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Formation of radicals in stepwise thermolysis of polyunsaturated polycarbosilane —[($Me_2SiC{\equiv}C$)$_4$$Me_2SiCH{=}CH$]$_n$— *

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The onset temperature of radical formation in the stepwise thermolysis of polyunsaturated polycarbosilane —[($Me_2SiC{\equiv}C$)$_4$$Me_2SiCH{=}CH$]$_n$— with $n > 2$ was found by ESR spectroscopy. Beginning from 230 °C two types of radicals are formed. The first radical arises on heating to 240 °C due to the delocalization of unpaired electrons over the polyunsaturated polymer systems to H atoms of the Et groups of the polymer. The second radical appears at temperatures ≥240 °C due to delocalization to H atoms of the Me groups through the vacant 3d-orbital of the Si atom.

Key words: polyunsaturated silicohydrocarbons, ESR, spin-spin interactions.

The formation of a silicocarbon matrix by thermolysis of polycarbosilane begins from the bond rupture and recombination stages. Under specified conditions, some unpaired electrons (UE) that released by bond rupture are stabilized in the formed system of the polyconjugated bonds of polyunsaturated polycarbosilane (PCS). Characteristics of such UE can be obtained with the use of ESR spectroscopy.[1,2]

To elucidate the mechanism of the initial stages of thermolysis of the polyunsaturated silicohydrocarbon —[$Me_2SiC{\equiv}C$)$_4$$Me_2SiCH{=}CH$]$_n$— ($n > 2$) (**1**) and to determine the onset temperature of the radical formation, we studied this process by ESR during heating the polymer from 30 to 260 °C.

The first, low-intensity spectrum in the region of ESR signals of the organic radicals was found at 230 °C (Fig. 1). When the temperature is increased to 240 °C, the amplitude of the ESR signal increases and a dublet of dublets appears. Splitting in the 3.2—3.5 G region is due to the nonequivalent *trans*-protons of the bridging Et group. The *g*-factor is 2.0029±0.0003. The singlet line appears in the center of the spectrum at 240 °C. After heating to 250 °C, the amplitudes of the dublet lines increare slower than that of the singlet line. It is seen from the differential ESR spectrum of the radicals formed in the temperature range of 240—250 °C (see Fig. 1) that the amplitude of the central line is higher than the sum of the amplitudes of the dublet lines.

When the temperature is elevated to 260 °C, the central singlet line mainly increases. The concentration of UE determining this line increases to ~10^{16} spin g^{-1}. The intense singlet masks the dublets (Figs. 2 and 3).

The fact that resolution of the dublets deteriorates and they transform to a triplet can be due to the UE spin-spin exchange interactions because of increase in their concentration and an increase in the melt viscosity upon the thermopolycondensation of the polymer. When the power level in the ESR resonator is enhanced to 30 mW, the saturation of resonance transitions of UE in PCS occurs at 260 °C. As a result, the intensity of the singlet decreases compared to that of the doublet lines and broadened doublet lines appear, which are saturated to a lesser extent (see Fig. 3). If the singlet was determined only by transformation of the doublets, then the relaxation time of the UE singlet would be shorter than that of the UE doublets, because transformation of the doublets to the triplet is due to a decrease in the relaxation time of the UE doublets. However, as can be seen in the saturated spectrum, the relaxation time of the UE singlet is longer. The difference in the UE relaxation times indicates that UE, which determine both the doublet and singlet lines, have different localization. This conclusion is supported by the anisotropy of the saturated spectrum, which gives evidence of different *g*-factors for the overlapping lines of the double doublet and singlet.

