Effect of Heat Treatment on the Dielectric Relaxation of Polyacrylonitrile. III. Role of Duration of Heat Treatment

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Synopsis

Dielectric relaxation of polyacrylonitrile (PAN) heat-treated at 120°C in vacuum for durations varying from 4 to 24 h is studied in order to investigate the effect of the duration of heat treatment. Decrease in dielectric constant increment and loss peak height and an increase in relaxation temperature on heat treatment are observed at all durations of heat treatment. At the studied temperature of heat treatment the observed changes in dielectric relaxation were found to increase with duration of heat treatment showing maxima at a 16 h duration and then a decrease at a higher duration of heat treatment. The results are discussed in terms of the variation of degree of intermolecularly bound nitrile groups with the duration of heat treatment. Glass transition temperature calculated from the dielectric data, through WLF theory, showed a variation, similar to that of the degree of bound nitrile groups, with duration of heat treatment. The observed variation of T_g is attributed to the interlinking effect produced by the bound nitrile group pairs on the segmental mobility.

INTRODUCTION

In papers I[1] and II[2] of this study, it was reported that the heat treatment of polyacrylonitrile (PAN) produced considerable changes in its dielectric relaxation in the glass transition region. Corresponding changes in structure and mechanical properties of PAN fibers on heat treatment were also observed.[3] The observed changes in dielectric relaxation were lower in magnitude in case of: (i) heat treatment at a higher temperature (i.e., 160°C) than those at a lower temperature (i.e., 120°C)[1]: (ii) heat treatment in air than those produced by heat treatment under vacuum at identical temperature of heat treatment.[2] The effect was attributed to the difference in the degree of intermolecularly bound nitrile groups in the PAN samples when heat treated at different temperatures[1] or under different atmospheres.[2]

The role of segmental mobility and dipole–dipole interactions between nitrile groups in producing the structural changes during the heat treatment, discussed in previous publications,[1-3] adequately explained both the above-mentioned effects of temperature (i) and atmosphere (ii) of heat treatment.

However, in the previous studies, the effect was studied by varying temperature or atmosphere of heat treatment at constant duration of heat treatment. In this paper we present the results of a study of the effect of duration of heat treatment on the dielectric relaxation of PAN heat-treated under vacuum at constant temperature (i.e., 120°C).

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EXPERIMENTAL

Materials. PAN samples, used in this work, were prepared by the method[4] of emulsion polymerization at 35°C in nitrogen atmosphere using potassium persulfate as initiator, sodium bisulfite as activator and sodium lauryl sulfate as emulsifying agent.

For heat treatment the predried (in vacuum oven at 50°C for more than 12 h) PAN powder was filled in glass tubes, which were then evacuated and sealed while still connected to the vacuum line. These tubes were then placed in an oven at constant temperature (viz., 120°C) for specified durations, viz., 4, 8, 16 and 24 h. The various heat-treated samples (heat-treated at 120°C under vacuum) are denoted as: PAN (4 h), PAN (8 h), PAN (16 h), and PAN (24 h), where the figures in the parentheses denote the duration of heat treatment. The untreated PAN sample is represented as PAN (U).

Measurements. Dielectric measurements in the frequency range 1–100 kHz and temperature range 30–170°C were carried out on a General Radio GR-716 CS Bridge, using a two-terminal connection for the sample cell. The sample cell was a parallel plate condenser, with adjustable electrode separation, enclosed in a thermostated chamber controlled within ±0.1°C. Specimen temperature was measured by a thermocouple placed in close vicinity to the sample. Measurements were made on pellets (thickness 0.1 cm and diameter 1.3 cm) prepared by compressing dried powder samples, and the disc surfaces were silver-coated for better electrode contact. To minimize the effects due to moisture absorption, the sample discs were stored in the desiccator.

