

Effect of Heat Treatment on the Dielectric Relaxation of Polyacrylonitrile. II. Heat Treatment under Vacuum and in Air

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Synopsis

Dielectric relaxation, infrared spectra, and X-ray diffraction data of polyacrylonitrile (PAN) heat treated at 120°C in air and under vacuum and of the untreated PAN are reported. The heat treatment resulted in (1) lowering of dielectric constant increment, dielectric dissipation factor, and increase in relaxation temperature and glass transition temperature; (2) lowering of the intensity of $\text{—C}\equiv\text{N}$ stretching band in the infrared spectra; and (3) increase in degree of order of the X-ray diffraction results. The changes produced by heat treatment under vacuum are found greater than those produced by heat treatment in air, which suggests that the observed effect is not caused by chemical changes in the PAN molecule under heat treatment. Interpretation of these results is attempted on the basis of the difference in the degree of bound nitrile group pairs (bound through intermolecular dipole-dipole interactions) in the structure of PAN heat treated under the different conditions.

INTRODUCTION

In part I of this study,¹ it was reported that the heat treatment of polyacrylonitrile (PAN) in air produced considerable changes in its dielectric relaxation in the glass transition region. A similar heat treatment of the PAN fibers showed some changes in their structure and mechanical properties.² The observed changes in dielectric relaxation were of lower magnitude in the case of heat treatment at higher temperatures (i.e., 160°C) than those at lower temperatures (i.e., 120°C).¹ This effect was attributed to the difference in the degree of intermolecularly bound nitrile groups in the PAN samples when heat treated at different temperatures.

Since the heat treatments in the above-mentioned studies were carried out in air, the possibility of attributing the observed effect to the chemical changes in the PAN molecule during heat treatment could not be ascertained. However, heat treatment at a higher temperature produced less change in the dielectric properties of PAN than heat treatment at lower temperature. This was considered¹ as an argument sufficient to reject the explanation based on chemical changes in the PAN molecule, since chemical changes at higher temperatures should be greater than those at lower temperatures.

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To obtain a better understanding of this point, we carried out in the present work an investigation of the effect of heat treatment on PAN in air and under vacuum at identical temperatures. Heat treatment in vacuum or inert atmosphere must produce fewer chemical changes than that in air or oxygen atmosphere.

Dielectric relaxation, infrared spectra, and X-ray diffraction studies were carried out on PAN samples heat treated at 120°C for 16 h in air atmosphere and under vacuum as well as on the untreated PAN sample.

EXPERIMENTAL

Materials

The PAN used in this work was prepared by the method of emulsion polymerization.³ Polymerization was carried out at 35°C in inert (nitrogen) atmosphere using potassium persulfate as initiator, sodium bisulfite as activator, and sodium lauryl sulfate as emulsifying agent. All chemicals were Analar grade and were purified before use.

For heat treatment, one part of the dried PAN powder (dried in vacuum oven at 50°C for 24 h) was placed in a glass tube which was evacuated and sealed. Another part of the sample was kept in air atmosphere in a closed flask. These were then kept in a constant-temperature oven at 120°C for 16 h. After heat treatment, the samples were left to cool at room temperature conditions.

The three samples studied, viz., the untreated sample and the samples heat treated at 120°C for 16 h in air and at 120°C for 16 h under vacuum, are denoted hereafter as PAN(U), PAN(air), and PAN(vac), respectively.

Measurements

Dielectric measurements in the frequency range 1–100 kHz and temperature range 30–170°C were done on a General Radio GR-716 CS bridge, using a two-terminal connection for the sample cell. Samples were in the form of discs (1.3 cm in diameter and 0.1 cm thick) prepared by compressing the dried powder. The disc surfaces were silver coated in order to achieve better electrode contact. The sample discs were placed in the parallel-plate test condenser whose distance between the plates could be adjusted according to the disc thickness. This test condenser was enclosed in a thermostated chamber controlled within $\pm 0.1^\circ\text{C}$. The specimen temperature was measured by a thermocouple placed in close vicinity of the sample. Since the data could not be corrected for the dc conductivity effects, precautions were taken to minimize effects due to moisture absorption by storing the sample discs in the desiccator.

Infrared spectra were recorded on Perkin-Elmer 580 B spectrophotometer for these samples by embedding the polymer powder in KBr pellets.

X-ray diffraction on these powder samples were recorded on a Philips-Norelco automatic recording diffractometer at identical settings of the instrument for all the samples. CuK_α radiation was used for this.

