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Photostimulated synchronous chlorination of polymers at low temperatures

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High yields of free radicals (10^{18}—10^{19} spin g^{-1}) were found upon the low-temperature (77 K) chlorination of solid synthetic polymers on irradiation with light with $\lambda \geq 360$ nm. The stage of radical formation was considered in the framework of the mechanism of concerted reactions in the polymolecular complex [polymer—Cl_2].

Key words: polymers, chlorination, photostimulation, synchronous reactions, chlorine, free radicals.

At low temperatures (150—240 K), molecular chlorine manifests selectivity and mainly interacts with double bonds of the olefin type in macromolecules of solid polymers and low-molecular-weight compounds. The chlorination process is accompanied by the efficient accumulation of free radicals.[1—3] The mechanism of stages of spontaneous radical formation was considered in terms of the model of multicenter synchronous reactions in the polymolecular complex formed of several reactant molecules. It was assumed that the endothermic effect of chemical bond cleavage is compensated by the heat of formation of new bonds in intermediate and final products in the same elementary act. As it was shown,[3] under cryogenic conditions, the process is initiated by molecular rather than atomic chlorine, because the temperature range of Cl_2 dissociation and spontaneous chlorination reactions lies higher than 370 K.[4] Therefore, higher enthalpies and activation energies of initiation should be surmounted to carry out the chlorination of aliphatic hydrocarbons with simple C—C and C—H bonds and aromatic compounds at low temperatures (<370 K). In this case, the physical treatment of the system (UV irradiation) is used in order to induce the dissociation of chlorine to atoms initiating the radical chain process.

This work is devoted to the study of some regularities of photostimulated synchronous reactions of radical chlorination at 77 K of polymers with simple aliphatic and aromatic bonds.

Experimental

Industrial synthetic and natural polymers manifesting no effect of molecular chlorination due to the high endothermicity of the process were used: polyethylene (PE), polypropylene (PP), polystyrene (PS), and cellulose. Low-density polyethylene (Gur´ev Plant, Gur´ev) was used as a powder without special additives (molecular weight ~500 000, degree of crystallinity ~5 mol.%); PP was manufactured in France as a 10-μm film containing antioxidants and photostabilizers (molecular weight ~300 000; block PS as a film with a thickness of 25 μm (Kuskovo Plant of Polymer Materials, Moscow, Russia; molecular weight ~250 000) was obtained by the thermal polymerization in a nitrogen flow containing <1% oxygen; and microcrystalline cellulose (LK trade mark, for column chromatography (SP 20—30 units) and bleached pulp (SP 480) as plates 1.5 mm thick were used. Cyclohexane served as a low-molecular-weight analog of PE.

Polymer weighed samples (~50 mg) as powders or thin films (10—25 μm) were placed in glass ESR tubes. After evacuation, Cl_2 (40—50 Torr) was frozen over the sample surface at 77 K in such a way that chlorine in the liquid state (at ~240 K) would wet the whole sample. The tubes were sealed, and immersed in a Dewar flask filled with liquid nitrogen for UV irradiation ($\lambda \geq 360$ nm, intensity ~$3 \cdot 10^{17}$ quantum cm^{-2} s^{-1}). The samples were heated at temperature higher than 77 K stage by stage in a thermostat cooled with liquid nitrogen vapor, storing the samples for ~10 min at a specified temperature. ESR spectra were recorded on an EPR-21 X-range radiospectrometer at 77 K and a power of the microwave field of ~10^{-5} W. The concentration of paramagnetic centers (PMC) was determined by the ESR spectra using a standard sample with the known number of spins. The stable signal of Cr^{3+} in a ruby crystal served as a "side" standard that controlled instrumental parameters. The absolute measurement error for PMC concentrations, including detection and double integration of the spectra, was ±15%. The IR spectra of the initial and chlorinated PS films were recorded on a Perkin—Elmer Spectrum-100 FTIR spectrometer at 300 K. The gaseous products of PP photochlorination were measured on an MI-1201 mass spectrometer at an energy of ionizing electrons of 70 eV.

