

# A Water-Sensitive Thermomechanical Transition in a Polyimide

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## Synopsis

The effect of water vapor on a polyimide has been investigated in the temperature region of  $-190$  to  $325^{\circ}\text{C}$  using an automated torsion pendulum. A damping peak,  $T_{\text{H}_2\text{O}}$  develops at  $-122^{\circ}\text{C}$  (1 Hz) in the thermomechanical spectra of the polymer which is due to water-polymer interactions. The peak intensifies as the humidity of the conditioning atmosphere, at both  $30^{\circ}$  and at  $325^{\circ}\text{C}$ , increases and attains a limiting value at about 3000 ppm<sub>v</sub> H<sub>2</sub>O. The process is reversible. It is concluded that the number of sites in the polymer for interaction with water is low and limited ( $<0.3$  molecule H<sub>2</sub>O per polymer repeat unit) and, assuming direct proportionality between the intensity of the loss peak and the amount of water adsorbed, that the adsorption of water vapor follows the Langmuir isotherm.

## INTRODUCTION

Water molecules associate strongly with polar polymers through hydrogen bond formation,<sup>1</sup> the exothermic heat of formation of which is in the range of 3.4 to 6.6 kcal/mol.<sup>2-4</sup>

Recent publications<sup>5,6</sup> have reported that a water-sensitive damping peak,  $T_{\text{H}_2\text{O}}$ , appears in the thermomechanical spectra of polyimides obtained using the torsional braid analysis (TBA) technique.<sup>7</sup> This damping peak is in the temperature range of  $-90$  to  $-120^{\circ}\text{C}$  and varies with the molecular structure of the polyimides.<sup>6</sup> In epoxy systems,<sup>8,9</sup>  $T_{\text{H}_2\text{O}}$  appears at higher temperatures (ca.  $-70^{\circ}\text{C}$ ) on the shoulder of a glassy state transition ( $T_{\text{sec}} = \text{ca. } -90^{\circ}\text{C}$ ); both transitions are coupled. The  $T_{\text{H}_2\text{O}}$  damping peak in poly(methyl methacrylates)<sup>10,11</sup> at ca.  $-100^{\circ}\text{C}$  is also on the shoulder of a glassy state transition [ $T_{\text{sec}} = 24^{\circ}\text{C}$  (1.24 Hz)] and also increases in intensity with the humidity level of the conditioning atmosphere. In polyaminoacids<sup>12</sup> two types of  $T_{\text{H}_2\text{O}}$  peaks were reported, at  $-120^{\circ}$  to  $-130^{\circ}\text{C}$  and at  $0^{\circ}$  to  $35^{\circ}\text{C}$ . Table I summarizes results obtained earlier in this laboratory. The effect of water on natural products, such as lecithin and human erythrocyte ghosts, has been investigated elsewhere using TBA.<sup>13</sup> High amounts of water in these materials (66%–100%) produced large differences between the wet and dry materials; distinct peaks developed in the vicinity of  $-120^{\circ}$ ,  $-25^{\circ}$ , and  $35^{\circ}\text{C}$  owing to the presence of water.

Since the location of  $T_{\text{H}_2\text{O}}$  varies with polymer structure, it may be concluded that the relaxations are due to specific associations of water molecules with polymeric materials and not merely to condensation of water on the surfaces of the materials.

The particular polyimide system examined in this work (Fig. 1) is especially suitable for investigating the water vapor effect since the  $T_{\text{H}_2\text{O}}$  damping peak is isolated from  $T_{\text{sec}}$  and is symmetric.

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TABLE I  
 $T_{H_2O}$  Transitions of Polymers

No.	Dianhydride	Diamine	$T_{H_2O}$ , °C	Reference
1			-80 (0.50 Hz)	5
2			-122 (1.01 Hz)	present investigation
3			-100 (0.90 Hz)	5
4			-100 (0.95 Hz)	5
5			-90 (0.88 Hz)	5
6			-100 (0.95 Hz)	5
7			-120 (0.96 Hz)	5
8			-100 (0.86 Hz)	5
9	Poly(methyl methacrylate) (atactic)		-103	10, 11
10	Epoxies		-90	8, 9
11	Polyaminoacids		-120 to -130, 0 to 35	12

Linear aromatic polyimides are formed usually from the reactions of dianhydrides of tetracarboxylic acids with diamines. When the dianhydride is treated in solution with the diamine at room temperature, a polyamic acid is formed; heating yields the polyimide (imidization). If the polyamic acid formation stage is undesirable, a tetraacid can be used in place of dianhydride; the two stages of the reaction then occur together by heating or by adding another anhydride (usually acetic anhydride) to the reaction mixture (Fig. 1). The high glass transition temperatures of the high-temperature polyimides, the low extents of softening which occur through their glass transition temperatures, and the thermal reactions which stiffen the materials on heating above the glass transitions prevent processing by conventional thermoplastic methods. They are therefore formed in the fabrication process from reactive precursors, imidization being completed *in situ*.

