

## Isomers of polystyrene cyclohexadienyl radical: Structure and photochemical behavior

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### ABSTRACT

Low-temperature (77 K) radiolysis of polystyrene (PS) was found to yield a mixture of the isomers of alkyl-substituted cyclohexadienyl (CHD) radical ( $R_{\text{CHD}}^{\bullet}$ ) formed upon addition of *in situ* generated hydrogen atoms to the double bonds of aromatic ring in positions 2–6. Two kinds of  $R_{\text{CHD}}^{\bullet}$  radicals with different thermal stability and photosensitivity have been identified by EPR and optical absorption spectroscopy. The radicals with unpaired electron on C<sub>2</sub>, C<sub>4</sub>, and C<sub>6</sub> carbon atoms of the phenyl ring, whose relative amount exceeds a statistically expected value ( $>3/5$ ), exhibit a lower stability and higher photosensitivity. Their EPR spectra exhibit a triplet structure with the hyperfine splitting constant  $\alpha_3 = 1.0$  mT while the absorption spectra, a band peaked at  $\lambda_{\text{max}} = 330$  nm ( $\epsilon \approx 9.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). The relative amount of radicals on C<sub>3</sub> and C<sub>5</sub> atoms of the ring is below 2/5. Their EPR spectra are quadruplets with  $\alpha_4 = 1.0$  mT, while the absorption spectra represent a band peaked at  $\lambda_{\text{max}} = 320$  nm ( $\epsilon \approx 7.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). The individual EPR spectrum of C<sub>3</sub> and C<sub>5</sub> isomers has been obtained for the first time.

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### 1. Introduction

As is known [1–3], the EPR spectrum of cyclohexadienyl (CHD) radical ( $R_{\text{CHD}}^{\bullet}$ ) is a broad triplet (hyperfine splitting constant  $\alpha_{2\text{H}}^{\beta} \approx 4.5$  mT) arising upon interaction of an unpaired electron in the aromatic ring with two  $\beta$ -protons in the  $\text{CH}_2$  group. In case of benzene, the components of the  $R_{\text{CHD}}^{\bullet}$  triplet additionally split into the quadruplet with  $\alpha_4 = 1.0$  mT due to hyperfine interaction of an unpaired electron with three ring protons:



Upon introduction of alkyl substituent into the benzene ring, there appear two EPR signals with hyperfine structure (HFS): triplet and quadruplet with  $\alpha = 1.0$  mT, depending on the position of H attachment [1]. Therefore, the alkyl-substituted CHD radical of polystyrene (PS), where alkyl is polymer chain, can be expected to appear in two isomeric forms giving rise to triplet and quadruplet HFS with  $\alpha = 1.0$  mT. In the recorded EPR spectra of  $\gamma$ -irradiated PS, predominant is the triplet of CHD radical ( $\alpha_{2\text{H}}^{\beta} = 4.5$  mT) whose outer lines exhibit a triplet hyperfine structure with  $\alpha_3 = 1.0$  mT. This can be associated either with predominance of radical struc-

tures with a triplet HFS (with  $\alpha = 1.0$  mT) or with the absence of radicals with a quadruplet hyperfine structure. An attempt to obtain the EPR spectra of individual  $R_{\text{CHD}}^{\bullet}$  isomers was made in [1] upon hydrogenation of phenyl group in PS with atomic hydrogen but in this case the EPR spectra exhibited only a triplet HFS with  $\alpha_3 = 1.0$  mT: a signal with a quadruplet hyperfine structure has not been observed altogether. Nonetheless, in this work we explored the isomers of CHD radical formed in  $\gamma$ -irradiated PS by means of EPR and optical absorption spectroscopy.

