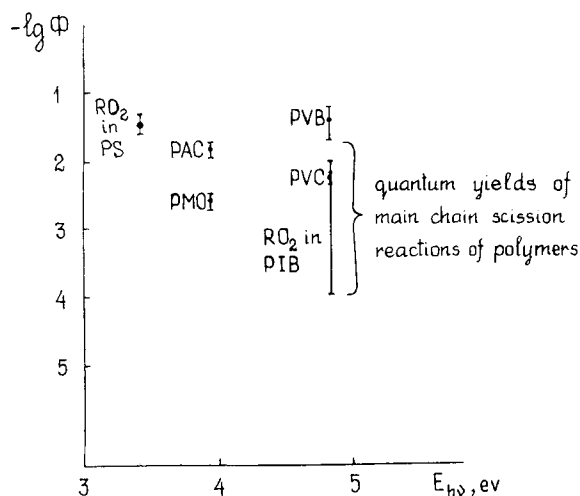


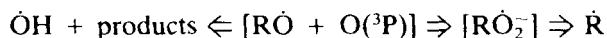
FIGURE 4 Quantum yields for the reaction of electronically excited macroradicals resulting in polymer main chain scission at 77 K.

TABLE III
Photochemical reactions of peroxide radicals "grafted" to SiO₂ surface³

Radical	Obtained paramagnetic products*	Assumed reactions
1. $\equiv\text{Si}\dot{\text{O}}\dot{\text{O}}$	$\equiv\text{Si}\dot{\text{O}}$ (0,8±0,1)	$\equiv\text{Si}\dot{\text{O}}\dot{\text{O}} \xrightarrow{h\nu} \equiv\text{Si}\dot{\text{O}} + \text{O}$
2. $\equiv\text{SiOCH}_2\text{O}\dot{\text{O}}$	$\equiv\text{Si}\dot{\text{O}}$ (0,5±0,1) $\equiv\dot{\text{S}}\text{H}$ (0,5±0,1)	$\equiv\text{SiOCH}_2\text{O}\dot{\text{O}} \xrightarrow{h\nu} \equiv\text{SiOCH}_2\dot{\text{O}} + \text{O}$ $\equiv\text{SiOCH}_2\dot{\text{O}} \rightarrow \equiv\text{Si}\dot{\text{O}} + \text{CH}_2\text{O}$ $\equiv\text{SiOCH}_2\dot{\text{O}} \rightarrow \equiv\text{SiOCHO} + \text{H}; \equiv\text{Si}:\text{H} \rightarrow \dot{\text{S}}\text{H}$
3. $\equiv\text{SiCH}=\text{CHO}\dot{\text{O}}$	$\equiv\text{Si}\dot{\text{C}}\text{HCHO}$ (0,7±0,1)	$\equiv\text{SiCHCHO}\dot{\text{O}} \xrightarrow{h\nu} \equiv\text{SiCHCHO} + \text{O}$ $\equiv\text{SiCHCHO}\dot{\text{O}} \rightarrow \equiv\text{Si}\dot{\text{C}}\text{HCHO}$
4. $\equiv\text{SiCH}_2\text{CH}_2\text{C}(\text{O})\dot{\text{O}}$	$\equiv\text{SiCH}_2\dot{\text{C}}\text{H}_2$ (0,7±0,1)	$\equiv\text{SiCH}_2\text{CH}_2\text{C}(\text{O})\dot{\text{O}} \xrightarrow{h\nu} \equiv\text{SiCH}_2\text{CH}_2\text{C}(\text{O})\dot{\text{O}} + \text{O}$ $\equiv\text{SiCH}_2\text{CH}_2\text{C}(\text{O})\dot{\text{O}} \rightarrow \equiv\text{SiCH}_2\dot{\text{C}}\text{H}_2 + \text{CO}_2$
5. $\equiv\text{SiCH}_2\text{CH}_2\text{O}\dot{\text{O}}$	$\equiv\text{SiOCH}_2\dot{\text{C}}\text{H}_2$ (0,8±0,1)	$\equiv\text{SiCH}_2\text{CH}_2\text{O}\dot{\text{O}} \xrightarrow{h\nu} \equiv\text{SiCH}_2\text{CH}_2\dot{\text{O}} + \text{O}$ $\equiv\text{SiCH}_2\text{CH}_2\dot{\text{O}} \rightarrow \equiv\text{SiOCH}_2\dot{\text{C}}\text{H}_2$
6. $\equiv\text{SiOCH}_2\text{CH}_2\text{O}\dot{\text{O}}$	$\equiv\text{SiO}\dot{\text{C}}\text{H}_2$ (0,7±0,1)	$\equiv\text{SiOCH}_2\text{CH}_2\text{O}\dot{\text{O}} \xrightarrow{h\nu} \equiv\text{SiOCH}_2\text{CH}_2\dot{\text{O}} + \text{O}$ $\equiv\text{SiOCH}_2\text{CH}_2\dot{\text{O}} \rightarrow \equiv\text{SiO}\dot{\text{C}}\text{H}_2 + \text{CH}_2\text{O}$

