

## Dynamic Mechanical Behavior of a Polyimide

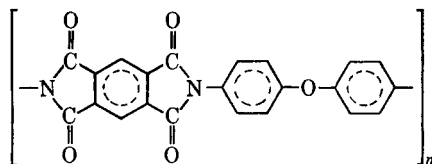
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### Synopsis

The dynamic mechanical properties of a polyimide (poly-4,4'-oxydiphenylene pyromellitimide) were studied from about 4 to 800°K. at audio frequencies. A prominent relaxation associated with absorbed water content occurs near 230°K. Below 270°K., the modulus undergoes a corresponding increase in value with increasing water content. Above 550°K. the onset of a major relaxation process is observed in the modulus data, and a maximum in the internal friction is observed at about 675°K. Minor relaxation peaks are also noted throughout the temperature range. Relatively minor differences are noted in the mechanical relaxation spectra for the polyimide when treated (after drying) with dimethylformamide, dimethylacetamide, and dimethylsulfoxide, whereas the treatment with water after drying has a marked effect on the relaxation behavior. A reactor radiation dose of 3000 Mrad also causes only minor alterations in the dynamic mechanical spectra.

### INTRODUCTION

Polyimides obtained by combining aromatic tetrabasic acid anhydrides with aromatic amines typically have useful high-temperature properties. One such polyimide, Polymer SP (E. I. du Pont de Nemours and Company; their product H-Film is also considered to be essentially the same formulation), which is essentially nonfusible, has been fabricated (by du Pont) in a high-temperature, high-pressure process into finished forms termed Vespel.<sup>1-3</sup> The repeat unit for this polyimide, referred to as poly-4,4'-oxydiphenylene pyromellitimide (POP), is considered to be of the form:<sup>2</sup>



The highly aromatic nature of this system, along with probable crosslinking,<sup>1</sup> tends to make the material relatively rigid over a broad temperature region, while the lack of aliphatic hydrogen makes the material peculiarly resistant to oxidation.

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From viscoelastic-property studies of polyimide polymers, Mair et al.<sup>1</sup> reported no sharp transition regions at temperatures from about  $-100$  to  $+500^{\circ}\text{C}$ ., in agreement with the work of Tatum et al.<sup>4</sup> Ikeda<sup>5,6</sup> has subsequently noted that the polyimide tested in his work exhibited two relaxation processes, one near  $200^{\circ}\text{K}$ . and the other near  $360^{\circ}\text{K}$ . The relaxations observed by Ikeda<sup>5,6</sup> have been confirmed in our laboratories and by others.<sup>7</sup>

This paper is a report on a study of the dynamic mechanical behavior of the polyimide Vespel from approximately  $80$  to  $600^{\circ}\text{K}$ . and, in one case, to  $800^{\circ}\text{K}$ . Since several solvents are important in the preparation and treatment of various polyimide systems, the investigation included the study of the effects of uptake of water, dimethylsulfoxide (DMSO), dimethylacetamide (DMAC), and dimethylformamide (DMF). The effect of reactor radiation on the dynamic mechanical properties also was studied for a dose of about  $3000$  Mrad.

### APPARATUS AND PROCEDURES

The primary apparatus used in this investigation is a modification of that reported elsewhere in the literature.<sup>8</sup> It is essentially a method which uses a free-free bar suspended horizontally and driven at resonance in the first transverse mode. Frequencies used in the investigation varied from about  $350$  to  $700$  cps. In calculations of the storage modulus  $E'$  from measurements of the resonance frequency, the room temperature dimensions and density were used in all cases. This results in an error in the apparent storage modulus as reported in the results but the error is usually not greater than a few per cent.

A longitudinal apparatus was used for obtaining data in the region from about  $4$  to  $100^{\circ}\text{K}$ . for frequencies between  $9300$  and  $9800$  cps. This apparatus is a modification of a type reported in the literature<sup>9</sup> and employs a configuration whereby the sample is driven in a longitudinal mode at one end and the sample response is noted by a detecting device located at the other end.

Materials of this investigation were received in the form of circular rods, which either were used in the as-received condition or were machined to a slightly smaller diameter. Densities and weights of the three samples (I, II, and III) are given in Table I. The densities were obtained by a displacement method. Two of the specimens, I and II, received multiple treatments (as indicated in the table) with dynamic mechanical testing (DMP) made after each treatment. The data for a given series of treatments thus refer to the same original sample although, admittedly, with a different thermal history.

