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Studies of Polyacetylene by Magnetic Resonance Methods

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Results obtained in studies of polyacetylene (PA) by magnetic resonance methods are discussed. The structure and properties of the paramagnetic centres in PA are examined, and compared with the structure and the chemical composition of pure and of doped PA (i.e. PA with added electron donors and acceptors).
The bibliography includes 116 references.

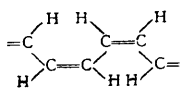
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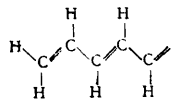
I. INTRODUCTION

In recent years polyacetylene (PA) has attracted much scientific interest because of its unusual electrical properties. An increase in electrical conductivity by 10–12 orders of magnitude has been obtained by adding donor or acceptor impurities (see Ref.1), equivalent to the transition from a dielectric to an "organic metal" with a conductivity $\sigma \cong 10^3\ \Omega^{-1}\ cm^{-1}$. In chemical composition polyacetylene $(CH)_x$ is the simplest of all the polymers with conjugated double bonds, whose conductivity is determined by the presence of impurities; therefore PA has been repeatedly chosen as a model system for studies of this unusual phenomenon. The properties observed in these studies appear to be general, and present in many other conjugated systems. Therefore the conclusions and hypotheses formulated from studies of the properties of PA may be equally applicable to other polymers with conjugated bonds. However, though PA is still the subject of most of the publications on polymers with conjugated bonds, papers on other similar systems have recently started to appear (polyphenylene and its derivatives, polypyrrole, etc.). These studies lack both the generality and the fullness of the work on PA, and in particular they do not provide a complete picture of the physical, chemical, and physicochemical changes resulting from the addition of impurities. Additional interest in the study of polymers with conjugated bonds has recently been stimulated by the development of effective methods of synthesis which allow the production of polymers with reproducible physicochemical properties.

We know[2-4] that the structure of PA consists of polymer chains in the *cis* or the *trans* form,



cis form



trans form

arranged in parallel bundles to form a fibre (or fibril) a few hundreds of Ångstroms thick and several thousands long. The long axes of these fibrils are randomly arranged, but they can be partially oriented by stretching the sample. Within each fibril the polymer chains are close-packed, and form a crystalline structure.[2,3] Thus PA is an unusual type of polycrystalline material, consisting of "crystalline fibrils".

This review discusses the properties of PA prepared by Shirakawa's method,[4] in which a stream of gaseous acetylene is directed at a thin layer of solution containing a Ziegler–Natta catalyst at 195 K. This produces a thin layer of polymeric material with a fibrillar structure. There are alternative methods of preparing PA, for example by first preparing an easily soluble polymer precursor and then heating it to give insoluble PA.[5,6] This material contains few defects, and is largely amorphous. However, most of the published work was done with PA prepared by Shirakawa's method.[4]

The fibrillar structure of PA facilitates its "doping", carried out as follows. The chemical additives ("dopants"), for example the electron-acceptor impurities I_2 or AsF_5, penetrate into the PA fibrils through their surface and interact with the polymer chains or among themselves. The result is the formation of the I_3^- or AsF_6^- anions, while part of the PA chain acquires a positive charge. Thus the addition of chemical impurities is only the first step in the doping of PA: the process includes several chemical changes and is completed by the partial conversion of the PA into an ion-radical salt containing charge transfer complexes.

Both doped and undoped PA have been extensively studied by magnetic resonance methods: ESR, NMR, electron–nucleus double resonance (ENDOR), dynamic nuclear polarisation (DNP), nuclear quadrupole resonance (NQR), and their time-resolved modifications. These methods offer varied and unique information on the structure of the polymer (bond length, size of conjugation regions, etc.), on the nature and properties of the paramagnetic centres, on the extent and nature of the doping, and on the distribution of charge and spin density in the polymer chains of undoped and of doped PA. This paper reviews the experimental studies of the structure and properties of PA by magnetic resonance methods. The theoretical foundations of the magnetic resonance methods and the apparatus used in this work are discussed in several monographs,[7-17] and will not be the object of this review. A generally

accepted model of the paramagnetic centre in PA has not yet been proposed, and as a result we still lack a unique terminology. In the present review we shall use general terms such as "paramagnetic defect", "unpaired electron", etc., avoiding as far as possible the term "soliton" applied by some workers to a particular model of defects in PA.

II. PARAMAGNETIC SUSCEPTIBILITY OF PURE PA

Like most conjugated systems, polyacetylene shows paramagnetism. This has been reliably established by studies of its static magnetic susceptibility (Faraday's method)[11] and by ESR measurements.[8,10,11] The paramagnetic susceptibility of *trans*-PA at room temperature is an order of magnitude greater than that of the *cis* isomer, and is equivalent on average to one paramagnetic centre per ~3000 CH units.[1,4,18–25] The molecular weight of the polymer is ~7000, i.e. the chains consist of approximately 400–500 CH units.[26] Obviously, this number depends on the method of synthesis of the PA. However, on average one paramagnetic centre is shared by 6–7 polymer chains.

In the ESR spectra of the *cis* and *trans* PA isomers we find a singlet line[19] with a g factor of 2.003, but in the *cis* isomer synthesised at 195 K the ESR signal with g = 2.003 is absent.[24,25,27,28] The signal appears only on raising the temperature, and at 300 K the concentration of paramagnetic centres reaches 10^{18} spins g^{-1} (i.e. one spin per 44 000 CH units). If the *cis* isomer at 77 K is irradiated with u.v. light[28] or treated with oxygen[24,25] it develops the same ESR signal as if the temperature is increased. On the other hand if a sample heated to room temperature is exposed to oxygen the amplitude of the ESR signal increases by almost an order of magnitude, and the width of the line (~8 Oe) stays almost unchanged.[24,25,27] The effect of u.v. irradiation and of oxygen on the *trans* isomer differs slightly from their effect on the *cis* isomer. The ESR signal is not increased by u.v. irradiation of the *trans* isomer. On exposure of this isomer to oxygen the signal initially increases, and then decreases,[24,29,30] while the width of the ESR line increases.[24,29]

Heating PA to 423 K produces a large increase in the number of paramagnetic centres according to the ESR results.[21,27,29] We know[31] that at 418 K an exothermic peak (attributed to *cis–trans* isomerisation) appears in the thermogram of polyacetylene. Heating of *cis*-PA produces two effects: *cis–trans* isomerisation and polymer degradation. It was reported[32] that the optimum region for the preparation of *trans*-PA is 413–423 K, because at these temperatures the rate of isomerisation is a maximum while the rate of degradation is still acceptably low.

It has been suggested[4] that the paramagnetism of PA is caused by the presence of defects: *cis*-PA has a more perfect structure, and it contains fewer defects than *trans*-PA. *Cis–trans* isomerisation results in an increase in the defect density of the polymer, accompanied by a corresponding increase in the absolute value of the paramagnetic susceptibility. Similar views are expressed in more recent papers (see, for example, Refs.21 and 27). The ESR signal observed in *cis*-PA at room temperature has been attributed[22,24] to the presence of ~5% of *trans*-PA in the sample. It was suggested that fragments of the *trans* isomer are localised at the ends of the polymer chain, where *cis–trans* isomerisation occurs most readily. Noting the similarity (Fig.1) between the temperature dependences of the concentration of *trans* isomers (obtained from the i.r. spectra) and of free radicals Zanobi and D'Ilario[28] suggested that isomerisation causes breaking of the double bonds with formation of regions containing an odd number of π electrons.

