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1962

SovietRxiv

Abstract

Full Text

Chemistry

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POLYAZINES–A NEW CLASS OF POLYMERS WITH CONJUGATED BONDS

Among polymers containing conjugated bonds in the main polymer chain, polyazines have practically not been investigated. However, these compounds are of considerable interest for elucidating the nature of the special electrophysical properties exhibited by polymers with conjugated bonds. The presence in polyazines of:

$$[= \mathrm{CX} - \mathrm{R} - \mathrm{CX} = \mathrm{N} - \mathrm{N} =]_n, \quad \text{where } \mathrm{X} = \mathrm{H}, \mathrm{CH_3}, \mathrm{C_6H_5}$$

nitrogen heteroatoms with free electron pairs creates favorable conditions for the maximum delocalization of the π-electrons of the conjugated bonds. We therefore undertook a study of the synthesis reaction of polyazines by polycondensation of hydrazine with glyoxal and with a series of diketones, and an investigation of the electrophysical properties of the polymers obtained. To study the influence of the degree of conjugation in the macromolecule on the electrical properties of polymers, we synthesized polyazines whose macromolecules contain methylene groups, as well as oxygen and sulfur atoms. The reaction of hydrazine with bifunctional aldehydes and ketones was first studied by Curtius ([1,2]). As a result of studying the reaction of a series of diketones with hydrazine, Zimmermann showed that in the case of α-diketones ([3]), with an equimolecular ratio of the reagents, linear polyazines are obtained. On the other hand, one should expect cyclic products to be obtained when hydrazine reacts with β- and γ-diketones, in view of the possibility of formation of five- and six-membered rings. Indeed, β-diketones in reaction with hydrazine give pyrazoles ([4,5]). In the reaction of γ-diketones with hydrazine in an equimolecular ratio, linear polymers are obtained along with cyclic products. Zimmermann isolated from the products of the interaction of acetylacetone with hydrazine both 3,6-dimethylpyridazine ([6]) and a linear polyazine with a molecular weight of about 20,000. This is the only case of obtaining a polyazine of such high molecular weight. Marvel ([7,8]) synthesized several polyazines and found that their molecular weight did not exceed 2000. He also drew attention to the fact that the ratio of the reagents affects the characteristic viscosity of the polymers. This feature is common to all types of polycondensation reactions, as has been shown in many examples ([9–11]). The presence of this dependence was also confirmed

Figure 1

Figure 1: Figure 1

in work (^{12}), in which the reaction of substituted dihydrazones with diketones was investigated. The molecular weight of the polyhydrazones obtained in this case did not exceed 5000.

We carried out the polycondensation of hydrazine with glyoxal, diacetyl, benzil, 4,4′-diacetyldiphenyl oxide, 4,4′-diacetyldiphenyl sulfide, 4,4′-diacetyldiphenylmethane, and 4,4′-diacetyldiphenyl ethylene glycol ether, as a result of which polyazines are formed. The polyazines obtained are solid substances colored in various colors. A darker coloration is characteristic of polyazines with an uninterrupted chain of conjugation. All the polyazines dissolve to a very limited extent in such solvents as methanol, benzene, chloroform, and somewhat better in

in tetrachloroethane and dimethylformamide (at high temperatures). In phenol and *m*-cresol at 120° polyazines dissolve completely. Most polyazines have a crystalline structure; polyazines from glyoxal and benzil are amorphous.

Fig. 1. Dependence of resistance on temperature for polyazines obtained from glyoxal (1), diacetyl (2), benzil (3), 4,4′-diacetyldiphenylmethane (4), 4,4′-diacetyldiphenyl sulfide (5), 4,4′-diacetyldiphenyl oxide (6), 4,4′-diacetyldiphenyl ether of ethylene glycol (7), glyoxal (product of thermal decomposition of polyazine) (8)

The IR spectra of polyazines show the presence of an intense absorption band at 1670 cm^{-1}, characteristic of stretching vibrations of the C=O bond, as well as a band at 1600 cm^{-1}, indicating the presence of C=N bonds. Polyazines are thermally unstable substances. Even the presence of a system of conjugated double bonds does not lead to an increase in the thermal stability of these polymers. Thus, the polyazine from glyoxal decomposes upon heating to 210°, and the decomposition proceeds in an explosive manner. The loss in weight, caused by the evolution of gaseous products, amounts to 67.5% of the initial weight of the polymer. Chromatographic analysis shows that the evolved gases contain: 67.49% nitrogen, 5.39% hydrogen, and 27.12% amines, hydrocarbons, and water (traces).

Polyazines from diacetyl and benzil decompose at 240 and 250°, respectively. It is possible that the facile thermal decomposition in the case of polyazines is due to azo–azine tautomerism:

$$[=\text{CX}{-}\text{CX}=\text{N}{-}\text{N}=]_n \rightleftarrows [-\text{CX}=\text{CX}{-}\text{N}=\text{N}-]_n, \quad \text{where } X=\text{H},\ \text{CH}_3,\ \text{C}_6\text{H}_5.$$

The azo compounds formed, being less stable, apparently decompose readily as follows:

$$[-\mathrm{CX}=\mathrm{CX}-\mathrm{N}=\mathrm{N}-]_n \rightarrow n\,\mathrm{N}_2+[-\mathrm{CX}=\mathrm{CX}-]_n.$$

Polyazines with aromatic rings in the chain are more stable and melt at high temperatures without decomposition, which can evidently be explained by the presence of conjugation with benzene rings. The evolution of a significant amount of nitrogen during the thermal destruction of polyazines may be used in the industrial production of foamed plastics. Similar work has been described in the literature (13).