TABLE II  
Transition Temperatures of Polyimides

No.	Structure		$T_g, ^\circ\text{C}$	Transitions		Reference
	Dianhydride	Diamine		$T_{sec}, ^\circ\text{C}$	$T_{sec}/T_g, \text{K}/^\circ\text{K}$	
1			>330	? 210	<0.80	5, 6
2			313	135	0.70	present investigation
3			283	112	0.69	5, 6
4			271	94	0.68	5, 6

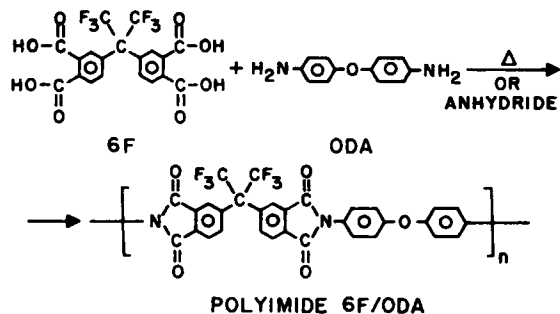


Fig. 1. Synthesis of polyimide.

The current report deals with a recently introduced commercial system (du Pont NR-150A2) which is outlined in Figure 1.<sup>14</sup> In particular, an attempt has been made to correlate the intensity of the H<sub>2</sub>O damping peak of the polyimide to the level of water vapor and to the temperature of the conditioning atmosphere.

## EXPERIMENTAL

### Materials and Sample Preparation

The precursor solution was made from a stoichiometric mixture of the 6F tetracarboxylic [2,2-bis(3',4'-dicarboxyphenyl)hexafluoropropane] and 4,4'-oxydianiline dissolved in a 3:1 mixture by weight of N-methylpyrrolidone and ethanol. A composite specimen of polymer precursor and glass braid was utilized for the torsion pendulum studies. After mounting a solution-impregnated braid, solvent was removed from the specimen and the imidization reactions were completed in the TBA apparatus *in situ* in He by heating the specimen to 325°C for 5 hr. After cure, the composite specimen contained 48% by weight of polymer. The intrinsic viscosity of such a polymer in concentrated H<sub>2</sub>SO<sub>4</sub> at 25°C is about 0.8 dl/g.<sup>14,15</sup>

### Instrumentation and Data Representation

#### *Torsional Braid Analysis (TBA)*

Thermomechanical TBA spectra were obtained using a fully automated torsion pendulum analysis system.<sup>7,16-18</sup> (A version of the system is commercially available from Plastics Analysis Instruments Inc., P.O. Box 408, Princeton, N.J.) A hard-wired analog computer (data reducer)<sup>17,18</sup> provided automatic alignment of the transducer, initiation of oscillations of the pendulum, printing of the values of the temperature (in mV, from an iron-Constantan thermocouple), period ( $P$ , in sec), and logarithmic decrement ( $\Delta$ ) of the damped oscillations [ $\Delta = (1/n) \ln (A_i/A_{i+n})$ , where  $A_i$  is the amplitude of deformation of the  $i$ th oscillation and  $n$  is the number of oscillations between two fixed arbitrary boundary amplitudes in each wave]. The reduced data were also presented on an XY recorder versus the temperature (or time) as the logarithm of the relative rigidity ( $1/P^2$ ) (which

is a good approximation<sup>19</sup> for the relative elastic shear modulus  $G'$ ) and the logarithm of  $\Delta$ .

Constant and different levels of water vapor in the atmosphere were obtained by mixing wet and dry gas streams of He.<sup>8</sup> The levels of water were measured by an electronic hygrometer in the outlet port of the apparatus and ranged from 20 to 10,000 ppm<sub>v</sub> (parts per million on a volume basis) of H<sub>2</sub>O in He.

### *TGA and DTA*

TGA and DTA measurements were recorded on a du Pont 950 thermogravimetric analyzer and on a du Pont 900 differential thermal analyzer. The precursor solution was used "as received."

## **Experiments**

### *TBA*

A single specimen was used. The uncured specimen was heated to 325°C at a rate of 1.5°C/min (the rate used in all the TBA experiments) and postcured by continued heating for 5 hr at 325°C in 20 ppm<sub>v</sub> H<sub>2</sub>O/He in order to provide a specimen which would be chemically inert at 325°C. A spectrum of the "dry" specimen was then recorded on decreasing and then on increasing the temperature (325° → -190° → 325°C) in order to check reversibility of the data. The specimen was conditioned at 325°C at a constant level of water vapor for a measured time and the spectrum was recorded, using the same input atmosphere used for conditioning, again in the two directions of change in the temperature (325° → -190° → 325°C) in order to investigate hysteresis phenomena, including the effect of condensation of water on the specimen. The specimen was cooled to 30°C and conditioned at the same level of water vapor and period of time; and then a plot was taken (30° → -190° → 30°C), again using the input atmosphere used for conditioning the specimen. The temperature was then increased to 325°C, and a new cycle with a different level of water vapor was undertaken.