A simple model of a defect in *trans*-PA is the formation of a cross-link between chains.[33] Cross-linking produces a fragment with an odd number of carbon atoms, which contains an unpaired electron. The model in which defects are identified with cross-links is discussed in Ref.34. After the cross-link is established one radical appears in each chain: the energy of this biradical state was calculated by the quantum-chemical INDO method. Other workers[27–29] have expressed similar views on the causes of the effect of oxygen on the ESR signal in PA. Oxygen catalyses the *cis–trans* isomerisation process in PA and initiates the chemical oxidation of PA, i.e. it acts as a dopant of the acceptor type. At the same time the oxygen takes part in chemical reactions with the PA which result in degradation of the latter.

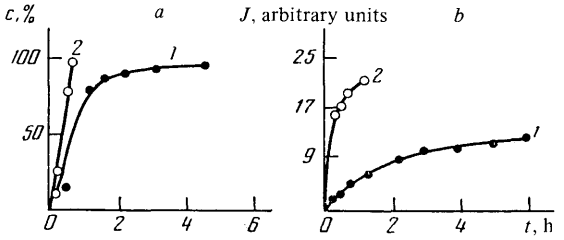


Figure 1. Kinetics of the change in the concentration of the *trans* isomer of PA (from i.r. data) (*a*) and in the concentration J of free radicals in PA (from ESR data) (*b*) as a function of the hold time t of the sample at 383 K (*1*) and 493 K (*2*) (from Ref.28).

No detailed studies of the effect of oxygen on the structure and properties of PA have yet been reported. Most workers give only a qualitative estimate of the effect of oxygen on their measurements (for example, they quote the dependence of a measured parameter on the time of exposure of the sample to air or to an oxygen atmosphere). However, oxygen has a marked effect on the paramagnetism of PA, as was clearly shown by Bernier and co-workers:[27] in the absence of oxygen these workers observed in *cis*-PA a broad signal from a catalyst present at a concentration of 0.2% of the number of CH groups, but after contact with oxygen this signal was completely suppressed, and was replaced by a narrow ESR signal of increasing intensity which was attributed to *trans*-PA.

Studies of the paramagnetic susceptibility χ of the *trans* isomer at 0.03–300 K have revealed the presence of Curie paramagnetism: the magnetic susceptibility χ_c is proportional to $1/T$.[4,16–18,35–41] Curie paramagnetism has also been observed[4,22,23] in *cis*-PA at 2–295 K. However, according to Tomkiewicz and co-workers[18] the magnetic susceptibility of the *cis* isomer is not described by Curie's law at 4–300 K. The reason for these discrepancies is not clear.

III. TYPES OF PARAMAGNETIC DEFECT IN PURE PA

All the experimental results obtained by ESR, ENDOR, and NMR methods indicate the presence of an unpaired electron in the π system. Careful measurements of the g-factor in undoped PA, and also in the *cis* and *trans* isomers doped with AsF_5, showed[19] that in every case

$g = 2.002634 \pm 0.000015$, which is much higher than the g-factor for the free electron (2.0023). These high values of the g-factor are characteristic of an unpaired electron in a π system.[10,11]

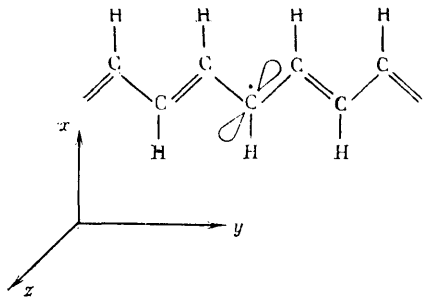


Figure 2. Orientation of the polymer axis with respect to the $2p$ π orbital of the paramagnetic defect in *trans*-PA.

In an ideal stretched film of $(CH)_x$ all the fibril axes (y) and therefore also the axes of the polymer molecules are oriented in the stretching direction. Partial orientation of the fibrils can be obtained by stretching the sample (film) in a particular direction.[42] The appearance of g-factor anisotropy in such a film can be explained in terms of the nature of the $2p$ π orbital of the paramagnetic defect (see Fig. 2): the unpaired π electrons occupy atomic orbitals perpendicular to the y axis (the fibril axis). ESR measurements[43] in the millimetric region gave very precise values of the g-tensor for the *cis* and *trans* isomers in oriented and in non-oriented samples at temperatures in the range 4.2–300 K. For *cis*-PA they found $g_{\parallel} = 2.004$ and $g_{\perp} = 2.003$ {where $g_{\parallel}$ and $g_{\perp}$ are for magnetic fields parallel and perpendicular (respectively) to the axis of the polymer chain}. These values of the g-tensor components agree with published data.[44]

The components of the g-tensor have also been calculated[43] by a special variant of the molecular orbital method[45] for *cis* and *trans* $(CH)_n$ fragments where n is an odd number between 5 and 15. In chains with $n \geq 9$ the g-factor has become independent of n, and can therefore be interpreted as the g-factor for a long fragment. The calculations were made for structures with C–C bonds of equal length and for structures with alternating double and single bonds. The g-tensors calculated for these two types of structure (with $n \geq 9$) were equal to the experimental values: according to the calculation $g_{\parallel} = 2.0034$ and $g_{\perp} = 2.0028$. The g-factor anisotropy ($|\Delta g| = |g_{\parallel} - g_{\perp}|$) for the $2p$ π electron in small molecules with conjugated bonds is usually 0.001–0.002.[46] The smaller value of this difference observed experimentally[43,44] can be attributed to a lower level of orientation of the polymer chains.

The components of the hyperfine interaction (HFI) tensor of the electron with the protons and the ^{13}C nuclei for *cis*-PA (with a 99% enrichment in ^{13}C) have been determined[43,47–49] by the ENDOR method (see Section IV). The symmetry of the tensors and the relative values of the isotropic and the anisotropic components suggest that the unpaired electron occupies a π orbital. This conclusion is confirmed by an ENDOR study[50] at 77 K of *cis*-PA films in which the polymer chains had been oriented by stretching the sample.

The presence of an unpaired electron in the π system is observed also in the NMR spectra, because local electronic configurations produce local anisotropic fields which interact with the magnetic nuclei. The high-resolution NMR technique has been used[51] to determine the diagonal elements of the chemical shift tensor (σ_{11}, σ_{22}, σ_{33}) on ^{13}C for the *cis* and *trans* isomers. Both isomers gave values of the tensor components typical of conjugated systems.

A study[52,53] of a mixture of PA isomers and of the pure *trans*-PA isomer by the electron spin echo (ESE) method showed that localised defects (possibly consisting of σ radicals) are present in PA in addition to the delocalised π defects. The concentration of localised defects is approximately 100 times lower than the concentration of delocalised defects, and therefore the magnetic behaviour of the system as a whole is determined mainly by the π defects.

IV. DELOCALISATION REGION OF THE UNPAIRED ELECTRON AND SPIN DENSITIES IN PURE PA

Table 1. Components of the HFI tensor (in MHz) for ^1H and ^{13}C (99% enrichment) in *cis*-PA, calculated from measurements at 136 K (Ref. 47).

