

## Thermomechanical and Thermogravimetric Analyses of Systematic Series of Polyimides

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### Synopsis

Twelve polyimides which differ systematically in chemical structure were investigated in nitrogen through the temperature range  $-190^{\circ} \rightleftharpoons 500^{\circ}\text{C}$  by torsional braid analysis. The degradative regions were also examined in nitrogen by thermogravimetric analysis. Relationships between chemical structure/thermal history, processibility, thermomechanical behavior, and weight loss are discussed. A logical thermal program for converting the precursor polyamic acid solutions to solid polyimides was developed. High-temperature, thermally induced chemical reactions could be regulated so as to preferentially freeze out longer-range relaxations and extend the glass state behavior to well above its original load-limiting  $T_g$ . Materials made from more flexible molecules had lower glass transitions, softened more through the  $T_g$ , and had simpler damping spectra and lower thermal stability than materials made from more rigid molecules. A commercially available polyimide film and polyimide-forming varnish of undisclosed structures were examined by torsional pendulum and torsional braid analyses, respectively. The thermomechanical spectra of the film and cured varnish were similar to the spectra of one structural type of polyimide.

### INTRODUCTION

Linear aromatic polyimides formed formally from the reaction of tetracarboxylic acids with diamines have been commercially available as laminating, coating, and adhesive varnishes, as molding compounds, and as films and machinable bulk solids since the early 1960's. The du Pont and Monsanto systems are probably based on pyromellitic dianhydride and benzophenone tetracarboxylic acid dianhydride, respectively. Polyimides are the best readily available organic materials for structural use at elevated temperatures ( $>250^{\circ}\text{C}$ ). Attributes include high-temperature oxidative stability and electrical insulating properties, toughness and flexibility at cryogenic temperatures, nonflammability, and resistance to radiation (ultraviolet and high energy). Polyimides are prime wire-coating materials. A major drawback of polyimide systems is that they cannot be processed by conventional thermoplastic methods. This is a consequence of their high glass transition temperatures, the low extent of softening which occurs through the glass transition regions, and the thermal reactions which stiffen the materials once soft. Precursors in the form of solutions of reac-

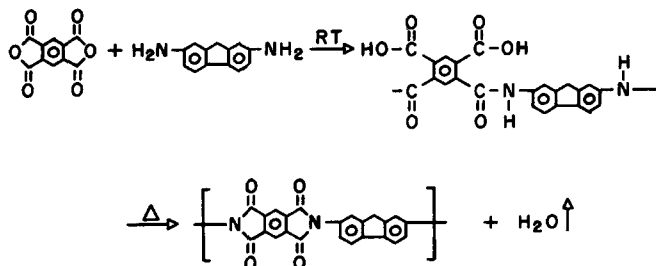


Fig. 1. Reaction of dianhydride + diamine  $\rightarrow$  polyamic acid  $\rightarrow$  polyimide.

tive polyamic acids are therefore used for fabrication, and a subsequent high-temperature in situ thermal step is necessary to remove solvent and complete imidation reactions (e.g., see Fig. 1). The by-products of the latter processes lead to problems and limit the use of polyimide materials.

The present report deals with relationships between chemical structure/thermal history, processibility, thermomechanical behavior, and degradation. Acute sensitivity of the thermomechanical spectra of the polar materials to trace amounts of water is also illustrated.

The basic problem is how to obtain the best thermomechanical properties from a reactive intermediate (which generates a by-product on cure). In principle, thermogravimetric analysis (TGA) could be used to determine the cure cycle by finding a temperature region where volatilization (due to removal of solvent and by-products) has ceased and degradation has not yet commenced. Torsional braid analysis<sup>1</sup> (TBA) could then be used to characterize thermomechanical behavior. However, a simple distinction between cure and degradation often cannot be made by TGA since weight is lost continuously. Furthermore, thermal crosslinking reactions might well occur and need not involve significant loss of weight. This raises another question since these latter reactions may be desirable for the final product. Is the process to be designed for obtaining a chemically pure polyimide or the best material from a polyimide? From the point of view of molecular control, the former is the goal, while for pragmatic use the latter is the objective.

## EXPERIMENTAL

The soluble precursors to the polyimides were synthesized and provided by Dr. V. L. Bell and Dr. N. Johnston of NASA, Langley Research Center, Hampton, Virginia. The provided prepolymer solutions of polyamic acid (10% in dimethylacetamide, weight/volume) were prepared by reacting equal moles of dianhydride and diamine in dimethylacetamide at room temperature. Polyimides were prepared from prepolymer solutions of polyamic acids in dimethylacetamide (bp = 166°C) by removing solvent and effecting a ring-closure reaction in situ (e.g., Fig. 1).

The experimental techniques employed for this investigation were torsional braid analysis<sup>1</sup> and thermogravimetric analysis.

## RESULTS AND DISCUSSION

## Effect of Cure

The thermomechanical spectra in dried nitrogen of two specimens prepared from the same prepolymer sample are shown<sup>2,3</sup> in Figure 2. The top