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Results and Discussion

The control experiments carried out before radical chlorination showed that no PMC appeared upon the irradiation of the studied polymers with $\lambda \geq 360$ nm at 77 K or heating (from 77 to 300 K) of the non-irradiated samples in the presence of chlorine. In addition, it was found that the efficiency of chlorination depends on the degree of mixing of the reactants. The system, where chlorine frozen over the sample surface was preheated above 170 K (melting point of Cl_2) and penetrated (in the liquid state) into the sample bulk turned out, to be optimal for the interaction of chlorine atoms with the substance. High concentrations of the free radicals were obtained upon the subsequent UV irradiation (at 77 K) of thus mixed reactants.

Polyethylene. The photochlorination of PE is accompanied by the generation of radicals, whose ESR spectrum consists of eight lines (Fig. 1, *a*, spectrum *1*). According to the number of components and the value of hyperfine splitting (HFS) constants $\alpha = 1.8$—2.2 mT, the spectrum corresponds to the signal of UV-irradiation PE (spectrum *3*), although the signals differ slightly in shape. The photochemical processes in PE were shown[5] to initiate mainly carbonyl groups (as industrial admixtures) *via* the Norrish 1 type mechanism of photolysis of carbonyls. The cleavage and subsequent cross-linking of fragments of the polymer chains afford terminal radicals of the allyl type, which are stabilized on defects of the structure. Their spectrum of eight lines (spectrum *3*) have different HFS constants on the β-protons of the methyl and methylene groups: $\alpha^{H}_{Me} = 1.8$ mT and $\alpha^{H}_{CH_2} = 2.2$ mT.

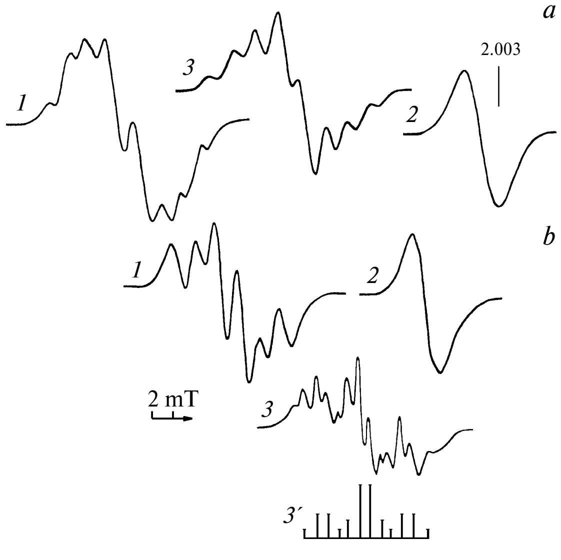


Fig. 1. ESR spectra of (*a*) photochlorinated at 77 K (*1*), heated to 300 K (*2*), and UV-irradiated at 77 K ($\lambda \geq 236$ nm) (*3*) polyethylene and (*b*) γ- (*1*), UV-irradiated (*2*), and photochlorinated at 77 K (*3*) cyclohexane; (*3´*) the scheme of the hyperfine structure lines of spectrum *3*.

Based on the obtained spectrum *1* (see Fig. 1, *a*), we may assume that during photochlorination the radical particle contains the methyl and methylene groups in the β-position and the free valence is conjugated with π-electrons of the double bond. Therefore, at least two chlorine molecules should interact with the fragment of the polymer molecule containing the Me group as a branching of the polymer chain to form such an allyl radical.

The formation of macroradicals upon the low-temperature photochlorination of PE can be presented in terms of the mechanism of multicenter synchronous reactions in the polymolecular complex if taking into account the initiation of atomic chlorine formed by the photodissociation of Cl_2.

