Orientation in Acrylonitrile Copolymers

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Synopsis

Rubber modified and unmodified poly(acrylonitrile/methyl acrylate) (75/25) copolymers [(Barex® resins) (Barex® is a registered trademark of Vistron Corporation, a subsidiary of The Standard Oil Company, Ohio)] were stretched at varying strain rates at different temperatures. Molecular orientation of the stretched samples at different extension ratios was determined using birefringence, the X-ray orientation factor, and infrared dichroism. The birefringence of rubber modified copolymers, which were prepared by graft copolymerization of the poly(acrylonitrile/methyl acrylate) copolymer with 10 parts (by weight) of a poly(butadiene/acrylonitrile) rubber, is found to be appreciably different as compared with the birefringence of unmodified poly(acrylonitrile/methyl acrylate) copolymer. The possible reasons for this difference are discussed. The orientation measured from the three techniques is compared, and the effects of temperature of stretching and of strain rate are discussed. The maximum values of the birefringence of these two copolymers and that of the polyacrylonitrile have been estimated. Transition moment angles for CH_2 and $C{\equiv}N$ stretching bonds are obtained. From the birefringence data at various temperatures and strain rates, the activation energies of these two copolymers have been obtained.

INTRODUCTION

This paper presents a comprehensive attempt to investigate and understand the mechanism of molecular deformation and orientation in acrylonitrile copolymers. The copolymers studied in this paper are unmodified and rubber-modified poly[acrylonitrile (AN)/methyl acrylate (MA)] (75/25) copolymer. Descriptions of these copolymers are given in the Experimental section. The rubber modified copolymer is an acrylonitrile copolymer having properties useful for packaging materials since it has low gas permeability, good chemical resistance, and a minimal amount of thermal and shear sensitivity. It contains 75% polyacrylontrile. A butadiene (BD) phase is also present to provide impact resistance. Previous investigation has shown that some of the glassy AN/MA copolymer is included in the rubber, giving rise to a honeycomb structure.[1] Impact strength has been related to this rubbery phase volume. Dynamic mechanical properties and stress–strain behavior for these copolymers have also been studied.[1,2]

A good deal of controversy exists in the literature as regards the crystal structure and molecular chain conformations in PAN. A number of workers consider PAN either as a one phase material or having some kind of order but not two distinct phases.[3,5–10] A number of authors favor a 2-dimensional

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order.[3-5] The lateral order of PAN is usually attributed to the dipolar intra-molecular repulsions. On the other hand, a number of workers have shown good evidence using techniques such as X-ray and electron diffraction that PAN crystallizes and has 3-dimensional order.[11-16] Imai et al.[15] have shown that PAN can be polymerized in amorphous or crystalline form using different polymerization techniques. In this manner they prepared two different amorphous PAN and crystalline PAN having hexagonal and orthorhombic unit cells. These samples were characterized by X-ray diffraction. In the literature, there is evidence that PAN can be atactic, isotactic, or syndiotactic, depending upon its preparation history.[15-23] Imai et al.[15] concluded that radically initiated polymer has nearly an atactic configuration while the radiation induced polymerization of AN in urea canal has predominantly isotactic configuration. Hinrichsen and Orth[12] concluded that syndiotactic PAN crystallizes in planar zigzag conformation. On the other hand, in a later publication, Colvin and Storr[16] established the conformation of crystalline PAN as a helix with a spacing per monomer unit of 1.774 Å. The optical anisotropy of PAN along with various other polymers has been calculated by Furukawa et al.[32] The molecular structure of acrylonitrile was determined by electron diffraction and infrared spectroscopy by Fukuyama and Kuchitsu.[24] The molecular conformation of PAN has been described as paracrystalline,[25] laterally ordered,[26] extended,[27] and rodlike crystals in a random matrix.[28]

The rheooptical properties of polybutadiene rubber have been studied by a number of authors.[29-32] The values of optical anisotropies have been calculated for various conformations,[32] and the experimental results of stress-optical coefficients discussed using the theory of Kuhn and Grün[33] and Treloar.[34] From the study of birefringence of poly(methyl methacrylate) (PMMA), Raha and Bowden[35] suggested that the molecular chains in PMMA are bound by cohesion points which are dissociated by increasing temperature or under the influence of plastic strain. It has been suggested that the cohesion points can be attributed to interactions between the dipoles of the ester side groups; this may be true in poly(methyl acrylate) (PMA) also. Temperature dependence of birefringence in poly(methyl acrylate) (PMA) has been studied by Andrews and Hammack.[36] The birefringence changes significantly with temperature, and an actual change of sign of birefringence from negative to positive occurs with increasing temperature. The crossover temperature is considerably above T_g in PMA.

The infrared spectra of PAN have been studied in detail by Liang and Krimm.[37] The orientation in PAN has been determined from infrared dichroism, wide-angle X-ray scattering (WAXS), and small-angle X-ray scattering (SAXS),[26] and in a second reference[38] from IR dichroism, WAXS, and birefringence. The structure of oriented PAN film has been obtained by Koenig and co-workers[39-41] using IR dichroism. The transitions have been studied in PAN, AN/MA copolymers, and in rubber-modified copolymers using infrared studies.[39]

The glass transition in PAN has been studied by Gupta and Chand.[42] Stupp and Carr[43] have proposed a two-phase structure for PAN. Comstock et al.[44] have observed a birefringence value of -0.005 in PAN film stretched to a draw ratio of 4. This value is in agreement with the birefringence of spun PAN fibers.[45] The absolute value of the birefringence is found to increase to -0.009 upon a combination of stretching and polarizing with an electric field (5.3×10^4 V/cm)
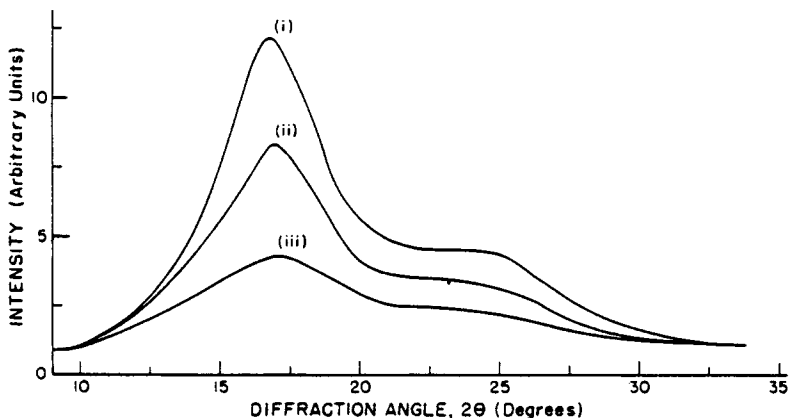
Fig. 1. Radial scans of WAXD in AN/MA and in rubber-modified copolymer at (i) $\phi = 0°$; (ii) $\phi = 30°$; (iii) $\phi = 90°$.

perpendicular to the stretching direction. This increase is attributed to an internal rearrangement of the dipolar groups into directions parallel to the persistent external field.

EXPERIMENTAL

The following two polymer systems were investigated:

(i) AN/MA copolymer: acrylonitrile/methyl acrylate (AN/MA) copolymer. 75% acrylonitrile and 25% methyl acrylate by weight. The AN/MA base resin was prepared by emulsion polymerization.

(ii) Rubber-modified copolymer (Barex® 210 resin): AN/MA copolymer grafted onto 10% butadiene/acrylonitrile (BD/AN) rubber. The BD/AN rubber was prepared by emulsion polymerization of approximately 30% acrylonitrile and 70% butadiene. Grafting was done by copolymerizing AN and MA monomer in the presence of BD/AN latex.

