polymer papers

Nuclear magnetic resonance and wide angle X-ray scattering in poly(acrylonitrile-co-methyl acrylate): 1. The influence of comonomer on structural characteristics and annealing behaviour

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The morphology, dynamics and annealing behaviour of acrylonitrile/methyl acrylate copolymer P(AN-co-MA) have been examined by means of broad-line nuclear magnetic resonance (^{1}H BL-n.m.r.) and WAXS methods. The difference in conformation between 'pure' acrylonitrile sequences and 'foreign' unit-centred triads has been revealed and a conformational model of the copolymer has been proposed. Three distinct steps in behaviour of P(AN-co-MA) on annealing have been distinguished and interpreted. The role of the comonomer units in molecular mobility as well as in structural and chemical changes on heat treatment has been emphasized. Both differences and similarities between polyacrylonitrile (PAN) and P(AN-co-MA) have been shown and an attempt has been made to explain the effect of the comonomer units on paracrystalline and amorphous regions.

(Keywords: polyacrylonitrile; poly(acrylonitrile-co-methyl acrylate); broad-line n.m.r.; WAXS; conformation; tacticity; morphology; annealing)

INTRODUCTION

Polyacrylonitrile (PAN) has been the centre of much interest for many years[1–8]. Studies of this polymer as a model compound are important in the recognition of the structure of acrylonitrile based copolymers. In spite of the industrial importance of these copolymers, the literature dealing with structural investigations is relatively scarce. In some works the problem of the modification of the physical properties of acrylic fibres by copolymerization is raised[9]. Other works consider the characteristics of acrylonitrile copolymers as precursors of carbon fibres[10].

An important contribution to structural investigations was made by Gupta *et al.*[11–14], who determined the effect of random copolymerization of acrylonitrile (AN) with methyl methacrylate (MMA)[14], methacrylonitrile (MAN)[12,14], hydroxyethyl methacrylate[11] and some silylated acrylic comonomers[13] on physical properties.

The aim of this work is to characterize the structure and dynamics of acrylonitrile/methyl acrylate copolymer for comparison with the previously studied homopolymer of acrylonitrile.

EXPERIMENTAL

Sample preparation

A random copolymer of acrylonitrile (AN, 93 mol%) and methyl acrylate (MA, 6 mol%), containing 1 mol% of itaconic acid (IA) was prepared by radical polymerization in 51 wt% aqueous solution of sodium thiocyanate (NaSCN) with azobisisobutyronitrile (AIBN) as initiator at 80°C. The polymer was precipitated with a mixture of water and methanol (1:1), filtered off, washed with boiling distilled water to remove NaSCN and then with methanol. It was dried at room temperature and then vacuum dried at 60°C.

For simplicity, the copolymer will be referred to as poly(acrylonitrile-co-methyl acrylate), P(AN-co-MA), itaconic acid being omitted in the designation due to its small amount.

Measurements

Investigations were made by means of broad-line nuclear magnetic resonance (^{1}H BL-n.m.r.) on a Varian WL-109 spectrometer at a resonance frequency of 30 MHz and wide-angle X-ray scattering (WAXS) on a DRON-1.5 diffractometer using CuKα radiation. 50.3 MHz ^{13}C-{^{1}H} n.m.r. spectra at room temperature and 100 MHz ^{1}H n.m.r. spectra at 155°C of the copolymer in DMF-d_7 solution, using TMS as an internal standard, were recorded on a Varian XL-200 and a Varian XL-100 spectrometer, respectively.

Infra-red spectra were recorded on a SPECORD M80 spectrophotometer, using copolymer samples in the form of pellets with KBr.

Numerical analysis of the BL-n.m.r. spectra was performed on a WANG 2200 B minicomputer. The results are the mean of several measurements. The widths of the individual components of the spectra were measured as the distance (in gauss*) between the extreme values of the derivatives of the components. The relative

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* 1 gauss (G) = 10^{-4} T

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amounts of the components in the absorption spectra were calculated on the basis of their first moment values.

RESULTS AND DISCUSSION

Shape of BL-n.m.r. lines

^{1}H BL-n.m.r. spectra of poly(acrylonitrile-co-methyl acrylate) in the form of the first derivatives of the absorption curves were recorded in the temperature range 20–200°C. *Figure 1* presents the copolymer spectra taken at 20, 110 and 135°C, with the corresponding spectra of polyacrylonitrile (PAN) for comparison.

The room temperature spectrum of PAN may be attributed to the rigid lattice state of the polymer[15]. Given the predominant contribution of AN sequences in the chemical composition of P(AN-co-MA) as well as its high T_g (see the next section), it is plausible that rotation of side groups of comonomer units is the only type of motion occurring at room temperature.

Numerical analysis of P(AN-co-MA) spectra was carried out by the method of Bergmann and Nawotki[16,17]. The calculated spectra were fitted to the experimental spectra according to Marquardt's iterative technique[18].

The spectrum recorded at 20°C was divided into two components described respectively by the first derivatives of a shape function appropriate to a rigid two-proton system[16,19] where H–H distance is 0.15 nm[15] and a Gaussian function. The components were designated α, β, respectively. The protons from CH_3 groups are assumed to contribute to the Gaussian, β component.

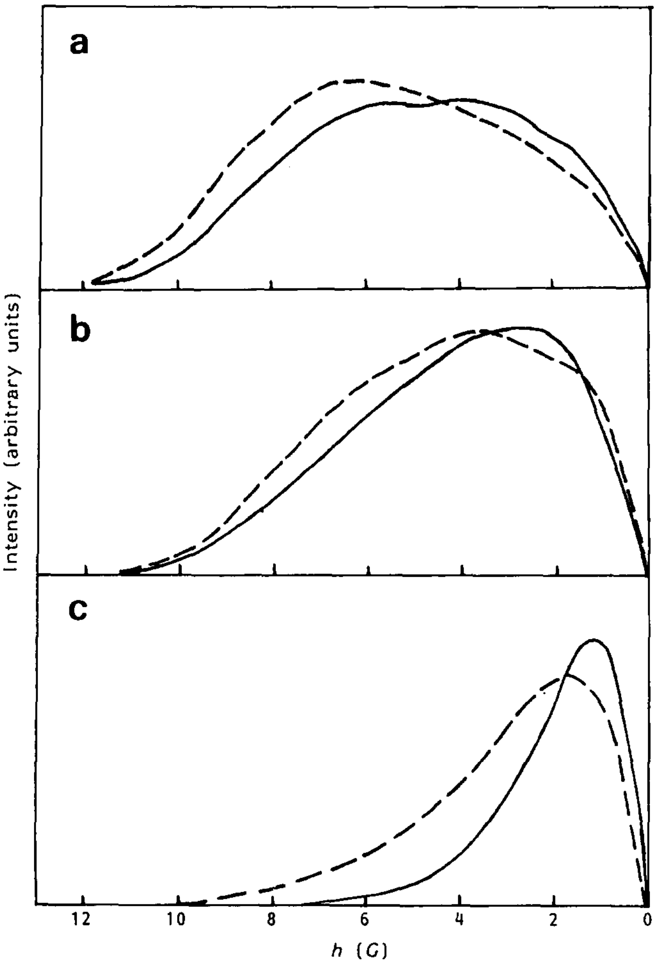


Figure 1 First-derivative (one-half shown) ^{1}H BL-n.m.r. absorption spectra (——) of poly(acrylonitrile-co-methyl acrylate) at (a) 20, (b) 110, and (c) 135°C. For comparison the corresponding spectra of polyacrylonitrile are shown (-----)

