

Mechanical Relaxation Processes in Polyacrylonitrile Polymers and Copolymers

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Synopsis

The dynamic mechanical properties of molded and cast polyacrylonitrile and copolymers have been measured by an automatic Rheovibron. The transitions are described for the amorphous, "paracrystalline," and crystalline phases. Based upon a number of polymer theories of multiple phases in polymeric systems, the transitions have been assigned to specific polymer motions. Three transitions are defined for the alpha transition region. The mechanical response is compared to x-ray diffraction and infrared to ascertain the transition assignments in decreasing order beginning with the highest temperature transition as (1) the main transition for the amorphous phase (T_1), (2) dipole-dipole interaction which is related to the "paracrystalline phase" (T_2), and (3) secondary transition for the amorphous phase (T_3).

INTRODUCTION

The transitions in polyacrylonitrile (PAN) have been the subject of several papers.¹⁻⁸ Minami¹ has studied the morphological properties of PAN fibers and has made assignments for the multiple relaxations. This work further amplifies his findings and extends the study to molded films. All work seems to exhibit three transitions in the general regions normally assigned as glass transitions, but some confusion exists as to the processes involved in the multiple relaxations. The glass transition in the 106°C range is recorded as the usual accepted transition. Since PAN exists as multiple phases, the presence of the large intermediate order, generally designated the paracrystalline phase, along with the crystalline phase has contributed to the confusion as to the behavior of such a complex system. The location of a melting point in PAN is also difficult because of degradation before melting.

EXPERIMENTAL

Preparation of Film Samples

Two experimental polymers made by emulsion free-radical polymerization of acrylonitrile were used (polymer A and polymer B). The molecular weights were established by measuring the intrinsic viscosity of dimethylformamide (DMF) solutions at 25°C and using the relation of Cleland and Stockmayer⁹

$$\eta_{25^\circ}^{\text{DMF}} = 24.3 \times 10^{-5} M^{0.75}$$

The calculated viscosity molecular weights for polymers A and B were 120,000 and 328,000, respectively. Polymer A was cast from a dimethylformamide(DMF)

solution, while polymer B was cast from dimethyl sulfoxide (DMSO) solution. Polymer B was also compression molded into a film.

Polyacrylonitrile is a difficult polymer to mold successfully because of degradation and poor flow characteristics. A successful film molding was achieved with polymer B after several attempts by preheating the mold to 220°C and then adding a thin layer of the powdered polymer. The powder was allowed to heat for 1 min, and then a molding pressure of 20 tons was rapidly applied. The molded film was quenched by cold water and annealed at 180°C.

The acrylonitrile copolymer was made by copolymerizing methyl vinyl ether and acrylonitrile by emulsion as described by Kenyon and Mottus.¹⁰ The resulting polymer contained 83.3% acrylonitrile and 16.7% methyl vinyl ether.

Dynamic Mechanical Properties

The dynamic mechanical properties of the PAN polymers were measured on a Rheovibron DDV II which had been converted to automatic operation by Kenyon, Grote, Wallace, and Rayford.¹¹ The instrument automatically recorded stress, strain, phase angle, length of sample, and temperature. The tension is automatically controlled to either constant strain or just sufficient tension to prevent slack in the sample. The principle of this modification has been previously described.¹¹ The heating rate was approximately 1°/min from room temperature to the decomposition point. The molded film samples were approximately 4.0 cm long by 0.24 cm wide. The thickness on some of the cast films were as thin as 0.0015 cm. The data in the form of digital output from the Rheovibron were logged on punch paper tape and processed on an IBM 370 computer coupled with a CalComp plotter. Each curve is generated by over 200 data points which are represented by the continuous curves; the large number of data points permits greater precision for locating minor transitions.

Many minor transitions are not capable of complete resolution because of the overlapping of the relaxations. The $\tan \delta$ curves for all the PAN polymers are very broad and would indicate multiple transitions, and the work of Minami¹ also indicated multiple transitions in the α region. These broad $\tan \delta$ curves were resolved into three relaxation regions by a du Pont curve resolver. The combined effects of the automation of the Rheovibron and du Pont curve resolver have improved the capability for resolving minor transitions. The automated Rheovibron has been proved to measure $\tan \delta$ to ± 0.001 when the $\tan \delta$ reaches a value greater than 0.005.

