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Fracture detection in polymers by electron paramagnetic resonance

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Summary

Electron paramagnetic resonance (EPR) spectroscopy is a form of microwave absorption spectroscopy in which transitions are induced between the Zeeman energy levels of unpaired electrons. Since bond breakage in polymers results in the production of unpaired electrons, or free radicals, EPR spectroscopy can be used to study the submicroscopic mechanisms of fracture in these materials. Using EPR techniques, bond breakage induced by uniaxial tension has been studied for a number of polymers. It has been possible to determine how many of which bonds are broken during fracture, and to monitor the bond breakage as a function of time so as to provide important new insights into the mechamism and kinetics of the fracture process. Highly crystalline, oriented fibers have proven most amenable to EPR analysis during tensile fracture, and this paper presents tensile data taken on drawn polycaprolactam (Nylon 6) fibers. Free radical concentrations in this material reach approximately 10^{17} spins per gram at fracture (in this case number of free radicals present). The kinetic behavior seems to imply that presently existing theories of bond rupture are oversimplified. Although the kinetics of free radical formation are complex, a correlation between stress and the steady-state free radical concentration was found, however, which took the form of a thermally-activated stress-aided process.

Introduction

At the First International Conference on Fracture, S. N. Zhurkov reported using electron paramagnetic resonance (EPR) spectroscopy to monitor the molecular bonds broken during the mechanical degradation of polymers. Since that time the authors have extended this technique to a variety of applications [1, 2]. A major purpose of this report is to discuss the possibilities and limitations of the method as used to detect bond rupture due to mechanical loading of the specimens at various time histories.

EPR spectroscopy is a special form of microwave absorption spectroscopy in which transitions are induced between the Zeeman energy levels of an assemblage of paramagnetic electrons. When homolytic rupture of a covalent bond of a polymeric molecule takes place, two unstable free radicals are formed whose paramagnetic character makes them amenable to detection and identification by an EPR spectrometer. Whenever the free radical concentration in the sample lies above the sensitivity limits of the spectrometer ($\sim 10^{12}$ radicals), a spectrum is produced whose size (intensity) is a measure of the number of unpaired electrons present, and

whose shape (the so-called 'hyperfine structure'), is a measure of the local chemical environment of the radicals. In principle at least, the EPR spectrometer is able to detect *how many* of *which* bonds have been broken, and to monitor the bond-breakage kinetics as a function of time.

The applicability of EPR to fracture studies is limited to those materials in which bond rupture produces paramagnetic electrons (metals and ionic crystals are thus eliminated) in concentrations exceeding the above experimental equipment limit. This requirement produces stringent limitations on the method, but the authors have found EPR to be an extremely valuable analytical technique in the study of many diverse types of covalent bond rupture [3]: γ-ray induced degradation, stress crazing, grinding, cutting, radiation or certain types of leukemia-induced blood cell rupture, and decay in teeth, to name a few. This paper presents some results of our EPR observations of bond breakage in uniaxial stressed nylon with different loading histories, and some correlations between these data and macroscopic fracture.

Experimental equipment

A Varian Associates E-3 EPR spectrometer was employed in the studies. This equipment operates at a microwave frequency of approximately 9·5 gHz and a magnetic field modulation frequency of 100 kHz. All the tests were made at low microwave power (~1 mw) to avoid saturation effects. A suitably modified Varian E-4557/E-9540 variable temperature accessory and controller make it possible to maintain the temperature of the sample at any value between −165 °C and +300 °C; this device also enabled the testing to be conducted in a controlled atmosphere.

A servo-controlled hydraulic loading system was designed and built to be used in conjunction with the EPR spectrometer so as to enable the application of a tensile load to a specimen in the spectrometer's microwave cavity. Signals from either load or displacement transducers could be used as response signals in the servosystem; using appropriate command circuitry, either load, strain, or stress could be controlled according to any desired time-dependent program. With this system it is possible to subject the specimens to almost any programmed stress or strain. The transducer signals were also recorded alongside the EPR signal on magnetic tape, which permitted data reduction and analysis on a Univac 1108 digital computer. The results could then be displayed by an IBM 1627 digital plotter.