RESULTS AND DISCUSSION

Dielectric Measurements

Results of dielectric measurements of the heat-treated and the untreated PAN samples are shown in Figures 1-3 as variations of dielectric constant (ϵ') and dissipation factor ($\tan \delta$) with temperature (T) at various frequencies. The relaxation represented by these data has been attributed to segmental mobility in the glass transition region.^{1,4}

Some essential differences in these data are represented in terms of quantities summarized in Table I. The difference in dielectric constants between the highest and the lowest temperature ($\epsilon'_{170} - \epsilon'_{30}$) is indicative of the total polarization produced in the various samples of PAN in the studied range of temperature (i.e., 30 to 170°C). The loss peak amplitude ($\tan \delta_{\max}$) compares the relative magnitudes of the dielectric loss in these samples. Variations of $\epsilon'_{170} - \epsilon'_{30}$ and $\tan \delta_{\max}$ as function of frequency are shown in Fig. 4. At any given frequency, values of $\epsilon'_{170} - \epsilon'_{30}$ and $\tan \delta_{\max}$ for the three samples of PAN decrease in the following order:

$$(\epsilon'_{170} - \epsilon'_{30})_{\text{PAN(U)}} > (\epsilon'_{170} - \epsilon'_{30})_{\text{PAN(air)}} > (\epsilon'_{170} - \epsilon'_{30})_{\text{PAN(vac)}} \quad (1)$$

$$(\tan \delta_{\max})_{\text{PAN(U)}} > (\tan \delta_{\max})_{\text{PAN(air)}} > (\tan \delta_{\max})_{\text{PAN(vac)}} \quad (2)$$

However, because the dc conductivity effects are apparent in the data at 1 kHz (Fig. 1) for which no correction could be applied to these data, the subsequent

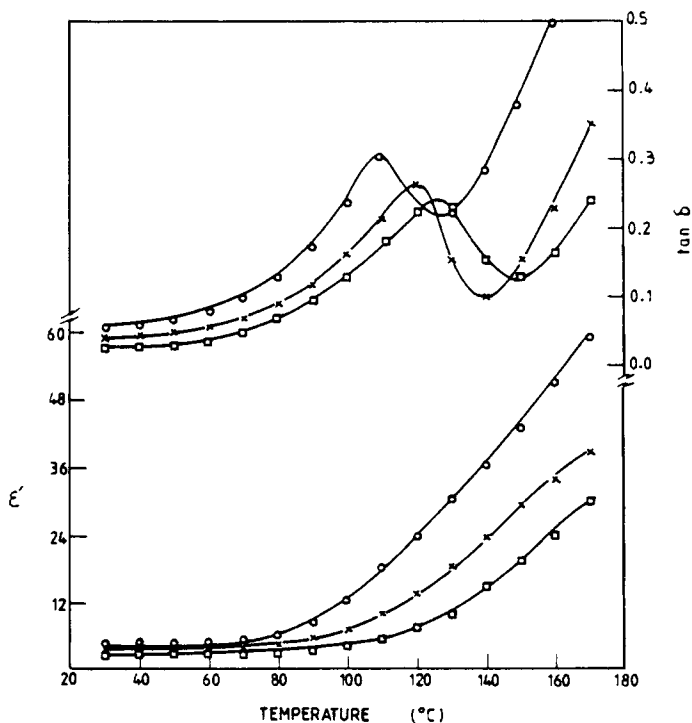


Fig. 1. Variation of dielectric constant ϵ' and dissipation factor $\tan \delta$ with temperature at 1 kHz for PAN(U) (O), PAN(air) (X), and PAN(vac) (□).

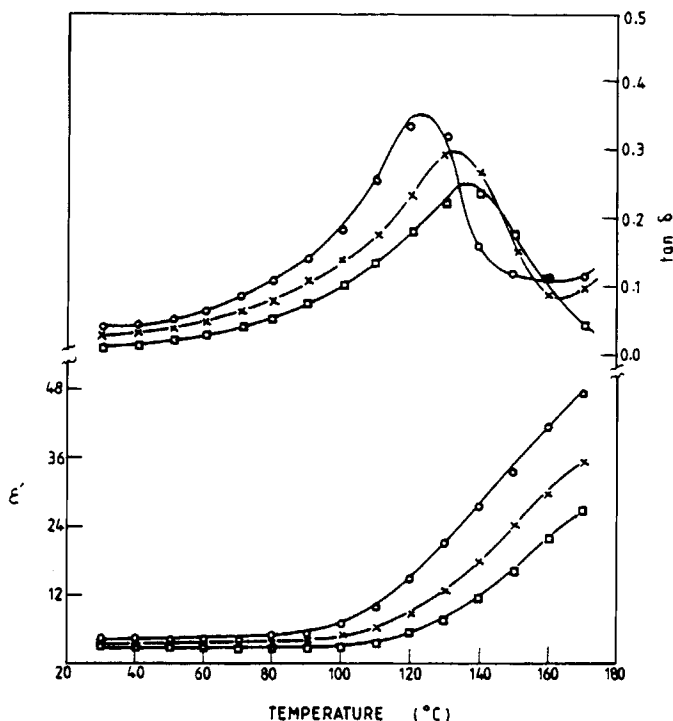


Fig. 2. Variation of dielectric constant ϵ' and dissipation factor $\tan \delta$ with temperature at 10 kHz for PAN(U) (O), PAN(air) (X), and PAN(vac) (□).

discussion about dipolar orientation phenomena will be based on the data at the higher two frequencies.