A study of the electrical properties of polyazines shows that, for all these substances, an exponential dependence of electrical conductivity on temperature is characteristic. The specific electrical conductivity of polymers with conjugated double bonds lies within the range $7.08 \cdot 10^{-12} \div 1.29 \cdot 10^{-14}$. Apparently, the introduction of side substituents into the main chain leads to a decrease in the electrical conductivity of the polymers and to an increase in the activation energy of conductivity. This also occurs when the substituent is a phenyl radical, although the double bonds of the phenyl nucleus are conjugated with the double bonds of the main chain. It is possible that the reasons for this phenomenon are analogous to those responsible for the increase in the resistance of semiconductor materials obtained on the basis of polyacrylonitrile upon adsorption of oxygen (an electron acceptor). The introduction of a methylene group between phenyl nuclei does not lead to a noticeable change

Table 1

Properties of polyazines

Name of the starting dicarbonyl compound	Structural formula	color	m.p., °C	mol. wt.	cryst.	activation energy, eV	pre-exponential factor, σ_0, $\Omega^{-1} \cdot \mathrm{cm}^{-1}$	specific electrical conductivity, σ_{293}, $\Omega^{-1} \cdot \mathrm{cm}^{-1}$
Glyoxal	O=CH – CH=O	black	decomposes at 210	–	amorph.	1.60	8.91	$7.08 \cdot 10^{-12}$
Diacetyl	O=C – C=O CH_3 CH_3	yellow-orange	decomposes at 240	–	cryst.	1.56	2.14	$1.32 \cdot 10^{-13}$
Benzil	O=C – C=O C_6H_5 C_6H_5	orange	decomposes at 250	4494*5200**	amorph.	2.11	$2.04 \cdot 10^4$	$1.29 \cdot 10^{-14}$

Name of the starting dicarbonyl compound	Structural formula	color	m.p., °C	mol. wt.	cryst.	activation energy, eV	pre-exponential factor, σ_0, $\Omega^{-1} \cdot cm^{-1}$	specific electrical conductivity, σ_{293}, $\Omega^{-1} \cdot cm^{-1}$
4,4′-Diacetyldiphenylmethane	$O{=}C{-}C_6H_4{-}CH_2{-}C_6H_4{-}C{=}O$	light green	237–238	1000*	cryst.	1.88	$1.17 \cdot 10^3$	$6.17 \cdot 10^{-14}$
				CH_3		CH_3		
4,4′-Diacetyldiphenyl sulfide	$O{=}C{-}C_6H_4{-}S{-}C_6H_4{-}C{=}O$	light green	270–271	–	cryst.	2.46	$4.37 \cdot 10^6$	$2.51 \cdot 10^{-15}$
			CH_3		CH_3			
4,4′-Diacetyldiphenyl oxide	$O{=}C{-}C_6H_4{-}O{-}C_6H_4{-}C{=}O$	pale green	280–298with partial decomposition	1789***	cryst.	2.63	$1.74 \cdot 10^6$	$2.88 \cdot 10^{-16}$
			CH_3		CH_3			
4,4′-Diacetyldiphenyl ethylene glycol ether	$O{=}C{-}C_6H_4{-}OCH_2{-}CH_2O{-}C_6H_4{-}C{=}O$	pale green	255–258	–	cryst.	2.82	$2.24 \cdot 10^6$	$1.12 \cdot 10^{-18}$
				CH_3			CH_3	

Name of the starting dicarbonyl compound	Structural formula	color	m.p., °C	mol. wt.	cryst.	activation energy, eV	pre-exponential factor, σ_0, $\Omega^{-1} \cdot$ cm^{-1}	specific electrical conductivity, σ_{293}, $\Omega^{-1} \cdot$ cm^{-1}
Glyoxal		black****	does not melt	–	amorph.	1.22	0.309	$6.45 \cdot 10^{-11}$

* Determined by the isopiestic method.
** Determined by the ebullioscopic method.
*** Determined according to Rast.
**** Product of thermal decomposition of the polyazine.

electrical properties of the polymer. This is consistent with the recently obtained data of Dulov, Slinkin, Liogon' kii, and Rubinshtein[1], indicating that a decrease in the degree of conjugation may be compensated by an increase in crystallinity.

The introduction of heteroatoms of oxygen and sulfur between phenyl nuclei somewhat lowers the conductivity of the polymer. When the phenyl nuclei are separated by two oxygen atoms and two methylene groups, a sharp decrease in the conductivity of the polymer occurs, despite its crystallinity.

The data characterizing the properties of the polymers are summarized in Table 1.

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Received
27 VIII 1962

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

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[1] A. A. Dulov, A. A. Slinkin, B. I. Liogon' kii, A. M. Rubinshtein, DAN, **143**, 1355 (1962).