RESULTS AND DISCUSSION

Dielectric Relaxation

Variations of dielectric constant (ϵ') and dissipation factor (tan δ) with temperature at various frequencies of measurements for the heat-treated and untreated PAN samples are shown in Figures 1–3. The relaxation represented by the observed loss peaks has been attributed to the segmental mobility in glass transition region.[5]

Differences in these data are represented in Table I in terms of the quantities defined below. The quantity ($\epsilon'_{170} - \epsilon'_{30}$), i.e., the difference between dielectric constants at the two extremes of the studied range of temperature (viz., 30–170°C), enables a comparison of the polarization produced in the various samples in the identical temperature range at the given frequencies. The quantity loss peak amplitude (tan δ_{max}) compares the relative magnitudes of dielectric loss at the relaxation temperature at given frequencies. The loss peak temperature, or the relaxation temperature, T_{max}, is related to the glass transition temperature T_g. Variation of T_{max} may be taken as an evidence of the variation of restrictions on segmental mobility. The quantity ($\epsilon'_0 - \epsilon'_\infty$), called dielectric relaxation strength (where ϵ'_0 and ϵ'_∞ are respectively the low and high frequency limiting values of ϵ' for the observed relaxation), is a measure of the mean square dipole moment of the relaxing segments.[6] From these data in the limited frequency range, ($\epsilon'_0 - \epsilon'_\infty$) was evaluated from the area under ϵ'' vs. $1/T$ plot (shown in Fig. 4) according to the procedure described elsewhere.[2,7,8] Also shown in Table I
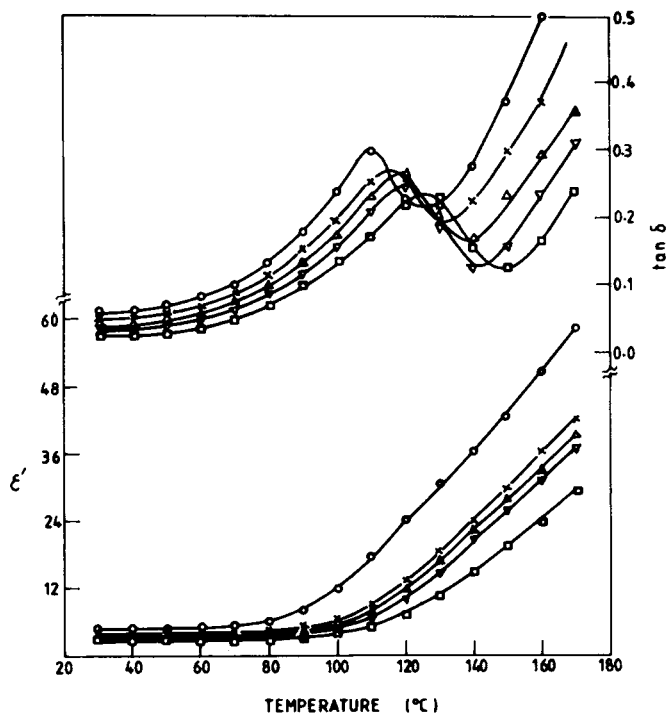
Fig. 1. Variation of dielectric constant ϵ' and dissipation factor tan δ with temperature at 1 kHz for the various samples of PAN (various durations of heat treatment):   (O) U; (X) 4 h; (△) 8 h; (□) 16 h; (▽) 24 h.

TABLE I
Values of Various Quantities Obtained from Dielectric Relaxation Measurements

