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Abstract

Full Text

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NUCLEAR MAGNETIC RESONANCE IN POLYMERS WITH A SYSTEM OF CONJUGATED BONDS

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Polymers with a system of conjugated bonds in the macromolecule, possessing a number of practically valuable properties that are also interesting from the theoretical point of view, have been the subject of numerous investigations (^{1}). However, a number of important problems remain unresolved: in particular, there is no direct experimental evidence for deciding whether the molecules of polyphenylenes and their derivatives have a planar structure or whether neighboring nuclei are noncoplanar. In the present work an attempt has been made to apply, for clarification of this question, the NMR method, which in recent years has been successfully used to study the structure of polymers (^{2}).

Fig. 1. NMR spectrum of polyphenylene at a temperature of 175°

The objects of the investigation were the following polymers with a system of conjugated bonds: the benzene-soluble fraction of polyphenylene (PP), obtained by the Wurtz-Fittig reaction; polyazophenylene (PAP) (unfractionated and benzene-insoluble samples); and methyl-substituted polyazophenylene (MPAP), obtained by decomposition of bisdiazotized benzidine and *o*-tolidine with salts of monovalent copper. PP was reprecipitated with methanol from benzene solution. PAP and MPAP, after purification from copper, were washed with methanol. Benzene-insoluble PAP was obtained by extraction of the unfractionated polymer with benzene in a Soxhlet apparatus. All the samples listed were evacuated at 100° and 10^{-3} mm Hg.

On the basis of a study of a number of chemical and physicochemical properties (^{3}), the following general formulas were proposed for the indicated polymers:

$$\left[\mathrm{X} - \text{benzene ring} - \mathrm{X}\right]_n , \qquad \mathrm{PP}\ (\mathrm{X} = \mathrm{Cl});$$

$$\left[\mathrm{X}-\text{substituted biphenyl unit}-\mathrm{X}\right]_m\left[-\mathrm{N}=\mathrm{N}-\text{substituted biphenyl unit}-\mathrm{X}\right]_n, \qquad \begin{array}{l}\text{PAP } (\mathrm{R}=\mathrm{H});\\ \text{MPAP } (\mathrm{R}=\mathrm{CH_3})\end{array}$$

The number-average molecular weights are 1000–3000. All samples of the polymers studied give an EPR signal with an intensity correspond-

of 10^{17}–10^{18} spins/g. As a model substance, samples of quaterphenyl, subjected and not subjected to vacuum distillation, were used. The NMR spectra were recorded at temperatures of −196°, 20°, and 175° on the spectrometer described in (4).

At a temperature of −196°, all the substances studied give a simple NMR line, close in shape to a Gaussian. In quaterphenyl the same line shape is retained at room temperature as well. The spectra of the PP preparation at 20° have a complex structure and consist of two components—narrow and broad. The complex structure of the NMR line appears even more strongly in the spectrum of PP recorded at 175° (Fig. 1). Such a structure of the NMR line is characteristic of two-phase systems in which there are two kinds of protons with different mobility; apparently, the narrow component of the line is associated with protons of relatively low-molecular-weight fusible fractions, while the broad component characterizes the mobility of protons of macromolecules of infusible PP fractions, which constitute the main mass of the substance. After evacuation of PP (10^{-3} mm Hg at 180°), the intensity of the narrow component sharply decreases, and it is not visible at 20° and is very weakly expressed at 175°. Samples of PAP and MPAP give two-component NMR lines at 20°, and at 175°—very narrow NMR lines. Probably, in this case too the narrow line is due to the mobility of protons of relatively low-molecular-weight fusible fractions. In accordance with the considerations expressed, in the insoluble PAP preparation freed of low-molecular-weight fusible fractions

Table 1

Sample	−196° δH, G	−196° ΔH_Γ^2, G^2	20° δH, G	20° ΔH_Γ^2, G^2	175° δH, G	175° ΔH_Γ^2, G^2
Polyphenylene	7.5	10.6	5.6	6.0	5.0	–
Polyphenylene, evacuated	7.8	10.4	5.9	6.3	4.8	4.8
Polyazophenylene, unfractionated	6.6	8.6	4.8	5.0	<0.1	–
Polyazophenylene, insoluble	7.0	9.5	5.1	5.2	4.0	3.6

Sample	−196° δH, G	−196° ΔH^2_Γ, G^2	20° δH, G	20° ΔH^2_Γ, G^2	175° δH, G	175° ΔH^2_Γ, G^2
Methyl-substituted polyazophenylene	6.3	9.4	5.4	6.5	<0.1	–
Quaterphenyl	9.9	12.9	8.0	8.4	–	–
Quaterphenyl, purified by vacuum distillation	9.1	12.6	–	–	–	–

at 20 and 175°, only one broad NMR line is observed. Table 1 gives the values of the width δH and the second moment ΔH^2_Γ of the NMR lines. The values in Table 1 are averages from 3–5 spectra. For lines of complex shape, δH is given for the broad component; the width of the narrow component under the spectral recording conditions used was determined by the amplitude of the magnetic-field modulation.

