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Abstract

Full Text

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On the Oxidation Products of High-Molecular-Weight Conjugated Polyenes

(Presented by Academician V. N. Kondrat’ eva, February 28, 1962)

Polymers with an acyclic conjugation system are characterized by a comparatively low excitation-energy value, which is manifested above all in their ability to absorb not only in the ultraviolet but also in the visible and near-infrared regions of the spectrum (1). In the absence of side aromatic groups, such polymers possess high reactivity toward oxygen, electrophilic reagents, and dienophiles (2–5). Recently it was shown that the products of mild dehydrochlorination of polyvinyl chloride react very vigorously with oxygen, changing from dark-colored substances into light-yellow polymeric substances of unknown nature and properties (6).

Fig. 1. Effect of the sodium amylate: polymer ratio and of temperature on the rate and extent of dehydrochlorination of polyvinyl chloride and perchlorovinyl.

It seemed of interest to us to investigate the mechanism of the process of mild ($t = 20^\circ$) oxidation of high-molecular-weight polyenes by oxygen and to determine the reactivity and dehydrating activity of the products formed. The acyclic polymers with a conjugation system required for the work were obtained by heterogeneous dehydrochlorination of polyvinyl chloride (PVC) with molecular weight 650,000 and perchlorovinyl (CPVC) with molecular weight 105,000 using sodium amylate, in an inert gas atmosphere (argon).

As can be seen from Fig. 1, practically complete dehydrochlorination of PVC is achieved at a relatively high ratio of sodium amylate to PVC. In the process of dehydrochlorination with sodium amylate, a side alkoxylation reaction takes place, causing disruption of the continuity of the conjugation chain. The insolubility of the dehydrochlorination products in organic solvents may be explained

Fig. 2. Rate of addition of O_2 and change in the electrical properties of dehydrochlorinated polyvinyl chloride and perchlorovinyl.

Figure 2: Fig. 2. Rate of addition of O_2 and change in the electrical properties of dehydrochlorinated polyvinyl chloride and perchlorovinyl.

by the formation of π-complex or network structures.

The presence in CPVC of vicinal and 1,1 structures (^{7}) contributes to an increase in the rate of thermal dehydrochlorination of the polymer. However, under the action of sodium alcoholates, CPVC is dehydrochlorinated incompletely and, even at high molar ratios of sodium amylate to CPVC, is converted into a polyene containing up to 20% firmly bound chlorine, apparently located directly at the double bond. The dehydrochlorinated polymers are black, insoluble, and do not soften up to the decomposition temperature (400–500°); they are brittle products showing a narrow EPR singlet corresponding to 10^{18} paramagnetic particles per 1 g. The width of the EPR signal for dehydrochlorinated PVC is 18.6 oersted, and for dehydrochlorinated CPVC 9.5 oersted. The narrower EPR signal in the latter case is an indication of

the presence of large exchange interactions of unpaired electrons, owing to an increase in the conjugation effect due to the electron-donor chlorine atoms of the chlorovinylene groups.

Oxidation of the dehydrochlorination products of PVC and CPVC was carried out at 20° and was sharply accelerated by illumination with visible or ultraviolet light. In the course of oxidation, the color of the polyvinylenes changes from black to light yellow, and the EPR signal disappears. The rate of oxidation and the amount of O_2 added in the case of dehydrochlorinated CPVC are considerably lower than in the case of dehydrochlorinated PVC (Fig. 2). Apparently, the presence of halogen in the conjugation chain reduces the ability of the polyene to undergo addition reactions, in the same way as occurs when a polyene chain is blocked by alkyl or aryl groups ($^{2-4}$).

Fig. 2. Rate of addition of O_2 and change in the electrical properties of dehydrochlorinated polyvinyl chloride and perchlorovinyl

It is interesting to note that disruption of the conjugated system as a result of addition of O_2, even at the initial stages of oxidation, leads to a sharp decrease in the electrical conductivity of the polymer. At the same time, in accordance with the rate of oxidation, the decrease in electrical conductivity of dehydrochlorinated PVC proceeds faster than in the case of dehydrochlorinated CPVC. Thus, the electrical conductivity of polyvinylene obtained from VC falls from 10^{-5} to $10^{-11}\ \Omega^{-1}\cdot\text{cm}^{-1}$ within 22 min after the start of oxidation, whereas for a similar decrease in the case of CPVC almost an hour is required (Fig. 2).

The product of complete addition of O_2 to the polyene obtained from PVC contained about 32.5% bound oxygen. The iodometric method of Baeyer and

Fig. 3

Figure 3: Fig. 3

Villiger (^{9}) indicates the presence of peroxide groups. However, owing to the insolubility of the product, this method gave very low values. In addition to peroxide groups, double bonds were found in the oxidized product. On the basis of elemental analysis and bromine numbers it was calculated that for one double unit there are 4 carbon atoms, or that for 4 carbon atoms there are approximately 2 oxygen atoms.

The chemical-analysis data agree with IR spectra indicating the presence of peroxide and methine groups (895, 1330, 1250, 2900 cm^{-1}) and isolated double bonds. Along with this, the IR spectra reveal the presence of hydroxyl and carbonyl groups (3400, 1650, 1150 cm^{-1}).