Sheets (approximately 0.015 in. thick) of both AN/MA copolymer and the rubber-modified copolymer were obtained by compression molding the resin between aluminum plates at 200°C. These sheets were used for birefringence and X-ray studies. For infrared studies comparatively thinner films (approximately 0.001 in. thick) were compression molded. These films were vacuum dried at 45°C for 24 h and then stretched to different draw ratios using an Instron Tensile Tester at 23°C, 50°C, 75°C, and 100°C and at strain rates of 2.5%, 125%, and 6250%/min. The films were marked before stretching to determine the local extension ratios.

After stretching to a definite draw ratio at a given temperature, the sample was brought back to room temperature and then taken off the clamps. The birefringence of these samples was measured using a Berek tilting compensator. For measuring the X-ray orientation, flat-plate photographs of the stretched samples were taken. From the photographs the radial scans at azimuthal angles of $\phi = 0°, 5°, 10°, \ldots, 90°$ were taken using a microdensitometer (Fig. 1). These scans resemble very well the scan of the amorphous PAN given by Imai et al.[15] In our copolymer systems there is no evidence of distinct crystalline and amorphous phases. Therefore, our calculation of an X-ray orientation factor are based on a one-phase structure.

The intensity of the scans at $2\theta = 16.7°$ (Fig. 1) was measured using a micro-densitometer. From these measured peak intensities, $I(\phi)$'s, the orientation factor for overall molecular orientation was calculated using the following equations:

$$\overline{\sin^2\phi} = \frac{\int_0^{\pi/2} I(\phi)\sin^3\phi\, d\phi}{\int_0^{\pi/2} I(\phi)\sin\phi\, d\phi} \tag{1}$$

$$f = 1 - \tfrac{3}{2}\overline{\sin^2\phi} \tag{2}$$

where $\phi = 0$ indicates the equator. From this, $f = 1$ for parallel orientation, $f = 0$ for random orientation, and $f = -\tfrac{1}{2}$ for perpendicular orientation.

For several samples the orientation was also determined by taking the areas of the scans in Figure 1 and replacing the intensity $I(\phi)$ in eq. (1) by the area of the corresponding scan. The two orientation values agree well within the limits of experimental error. Another point which should be mentioned here is that this determination of molecular orientation is based on the principle of orientation determination of crystal planes and therefore the accuracy of this method in determining the overall molecular orientation is limited for a system such as this in which the degree of ordering of the structure is not well defined.

In order to determine the dichroic ratios, two infrared spectra were obtained for each sample using Fourier-transform infrared spectrometry (FTIR): one with the electric vector polarized parallel to the stretching direction and a second with the electric vector polarized perpendicular to the stretching direction. Two background scans with two different positions of the polarizer (without sample) were taken; $I_{0\parallel}$ and $I_{0\perp}$, which are the incident intensities in the two directions of the polarizer. These can differ if the incident beam is self-polarized. Therefore, two backgrounds in the two directions of the polarizer are required to correct for the effect of self polarization. The optical densities $\epsilon_\pi = \log I_{0\parallel}/I_\parallel$ and $\epsilon_\sigma = \log I_{0\perp}/I_\perp$ were calculated with $I_\parallel$ and $I_\perp$ being the two transmitted intensities. The dichroic ratio D is given as the ratios of these optical densities, $\epsilon_\pi/\epsilon_\sigma$.

In each FTIR measurement, an average of 300 scans was taken. In this work the dichroic ratios of CH_2 stretching (at 2936 cm^{-1}), $C{\equiv}N$ stretching (at 2241 cm^{-1}), CH_2 bending (at 1426 cm^{-1}), and $CH{=}CH$ out of plane deformation (at 967 cm^{-1}) were determined. If in a polymer system there is some frequency shift for a particular band, then the accuracy of the dichroic ratio of that band will be limited. The width of the peak in the parallel and perpendicular spectrum may also vary. In order to determine if there are any frequency shifts and or variations of peak width, a spectra of $\log(I_{0\perp}/I_\perp) - \log(I_{0\parallel}/I_\parallel)$ was taken as shown in Figure 2. Now if there is any frequency shift for a peak, for a part of that peak the value of $\log(I_{0\perp}/I_\perp) - \log(I_{0\parallel}/I_\parallel)$ will be above the base line of the spectrum, and for the remaining part it will be below the base line. In the case of peak width variation, the peak splits into two. Therefore, from the shape of the CH_2 stretching, CN stretching, and CH_2 bending peaks in Figure 2, it is obvious that there are no peak width variations and that the variation in the frequency shifts is not significant.

In order to determine the statistical error of the dichroic ratios, a sample was
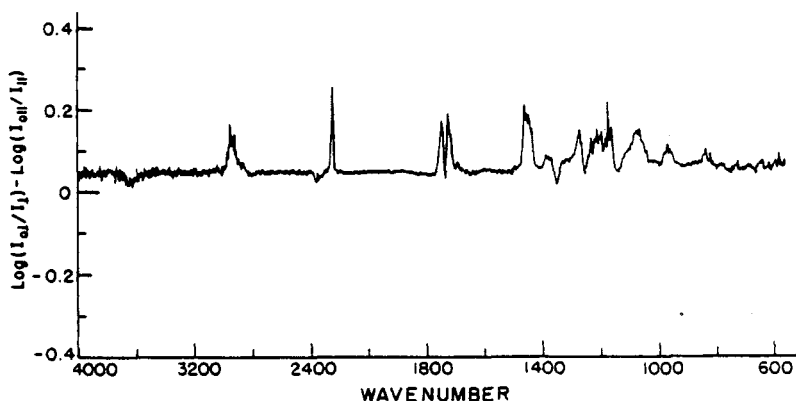
Fig. 2. Infrared spectra of $[\log(I_{0\perp}/I_{\perp}) - \log(I_{0\parallel}/I_{\parallel})]$ of rubber-modified copolymer.

mounted seven times and every time an average of 300 scans was taken. The seven individual measurements of dichroic ratios in one sample revealed that the dichroic ratios of CH_2 (stretching), $C≡N$ (stretching), and CH_2 (bending) and that of $CH=CH$ (out of plane deformation) were found accurate to within a limit of ± 0.02. For the results of the dichroic ratios presented in this paper the deviation is more than ± 0.02 in some cases. This is because all the dichroic ratios presented are the result of a single test.

The relationship between the infrared dichroism D, molecular orientation f, and the direction of transition moments is given by the following relation[46]:

$$f = (D - 1)(D_0 + 2)/(D + 2)(D_0 - 1) \qquad (3)$$

where D_0 is the dichroic ratio of an ideally oriented polymer. D_0 is related to the transition moment angle α_ν by the expression

$$D_0 = 2 \cot^2 \alpha_\nu \qquad (4)$$

Samuels[47] has shown that the molecular orientation function f in eq. (3) is the same as Herman's orientation function [eq. (2)].

RESULTS

Birefringence Studies

The variation of birefringence of both AN/MA copolymer and of rubber-modified copolymer, stretched at 75°C and at strain rates of 2.5%, 125%, and 6250%/min, is given in Figure 3. The birefringence variations of these two copolymers, stretched at 23°C, 50°C, 75°C, and at 100°C and at a strain rate of 125%/min are given in Figure 4. From these figures we observe the following points:

(i) Birefringence of both AN/MA and rubber-modified copolymers is negative and stays negative at all strains (greater than 25%), strain rates, and temperatures of stretching.

(ii) The absolute value of the birefringence of AN/MA copolymer is much higher than the birefringence of rubber-modified copolymer.

