INDIRECT ELECTROCHEMICAL REDUCTIVE DEGRADATION OF POLYCARBONATES

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We have studied the kinetic characteristics of degradation of polycarbonates with different structures in dimethylformamide when treated with the products of electrochemical reduction of a \((\text{C}_4\text{H}_8)_4\text{NCIO}_4\) solution in dimethylformamide (supporting solution). We have shown that this process (which can be described as indirect electrochemical reductive degradation) occurs according to a nucleophilic catalytic mechanism.

Earlier [1] we established the feasibility of electrochemical reduction of polycarbonate based on bisphenol A followed by its subsequent degradation to the starting bisphenol in dimethylformamide (DMF) solution in the presence of \(\text{N}(\text{C}_4\text{H}_8)\text{NCIO}_4\) for high cathodic potentials (< -2.5 V relative to the saturated calomel electrode). In this case, we showed that under such conditions degradation of polycarbonate occurs not only as a result of direct electron transfer from the cathode to the electron-acceptor carbonate groups, but also via an indirect route under the influence of the electrochemical reduction products (negatively charged and neutral) of the supporting solution (the supporting solution is capable of electrochemical reduction at the same cathode potentials as polycarbonate) [2]. This type of degradation was described as indirect electrochemical reductive degradation of polymers [1, 2] and probably can be used in reactions of electrochemical [3] and subsequent chemical functionalization of macromolecules.

Our goal was to investigate the kinetic characteristics of indirect electrochemical reductive degradation of polycarbonates and to evaluate the effect of the structure of the elementary unit on the kinetics of this process.

As the primary objects for the investigation, we used polycarbonate based on bisphenol A (polycarbonate) with molecular mass \(M = 36000\) and diphenylcarbonate (DPC) (Aldrich), modeling the elementary unit of polycarbonates. We also studied indirect electrochemical reductive degradation of polycarbonate based on 3,5,3',5'-tetramethyl-substituted bisphenol A (PCtm) with \(M = 35000\) and the copolymer of polycarbonates based on bisphenol A (70%) and 3,3,5-trimethylcyclohexane (30%) (PCcp) (Bayer).

Before use, the dimethylformamide was purified according to the procedure in [4]. As the supporting electrolyte, we used \((\text{C}_4\text{H}_8)_4\text{NCIO}_4\) synthesized as in [5].

To investigate indirect electrochemical reductive degradation of polycarbonates, we carried out preliminary reduction of the catholyte: 0.05 M \((\text{C}_4\text{H}_8)_4\text{NCIO}_4\) in DMF, under galvanostatic electrolysis conditions at the platinum cathode for current density \(i = 6 \text{ mA/cm}^2\), which corresponded to a potential \(E = -2.6 \text{ to } -2.7 \text{ V}\) relative to the saturated calomel electrode in the presence of molecular sieves and for continuous purging with dry argon. When electrolysis was complete, the reduced catholyte was added to solutions of polycarbonates in DMF (in spectrophotometric cuvettes, \(l = 0.1 \text{ cm}\)).

We monitored the indirect electrochemical reductive degradation of the objects of investigation by spectrophotometry (Specord M-40) from the growth in the intensity of the absorption band of the degradation products of the polycarbonates (the corresponding bisphenols, at a wavelength \(\lambda = 289 \text{ nm}\) and from the increase in the intensity of the absorption band of the degradation product of diphenylcarbonate (phenol, at \(\lambda = 284\) 

Fig. 1. Electronic absorption spectra of solutions in DMF: 1) polycarbonate; 2) diphenylcarbonate; 3) PCtm (C = 2·10⁻³ M/L). Products of indirect electrochemical reductive degradation: polycarbonate (4); diphenylcarbonate (5); PCtm (6); 4-0 bisphenol A; 5-0 phenol; 6-0 tetramethyl-substituted bisphenol A (C = 2·10⁻³ M/L).

nm) (Fig. 1). The reactions were carried out until conversion of the carbonates was complete.

Before the experiments, we established that indirect electrochemical reductive degradation of polycarbonates occurs at a very high rate. So to effectively monitor the reaction, as in [6] about a 100-fold excess concentration of the substrates was used compared with the concentrations of the active nucleophilic species Nu⁻.

In the literature, we find information indicating that during electrochemical reduction of solutions of tetraalkylammonium salts in DMF, nucleophiles also appear: N(C₄H₉)₄, HN(CH₃)₂, “N(CH₃)₂, (CH₃)₂NCHO” etc. [2]. The broad spectrum of the products of electrochemical conversions of solutions of N(C₄H₉)₄ClO₄ in DMF and their different activities in reactions of indirect electrochemical reductive degradation are a very serious impediment to kinetic study of this process. So we were forced to simplify the scheme for indirect electrochemical reductive degradation, eliminating participation of such products as tributylamine and dimethylamine. Thus, by means of control experiments we showed that tributylamine does not react with polycarbonates. The dimethylamine, which can cause degradation of polycarbonates [9], was completely removed from the reduced catholyte by continuous purging with argon. This allowed us to hypothesize participation of only one type of nucleophilic product in indirect electrochemical reductive degradation of polycarbonates under the studied conditions: the negatively charged species Nu⁻. Possibly “N(CH₃)₂ anions stabilized by [N(C₄H₉)₄]⁺ cations might claim the role of the latter, but prolonged existence of such species, as for the radical anion (CH₃)₂NCHO⁻, seems quite unlikely.

We are currently attempting to establish the nature of the negatively charged nucleophiles causing rapid degradation of polycarbonates and will present our results in a separate paper.

Since consumption of electricity in reduction of solutions of tetraalkylammonium salts in DMF for a series of parallel reactions [8] does not allow us to use Faraday's law to calculate the number of active charged particles, we determined this using selective reaction of the charged particles with a trap: o-nitrochlorobenzene. Adding o-nitrochlorobenzene to freshly reduced supporting electrolyte is accompanied by yellow coloration of