A broad-line nuclear magnetic resonance investigation of polyacrylonitrile phase structure and chain conformation

J. Grobelny, P. Tekely and E. Turska
Institute of Polymer Chemistry, Polish Academy of Sciences, 41-800 *Zabrze, Poland*
(*Received* 5 *September* 1980)

The investigation of polyacrylonitrile (PAN) phase structure has been carried out in connection with its chain conformation by means of analysing the shape, width and the second moment of ^{1}H *BL*-n.m.r. lines. A complex structure of the n.m.r. lines within the range of temperatures between −180°C and 115°C is interpreted as resulting from the presence of a specific conformation in the iso- and heterotactic sequences of PAN. A complex shape of the lines in temperatures above 115°C may be explained by heterogeneity of phase structure or by the polymer's microstructure. The line width was found to narrow in the vicinity of 95°C and within the range of 120°C and 160°C, which was attributed to certain changes in the nature of molecular motion. Theoretical and experimental values of the second moment of ^{1}H *BL*-n.m.r. line for rigid lattice of PAN were compared. The n.m.r. spectra of two polyacrylonitrile samples heat-treated at 200°C and deuterated respectively, were studied to confirm the presence of specific chain conformation.

INTRODUCTION

It is difficult to resolve PAN's morphology in detail. It belongs to the category of neither conventionally amorphous nor semicrystalline polymers. Lindenmeyer and Hosemann[1] suggested that PAN is paracrystalline. It is evident from X-ray analysis carried out by Bohn, Shaefgen and Statton[2], that PAN is a laterally ordered polymer, its nearest interchain distance being about 6 Å. These authors treat PAN as a polymer consisting of one phase combining some of the properties of both crystalline and amorphous phases. They also found a lack of order along the chain, independent of the conditions in which the sample was prepared. Hayakawa *et al.*[3], using the dielectric relaxation method, also treat this polymer as paracrystalline. In works by Andrews[4,5] it is suggested that PAN may be characterized as a polymer of 'heterobonded' solid-state structure, consisting of two different amorphous phases with various types of secondary intermolecular forces and of one crystalline phase[6]. Birefringence studies[7] of oriented PAN film also indicated at least a two-phase structure of this polymer, its well-ordered rigid phase being imbedded in a more easily softened matrix. This corroborates with the results presented by Hinrichsen and Orth[8−9], obtained by means of low-angle X-ray and electron microscope investigations as well as by means of dynamic methods—Imai *et al.*[10].

Kenyon and Rayford[11] showed, using mechanical relaxation, that PAN consists of three phases, namely: amorphous, paracrystalline and crystalline. The chain conformation of PAN was studied by Krigbaum and Tokita[12], who found that in isotactic sequences energetic factors determine the same type of helical conformation accepted for crystalline isotactic polyolefins. For syndiotactic sequences a different type of helical conformation is determined. A planar zigzag conformation was accepted by Hinrichsen and Orth[8] for syndiotactic structures. The same authors stated that these sequences belong to better ordered areas in a preferred manner.

The aim of this work was to analyse the structure of unoriented, atactic PAN in connection with its chain conformation by means of broad-line nuclear magnetic resonance investigations. This method enables observation of the differences between various areas of the polymer with regard to their order and molecular mobility. In some cases it is possible to record the fine shape of the n.m.r. line resulting from the presence of weakly interacting atomic groups in the macromolecule, thus making it possible to draw some conclusions concerning the conformation of the polymer chains.

EXPERIMENTAL

Preparation of the sample

Powdered PAN was prepared by radical polymerization of acrylonitrile in dimethylformamide solution with azoisobutyronitrile (AIBN) as the initiator at 60°C. The polymer was precipitated from 2% DMF solution with boiling distilled water, filtered off and vacuum dried at 40°C during 5 h. Afterwards it was washed with distilled water and dried again in the same conditions. The PAN contained some DMF residues, which was confirmed by i.r. spectrum analysis.

It is difficult to remove residual DMF because of the strong molecular interactions of a highly polar molecule of this solvent and PAN macromolecules containing strong nitrile dipoles. Despite extended vacuum drying the PAN still contains DMF residues[13]. The viscosity-average molecular weight of PAN was about 110.000.

The microtacticity of PAN was estimated by the $^{13}C-\{^1H\}$ n.m.r. method on a Varian CFT-20 spectrometer. The polymer consists of almost equal amounts of iso- and syndiotactic triads (each about 25%) and of 50% heterotactic triads[14].