A proposed fracture model based on EPR observations

To date detectable EPR signals have been produced during tensile fracture only for a very restricted class of polymeric materials: i.e. the highly oriented drawn fibers of high tensile strength. All samples in bulk

form (amorphous or spherulitic morphology) have generated at best a marginally detectable full radical concentration. The number of bonds broken during fracture of the fibers (10^{17} bonds/gram) is at least five orders of magnitude larger than that in the bulk polymers or even the low-strength fibers.

It is significant that the above classes of polymers exhibit markedly distinct macroscopic fracture properties. Amorphous materials such as polymethylmethacrylate and polystyrene are characterized by a brittle, notch-sensitive fracture at relatively low stresses, while bulk spherulitic polymers such as nylon and high-density polyethylene are tougher and stronger. The drawn fibers are the strongest of all polymers: drawn nylon fibers have tensile strengths near 120 ksi and actually surpass steel on a strength-per-weight basis.

On a molecular level, these distinctions must stem from the different morphologies and chain mobilities of the materials. If one views fracture as a process which involves the nucleation and growth of submicroscopic flaws by a thermally-activated stress-aided bond rupture process describable by reaction rate theory, then the catastrophic propagation of one of these flaws once it has exceeded some critical size is described by the Griffith-Williams (viscoelastic) fracture theory. At temperatures far below the glass transition temperature (~100 °C), molecular chain motion is so restricted that the material loses its polymeric mechanical nature and behaves as a brittle elastic solid; this will be true for amorphous and crystalline polymers alike. In this 'frozen' state, the material is unable to adjust itself so as to relax its internal stress concentrations. Initial bond rupture then occurs primarily at these relatively sparse locations, resulting eventually in a critical size flaw without having generated comparable bond rupture throughout the entire volume of the sample. Since relatively few chemical bonds are brought to bear as load supporters, these solids are characteristically weak.

In the vicinity of the glass transition temperature, on the other hand, chain mobility is sufficient to allow stress relaxation and redistribution around the internal stress risers. The result is a complex phenomenon in which bonds are breaking according to reaction-rate theory, but in a redistributed stress field which is decaying according to some undetermined kinetic behavior. These solids are stronger and less brittle since more bonds are able to help support the load. The number of bonds ruptured during loading to fracture will now be a function of the material's morphology. In amorphous polymers with little interchain cohesion, chain slip and flow play important roles: even though bonds do of course break under the stress, the formation and growth of a flaw might be greatly facilitated by chain rearrangements. The effect is similar in the spherulitic crystalline polymers, but here the chains are more restricted due to

secondary bonding in the crystal lamellae; chain rearrangements are primarily due to crystal tilt and twinning as in cold-drawing. More bonds must be broken before a critical flaw is germinated and the material is correspondingly stronger. For the drawn fibers, where a two-phase folded-micelle model for morphology appears reasonable [4], the chain ends are tightly enclosed in the lamellae and the rupture takes place in the relatively thin tie-chain-containing amorphous regions between the lamellae. The tie chains undergo conformational change and permit stress relaxation, but chain slip and flow is prohibited. Hence, extensive bond rupture must occur throughout the interior of the sample before a catastrophic flaw is created.

Although the above description is in many ways rather speculative, it is in basic agreement with the lack of a large radical concentration in all but the high-strength fibers, as well as with the observed bond rupture kinetics which will now be presented. Of particular importance in this latter regard is the ability of the polymeric solid to permit a time-dependent relaxation of stresses within its interior.

EPR observations of bond rupture kinetics

The material most amenable to EPR analysis during tensile fracture has been drawn (4 to 1) Nylon 6 (polycaprolactam) fibers provided by Allied Chemical Corporation. X-ray fluorescence of these fibers by Allied Chemical Corporation indicated that the only inorganic ions present in substantial amounts were copper, 61 ppm; iodine, 0·2%, and all other metals less than 2 ppm. The fibers exhibit no residual EPR signal, and their fracture yields particularly high free radical concentrations. The data presented here will be for these fibers exclusively, as they are not untypical of other high-strength fibers tested.* Stress-induced EPR signals are generated in these Nylon 6 fibers at stresses above approximately 60% of the fracture stress. Fig. 1 shows the spectrum, which exhibits here a typical growth during stepwise-increasing loads. The second integral of these curves is proportional to the number of broken bonds.

