# Effect of Copolymerization with Methacrylonitrile on the Dielectric Relaxation of Polyacrylonitrile

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## Synopsis

Dielectric relaxation in the glass transition region of polyacrylonitrile (PAN), polymethacrylonitrile (PMAN), and their random copolymers containing 6–46 wt % MAN has been studied in the frequency range $10^2$–$10^5$ Hz and temperature range 40–160°C. Changes in the dielectric constant increment, relaxation temperature, and the loss peak amplitude with changing MAN content in the copolymers were observed. Dielectric constant increment and loss peak amplitude showed maxima around 6–12 wt % MAN content while the relaxation temperature increased continuously over the entire range. The results are discussed in terms of the possible structural differences arising from the effect of the introduction of MAN units on the dipolar interactions between the nitrile groups.

## INTRODUCTION

Dielectric relaxation of polyacrylonitrile (PAN) due to segmental mobility in the glass transition region is significantly affected by the dipole–dipole interactions between the nitrile groups.[1-5] Intermolecular interactions between the nitrile groups are strongly attractive[6] and thus give rise to some kind of interlinking effect between the neighboring segments through the bound nitrile group pairs (bound through their dipolar interactions). These bound nitrile group pairs result in a reduction of the mean square dipole moment of the segments and greater restrictions on the mobility of the segments.

Changes in the degree of bound nitrile groups in the structure of PAN are produced by the heat treatment at temperatures above the glass transition temperature.[3,5,7] During the course of heat treatment, as the specimen is held at high temperature for a certain duration, the processes of formation and breaking of bound nitrile group pairs occur simultaneously, which gives rise to a variation of equilibrium value of degree of bound nitrile group pairs with temperature, duration, and atmosphere of heat treatment. After the heat treatment, as the specimen is cooled to room temperature (i.e., below glass transition temperature) the final equilibrium value of the degree of bound nitrile groups becomes stable, owing to the absence of segmental mobility. The observed dependence of degree of bound nitrile groups on the temperature,[3] atmosphere,[5] and duration[7] of heat treatment enabled us to ascertain the nature of these structural changes in PAN on heat treatment.[2-5] The effect of heat treatment on the dielectric relaxation[2,3,5] and mechanical properties[4] of PAN were found well accounted for by the above-stated structural changes.

However, it may be remarked that even in the PAN which has not undergone any thermal treatment, the degree of bound nitrile groups may be finite and may differ in samples prepared by different methods. Chapiro et al.[8] have reported that the polarity of the medium of polymerization results in considerable differences in the structure and $T_g$ of PAN, which imply the differences in the dipolar interactions between the nitrile groups. Effect of random copolymerization of PAN with hydroxyethyl methacrylate (HEMA),[9,10] methacryloyloxy ethoxytrimethyl silane (MAETMS),[11] and methacryloyloxy propoxytrimethyl silane (MAPTMS)[11] showed some changes in the dielectric relaxation and X-ray diffraction and thermal properties of PAN, which were found attributable to the changes in the dipolar interactions between the nitrile groups in the structure of PAN.

In this work, we have carried out a study of the effect of copolymerization with methacrylonitrile (MAN) on the dielectric relaxation of PAN in the glass transition region, with the aim to achieve better insight into the effect of copolymerization on the formation of interacting nitrile group pairs in the structure. The comonomer MAN has a special feature that, unlike the case of the comonomers studied earlier,[9-11] the replacement of acrylonitrile units by MAN does not change the number of nitrile groups in the molecular chain while some methyl groups are introduced in place of hydrogen atoms.

## EXPERIMENTAL

### Samples

Homopolymers of acrylonitrile and methacrylonitrile and their copolymers were prepared by the method described elsewhere[12] by emulsion polymerization in aqueous medium at 35°C in inert atmosphere using potassium persulfate as initiator. In the case of copolymers, the polymerization was carried out using the stipulated proportion of the two monomers. Compositions of the copolymer were finally determined from infrared spectra.

The various copolymers are denoted as $M_1$, $M_2$, $M_3$, $M_4$, and $M_5$, which contain respectively 6, 12, 24, 35, and 46 wt % MAN.