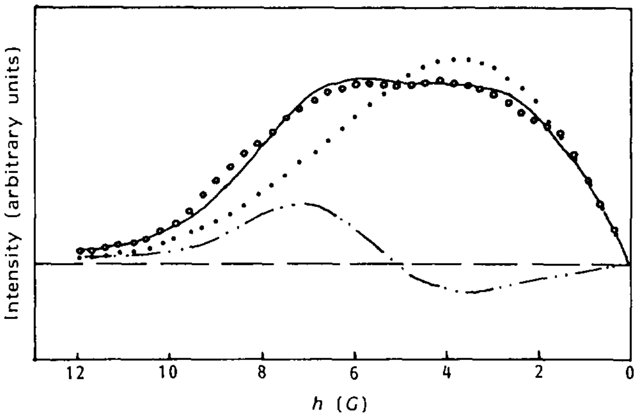


Figure 2 First-derivative (one-half shown) ^{1}H BL-n.m.r. absorption spectrum of poly(acrylonitrile-co-methyl acrylate) and its components at 20°C: ○, experimental; ——, calculated; —·—, α component; ····, β component

Table 1 Experimental and calculated values of the amounts of components in the ^{1}H BL-n.m.r. absorption spectrum of P(AN-co-MA) at 20°C

Experimental		Calculated			
		Case I[a]		Case II[b]	
α	β	α	β	α	β
17	83	21.7	78.3	18.5	81.5

α, Component of a rigid two-proton system, where H–H distance is 0.15 nm

β, Gaussian component

[a] Conformation of all sequences is the same as in homopolymer[15]

[b] Conformation of 'pure' AN sequences is the same as in homopolymer[15]; conformation of MA- or IA-centred sequences is diverse

Figure 2 presents a room temperature spectrum of P(AN-co-MA) divided into α and β components.

The experimental and theoretical values of the relative amounts of individual components are collected in *Table 1*. Assuming that the conformation of all AN sequences in P(AN-co-MA) is the same as in PAN, it was calculated that the amount of the α component in the copolymer spectrum is ≈22% (in PAN≈25%[20]). However, *Table 1* shows that the experimental value is only ≈17%. On the contrary, good agreement with the experimental values can be obtained under the following two assumptions: first, the conformation of the 'pure' AN triads is the same as for the homopolymer, i.e. twisted, in which the protons from terminal H–C–CN groups in the triads approach each other at a distance of 0.15 nm, constituting relatively isolated pairs of spins, thus giving rise to the α component in the BL-n.m.r. spectra[15,20]; second, the triads with the 'foreign' unit in the central position have a diverse conformation, in which protons from H–C–CN groups do not form such pairs, so they do not contribute to the α component; thus their conformation would be more straightened, or less twisted, than for 'pure' AN triads, and for these a smaller diameter of 'molecular rod' could be accepted.

The BL-n.m.r. spectra recorded above room temperature to 105°C were analysed by considering them as the sum of the α and β components.

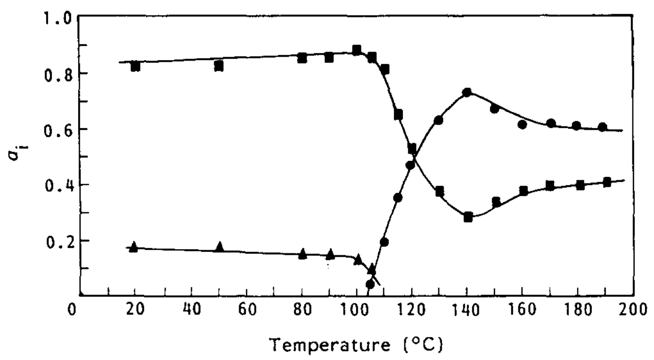


Figure 3 Relative amounts of the components of ^{1}H BL-n.m.r. absorption spectra of poly(acrylonitrile-co-methyl acrylate) as a function of temperature: ▲, α; ■, β; ●, γ

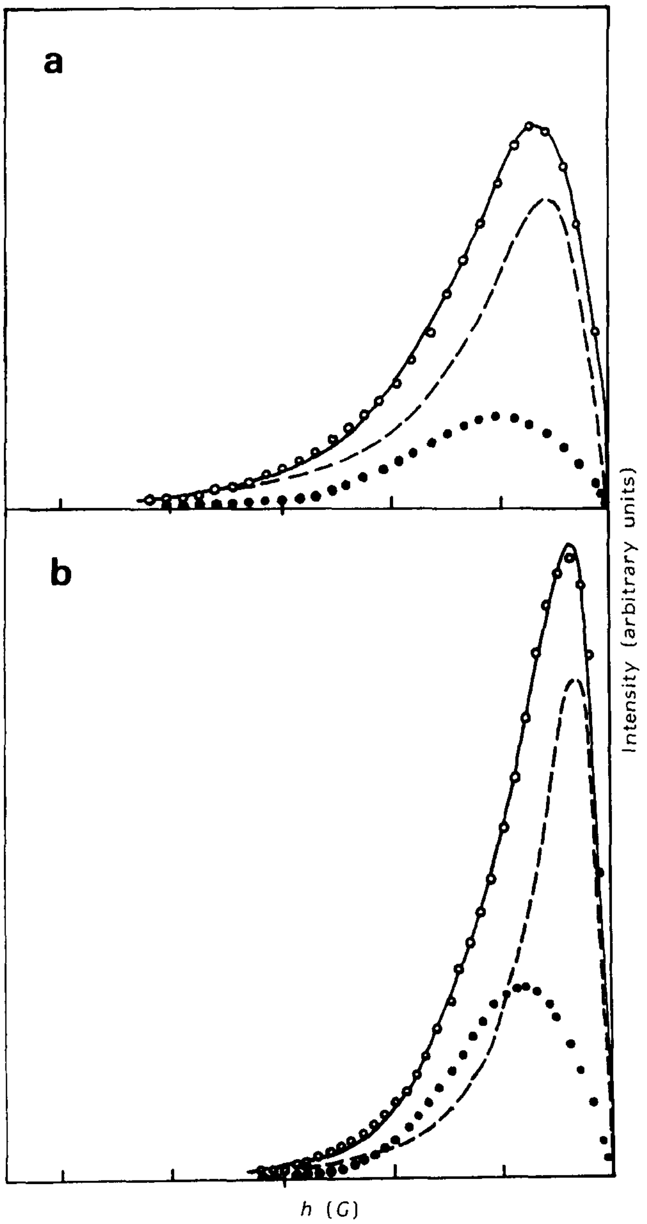


Figure 4 First-derivative (one-half shown) ^{1}H BL-n.m.r. absorption spectra of poly(acrylonitrile-co-methyl acrylate) and its components at (a) 140 and (b) 190°C: ○, experimental; ——, calculated; ····, β component; – – –, γ component