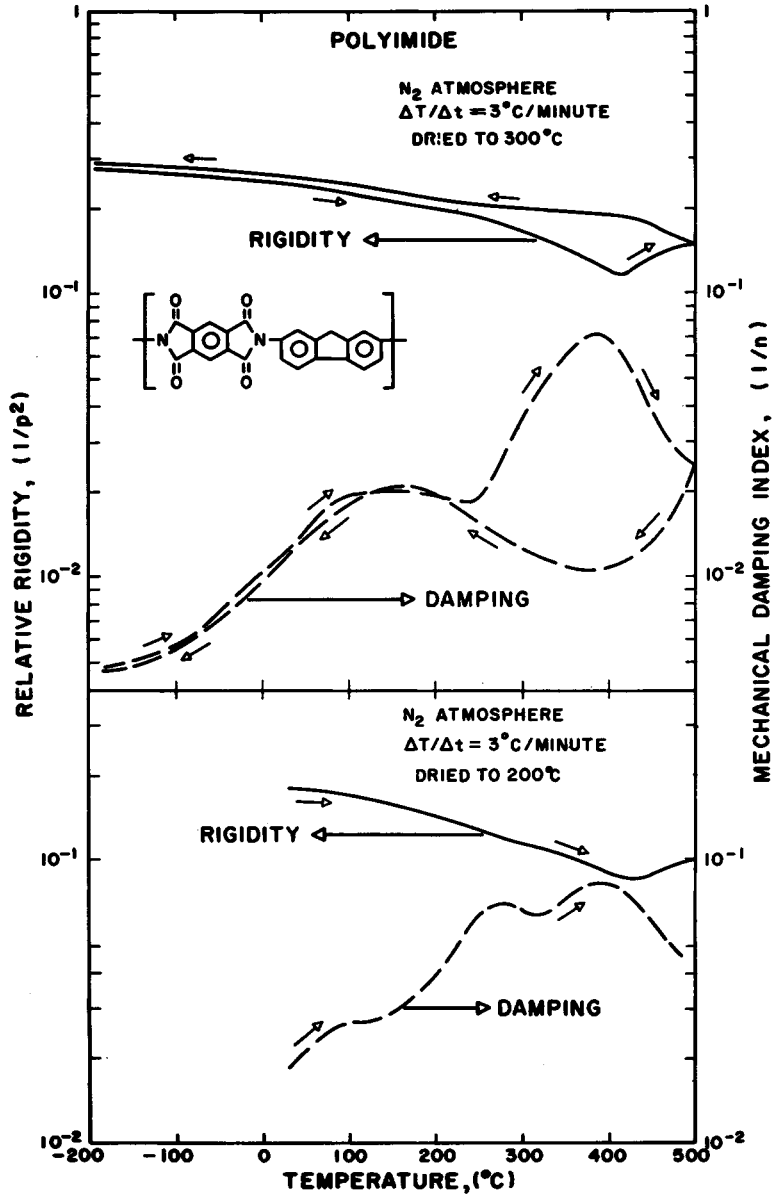


Fig. 2. Effect of thermal prehistory on polyimide. Experimental data:  $-180^{\circ} \rightarrow 500^{\circ}$   
 $\rightarrow -180^{\circ}\text{C}$ .

set of data ( $-180^{\circ} \rightarrow 500^{\circ} \rightarrow -180^{\circ}\text{C}$ ) was generated after a drying/curing cycle of  $25^{\circ}\text{C}$  to  $300^{\circ}\text{C}$  at  $2^{\circ}\text{C}/\text{min}$ . The lower set of data ( $25^{\circ} \rightarrow 500^{\circ}\text{C}$ ) was generated after a prior history of heating from  $25^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  at  $2^{\circ}\text{C}/\text{min}$ . The specimen which was dried to  $200^{\circ}\text{C}$  displayed an additional damping peak and an inflection in the rigidity curve in the  $200^{\circ}$ – $300^{\circ}\text{C}$  region of the heating part of the experiment. This difference can be attributed to either the removal of associated solvent that remained absorbed to the polymer more than  $30^{\circ}\text{C}$  above its boiling point and/or to the continuation of the ring-closure reaction which is not completed during the  $25^{\circ}$ -to- $200^{\circ}\text{C}$  cure cycle.

### Effect of High Temperature

Figure 3 (see also Fig. 2, top) displays the thermomechanical behavior ( $-180^{\circ} \rightarrow 500^{\circ} \rightarrow -180^{\circ}\text{C}$ ) of the material which resulted from heating a prepolymer to  $300^{\circ}\text{C}$  at  $2^{\circ}\text{C}/\text{min}$  in dried nitrogen. The glass transition region was shifted from about  $370^{\circ}\text{C}$  to  $>500^{\circ}\text{C}$ , whereas the glassy state relaxation, with a damping peak at about  $160^{\circ}\text{C}$ , was virtually unaffected by the thermal treatment to  $500^{\circ}\text{C}$  of the experiment. These results are explained by suggesting that crosslinking and/or chain-stiffening reactions, which increase the modulus above  $460^{\circ}\text{C}$ , are of sufficient density to affect the longer-range motions which are associated with the glass transition and yet are of insufficient density to affect the more localized motions associated with the glassy state relaxation. Since the damping peak in the glassy phase ( $160^{\circ}\text{C}$ ) was observed after cure to  $300^{\circ}\text{C}$  and also after pyrolysis to  $500^{\circ}\text{C}$ , it represents a relaxation of the polyimide *per se* (cf. effect of solvent and/or curing reaction, as above). (The major glassy state transition of each of the polymers listed in Table I was retained after heating to  $500^{\circ}\text{C}$ .) Furthermore, the controlled pyrolysis to  $500^{\circ}\text{C}$  resulted in a new material which differed in having a higher load-limiting glass transition region, but had much the same thermomechanical properties as its precursor polyimide in the glassy state. That is, thermally induced chemical reactions can be regulated so as to freeze out preferentially longer-range relaxations, thereby extending the glassy state behavior and the utility of the material to higher temperatures.