Furthermore, as the dc conductivity effect is known to affect the magnitude of $\tan \delta$ and not generally the position of loss peak on the temperature scale, the relaxation temperature (T_{\max}) may be considered reliable at 1 kHz also. The trend in the variation of the relaxation temperature at identical frequency for these samples is as follows:

$$(T_{\max})_{\text{PAN(U)}} < (T_{\max})_{\text{PAN(air)}} < (T_{\max})_{\text{PAN(vac)}} \quad (3)$$

A higher value of the relaxation temperature implies greater restrictions on segmental mobility.

TABLE I
Values of Dielectric Parameters for PAN(U), PAN(air), and PAN(vac)

Sample	Frequency, kHz	$\epsilon'_{170} - \epsilon'_{30}$	$\tan \delta_{\max}$	$T_{\max}, ^\circ\text{C}$
PAN(U)	1	54.0	0.295	110
	10	43.0	0.350	122
	100	35.5	0.455	138
PAN(air)	1	35.0	0.260	120
	10	31.5	0.300	132
	100	26.4	0.370	147
PAN(vac)	1	27.0	0.235	126
	10	23.5	0.256	137
	100	20.0	0.330	151

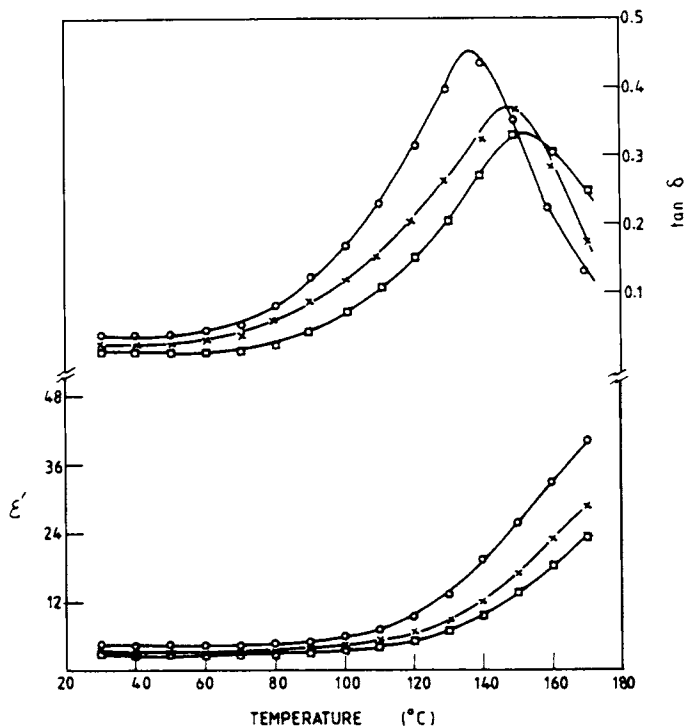


Fig. 3. Variation of dielectric constant ϵ' and dissipation factor $\tan \delta$ with temperature at 100 kHz for PAN(U) (O), PAN(air) (x), and PAN(vac) (□).

Arrhenius plots of these data, shown in Figure 5, are almost parallel for the two heat-treated samples giving an activation energy $\Delta E = 55$ kcal/mol for PAN(air) and PAN(vac), and $\Delta E = 48$ kcal/mol for PAN(U). These activation energy values are comparable with the generally observed value for glass transition relaxation.⁴ T_{\max} is related to the glass transition temperature T_g through the frequency of measurements⁵⁻¹⁰ as discussed below.

As revealed by the ϵ' -vs.- T curves (Figs. 1-3), ϵ' changes inappreciably with temperature up to a temperature T' (which is in the range 80-120°C for the various samples) and then rises rapidly with temperature for $T > T'$. This temperature T' is indicative of the glass transition of the sample, because below this temperature the segmental dipole moments do not contribute to the value of the dielectric constant due to frozen segmental mobility in the glassy state of the polymer. Above T' , the increase in dielectric constant with temperature is attributable to the dielectric relaxation due to segmental mobility, as the polymer is above its glass transition temperature. The trend in the variation of T' apparent in these data is as follows:

$$T'_{\text{PAN(U)}} < T'_{\text{PAN(air)}} < T'_{\text{PAN(vac)}} \quad (4)$$

which is in agreement with the trend in the variation of T_g of these samples, as subsequently described.

The dielectric relaxation strength $\epsilon'_0 - \epsilon'_\infty$, where ϵ'_0 and ϵ'_∞ are the low and high frequency limiting values of ϵ' for the observed dielectric relaxation, may be evaluated from these data in the limited frequency range through the area under the ϵ'' -vs.- $1/T$ plot using the relation¹⁰

