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Abstract

Full Text

PHYSICAL CHEMISTRY

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**ON THE DISRUPTION OF COPLANARITY
AND CONJUGATION IN CRYSTALLIZING
POLYMERS**

(Presented by Academician V. A. Kargin on 14 VII 1964)

In the present work we attempted to determine to what extent the emergence of crystalline formations during the formation of the solid phase is accompanied by disruption of conjugation between parts of the macromolecule because individual blocks of a polyconjugated system are brought out of coplanarity, and how this affects the optical, paramagnetic, and semiconducting properties. Since the question concerns the influence of the crystallinity* of a polymer on the properties of an individual macromolecule, the present work is a development, as it were "at the molecular level," of ideas about the influence of supramolecular structure on the properties of a polymer.

Whereas conformational changes due to rotation about an ordinary bond during the formation of crystalline regions in nonconjugated polymers have little effect on the properties of individual macromolecules, in polyconjugated systems analogous changes strongly affect the entire complex of chemical, optical, magnetic, and electrical properties of polymers, because individual blocks of the macromolecules are brought out of coplanarity and the associated disruption of conjugation arises.

When comparing the properties of a number of polymers with a system of conjugated bonds (molecular weight from 1500 to 8000), belonging mainly to the class of polyazines and poly-Schiff bases (Table 1), it is seen that the properties characteristic of polyconjugated systems are manifested to a greater extent in those substances which in the solid state have an amorphous structure.

Confirmation that amorphous polymers are characterized by a greater degree of delocalization of π -electrons is provided by: a shift into the red region of the long-wavelength edge in the electronic absorption spectra (the presence of a deeper coloration); the presence of an elevated background level in the IR spectra; and an increased intensity of the ESR signal, as a rule exceeding by 1-3 orders of magnitude the signal intensity of crystalline polymers having the same number of double bonds between phenyl rings.

In polymers whose X-ray diffraction patterns indicate high crystallinity, the properties inherent in polyconjugated systems are considerably weakened. This is especially clearly manifested when considering the properties of polyazines. Of the 10 polyazines synthesized in our laboratory, only 2 are X-ray amorphous, and it is precisely these polymers that possess a dark coloration, give a signal in the ESR spectrum, and have an elevated background level in the IR spectrum. Crystalline polyazines, in coloration, in the sharpness of the IR spectrum, and also in the absence of a signal in the ESR spectrum, are to a considerable degree similar to polyazines in which the conjugation segments are separated by atoms of oxygen, sulfur, methylene, and oxymethylene groups, although in the value of the activation energy of electrical conductivity and in their behavior during thermal destruction they differ from the latter, approaching amorphous polymers.

* By crystallinity here and below should be understood the detection of sharp reflections in X-ray structural investigations.

Table 1

No.	Polymers	Crystallinity	Color	e.p.r.	E , eV
1	[-CH-CH=N-]_n	amorph.	black	$7 \cdot 10^{17}$	2.6
2	[-C-C-N-]_n	cryst.	yellow	$1 \cdot 10^{14}$	2.2
3	[-C-C-N-]_n $\text{CH}_3 \text{CH}_3$	cryst.	yellow	$1 \cdot 10^{14}$	2.6
4	[-C-C-N-]_n $\text{C}_6\text{H}_5 \text{C}_6\text{H}_5$	cryst.	yellow	$1 \cdot 10^{14}$	—
5	[-N-C-C-]_n	cryst.	yellow	$1 \cdot 10^{14}$	2.6
6	[-C-C-N-]_n $\text{C}_6\text{H}_3(\text{CH}_3)-$ $\text{C}_6\text{H}_3(\text{CH}_3)-$ C= N-N-	cryst.	yellow	$1 \cdot 10^{14}$	2.8