On cooling below 0°C water freezes on the walls of the apparatus, and the level of water vapor in the atmosphere around the specimen decreases (Fig. 2). However, the amount of trapped water in the polymer remains unchanged.<sup>8</sup> As the temperature is raised through 0°C, the condensed water evaporates, thus increasing the level of water in the atmosphere; at higher temperatures it decreases to the original level. Since the polymer was exposed to high humidity during this process, the specimen was heated to 325°C in order to eliminate water prior to reequilibration with a different level of water vapor.

### *TGA*

Prepolymer solution (~8 mg) was used "as received." The relative weight was recorded versus temperature to 325°C in N<sub>2</sub> (5 ppm<sub>v</sub>H<sub>2</sub>O). At 325°C an isothermal experiment was run for 135 min, and then the sample was heated to 750°C (Fig. 5,  $\Delta T/\Delta t = 5^\circ\text{C}/\text{min}$ ).

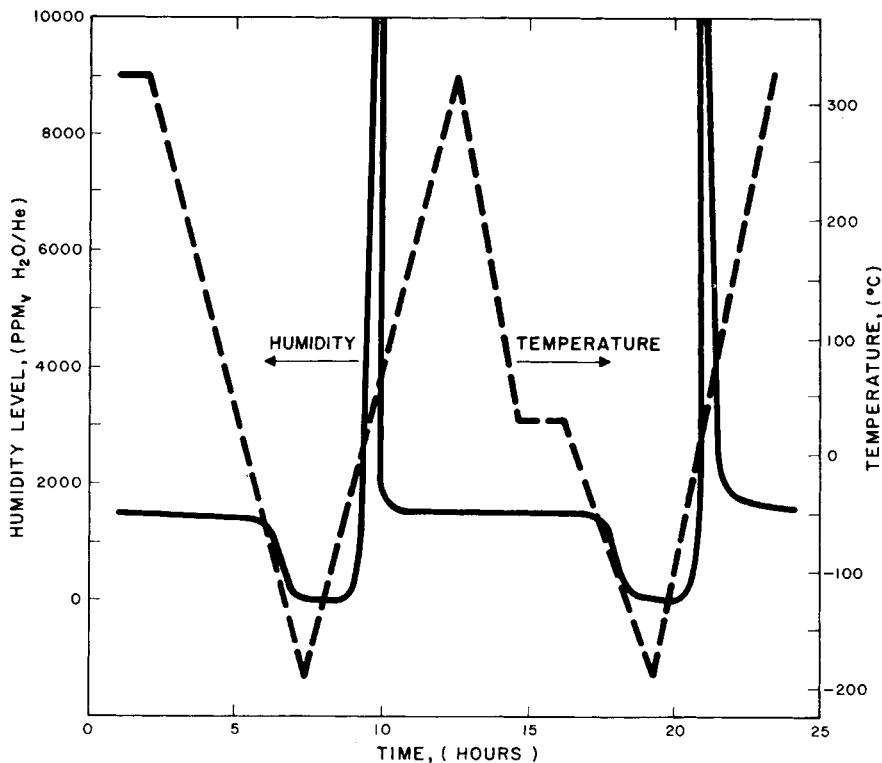


Fig. 2. Temperature and humidity level (expressed as parts per million of water in helium on a volume basis) for a constant setting of the humidity system vs time in the TBA system. Conditioning at 325°C and at 30°C was at 1500 ppm H<sub>2</sub>O.

## RESULTS AND DISCUSSION

### Cure

The thermomechanical data of Figure 3 show the changes that occur on heating the unreacted "as received" material to 325°C. It is evident that the removal of solvents and the imidization reaction proceed rapidly in the vicinity of 170°C. This is in accord with other experiments.<sup>14,15</sup>

After the above cure, the transitions were (Fig. 3):  $T_g = 313^\circ\text{C}$  (0.62 Hz),  $T_{\text{sec}} = 135^\circ\text{C}$  broad (1.0 Hz),  $T_{\text{H}_2\text{O}} = -117^\circ\text{C}$  (1.1 Hz). The latter ( $T_{\text{H}_2\text{O}}$ ) relaxation is not observed after postcuring at 325°C for 5 hr in a dry atmosphere (20 ppm<sub>v</sub> H<sub>2</sub>O/He) (Fig. 4) but reappears after exposure to water vapor (Fig. 6). After the postcure, the  $T_g$  had risen to 319°C (0.61 Hz), but  $T_{\text{sec}}$  was unchanged. Another glassy state relaxation,  $T < -190^\circ\text{C}$ , is apparent in the dry material (Fig. 4). Hysteresis is observed immediately below  $T_g$  (Fig. 4).

