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INVESTIGATION OF POLY(p-PHENYLENE) OBTAINED BY ELECTROCHEMICAL OXIDATION OF BENZENE IN A BuPyCl-$AlCl_3$ MELT

L. M. GOLDENBERG, A. E. PELEKH, V. I. KRINICHNYI, O. S. ROSHCHUPKINA, A. F. ZUEVA, R. N. LYUBOVSKAYA and O. N. EFIMOV

Institute of Chemical Physics, U.S.S.R. Academy of Sciences, Chernogolovka 142 432 (U.S.S.R.)

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Abstract

Poly(p-phenylene) has been obtained by electrochemical oxidation of benzene in a BuPyCl-$AlCl_3$ melt. The conductivity of the fresh film is 10 - 100 S/cm. Even when the film is stored in a dry inert atmosphere, its conductivity is reduced. Electrochemical properties and IR and ESR spectra have been investigated. The polymer has an average chain length of 29 - 30 units.

Introduction

Poly(p-phenylene) (PPP) is one of the most unusual electroconducting polymers. The most widely used method of PPP production is benzene oxidation with a Friedel-Crafts catalyst (the Kovacic method) [1], which yields a polycrystalline powder. But for investigations thin PPP films are more suitable. Their synthesis is performed by the anodic oxidation of benzene, diphenyl and other benzene oligomers [2-11] or by the cathodic reduction of dibromobenzene [12]. Thin films of low conductivity (10~^{3}- 10~^{s} S/cm [2, 3, 5, 6, 11]) are usually obtained; in some cases this value reaches 100 S/cm [4,7,8].

Recently a report [13] has been published on the production of PPP films by the anodic oxidation of benzene in a BuPyCl-$AlCl_3$ (BPA) melt. This method was proposed earlier by Osteryoung *et al.* for the production of polypyrrole and polythiophene [14, 15]. A Meissner effect (levitation) was observed in the films in a magnetic field at 268 K. Later the same authors reported results of a study of PPP films (a = 10^4 S/cm) obtained analogously in a cetylpyridinium chloride-$AlCl_3$ melt [16].

The present paper reports on investigations of the properties of PPP obtained by benzene electrooxidation in a BPA melt.

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Experimental

BuPyCl was obtained by reaction of pyridine with BuCl in DMF at 120 °C; it was recrystallized five times from a mixture of MeCN/EtOAc with charcoal, then dried over P_2O_5 at 60 °C for 30 h. Chemical-grade benzene was distilled over P_2O_5. 1,1,2-Trichloroethane (TCE) and dichloromethane (DCM) were purified by subsequent treatment with cone. H_2SO_4, Na_2CO_3 solution and water, dried over K_2CO_3, distilled over P_2O_5 and stored over K_2CO_3. All the procedures were performed in a dry argon atmosphere in a glove box. Before the experiment, benzene, TCE and DCM were purified by vapour freezing from the vessel with P_2O_5 under vacuum into a trap cooled by liquid nitrogen.

The melt components were mixed with the addition of small portions of purified $A1C1_3$ to the BuPyCl to prevent high heating of the mixture. A light yellow liquid was formed which was purified by prolonged electrolysis, according to ref. 17. Freshly distilled benzene was added to the melt (vol./vol. ratio 10:1). A 15 - 20 min electrolysis was carried out in a cell (6 cm^3) with two Pt electrodes (12 cm^2 surface) at a current density of 1.5 mA/cm^2. The black thin film so obtained was carefully washed off from the melt by TCE and benzene or several times with DMC and peeled off from the electrode. Elemental analysis showed that even after continuous washing the film contained nitrogen, which was evidence of the presence of butylpyridinium cations resulting from cointercalation with chloraluminate anions.

A neutral PPP film was obtained by water treatment, by soaking in a 25% ammonium solution for 24 h, then washing off with water, alcohol and ester.