No.	Polymers	Crystallinity	Color	e.p.r.	E , eV
7	$\left[\begin{array}{l} \text{N} - \text{N} = \\ \text{C}(\text{CH}_3) - \\ \text{C}_5\text{H}_3\text{FeC}_5\text{H}_3 - \\ \text{C}(\text{CH}_3) = \end{array} \right]_n$	amorph.	black	$2 \cdot 10^{15}$	1.5
8	$\left[\begin{array}{l} \text{C}(\text{CH}_3) - \\ \text{C}_6\text{H}_4 - \\ \text{O} - \\ \text{C}_6\text{H}_4 - \\ \text{C}(\text{CH}_3) = \\ \text{N} - \text{N} = \end{array} \right]_n$	cryst.	green	$1 \cdot 10^{14}$	3.2
9	$\left[\begin{array}{l} \text{C}(\text{CH}_3) - \\ \text{C}_6\text{H}_4 - \\ \text{CH}_2 - \\ \text{C}_6\text{H}_4 - \\ \text{C}(\text{CH}_3) = \\ \text{N} - \text{N} = \end{array} \right]_n$	cryst.	green	$1 \cdot 10^{14}$	3.2
10	$\left[\begin{array}{l} \text{C}(\text{CH}_3) - \\ \text{C}_6\text{H}_4 - \\ \text{S} - \\ \text{C}_6\text{H}_4 - \\ \text{C}(\text{CH}_3) = \\ \text{N} - \text{N} = \end{array} \right]_n$	cryst.	green	$1 \cdot 10^{14}$	3.4
11	$\left[\begin{array}{l} \text{C}(\text{CH}_3) - \\ \text{C}_6\text{H}_4 - \\ \text{OCH}_2\text{CH}_2\text{O} - \\ \text{C}_6\text{H}_4 - \\ \text{C}(\text{CH}_3) = \\ \text{N} - \text{N} = \end{array} \right]_n$	cryst.	green	$1 \cdot 10^{14}$	4.1
12	$\left[\begin{array}{l} \text{CH} - \\ \text{CH} = \\ \text{N} - \\ \text{C}_5\text{H}_4\text{N} = \end{array} \right]_n$	amorph.	brown	$3 \cdot 10^{17}$	2.0
13	$\left[\begin{array}{l} \text{CH} - \\ \text{CH} = \\ \text{N} - \\ \text{C}_4\text{H}_2\text{N}_2 = \end{array} \right]_n$	amorph.	brown	$2 \cdot 10^{16}$	2.1

No.	Polymers	Crystallinity	Color	e.p.r.	E , eV
14	$\text{[-C(CH}_3\text{)-C(CH}_3\text{)=N-C}_6\text{H}_4\text{-N]}_n$	amorph.	brown	$2 \cdot 10^{16}$	2.0
15	$\text{[-C(C}_6\text{H}_5\text{)-C(C}_6\text{H}_5\text{)=N-C}_6\text{H}_4\text{-N]}_n$	cryst.	yellow	$3 \cdot 10^{15}$	2.6
16	$\text{[-C(C}_6\text{H}_5\text{)-C(C}_6\text{H}_5\text{)=N-C}_4\text{H}_2\text{N}_2\text{-N]}_n$	cryst.	yellow	$1 \cdot 10^{15}$	2.0
17	$\text{[-CH=CH-CH=N-C}_4\text{H}_2\text{N}_2\text{-N]}_n$	amorph.	black	$1 \cdot 10^{18}$	1.7
18	$\text{[-CH=C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-N]}_n$	cryst.	yellow	$1 \cdot 10^{15}$	2.4
19	$\text{[-CH=C}_6\text{H}_4\text{-CH=N-C}_4\text{H}_2\text{N}_2\text{-N]}_n$	cryst.	yellow	$5 \cdot 10^{15}$	2.1

No.	Polymers	Crystallinity	Color	e.p.r.	E , eV
20	[- CH - CH = CH - CH = CH - CH = CH - CH = N - $\text{C}_6\text{H}_4 -$ $\text{N =}]_n$	amorph.	black	$4 \cdot 10^{18}$	—
21	[- CH - $\text{C(CH}_3\text{) =}$ CH - CH = CH - CH = $\text{C(CH}_3\text{)-}$ CH = N - $\text{C}_6\text{H}_4 -$ $\text{N =}]_n$	amorph.	brown	$2 \cdot 10^{18}$	—
22	[- CH - CH = CH - CH = CH - CH = CH - $\text{C}_6\text{H}_4(\text{CH =}$ $\text{N})(\text{N =}$ $\text{)-}]_n$	amorph.	brown	$9 \cdot 10^{16}$	—

(continued)