The reported<sup>14</sup>  $T_g$  (285°C) is lower than the present results due to the undercure of the different thermal treatments. TGA experiments (Fig. 5) show that a small loss of weight occurs particularly during the first 2 hr of postcure at 325°C. The polymer is then stable to above 500°C.

The thermomechanical behavior of the polyimide is consistent with previous investigations.<sup>5,6</sup> As expected, the damping curve of the polyimide is similar to those of polyimides derived from benzophenonetetracarboxylic acid and from

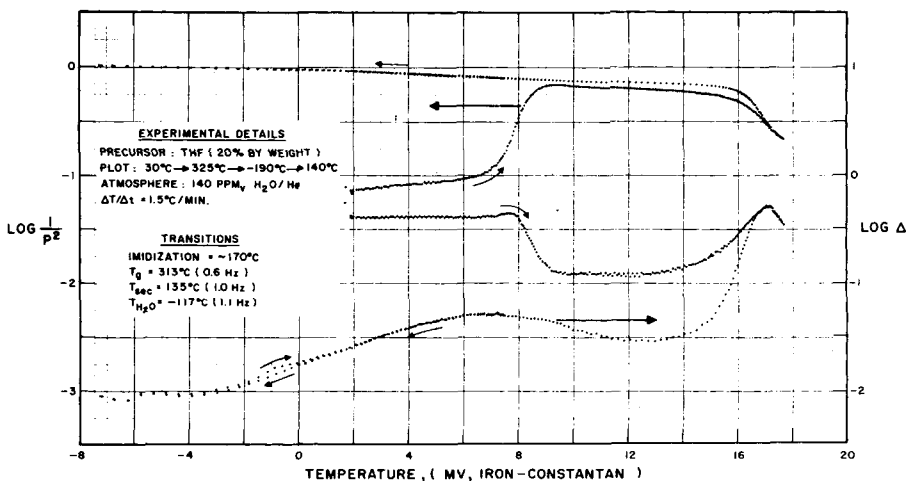


Fig. 3. Thermomechanical spectra of polyimide precursor (30° → 325°C) and polyimide (325° → -190° → 140°C).

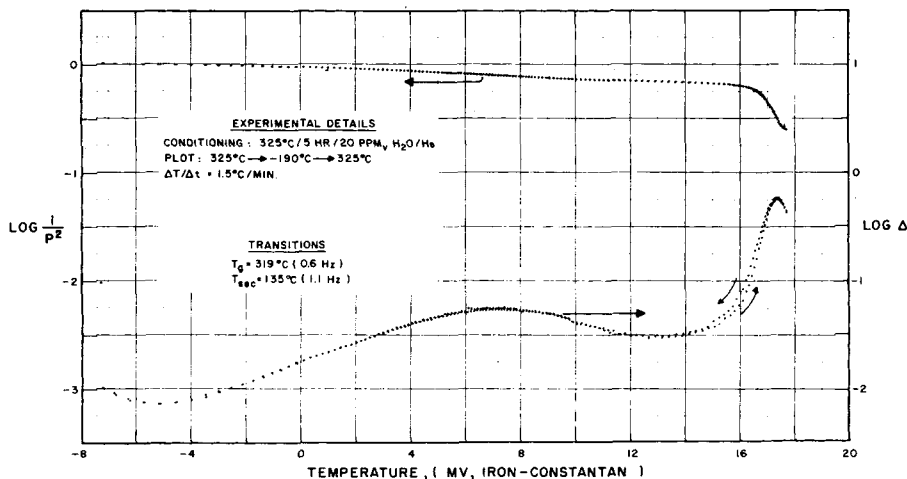


Fig. 4. Thermomechanical spectra of polyimide after conditioning in a dry atmosphere.

$[(\text{COOH})_2\text{C}_6\text{H}_3]_2\text{Si}(\text{CH}_3)_2$  with 4,4'-oxydianiline (Table II, polymers 3 and 4). In these three cases the spectra consist of sharp  $T_g$  and broad  $T_{\text{sec}}$  transitions. Although  $T_g$  depends on the specific structure of the polymer, the ratio  $T_{\text{sec}}/T_g$  ( $^{\circ}\text{K}/^{\circ}\text{K}$ ) is unchanged (0.68–0.70) for both the reported and for the present work. A water-sensitive loss peak in the vicinity of  $-100^{\circ}\text{C}$  is also observed in the three polymers.