Index	^1H			^{13}C		
	A_x	A_y	A_z	A_x	A_y	A_z
1	−0.5	−2.1	−1.1	−1.3	−1.3	−2.1
2	−1.8	−7.0	−3.9	−3.1	−3.1	7.0

Detailed studies of spin densities in solids are usually made by the ENDOR method. Table 1 shows the components of the HFI tensors obtained[43,47–49,54] from the characteristic ENDOR frequencies of *cis*-PA 99% enriched in ^{13}C. The experimental ENDOR spectrum for ^1H and ^{13}C is described by two pairs of tensors (of index 1 and 2) corresponding to the two types of carbon and hydrogen atom. The HFI tensor components given in Table 1 were obtained by numerical modelling of the experimental spectrum allowing for all the interactions of the electronic and nuclear spins in all the magnetic fields present in the system and using the appropriate relaxation times. As Table 1 shows, the HFI tensor for ^{13}C is characterised by an axial symmetry and small values of the isotropic HFI constants, typical of defects in the π system. The symmetry and the relative values of the diagonal elements of the tensor for the HFI with the ^1H nuclei are the same as for the α protons.[13] Thus both the symmetry and the value of the tensor elements for ^{13}C and for ^1H unambiguously indicate the presence of a paramagnetic defect (unpaired spin) on a π orbital and the existence of two types of carbon atom with an unpaired electron.

The following spin densities of the unpaired electron on carbon were calculated from the HFI tensors for ^{13}C (Table 1): $|\rho(C_1)| = 0.06$ and $|\rho(C_2)| = 0.02$.[47] Studies by triple electron–electron resonance[47] showed that the spin densities on these two types of carbon atoms have different signs: $\rho(C_1)$ is positive and $\rho(C_2)$ is negative, and these densities are alternating along the polymer chain. The signs and amplitudes of the spin densities suggest a substantial delocalisation of the π orbital on a region of the

chain approximately 47 CH units long (i.e. ~100 Å). An estimate of the total number of atoms ($2n + 1 \cong 47$) in the paramagnetic fragment is obtained from the condition $n\rho(C_2) + (n + 1)\rho(C_1) = 1$.[43] The interaction of the paramagnetic defect with the protons in 70% *cis*-PA is also thought[55] to be characterised by two sets of HFI parameters, corresponding to two values of the spin density on the carbon atoms differing in magnitude and in sign. In 70% *cis*-PA the delocalisation region of the unpaired electron was calculated[55] to be 93 CH units, i.e. double the value given in Refs.43 and 47.

The spin density has been calculated[43] by the methods of Hückel and McLachlan (of which the latter gives a negative spin density in π radicals) for $(CH)_n$ fragments with odd values of n between 3 and 99. Two types of structure were considered: with bonds of equal length and with alternating bond lengths. The latter model of the $(CH)_n$ fragments gave a qualitative agreement with experiment: an alternation of the signs along the chain, but the absolute density values show a large scatter which should prevent the formation of a resolved ENDOR spectrum (though such a spectrum is observed experimentally). The hypothesis of uniform bond lengths in $(CH)_n$ fragments with odd values of n has not so far been tested by any other method. Since the total number of carbon atoms associated with one spin in *trans*-PA is ~3000,[22] the 47 carbon atoms in the fragment with an unpaired electron and equal bond lengths accounts for only 1.6% of the total number of carbon atoms in the sample.[43] A calculation[50] of the frequencies of the ENDOR spectrum using the spin densities specified by the soliton theory[56,57] gave the best agreement with experiment when the corrections for negative spin densities were used. However, no definite conclusion as to the distribution of spin densities could be reached[50] from the ENDOR spectra obtained in this work.

The ENDOR spectrum of *trans*-PA is reported[55,58] to be singlet. The delocalisation of the paramagnetic defect in *trans*-PA is thought[55] to be very extensive, i.e. each carbon atom in the delocalisation region carries only a small fraction of the spin density. Therefore the hyperfine structure (HFS) is unresolved even when the ENDOR method is used.

V. VIEWS ON THE MOTION OF A PARAMAGNETIC DEFECT IN PA

The DNP method[12] has been widely used in studies of the static and dynamic characteristics of unpaired electrons in solids. It was first applied to the study of paramagnetic defects in PA by observing the NMR proton signal[59–61] in a saturated u.h.f. transition at a frequency close to the ESR resonance frequency (ν_e = 8190 MHz). Two extreme cases are possible, depending on whether the electron–nucleus interaction is static or dynamic.[9] For a static interaction the unpaired electrons are "fixed" in space (at least, their jumping frequency is smaller than the NMR frequency, ν_n), and forbidden transitions at the frequency $\nu_e \pm \nu_n$ are induced by the electromagnetic field. This is the so-called solid effect. On the other hand if the unpaired electrons are mobile (on the time scale of the frequency ν_e) the intensity of the NMR signal may be increased at the frequency ν_n (the Overhauser effect). In pure *trans*-PA at 300 K a single Overhauser effect was observed,[61] whereas a mixture of the *cis* and *trans* isomers gave a superposition of the Overhauser effect and of the solid effect. In the mixed samples the proportion of the Overhauser effect increases with the content of the *trans* isomer (see Fig.3).

In Ref.62 the same signal is obtained as in Ref.61 for the mixture of isomers, but a weak solid effect is reported, in addition to the Overhauser effect, for the pure *trans*-PA. This discrepancy may be due to an impurity of the *cis* isomer in the latter case.[62] The following conclusions were formulated from the results of Ref.61: 1) in the *trans* isomer the unpaired electrons are mobile, and the lower limit of their diffusion rate is ~5×10^{10} rad s^{-1} (determined from the ESR working frequency ν_e); 2) in *cis*-PA the unpaired electrons are fixed; 3) during the *cis–trans* isomerisation some previously fixed unpaired electrons become mobile.

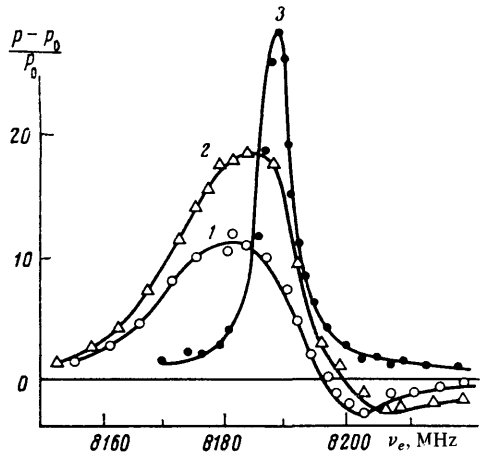


Figure 3. Increase in the amplitude of the ^1H NMR signal at different frequencies ν_e of the saturating field for concentrations of the *trans* phase in undoped PA of 50 (*1*), 65 (*2*), and 100% (*3*); T = 300 K (P_0 and P are the NMR signals without microwave saturation and with saturation respectively).