### Effect of Trace Moisture

A well-known characteristic of many polymers is the ability of polar groups to attract and associate with water. The data<sup>2,3</sup> in Figure 4 are mechanical spectra of two specimens of the same polymer obtained after heating prepolymer solutions to  $300^{\circ}\text{C}$  at  $2^{\circ}\text{C}/\text{min}$  to effect solvent removal and chemical ring-closure. The top set of data was obtained using an atmosphere of "Hi-Pure" nitrogen, which is specified as 99.996% pure with 5 ppm water and 10 ppm oxygen. It is apparent that the cooling and subsequent heating data below  $130^{\circ}\text{C}$  are not reproducible and that there is a damping peak at about  $-80^{\circ}$ . After these low temperature experiments, the specimen was held overnight at  $130^{\circ}\text{C}$ . The damping returned

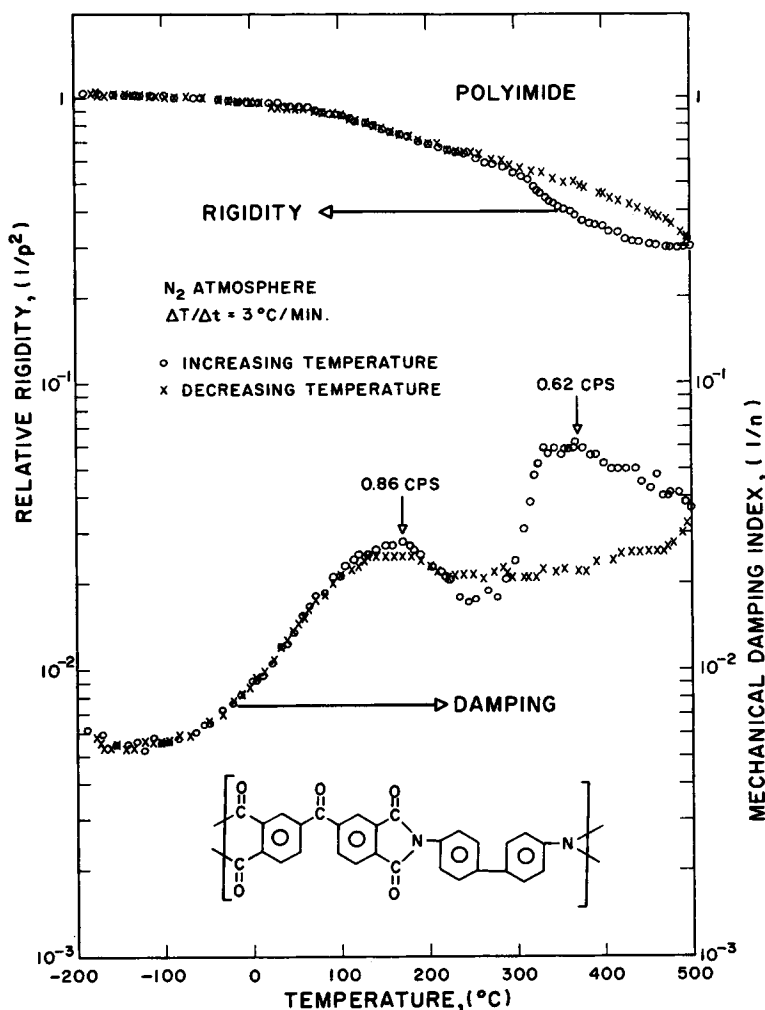


Fig. 3. Effect of high temperature on polyimide. Experimental data:  $-180^{\circ} \rightarrow +500^{\circ} \rightarrow -180^{\circ}\text{C}$ .

overnight to the level of the pre-low temperature experiment, which implies that the associated water was driven off by heating overnight. The lower set of data was obtained using "Hi-Pure" nitrogen that was passed through liquid nitrogen cold traps and drying columns. The up-and-down reproducibility of the low-temperature region and the absence of the  $-80^{\circ}\text{C}$  peak are noteworthy. (After being held overnight at  $130^{\circ}\text{C}$ , both specimens were taken from  $100^{\circ}$  to  $500^{\circ}\text{C}$ .)

#### Effect of Chemical Structure

The chemical formulae and data showing the thermomechanical behavior ( $-180^{\circ} \rightarrow 500^{\circ}\text{C}$ ) of two series of polyimides in dried nitrogen are

TABLE I  
Structural formulae, inherent viscosities, and transitions of polyimides

STRUCTURE		VISCOSITY <sup>(a)</sup>	TRANSITIONS <sup>(b)</sup>			
DIANHYDRIDE	DIAMINE		T <sub>g</sub> (CPS)	T <sub>1</sub> (CPS)	T <sub>2</sub> (CPS)	T <sub>3</sub> (CPS)
	①	1.55	>330°C (0.74)	210°C (0.81)	50°C (0.81)	-100°C (0.90)
	②	1.41	>330°C (0.79)	200°C (0.88)	20°C (0.88)	-100°C (0.95)
	③	1.25	>330°C	—	0°C (0.83)	-90°C (0.88)
	④	1.71	>330°C (0.47)	154°C (0.47)	—	—
	⑤	1.19	>330°C (0.46)	145°C (0.46)	—	—
	⑥	2.70	>330°C (0.83)	230°C (0.83)	50°C (0.92)	—
	①	1.01	281°C (0.50)	115°C (0.88)	—	-100°C (0.95)
	②	1.41	283°C (0.49)	110°C (0.85)	—	-120°C (0.96)
	③	0.70	282°C (0.51)	120°C (0.78)	—	-100°C (0.86)
	④	0.93	328°C (0.31)	171°C (0.46)	—	—
	⑤	1.18	320°C (0.32)	180°C (0.46)	—	—
	⑥	1.30	>330°C (0.88)	160°C (0.88)	—	—

<sup>a</sup> Inherent viscosity of polyamic acid, dl/g (0.5% in dimethylacetamide at 25°C).