### Measurements

Dielectric measurements in the frequency range $10^2$–$10^5$ Hz and temperature range 40–160°C were made on a General Radio GR-716-CS bridge using a two-terminal connection for the cell. Sample discs (about 1 mm thickness and 1.3 cm diameter) were prepared by compressing the vacuum dried polymer powders. The disc surfaces were silver-coated for achieving better electrode contact. The specimen cell was kept in a thermostated chamber controlled within ±0.1°C. Temperature was measured by a thermocouple placed in good thermal contact with the sample disc.

## RESULTS AND DISCUSSION

Results of dielectric measurements at the various frequencies are shown as variations of dielectric constant $\epsilon'$ and dissipation factor $\tan \delta$ with temperature
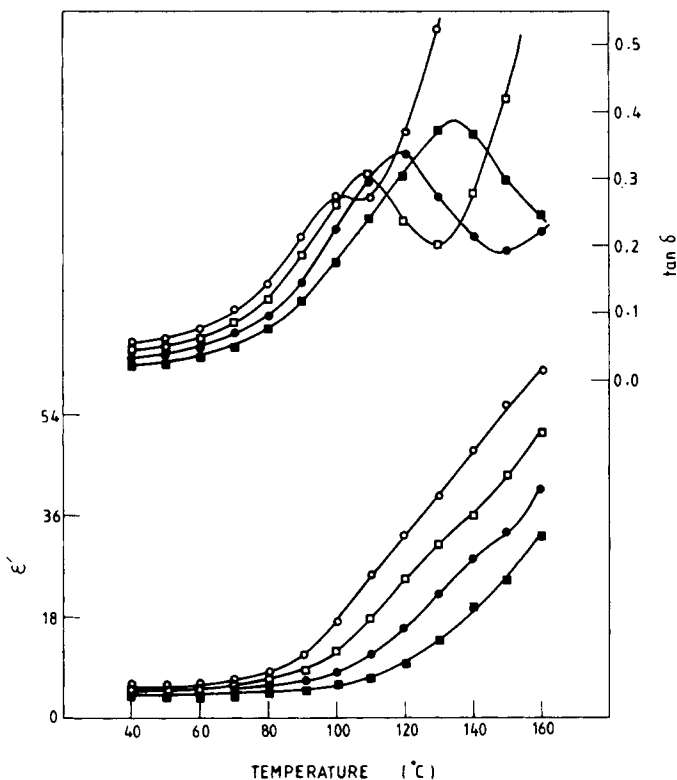
Fig. 1. Variation of dielectric constant $\epsilon'$ and dissipation factor tan $\delta$ with temperature at various frequencies (Hz) for PAN: (O) $10^2$; (□) $10^3$; (●) $10^4$; (■) $10^5$.

in Figures 1–4 of PAN, PMAN, and two copolymers $M_1$ and $M_4$, as typical examples of these data on the various samples studied. These data at the lower frequencies show considerable dc conductivity effect, for which correction could not be applied. Hence these lower frequency data may be taken reliable only for the value of relaxation temperature and not for the magnitudes of tan $\delta$ and $\epsilon'$. In the subsequent discussion about the variation of the values of tan $\delta$ and $\epsilon'$, we will refer to the data at frequency $10^5$ Hz unless otherwise stated.