The hyperfine structure of the Nylon 6 spectrum is the same as that reported extensively for γ-ray induced polymer degradation [5]. It has been analyzed as corresponding to the radical

$$-CO-NH-\dot{C}H-(CH_2)_4-$$

It can be shown quite unambiguously that this radical corresponds to a side-proton removal rather than a main-chain scission, and hence it is expected that it represents not the originally-broken bond, but rather the

* Similar results have been obtained from drawn polyethylene, Nylon 66, and polyester fibers; testing is presently planned for natural silk, and isotactic polypropylene fibers.

most stable site to which the highly active primary radical quickly migrates. EPR studies of mechanical degradation at liquid nitrogen temperatures, where this migration process is strongly retarded, produce a different spectrum which corresponds to chain scission at two equivalent sites [6, 7]:

$$-CO-NH-CH_2+(CH_2)_3+CH_2-$$

If one assumes that the radicals of Fig. 1 represent a one-to-one correspondence with the originally-broken bonds, the EPR spectrometer can be used to monitor the kinetics of bond rupture during tensile loading to fracture. For sensitivity and other reasons typical EPR spectra as shown in Fig. 1 are first derivatives of absorption curve, so the second integral of this spectra is proportional to number of free radicals present. If, however, the spectra can be approximated by either a Lorentzian or Gaussian type curve, the height of this spectral curve is proportional to this second integral. If the magnetic field of the spectrometer is fixed at a value corresponding to one of the resonance peaks, then the magnitude of this EPR signal, proportional to the number of bonds, can be recorded continuously as a function of time as the sample is loaded. By employing a standard EPR sample with a known number of free radicals, the height of the resonance peak chosen can be calibrated to measure the number of radicals present in the stressed sample.

Fig. 2 shows the results of a typical computer treatment of data taken during a constant-load test. It is seen that the bond breakage rate decreases monotonically after application of the load, falling eventually to zero. Although the curve approaches an asymptotic value, it is not an exponential. This effect is absolutely reproducible and has been found in other drawn fibers as well [7].

The general shape of these curves are in marked conflict with most theoretical reaction-rate treatments of polymeric bond rupture [8], in which the assumption of a uniform (or at best, a statistical but still time-independent) distribution of stresses among the unbroken bonds predicts a constant or accelerating rate of bond breakage during a constant load test. These curves argue strongly for the stress-relaxation model of fiber strength mentioned above. Almost certainly, they represent rearrangements of the amorphous sections of the fiber which distribute the stresses more evenly among all the chemical bonds, which then bear the load without further appreciable bond rupture. These rearrangements likely take the form of both chain conformational changes and actual chain scission at stress concentrations. It is thus concluded that even the more elaborate reaction-rate models of polymeric bond rupture are oversimplified unless they take a decaying stress field into account. It appears that the model of Knauss [9], which can do so at least implicitly,

can be fitted to the EPR data. Such a fit provides an independent check of the model, and will be published shortly.

It should be noted that the above involves a disparity with the conclusions reached by S. N. Zhurkov [10], who reported that EPR tests have corroborated the relation

$$\dot{C} = A \exp(B\sigma) \tag{1}$$

i.e., bonds are broken at a constant rate for any given applied stress σ, and that this rate is exponential in the stress. In light of Fig. 2, where it is clear that the bond breakage rate is certainly not constant, such a conclusion seems confusing at best. Apparently Zhurkov did not use constant-load tests to reach this conclusion, however, but rather constant-load-*rate* tests [11]. To investigate this approach, the authors conducted a series of constant-load-rate tests at various temperatures; a typical test on Nylon 6 fibers is depicted in Fig. 3. The free-radical curve itself is not an exponential but its first derivative, i.e., the *rate* of bond breakage, is. A typical numerical differentiation of a constant-stress-rate free-radical curve is shown in Fig. 4.

The authors feel, however, that this result does not justify the assertion that the bond breakage rate is exponential in the stress for all other loading modes as well. Even though this conclusion led Zhurkov to some impressive correlations with his thermo fluctuation mechanism of creep rupture [10], it may be misleading on several points. First, it is directly contradictory to the very reproducible results of Fig. 2. (Zhurkov also reports curves of this type [11].) Second, the activation constant B does not obey an Arrhenius relation $B = (\text{constant})/kT$ as would be expected in a process of this kind. Third, our numerical values, and in particular the slope of the line in Fig. 4, are in substantial disagreement with those reported by Zhurkov. Equation 1 is well-justified on the basis of reaction-rate theory and would likely be valid if σ were taken to be the local time-dependent stress rather than the overall applied stress, but it fails to account for the complex and changing morphology of real polymeric solids.

