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Academician A. N. NESMEYANOV, A. M. RUBINSHTEIN, A. A. DULOV,

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Abstract

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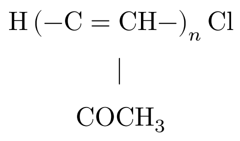
Academician A. N. NESMEYANOV, A. M. RUBINSHTEIN, A. A. DULOV, A. A. SLINKIN, M. I. RYBINSKAYA, and G. L. SLONIMSKII

INVESTIGATION OF THE CATALYTIC PROPERTIES OF POLYMERS OBTAINED ON THE BASIS OF METHYL-β-CHLOROVINYL KETONE

In a work published earlier (1), the synthesis of polymers based on methyl-β-chlorovinyl ketone (2) was reported. It turned out that these polymers have very interesting electrical and magnetic properties and possess catalytic activity in reactions of oxidation and dehydrogenation of alcohols.

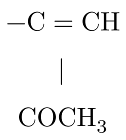
In the present work the study of the physical properties of these polymers and, especially, of their catalytic activity was continued. The preparation of the initial polymers was carried out as follows. Methyl-β-chlorovinyl ketone, on standing for 25–30 days, undergoes spontaneous polycondensation with liberation of hydrogen chloride. As a result, a mixture of polymers is obtained, to which, on the basis of chemical properties (1) and elemental-analysis data, the general formula is assigned



$$\mathrm{H}\,(-\underset{\substack{|\\ \mathrm{COCH_3}}}{\mathrm{C}}=\mathrm{CH}-)_n\,\mathrm{Cl}$$

(C 72.12%; H 5.41%; Cl 1.6%).

Calculated for



$$-\underset{\substack{|\\ \mathrm{COCH_3}}}{\mathrm{C}}=\mathrm{CH}$$

C 70.59%; H 5.88%. The polymer analyzed had been treated for a long time with boiling glacial acetic acid (for the most complete liberation of hydrogen chloride). The best results are obtained when the polycondensation is carried out in a sealed ampoule. In a poorly closed vessel or upon dilution with a neutral solvent, a large amount of the cyclic trimer—triacetylbenzene—is formed. Additions of metal chlorides, of the Friedel-Crafts catalyst type, considerably accelerate the polycondensation. When anhydrous ferric chloride was used as catalyst, a polymer was obtained containing C 70.87; H 5.90; Cl 2.72. In order to avoid contamination of the polymers by metal ions, to accelerate the polycondensation a small amount of semiliquid polymeric mass taken from an opened ampoule was added to freshly prepared monomer.

Table 1

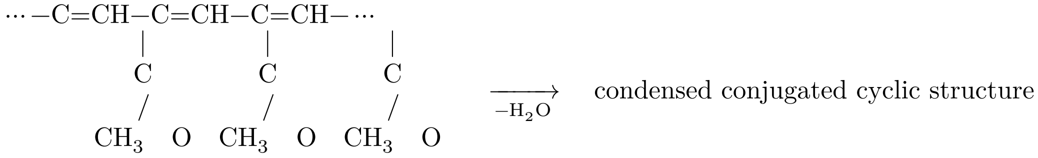
T, °C/mm	Time, hr	Analysis data*, %	Analysis data*, %
		C	H
300°/12	6	88.11	5.01
400°/12	6	89.35	4.45
700°/12	6	94.77	3.31

* Calculated data for the polymer, %:

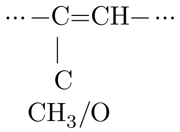
C 96; H 4

Investigation showed that these polymers, upon prolonged heating in vacuum (12 mm), slowly change (with liberation of water) in the direction of an increase in carbon content (Table 1). Apparently, crotonic polycondensation takes place at each of two adjacent acetyl groups within one chain (I), or interchain polycondensation at the expense of acetyl-

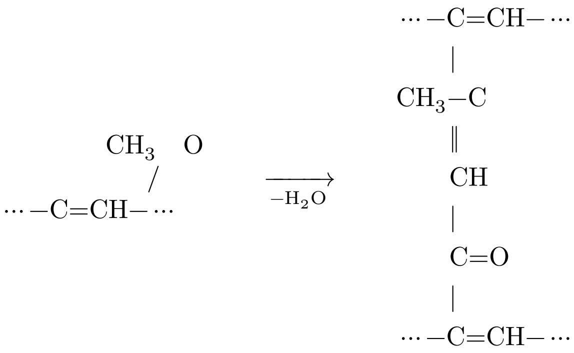
···groups (II), which can be represented by the scheme:



(I)



$$\cdots-\underset{\underset{CH_3/O}{C}}{\underset{|}{C}}=CH-\cdots$$



$$\begin{array}{c} \mathrm{CH_3}\quad \mathrm{O} \\ / \\ \cdots-\mathrm{C{=}CH}-\cdots \end{array} \xrightarrow[-\mathrm{H_2O}]{} \begin{array}{l} \cdots-\mathrm{C{=}CH}-\cdots \\ \quad| \\ \mathrm{CH_3-C} \\ \quad\| \\ \quad\mathrm{CH} \\ \quad| \\ \quad\mathrm{C{=}O} \\ \quad| \\ \cdots-\mathrm{C{=}CH}-\cdots \end{array}$$

(II)

In practice, apparently both processes occur, since some amount of oxygen always remains in the polymer owing to the carbonyl groups.