The amount of α component was found to decrease with increasing temperature, as in the case of PAN[15]. This points to the gradual untwisting of the 'pure' AN sequences, causing the distance between protons from H–C–CN groups to increase. As seen in *Figure 3*, the α component disappears from the spectra at about 105°C, i.e. at a temperature $\approx$10°C lower than for PAN[15].

From 105 to 200°C the best fit of the calculated to the experimental spectra was achieved by dividing the spectra into Gaussian (β) and Lorentzian (γ) components. *Figure 4* shows the spectra recorded at 140 and 190°C, divided in this way. The γ component reflects the amorphous regions, while the β component could be attributed to paracrystalline areas. At lower temperatures in the range 105–200°C, part of the amorphous material would also contribute to the β component.

Quantitative determination of the amount of paracrystalline and amorphous regions in P(AN-co-MA) is not possible because the amounts of β and γ components are not constant at higher temperatures (see *Figure 3*). The increase in the amount of β component to about 40% at 200°C could be misinterpreted as resulting from the increase in paracrystallinity on annealing. However, WAXS analysis shows (see below) that annealing of the copolymer at temperatures above 150°C involves a reduction of the degree of ordering due to the cyclization and crosslinking reactions. Thus, it may be concluded that the β component in BL-n.m.r. spectra recorded at these temperatures represents not only paracrystalline regions of the copolymer, but also some stiffened structures formed in these reactions.

Widths of the components of BL-n.m.r. spectra

Temperature dependences of the widths of individual components of P(AN-co-MA) BL-n.m.r. spectra are shown and compared with corresponding plots for the previously studied PAN in *Figure 5*. The observed drop in the widths are connected with changes in the character of the molecular motion[21].

The width of the Gaussian β component decreases from $\approx$7.5 to 6.7 G near 85°C. Within the temperature range 110–150°C there is a narrowing of both the Gaussian β component, from $\approx$6.7 to 2.7 G, and the Lorentzian γ component, from $\approx$3.5 to 1.3 G. The character of these changes is then very close to the analogous dependences observed for PAN. The principal difference is the 10°C shift downwards of the width-drop temperature ranges

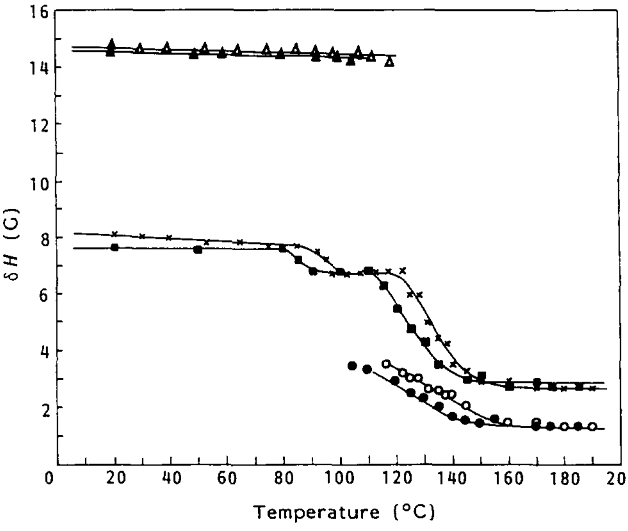


Figure 5 Width of ^{1}H BL-n.m.r. lines *versus* temperature for polyacrylonitrile (△, ×, ○) and poly(acrylonitrile-co-methyl acrylate) (▲, ■, ●); △, ▲, α component; ×, ■, β component; ○, ●, γ component

for both components. The lower-temperature transition may be ascribed to thermally induced oscillations, while the higher-temperature transition may be considered as resulting from cooperative rotational and translational motions, typical for a glass transition both in amorphous and paracrystalline regions[15].

The shift of T_g cannot result from the slight difference in tacticity between P(AN-co-MA) and PAN (for tacticity analysis see Appendix A), because the T_g range for both atactic PAN and isotactic-rich polymer is situated within the same limits[21]. Thus it may be concluded that the depression of T_g results mainly, if not exclusively, from the presence of the comonomer units. The value of this shift confirms the finding of Rosenbaum, who observed a decrease in T_g of about 1°C $(\mathrm{mol}\%)^{-1}$ methyl acrylate comonomer[22].

From the considerations presented in the previous section it is apparent that the presence of the 'foreign' units leads to a reduced number of AN units involved with the rigid irregular helical conformation. On the other hand, as shown previously[15], such conformation is primarily responsible for the T_g value of PAN. Thus the decrease in T_g is probably due to the contribution of sequences of AN–MA–AN or AN–IA–AN type with a diverse, less rigid conformation. The presence of such sequences must lead to an enhanced net effective flexibility of the chain.

As in the case of PAN[15], the similarity of the T_g ranges for amorphous and paracrystalline regions (represented in the spectra recorded in the range 110–150°C by the γ and β components, respectively; see *Figure 5*) points to a similar conformation of the chains in both these regions. The fact that a depression in T_g is observed both in amorphous and in paracrystalline regions indicates that the 'foreign' units are also incorporated into the ordered areas, affecting the molecular mobility of their chains.

As already stated, the α component is attributed to the protons disposed in a preferred manner at a distance of 0.15 nm. Within the range 20–100°C the widths of this component in the spectra of P(AN-co-MA) and PAN are very similar (about 15 G as seen in *Figure 5*). This confirms the possibility of accepting the same conformational model for the 'pure' AN sequences of the copolymer as for PAN. On the other hand, at temperatures $< T_g$ the width of the β component, reflecting all the other protons in the system, decreases from 8 G for PAN to 7.5 G for P(AN-co-MA), which is connected with first, longer distances between protons in 'foreign' unit-centred sequences, implying more extended (untwisted) conformation of these sequences, and, second, rotation of side groups of the comonomer units.

The second moment

The second moment of the resonance line is defined as[21]

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

where h is the deviation of the magnetic field from its value at the midpoint of the absorption envelope and $g(h)$ is the absorption function. The experimental value of the second moment can be determined directly from the spectrum recorded in the form of the first derivative of the absorption curve and compared with the theoretical value calculated for an assumed structure[21].