The ESR spectra (3-cm range) were recorded at 300 and 77 K on an ESR-V spectrometer. The high-resolution ESR spectra (2-mm wave range) were recorded on an ESR-5-01 spectrometer, according to ref. 18. The magnetic field was calibrated using single crystals of the ion-radical salt $DBTTF_3$-$PtBr_6$ as a standard. The magnetic microwave field (#j) in the centre of the 2-mm wave range resonator was calculated from the expression [19]

$$\Delta H = \Delta H_0(1 + \gamma^2 H_1{}^2 T_1 T_2)$$

for the linewidth of the fluoranthene cation-radical salt (T_1 T_2 — the electron relaxation time). The a.c. specific conductivity (f = 10 GHz) and the electron relaxation time were determined from the asymmetry factor of the ESR spectra (A/B) according to refs. 20 and 21. The (pyrimidine)$(TCNQ)_2$ salt (2 G linewidth) was used as the standard to calibrate the absolute unpaired spin concentration.

The IR spectra were registered on a Specord-75IR instrument in a hermetic cell with KBr windows.

The d.c. conductivity measurements were obtained using the four-probe method with contacts retained against the sample. Detection of superconductivity was determined by a magnetometer as well as from the hysteresis of the microwave power (*f* = 10 GHz) reflection from the samples depending on the magnetic field scanning rate at 77 K, according to ref. 22. Superconductivity was not detected.

Results **and** discussion

The anodic oxidation of benzene in BPA (1:1,1:2) at a current density of 1.5 mA/cm^2 proceeds at potentials close to those at which chloraluminate anions discharge with the formation of a dense black film about 10-/xm thick. The side facing electrode was bright and smooth, the other was dull. As seen from Fig. 1, PPP has a granular morphology. At lower current densities the time required for film production increases; an increase in current density results in the formation of a loose precipitate.

Fig. 1. SEM micrograph of the PPP film.

When the film is washed free of the melt admixtures, its d.c. conductivity is 10 - 100 S/cm at 300 K. Even when the film is stored in a dry inert atmosphere, its conductivity is reduced by two to three times per day. At the same time, evaluation of the conductivity with respect to the asymmetry factor of the ESR spectra (Table 1) gives a value of 2 to 4x10^3 S/cm, which

TABLE 1

Magnetic and electric parameters of PPP: A/B is the asymmetry factor; ΔH_O is the half-width of the ESR line; $[R]_o$ is the concentration of the paramagnetic centres at 300 K; $[R]/[R]_O$ is its relative change when the sample is cooled to 77 K; σ_{MW} and σ_{dc} are the conductivity values measured from the ESR spectra and d.c. studies

Sample	A/B	DH_O (G)	$[R]_o$ x 10^{18} (spin/g)	$[R]/[R]_O$	T_2 (µs)	σ_{MW} (S/cm)	σ_{dc} (S/cm)
PPP1	2.3	0.9	12	17.0	0.41	3×10^3	10-100
PPP2	2.5	1.2	32		0.44	4×10^3	
PPP3	1.4	2.2	21	3.5	0.16	1.4×10^3	
PPP4		3.7[a]	0.4	2	100-1000		10^{-8}
PPP5		4.7[a]	0.06	0.1			10^{-2}

[a] The half-width for gj^.

remains practically constant when the film is stored in an evacuated ampoule for 4 days (PPP2, Table 1). This suggests that the PPP film doped with chloraluminate anions is extremely moisture sensitive. In air or during the washing by MeCN, ester and acetone the film turns brown-red and its conductivity decreases down to 10^{-8} S/cm. All these effects may be caused by the destruction of the highly doped PPP as a result of a redox process involving chloraluminate anion oxidation with further radical decay and polymer chlorination

$$\dot{\mathrm{P}}\mathrm{PP}^{+}\mathrm{AlCl_4}^{-} \rightleftharpoons \mathrm{PPP}^{0}\mathrm{AlCl_4}^{\cdot} \rightleftharpoons \mathrm{PPP}^{0} + \mathrm{AlCl_3} + \mathrm{Cl}^{\cdot} \rightleftharpoons \mathrm{PPP(Cl)} + \mathrm{HCl}$$

As shown earlier [23, 24], such reactions with the AsF_6~ anion lead to PPP fluorination; the fluorine atoms attack the terminal benzene rings. Since the rate of AsF_6^- consumption is controlled by diffusion, it appears that the dopant radical decays on entering the polymer free volume, followed by rapid PPP fluorination.