### 2. Experimental technique

In experiments, we used the commercially available bulk PS ( $MW \approx 7.5 \times 10^5$ ) produced by thermal polymerization in the absence of technological additives. The samples in the form of powder (particle size 0.2 mm) or cast films (25  $\mu\text{m}$  thick) were  $\gamma$ -irradiated ( $^{60}\text{Co}$ ) at 77 K (KU-150000 source) at a dose rate around 10 Mrad  $\text{h}^{-1}$ .  $\gamma$ -Irradiated samples were illuminated with either unfiltered ( $\lambda_{\text{ex}} \geq 236$  nm) or filtered ( $\lambda_{\text{ex}} \geq 360$  nm) UV radiation from a 1000-W high-pressure Hg-arc lamp. We did not take into account the radicals formed upon photolysis being sure that their concentration is 1–2 orders of magnitude lower than of those formed during  $\gamma$ -irradiation. The photolysis of PS was carried out at 77 K in vacuum at  $\lambda \geq 236$  nm and  $\lambda \geq 300$  nm. EPR spectra were recorded at 77 K with an EPR-2 radiospectrometer (microwave energy output about  $10^{-4}$  W, modulation amplitude 0.4 mT). Concentration of paramagnetic centers was determined by standard method using a reference sample of stable nitroxyl radical with a

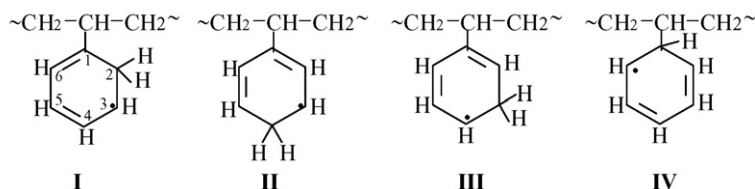
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known amount of spins. The absolute error of EPR measurements (including recording and double integration of spectra) had a typical value of  $\pm 15\%$ . Optical absorption spectra were taken at 77 K with a Unicam UV-VIS spectrophotometer.

### 3. Results and discussion

#### 3.1. Radicals structure

Upon equiprobable attachment of H atoms to positions 1–6 in the phenyl group of PS, the following four radical structures can be expected to form:



Three radical structures – two of type **I** and one of type **II** – give a main triplet signal with  $\alpha_{2H}^{\beta} = 4.5$  mT and additional triplet HFS with  $\alpha_3 = 1.0$  mT (due to interaction of an unpaired electron with protons at  $C_3$  and  $C_5$ ). For radical **III**, typical is a triplet with  $\alpha_{2H}^{\beta} = 4.5$  mT and a quadruplet HFS with  $\alpha_4 = 1.0$  mT (interaction with protons at  $C_2$ ,  $C_4$ , and  $C_6$ ). Radical **IV** can be expected to give a doublet with  $\alpha_H^{\beta} = 4.5$  mT (interaction of an unpaired electron with a proton at  $C_1$ ) and a quadruplet HFS with  $\alpha_4 = 1.0$  mT (interaction with protons at  $C_2$ ,  $C_4$ , and  $C_6$ ).

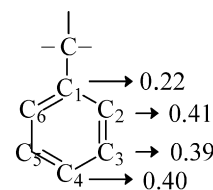
Fig. 1 shows the recorded EPR spectrum of PS  $\gamma$ -irradiated (77 K, in vacuum) to a dose of 1000 kGy (spectrum 1). It is a typical triplet of CHD radical with the hyperfine splitting constant  $\alpha_{2H}^{\beta} = 4.5$  mT. The central component is stronger (1:6:1) and, in contrast to outer lines, exhibits no hyperfine structure (due to overlapping with the spectra of hydrogen abstraction radicals and with the singlet of stabilized electrons). The overall EPR spectra of  $\gamma$ -irradiated PS exhibit no doublet with  $\alpha_H^{\beta} = 4.5$  mT corresponding to radical **IV**.

Based on spectrum 1 (with  $\alpha_3 = 1.0$  mT), it can be assumed that, during low-temperature radiolysis of PS, atomic hydrogen reacts largely with the  $C_2$ ,  $C_4$ , and  $C_6$  carbon atoms to yield isomers **I** and **II**. But if we admit equiprobable H attachment to  $C_2$ – $C_6$  carbons, then the 3-isomers with a triplet HFS ( $\alpha_3 = 1.0$  mT) would be expected to dominate over the 2-isomers with a quadruplet HFS, so that the quadruplet structure with  $\alpha_4 = 1.0$  mT would be unnoticeable in the overall EPR spectrum. Moreover, in their study on hydrogenation of solid PS with atomic hydrogen [1], the authors assumed that the number of isomers with a triplet HFS may exceed a statistical value, that is, H atoms more readily react with the  $C_2$ ,  $C_4$ , and  $C_6$  rather than with  $C_3$  and  $C_5$  carbons. Only under such assumption, the measured spectra were found to best fit the computer-modeled ones.

