Polyazopolyarenes (PA's) derived from chrysoidine and its derivatives have catalytic activity with respect to the liquid-phase oxidation of cumene and tetralin (TL) to the corresponding hydroperoxides (HP's) [1, 2]. Small amounts of bound copper in the polymer are required to initiate its action [2]. In the present work, we have used ESR to analyze the structure of the copper-containing centers in PA's and to examine the changes undergone by these centers under the influence of various reagents.

**EXPERIMENTAL**

The chrysoidine, methylchrysoidine, and butoxychrysoidine polyazopolyarenes (PA's) investigated were prepared by oxidizing the corresponding diamines in pyridine solution in the presence of CuCl. Excess copper was removed from the polymers by repeated washing with 10% HCl solution and aqueous solutions of NaOH or NH₃. After each treatment, the polymer was fractionated by selective dissolution in DMF [1].

The ESR spectra of the polymers were recorded for solutions in DMF, chlorobenzene, or chloroform. The tetralin (TL) and cumene used in a number of experiments were first purified to remove hydroperoxide (HP) by distillation in vacuo over Na. The copper content of the polymers was determined by atomic-absorption analysis and was estimated from the ESR spectra.

**DISCUSSION OF RESULTS**

The ESR spectra of the PA's with different copper contents exhibit two types of Cu(II) signal, obviously corresponding to complexes with different structures. Hyperfine splitting due to N nuclei is clearly visible in the spectrum of one of the complexes (I) (Fig. 1a) but was not observed in the spectrum of the other complex (II) (Fig. 2a), which has a higher g-factor. Copper ions stabilized in the chrysoidine, methylchrysoidine, and butoxychrysoidine polymers gave similar spectra. Because of its high solubility, we concentrated mainly on the ESR spectrum of the butoxychrysoidine* polymer (PBC).

The copper content of the PBC samples was varied from 0.04 to 1.3% according to the extent of washing. The amount of Cu(II) bound in the polymer can be increased by adding Cu(II) bis(0,0-di-2-ethylhexyl phosphate) to the polymer solution. In TL solution, this copper phosphate occurs in the form of associates and gives a strongly broadened signal. Addition of this salt to a solution of the polymer in TL increased the intensity of the signal from the polymer centers primarily on the part of complex (II) and to a lesser extent on the part of complex (I). The maximum number of Cu²⁺ ions that can be bonded to PBC in the form of complexes (I) and (II) corresponds on average to one copper-containing center per 7000 molecular-weight units.

The Cu(II) spectra recorded at 20°C, even in low-viscosity solvents such as chloroform, differed little in shape from the spectra observed in vitrified solvents at the temperature of liquid N₂. Consequently, the size of the individual polymer macromolecules containing the Cu²⁺ ions is sufficiently large, and their motion in the liquid solution is sufficiently slow, not to average out the anisotropy of the g-factor and hfs.

*Butoxychrysoidine = 2,4-diamino-5-butoxyazobenzene.
Fig. 1. The ESR spectra of PBC in DMF glass: a) containing 0.2% Cu, complex (I); b) after contact with tetralin HP, complex (II); c) after addition of CH₃COOH, complex (III); d) after oxidation of tetralin, complex (IV).

Fig. 2. The ESR spectra of PBC in TL: a) polymer containing 1.2% Cu; b) polymer containing 0.2% Cu after heating at 80°C in the presence of tetralin HP (0.1 M); c) polymer containing 1.2% Cu after heating at 80°C in TL without admission of O₂; d) signal recorded in TL solution at 20°C.

In the polymers containing >1% copper, some of the ions are evidently stabilized in sites different from complexes (I) and (II). These ions are responsible for the slight broadening at the wings of the Cu(II) signal (see Fig. 2a) and, after adding pyridine (~1 M) to the solution, give a spectrum corresponding to a tetrapyridine complex, whereas the ESR spectra of complexes (I) and (II) remain unchanged on addition of pyridine.

The addition of acetic acid or 0,0-di-2-ethylhexyl phosphoric acid to solutions of PBC in DMF, chlorobenzene, or chloroform resulted in the appearance of a new complex (III) (Fig. 1c) with an appreciably higher g-factor (Table 1). Complex (III) in chloroform was formed at lower acid concentrations than in DMF. The addition of DMF to a solution of PBC in chloroform containing the minimum amount of acid necessary for the formation of complex (III) resulted in the reappearance of the signals from complexes (I) and (II). Consequently, the formation of complex (III) is not due to destruction of copper-containing centers and is reversible in character.

In solutions containing acid and pyridine, the Cu(II) ions are extracted from the polymer structure and give a spectrum characteristic of the tetrapyridine complex.