Dielectric constant of PAN shows inappreciable variation with temperature in the lower temperature region up to about 80°C and thereafter it increases with temperature to considerably high value at the high temperature extreme of these measurements, viz., 160°C. $\epsilon'_{160}$ (the dielectric constant at 160°C) is 33 at $10^5$ Hz and increases with increasing frequency showing a value $\epsilon'_{160} \simeq 60$ at $10^2$ Hz. Such a high increase of dielectric constant of PAN in the stated range of temperature is also observed in the data on PAN reported by other authors.[1,13–15] This increase of dielectric constant to such high values may be attributed to the orientation of highly polar segments of PAN and/or to the high conductivity, which is common with pressed powders particularly at low frequencies. High dipole moments of the PAN molecular segments is due to the presence of strongly polar nitrile groups. The peak or plateau in $\epsilon'$ around 160°C would be due to the polar segments, but the elevated values of dielectric constant might be partly
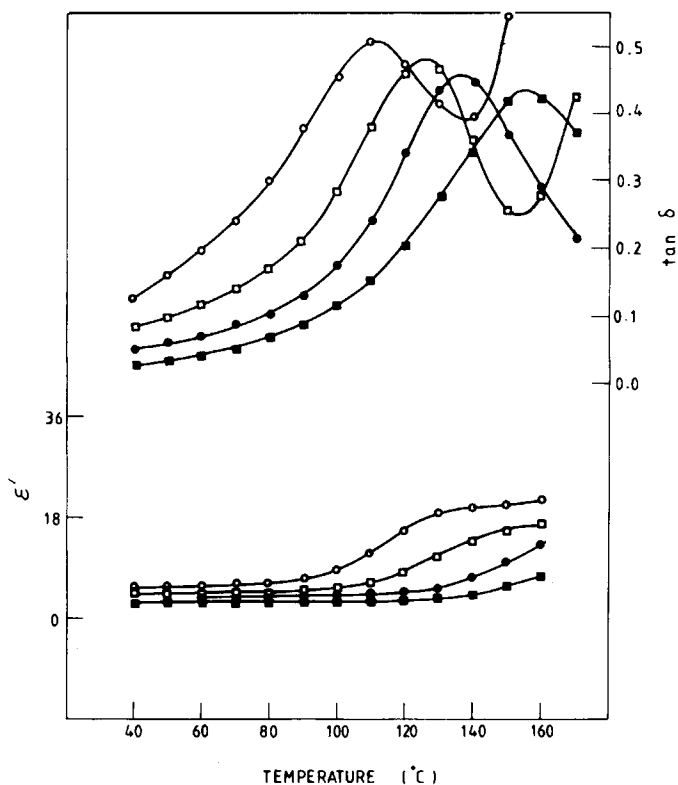
Fig. 2. Variation of dielectric constant $\epsilon'$ and dissipation factor tan $\delta$ with temperature at various frequencies (Hz) for PMAN: (O) $10^2$; ($\square$) $10^3$; ($\bullet$) $10^4$; ($\blacksquare$) $10^5$.

due to the dipole moment of the segments and partly due to the rapidly rising base line caused by charge flow at high temperatures.[14]

For PAN two transitions are reported by various authors,[16–18] one in the vicinity of 90°C and the other around 140°C. The former is attributed to the glass transition while the latter to the breaking of dipolar interactions of nitrile groups,[16,18] which are well confirmed by the observed[19] structural changes of PAN on heat treatment at both these temperatures. The glass transition temperature $(T_g)$ of PAN is reported in the literature[16,20] in the range 80–104°C. The present data show a relaxation which is attributable to the first one of the above-stated two transitions of PAN, viz., the glass transition, as discussed in detail elsewhere.[1]

The observed variation of $\epsilon'$ vs. $T$ in these data, i.e., $\epsilon'$ remains almost unchanged up to a temperature (which we will call $T'$) which is close to the $T_g$ of PAN, and above this temperature $\epsilon'$ increases with increasing temperature. At temperatures lower than $T'$ (or $T_g$), since the polymer is in its glassy state, the molecular segments being immobile, the segmental dipole moments do not contribute to the dielectric constant value. At temperatures above $T'$ (or $T_g$), since the segments are mobile, dipolar orientations of polar segments may produce the observed polarization effect or the increase in dielectric constant value.
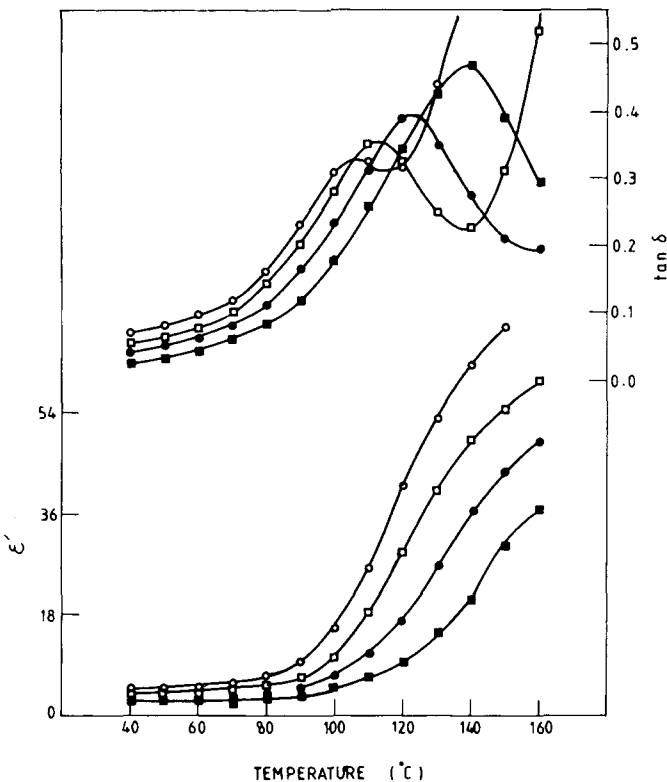
Fig. 3. Variation of dielectric constant $\epsilon'$ and dissipation factor tan $\delta$ with temperature at various frequencies (Hz) for the copolymer $M_1$ of acrylonitrile and methacrylonitrile containing 6 mol % MAN:  (O) $10^2$; (□) $10^3$; (●) $10^4$; (■) $10^5$.

