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Molecular Motion in Poly(acrylonitrile) As Determined by Deuteron NMR

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ABSTRACT: Samples of poly(acrylonitrile) which were deuterated in the α-position (PAN-α-d_1) and in the β-position (PAN-β,β-d_2) were heated from room temperature to 180 °C. The longitudinal relaxation curves and the NMR spectra of the deuterons were measured as a function of temperature. It was found that the longitudinal relaxation curve could be separated into two exponential curves. The fraction of the component showing the larger relaxation time T_1 decreased with increasing temperature. The shape of the NMR spectra changes from a Pake spectrum at room temperature to a spectrum typical for rapid crankshaft motion at 180 °C. The spectrum did not change its shape when the "waiting time τ_w" was varied. From this it is concluded that the NMR results favor a single-phase model for the structure of PAN more than a two-phase model.

Introduction

Poly(acrylonitrile) (PAN) is an important polymer for fiber production. Though this polymer has now been used for many years, its structure is still discussed controversially. The wide-angle X-ray scattering (WAXS) shows a strong crystal reflection, indicating that there exists a hexagonal packing of the chains. In addition a diffuse scattering is observed. Some researchers[1-4] assume that PAN forms a single phase consisting of strongly disturbed hexagonal crystals. Others consider a two-phase system of crystalline and amorphous regions[5-7] or even a three-phase system showing some sort of intermediate phase in addition to the crystalline and amorphous phases.[8,9] There also exists some disagreement concerning the chain conformations. While usually a helical conformation is assumed, according to a new evaluatin of the WAXS, a disturbed planar zigzag structure[4] was postulated.

It was possible to grow single PAN crystals from solution[11,12] which, however, show an orthorombic lattice in contrast to the hexagonal lattice observed in the bulk material. An orthorombic lattice was also obtained when the material was crystallized from the gel state by evaporation of the solvent.[13] Studies of the melting process and the corresponding disappearnace of the crystal reflection are not possible because chemical decomposition by cyclization reactions starts before melting occurs. These reactions are the first steps in the formation of carbon fibers.

There exist some investigations of molecular mobility in PAN by dielectric relaxations,[3] dynamic mechanical measurements,[11] and ^{1}H NMR.[14] A glass transition temperature of 100 °C was found.[15] From the ^{1}H NMR measurements it was concluded that thermally induced rotational oscillations start at about 95 °C, and a cooperative motion, typical for a glass transition, is developed in the temperature range from 120 to 160 °C.

Deuteron NMR is a very powerful method for investigation of molecular mobility.[16,17] Different kinds of motion result in different line shapes. Thus, by deuteron NMR it becomes possible to determine the kind of motion which is performed by the chains in some detail than by the other methods. In addition, by deuterating different positions of the molecules the mobility of different atoms can be determined separately. Furthermore, by applying different waiting times τ_w the motion in regions with different chain mobilities is studied separately.

In this paper we present some results on molecular mobility obtained by deuteron NMR. As, usually, crystalline and amorphous regions show different chain mobility, by such measurements it should be possible to decide whether PAN forms a one- or a two-phase system. Furthermore, we study at which temperature NMR-relevant molecular motion starts and of which type this motion is.

Some results on deuterated acrylonitrile and PAN have been presented in a quite recent paper by Mathias and Colletti.[18] The shape of the NMR line and values of T_1 and T_2 were measured at temperatures up to 160 °C. However, the "waiting time" was not changed, and higher temperatures, where important changes in motion occur, were not applied. Thus, the questions of semicrystallinity and the kind of molecular motion, which are raised in the present paper, were not investigated.

Experimental Section

Sample Preparation. Two different materials were investigated: PAN which was deuterated in the α-position (PAN-α-d_1) and PAN deuterated in the β-position (PAN-β,β-d_2). The materials were synthesized by radical polymerization of correspondingly deuterated monomers.

Monomer Synthesis. Acrylonitrile-α-d_1 (AN-α-d_1) was prepared by H/D exchange in D_2O with CaO as a catalyst.[19] The exchange reaction was repeated twice after the isolation of the partially deuterated intermediates. Yield: approximately 15.0%, based on the acryloniteile starting material. Degree of deuteration: 97.5%.

Acrylonitrile-β,β-d_2 (AN-β,β-d_2) was prepared starting from acetaldehyde-d_3[19-21] via the intermediates lactic-d_3 acid nitrile (prepared by HCN addition) and lactic-d_3 acid nitriloacetate (prepared by acetylation with acetic acid anhydride) and subsequent pyrolytic cleavage (680 °C). Yield: 23%, based on the acetaldehyde-d_3 starting material. Degree of deuteration: >98%.