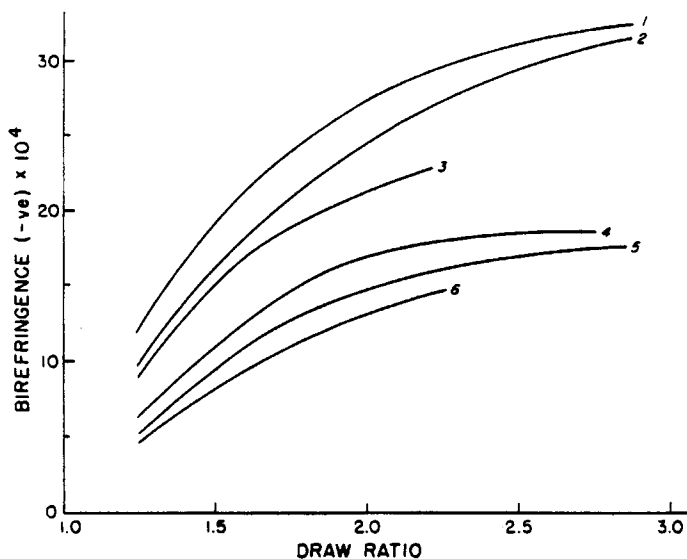(iii) Below the glass transition temperature, the absolute value of birefringence

Fig. 3. The variation of birefringence with draw ratio (effect of strain rate): (1,2,3) AN/MA copolymer; (4,5,6) rubber-modified copolymer. Stretching temp = 75°C; strain rate (%/min); (1,4) 2.5; (2,5) 125; (3,6) 6250.

increases with decreasing strain rate in both AN/MA and rubber-modified copolymers.

(iv) In both copolymers the absolute value of birefringence increases with initial increase in stretching temperature. But both copolymers stretched at 100°C have lower birefringence than the corresponding values for the samples stretched at 75°C.

The comparatively large differences in the birefringence values of AN/MA
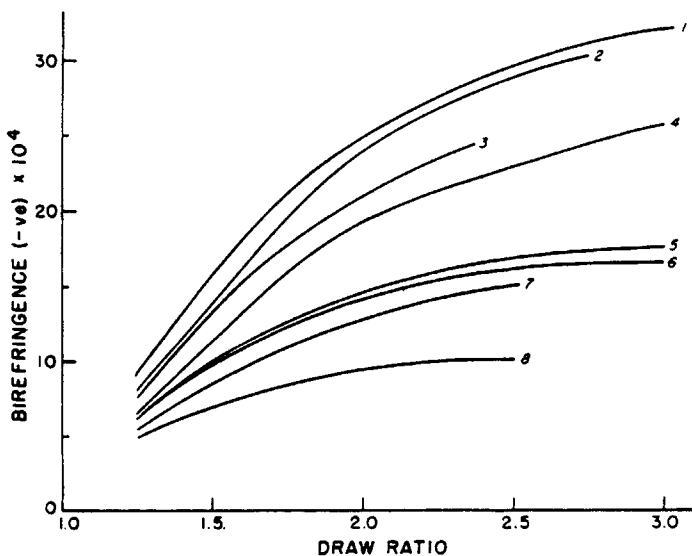

Fig. 4. The variation of birefringence with draw ratio (effect of stretching temperature): strain rate = 125%/min; stretching temp (°C): (3,8) 23; (2,7) 50; (1,5) 75; (4,6) 100; (1–4) AN/MA copolymer; (5–8) rubber-modified copolymer.

copolymer and the rubber-modified copolymer arise only due to approximately 7% (by weight) of butadiene. This suggests that either butadiene has high positive birefringence or that the molecular orientation in the rubber-modified copolymer is significantly less than the molecular orientation at the corresponding draw ratio in AN/MA copolymer. But the differences in molecular orientation in the two copolymers as determined from wide-angle X-ray diffraction (Fig. 7) are not sufficiently high to account for the birefringence difference. This leaves us with the possibility of a high positive birefringence of the butadiene component. As discussed later in this paper, Fukuda et al.[30] and Furukawa et al.[32] have given birefringence values of *cis*- and *trans*-1,4-polybutadiene that are high and positive.

Below the glass transition temperature, the birefringence is high at small strain rates. Deformation changes molecular bond angles and bond lengths. This changes the molecular polarizability and therefore the birefringence. At these temperatures, slow strain rates allow more time for chains to orient, whereas, at fast strain rates, molecular chains do not respond fast enough. Consequently, birefringence increases as the strain rate decreases when these copolymers are deformed under these conditions.

The birefringence increases (Fig. 4) with the initial increase in stretching temperatures from 23°C to 75°C, but decreases for the samples stretched at 100°C. This suggests that, for these two copolymers, the glass transition temperature is between 75°C and 100°C. This result is in agreement with the dynamic mechanical data.[1,2,48]

Activation energy can be calculated from the birefringence results at different temperatures and at different strain rates. For a single relaxation time process

$$\tau = \tau_0 \exp(\Delta E_a / RT)$$

or

$$\ln\left(\frac{\tau_1}{\tau_2}\right) = \frac{\Delta E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where $\tau_1/\tau_2 = a_T$ (shift factor). Therefore, the activation energy is given by the following equation:

$$\Delta E_a = R \frac{d(\ln a_T)}{d(1/T)} \tag{5}$$

From our birefringence results, part of which is presented in Figures 3 and 4, we attempted a time–temperature superposition. The birefringence at different temperatures was plotted as a function of log (strain rate). The birefringence curves at 25°C and at 50°C were horizontally shifted to the one at 75°C. The shift factors, a_T's, obtained are plotted as a function of temperature^{-1} in Figures 5(a) and 5(b) for the AN/MA and rubber-modified copolymers, respectively. Activation energies calculated using eq. (5) and Figures 5(a) and 5(b) are 40 kJ/mol and 183 kJ/mol for the AN/MA copolymer and rubber-modified copolymers, respectively.

The birefringence relaxation in the two copolymers is given in Figure 6. AN/MA copolymer and rubber-modified copolymer were stretched at 75°C and at a strain rate of 125%/min. After stretching up to a draw ratio of 2.4, the
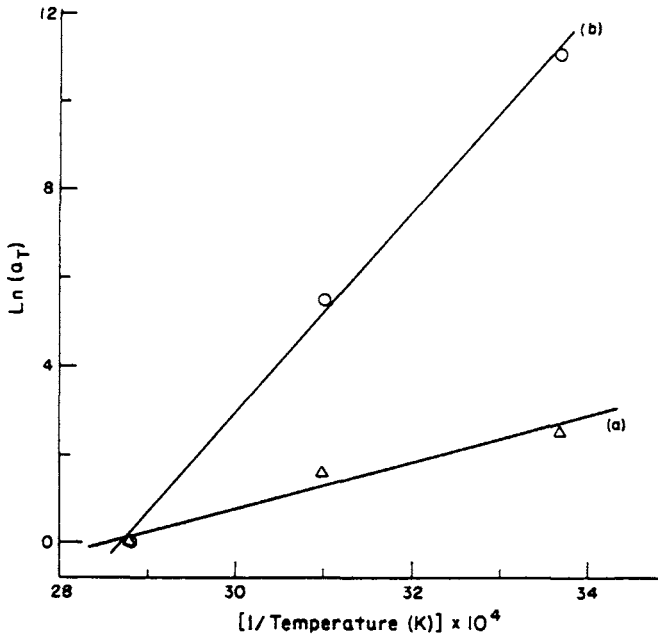
Fig. 5. Logarithm of horizontal shift factor vs. 1/temperature: (a) AN/MA copolymer; (b) rubber-modified copolymer.