No.	Polymers	Crystallinity	Color	e.p.r.	E , eV
23	$\left[\begin{array}{l} \text{CH} - \\ \text{C}(\text{CH}_3) = \\ \text{CH} - \\ \text{CH} = \\ \text{CH} - \\ \text{CH} = \\ \text{C}(\text{CH}_3) - \\ \text{CH} = \\ \text{N} - \\ \text{phenylene} - \\ \text{N} = \end{array} \right]_n$	amorph.	brown	$3 \cdot 10^{17}$	—
24	$\left[\begin{array}{l} \text{CH} - \\ \text{CH} = \\ \text{CH} - \\ \text{CH} = \\ \text{CH} - \\ \text{CH} = \\ \text{CH} - \\ \text{CH} = \\ \text{N} - \\ \text{triazine ring} - \\ \text{N} = \end{array} \right]_n$	amorph.	brown	$3 \cdot 10^{18}$	—
25	$\left[\begin{array}{l} \text{CH} - \\ \text{C}(\text{CH}_3) = \\ \text{CH} - \\ \text{CH} = \\ \text{CH} - \\ \text{CH} = \\ \text{C}(\text{CH}_3) - \\ \text{CH} = \\ \text{N} - \\ \text{pyridine ring} - \\ \text{N} = \end{array} \right]_n$	amorph.	brown	$4 \cdot 10^{18}$	—
26	$\left[\begin{array}{l} \text{CH} - \\ \text{C}(\text{CH}_3) = \\ \text{CH} - \\ \text{CH} = \\ \text{CH} - \\ \text{CH} = \\ \text{C}(\text{CH}_3) - \\ \text{CH} = \\ \text{N}(\text{anisyl}) - \\ \langle \text{anisyl} \rangle \text{N} = \\ \end{array} \right]_n$	amorph.	mustard	$2 \cdot 10^{17}$	—

No.	Polymers	Crystallinity	Color	e.p.r.	E , eV
27	$\begin{array}{l} \text{[CH -} \\ \text{C(CH}_3\text{) =} \\ \text{CH -} \\ \text{CH =} \\ \text{CH -} \\ \text{CH =} \\ \text{C(CH}_3\text{) -} \\ \text{CH =} \\ \text{N(phenylene) -} \\ \text{(phenylene)N =} \\ \text{]}_n \end{array}$	amorph.	brown	$2 \cdot 10^{17}$	—
28	$\begin{array}{l} \text{[CH -} \\ \text{CH =} \\ \text{CH(phenylene)CH =} \\ \text{CH -} \\ \text{CH =} \\ \text{N(phenylene)N =} \\ \text{]}_n \end{array}$	cryst.	orange	$4 \cdot 10^{16}$	—
29	$\begin{array}{l} \text{[N -} \\ \text{thiazole ring -} \\ \text{CH =} \\ \text{N(phenylene)N =} \\ \text{]}_n \end{array}$	cryst.	orange	$3 \cdot 10^{16}$	—
30	$\begin{array}{l} \text{[} \\ \text{C(C}_6\text{H}_5\text{) -} \\ \text{C(C}_6\text{H}_5\text{) =} \\ \text{N - N =} \\ \text{C(CH}_3\text{) -} \\ \text{C(CH}_3\text{) =} \\ \text{]}_n \end{array}$	amorph.	brown	$4 \cdot 10^{17}$	—
31	$\begin{array}{l} \text{[} \\ \text{C(C}_6\text{H}_5\text{) -} \\ \text{C(C}_6\text{H}_5\text{) =} \\ \text{N - N =} \\ \text{C(CH}_3\text{) -} \\ \text{C(CH}_3\text{) =} \\ \text{]}_n \end{array}$	amorph.	brown	$5 \cdot 10^{17}$	—
32	$\begin{array}{l} \text{[} \\ \text{C(C}_6\text{H}_5\text{) -} \\ \text{C(C}_6\text{H}_5\text{) =} \\ \text{N - N =} \\ \text{CH(phenylene)CH =} \\ \text{]}_n \end{array}$	amorph.	brown	$2 \cdot 10^{17}$	—

Copolymers 30 and 31 were obtained at benzil-to-diacetyl ratios of 75 : 25 and 50 : 50, respectively.