Though the above-mentioned parameter $T'$ is not talked about in the literature, its coincidence with literature value of $T_g$, and the ability to explain the variation of $\epsilon'$ and $T'$ in terms of glass transition behavior, seem to suggest the relevance or relationship of $T'$ with $T_g$.   Furthermore, a variation of $T'$ with frequency apparent on these data is in good qualitative agreement with the well-believed variation[1] of relaxation temperature with frequency.

These data for all the samples at one frequency ($10^5$ Hz) are represented in Figure 5, which reveals more clearly the differences in these data for the various samples.

Increases in polarization over the measured temperature range, as indicated by the difference between the values of dielectric constant at two extreme temperatures (i.e., $\epsilon'_{160} - \epsilon'_{40}$), varies with MAN content in the copolymers.   The values of ($\epsilon'_{160} - \epsilon'_{40}$) for these samples at $10^5$ Hz are shown in Table I.   Also shown in this table are the values of relaxation temperature $T_{max}$, corresponding to the position of the maxima in tan $\delta$ vs. $T$ curves, and the loss peak amplitude tan $\delta_{max}$ for these samples at the stated frequency.

The observed relaxation of PAN has been attributed to the glass transition[1] and the relationship of the relaxation temperature with $T_g$ is discussed through the dependence of relaxation temperature on the frequency of measure-
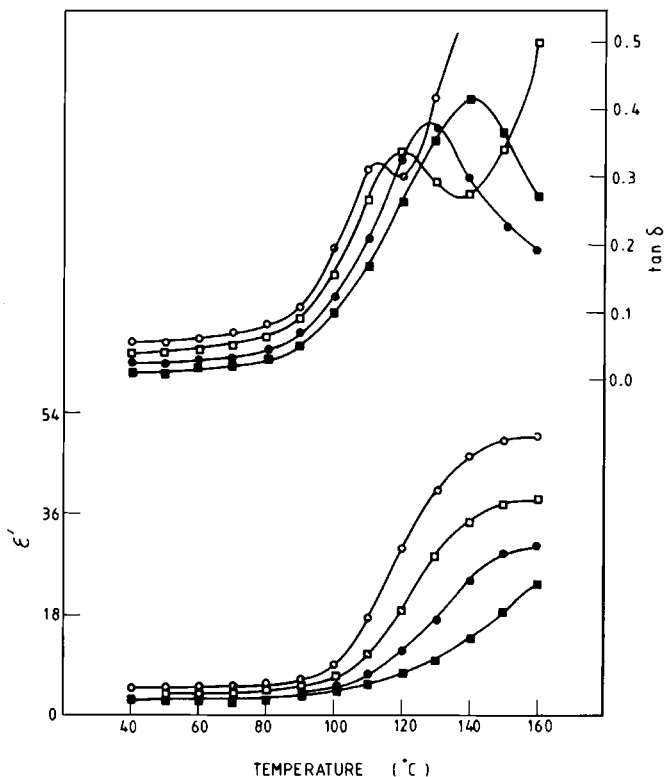
Fig. 4. Variation of dielectric constant $\epsilon'$ and dissipation factor tan $\delta$ with temperature at various frequencies (Hz) for the copolymer $M_4$ of acrylonitrile and methacrylonitrile containing 35 mol % MAN:  (○) $10^2$; (□) $10^3$; (●) $10^4$; (■) $10^5$.

ment.[1,21-25]  Variations of $T_{max}$ with frequency in these data are represented at the Arrhenius plots shown in Figure 6.   The nonlinear nature of Arrhenius plots for the glass transition process is a well-reported observation and is also predicted by the theories.[1,24,25]  Activation energy $\Delta E$, calculated from the slope of the linear portion of these Arrhenius plots in the frequency range $10^4$–$10^5$ Hz are shown in Table I, to illustrate its variation in the identical range of frequency of measurements.   In the subsequently described calculation of dielectric relaxation strength from the data at $10^5$ Hz, these values of $\Delta E$ are used.