Incorporation of the perfluoroisopropylidene group between the aromatic rings results in increased chain flexibility over that of pyromellitic dianhydride (PMDA). However, motion between the two aromatic rings of the tetraacid is restricted by the trifluoromethyl groups in comparison with the effect of the carbonyl and  $\text{Si}(\text{CH}_3)_2$  linkages. The result is a higher  $T_g$  than for polymers 3 and 4 but lower than for the more rigid polymer 1 (Table II).

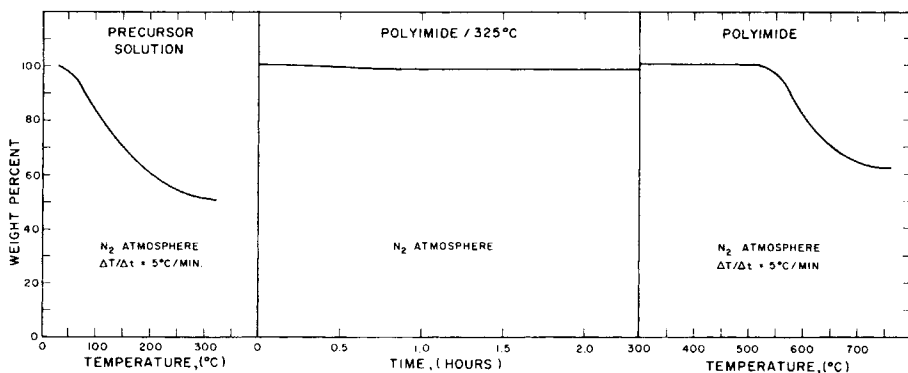


Fig. 5. Thermogravimetric analysis of polyimide.

### Effect of Water

When water vapor is introduced in the atmosphere a  $T_{\text{H}_2\text{O}}$  peak at  $-122^\circ \pm 2^\circ\text{C}$  (1.0–1.1 Hz) emerges in the polyimide spectra (e.g., Fig. 6). According to previous publications,<sup>5,6</sup>  $T_{\text{H}_2\text{O}}$  appears in polyimide spectra even when the atmosphere is "dry." Water elimination was effected in some of the polymers only when the polyimide was heated overnight at  $130^\circ\text{C}$ , i.e., below  $T_g$  (e.g., Table I, polymer 1). Drying could be accomplished with the presently examined polyimide only by heating above the  $T_g$  of the polymer, where diffusion is facilitated.<sup>20</sup>

Experimental results showing the  $T_{\text{H}_2\text{O}}$  transition versus level of water vapor in the conditioning atmosphere at  $30^\circ\text{C}$  are summarized in Figures 7 and 8. (The time for equilibration was found to be less than 1 hr at  $30^\circ\text{C}$ .) The peak is isolated from  $T_{\text{sec}}$  and does not affect  $T_g$  and  $T_{\text{sec}}$ . Since it is also symmetric and its location is not affected by its intensity (Table III), the observance of its change as a function of the external humidity is simplified. Its intensity reaches a limiting value in the vicinity of levels of 3000 ppm  $\text{H}_2\text{O}$ .

When a humid atmosphere is introduced into the TBA apparatus at temperatures below the frost point of water (on heating or cooling),  $T_{\text{H}_2\text{O}}$  does not ap-

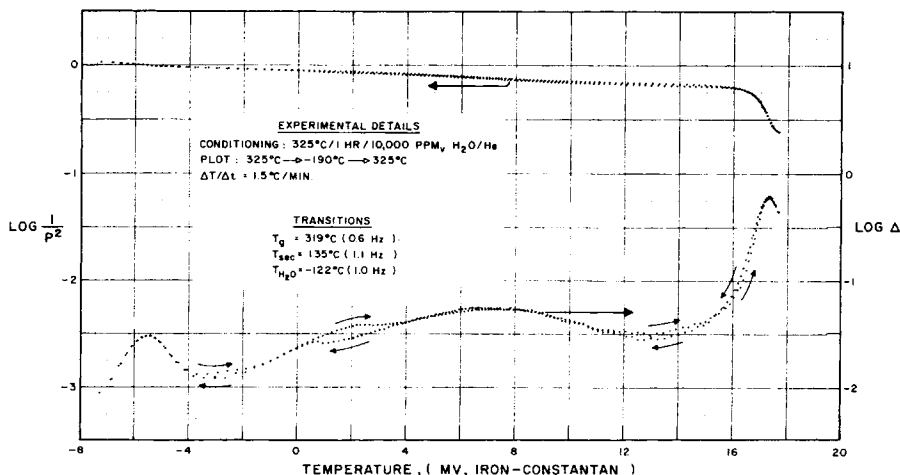


Fig. 6. Thermomechanical spectra of polyimide after conditioning in a humid atmosphere.



