

Nuclear magnetic resonance and wide-angle X-ray scattering in poly(acrylonitrile-*co*-methyl acrylate): 2. The influence of comonomer on swelling behaviour

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The changes of conformation and supermolecular structure of poly(acrylonitrile-*co*-methyl acrylate) on swelling have been revealed by combining ¹H broad-line nuclear magnetic resonance and wide-angle X-ray scattering techniques. The similarities and differences in swelling behaviour and the resulting structure between polyacrylonitrile and the copolymer have been presented and interpreted.

(Keywords: polyacrylonitrile; poly(acrylonitrile-*co*-methyl acrylate); wide-angle X-ray scattering; broad-line nuclear magnetic resonance; swelling; morphology; conformation)

INTRODUCTION

Acrylonitrile-based copolymers have been found to be materials of great industrial importance. They can yield acrylic fibres¹ as well as precursors of carbon fibres². The utility of the copolymers has provided the impetus for the interest in their structure and properties³⁻¹⁰.

Our previous paper¹¹ dealt with the influence of methyl acrylate on the structural characteristics and annealing behaviour of poly(acrylonitrile-*co*-methyl acrylate), P(AN-*co*-MA). The role of the comonomer units in molecular mobility and changes in supermolecular structure on heat treatment have been shown.

The aim of the present work is to reveal the effect of the comonomer on the copolymer behaviour and structural changes upon swelling.

EXPERIMENTAL

Sample preparation

A terpolymer of acrylonitrile (AN, 93 mol%), methyl acrylate (MA, 6 mol%) and itaconic acid (IA, 1 mol%) was used in the work reported here. The conditions of synthesis and preparation as well as the general chemical formulae were described earlier¹¹. The polymer will be referred to as poly(acrylonitrile-*co*-methyl acrylate) throughout the paper and abbreviated as P(AN-*co*-MA). Powdered samples were swollen in nitromethane at different temperatures.

Measurements

X-ray diffraction traces were recorded on a Dron-1.5 diffractometer, using Cu K α radiation. ¹H broad-line nuclear magnetic resonance (b.l. n.m.r.) spectra were taken on a Varian WL-109 spectrometer at a resonance frequency of 30 MHz. The numerical analysis of these spectra was carried out by means of a Wang-2200 B minicomputer. A Specord M80 spectrophotometer was used to obtain i.r. spectra.

RESULTS AND DISCUSSION

Swelling

Nitromethane was chosen as the swelling agent for P(AN-*co*-MA). This selection was made based on the results of our previous investigation of PAN swelling behaviour^{12,13}. A known amount of powdered copolymer was immersed in the proper volume of nitromethane, giving samples with the required degree of swelling. Degrees of swelling were determined as the ratio of the mass of absorbed liquid to the mass of the copolymer.

The copolymer samples reached significantly higher degrees of swelling as compared to the homopolymer swollen under the same conditions¹². For example, at 30°C the equilibrium degree of swelling of P(AN-*co*-MA) is ~200 wt%, while at 90°C it reaches the value of ~400 wt%. The corresponding values for PAN were 50 and 130 wt%¹². Moreover, the homopolymer samples do not change macroscopically in a significant manner—they look like a wet powder. In the case of the copolymer, drastic changes are observed—the powdered P(AN-*co*-MA) samples undergo gelation on swelling, becoming yellow and transparent. The reasons for these differences are discussed in subsequent sections.

¹H b.l. n.m.r. spectra of swollen P(AN-*co*-MA) samples

The swelling of P(AN-*co*-MA) samples for n.m.r. measurements was performed in nitromethane-*d*₃ directly in the n.m.r. sample tubes at different temperatures in the range 20 to 100°C. The degree of swelling was set at 100 wt% in all cases.

The ¹H b.l. n.m.r. spectra were recorded at room temperature after several hours of sample swelling at a given temperature. In *Figure 1* the spectra of the copolymer swollen at 20, 50 and 80°C are displayed.