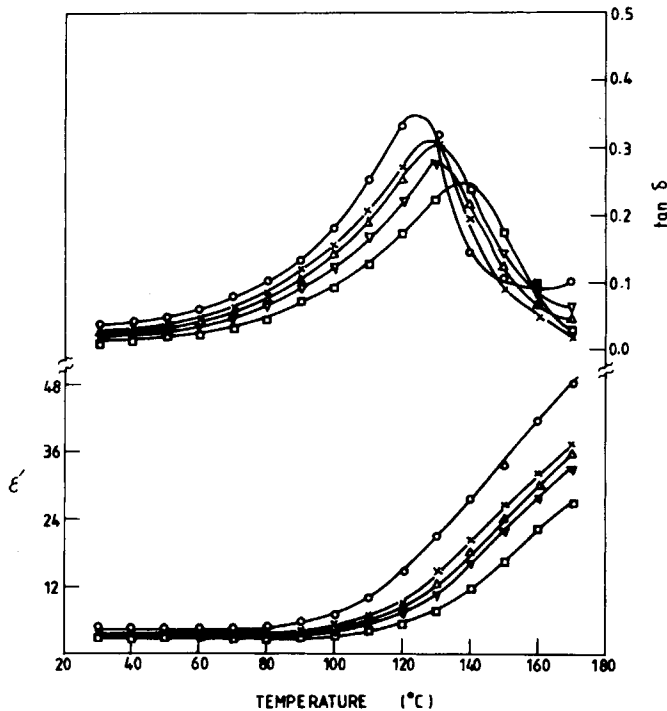| Sample	Frequency (kHz)	$(\epsilon'_{170} - \epsilon'_{30})$	tanδ_{max}	T_{max} (°C)	ΔE (kcal/mol)	$(\epsilon'_0 - \epsilon'_\infty)$
PAN (U)	1	54	0.295	110		
	10	43	0.350	122		
	100	35	0.455	138		
					48	45.3
PAN (4 h)	1	38	0.270	115		
	10	33	0.315	127		
	100	29	0.395	143		
					52	39.7
PAN (8 h)	1	36	0.260	117		
	10	32	0.300	129		
	100	27	0.380	144		
					52	36.4
PAN (16 h)	1	27	0.240	126		
	10	23	0.255	137		
	100	20	0.325	151		
					55	30.0
PAN (24 h)	1	34	0.250	121		
	10	29	0.295	132		
	100	26	0.365	146		
					52	34.8

Fig. 2. Variation of dielectric constant ϵ' and dissipation factor tan δ with temperature at 10 kHz for the various samples of PAN (various durations of heat treatment): (O) U; (X) 4 h; ($\triangle$) 8 h; ($\square$) 16 h; (∇) 24 h.

is the activation energy ΔE obtained from the slopes of Arrhenius plots of these data.

General features about the effect of heat treatment on these dielectric data are discussed in detail in the previous publications.[1,2] Present discussion will, therefore, be confined to the variations in these results with duration of heat treatment.

Variations of ($\epsilon'_{170} - \epsilon'_{30}$), tan δ_{max}, and T_{max} at 100 kHz and the frequency independent quantity ($\epsilon'_0 - \epsilon'_\infty$) with duration of heat treatment, shown in Figures 5 and 6, show reversals of the trends in variations of all these quantities at 16-h duration of heat treatment for these samples. ($\epsilon'_0 - \epsilon'_\infty$) and tan δ_{max} first decrease with increasing duration of heat treatment up to 16 h, and thereafter both these quantities start increasing with increasing duration of heat treatment. T_{max}, on the other hand, first increases with increasing duration of heat treatment, showing a maximum at 16 h and then decreases for higher durations of heat treatment. Data at other frequencies also showed similar behavior. This indicates that the structural changes produced by heat treatment of PAN at 120°C under vacuum are greatest when the duration of heat treatment is 16 h.