0032-3861/81/121649-06$02.00

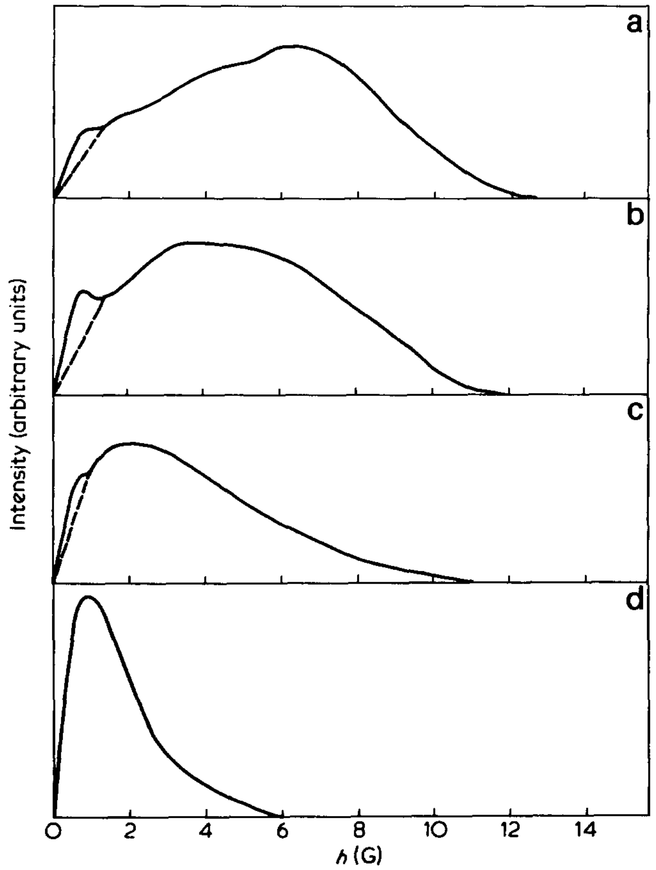

Figure 1 First derivative ^1H *BL*-n.m.r. absorption spectra of polyacrylonitrile (one-half shown) at (a) 20°C; (b) 97°C; (c) 122°C; (d) 160°C

Measurements

Measurements were carried out on a broad-line Varian WL-109 spectrometer at a resonance frequency of 30 MHz. The temperature was stabilized with an E-257/WL-257 device and measured with Ni-CrNi thermocouple, to within ±1°. ^1H *BL*-n.m.r. lines were recorded in conditions preventing saturation and overmodulation. The numerical analysis of the n.m.r. lines was performed on a WANG-2200B minicomputer.

The X-ray diagram of the PAN under study was performed on a DRON-1.5 diffractometer, while the i.r. spectrum on a SPECTROMOM 2000 spectrophotometer.

RESULTS AND DISCUSSION

Analysis of the line shape

The spectra of broad-line nuclear magnetic resonance ^1H *BL*-n.m.r. were taken as the first derivatives of the absorption curves. *Figure 1* presents the *BL*-n.m.r. lines observed for several temperatures. The line recorded at 20°C resembles the line observed at −180°C as far as the shape and value of their second moments are concerned. Therefore it is assumed that any analysis concerning the rigid lattice of PAN are of equal validity at room temperature. Within the wide temperature range the lines under study show a narrow component, originating from mobile DMF protons. This component is overmodulated in the recording conditions necessary to obtain a satisfactory spectral intensity. It was not taken into consideration when analysing the line shape.

To perform a detailed analysis of n.m.r. lines, the lines were divided into normalized components $y_i'(x,b_i)$ according to the equation[15]:

$$Y'_{\mathrm{calc}} = \sum_{i=1}^{n} a_i y_i'(x,b_i) \qquad (1)$$

where a_i is the relative amounts of the line components, and b_i, the parameters of the line broadening, resulting from interaction of proton groups.

The experimental spectrum y'_{exp} was compared to the spectrum calculated according to equation (1), minimizing the sum of squares of errors:

$$\varphi = \sum_{j=1}^{m} (Y'_{j,\mathrm{exp}} - VY'_{j,\mathrm{calc}})^2 \qquad (2)$$

in points $x_j = j \cdot 0.3$ G by the systematic change of the unknown values according to Marquardt's iterative method[16]. V in equation 2 is the n.m.r. spectrometer amplification factor. The best fit to the experimental lines within the temperature range 20°–115°C was obtained when dividing them into two components described with a normalized Gaussian function and the function $p(h)$ for a rigid two-spin system and taking into account the Gaussian broadening effect[17]:

$$y(x) = \int_{-\infty}^{+\infty} p(h) \cdot S(x-h)\mathrm{d}h \qquad (3)$$

The spectrum of a rigid, isolated pair of protons $p(h)$ consists of two lines, determined by equation [17]:

$$H = H_0 \pm \alpha(3\cos^2\theta - 1) \qquad (4)$$

where

$$\alpha = \frac{3}{2}\mu r^{-3} \qquad (5)$$

In equations 4 and 5, μ designates the magnetic moment of the proton, r, the distance between interacting protons, θ, the angle between the line connecting both protons and the direction of the external magnetic field H_0.