Similarly as for the swollen acrylonitrile homopolymer (PAN)¹³, the spectra were divided into three components, designated α , β and γ , and described respectively by: (1) a shape function appropriate to a rigid two-proton

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system^{14,15} with H-H distance being 1.5 Å¹⁶; (2) a Gaussian function; and (3) a shape function of the narrow component recorded under conditions of overmodulation¹⁷. The sum of the α and β components will hereafter be referred to as the broad part of the spectrum.

The α component was assigned to H-C-CN protons, which mutually approach to a mean distance of ~ 1.5 Å¹⁶ due to the strong repulsion between nitrile dipoles, resulting in a specific twisted chain conformation^{3,8}. This component is connected with a conformational model previously proposed for the PAN chain^{16,18} and for the

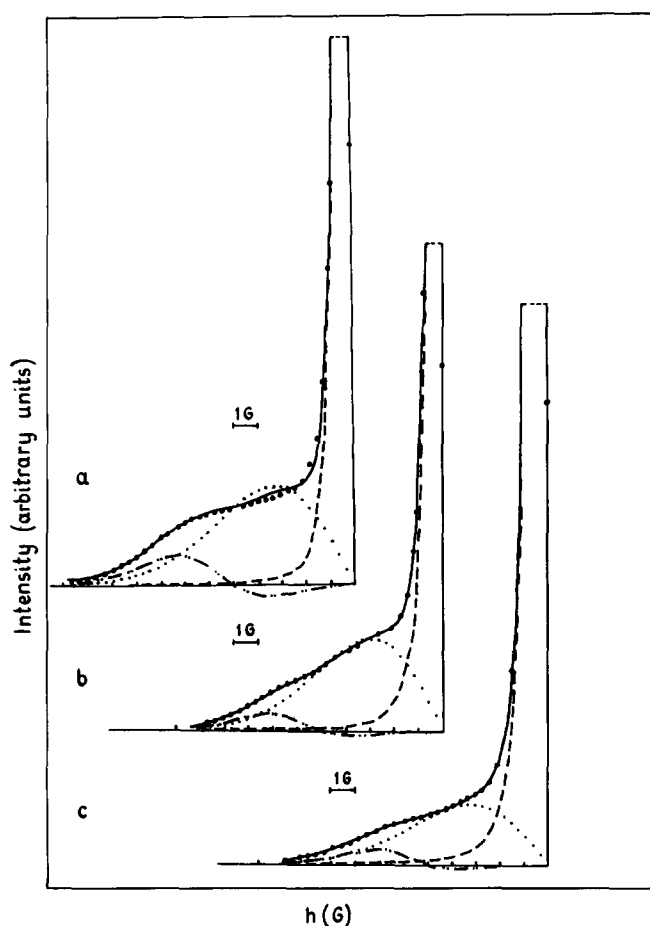


Figure 1 Room-temperature first derivative (one-half shown) ¹H b.l. n.m.r. absorption spectra of P(AN-co-MA) swollen in nitromethane-d₃ at (a) 20°C, (b) 50°C and (c) 80°C: (—●—) experimental; (---) calculated; (·····) α component; (-·-·-) β component; (----) γ component

majority of AN sequences in P(AN-co-MA)¹¹ within both the paracrystalline regions of hexagonal packing and amorphous areas. All the other protons of the chains belonging to the ordered regions and to the part of amorphous areas that does not experience a significantly enhanced molecular mobility are assumed to give rise to the β component. Then the γ component may be ascribed to the remaining part of disordered regions involved in a rapid molecular motion.

The numerical analysis of the spectra of the copolymer swollen in nitromethane-d₃ made it feasible to yield the relative amounts of the individual components and their widths. The experimental values of the amounts of these components are given in Table 1. These results show that an expected increase in the amount of γ component with increasing swelling temperature ensues, pointing to an increasing amount of disordered regions of extensive mobility. Simultaneously a decrease in the amounts of β and α components is observed. More interestingly, the amount of the latter in the broad part of the spectrum reduces on swelling, indicating the occurrence of conformational changes of the chains encompassed by the broad part of the spectrum.

