A new mechanism of the dioxygen effect on ESR spectra of polyaniline

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The effect of dioxygen on the ESR spectra of powders of emeraldine salts at 170–230 K was found to depend on the time of storing of the samples at a specific temperature. The kinetics of changes in the ESR spectra reflects the conformational mobility of the polyaniline chains and its supramolecular structure. A new mechanism of the dioxygen effect on the ESR spectra of polyaniline at 50–100 K associated with the condensation of dioxygen in polyaniline pores was proposed.

Key words: polyaniline, ESR, dioxygen, morphology.

The specific features of the dioxygen effect on the linewidth of the ESR spectra of polyaniline are usually explained in the framework of a model,[1] according to which a paramagnetic O_2 molecule adds to the polymer and the exchange interaction at the instant of collision between spins of the motionless O_2 molecule and the mobile polaron broadens the ESR line of the polaron. We have previously found[2] that the broadening of the ESR line in the spectrum of polyaniline by dioxygen in the temperature region of 140–290 K has a maximum at 250 K. Analysis of the data in the framework of the model presented above estimated the rate of jumps of the polarons ($\sim 10^{13}$ s^{-1}). The maximum was assessed to the transition from weak to strong interaction with a temperature decrease. The amount of sorbed dioxygen was assumed to remain unchanged when the temperature changes. In this work, we showed that the amount of sorbed dioxygen increases with temperature decrease, but the rate of its addition to polyaniline decreases to such an extent that equilibrium is not achieved within a reasonable time. In addition, a new mechanism of the dioxygen effect at low temperatures was found.

Experimental

The polyaniline powders PAN1 and PAN2 used in the work were prepared as follows. Polyaniline PAN1 was synthesized for 2 h at −20 °C in water containing 0.1 *M* aniline, 0.08 *M* $(NH_4)_2S_2O_8$, and 0.1 *M* $HClO_4$, followed by drying of the samples at −20 °C. Polyaniline PAN2 was synthesized for 5 h at a lowered temperature in acetonitrile containing 1 *M* aniline and 1 *M* $HClO_4$ with gradual addition of 1 *M* $(NH_4)_2S_2O_8$; the precipitate was repeatedly washed with acetonitrile, water, and 0.1 *M* $HClO_4$ (to obtain the acidic salt of polyaniline) and dried at 40 °C. The protonation degrees determined as the ratio [Cl]/[N] are 0.56 and 0.13 for PAN1 and PAN2, respectively.

The samples were evacuated for 2 h under 10^{-4} Torr, and then O_2 was supplied under different pressures.

ESR spectra were recorded on an Radiopan SE/X-2544 radiospectrometer (Poznan, Poland) equipped with a temperature unit for work at temperatures >100 K and a home-made attachment for the work at helium temperatures. The ESR spectra were detected at low magnetic modulation amplitude and SHF-field power, at which the distortion of the line shape is negligible. The linewidth ΔH was measured between the extremes of the first derivative with an accuracy of ±2%. The *g* factor was calculated from the magnetic field strength and SHF radiation frequency for the intersection point of the ESR and basic lines. The relative error of the *g* factor measurement was $2 \cdot 10^{-5}$; however, the absolute error was $1 \cdot 10^{-4}$ because of the magnetic field gradient between the sensor of the magnetometer and the center of the cavity.

Results and Discussion

We found a new mechanism of the dioxygen effect in our study of the influence of dioxygen on the ESR spectra of PAN2 in a wider temperature range (Fig. 1). In addition to the previously found maximum of the ESR linewidth at 250 K, a maximum at 60–90 K was revealed. When the temperature decreases, the width of this maximum increases jumpwise at ~90 K and decreases at ~60 K. These temperatures are close to the liquation (90 K) and solidification points (54 K) of dioxygen. The broadening at 60–90 K is explained by spin exchange upon collision of polarons with mobile dioxygen molecules localized in the liquid phase. The volume of condensed dioxygen is insufficient to cover the completely immersed polyaniline powder in the ampule. Probably, dioxygen is condensed in polyaniline pores. At all temperatures, the line shape of the ESR spectra of polyaniline in both oxygen and a vacuum is close to the Lorentzian shape.

The *g* factors in a vacuum and an oxygen atmosphere differ (see Fig. 1). At >90 K in the presence of oxygen, the *g* factor decreases due to the spin exchange between sorbed oxygen and the polaron.[1] The changes in the ESR linewidth in oxygen at 60–90 K are accompanied

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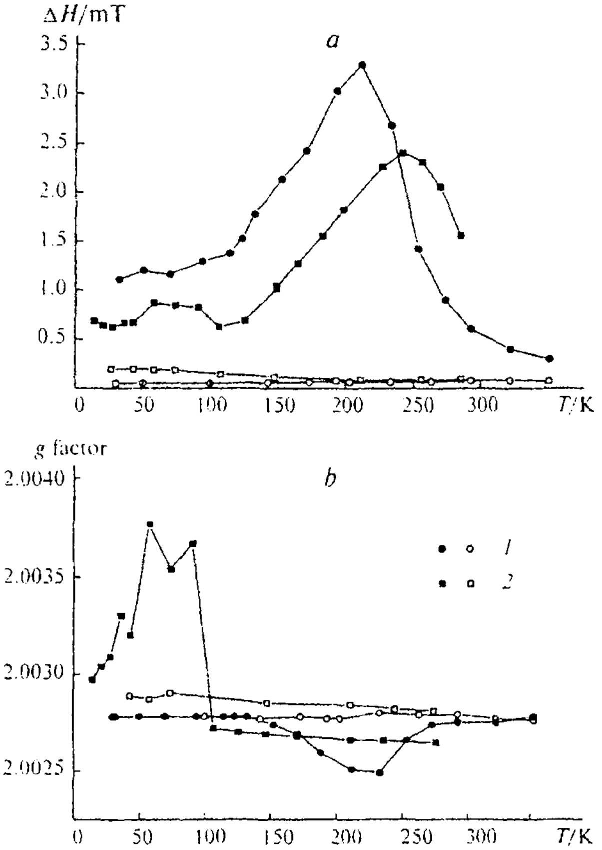

