

Effect of Heat Treatment on Dielectric Relaxation of Polyacrylonitrile: Reversible Thermally Induced Structural Change

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Synopsis

The effect of heat treatment on the dielectric relaxation of polyacrylonitrile (PAN) was studied. Dielectric measurements, in the frequency range 0.1–100 kHz and temperature range 30–170°C, on PAN heat treated at two temperatures (120 and 160°C) and the untreated PAN are reported. The loss peak height, the dielectric relaxation strength, loss peak width, and the loss peak temperature were found to vary systematically with the temperature of the heat treatment. The changes in dielectric relaxation produced by heat treatment at the higher temperature (i.e., 160°C) were considerably less than those produced by heat treatment at 120°C. The results are discussed and attributed to the variation of the degree of bound nitrile groups (through their dipole–dipole interaction) with heat treatment temperature. Heat treatment of the higher temperature (160°C) results in lower degree of bound nitrile groups in the structure than heat treatment at the lower temperature (120°C).

INTRODUCTION

Some controversies over the structure and dielectric relaxation of polyacrylonitrile (PAN) have been discussed in a previous publication.¹ The dielectric relaxation in the same temperature and frequency range reported from four different laboratories^{1–4} showed some differences which seem attributable to the difference in the structure of PAN sample used. Difference in the structure of PAN could be expected due to various reasons: (1) different methods of chemical synthesis of PAN, (2) film preparation from solutions in different solvents and under different conditions of drying, and (3) the different thermal treatment of the specimen.

In the comparative study¹ of the four different sets of dielectric data on PAN, some major differences were found in the data of Hayakawa et al.² from the other three sets of data.^{1,3,4} The essential differences in the samples used were the following: (1) Hayakawa et al. used a solution-grown film while the other studies were on PAN in powder form. (2) Hayakawa et al.'s sample was heat treated at 130°C for 30 h for removing traces of solvent from the films while the three sets of data were on samples which did not undergo any heat treatment. Structural changes may occur both during film growing and heat treatment. Thus, the differences in the dielectric data of Hayakawa et al.² from those of the other authors^{1,3,4} seem attributable to either one or both of these causes.

In the present work, we investigate the effect of heat treatment on the dielectric

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relaxation of PAN. Dielectric measurements are carried out on PAN samples identical in all other respects and differing only in the thermal treatment.

Choice of heat treatment temperature and time was governed by the conditions used in the work of Hayakawa et al., as stated above. The heat treatment was carried out for 24 h at two temperatures, one (120°C) was just above the glass transition temperature (T_g) and the other (160°C), much above the T_g .

EXPERIMENTAL

PAN used in this work was prepared by free radical polymerization of acrylonitrile in dimethylformamide in inert medium using α, α' -azobisisobutyronitrile as the initiator by a method described in detail elsewhere.⁵

Measurements were made on three samples, two of which were heat treated in air in a closed container at 120 and 160°C for 24 each (called hereafter PAN(120) and PAN(160), respectively), and one which was not given any heat treatment (hereafter called PAN(U)).

Specimen discs about 1 mm thick and 1 cm in diameter were prepared by compressing at 8 tons/in.² pressure the PAN powder (dried in vacuum oven at 40°C) under vacuum. The disc surfaces were silver coated to achieve better electrode contact.

Dielectric measurements were done in the frequency range 0.1–100 kHz and temperature range 30–170°C on a General Radio (GR 716-CS) bridge. The temperature change was stepwise in a cycle of increasing temperature, and the overall average heating rate was about 0.5°/min. The specimen was kept in a thermostated chamber maintained at temperatures within $\pm 0.1^\circ\text{C}$. The temperature of the specimen was measured by a thermocouple kept in close vicinity of the specimen.

RESULTS AND DISCUSSION

Dielectric measurements data on PAN(U), PAN(120), and PAN(160) are shown in Figures 1–6 as variations of dielectric constant (ϵ') and dissipation factor ($\tan \delta$) with temperature at various frequencies. The differences apparent on these data for the three samples are described in some quantitative terms in Table I.