For acrylonitrile homopolymer (PAN) swollen in nitromethane at temperatures above 30°C, the value of the amount of α component indicated the total change of conformation in each chain sequence in the paracrystalline regions¹³. Such changes were shown to precede the reorganization of supermolecular structure, consisting of the change of chain packing type within these areas from hexagonal to orthorhombic¹². As mentioned above, the analysis of the amount of the α component in the ¹H b.l. n.m.r. spectra of the swollen copolymer also points to the occurrence of such changes. In order to determine their extent, the theoretical amounts of this component were calculated for two cases, as for the homopolymer¹³. In the first case it was accepted that the α component originates from the proton pairs of a part of disordered regions contributing to the β component as well as paracrystalline ones. With this assumption, the amount of the α component in the broad part of the spectrum would remain constant regardless of the amount of γ component and equal to the value calculated for non-swollen copolymer, i.e. $\sim 18.5\%$ ¹¹.

The second case assumes that the α component represents the proton pairs in the chains belonging exclusively to disordered regions (naturally excluding the part which contributes to the γ component).

The comparison of the data in Table 1 shows that the

Table 1 Experimental and calculated values of the amounts of components in the ¹H b.l. n.m.r. absorption spectra of P(AN-co-MA) swollen in nitromethane-d₃ ($T = 20^\circ\text{C}$ = measurement temperature; T_{sw} = swelling temperature)

T_{sw} (°C)	Experimental ^a					Calculated					
						Case I ^b			Case II ^c		
	$a_\alpha + a_\beta$	a_γ	a_α	a_β	a_α^*	a_α	a_β	a_α^*	a_α	a_β	a_α^*
20	85	15	14	71	16.4	15.7	69.3	18.5	10.2	74.8	12
50	70	30	10	60	14.2	12.9	57.1	18.5	7.4	62.6	10.6
80	55	45	8	47	14.5	10.2	44.8	18.5	4.6	50.4	8.4

^a a_α , a_β , a_γ = relative amounts of the components in the total spectrum (%); a_α^* = relative amount of the α component in the broad part of the spectrum (%)

^b The α component originates from both immobile amorphous and paracrystalline regions

^c The α component originates only from immobile amorphous regions

experimental amounts of α component are intermediate between those calculated for the two cases. As this component describes the protons whose disposition results from the twisted chain conformation, the data indicate that only a part of the AN sequences is involved in the conformational change of the chains within paracrystalline areas. In our previous work¹¹ a conformational model for the P(AN-co-MA) chain has been proposed which presents the copolymer macromolecule in the form of alternating longer fragments of 6 Å diameter 'molecular rod', comprising 'pure' AN sequences, and shorter ones, containing chain triads with 'foreign' units in the central position. For these short fragments a smaller diameter of the 'rod', as a consequence of a more untwisted conformation, has been accepted. It seems that these sites are the starting points for further conformational changes on swelling leading to the lengthening of the smaller-diameter fragments. Figure 2 presents schematically the supposed picture of the changes of the copolymer chain's shape on swelling.

The width of the β component in the spectrum of swollen P(AN-co-MA) is ~ 6.4 G and the second moment ΔH_2^2 of this component is 10.2 G². The respective values for non-swollen P(AN-co-MA)¹¹ are 7.5 G and 14 G². The decrease of the width and the second moment of the β component on swelling are consistent with the view of conformational changes within the chains of paracrystalline areas presented above on the basis of the analysis of the amount of α component. By analogy with the swelling behaviour of the homopolymer¹³, the conformational transition of an irregular helix to zig-zag type can be assumed. However, the theoretical value of ΔH_2^2 for the β component when regarding a zig-zag conformation along the whole chain fragment, belonging to the paracrystalline region, is found to be ~ 12.7 G². Taking into account a merely partial change of conformation evidenced by the analysis of the amount of α component, the theoretical value would be still higher, thus making a rather large discrepancy with the experimental value of 10.2 G². This mismatch seems to indicate some

increase in mobility of the chains within disordered regions, which contribute to the β component, resulting in the reduction of its experimental ΔH_2^2 value.