Figure 2a presents an example of a line divided in this way assuming isotropic distribution of such pairs. Between temperatures 20°C and ~115°C the α value for component 1 in *Figure 2a* changes within the narrow limits of 6.3 to 6.0 G, which corresponds with the change of the distance r between the two interacting protons within the range from 1.50 Å to 1.52 Å, this being accompanied by a simultaneous drop in the relative amount of this component in the spectrum from about 17% to 6% (*Figure 3*).

The observed change of the line characteristic for a two-proton system is not due to $-CH_2$ groups present in the polymer; otherwise the H–C–H angle necessary to bring the two protons to the distance of 1.5 Å would have to be distorted from its normal value of 109° 28′ to 88° 52′, which is clearly not possible.

To explain the origin of the observed shape of the line we assumed, here, such a conformation of the macromolecule chain of PAN, which would enable it to bring two protons to the distance calculated above ~1.5 Å. This is made possible by an irregular helical

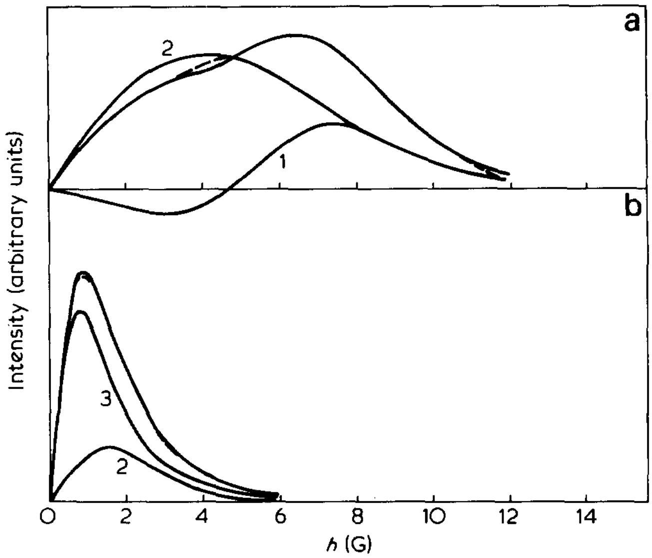

Figure 2 First derivatives ^{1}H *BL*-n.m.r. absorption spectra of polyacrylonitrile and their components (——) calculated; (– – –) experimental, at (a) 20°C and (b) 160°C: 1, component of two-spin system with Gaussian broadening; 2, normalized Gaussian component; 3, normalized Lorentzian component

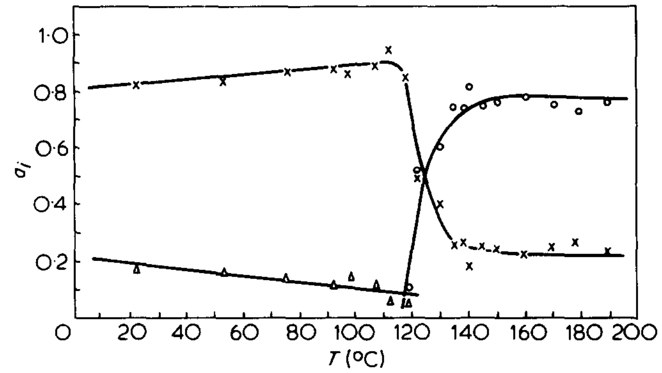

Figure 3 Relative amounts of the components of ^{1}H *BL*-n.m.r. spectrum of polyacrylinitrile as a function of temperature. △, Component of two-spin system with Gaussian broadening; x, normalized Gaussian component; ○, normalized Lorentzian component

conformation resulting from steric and dipolar intramolecular interactions leading to chain stiffening[2,18]. The existence of kinks and jogs[2,19] is characeristic for such a conformation. According to our opinion, it can make two protons from H–C–CN groups approach each other to the desired distance of 1.5 Å, these protons would constitute a relatively isolated pair of spins.

Because of dipolar and steric reasons[12] the possibility of bringing two protons to the distance of 1.5 Å exists in iso- and heterotactic triads of PAN, exclusively. This is confirmed by the amount of component 1 in ^{1}H *BL*-n.m.r. spectrum for a rigid lattice, amounting to about 17%. The calculations performed on the basis of ^{13}C–{^{1}H} n.m.r. spectrum lead to the conclusion that the amount of the analysed proton pairs should be 16.6%, there are 9 protons in PAN triads, of which only two protons can form a pair at a distance of about 1.5 Å.