crosshead of the Instron tensile tester was stopped and the birefringence of the samples was measured with a Babinet compensator, which is attached to the Instron. These samples were allowed to relax, while clamped in the Instron jaws and maintaining the temperature of 75°C. In this way the birefringence was measured up to a relaxation time of 30 min. After this time, the sample was brought to room temperature and again the birefringence was measured. From
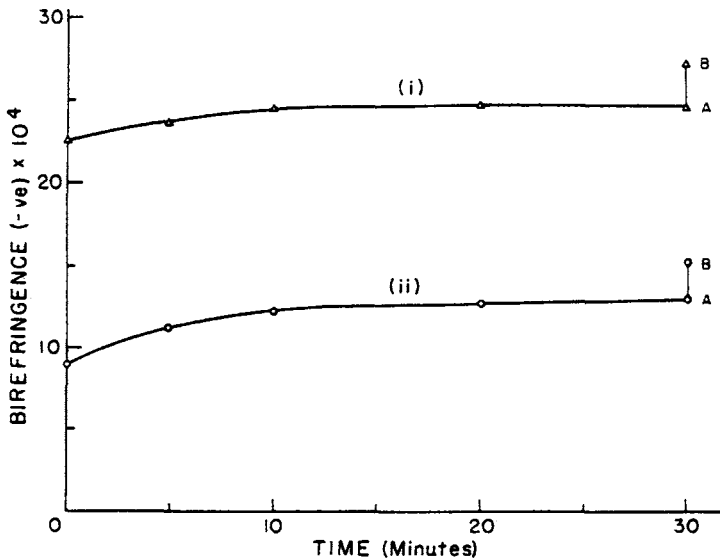

Fig. 6. The variation of birefringence on relaxation time: (i) AN/MA copolymer; (ii) rubber-modified copolymer. Draw ratio = 2.4.

the birefringence relaxation results presented in Figure 6 we note that relaxation is faster in AN/MA copolymer [Fig. 6(i)] as compared to rubber-modified copolymer [Fig. 6(ii)]. In the AN/MA copolymer the complete relaxation seems to have taken place in about 15 min, while in the rubber-modified copolymer there are long relaxation processes taking 30 min or more. This is despite the fact that the relaxation of rubber may increase the birefringence in the positive direction. In Figure 6, point A represents the birefringence measured at 75°C and point B is the birefringence at 23°C. Therefore, birefringence increases towards positive values with increasing temperature. Andrews and Hammack[36] studied the temperature dependence of birefringence in polystyrene, PMA, and PMMA. In polystyrene, the birefringence increases in the negative direction with temperature, while in PMA and PMMA the birefringence increases towards the positive direction with temperature. The results of AN/MA copolymer and of rubber-modified copolymer follow the behavior of PMA and PMMA.

The birefringence value of point B in Figure 6 has a lower value (in a negative sense) than the 125%/min value at a draw ratio of 2.4, in Figure 3. This would be possible if relaxation can take place at room temperature, because there was a long delay in stretching and measuring the birefringence in Figure 3 as compared to the one in Figure 6. This means that the sample used for Figure 3 had relaxed more than the sample in Figure 6.

The average molecular orientation as measured from X-ray diffraction is given in Figure 7. From this we observe that the molecular orientation in AN/MA copolymer is slightly higher than in the rubber modified copolymer. The X-ray orientation in Figure 7 is for samples stretched at 75°C at strain rates of 125%/min. The molecular orientation measured on the samples which were stretched at other strain rates and at temperatures of 23°C and 50°C shows similar behavior. The X-ray orientation approaches a maximum value at a draw ratio of 3.5–4. This is in agreement with Choi,[48] who concluded that a limiting maximum orientation in the draw ratio range of 3.5–4.0 was observed; further
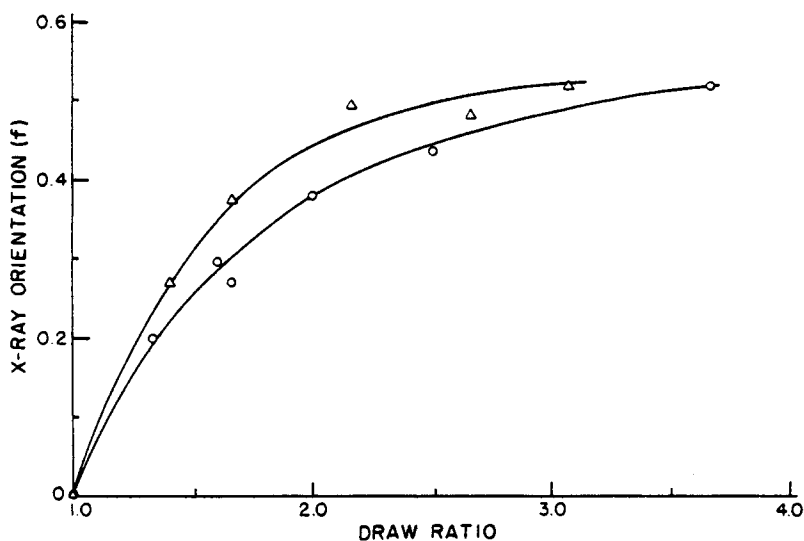

Fig. 7. The variation of X-ray orientation factor on draw ratio in AN/MA copolymer (△) and in rubber-modified copolymer (○); stretching temp = 75°C; strain rate = 125%/min.

stretching of the polymer produced no appreciable effect on birefringence, or on static and dynamic mechanical properties.

In order to estimate the maximum attainable value of birefringence in the AN/MA copolymer and in the rubber-modified copolymer, the birefringence of the samples, stretched at various temperatures and strain rates, was plotted as a function of molecular orientation determined from X-ray diffraction. These plots for the two copolymers are given in Figure 8. From this figure we observe that the relationship of X-ray orientation with birefringence is different for AN/MA and rubber-modified copolymers. However, birefringence and X-ray orientation correlate linearly in both copolymers. By extrapolation of the line to an ideal orientation ($f = 1$), we obtain the maximum value of birefringence. The maximum value of birefringence thus obtained for AN/MA copolymer is −0.0060 and that for the rubber-modified copolymer is −0.0036.

According to the theory of Kuhn and Grün[33] for amorphous polymers, birefringence should have a straight line relationship with ($\lambda^2 - 1/\lambda$), where λ is the draw ratio. Our results show a significant deviation from the straight line relationship (not shown in the figures). One explanation for this type of observation is that by Raha and Bowden[35] on the basis of strain induced dissociation of cohesion points. For such a case, the equation relating birefringence and draw ratio is

$$\Delta n = CN_0(T,\dot{\epsilon})(\alpha_1 - \alpha_2)(\lambda^2 - 1/\lambda) \exp(-k\epsilon') \qquad (6)$$

where $N_0(T,\dot{\epsilon})$ is the thermal equilibrium value of chain density prior to any breakdown of cohesion points as a result of strain (ϵ), k is a constant determined by the extensibility of the chain, N_0 is a function of temperature (T) and strain rate $\dot{\epsilon}$, and ($\alpha_1 - \alpha_2$) is the optical anisotropy of the repeat unit of the chain. ϵ' is of the form ($\lambda - \lambda^{-1/2}$). Rearranging eq. (6):

$$\ln[\Delta n(\lambda^2 - 1/\lambda)] = \ln[CN_0(T,\epsilon')(\alpha_1 - \alpha_2)] - k(\lambda - \lambda^{-1/2}) \qquad (7)$$