Like the results of the previous two studies,[1,2] these results clearly indicate that the observed effect on dielectric relaxation of the heat treatment of PAN is not attributable to the chemical changes in PAN molecule. If the changes in relaxation were due to the chemical changes, then they should be greater for the
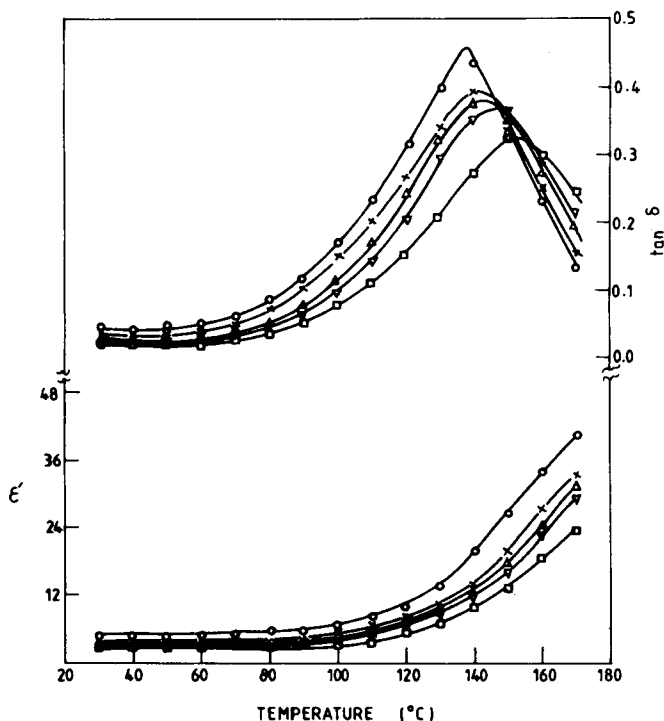
Fig. 3. Variation of dielectric constant ϵ' and dissipation factor tan δ with temperature at 100 kHz for the various samples of PAN (various durations of heat treatment): (O) U; (×) 4 h; (△) 8 h; (□) 16 h; (▽) 24 h.

case of 24-h duration of heat treatment than the case of 16 h, which is contrary to the present results.   Furthermore, though the controversy over the two possible explanations [viz., (i) variation of degree of bound nitrile group pairs and (ii) chemical changes in the PAN molecule] for the origin of the observed effect of heat treatment on dielectric relaxation seems well resolved from the previously reported results on the effect of temperature[1] and atmosphere[2] of heat treatment, the present results on the effect of duration of heat treatment provide an additional point for discarding explanation (ii).   The compatibility of the present results with explanation (i) will be discussed below.

If one considers the structure of heat-treated PAN samples as containing a greater number of intermolecularly bound nitrile groups than the untreated PAN, then the relaxing units (i.e., the molecular segments) would have a lower dipole moment (owing to the lower number of free nitrile groups) and greater restrictions on the segmental mobility (owing to the interlinking of segments through the intermolecularly bound nitrile groups) in the case of heat-treated samples than the PAN (U).   Lower values of $(\epsilon_0' - \epsilon_\infty')$ and tan δ_{max} and higher values of T_{max} for the heat-treated samples than PAN (U) (Table I) indicate a higher degree of bound nitrile groups in heat-treated samples than PAN (U).

Values of the square root of $(\epsilon_0' - \epsilon_\infty')$, which is proportional to the root mean square dipole moment $(\overline{\mu^2})^{1/2}$ of the segments,[6] are shown in Table II for the various samples.   If one assumes that, on the average, each nitrile group has equal
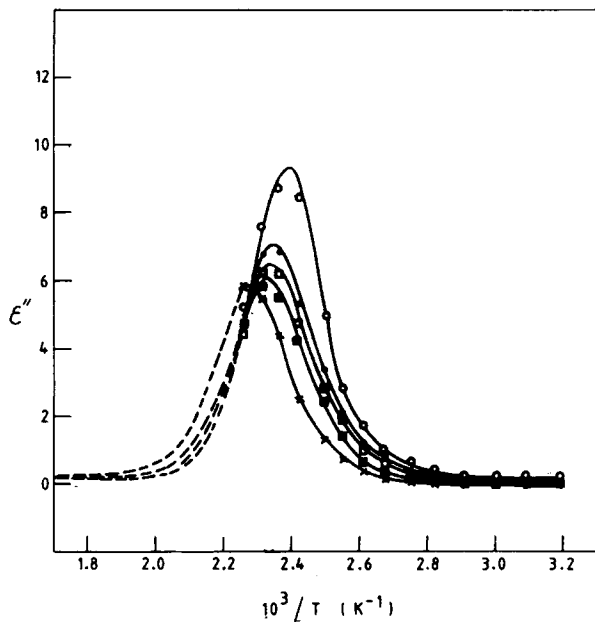
Fig. 4. Variation of dielectric loss factor (ϵ'') with reciprocal of temperature ($1/T$) at 100 kHz for the various samples of PAN (various durations of heat treatment): (O) U; (●) 4 h; (□) 8 h; (×) 16 h; (■) 24 h.