On cooling *trans*-PA we produce a change in the DNP signal: the characteristic signal of the pure Oberhauser effect (observed at room temperature) is replaced at 5.5 K by a signal corresponding to the solid effect.[63,64] The electrons which are mobile at high temperatures are slowed down, and their characteristic frequency, inversely proportional to the time of residence of the unpaired electron near the nucleus (i.e. the characteristic velocity of the electron), becomes smaller than the NMR frequency (10^7 s^{-1}). A smooth change from the Oberhauser effect to the solid effect has been observed[65] during temperature changes from 300 to 4 K (the two effects being comparable at 40–50 K). The exposure of *trans*-PA to oxygen produces the same effect as cooling the sample:[60] the presence of O_2 "freezes" the motion of the unpaired electron. The superposition of the signals corresponding to the Oberhauser effect and to the salt effect in the presence of air has been observed previously in other conjugated polymers.[66]

The study of the components of the g-tensor (ESR in the millimetre band) and of the HFI tensors (ENDOR spectra) for PA at 4–300 K led to the conclusion[43,47] that the paramagnetic centres are mobile in the *trans* isomer and fixed in the *cis* isomer. The presence of mobile paramagnetic centres in *trans*-PA is indicated also by ESE measurements on protonated and deuteriated samples at 4–300 K.[51–53,67,68] Masin

and co-workers[69] concluded from the kinetics of the damping of the NMR signal of ^{13}C that unpaired electrons are not generally found in PA. However, it has been pointed out[70] that this conclusion may be valid only for the particular samples studied in that work.[69]

VI. QUANTITATIVE CHARACTERISTICS OF A MOBILE PARAMAGNETIC DEFECT

The motion of the paramagnetic centre in PA is usually described in terms of the measured nuclear (T_{1n}) and electronic (T_{1e}) relaxation times by using formulae for two models of the motion: one-dimensional diffusion of the paramagnetic centre along the polymer chain and three-dimensional diffusion of the nuclear spin polarisation towards a fixed paramagnetic centre. For the first model of the motion a theoretical expression which had been previously applied in studies of the conducting tetracyanoquinodimethane (TCNQM)[61] has been proposed:[71-73]

$$T_1^{-1}(n) = kT\chi\left[\frac{3}{5}d^2\,\mathrm{i}(\omega_e) + \left(a^2 + \frac{7}{5}d^2\right)\mathrm{f}(\omega_e)\right] \qquad (1)$$

Here χ is the normalised spin susceptibility ($\chi = \chi_{mol}/\nu(g\mu_B)^2$, where ν is the concentration of paramagnetic centres); a and d are the constants for the isotropic and the dipolar electron–proton interaction respectively; $f(\omega)$ is the spectral density function; ω_n and ω_e are the Larmor frequencies of the nuclear and the electron spin respectively; μ_B is the Bohr magneton.

Eqn.(1) is valid when the electronic and the nuclear Zeeman energies are much less than kT, i.e. at relatively high temperatures ($T > 4$ K). For the one-dimensional diffusion of the paramagnetic centre, allowing for the HFI, the function $f(\omega)$ takes the form[74]

$$\mathrm{f}(\omega) = \frac{1}{(2W_{\parallel}\omega)^{1/2}} - C_L;\ C_L \approx 0{,}37\,\frac{L}{W_{\parallel}} \qquad (2)$$

where $W_{\parallel}$ is the diffusion rate of the electron along the chain, and L is the size of the delocalisation region.

The quantity $W_{\parallel}$ is related to the diffusion constant $D_{\parallel}$ by the expression

$$W_{\parallel} = D_{\parallel} b^{-2}$$

where b is the distance between the CH fragments along the chain of *trans*-PA ($b = 2.46$ Å). At low frequencies the one-dimensional diffusion can be perturbed by inter-chain jumps, so that the system behaves as two- or three-dimensional. The transition from one-dimensional to two- or three-dimensional motion occurs at the frequency $\omega_c = W_{\perp}$, where $W_{\perp}$ is the rate of inter-chain diffusion.

In the model which assumes diffusion of the polarisation of the nuclear spin towards a fixed paramagnetic centre the expression for $T_1^{-1}(n)$ is[9]

$$T_1^{-1}(n) = \frac{4}{3}\pi\rho T_{1e}^{-1/4}(\mu_B/\gamma_n)^{1/2}\bar{D}^{3/4}\omega_n^{-1/2} \qquad (3)$$

where $\bar{D}$ is the diffusion constant of the polarisation of nuclear spins and ρ is the electronic spin density.

It follows from the usual model[9] of the diffusion of nuclear spin polarisation that $T_1^{-1}(n)$ is independent of the magnetic field strength at a frequency below the value for which $\tau_c < \omega_n^{-1}$, where τ_c is the characteristic damping time of the z-component of the magnetisation of the unpaired electron (assuming an exponential decay), located in the vicinity of a relaxing nucleus. The quantity τ_c is determined by the electronic relaxation time T_{1e} or by the electronic "flip–flop" transition time (more accurately, by the shorter of these two times). Under these conditions $T_1^{-1}(n)$ should be independent of temperature in the region of weak magnetic fields.

Since all the quantities which appear in formulae (1) and (3) are experimentally known we can determing $\bar{D}$ or $W_{\parallel}$ by measuring $T_1^{-1}(n)$. This determination of the diffusion coefficients of the electronic or the nuclear polarisation becomes incorrect if the system of nuclear spins cannot be characterised by a single spin temperature. Experimental dependences of $T_1^{-1}(H)$ on ω_n at different temperatures have been obtained[61,66,71,75,76] for the protons of *trans*-PA. As Fig.4 shows, the dependence of $T_1^{-1}(H)$ on $\omega_n^{-1/2}$ is linear in the experimental temperature range 0.45–295 K, and the straight line for room temperature passes through the origin whereas the lines for lower temperatures give a finite intercept ($\sim C_L$) on the horizontal axis.[75] Various workers[60,61,66,71,75,77,78] have explained the experimentally observed dependences of $T_1^{-1}(H)$ on T and ω_n by postulating one-dimensional diffusion of the unpaired electron. Some believe[71,75] that even at 4 K 1.5% of the paramagnetic centres are mobile. Values of $W_{\parallel} = 4 \times 10^{13}$ rad s^{-1} and $D_{\parallel} = 4 \times 10^{-3}$ cm^2 s^{-1} were calculated[71] for 300 K. This value of the D diffusion coefficient is too high for a dielectric such as polyacetylene, and comparable with the D value for the metallic TCNQM salts.[72]

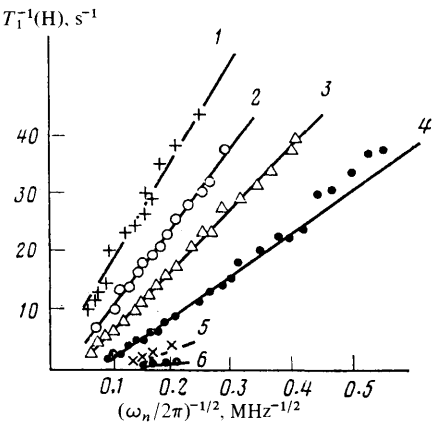


Figure 4. Rate of proton relaxation $T^{-1}(H)$ in *trans*-PA against $\omega_n^{-1/2}$ at 295 (*1*), 77 (*2*), 30 (*3*), 4.2 (*4*), 1 (*5*), and 0.45 K (*6*) (Ref.75).