Plots of $\ln[\Delta n/(\lambda^2 - 1/\lambda)]$ as a function of ($\lambda - \lambda^{-1/2}$) for AN/MA and rubber-modified copolymers are given in Figure 9, from which we see that there is a
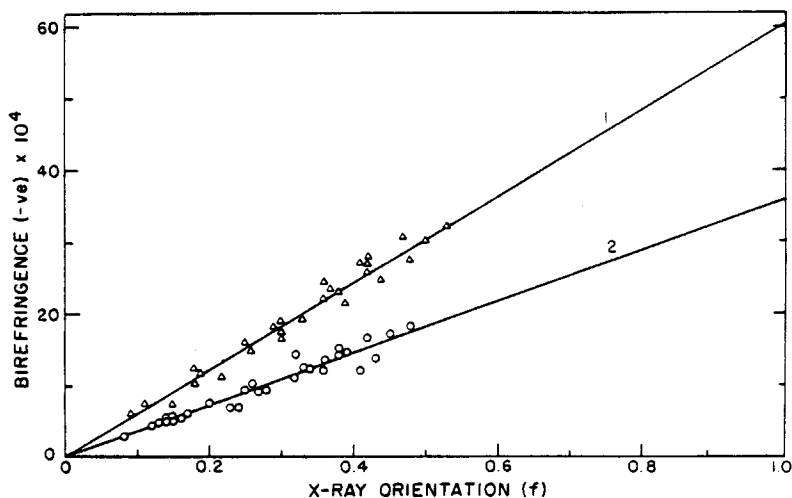

Fig. 8. Plot of birefringence vs. X-ray orientation factor in (1) AN/MA copolymer (Δn_{max} = −0.0060) and (2) in rubber-modified copolymer (Δn_{max} = −0.0036).
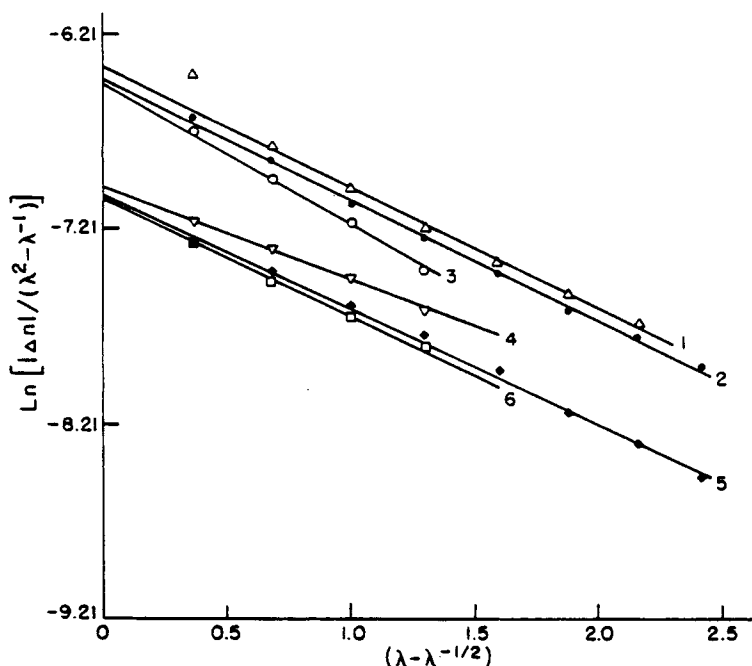
Fig. 9. Plot of $\ln[\Delta n/(\lambda^2 - \lambda^{-1})]$ vs. $(\lambda - \lambda^{-1/2})$. (1–3) AN/MA copolymer; (4–6) rubber-modified copolymer; stretching temp = 75°C; strain rate (%/min): (1,4) 2.5; (2,5) 125; (3,6) 6250.

straight line relationship as predicted by eq. (7), the slope of which is $-k$ and intercept $\ln[CN_0(T,\acute{\epsilon}')(\alpha_1 - \alpha_2)]$. The intercepts of these lines are different because of the variation of N_0 with temperature and strain rate. The slopes of the lines also vary in Figure 9, which shows that the variation in k, i.e., the extensibility of the chains, vary with strain rate.

Alternatively, the deviation may be accounted for on the basis that AN/MA is not an amorphous polymer but may be partly crystalline. The orientation of the crystalline portion would not be expected to follow the Kuhn–Grün equation which is implicit in eq. (6).

Furukawa et al.,[32] using the bond polarizabilities given by Denbigh,[49] calculated the polarizabilities of the polymeric units of a number of polymers. The polarizabilities for polybutadiene and polyacrylonitrile calculated by Furakawa et al.[32] are listed in Table I, where $\alpha_\parallel$ is the polarizability along the polymer chain and $\alpha_\perp$ is the polarizability perpendicular to the polymer chain. These polarizabilities were calculated on the basis of the structures given in Figure 10. The polarizability values for cis- and trans-1,4-polybutadiene have also been given

TABLE I
Calculated Polarizabilities of Polymeric Units of Polyacrylonitrile and Polybutadiene[32]

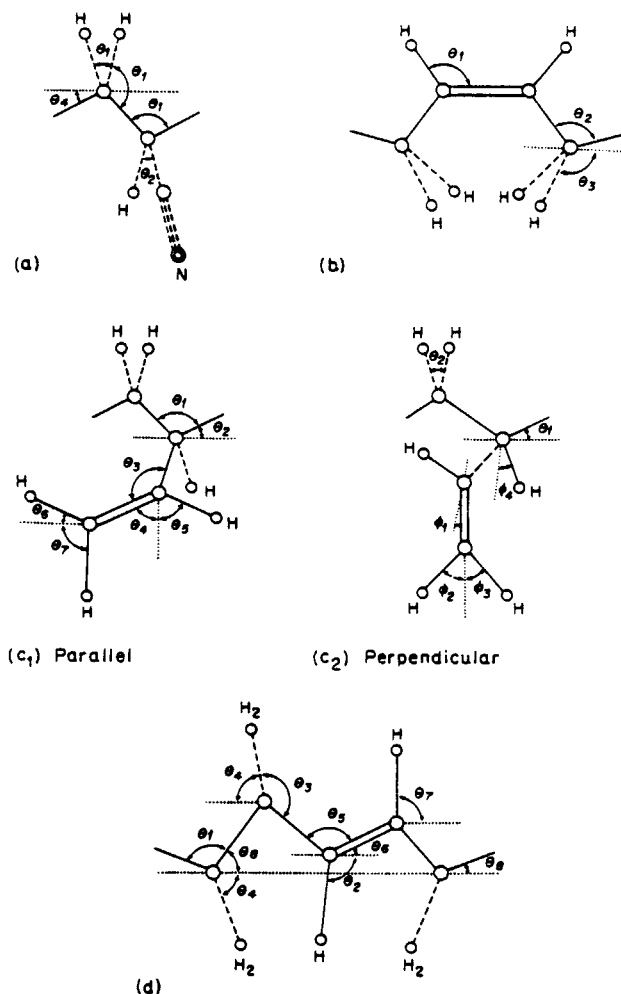| Polymer	$\alpha_\parallel$ (10^{-25} cm^3)	$\alpha_\perp$ (10^{-25} cm^3)
cis-1,4-polybutadiene	95.7	64.2
1,2-polybutadiene	70.8	76.8
trans-1,4-polybutadiene	98.7	62.9
polyacrylonitrile (A)	56.8	59.0