PAN does not show a transition (T_m) due to melting because degradation occurs before the melt process. For the purpose of clarity, this work assigns the transitions in the upper temperature region which has been designated as the α -transition region as T_1 , T_2 , and T_3 , where T_1 is the transition occurring at the highest temperature and T_3 , at the lowest. In some cases, the storage modulus shows an increase with increased temperature, which indicates degradation. No data occurring in the degradation regions are used in the interpretation of transitions.

DATA AND DISCUSSION

Mechanical Properties

Plots of the storage modulus E' , loss modulus E'' , and $\tan \delta$ as a function of temperature are shown in Figures 1 and 2. The transitions are summarized in Table I. The transitions were resolved by use of the du Pont curve resolver using the linear plots of the $\tan \delta$ as shown for a representative sample in Figure 3. The curve resolver is capable of selecting either Gaussian- or Lorentian-type distributions. It was not possible to obtain a distribution to match the experimental curve with the sum of two Gaussian or Lorentian distributions regardless of the breadth or skewness tried. Reasonably good fits could be obtained with three

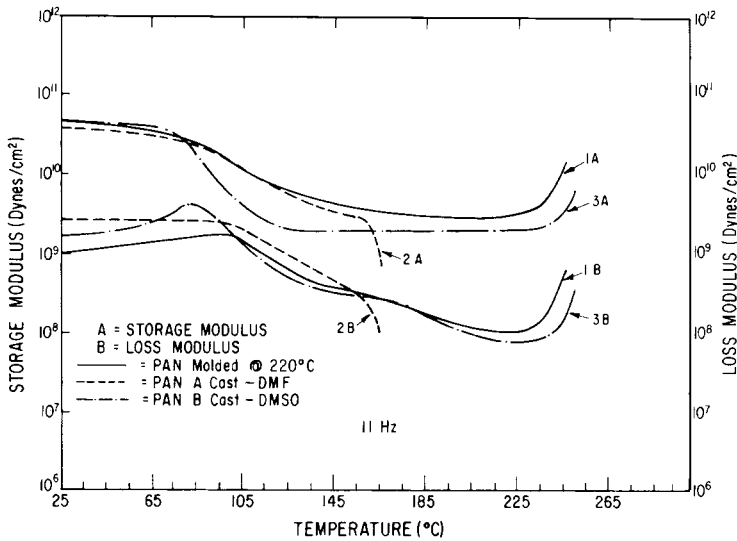


Fig. 1. Dynamic mechanical properties of PAN: storage and loss moduli as function of temperature.

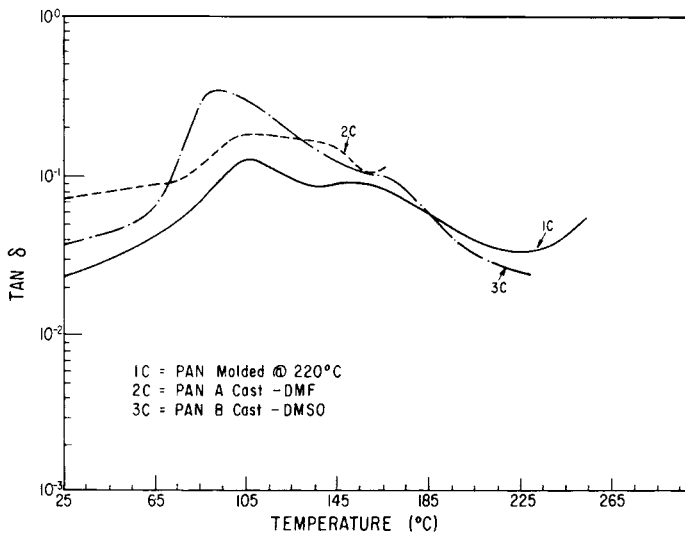


Fig. 2. Dynamic mechanical properties of PAN: $\tan \delta$ as a function of temperature.