Predominant reactivity of H atoms with the  $C_2$ ,  $C_4$ , and  $C_6$  carbons can also be explained in terms of the free valence index  $F$  which affords to determine a most probable site for the attack of radical reagent (in our case, H atom). According to [4],  $F$  is defined as a difference between the maximally possible ( $N_{max}$ ) and real ( $N_r$ ) number of bonds of the  $r$ -th atom in a given molecule:  $F = N_{max} - N_r$ . For C atoms in organic compounds,  $N_{max}$  usually has a value of 4.732.

In case of benzene,  $N_r$  for carbon atoms is a sum of three  $\sigma$  and two  $\pi$  bonds (the order of the  $\sigma$  and  $\pi$  bonds being 1.0 and 0.667, respectively). In this case, we obtain  $N_r = 4.334$  and  $F = N_{max} - N_r = 0.398$ . In benzene, all carbon atoms have the same value of  $F$  (0.398) and equally participate in formation of bonds. The presence of alkyl substituent in the ring gives rise to some displacement of  $\pi$  electrons (formation of some dipole moment), which leads to small changes in  $F$ . But the displacement of electrons and order of bonds are known to be slightly dependent on the length of

alkyl substituent. For this reason, the available [4] bond orders for toluene (and ethylbenzene) can be safely used to determine the  $F$  values (indicated below) for carbon atoms in the alkyl-substituted benzene ring of PS.



It follows that the most probable sites for the attack of H atom are the  $C_2$ ,  $C_4$ , and  $C_6$  carbons. The least probable is the  $C_1$  carbon because of its lower  $F$  value (0.22) and higher steric hindrance. In view of this, a contribution from radical **IV** can be expected to be below a statistical value (<16%). Anyhow, a doublet with  $\alpha_H^{\beta} = 4.5$  mT is absent in the EPR spectrum of  $\gamma$ -irradiated PS.

Therefore, it is safe to conclude that, during low-temperature radiolysis of PS, the reaction of atomic hydrogen with  $C_2$ – $C_6$  carbons yields a mixture of isomeric CHD radicals in which structures **I** and

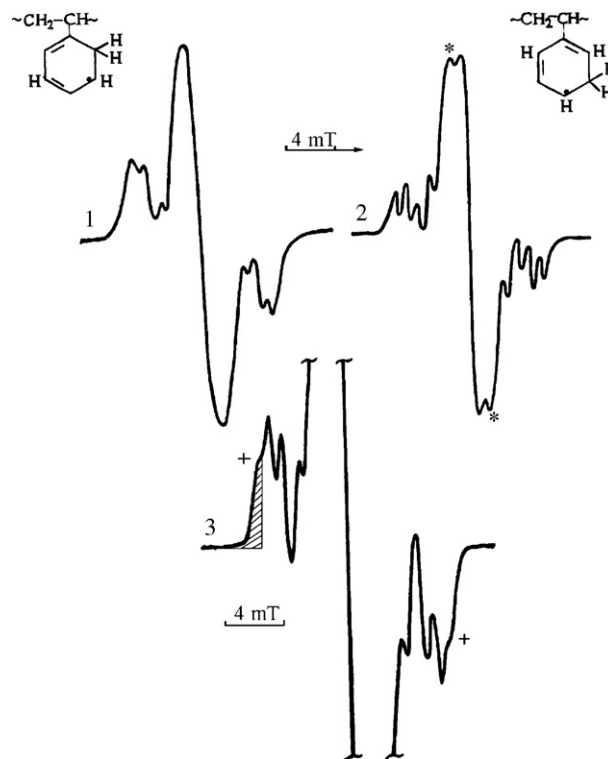


Fig. 1. EPR spectra of: (1) PS  $\gamma$ -irradiated (77 K, in vacuum) to a dose 1000 kGy, (2) the same sample after photolysis ( $\lambda_{ex} \geq 360$  nm) at 270 K, and (3) PS  $\gamma$ -irradiated (77 K, in vacuum) to a dose of 2000 kGy and heated up to 300 K. Spectra 1 and 2 were recorded at 77 K while spectrum 3, at 300 K. In spectrum 2, the triplet components of the  $R_{CHD}^{\bullet}$  radical are indicated by an asterisk; in spectrum 3, the fourth component of the outer lines of the  $R_{CHD}^{\bullet}$  spectrum that was subjected to double integration is shaded. The structural formulas of  $R_{CHD}^{\bullet}$  show only those H atoms of aromatic ring (except for  $CH_2$  groups) which provide a hyperfine structure with  $\alpha = 1.0$  mT.