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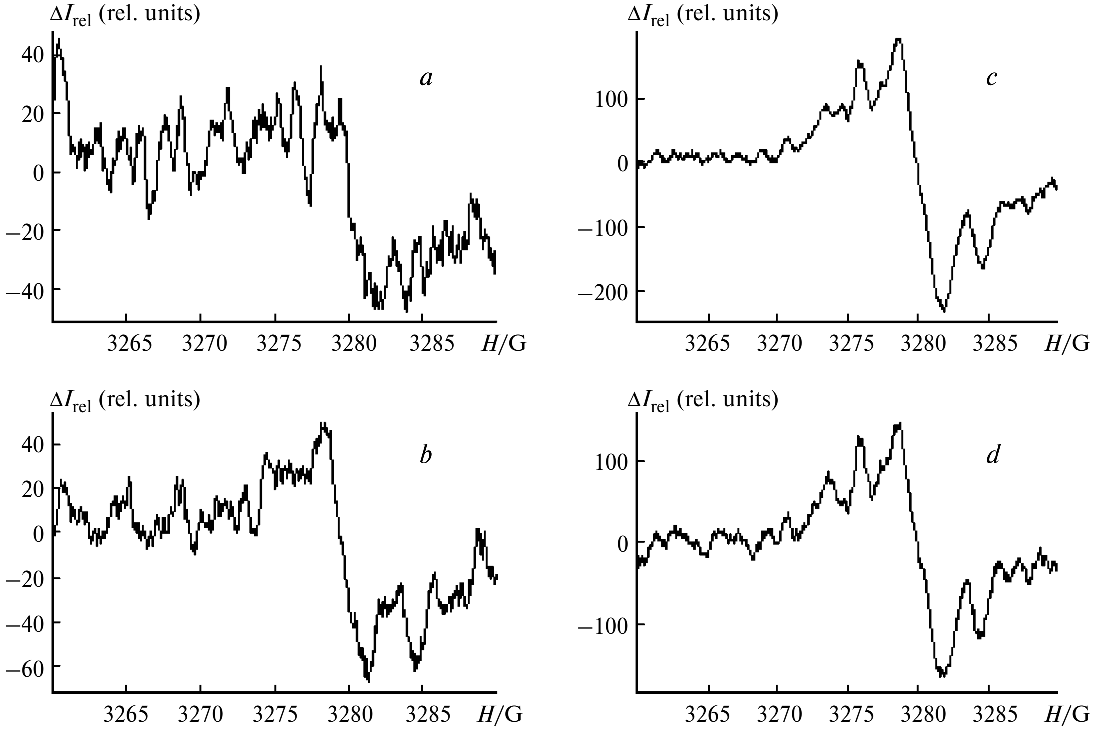

Fig. 1. ESR spectra of radicals formed on heating of PCS **1** in argon up to (*a*) 230, (*b*) 240, (*c*) 250; and (*d*) 240—250 °C (differential spectrum at 250 and 240 °C is presented).

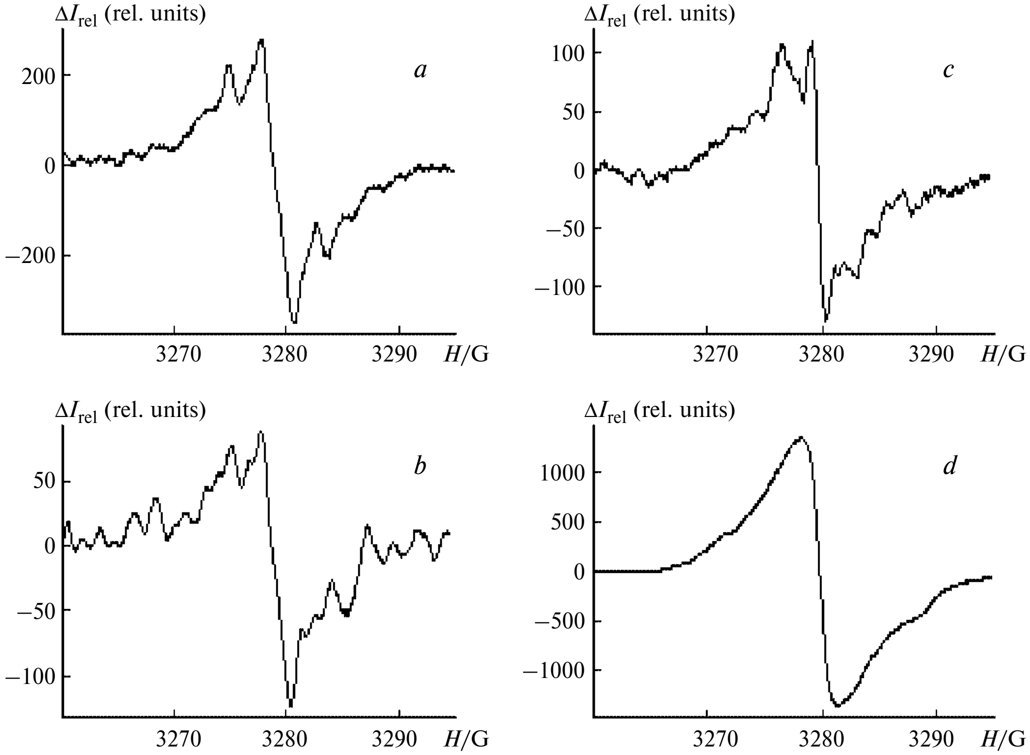

Fig. 2. ESR spectra of radicals formed on heating of PCS **1** in argon up to 260 °C (*a*); differential spectra obtained during heating PSC from 250 to 260 °C (*b*) and storage at 260 °C for 60 and 90 min (*c*) and 10 and 180 min (*d*).