The specimens were dried (after receiving the initial DMP test in the as-received condition) by being placed in a vacuum oven at  $100^{\circ}\text{C}$ . until no appreciable weight change was noted between adjacent weighing periods. The typical time for this drying was  $25$ – $50$  hr. In the preparation of specimen II-B the specimen was submerged in a sealed flask with distilled

TABLE I  
 Characteristics of Specimens

Specimen designation <sup>a</sup>	Density before test at room temp.	Weight, g.		Additive content, wt.-%
		Before test	After test	
I (dried)	1.4267	2.7882	2.7874	—
I (irradiated) 3000 Mrad reactor irradiation	1.4258	2.7848	—	—
II-A (as received)	1.4335	2.8328	2.7910	as received
II-B (dried)	1.4226	2.7906	2.7889	—
II-C (H <sub>2</sub> O)	1.4323	2.8272	2.7931	1.37 H <sub>2</sub> O
II-D (DMSO)	1.4240	2.7996	2.7908	0.23 DMSO
II-E (DMF)	1.4211	2.8003	2.7904	0.35 DMF
II-F (DMAC)	1.4258	2.7972	2.7906	0.24 DMAC
III (as received) <sup>b</sup>	1.431	—	—	—

<sup>a</sup> The prefix I, II or III, refers to the particular sample. The other designation refers to the treatment received.

<sup>b</sup> The sample tested on the longitudinal apparatus was received at a different date but was reported to be of the same batch from which samples I and II were obtained.

water at 50°C. for approximately 100 hr. In subsequent cases, in which other organic liquids (e.g. DMSO, DMF, or DMAC) were added to the sample, specimens were first dried and then similarly submerged in the organic liquid at about 50°C. for 100 hr.

Specimen I was irradiated at The Pennsylvania State University Nuclear Reactor Facility to a dose of approximately 3000 Mrad. At the irradiation position used, the gamma dose rate was about 11.6 Mrad/hr. and the neutron dose rate was about 6.2 Mrad/hr. The temperatures of irradiation were estimated from other similar experiments to be about 40°C. The sample was encapsulated in a triple container of glass, polyethylene, and aluminum before irradiation and the first postirradiation test was carried out within approximately 10 days after the irradiation was completed.

## RESULTS

The dynamic-modulus and mechanical-loss data for specimen II in the as-received, dried, and water-added conditions are shown in Figure 1. From the data of this figure, the as-received polyimide material, designated II-A, is seen to have an internal friction value  $Q^{-1}$  of approximately  $5 \times 10^{-3}$  at 100°K. It rises steadily with increasing temperature from this value to a peak value of about  $3 \times 10^{-2}$  at 230°K. and then falls before going through another broad peak with a height of about  $2 \times 10^{-2}$  in the range of 350 to 400°K. Near 550°K. the internal friction starts to rise and continues to do so, until the highest test temperature (slightly above 600°K.) is attained. The data of Figure 1 also give some evidence of a possible dual peak in

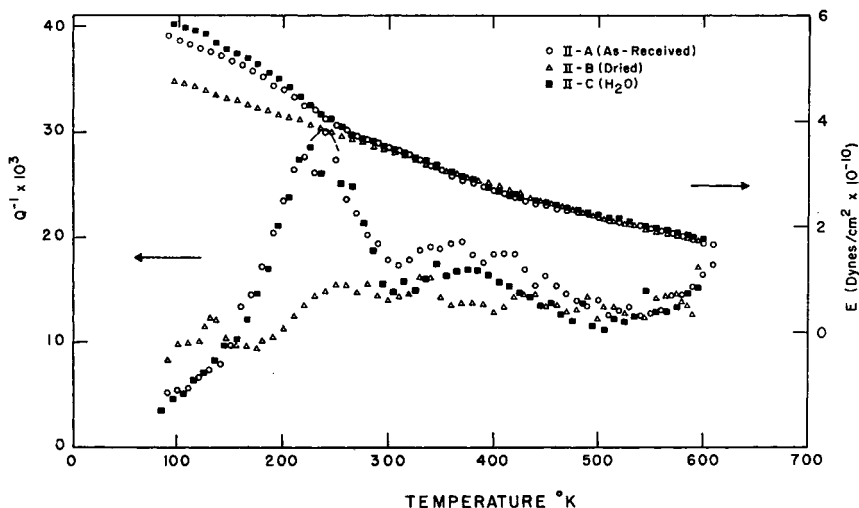


Fig. 1. Elastic modulus and mechanical loss for sample II (A, B, C).

the temperature region near 230°K. and other minor peaks from 300 to 500°K.