contribution on the mean square dipole moment of the segments, or, in other words, $(\overline{\mu^2})^{1/2}$ is proportional to the number of nitrile groups in the segments, then the observed decrease of $(\epsilon'_0 - \epsilon'_\infty)^{1/2}$ with duration of heat treatment (Table II) may enable us to estimate the relative fraction of intermolecularly bound
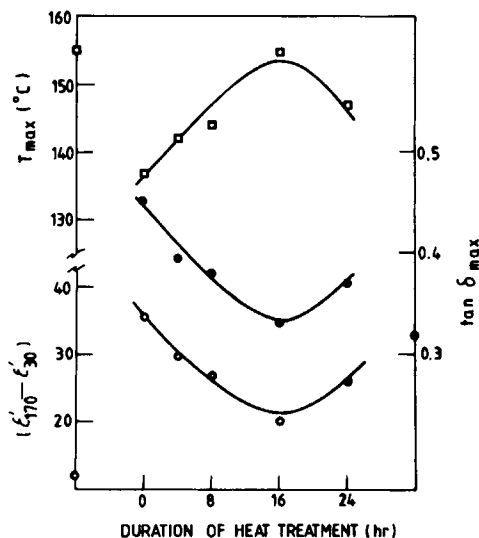

Fig. 5. Variation of dielectric constant increment ($\epsilon'_{170} - \epsilon'_{30}$), loss-peak height (tan δ_{max}), and relaxation temperature T_{max} with duration of heat treatment. Data at zero duration of heat treatment are those for the sample PAN (U).
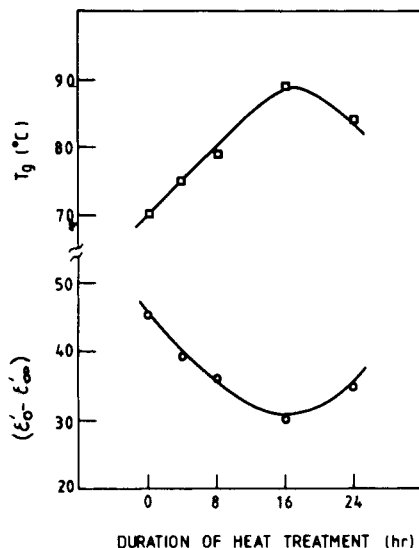
Fig. 6. Variation of $(\epsilon'_0 - \epsilon'_\infty)$ and glass transition temperature (T_g) with duration of heat treatment of PAN at 120°C under vacuum. Data at zero duration of heat treatment correspond to the untreated PAN sample.

nitrile groups in these samples. As indicated in the last column of Table II, out of the free nitrile groups occurring in the segments of PAN (U), about 19% are bound in PAN (16 h) while only about 12% are bound in PAN (24 h).

At the temperature of heat treatment, the system is in its state above glass transition temperature; hence there occurs segmental mobility in the amorphous phase. Segmental mobility induces nitrile-group pairing by providing the nitrile groups of neighboring segments the opportunity to approach each other. The dipole–dipole interaction energy of the nitrile-group pairs would be attractive for these intermolecular nitrile-group pairs and would depend on their mutual alignment.[2,9] Thus, depending on their mutual alignment, some of the nitrile-group pairs would be strongly bound while others may be weakly bound through their dipolar interaction forces. The continuously occurring segmental mobility would produce the following two effects on these nitrile group pairs: (1) changing their mutual alignment and thereby bringing them to the positions of stronger

TABLE II

Variation of $(\epsilon'_0 - \epsilon'_\infty)^{1/2}$ and Estimated Fraction of Bound Nitrile Groups with Duration of Heat Treatment

Sample	$(\epsilon'_0 - \epsilon'_\infty)$	$(\epsilon'_0 - \epsilon'_\infty)^{1/2}$	% Decrease relative to PAN (U)
PAN (U)	45.3	6.73	0
PAN (4 h)	39.7	6.30	6.4
PAN (8 h)	36.4	6.03	10.4
PAN (16 h)	30.0	6.48	18.6
PAN (24 h)	34.8	5.90	12.4

attractive interaction between them, and (2) breaking some of the weakly bound pairs.