The proposed destruction mechanism of PPP doped with chloraluminate anions is confirmed by the appearance of a band at 750 cm^{-1} in the IR spectra of the neutral PPP film, corresponding to C—C1 bond vibrations. The presence of moisture or a polar solvent may cause $A1C1_4$* radical decay promoted by solvation or hydrolysis.

To increase the stability of the p-doped film, an electrochemical exchange of chloraluminate anions by BF_4^- was undertaken by anodic oxidation of the freshly prepared film in 1 M $LiBF_4$ in propylene carbonate (PC) at the potential of 4.0 - 4.1 V (versus Li/Li^+) for 8 h (~0.1 mA). After such treatment the film is air-stable and its conductivity is $10{\sim}^{2}$ to $10{\sim}^{3}$ S/cm.

The electrochemical behaviour of the film is in general characteristic of polyconjugated polymers. In the cyclic voltammograms (CVA) a slightly pronounced oxidation peak *(El* = 3.85 V) and an intense one *(E* = 4.3 V) were observed when the potential was swept from the initial value of +3.2 V (corresponding to the lightly doped PPP film) to +4.5 V (i.e. the region of initial discharge of the supporting electrolyte). The peak *El* = 4.2 V only

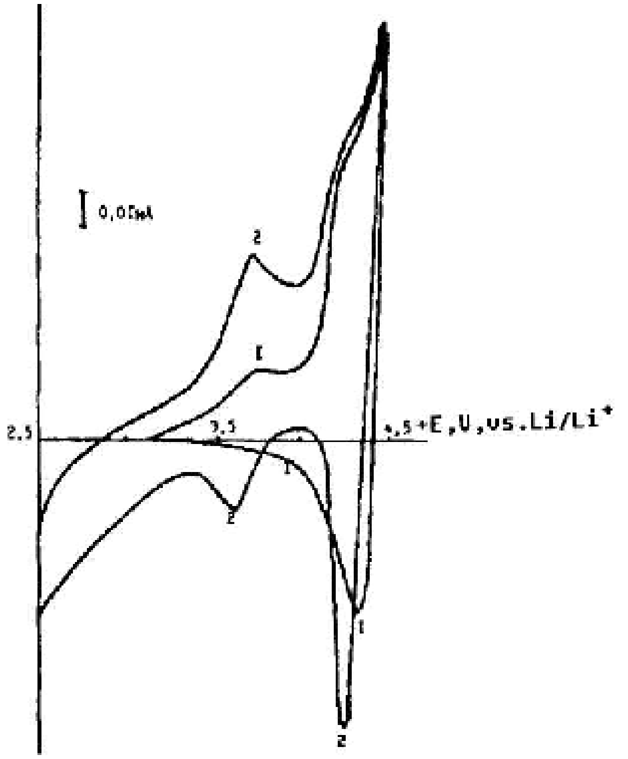


Fig. 2. CVA for the PPP film synthesized from BPA melt in propylene carbonate with 1 M $LiBF_4$. The scan rate was 1 mV/s. (1) The film redoped in propylene carbonate with 1 M $LiBF_4$. (2) Moulded electrode from the PPP film (1.5 mg), milled with carbon additive.

appears when the potential is reversed (Fig. 2). According to ref. 25 the peak E_a^1 = 3.85 V is the signature of neutral PPP doping, and its low density may be conditioned by the high resistance of a slightly doped film and the low value of the charge, which is injected under CVA oxidation. The absence of a backward peak, E_c^1, may be caused by the insulating layer formed at E_c^2 near the film-electrode interface reduction, which hinders further charge removal, as suggested in ref. 25. Indeed, in a blend prepared by mixing milled PPP and conducting carbon additive there appears a well-defined oxidation peak (E_a^1 = 3.76 V), the reversibility of which is confirmed by the appearance of the backward peak E_c^1 = 3.62 V. However, removal of the remnant charges proceeds when the potential is still decreasing. It is apparently connected with hindrances in the anion de-intercalation from the dense PPP film. The PPP samples synthesized via the Kovacic method and anodic oxidation of benzene in liquid HF in the mixture with the conducting

