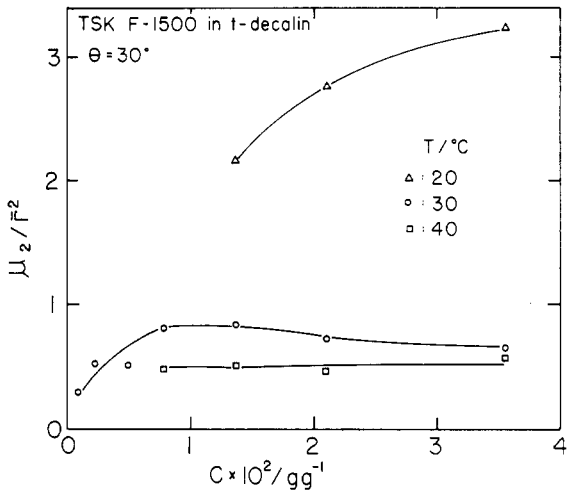

Figure 17. Plots of $\mu_2/\bar{\Gamma}^2$ vs. concentration (g/g of solution). We used $\mu_2 = A_f A_s(\bar{\Gamma}_f - \bar{\Gamma}_s)^2 + A_f\mu_{2f}$ and $\bar{\Gamma} = A_s\bar{\Gamma}_s + A_f\bar{\Gamma}_f$.

at $K\langle r_g^2\rangle_z^{1/2} > 1$ and partly because under actual experimental conditions laser light scattering can detect the different modes over large ranges in the $K\langle r_g^2\rangle_z^{1/2} - C/C^*$ plane. The boundaries specified for the various domains (I, II, and III) are not sharp, and definitive quantitative answers are available only in the asymptotic limit. Experiments which try to examine some of those limits involve a high molecular weight polymer dissolved in a good solvent, and a more complete analysis including experimental data obtained by classical means[12-20] is in progress. Further theoretical refinement in the transition regions corresponding to most actual experimental conditions should be of interest.

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Mechanical Properties of Cast Acrylonitrile Polymers. 1. Polyacrylonitrile

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ABSTRACT: The mechanical properties of polyacrylonitrile (PAN) cast from its monomer have been investigated, and shear creep compliance and free torsion pendulum results are reported in the 25–175 °C range for cast PAN and for PAN samples heat treated at 125 and 160 °C. Both the creep compliance and the storage modulus decrease by only slightly over one order of magnitude above the main transition region, indicating that the glass transition behavior of PAN is not analogous to that of typical amorphous polymers. Further, both the activation energies for creep and the loss modulus indicate two loss peaks, one at about 100 °C and a higher one at about 125 °C. Finally, heat treatment results in an increase in the modulus, especially above the transition region, and in the elimination of the second, higher-temperature loss peak. These results are discussed in terms of reaction of nitrile groups along the PAN backbone.

In recent years polyacrylonitrile has received widespread attention. This interest has developed principally because of the great commercial importance of polymers based on acrylonitrile, and considerable effort has been devoted to the problems of processing and fiber formation. Further, the polymer itself also has been studied extensively, not only in support of applied projects but also because of a number of interesting and sometimes unusual or unique properties. In particular, many papers have appeared dealing with color formation and decomposition and, to a lesser extent, with glass transition and multiple transition behavior and mechanical and dielectric properties. It is primarily the mechanical properties that are of interest here, but the question of heat treatment and decomposition will be seen to be of importance.

Relatively little data concerning the mechanical properties of polyacrylonitrile have appeared. Schmieder and Wolf[1] report torsion pendulum results from about −160 to 230 °C, Cotten and Schneider[2] vibrating reed results at three frequencies from about 30 to 150 °C, and Ohajima et al.[3] stretching vibrometer results from 20 to 180 °C. Further, Andrews and Okuyama[4] report creep and creep recovery studies between 70 and 160 °C and Furusho et al.[5] limited data using torsional braid analysis. The reason for the scarcity of data is mainly the difficulty in fabricating suitable test specimens, especially for creep or stress relaxation studies. The results referred to above were all obtained using either fibers or films cast from solution, since, until recently, methods for obtaining polyacrylonitrile by bulk polymerization from its monomer were

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unknown. The main purpose of this report is to extend the limited amount of data presently available with results of shear creep compliance and torsion pendulum measurements over a wide temperature range obtained using polyacrylonitrile cast from its monomer.