Fig. 10. (a) Structure of polymeric unit of polyacrylonitrile: $\theta_1 = 109°30'$; $\theta_2 = 122°$; $\theta_3 = 122°$; $\theta_4 = 35°15'$; $\theta_5 = 122°36'$. (b) Polymer unit of *cis*-polybutadiene: $\theta_1 = 125°$; $\theta_2 = 109°30'$; $\theta_3 = 109°45'$. (c) Polymeric unit of 1,2-polybutadiene: (c1) $\theta_1 = 109°30'$; $\theta_2 = 35°15'$; $\theta_3 = 125°$; $\theta_4 = 55°$; $\theta_5 = 75°$; $\theta_6 = 20°$; $\theta_7 = 90°$, (c2) $\theta_1 = 35°15'$; $\theta_2 = 109°30'$; $\phi_1 = 15'$; $\phi_2 = 54°45'$; $\phi_3 = 35°15'$; $\phi_4 = 54°45'$. (d) Polymeric unit of *trans*-polybutadiene: $\theta_1 = 109°30'$; $\theta_2 = 83°45'$; $\theta_3 = 125°15'$; $\theta_4 = 83°45'$; $\theta_5 = 122°$; $\theta_6 = 29°$; $\theta_7 = 87°$; $\theta_8 = 41°30'$.

by Fukuda et al.[30] According to Fukuda et al. $(\alpha_\parallel - \alpha_\perp)$ for *cis*-1,4-polybutadiene is 31.7×10^{-25} cm³ and for *trans*-1,4-polybutadiene it is 36.3×10^{-25} cm³. These values are in very good agreement with the values given by Furukawa et al.[32] The corresponding values given by Furakawa et al. are (from Table I) 31.5 $\times 10^{-25}$ cm³ and 35.8×10^{-25} cm³. For purposes of calculation, the butadiene component in the rubber-modified copolymer is considered to be an equal mixture of *cis*- and *trans*-1,4-polybutadiene. The values of refractive indices, $n_\parallel$ and $n_\perp$ and birefringence Δn can be calculated for PAN crystal by substituting the molecular polarizability values into the Lorenz–Lorenz expression:

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = \frac{4}{3} \pi N \alpha \qquad (8)$$

where n is the appropriate ($n_{\parallel}$ or $n_{\perp}$) refractive index, M = molecular weight per repeat unit, d = density of the substance, N is Avogadro's number, and α is the appropriate ($\alpha_{\parallel}$ or $\alpha_{\perp}$) polarizability of the whole repeat unit of a polymer chain. For PAN, using $M = 53.06$, $d = 1.17$,[50] and the polarizabilities given in Table I, the refractive indices are $n_{\parallel} = 1.5446$ and $n_{\perp} = 1.5703$. From these the birefringence of PAN is -0.0257. The birefringence of real amorphous chains can be determined by using the Flory,[51] Gotlib,[52] and Volkenstein[53] approaches. It is well known that the birefringence of PAN is negative but not as high as -0.0257. As previously indicated, Comstock et al.[44] have obtained a value of -0.0090 on stretched and polarized PAN. This value probably approaches the experimentally measured maximum value of birefringence in PAN. Considering the reasons for the difference in calculated and experimental values of birefringence, it is important to point out here that this calculation was based on assuming a planar zigzag chain in the polymer. But at least one paper[16] has suggested that PAN has a helical structure. However, a detailed molecular conformation of the helical structure has not yet been given, and this can account at least partly for the difference in calculated and measured birefringence. A related point which will be discussed in detail in the next section is the angle which $C\equiv N$ and $C-H$ bonds make with the molecular chain. Theoretically, both angles have been given at 90° for the planar zigzag conformation. However, measurements have shown that this angle can be considerably different from 90°.[26,54] This change in bond angle suggests that the assumed planar zigzag structure is not correct and would also vary the calculated birefringence.[16]

Now considering Δn_{max} (PAN) = -0.0090, Δn_{max} (AN/MA) = -0.0060, and Δn_{max} (AN/MA/BD) = -0.0036 (the latter two values as obtained from Fig. 8), an estimate of Δn_{max} for the methyl acrylate and butadiene components is obtained using the following expression, based on the principle of additivity of birefringence[55].

$$\Delta n_{max} \text{ (AN/MA/BD)} = V_{AN/MA} \, \Delta n_{max} \text{ (AN/MA)} + V_{AN/BD} \, \Delta n_{max} \text{ (AN/BD)}$$

$$(9)$$

$$\Delta n_{max} \text{ (AN/MA)} = V_{AN1} \, \Delta n_{max} \text{ (AN)} + V_{MA} \, \Delta n_{max} \text{ (MA)} \qquad (10)$$

$$\Delta n_{max} \text{ (AN/BD)} = V_{AN2} \, \Delta n_{max} \text{ (AN)} + V_{BD} \, \Delta n_{max} \text{ (BD)} \qquad (11)$$

where V represents the volume fractions of the various components. Densities of acrylonitrile and methyl acrylate are usually quoted in the range of 1.17–1.18. The fraction of butadiene component is very small. Therefore, approximating the weight fractions equal to volume fractions, viz. $V_{AN/MA} = 0.90$, $V_{AN/BD} = 0.10$, $V_{BD} = 0.70$, $V_{AN1} = 0.75$, $V_{MA} = 0.25$, and $V_{AN2} = 0.30$, we obtain Δn_{max} (BD) = 0.0296 and Δn_{max} (MA) = 0.0030.

Infrared Studies

Typical infrared spectrum of AN/MA copolymer and that of the rubber modified copolymer are given in Figures 11(a) and 11(b), respectively. The spectra of the two copolymers are identical except that in the rubber-modified copolymer an extra absorption peak appears at 967 cm^{-1}, arising from the out-of-plane deformation of the $CH=CH$ bond of butadiene. In addition to the $CH=CH$ bond, the dichroic ratio has been determined for CH_2 stretching (at
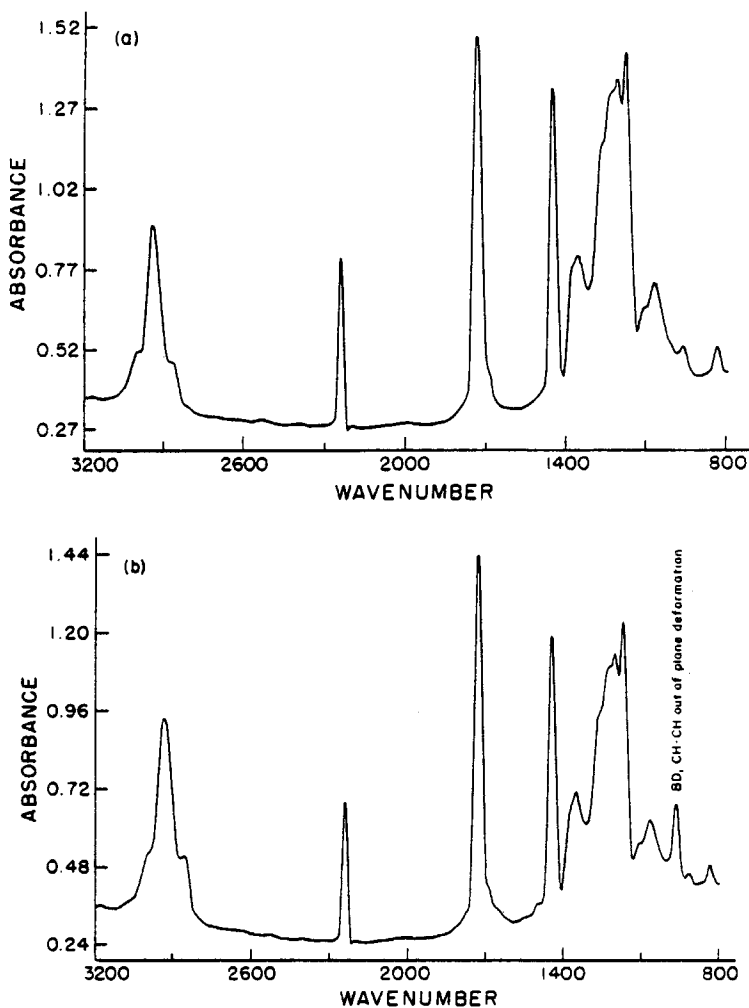
Fig. 11. Infrared spectrum of (a) AN/MA copolymer and (b) rubber-modified copolymer.