Thus the segmental mobility, which helps in initial formation of nitrile-group pairs, plays a significant role on the stability of the bound nitrile groups pairs. Equilibrium value of the degree of bound nitrile group pairs at any instant of time may differ from that at another instant of time. The equilibrium value of degree of bound nitrile group pairs at the instant of termination of the heat treatment process becomes the ultimate structural feature of the sample, due to the ceasing of the segmental mobility, when the sample is cooled to room temperature (i.e., below T_g).

The structural differences in the samples heat-treated for different durations should therefore provide information about the variation of the equilibrium value of degree of bound nitrile-group pairs with time during the process of heat treatment.

For the present case of heat treatment of PAN at 120°C under vacuum, it is apparent from these results that at the stated experimental conditions the bound nitrile-group pairs are sufficiently stable up to 16 h. At longer durations their stability seems poorer. Below 16-h duration the segmental mobility helps in gradually readjusting the mutual alignment of nitrile-group pairs to the positions of stronger force of dipolar interaction, thus accounting for the observed increase of degree of bound nitrile groups with increasing duration of heat treatment. Beyond 16-hr duration, since the bound pairs are subjected to a sufficiently prolonged thermal agitation due to segmental mobility, dissociation of some bound pairs may occur, which should account for the observed lower degree of bound nitrile group pairs in PAN (24 h) than PAN (16 h).

Glass Transition Temperature

The glass transition temperatures (T_g) of the various samples are determined from these data according to the method described elsewhere.[2] The following expression for T_s (the reference temperature in the WLF equation[10]) in terms of the relaxation temperature at two frequencies has been derived from the WLF equation[11,12]:

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

where T_1 and T_2 are the relaxation temperatures at frequencies f_1 and f_2, respectively, and C_1 and C_2 are the constants of the WLF equation, whose universal values, $C_1 = 8.86$ and $C_2 = 101.6$, corresponding to the case $T_s = T_g + 50$, and $C_1 = 17.4$ and $C_2 = 51.6$, corresponding to the case $T_s = T_g$, are valid for wide variety of polymers.[10,13] However, values of these constants for PAN are reported[5] to be somewhat different from the universal values. In this calculation we have used the values of the constants reported for PAN[5] (viz., $C_1 = 5.7$ and $C_2 = 75$ for the case of $T_s = T_g + 50$). For the present data at three frequencies, three data pairs are possible for each sample. Calculations from the various data pairs lead to the values of T_s. The T_g values, obtained from the different data pairs for any given sample, are quite consistent and show deviations less than ±3°C around the mean values, stated in the last column of Table III, for each sample.

TABLE III
Values of T_g Calculated from Various Pairs of Dielectric Relaxation Data

Sample	f_1 (kHz)	f_2 (kHz)	T_1 (°C)	T_2 (°C)	T_g (°C)	Mean T_g (°C)
PAN (U)	1	10	110	122	69.1	
	1	100	110	138	70.4	
	10	100	122	138	71.9	
						70.5
PAN (4 h)	1	10	115	127	74.1	
	1	100	115	143	74.4	
	10	100	127	143	76.9	
						75.1
PAN (8 h)	1	10	117	129	76.1	
	1	100	117	144	78.3	
	10	100	129	144	81.1	
						78.5
PAN (16 h)	1	10	126	137	87.7	
	1	100	126	151	89.3	
	10	100	137	151	91.3	
						89.4
PAN (24 h)	1	10	121	132	82.7	
	1	100	121	146	84.3	
	10	100	132	146	86.3	
						84.4