On examining the corresponding quantities in the sequence PAN(U), PAN(120), PAN(160), one finds that at any given frequency:

- (1) Loss peak temperature (T_{\max}) first increases, then decreases.
- (2) Width of the loss peak first increases, then decreases.
- (3) Loss peak height ($\tan \delta_{\max}$) first decreases, then increases.
- (4) Dielectric constant increment over the studied temperature range ($\epsilon'_{170} - \epsilon'_{30}$) first increases and then decreases. The equivalence of ($\epsilon'_{170} - \epsilon'_{30}$) with the relaxation strength ($\epsilon'_0 - \epsilon'_\infty$) is discussed elsewhere.⁶

All these trends of variation in the dielectric relaxation curves indicated that the heat treatment at 120°C produces greater change in the relaxation than that at the higher temperature, i.e., 160°C.

Since the heat treatments on these samples were carried out in air, the possibility of some chemical change such as aromatization or thermal polymerization cannot be ruled out. However, major chemical changes in PAN are reported⁷

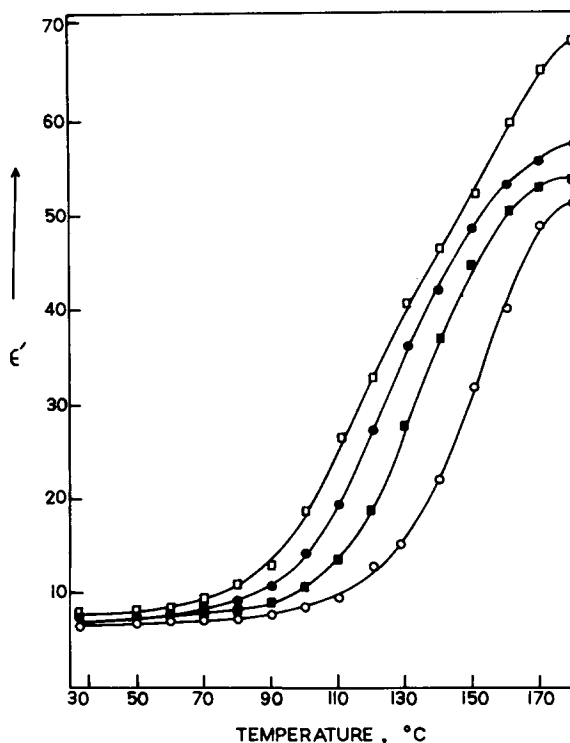


Fig. 1. Variation of dielectric constant (ϵ') with temperature for PAN(U) at various frequencies: (□) 0.1 kHz, (●) 1 kHz, (■) 10 kHz, (○) 100 kHz.

only above 200°C. The observed changes in the dielectric relaxation do not seem attributable to such chemical changes, because the heat treatment at the higher temperature (160°) produces less change in the dielectric relaxation than the heat treatment at the lower temperature (120°C). Moreover, infrared analysis⁸ gave indications of the association of nitrile (CN) groups through dipolar interactions. In the IR spectra, the CN stretching band occurring at 2240 cm^{-1} showed changes in intensity (ratio of CN stretching and CH stretching band heights), such that the intensity was lower for PAN(160) and lowest for PAN(120) as compared to PAN(U). Lower intensity of the band implies a lower number of free nitrile groups, which in turn suggests a higher degree of bound nitrile groups in the structure.

The relaxation shown by these dielectric data has been attributed to the polymer segment mobility characteristic of glass transition as discussed earlier in detail.¹ For the relaxation due to glass transition of polymers, magnitudes of the dielectric parameters depend not only on the dipole moment of the relaxing units (chain segments) but also on the restrictions on the freedom of movement of the polar groups. A polymer having high dipole moment groups may have a low dielectric constant in the glassy state and higher value above the glass transition temperature. Due to the absence of segment mobility in the glassy state of the polymer, the dipole moments of the chain segments do not contribute to the polarization responding at the frequency of the applied field. The low dielectric constant of the polymer in its glassy state is due to some low-scale polarizations (implying smaller groups) in the system. At temperatures above