Upon drying of the polyimide, it is noted from Figure 1 (sample designation II-B) that the internal friction changes radically. At low temperatures the internal friction is higher and seems to peak slightly near 130°K. A second peak having a value of  $1.5 \times 10^{-2}$  occurs in the data for the dried sample at about 260°K. while other minor peaks occur near 340 and 420°K. Near 600°K. there is some indication that the internal friction rises as in the as-received sample.

From the data of Figure 1 it is noted that the addition of water to the material (specimen II-C) to the extent of about 1.37 wt.-% results in an internal friction spectrum at 100 to 300°K. which somewhat approximates that of the as-received material near 360°K.; beyond 500°K., however, the internal friction rises in a manner similar to the as-received material. It should be noted that from 80 to 200°K. the data for II-A and II-C are very nearly identical and the data for II-B below 150°K. rise above that of II-A and II-C.

The dynamic moduli data of Figure 1 also indicate that the as-received sample (II-A) undergoes a large relaxation near 230°K. Minor inflection points are also present near 360 and 420°K. Upon drying of the polyimide, the moduli data for II-B are almost devoid of the large inflection near 230°K. and throughout the entire temperature region only slight and gradual deviations from straight-line behavior occur. Upon addition of water to the polymer (II-C), the dynamic modulus again exhibits a relatively severe inflection near 230°K. Beyond about 270°K. the data for II-A, II-B, and II-C follow nearly the same curve but close observations show that there are minor differences.

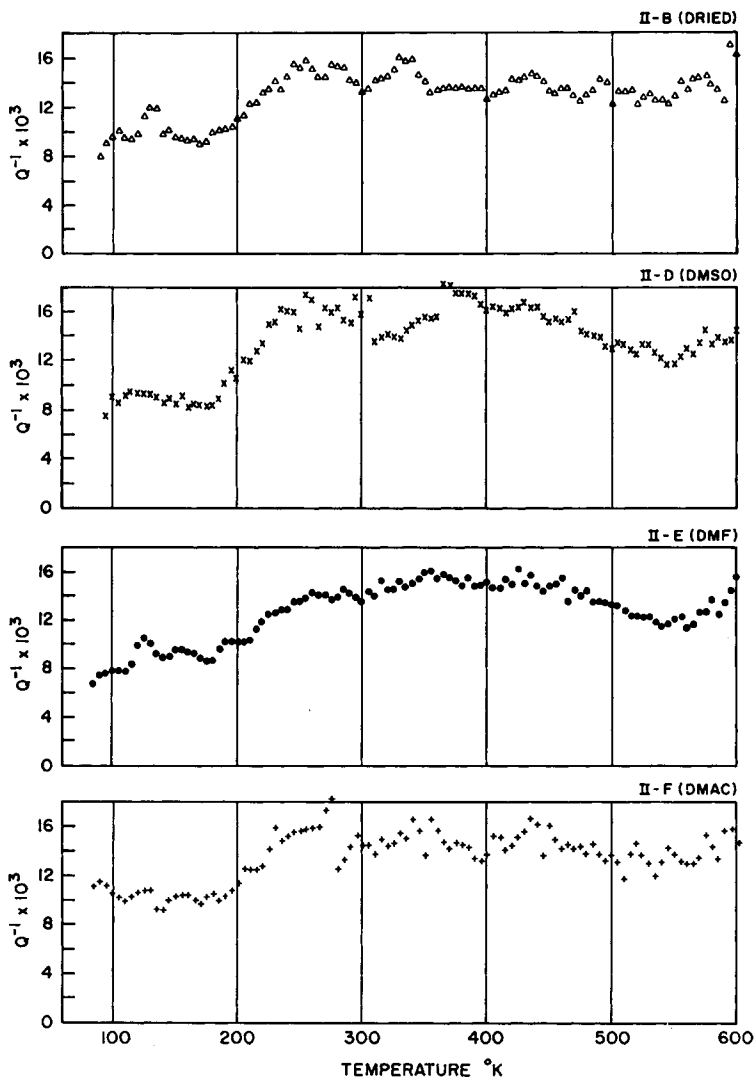


Fig. 2. Mechanical loss for sample II (B, D, E, F).

