polymer communication

New route for producing acrylic acid copolymers, based on electrochemical carboxylation of poly(vinyl halide)s and polybutadiene

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The electrochemically activated direct introduction of CO_2 into poly(vinyl chloride), poly(vinyl bromide) and polybutadiene to form the corresponding acrylic acid copolymers is shown. It is demonstrated that the maximum extent of carboxylation is attained in the case of poly(vinyl chloride), when conducting controlled-potential electrolysis in dimethylformamide using a platinum cathode and sacrificial anode in an undivided cell. Possible pathways for the explored reactions are suggested.

(Keywords: acrylic acid copolymers; poly(vinyl halide)s; polybutadiene)

Introduction

Acrylic acid copolymers are routinely used in diverse areas. Traditional procedures to obtain such materials rely primarily upon copolymerization of acrylic acid with various monomers. At the same time, certain alkyl halides and olefins are known[1,2] to be capable of reacting with carbon dioxide under electrochemical activation to form carboxylic acids. Allowing for the similarity principle regarding the reactivity of molecules and macromolecules containing the same functional groups, we have explored for the first time the possibility of direct cathodic introduction of carboxy groups into poly(vinyl chloride) (PVC), poly(vinyl bromide) (PVB) and polybutadiene (PB), in order to develop new processes for producing corresponding copolymers of acrylic acid and its derivatives. This modification of the available polymer would avoid the need for separate synthesis of monomers followed by their copolymerization, frequently run under severe conditions using initiators, emulsifiers and other components.

Experimental

Voltammetric investigations were carried out on a PI-50-1 potentiostat. Preparative electrolysis was conducted in gas-tight cells with CO_2 being continuously passed through the solution. When the electrolysis was accomplished, the resulting polymeric product was isolated either by distilling off the solvent under low pressure or by precipitating with water from the working solution and subsequently washing with water. To transform the polymer into its acidic form it was treated with hydrochloric acid at 25°C, washed with water and dried. PVC with a molecular weight of 100 600 was used. PVB with a molecular weight of 82 300 was synthesized by vinyl bromide block polymerization[3]. The PVB was cleaned through reprecipitation (hexane/acetone). Dimethylformamide (DMFA) was vacuum distilled, held over 4 Å sieves and redistilled prior to use. Tetrahydrofuran (THF) was cleaned as indicated in ref. 4. Tetraalkylammonium salts were obtained and cleaned as described in ref. 5.

Results and discussion

The PVC and CO_2 exhibited similar electrochemical activity on a platinum electrode in a DMFA + 0.1 M Et_4NBr solution and could be irreversibly reduced in the -2.3 to -2.7 V potential region vs. Ag/AgCl (broad waves for PVC with $E_p = -2.65$ V, and for CO_2 $E_p = -2.34$ V). In view of this fact, preparative controlled-potential electrocarboxylation of PVC was effected by joint cathodic reduction of the polymer and CO_2 ($E = -2.4$ V; undivided cell, Pt cathode, Zn anode; DMFA + 0.1 M Et_4NBr; polymer concentration per repeat unit molecular weight was 0.1 M). In addition to PVC absorption bands, the i.r. spectrum of the isolated product featured an intensive band at $1710\,cm^{-1}$ plus a broad band in the region of $3500\,cm^{-1}$, which are similar to those attributable to carboxy group C=O and O–H bond vibrations in the i.r. spectrum of poly(acrylic acid). Treatment of the isolated polymer with alkali led to the total disappearance of the OH group vibration band ($3500\,cm^{-1}$) in the spectrum, while the carbonyl vibration band shifted $40\,cm^{-1}$ towards lower wavenumbers. Polymer film retreatment with acid fully restored the initial spectrum. Consequently, as evidenced by i.r. spectroscopy data, in the course of joint PVC–CO_2 electrolysis, electrochemically activated introduction of CO_2 into the polymer took place, to form acrylate fragments.

The carboxy group content of the resulting polymer was evaluated by potentiometric titration with 0.1 M KOH solution of a polymer sample dissolved in THF, and by weight analysis (as $KHSO_4$)[6]. The current efficiency (CE: ratio of the amount of electricity theoretically needed for introduction of carboxy group number found in the polymer to that passed through the polymer solution) of PVC carboxylation under the above condition was 10.1% and the yield (Y: ratio of the number of carboxylated repeat units to the total number

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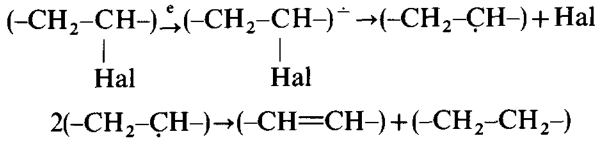
of units in initial polymer) was 8.2%. Comparable values (CE = 8.1%; Y = 5.7%) are also found in the case of controlled-current PVC carboxylation with carbon dioxide (current density 5 mA cm^{-2}; Pt cathode; Zn anode; DMFA + 0.1 M Bu_4NBr; $C_{pvc} = 0.1$ M). Increasing polymer concentration to 0.2 M leads to a substantial decline in the carboxylated product yield (Y = 2–3%). This may be relevant to the increase in solution viscosity and passivation of the electrodes. A similar effect is produced by the use of a platinum cathode and anode in a cell divided by a glass filter. In this case carboxylation is accompanied by the partial dehalogenation of the polymer and the formation of C=C bonds. This is evidenced by the appearance of the absorption band at 1650 cm^{-1} in the i.r. spectrum and by elemental analysis data. According to the latter, decreasing chlorine content in the final product perceptibly exceeds its carboxy group content.