<sup>b</sup> T<sub>g</sub> = main glass transition, T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub> = glassy state transitions.

shown in Figures 5 and 6. Table I also summarizes data on the various transitions. The specimens were prepared from solutions of the precursor polyamic acids by heating to 300°C ( $\Delta T/\Delta t = 2^\circ\text{C}/\text{min}$ ) in dried nitrogen. The curves for the relative rigidity parameter have been shifted vertically so that the rigidity is the same for each series of the polymers at  $-180^\circ\text{C}$ . This normalization facilitates comparison of materials and is made possible by having the specimens, which are to be compared, have approximately the same polymer content. (Solutions of the same concentration and approximately the same viscosity (Table I) were used to prepare specimens.) For clarity the damping curves have been displaced vertically by arbitrary amounts.

The data support the *a priori* prediction which could be made on the basis of the relative flexibilities of the molecules that there would be several



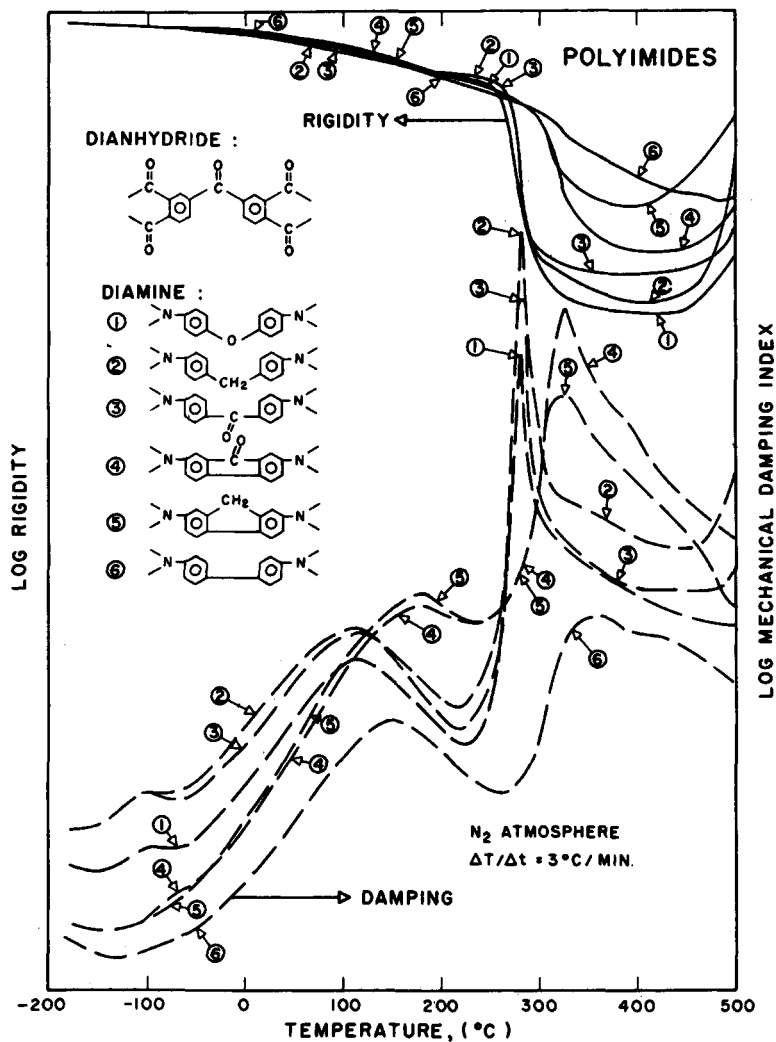


Fig. 5. Polyimides based on pyromellitic dianhydride; effect of chemical structure. Experimental data:  $-180^{\circ} \rightarrow 500^{\circ}\text{C}$ .

distinct types of behavior. Polymers formed using benzophenonetetracarboxylic acid dianhydride (BTDA) would be expected to be more flexible than those formed by using pyromellitic dianhydride (PMDA), since the former is less double-stranded with rigid linkages than the latter. Polyimides which are derived from BTDA do have lower glass transitions and soften more through  $T_g$  than do the polyimides made from PMDA. On the other hand, the presence of methylene versus carbonyl linkages in the backbone would have less influence on the molecular flexibility and intermolecular forces, and hence on the thermomechanical behavior. Indeed, very similar thermomechanical behavior is displayed by polyimides syn-