TABLE I
 Transitions (in °C) of PAN^a

Transition	Cast film					
	DMF		DMSO		Molded film	
	Initial	Annealed	Initial	Annealed	Initial	Annealed
T_1	128	144	157	157	154	156
T_2	90	103	99	99	106	106
T_3	64	60	79	79	65	55

^a At 11 Hz.

Gaussian curves. The transition occurring at the lowest temperature (T_3) represents small, and not clearly defined, relaxations. T_1 and T_2 are more clearly defined in the $\tan \delta$ curves and can be accurately located.

Many polymeric systems, and especially those polymers which have the possibility of more than a single phase, exhibit multiple transitions. Many workers¹²⁻¹⁵ have observed that the transitions usually are related to each other in an empirical manner. Their resulting equations have been used to assign the transitions. The ratio of the β transition to the main glass transition of the amorphous polymer is approximately 0.75. In crystalline polymers, which have a definite melting point, the ratio of the glass transition temperature (T_g) to the melting temperature (T_m) has been found to approximate 0.75. These empirical relations between transitions have been observed when the transitions were expressed on an absolute temperature scale. Since the melting point for the homopolymer of acrylonitrile cannot be determined because of degradation, the melting point of 319°C was obtained from extrapolated data of Krigbaum and Takita¹⁶ using the melting points of varying copolymer compositions.

The transitions in polymers are usually expressed as α , β , and γ regions, with the α transitions occurring at the highest observable range. The transitions discussed in this work relate to those normally considered as α transitions. Since the assignment of the transitions are somewhat in question, the relaxation processes are designated as T_1 , T_2 , and T_3 . These designations are used in order to later assign the relaxation processes. Boyer¹² has discussed the mechanical properties of polymers showing multiple transitions in semicrystalline polymers. He arbitrarily assigned a number to the transition in order to descending temperature position such as T_1 , T_2 , etc., and then took ratios between the numbered

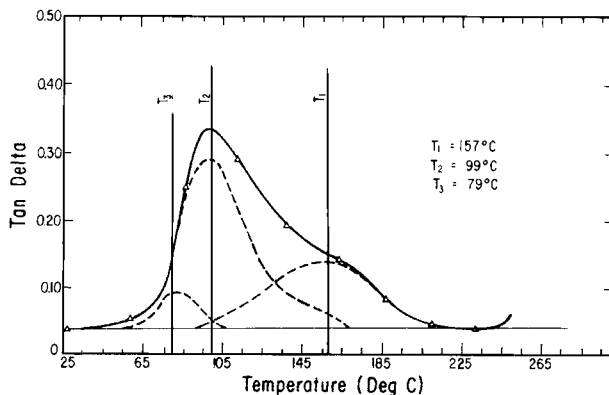


Fig. 3. Resolution of transitions by du Pont curve resolver. PAN cast film.

transitions. Since the transitions show an empirical ratio to one another, it is possible to deduce the correct assignment.

Table II shows the results of the ratios of the transitions. The first group of transition ratios consider T_1 as the main glass transition of the amorphous phase and T_2 and T_3 as secondary transitions. The ratios were further extended to consider T_2 and T_3 as the main glass transition. The value T_m represents the melting point of the homopolymer of acrylonitrile.

The first group of ratios consider the main glass transition in respect to the melting point. The T_1/T_m ratio is closer to the predicted ratio of 0.75 than the other ratios (T_2/T_m and T_3/T_m). Both T_2 and T_3 transitions occur too far below the melt to be considered as the main glass transition of the amorphous phase. On this basis T_1 is assigned as the main glass transition.

Likewise, the secondary transition of the amorphous phase (T_3) and the main transition (T_1) have a ratio in the region of 0.75. The ratios of T_2 and T_3 were taken with respect to the other transitions and are shown in Table II. The T_3/T_1 ratio more closely approximates the expected value; therefore the T_3 transition could be related to the secondary transition of the amorphous phase. These ratios further show that the middle transition (T_2) does not fit the expected values, so this relaxation must not involve the truly amorphous phase. The T_2 transition must therefore be related to some form of ordered phase which has been defined as a paracrystalline region. It can only involve that portion of the ordered region which is mobile.

