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1963

SovietRxiv

Abstract

Full Text

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INFRARED SPECTRA OF POLYYNES

In order to elucidate the structure, and also the possibility of spectrally determining the molecular weight of polyynes, the IR absorption spectra were studied for a series of products of the joint oxidative polycondensation of acetylene, phenylacetylene, *p*-diethynylbenzene, and *p*-nitrophenylacetylene (Table 1),

Table 1

Name	Formula	Fig.
Polyacetylene (carbyne)	$\mathrm{H}\,[-\mathrm{C}\equiv\mathrm{C}-]_n\,\mathrm{H}$	1a
Phenylacetylene	$\mathrm{Ph}-\mathrm{C}\equiv\mathrm{CH}$	1d
Diphenylacetylene (tolane)	$\mathrm{Ph}-\mathrm{C}\equiv\mathrm{C}-\mathrm{Ph}$	1b
Diphenylbutadiyne	$\mathrm{Ph}-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}\equiv\mathrm{C}-\mathrm{Ph}$	1v
Product of polycondensation of acetylene and phenylacetylene (benzene-soluble fraction, mol. wt. = 330)	$\mathrm{Ph}-\mathrm{C}\equiv\mathrm{C}\,[-\mathrm{C}\equiv\mathrm{C}-]_5\,\mathrm{C}\equiv\mathrm{C}-\mathrm{Ph}$	1g
p-Diethynylbenzene	$\mathrm{HC}\equiv\mathrm{C}-\mathrm{C}_6\mathrm{H}_4-\mathrm{C}\equiv\mathrm{CH}$	2a
Polymer of *p*-diethynylbenzene	$\mathrm{H}\,[-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}_6\mathrm{H}_4-\mathrm{C}\equiv\mathrm{C}-]_n\,\mathrm{H}$	2b
Product of polycondensation of *p*-diethynylbenzene with phenylacetylene (benzene-soluble fraction, mol. wt. = 450)	$\mathrm{Ph}-\mathrm{C}\equiv\mathrm{C}\,[-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}_6\mathrm{H}_4-\mathrm{C}\equiv\mathrm{C}-]_2\,\mathrm{C}\equiv\mathrm{C}-\mathrm{Ph}$	2v
(insoluble fraction)	$\mathrm{Ph}-\mathrm{C}\equiv\mathrm{C}\,[-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}_6\mathrm{H}_4-\mathrm{C}\equiv\mathrm{C}-]_n\,\mathrm{C}\equiv\mathrm{C}-\mathrm{Ph}$	2g

Fig. 1

Figure 1: Fig. 1

Name	Formula	Fig.
Product of polycondensation of *p*-diethynylbenzene with *p*-nitrophenylacetylene	$O_2N-C_6H_4-C\equiv C\left[-C\equiv C-C_6H_4-C\equiv C-\right]_n C\equiv C-C_6H_4-NO_2$	2d
Product of polycondensation of *p*-diethynylbenzene with acetylene (benzene-soluble fraction)	$H\left[-C\equiv C-C_6H_4-C\equiv C-\right]_n\left[-C\equiv C-\right]_m H$	2e
(insoluble fraction)	same	2zh

obtained by the reaction of bis-acetylenes with aqueous solutions of salts of divalent copper and subsequent oxidation of the polymeric acetylides formed (^{1}).

The spectra were recorded on a double-beam IKS-14 spectrophotometer in the region 300–4000 cm^{-1} (KBr, NaCl, and LiF prisms). Powder samples were prepared in the form of tablets pressed with potassium bromide.

An X-ray study of carbyne (^{2}) showed the presence of rectilinear macromolecules grouped into bundles with a period in the molecular chain $d_C = 2.62$ Å, somewhat greater than the sum of the lengths of the triple ($d_{\mathrm{C\equiv C}} = 1.19$ Å) and single ($d_{\mathrm{C-C}} = 1.36$ Å) bonds in the diacetylene molecule (^{3}).

The relatively sparse spectrum of carbyne (Fig. 1a) includes absorption bands characteristic of stretching vibrations of the triple bond of disubstituted acetylene groups $R_1-C\equiv C-R_2$ at 2200 cm^{-1} and of terminal monosubstituted groups $R-C\equiv C-H$ at 2100 cm^{-1}, as well as stretching vibrations $\equiv C-H$ at 3250 cm^{-1} and 3300 cm^{-1}. The two bands at 1960 cm^{-1} (very strong) and at 1070 cm^{-1} (weak) should be assigned to stretching and skeletal vibrations of the carbon chain with cumulated double bonds $=C=C=C=$.

The presence of the listed bands in the spectrum indicates a partially cumulated structure of the polyyne hydrocarbon chains.

The spectra of diphenylbutadiyne (Fig. 1*b*) and of the product of the joint condensation of acetylene with phenylacetylene (Fig. 1*c*) differ little and are very similar to the spectrum of diphenylacetylene (Fig. 1*b*). In their spectra, however, a band appears at 2146 cm^{-1}, characteristic of the disubstituted acetylene group R_1—$C\equiv C$—R_2 with different substituents.

Fig. 1

The spectra of diethynylbenzene (Fig. 2*a*) and of its polymer (Fig. 2*b*) contain bands characteristic of para-disubstituted aromatic rings at 550 cm^{-1} (for the polymer 540 cm^{-1}), 832 cm^{-1} (very strong), 1016 cm^{-1}, and 1160 cm^{-1} (very weak for the monomer).