Since at low temperatures molecular "chlorine" is prone to dimerization,[6] the polymolecular complex will include the dimer $Cl_2...Cl_2$ and the fragment of the macromolecular with the branching containing the Me group. When the complex is irradiated at the absorption band of dichlorine (≥360 nm), Cl_2 dissociates to atoms, their interaction with the CH and CH_2 groups of the polymer results in synchronous reactions of C—H bond cleavage and multiple bond formation in the macromolecule, and HCl appears in the reaction products; the Cl continues the kinetic chain.

The exothermic effect of the transformation of the complex in reaction (1) can be ~66 kcal mol^{-1}.

$$[\sim CH_2{-}CH(CH_3){-}CH_2{-}CH_2{-}CH_2\sim] \xrightarrow{i}$$

$$\longrightarrow 3\,HCl + \sim CH_2{-}C^{\cdot}(CH_3){-}CH{=}CH{-}CH_2\sim + Cl^{\cdot} \quad (1)$$

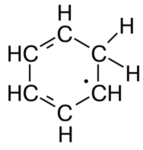
i. $Cl_2...Cl_2$; UV irradiation.

The intensity ratio of the lines in spectrum *1* (see Fig. 1, *a*) is close to binomial, indicating the predominant accumulation of one type of particles, and the spectral shape remained unchanged upon prolong irradiation. After photolysis for 5 min, the concentrations of the radicals attained values of $\sim 2 \cdot 10^{18}\ g^{-1}$, while 2 h after they increased by an order of magnitude ($1.9 \cdot 10^{19}\ g^{-1}$). The quantum yield of photochlorination radicals was estimated in the approximation of full absorption of the light incident on the sample. This gave $\varphi_R \approx 2.2 \cdot 10^{-1}$, which two orders of magnitude exceeds the quantum yield of radicals during the direct photolysis (77 K) of PE with $\lambda \geq 236$ nm ($2.3 \cdot 10^{-3}$) (see Ref. 7). It was found[8] that the rate of radical chlorination of solid PE (at 100 °C) was directly proportional to the chlorine pressure and concentration of the CH_2 groups on the polymer surface, whereas the activation energy and pre-exponential factor of the bimolecular reaction were $E_a = 35.8$ kJ mol^{-1} (8 kcal mol^{-1}) and $K_0 = 0.09$ $atm^{-1}\ h^{-1}$, respectively.

The PMC concentration decreased with an increase in the temperature of the irradiated PE—Cl_2 system, and the spectrum of eight lines loses the hyperfine structure and at 300 K is completely transformed into a singlet with the width $\Delta H \approx 4.0$ mT, $g = 2.003$ (see Fig. 1, *a*, spectrum *2*). According to the published data,[9] the singlet belongs to the dienyl radical in which the free valence is conjugated with π-electrons of two double bonds. Therefore, the chlorination of PE continues during heating of the photolyzed system, unsaturation in the polymer chain increases, and allyl radicals are transformed into dienyl radicals. They are retained in the chlorinated samples (when dichlorine is completely consumed) at temperatures exceeding room temperature. Thus, the radical intermediates of chlorinated PE are similar to the radicals of photolyzed PE. An unpaired electron in the radical is conjugated with the π-electrons of the double bond. As during photolysis, the radicals are stabilized in the sites of distortion of an ideal polymer chain: for photolysis, these are the sites of inclusion of the carbonyl group; for chlorination, the radicals are stabilized in the sites of branching of polymer chains. The distinction in the shape of spectra *1* and *3* (see Fig. 1, *a*) can be due to the fact that the radicals formed during photolysis are terminal, while those formed by photochlorination are middle. The more resolved spectrum (spectrum *3*) corresponds to the more mobile terminal radicals.