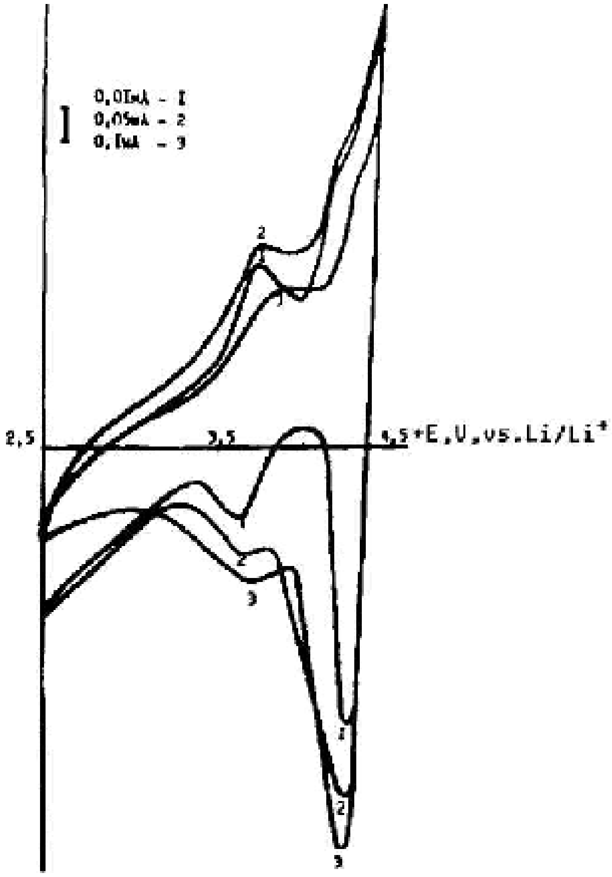


Fig. 3. CVA for PPP blends prepared by mixing the PPP sample with 15 wt.% carbon black and 15 wt.% teflone in propylene carbonate with 1 M $LiBF_4$. The blends were moulded (100 kg/cm^2) into a disc, which had a surface of 0.078 cm^2. The current collector was of Pt mesh. The scan rate was 1 raV/s. (*1*) The PPP film (1.5 mg) synthesized from BPA melt and milled with the carbon additive. (*2*) The PPP (22 mg) synthesized by benzene electro-oxidation in liquid HF. (*3*) The Kovacic PPP (76 mg).

carbon black additive exhibit similar behaviour and at potentials ranging from 3.6 to 3.8 V there is a reversible peak of PPP oxidation in the CVA in all cases (Fig. 3).

The reason for the appearance of the E_a^2 peak in the region of discharge of the supporting electrolyte is not clear and requires a more detailed study. The appearance of the backward peak suggests that the process is reversible, which does not essentially affect the PPP structure. The anodic process probably includes anion oxidation with the formation of the radical BF_4^-, which oxidizes PPP (analogously to p-doping)

$$BF_4^- - e \longrightarrow BF_4^\bullet$$

$$PPP^0 + BF_4^\bullet \longrightarrow PPP^+BF_4^-$$

The probability of the mechanism is supported by the dependence of the potential and the *El* peak height on the nature of the anion in the sequence: BF_4^-, ClO_4^-, AsF_6^-, $SO_3CF_3^-$ (Fig. 4).