The disordered areas of P(AN-co-MA) not only appear in the b.l. n.m.r. spectra of the swollen copolymer in the form of the narrow, γ component, but they also partially contribute to the β component. The amount of the γ component in the spectra recorded at room temperature increases considerably with the swelling temperature (see Table 1), reaching 45% for $T_{sw} = 80^\circ\text{C}$ (while being only 20% for PAN¹³). In the case of PAN the analysis of the amount of γ component demonstrated¹³ that in the disordered part of the homopolymer two kinds of regions differing in degree of order and molecular mobility may be distinguished: truly amorphous areas, giving rise to the γ component, as well as non-ordered ones with a rather high degree of correlation between the positions of neighbouring chains. In comparison with PAN, the considerably higher amount of the γ component in the copolymer spectra may thus indicate the increased contribution of the truly amorphous regions in the disordered part. This can imply a higher total accessibility of the copolymer to swelling (mentioned in the relevant section) as compared with PAN and a lower effective degree of swelling of paracrystalline areas. This could explain why in the first approach the chains of these areas in P(AN-co-MA) undergo only a partial change of conformation as opposed to the homopolymer for which a total conformational change takes place. Moreover, the increased contribution of amorphous areas, involved in rapid motion on swelling, can influence the dynamics of the chains within the remaining part of disordered regions and probably also paracrystalline ones. This effect could be responsible for the mentioned decrease of the β component's second moment below the expected value.

These considerations may also lead to an additional source of T_g lowering of P(AN-co-MA) relative to PAN¹¹. This depression, on the one hand, could thus be explained by the enhanced flexibility of the chain as a consequence of incorporation of 'foreign' units¹¹ (internal plasticization) and, on the other, could be connected with the increased contribution of the truly amorphous regions, affecting the molecular mobility of their neighbours.

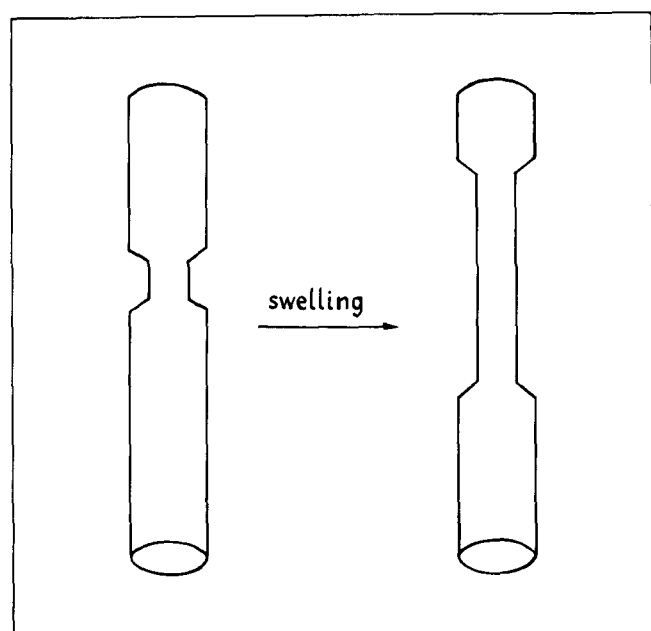


Figure 2 Schematic representation (not to scale) of the effect of swelling by nitromethane on chain conformation of P(AN-co-MA)

X-ray study of swollen P(AN-co-MA): mechanism of swelling

In order to describe the structural changes occurring in P(AN-co-MA) on swelling as well as the influence of the 'foreign' chain units on the swelling mechanism, the X-ray traces of P(AN-co-MA) samples swollen for 24 h in nitromethane at different temperatures in the range 25–95°C were recorded. X-ray traces were taken at room temperature after several weeks of drying at 30°C.