The investigation and interpretation of transitional phenomena manifested by polyacrylonitrile have also been of considerable interest. At least two transitions (perhaps more appropriately called "relaxations" or "processes") are generally recognized. These are: (1) a transition in the 80–105 °C range which is usually referred to as the glass transition, although several authors denote this the β transition; and (2) a transition above the β transition in the 140 °C range which is sometimes denoted the α transition. Schmieder and Wolf,[1] Cotten and Schneider,[2] and Meredith and Hsu[6] all found these transitions as evidenced by dynamic mechanical loss peaks. Also, the birefringence studies of Kimmel and Andrews[7] and the dielectric studies of Ishida et al.[8,9] and Van Beek[10] lend support to the existence of two transitions in polyacrylonitrile above room temperature, and the infrared spectroscopic studies of Ogura et al.[11] and the reciprocal chromatography studies of Calugaru and Schneider[12] indicate the existence of three or more transitions in the 50–150 °C range. It is, therefore, of interest to investigate the transitional behavior of cast polyacrylonitrile, using both torsion pendulum and creep compliance measurements, and the results of these studies are presented.

Numerous studies have appeared devoted to the thermal behavior and decomposition of polyacrylonitrile, and it is well known that thermal history can have a marked effect on its properties. For example, Van Beek[10] found that by heat treating samples, a dielectric loss peak originally found at 140 °C disappeared. As a final point in this report, the effect of heat treatment on the dynamic mechanical properties is discussed.

Experimental Section

It is well known that the bulk polymerization of acrylonitrile to form polyacrylonitrile (hereafter denoted PAN) proceeds in a heterogeneous fashion, and several studies have appeared devoted to the kinetics and other aspects of this reaction.[13] However, it was discovered several years ago that under suitable conditions PAN could be cast from its monomer.[14] Although the polymerization proceeds in a heterogeneous fashion at first, if a layer of monomer is maintained over the polymerizing cake, at high conversion the center portions of the cake tend to become clear and form a homogeneous mass.

Acrylonitrile (American Cyanamid Co.) was purified by washing it successively with 10% phosphoric acid, 1% sodium bicarbonate, and water, drying it with calcium hydride, and distilling it at atmospheric pressure. The monomer was catalyzed with 0.25% by volume *tert*-butyl peroxypivalate (Wallace and Tiernan, Inc.). The polymerizations were carried out between 6 in. × 6 in. glass plates, using $^3/_{32}$ in. or $^1/_8$ in. poly(vinyl chloride) gasket material to form the cell. The system was maintained at 40 °C for about 3 days, 55–60 °C for 1 day, and finally 80 °C for 8–12 h. The results of the polymerizations were rather unpredictable, although usually at least some clear polymer formed; the most successful attempts produced masses 4 in. × 5 in. in area with plane parallel sides. The cast PAN was perfectly transparent, with a very pale yellow color. It was completely soluble in dimethylformamide and had an intrinsic viscosity in this solvent of 5.2 dL/g, or from the expression $[\eta] = 2.43 \times 10^{-4}\ M^{(0.75)}$,[15] a viscosity-average molecular weight of 600 000. By chromatographic techniques, the residual monomer concentration was found to be less than 0.20–0.30% by weight.[14]

Specimens used for both creep and torsion pendulum studies were prismatic bars with rectangular cross sections. They were fashioned by cutting a strip from a sheet of cast polymer, milling the cut faces, and finally polishing these faces with fine sandpaper. A typical specimen used for creep measurements had dimensions of about $^1/_8$ in. × $^1/_8$ in. × 1 in., and for the torsion pendulum the measurements $^3/_{32}$ in. × $^3/_{32}$ in. × 2 in.