*part of corresponding paramagnetic products

behaviours are the reason, in our opinion, for the observed differences in the pathways and efficiencies of the photochemical reactions of peroxide radicals.



It is important to note that the photochemical reactions of peroxide radicals resulting in C—C bond scission of the main polymer chain and the formation $\dot{\text{O}}\text{H}$ radicals—low molecular carriers of free valence, effectively induce the oxidative processes during the photoradical chain reactions (Table IV).

It was found that under the action of light on thiylperoxide radicals $\text{RSO}\dot{\text{O}}$ produced during the photooxidation of some S-containing polymers resulted in the formation of sulphonyl radicals, RSO_2 , i.e., a new type of process was realized for peroxide radicals. The peculiarity of this reaction is the possibility of its occurring also under IR-radiation ($\lambda \geq 850 \text{ nm}$) with the formation of the same radical products—sulphonyl radicals. This process is the first and, as far as we know, a unique case of a radical photochemical reaction occurring under IR-radiation.

TABLE IV

Quantum yields for reactions of electronically excited peroxide macroradicals resulting in polymer main chain scission at 77 K

Polymer	Peroxide macroradical	Quantum yield	
		254 nm	313 nm
polyisobutylene	$\sim\text{C}(\text{CH}_3)_2\underset{\text{OO}}{\overset{\cdot}{\text{C}}}\text{HC}(\text{CH}_3)_2\sim$	$10^{-1}-10^{-2}$	-
polystyrene	$\sim\text{CH}_2\underset{\text{Ph}}{\overset{\cdot}{\text{C}}}(\text{OO})\text{CH}_2\sim$	-	$2,7 \cdot 10^{-2}$

TABLE V

Quantum yields for the abstraction of hydrogen an atom from electronically excited macroradicals in some polymers at 77 K

Polymer	Radical	Quantum yield
polyethylene	$\sim\text{CH}=\overset{\cdot}{\text{C}}\text{H}\sim$	$\approx 0,1$ (365 nm)[4]
polystyrene	$\sim\text{CH}_2\overset{\cdot}{\text{C}}\text{H}\sim$	$0,14 \pm 0,03$ (510 nm)
	$\underset{\text{C}_6\text{H}_7}{\overset{\cdot}{\text{C}}}$	$0,07 \pm 0,02$ (559 nm)
	$\sim\text{CH}_2\underset{\text{Ph}}{\overset{\cdot}{\text{C}}}\sim$	$(4-6) \cdot 10^{-4}$ (313 nm)*[5]

* -quantum yield of photochemical reactions in model low-molecular compound

Less frequently we deal with the reactions of electronically excited macroradicals in which they abstract a hydrogen atom from the polymer molecule (photosubstitution reactions). These processes are typical of allyl (in polyolefins), cyclohexadienyl (in longwave $D_0 \Rightarrow D_1$ transitions and middle macroradicals (in polystyrene) and some other types of macroradicals. The data on the quantum yields of these reactions, which cause the migration of free valence and photorecombination of macroradicals, are shown in Table V. In the literature, there is no reliable data about the influence of these reactions on the changes in polymer properties.