Modulus behavior of film cast from DMF shows some plasticization effect by the solvent and the inability to completely remove the last traces of solvent. The plasticization effect is indicated by the slope of the modulus curve, the breadth of the $\tan \delta$ curve, and the lowering of the absolute value of the storage modulus below the glass transition.

Comparison of the modulus curves for the PAN samples shows different modulus behavior above the main glass transition due to variation in the amounts of the three phases. Above the glass transitions, the amorphous phase no longer can hold the modulus at high levels (greater than 10^7 dynes/cm²). The high modulus above the T_g in the polyacrylonitrile polymers might be caused by the presence of the crystalline and ordered phases.

PAN has been the subject of a number of papers describing the paracrystalline behavior ranging from 0% to 100%. Bohn, Schaefer, and Stratton¹⁷ claim 100% paracrystalline structure. The dynamic modulus curves show the presence of multiple transitions and modulus values in the range of 10^9 dynes/cm². The $\tan \delta$ values show the presence of several transitions in the amorphous region. Since

TABLE II
Relaxation Relations in PAN^a

Relation	DMF		DMSO		Molded	
	Initial	Annealed	Initial	Annealed	Initial	Annealed
T_1/T_m	.67	.70	.73	.73	.71	.74
T_2/T_m	.61	.63	.63	.63	.64	.64
T_3/T_m	.57	.56	.60	.60	.57	.57
T_3/T_1	.83	.80	.83	.82	.79	.78
T_3/T_2	.92	.89	.92	.92	.89	.89
T_2/T_1	.90	.90	.89	.89	.88	.88

^a At 11 Hz.

PAN may be considered a polyblend of crystalline, amorphous, and paracrystalline phases, some estimate of the phase concentrations should be possible. Nielsen¹⁸ has approximated the crystalline content from the shear modulus by the relation

$$\log_{10} G' \approx 6.763 + 4.77W_c \quad (1)$$

where W_c is the fraction of crystallinity. This equation is based upon a two phase system where the crystalline phase has a greater modulus than the amorphous phase, and it assumes a shear modulus of 3.4×10^{11} dynes/cm² for polymer crystals and 5.7×10^6 dynes/cm² for the rubber phase. Only those molecules which have a three-dimensional order as in a true crystal will be measured by the modulus.

Gray and McCrum¹⁹ used the decrease in damping as a measure of the crystalline content and expressed the relation as

$$\tan \delta = (1 - W_c) \tan \delta(a), \quad (2)$$

where $\tan \delta(a)$ is the damping for a completely amorphous phase. The use of the damping function will include all the molecules which cannot relax at the temperature and frequency. Damping would therefore include those molecules which are strongly bound in a two-dimensional order such as "paracrystallinity" crystalline region. To use the Gray-McCrum equation, the damping for a completely amorphous polyacrylonitrile must be known. Since a 100% amorphous polyacrylonitrile is impossible, the mechanical properties of the AN/MVE copolymer were used as a measure of a completely amorphous polymer as shown in Figure 4. Table III shows the calculated values of the shear modulus, the sum of the $\tan \delta$ values for the amorphous region (T_1, T_2, T_3), and crystallinity cal-