On the basis of the above, it may be assumed that the interaction of the high-molecular-weight polyenes studied by us with O_2 proceeds analogously to what has been shown for monomeric cyclodienes and acenes (^{10,11}):

$$-\mathrm{CH{=}CH}-\mathrm{CH{=}CH}- \xrightarrow[E,h\nu]{O_2} -\mathrm{CH}-\mathrm{CH{=}CH}-\mathrm{CH}- \qquad \text{(I)}$$

$$|\quad \mathrm{O}-\mathrm{O} \quad|$$

Considering O_2 as a kind of philodiene, and the high-molecular-weight polyene as a substance analogous, in excitation energy and reactivity, to polynuclear acenes (^{1,2}), one may suppose that peroxides of type I should, in their properties, be close to the corresponding endoperoxides (^{12}). Experiments have established that, upon heating oxidized polyenes at $t \geq$ 150-200° without access of air, under pressure, in vacuum, or in an atmosphere of inert gas, a deepening of the color is observed.

from light yellow to brown and then black. In this process products are formed which again show a narrow EPR singlet, without hyperfine structure, corresponding to a content of 10^{17}–10^{18} paramagnetic particles per 1 g. At the same time the electrical conductivity increases sharply.

Fig. 3. Thermal decomposition upon heating in air of the oxidized product of dehydrochlorination of PVC.

The thermally colored polymer obtained after heat treatment differs from the initial polyene in elemental composition (it contains up to 15% bound oxygen) and in greater resistance to the action of O_2 at room and elevated temperatures. All this suggests that, when the peroxides under study are heated, they are converted into a new polymer with another, apparently aromatic, type of conjugation. To clarify the probable mechanism of this complex process, a

Fig. 4

Figure 4: Fig. 4

mass-spectrometric study was carried out of the gaseous products formed when the peroxide polymer, obtained from dehydrochlorinated PVC, was heated in vacuum at a temperature of 200°.

The study was performed using an MX-1302 mass spectrometer. The sample was first degassed for 1 hour at a temperature of 100° and a vacuum of 10^{-3} mm Hg.

Analysis of the mass spectrum shows that the substances evolved are chiefly water, CO_2, alcohols and unsaturated hydrocarbons, and benzene. It is significant that oxygen is practically absent among the evolved gases. At the same time, the data of elemental analysis of the brown polymer formed under the conditions in which the mass-spectral study was carried out indicate the loss of about half of all the oxygen. The brown polymer again exhibits a narrow EPR signal with a concentration of unpaired electrons of 10^{17} per 1 g and a width of 8.7 oersted, and an increase in electrical conductivity at room temperature by 2 orders of magnitude. The absence of oxygen and the presence of relatively large amounts of water and benzene in the gaseous products of thermolysis of the polymeric peroxide give grounds to assume that under such treatment decomposition of the peroxide and cyclization of the products formed take place, accompanied by the conversion of the resulting alicyclic structures into aromatic ones. Along with this, destructive processes also occur, causing the formation of CO_2 and a number of other products.

Fig. 4. Thermomechanical curves recorded on the Tsetlin apparatus in nitrogen under a load of 0.8 kg/cm^2.
1 –initial PVC (pressed at 20° and 4500 kg/cm^2); 2, 3 –dehydrochlorinated and oxidized PVC: 2 –pressed at 20° and 4500 kg/cm^2, 3 –at 150° and 100 kg/cm^2.

The conclusion that peroxides of polymeric polyenes are capable, under comparatively mild conditions, of dehydrogenating alicyclic compounds with the formation of aromatic hydrocarbons was confirmed experimentally, since it turned out that such peroxides are capable, in the absence of O_2 at 150°, of converting tetralin into naphthalene in considerable yield. In this process the peroxide, giving up part of its oxygen, is converted into a dark-brown polymer showing characteristic EPR spectra (see above).

It is curious to note that heating, in air, the peroxides of polyenes obtained by dehydrochlorination of PVC does not lead to their progressive decomposition, as is the case for ordinary peroxides and hydroperoxides. In our case, on the contrary, even a certain increase in thermal stability is observed with increasing duration of heat treatment (Fig. 3). The "stepwise" course of the destruction curve shown in Fig. 3 is observed for polymers with a system of conjugated bonds, or for polymers capable, during heat treatment, of forming such structures (2).

Thus, the investigated peroxides of high-molecular-weight polyenes, like endoperoxides, undergo mainly not destructive decomposition but complex chemical transformations leading to more energetically favorable structures. The absence in the peroxides studied of a developed conjugation system accounts for the greater flexibility of the macromolecules and sharply reduces their ability to form intermolecular π-complexes.

Indeed, as is evident from Fig. 4, the oxidized polymer exhibits highly elastic properties at temperatures above 70°. At elevated temperatures, processes occur that lead to the formation of three-dimensional structures. A specimen molded at 150° (the onset of decomposition of the oxidized product) is characterized by a complete loss of highly elastic properties. Molding oxidized polyvinylene at temperatures of 150–250° and at pressures of the order of 300–500 kg/cm^2 makes it possible to obtain fairly strong plastics characterized by increased heat resistance.

The use of peroxides of high-molecular-weight polyenes as a binder not only does not impair, but in a number of cases even improves (Table 1) the electrical characteristics of the material, apparently as a result of oxidative dehydrogenation of saturated groups, which disrupt the conjugation chain in the macromolecules of the polymer ingredients.

Table 1

Electrical properties of compositions obtained on the basis of powdered nonpressable polymeric substances and the oxidized product of PVC dehydrochlorination

Material	Ratio of ingredients (powder : oxidized substance), parts by wt.	Pressing conditions: temperature, °C	Pressing conditions: pressure, kg/cm^2	Pressing conditions: holding time, min	E, eV	$\lg \sigma_{300}$	$\lg \sigma_0$
Oxidized product of PVC dehydrochlorination (OP)	–	20	4500	15	0.328	−14.93	−9.48
Substance I	–	–	–	–	0.087	−5.0	−3.6
Substance II	–	–	–	–	0.426	−7.0	0.30
Substance I + OP	70 : 30	200	500	15	0.123	−4.04	−1.48
Substance II + OP	70 : 30	200	500	15	0.275	−5.71	−1.11

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Note: Figure translations are in progress. See original paper for figures.