**II** are predominant. As a result, in the overall EPR spectrum of the mixture (containing radicals **I** and **II** in amount higher than 3/5 and radical **III** in amount below 2/5) the quadruplet HFS with  $\alpha_4 = 1.0$  mT is masked by a stronger triplet structure. Meanwhile, in this work we managed to isolate isomers **III** and to obtain their EPR spectrum.

### 3.2. Photochemical separation of $R_{\text{CHD}}^{\bullet}$ isomers

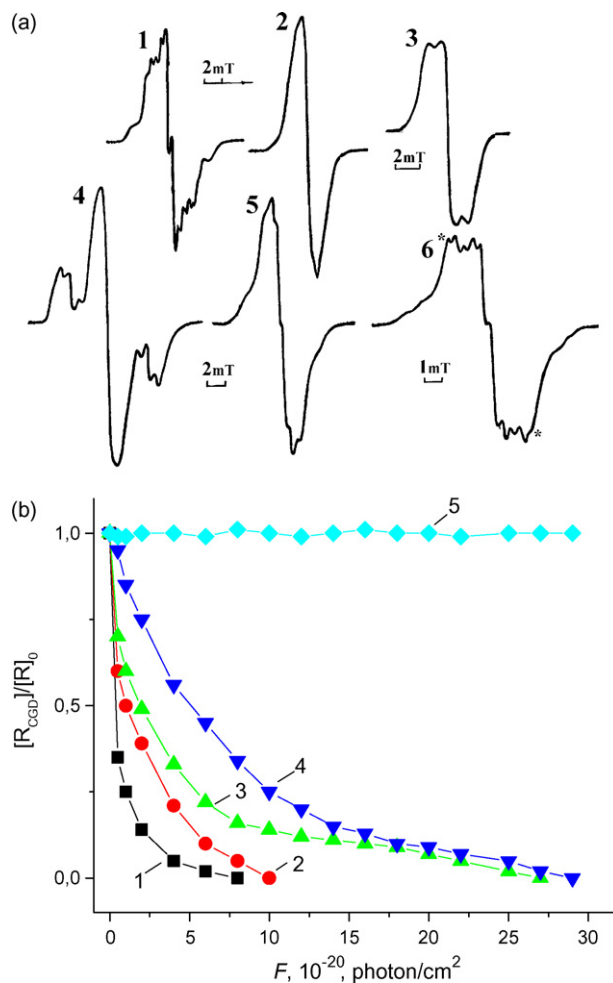
We have found that the isomers of CHD radical exhibit different thermal stability. Upon warm-up of  $\gamma$ -irradiated PS from 77 to 300 K, the outer lines of the ESR spectrum exhibited a weak quadruplet hyperfine structure with  $\alpha_4 = 1.0$  mT, thus evidencing an elevated thermal stability of radicals **III** compared to that of **I** and **II** (in spectrum 3, Fig. 1, the weak fourth components are indicated by a cross).