TABLE I
 Values of Loss Peak Temperature (T_{\max}), Peak Width at Half-Height (ΔT), Peak Height ($\tan \delta_{\max}$), and Dielectric Constant Increment Over the Studied Range of Temperature ($\epsilon'_{170} - \epsilon'_{30}$) for PAN(U), PAN(120), and PAN(160) at Various Frequencies

Frequency kHz	T_{\max} , °C			ΔT , °C ^a			$\tan \delta_{\max}$			$\epsilon'_{170} - \epsilon'_{30}$		
	PAN(U)	PAN(120)	PAN(160)	PAN(U)	PAN(120)	PAN(160)	PAN(U)	PAN(120)	PAN(160)	PAN(U)	PAN(120)	PAN(160)
0.1	102	108	105	16.5	25	20	0.19	0.11	0.17	57	28	46
1	113	120	115	15	22	20	0.27	0.12	0.21	48	25	38
10	125	131	128	17.5	22.5	20.5	0.36	0.15	0.30	45	23	36
100	138	150	145	---	---	---	0.48	0.25	0.37	41	19	33

^a Based on extrapolation of the loss peaks symmetrical to the low temperature end of the curve.

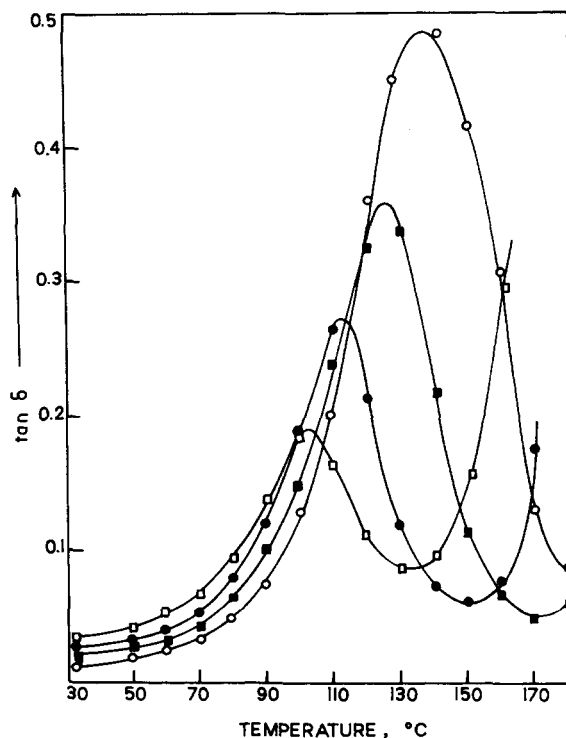
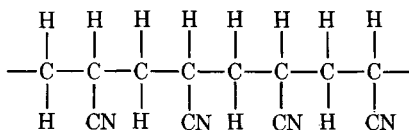


Fig. 2. Variation of dissipation factor ($\tan \delta$) with temperature for PAN(U) at various frequencies. (\square) 0.1 kHz, (\bullet) 1 kHz, (\blacksquare) 10 kHz, (\circ) 100 kHz.

the glass transition temperature (T_g) of the material, the chain segments become mobile and thus their dipole moments start contributing to the polarization responding to the applied electric field of the particular frequency and thereby increasing dielectric constant value. Variations of dielectric constant with temperature observed on these samples (Figs. 1, 3, and 5) clearly show similar behavior. The dielectric constant shows an insignificant variation with temperature up to about 90°C , which is believed to be the T_g of PAN, and then it increases as the segment mobility increases with temperature.

