

INVESTIGATION OF POLY-(*p*-PHENYLENE) OBTAINED IN ELECTROCHEMICAL OXIDATION OF BENZENE IN THE BuPyCl-AlCl₃ MELT AND IN ORGANIC SOLVENTS WITH OLEUM

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ABSTRACT

Poly-(*p*-phenylene) has been obtained in electrochemical oxidation of benzene in the BuPyCl-AlCl melt. The conductivity of the fresh film is 10 - 100 S/cm. Even when the film is stored in the dry inert atmosphere, its conductivity reduces. Poly-(*p*-phenylene) has been also obtained in electrooxidation of benzene with oleum or P O Electrochemical properties and IR and ESR spectra have been investigated. The SEM data on the film morphology have been also discussed.

INTRODUCTION

The films of poly(*p*-phenylene)(PPP) are object of great interest for physical and electrochemical investigations as well as possible practical applications. The properties of the films mainly depend on their structure and consequently on the method of obtainment. Recently there has appeared information [1] on the production of PPP films by the anodic oxidation of benzene in the BuPyCl-AlCl (BPA) melt. Meissner effect (levitation) was observed in the films in the magnetic field at 2.68 K. Later the same authors reported on the results of the study of PPP films ($\sigma = 10^4$ S/cm) obtained analogously in the cetylpyridinium chloride - AlCl₃ melt [2]. Simple and suitable ways of PPP production have been also proposed, in which drying additions (strong proton or Lewis acid) are used for electrochemical polymerization of benzene in organic solvents. Thus P.C.Lacaze et al introduced P₂O₅ into the organic solvents [3] and found CH₂Cl₂ and MeNO₂ to be the most suitable solvents. The

films of 10^{-1} S/cm conductivity and average degree polymerization (DP) of about 9 units (from IR spectra) were obtained in these systems.

In this paper properties of PPP obtained by benzene electrooxidation in a BPA melt and in organic solvents with oleum or P_2O_5 are presented.

RESULTS

The PPP films were obtained in benzene oxidation (10% vol.) on Pt electrodes (10 cm^2) under constant current ($1.5\text{-}2\text{ mA/cm}^2$). The electrode were washed with CH_2Cl_2 after electropolymerization and the films formed were peeled off from the electrode. When systems *D* and *G* (see the Table) the films would be peeled off only after washing with water or alcohol, though in the case of *G* the films tore into pieces under the internal tension. In the majority of cases, flexible films of $10\text{ }\mu\text{M}$ order thick form, whereas thick loose film form in the system *H*. The Table present the data on the conductivity and DP derived from the formula proposed in [4]. The films obtained in BPA melt have rather high conductivity, but even the film is stored in glove box, its conductivity is reduced by two to three times per day. In air or during the washing by MeCN or ether the films turns into neutral form with conductivity 10 S/cm . All these effects may be caused by the destruction of the highly doped PPP with polymer chlorination as it shown for PPP doped AsF_5 [5]. This process may be accelerated by moisture as in the case of PPP obtained in benzene electrooxidation with $CuCl_2$. [6].

The absorption band intensities at 760 and 690 cm^{-1} were used in the calculations which led to different values of DP for all cases. The films *A-C* of higher DP obtained in OH_2Cl_2 and in BPA melts do not have cross-linking, whereas there appears the band of 875 cm^{-1} that corresponding to 1,2,4-substitution in benzene in all other cases. Besides, in the spectra of the films *A-C* systems there is a 1600 cm^{-1} band, which is an overtone of the 800 cm^{-1} band and the evidence for the chain linearity [7], the spectra of other films contain the band 1590 cm^{-1} , which reveals their branching [4]. It should be noted that high DP in the films *A-C* compared with that for PPP obtained in SO_2 [4]. The higher DP in the films *B,C* in comparison with films *D,E* may be connected with possible higher solubility of PPP's oligomers in CH_2Cl_2 . The another confirmation of high DP and linear structure is that film *B* do not soluble in *N*-methylpyrrolidone as PPP with cross-linking [8].