CHD radicals of PS are known to be photosensitive: upon illumination ( $\lambda = 236$ –540 nm) at 77 K, these radicals undergo quantitative transformation into alkyl and allyl radicals [5]. Just as in case of PS photolysis [6], the type of photoconverted radicals depends on the spectral composition of incident light. Photoinduced transformations of CHD radicals in  $\gamma$ -irradiated PS can be directly identified from the changes in their EPR spectra caused by illumination with light of different spectral composition. In order to make clearer the identification of photoconverted radicals, let us enumerate the EPR spectra of the radicals formed upon photolysis of PS at 77 K. A primary product of PS photolysis at  $\lambda \geq 236$  nm is the benzyl-type radical  $\sim\text{CH}_2-\text{C}^{\bullet}(\text{Ph})-\text{CH}_2\sim (R_{\text{C}}^{\bullet})$ . It gives a quintuplet signal ( $\alpha_{\beta}^{\text{H}} = 2.0$  mT) with an additional hyperfine structure from three ring protons ( $\alpha_{\text{ph}}^{\text{H}} = 0.5$  mT) [6,7], see Fig. 2a, spectrum 1. Upon prolonged photolysis,  $R_{\text{C}}^{\bullet}$  undergoes transformation into the allyl-type radical  $\sim\text{CH}_2-\text{C}^{\bullet}(\text{Ph})-\text{CH}=\text{C}(\text{Ph})-\text{CH}_2\sim (R_{\text{all}}^{\bullet})$  giving a singlet ( $\Delta H = 2.0$  mT) signal (Fig. 2a, spectrum 2). But UV irradiation of PS at  $\lambda \geq 300$  nm results in formation of two radicals— $R_{\text{C}}^{\bullet}$  and  $\sim\text{CH}(\text{Ph})-\text{C}^{\bullet}(\text{OH})-\text{CH}(\text{Ph})\sim (R_{\text{T}}^{\bullet})$ —through intramolecular reduction of excited carbonyl groups [6]. (Carbonyl groups are present as impurity chromophores almost in all commercially available polymers, which is evidenced by a band peaked at  $1740\text{ cm}^{-1}$  in the IR spectrum of starting PS.) The binomial triplet of the  $R_{\text{T}}^{\bullet}$  radical ( $\alpha_{\beta}^{\text{H}} = 1.8$  mT) is given in Fig. 2a, spectrum 3. This thermostable radical is formed upon both photolysis ( $\lambda \geq 300$  nm) and radiolysis of PS at 300 K.

Now let us consider the changes in the EPR spectra taking place during photoinduced transformations of CHD radical in  $\gamma$ -irradiated PS. Fig. 2a (spectra 4–6) illustrates the changes at 77 K in the EPR spectra of CHD radicals formed upon  $\gamma$ -irradiation (spectrum 4), illumination at  $\lambda \geq 236$  nm (spectrum 5), and illumination at  $\lambda \geq 300$  nm (spectrum 6). Fig. 2b shows a change in the concentration of CHD radicals caused by illumination with light of different spectral composition (within the range 236–540 nm). During illumination at 77 K, the overall concentration of radicals remains constant (curve 5 in Fig. 2b), which implies that there is no decay of CHD radicals. As can be inferred from spectrum 5, photoexcitation within the spectral range of PS absorption (240–280 nm) results in complete phototransformation of CHD radicals largely into allyl radicals  $R_{\text{all}}^{\bullet}$ .

The singlet signal from this radical is seen to slur over the HFS of the overall spectrum 5. But upon illumination at  $\lambda \geq 300$ –360 nm, CHD radicals yield two radicals,  $R_{\text{C}}^{\bullet}$  and  $R_{\text{T}}^{\bullet}$ . From the elements of the HFS ( $\alpha_{\text{ph}}^{\text{H}} = 0.5$  mT) present on the lines of the binomial triplet with  $\alpha_{\beta}^{\text{H}} = 1.8$  mT (indicated with an asterisk in spectrum 6), it can be inferred that, upon illumination at  $\lambda \geq 300$  nm, CHD radicals undergo transformation into the  $R_{\text{C}}^{\bullet}$  and  $R_{\text{T}}^{\bullet}$  alkyl radicals.

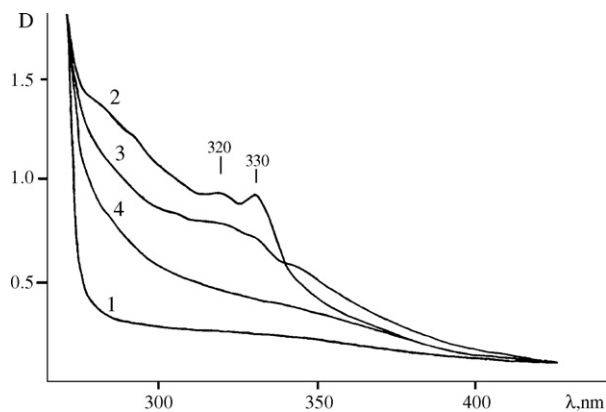
At 77 K and  $\lambda \geq 236$  nm, CHD radicals rapid transform almost completely into the alkyl and allyl radicals of PS (at  $\lambda_{\text{ex}} = 340$ –360 nm quantum yield of photoisomerization  $\varphi \approx 0.03$ ).