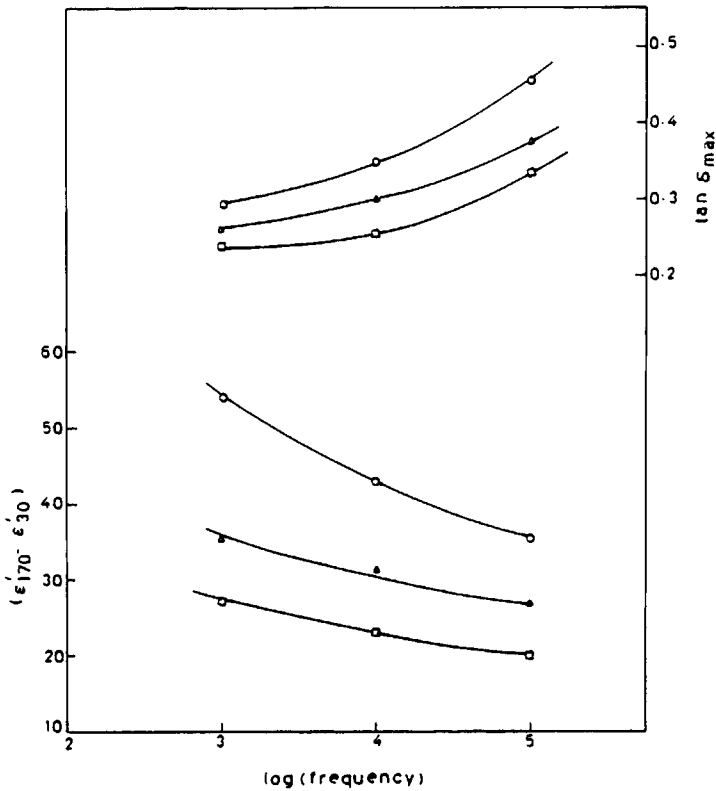


Fig. 4. Variation of $\epsilon'_{170} - \epsilon'_{30}$ and $\tan \delta_{\max}$ with log frequency for PAN(U) (O), PAN(air) (Δ), and PAN(vac) (\square).

$$\epsilon'_0 - \epsilon'_\infty = \frac{2 \cdot \Delta E}{\pi R} \int_{-\infty}^{\infty} \epsilon'' d(1/T) \quad (5)$$

where ΔE is the activation energy and R is the universal gas constant. Calculations from these data at 100 kHz give the values of $\epsilon'_0 - \epsilon'_\infty$ shown in Table II. Areas under ϵ'' -vs.- $1/T$ curves were determined by symmetrical extrapolation of these curves shown in Figure 6.

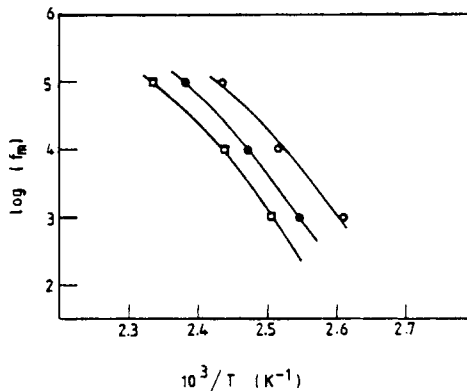


Fig. 5. Arrhenius plots obtained from the dielectric relaxation data on PAN(U) (O), PAN(air) (\bullet), and PAN(vac) (\square).

TABLE II
Dielectric Relaxation Strength ($\epsilon'_0 - \epsilon'_\infty$), Degree of Order (X) (from X-Ray Diffraction), I_{2240}/I_{1460} (from Infrared Spectra), and T_g (from Eq. (10)) for PAN Samples

Sample	$\epsilon'_0 - \epsilon'_\infty$	$X, \%$	I_{2240}/I_{1460}	$T_g, ^\circ\text{C}$
PAN(U)	45.3	28.5	1.2	74
PAN(air)	36.6	32.0	0.9	84
PAN(vac)	30.0	34.5	0.7	94

The relation of $\epsilon'_0 - \epsilon'_\infty$ to the mean square dipole moment and number density N_s of the relaxing unit (i.e., the polymer segments), as stated by Sato and Yashiro,¹¹ is

$$\epsilon'_0 - \epsilon'_\infty = \frac{4\pi}{3kT} \frac{3\epsilon'_0}{2\epsilon'_0 + \epsilon'_\infty} \left(\frac{\epsilon'_\infty + 2}{3} \right)^2 N_s \bar{\mu}_s^2 \quad (6)$$

where k and T are Boltzmann's constant and absolute temperature, respectively. Thus, considering the direct proportionality of $\epsilon'_0 - \epsilon'_\infty$ with $N_s \bar{\mu}_s^2$, it is clearly apparent from the variation of dielectric relaxation strength (Table II) that

$$(N_s \bar{\mu}_s^2)_{\text{PAN(U)}} > (N_s \bar{\mu}_s^2)_{\text{PAN(air)}} > (N_s \bar{\mu}_s^2)_{\text{PAN(vac)}} \quad (7)$$

Hence, the observed decrease in $\epsilon'_0 - \epsilon'_\infty$ upon heat treatment of PAN may imply a decrease in $\bar{\mu}_s^2$ or N_s , or both.