In PAN molecules, each alternate carbon atom of the main chain has attached to it a nitrile (CN) group, which possesses a high dipole moment and a strong dipole-dipole attractive interaction between two nitrile groups of neighboring segments⁹:



So long as the polymer is at temperatures below its T_g , chain segments have almost no mobility; therefore, the nitrile groups, if separated from each other by distances greater than the range of their dipole-dipole interactions, will remain in the unbound state. At temperatures above T_g , owing to the segmental mobility, and possibility of nitrile groups coming in close proximity of other nitrile

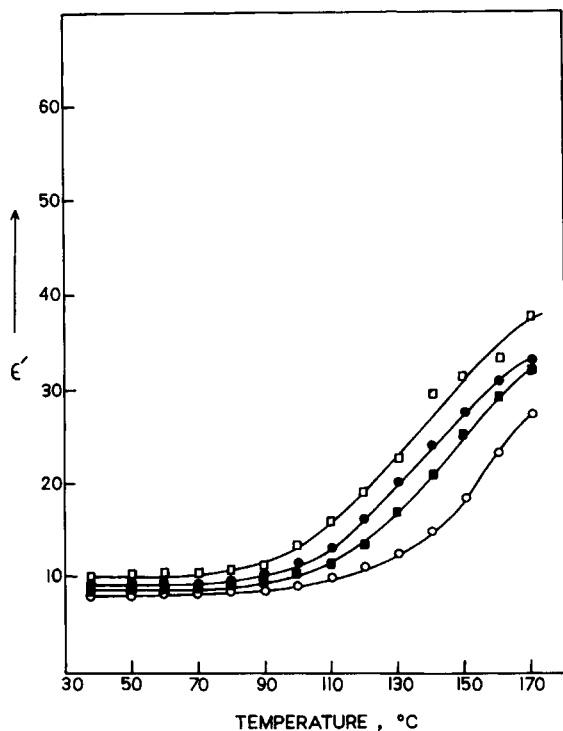


Fig. 3. Variation of dielectric constant (ϵ') with temperature for PAN(120) at various frequencies: (□), 0.1 kHz, (●) 1 kHz, (■) 10 kHz, (○) 100 kHz.

groups will increase, which may result in the formation of bound nitrile group pairs through their dipole-dipole interactions. As the temperature rises further, thermal energy of the segmental motion increases, which tends to break the bound nitrile group pairs. In other words, the segmental mobility acts in competition with the dipolar interaction forces, and hence one may expect a decrease in the stability of bound nitrile group pairs with increasing temperature.

Thus, the structure of the three samples of PAN would differ in their number of bound nitrile group pairs (or, as we shall call it hereafter, the "degree of bound nitrile groups"). Let $\chi_{\text{PAN(U)}}$, $\chi_{\text{PAN(120)}}$, and $\chi_{\text{PAN(160)}}$ denote the degrees of bound nitrile groups in PAN(U), PAN(120) and PAN(160), respectively. As stated, the magnitudes of dielectric parameters depend on the number of free dipole units in the relaxing chain segments. Thus, the higher the degree of bound nitrile groups, the lower will be the number of free nitrile groups, hence the lower will be the magnitudes of the dielectric parameters of the observed relaxation. The observed variations of dielectric constant increment and the loss peak height with heat treatment temperature,

$$(\epsilon'_{170} - \epsilon'_{30})_{\text{PAN(U)}} > (\epsilon'_{170} - \epsilon'_{30})_{\text{PAN(160)}} > (\epsilon'_{170} - \epsilon'_{30})_{\text{PAN(120)}}$$

and

$$(\tan \delta_{\text{max}})_{\text{PAN(U)}} > (\tan \delta_{\text{max}})_{\text{PAN(160)}} > (\tan \delta_{\text{max}})_{\text{PAN(120)}}$$