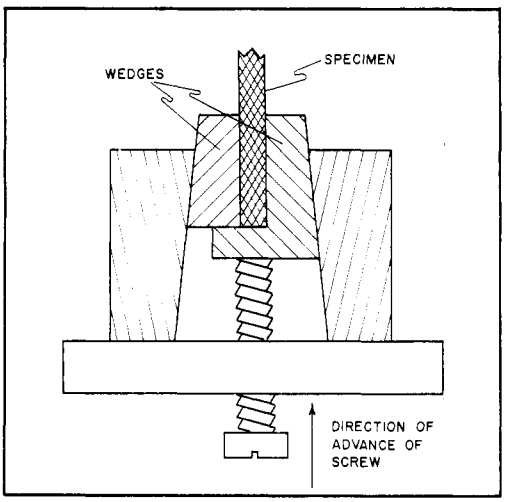

Figure 1. Clamping arrangement for creep compliance and torsion pendulum apparatus.

The specimens used for the torsion pendulum studies were subjected to two heat treatments after the initial measurements were made, the first being 30 h at 125 °C and the second 24 h at 160 °C. After the first treatment, the samples were of a relatively deep, uniform orange-red color and perfectly clear; after the second they appeared black, although a thin section showed the samples to be clear and of a very deep red color.

Shear creep compliance measurements were made using an apparatus and recording system similar to one already described by us.[16] However, since specimens with rectangular cross sections were used in the present study, the method of clamping was modified, employing a series of wedges which assured that the specimen remained collinear with the overall axis of the apparatus. (The details of the clamping arrangement are shown in Figure 1.) Briefly, the apparatus consisted of a base and frame to which one end of the specimen was rigidly attached; to the other end was fastened a torsion arm which could be twisted by a pair of weights hung over pulleys. Also attached to the torsion arm and collinear with the specimen was a rotary variable differential transformer (Schaevitz, model R3B255), the output of which was proportional to the angular deflection. Two recorders were used: (1) a Model GPO 460 oscillograph (Century) for times for about 0.25–5 s; and (2) a Model VOM7 stripchart recorder (Bausch and Lomb) with an AC converter for times greater than 5 s. Torsion pendulum measurements were made using the same apparatus and the oscillations recorded with the oscillograph mentioned above.

Experimental Results

Creep Compliance Data. The response of the cast PAN specimens to applied static load was measured between 25 and 165 °C over time spans of 0.5 to as long as 1000 s. Care was taken to insure that the ratio of response to applied load did not depend on the magnitude of the load itself; that is, it is important that the measured response corresponds to linear viscoelastic behavior. Empirically, we determined that at strain levels below about 1% the measurements were well within the linear region.

The specimens used in this study were prismatic bars with rectangular cross sections, and for this geometry the time-dependent shear creep compliance $J(t)$ is given by[17]

$$J(t) = \frac{ws^3}{3h}\left[\frac{1}{3} - k\right]\frac{\theta(t)}{T} \qquad (1)$$

where w, s, and h are the width, thickness, and length, respectively, of the specimen; $k = 16s/(\pi^5 w) \tanh(\pi w/2s)$, a constant depending on the ratio s/w; T is the applied torque (which for creep experiments is constant and calculated from the values of the applied load and radius of

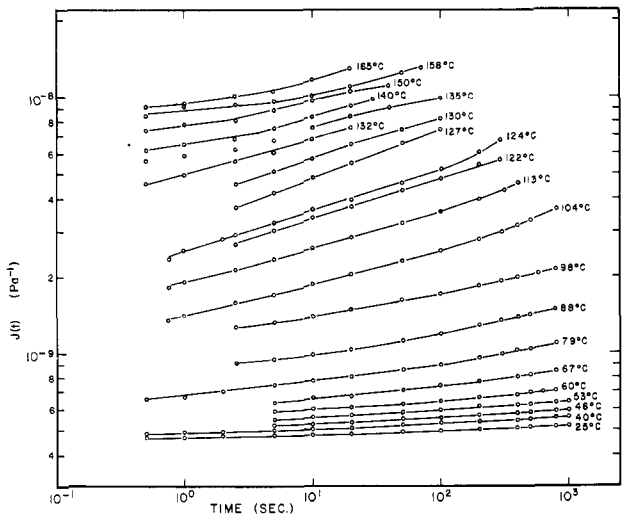

Figure 2. Shear creep compliance of cast polyacrylonitrile between 25 and 165 °C.