The energy dissipated in the dipolar orientation process (i.e., $\tan \delta$) will be higher when either (a) the restrictions on the mobility of the orienting units is higher; (b) the number of orienting units N_s is higher; or (c) the dipole moment of the orienting units $\bar{\mu}_s^2$ is higher. Indication of higher restrictions on segment

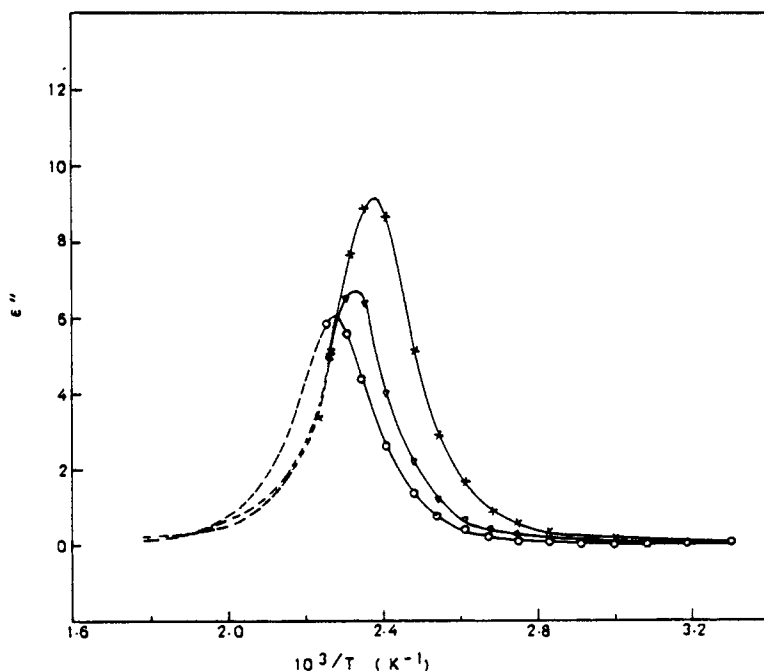


Fig. 6. Dielectric loss factor ϵ'' as function of reciprocal temperature at 100 kHz for PAN(U) (x), PAN(air) (Δ), and PAN(vac) (O).

mobility in the heat-treated PAN than the untreated PAN is provided by the T_{\max} value, which is higher for heat-treated than untreated PAN. Hence, the observed lower values of $\tan \delta_{\max}$ for heat-treated PAN than untreated PAN suggest that the effects of changes in N_s and $\bar{\mu}_s^2$ are predominant in the magnitude of $\tan \delta_{\max}$. The decrease in $\tan \delta_{\max}$ on heat treatment may be due to the decrease in either one or both the parameters N_s and $\bar{\mu}_s^2$. Decrease in N_s is possible only in cases of an extremely high degree of intermolecularly bound nitrile groups which might render some segments immobile so as not to participate in the dielectric relaxation process. However, in the present results, the decrease in $\bar{\mu}_s^2$ seems a more predominant effect to account for the observed decrease in $\epsilon'_0 - \epsilon''_0$ on heat treatment. The heat treatment may not only introduce intermolecular nitrile group bonding but may also modify the intramolecular nitrile group interactions so as to result in a lower value of $\bar{\mu}_s^2$ in the heat-treated samples. Further investigation would be required to ascertain this point. However, the significance of $\bar{\mu}_s^2$ in affecting the value of dielectric loss was stated earlier,⁴ where it was found that unlike various nonpolar or less polar polymers, PAN showed a considerable increase in loss peak amplitude with increasing frequency.

These observed differences in the results for the three samples of PAN show two general trends of variation: (a) Heat treatment of PAN in air or under vacuum produces a change in polarization, dielectric loss, relaxation temperature and dielectric relaxation strength. (b) The changes in all the above-mentioned dielectric parameters are greater in magnitude for PAN(vac) than PAN(air).

The general effect of heat treatment described by trend (a) may be explained by the formation of bound nitrile group pairs due to intermolecular dipole-dipole interactions of nitrile groups. These bound nitrile group pairs may produce interlinking between the segments which should be responsible for the restrictions of segment mobility and thus for the increase in T_{\max} .

The dipole-dipole interaction energy E between two dipoles of dipole moments μ_1 and μ_2 at a given distance r is expressed,¹² for the case when r is large compared to the charge separation within the dipoles, as follows:

$$E = \frac{\mu_1 \mu_2}{r^3} (\cos \phi - 3 \cos \delta_1 \cos \delta_2) \quad (8)$$

The angles ϕ , δ_1 , and δ_2 and the vectors μ_1 and μ_2 are described in Figure 7. For the case of PAN, any two interacting nitrile group dipoles (dipole moment $\mu_1 = \mu_2 = \mu$) may have various possibilities of mutual alignment described by the values of δ_1 , δ_2 , and ϕ . The three extreme situations of mutual alignment may be described as (1) antiparallel ($\delta_1 = 90^\circ$, $\delta_2 = 270^\circ$, and $\phi = 180^\circ$), $E = -\mu^2/r^3$; (2) parallel end-to-end ($\delta_1 = \delta_2 = 0^\circ$ and $\phi = 0^\circ$), $E = -2\mu^2/r^3$; (3) parallel side-by-side ($\delta_1 = \delta_2 = 90^\circ$ and $\phi = 0^\circ$), $E = +\mu^2/r^3$.