The indicated correlation between the amorphous nature of polymers and their properties as polyconjugated systems also holds for poly-Schiff bases, although it is expressed somewhat less distinctly. Along with the enumerated features of polyconjugated systems, one should emphasize the increased activity of amorphous poly-Schiff bases, in comparison with crystalline ones, as photosensitizing agents in the reaction of photosensitized oxidation of ascorbic acid.

Like polyazines, poly-Schiff bases having a crystalline structure approach polymers with separated conjugation segments in the depth of color, the character of the IR spectrum, and paramagnetic properties, although in thermal stability and in the value of the activation energy of electrical conductivity they differ considerably from them.

The weakening, in crystalline polymers, of properties characteristic of polyconjugated systems can be explained by the following reasons. The maximum interplanar distances both in crystalline polyazines and in poly-Schiff bases do not exceed 8-11 Å. The length of the polymers studied (calculated from bond lengths), as a rule, exceeds this value severalfold. As is known, macromolecules of polymers, owing to their large dimensions, enter various crystalline formations as separate portions.

In addition, departure from coplanarity will always be energetically justified when dense packing of macromolecules in the crystal is incompatible with preservation of coplanarity. The energy expenditures associated with the loss of conjugation energy due to rotation about C-C or C-N bonds

(6-10 kcal/mol), can be compensated by the heat of crystallization, judging from the considerable endothermic effect of polymer melting, as was shown in a thermogravimetric study of the melting of polyazines.

A direct confirmation that the weakening of conjugation between individual parts of the macromolecule may be caused by a departure from coplanarity during crystallization would be the detection of shifts into the long-wavelength region of the electronic absorption spectrum upon melting or amorphization of crystalline polymers. However, polyschiff bases decompose upon melting, and crystalline polyazines cannot be amorphized, since on transition to the melt they are characterized by the presence of a liquid-crystalline state. Moreover, the latter persists up to the decomposition temperature of the polymers.

To obtain deliberately amorphous polyazines, we made use of the fact that disruption of the regular alternation of substituents in the main chain should hinder the formation of crystallizing polymers. We synthesized several copolymers by polycondensation of hydrazine with a mixture of dicarbonyl compounds, each of which individually forms with hydrazine a crystalline, diamagnetic, weakly colored polyazine. In the polycondensation of hydrazine with a mixture of diacetyl and benzil, and also of diacetyl and terephthalaldehyde, X-ray-amorphous poly-

mers were indeed obtained. As we expected, these polymers have a dark-brown color, give an EPR signal corresponding to a concentration of $2-5 \cdot 10^{17}$ spins/g, and in the IR spectra of these substances there appears the elevated background level characteristic of polyconjugated systems.

Thus, prevention of crystallization promotes preservation of coplanarity, which is expressed in the appearance in the polymers of the whole complex of properties inherent in polyconjugated systems.

All that has been said confirms our point of view that crystallization of polymers is accompanied by disruption of conjugation as a result of the departure from coplanarity of individual parts of the macromolecule. Everything discussed in the present article applies to linear polyconjugated systems in which, to take the macromolecule out of coplanarity, it is sufficient to rotate about $C-C$ or $C-N$ bonds.

Detection of the indicated regularity is made difficult when a crystalline phase is present in an amorphous polymer.

However, as is evident from the data of Table 1, the viewpoint advanced in the present work concerning the correlation of the properties of polyconjugated polymers with their crystallinity is confirmed in the overwhelming majority of cases.

As is known, the electrical conductivity of a substance is determined by the product of the concentration of charge carriers and their mobility ($\sigma = enu$).

Dense packing and regularity of structure, due to the crystallinity of the polymer, should apparently promote an increase in the mobility of the carriers; but at the same time, precisely as a result of crystallization, the lengths of the coplanar conjugated segments of the macromolecule decrease, which is accompanied by a decrease in the concentration of charge carriers owing to an increase in the excitation energy of the molecule. Since in polyconjugated systems with incompletely equalized bonds both the increase in concentration and the transfer of charge carriers from molecule to molecule are apparently activation processes, the influence of crystallinity on the semiconducting properties of polymers is determined in each individual case by the ratio of the changes in the activation energies of these processes.

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

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