The $W_{\parallel}$ value obtained from the ESE spectra[67,68,79] was three orders of magnitude lower than the above. The reason for this discrepancy is not clear, but a likely explanation is inadequacy of the chosen diffusion model. The $W_{\parallel}(T)$ dependence has been determined[71,75] from experimental data on the dependence of $T_1^{-1}(H)$ on ω_n at different temperatures and on the dependence of the width of the ESR line (ΔH) on T. A similar $W_{\parallel}(T)$ dependence, i.e. an increase in $W_{\parallel}$ with T, was obtained from an analysis of the ESE spectra.[67,68,79]

The results of a study of the effect on $T_1^{-1}(n)$ of the isotopic replacement of hydrogen by deuterium[65] at 4.2 K were interpreted[65] by the model of the diffusion of nuclear spin polarisation towards a fixed unpaired electron. The calculated[65] threshold value of the magnetic field for which the $T_1^{-1}(n) \propto \omega^{-1/2}$ dependence (characteristic of one-dimensional

diffusion) ceases to apply and the $T_1^{-1}(n)$ dependence becomes independent of the magnetic field is ~3 Oe, which is acceptably close to the experimental value (20 Oe). More recent results obtained[80] with *trans*-PA films (deuteriated, and enriched in ^{13}C) at room temperature are shown in Table 2. The $T_1^{-1}(n)$ values were measured on three samples containing different amounts of ^1H and ^{13}C. We can see from the Table that in the sample with a high concentration of magnetic nuclei $T_1^{-1}(H)$ exceeds $T_1^{-1}(^{13}C)$ by more than an order of magnitude. A similar result is reported in Ref.81, with $T_1^{-1}(H) \propto \omega^{-1/2}$, whereas $T_1^{-1}(^{13}C)$ is independent of frequency. The ^{13}C nuclei (in contrast to the ^1H and ^2H nuclei) show a non-exponential decay: the extent of damping varies with t approximately by a $t^{1/2}$ law. It was found[72] that the ^{13}C nucleus relaxes with two characteristic times (0.3 and 1.5 s), so that we should consider two different velocities: $T_1^{-1}(^{13}C) \cong 3\ s^{-1}$ and $T_1^{-1}(^{13}C) \cong 0.7\ s^{-1}$. Therefore the $T_1^{-1}(^{13}C)$ values given in Table 2 should be interpreted at best as the average of two velocities.

Table 2. Values of $T_1^{-1}(n)$ for three samples of *trans*-PA of different isotopic composition.

Sample	Isotope concentrations		ν, MHz	$T_1^{-1}(H)$, s^{-1}	$T_1^{-1}(^{13}C)$, s^{-1}
	[^1H], %	[^{13}C], %			
1	100	98	90	18±1	—
1	100	98	23	37.3±2	1.9±0.1
1	100	98	11.5	45±3	1.9±0.1
2	2	90	23	—	2.6±0.2
2	2	90	12	—	2.6±0.1
3	2	20	12	—	0.9±0.2
3	2	20	23	—	0.9±0.2

In planning the experiment with samples enriched in ^{13}C it was assumed[80] that $T_1^{-1}(H)$ and $T_1^{-1}(^{13}C)$ would have the same frequency dependence and absolute value, since the HFI constants of the unpaired electron in ^1H and ^{13}C are similar.[10,48,49,68] The assumption is valid if all the nuclear relaxation processes are determined exclusively by interactions with a mobile unpaired electron. From the lack of frequency dependence of $T_1^{-1}(^{13}C)$ (see Table 2) it follows that the results of the ^{13}C are not correctly described by the models which assume diffusion of the polarisation of electrons or nuclei. The following qualitative model of the relaxation for isotopic nuclei in the polymer chain was proposed.[80] In the case of nuclei in a polymer fragment containing a mobile paramagnetic defect the main relaxation channel is the HFI. Equilibrium between these nuclei and the others is reached as a result of the diffusion of nuclear spin polarisation: in other words, according to this model the system of nuclear spins cannot be characterised by a single spin temperature. Obviously, for a quantitative description of the experiments with ^{13}C further theoretical development of the unpaired electron diffusion model is required.† It has been suggested[65] that the views expressed in Ref.80 are the most likely to lead to a convincing explanation of the increasing volume of experimental $T_1^{-1}(n)$ data.

†A further theoretical development of this model has appeared in a paper by P.K.Kahol, M.Mehring, and X.Wu (J.Phys.(Paris), 1985, v.46, p.1683).

The rate of electronic spin–lattice relaxation T_{1e}^{-1} has been studied[84] in *trans*-PA in the frequency range 5–450 MHz at room temperature. For protonated and deuteriated samples the T_{1e}^{-1} values at frequencies $\geq$ 20 MHz are accurately described by the $T_{1e}^{-1} \propto \omega^{-1/2}$ relationship, previously established for the rates of proton relaxation.[61,66,71,75,76] The same relationship was obtained by other workers[68,82,83] at higher frequencies (9–17 GHz). At a frequency of ~20 MHz (with a field of ~6 Oe) a deviation from this relationship was observed,[84] and at frequencies < 10 MHz T_{1e}^{-1} was independent of frequency. The T_{1e}^{-1} values for deuteriated PA samples are somewhat lower (by ~50%) than the values for the protonated samples. The observed $T_{1e}^{-1}(\omega)$ frequency dependence was ascribed[84] to the one-dimensional diffusion of the unpaired electron along the polymer chain, and the frequency 10 MHz (3 Oe) was assigned to the inter-chain jumps.

As was stated above, the measurement of $T_1^{-1}(H)$ suggested that the diffusion ceases to be one-dimensional at a field strength of ~20 Oe, which is close to the value inferred from T_{1e}^{-1} data. A study[84] of the dependence of T_{1e}^{-1} on the concentration of paramagnetic centres in PA showed that the T_{1e}^{-1} value is determined by the dipole and hyperfine interactions of the unpaired electron with the protons. The coefficients and rate constants for diffusion of the unpaired electron were also determined,[84] and found to be close to the values determined[60,61,71] from measurements of $T_1^{-1}(H)$. We should stress that the interpretation of the T_{1e}^{-1} data is more unambiguous than the interpretation of the $T_1^{-1}(n)$ data, since the relaxation rate T_{1e}^{-1} is associated only with the diffusion of the unpaired electron.

The addition of dopants (Br_2, I_2, AsF_5) to PA has no effect[61,77,78] on the frequency dependence of the rate of proton relaxation $T_1^{-1}(H) \propto \omega_n^{-1/2}$, but it makes the relaxation rates $T_1^{-1}(H)$ and $T_1^{-1}(^{13}C)$ lower than in the pure PA.[1,67,69,77,78,85] The most marked decrease in these quantities is found by using AsF_5; I_2 and Br_2 have similar effects, almost an order of magnitude lower than that of AsF_5. The value $W_\parallel = 1.7 \times 10^{17}$ rad s^{-1} has been calculated[61] for PA doped with AsF_5: this is 10^3 times higher than the analogous value for undoped PA. The anisotropy ($W_\parallel/W_\perp$) is also not very different from that of the undoped polymer, i.e. ~10^6.

VII. PROPERTIES OF THE PARAMAGNETIC CENTRES IN PURE PA INFERRED FROM THE SHAPE OF THE ESR LINE

The shape of the ESR line depends on the properties of the paramagnetic centres in PA, but its analysis yields little quantitative information.# Early studies of the application of ESR to PA are mainly of historical interest, due to the fact that they stimulated the application of more advanced methods to the study of PA (ESE, ENDOR, and DNP).

The ESR signal in *cis* and *trans* PA is a singlet with $g = 2.0036$ (the measurements of the g-factor and g-tensor are discussed in Section III). Large differences are found between the determinations of the line width (ΔH) by various workers: from 7 to 9.5 Oe for the *cis* isomer[4,23,24,28,5] and from 0.28 to 5 Oe for the *trans* isomer,[60] i.e. the largest scatter occurs in the ΔH values for *trans*-PA. This is

#The same view is expressed in the theoretical paper by P.K.Kahol and M.Mehring (J.Phys.C, Solid State Phys., 1986, v.19, p.1045), whose aim was to demonstrate the unsuitability of the ESR method for determining spin densities and the delocalisation region of the unpaired electron from an analysis of the shape of the ESR line.

apparently due to differences in the preparative techniques used by different workers, since the parameter ΔH depends on the duration and temperature of the *cis–trans* isomerisation process, on the presence of oxygen, etc.