Figure 3 presents the X-ray traces of the copolymer samples swollen to 50, 100 and 200% at 30 and 95°C. In all cases of swollen P(AN-co-MA) samples, the main reflection at $2\theta = 17^\circ$ is split into two broad maxima. Their positions seem to be close to the values of 16.8° and 17.6° observed for PAN¹² (the third reflection at $2\theta = 29.5^\circ$ is present only for samples of moderate degrees of swelling). Regardless of swelling temperature, the shape of the X-ray traces of P(AN-co-MA) swollen in nitromethane resembles the shape of the X-ray traces of

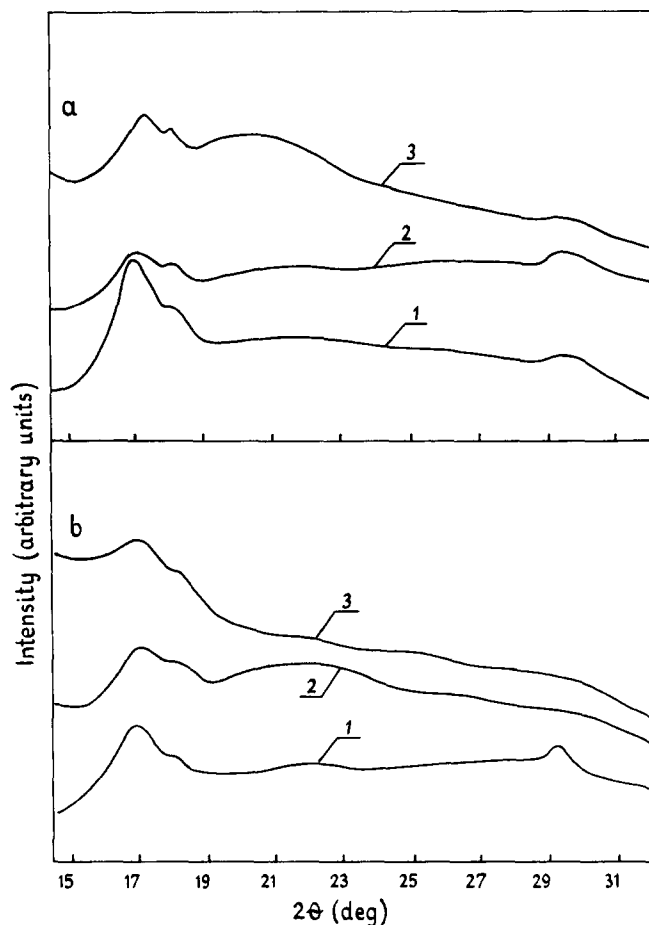


Figure 3 Wide-angle X-ray diffraction traces of P(AN-co-MA) swollen in nitromethane at (a) 30°C and (b) 95°C. Degree of swelling: (1) 50 wt%, (2) 100 wt% and (3) 200 wt%

PAN swollen in the same liquid at temperatures up to 30°C. In X-ray traces of PAN samples swollen under such conditions, only a strong deformation of the main reflection has been observed¹², the deformation being due to a superposition of two broad reflections from an orthorhombic lattice. However, for PAN the sharpening of the reflections has been observed with increase in swelling temperature¹². According to the literature^{4,19}, such a splitting has been interpreted as being connected with the changes of chain arrangement within paracrystalline areas of the polymer from hexagonal to orthorhombic¹². The similarity of the shape of the X-ray traces of the unswollen homo- and copolymer points to the similarity of the supermolecular structures of the polymers^{11,18}. On the other hand, the splitting of the main reflection at $2\theta = 17^\circ$ observed for PAN¹² as well as for P(AN-co-MA) swollen in nitromethane suggests a similar course of the swelling process in both cases. Thus it seems that the swelling mechanism proposed by us for PAN^{12,13} can be accepted also in the case of P(AN-co-MA).

The forces effective in PAN result predominantly from interactions of the strongly polar CN groups. The intramolecular repulsion of adjacent nitrile groups compels the individual macromolecules into a somewhat irregular helical conformation. Such a macromolecule may be thought of as a molecular rod fitting within a cylinder of about 6 Å diameter^{3,8}. The molecular rods (cylinders) packed side-by-side and laterally bonded by intermolecular dipolar interactions form hexagonally