Cyclohexane. Cyclohexane (CyH) was chosen for photochlorination as a low-molecular-weight analog of PE. Cyclohexane is often used as a model compound containing one type of C—C and C—H bonds. Radiolysis of CyH was studied in detail.[10] We studied the low-temperature radiolysis and photolysis of CyH by the ESR method to compare the PMC formed in these two processes with the intermediates of radical chlorination. Upon the γ-irradiation of CyH (77 K), the PMC are accumulated with the radiation yield $G_R \approx 3$ per 100 eV, which is within the range of values of G known[10] for CyH. The ESR spectrum is a signal of six lines with the splitting $\alpha = 2.25$ mT, which belongs, according to the published data,[9] to the alkyl radical ($\sim CH_2—C^{\bullet}H—CH_2\sim$) formed in the ring due to C—H bond dissociation (see Fig. 1, *b*, spectrum *1*). Photolysis of CyH was studied to a less extent. Simple C—C and C—H bonds of cyclic hydrocarbon absorb in the vacuum UV region, and neat CyH should not undergo destruction under the medium-UV irradiation. However, a weak singlet ESR spectrum ($\Delta H = 2.0$ mT, $g = 2.0029$) was observed upon the irradiation of CyH with $\lambda \geq 236$ nm at 77 K (see Fig. 1, *b*, spectrum *2*). It is most likely that the signal is related to the PMC formed due to photolysis induced by photosensitive impurities in technical CyH.

The results of low-temperature CyH photochlorination are interesting and differ from those in the cases of radiolysis and photolysis. A broad binomial triplet ($\alpha_3 = 4.5$ mT) of quadruplets ($\alpha_4 = 1.0—1.1$ mT) with $g = 2.003$ appears in the ESR spectrum from the very beginning of irradiation of the CyH—Cl_2 system, and its shape remains unchanged during irradiation (see Fig. 1, *b*, spectrum *3*). The spectrum corresponds by parameters to cyclohexadienyl (CyHD) radicals (**A**) formed due to the hydrogenation of double bonds of the aromatic ring with atomic hydrogen.

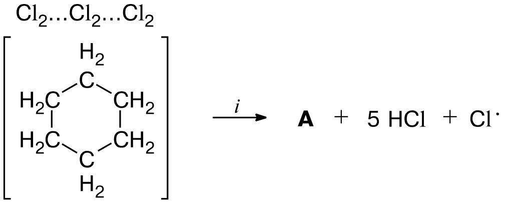


A

The triplet with the HFS constant $\alpha_\beta{}^H = 4.5$ mT is formed due to the interaction of the unpaired electron with two protons of the methylene group, and the additional splitting into four lines with $\alpha_{Ph}{}^H = 1.0—1.1$ mT appears because of the interaction with three protons of the ring.[11]

The maximum concentrations of the radicals upon the photolysis of the CyH + Cl_2 system within 10 min were $(2.5—3.0) \cdot 10^{17}$ spin g^{-1} (quantum yield $\varphi_R \approx 1.7 \cdot 10^{-3}$). With an increase in the temperature of the chlorinated samples, the spectrum of the CyHD radicals disappeared at ~120 K, *i.e.*, long before melting of residual chlorine (170 K) and cyclohexane (280 K). In the γ-irradiated CyH, the alkyl radicals ($\sim CH_2—C^{\bullet}H—CH_2\sim$) retain stability up to 225 K, which is ~100 K higher.

The interaction of at least three chlorine molecules with the CyH molecule is necessary for the CyHD radical to form; *i.e.*, the minimal composition of the polymolecular complex can be [CyH + 3 Cl_2]. The interaction of chlorine atoms with the CH_2 groups of the CyH molecule (reaction (2)) following the mechanism of multicenter synchronous reactions results in the cleavage of five C—H bonds, formation of two double bonds in the ring, and evolution of hydrogen chloride. The exothermic effect of reaction (2) is 80 kcal mol^{-1}.



(2)

i. UV irradiation.