The experimental ΔH_2^2 value of BL-n.m.r. spectra of PAN at room temperature is 17.5 G^2 (ref. 15) and the corresponding value for the copolymer is 15 G^2. To explain the difference, theoretical values for the second moment were calculated with the assumptions that the conformation of 'pure' AN sequences is the same as in the homopolymer[15], while in AN sequences with the 'foreign' unit in the central position the arrangement of protons is similar to the 'zig-zag' conformation. These calculations (presented in Appendix B) established that the theoretical ΔH_2^2 value for the copolymer was $\approx 17\,\mathrm{G}^2$, $\approx 2.4\,\mathrm{G}^2$ less than the appropriate value determined for the homopolymer. Thus the difference between the experimental values of the second moment ($\approx 2.5\,\mathrm{G}^2$) is close to the difference between the theoretical values calculated for PAN and P(AN-co-MA). This accordance confirms the existence of short sequences distinguished by untwisted conformation. On the other hand, for both PAN and P(AN-co-MA), the absolute values of theoretical second moment do not correlate well with the corresponding experimental values. Previously[15], we tried to get better agreement between theoretical and experimental values of ΔH_2^2 for PAN by assuming for a syndiotactic triad the ΔH_2^2 value of 11.5 G^2, corresponding to planar zig-zag conformation. However, subsequent examination of isotactic-rich polymer indicated the possibility of adopting the same model of twisted conformation for all PAN chain sequences, independent of their tacticity[20]. Thus it seems that the above mentioned discrepancy between theoretical and experimental ΔH_2^2 values for both homopolymer and copolymer, is rather due to some oversimplifications adopted in the calculation[15,20].

Wide angle X-ray diffraction traces of P(AN-co-MA)

The X-ray trace of P(AN-co-MA) shown in *Figure 6* is very similar to the diffractogram of PAN[20].

The similar character of the X-ray traces of PAN and P(AN-co-MA) is evidence for a similar supermolecular structure for both polymers. Thus is seems possible to describe the phase structure of P(AN-co-MA) using the same model as previously proposed for PAN[20]. The model assumes that PAN forms a heterogeneous system composed of amorphous and paracrystalline, hexagonally ordered[15,20] regions.

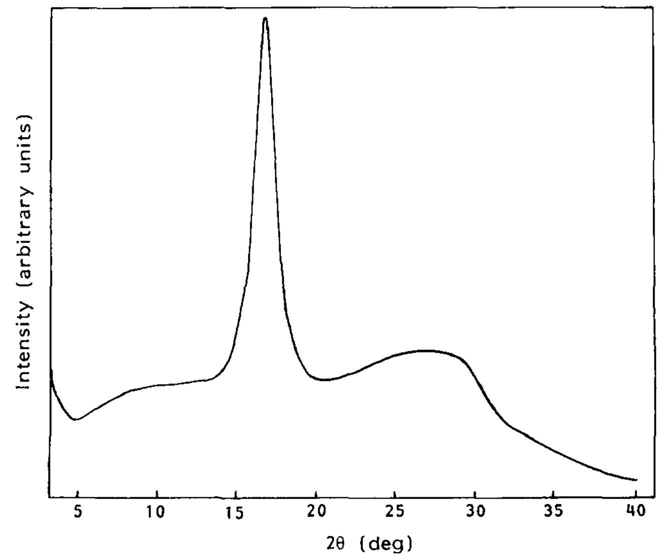


Figure 6 Wide-angle X-ray diffraction trace of P(AN-co-MA)

However, some differences are observed in X-ray traces of P(AN-co-MA) and PAN as far as the values of half-breadth $\Delta\omega$ of the main reflection at $2\theta = 17°$ and amount of ordered regions are concerned. In general, the half-breadth $\Delta\omega$ is a measure of size and/or perfection of ordered regions. The half-breadth values of the main reflection for PAN and P(AN-co-MA) are 0.73 and 0.93°, respectively, which are connected with lower perfection of the structure in the copolymer and/or smaller sizes of its paracrystalline regions compared with PAN.

The amounts of ordered regions estimated by the method of Hendus–Hinrichsen[4] are $\approx 27\%$ for PAN[20] and $\approx 22\%$ for P(AN-co-MA).

Heat treatment

To describe the structural changes occurring in P(AN-co-MA) on annealing, X-ray traces were recorded for copolymer samples annealed for 1 h at temperatures in the range 20–210°C.

The results, as well as our previous data on PAN[20] completed with some additional mesurements made for the annealing range 20–100°C, were compared. *Figure 7* shows the change in the half-breadth of the main reflection at $2\theta = 17°$ for the homopolymer and copolymer samples as a function of the annealing temperature. The curve for the copolymer reveals a three-step nature. In the first step, there is a drop from 0.93 to 0.83° in the temperature range 20–80°C; in the second step there is a decrease from 0.82 to 0.55° in the temperature range 80–160°C; and in the third step, corresponding to the temperature range 160–210°C, there is an increase from 0.55 to 0.62°, with a simultaneous reduction of the amount of paracrystalline regions.

The first and second steps correspond to a progressive change in the half-breadth of PAN[20]. Interpretation of the two-step nature of the half-breadth decrease of PAN samples examined previously (atactic sample with a larger amount of amorphous regions and isotactic-rich sample) led us to the conclusion that during the first step (below T_g) there is an improvement in the paracrystalline regions and that in the second step (above T_g) further improvement is accompanied by an increase in the size of these regions[20].

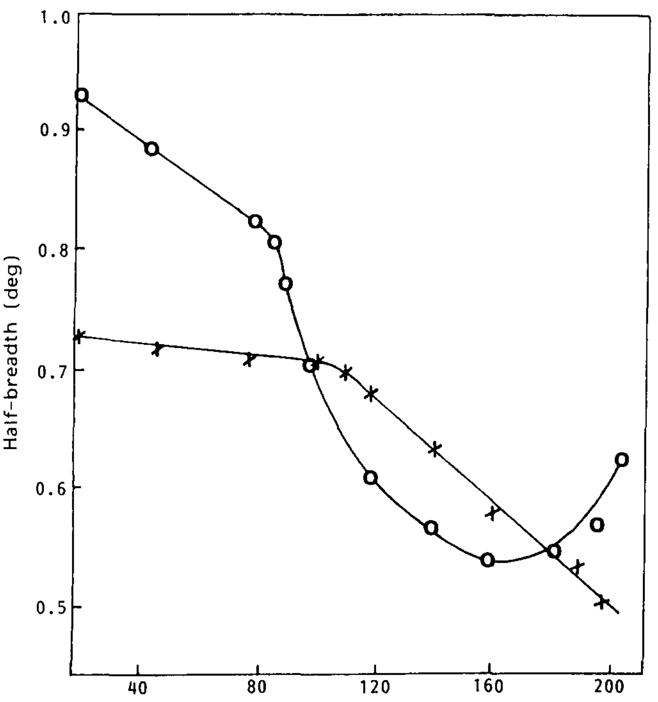


Figure 7 Half-breadth of the main reflection at $2\theta = 17°$ *versus* temperature of annealing for (×) PAN and (○) P(AN-co-MA)

For atactic PAN (as used in the present study), only the second step was observed, since the maximal temperature of thermal treatment during sample preparation (i.e. 100°C) was taken as the starting annealing temperature. However, it appears that additional annealing in the temperature range 20–100°C produces a slight decrease of half-breadth from 0.73 to 0.70° (*Figure 7*).

