ELECTROCHEMICAL DEHYDROCHLORINATION
INITIATION FOR VINYLIDENE CHLORIDE –
VINYL CHLORIDE COPOLYMERS

Yu. V. Kontsur, G. S. Shapoval, and A. A. Pud

Direct electrochemical initiation of dehydrochlorination is possible for polyvinylidine chloride VDC and copolymers of VDC with vinyl chloride VC. The ratio of the VDC and VC links in the initial polymer affects the rate of the dehydrochlorination and the structure of the products.

Chlorine-bearing carbon-chain polymers such as polyvinyl chloride PVC and polyvinylidine chloride PVDC are destroyed by various chemical agents and high-energy processes as described in numerous papers [1, 2].

As a rule, such processes occur at appreciable rates above 70°C. We have found that PVC can undergo electrochemical destruction at room temperature [3, 4]. When a solution of this polymer in dimethyl formamide DMFA is electrolyzed in the presence of a tetraalkylammonium salt TAA at low potentials, HCl is split off and conjugated multiple bonds are formed in the main chain, as well as cross links. A similar process occurs when PVC is treated with a freshly reduced solution of a TAA salt in DMFA immediately after the electrochemical reduction [3, 4].

On the other hand, it is not known whether other chlorine-bearing carbon chain polymers having high chlorine contents in the elementary links can participate in such processes. The present paper demonstrates electrochemical destruction for PVDC and copolymers of VDC when a previously reduced solution of tetralkylammonium perchlorate in DMFA is used. We also examine how the structure of an elementary link in the polymer affects the rate of the reduction and the structure of the products.

We used PVDC containing 67% chlorine. SP-1 block copolymer having a ratio for VC and VDC links of 49.2:50.8% and a chlorine content of 61%, and SP-2 block copolymer having a 19.5:80.5% ratio of VC and VDC links and a chlorine content of 66%. For comparison, we used PVC under the same conditions with a chlorine content of 54%.

The DMFA and tetrabutylammonium perchlorate (TBAP) were purified and dried by the [5, 6] methods.

A solution of 0.05 M TBAP in DMFA was electrolyzed under galvanostatic conditions at a current density of 2 mA/cm², which corresponded to the range in potential E from -1.8 to -2.5 V relative to a saturated calomel reference electrode in a two-chamber cell having a volume of 65 ml, where the cathode and anode spaces were separated by a Schott No. 3 filter in an argon atmosphere. The working and auxiliary electrodes were platinum plates having working areas of 6.5 cm² each. The reduced catholyte immediately after electrolysis was treated with a powder of insoluble PVDC and with 0.25% solutions of PVC, SP-1, and SP-2 in DMFA.

The extent of reaction was judged from the amounts of conjugated multiple bonds formed as indicated by spectrophotometry. We used the relative integral intensity I characteristic of polyene structures in the range 280-600 nm in solutions of these polymers after reaction with the catholyte.

We used Spector M-40 and Specord M-80 instruments respectively for spectrophotometry and IR spectroscopy of the altered polymers.

We derived an approximate length distribution for the polyene sequences in the products by the [1] method from

\[ P_n = \frac{D_n}{\varepsilon_n C_n} \]
Fig. 1. a) UV spectra of polymer solutions after catholyte treatment: 1) SP-1; 2) SP-2; 3) PVC; 4) PVDC; b) relative integral intensities in UV spectra (280-600 nm) from dehydrochlorination products in relation to electrolysis time: 1) SP-1; 2) SP-2; 3) PVC.

in which \( P_n \) is the probability of formation of a polynene part containing \( n \) conjugated double bonds, \( D_n \) is the optical density in the spectrum for the polynene part, \( e_n \) is the optical density in the spectrum for the polynene part, \( e_n \) the extinction coefficient for the long-wave absorption maximum of the polynene, and \( C \) the polymer concentration. In accordance with [1], we took \( P_3 \) for the trimer as unit and plotted \( P_n \) against \( n \).

When the reduced catholyte interacts with PVDC powder, the surface of the latter becomes dark brown, while the solution acquires a gray-brown tinge. The IR spectra of the treated PVDC show bands in the region 1600-1700 cm\(^{-1}\) characteristic of conjugated C=C bonds and reduced intensities for the vibration bands of the C-Cl bonds at 600-700 cm\(^{-1}\) [7]. The UV spectrum of the solution showed weak absorption at 280-500 nm characteristic of polynene structures [8], whose intensity hardly altered as the contact time of the PVDC with the catholyte increased (Fig. 1a). It seems that the reduced catholyte localizes the dehydrochlorination in the surface of the PVDC. The products are formed in small amounts and dissolve slightly in the DMFA.

Adding freshly reduced catholyte to the SP-1 and SP-2 solutions led to their instantly becoming brown; the UV spectra showed a broad absorption at 280-600 nm characteristic of polynene structures (Fig. 1a). The IR spectra of polymers isolated from the solutions show considerable reduction or practically complete loss of the C-Cl stretching bands in the 600-700 cm\(^{-1}\) region and the production of bands in the 1600-1700 cm\(^{-1}\) region (conjugated C=C bonds), i.e., the picture is analogous to that when such a solution interacts with PVC [3] and suggests that the DMFA reduction products also initiate the dehydrochlorination of VC and VDC copolymers, which is accompanied by the formation of polynene structures:

\[
(\text{CH}_3)_2\text{NCHO} \rightarrow \text{Nu}^-, \quad \text{Nu}^- + \text{H}^+. \]

The PVC and copolymer spectrometry data indicate that \( I \) is proportional to the amount of electricity passed during electrolysis, and thus to the concentration of active species that initiate the destruction (Fig. 1b). This is most extensive for PVC. When a polymer contains VC links, the extent of reaction increases, and the latter is largest for SP-1, in which the numbers of VC and VDC links are similar. However, I indicates that a higher content of VDC links (SP-2) reduces the number of multiple bonds in the products.

On the other hand, the shapes of the UV spectra indicate that the dehydrochlorination products from these polymers differ in the relation between the numbers of long and short polynene sequences.

The approximate calculations on the polynene length distribution show that \( P_n \) for all the polymers decreases monotonically as \( n \) increases, but the proportion of longer polynene sequences increases as the number of VDC links in the initial polymer decreases and correspondingly as the chlorine content decreases (Fig. 2). An analogous effect has been observed in [9]: dehydrochlorination by a DMFA-LiCl complex at an elevated temperature was applied to VDC polymers containing up to