The CyHD radicals are usually formed in the hydrogenation of the benzene ring upon the low-temperature radiolysis of aromatic compounds.[9] The photochlorination of CyH (2) can be considered as a backward reaction: dehydrogenation (aromatization) of the six-membered ring of cyclohexane. In this respect, this reaction is close to the classical Zelinsky[12] dehydrogenation of CyH at 300 °C in the presence of palladium black to benzene. Thus, the model system CyH + 3 Cl_2 distinctly models the main reaction of hydrocarbon photochlorination, namely, the dehydrogenation of C—H bonds, with the formation of unsaturation in the molecule and hydrogen chloride evolution.

Polypropylene. Samples of PP were used as films with the thickness 10 μm. The concentrations of the radicals

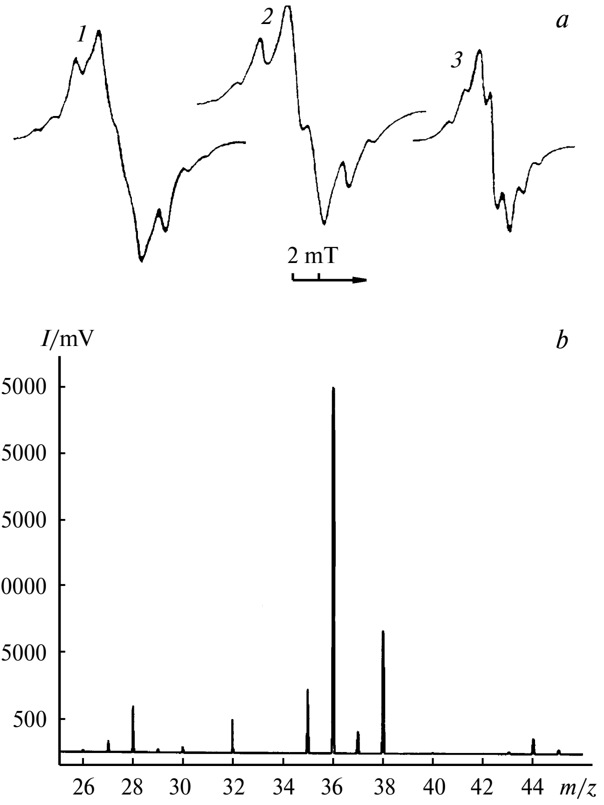


Fig. 2. (*a*) ESR spectra of photochlorinated at 77 K (*1*) and heated to 170 (*2*) and 240 K (*3*) polypropylene and (*b*) the mass spectrum of the products of polypropylene photochlorination.

after the UV irradiation of the PP—Cl_2 system for 10 min reached $3.5 \cdot 10^{18}$ spin g^{-1} (quantum yield $\varphi_R \approx 2 \cdot 10^{-2}$). Complicated spectrum *1* (Fig. 2, *a*) belongs to several radicals, and its shape changes several times during heating of the sample. At ~170 K, a distinct sextet appears with the HFS constant α = 2.4—3.0 mT and the ratio of line intensities close to binomial (spectrum *2*), which is similar by shape and parameters to the spectrum of γ-irradiated PE. At ~240 K, the sextet is transformed into a signal of seven lines of the allyl radical (α = 1.5 mT) ~$CH(CH_3)—C^{\cdot}H—C(CH_3)=CH—CH(CH_3)$~,[9] which is retained up to 300 K (spectrum *3*); in this case, the PMC concentration is ~7% of the initial value. This ESR signal is also observed upon the prolong radiolysis of PP at room temperature.

The scheme of PP photochlorination involving two chlorine molecules and resulting in the formation of the allyl radical and HCl can be presented as follows:

$$[\sim CH(CH_3)—CH_2—CH(CH_3)—CH_2—CH(CH_3)\sim] \xrightarrow{i}$$

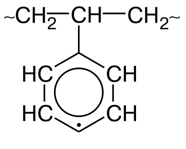
$$\longrightarrow 3\ HCl + Cl^{\cdot} + H_3C—C^{\cdot}H—C(CH_3)=CH—CH(CH_3)\sim$$

$$(-66\ kcal\ mol^{-1}). \qquad (3)$$

i. $Cl_2...Cl_2$; UV irradiation.