The internal friction and dynamic modulus of specimens II-D, II-E, and II-F containing, respectively, small amounts of DMSO, DMF, and DMAC, are presented in Figures 2 and 3. Data for the dried sample II-B are also presented for comparison. For specimen II-D, to which 0.23% DMSO has been added, a slight peak appears near 130°K. and a second slight peak also occurs near 260°K. A very broad peak encompassing the range of 300 to 500°K. also is noted for sample II-D. At high temperatures (>550°K.) the internal friction is again beginning to rise with temperature.

The introduction of DMF in the amount of 0.35 wt.-% results in an internal friction behavior (sample II-E) which is similar to that of sample

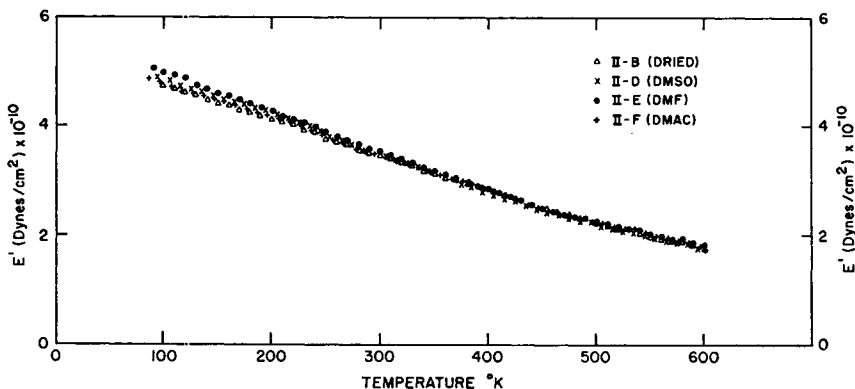


Fig. 3. Elastic modulus for sample II (B, D, E, F).

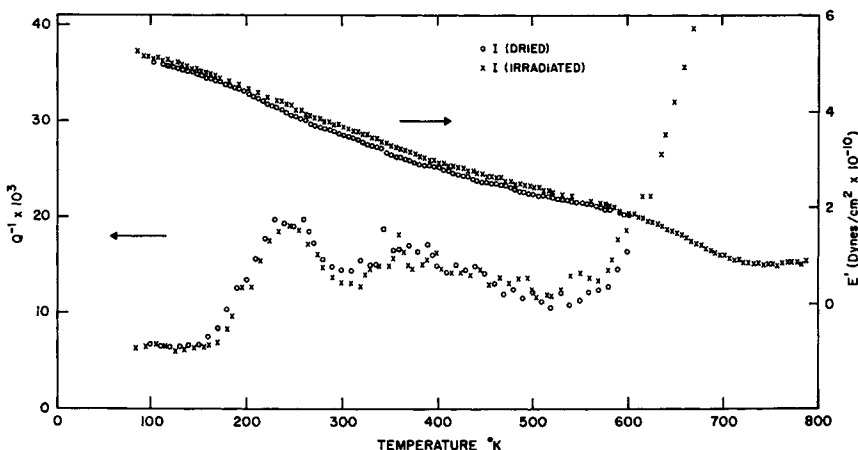


Fig. 4. Elastic modulus and mechanical loss for sample I.

II-B but only traces of a peak from 200 to 300°K. remain. Once again the values at lower temperatures (150°K.) are higher than those for the as-received sample. A broad, smooth peak is centered just below 400°K.

Internal friction data for specimen II-F, to which 0.24% DMAC has been added, are quite similar to the data of the dried sample II-B. Evidence of very slight peaks is present near 260, 340, and 440°K. Below 100°K. the internal friction is the highest recorded in all tests.

Above about 300°K. the modulus behavior of samples II-D through II-F (Fig. 3) is very nearly identical. Below 300°K. the behavior differs slightly from the dried sample (II-B). Specimen II-B has the lowest modulus value in this region and is followed by a slightly higher modulus value for the samples to which DMAC, DMSO, and DMF have been added. As noted earlier, specimens designated II, i.e. II-A-II-F, refer to the same physical sample as reported in Table I.