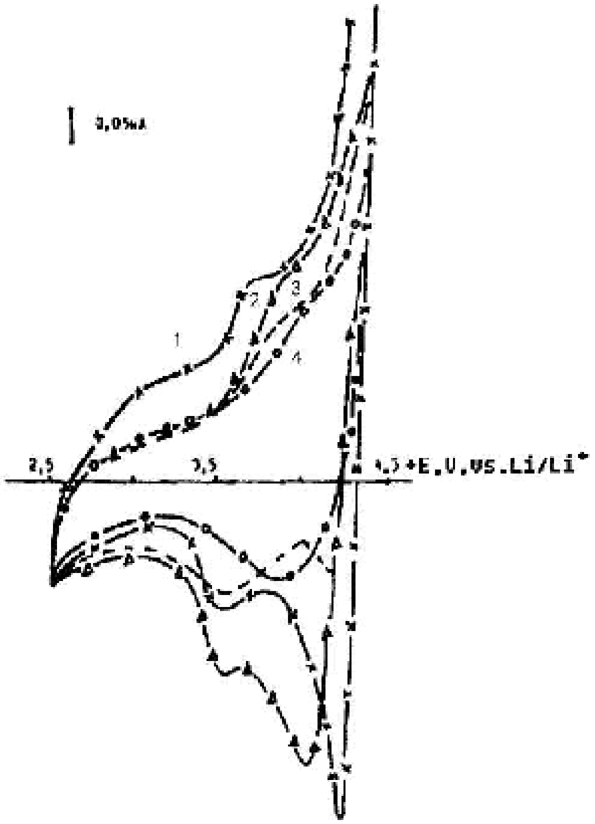
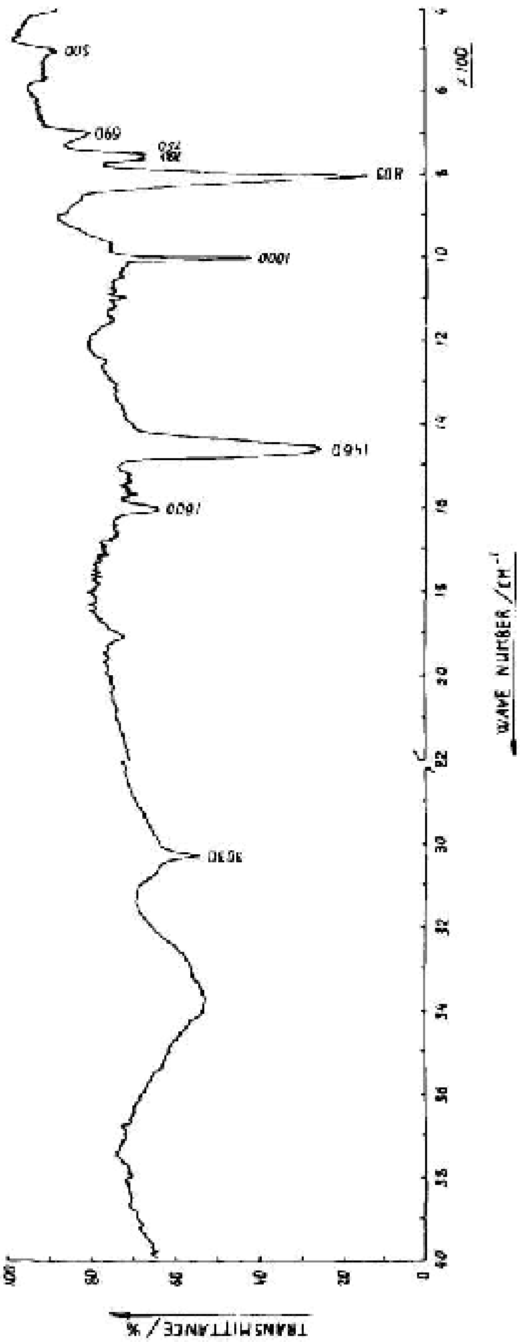


Fig. 4. CVA for the blend prepared by mixing Kovacic PPP (76 mg) with 15 wt.% carbon black and 15 wt.% teflone in a PC solution of various lithium salts. The scan rate was 1 mV/s. (*1*) $LiBF_4$; (*2*) $LiClO_4$; (*3*) $LiSO_3CF_3$; (*4*) $LiAsF_6$.