It was initially thought that the two conclusions could be reconciled if the asymptotic nature of Fig. 2 were taken to reflect a balance between radical production and first-order radical decay:

$$\dot{C} = \dot{C}_{\text{production}} - \dot{C}_{\text{decay}} = A \exp B\sigma - C/\tau \tag{2}$$

where τ is the characteristic decay time. The decay did in fact approximate first-order kinetics in these tests, and τ can be measured easily by unloading the sample and monitoring the signal decay as a function of time. The relaxation time so measured was approximately 800 seconds. Equation 2 cannot be fitted to the observed EPR data, however, unless τ is chosen some twenty times smaller than this. Although the contradiction might be explained in terms of some sort of stress-assisted relaxation process, such a mechanism is difficult to envision and it appears that the simple equation (2) does not properly describe the bond rupture kinetics.

Further evidence against this formation-decay model is provided by long-time constant load tests in which the signal is observed to decay slowly (at $\tau \sim 800$ sec) after reaching 'steady-state' level. This decay is due to the addition of the asymptotic bond rupture curve and the first-order decay curve; it is clear that radical production has stopped or at least markedly decreases even though the gross stresses remained constant. Another test which indicates the importance of morphological rearrangements and the erroneous character of either equation 1 or 2 involves loading a sample so as to produce a strong EPR signal, then unloading it and allowing the signal to anneal away at room temperature. When the sample is reloaded to the original level, the EPR signal does not reappear; a detectable free radical concentration is not formed until the stress (and strain) is increased above this level as indicated in Fig. 5. Clearly, the response of the material to the second loading is different than to the first and this behavior cannot be justified with equations 1 or 2.

A correlation between EPR data and applied stress

Most of the above conclusions appear rather negative in nature: the atomistics of polymer fracture seem more complex than even the already nearly intractable reaction-rate models portray them, and one should regard a simplified model with great caution. It does appear, however, that there exists a significant correlation between the steady-state concentration of radicals in a constant-stress test and the applied macroscopic stress. If we assume that the combined bond rupture and stress relaxation mechanisms are a thermally-activated stress-aided process, then the steady-state concentration C_{ss} should be expected to obey an equation of the form

$$C_{ss} = \alpha \exp[(\beta\sigma - \gamma)/kT] \tag{3}$$

Here σ is the applied stress; T is the absolute temperature; k is Boltzmann's constant; and α, β, and γ are material constants. For isothermal conditions, this reduces to

$$C_{ss} = \delta \exp(\zeta\sigma) \tag{4}$$

where $\delta = \alpha \exp(-\gamma/kT)$ and $\zeta = \beta/kT$. Equation 4 implies that a plot of $\log(C_{ss})$ versus σ should be linear; this has been found to be the case for all fibers tested so far which produce detectable EPR signals. Fig. 6 shows the plot for drawn Nylon 6 fibers. This relationship also holds over a wide range of temperatures.

To further check this model, the activation constant ζ was plotted against $1/T$. This plot is shown in Fig. 7. The data does plot as a straight line passing through the origin in agreement with $\zeta = \beta/kT$. The activation volume β can be computed from the slope of this line; for Nylon 6 fibers, $\beta = 2{\cdot}28 \times 10^{-24}$ in^3. Another check is provided by the pre-exponential factor δ in equation 4. Since $\delta = \alpha \exp(-\gamma/kT)$, a plot of $\log \delta$ versus $1/T$ should be linear and this is shown to be the case in Fig. 8. The thermal activation energy γ can be found from the slope of this line and the constant α can be read as the intercept with the vertical axis. For Nylon 6, $\gamma = 4{\cdot}32 \times 10^{-19}$ inch-pounds and $\alpha = 6{\cdot}1 \times 10^{16}$.

It should be noted that the activation volume (ζ) corresponds to a cube 3·6 Å on a side, almost exactly the distance found by Gubanov [12] (~3½) as the elongated chemical bond length just prior to rupture. Attaching too much significance to this result is probably ill-advised since the concept of an activation volume is rather artificial. However, the activation volume for metals seems to coincide with the volume of a diffusing vacancy and perhaps we have found a similar correlation for polymer fracture.