Polymerization. The polyacrylonitriles PAN-α-d_1 and PAN-β,β-d_2 were prepared from the deuterated acrylonitriles AN-α-d_1 and AN-β-d_2 by a radically initiated precipitation polymerization. A semibatch polymerization was applied using the following

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Table I
Yield, Intrinsic Viscosity in DMF [η], and Molecular Weight M_w for the Two Samples Investigated

	PAN-α-d_1	PAN-β,β-d_2
yield (%)	75	73
$[\eta]_{DMF}$ (dL/g)	2.8	3.3
M_w	390 000	300 000

concentrations: 76.6 wt % H_2O (30% in the reaction vessel and 70% in the addition vessel), 23.2 wt % AN (7% in the reaction vessel and 93% in the addition vessel), 0.12 wt % K_2SO_8, based on AN (15% in the reaction vessel and 85% in the addition vessel), 0.70 wt % $Na_2S_2O_5$, based on AN (10% in the reaction vessel and 90% in the addition vessel), and 0.01 wt % H_2SO_4, based on AN (50% in the reaction vessel and 50% in the addition vessel). The polymerization was carried out at 55 °C in the reaction vessel with simultaneous addition of the aforementioned reagents at 55 °C over 4 h. The AN and both of the aqueous initiator solutions were added from separate vessels.

The molecular weight was determined by viscosimetry[22] using the equation $[\eta] = aM^{\alpha}$ with $a = 17.7 \times 10^{-3}$ mL/g and $\alpha = 0.78$. Table I shows the yield, the viscosity, and the molecular weight for the two materials investigated.

NMR Measurements. The ^{2}H NMR measurements were performed on a Bruker MSL 300 FT NMR spectrometer using a sample holder made of Vespel in our laboratory. This sample holder could be heated up to 300 °C. The NMR line was measured by the solid echo method: First, a progressional saturation pulse sequence consisting of 10 90°$-x$ pulses was applied. As a result of these pulses, the net magnetization becomes zero. After a waiting time τ_w, a solid echo pulse sequence followed, consisting of a 45°$-x$ and a 45°$-y$ pulse separated by a time τ. The duration of the 45° pulse was about 4.5 μs. The distortions due to these finite pulse lengths[23,24] were taken into account by also assuming such a finite pulse length in the calculation of the spectra. τ_w was varied between 0.2 and 2 s; τ was 20 μs. The NMR spectrum was obtained by Fourier transformation of the echo signal observed after the last of the pulses. About 2×10^3 spectra had to be accumulated during each measurement.

In order to measure the longitudinal relaxation, the waiting time τ_w was varied and the maximum intensity of the echo was determined as a function of the waiting time τ_w (saturation recovery). In these experiments waiting times up to 10 s were applied.

For the evaluation of the longitudinal relaxation curve it was assumed that this curve can be represented by a superposition of exponential curves. Thus, the longitudinal magnetization M_z (τ_w) is given as a function of the waiting time τ_w by the equation

$$M_z(\tau_w) = M_0[1 - \sum x_i \exp(-\tau_w/T_1^{(i)})] \qquad (1)$$

Calculation of the NMR Line Shape. For the evaluation of the NMR results, the shapes of the ^{2}H NMR lines were calulated under the assumption of different kinds of motion by means of a computer program originally developed by Spiess et al.[16] and modified in such a way that it could be used on a PC.

According to the program, the calculation was performed in the following way: One octant of the total sphere representing different orientations of the CD bonds was divided into 3294 parts of equal area, each of them characterized by the two Eulerian angles θ and Φ, describing the orientation of the CD bond with respect to the static magnetic field. For each pair of θ and Φ the line shape was calculated assuming a jump Markov process. Due to the assumption of a limited number of distinct orientations rather than a continuous orientation distribution, this procedure results in spectra consisting of distinct sharp lines. As, in reality, the orientation distribution is continuous and, in addition, due to the limited lifetime of a spin, each line is broadened, the calculated lines were superimposed by a Gaussian function. For the spectra with variable jump frequency Ω, the width σ of the Gaussian function was chosen to be 0.06δ, the smallest value which gave a sufficient smoothing in the region of intermediate jump rates. For the spectra relating to slow and fast exchange rates, it was sufficient to choose $\sigma = 0.02\delta$, which also gave the best fit to the experimental spectra.