Of these three kinds of alignment, the parallel end-to-end alignment is sterically not feasible in polymer molecules. The parallel side-by-side alignment concerns the intramolecular interaction between adjacent nitrile groups. Such an interaction is repulsive in nature and gives rise to the formation of an irregular helical conformation of the PAN molecule as described by some authors.^{12,13} The irregular helical conformation of the PAN chain is shown to fit in a cylinder of diameter about 6 Å, as shown in Figure 1 of Ref. 12. Some nitrile groups projecting out of the boundaries of this cylinder are potentially available for intermolecular dipole-dipole interactions. In the amorphous phase of PAN,

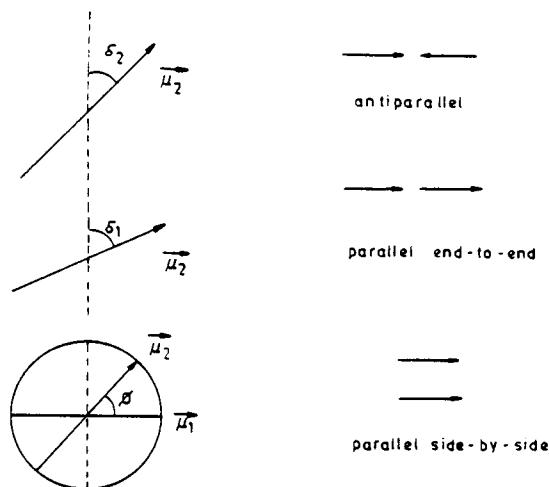


Fig. 7. Description of angles δ_1 , δ_2 , and ϕ of eq. (8) for the case of two dipole moment vectors μ_1 and μ_2 , and the representation of the three extreme cases of mutual alignment of dipoles discussed in the text.

this cylinder, representing the PAN molecule in its irregular helical conformation, may be viewed as a flexible cylinder (or flexible rod) whose different portions may be considered as the segments responsible for glass transition behavior.

During the course of heat treatment at a temperature above the T_g , the segmental mobility will assist in bringing these free nitrile groups of the neighboring segments in close vicinity at mutual alignments ideally antiparallel or with some deviations from ideally antiparallel alignment. Dipole-dipole interaction energies of the various nitrile group pairs will differ depending on the values of δ_1 , δ_2 , and ϕ according to eq. (8). Owing to the attractive nature of their dipolar interaction, these nitrile group pairs will form bound nitrile group pairs. However, in the course of long duration of heat treatment, some readjustments in these bound nitrile group pairs are possible in which (1) some pairs may become more strongly bound due to the segmental mobility which assists in changing their mutual alignment to the positions of optimum attractive interaction; and (2) some weakly bound nitrile group pairs, which cannot withstand the opposing force exerted by segment mobility tending to break the bound pair, may dissociate.

Thus, the ultimate degree of bound nitrile group pairs may differ in the PAN samples heat treated under different conditions. As reported earlier,¹ the heat treatment of PAN at different temperatures results in different degrees of bound nitrile group pairs. Furthermore, the nitrile groups involved in these dipole-dipole interactions may not contribute to the total dipole moment of the polymer segments like the other free nitrile groups. Hence, a lower value of the mean square dipole moment of the segments may be expected in the heat-treated PAN samples than in the PAN(U). The greater the degree of bound nitrile groups, the lower would be the expected value of segmental dipole moment.

Trend (b) in the variation of these dielectric relaxation data, viz., that the changes produced by heat treatment under vacuum are greater than those produced by heat treatment in air, is an important finding of this work. This helps to ascertain whether the observed effect of heat treatment is attributable to the

formation of bound nitrile group pairs or to chemical changes in the PAN molecule. The following arguments seem to favor the former explanation: First, the chemical changes in PAN at the temperature of heat treatment (i.e., 120°C) are believed to be inappreciable. Secondly, vacuum or inert atmosphere should prevent or decrease considerably any chemical changes, while air or oxygen atmosphere should aggravate such chemical changes.

These dielectric relaxation data on PAN(U), PAN(air), and PAN(vac) suggest that the degree of bound nitrile group pairs in PAN(vac) is higher than that in PAN(air). The ultimate degree of bound nitrile group pairs in the structure after heat treatment is governed by the net result of two effects: (1) the dipole-dipole interaction force (which holds the pairs bound), and (2) the energy of segment mobility (which tends to break the bound pairs). The segment mobility also plays a helping role in the formation of the bound nitrile group pairs by initially bringing the nitrile groups close to each other and further improving the mutual alignment of the interacting dipoles to positions of optimum attractive interaction. This helping role may be played equally successfully by very low or very high energy of segment mobility, since the duration of the heat treatment was sufficiently long. The role of the energy of segment mobility in breaking the bound nitrile group pair would clearly differ depending on the energy of segment mobility. Since the heat treatment in PAN(air) and PAN(vac) was done at identical temperatures, the possible reason for higher segment mobility in case of heat treatment in air atmosphere might be that the diffusion of gases from air may produce plasticization which enhances segment mobility. Since such an effect is not operative in the case of heat treatment under vacuum, the ultimate degree of bound nitrile group pairs in PAN(vac) is higher than that in PAN(air).