The photoionization reaction of macroradicals may exert a strong influence on the dielectric properties of some polymers. However, the data we have obtained show that the role of this process in the photoradical reactions in organic solids has been overstated. Information about the quantum yields of the photodissociation and photoionization reactions in polymers is given in Table VI. It may be seen

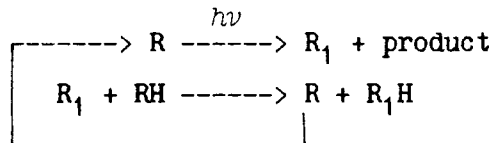
TABLE VI

The ratio of quantum yields of photodissociation (Φ_D) and photoionization (Φ_I) reactions for some types of radicals in organic solids at 77 K

Type of radical	Φ_D/Φ_I
$\sim\dot{C}\sim$	≈ 100 (254 nm)
$\begin{array}{c} \\ OH \end{array}$	≈ 1500 (313 nm)
$>\dot{C}OC<\sim$	≈ 500 (254 nm)
	≈ 1500 (313 nm)

that the quantum yields for the photodissociation of macroradicals are more than two orders of magnitude greater than the values for photoionization efficiency.

During our studies of the photochemical reactions of low- and high-molecular weight radicals we have discovered the phenomenon of photoradical chain reactions. These are chain reactions proceeding in substances which contain free radicals in which propagation proceeds by light induced activation of the radicals. These photoradical chain reactions result in the formation of stable products and recovery of the initial radicals, which can absorb light again resulting in multiple replications of the conversion cycle:



defining the efficiency of continuing thermal reactions having a radical lifetime, τ . The following quantitative relationship defines the condition in which the photoradical chain reactions may occur:

$$2.3 \cdot \epsilon \cdot \Phi \cdot I \cdot \tau > 1$$

Using this criterion and the values of ϵ and Φ as well as the data on thermal stability of macroradicals in polymers, it is quite possible to define clearly the conditions under which photoradical chain reactions will result. These are, first of all, low temperature chemical processes, in particular, radical processes in polymers below the vitrification temperature or melting point and characterized by large values of τ .

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

The most characteristic features of photoradical chain reactions are following.

1. Anomalously high yields of stable radical transformation products, exceeding dozens and hundreds of times the stationary concentrations of radicals.

2. The photorecombination of the radicals in a temperature range which rules out their translational mobility in the dark. The change in radical concentration in this case is expressed by the following dependence:

$$[R]^{-1} = [R]_0^{-1} + 4.6k_3 \cdot \Phi \cdot I_0 \cdot \epsilon \cdot l \cdot t / k_2 \cdot [RH]$$

where $[R]$ and $[R]_0$ are the current and initial concentrations of the radicals, k_2 and k_3 are propagation and termination rate constants, and l is optical length.

Regardless of the specific mechanism of photoradical chain reactions, this expression is valid for processes of photorecombination of radicals in PU, polyacrylic acid and polyacryl amide, etc. (Figure 5).

3. In the case where radicals are generated in the polymer prior to its exposure to light, growth of the chain length of the photoradical chain reaction is linear with photolysis time (Figure 6). The maximum chain length in the photoradical chain processes studied until now, in polymers, exceeds $\approx 10^3$.⁶

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

Concerning the efficiency of these photochemical reactions of macroradicals, we would like to consider the major factors influencing the quantum yields of the dissociation of the macroradicals. In the first place, it should be noted that the data available until now show the efficiency of the dissociation of polymer radicals in the solid phase to be satisfactorily described by the assumptions of "free volume" representations relating the quantum yield of the process to the dimensions of the product species of radical dissociation and to the thermodynamic mean free volume per matrix molecule⁷: $\Phi = \exp(-\alpha \cdot v_r/v)$. Figure 6 shows the applicability of the free volume model to the determination of the ratio of quantum yields for the dissociation of electronically excited macroradicals by different pathways.

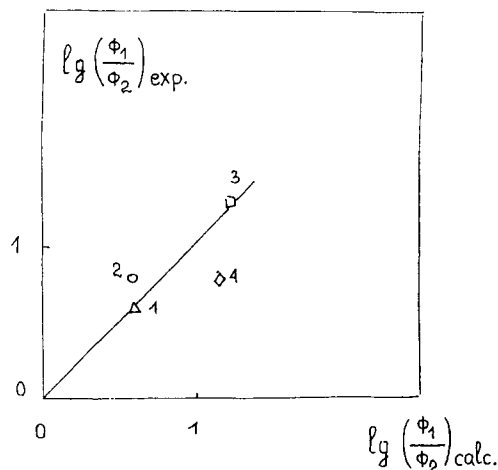


FIGURE 5 Calculated and experimental quantum yields for the dissociation of electronically excited radicals at 77 K: 1—polyethylene, 2—polyacrylic acid (PAA), 3—polyisobutylene, 4—PMMA.