ordered areas of polymer³. Swelling of these areas could be possible only in the case of lowering of the diameter of the molecular cylinders. This in turn requires a change of the helical conformation into a conformation featuring a smaller cylinder diameter, e.g. zig-zag type. Such a conformational change could be the result of replacing dipole-dipole interactions of the polymer molecules by interactions of the polymer CN groups with dipoles of the swelling agent⁸. As a consequence the change of the chain arrangement within the ordered areas from hexagonal to orthorhombic may become possible^{12,20}. Since a 'zig-zag' type conformation is not energetically favourable^{21,22}, one can expect that removing a swelling agent will cause the restoration of the helical conformation and hexagonal arrangement of the chain fragments building up the ordered regions. In fact, such an effect has been observed for PAN^{12,13}. In the case of the copolymer P(AN-co-MA), the orthorhombic structure is preserved after removing the swelling agent. Thus, as a result of swelling, a stable but disturbed orthorhombic structure is obtained, and annealing leads to its improvement as reflected by the sharpening of the reflections (Figure 4).

From the comparison of the X-ray traces of the homopolymer swollen at temperatures up to 30°C¹² with the X-ray traces of the copolymer swollen at temperatures in the range 20–95°C as well as from ¹H b.l. n.m.r. results, the following conclusions can be drawn:

(i) ordered regions of P(AN-co-MA) become orthorhombic on swelling, the degree of disturbance being higher than in PAN; and

(ii) in swollen P(AN-co-MA) only a partial change of conformation of the chain fragments forming the ordered areas takes place, regardless of the swelling temperature.

The interpretation of the differences and similarities in WAXS and ¹H n.m.r. spectra of homo- and copolymer led us to accept a structural model for P(AN-co-MA)¹¹. The model as compared to PAN assumes the presence of intramolecular defects (i.e. AN-MA-AN or AN-IA-AN sequences) as well as the occurrence of intermolecular defects, which disturb the parallelism of molecular rods within the paracrystalline regions ('hinge' effect). Based upon the proposed model, conclusion (i) may be completed with the assumption that in ordered regions of the swollen copolymer different conformational forms

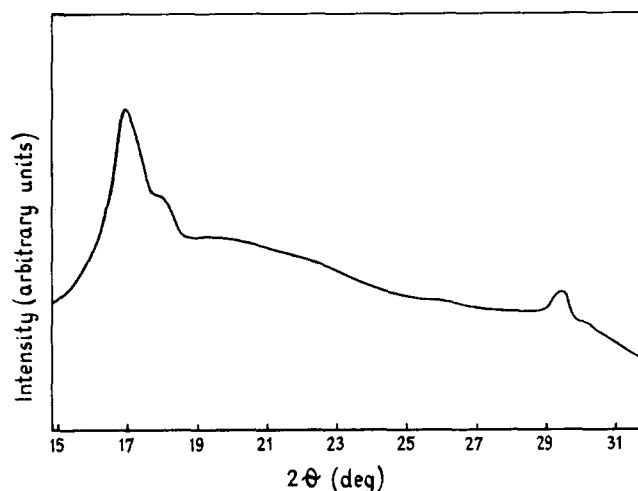
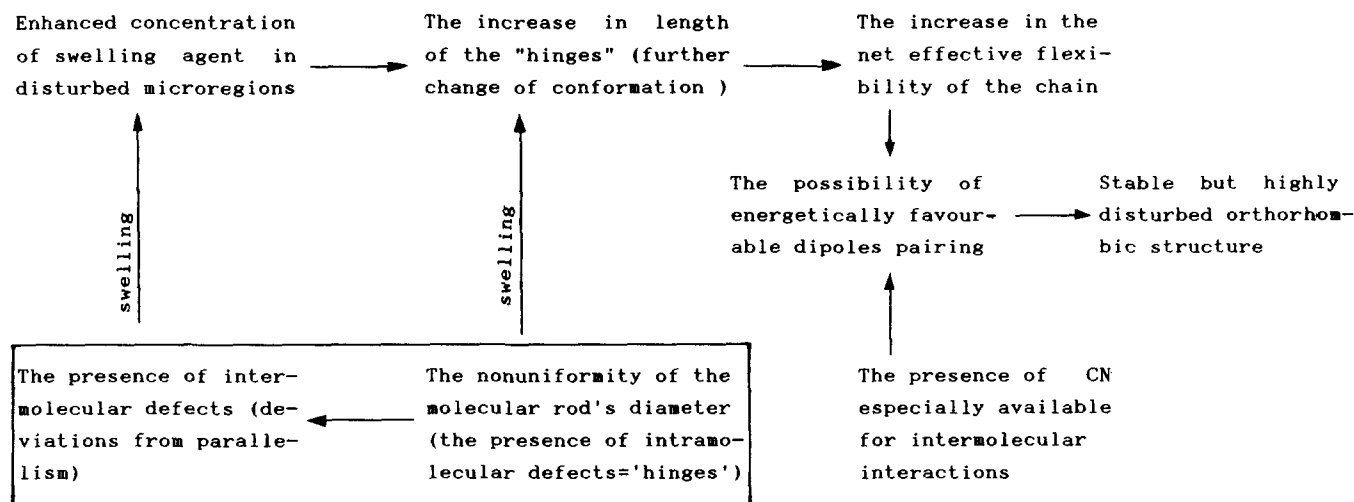