The glass transition temperature of P(AN-co-MA) is $\approx 90°C$ (T_g of PAN ≈ 100–$110°C$), as revealed by WAXS. The half-breadth value corresponding to the T_g reaches 0.77° (homopolymer half-breadth at $T_g = 0.70°$).

The relative difference between the values of half-breadth of PAN and P(AN-co-MA) at their glass transition temperatures

$$\Delta = [\Delta\omega(T_g, \text{co}) - \Delta\omega(T_g, \text{homo})]/\Delta\omega(T_g, \text{co})$$

is much smaller ($\Delta \approx 10\%$) than that of the untreated samples ($\Delta \approx 30\%$). According to the previously proposed model of structural changes occurring on annealing[20] (below T_g only improvement of the structure), the larger value of the half-breadth of the untreated copolymer may be due to the larger amount of imperfections in the paracrystalline copolymer lattice. On the other hand, the rate of the half-breadth decrease for the copolymer indicates the facility of elimination of the defects. Certainly, in ordered regions the 'foreign' units as such constitute a kind of lattice imperfection. But it seems that the possibility of existence of short comonomer unit-containing sequences with a conformation more flexible than the irregular helical conformation of pure AN sequences involves much more important structural consequences.

These short chain fragments of AN–MA(or IA)–AN type can be defined as intramolecular defects. Because of their flexible conformation the intramolecular defects can be a source of intermolecular defects by disturbing the parallelism of the chains within ordered regions. This action will be called here the 'hinge' effect.

Gupta and Singhal[14] expect the presence of comonomer units in ordered regions only above a critical comonomer content, which is characterstic of a given comonomer. They state that up to this value there is no change in the Bragg spacing corresponding to $2\theta = 17°$. The constant Bragg spacing implies, in their opinion, that the lattice of the copolymers studied (with low comonomer content) is like that of PAN, suggesting the occurrence of uninterrupted AN sequences in the ordered regions.

For the copolymer P(AN-co-MA), the position of the main reflection in the X-ray trace (see *Figure 6*) is the same as for PAN[20]. Nevertheless, in the proposed structural model we do not exclude the possibility of the presence of comonomer units either at the boundaries of or inside the copolymer ordered regions.

Figure 8 shows two possible representations of the P(AN-co-MA) ordered region. It may be considered either as a parallel arrangement of 'pure' AN sequences in the form of molecular rods 0.6 nm in diameter (dashed lines in *Figure 8*) or as an arrangement of AN sequences containing 'foreign' units (dotted line in *Figure 8*). In the former case, X-ray peak broadening would be attributed

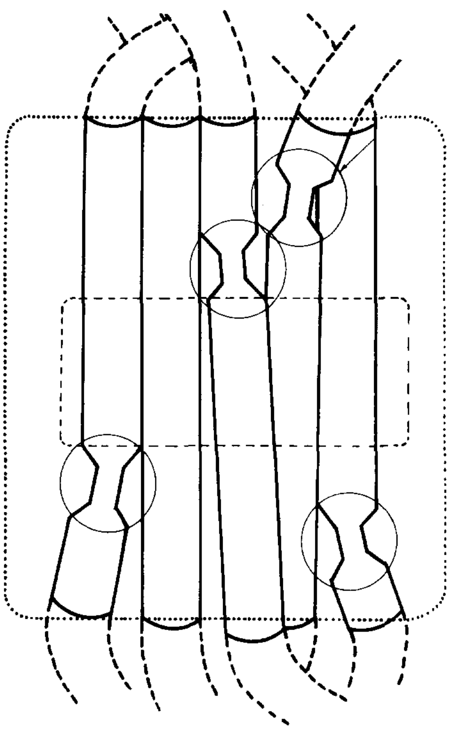


Figure 8 Possible representations (not to scale) of the P(AN-co-MA) ordered region

first to the small size of such a region; in the latter case, to the presence of the short chain fragments of diverse conformation (intramolecular defects characterized above and marked by circles, in *Figure 8*) and to deviations of the parallelism of the molecular rods resulting from the 'hinge' effect. An additional important point confirming the presence of comonomer units in the paracrystalline regions, is the lowering of T_g from 100–110°C for PAN ('pure' AN sequences) to 90°C for P(AN-co-MA). The BL-n.m.r. data are in good agreement with the results obtained by WAXS.

In the annealing temperature range 100–160°C (the second step), the copolymer half-breadths reach lower values than for PAN (*Figure 7*). This means that at these temperatures the paracrystalline regions of the copolymer feature a more perfect structure and/or larger sizes than in PAN. As mentioned above, the presence of 'foreign' units results in structural imperfections of the untreated copolymer structure. On the other hand, it seems that the ability to improve the order (during the second step of annealing to an even greater extent than in PAN) may also be attributed to them. In both cases the same 'hinge' action is supposed to be responsible for the observed phenomena. In P(AN-co-MA) the presence of flexible fragments ('hinges') would produce the increase of effective chain flexibility, manifested by the lowering of T_g, as well as facilitating parallel alignment of chain segments in the second step of annealing. On the other hand, a more 'untwisted' conformation of the 'hinges' would result in the presence of CN groups not involved with intramolecular interactions.

The presence of such 'unblocked' CN groups especially available for intermolecular interactions would, along with the parallel chain alignment, facilitate the formation of dipole pairs. Thus the effect of such intermolecularly bonded nitrile groups would be an increase of order and of the size of the ordered region.

The proposed picture of ordering processes occurring in P(AN-co-MA) on annealing is presented in *Scheme 1*.

For PAN the increase of order on annealing is also connected with the increase of intermolecularly bonded dipole pairs[14]. However, random locations of CN groups, as well as lower chain mobility, make optimal dipole pairing difficult[1].

On the basis of the above comparison, one can suppose that the probability of optimal dipole pairing is higher in P(AN-co-MA) than in PAN. Thus this seems to be the reason for the lower value of copolymer half-breadth in the second step of annealing compared with PAN (*Figure 7*).