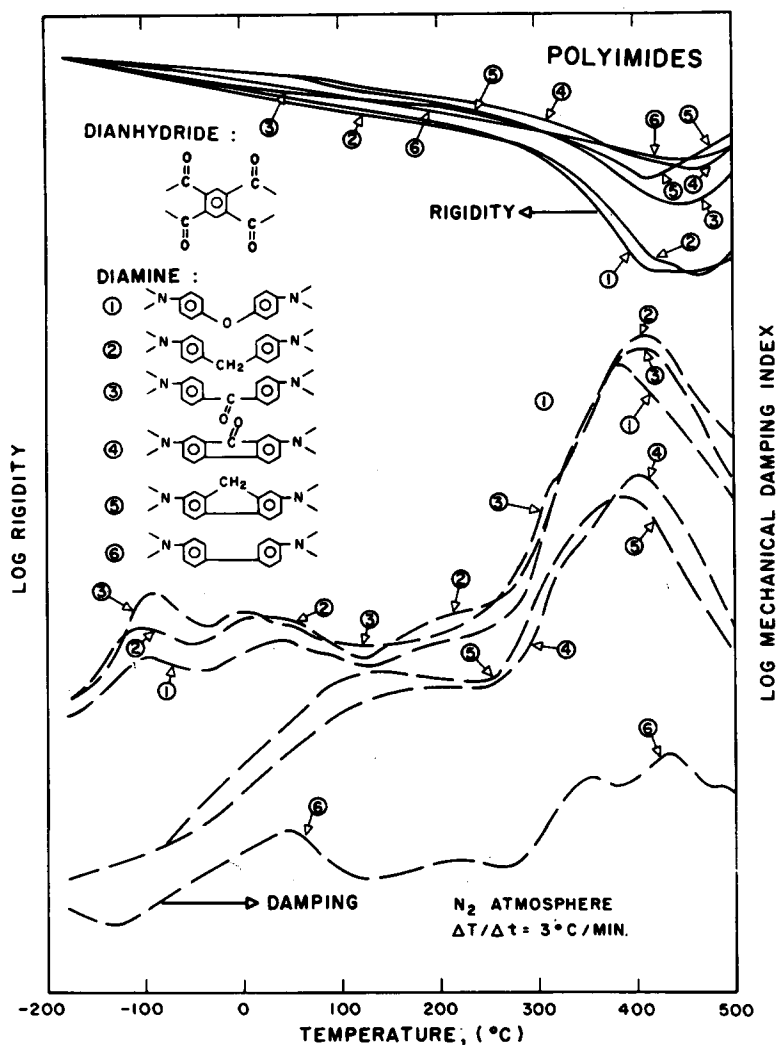


Fig. 6. Polyimides based on benzophenone tetracarboxylic acid; effect of chemical structure. Experimental data:  $-180^{\circ}\text{C} \rightarrow 500^{\circ}\text{C}$ .

thesized from fluorenediamine and fluorenonediamine. Likewise *p,p'*-diaminodiphenylether-derived, *p,p'*-methylenedianiline-derived, and *p,p'*-diaminobenzophenone-derived polyimides show similar behavior to one another.

The data on the two series of polyimides (Figs. 5 and 6) bear further on the molecular interpretation of the thermomechanical behavior. The polyimides with incorporated BTDA residues have thermomechanical spectra which are not unlike those of simpler amorphous polymers such as amorphous isotactic, syndiotactic, and atactic poly(methyl methacrylates) which display as main features a glassy state damping region ( $\beta$ -peak) and a

glass transition region. The ratio  $T_\alpha/T_\beta$  for the poly(methyl methacrylates)<sup>4</sup> is 1.23 to 1.34 at about 1 cps. The corresponding ratio is 1.31 to 1.45 for polyimides prepared by heating to 300°C, and is a function of the specific thermal prehistory used to obtain the polyimides. On the other hand, the thermomechanical spectra of polyimides containing PMDA residues can be more complex in displaying multiple damping peaks. This suggests that highly discrete modes of submolecular motion are activated in raising the temperature in some of these polymers. In contrast, a more continuous mode of activation of submolecular motions is suggested for the polyimides made from BTDA. Since insertion of PMDA (versus BTDA) residues results in more change in thermomechanical spectra than is produced by the other changes in molecular architecture, it may well be that this special influence is due to the high density of polar carbonyl groups in a very rigid anhydride residue which drastically affects intermolecular interactions and controls the thermomechanical behavior. In contrast, intramolecular flexibility appears to

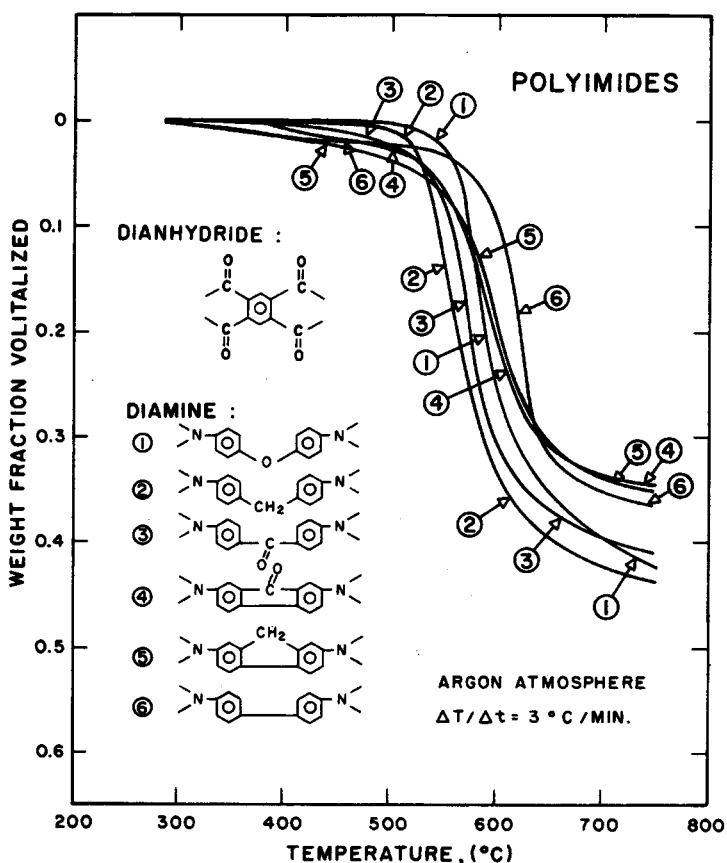


Fig. 7. Thermogravimetric analyses of polyimides based on pyromellitic dianhydride.

control the thermomechanical behavior of the polyimides synthesized from BTDA.

The glass transitions of the polyimides containing PMDA residues are ill defined. This is a consequence of thermally induced chemical reactions which compete with the softening process of the glass transition. In all the polymers, these reactions cause an increase in rigidity. The region of low rigidity ( $>T_g$ ) for the BTDA-derived polyimides has a wider temperature range than that of the PMDA-derived polyimides. Should advantage be taken of the high-temperature (400°–500°C) reactions to form engineering polymeric materials which would have significant strength and modulus in the temperature range 400°–500°C, then there may well be advantages in fabricating (e.g., forming) with the more fusible polymer and then pyrolyzing in situ. However, variations in the amount of volatiles formed on degradation versus molecular structure would have to be taken into account.

