Reports of the Academy of Sciences of the USSR

1964

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Volume 156, No. 3

PHYSICAL CHEMISTRY

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ON THE RELATION BETWEEN THE PARAMAGNETIC AND ELECTRICAL PROPERTIES OF SOME ORGANIC SEMICONDUCTORS

(Presented by Academician A. N. Frumkin, 12 II 1964)

At present it is generally accepted that the possible nature of paramagnetism in various carbonization products may be due to structural defects of the following type: 1) broken bonds arising during the growth of ring structures when the temperature of thermal treatment is increased ([1,2]), 2) charge-transfer complexes (CTC) ([3]). In pyropolymers exhibiting semiconductor properties, there is usually no correlation between the unpaired electrons responsible for the EPR spectrum and the current carriers ([4]). However, in ([3]) it is assumed that the formation of current carriers is caused by the thermal dissociation of CTCs responsible for paramagnetism. Paramagnetic resonance in some high-temperature coals is associated with charged current carriers ([5]). In ([6]) it is proposed that unpaired electrons are connected with the specific characteristics of strongly conjugated systems. This conclusion is based on experimental data according to which adsorption of one oxygen molecule leads to the reversible disappearance of 70 paramagnetic centers (p.m.c.) in sugar coke treated at 600° in air. In previously published works ([7,8]), devoted to the study of the structure of products of radiation-thermal modification of polyethylene (RTMP), it was shown that, under deep radiation exposure, regions of preferential polyconjugation arise in polyethylene, separated by dielectric interlayers, and that these regions grow as the temperature of subsequent thermal treatment (TTT) is increased. In RTMP pyrolyzed at 720° (RTMP 720°), adsorption of one oxygen molecule leads to the reversible disappearance of approximately two paramagnetic centers (p.m.c.).* On this basis it was concluded that the paramagnetism of RTMP products is not determined by the specific characteristics of strongly conjugated systems, but is due to the presence in the system of delocalized unpaired electrons. It was also shown earlier ([9]) that in RTMP products the character and dimensions of the dielectric interlayers determine the activation energy (ΔE) of mobility

Figure 1. Dependence of the concentration of p.m.c. (I) and the concentration of charged carriers (II) on TTO. III $-\lg(R-n) = f(\mathrm{TTO})$

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and, consequently, conductivity, whereas the concentration of carriers does not depend on the temperature of the current. An estimate of the concentration of current carriers n can be obtained from the electrical characteristics of RTMP products, taking into account that $n = \frac{\sigma}{e\mu}$ and $\mu = \mu_0 e^{-\frac{\Delta E}{kT}}$. As was shown ([9]), $\mu_0 \simeq 10 \div 100$ cm^2/V $\cdot$ sec. If one takes $\mu_0 = 50$ cm^2/V $\cdot$ sec and the experimentally obtained values of ΔE and σ ([7]) for different TTTs, one can obtain the dependence of the concentration of charged carriers on TTT. A comparison of the concentration of p.m.c. R and the concentration of current carriers calculated in this way as a function of the temperature of two-hour vacuum thermal treatment is given in Fig. 1 (curves I and II, respectively). The accuracy of determining the absolute values of the concentration of p.m.c. is $\pm 40\%$; relative measurements are considerably

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* Experimental materials will be published in the *Journal of Structural Chemistry* in 1964.

more accurate. It is seen from the figure that at TTO $< 800^\circ$ the concentration of p.m.c. exceeds the concentration of charged carriers by several orders of magnitude. Consequently, the paramagnetism of RTMP products treated at TTO $< 800^\circ$ cannot be associated with current carriers. From this it may be concluded that the EPR signal in RTMP treated at TTO $< 800^\circ$ is due to structural defects. These defects apparently are not sources of carriers—for example, charge-transfer complexes—since, as TTO increases in the range from 600 to 850°, the concentration of p.m.c. decreases, while the concentration of current carriers increases (see Fig. 1). With very careful removal of oxygen, the EPR spectrum of these materials is a single Lorentzian line of width $\Delta H_{\max} = 0.5 \pm 0.1$ oersted, independent of TTO (7). The concentration of p.m.c. does not depend on the measurement temperature. In the case TTO $> 800^\circ$, the concentrations of p.m.c. and carriers have similar values (see Fig. 1). If it is assumed that in this case current carriers are responsible for the paramagnetism, then from the characteristics of the EPR spectra one can obtain an approximate estimate of their mobility. Elliott' s formula (10)