**Fig. 2.** (a) EPR spectra of the  $R_{\text{C}}^{\bullet}$  (1),  $R_{\text{all}}^{\bullet}$  (2), and  $R_{\text{T}}^{\bullet}$  (3) radicals in UV-irradiated PS ( $\lambda \geq 236$  nm and  $\lambda \geq 300$  nm, 77 K) and a change at 77 K in the EPR spectrum of  $\gamma$ -irradiated PS (spectrum 4) caused by illumination at  $\lambda \geq 236$  nm (spectrum 5) and at  $\lambda \geq 300$  nm (spectrum 6); (b) changes in the concentration of CHD radicals during illumination at  $\lambda \geq 236$  nm (1),  $\lambda \geq 300$  nm (2),  $\lambda \geq 440$  nm (3), and  $\lambda \geq 540$  nm (4). During phototransformations at 77 K, the overall concentration of radicals  $[R^{\bullet}]_0 = [R^{\bullet}]_{\text{CHD}} + [R^{\bullet}]$  remained unchanged (curve 5) and equal to  $4.5 \times 10^{18} \text{ g}^{-1}$ .

At elevated temperatures, phototransformation of  $R_{\text{CHD}}^{\bullet}$  is also accompanied by the decay of starting  $R_{\text{CHD}}^{\bullet}$  and newly formed radicals. Keeping in mind an elevated thermal stability of radicals **III**, we used elevated temperature (270 K) and short-term (several min) illumination of  $\gamma$ -irradiated PS at  $\lambda \geq 360$  nm and, in these conditions, we managed to separate the EPR spectrum of isomers **III**. Photolysis at 270 K induced rapid transformation of some fraction of CHD radicals into the  $R_{\text{C}}^{\bullet}$  and  $R_{\text{T}}^{\bullet}$  alkyl radicals (at the expense of **I** and **II**). But at 270 K the “middle” radical  $R_{\text{C}}^{\bullet}$  is not preserved (it is stable only below 240 K [6]). The absence of the quintet derived from  $R_{\text{C}}^{\bullet}$  markedly simplifies the overall EPR spectrum which now becomes a superposition of the binomial triplet derived from the stable radical  $R_{\text{T}}^{\bullet}$  (its lines with  $\alpha_{2\text{H}}^{\beta} = 1.8$  mT are marked with an asterisk) and the triplet of the  $R_{\text{CHD}}^{\bullet}$ . In this case, the outer lines of the  $R_{\text{CHD}}^{\bullet}$  spectrum clearly show the presence of the quadruplet HFS with  $\alpha_4 = 1.0$  mT belonging to the more stable isomer **III** (Fig. 1, spectrum 2).

Note however that UV irradiation may also induce (along with transformation of CHD radicals into the alkyl and allyl ones) a hydrogen shift from positions 2, 4, and 6 to positions 3 and 5. Similar transformation of  $\alpha$ - to  $\beta$ -isomer was observed (by absorption spectroscopy) upon UV irradiation of hydronaphthyl radicals [3].



**Fig. 3.** Absorption spectra of: (1) starting PS film (25  $\mu\text{m}$ ), the same film after (2)  $\gamma$ -irradiation at 77 K to a dose of 2500 kGy (total concentration of radicals  $6 \times 10^{18} \text{ g}^{-1}$ ), (3) photolysis at  $\geq 236 \text{ nm}$ , and (4) heating up to 300 K (complete decay of radicals). All spectra were recorded at 77 K.

We checked out such a possibility in the following way. By the method of double graphical integration, we traced the evolution of the surface area enveloped by the fourth component (with  $\alpha_4 = 1.0 \text{ mT}$  in low fields) during photolysis of  $\gamma$ -irradiated PS (in spectrum 3, Fig. 1, this area is shaded). We have found that UV irradiation decreases the surface area enveloped by the fourth component, while hydrogen shift would have increased it. Photolysis is also accompanied by a decrease in the concentration of radicals **I** and **II**. Due to a decrease in the amount of **I** and **II**, the contribution from the triplet HFS with  $\alpha_3 = 1.0 \text{ mT}$  to the outer lines of overall EPR spectrum also decreased, thus favoring a better resolution of the quadruplet component with  $\alpha_4 = 1.0 \text{ mT}$  and evidencing the presence of radicals **III** in the mixture of isomers.