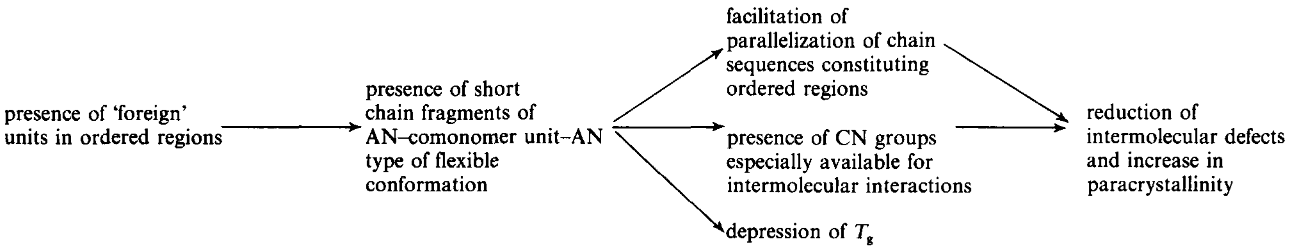
The third step of half-breadth changes corresponds to the temperature range 160–210°C. In this step the copolymer half-breadth increases from 0.55 to 0.62° and the amount of paracrystalline regions decreases from 34% (at 160°C) to 19% (at 210°C). For PAN annealed in the same temperature range, a continuous decrease of the main reflection's half-breadth and an increase in the paracrystallinity are observed[4,20]. Comparison of the behaviour of the copolymer and PAN at temperatures above 160°C shows that for P(AN-co-MA) disordering processes start to compete with the improvement and growth of the copolymer paracrystalline regions.

Discolouring of the copolymer samples studied due to chemical reaction of CN groups[10,23–26] can already be seen at ≈90°C (for PAN at ≈150°C).

The changes observed in X-ray traces of P(AN-co-MA) samples annealed above 160°C as well as the discoloration of the samples can indicate the chemical processes occurring on annealing. It was decided to observe these processes by investigating the changes of half-breadth of P(AN-co-MA) and PAN with time of annealing at 200°C (*Figure 9*) as well as by means of infra-red (i.r.) methods (next section).

In the time range of annealing 1–24 h only a slight increase of PAN half-breadth is observed, indicating that the chemical processes do not significantly influence the PAN structure at this temperature, which is in accord with the literature[1,27].

The corresponding data for the copolymer show the



Scheme 1 Schematic representation of the influence of 'foreign' units on the ordering processes in P(AN-co-MA) on annealing

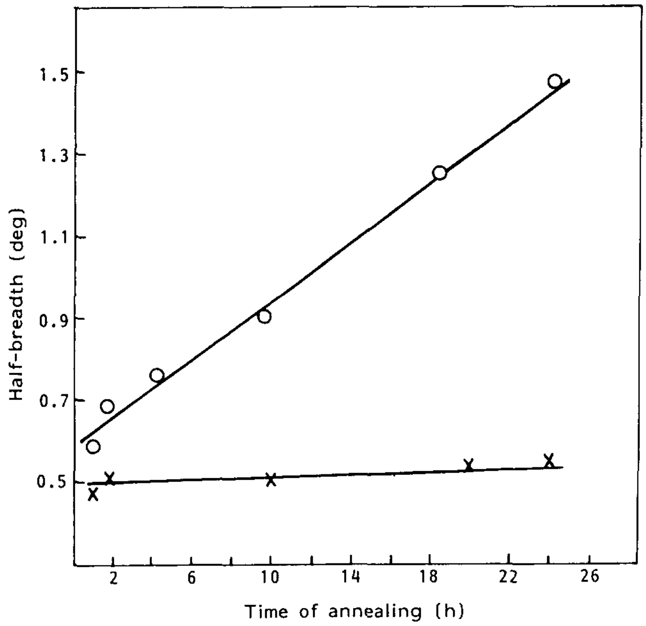


Figure 9 Half-breadth of the main reflection at $2\theta = 17°$ *versus* time of annealing at 200°C for (×) PAN and (○) P(AN-co-MA)

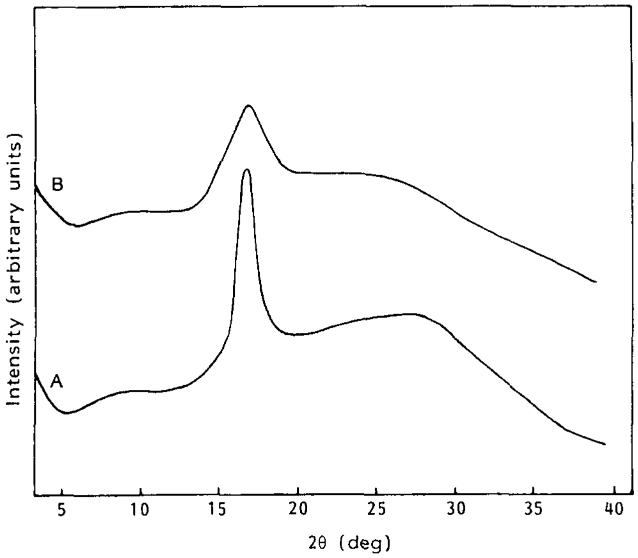


Figure 10 Wide-angle X-ray diffraction traces of P(AN-co-MA) annealed for (A) 1 h and (B) 24 h at 200°C

strong dependence of the half-breadth on annealing time at 200°C. The half-breadth increases more than twofold from 0.6° (after 1 h of annealing at 200°C) to 1.5° (after 24 h) and the intensity of the reflection at $2\theta = 17°$ dramatically decreases (*Figure 10*).

This effect confirms the supposition of chemical changes occurring in the copolymer structure on annealing at higher temperatures.

Since such chemical changes require a proper conformation[26], it seems that the hypothesis of the role of comonomer units as a conformation-modifying factor is also confirmed.

I.r. study

Figure 11 shows i.r. spectra of PAN and P(AN-co-MA), annealed for 2 h at 190°C (*Figure 11a*) and for 24 h (*Figure 11b*) as well as i.r. spectra of the untreated polymers (*Figure 11c*). As seen from the figure, the same direction of spectral changes is observed for the polymers. In the spectra presented (*Figures 11a* and *b*) the bands at 2960, 2240, 1480 and 1100 cm^{-1} appropriate to ν(CH), ν(CN), $\delta(CH_2)$ and ν(CC) vibrations[28] reduce in intensity with time of annealing. Simultaneously, growth of the wide band in the range 1600–1800 cm^{-1} is observed. However, for P(AN-co-MA) these changes are greater and their rate is higher than for PAN. After 2 h of annealing at 190°C the i.r. spectrum of PAN is close to the spectrum of the untreated homopolymer, whereas the corresponding comparison made for P(AN-co-MA) leads to the conclusion that 2 h of annealing at 190°C is sufficient for considerable chemical changes in the copolymer structure to occur.