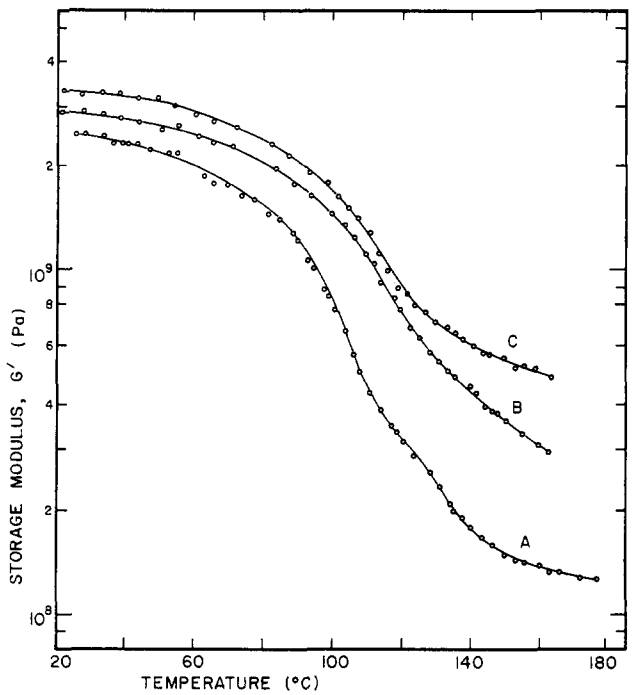

Figure 3. Storage modulus of three polyacrylonitrile test specimens: curve A, untreated; curve B, heat treated at 125 °C for 30 h; curve C, heat treated at 160 °C for 24 h.

the torsion arm); and $\theta(t)$ is the time-dependent angular deflection.

The results of the calculation of $J(t)$ using eq 1 are shown in Figure 2, where the circles represent times for which $J(t)$ was actually calculated from the continuous oscillograph or recorder outputs.

Torsion Pendulum Data. Torsion pendulum measurements were made over the temperature range 28–176 °C, using the Century optical oscillograph mentioned above. From the resulting oscillographs, the frequency of the free oscillation ω and the logarithmic decrement Δ were determined. For free oscillations in the region of linear viscoelastic response, the storage modulus G' and loss modulus G'' are given by[18]

$$G' = \frac{I\omega^2}{F}\left[1 + \left(\frac{\Delta}{2\pi}\right)^2\right] \quad (2)$$

$$G'' = \frac{I\omega^2}{F}\frac{\Delta}{\pi} \quad (3)$$

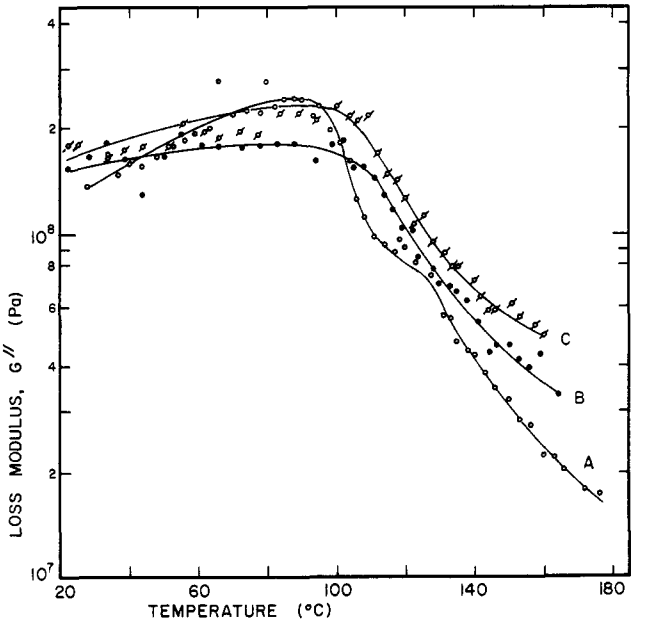

Figure 4. Loss modulus of three polyacrylonitrile test specimens: curve A, untreated; curve B, heat treated at 125 °C for 30 h; curve C, heat treated at 160 °C for 24 h.