Dielectric relaxation strength $(\epsilon'_0 - \epsilon'_\infty)$, where $\epsilon'_0$ and $\epsilon'_\infty$ are the low and high frequency limiting values of the dielectric constant for the observed relaxation, is related to the mean square dipole moment of the relaxing units (i.e., the polymer segments).[26]  For these data in the limited frequency range, $(\epsilon'_0 - \epsilon'_\infty)$ may be evaluated from the area under the $\epsilon''$ vs. $1/T$ plot according to the relation[25,26]

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

where $\Delta E$ is the activation energy and $R$ is the universal gas constant.   Due to the presence of dc conductivity effects in the data at the lower frequencies, these calculations are done on the data at $10^5$ Hz.   Areas under the $\epsilon''$ vs. $1/T$ plots were
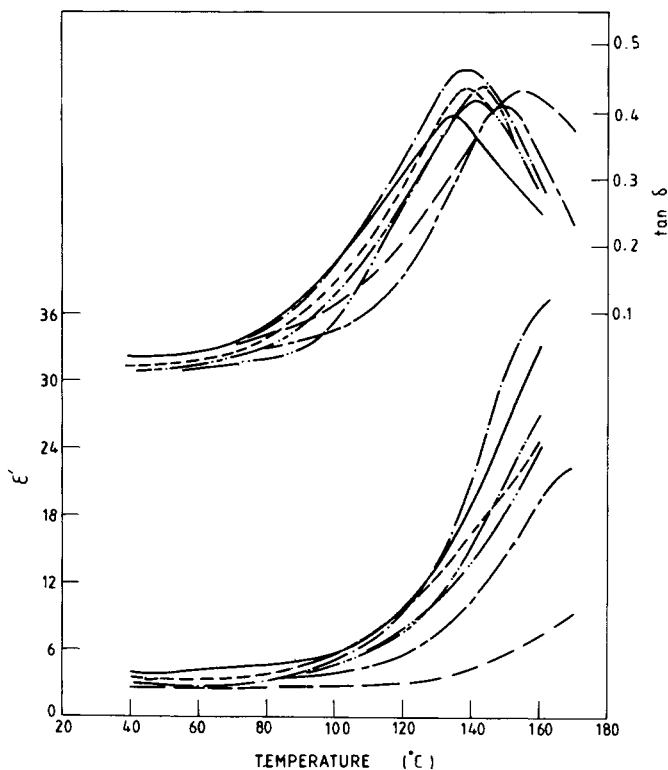
Fig. 5. Comparison of the $\epsilon'$ vs. $T$ and tan $\delta$ vs. $T$ curves at $10^5$ Hz for PAN (——), PMAN (- -), and the copolymers $M_1$ (–··–), $M_2$, (- - -), $M_3$ (—·—·—), $M_4$ (— ·· —), and $M_5$ (— — —).

determined after symmetric extrapolation of the loss peaks.   Values of $(\epsilon_0' - \epsilon_\infty')$ thus obtained for the various samples are shown in Table I.

Considering PAN and PMAN as the extreme cases of copolymer composition respectively representing 0% and 100% MAN contents, variations of these dielectric relaxation parameters with copolymer composition may be represented as shown in Figure 7.   These results show that:

(i) The dielectric constant increment, $(\epsilon_0' - \epsilon_\infty')$, initially increases with increasing MAN content up to a maximum value for 6–12% MAN content, and then decreases to a value almost equal to that of PAN for the copolymers containing 25–46% MAN.   The value of $(\epsilon_0' - \epsilon_\infty')$ for PMAN is much lower than that of PAN.

TABLE I
Values of $(\epsilon_{160}' - \epsilon_{40}')$, $T_{max}$, and tan $\delta_{max}$ at $10^5$ Hz and $\Delta E$ and $(\epsilon_0' - \epsilon_\infty')$ for Various Samples