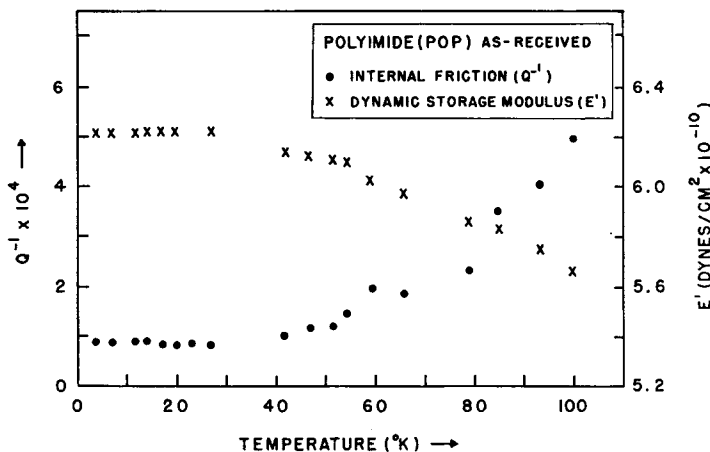


Fig. 5. Elastic modulus and mechanical loss for sample III.

In Figure 4 dynamic mechanical data for an irradiated sample are presented along with the data for the unirradiated sample. The specimen designated I (irradiated) was irradiated and tested in essentially a dried condition (Table I) and is therefore compared to specimen I (dried). From 80 to 300°K. the results are very nearly identical: the height of the peak at 230°K. for both I (dried) and I (irradiated) is higher than that of the other dried sample (II-B) but this may be attributable to a higher residual moisture content, since the density for both of these is higher than the density of II-B (see Table I) and the density appears to increase with increasing water content. Above 300°K. there are some very small differences in the internal-friction spectra of I (dried) and I (irradiated) but their importance is difficult to ascertain. The specimen I (irradiated) was further tested to higher temperatures (800°K.), since it was not needed for further testing. After testing to about 800°K. the sample was badly damaged and would have been essentially unusable. However, evidence of a relaxation process near 675°K. was obtained from the rise in  $Q^{-1}$  and the inflection in the modulus. Below 600°K. irradiation resulted in a slight overall increase in the storage modulus  $E'$ .

Figure 5 presents the dynamic-modulus and the mechanical-loss data for an as-received sample (III) as obtained with the longitudinal apparatus. The modulus appears to be rather temperature-independent from about 4 to 30°K. Above 30°K. it decreases gradually with increasing temperature and there is some evidence of a slight inflection near 100°K. Although the test frequencies are higher (9300–9800 cps) for this apparatus than those for the transverse apparatus (350–700 cps), the modulus values are comparable where the two temperature ranges overlap. As noted in Figure 5, the mechanical loss or internal friction ( $Q^{-1}$ ) for sample III rises from a low value of less than  $10^{-3}$  near 4°K. to about  $5 \times 10^{-3}$  at about 100°K. The  $Q^{-1}$  value at 100°K. compares favorably with that obtained on the transverse apparatus for sample II-A (as received); see Figure 1. There

is some evidence that at least one minor peak is present in the  $Q^{-1}$  data between 4 and 100°K. (near 60°K.).

## DISCUSSION

### Low-Temperature Behavior

Results for the polyimide studied in this investigation show that there is evidence of relaxation processes over the temperature range 80–800°K. The strong relaxation in the as-received material (II-A) near 230°K. appears to be associated with absorbed water. Upon drying in vacuum at 100°C. for 50 hr., this relaxation is substantially reduced (sample II-B), while subsequent soaking in a high-humidity atmosphere for 100 hr. at 50°C. (sample II-C) causes it to reappear at approximately the same strength.

Dynamic-modulus data for the as-received polyimide (Fig. 1) exhibit an inflection point near 230°K., confirming the presence of the relaxation process noted in the damping. Upon drying the inflection is essentially eliminated whereas upon subsequent soaking in water it reappears. The rise in modulus with the addition of water indicates that the water molecules do not act as a plasticizer in this temperature range but instead tend to make the structure more rigid at low temperature.<sup>5</sup> It seems probable that water molecules are involved in hydrogen bonding with the carbonyl oxygen present in the polyimide structure. Since the moduli for samples II-A, II-B, and II-C tend to assume very nearly the same value about 270°K., the bonding action is apparently largely broken by the time this temperature is reached.