Equation 4 is interesting in light of the fact that time to fracture in creep is also often exponential in the applied stress. There is, therefore, a direct relation between the lifetime under load and the steady-state concentration of broken bonds within the sample, at least for the drawn fibers. The following proposed explanation is consistent with these observations: the time to fracture may be directly related to the size of the internal microflaws which will eventually coalesce into a catastrophically-propagating crack. These microflaws, each of which can be viewed as an aggregation of broken bonds, have sizes which are directly related to the steady-state free-radical concentration.

The association between radical concentration and creep lifetime is not a simple proportionality, however; a cross-plot between $\log C_{ss}$ and $\log t_f$ (t_f being the lifetime) shows that the lifetime varies with approximately the fifth power of the radical concentration. In other words, if the applied stress is raised enough to increase the radical concentration by one order of magnitude, the sample's lifetime is reduced by five orders of magnitude. The lack of a direct-proportion relation seems to indicate that other factors – perhaps chain entanglements, crystallite growth, etc. – besides bond breakage play important roles in the fracture lifetime of solids.

Acknowledgment

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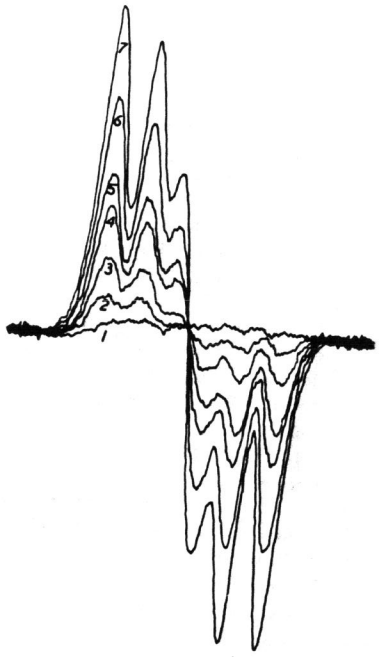

Fig. 1. Quasi steady state EPR spectra for stepwise increases in load. Increasing loads are zero, 100, 110, 115, 120, 127, and 130 ksi.

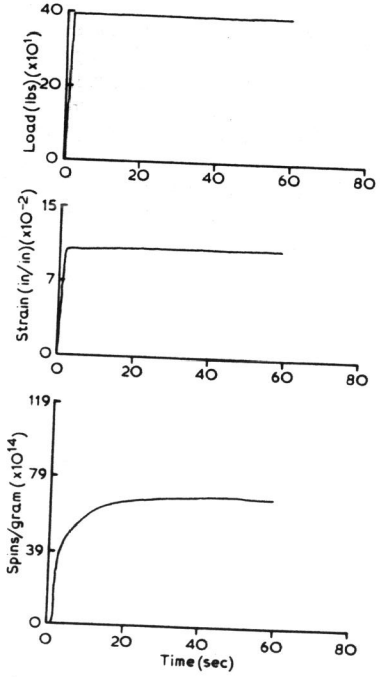

Fig. 2. Free radical production during a constant-load test of drawn Nylon 6 fibers. Samples predessicated and tested in dry N_2 atmosphere at 25° C.

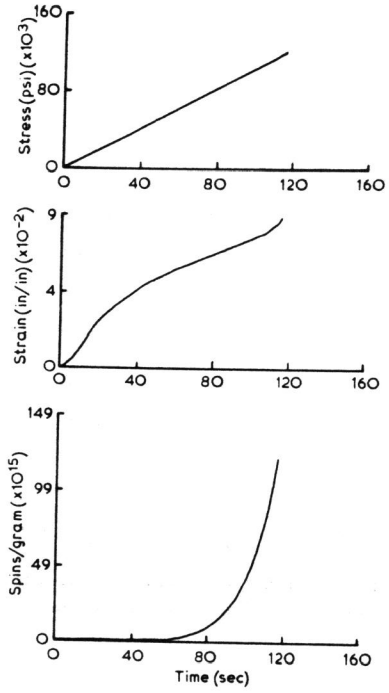

Fig. 3. Free radical production during a constant-load-rate test of drawn Nylon 6 fibers. Sample predessicated and tested in dry N_2 atmosphere at 80° C.