In order to verify some of the suppositions stated above, parallel ESR and IR investigations of the samples were carried out. The as-synthesized PPP sample showed a broad absorption in the IR region (4000 - 400 cm^{-1}) characteristic of deeply doped conducting polymers because of the electron-vibration interaction. This broad IR absorption vanishes when the sample degrades with conductivity loss and some separate bands appear typical of PPP.


TRANSMITTANCE / %
0
20
40
60
80
100
WAVE NUMBER / CM⁻¹
x 100
40
38
36
34
32
30
22
20
18
16
14
12
10
8
6
4
3030
1600
1460
1000
803
720
690
500

The IR spectrum of the neutral PPP (Fig. 5) consists of the following absorption bands: 685 and 760 cm^{-1} ($\delta_{\perp}$CH of mono substituted phenyl rings); 803 cm^{-1} ($\delta_{\perp}$CH of para-substituted rings); 1000 cm^{-1} ($\delta_{\perp}$CH of para-substituted rings); 1460 cm^{-1} (v (CC_{Ar})) [10].

The presence of the band at 1600 cm$'^{1}$ (the 5iCH overtone at 803 cnoT^{1}) as well as the absence of the absorption band in the region of 1,2,4-substituted benzenes (860 - 900 cm^{-1}) provide evidence of a low degree of polymer chain branching [10]. The absorption band at 750 cm^{-1} can be assigned to y(CCl).

The average chain length was estimated from the empirical equation with the use of the band intensity ratio at 803 and 685 cm^{-1} ($\delta_{\perp}$CH of *para*- and mono substituted rings, respectively) [10]. It appeared to be equal to 29 - 30 units, i.e. the electrosynthesis in the melt yields average chain lengths similar to that formed in the anodic oxidation of benzene in liquid SO_2 [10], and much higher than in the Kovacic PPP (9-14 units) [1].

Some samples of PPP films were studied by the ESR method: a freshly prepared film (PPP1); the same film after 4 days storage in an evacuated ampoule (PPP2); that exposed for a short time to air (PPP3); after dopant removal (PPP4); and after BF_4^- redoping of the film (PPP5).

The PPP1-PPP3 ESR spectra in the 3-cm wave range are asymmetric singlets with a well-pronounced Disonian line shape (Fig. 6(a)). The magnetic parameters of these samples (namely g factor and half-width of the line) are close to those for PPP synthesized by anodic oxidation of benzene in liquid HF, which have the following magnetic parameters: g = 2.0092, ΔH = 2.1 G for the native sample, and g = 2.0035, ΔH = 3.5 G for the washed-off sample. On dopant removal, i.e. at the transition from PPP1 to PPP4, the above spectra transform to the axially symmetrical ones with anisotropic g factors: $g_{\perp}$ = 2.00337, $g_{\parallel}$ = 2.0020 (Fig. 6(c)). Such a transition is accompanied by a sharp decrease in the concentration of the spin carriers and broadening of the line (Table 1). It is worth noting that in earlier reports

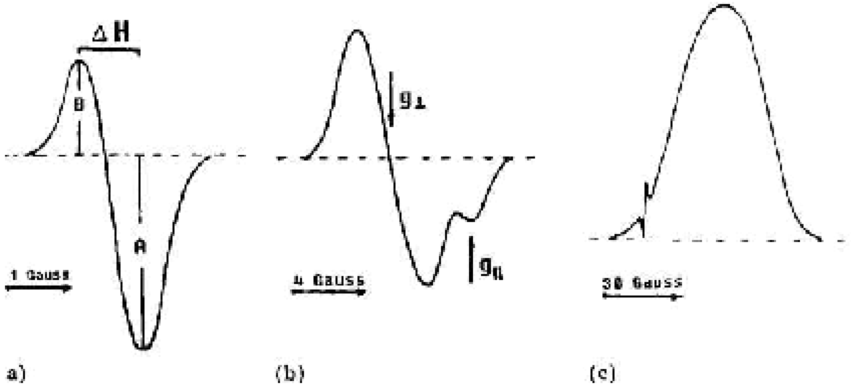


Fig. 6. The ESR spectra of the PPP films: (*a*) PPP1-PPP3 in the 3-cm wave range; (*b*) PPP4, PPP5 in the 3-cm wave range; (*c*) PPP4 in the 2-mm wave range.