Separate experiments on a similar material<sup>7</sup> indicate that the peak height is not directly proportional to the percentage of water present. Tatum et al.<sup>4</sup> list the equilibrium value of 3% for the per cent water absorbed by polyimide in a 100% relative-humidity environment at room temperature (23°C.). Torsion pendulum experiments<sup>7</sup> also indicate that the peak is centered near 186°K. for a frequency of 1.6 cps, and the peak height for approximately the same percentage of water content is essentially equivalent. By means of the data given above<sup>7</sup> and those of the present investigation (230°K., 576 cps), the activation energy of the process may be estimated to be 11.4 kcal./mole.

Ikeda<sup>5,6</sup> has presented data indicating a strong relaxation in the  $G''$  data near 193°K. and a lesser relaxation near 353°K. at a frequency of 1 cps for a film polyimide of pyromellitic acid and 4,4'-oxydianiline. The film had an x-ray crystallinity index of 13%. A molded form with a crystallinity index of 26% exhibited a lower peak at 178°K. and essentially no relaxation process in the 350°K. temperature region. No record of water content was presented. In Ikeda's work it is possible that the higher magnitude of the peak at 193°K. for the film sample is associated with a difference in water content, although differences in crystallinity between the molded and machined samples could conceivably also be a factor.



The repeat unit for the polyimide tested has a molecular weight of 382. For water to be involved in bonding with all the carbonyl oxygens, 4.0 molecules per polyimide repeat group, or about 16% water, would be required. In the present experiments sample II-C absorbed only 1.3% water. Although longer times in a high-humidity atmosphere would cause a further increase in water content, it is doubtful that the percentage would approach 16%. It thus appears that only a fraction of the possible sites can be occupied by water molecules.

NOTE: Heacock and Berr<sup>10,11</sup> list moisture absorption at room temperature in the closely related polyimide H-film as 1.3% at 50% relative humidity and 3.0% at 100% relative humidity.

Weight and density measurements show that absorption of the water is accompanied by some expansion of the material at room temperature. However, the density increases with water content, demonstrating that part of the water molecules tend to occupy space already available in the dried polymer. A coefficient of hygroscopic expansion is given for a similar polyimide, H-film, as  $2.2 \times 10^{-5}$  cm./cm./%RH.<sup>4</sup>

Thus from the evidence now accumulated, it appears that the prominent relaxation occurring near 230°K. in the present investigation, and at lower temperatures for lower frequencies of investigation, is directly associated with water molecules present in the material. It seems probable that the water molecules are attracted and held by hydrogen bonds to carbonyl oxygen atoms in the polyimide chain and that the onset of hindered movement of the water molecules with increasing temperature gives rise to the internal friction peak at 230°K. The bonding of the water results in a higher modulus at lower temperatures but as the temperature approaches 270°K. the bonding gradually decreases and the modulus decreases proportionately. In nylon, absorption of water is known to produce an internal friction peak near 240°K.<sup>12</sup>

The data for sample II-B indicate that a relatively small peak remains near 250°K. after the drying process. It is probably a result of traces of water that remain. However, drying also results in a distinct rise in internal friction below 150°K.; see Figure 1 (this is also noted in torsional-pendulum studies).<sup>7</sup> The addition of water to the system apparently restricts motion at low temperatures, causing the internal friction to drop. The addition of small amounts of DMSO, DMF, or DMAC (Fig. 2) to the dried sample (II-B) does not appear to lower the values of internal friction to the level of sample II-B in the region near 100°K.; see Figure 2. It is noted, in addition, that the uptake of these chemicals is much less on a percentage basis (0.23–0.35%).

The data of Figure 2 show that the addition of small amounts of DMSO, DMF or DMAC has little effect on the relaxation spectrum of dried polyimide in general. This may be largely a result of the relatively low solubilities of these chemicals. However, Figure 3 demonstrates that the low-temperature modulus values increase in each case over those of the dried sample

(II-B), and that DMF, a small molecule (mol. wt., 73), which was absorbed by the polyimide to the extent of 0.35% (compared to 0.23% for DMSO, m. w., 78, and 0.24% for DMAC, m. w., 87), produces the greatest effect.