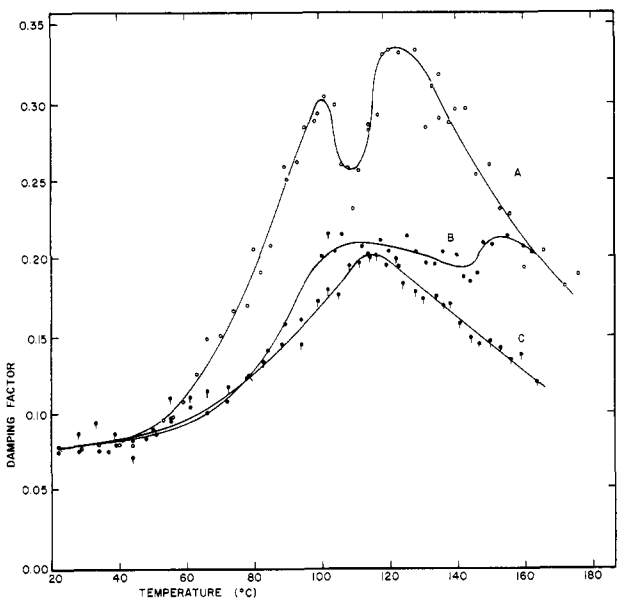

Figure 5. Damping factor of three polyacrylonitrile test specimens: curve A, untreated; curve B, heat treated at 125 °C for 30 h; curve C, heat treated at 160 °C for 24 h.

where I is the moment of inertia of the system, and $F = ws^3\mu/16h$, where w, s, and h have the same meaning as above and μ is a shape factor depending on the ratio s/w.[19] For eq 2 and 3 to be valid it is necessary that $G' \gg G''$, that is, the loss be relatively small. For the results presented here, the ratio G'/G'' is about equal to 10 in the regions of greatest loss and much less elsewhere. Also, the term $(\Delta/2\pi)^2$ is never greater than about 0.25% of unity.

The results of the calculation of G' and G'' for cast PAN are shown as curve A in Figures 3 and 4, respectively. Further, the damping factor (or loss tangent) which is proportional to the ratio G''/G' is shown as curve A in Figure 5. We have included the damping factor because it tends to accentuate loss peaks as compared to the loss modulus G'' itself, and for the purposes of this report the loss peaks are of particular interest. Finally, G', G'', and the damping factor are shown in Figures 3, 4, and 5, respectively, for the two heat-treated samples described in

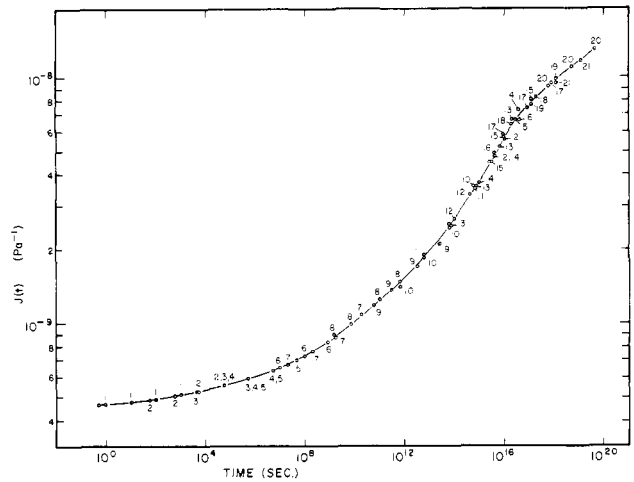

Figure 6. Master shear creep compliance curve of cast polyacrylonitrile: (1) corresponds to 25 °C; (2) 40 °C; (3) 46 °C; (4) 53 °C; (5) 60 °C; (6) 67 °C; (7) 79 °C; (8) 88 °C; (9) 98 °C; (10) 104 °C; (11) 113 °C; (12) 122 °C; (13) 124 °C; (14) 127 °C; (15) 130 °C; (16) 132 °C; (17) 135 °C; (18) 140 °C; (19) 150 °C; (20) 158 °C; (21) 165 °C. The reference temperature is 25 °C.

the previous section, namely, 30 h at 125 °C (curves B) and 24 h at 160 °C (curves C).