The mass spectrometric analysis of the gaseous products of PP photochlorination showed hydrogen chloride (see Fig. 2, *b*, mass numbers 36 and 38 for isotopes ^{35}Cl and ^{37}Cl, respectively). This suggests that the single low-molecular-weight product of hydrocarbon photochlorination at 77 K is HCl. The photochlorination of PP at 77 K can be compared by efficiency with the prolong radiolysis of the polymer at room temperature.

Polystyrene. For the photochlorination of PS, the concentration of PMC after irradiation for 30—40 min attained ~$4 \cdot 10^{18}$ spin g^{-1} (quantum yield $\varphi_R \approx 6 \cdot 10^{-3}$). The ESR spectrum at 77 K is shown in Fig. 3 (spectrum *1*). The spectrum represents a superposition of the triplet with α = 2.2—2.4 mT and a singlet line with the width $\Delta H \approx$ 4.0 mT. The ratio of intensities of the triplet lines is close to binomial, which is noticeable with the temperature of the chlorinated sample increases (spectrum *2*). By the values of the HFS constants and thermal stability (the lines of the triplet disappears at ~220 K), the triplet signal should be attributed, most likely, to the phenyl radicals formed due to the dissociation of the C—H bonds of the aromatic ring[13] (**B**).



B

In the phenyl radical, the unpaired electron is mainly localized on the antibonding σ-orbital and its hyperfine interaction with the protons of the ring is not uniform. The maximum interaction is characteristic of the *ortho*-protons (α = 2.3 mT) and results in the formation of the triplet; a weaker interaction with the *meta*-protons (α = 0.3—0.4 mT) is detected in the spectra of the liquid samples and is not detected in the solid phase.[13,14] After the decay (above 240 K) of the phenyl radicals, the ESR spectra of chlorinated PS contain a singlet line with the width ΔH = 4.0 mT with g = 2.003, which becomes

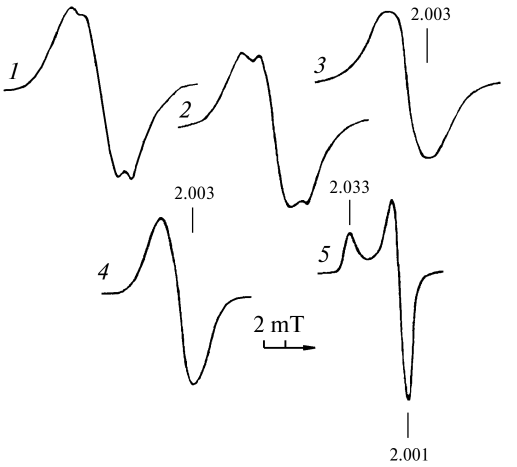


Fig. 3. ESR spectra of photochlorinated at 77 K (*1*) and heated to 180 (*2*), 240 (*3*), and 370 K (*4*) polystyrene and (*5*) the spectrum of the sample (*1*) heated to 190 K in the presence of oxygen.

narrower to $\Delta H = 2.0$ mT with temperature (see Fig. 3, spectra *3* and *4*). The latter signal corresponds by parameters to the spectrum of the allyl radical $\sim CH_2—C^{\bullet}(Ph)—CH{=}CH(Ph)\sim$. This radical is also formed by the photolysis of PS. The overall quantum yield of radical accumulation in PS for direct photolysis (at 77 K) with $\lambda \geq 236$ nm is $\varphi_R \approx 3 \cdot 10^{-5}$,[15] which is considerably lower than the quantum yield $[R^{\bullet}]$ of photochlorination ($6 \cdot 10^{-3}$).

