

COLLOID CHEMISTRY
AND ELECTROCHEMISTRY

Electrochemistry Behavior of Benzene, Diphenyl and *p*-Terphenyl
in Room-Temperature Ionic Liquid Butyl Pyridinium Chloride–AlCl₃

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Abstract—The cyclic voltammetry method was used for studying the electrochemical oxidation of benzene, diphenyl and *p*-terphenyl in ionic liquid butyl pyridinium chloride–AlCl₃ (1 : 1.5) at 30°C. Comparative analysis of peaks obtained for each initial monomer was performed. The assumptions on the differences in the mechanisms of electrochemical synthesis of polyphenylenes in the ionic liquid from benzene, diphenyl and *p*-terphenyl were made.

Keywords: electrochemical oxidation, mechanism, cyclic voltammetry method, ionic liquid

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Polyphenylenes can be electrochemically synthesized not only from benzene, but also from diphenyl and *p*-terphenyl [1]. The use of ionic liquids as electrolytes [2–5] makes it possible to synthesize conductive polymers that cannot be synthesized in usual electrolytes [3–14]. The absence of heteroatoms or functional groups in substrate molecules makes it possible to suppress side reactions, the number of possible products will be limited, and variation of the properties of polyphenylenes will depend, for the most part, on the length of the polymer chain, rather than on the number and quality of different branches [15]. The ionic liquids derived from pyridine and aluminum chloride are of a certain interest as electrolytes in organic electrosynthesis [2]. Synthesis of polyphenylenes from benzene at a controlled current has been carried out, and polymeric films of a product have been prepared directly on a working electrode [16]. It is considered that AlCl₃-based ionic liquids, due to chlorine release which significantly reduces the quality of polymer films, have not been extensively investigated [17]. This opinion was due to the choice of conditions for the synthesis of polyphenylenes at the controlled current, which, being not optimal, could lead to uncontrolled chlorine release [16, 18]. In our opinion, carrying out synthesis at the controlled potential will solve this problem [19]. This requires cyclic voltammetry measurements.

EXPERIMENTAL

All voltammograms were obtained on a platinum electrode (a disk with the diameter of 1 mm) at a potential sweep rate of 50 mV/s. The platinum disk sealed in a glass holder was applied as a working electrode. The 3-electrode cell with the working volume of 3 mL was used. Chambers for working and counter electrodes were separated by a glass filter membrane. Aluminum wire (99.99% purity) sealed in a glass holder and located in the studied electrolyte (in a separate chamber) was used as a reference electrode. All potentials are given vs an aluminum reference electrode [16, 20]. Platinum wire sealed in a glass holder served as a counter electrode. The test solution was prepared upon blowing the system with argon. Before measurements, the electrolyte was purged with argon for 20 min, after that the electrodes were placed in the cell, and the cell was closed hermetically. All measurements were carried out at 30°C.

The ionic liquid of the following structure was investigated: [BuPyCl]Al₂Cl₆, where Py is pyridinium, Bu is butyl. This ionic liquid was synthesized by the reaction of BuPyCl (0.2 mol) with AlCl₃ (0.3 mol), both being dissolved in CH₂Cl₂ (100 mL) with further removal of the solvent using a rotor evaporator.

RESULTS AND DISCUSSION

Figure 1 shows a cyclic voltammogram in the case of diphenyl oxidative polycondensation. The first cycle starts of the scan from the stationary potential at