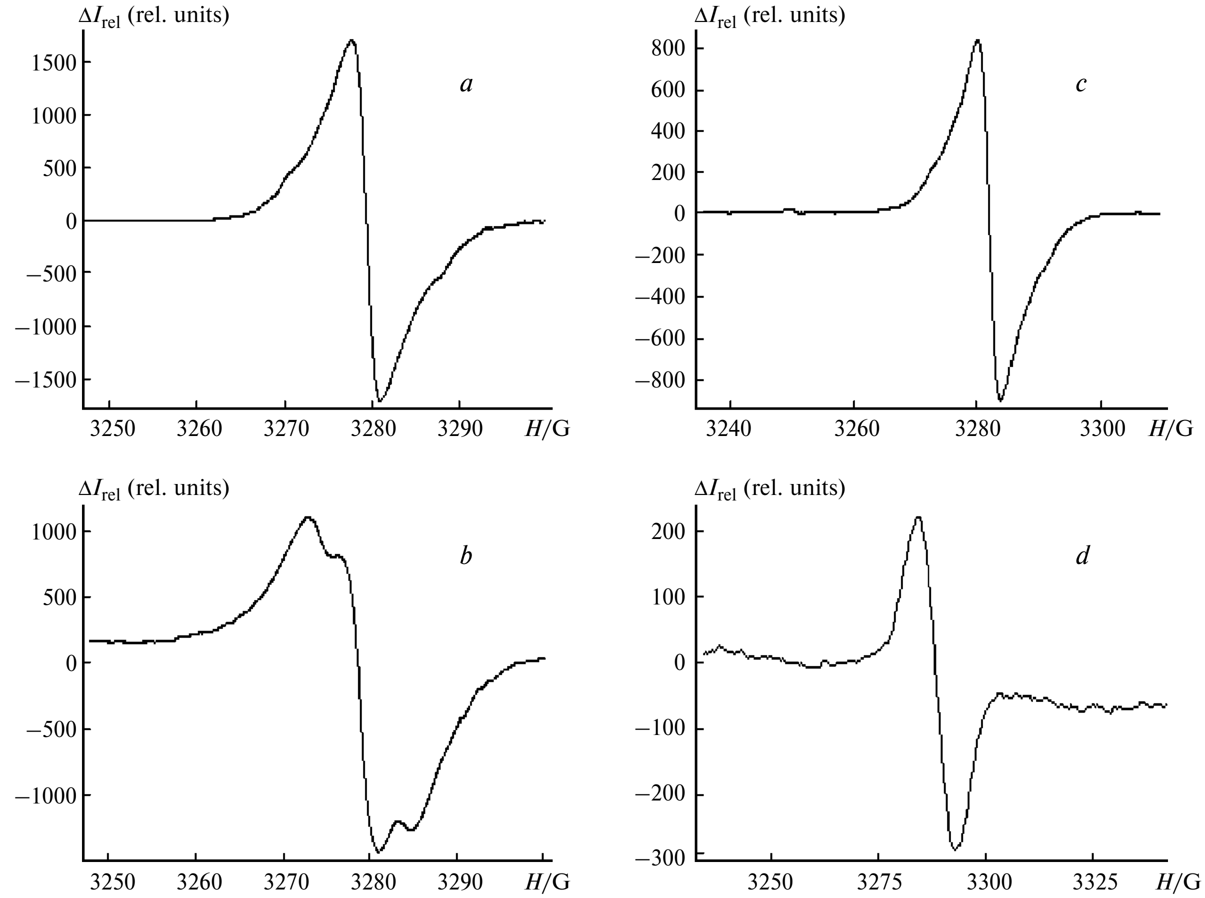

Fig. 3. ESR spectra of radicals formed on heating of PCS **1** in argon at 260 °C for 240 min (*a*); upon saturation of resonance transitions of unpaired electrons of radicals with excess MV-radiation (~30 mW) at 260 °C (*b*); after cooling the sample in argon down to 20 °C (*c*); after storage in air at 20 °C for three months (*d*).