Based on the above data, it can be concluded (i) that radicals **III** are not formed in photochemical reactions of  $\text{R}_{\text{CHD}}^{\bullet}$ , they appear (together with **I** and **II**) in the course of PS radiolysis and (ii) that the photosensitivity of CHD radicals is different, isomers **I** and **II** being more sensitive and stronger UV-absorbing compared to isomers **III**.

### 3.3. Absorption spectra of $\gamma$ -irradiated polystyrene

In the light of above findings, let us consider the absorption spectra of  $\gamma$ -irradiated PS containing CHD radicals. Due to the presence of an unpaired electron in macroradicals, one can also expect the occurrence of electronic transitions at longer wavelengths. As is known [2,3], allyl radicals exhibit two absorption bands: one peaked around 250 nm is attributed to the  $p \rightarrow \pi^*$  transition of the unpaired electron to anti-bonding  $\pi$  orbital while another peaked around 400 nm, to the  $\pi \rightarrow p$  transition of bonding electron to the anti-bonding orbital of the unpaired electron. For CHD radicals of alkyl-substituted benzenes, the  $\pi \rightarrow p$  band shows [8] a maximum around 330 nm (edge at  $\sim 610 \text{ nm}$ ), the type of substituent having little or no influence on  $\lambda_{\text{max}}$ . Like their low-molecular analogs, the CHD radicals formed (in an amount of  $6 \times 10^{18} \text{ g}^{-1}$ ) in  $\gamma$ -irradiated

films (dose 2500 kGy, 77 K) exhibit an absorption band peaked at 320–330 nm and an edge around 640 nm (Fig. 3, curve 2). The spectrum is seen to exhibit two maxima (at 320 and 330 nm) which can be attributed to two different CHD radicals.

Illumination of  $\gamma$ -irradiated PS at  $\lambda \geq 236 \text{ nm}$  (77 K) led to rapid disappearance of these bands (Fig. 3, curve 3). This was accompanied by disappearance of signals from CHD radicals in the EPR spectrum. Apparently, the band with  $\lambda_{\text{max}} = 330 \text{ nm}$  can be attributed to radicals **I** and **II** exhibiting elevated photosensitivity while the band with  $\lambda_{\text{max}} = 320 \text{ nm}$ , to radicals **III**. Knowing the relative amount of radicals **I**+**II** and **III** in the mixture (3/5 and 2/5, respectively), we can estimate the extinction coefficients  $\epsilon$  for the above radicals from the EPR spectra and the data of Fig. 3:  $\epsilon^{330}(\text{I, II}) \approx 9.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon^{320}(\text{III}) \approx 7.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ . At the spectral edges, a difference between the above  $\epsilon$  values can be expected to be still higher.

## 4. Conclusions

Low-temperature (77 K) radiolysis of polystyrene yields a mixture of the isomers of alkyl-substituted cyclohexadienyl radical formed upon addition of *in situ* generated hydrogen atoms to the double bonds of aromatic ring in positions 2–6. Analysis in terms of the free valence index has shown that the  $\text{C}_2$ ,  $\text{C}_4$ , and  $\text{C}_6$  carbon atoms of the phenyl ring are more favorable for the attack of H atoms, so that the relative amount of radicals on the  $\text{C}_2$ ,  $\text{C}_4$ , and  $\text{C}_6$  atoms is somewhat higher than a statistical value (above 3/5). Radicals **I** and **II** are spectrally indiscernible: both exhibit a triplet HFS with  $\alpha_3 = 1.0 \text{ mT}$  in the EPR spectra and a band peaked at  $\lambda_{\text{max}} = 330 \text{ nm}$  in optical absorption spectra. The relative amount of the  $\text{C}_3$  and  $\text{C}_5$  isomers (radicals **III**) is below 2/5. Their individual EPR spectrum with a quadruplet HFS ( $\alpha_4 = 1.0 \text{ mT}$ ) was recorded for the first time. In optical absorption spectra, the  $\text{C}_3$ - and  $\text{C}_5$ -isomers exhibit a band with  $\lambda_{\text{max}} = 320 \text{ nm}$ .

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