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Abstract

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Investigation of the Properties and Structure of Carbyne

The present work gives the results of a study of the infrared absorption spectra and electron paramagnetic resonance spectra of polymers containing conjugated poly-yne groupings in the chain. Earlier (^{1}), the preparation of polyyne by the reaction of oxidative polydehydrocondensation of acetylene was described, and some physical properties of this product were reported. In (^{2,3}), the IR absorption spectrum of polyyne was given. Interpretation of the IR spectra and X-ray structural analysis data led to the supposition that polyyne (carbyne) consists, at least in part, of cumulated carbon chains.

For a more detailed investigation of the structure of carbyne by IR spectroscopy, we carried out a counter synthesis of polymers of polyyne structure by dehydrochlorination of polyvinylidene chloride (PVDC). In carrying out the dehydrochlorination reaction, we proceeded from the premise that, to form the required structure, strong bases should be used for the elimination of hydrogen chloride under the mildest possible conditions. Under harsh conditions, dehydrochlorination could lead to the formation of crosslinked structures. It was also necessary to take into account that the first stage (formation of the chlorinated polyene) proceeds considerably more readily than the second (formation of polyyne), since the chlorine atoms in the chlorinated polyene have reduced chemical activity (halogen at a carbon atom with a double bond).

The scheme for the transformation of polyvinylidene chloride into polyyne is presented below:

$$|{-}\mathrm{CCl_2}{-}\mathrm{CH_2}{-}|_n \longrightarrow |{-}\mathrm{CCl}{=}\mathrm{CH}{-}|_n \longrightarrow |{-}\mathrm{C}{\equiv}\mathrm{C}{-}|_n.$$

Proceeding from the considerations set out above, we chose alkali-metal amides in liquid ammonia as the principal dehydrochlorinating agents.

The IR spectra of the products of successive dehydrochlorination of polyvinylidene chloride were compared with the IR spectrum of polyyne obtained by oxidative polydehydrocondensation of acetylene. The carbyne sample was thoroughly washed free of mineral impurities and dried by heating under reduced pressure.

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

The spectra were recorded on an IKS-14 infrared spectrophotometer. The samples were pressed into pellets with potassium bromide.

In the IR spectrum of PVDC (Fig. 1; Ib), treated with sodium amide in liquid ammonia for 40 hr, the structural bands of the starting polymer (Fig. 1; Ia) are still clearly visible. Along with this, an absorption band appears in the region of stretching vibrations of double bonds, and an absorption band with a maximum at 2140 cm^{-1}, attributed to the stretching vibrations of the triple bond $C \equiv C$. The absorption band (2140 cm^{-1}) in the spectrum of PVDC treated under the same conditions for 100 hr (Fig. 1; Ic) is noticeably more intense.

In the second series of experiments, the elimination of HCl from PVDC was also carried out with sodium amide, but with heating in a tetrahydrofuran medium. In the spectrum of this sample, ···

sample (Fig. 1; I) the structural bands are less pronounced. The absorption band corresponding to the valence vibrations of the triple bond has a maximum at 2195 cm^{-1}. Further treatment of this polymer with sodium methylate in boiling methyl alcohol leads to the formation of a polymer containing 8% chlorine. In the IR spectrum of this polymer (Fig. 1; I) the initial structure of PVDKh is no longer visible, but the vibration frequency of the triple bond retains its value (2195 cm^{-1}).

Fig. 1. IR spectra of PVDKh and of the products of its dehydrochlorination: *a*—PVDKh; —PVDKh treated with $NaNH_2$, 40 h; —PVDKh treated with $NaNH_2$, 100 h; —PVDKh treated with $NaNH_2$ in tetrahydrofuran; —PVDKh treated with sodium methylate in CH_3OH; —PVDKh fused with Na

Fig. 2. IR spectra of polyynes: *a*—not containing copper; —the same; ,—at different stages of washing from copper

Fusion of a PVDKh sample with metallic sodium leads to the production of a polymer containing no chlorine; in the spectrum of this sample (Fig. 1; I) the structural bands of the initial polymer, as well as the vibration frequencies of the triple bond, are absent.

On comparing the IR spectra of the samples of dehydrochlorinated PVDKh with the IR spectrum of polyine (carbyne) obtained by oxidative polydehydrocondensation of acetylene (Fig. 2; IIa and II), a close coincidence of the vibration frequencies of the triple bonds is clearly seen. (The frequency 2100 cm^{-1} in IIa and the frequency 2140 cm^{-1} in I and I . The frequency 2195 cm^{-1} in II , I , and I . Figs. 1 and 2.)