A special study[60] of the scatter in the measured values of ΔH suggested that the presence of uncontrolled amounts of oxygen is the main reason for the disagreement between the results of different workers. The smallest width of the ESR line obtained[60] by the meticulous application of all possible measures to prevent the access of oxygen to the system during all stages of the sample preparation and of the measurements was 0.44 Oe. This value is slightly higher than the value $\Delta H = 0.28$ Oe given in Ref.86. The line width $\Delta H = 1$ Oe in the spectrum of *trans*-PA is attributed[60] to the presence of 50 p.p.m. of oxygen. Special protective measures are needed to eliminate these very small contaminations.

The change from protonated to deuteriated PA produced a substantial narrowing of the ESR signal,[21,22,40] but a broadening of the ESR line was also reported[24] following the enrichment of *cis* and *trans* isomer samples with ^{13}C. The inconsistent changes in ΔH caused by isotopic replacement are due to differences in the magnetic moments of the nuclei ^1H, ^2H, and ^{13}C, and suggest the presence of an unresolved HFS. The absence of a resolved HFS in PA was initially attributed to exchange narrowing of the signal (see, for example, Refs.18, 19, 29, and 40). However, this work revealed a strong dependence of ΔH on T, which would not be expected for line narrowing by the exchange mechanism.[22,24,40,87] Fast one-dimensional motion of the paramagnetic centres has been suggested[22,40,60,63,87] as the reason for the narrowing of the ESR line.

The ESR line for *cis*-PA is Gaussian.[1] For the *trans* isomer in the temperature range 0–296 K a Lorentzian line, characteristic of exchange interaction, has been observed.[19] A Lorentzian line was reported[87] even when the temperature was lowered to 2 K, but deviations from this form were later observed. There have been attempts[22,56,60,63] to model the experimental spectrum by allowing for dipole–dipole and hyperfine interactions, repulsion between the electrons, and the one-dimensional diffusion of the unpaired electron along the chain. The model proposed in Ref.60 gives the best description of the experimental results. An analysis of the experimental line by this model showed[60,63] that the shape of the ESR line is different in different samples, and that it depends on temperature and on the presence of oxygen. In other words, it was made clear that the shape of the ESR line is not a fundamental property of PA itself. The width of the ESR line was not calculated exactly,[60] but the broadening due to the motion of the unpaired electron ($\Delta H = 0.15$ Oe) was estimated, and used to calculate the rate of diffusion along the chain $W_{\parallel} = 8 \times 10^{12} - 8 \times 10^{13}$ rad s^{-1}. This value of $W_{\parallel}$ agrees well with the value deduced from measurements of $T_1^{-1}(H)$ (6×10^{13} rad s^{-1}).[59]

This work[60] is the only reported instance of consistent diffusion rates $W_{\parallel}$ obtained from ESR and NMR measurements. The $W_{\parallel}$ values obtained by the two methods usually differ by a factor of 10–10^3.[60,88] According to calculations[22] based on an analysis of the ESR line shape ($\Delta H = 4$ Oe) the delocalisation region of the paramagnetic centre in *cis*-PA is ~14 CH units. For *trans*-PA a calculation of the second component M_{2e} of the ESR line[71] gives a delocalisation region of ~10 CH units for the soliton model of the distribution of spin density[56,89] or ~7 CH units if the spin density is assumed to be constant within the delocalisation region. However, by using the ENDOR values[43] of the spin density (see Section IV), which correspond to a delocalisation length of ~50 CH units, we again obtain good agreement between experiment and calculation for M_{2e} in protonated and in fully deuteriated PA. The calculation of the difference ΔM_{2e} by the formula[71]

$$\Delta M_{2e} = M_{2e} - M_{2e}^{*} = 140\Sigma\rho_i^2 \qquad (4)$$

where M_{2e} and M_{2e}^{*} are the second components of the ESR line for protonated and for deuteriated PA respectively, gives similar values for substantially different distributions of the spin density. Thus, $\Delta M_{2e} = 20$ Oe^2 for a constant ρ_i over a fragment 7 CH units long and $\Delta M_{2e} = 14$ Oe^2 for the model in which ρ_i is distributed (with a sign alternation) over 47 CH units.[43] The experimental value of ΔM_{2e} is 20 ± 4 Oe^2.[80]

VIII. CHARACTERISTICS OF DOPED PA FROM THE CHANGES IN PARAMAGNETIC SUSCEPTIBILITY AND FROM THE ESR SPECTRA

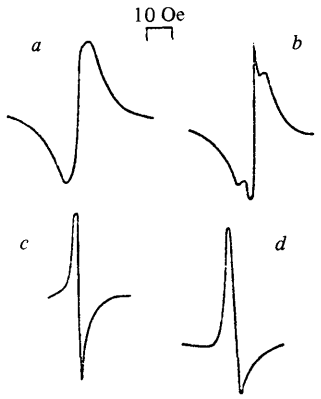


Figure 5. ESR spectra of *cis*-$[CH(AsF_5)_y]_x$ at room temperature and different dopant concentrations: (*a*) pure PA, (*b*) $y = 5 \times 10^{-4}$, (*c*) $8 \times 10^{-3} \leq y \leq 2 \times 10^{-2}$, (*d*) $y = 0.08$ (Ref.95).

The addition of the dopant Z (at concentration§ y) to PA produces a doped PA of composition $(CHZ_y)_x$ which has some of the properties of a metal, including electrical conductivity. According to Dyson's general theoretical considerations[90] on paramagnetic additives in metals an increase in y for $(CHZ_y)_x$ can result in asymmetry of the ESR line. In a large enough sample of doped PA, for which the sample thickness is greater than the depth of the skin effect at the ESR frequency, a typical Dyson (asymmetric) ESR line is observed (see Fig.5).[83,86,91–95] If the PA sample is thinner than the skin layer the line stays symmetrical even at high values of y.[96–99] Some workers[3,96,97] observed only one ESR line in PA doped with Li, Na, or Br_2, others[84,86,91,95,98] found two lines for *p*- and *n*-type dopants at low y, with different widths and a *g*-factor equal to that of the free electron, but at high doping levels ($y \geq 0.03$) only one line was observed (Fig.5). The combination of a broad and a narrow line is characteristic of different dependences of the intensity and shape of the line on the temperature, u.h.f.

§ The concentration y is defined as the number of molecules of dopant per CH unit.

power, and on the presence of NH_3 impurities. The broad line has been assigned[86,91,95,98] to a *trans* fragment in *cis*-PA, and the narrow line to *trans*-PA. According to some workers[86,95,97,98] the change in shape of the ESR line of *cis*-PA as a function of y suggests a large non-uniformity in the distribution of the dopant in the polymer, uniform doping in *cis*-PA being effectively impossible because of the presence of segments of the *trans* isomer. In this sense *trans*-PA is more easy to dope uniformly, but even for this isomer we can only expect a moderate degree of uniformity in the distribution of dopants in the sample.