I.r. spectra taken after 24 h of annealing also show that in P(AN-co-MA) the chemical reactions are more advanced than in PAN.

According to the literature[10,23–26], the changes observed in i.r. spectra of the polymers under study indicate the formation of ladder like structures. Shimada *et al.*[28] gave evidence, on the basis of the i.r. studies of PAN and one of the copolymers of AN, for the facilitating

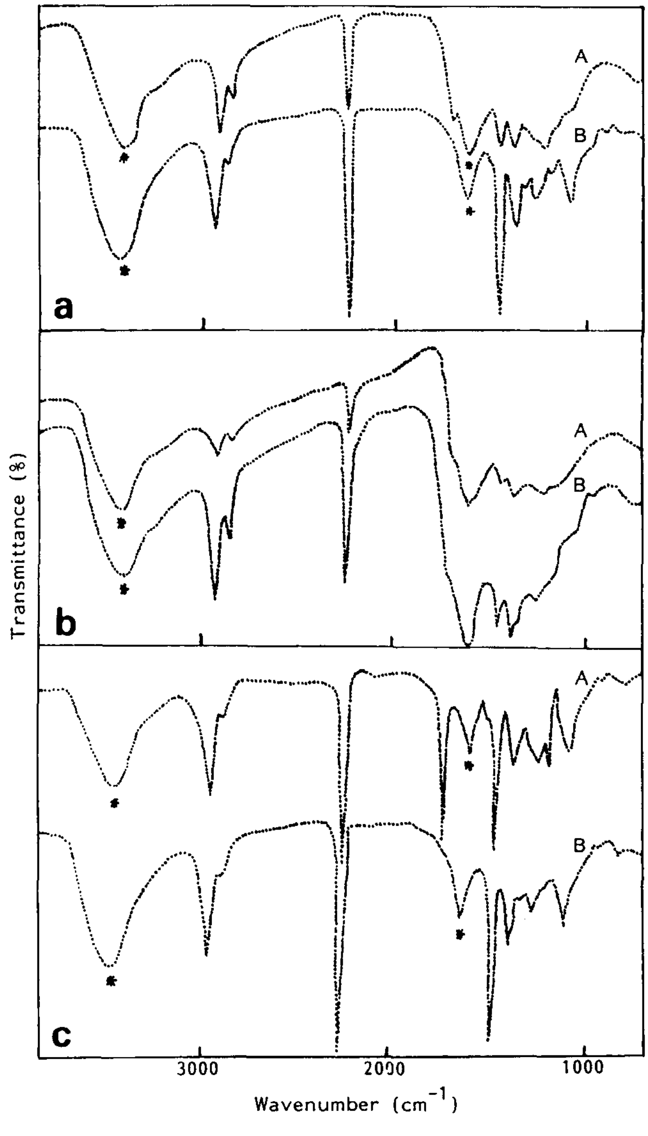


Figure 11 I.r. spectra of (A) P(AN-co-MA) and (B) PAN annealed at 190°C for (a) 2 h, (b) 24 h, and (c) untreated. The bands marked by an asterisk are due to moisture in KBr

and accelerating influence of the comonomer unit on the rate of the chemical processes.

The results of i.r. studies presented are not sufficient to characterize the annealing behaviour of the copolymer at higher temperatures. However, it seems that they confirm the hypothesis of the role of the comonomer units as a factor generating and accelerating the chemical changes through their influence on the conformation of the chain fragments near the comonomer units.

CONCLUSIONS

Investigations carried out by means of WAXS, ^{1}H BL-n.m.r. and i.r. methods have shown both the differences and similarities between the structure, molecular mobility and behaviour on annealing of PAN and P(AN-co-MA). On the basis of ^{1}H BL-n.m.r. results a conformational model describing the copolymer chain was proposed. In this model it was assumed that: (1) 'pure' AN sequences feature a rigid, twisted conformation, the same as for homopolymer[15]; and (2) the conformation of sequences with an MA or IA unit in the central position is more extended (of zig-zag type). Thus P(AN-co-MA) macromolecules can be thought of as alternating longer fragments of molecular rod of 0.6 nm diameter and shorter fragments fitting within a cylinder of a smaller diameter. The mean length of the 'thicker' fragments of such non-uniform 'molecular rods' would obviously depend on the number of 'foreign' units in the chain.

Comparative analysis of X-ray traces of PAN and P(AN-co-MA) showed that the 'foreign' units do not produce a change in lateral hexagonal type chain packing in paracrystalline regions. However, this structure is less perfect for the copolymer, suggesting the presence of 'foreign' unit-containing sequences within these regions. The short chain fragments containing 'foreign' units may be considered as intramolecular defects of the hexagonal lattice. These, in turn, would be responsible for intermolecular defects, i.e. deviations of 'molecular rods' fragments of 0.6 nm diameter from the parallelism.

The structure of the paracrystalline regions of the copolymer improves on annealing at temperatures up to about 100°C (the first step), while in the annealing temperature range 100–150°C (the second step) there is an increase in the size of these regions accompanied by their further improvement. In the second step of annealing the copolymer's structure is more perfect than in PAN. In our opinion, the explanation of this rather unexpected phenomenon may also be connected with the presence of the 'foreign' units, resulting in the existence of the chain fragments of flexible conformation. The influence of these fragments on the structural changes on annealing would consist of (1) facilitating parallelization of the molecular rods comprising 'pure' AN sequences (the 'hinge' effect); and (2) increasing the possibility of optimal pairing between nitrile dipoles of neighbouring chains.

At higher annealing temperatures (150–210°C, the third step) some chemical changes compete with the ordering processes, leading to a decrease of the amount of paracrystalline regions and the degree of their perfection. This phenomenon is undoubtedly connected with the presence of the comonomer units and their facilitating and accelerating influence on the intra- and intermolecular chemical reactions (i.e. the cyclization and crosslinking)[10,23–26].

The influence of the comonomer units on molecular mobility of P(AN-co-MA) chains compared with PAN chains is also evident. The existence of short chain fragments of less rigid conformation leads to an increase in the net effective flexibility of the chain and a consequent depression of T_g. The shift of the T_g range towards lower temperatures is observed both for amorphous and paracrystalline regions. This would confirm the possibility of 'foreign' units being incorporated into ordered areas of the copolymer.

Thus the interpretation of the differences and similarities between WAXS and ^{1}H BL-n.m.r. spectra of the homopolymer and the copolymer led us to accept a structural model for P(AN-co-MA) which, compared with PAN, assumes: (1) the presence of intramolecular defects giving rise to an enhanced non-uniformity in the thickness of molecular rods forming the paracrystalline regions (i.e. the existence of fragments with rigid and flexible conformation alternating in the chain); and (2) the occurrence of intermolecular defects which disturb the supermolecular structure, but which may be efficiently eliminated due to the existence of intramolecular defects.