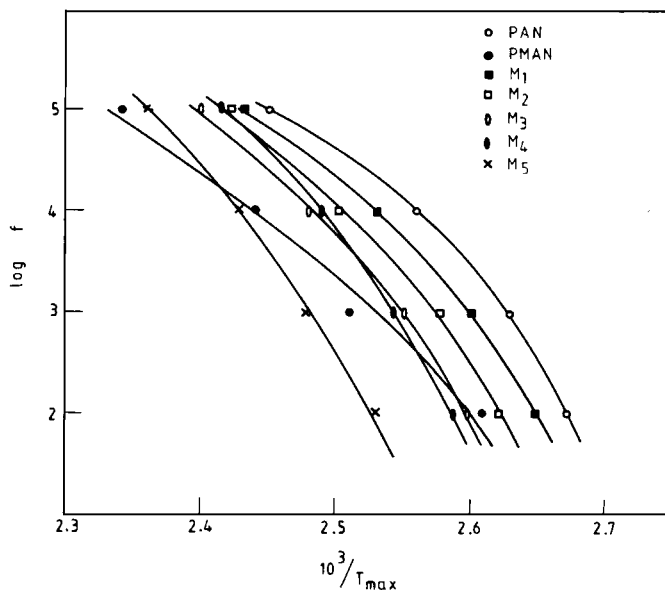| Samples | $(\epsilon_{160}' - \epsilon_{40}')$ | $T_{max}$ (°C) | tan $\delta_{max}$ | $\Delta E$ (kcal/mol) | $(\epsilon_0' - \epsilon_\infty')$ |
|---|---|---|---|---|---|
| PAN | 28.5 | 135 | 0.40 | 43.3 | 41.4 |
| $M_1$ | 32 | 139 | 0.47 | 44.9 | 47.9 |
| $M_2$ | 21 | 138 | 0.44 | 60.2 | 47.4 |
| $M_3$ | 23 | 143 | 0.43 | 57.0 | 42.2 |
| $M_4$ | 19 | 141 | 0.42 | 60.3 | 42.3 |
| $M_5$ | 18 | 150 | 0.42 | 68.0 | 40.9 |
| PMAN | 9 | 155 | 0.43 | 45.0 | 10.4 |

Fig. 6. Arrhenius plots from the dielectric relaxation data for PAN (O), PMAN (●), and the co-polymers $M_4$ (■), $M_2$ (□), $M_3$ (O), $M_4$ (●), and $M_5$ (×).

(ii) The relaxation temperature $T_{max}$ increases continuously with MAN content over the whole range of composition.

(iii) The loss peak amplitude tan $\delta_{max}$ first increases for the low MAN content and then suddenly drops to a value almost equal to that of PMAN.

Before discussing the observed differences in the variations of the three quantities, it may be stated that the value of $(\epsilon'_0 - \epsilon'_\infty)$ depends on mean square dipole moment and that of $T_{max}$ depends on the restrictions on the mobility of the segments, while the magnitude of tan $\delta_{max}$ would have the contributions from both the above-mentioned factors. Greater restrictions on segment mobility as well as the higher polarity of the relaxing units may account for higher magnitude of dielectric loss. However, the existing theories do not seem to describe the separate contributions of these two factors on the magnitude of tan $\delta$. As apparent from these results (Fig. 7), the magnitude of tan $\delta_{max}$ seems to be a more complicated function than the simple addition or multiplication of $(\epsilon'_0 - \epsilon'_\infty)$ and $T_{max}$.