When taking the amounts of isotactic triads (25%) and heterotactic triads (50%), we obtain:

$$\tfrac{2}{9}\cdot 25\% + \tfrac{2}{9}\cdot 50\% = 16{\cdot}6\%$$

The above considerations lead us to accept the conformation of PAN chains, for which iso- and heterotactic triads are characteristic in the existence of a specific conformation due to kinks and jogs.

Figure 4 shows the proposed conformation of iso- and heterotactic sequences.

For temperatures above 115°C the best fit of the calculated and experimental lines was obtained by dividing them into the normalized Gaussian component (component 2) and normalized Lorentzian component (component 3). In *Figure 2b* we present such a line, divided in this way, taken at 160°C, whereas *Figure 3* shows the change of the relative amount of line components with temperature.

The origin of a complex shape of a line in this temperature range cannot be explicitly interpreted at the present state of research. The occurrence of two line components may be due to the existence of chain fragments with different microstructure or to the phase heterogeneity of PAN. To solve this problem it seems to be necessary to perform analogical analysis of the swollen PAN. It is expected that in the analysed PAN there exists both amorphous and paracrystalline areas. The presence of the paracrystalline areas is confirmed by the X-ray diagram we obtained, which is typical for paracrystalline polymers[2,20].

Width of the line

The line width was measured as the distance between the extreme values of the absorption curve's derivative. Temperature dependencies of the widths of individual line components are shown in *Figure 5*. Line widths were

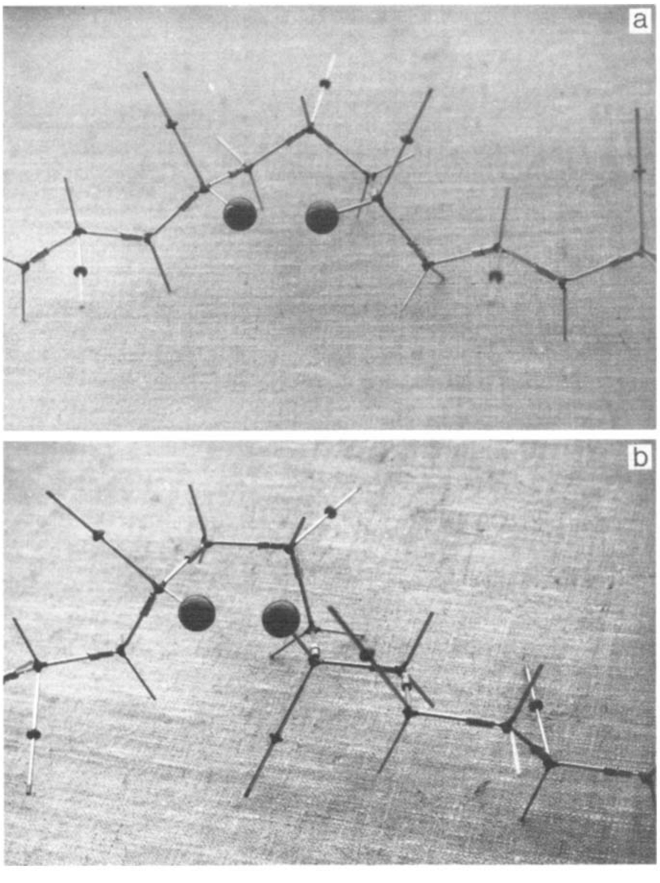

Figure 4 Proposed conformation of (a) iso- and (b) heterotactic sequences of polyacrylonitrile

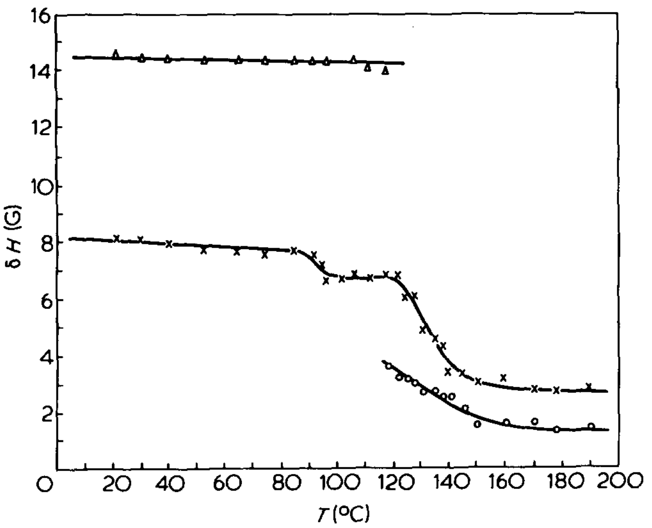

Figure 5 Plots of the width of ^{1}H *BL*-n.m.r. lines vs. temperature for polyacrylonitrile: △, component of two-spin system with Gaussian broadening; x, normalized Gaussian component; ○, normalized Lorentzian component

found to decrease, which is connected with changes of the character of molecular motion. The Gaussian component's width decreases from about 7.7 G to 6.7 G in the vicinity of 95°C and from 6.7 G to 2.7 G within the temperature range 120°–160°C (the main transition).