According to Shirakawa[42] the Curie paramagnetic susceptibility χ_C is very sensitive to the degree of doping non-uniformity: the more uniform the dopant distribution, the lower is χ_C. Various methods of doping have been suggested to improve the uniformity: slow doping at low pressure,[36,37] cylic doping,[95] modified doping,[3] electrochemical doping,[96] etc. The structure of the dopant and its physicochemical properties[95] can also affect the doping uniformity.¶ The I_3^- ion is a linear cylindrical molecule with a diameter of 3.37 Å, and behaves as a weak electron acceptor; AsF_5 and SbF_5 are octahedral [owing to fluorine sharing (Editor of Translation)], with a maximum diameter of 6.24 Å, and have high oxidising power. These properties of AsF_5 and SbF_5 hinder their penetration into the fibrils, and therefore doping with iodine is more uniform than doping with AsF_5 or SbF_5. The formation of a concentration gradient of dopant within the fibril has been suggested[37] as part of a simple model of the dopant distribution which gives a good agreement between calculated and experimental values of the magnetic susceptibility.

Studies[86,91,95] of the ESR spectral changes of *cis*-PA caused by doping showed that doping can initiate *cis–trans* isomerisation, and that this effect is a characteristic of PA. Electrochemical doping of *cis*-PA with lithium did not produce significant changes in the intensity of the ESR signal.[91,96] Doping (like isomerisation) takes place at the surface of the sample in the initial stages). This accounts for the appearance of a compensation effect† in the ESR signal in the initial stages, resulting in slight swelling of the polymer and a small change (by ~15%) in the *cis/trans* isomer ratio.[86,95] Lengthy exposure to the dopant results in diffusion along the fibrils,[86,91] which is a slow process, and the *cis-trans* isomerisation now takes place in the bulk of the sample. At this stage of doping the concentration of defects can no longer be significantly decreased by compensation effects.[86]

A threshold concentration of dopant is needed to initiate the isomerisation;[91,96] its value is largely determined by the chosen doping technique.

It has been reported[91] that high rates of introduction of the additive yield smaller y values than lower rates. This is because at high rates the concentration of dopant on the fibril surface can rapidly reach the value which initiates isomerisation. At low doping rates there is time for the dopant to diffuse into the fibril and reach a *trans* segment. Since in *trans*-PA the oxidation potential (ionisation potential) is slightly lower[96] than in *cis*-PA we may expect preferential doping of the *trans* segment. In PA samples containing a large proportion of the *cis* isomer the addition of impurities at first initiates *cis–trans* isomerisation, followed by doping of the *trans* segments. The slight inconsistencies between the threshold values (y) of the dopant concentration reported by different workers can be attributed to differences in the isomer composition of the initial sample or to differences in the doping techniques.[91]

The isomerisation process is followed by charge transfer to the paramagnetic defect, which converts it into the diamagnetic state. This mechanism was established[91] from the time-changes of the ESR spectrum after doping. If the doping process is stopped at the instant when two superimposed singlets appear, after some time (~1 h) the narrow singlet from *trans*-PA disappears, leaving only the signal from *cis*-PA.

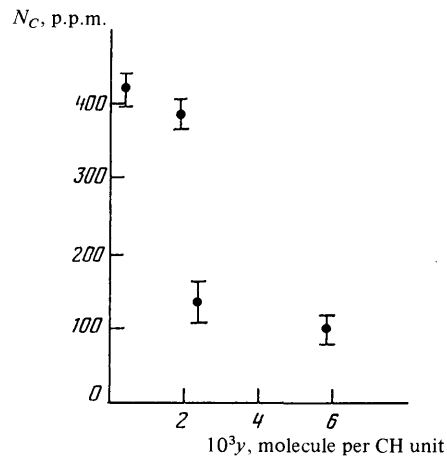


Figure 6. Change in the concentration of Curie spins N_C with the concentration of AsF_5 (y) in *trans*-PA (Ref.36).

By combining the ESR method with the Faraday compensation method it was shown that the addition of dopants to the *cis* and the *trans* isomers affects the nature and magnitude of the paramagnetism.[18,20,35–39,83,86] Thus, adding AsF_5 to *trans*-PA was found[36] to lower χ_C more than 400-fold for an increase in dopant concentration from 0.001 to 0.05. The change in spin concentration N_C corresponding to the paramegnetic Curie susceptibility for low concentrations of AsF_5 is shown in Fig.6. For *cis*-PA lightly doped with lithium ($y < 0.003$) the parameter χ_C decreases as y increases.[91] Under these conditions the temperature-independent Pauli paramagnetism is still insignificant (Pauli paramagnetic susceptibility $\chi_P \leqslant 5 \times 10^{-8}$ cm^3 mole^{-1}). In PA samples with a high concentration of AsF_5 only Pauli paramagnetism was observed[18–20,23,25,35–37,83,93] ($\chi_P \cong 10^{-6}$ cm^3 mole^{-1}). Doping with iodine did not produce Pauli paramagnetism even at high dopant concentrations.[38,39,99] Using AsF_5,[20,36] I_2,[37] and Na[97] as dopants produced a discontinuous increase in χ_P at concentrations in the region of 0.04–0.07. Fig.7 shows the dependence of χ_P on y[100] for samples doped with I_2 and AsF_5, and also the dependence of the conductivity σ on y. Clearly, we have a concentration range ($y < 0.05$) in which χ_P is still small but σ is already approaching the value corresponding to the metallic state. In contrast to

¶ See also J.C.W.Chien, J.M.Warakomski, and F.E.Karasz, J.Chem.Phys., 1985, v.82, p.2118.

†The compensation effect can be described as follows: at low doping levels the effects of donor (or acceptor) additives are suppressed by the subsequent addition of impurities of the "opposite" type i.e. acceptor (or donor) additives respectively.

this report, Pauli paramagnetism was observed[35] at very low concentrations of AsF_5 ($y \cong 0.005$), coupled with a smooth increase in χ_P with increasing y. Later work[101] showed the reason for this discrepancy between the experimental results. In Ref.35 the concentration of paramagnetic centres was determined by the ESR method, which gives a large error in the double integration due to the large asymmetry of the line. In Refs.36 and 100 the Schumacher–Slichter method[102,103] was used, which allows the absolute value of the paramagnetism to be calculated more precisely than the ESR method.

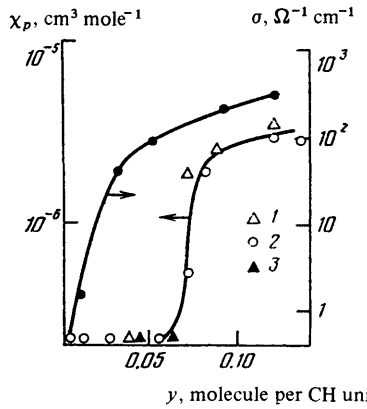


Figure 7. Dependence of the Pauli magnetic susceptibility χ_P and of the conductivity σ on the concentration of AsF_5 and I_3^- dopants.[100] The χ_P value for AsF_5 was obtained by the Faraday method (*1*) and from ESR data (*2*); the value for I_3^- by the Faraday method (*3*).

It has been suggested[4] that the carriers of charge and of paramagnetism are different species in PA, since the conductivity and the magnetic susceptibility have different temperature dependences: $\sigma \propto \exp(-AT^{-1})$ and $\chi_C \propto T^{-1}$. Other workers[19] came to the same conclusion. No correlation was observed[20] between the increase in magnetic spin susceptibility and the increase in σ when small amounts of AsF_5 were added to *trans*-PA (see also Fig.7). Different views are held at present on this behaviour of the electrical and magnetic characteristics of doped polyacetylene.

Some workers[19,20,36,37] interpret their experimental results on the changes in magnetic susceptibility of lightly doped PA in terms of the neutral soliton model.[56,89] However, a detailed examination of the experimental data from this standpoint reveals a number of inconsistencies (see, for example, Refs.20 and 54). Furthermore, neither the results of experiments with strongly doped PA nor the existence of a transition region in the $\chi_P(y)$ relationship are explicable in terms of the soliton model.