The results of thermogravimetric analysis for the two series of polyimides are shown in Figures 7 and 8. The prehistory for all of the polymers was the same as for the thermomechanical experiments. Comparative thermal stability in the decomposition range was estimated in three ways: (1) using the temperature of onset of increasing rate of weight loss; (2) using the relative weight loss incurred by a particular temperature (e.g., 550°C); and (3) using the relative temperatures by which a particular fraction (e.g., 10%) has volatilized. Regardless of the technique employed, the order of stability and inflexibility for both series was benzidine, 6, >fluorenonediamine, 4, >fluorenediamine, 5, >benzophenonediamine, 3, >methylenedianiline, 2. (Ether dianiline, 1, did not fit into the general pattern.) Similarly, incorporation of the flexible BTDA residues lowered the stability. Ease of processibility would appear to be in the opposite order to molecular stability and inflexibility.

### Thermomechanical Spectra as "Fingerprints" for Identification

The thermomechanical spectra of the polyimides are sufficiently complex to serve as "finger prints" for purposes of identification. A comparison of TBA and torsional pendulum data on a commercially available polyimide-forming varnish and a polyimide film, of undisclosed structures, indicates that each material is based on the same chemical structure and that the structure is closely related to one of the known types discussed above. The data<sup>3</sup> on the commercially available materials are shown in Figure 9.

The materials, available from du Pont, were: (1) Kapton ("H"-film) as a free film with dimensions 0.0045 in.  $\times$  0.17 in.  $\times$  5 in.; tensile stress <70 psi, and (2) Pyre-M.L. enamel; the braid was impregnated with the 7.5% polyamic acid solution in dimethylacetamide (bp = 166°C) with N-methyl-2-pyrrolidone (bp = 202°C).

Both specimens were heated from 25° to 300°C at 3°C/min in dried nitrogen. In the case of the Pyre-M.L. varnish, this was a drying (removal of

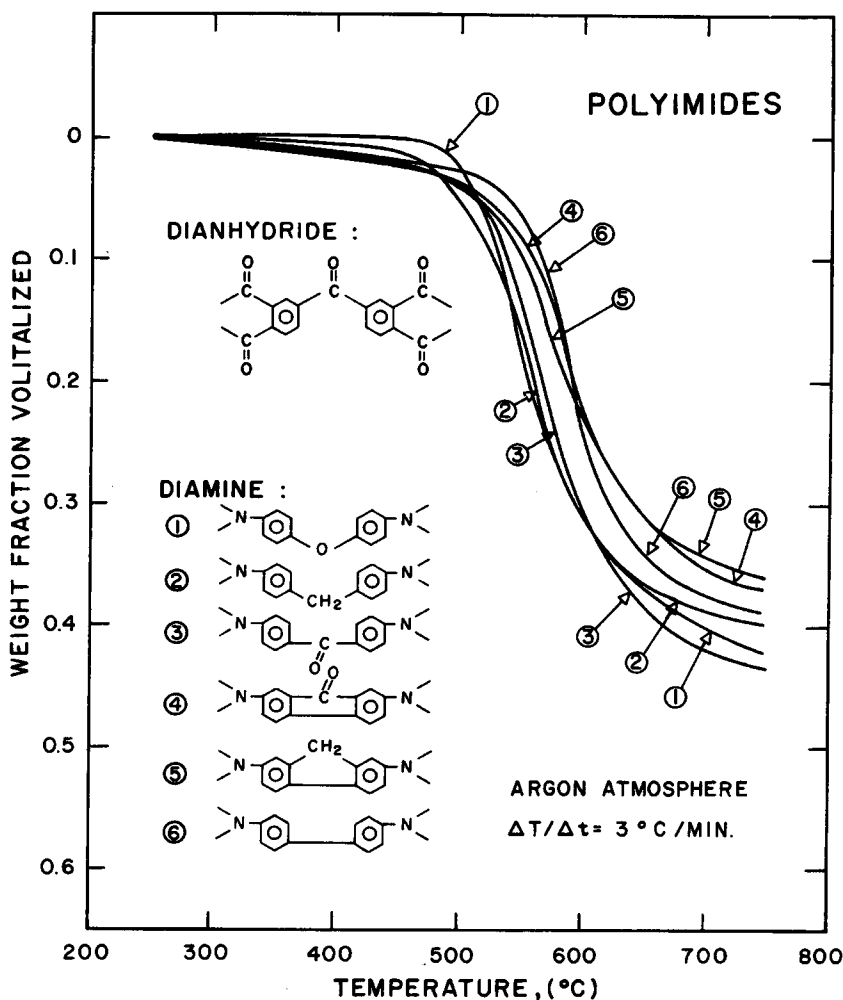


Fig. 8. Thermogravimetric analyses of polyimides based on benzophenonetetracarboxylic acid dianhydride.

solvent) and curing (ring-closure) cycle. In the case of the "H"-film, this was done in order to duplicate the prehistory of the Pyre-M.L. (and tacitly assumed that previous thermal treatment of the "H"-film was to less than 300°C) and to remove any moisture or residual solvent present.