Discussion

In Figure 2 $J(t)$ is shown for relatively short time spans of 10^0–10^3 s or less for 21 different temperatures. For the purposes of better understanding the nature of $J(t)$ and for comparing the creep and dynamic results, it is desirable to reduce the data to a single reference temperature over an extended time span. This can be accomplished by employing the well known time–temperature superposition principle,[18] and the result is shown in Figure 6. In obtaining the master creep curve only horizontal shifts were used (this point will be discussed in greater detail later). Each temperature is represented by points for t = 1, 10, 100, and 1000 s and is identified by a number. Generally, two successive $J(t)$ vs. time curves overlap for about one to three decades of time, and, considering the relatively complex dependence of $J(t)$ on temperature, the superposition is remarkably good. The reference temperature is, of course, arbitrary and has been chosen as 25 °C. The master creep curve is seen to be roughly the reciprocal of curve A in Figure 3, as would be expected, and a minor inflection is seen in both (at about $t = 10^{16}$ s in the $J(t)$ curve and in the T = 130 °C range in the G' curve).

There is considerable evidence to suggest that the main transition in PAN is not an ordinary glass transition as manifested by amorphous polymers in general.[20] This unusual behavior is usually explained in terms of the relative inflexibility of the PAN backbone and the paracrystalline nature of PAN. In Figure 3 it is seen that the modulus of cast PAN drops by barely an order of magnitude, unlike a typical amorphous polymer where at the glass transition a drop of 2 or 3 orders of magnitude is observed. Correspondingly, in Figure 6 the increase in $J(t)$ is about a factor of 10. These observations are in agreement with the results obtained using other forms of PAN.

We noted in the introduction above that several investigators have reported the occurrence of multiple transitional behavior in PAN in the 80–140 °C range. Referring to curve A of Figure 5, we observe loss peaks at 100 and 125 °C, and thus two transitions or processes manifest themselves in cast PAN as in other forms of PAN. It has been suggested that the lower-temperature transition (the glass transition) involves the onset of concerted backbone motions[6] or alternatively involves rotational vibration in

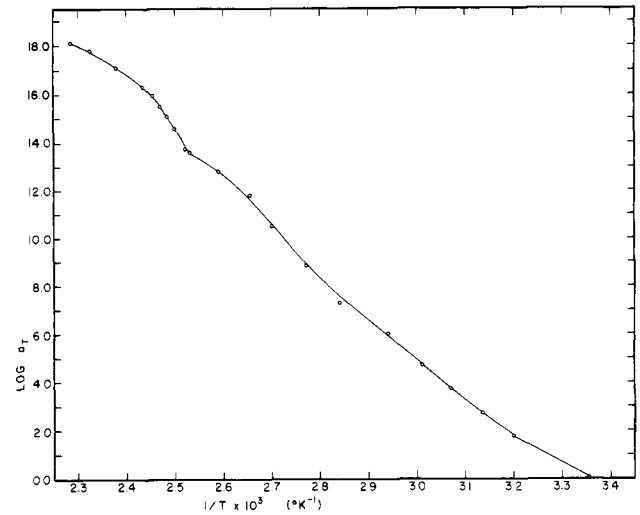

Figure 7. Log a_T vs. $1/T$ from shear creep compliance measurements for cast polyacrylonitrile. The reference temperature is 25 °C.

the paracrystalline region[20] while the upper-temperature transition (the α transition) is the result of an association–dissociation phenomenon between nitrile dipoles on adjacent chains.[7] However, the exact nature of the amorphous-paracrystalline phases in PAN and other structural details remain to be elucidated, and it is, therefore, probably premature to assign molecular interpretations to the observed "transitions". We will comment again on the α transition toward the end of this section.