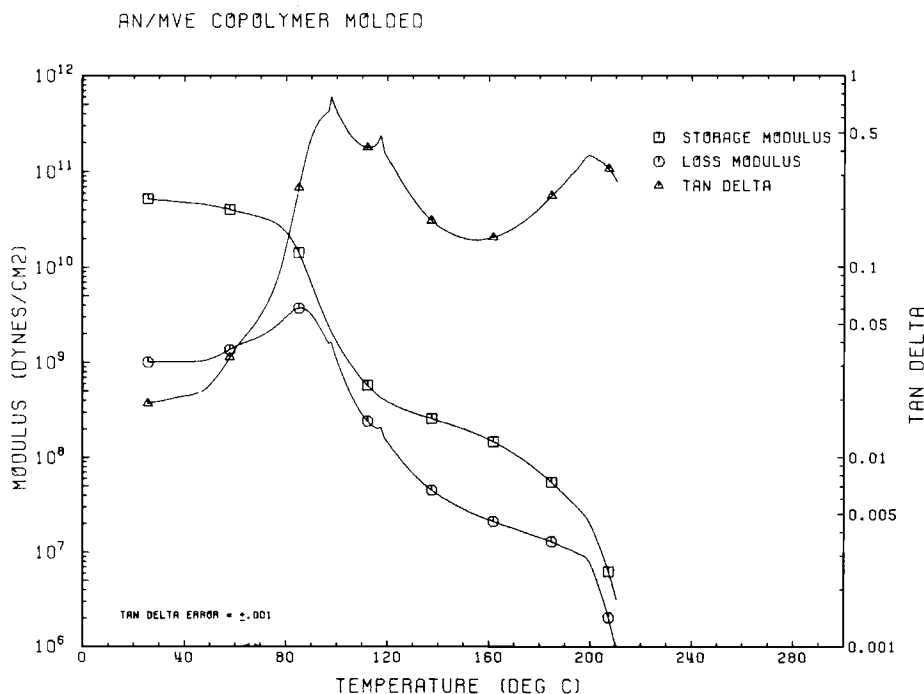


Fig. 4. Dynamic mechanical properties of acrylonitrile-methyl vinyl ether copolymer.

TABLE III

Sample	Calculated $G \times 10^{-9}$	Σ tan δ	W_c from G^1	W_c from tan δ	ΔW_c	W_c from XRD
1. PAN B molded at 220°	1.06	.278	0.47	0.72	0.25	0.46
2. PAN B molded-annealed	.866	.216	0.45	0.79	0.34	
3. PAN B cast	.6	.48	0.42	0.52	0.10	
4. PAN A cast-annealed	.766	.333	0.44	0.67	0.23	0.45

culated from shear modulus and tan δ as defined in eqs. (1) and (2). It is seen that the amount of crystallinity ranges from 0.42 to 0.47 based upon the shear modulus. When the crystalline fraction is calculated by the loss of damping, the fraction varies from 0.52 to 0.79. The crystallinity based upon the damping would contain the true crystalline and paracrystalline phases. The difference between the fractions calculated from damping and shear modulus could be a means of estimating the paracrystallinity phase which maintains ordering even at the highest temperatures.

By combining the measurements of XRD and modulus, an estimate of the fraction of each of the three phases present (Table IV) can be made. The data show little change in the crystalline phase in either a molded or cast film. Large differences are shown for the amorphous phase and paracrystalline phase depending on whether the polymer was cast or molded. Even though the crystals were destroyed when dissolved, they were reformed in the casting operation to the same overall fraction.

Copolymer Theory

The prior measurements were used to assign relaxation processes in the PAN system where only homopolymers were considered. However, when copolymers are made, the comonomer will have an effect on the transition. We have used the principle of copolymers to further verify the assignment of T_1 , T_2 , and T_3 transitions.

According to copolymer theory, the resulting glass transition of a copolymer will be dependent upon the content of each monomer and the respective glass transitions for each of the homopolymers. Fox²⁰ expressed the relation for the glass transition of the copolymer as follows:

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \quad (3)$$

where W is the weight fraction of each monomer and T_g (1 and 2) are the glass transitions of the respective homopolymer. This same relation holds for a blend of the two different homopolymers. The copolymer theory has been applied to a copolymer of AN and methyl vinyl ether as a means of assigning the α