The triple bonds in the spectrum of the monomer are reflected by stretching-vibration bands at 2100 cm^{-1} and by a very strong stretching-vibration band of $\equiv CH$ at 3260 cm^{-1}. In the spectrum of the polymer, in addition to these bands (of low intensity), there is a comparatively intense triple-bond band at 2200 cm^{-1}, characteristic of disubstituted groups $R_1—C \equiv C—R_2$. For the spectra of the products of co-polycondensation of acetylene with phenylacetylene, as well as for phenylacetylene itself, the presence of bands is characteristic

absorption bands of groups with double bonds at 915 cm^{-1}, 1070 cm^{-1}, 1437 cm^{-1}, 1940 cm^{-1}, 2840 cm^{-1}, 2920 cm^{-1}, which could be assigned to tautomeric groups with divalent carbon and cumulated double bonds.

Fig. 2

This also applies to samples of the copolymer of *n*-diethynylbenzene with phenylacetylene.

The possibility is not excluded of tautomeric rearrangements of this type also for paradiethynylbenzene and its polymers

$$\mathrm{C} = \mathrm{C} - \langle\text{benzene ring}\rangle - \mathrm{C} = \mathrm{CH_2},$$

if one takes into account the appearance of bands at 960 cm^{-1}, 1390 cm^{-1}, 1665 –1676 cm^{-1}, 1960 cm^{-1}, 2840 cm^{-1}, and 2920 cm^{-1}. In a similar way one can also explain the appearance of bands characteristic of groupings with double bonds $= CH_2$ in the spectrum of carbyne.

In Fig. 2 the spectrum is shown of a polymer of *n*-diethynylbenzene with phenylacetylene, soluble in benzene, whose molecular weight, measured by the cryoscopic method, is 450. The molecule of this polymer contains two mono- and two para-substituted aromatic rings.

In Fig. 2 the spectrum of an insoluble polymer is shown. To determine the molecular weight it was convenient to use a quantitative comparison of the integral intensities of the closely situated bands at 757 cm^{-1} (mono) and 832 cm^{-1} (para).

In Fig. 3 a series of spectra is shown in the region of these absorption bands for polymers of different molecular weights, calculated from the spectra. The calculation was carried out under the assumption of a linear dependence of the integral intensity A of a band on the number (m_m) of monosubstituted or, respectively, (m_p) para-substituted aromatic rings,

Fig. 3. Infrared spectral fragments with labels: $m_{\mathrm{p}} = 2,\ \mu = 450$; $m_{\mathrm{p}} = 4,\ \mu = 698$; $m_{\mathrm{p}} = 6,\ \mu = 946$; $m_{\mathrm{p}} = 14,\ \mu = 1938$; $m_{\mathrm{p}} = 18,\ \mu = 2434$; $m_{\mathrm{p}} = 28,\ \mu = 3674$; $m_{\mathrm{p}} = 44,\ \mu = 5658$; $m_{\mathrm{p}} = 72,\ \mu = 9130$.

Figure 2: Fig. 3. Infrared spectral fragments with labels: $m_{\mathrm{p}} = 2,\ \mu = 450$; $m_{\mathrm{p}} = 4,\ \mu = 698$; $m_{\mathrm{p}} = 6,\ \mu = 946$; $m_{\mathrm{p}} = 14,\ \mu = 1938$; $m_{\mathrm{p}} = 18,\ \mu = 2434$; $m_{\mathrm{p}} = 28,\ \mu = 3674$; $m_{\mathrm{p}} = 44,\ \mu = 5658$; $m_{\mathrm{p}} = 72,\ \mu = 9130$.

$$A_{\mathrm{p}} = k_{\mathrm{p}} m_{\mathrm{p}} \quad \text{and} \quad A_{\mathrm{m}} = k_{\mathrm{m}} m_{\mathrm{m}},$$

whence

$$\frac{m_{\mathrm{p}}}{m_{\mathrm{m}}} = \frac{k_{\mathrm{m}}}{k_{\mathrm{p}}} \cdot \frac{A_{\mathrm{p}}}{A_{\mathrm{m}}} = k \frac{A_{\mathrm{p}}}{A_{\mathrm{m}}},$$

where k is the ratio of the molar absorption coefficients of mono- and para-substituted aromatic rings.

Measurement of the ratio of the integral intensities $A_{\mathrm{m}}/A_{\mathrm{p}}$ of the bands at 750 cm^{-1} and 830 cm^{-1} in the spectra of the soluble polymer with mol. wt. = 450 and $m_{\mathrm{m}} = m_{\mathrm{p}} = 2$ gives the value $k = 4$.

The number of para-substituted aromatic rings for polymers with any length of the molecular chain ($m_{\mathrm{m}} = 2$ for all polymers) is expressed by the following simple formula:

$$m_{\mathrm{p}} = 8\,\frac{A_{\mathrm{p}}}{A_{\mathrm{m}}}.$$

Fig. 3

Comparison of the spectra of the products of joint condensation of paradiethynylbenzene with phenylacetylene (Figs. 2 and 2) and with *p*-nitrophenylacetylene (Fig. 2) shows the presence of very intense bands of the NO_2 groups and a substantial change in the intensities and frequencies of the principal absorption bands under the influence of the terminal nitro groups in the polymer molecule.

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Received
25 VI 1963

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