An alternative model[18,35] assumes the formation of metal-like regions, analogous to metal granules embedded in a dielectric. However, the application of this model also encounters serious difficulties.

IX. STRUCTURAL CHARACTERISTICS OF PURE AND OF DOPED PA FROM ^{13}C NMR DATA

The NMR signal from ^{13}C nuclei (at their natural enrichment level of 6%) for pure PA, obtained by rotation through the "magic angle", is a narrow line located at 127 p.p.m. for *cis*-PA and 137.4 p.p.m. for *trans*-PA (relative to the Me_4Si signal).[51,52,104] In samples of *trans*-PA with a 30% enrichment in ^{13}C a weak additional peak is observed at 47 p.p.m. (its intensity is 3.4% of that of the main peak). This peak has been attributed[104] to carbon atoms in a state of sp^3 hybridisation, i.e. the carbon atoms of the methylene groups. These groups interrupt the continuous conjugation of the polymer chain, giving an average length of the conjugated regions in *trans*-PA of about 30 CH groups. A content of methylene groups of 3.4% is confirmed by the element analysis, according to which the formula of PA is more accurately written as $(C_{1.00}H_{1.03})_x$ than as $(CH)_x$.

The changes in intensity, shape, and position of the two ^{13}C NMR peaks (127 and 137 p.p.m.) produced as a result of *cis–trans* isomerisation by heating pure *cis*-PA have been studied.[104] The *cis*-PA line is lowered by heating, but its width and position are unaffected. The *trans*-PA line undergoes changes in width and position (by ~1 p.p.m.) as the amount of *trans* isomer increases. This has been interpreted[104] as evidence that 1) the structure of partially isomerised *trans*-PA is different from that of pure *trans*-PA, and very inhomogeneous, and 2) the *cis* isomer has an ordered structure.

Nutation NMR[105] on pure PA prepared from acetylene enriched in ^{13}C (initially containing 6% of $H^{13}C{\equiv}{}^{13}CH$ molecules) showed that two types of bond are present in *trans*-PA, of length# 1.37 and 1.43 Å. The splitting in the nutation NMR spectrum of the two peaks corresponding to these bond lengths is ~300 Hz. If fast interconversion of the two types of bond were possible (as the soliton model stipulates) the two peaks would be replaced by a single peak. Hence we conclude that the interconversion does not take place, or that it takes place slowly (with a frequency much lower than 300 Hz).

Measurements of the second component of the ^1H NMR proton line led to the conclusion[106] that even a small concentration of I_2 ($y \cong 0.05$) causes almost complete *cis–trans* isomerisation, whereas according to ^{13}C NMR data the isomerisation is not complete even at higher doping levels.[107–111] This discrepancy may be attributed to differences in doping method (see Section VIII).

Studies of the ^{13}C NMR spectra of samples of composition *trans*-$[CH(AsF_5)_{0.07\text{б}}]_x$ and *trans*-$[CHK_{0.09}]_x$ showed[108] that the line shifts produced by doping towards lower fields (+9 p.p.m.) for AsF_5 and towards higher fields (−12 p.p.m.) for K (relative to the line for pure *trans*-PA) are chemical shifts (as also stated in Ref.109). In some earlier work[100,110] a different interpretation of these shifts had been proposed: the Knight shift. However, the Knight shift calculated[108] for these concentrations is only +2 p.p.m. Thus doping produces a change in the π electron density on the carbon atoms. As the π electron density is decreased (or increased) by one electron in the calculation the shift of the ^{13}C NMR line towards lower (or higher) fields is ~160 p.p.m. The reported[108] chemical shifts are satisfactorily consistent with the theoretical estimates (+12 and −14 p.p.m.) for the concentrations of AsF_5 and K used in those experiments.

The analysis of the ^{13}C NMR spectrum of the *trans*-$(CHI_{0.08})_x$ sample[108] showed (allowing for the fact that the true dopant was the I_3^- ion) that practically all the iodine atoms are converted into the I_3^- state and contribute to the charge transfer, and also that the peak at 47 p.p.m. for sp^3 hybridised carbon atoms is significantly stronger than in pure PA. This suggests a very slight degree of chemical compound formation between the iodine and the polymer,

#Similar values for the length of the C–C bonds were obtained by M.J.Duijvestijn, A.Manenchijn, J.Smidt, and R.A.Wind, J.Magnetic Resonance, 1985, v.64, p.461.

giving the fragment –CHI–. The volume of the undoped region was estimated[108] as 50%, since in the doped region the concentration of dopant was about double the average.

The ^{13}C NMR spectra for *trans*-$(CHBr_y)_x$ with $y = 0.661$ and $y = 0.103$ contain strong peaks in the 50 p.p.m. region. This indicates not only a high level of chemical compound formation between the bromine and the polymer (formation of the –CHBr– fragment) but also the formation of cross-links between neighbouring polyacetylene chains (the C atoms in the region of the cross-links are also in the sp^3 hybridisation state).[108]

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The results of magnetic resonance studies have given valuable information on the structure and properties of pure and of doped PA. The average length of the continuous conjugation regions in the polymer chains has been determined (about 30 CH units), and the alternation of bond length in the chain has been confirmed. It was shown that the paramagnetic centre or defect mainly responsible for all the magnetic properties of PA is the π electron. The delocalisation region of the paramagnetic π defect is found to vary between 7 and 93 CH units. In the *cis* isomer the paramagnetic defects are immobile, but in the *trans* isomer they are mobile at $T \gtrsim 50$ K and immobile at $T \lesssim 50$ K. Doping produces various structural and chemical changes in PA (*cis–trans* isomerisation, chemical changes of the dopant additives, reaction of the additives with the polymer, etc.). None of the models so far proposed can explain all the results obtained by magnetic resonance methods for PA: there is no generally accepted account of the mechanism of electronic and nuclear relaxation, various estimates of the size of the delocalisation region of the unpaired π electron are inconsistent, and existing models of the paramagnetic defect cannot explain the extensive group of reported magnetic measurements in a manner consistent with the results of electrical measurements. The ^{13}C high-resolution NMR method (and some of its modifications) appear to be the most promising approach to the structural study of PA.

While this review was being prepared the proceedings of two international conferences and of an international school on organic conductors, including PA, were published.[112–114] Most of the recent publications are new developments of previously formulated ideas, and they do not affect the main conclusions of the present review on the structure of PA. However, two recent papers deserve special mention for suggesting new ideas as well as improved experimental approaches.[115,116]

Holczer and co-workers[115] suggested that many of the effects observed in *trans*-PA could be attributed to surface phenomena, determined by specific aspects of the morphology of the polymer. Calculation shows that in PA synthesised by Shirakawa's method, with a specific surface of $10–100\ m^2\ g^{-1}$, ~20% of all the chains (1/5 of the total volume) are in contact with the surface, whereas in a normal solid the proportion of the atoms located in the first surface layer is $\sim 10^{-8}$.

Chien and Schen[116] studied by ESR the effect of the molecular weight (MW) of PA on the magnetic properties. They found that many of the characteristics of PA (concentration of paramagnetic centres in undoped and in doped PA, relaxation times T_{1e} and T_{2e} in the doped isomers) are insensitive to changes in MW between 500 and 870 000. However, in undoped PA the time T_{1e} decreases as the MW increases.

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