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APPENDIX A TACTICITY ANALYSIS

Figure 12 presents the 100 MHz ^{1}H-n.m.r. spectrum of poly(acrylonitrile-co-methyl acrylate) in DMF-d_7 solution. The spectrum consists of the multiplet originating from the methine protons at lower field (at around $\delta = 3.25$ ppm) and the multiplet assigned to the resonance of the methylene protons at higher field (at around $\delta = 2.25$ ppm). The CH_2 signal is considered[29] as a result of two overlapping triplets connected with isotactic and syndiotactic sequences.

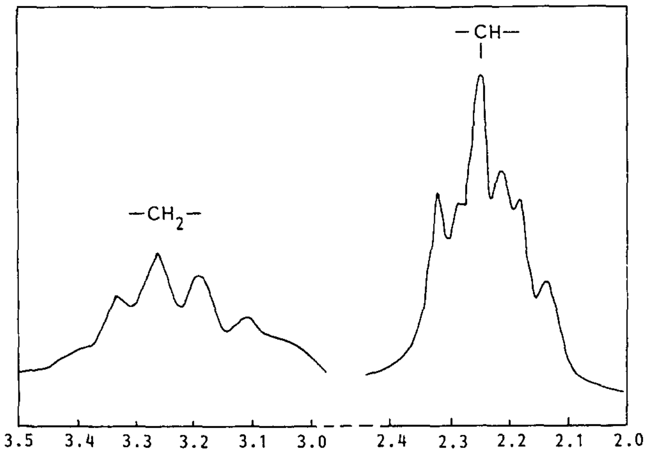

Figure 12 100 MHz ^{1}H n.m.r. spectrum of poly(acrylonitrile-co-methyl acrylate) in DMF-d_7 at 155°C (Varian XL-100, TMS)

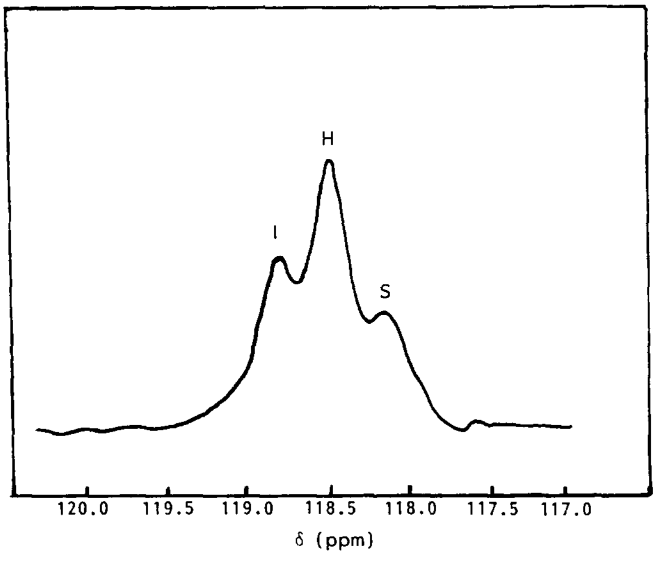

Figure 13 50.3 MHz $^{13}C\{^1H\}$ n.m.r. spectrum of poly(acrylonitrile-co-methyl acrylate) in DMF-d_7 at room temperature (Varian XL-200, TMS), cyano group signal

Analysis of the tacticity of AN sequences in the examined copolymer was performed on the basis of the $^{13}C\{^1H\}$ n.m.r. signal of the cyano group's carbon, as the most stereosensitive signal. The appropriate spectrum is shown in *Figure 13*.

The visible splittings of the signal were assigned according to the literature[30] to isotactic (I), heterotactic (H) and syndiotactic (S) triads, respectively, from lower to upper field. The amounts of the triads were calculated: $I = 30\%$, $H = 50\%$ and $S = 20\%$, and on this basis, according to the following equations[31]:

$$i = I + 0.5H \tag{1}$$

$$s = S + 0.5H \tag{2}$$

the diad stereoregularity was determined. The values obtained, i.e. $i = 55\%$ and $s = 45\%$, indicate that the AN sequences in the copolymer are slightly isotactic-rich.

APPENDIX B CALCULATION OF THEORETICAL VALUES OF SECOND MOMENT

The second moment was determined by adding up the contribution of each of the various structural proton groups to the total absorption. The calculations were made using the appropriate form of Van Vleck's formula[32]:

$$\Delta H_2^2 = \frac{18}{5} \frac{\mu^2}{N} \sum_{j>k} r_{jk}^{-6} \tag{3}$$

where r is the distance between the protons, μ is the magnetic moment of the protons and N is the number of protons analysed. The intramolecular part of the second moment, originating from the interactions of protons within separate groups and from the interactions external to the groups themselves within the same molecule, was calculated for P(AN-co-MA) chain triads. The contribution to the second moment due to interactions of protons from neighbouring chains (i.e. the intermolecular part of the second moment) was neglected for reasons discussed elsewhere[15,33]. The respective H–H distances in AN sequences in P(AN-co-MA) result from the presumed conformational model of PAN chain[15].

For P(AN-co-MA) the total second moment can be divided into four terms:

$$\Delta H_2^2 = aA + bB + cC + dD \tag{4}$$

where A and B are the second moment values connected with the pairs of the approached protons from H–C–CN groups and the remaining protons of 'pure' AN triads, respectively, which feature the same conformation as the homopolymer[15,20]; C is the second moment of the comonomer unit, centred triad; and D is the contribution of methyl groups to the second moment reduced by a factor of $\frac{1}{4}$ due to their rotation about the symmetry axis[34]. The relative amounts of the proton groups contributing the A, B, C and D components to the total second moment are a, b, c and d, respectively. These were calculated on the basis of the chemical composition of the copolymer and on the assumption that the conformation of a triad with the 'foreign' unit in the central position differs from the conformation of a 'pure' AN triad. For A and B the same values as for homopolymer were taken; for C a value of $11.5\,\mathrm{G}^2$, corresponding to the 'zig-zag' conformation, was accepted[15] and for D[35]:

$$D = \tfrac{1}{4}(22.5 + 1.5)\,\mathrm{G}^2 = 6\,\mathrm{G}^2 \qquad (5)$$

Thus, if methyl groups rotate about their symmetry axes, while the chains are otherwise motionless, the value of the second moment to be expected is:

$$\begin{aligned}\Delta H_2^2[\mathrm{P(AN\text{-}co\text{-}MA)}] &= 0.162 \times 33.7 + 0.577 \times 15.3 \\ &\quad + 0.205 \times 11.5 + 0.056 \times 6 \\ &= 17.0\,\mathrm{G}^2\end{aligned}$$

For comparison the value of the PAN second moment is $19.4\,\mathrm{G}^2$ (refs. 15, 20).