In the photochlorination of PS, the phenyl and allyl radicals $\sim CH_2—C^{\bullet}(Ph)—CH{=}CH(Ph)\sim$ (with the unpaired electron in the polymer chain) are accumulated in equal amounts, *i.e.*, ~50% of the initial concentration of the PMC for each radical. Based on these data, we may suggest that the cleavage of the C—H bonds in the ring and polymer chain is almost equivalent for the chlorination of PS, although the dissociation energies of C—H bonds of three types in PS, namely, at the tertiary and secondary carbon atoms of the chain and in the benzene ring, differ significantly, being 71, 76, and 104 kcal mol^{-1}, respectively.[16] The allyl radical of PS can be oxidized, and in the presence of oxygen at ~190 K the isotropic singlet of the allyl radical is transformed into the asymmetric singlet of peroxide radicals $ROO^{\bullet}$ (see Fig. 3, spectrum *5*), which confirms the high reactivity of the PMC. Thus, when PS is photochlorinated, the attack of atomic chlorine is equally directed at the C—H bonds of both the polymer chain and phenyl groups, resulting in the formation of phenyl and allyl radicals in almost equal amounts. Double bonds are formed in the polymer chains and hydrogen chloride is evolved. Note that phenyl radicals were detected for the first time in the radical intermediates of PS photochlorination, and they were not found among the products of photolysis and radiolysis of the polymer (according to the ESR spectra).

The changes in the molecular structure of the polymer subjected to photochlorination confirm the IR spectroscopic data. The IR spectra of the PS films before (spectrum *1*) and after low-temperature photochlorination for 3 h under a chlorine pressure of 70—80 Torr (spectrum *2*) are presented in Fig. 4.

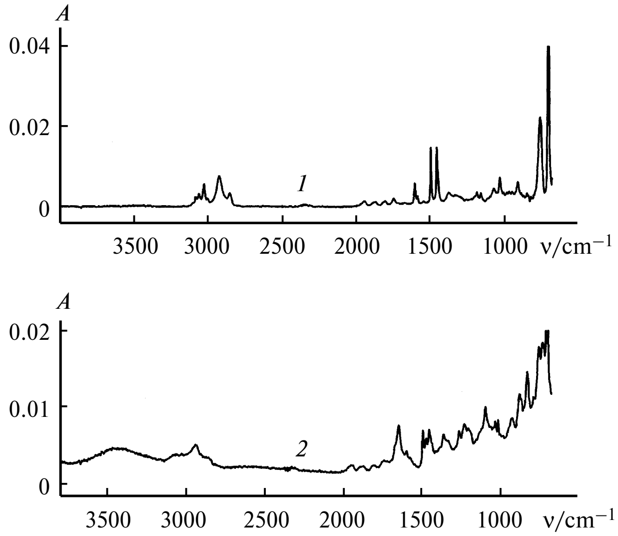


Fig. 4. IR spectra of the initial (*1*) and photochlorinated at 77 K (*2*) polystyrene. The spectra were recorded at 300 K.

Spectrum *2* exhibits the sharp and synchronous decrease in the intensity of bands in three spectral regions related to the stretching and bending vibrations of the C—H and C=C bonds of the aromatic ring (at 3000, 1600—1500, and 700 cm^{-1}). Therefore, photochlorination decreases the amount of phenyl groups in PS, which agrees with the ESR spectroscopic data on the efficient accumulation of phenyl radicals as a primary act of aromatic ring destruction. The decrease in the intensity of bands of the stretching vibrations of the CH_2 and CH bonds of the polymer chain (2920 and 2850 cm^{-1}) and the appearance of a new band at 1670—1650 cm^{-1} related to the stretching vibrations of the conjugated C=C bonds indicate a decrease in the hydrogen content in the macromolecule and the formation of unsaturation. The initial IR spectrum (see Fig. 4, spectrum *1*) of industrial PS almost always contains the band at ~1680 cm^{-1}, which is usually assigned to the impurity (olefinic) bonds in the main polymer chain. The intensity of this band decreases upon photochlorination (see Fig. 4, spectrum *2*). The suppression of this band can be explained by the chlorination of isolated double bonds, evidently, at the stage of kinetic chain propagation, due to which the weight of the samples increases (according to the elemental analysis data, the content of chlorine was 4%). The absorption bands of polysubstituted C—Cl bonds appear in the IR region at 880—830 cm^{-1}, where the intrinsic absorption of PS is absent. The broad band at 3450 cm^{-1} indicates the presence of OH groups; *i.e.*, the polymer is oxidized, most likely, due to residual (incompletely removed by evacuation) oxygen in parallel with photochlorination.