Thus, the dehydrochlorination reaction of polyvinylidene chloride can serve as a counter-synthesis of carbyne, at least of its fragments.

Fig. 3. EPR spectra of polyynes: a—polyyne containing no copper; b—polyyne containing Cu+; c, d—polyyne containing Cu2+

Figure 2: Fig. 3. EPR spectra of polyynes: a—polyyne containing no copper; b —polyyne containing Cu+; c, d—polyyne containing Cu2+

Earlier (^1) we put forward the supposition that the cumulene structure of carbyne owes its appearance to copper bound in a complex, or to copper in the form of acetylenides. It was noted (^4) that in the IR spectrum of eicosadiyne-1,19 acetylenide the characteristic frequency of the C C bond was not observed. At the same time, a band appears in the IR spectrum in the region of 1620 cm^-1, whose origin was explained by the fact that the π-electrons of the C C bond are shifted toward the copper atoms. Studies of the IR spectra of other acetylenides, carried out by Coates and Parkin (^5), showed very low values of the characteristic frequencies of the C C bond (1929–1955 cm^-1).

Fig. 3. EPR spectra of polyynes: *a*—polyyne containing no copper; *b*—polyyne containing Cu^+; *c*, *d*—polyyne containing Cu^2+

To prove the influence of the presence of copper on the structure of carbyne, we compared the IR spectra of carbyne gradually freed from copper with the spectrum of carbyne containing no copper and having only the characteristic stretching vibrations of the C C bond: 2102 cm^-1 (Fig. 2; *IIa*) and 2194 cm^-1 (Fig. 2; *IIb*).

In the IR spectrum of freshly prepared carbyne not freed from copper (Fig. 2; *IIv*) a series of characteristic frequencies is observed: 2200 cm^-1 (stretching vibrations of the C C bond), 2050 and 2015 cm^-1 (stretching vibrations of the C=C=C bond). The IR spectrum of a carbyne sample partially washed free of copper (Fig. 2; *IIg*) shows the presence of absorption bands in the region of 2080 cm^-1 (C C) and 2042 cm^-1 (C=C=C). More thorough removal of copper leads to the appearance of only one absorption band at 2085 cm^-1, characteristic of stretching vibrations of the C C bond (Fig. 2; *IId*).

All the investigated samples obtained by dehydrochlorination of PVDC or by oxidative polydehydrocondensation of acetylene give a narrow EPR signal (Fig. 3; *IIIa*) with a g-factor close to the g-factor of a free electron, and with a line width (determined between the points of maximum slope) from 5 to 9 oersteds. The concentration of unpaired electrons increases as the degree of dehydrochlorination of polyvinylidene chloride rises: from 1.25 • 10^17 for sample *Ib*, 2.63 • 10^18 for sample *Id*, to 1.4 • 10^21 for sample *Ie*. Samples obtained by oxidative polycondensation of acetylene, and samples obtained from PVDC with a low chlorine content, gave narrow EPR signals with coincident spin-lattice relaxation times T_1 of 10^-6 sec, whereas samples of a low degree of dehydrochlorination had considerably longer relaxation times T_1, 10^-4 sec.

In these samples, transmission effects are observed that are characteristic of chemically carbonized substances. The spin-lattice relaxation time T_1 gradually decreases with increasing degree of dehydrochlorination of PVC.

It is also of interest that in the carbyne sample (*IIb*), not yet washed free of copper, there is no EPR signal corresponding to divalent copper (Fig. 3; *IIIb*), whereas for partially washed carbyne (sample *IIa*) both a narrow signal and a broad signal with weak resolution, characteristic of divalent copper, are already observed (Fig. 3; *IIIb*).

When the samples are kept in air, these signals change with time; the intensity of the narrow signal decreases by at least a factor of three, and the resolution of the broad signal is no longer observed (Fig. 3; *IIIe*).

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REFERENCES

1. V. V. Korshak, V. I. Kasatochkin et al., DAN, **136**, 1342 (1961).
2. V. I. Kasatochkin, O. I. Egorova, Yu. G. Aseev, DAN, **151**, 125 (1963).
3. V. I. Kasatochkin, A. M. Sladkov et al., DAN, **153**, 346 (1963).
4. V. V. Korshak, A. M. Sladkov, Yu. P. Kudryavtsev, *High-Molecular Compounds*, **2**, 1824 (1960).
5. I. E. Coates, C. Parkin, *Advances in the Chemistry of the Coordination Compounds*, No. 4, 1961, p. 173.

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