From the data ( $-180^\circ \rightarrow 500^\circ \rightarrow -180^\circ\text{C}$ , Fig. 9), generated at 3°C/min in dried nitrogen, both polyimides appear to be mechanically identical, with damping maxima peaking at about  $-90^\circ$ ,  $+30^\circ$ ,  $+200^\circ$  (a shoulder), and  $+400^\circ\text{C}$ . In terms of the modulus, both materials display a steady decline from  $-180^\circ\text{C}$  to about 300°C, with subtle inflections at temperatures roughly corresponding to those of the damping peaks. Above 300°C, both modulus curves decrease at an increasing rate to a minimum at about 450°C and then display a small rise at 500°C. The large decrease in modulus,

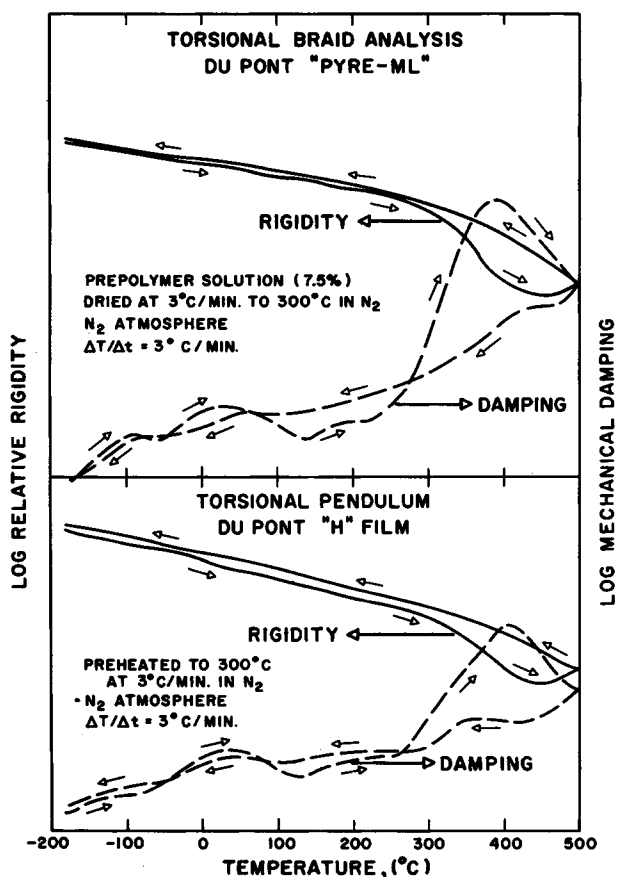


Fig. 9. Torsional braid and torsional pendulum analyses as "finger prints" of thermomechanical behavior. Upper figure shows thermomechanical behavior of a cured polyimide-forming varnish, while lower figure shows thermomechanical behavior of a polyimide film.

coupled with the magnitude of the 400°C damping peak (relative to the peaks at lower temperatures) is indicative of the glass transition region. In both materials the peak is broad and skewed. The shape of the damping peak and the corresponding upturn in the relative modulus indicate that a degree of chain stiffening and/or crosslinking occurred in the  $T_g$  region, where molecular motion and diffusive rate processes increase by orders of magnitude. For both polymers, the thermal cure to 500°C has raised and broadened the glass transition region. On the other hand, retention of low-temperature glassy state relaxations implies that whatever the mechanism of the stiffening process, it is of long enough range so as not to interfere with the short-range motions associated with the low-temperature damping peaks.

The thermomechanical spectra (Fig. 9) correspond closely with those in the group of polyimides (Fig. 5) synthesized from pyromellitic dianhydride

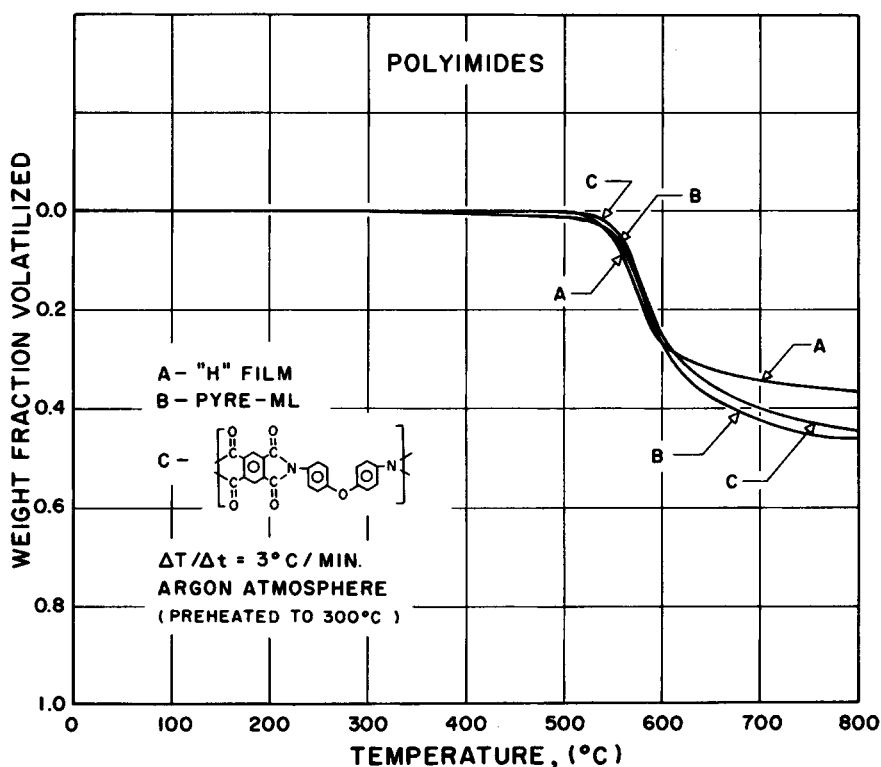


Fig. 10. Thermogravimetric analyses of Kapton "H"-film, cured Pyre-M.L. varnish, and the polyimide synthesized from pyromellitic dianhydride and *p,p'*-diaminodiphenyl ether.

and one of the three diamines: *p,p'*-diaminodiphenyl ether, 1; *p,p'*-methylenedianiline, 2; and *p,p'*-diaminobenzophenone, 3.