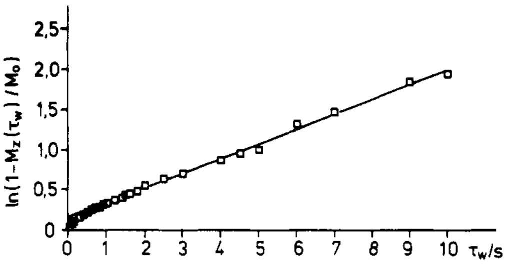

Figure 1. Semilogarithmic plot of the longitudinal magnetization M_z against the waiting time τ_w for PAN-β,β-d_2 at 27 °C: (□) experimental data; (—) straight line fitted at large values of τ_w, yielding $x_1 = 0.86$ and $T_1^{(1)} = 5.4$ s.

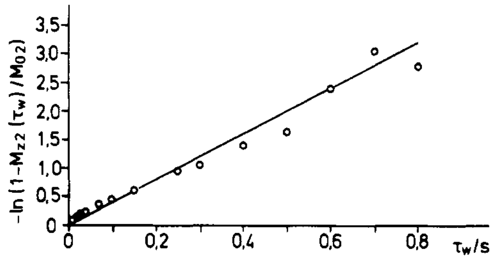

Figure 2. Semilogarithmic plot of the difference in longitudinal magnetization M_{z2} against the waiting time τ_w for PAN-β,β-d_2: (○) data from experiment; (—) straight line fitted to the data, yielding $x_2 = 0.14$ and $T_1^{(2)} = 0.25$ s.

Table II
Longitudinal Relaxation Times $T_1^{(i)}$ and Weight Fractions x_i of PAN-β,β-d_2 at Different Temperatures T

T (°C)	x_1 (%)	$T_1^{(1)}$ (s)	x_2 (%)	$T_1^{(2)}$ (s)
27	86 ± 1	5.4 ± 0.2	14 ± 1	0.25 ± 0.04
108	43 ± 3	0.58 ± 0.04	57 ± 3	0.108 ± 0.005
129	28 ± 2	0.50 ± 0.07	72 ± 2	0.055 ± 0.003
162	0	0	100	0.0140 ± 0.0004

Results

Figure 1 shows the decay of the longitudinal magnetization M_z of the β deuterated material, PAN-β,β-d_2, in a semilogarithmic plot corresponding to eq 1 as measured at 27 °C (squares) together with a straight line fitted to the tail of the curve given by the squares. M_0 stands for M_z at $\tau_w = \infty$. As one can see, the straight line does not fit the measured points at small values of τ_w, indicating that the measured curve is not exponential. Therefore, the values corresponding to the straight line were subtracted from the measured values, and the differences of the M_z values, we call them M_{z2}, were again plotted in the semilogarithmic scale (Figure 2). The value at $\tau_w = \infty$ is denoted by M_{02} and is equal to M_0x_2. As demonstrated in the figure, these values can be fitted over the whole regions by a straight line. This shows that the relaxation curves can be separated into two exponentional components. In a similar way the relaxation curves obtained at other temperatures were evaluated.

Table II shows the weight fractions w_1 and w_2 together with the relaxation times $T_1^{(1)}$ and $T_1^{(2)}$ of the two components at various temperatures. x_1, the weight fraction with the larger relaxation time T_1, decreases with increasing temperature and becomes zero at 162 °C. The values of $T_1^{(1)}$ and $T_1^{(2)}$ also decrease considerably when the temperature is raised.

Figure 3 shows the NMR lines measured at different temperatures during heating. Up to about 120 °C no change in the spectrums is found; a pake diagram is obtained which indicates that there occurs no molecular motion which is relevant for the shape of the NMR line. Above this temperature the line changes its shape due to

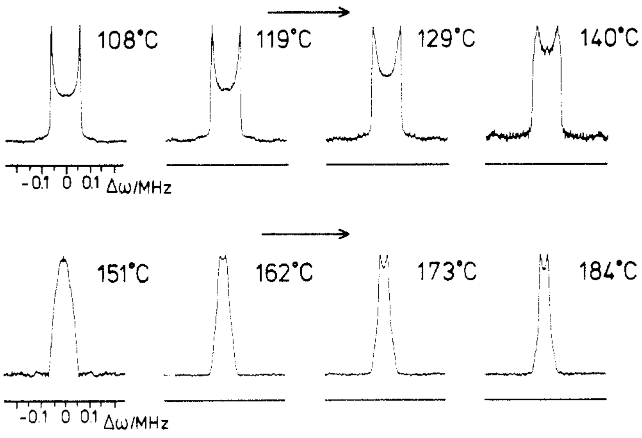

Figure 3. ^{2}H NMR spectra of PAN-β,β-d_2 measured at different temperatures. τ_w = 2 s.