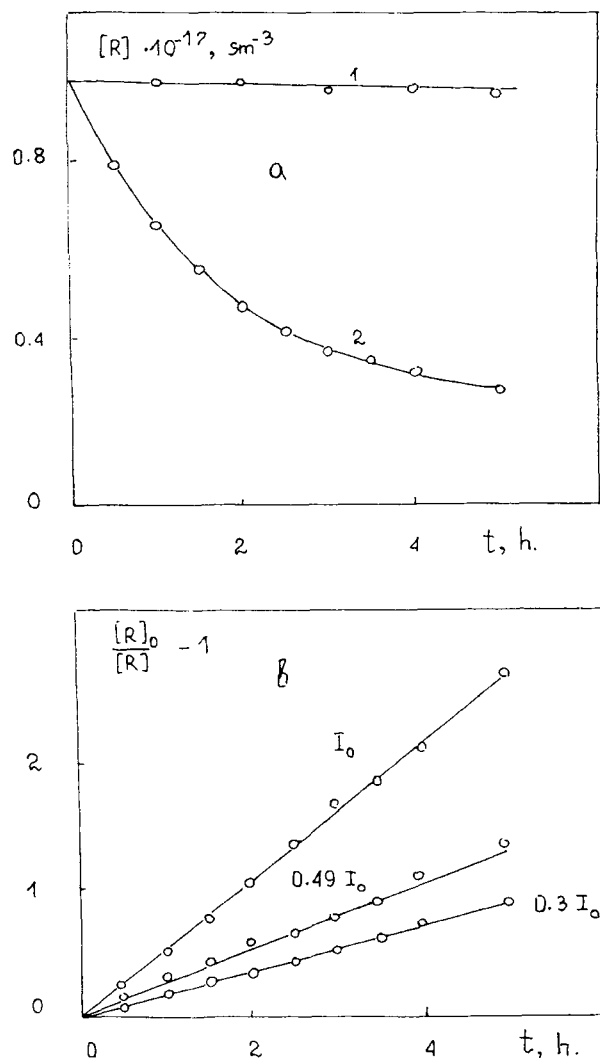


FIGURE 6 The kinetics of the change in concentration of $\sim\text{CH}_2\text{OCONH}\dot{\text{C}}\text{HCH}_2\sim$ radicals in 4,6-polyurethane (a) at 293 K in the dark (1) and under the action of 365 nm light (2) and linear anamorphoses (b) of kinetic curves for the photorecombination of $\sim\text{CH}_2\text{OCONH}\dot{\text{C}}\text{HCH}_2\sim$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

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 photon energy (Figure 7). On the other hand, for quantum yields exceeding ≈ 0.1 this dependence disappears. This indicates, in many instances, that the governing role of structural processes of reorganization of the matrix are 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 weight radicals of the same type manifest cardinally different depen-

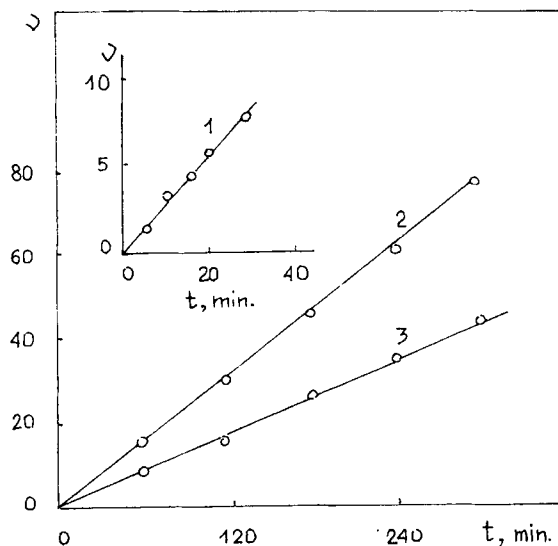


FIGURE 7 Relationship between photoradical reaction chain length and duration of photolysis at 77 K for different polymers: 1—polyvinyl acetate (PVA), 2—polyacrylamide, 3—PAA.