Figure 4 Wide-angle X-ray diffraction trace of P(AN-co-MA) after swelling in nitromethane at 30°C (degree of swelling 100 wt%) and annealing for 24 h at 150°C



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

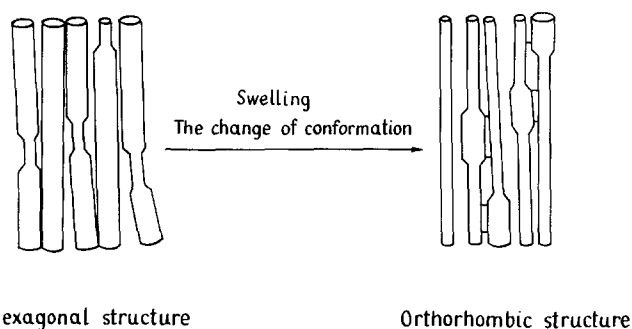


Figure 5 Schematic representation (not to scale) of the effect of swelling by nitromethane on P(AN-co-MA) structure

exist simultaneously (Figure 5). Thus in the original PAN, a uniform* helical conformation changes on swelling into a likewise uniform* 'zig-zag' conformation, whereas in P(AN-co-MA) both conformational types are present before swelling (pure AN sequences forming a helix and AN-MA-AN sequences a 'zig-zag' type conformation). Upon swelling, only their proportion varies.

In unswollen P(AN-co-MA), the helical form is predominant, while swelling causes an increase of 'zig-zag' type sequences. The main reason for the conformational non-uniformity in P(AN-co-MA) is the presence of 'foreign' units in the copolymer chain and thereby intra- and intermolecular defects¹¹. Moreover, the intermolecular defects disturbing the chain parallelism in P(AN-co-MA) ordered regions increase the probability of liquid penetration of micro-areas containing the defects (Figure 5). Thus the swelling agent concentrates in such micro-areas and the swelling becomes inhomogeneous. Along with the highly swollen micro-regions, there can exist unswollen ones, in which temperature is the main factor influencing the structure. In such micro-regions the helical conformation of the chain fragments and their hexagonal arrangement ought to be preserved as in the case of annealing¹¹. On the other hand, the 'zig-zag' type conformation may be expected in the swollen micro-regions as in swollen PAN¹³. This means that short chain fragments containing 'foreign' units ('hinges') undergo elongation on swelling. The 'hinge' elongation causes the increase in