In Figure 6 we may observe the creep behavior of polyacrylonitrile from essentially elastic response, through a major transition region, to the onset of a rubbery-like response. To understand the transition region better and for the purpose of comparing the creep and dynamic results, it is desirable to investigate the shift factors a_T obtained from time–temperature superposition and their temperature dependence. A particular value of a_T is, of course, a measure of the extent to which a $J(t)$ curve at some temperature T must be shifted along the time scale to superimpose it on the master curve at the reference temperature T_0, in this case 25 °C. For most polymers below their glass transition temperatures, it is found that an Arrhenius type of expression of the form

$$\ln a_T = \frac{\Delta H_c}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{4}$$

is valid,[21] where ΔH_c is the activation energy for creep, roughly a measure of the height of the potential energy barrier which opposes the motion of a unit of flow, and R is the ideal gas constant. A plot of log a_T vs. $1/T$ is shown in Figure 7, and the dependence is clearly not linear, that is, ΔH_c is not constant. Nevertheless, values of ΔH_c are easily obtained by computing the slope $da_T/d(1/T)$ at a given point, and the resulting ΔH_c vs. T curve is shown in Figure 8. Two maxima are observed in Figure 8, and these correspond almost exactly to the two loss peaks observed in curve A in Figure 5. Thus, evidence of two distinct transitions or processes is found in both the creep and dynamic data for cast PAN.

We pointed out above that only horizontal shifts were used in obtaining the master creep curve and values of a_T. This is not strictly correct since in certain cases, at least, it is known that vertical shifts, or corrections, are needed. For example, the theory of rubber elasticity leads to the well known temperature–density correction for the temperature dependence of the modulus and thus to the

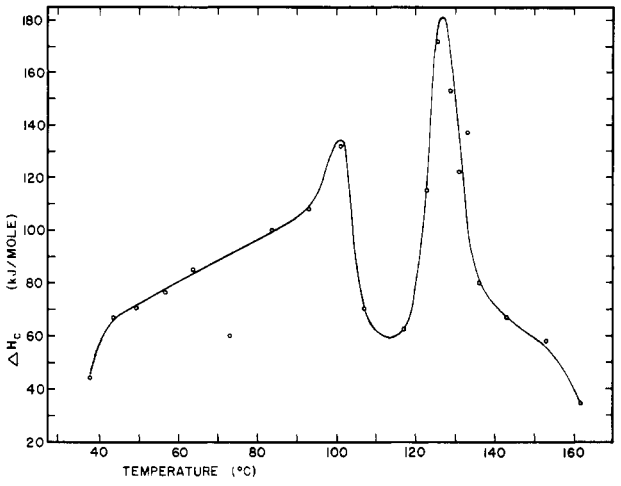

Figure 8. Activation energy for creep vs. temperature derived from shear creep compliance measurements for cast polyacrylonitrile.

prediction of a small vertical shift factor, and more recently McCrum and Morris[22] have developed a method for estimating vertical shift factors for glassy polymers. Because we have not employed such corrections here, the values of ΔH_c reported here would not be comparable with an activation energy of internal friction obtained from, say, a dielectric constant measurement. For our purposes, however, this distinction is not important.

It is well known that PAN undergoes profound changes upon heat treatment, and in the introduction to this paper we commented briefly on color formation and changes in mechanical and dielectric properties. In particular, in Figure 3 we observe a gradual increase in G' upon heat treatment (curve A to curve C), especially above the glass transition region, indicating a stiffening of the overall backbone structure or some other structural change. Further, in Figure 5 it is seen that the second damping peak disappears, with the result that the heat-treated sample represented by curve C yields a single less intense damping peak. This behavior appears to be in agreement with the observation cited earlier that the dielectric loss peak associated with PAN in the 130–140 °C region also disappears.[10] Van Beek[10] associated this region of dielectric loss in PAN with coordinated motions of nitrile groups and that fixation of nitrile groups in conjugated chains by pyrolysis would restrict their orientation and thus lead to a decrease in the loss peak. The increase in storage modulus from curve A to curve C seen in Figure 3, the color changes that take place during heat treatment, and the elimination of the higher-temperature loss peak seen in Figure 5 would seem to suggest that similar cyclization reactions take place in cast PAN and support the interpretation of the 140 °C transition advanced by Van Beek[10] and Kimmel and Andrews.[7] However, it should be noted that recent studies of electrically polarized PAN indicate the possible formation of double bonds in the backbone itself,[23] and this phenomenon could also explain the observed mechanical and loss behavior. Thus, we conclude that until the structure of PAN pyrolyzates is more fully understood, it will not be possible to completely resolve the question of the molecular interpretation of the observed transitional behavior of PAN.

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