none of the axially symmetrical ESR spectra for the π-conjugated polymers, including Kovacic PPP, were registered in the 3-cm wave range. We registered the axially symmetrical spectra of polythiophene doped with various anions only in the 2-mm wave range [18]. With PPP doped with BF_4^- anions (PPP5) the spectrum shape retains, however, a slight decrease in the concentration of paramagnetic centres and a change in the sign of its dependence on temperature is observed (Table 1).

In the 2-mm wave range the spectral resolution increases. Also the cross-relaxation between the spin packets decreases in a strong field (about 50 kG), therefore it seems possible that there is a much slower efficient relaxation time of the paramagnetic centres. When the condition $T_2 >> T_{run} > T_{prec}$ (where T_2 is the electron relaxation time, $T_{run} = H_l/\omega_m H_m$ is the time of the resonance condition running, $T_{prec} = l/\gamma H_1$ is the time of the spin precession, H_1 is the magnetic component of the MW oscillations in the centre of the cavity, γ is a gyromagnetic ratio, ω_m and H_m are the frequency and amplitude of the high-frequency modulations, respectively) is valid, in the ESR spectrum there appears a bell-like signal of dispersion π out of phase to the modulating high-frequency field. Such a form is typical of paramagnetic centres registered at fast adiabatic running of the resonance conditions [20] and shows that the relaxation processes do not essentially affect the character of reorientation of their magnetization vector.

In the 3-cm wave range there is the possibility of determining the electron relaxation time only for highly-doped conducting polymers within T_2 = 0.1 - 1.0 /us [20]. This interval is extended to the value T_2 = 0.1 μs to 1.0 ms at the 2-mm wave of ESR, since in this case T_2 can be estimated both from the A/B factor for deeply doped samples and from the dispersion contribution to the ESR signal for lightly doped ones.

In the case of PPP4 with fast running of the resonance conditions and weak non-adiabaticy in a wide range of $H_{1,}$ H_m changes occur (Fig. 6(c)), the time of the electron relaxation of the paramagnetic centres of the neutral sample being equal to T_2 - 0.1 to 1.0 ms.

Thus, the ESR data allow us to conclude that in PPP4 the paramagnetic centres are located on the polymer chain (defects), and they have axially symmetrical ESR spectra. In the deeply doped PPP1, charge transfer is performed by the spin carriers (s = 1/2), whereas in PPP5 after $AlCl_4^-$ substitution for BF_4^- charge transfer occurs by spinless carriers. This change in the conductivity mechanism at the transition from PPP1 to PPP5 can be explained in the framework of the polaron-bipolaron model.

In electrochemical substitution of chloraluminate anions for BF_4^-, the location of the latter may differ from that of the dopant in the initial PPP; the morphology of the BF_4^--redoped PPP may be close to that of the neutral film. A geometrical distortion from the aromatic to the planar quinoid form is known to occur [26]. A strictly ordered structure is expected to be formed in the melt in the process of electrosynthesis. However, this prevents coupling of the charge-spin carriers in the deeply doped polymer. The process of dopant removal results in compression of polymer volume. In this case there may arise hindrances to the electrochemical intrafibrillous doping by the BF_4^- anions, which may be located in the interfibrillous interface of the free volume in the polymer matrix. The change in the mechanism of the charge transfer in the PPP under study results from such a conformational transition.

Conclusions

The method of PPP production by anodic oxidation in a BuPyCl-$AlCl_3$ melt yields strictly ordered films with high conductivity without transverse cross linkages between the chains. The film instability caused by the extremely high sensitivity of chloraluminate anions to hydrolysis, as well as probable destruction of the polymer caused by the anion oxidation and polymer chlorination, may be partially overcome by electrochemical substitution by more stable BF_4^- anions, although this induces a decrease in conductivity and changes in the conductivity mechanisms.

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