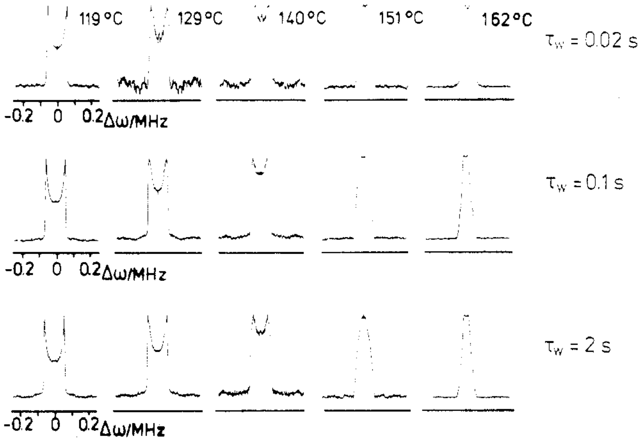

Figure 4. ^{2}H NMR spectra of PAN-β,β-d_2 measured at different temperatures using three different values for the waiting time τ_w, namely, 0.02, 0.1, and 2 s.

molecular motion. When the sample is cooled, at each temperature the same line shape is obtained as during heating. Thus, the change of the line shape with temperature is completely reversible. If the samples are heated above 190 °C, the changes in the line shape become irreversible. This effect is explained by cyclization reactions and is the subject of another publication.[25]

If the components having different longitudinal relaxation times T_1 could be attributed to atoms performing different kinds of molecular motion, one would be able to separate the NMR lines of these atoms by varying τ_w. Figure 4 shows the NMR lines obtained at various temperatures by applying three different waiting times, namely, 2, 0.1, and 0.02 s. No influence of τ_w on the line shape is visible.

The results obtained on PAN-α-d_1 are similar to those on PAN-$\beta,\beta d_2$.

Discussion

Interpretation of the Two Components of the Longitudinal Relaxation Curve. In semicrystalline polymers, the component with the largest relaxation time T_1 is attributed to the crystalline fraction whereas all components having smaller values of T_1 are attributed to the amorphous regions. As mentioned in the Introduction, some researchers[5-7] assume that PAN is semicrystalline, estimating the degree of crystallinity to be 30–50% depending on the method of evaluation, while other researchers[1-4] assume a one-phase model. We believe that an assignement of the two exponential components to crystalline and amorphous regions would not be correct because the spectra measured by using different waiting times τ_w do not differ from each other even at temperatures considerably higher than the glass transition temperature. At such high temperatures the amorphous regions due to the isotropic motion should give rise to a central narrow line which is not observed. Furthermore, the value of x_1 at room temperature (0.86) is much larger than the values of the degree of crystallinity reported[5-7] (up to 0.50).

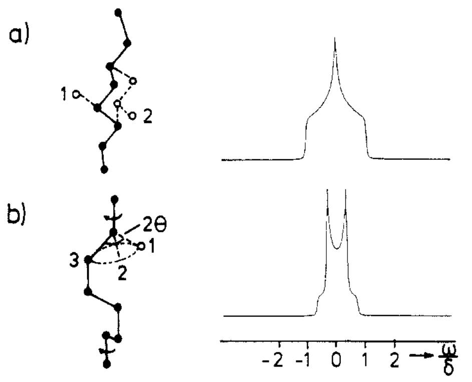

Figure 5. Schematic representation of two possible mechanisms of molecular motion in PAN together with the corresponding line shapes in the fast motion limit: (a) kink motion, affecting three bonds, (b) crankshaft motion, affecting five bonds. The solid circles represent the carbon atoms; the open circle respresents one of the deuterons. The numbers 1–3 indicate the three possible positions of this deuteron on a cone with an opening angle of 2θ.

There exist two possible ways to explain the NMR results: (i) One can assume a one-phase model as suggested by different researchers[1-3] and explain the nonexponential decay of longitudinal relaxation by a nonexponential correlation function of the motion. (ii) One can assume that there exist two kinds of regions giving rise to the two exponential components of the longitudinal relaxation curve. Then, from the results one can conclude that the nature of the molecular motion is the same in the different regions; however, the frequencies are different, lying within a window in which the relaxation times T_1 but not the line shapes are influenced. However, one cannot assume that one kind of region is amorphous. This would be possible only if one pretends that the glass transition temperature is considerably higher than the value of approximately 100 °C usually assumed.[15] Otherwise one cannot explain that no central narrow line is observed even at 184 °C. Unfortunately it is not possible to perform measurements above this temperature because cyclization reactions occur.[24]

In other semicrystalline polymers a behavior like in PAN has not been observed. In addition, it seems difficult to understand that the different frequencies of the two regions lead to the same line shape while an increase of temperatures changes the line shape. Therefore, we believe that the one-phase model is more supported by our results than the semicrystalline model.