The Lorentzian component shows a narrowing of its width from about 3.5 G to 1.3 G between 120° and 160°C.

The majority of authors agree as to the existence of a glass transition between temperatures of 85°C and 110°C[21]. Andrews[4–6] claimed that the transition in the vicinity of 90°C corresponds to the glass transition of an amorphous phase with weaker cohesive forces. Other authors [2–3,10–11] relate this transition to a certain type of molecular motion in the paracrystalline phase.

The value of the n.m.r. line width's decrease within this temperature range (*Figure 5*) suggests that it is the result of thermally induced oscillations. In our opinion, this type of motion occurs mainly in amorphous areas of PAN.

At higher temperatures, Andrews[4–7,22] noticed a subsequent transition at 140°C, which is interpreted by the authors as the second glass transition, but this time for a more ordered or strongly cohesively bonded amorphous phase.

Studying oriented fibres of PAN by means of the *BL*-n.m.r. method, Olf[23] found that two transitions exist: at 120°C and at 175°C. This may be evidence for the existence of 'two major processes of chain segmental motion'. The author suggests that the transition at 120°C should not be called a glass transition.

Imai *et al.*[10] and Kenyon and Rayford[11] claimed that the transition observed by means of dynamic method at 140°C is related to the molecular motion in the amorphous area of the polymer.

In our opinion, the decrease in both the Lorentzian and Gaussian component widths in the temperature range 120°–160°C (*Figure 5*) result from the cooperative rotational and translational motions, typical for a glass transition T_g. Such a motional nature is confirmed by a high value of activation energy calculated below. The lack of difference in temperatures of these motion activations for both components (*Figure 5*) may prove that the chain conformation is identical in the amorphous and paracrystalline areas, assuming that both components originate from the phase heterogeneity of the polymer.

This conformation is determined by intramolecular interactions and is first of all responsible for the value of T_g. Constant values of the line components above a temperature of 160°C might indicate that the paracrystalline phase fraction is ~20%, and the amorphous phase ~80%.

The difference between the Gaussian and Lorentzian component widths above T_g may be a result of some order maintenance in the paracrystalline areas, as this order limits the mobility even above this point. X-ray investigations, carried out by Bohn *et al.*[2] proved that only at temperatures from 250°C to 270°C this characteristic order gradually deteriorate and disappear.

Calculation of correlation times and activation energy of the main transition

Time correlation value, τ_c, is described by the modified[24,25] theory by Bloembergen, Purcell and Pound[26]

$$\tau_c = \frac{8\ln 2}{\gamma\cdot\delta H} tg\left[\frac{\pi}{2}\left(\frac{\delta H - B^2}{C^2 - B^2}\right)\right] \qquad (6)$$

where γ is the gyromagnetic ratio of the nucleus under study, δH[G] designates the line width in the transition range, B, C[G] are the line widths above and below the transition temperature range, respectively. On the basis of the obtained experimental data we calculated correlation time values for the main transition temperature range. The activation energy value E_a was calculated from the Arrhenius equation:

$$\tau_c = \tau_0 \exp(E_a/RT) \qquad (7)$$

The plot of the function $\ln\tau_c = f(1/T)$, presented in *Figure 6*, was prepared on the basis of the results obtained. The

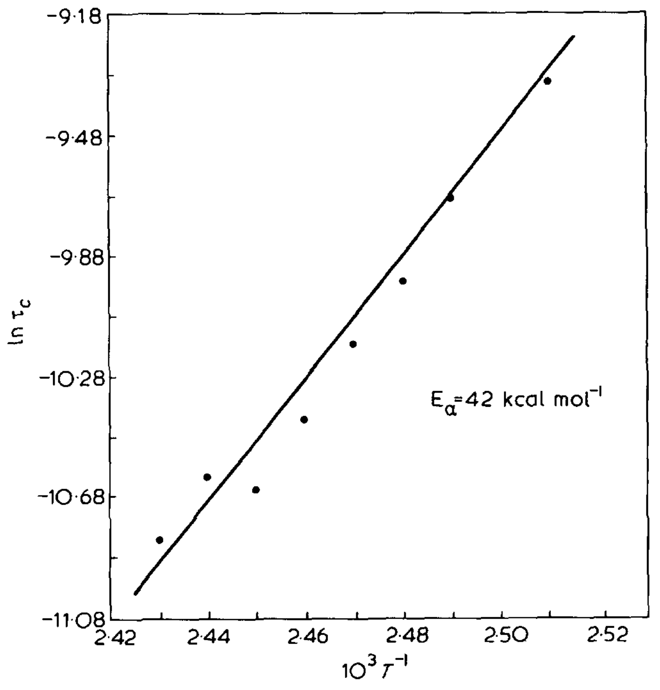

Figure 6 Variation of the correlation time with temperature in the range of main transition for polyacrylonitrile