Along with PVC, we studied the possibility of electrochemical carboxylation of PVB with carbon dioxide. The controlled-potential ($E = -2.3$ V) process was run in an undivided cell (Pt cathode, Zn anode, DMFA + 0.1 M Bu_4NBr; $C_{pvb} = 0.1$ M); the joint electrochemical activation of PVB and CO_2 was found, just as in the case of PVC, to lead to carboxylated polymer: CE = 7.2%; Y = 5.2%.

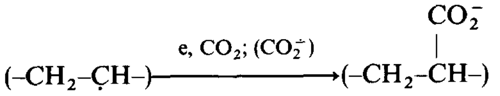
Thus, as evidenced by the results of this investigation, electrochemical activation promotes the direct introduction of CO_2 into poly(vinyl halide)s to form acrylic acid–vinyl halide copolymers. At present it is rather difficult to draw unambiguous conclusions about the fine details of the mechanism of the processes found. We can only suggest several possible pathways for their progress. When cathodically activated in DMFA, poly(vinyl halide)s were shown[7] to be capable of undergoing dehalogenation to form double C=C bonds in the polymer, which can be visualized by the following scheme:



$$(\text{-CH}_2\text{-}\underset{\text{Hal}}{\underset{|}{\text{CH}}}\text{-}) \xrightarrow{e} (\text{-CH}_2\text{-}\underset{\text{Hal}}{\underset{|}{\text{CH}}}\text{-})^{\cdot -} \rightarrow (\text{-CH}_2\text{-}\underset{\cdot}{\text{C}}\text{H-}) + \text{Hal}^-$$

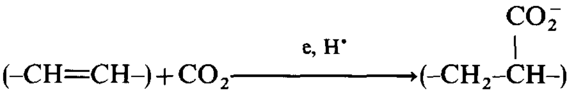
$$2(\text{-CH}_2\text{-}\underset{\cdot}{\text{C}}\text{H-}) \rightarrow (\text{-CH=CH-}) + (\text{-CH}_2\text{-CH}_2\text{-}) \quad (1)$$

Under the conditions of electrochemical carboxylation, when simultaneous reduction of poly(vinyl halide)s and CO_2 is realized, the active intermediates formed (radicals, anion radicals of polymer fragments, etc.) interact either with CO_2 or with its anion radical $CO_2^{\cdot -}$, which may ultimately lead to carboxylation of the polymer:



$$(\text{-CH}_2\text{-}\underset{\cdot}{\text{C}}\text{H-}) \xrightarrow{e,\ CO_2;\ (CO_2^{\cdot -})} (\text{-CH}_2\text{-}\overset{CO_2^-}{\overset{|}{\text{CH}}}\text{-}) \quad (2)$$

Since, as was shown[7], double C=C bonds are likely to be formed in the course of cathodic activation of poly(vinyl halide)s, one cannot rule out the possibility of electrochemical carboxylation involving such fragments:



$$(\text{-CH=CH-}) + CO_2 \xrightarrow{e,\ H^{\cdot}} (\text{-CH}_2\text{-}\overset{CO_2^-}{\overset{|}{\text{CH}}}\text{-}) \quad (3)$$

To verify this supposition we explored the possibility of electrochemical carboxylation of PB using CO_2. The preparative electrolysis of PB in THF in the presence of CO_2 was carried out in an undivided cell (Pt cathode; Zn anode; 0.1 M Bu_4NBr) at a cathode potential of −2.4 V. In the i.r. spectrum of the isolated polymeric product there are absorption bands of C=O (1710 cm^{-1}) and O–H (3500 cm^{-1}) stretches, which points to the presence of acrylate fragments in the polymer; the extent of carboxylation, however, comes to Y = 2.5%. This gives reason to believe that although electrochemical poly(vinyl halide) carboxylation processes involving double bonds may well be in progress, it is less preferable compared to that proceeding according to reaction (2).

Conclusions

In this paper we have demonstrated the possibility of electrochemically activated direct carboxylation of halogen-containing (PVC, PVB) and unsaturated (PB) polymers using carbon dioxide, which makes it possible to produce the corresponding acrylic acid copolymers in one step under mild conditions. Possible routes for the cathodic carboxylation of poly(vinyl halide)s have been proposed: halogen atom substitution for the cathodic carboxylation of poly(vinyl halide)s, or carbon dioxide addition to the double bond of the polymer in the course of their joint reduction. To determine the contribution of each route to the progress of such processes calls for further, more detailed investigation.

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