In the present work the properties were studied of polymers heated for 6 h at 400°/12 mm, obtained both with an addition of ferric chloride and without it. The catalytic properties of the above-described polymers were compared with the catalytic properties of natural carbon polymers: activated charcoal and graphite. Activated charcoal and graphite were carefully washed free of paramagnetic impurities with hydrochloric acid; this was monitored by the value of the specific magnetic susceptibility (χ) and by its dependence on the field strength after treatment of the samples with hydrogen at 400°C. The EPR spectra of the substances studied were recorded on an apparatus of the type described in papers (^{3,4}). Magnetic susceptibility was measured by Faraday' s method in magnetic fields from 3000 to 4500 Oe. The specific surface area of the compounds investigated was determined from argon adsorption at 20°. The electrical conductivity of the polymers and its temperature dependence were studied in a vacuum apparatus (10^{-3}—10^{-4} mm Hg) using a quartz cell and nickel electrodes.

Fig. 1. Change in specific electrical conductivity and calculated activation energies: I —polymer obtained with $\mathrm{FeCl_3}$, $E_\sigma = 0.8$ eV; II —polymer obtained without additives, $E_\sigma = 0.86$ eV.

Table 2

Sample	S, m^2/g	$\chi^*_{20} \cdot 10^6$	Number of unpaired spins per 1 g	$\lg \sigma_{200^\circ}$, ohm^{-1} · cm^{-1}	E_σ, eV
Polymer obtained with FeCl$_3$	0.32	−0.3	$\sim 10^{19}$	−11.7	0.8
Polymer obtained without additions of metal ions	0.3	−0.5	$\sim 10^{19}$	−12.8	0.85
Activated charcoal	$\sim$ 600	−0.4	–	–	–
Graphite	20.0	−3.0	–	–	–

* Without correction for diamagnetism.

The main physical characteristics of the polymers studied, as well as of activated carbon and graphite, are given in Table 2 and in Fig. 1.

As follows from the data in Table 2, the polymers have a very small specific surface area (S) in comparison with activated carbon and a relatively large number of unpaired spins. It should be noted that the EPR signal of these polymers, in contrast to the EPR signal of carbons ([5,6]), does not change at all in the presence of oxygen, and therefore the EPR of these polymers can be measured in air. Evacuation of the polymer in vacuum (10^{-3} mm) at 100° for 6 h does not lead to a change in the width or intensity of the signal.

Figure 1 gives data on the change in specific electrical conductivity (σ) with temperature, from which the activation energies of conduction (E_σ) were calculated (Table 2). In the temperature range studied (160–350°), these polymers are possibly intrinsic semiconductors with a band gap of 1.6 eV.

The catalytic activity of the polymers, as well as of activated carbon and graphite, was studied using the reaction of oxidation of toluene by air at 370–380° in a flow apparatus with 3.0–5.0 cm^3 of catalyst. Benzoic acid and benzaldehyde, identified as the 2,4-dinitrophenylhydrazone, were isolated from the condensate.

Table 3

Sample	S, m^2/g	Experimental temperature, °C	Volume rate of toluene feed, h^{-1}	Air feed rate, l/h	Conversion based on passed toluene, wt. %, to aldehyde	Conversion based on passed toluene, wt. %, to acid	Conversion based on passed toluene, wt. %, total	Melting point of isolated dinitrophenylhydrazone*, °C	Melting point of isolated benzoic acid*, °C
Polymer obtained with $FeCl_3$	0.32	380	0.33	0.5	0.7	3.0	3.7	239.2–240.2	121.0–122.0
Polymer obtained without addition of metal ions	0.30	380	0.33	1.2	0.4	1.6	2.0	239.0–240.0	121.5–122.0
Activated carbon	600	370	0.20	0.5	0.5	3.4	3.9	239.2–240.0	–
Graphite	20.0	370	0.33	0.5	0.5	0.2	0.7	239.0–240.0	121.0–122.0
Blank experiment	–	390	–	0.5	Oxidation does not proceed	Oxidation does not proceed	Oxidation does not proceed	Oxidation does not proceed	Oxidation does not proceed

* Mixed samples with authentic specimens do not give a depression of the melting point.

Table 3 gives the conditions and results of the study of the catalytic properties of the polymers, activated carbon, and graphite in the reaction of oxidation of toluene to benzaldehyde and benzoic acid. As can be seen from the data in Table 3, the polymers obtained show significant activity in the reaction of toluene oxidation. In evaluating these data, it should be taken into account that the oxidation reaction of toluene, which usually takes place on oxides of transition elements of the first long period, is carried out under more severe conditions (^{7}) (temperature 450–500°, volume rates of toluene 0.01–0.06 h^{-1}), and therefore the results obtained are of undoubted interest.

A second important point is that the polymer, having a specific surface area of ~ 0.3 m^2/g, gives the same yield of oxidation products as activated carbon, which has a surface area of about 600 m^2/g; i.e., the specific activity of the polymer exceeds the specific activity of carbon by three orders of magnitude. It is still unclear what accounts for such a significant activity of the polymer. It is possible that this is caused by the increased concentration of spins on such a small surface of the polymer. In any case, further parallel

catalytic and physical methods of investigating similar compounds will help answer this question.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

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