2936 cm^{-1}), C$\equiv$N stretching (at 2241 cm^{-1}), and CH$_2$ bending (at 1426 cm^{-1}). A complete assignment of the fundamental vibrational frequencies and a detailed analysis of the polyacrylonitrile spectrum has been presented by Liang and Krimm.[37]

The dichroic ratios as a function of draw ratio for various bonds in the AN/MA copolymer and in the rubber-modified copolymer are given in Figures 12 and 13; respectively. This study was done by stretching the copolymer films at 75°C and at a strain rate of 125%/min. The dichroic ratio does not change as sharply with draw ratio as does birefringence and X-ray orientation. This behavior has also been noticed in PAN fibers by Bohn et al.[26] From a comparison of Figures 12 and 13, we observe that the CH$_2$ and C$\equiv$N bonds are only slightly more oriented in the AN/MA copolymer than in the rubber-modified copolymer. In the rubber-modified copolymer, butadiene is also contributing to the dichroic ratios of the CH$_2$ bond. These results are in accordance with the X-ray orientation results where AN/MA copolymer has slightly higher orientation than the rubber modified copolymer (Fig. 7).
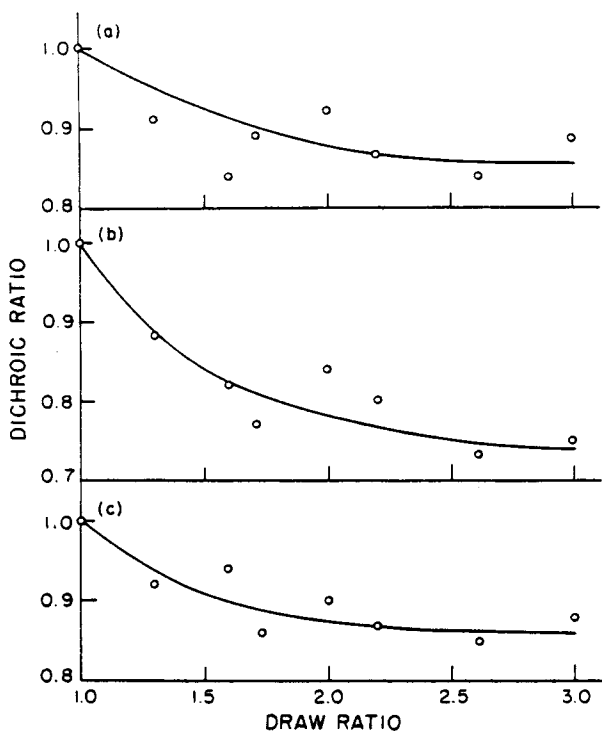
Fig. 12. Infrared dichroism vs. draw ratio for AN/MA copolymer stretched at 125%/min at 75°C: (a) CH_2 stretching; (b) $C\equiv N$ stretching; (c) CH_2 bending.

Using our results of dichroic ratio and molecular orientation (determined from X-ray) and eqs. (3) and (4), we can determine the transition moment angles of various bonds. The orientation factor f is plotted as a function of $(D - 1)/(D + 2)$ in Figure 14(a) for AN/MA copolymer and in Figure 14(b) for the rubber-modified copolymer. From eq. (3) the slope of these lines is given by $(D_0 + 2)/(D_0 - 1)$, while D_0 is related to the transition moment angle as given in eq. (4). Therefore, the transition moment angles of CH_2 stretching (at 2936 cm^{-1}) and $C\equiv N$ stretching (at 2241 cm^{-1}) in the two copolymers can be determined from the slopes of the lines. The transition moment angle in AN/MA copolymer for CH_2 stretching (2936 cm^{-1} band) is 58.3° and for $C\equiv N$ stretching (2241 cm^{-1} band) is 61.5°, while these angles in rubber-modified copolymers come out to be 59.0° and 62.0°, respectively.

Generally in PAN a syndiotactic planar zigzag chain is considered as the most simple model and has been used for calculations of normal vibrations.[56,57] For this structure the transition moment angle of $C\equiv N$ stretching and $CH_2(\nu_a)$ is 90°, which is considerably different from the range of 58–62° reported above. The difference is certainly outside experimental error.

A possible reason for the discrepancy is the assumption of the planar zigzag chain conformation as the reference oriented state. It is likely that the PAN is not entirely syndiotactic.[15] The isotactic structure could not reasonably assume a planar zigzag conformation because of steric hinderance and would probably take on a helical conformation in which the CH_2 transition moment axis may be other than at 90°. However, even in syndiotactic conformation a
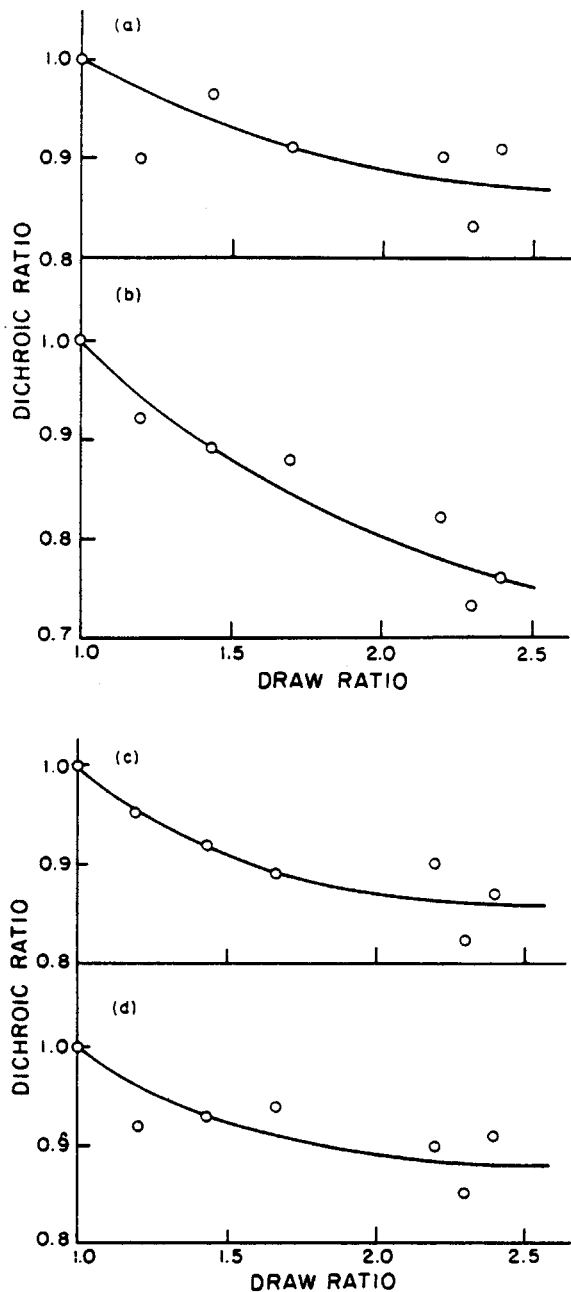
Fig. 13. Infrared dichroism vs. draw ratio for rubber-modified copolymer stretched at 125%/min at 75°C: (a) CH_2 stretching; (b) C≡N stretching; (c) CH_2 bending; (d) CH=CH (out of plane deformation.

helical structure has been proposed for PAN.[16]   Chain conformation of PAN is not completely known.   However, if one assumes a 3/1 helical conformation as in polypropylene,[58] the transition moment direction calculated using the atomic coordinates given by Keedy et al.[59] is still 90°.