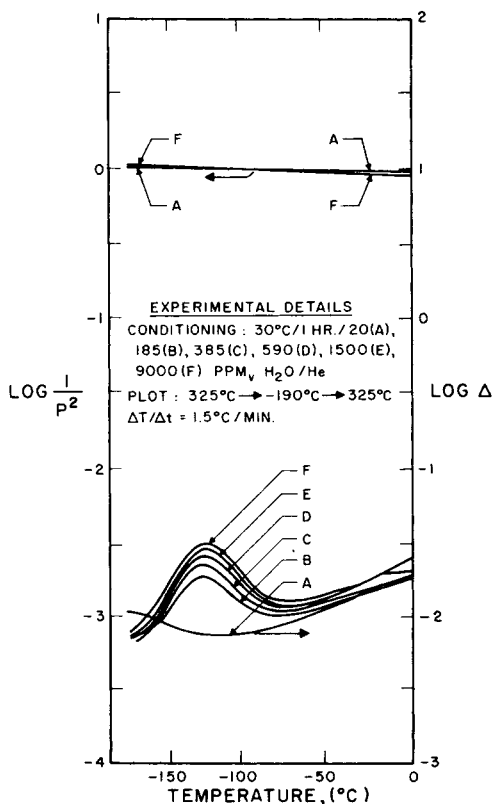


Fig. 7.  $T_{H_2O}$  transition after conditioning at 30°C at different humidity levels.

pear.<sup>8,9</sup> Thus, it is concluded that  $T_{H_2O}$  is due to polymer-water interactions and not simply to an intrinsic property of condensing water. This interaction is probably caused by hydrogen bonding, which is observed in the IR spectra of the polyimide.<sup>15</sup>

The maximum capacity of water in the polymer, assuming five binding sites per repeat unit, is 12.9% (weight water/weight "moist" polymer). The actual take-up of water in the plateau region after conditioning at 30°C was found to be less than 1% by weight measurement. This low water absorption agrees with results of other workers.<sup>14,15</sup> The low pickup of water is related to the hydrophobic character of the polymer, which contains six fluorine atoms and four aromatic groups in each repeat unit. The reversibility of the water effect is apparent from a comparison of Figures 9 and 4. When the polymer was dried at 325°C (5 hr), the peak at  $T_{H_2O}$  diminished almost to the original intensity.

Two different temperatures for conditioning were chosen, one above the glassy state (325°C) and one close to room temperature (30°C). The specimen was conditioned at the desired level of water vapor and temperature for 1 hr. Longer times (5 hr) did not affect the results. As is seen in Figure 8, larger values of  $\Delta$  were obtained at 30°C than at 325°C for low levels of water vapor (up to ca. 2000 ppm H<sub>2</sub>O/He). At higher levels of water vapor, the same plateau value for  $\Delta$  was reached for both temperatures. Since the equilibration time is relatively short, a reequilibration occurs as the temperature decreases to 30°C during the thermomechanical experiment. Therefore, the real difference of the water pickup

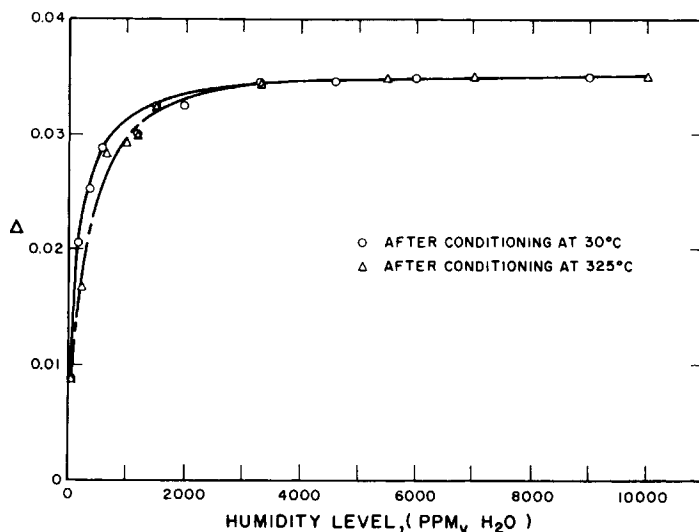


Fig. 8. Plot of  $\Delta$  at  $T_{H_2O}$  vs humidity level of conditioning atmosphere at 30°C: (○) after conditioning at 30°C; (△) after conditioning at 325°C.