Motion Performed by the CH$_2$ and by the CH Groups. The double peak observed up to 184 °C in the spectra proves that the motion of the segments is not isotropic. What kind of motion do the atoms perform?

In the PAN chain two different kinds of motion of the carbon atoms are possible: (i) A Kink motion in which three carbon atoms are involved. Each C–^{2}H bond performs 180° jumps on a cone having an opening angle of 54.74° (Figure 5a). (ii) A crankshaft motion in which five carbon atoms are involved. Each C–^{2}H bond moves on a cone having an opening angle of 70.5° (Figure 5b). According to a potential calculation performed by Krigbaum and Tokita,[26] this motion probably consists of 120° jumps.

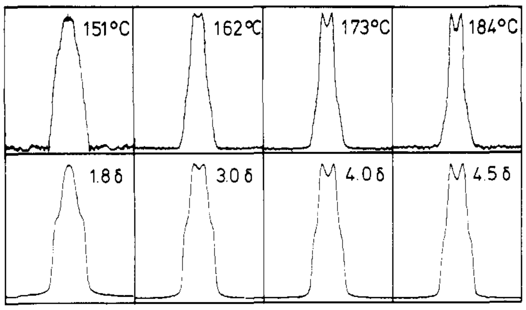

Figure 6. Comparison of spectra measured at different temperatures (upper row) and spectra which where calculated assuming a crankshaft motion consisting of 120° jumps (lower row). The jumping frequency is given in units of $\delta = 2\pi \times 60$ MHz.

The shape of the lines observed in the limit of high-frequency motion is quite different as it can be seen in Figure 5.

We have calculated the line shape assuming different jump frequencies for both kinds of motion and compared the calculated with the measured curves. Figure 6 shows that good agreement is obtained if a crankshaft motion is assumed. The jump frequency of the motion increases from 1.8δ to 4.5δ, where δ is the coupling constant. From the distance of the peaks in the Pake diagram it was found that $\delta = 2\pi \times 60 = 377$ kHz.

We have to mention that the distance of the peaks found at 184 °C is $^1/_4$ of the distance found in the Pake diagram at room temperature. According to theoretical calculations, the crankshaft motion should decrease the distance to $^1/_3$ of its value. This factor however is very sensitive to the opening angle 2θ of the cone on which the C–H bond moves. If 66° instead of 70.5° is assumed for θ, which implies a small deviation from the tetrahedral angle, the factor $^1/_4$ is obtained by calculation instead of $^1/_3$. Therefore, we believe that due to the different substituents at the C atoms in PAN, θ is reduced to 66°. As the calculations in Figure 5 were performed assuming $\theta = 70.5$ the distance between the peaks in the calculated spectra is slightly larger than in the measured spectra.

We point out that a decrease of the peak distance to $^1/_4$ of the distance found in the Pake diagram can also be explained by assuming a librational motion covering an angle of 20° in addition to the jumps. Such a librational motion also might be the reason for the smaller peak distance. One could also assume mainly librational motion instead of the jumps; however, it seems difficult to distinguish between jumps and librations on the basis of the line shape.[27]

It is interesting to note that the change of the spectrum with increasing temperature can be interpreted by assuming an increase of the jump frequency ν rather than an increase of a fast-moving fraction of material which was observed, for example, in copolyesters of PHB.[28] While a gradual increase of a fast-moving fraction indicates the presence of a broad distribution of activation energies,[29,30] the present result shows that in the case of PAN the motion observed is associated with a single activation energy E_a (or a very narrow spectra of activation energies). This result, too, is in favor of a single-phase model for the structure in PAN. From a plot of $\ln \nu$ against $1/T$ a value of 45 kJ/mol is obtained.

Conclusions

From the analysis of the shape of the spectra it is concluded that the molecular motion in bulk PAN is quite uniform throughout the sample. In other words, there do not exist regions showing different kinds of mobility like crystals and amorphous regions. With increasing temperature, in the range from 150 to 180 °C a crankshaft motion involving five carbon atoms is developed. This motion is associated with a single activation energy. An isotropic segmental motion as occurring in amorphous polymers can be excluded. Though a two-phase model cannot be completely excluded, these results favor a single-phase model for the structure of PAN, according to which all PAN molecules are organized in hexagonal crystals which, as revealed by the poor WAXS reflections, are strongly disturbed. The crankshaft motion indicates that these crystals may be conformationally disordered.

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