Infrared Spectra

The IR spectra of these samples are shown in Figure 8. The absorption band at 2240 cm^{-1} due to nitrile ($-\text{C}\equiv\text{N}$) bond stretching^{14,15} is quite intense and occurs at the same frequency for all the three samples of PAN. However, the intensity of this band shows a systematic variation. The relative intensity of this band, estimated by the ratio I_{2240}/I_{1460} of the heights of $\text{C}\equiv\text{N}$ stretching (2240 cm^{-1}) and CH bending band (1460 cm^{-1}) for the various samples, is shown in Table II.

This observation is a little strange because, in most previous works, the decrease in the intensity of the 2240 cm^{-1} band has been attributed¹⁶ to the decrease in the concentration of $\text{C}\equiv\text{N}$ groups which are not converted to $\text{C}=\text{N}$ or other chemical structures. In the present case, the intensity of the 2240 cm^{-1} band is lower for the case where the possibility of chemical change is lower, i.e., PAN(vac), than for the case with greater possibility of chemical change, i.e., PAN(air). Since the intensity of the 2240 cm^{-1} band decreases in the same order as the degree of intermolecularly bound nitrile groups through their dipole-dipole interactions, it seems tempting to say that for such a bound nitrile group pair the $\text{C}\equiv\text{N}$ band stretching mode is affected.

It may be noted that for these heat-treated samples as well as for PAN(U), the band around 2220 cm^{-1} , generally attributed $\text{C}=\text{N}$, is not apparent in these spectra. This confirms the absence of the chemical changes in these samples. Color change on heat treatment was also inappreciable in these samples.

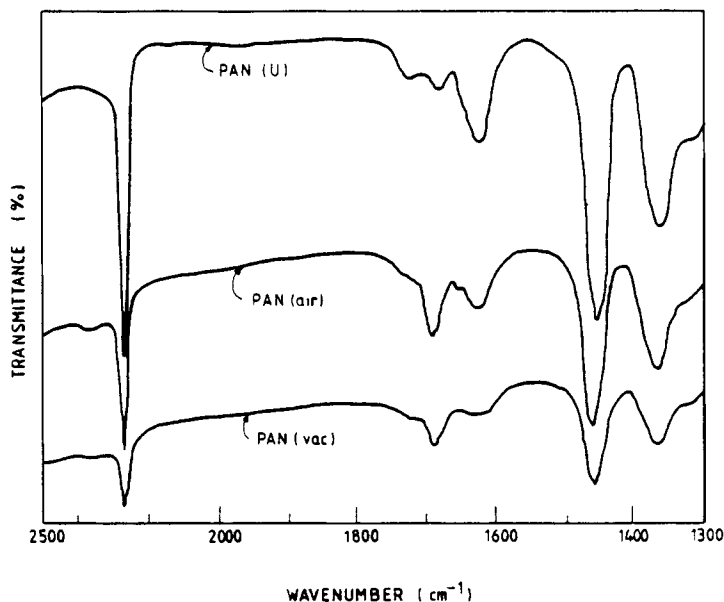


Fig. 8. Infrared spectra of PAN(U), PAN(air) and PAN(vac).

X-Ray Diffraction

X-ray diffraction patterns for these PAN samples, represented in Figure 9 as the intensity (I)-vs.-diffraction angle (2θ) plots, show an intense sharp reflection at $2\theta = 16.5^\circ$ (peak 1) and another less intense sharp reflection at $2\theta = 29.5^\circ$ (peak 2), and a broad diffuse scattering in the region between these two sharp peaks. X-Ray diffraction patterns for PAN with the same characteristic features have been reported by various authors.¹⁷⁻²¹ The intense reflection at $2\theta = 16.5^\circ$

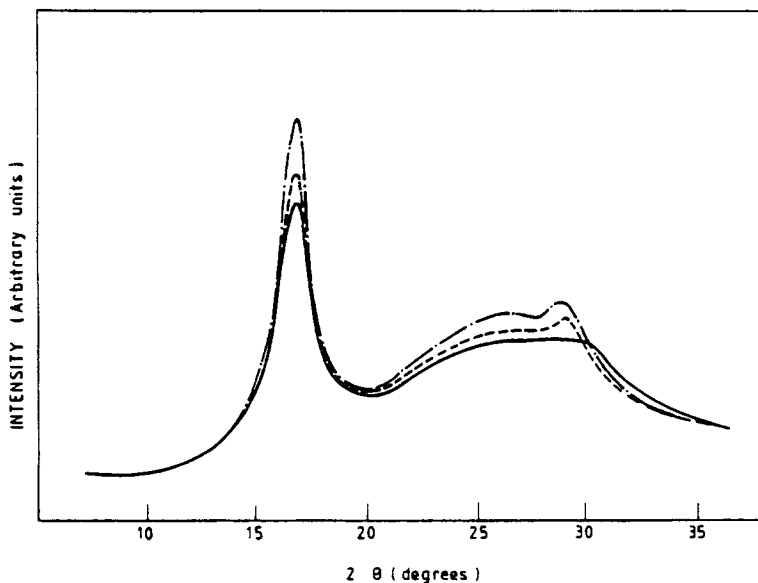


Fig. 9. X-ray diffractograms for PAN(U) (—), PAN(air) (- - -), and PAN(vac) (- · -).