TABLE III  
 $T_{H_2O}$  Transition at Different Humidity Levels After Conditioning at 30°C

ppm <sub>v</sub> H <sub>2</sub> O/He	$T_{H_2O}$ , °C	Frequency, Hz	$\Delta$
20	-118	1.10	0.00854 ( $\Delta_0$ )
180	-121	1.11	0.02088
385	-120	1.10	0.02529
590	-120	1.10	0.02878
1200	-124	1.12	0.02998
1500	-122	1.10	0.03248
2000	-122	1.12	0.03248
3300	-121	1.11	0.03457
4600	-124	1.11	0.03469
6000	-120	1.10	0.03498
9000	-121	1.10	0.03492
>10000	-119	1.10	0.03511 ( $\Delta_{max}$ )

at these two temperatures should be higher than that observed. The additional thermal hysteresis in the temperature region of 190° to 280°C (cf. Figs. 4 and 6) provides supporting evidence for polymer-water interactions, even in the high-temperature region. Because of the low pickup of water and the low retention of it at high temperatures, no significant decrease in  $T_g$  could be observed on account of plasticization by water.

In previous investigations on epoxy systems,<sup>8</sup> it has been shown that higher absorbance of water at low temperatures, as in the present system, supports a theory of bond formation between water and the polymer rather than simple mixing. According to a parallel approach, the free water molecules in the external atmosphere are in equilibrium with the bound water. Since the formation of hydrogen bonds is an exothermic process, the value of the equilibrium constant ( $\alpha$ ) is decreased by increasing temperature ( $d \ln \alpha / dT = \Delta H / RT^2$ , where  $\Delta H$  is the heat of interaction). A decrease in  $\alpha$  at higher temperatures leads to a decrease in the equilibrium conversion, which leads to a lower pickup of water, as was obtained.

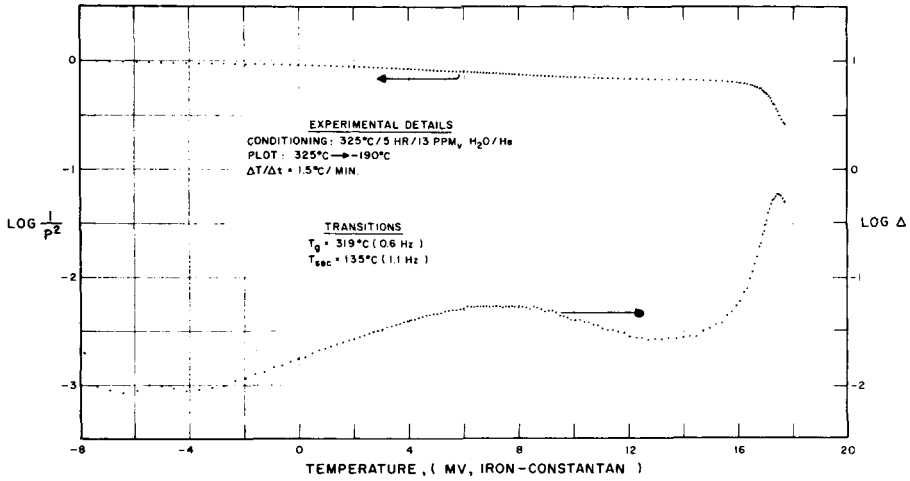


Fig. 9. Thermomechanical spectra of polyimide dried after conditioning in the sequence of humid atmospheres used in the experiments.

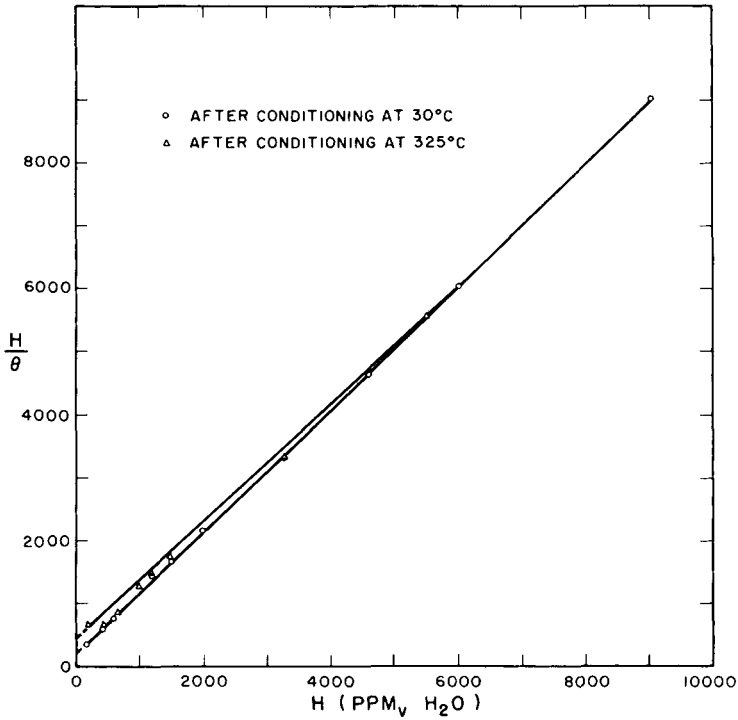


Fig. 10. Langmuir plots of  $H/\theta$  vs  $H$  (see text): (O) after conditioning at 30°C; ( $\Delta$ ) after conditioning at 325°C.