Fig. 1. Dependence of the concentration of p.m.c. (I) and the concentration of charged carriers (II) on TTO. III $-\lg(R-n) = f(\mathrm{TTO})$

$$T_1 \simeq \frac{1}{30} \cdot \frac{\tau_R}{(\Delta g)^2} \tag{1}$$

relates the spin-lattice relaxation time T_1 to the electron relaxation time τ_R. Here $\Delta g = g_{\text{RTMP}} - g_{\text{free el.}}$, $g_{\text{free el.}} = 2.0023$. The carrier mobility is determined by the formula

$$\mu = \frac{e}{m}\tau_R, \tag{2}$$

where e is the electron charge, and m is the effective mass of the carrier, taken equal to the mass of a free electron. It is known that in a system with strong delocalization of spins $T_1 \simeq T_2$ (11), where T_2 is the spin-spin relaxation time, determined from the line width. Thus, to calculate μ it is sufficient to measure $\Delta H_{\max}$ and the position of the g-factor. Measurements of these quantities were carried out on RTMP 930° samples. It turned out that the RTMP 930° line is shifted upfield from the line of the DPPH reference sample by 0.6 ± 0.2 Oe. This means that $g_{\text{RTMP}} \simeq 2.0027$, since $g_{\text{DPPH}} \simeq 2.0039$. Hence $\Delta g \simeq 4 \cdot 10^{-4}$. The line width of evacuated RTMP 930° is $\Delta H_{\max} = 3.5 \pm 0.2$ Oe, i.e., $T_2 = 1.5 \cdot 10^{-8}$ sec. Substituting the corresponding values into formulas (1) and (2), we obtain $\mu = 70(\pm 50)$ cm^2/(V · sec). As was shown by electrical measurements, in RTMP 930° the activation energy of conductivity is close to zero, i.e. $\mu \simeq \mu_0$, and in magnitude agrees with the value given above. The conductivity value calculated from EPR data, $\sigma = R \cdot e \cdot \mu$ ($R = n$), is close to the experimentally measured value $\sigma \simeq 56\ \Omega^{-1} \cdot \text{cm}^{-1}$. As is seen from Fig. 1, on going from RTMP 930° to RTMP 1100°, the concentration of p.m.c. increases approximately twofold, while the conductivity increases by ~ 1.5 times. The concentration of both p.m.c. and charged carriers does not depend on the measurement temperature. The agreement of the data presented makes it possible to ascribe the paramagnetic resonance in RTMP treated at TTO $> 850°$ to charged current carriers.

The RTMP 850° material, whose vacuum thermal treatment lasted ~ 120 hours, has the intrinsic property of highly conducting mate-

an asymmetric line with an asymmetry of the shoulders $A/B = 2.7$. Estimates of the concentration of paramagnetic centers and the line width were carried out after grinding with Al_2O_3 and proved to be, respectively, $R \simeq 2 \cdot 10^{19}$ pmc/g, and $\Delta H_{\max} = 35 \pm 3$ Oe.

Assuming that the EPR signal is associated with current carriers, one can calculate the conductivity of the material by formula [12]:

$$\sigma = R \cdot e \frac{3\delta^2}{2T_{\text{d}}\left(\frac{kT}{e}\right)}, \tag{3}$$

where T_{d} is the diffusion time of an unpaired electron through the skin layer, estimated from the asymmetry of the shoulders; at $A/B \simeq 3$, $T_{\text{d}} \simeq 3T_2$ [12]; the spin-spin relaxation time calculated from the line width is $T_2 = 1.5 \cdot 10^{-9}$ sec; consequently,

$$T_{\text{d}} = 4.5 \cdot 10^{-9} \text{ sec}; \quad \delta = 0.03\sqrt{\frac{\lambda}{\sigma}} \text{ [cm]}$$

is the thickness of the skin layer. Substituting the corresponding values into formula (3), we find $\sigma \simeq 1 \cdot 10^4\ \Omega^{-1} \cdot \text{cm}^{-1}$ and $\delta \simeq 5 \cdot 10^{-4}$ cm. Direct measurement of the conductivity gave the value $\sigma \simeq 10^3\ \Omega^{-1} \cdot \text{cm}^{-1}$. Since such a highly conducting material is in powder form, owing to contact phenomena the conductivity of the entire sample may be less than the conductivity of the individual grains, which is determined from the EPR data. Thus, in PTMP products the paramagnetism is apparently due to structural defects of the broken-bond type only in the case when TTO $< 800°$, the number of such defects decreasing rapidly at TTO $\sim 850°$ (see Fig. 1, curve III). At TTO $> 850°$, the paramagnetism is apparently associated with charged current carriers.

The authors express their deep gratitude to N. A. Bakh for valuable advice.

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Received
6 II 1964

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Note: Figure translations are in progress. See original paper for figures.