suggest that

$$\chi_{\text{PAN(U)}} < \chi_{\text{PAN(160)}} < \chi_{\text{PAN(120)}}$$

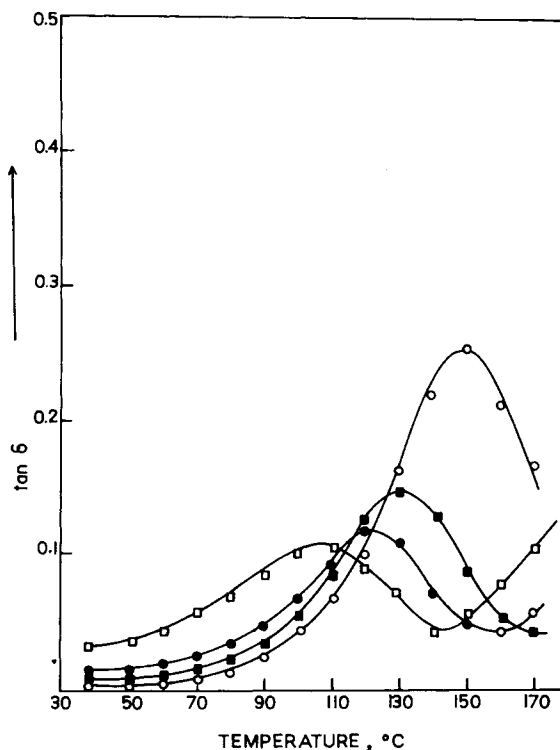


Fig. 4. Variation dissipation factor ($\tan \delta$) with temperature for PAN(120) at various frequencies: (□) 0.1 kHz, (●) 1 kHz, (■) 10 kHz, (○) 100 kHz.

As discussed above, the degree of bound nitrile groups formed during the heat treatment of PAN would depend on the resultant effect of two forces: one due to the thermal energy of segment mobility and the other due to the dipole-dipole interaction of the nitrile groups. A higher degree of bound nitrile groups in PAN(120) than in PAN(160) may result owing to the lower thermal energy of segment mobility during the heat treatment. The lower $\chi_{\text{PAN(U)}}$ value seems attributable to the fact that PAN(U) was not subjected to temperatures higher than 60°C (its polymerization temperature); and during the polymerization and subsequent drying, only a lower degree of bound nitrile groups could be achieved.

In addition, these results show that the loss peak temperature, T_{max} , at identical frequencies varies as

$$(T_{\text{max}})_{\text{PAN(120)}} > (T_{\text{max}})_{\text{PAN(160)}} > (T_{\text{max}})_{\text{PAN(U)}}$$

This indicates a higher T_g , or more restricted mobility of chain segments in PAN(120), than the other two samples. This behavior seems well explained by the above described structural differences of these samples. The presence of bound nitrile groups would restrict the mobility of the chain segments, and thus a higher temperature (or thermal energy) will be needed for the relaxation.

Furthermore, a broadening of the loss curves is apparent in these results (half-widths of the peak shown in Table I). Broadening of loss curves is a common feature in dielectric relaxation when the distribution of relaxation time becomes wider. It seems that the formation of bound nitrile groups during the

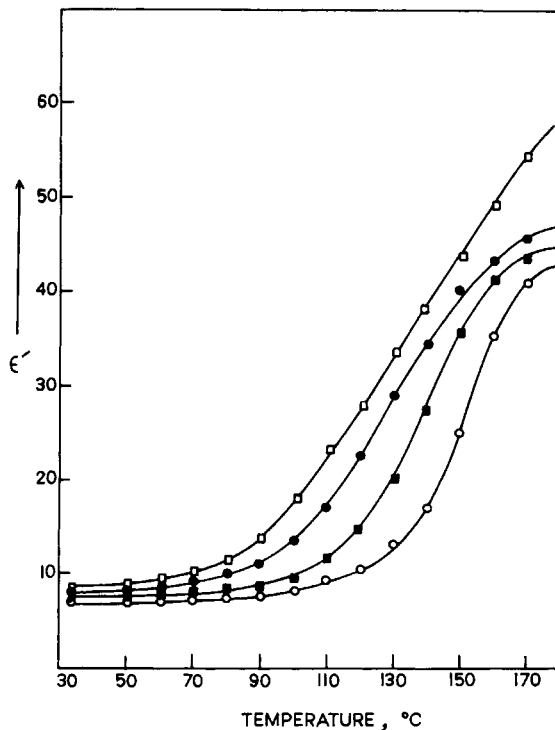


Fig. 5. Variation of dielectric constant (ϵ') with temperature for PAN(160) at various frequencies: (\square) 0.1 kHz, (\bullet) 1 kHz, (\blacksquare) 10 kHz, (\circ) 100 kHz.

heat treatment occurs at positions randomly spaced along the molecular chain; hence, it results in unequal lengths of segments with free nitrile groups. Such a distribution of segment lengths might account for the observed wider distribution of relaxation time in the heat treated PAN samples.