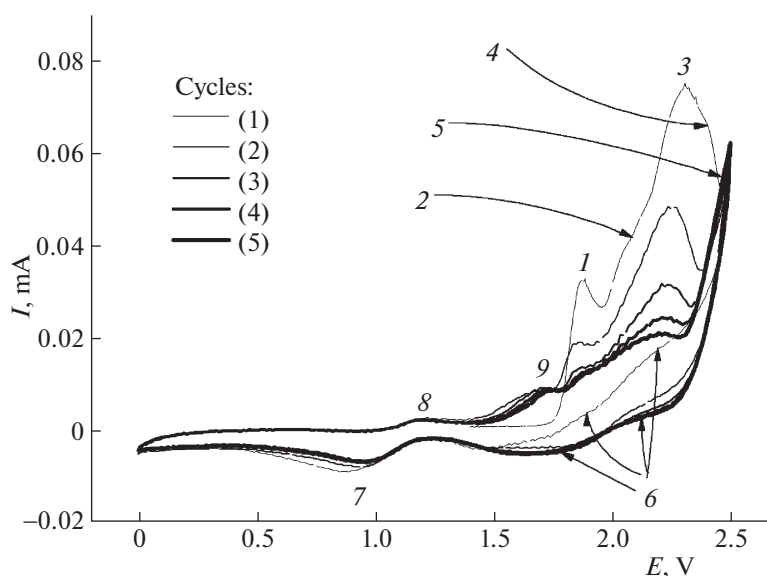


Fig. 1. Cyclic voltammograms of diphenyl ($C = 1.6 \times 10^{-2}$ M) on the Pt-electrode (disk with diameter 1 mm) in BPC : AlCl_3 (1 : 1.5) vs. $E_0(\text{Al}/\text{Al}^{3+})$ at the scan rate 50 mV/s ($t = 30^\circ\text{C}$).

1.4 V. The peak 1 corresponded to the oxidation of the diphenyl molecule to the cation-radical (reaction a). After the chemical stage of addition of the neutral molecule to the cation-radical (reaction b), there is a sequential separation of electrons from the intermediate as follows: peaks 2, 3 and 4 (reaction c). When the scanning rate is reduced, the peaks 2, 3, 4 are well resolved. The peak 5 indicates the anode boundary of the electrochemical stability window of the ionic liquid itself (approximately 2.4–2.5 V). The set of peaks 6 is assigned to partial cathodic reduction of cation-radicals and intermediates and, has no significant effect on the progress of the main processes. On the contrary, the peak system 7 and 9 shows the appearance of new polymer products with each subsequent cycle. The decrease in the values of the peaks 1–4 is associated with a decrease in the “effective” surface of the electrode on which oxidation takes place. The weak visible peak 8 is likely attributed to the oxidation of impurities contained in the ionic liquid and the products of side reactions of impurities with intermediates. The small value of peak 8 indicates a very weak influence of impurities on the progress of the main reaction.

Figure 2 shows a cyclic voltammogram of *p*-terphenyl. Comparison of Figs. 1 and 2 shows a cathodic shift of the peaks almost by 0.2 V, but the relative location and number of peaks do not change. The system corresponding to peaks 2, 3, 4 (reaction c) is somewhat more complicated than for diphenyl. At a lower scan rate (10 mV/s), the system is resolved into more than three peaks. It is likely that more electrons are transferred sequentially than in the case of diphenyl. This is presumably due to the increased “capacity” (additional phenyl ring per substrate molecule) and there-

fore the ability to delocalize the additional charge on the intermediate. Such stabilization can lead to two opposite results. In the first case, significant polymer chain growth can be expected due to the relatively slow addition of neutral molecules to the cation-radical because the probability of recombination of such resistant radicals is low. In the second case, the stable intermediate may be so low-active that the chain growth will end at the dimerization stage, or, at the maximum, trimerization.

Figure 3 shows a cyclic voltammogram for benzene. The problem with the control of the initial concentration of benzene in the ionic liquid caused the use of a saturated benzene solution in the experiment. Benzene was added in excess, which formed a layer in the working chamber of the cell. This caused the currents corresponding to reaction a to increase, making it impossible to resolve 1 as a single peak or wave. There are no 2, 3, 4 and 6 peaks. Peaks 7 and 9 continue to grow with each cycle, indicating a significant growth of the film or precipitate of the conductive polymer. Under these conditions, the product is already a good current conductor. This is evidenced by the increase of the peak 1 with each cycle, i.e. the “effective” electrode surface increases with each cycle.