The singlet line may contain the unresolved spectrum of UE interacting with protons of the Me groups at the silicon atoms. The HFS on the protons of the Me groups is poorly seen on the wings of the spectrum of the radicals formed at 260 °C (Fig. 4). The interaction of the unpaired electrons of the Ph groups with the protons of the Me groups through the Si atoms, which manifests itself in the HFS of the ESR spectrum of its radical ion, is known.[3]

After the PCS was cooled to room temperature, the ESR spectrum of the radicals does not markedly change in intensity and the doublets disappear (see Fig. 3). This can be due to their transformation to the singlet upon the melt—solid transfer because of a change in the relaxation time. The singlet linewidth increases up to ~4 G. After of the PCS sample was stored at room temperature in air for 3 months, the concentration of the paramagnetic centers (PMC) does not substantially change. A decrease in the amplitude of the spectrum is due to the line broadening from ~4 to ~9 G.

Such a high stability at these temperatures of the radicals formed is not typical of melts of hydrocarbon polymers. The stabilization can be due to UE delocalization through the vacant 3d-orbital of the silicon atom (p_π—d_π-interaction) to the system of the polyconjugated π-electrons in the polymer chain.[1—9] A loss in transparency and darkening of PCS to a dark brown color upon

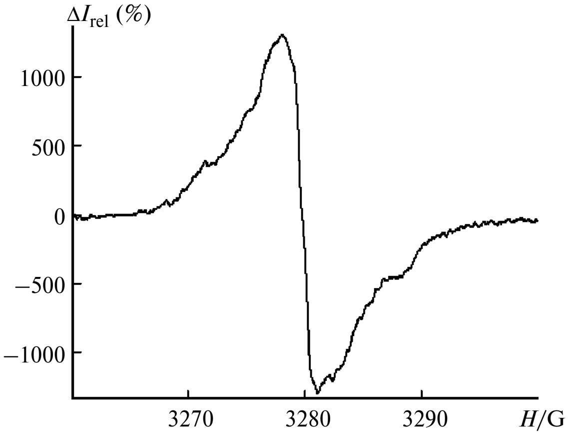

Fig. 4. ESR differential spectrum of the PCS radicals formed at 260 °C after storage during 3 to 180 min (difference spectrum).

heating above 230 °C also indicate the formation of the polyconjugation system.

Summing up, the study of the thermochemical transformations of PCS $-[Me_2SiC\equiv C)_4Me_2SiCH=CH]_n-$ ($n > 2$) during heating showed that the radicals in the polymer are formed at temperatures ≥230 °C. It follows from the ESR spectra that the double doublet, which appears at temperatures ≥240 °C, can be due to the UE interacting with protons in the *trans*-position of the Et groups in the polymer chain. The singlet line occurring in the ESR spectrum at 240 °C can be a sum of the unresolved lines of the spectrum of UE interacting with protons of the Et groups and electrons interacting with protons of the Me groups at the silicon atoms.

Experimental

The initial PCS was synthesized according to a procedure described elswhere.[10] The melting point of the polymer was 135 °C.

ESR spectra were recored in the X-range on an SE/X 2540 radiospectrometer (Radiopan, Poland) with a Radiopan UTS-211 temperature attachment that controlled the sample temperature with an accuracy of ±5 °C. The ESR spectra were recorded and processed with the WIN-EPR program (Bruker, Germany).

The concentration of PMC was estimated according to a standard procedure: the single crystal of $CuCl_2 \cdot 2H_2O$ was used as the side standard; the sample with Mn^{2+} ions in MgO (VNIIFTRI standard) served as the standard for determination of the PMC concentration.

The PCS sample (0.008—0.016 g) was placed in a quartz ampule with an inner diameter of 2 mm. Before the experimental run, argon was passed through a capillary inserted in the ampule for 10 min. Then the ampule was heated from 30 to 260 °C in an Ar flow in the resonator of the ESR spectrometer with a stepwise temperature increase. The ESR spectra were recorded at 30, 100, 150, 200, 230, 240, 250, and 260 °C.

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