Cellulose. Unlike the synthetic polymers, cellulose is poorly chlorinated. After the UV irradiation of the system bleached pulp—Cl_2 for 1 h and irradiation of monocrystalline cellulose mixed with chlorine for 2 h, the ESR spectra exhibited weak signals with features of the triplet structure $\Delta H \approx 3.0$ mT. There is no efficient chlorination, because Cl_2 poorly penetrates, most likely, into the matrix and the concentration of chlorine atoms is low, while the latter could freely react with the C—H bonds of macromolecules. The low solubility of Cl_2 is related to a specific feature of the supermolecular structure of cellulose in which the macromolecules is tightened with the three-dimensional network of inter- and intramolecular hydrogen bonds impeding the penetration of gas molecules inside the polymer sample. In this respect, the behavior of Cl_2 is similar to that of oxygen, which also poorly penetrates and is weakly dissolved in cellulose.[17] Note that molecular fluorine (unlike Cl_2) efficiently interacts with cellulose at both the temperature of liquid nitrogen and close to that temperatures of liquid helium (45—77 K), which is indicated by the high concentrations of free radicals detected**18** by the ESR method.

Thus, the photochlorination of hydrocarbons at 77 K follows the radical chain mechanism. Unlike molecular chlorine reacting with double bonds of the olefinic type at low temperatures, atomic chlorine exhibited no selectivity to the dehydrogenation of CH and CH_2 groups of the aliphatic or aromatic type. The results showed a high efficiency of accumulation of free radicals upon the interaction of atomic chlorine with solid synthetic polymers. Under chlorine pressures of 40—50 Torr, the concentrations of the radicals after irradiation with the relatively mild UV light at $\lambda \geq 360$ nm for 5—10 min attained 10^{18}—10^{19} spin g^{-1}, which is comparable with the concentrations of $R^{\cdot}$ stabilized in the polymers upon radiolysis with doses of several tens (or hundreds) of megaradian. When the Cl_2 chromophore was introduced into the system, the quantum yield of free radicals upon irradiation with $\lambda \geq 360$ nm increased by two—three orders of magnitude compared to pure photolysis ($\lambda \geq 236$ nm).

The generation of radicals in the polymers by photochlorination is much more efficient than the generation by direct photolysis or radiolysis. High concentrations of radicals, which are easily obtained by the simple method of hydrocarbon photochlorination, can be of interest for the initiation of polymerization, copolymerization, grafting, and chemical modification of polymer materials.

The radicals of photochlorination of polymers are classified as hydrocarbon radicals with double bonds, *i.e.*, allyl or dienyl, and they often coincide with the known paramagnetic centers formed upon the UV or γ-irradiation of polymers. No formation of chloroalkyl radicals characteristic of the molecular chlorination of olefins was observed under the conditions of photoirradiation and subsequent heating of the chlorinated samples (from 77 to 300 K). However, an increase in the amount of the photochlorinated samples and the appearance of the C—Cl bonds in the IR spectra indicate the addition of chlorine to the polymer molecule, most likely, at the stage of kinetic chain propagation. The data of IR spectroscopy also confirm an increase in unsaturation in the macromolecules.

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