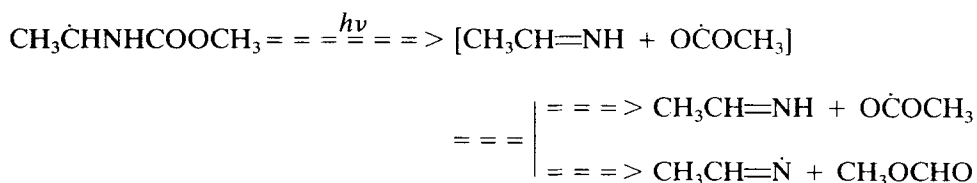
dences on the energy of the photon. In terms of the free volume model, this means that for two processes featuring great similarity in their chemical mechanism to occur, substantially different free volumes are required.

The effect of pressure on the efficiency of the 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 usually smaller than that of the corresponding molecules,⁸ 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, a pressure increase will also alter the rate of radiationless processes. For phototransformation reactions of radicals taking several channels and characterized by different activation volumes, pressure change can be used for preferably carrying out a reaction having a smaller activation volume.

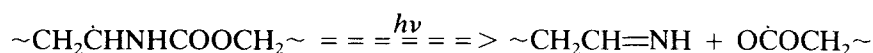
A change in the energy of the photon and a switch from one electronic absorption band to another may alter not only the quantum efficiency of the process but also its direction. Thus, cyclohexadienyl radicals, on excitation in the $D_0 - D_2$ electron transition band, dissociate to give hydrogen atoms while in the $D_0 - D_1$ transition band they detach an excited state hydrogen atom from a molecule of the medium, with the quantum yield in a polystyrene (PS) matrix changing from 0.21 to 0.07. 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 factor in the processes of dissociation of electronically cited 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 determined by the molecular organization

of the system. This 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 PU formed from hexamethylene diisocyanate and 1,4-butane- and 1,6-hexanediols gives only alkoxy carbonyl radicals



This difference should be ascribed to the 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.

In order to deliberately change the properties of a polymeric material, it is convenient to make use of the numerous cases where thermal and photochemical reactions of macroradicals alter differently the properties of polymers. Thus, photochemical reactions of alkyl macroradicals in PVB lead to destruction of the main

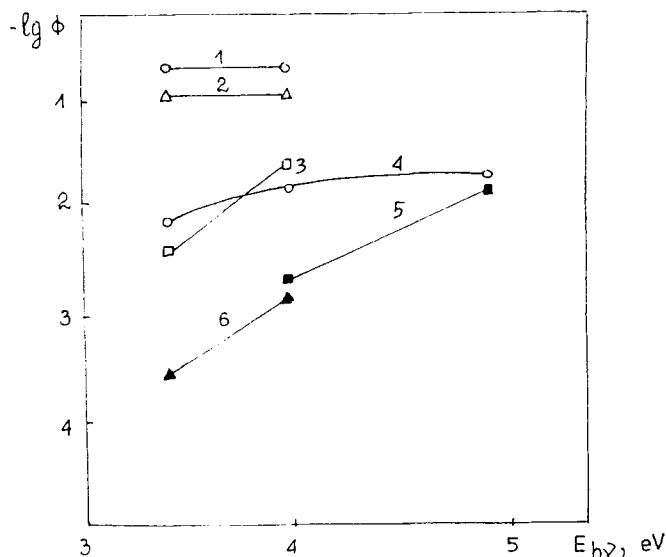


FIGURE 8 Dependence of quantum yields of dissociation of electronically excited radicals on photon energy at 77 K: 1—polyvinyl pyrrolidone, 2—PVA, 3— $\text{R}\dot{\text{S}}\text{O}_2$ in polypropylene, 4—polyvinylene carbonate, 5—polyvinyl butiral (PVB), 6— $\text{R}\dot{\text{S}}\text{O}_2$ in tetrafluoroethylene-hexafluorpropylene copolymer.