An alternative explanation for these results might be that at 120°C, which is above T_g but below T_m (melting temperature), there is crystallization whereas at 160°C, which would be nearer the T_m , there might be less crystallization. As the amount of crystallization increases, the glassy phase would diminish and this would reduce the relaxation peak height and the relaxation strength. Although such an explanation seems logical, some readers may question the crystallization of PAN in the conventional sense of crystallization in other polymers; and, moreover, the concept of melting point of PAN is not fully clear. However, both these explanations may look like different words used for expressing the same idea, as discussed below.

Opinions of authors are divided over the structure of PAN. Some authors^{1,3,4,6,11-17} believe in a two-phase (crystalline and amorphous) structure, and others^{2,18} believe in one phase (paracrystalline) structure of PAN. The two models may be considered similar if (1) in the two-phase model the regions of high degree of bound nitrile groups are considered as crystalline and the regions with the lowest degree of bound nitrile groups as the amorphous phase; and (2) in the one-phase paracrystalline model, the whole structure is viewed as a single phase with bound nitrile groups and unbound nitrile groups distributed at random along the whole structure as defects in the crystalline structure. Thus, if

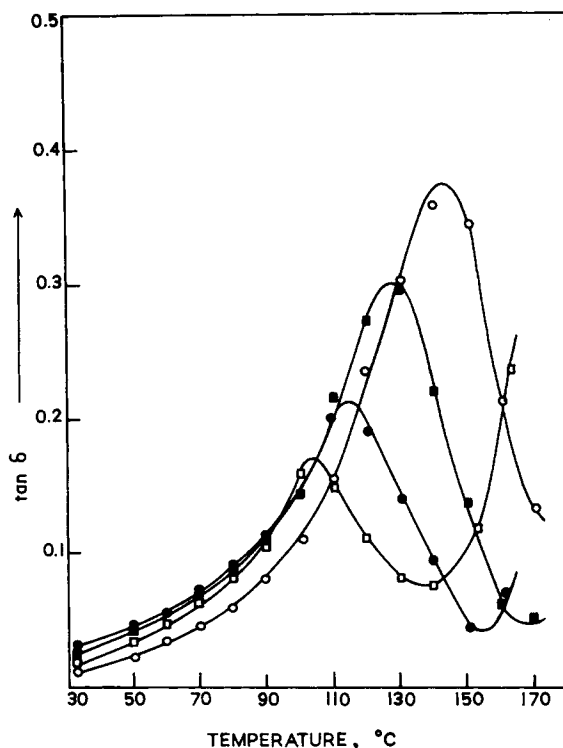


Fig. 6. Variation dissipation factor ($\tan \delta$) with temperature for PAN(160) at various frequencies: (\square) 0.1 kHz, (\bullet) 1 kHz, (\blacksquare) 10 kHz, (\circ) 100 kHz.

one views the formation of bound nitrile groups as a process similar to crystallization, then both the above-mentioned explanations would appear similar.

CONCLUSION

This study thus suggests that heat treatment at 120°C increases considerably the degree of bound nitrile groups in PAN. Such a structural change can be reversed to a great extent if the heat treatment is done at a higher temperature. As this study was limited to only two temperatures and a fixed duration of heat treatment, it was not possible to suggest the best temperature and duration of heat treatment for achieving the maximum degree of bound nitrile groups in PAN and what temperature would be required to achieve the lowest degree of bound nitrile groups. Further investigations would be necessary for a better understanding of this reversible structural change in PAN. Such an effect may find its applications in technology, as, for example, in acrylic fibers one structure (with low degree of bound nitrile groups) may be preferable for dyeing and texturizing, etc., and the other structure (with high degree of bound nitrile groups) may be preferable for the ultimate mechanical properties of the fibers.

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