corresponds to a lateral repeat distance of 5.4 Å and has been attributed to the (100) reflection of a hexagonal lattice.¹⁴ Rosenbaum,¹³ however, attributed this reflection to the intermolecular distances (close packing of the above described irregularly helical conformation) in drawn PAN fibers. The reflection at $2\theta = 29.5^\circ$ conforms to the second-order reflection of peak 1.²⁰ The general diffuse scattering covering an extensive portion of the pattern indicates that the disordered phase is distributed throughout the structure in a nondiscrete manner.¹⁴

In these diffraction patterns, the positions of the sharp reflection peaks on the 2θ axis remain unchanged for all the samples, and no new reflection seems to occur in the case of heat-treated samples. This suggests that the ordered structure (crystalline lattice) of PAN remains unaffected by heat treatment. Furthermore, like the results of Bohn et al.,¹⁴ the present results negate the formation of orthorhombic lateral order in PAN as a result of heat treatment, as suggested by some authors,²² since there is no additional reflection occurring in the diffraction pattern for the heat-treated samples.

Extrapolation of the sharp and diffuse reflections according to the method used by Bell and Dumbleton¹⁸ leads to the degree of order (or crystallinity index) shown in Table II for these samples. Since the increase in the degree of order is apparently accompanied by an increase in the degree of bound nitrile group pairs, it seems that the intermolecular nitrile group bonding produces a similar kind of order as existed in the untreated PAN sample. In other words, as Rosenbaum¹³ interpreted, if the reflection at $2\theta = 16.5^\circ$ were due to parallel close alignment of molecular irregular helices, then the heat treatment would result in a greater degree of such alignment and thus a higher degree of intermolecular nitrile group bonding.

Glass Transition Temperature

The relationship of the relaxation temperatures at various frequencies to the conventional calorimetric or dilatometric glass transition temperature T_g is discussed elsewhere.^{6,7} A simplified expression for T_g in terms of the relaxation temperatures at two frequencies is derived on the basis of the WLF equation. According to the WLF equation,²³ the temperature dependence of the relaxation time is expressed as

$$\log \frac{\tau}{\tau_s} = \frac{-C_1(T - T_s)}{C_2 + T - T_s} \quad (9)$$

where τ and τ_s are the relaxation times at any temperature T and at a reference temperature T_s , respectively. C_1 and C_2 are the constants whose universal values, valid for a large number of polymers, are $C_1 = 8.86$ and $C_2 = 101.6$ for $T_s = T_g + 50^\circ\text{C}$.²³

The expression for T_s derived from eq. (9) is⁷

$$T_s = C_2 + \frac{1}{2}(T_1 + T_2) - \frac{1}{2} \left[(T_1 - T_2)^2 - \frac{4C_1C_2(T_1 - T_2)}{(\log f_2 - \log f_1)} \right]^{1/2} \quad (10)$$

where the relaxation times τ_1 and τ_2 at temperatures T_1 and T_2 are replaced by the corresponding frequencies f_1 and f_2 [$\tau = 1/(2\pi f)$]. Equation (10) thus enables the evaluation of T_s from the relaxation temperature data at two frequencies.

Values of the WLF constants C_1 and C_2 for PAN have been reported⁴ as $C_1 = 5.7$ and $C_2 = 75.0$. Using these values and the relaxation temperature data at the higher two frequencies 10^4 and 10^5 Hz, we obtain T_s values for the various samples presented in the Table II as $T_g (= T_s - 50^\circ\text{C})$.

These T_g values, though in good agreement with the T_g value reported for PAN in the literature,²⁴ may be emphasized for their comparative values for the three samples and not for their absolute magnitude. For these three samples, T_g increases in the same order as the degree of bound nitrile group pairs in the structure. Heat treatment under vacuum increases T_g of PAN more than heat treatment in air. This increase in T_g is accompanied by an increase in the degree of order obtained from X-ray diffraction results and also by an increase in the degree of bound nitrile group pairs obtained from dielectric results.

CONCLUSIONS

The present investigation of heat treatment of PAN in air and under vacuum at identical temperatures clearly supports that the observed effect is not attributable to the chemical changes in the PAN molecule caused by the heat treatment. This is further supported by our earlier observation¹ that heat treatment at a higher temperature produced less change in dielectric relaxation than that at a lower temperature.

The lower values of dielectric relaxation strength and the dissipation factor for heat-treated samples than for the untreated PAN seem to be predominantly due to the decrease in the mean square dipole moment of the relaxing segments.

The observed effect of heat treatment can be attributed to the degree of intermolecularly bound nitrile groups which is found to be larger in the sample heat treated under vacuum than in the sample heat treated in air.

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