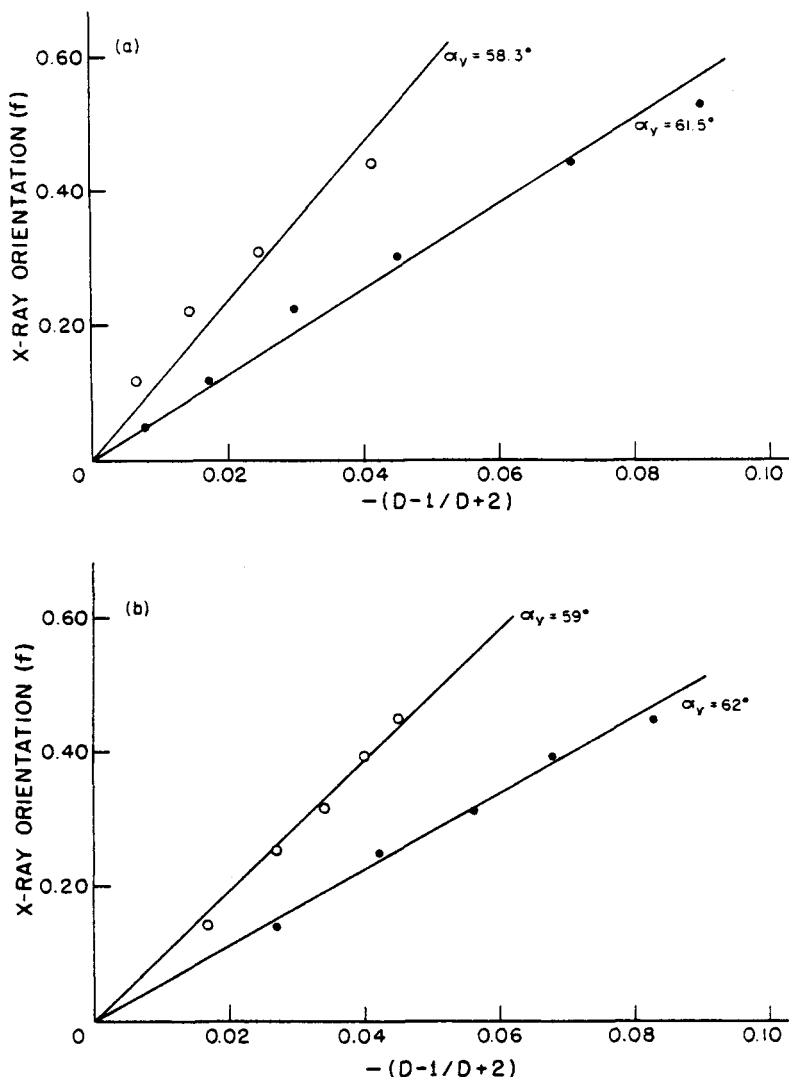The transition moment direction depends upon molecular structure.   For

Fig. 14. Determination of transition moment angle of C—H and C≡N stretching in (a) AN/MA copolymer and in (b) rubber-modified copolymer: (O) CH_2 stretching; (●) C≡N stretching.

example, it is pointed out by Bradbury et al.[60] that, in crystalline polyethylene suberate, six CH_2 groups have their transition moments perpendicular to the crystal c axis, but two CH_2 groups have their transition moments at 82° for the symmetrical CH_2 stretching mode and 71°34' for the antisymmetrical mode. While the crystal structure for polyethylene suberate does not bear a relationship to the chain structure for oriented PAN, this does illustrate the dependence of transition moment angle on the reference chain conformation.

There are other cases in the literature where the transition moment angle differs from the theoretically expected value.   For example, Samuels[47] concluded from the data of Stein and Norris[55] that the transition moment angle for the CH_2 rocking frequency for polyethylene crystals at 730 cm^{-1} was 83°, as compared with the theoretically accepted value of 90°.   A possible reason is a contribution from the less dichroic amorphous contribution to the band at 720 cm^{-1}.

Zbinden[54] has compared theoretical and measured transition moment angles in polyethylene for CH_2 rocking, bending, and stretching vibrations and reports a much greater discrepancy for bending and stretching than for rocking. For example, for stretching, an experimental angle of 68–71° is found as compared with the theoretically expected value of 90°. His explanation is that while 90° is the transition moment angle if the rest of the molecules were in a static conformation, the angle actually oscillates about this value with an amplitude δ because of other lower frequency vibrations (e.g., CH_2 wagging). This has the effect of lowering the dichroism of the higher frequency CH_2 stretching vibration and leads to an effective transition moment angle differing somewhat from 90°.

Zbinden[54] also compares theoretical and experimental transition moment angles for crystalline bands of isotactic polystyrene. In most cases, the agreement is rather good. A notable exception is with the asymmetric CH_2 stretching frequency where the experimental angle calculated from dichroism is 63° as compared with a theoretical value of 90° calculated from the crystalline coordinates of Natta et al.[61]

Another factor is that our observations are on a copolymer of AN with MA. The chain conformation of the AN portion of the chain will be perturbed and also, there will be a CH_2 (ν_a) contribution from the MA regions of unknown conformation. Dichroic ratios for poly(acrylonitrile/methylacrylate) (94:6) has also been given by Siesler and Holland-Moritz.[62] Transition moment angles of CH_2 stretching and bending and of $C\equiv N$ stretching have been given in the range of 62–65° by Bohn et al.[26]

The CH_2 motions are coupled with those of other portions of the chain. Evidence for this comes from the observation that the CH_2 (ν_a) appears at 2924 cm^{-1} in polyethylene,[63,64] but at 2940 cm^{-1} in PAN.[37,38,41] Such coupling may affect the transition moment direction, especially if the motion of the CH_2 group is associated with even a small motion of a high polar grouping such as $C\equiv N$.

CONCLUSIONS

1. The absolute value of birefringence measured at room temperature increases with the initial increase in stretching temperature. This trend is reversed at the glass transition temperature.

2. Below the glass transition temperature, the absolute value of birefringence increases with decreasing strain rate.

3. The absolute value of birefringence in the AN/MA copolymer is much higher as compared to the rubber-modified copolymer. This is primarily because of the positive birefringence of the butadiene.

4. Activation energies of the orientation process obtained from birefringence results (in between 23°C and 75°C) are 40 kJ/mol and 183 kJ/mol in AN/MA copolymer and in rubber-modified copolymer, respectively.

5. Orientation time in the AN/MA copolymer is less than in rubber modified copolymer.

6. The absolute value of birefringence decreases (increases towards positive values) with increasing temperature.

7. The two copolymers reach a limiting orientation at a draw ratio of 3.5–4.

8. The Δn_{max} for the AN/MA copolymer is −0.0060 and for the rubber-

modified copolymer is −0.0036. The maximum birefringence of PAN is −0.0090.

9. Orientation at the corresponding draw ratios is more in the AN/MA copolymer than in rubber-modified copolymer.

10. The transition moment angle of the CH_2 stretching bond is 58.3–59° and that of the $C\equiv N$ stretching bond is 61.5–62°.

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