Table

System	Conductivity, S/cm	DP on 760 cm ⁻¹	DP on 690 cm ⁻¹
A BPA	10 - 100	13 - 14	29 - 30
B CH ₂ Cl ₂ /BF ₄ /oleum	10 ⁻²	14 - 18	35 - 70
C CH ₂ Cl ₂ /BF ₄ /P ₂ O ₅	10 ⁻¹ - 10 ⁻²	13 - 15	25 - 60
D MeNO ₂ /BF ₄ /P ₂ O ₅	10 ⁻²	6	10
E MeNO ₂ /BF ₄ /oleum	10 ⁻²	6 - 7	13 - 15
F MeNO ₂ /F(HF) _n /oleum	10 ⁻²	5	9
G MeNO ₂ /F(HF) _n /P ₂ O ₅	10 ⁻³	5	7
H CH ₂ Cl ₂ /F(HF) _n /P ₂ O ₅	10 ⁻²	-	-

The SEM data of the film surface show it to be dependent on the growth conditions and as a rule represented by globular formations. The films *D* and *G* are smooth, though surface of film *G* is covered with wrinkles. There are pronounced globules of small height (2-4 μm) in the films *B* and *E*. Strongly pronounced globular morphology is obtained in the films *A* and *C*. These films are likely to be porous. Obviously the high porosity is characteristic of film *H*, which consist of cone-like formations of an order 100 μm in size.

In the cyclic voltammograms of the film *A* two oxidation peak (3.85 V and 4.3 V vs. Li/Li⁺) are observed. In the work [6] analogous behavior was considered as two-step oxidation. In our case the potential and peak height of the second peak depend on the nature of the anion in supporting electrolyte, so we suppose that second oxidation step includes anion oxidation with the formation of the radical, which oxidizes PPP.

The PPP *B-H* ESR spectra at 3 cm wave band are singlets with $\Delta H = 1.6 - 2.4$ G (for undoped sample $\Delta H = 3.5$ G). However the PPP *A* ESR spectrum at this wave band is Disonian singlet with ΔH about 1 G, $g = 2,00290$ and asymmetric factor about 2.5. Electron relaxation time and ac conductivity were determined from this spectrum. They consisted of $4 \cdot 10^{-7}$ and $\sim 10^3$ S/cm respectively. The conductivity value remains practically constant when the film is stored in an evacuated tube at least for 3 months.

The ESR spectrum of neutral (undoped) PPP A film is the axially symmetrical one with $\Delta H = 4$ G, $g_{\perp} = 2.00337$, $g_{\parallel} = 2.00200$. Spin carriers concentration decreased about 50 times as compared with doped film. Electron relaxation time being equal to $(1 - 10) \cdot 10^{-3}$ s was determined from 2 mm wave band ESR spectrum [7]. The excitation energy of electron transition corresponds to about 7 eV, because difference between g_{\perp} and g_e is $1.0 \cdot 10^{-3}$. This energy is close to the first ionization potential of polycyclic aromatic hydrocarbons [9]. Consequently paramagnetic centres in neutral PPP A film may be localized at cross-linking through polycyclic hydrocarbons. This structure was shown [3] to exist in PPP. Apparently in our samples the concentration of such defects is insufficient for registration by IR method.

From the analysis of line shape at 3 cm and 2 mm wave band ESR the spin packets exchange velocity in neutral film $4 \cdot 10^{-7}$ s was determined. This value increases up to $1.8 \cdot 10^8$ s for doped film because of mobility of paramagnetic centres. The calculated half-width of PPP will be 0.04 G in zero magnetic field approach. Isotropic g factor of neutral sample is equal to g factor of doped one. It shows that the g tensors components of paramagnetic centers in doped sample are averaged due to their mobility. These data confirm supposition [7] about the existence of mobile charge carriers in doped PPP A film.

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