Experiments on a separate as-received sample (III) with a longitudinal apparatus at 9300 to 9500 cps (Fig. 5) indicate that the internal friction continues to drop as the temperature is lowered below 80°K., reaching a  $Q^{-1}$  value of about  $1.0 \times 10^{-3}$  near 40°K. and of  $0.92 \times 10^{-3}$  near 4°K. Data from the longitudinal apparatus also indicate that  $E'$  continues to rise with decreasing temperature from  $5.67 \times 10^{10}$  dynes/cm.<sup>2</sup> at 100°K. to slightly more than  $6.2 \times 10^{10}$  dynes/cm.<sup>2</sup> near 30°K. and then becomes approximately temperature-independent as the temperature is further decreased toward 4°K. The slight bump in the  $Q^{-1}$  data of Figure 5 near 60°K. and the minor inflection in the elastic modulus in this temperature range suggest that there may be a small relaxation in the as-received material near 60°K. This may indicate the onset of limited oscillation of the phenyl groups or of small segments of additives or impurities.

Although others<sup>5,6</sup> have indicated that crystallinity has been detected in polyimide materials, the x-ray diffraction studies of the material used in this investigation did not result in a crystalline x-ray pattern. This would seem to confirm that the relaxation phenomena noted above are occurring in an amorphous medium in a glasslike phase. Infrared studies of the undried polyimide at room temperature suggest that the water present is relatively unbonded. (The x-ray and infrared studies were made by P. R. Young, of the Spacecraft Materials Research Section, NASA-Langley.) This would appear to be consistent with the observations noted above in which the differences in the magnitude of the modulus, which occur for dried specimens versus specimens containing significant amounts of water, were seen to largely disappear as the temperature was raised from 80 to about 270°K.

### Behavior above Room Temperature

As previously noted, Ikeda<sup>5,6</sup> has reported a broad relaxation peak (about 150°C. in width) occurring in polyimide film near 353°K. (ca. 1 cps), whereas only a trace of a peak at this temperature is noted in the molded sample. He suggested a process analogous to the proposed interplane-slippage process in graphite to explain this loss mechanism. From x-ray studies Ikeda reported that a uniplanar structure existed in his specimens, similar to the graphite structure, with "diffraction planes" of 4 to 5 Å. spacing in the film sample.

From the data of samples II-A and II-C of the present work, one notes a broad relaxation peak centered between 350 and 400°K. In the dried sample (II-B) the broad peak is not discernible. It is doubtful that this loss mechanism is associated with an interplane-slippage process, since there was no evidence of x-ray crystallinity in the sample. All samples (I and II-A-II-F) tend to show a multiplicity of minor peaks superimposed on the data from about 300 to 550°K.

If one assumes that the materials used here are essentially the same as those of Ikeda,<sup>5,6</sup> and if 378°K. is chosen for the temperature of the relaxation peak in the present work (522 cps), i.e. for sample II-C, an estimate of 65 kcal./mole for the activation energy can be obtained. Although multipeak structure has been suggested in studies of other polymers, the origin of the possible multipeak modulation in the data of the present investigation does not appear to be explainable at this time. However, in polyethyleneterephthalate a carbon backbone motion, including that of the phenyl groups, probably occurs by 375°K.<sup>11</sup> Barriers to large-scale rotation of phenyl groups associated with the bis(4-amino phenyl) ether unit might be expected to be somewhat equivalent, and thus a relaxation associated with the onset of this process might be logically expected below 400°K. in the polyimide.

As noted earlier, Mair et al.<sup>1</sup> have reported results of viscoelasticity studies for about 180–785°K. They also reported that the elastic modulus changed but little over a very wide temperature range and that no sharp molecular transition takes place within the region. However, data that they<sup>1</sup> present from their Gehman apparatus appear to show some evidence of inflections in the modulus curves and Cooper et al.<sup>2</sup> present data having an inflection near 675°K. or so. For instance, at the lowest temperature<sup>1</sup> (near 180°K.) the 10 sec. modulus  $E$  (10) or  $3G$  (10) is rising rapidly with decreasing temperature, suggesting that a transition is imminent. Since their measurements correspond to essentially a zero-frequency measurement, one would expect the relaxation peak to appear below 186°K. (186°K. at 1.6 cps).<sup>7</sup> Another indication of a modulus inflection appears near 340°K.,<sup>1</sup> which may be compared with the 350 to 400°K. inflection in the present study for the modulus inflection and relaxation peak (Fig. 1, samples II-A and II-C).