The plateau value of  $\Delta$  (Fig. 8), which is reached at relatively low levels of water vapor (ca. 3000 ppm), and the small change in the value of  $1/P^2$  (Fig. 7) (the relative value of  $1/P^2$  is dependent on the dimensions of the specimen) indicate that at high humidity there is no significant change in the mass of the specimen—implying that the observed  $T_{H_2O}$  is not due to water condensed on the polymer.

Thermal hysteresis develops in the temperature range of  $-45^{\circ}$  to  $20^{\circ}\text{C}$  at low levels (180 ppm) and shifts up to from  $4^{\circ}$  to  $77^{\circ}\text{C}$  at higher levels (10,000 ppm) of water vapor. A significant change in maximum values of  $\Delta$  is also observed, i.e., 0.02545 ( $-4^{\circ}\text{C}$ , 1.07 Hz) for the former and 0.04495 ( $52^{\circ}\text{C}$ , 1.02 Hz) for the latter. As can be seen from Figure 6, small changes in the values of  $1/P^2$  exist in this region which depend on the direction of temperature change. The hysteresis loop differs from  $T_{\text{H}_2\text{O}}$  (Table III) in that it increases with the humidity level without reaching a limit, and it is coupled with the water flash-off from the apparatus (Figs. 2 and 6). Therefore, it is concluded that this hysteresis is due to plasticization of the polymer by water. The shift in the hysteresis region results from elimination of the plasticizing water which occurs at higher temperatures for higher levels of water vapor in the atmosphere.

That the  $T_{\text{H}_2\text{O}}$  transition of the polyimide occurs at a lower temperature ( $-122^{\circ}\text{C}$ ) than for poly(methyl methacrylate) ( $-100^{\circ}\text{C}$ ) suggests that the water bound to a polar site in the rigid polyimide backbone moves more readily (i.e., at lower temperatures) than when bound to the polar site of the ester side group. In polyimide the water transition is not coupled to an obvious secondary relaxation of the polymer, whereas it is presumably coupled to the motions of the ester group in poly(methyl methacrylate).

In order to investigate the effect of water vapor on the polyimide quantitatively, the external humidity was increased incrementally and the development of the thermomechanical spectra was followed. A plot of  $\Delta$  at the maximum of  $T_{\text{H}_2\text{O}}$  versus the humidity level expressed as ppm<sub>v</sub> H<sub>2</sub>O in He (Fig. 8) is similar to the plot of amount of gas adsorbed versus its pressure for the case of one molecule occupying a single site.<sup>21,22</sup>

Assuming that  $\Delta$  at the peak is proportional to the volume fraction of the lossy part of the solid,<sup>23</sup> and using the direct proportionality of level of water vapor (ppm<sub>v</sub> H<sub>2</sub>O/He) to the partial vapor pressure of water in the gas mixture, Langmuir's equation<sup>21</sup> should be applicable:

$$\frac{p}{\theta} = \frac{1}{a} + p$$

Where  $p$  is the gas pressure,  $\theta$  is the fraction of the occupied sites, and  $a$  is a factor which is considered to be dependent on the temperature alone and is defined as follows:

$$\frac{1}{a} = \left( \frac{K}{\delta} \sqrt{2Mkt} \right) e^{-q/RT}$$

Here,  $K$  is a velocity constant of desorption,  $\delta$  is a probability factor,  $M$  is the molecular weight of the adsorbed species,  $k$  is the Boltzman constant,  $T$  is the temperature in  $^{\circ}\text{K}$ ,  $q$  is the heat of adsorption per gram molecule, and  $R$  is the gas constant.

If  $\Delta - \Delta_0$  (for the same specimen) is linearly dependent on the water concentration in the polymer, as assumed, then

$$\theta = \frac{\Delta - \Delta_0}{\Delta_{\text{max}} - \Delta_0}$$

where  $\Delta_0$  and  $\Delta_{\text{max}}$  are the minimum and the maximum values respectively, of  $\Delta$  at  $T_{\text{H}_2\text{O}}$ .

A plot of  $H/\theta$  versus  $H$  (humidity level, in ppm<sub>v</sub>) gives a straight line (Fig. 10)

with slope  $45^\circ$ , as expected. The increase of the intercept with the temperature also agrees with the anticipated behavior of  $1/\alpha$ .

## CONCLUSIONS

The present investigation demonstrates the utility of the TBA method in detecting the presence of small amounts of water in polyimide systems. More specific correlations between the peak intensity, location (temperature) and molecular architecture of polymers will be sought using systematic series of polymers and reactants.

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