Based on cyclic voltammograms, the synthesis potentials of polyphenylenes from different substrates were selected. The product polymerization degree was determined by FTIR spectroscopy [1, 16, 19]. At the same synthesis potentials, the degree of polymerization benzene to produce polyphenylene exceeds 60, and for diphenyl and terphenyl it is not more than 8 and 6, respectively. The production of polymer products with a higher molecular weight from biphenyl and terphenyl at potentials above 2.5 V is not possible due

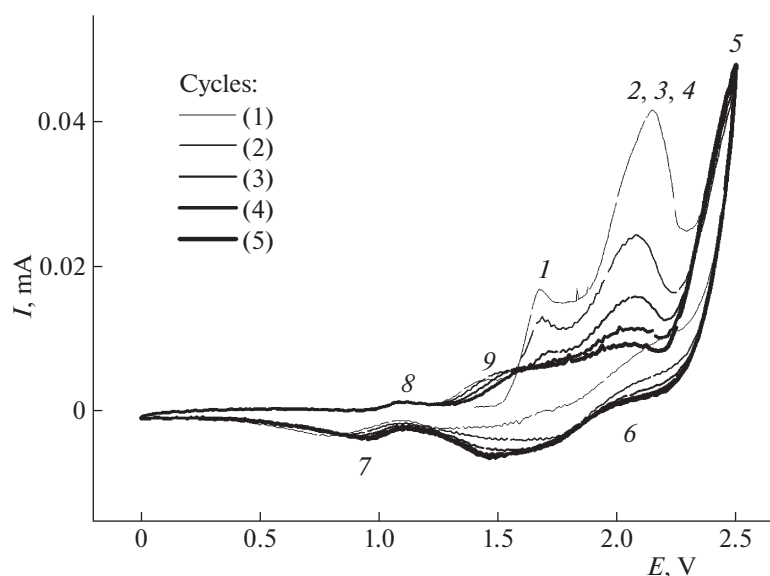


Fig. 2. Cyclic voltammograms of *p*-terphenyl ($C = 1.1 \times 10^{-2}$ M) on Pt-electrode (disk with 1 mm diameter) in BPC : AlCl₃ (1 : 1.5) vs. $E_0(\text{Al}/\text{Al}^{3+})$ at the scan rate 50 mV/s ($t = 30^\circ\text{C}$).

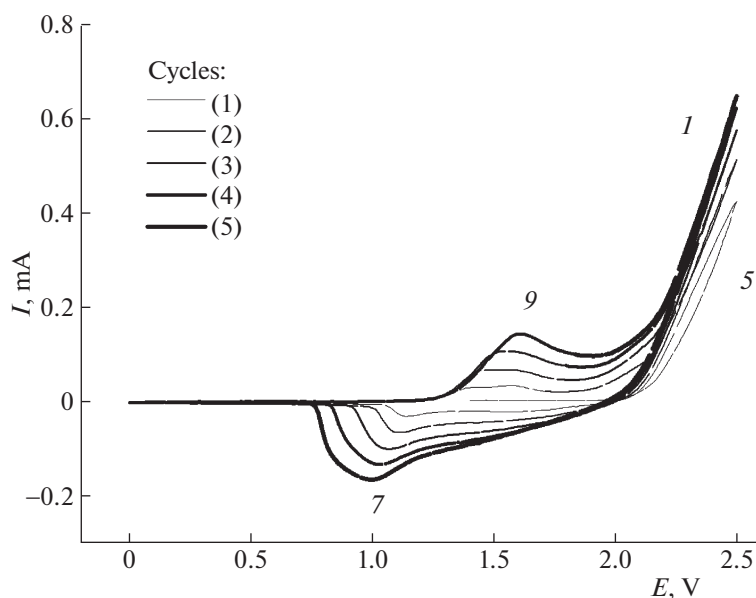


Fig. 3. Cyclic voltammograms of benzene (saturated solution) on Pt-electrode (disk with 1 mm diameter) in BPC : AlCl₃ (1 : 1.5) vs. $E_0(\text{Al}/\text{Al}^{3+})$ at the scan rate 50 mV/s ($t = 30^\circ\text{C}$).

to the anode boundary of the electrochemical stability window of the selected ionic liquid.

CONCLUSIONS

Thus, the degree of polymerization data supports the assumptions made. Formation of low-molecular weight intermediates (dimers-oligomers) is not a necessary stage (as in the case of benzene) and even unwanted for the formation of polymers with a high number of units (as for diphenyl and terphenyl).

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