In the present work, a clear indication of the onset of a major relaxation appears beginning near 550°K. in the damping data (Figs. 1 and 3). In the work of Mair et al.<sup>1</sup> there appears to be evidence of a third possible inflection in  $E$  (10) or  $3G$  (10) near 530°K. and above. According to the modulus data of Figure 4 the high-temperature dispersion for sample I (irradiated) appears to center near 675°K. Since the upswings for both the unirradiated and the irradiated cases are rather parallel and little radiation damage is expected,<sup>3</sup> this is probably the approximate peak temperature for the high-temperature dispersion in the modulus of the unirradiated material as well. Tests of a sample from another batch confirmed the presence of this relaxation in the unirradiated material. The fact that the relaxation is not strong compared with that of other polymer systems might be expected, because the polyimide structure is quite rigid and it is reported to be significantly crosslinked in typical cases.<sup>1</sup> The relaxation in the 675°K. region appears to be associated primarily with large-scale, backbone-chain motion, including the anhydride segments. Dynamic electrical data<sup>4</sup> further tend to confirm the existence of relaxation processes through the evidence of electrical damping peaks and comple-

mentary changes in the dielectric constant. Data presented for measurements as a function of temperature (room temperature to 500°K.) and frequency suggest that mechanical relaxations near 1 kc./sec. could be expected both below room temperature and above 500°K. There is also some slight evidence of a third relaxation slightly above room temperature.

The data of Figure 4 suggest that reactor irradiation to approximately 3000 Mrad. at temperatures near 315°K. has little effect on the dynamic mechanical properties, especially between 80 and 600°K. The slight differences between the irradiated and unirradiated cases may be primarily a result of further conversion of the polyimide during the previous high-temperature tests and during the irradiation treatment. Above about 725°K. the modulus of I (irradiated) is very nearly temperature-independent (Fig. 4). The slight rise might be an indication of crosslinking. Supplementary experiments carried out on a different piece of material presumed to be from the same batch confirm that the unirradiated material rises to a large internal-friction value above 550°K. and that the modulus also increases with temperature (rather rapidly) above 700°K. Appreciable thermal degradation occurs during testing at these higher temperatures.

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### References

1. A. D. Mair, M. C. Shen, and A. V. Tobolsky, "High-temperature polymers: H-Film and SP-Polymer," ONR Tech. Rept., Aug. 1964.
2. S. Cooper, A. D. Mair, and A. V. Tobolsky, *Textile Res. J.*, **35**, 1110 (1965).
3. C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Olivier, *J. Polymer Sci. A*, **3**, 1373 (1965).
4. W. E. Tatum, L. E. Amborsky, C. W. Gerow, J. F. Heacock, and R. S. Mallouk, Minutes 5th Conf. Elec. Insulation Conf., Sept. 19, 1963, p. 1.
5. R. M. Ikeda, Div. Polymer Chem., *Am. Chem. Soc., Polymer Preprints*, **6-2**, 807 (Sept. 1965).
6. R. M. Ikeda, *Polymer Letters*, **4**, 353 (1966).
7. J. A. Sauer, private communication.
8. D. E. Kline, *J. Polymer Sci.*, **22**, 449 (1956).
9. J. M. Crissman and R. D. McCammon, *J. Acoust. Soc. Am.*, **34**, 1703 (1962).
10. J. F. Heacock and C. E. Berr, *Stability of Plastics Preprints*, Soc. Plastics Engrs., Inc., Baltimore-Washington Section, June 1964, p. 344.
11. J. F. Heacock and C. E. Berr, *Soc. Plastics Engrs. Trans.*, **5-2**, 105 (1965).
12. A. E. Woodward, J. M. Crissman, and J. A. Sauer, *J. Polymer Sci.*, **44**, 23 (1960).
13. A. E. Woodward and J. A. Sauer, in *Physics and Chemistry of the Organic Solid State*, Vol. II, Interscience, New York, 1965, pp. 637-723.

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