These results show a continuous increase of $T_{max}$ with increasing MAN content whereas $(\epsilon'_0 - \epsilon'_\infty)$ and tan $\delta_{max}$ show initially an increase and then a decrease. Increase in $(\epsilon'_0 - \epsilon'_\infty)$ implies an increase of the dipole moment of the segments. Such an increase of dipole moment is possible if some nitrile groups are released from their dipolar interactions. At low MAN content, the $CH_3$ groups introduced in the structure might produce some steric hinderances, which prevent the pairing of some nitrile groups for their dipolar interactions. Thus a lower degree of in-termolecularly bound nitrile groups may be expected in these copolymers con-taining 6–12% MAN. On the other hand, at higher MAN content (greater than 12%), as the number of $CH_3$ groups at random positions along the molecular chain increases, their role in increasing the free volume becomes more predominant;
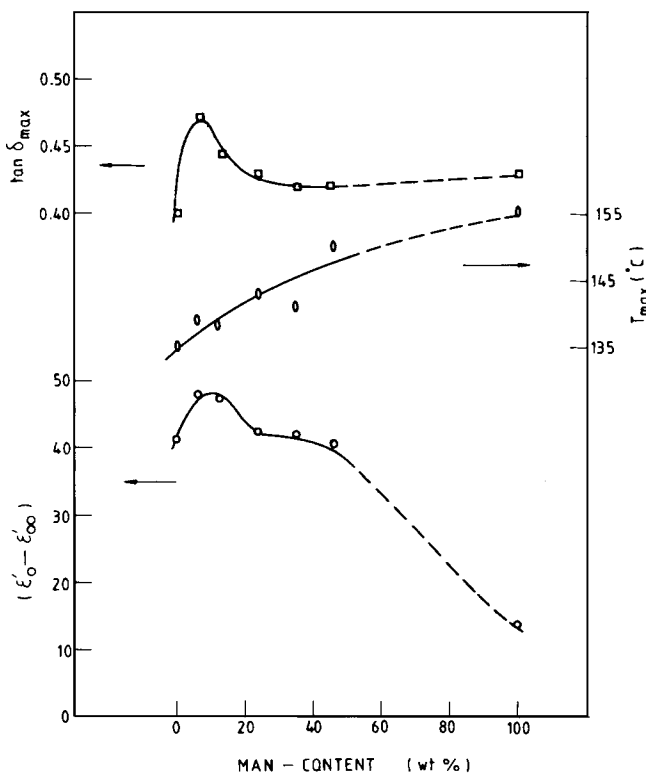
Fig. 7. Variation of dielectric relaxation strength ($\epsilon'_0 - \epsilon'_\infty$), less peak amplitude (tan $\delta_{max}$), and the relaxation temperature ($T_{max}$) with copolymer composition.

hence the segments find it easier to readjust to a structure with greater number of paired nitrile groups which results in a higher degree of bound nitrile groups in the structure. This higher degree of bound nitrile group pairs might account for lower value of dipole moment of the segments, which seems responsible for the observed decrease of ($\epsilon'_0 - \epsilon'_\infty$) for the copolymers of MAN content greater than 12%.

However, the increase of $T_{max}$ suggests that the introduction of $CH_3$ groups increases the bulkiness of the segments. The bulkier the relaxing unit the greater will be the thermal energy required for its relaxation at a given frequency of measurement. $T_{max}$ increases continuously with increasing MAN content irrespective of the degree of bound nitrile group pairs in the structure. Furthermore, the restrictions posed by intermolecularly bound nitrile group pairs on the segment mobility would also be inherent in this observed variation of $T_{max}$ with copolymer composition. Any abnormality in the variation of $T_{max}$ around the copolymer composition 6–12% MAN could not be detected, as these data show a considerable scatter in the values of $T_{max}$.

Variation of tan $\delta_{max}$ with copolymer composition shows a maximum around the same composition, where ($\epsilon'_0 - \epsilon'_\infty$) showed a maximum (Fig. 7). As already stated, this maximum may be a combined effect of the value of the diple moment of the segments as well as that of the restrictions on segmental mobility due to the bulkiness, steric hinderances, free volume, and bound nitrile group pairs.

In these experiments the copolymer composition between 50% and 100% MAN content is not investigated; hence the variations in this range (Fig. 7) are represented through dashed curves joining the data for the samples $M_5$ and PMAN. Abnormalities in the variation of these quantities in this region cannot be ruled out without further investigations.

The lower value of $(\epsilon_0' - \epsilon_\infty')$ for PMAN than PAN seems to imply that the steric effects due to the presence of $CH_3$ groups allow the formation of a greater degree of bound nitrile groups in PMAN than in PAN. The higher value of relaxation temperature $T_{max}$ of PMAN than PAN may also be partly due to the restrictions of segmental mobility due to higher number of bound nitrile group pairs in PMAN. Furthermore, it is also seen that for PMAN $(\epsilon_0' - \epsilon_\infty')$ is lower and $T_{max}$ is higher than PAN while tan $\delta_{max}$ is of comparable magnitude in both these homopolymers.

## CONCLUSION

The observed changes in the glass transition relaxation of PAN with copolymerization with methacrylonitrile suggest that in the copolymers with MAN content around 6–12 wt %, there is a lower degree of intermolecularly bound nitrile groups in the structure. Thus the amorphous phase has less intersegment interactions, or, in other words, the amorphous structure is more open for diffusion of penetrants such as, for example, the water or dye molecules. Thus, this composition seems recommendable for PAN fibers based on MAN as the comonomer. The segment mobility, however, is somewhat lower for these copolymers than for PAN. As regards the two homopolymers, the degree of bound nitrile groups seems greater in PMAN than in PAN.

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