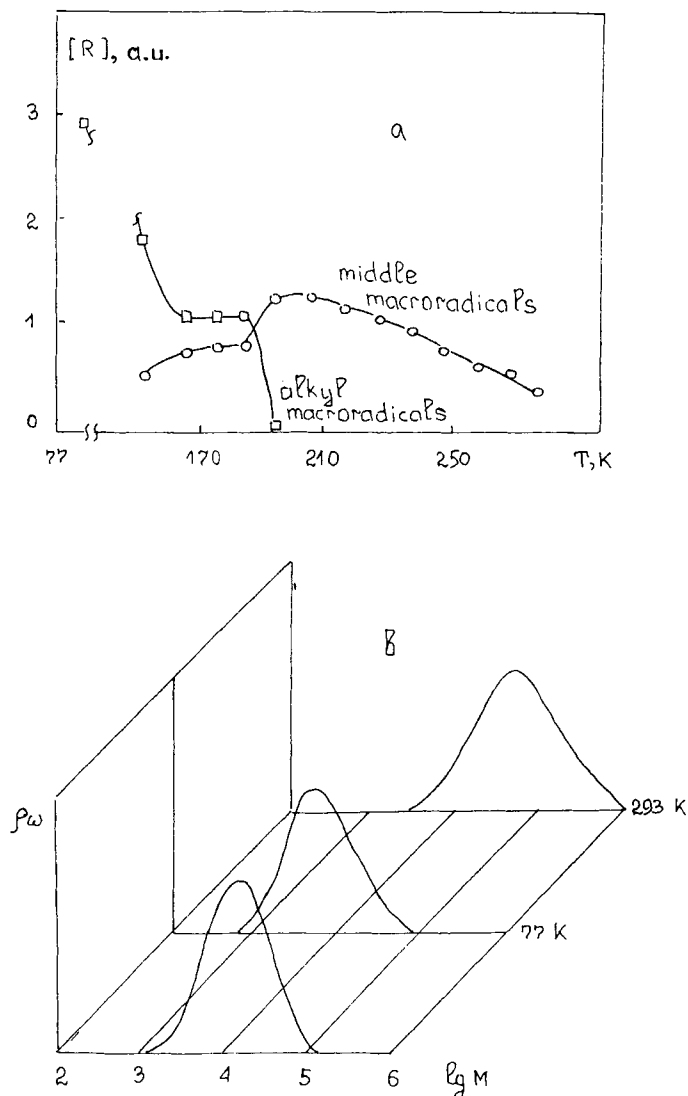


FIGURE 9 Change of radical concentration (a) and molecular mass distribution of PVB depending on the temperature of photoradical ageing (b).

chain whereas thermal reactions of the same radicals, lead to polymer cross-linking. By carrying out the process at temperatures below 180 K (a region of thermal stability for the alkyl macroradicals) and using light with $\lambda \leq 300$ nm, one can degrade the polymer; on the other hand, longer-wave length light or higher temperatures will lead to its cross-linking (Figure 9).

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

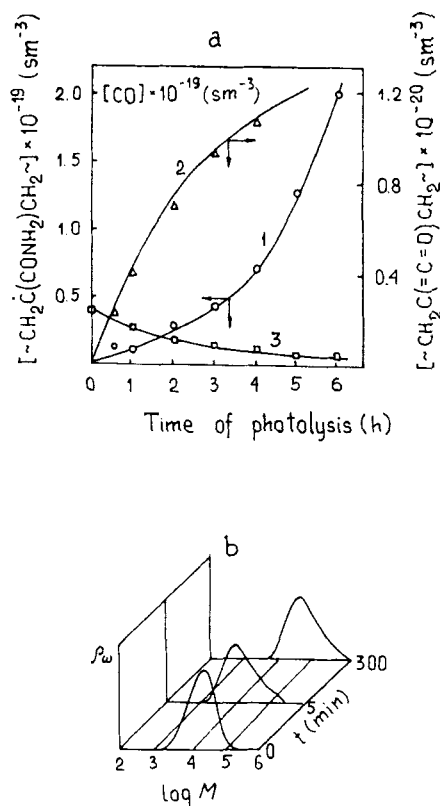


FIGURE 10 (a) Kinetic curves for the accumulation of carbon monoxide (1) and ketene (2), and consumption of middle macroradicals (3) during the photolysis at $\lambda \geq 280$ nm of PAA at 77 K. (b) Change of molecular mass distribution in PAA depending on the time of photoradical ageing.

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, and the introduction of additives entering into thermal chemical reactions with the intermediate product. This statement can be exemplified by the situation which takes place during photoradical ageing of polyacrylic acid and polyacrylamide where photochemical reactions of middle macroradicals gives rise to ruptures in the main chain, ketene accumulation and photochemical reactions of ketene to polymer cross-linking. As a result, the character of MWD changes as function of time of photolysis (Figure 10).

It follows from the data presented above that by 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 for each particular class of polymers have 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 the 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 definite 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 (increase of the glass transition temperature, reduction of deformation, increase in mechanical strength, etc.).

The most promising way to modify various 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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