* In terms of molecular-rod diameter

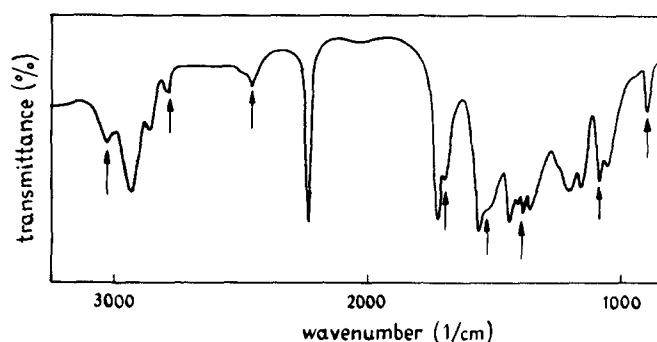


Figure 6 I.r. spectrum of P(AN-co-MA) swollen in nitromethane at 95°C (degree of swelling 100 wt%). The bands marked by arrows are due to nitromethane

net effective flexibility that is evidenced by d.s.c. measurements (e.g. the T_g of P(AN-co-MA) swollen to 50 wt% at 60°C is about -8.6°C). Moreover, it increases the number of CN groups available for intermolecular interactions. Both these factors are essential for energetically optimal dipole pairing. Such energetically optimal dipole pairs 'freezing' the new conformation of the chain sequences would be responsible for the stability of the orthorhombic structure. However, they would block further change of chain conformation on swelling. Thus, in that way, intramolecular defects of the orthorhombic lattice would arise—e.g. short chain sequences with 'frozen' helical conformation (Figure 5). The defects of the orthorhombic lattice and the presence of dipole pairs restrain the reorientation of chains in the swollen ordered regions. As a result the orthorhombic structure becomes highly disturbed. Scheme 1 presents the proposed swelling mechanism of P(AN-co-MA). In consequence of inhomogeneous swelling of the paracrystalline regions, the non-uniformity of the chain conformation becomes greater. It seems that conformational non-uniformity is a factor favouring energetically optimal dipole pairing, and thus it is a factor favouring physical crosslinking. Gelation (physical crosslinking) of P(AN-co-MA) samples swollen in nitromethane would confirm the hypothesis, especially in view of the fact that no gelation of PAN samples swollen in nitromethane has been observed (homogeneous swelling). Gel P(AN-co-MA) samples are soluble in dimethylformamide independently of swelling temperature. I.r. investigations of

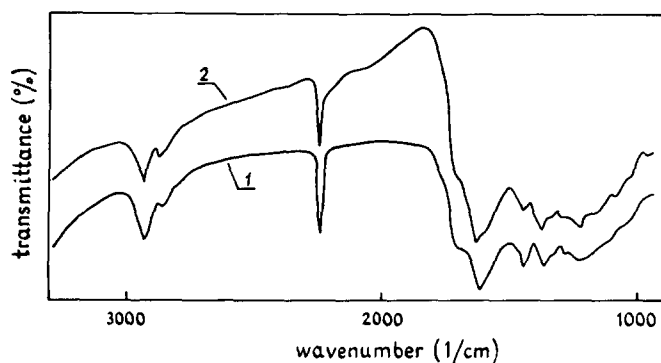


Figure 7 I.r. spectra of P(AN-co-MA): (1) after swelling in nitromethane at 30°C (degree of swelling 100 wt%), drying at 30°C and annealing for 24 h at 150°C; and (2) unswollen sample after annealing for 24 h at 200°C

all swollen samples of P(AN-co-MA) do not show chemical changes (Figure 6, ref. 11). These are observed only in i.r. spectra of P(AN-co-MA) samples annealed after swelling for 24 h at 150°C (Figure 7). Thus they take place at lower temperatures than for unswollen P(AN-co-MA)¹¹. This fact confirms the supposition of the formation of energetically optimal dipole pairs on swelling, since the presence of CN groups particularly available for dipole interactions is connected with a conformation favouring chemical changes²³⁻²⁶, and physical crosslinking is also an important factor facilitating chemical changes²⁷.

CONCLUSIONS

Swelling of P(AN-co-MA) in nitromethane causes a partial change of conformation connected with a change of chain packing within paracrystalline regions from hexagonal to orthorhombic.

The copolymer structure resulting on swelling is more disturbed but stable as compared to the homopolymer.

The influence of swelling temperature on improvement of the orthorhombic structure is of no significance as opposed to the homopolymer.

The annealing of the swollen P(AN-co-MA) samples results in the chemical changes occurring at lower temperatures than in unswollen copolymer.

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