TABLE IV
Estimate of Phases in PAN

Sample	Crystalline	Paracrystalline	Amorphous
1. PAN B molded at 220°	.47	.25	.28
2. PAN B molded-annealed	.45	.34	.21
3. PAN B cast	.42	.10	.48
4. PAN A cast-annealed	.44	.23	.33

transitions in PAN. A copolymer of acrylonitrile and methyl vinyl ether (83.3% AN and 16.7% methyl vinyl ether) was used to determine the relaxation assignments, as shown in Figure 4. The addition of the methyl vinyl ether comonomer causes an interruption of the AN sequences and will show its effect primarily in the amorphous phase. Since some shortening of the AN sequences occurs in the copolymerization, some reduction in the transition temperature for the crystalline regions is expected. The methyl vinyl ether units will be excluded from the paracrystalline or crystalline phases of the polyacrylonitrile. The copolymer theory for depressing the glass transitions has been applied to the three α transitions of PAN (T_1 , T_2 , and T_3). The following transitions were used to calculate the resulting T_g : (1) poly(methyl vinyl ether) = 270°K (5); (2) polyacrylonitrile $T_1 = 441^\circ\text{K}$, $T_2 = 396^\circ\text{K}$, $T_3 = 364^\circ\text{K}$.

The transitions for the pure PAN were the measured values from a solvent-cast film. The glass transition for poly(methyl vinyl ether) has been increased over the reported literature value of 260°K to allow for the transition shift due to increased frequency. The calculated transitions for the copolymer were calculated by eq. (3) on the basis of the pure homopolymers and compared to the observed values in Table V.

The calculated and observed T_1 and T_3 show agreement, while the observed value for T_2 differs from calculated value. The transition for T_2 is not depressed as much as expected upon the addition of the methyl vinyl ether comonomer which shows the copolymer preferentially altering the amorphous regions of the PAN. The transition T_2 , which is caused by the dipole-dipole interaction in the paracrystalline phase and consists of acrylonitrile sequences, has been partially reduced by the addition of the comonomer due to a shortening of the sequences.

Ogura, Kamamura, and Sobue²¹ studied transitions of PAN using infrared dichroism as a means of detecting changes in structures by observing the molecular motions of the CH and C \equiv N groups. Three transitions were clearly reported; however, only one transition (110°) showed changes in the CN group motions. They did not assign the molecular arrangement corresponding to the observed transitions. Motions involving the CH group did not show differences in any of transition regions. The paracrystalline region which involved dipole-dipole interaction between the C \equiv N groups would be expected to alter the IR spectra when the CN groups were free to move. They did not observe changes in the C \equiv N or CH motion regions for two transitions which according to the mechanical data would be assigned to the transitions involving the amorphous regions (T_1 and T_3). The IR data of Ogura²¹ would support the assignment of the 110° (T_2) transition to the dipole-dipole forces within the paracrystalline phase and T_1 and T_3 as the relaxations caused by the amorphous region. T_3 would correspond to the secondary relaxation of the amorphous region.

TABLE V
Comparison of Calculated and Observed Relaxation (in °C) of AN Copolymer

Relaxation	Calculated	Observed	Δ
T_1	124	124	0
T_2	93	100	7
T_3	70	70	0

CONCLUSIONS

1. PAN is a heterogeneous polymer system containing three phases; namely, amorphous, paracrystalline, and crystalline. It was not possible to show the presence of a single phase in any of the samples.

2. Modulus and slope modulus curve shows multiple-phase behavior. The high modulus above the T_g 's indicates some form of dipole-dipole interaction or crystallinity still present up to the point of degradation.

3. The broad $\tan \delta$ in the upper temperature region (α) can be separated into three separate transitions, namely, two amorphous regions and one dipole-dipole interaction. T_1 can be assigned as the transition of the totally amorphous phase. T_3 will be the β transition of the amorphous phase, and T_2 , which has been considered as the glass transition for PAN, results from a dipole-dipole release.

4. Assignment of relaxations have been based upon (a) copolymer theory of depression of the glass transition, (b) theoretical expressions of the interrelations of transitions, and (c) correlation with published infrared data on the relaxations.

The study of structure of the polyacrylonitrile system arose from discussions with Drs. Fred Kanel and Bruce Frushour, Monsanto Textiles Company. The AN copolymer was prepared by Dr. E. H. Mottus, CRL. The authors also express appreciation to Dr. D. Dahm and Frank May for the x-ray diffraction measurements. The discussions with Dr. L. E. Nielsen are gratefully acknowledged. The assistance of Don Wallace and Roger Young, CRL, who developed the computer programs which permitted data reduction and plotting is gratefully acknowledged.

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