Fig. 1. Temperature functions of the width ΔH (*a*) and *g* factor (*b*) of the ESR lines of PAN1 (*1*) and PAN2 (*2*) powders *in vacuo* (light markers) and in O_2 (dark markers). The O_2 pressures for PAN1 and PAN2 are 0.15 and 1 atm, respectively.

by significant changes in the *g* factor (see Fig. 1), and the sign of the change is opposite to that at temperatures >90 K. Such considerable changes in the *g* factor can be explained by conformational transitions in the polymeric chain upon liquation and solidification of O_2.

When the pressure of O_2 was halved (to 0.5 atm), its influence on the linewidth and *g* factor at temperatures >100 K decreased and at 60—90 K remained unchanged.

Oxygen affects the ESR linewidth of polyaniline PAN1 much more strongly than that of PAN2, and the specific features found for PAN2 at 60—90 K are absent (see Fig. 1). In addition, at <220 K the line shape noticeably differs from the Lorentzian shape. Unlike PAN2, the linewidth of PAN1 *in vacuo* decreases with temperature decrease.

The temperature changes in the *g* factor and linewidth (see Fig. 1) measured during slow (~10—15 min per point) decrease and increase in the temperature are close. When the temperature changes are fast, the amplitudes of the ESR lines for both PAN1 and PAN2 vary in time: they decrease after a fast temperature decrease and increase after a fast increase. This is explained by a change in the number of dioxygen molecules sorbed on polyaniline after the temperature change, and the sorption-desorption process is slow and reflects, probably, conformational changes in polyaniline. The conformation of the polyaniline chains can affect either oxygen diffusion in the pores or directly the addition of oxygen to the polymer. The possibility of conformational changes in the polyaniline structure is confirmed by the absence of the influence of oxygen admitted at 77 K on the ESR linewidth.

At $T > 220—230$ K, a decrease in the amplitude A is accompanied by an increase in the linewidth ΔH, so that the product $A \cdot \Delta H^2$, which is proportional to the number of spins in the sample, remains unchanged. At $T < 220—230$ K, the product $A \cdot \Delta H^2$ decreases in time. This occurs because a part of the paramagnetic centers (~50%) broadens so much that their ESR spectrum cannot be recorded. According to the previous data,[3] the volumes of the amorphous and crystalline phases in polyaniline are comparable. It is most likely that the paramagnetic centers whose ESR spectra are strongly broadened by dioxygen are arranged in the amorphous regions, and those of the centers in the crystalline regions are broadened less due to the impeded access of dioxygen to these centers. The size of the crystalline lattice of the emeraldine salt is 7.0×8.6×9.5 Å and, hence, for the dioxygen molecule of 3.6 Å, the penetration of dioxygen into the crystalline phase at low temperatures can be hindered.

The change in the amplitude of the signal in time is well described by the formula $A_1\exp(-t/\tau) + A_2$ after a jumpwise temperature decrease from ~20 °C or by the formula $A_1[1 - \exp(-t/\tau)] + A_2$ after a jumpwise temperature increase. The τ values determined at the same temperature after a decrease or an increase in the temperature are close. The Arrhenius plots of τ for PAN1 and PAN2 are presented in Fig. 2. The activation energies of the conformational transitions to PAN1 and PAN2 are equal and amount to 3.3 kcal mol^{-1}. Dioxygen adds to PAN1 more rapidly. Perhaps, this results in a situation that oxygen adds in a greater amount during a

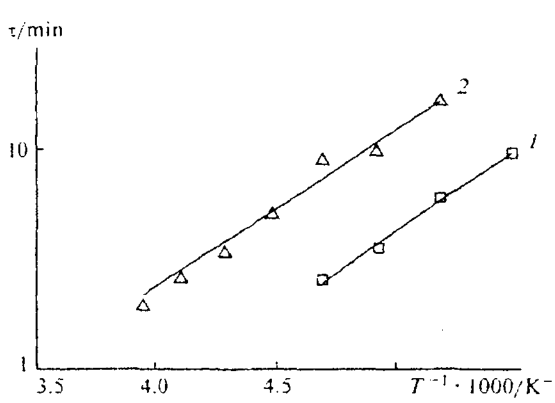

Fig. 2. Arrhenius plots of the characteristic times of changes in the amplitude of the ESR line of two polyaniline forms PAN1 (*1*) and PAN2 (*2*) after fast temperature decrease from ~20 °C.

comparable time and strongly broadens the ESR spectra of PAN1 as compared to those of PAN2.

The necessity of conformational transitions in polyaniline for the addition of oxygen restricts the amount of sorbed dioxygen. A considerable increase in the amount of sorbed dioxygen was found only for the temperature decrease to 210—220 K, then the sorption was retarded, and the equilibrium value was not achieved within the time of the experiment. These specific features of dioxygen sorption should be taken into account in analysis of the temperature plots of the spectral linewidth in the presence of oxygen. The decrease in the linewidth with the temperature decrease below 220—250 K (see Fig. 1) is explained, as previously,[2] by the retardation of polarons at an unchanged oxygen content. The linewidth increase upon temperature decrease from ~20 °C, which has previously been explained by a weak exchange, is stipulated by an increase in the amount of sorbed oxygen.

Our results show that the study of the dioxygen effect on the ESR spectra of polyaniline is a promising method for investigation of the supramolecular structure and molecular dynamics of polyaniline.

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