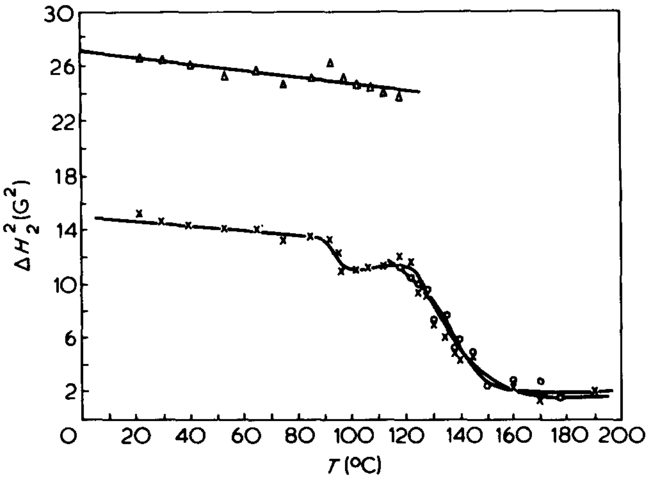

Figure 7 Plots of the second moment of ^1H *BL*-n.m.r. lines vs. temperature for polyacrylonitrile. △, Component of two-spin system with Gaussian broadening; x, normalized Gaussian component; ○, normalized Lorentzian component

activation energy value of the transition between 120°C and 160°C was calculated to 42 kcal mol^{-1}, which is shown to be in accordance with the value given by Andrews[6].

Second moment of the line

The second moment of the resonance line is defined by the equation[27]:

$$\Delta H_2^2 = \int_{-\infty}^{+\infty} h^2 g(h) \mathrm{d}h \tag{8}$$

where h designates the external magnetic field deviation from the resonance value, and $g(h)$ stands for the absorption function. Temperature dependency plots of the second moment's value shown in *Figure 7* have a similar course as in the case of the line widths. The conformation of PAN chain, may be confirmed on the basis of comparing theoretical and experimental values of ΔH_2^2, with the following requirements to be fulfilled:

(i) experimental values of the second moment should be taken from the spectrum for the polymer rigid lattice;

(ii) the intermolecular region of the second moment of the line ought to be negligibly small as compared with the intramolecular one.

The first requirement is fulfilled, whether we consider the spectrum taken at room temperature, or at −180°C, as the values of ΔH_2^2 for both of the components and of the total n.m.r. line are similar in both cases. It is clear when connected with greater stiffness of the PAN macromolecule[2,12,18]. The intermolecular part of the second moment may be neglected because of the large interchain distance. The latter, calculated from the X-ray diagram, is about 6 Å. A similar value was obtained[2] for oriented PAN fibres. Krigbaum and Tokita[12] found that enthalpy and entropy of melting has a low value in connection with a high value of the melting point, which lead Bohn *et al.*[2] to the conclusion that PAN consists of stiff chains with weak interchain forces. Thus, the second requirement may be assumed as fulfilled. The total experimental value of the second moment at −180°C is 17.5 G^2. The calculated value of the second moment for PAN triads, in which two protons approach each other to the distance of about 1.5 Å, is 19.4 G^2. For triads, in which no such approach can be found (i.e. for syndiotactic triads, that give 25% of the analysed polymer), a value, corresponding to a planar zigzag conformation amounting to 11.5 G^2, was accepted. Therefore, the calculated value of the second moment for PAN chain is:

$$\Delta H_2^2 = 19.4 \cdot 75\% + 11.5 \cdot 25\% = 17.4 \text{ G}^2$$

The theoretical values ΔH_2^2 were found on the basis of the equation[28]:

$$\Delta H_2^2 = \frac{18}{5} \frac{\mu^2}{N} \sum_{j>k} r_{jk}^{-6} \tag{9}$$

where r is the distance between the protons, μ designates the magnetic moment of the proton, and N stands for the number of analysed protons (for a PAN triad, $N = 9$). The calculated value approximately equals the experimental value of the second moment, this leads us to the conclusion that the assumed conformation of PAN chains seems to be correct. Both the observed shape and the second moment value of ^1H *BL*-n.m.r. line are well explained by the assumed conformational model of PAN chains, in which two protons from H–C–CN groups approach each other to about 1.5 Å. However the possibility of other protons mutually approaching, which would similarly effect the shape and the second moment value of the n.m.r. line, can also be taken into account. At the present state of research the above model is treated as satisfactory, because of the simplicity of the model of two interacting protons and its good accordance with the experiment, achieved within its framework.