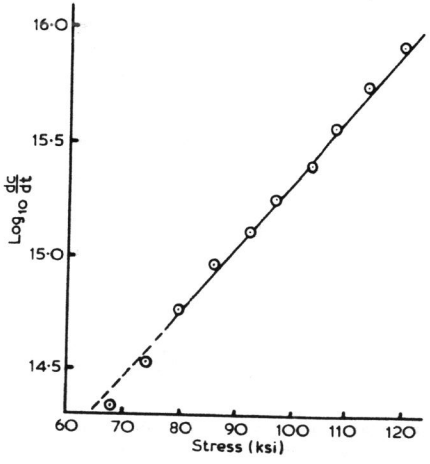

Fig. 4. Bond breakage rate versus stress during a constant-load-rate test. Sample predessicated and tested in dry N_2 atmosphere at 80° C.

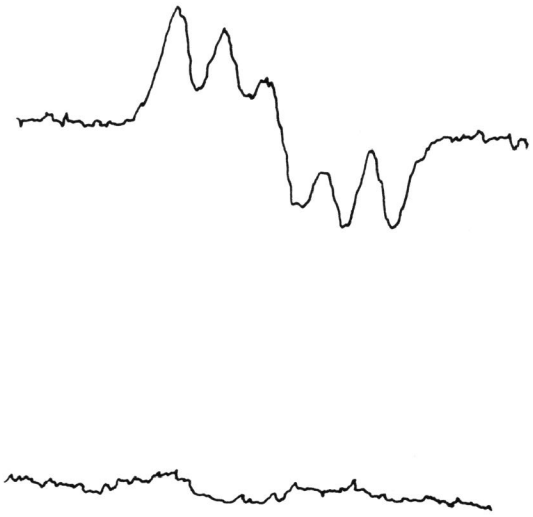

Fig. 5. Upper Curve: EPR spectrum of Nylon 6 fibers after loading at 80,000 psi. Lower Curve: EPR spectrum of same sample after unloading for 24 hours and reloading to 80,000 psi.

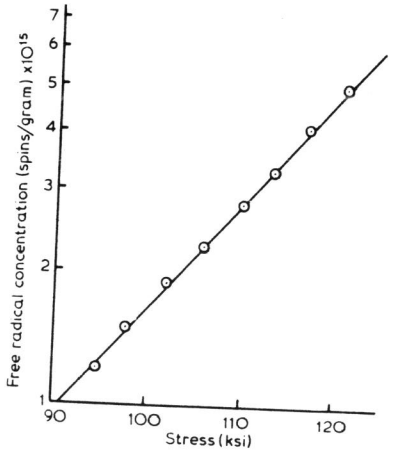

Fig. 6. Steady state free radical (spin) concentration versus stress for drawn Nylon 6 fibers. Samples predessicated and tested in dry N_2 atmosphere at 60° C.

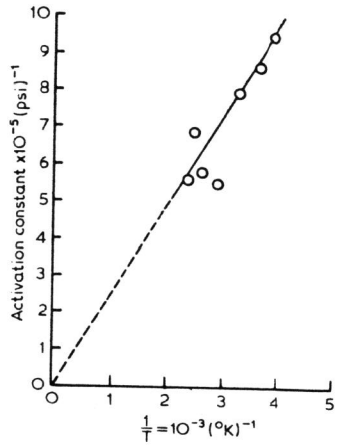

Fig. 7. Activation constant versus reciprocal temperature for drawn Nylon 6 fibers. Samples predessicated and tested in dry N_2 atmosphere.

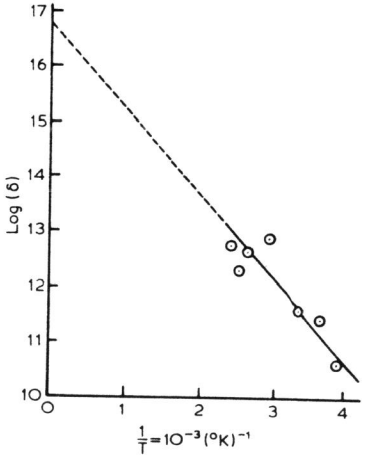

Fig. 8. Logarithm of pre-exponential factor δ versus reciprocal temperature for drawn Nylon 6 fibers. Samples predessicated and tested in dry N_2 atmosphere.