These values of T_g, though in good agreement with the literature value[14,15] of T_g for PAN (viz., 80–104°C) may be emphasized only for their comparative values for the various samples and not for their absolute magnitudes. T_g for the untreated PAN sample of the present study (viz., 71°C) is, however, slightly lower than the value for PAN (U) (viz., 74°C) of the previous study.[2] This difference of T_g may be either considered inappreciable or might be taken to imply some structural differences arising in the PAN samples when they are prepared in different batches by the same process of polymerization, keeping all other conditions identical. It may be noted that the samples of this study and one[2] of the previous two studies were synthesized under identical conditions but in different batches. Variations in the structure of PAN and its glass transition temperature with conditions and medium of polymerization is reported by Chapiro and Mankowski.[16] Variation of T_g with duration of heat treatment is relatively more significant. At lower durations (4 h and 8 h) of heat treatment, T_g increased by 4–8°C whereas its maximum value for PAN (16 h) is about 19° higher than the T_g of the untreated PAN sample. At higher duration (24 h), T_g drops down by 5°C from its maximum value for the case of PAN (16 h). The trend in variation of T_g with duration of heat treatment (shown in Fig. 6) is identical with that of the degree of bound nitrile groups shown by the dielectric data. The interlinking of segments through intermolecularly bound nitrile groups may produce restrictions on segmental mobility like the crosslinks in a crosslinked polymer. Thus the observed increase of T_g with increasing degree of bound nitrile groups in PAN seems an effect similar to the well-known effect of degree of crosslinking on the T_g of polymers.

CONCLUSIONS

This study shows that the heat treatment for a shorter duration (viz., 16 h) produced greater change in the dielectric relaxation of PAN than the similar heat treatment for a longer duration (viz., 24 h). This confirms the point already made in the previous papers[1,2] that the observed effect of heat treatment is not attributable to the chemical changes in the PAN molecule, because, for the case of the chemical changes, the longer duration of heat treatment should produce greater change in the relaxation than the shorter duration.

Furthermore, in addition to supporting the already proposed view on the variation of degree of bound nitrile groups produced by heat treatment of PAN, this study provides information about the stability of the bound nitrile group pairs during the process of heat treatment. At the studied conditions, viz., at 120°C and under vacuum, the bound nitrile group pairs seem sufficiently stable up to 16 h. Further studies of heat treatment at different temperatures would reveal information about the role of thermal energy of segmental mobility on the stability of bound nitrile group pairs.

References

1. A. K. Gupta, R. P. Singhal and V. K. Agarwal, *J. Appl. Polym. Sci.*, **26**, 3599 (1981).

2. A. K. Gupta, R. P. Singhal, A. K. Maiti, and V. K. Agarwal, *J. Appl. Polym. Sci.*, **27**, 4101 (1982).

3. A. K. Gupta and A. K. Maiti, *J. Appl. Polym. Sci.*, **27**, 2409 (1982).

4. W. R. Sorenson and T. W. Cambell, *Preparative Methods of Polymer Chemistry*, 2nd ed., Wiley-Interscience, New York, 1968, p. 236.

5. A. K. Gupta and N. Chand, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1125 (1980).

6. Y. Sato and T. Yoshiro, *J. Appl. Polym. Sci.*, **22**, 2141 (1978).

7. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967, p. 122.

8. J. F. Rabek, *Experimental Methods in Polymer Chemistry*, Wiley, New York, 1980, p. 544.

9. G. Henrici Olivé and S. Olivé, *Adv. Polym. Sci.*, **32**, 125 (1979).

10. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

11. A. K. Gupta, *Makromol. Chem. Rapid Commun.*, **1**, 201 (1980).

12. A. K. Gupta and A. K. Maiti, *Angew. Makromol. Chem.*, **97**, 91 (1981).

13. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, p. 216.

14. H. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd ed., Wiley, New York, 1975, p. V-37.

15. R. M. Kimmel and R. D. Andrews, *J. Appl. Phys.*, **36**, 3063 (1965).

16. A. Chapiro and Z. Mankowski, *Eur. Polym. J.*, **17**, 457 (1981).