Effect of heat treatment and deuteration of PAN on ^1H BL-n.m.r. spectral characteristics

To obtain additional confirmation of the assumed interpretation of the shape of ^1H *BL*-n.m.r. line and connected with it the suggested PAN chain conformation, the following procedure was performed: the polymer was heat treated at 200°C while n.m.r. and i.r. spectra were recorded at room temperature after time $t_{\text{heat treat}} = 2, 4, 6, 8$ and 10 h of thermal treatment. As previously described[21,29], at 200°C an autocatalytic cyclization reaction is the main process taking place in the polymer. Isotactic chain configuration is required[29,30]. The analysis of i.r. spectra indicates that the intensity of the absorption band of the CN group gradually decreases (at about 2250 cm^{-1}) and that at about 1600 cm^{-1} a band appears, the intensity of which is found to increase. This band is attributed to the  $\text{>C=N—}\overset{|}{\text{C}}\text{=N—}$ system formed after the cyclization. Simultaneously on ^1H *BL*-n.m.r. spectra we can see, together with the heat-treatment time, a decrease in the two-spin component amount (protons at a distance of 1.5 Å). The cyclization reaction may take place only at a suitable nearing of nitrile groups. Therefore, during heat-treatment it was necessary to change the assumed isotactic sequence conformation, causing the pair of protons to depart. Such reasoning is confirmed by the decrease in the relative amount of component, originating from such a pair on the ^1H *BL*-

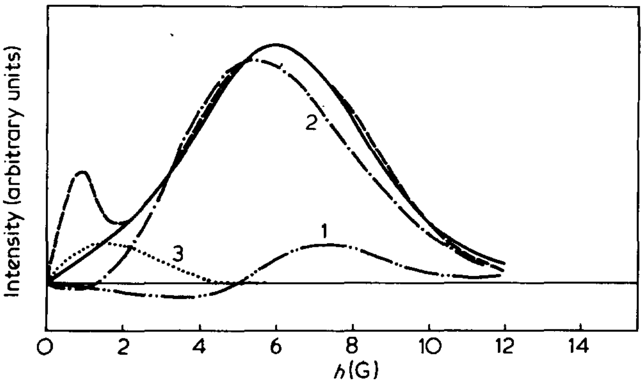

Figure 8 First derivative ^{1}H *BL*-n.m.r. absorption spectrum of deuterated polyacrylonitrile (PAN – αd$_1$) and its components (——) calculated; (– – – –) experimental at 20°C: 1, component of two-spin system, where H–H distance is 1.5 Å; 2, component of two-spin system, where H–H distance is 1.79 Å (CH$_2$ group); 3, normalized Gaussian component

n.m.r. spectrum. Thus, it can be assumed that investigation of the shape of ^{1}H *BL*- n.m.r. line of a heat treated PAN also confirms the concept of its chain conformation, presented here.

The concept of PAN chains conformation assumed by us may also be affirmed by the analysis of the ^{1}H *BL*-n.m.r. line of PAN deuterated in α position (PAN – αd$_1$). PAN – αd$_1$ was obtained analogically to undeuterated PAN by polymerization of a monomer deuterated according to the mode described by Leitch[31].

High resolution proton magnetic resonance spectra of both a monomer and polymer indicate a considerable degree of deuteration.

^{1}H *BL*-n.m.r. line of a deuterated polyacrylonitrile taken at room temperature is shown in *Figure 8*. The numerical analysis of the line was carried out without considering the presence of the narrow component which originates from DMF protons. The analysis proved that the other part of the line may be best divided into three components, described respectively by:

(1) function for a rigid two-spin system, where H–H distance is 1.5 Å; (2) function for a rigid two-spin system, where H–H distance is 1.79 Å (CH$_2$ group); (3) normalized Gaussian function.

The new component's (2) manifestation was possibly due to the decrease in intramolecular interaction, which results from the replacement of some of the protons from the H–C–CN groups with deuterons. This fact seems to support the concept that protons from CH$_2$ groups do not take part in nearing of the protons described by component 1. The conclusion may be formulated that the latter component may be attributed to pairs of protons at the distance of about 1.5 Å, the protons being from H–C–CN groups. The relative amount of component 1 decreased as compared with its amount in the spectrum of undeuterated PAN. Component 3 in our model describes the rest of the protons from H–C–CN groups, which do not take part in the nearing.