The TGA data in argon for "H"-film and Pyre-M.L. are included<sup>3</sup> in Figure 10; both were preheated to  $300^\circ\text{C}$  at  $3^\circ\text{C}/\text{min}$  in argon. In an inert atmosphere, both polymers were stable to 98% of their postdrying sample weight to  $500^\circ\text{C}$ . Both thermograms were basically the same until beyond  $600^\circ\text{C}$ , where the Pyre-M.L. lost weight at a faster rate, which provides evidence for some differences between the "H"-film and cured Pyre-M.L. polyimides. The TGA data for the preheated Pyre-M.L. and for the polyimide, formed by heating the polymer from pyromellitic dianhydride and *p,p'*-diaminodiphenyl ether to  $300^\circ\text{C}$  at  $3^\circ\text{C}/\text{min}$  in argon, are very similar (Fig. 10).

The thermomechanical behavior ( $-180^\circ \rightarrow 625^\circ \rightarrow -180^\circ\text{C}$ ) in dried nitrogen of Pyre-M.L., cured by heating the varnish to  $300^\circ\text{C}$  with  $\Delta T/\Delta t = 3^\circ\text{C}/\text{min}$ , is displayed<sup>3</sup> in Figure 11. The high-temperature data display the same features as in Figure 9 to  $500^\circ\text{C}$ . Above  $570^\circ\text{C}$ , the modulus curve continues to rise to a level above the highest rigidity experienced by the  $300^\circ\text{C}$ -cured polymer in the  $-180^\circ\text{C}$  to  $500^\circ\text{C}$  range. The damping

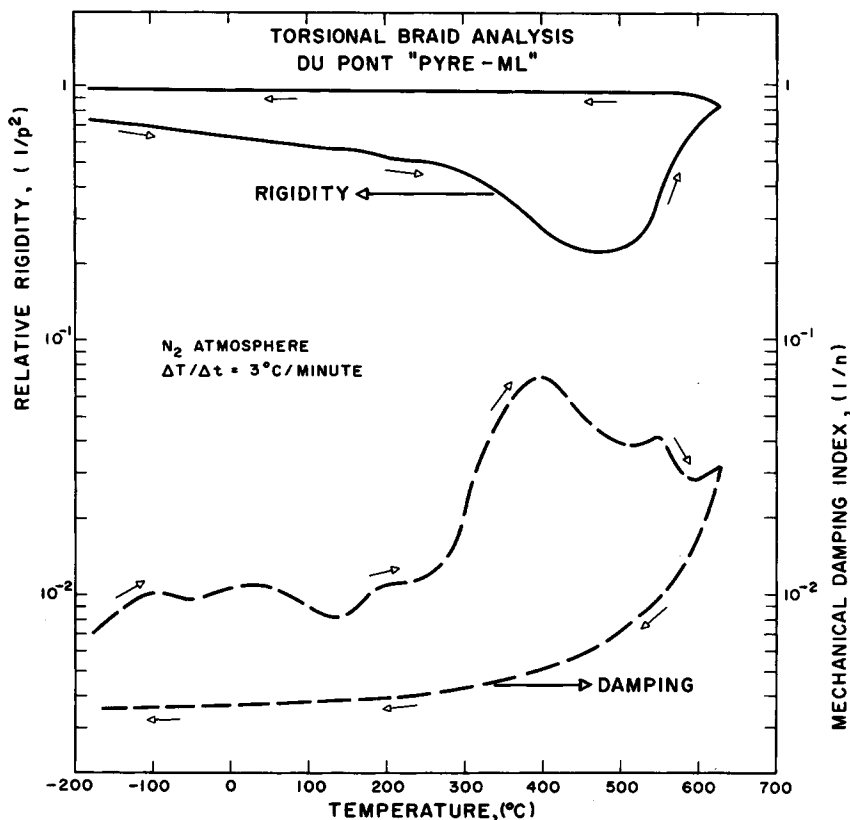


Fig. 11. Thermomechanical spectra ( $-180^{\circ} \rightarrow 625^{\circ} \rightarrow -180^{\circ}\text{C}$ ) of Pyre-M.L.

displays a peak near  $560^{\circ}\text{C}$ , then decreases to  $600^{\circ}\text{C}$ , and rises again. On cooling, the damping drops off to a low flat level below about  $300^{\circ}\text{C}$ . The  $50^{\circ}\text{C}$  and  $-90^{\circ}\text{C}$  peaks are no longer present. This indicates that the large weight loss (35% by  $625^{\circ}\text{C}$ ) and corresponding stiffening reactions were of such a character as to modify the original structure to an extent that the submolecular motions corresponding to those peaks were eliminated.

#### Comments on Structure-Property Relationships in Complex Polymers

The different damping patterns of the various polyimides in the glassy state (as well as in the glass transition region) are of practical significance, for it is differences in submolecular motions which confer differences in mechanical behavior.

It might also be noted that systematic studies of structure-property relationships in (high-temperature ring-containing) polymers is meaningful only when the structures are well defined. The synthetic routes which lead to polymers containing fused rings in their backbone generally lead to a complex mixture of isomers of the cis/trans type. On the other hand, polyimides are unique in that the symmetry of the imide rings precludes

this type of imperfection. However, other types of imperfection may well be present, such as incomplete ring-closure and intermolecular chemical links. Since the results of this study do show very definite structure-dependent similarities and differences, they serve to substantiate both the validity of the syntheses and the thermomechanical spectra.

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