INVESTIGATION OF THE MECHANISM OF THE THERMAL
CARBONIZATION OF CHLORINE-CONTAINING CARBON-CHAIN
POLYMERS

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It has been shown earlier [1] that the activation energy of the initial stages of the dehydrochlorination reaction
is substantially below the energy of cleavage of the C–Cl bond and depends both on the chlorine content in the
polymer and on its distribution in the macromolecule (table).

These results confirm the existing representations of the formation of more reactive hydrogen or halogen atoms,
situated in the α-position to the C = C bonds, at the initial stages of the process [2].

In this investigation we studied the structural transformations of the indicated polymers on the same samples
(see table), within a broad range of temperatures of heat treatment, by the methods of x-ray diffraction study and
IR spectroscopy, and also studied the dependence of the rate of evolution of volatile substances and that of the varia-
tion of the elementary composition on the temperature of heat treatment.

EXPERIMENTAL

Fig. 1 presents the differential curves of the evolution of volatile substances for polyvinyl chloride (PVC),
chlorinated polyvinyl chloride (CPVC), polyvinylidene chloride (PVDC), and the copolymer of vinyl chloride and
vinylidene chloride (CP). The measurements of the weight loss were conducted on a setup with a quartz spring
balance in a stream of nitrogen on 0.15-g samples, raising the temperature at a rate of 2°/min. Two distinct maxi-
ma at 270° (evolution of HCl) and 450° (evolution of hydrogen, methane, etc.) are observed on the curve for PVC,
which indicates two steps of carbonization. The presence of the second maximum on the differential curves of the
weight loss within this temperature interval is probably due to the destruction of the side chains and growth of the
aromatic condensed structures. For samples of CPVC, CP, and PVDC, the secondary evolution of volatile substances
is not expressed as a distinct maximum, but extends over a broad region of temperatures of treatment. This corres-
donds to a different character of the liberation of volatile substances in the second stage of carbonization, indicating
peculiarities of the structural transformations in the carbonaceous products.

The different course of carbonization of the polymers studied is also illustrated by the different character of
the dependence of the ratio of the carbon content to hydrogen (C/H) in the carbonization products on the temperature
of treatment (Fig. 2). An x-ray diffraction study of a series of products of heat treatment in a broad range of tem-
peratures was conducted to characterize the structural transformations of carbon during the process of carbonization
of the polymers. Fig. 3 presents photomicrograms of the x-ray diffraction patterns of the carbonization products,
under conditions of rapid heating of the initial polymer and exposure at a set temperature for 120 min.

All the polymers studied, treated at 800°, give x-ray diffraction patterns with pronounced interference maxima,
characterizing the formation of flat layers of condensed aromatic carbon (maximum 100) and packets of carbon lay-
ers (maximum 002). A relatively great sharpness of the maximum 002 may be noted for PVC, indicating compara-
tively high order of the carbon layers in the packets. The formation of condensed aromatic layers is already notice-
able for PVC at 250°, while for PVDC it is noted on the x-ray diffraction patterns only at temperatures of treatment.
Polymer | Predominant arrangement of Cl in the macromolecule | Elementary composition, % | E, kcal/mole
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Polyvinyl chloride (PVC) | CH₂–CHCl–CH₂CHCl (1,3) | 38,40 5,50 56,80 | 33,5
Chlorinated polyvinyl chloride (CPVC) | CH₂–CHCl–CHCl–CHCl (1,3 and 1,2) | 33,45 4,38 61,32 | 31,8
Polyvinylidene chloride (PVDC) | CCl₂–CH₂–CCl₂–CH₂– (1,1) | 25,00 2,34 72,74 | 28,7
Copolymer (CP) of 31,5% VC and 68,5% VDC | CH₂–CCl₂–CH₂–CHCl (1,3) | 29,25 2,95 67,50 | 27,5

Fig. 2. Ratio of the carbon content to hydrogen in the carbonization products of the polymers: 1) PVDC; 2) CP; 3) CPVC; 4) PVC.

Above 400°C. We should also mention the interesting effect of randomization of the layers in the carbonization products of PVC at 400°C, which leads to a broadening of the interference band 002 on the x-ray diffraction pattern. A comparison of the course of the variation of the x-ray diffraction patterns as a function of the temperature of treatment leads to the conclusion that the mobility of the structure of carbon in the carbonization products of PVC is comparatively great, and the temperatures of transformation of the aliphatic carbon chains to a condensed aromatic structure are comparatively lower in comparison with PVDC. The polymers CPVC and CP occupy an intermediate position. Further structural transformations of carbon in high-temperature treatment are determined by the structure of the carbonization product at low temperatures of treatment. As is well known, the carbonized products from PVC are homogeneously graphitized [3, 4] during high-temperature treatment (> 1900°C). In contrast to this, the products from PVDC, CPVC, and CP are not homogeneously graphitized.

The formation of thermally stable side bonds of the cumulene and polyyne type along the packets of aromatic layers, preventing azimuthal ordering of the layers in the crystal lattice of graphite, was indicated earlier [5] for a number of different nongraphitizing carbonaceous substances. During the process of carbonization of vinyl polymers with a large chlorine content, one might expect the formation of portions of the carbon chain with conjugated triple and cumulative double bonds, which would prevent crystallization of the carbon during high-temperature treatment. For a more detailed clarification of the intermediate structures formed in the process of carbonization, the IR spectra of the products of heat treatment were studied at various temperatures. Fig. 4 presents the spectra of certain samples of carbonized products of PVC and PVDC, which were taken in the form of tablets, pressed with potassium bromide, on the IKS-14 two-beam spectrometer in the region of 670-2000 cm⁻¹. The polymer samples were carbonized in a