As it is evident from the above considerations, the analysis of ^{1}H *BL*-n.m.r. line of the deuterated PAN also confirms our conclusions concerning chain conformation of this polymer.

CONCLUSIONS

(a) The analysis of the ^{1}H *BL*-n.m.r. line as regards its shape and its second moment proved that the conformation assumed for PAN chains leads to a high proton nearing in the iso- and heterotactic sequences.

(b) Temperature increase leads to the activation of two types of molecular motion in PAN: in the vicinity of 95°C, attributed to thermally induced rotational oscillations in the amorphous areas and within the range from 120°C to 160°C, attributed to cooperative motions, typical for a glass transition, of longer fragments of macromolecules in the whole polymeric material.

(c) The complex shape of the n.m.r. lines at temperatures above 115°C may result from either the phase heterogeneity of the investigated PAN or the existence of chain fragments of various tacticity values.

REFERENCES

1 Lindenmeyer, P. H. and Hoseman, R. J. *Appl. Phys.* 1963, **34**, 42
2 Bohn, C. R., Schaefgen, J. R. and Statton, W. O. *J. Polym. Sci.* 1961, **55**, 531
3 Hayakawa, R., Nishi, T., Arisawa, K. and Wada, Y. *J. Polym. Sci.* (*A-2*) 1967, **5**(**1**), 165
4 Andrews, R. D. and Kimmel, R. M. *J. Polym. Sci.* (*B*) 1965, **3**, 167
5 Andrews, R. D. *J. Polym. Sci.* (*C*) 1966, **14**, 261
6 Andrews, R. D., Miyachi, K. and Doshi, R. S. *J. Macromol. Sci.-Phys.* (*B*) 1974, **9**(**2**), 281
7 Andrews, R. D. and Okuyama, H. *J. Appl. Phys.* 1968, **39**, 4909
8 Hinrichsen, G. and Orth, H. *J. Polym. Sci.* (*B*) 1971, **9**, 529
9 Hinrichsen, G. *J. Polym. Sci.* (*C*) 1972, **38**, 303
10 Imai, Y., Minami, S., Yoshihara, T., Joh, Y. and Sato, H. *J. Polym. Sci.* (*B*) 1970, **8**, 281
11 Kenyon, A. S. and Rayford, Mc. C. J. *J. Appl. Polym. Sci.* 1979, **23**(**3**), 717
12 Krigbaum, W. R. and Tokita, N. *J. Polym. Sci.* 1960, **43**, 467
13 Stupp, S. I. and Carr, S. H. *J. Polym. Sci.* (*A-2*) 1977, **15**(**3**), 485
14 Turska, E., Gorbelny, J., Dworak, A. and Adamowicz, H. *Acta Polym.*, in press
15 Bergmann, K. and Nowotki, K. *Kolloid Z. Z. Polym.* 1967, **219**, 132
16 Marquardt, D. W. *J. Soc. Ind. Appl. Math.* 1963, **11**, 431
17 Pake, G. E. *J. Chem. Phys.* 1948, **16**, 327
18 Olive, G. H. and Olive, S, Advances in Polymer Science—32, Springer Verlag, Berlin–Heidelberg–New York, 1979
19 McCullough, R. L. *J. Macromol. Sci.-Phys.* (*B*) 1974, **9**(**1**), 97
20 Corradini, P., Stereochemistry of Macromolecules Vol. 3, J. Wiley and Sons, New York, 1966
21 Kimmel, R. M. and Andrews, R. D. *J. Appl. Phys.* 1965, **36**(**10**), 3063
22 Miyachi, K. and Andrews, R. D. *Appl. Polym. Symp.* 1974, **25**, 127
23 Olf, H. G. *Appl. Polym. Symp.* 1974, **25**, 103
24 Kubo, R. and Tomita, K. *J. Phys. Soc. Jpn.* 1954, **9**, 888
25 Gutovsky, H. S. and Pake, G. E. *J. Chem. Phys.* 1950, **18**, 162
26 Bloembergen, N., Purcell, E. M. and Pound, R. V. *Phys. Rev.* 1948, **73**, 679
27 Slonim, I. Ya. and Lyubimov, A. N., The NMR of Polymers, Plenum Press, New York, 1970
28 Odajima, A. and Sohma, J. *J. Phys. Soc. Jpn.* 1957, **12**(**3**), 272
29 Maklakov, A. J. and Pimenov, G. G. *Dokl. Akad. Nauk. SSSR* 1964, **157**(**6**), 1413
30 Kubasova, N. A., Din, D. S., Heiderich, M. A. and Shishkina, M. V. *Polym. Sci. USSR* 1971, **13**, 184
31 Leitch, L. C. *Can. J. Chem.* 1957, **35**, 345