For judging the structure of the substances, the value of the second moment at low temperature is of greatest importance: the experimental values of ΔH^2_Γ can be compared with theoretical ones calculated by the Van Vleck formula (5). The crystalline structure of quaterphenyl at room temperature is known from X-ray data (6).

The intramolecular contribution to the second moment calculated for this structure is $(\Delta H^2_\Gamma)_\text{v} = 8.8$ G^2, and the intermolecular contribution is $(\Delta H^2_\Gamma)_\text{m} = 2.7$ G^2. It may be assumed that upon cooling to −196°, the interatomic distances in the molecule change insignificantly, and only the distances between molecules are shortened. To estimate the increase in $(\Delta H^2_\Gamma)_\text{m}$, let us assume that the crystalline

the lattice contracts in the same way as in solid benzene (7), i.e., on average by 3%, which leads to an increase in $(\Delta H^2_r)_\text{m}$ by 20%, i.e., to 3.2 G^2. The total theoretical second moment for the rigid structure of quaterphenyl is therefore equal to 12.0 G^2. The experimental value of ΔH^2_r for the purified sample is 12.6 G^2. The agreement is quite satisfactory if one takes into account the accuracy of measuring the second moment, ±5%. Thus, the NMR data confirm the coplanarity of the quaterphenyl molecule.

To calculate the theoretical value of ΔH^2_r for PP, we shall initially assume a planar structure of the molecule, as in diphenyl, terphenyl, and quaterphenyl structural formula

Figure 2: structural formula

(8). The distances in the nuclei are C—C = 1.42 Å, between the nuclei C—C = 1.48 Å, C—H = 1.08 Å, and the angles between bonds are 120°.

For such a structure, $(\Delta H_r^2)_\mathrm{v} = 11.6$ G^2; of this value, 1.5 G^2 is due to the interaction of protons in a nucleus of the type $H_{(1)}$—$H_{(2)}$, and 9.9 G^2 to the interaction of protons of neighboring nuclei of the type $H_{(2)}$—$H_{(3)}$. For the value $(\Delta H_r^2)_\mathrm{m}$, one may apparently, without significant error, take the same value as for quaterphenyl–3.2 G^2. The total theoretical second moment for the planar structure of PP is then obtained as 14.8 G^2; allowing for possible errors in determining interatomic distances and in estimating the intermolecular contribution, we take the value 14.8 ± 1.5 G^2. The experimental value, taking into account the experimental error, is 10.5 ± 0.5 G^2, i.e., considerably smaller than the theoretical one. It is evidently impossible to explain such a large discrepancy by molecular motion, since at the temperature of liquid nitrogen the phenyl groups should be practically immobile. The only probable explanation remains the noncoplanarity of neighboring nuclei. Upon rotation of nucleus (a) relative to nucleus (b) about the C—C bond by $37 \pm 5°$, the interproton distance $H_{(2)}$—$H_{(3)}$ increases from 1.82 Å to 2.142—2.46 Å; the corresponding contribution to $(\Delta H_r^2)_\mathrm{v}$ decreases, and the theoretical value coincides with the experimentally determined quantity. An analogous conclusion can also be drawn for PAPh. For a planar structure with one azo group on average per 7 phenyl nuclei, $(\Delta H_r^2)_\mathrm{v} = 10.2$ G^2, $(\Delta H_r^2)_\mathrm{m} = 2.8$ G^2, the theoretical second moment is 13.0 G^2, and the experimental value at $-196°$ is $\Delta H_r^2 = 9.5$ G^2. The discrepancy corresponds to the same angle between the planes of neighboring nuclei. The introduction of CH$_3$ groups into the phenyl nuclei in the case of a rigid lattice should have significantly increased the second moment. An exact calculation of the theoretical value of ΔH_r^2 for MPAPh is difficult, since the position of the protons of the CH$_3$ groups is not determined. However, even without taking into account the interaction of methyl protons with the protons of the benzene nuclei, the increase in the second moment as compared with PAPh should be about 5 G^2. The experimentally determined value of ΔH_r^2 for MPAPh is no higher than for PAPh. This proves, first, that the methyl groups in MPAPh rotate already at a temperature of $-196°$, and, second, that neighboring nuclei are noncoplanar. The conclusion that, at low temperature, CH$_3$ groups bonded to benzene nuclei rotate is not unexpected: the same result was obtained for methyl-substituted polystyrenes at $-196°$ (9) and for hexamethylbenzene (10) even at helium temperatures.

The conclusion regarding the noncoplanarity of polyphenylene and polyazophenylene molecules agrees with our general ideas about the structure of polymers with a system of conjugated bonds (1,3) and may be due to recombinachemical reaction scheme

Figure 3: chemical reaction scheme

of excited biradical blocks in the process of polymer synthesis and by the formation of stable macromolecular double radicals of the type

and also by the fact that an increase in the length of the polyphenylene chain decreases the probability of the existence of a planar structure of the macromolecule.

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