Metal Ion Additive–Polyimide Interactions Employing Thermogravimetry*

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Synopsis

Solutions of poly(amic acid), a polyimide precursor prepared from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride and 4,4'-oxydianiline, containing metal ions such as Pd, Pt, and Sn in a variety of chemical states were prepared. The polymer–metal ion solutions and each component thereof were analyzed by thermogravimetry. Summation of the calculated contribution of each component of the polymer solution mass loss curve yields a calculated TG curve. Subtraction of the calculated curve from the actual curve for the polyamic acid–metal ion solution results in a difference TG curve. From the difference TG curve information about polymer/additive interactions can be obtained.

INTRODUCTION

Most often polymers are combined with additives to yield unique engineering materials for a specific end-use application. The resulting products add yet another dimension to the complexity of polymeric materials. Thermal methods of analysis are well suited for the characterization of these polymeric materials[1-4] for two main reasons. First, temperature changes can be used to accelerate tests for the evaluation and comparison of polymeric samples whose properties would otherwise require excessive experimentation time.[5] Second, since many polymers are used at temperatures other than ambient temperature, the availability of instrumentation that scans specimen properties over a wide temperature range is valuable to the materials scientist.

Highly aromatic polyimides characterized by excellent chemical and thermal stability and electrical insulative properties are being used in aerospace, electronics, and speciality consumer markets. Many of these polyimides are currently available as films, fibers, adhesives, resins, and/or a stabilized solution of a polyimide acid precursor (i.e., polyamic acid). Our research group has been studying the effect of metal ion incorporation into polyimides.[6-9] The goals are to enhance the electrical conductivity of polyimide films while maintaining high mechanical integrity and retaining high thermal stability. Toward this end thermogravimetry (TG) is being used to evaluate polymer/additive interactions on a quantitative basis.

Thermogravimetric analysis is often a suitable method for compositional analysis of blends which contain components that do not ineract. The technique relies on the fact that the sample mass loss profile is not responsive

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to component interactions. Thus, compositional analysis of polymer and elastomer formulations by thermogravimetry has been possible.[10] Duval[11] was able to characterize mixtures containing calcium oxalate and magnesium oxalate via this method because each behaved independently. The chemical independence of the two components of the mixture can be demonstrated by subtracting from the authentic TG curve of the mixture the appropriate contribution from each component. The resulting mass difference vs. temperature plot, if no chemical or physical interactions are present, results in a horizontal line. Interactions are observed as deviations from the straight line.

In this study polyamic acid solutions (i.e., polyimide precursor) were prepared from the room temperature polycondensation reaction between 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 4,4'-oxydianiline (ODA) in N,N-dimethylacetamide (DMAc). Polymer additive which was either $SnCl_4 \cdot 2DMSO$, $PdCl_2 \cdot 2DMSO$, or $PtCl_2 \cdot 2DMSO$ was then added to each solution. The resulting polyamic acid solutions and their individual components have been analyzed by thermogravimetry. Summation of the contribution from each component to the polymer/additive solution mass loss curve yields a calculated (no interaction) TG curve. Subtraction of the calculated curve from the actual curve results in a difference TG curve. From the resulting difference curve, information about polymer/additive interactions has been obtained.

EXPERIMENTAL

Materials. BTDA was obtained from commercial sources and purified by sublimation at 215°C at less than 1 torr. ODA was obtained from commercial sources and purified by recrystallization. Reagent grade DMAc distilled in glass was obtained from Burdick and Jackson. The solvent was stored over molecular sieves and sparged with dry nitrogen which had been passed through a column containing Drierite and molecular sieves. $SnCl_4 \cdot 2DMSO$, $PtCl_2 \cdot 2DMSO$, and $PdCl_2 \cdot 2DMSO$ were prepared according to literature references.[12]

Polymer Solution Preparation. Polyamic acid solutions were prepared at room temperature by placing 4.00 mmol ODA into a glass nitrogen-purged bottle. To this was added 6 mL DMAc with magnetic stirring. As a single portion 4.00 mmol BTDA was next added to the solution with 2 mL additional DMAc. The resulting solution was stirred at least 1 h prior to the addition of the metal ion additive. To assure homogeneity, the final solution was stirred at least four more hours prior to analysis by thermogravimetry. The syntheses of the undoped control (route 1) and the metal-ion doped polyimide (route 2) are shown in Figure 1.

Instrumentation. Thermogravimetric analysis was performed on a Perkin-Elmer Thermogravimetric System (Model TGS-2) under a dynamic nitrogen purge (30 cc/min). Each sample was placed directly on the platinum sample pan and heated at 5°C/min. The sample mass and temperature were recorded directly on a Fisher Scientific Series 5000 dual pen analogue strip chart recorder. Data points, manually digitized and entered into a Hewlett-Packard 85 computer system, were stored and plotted.
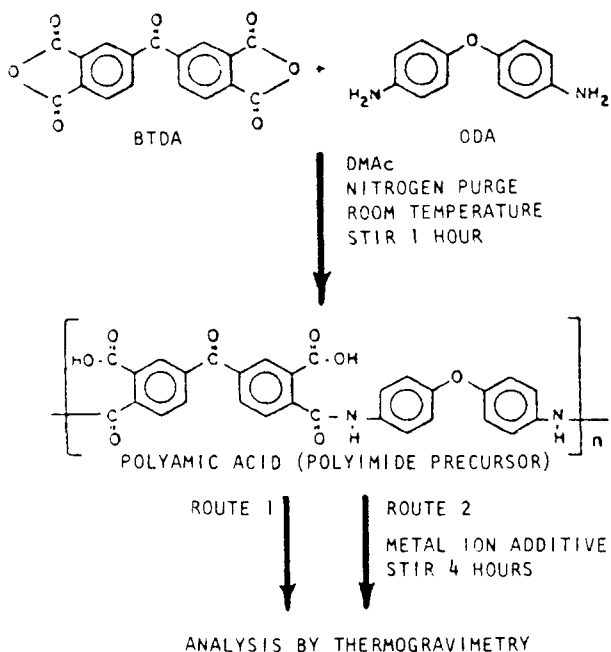
Fig. 1. The synthesis of the polymer control and the metal ion doped polymer.

RESULTS AND DISCUSSION

The composition of samples analyzed by thermogravimetry is shown in Table I. The TG curves of $SnCl_4 \cdot 2DMSO$ and BTDA–ODA polyamic acid solution are shown in Figure 2. The TG curve of BTDA–ODA shows mass loss of 78.4% at 174°C and 81.4% at 494°C. Based on the amount of solvent used in this polyamic acid solution (see Table I) and the mass loss due to the cyclodehydration of the polyamic acid (1.51 mg) with formation of polyimide, the expected total mass loss is 80.8%. Thus, the TG curve indicates that the solvent is removed and imidization occurred, resulting in the thermally stable polymer as residue. The TG curve of $SnCl_4 \cdot 2DMSO$ shows slight initial mass loss (1.5%) up to 100°C. This additive contains two am-

TABLE I
The Compositions of Samples Analyzed by Thermogravity and Used in This Study

Sample	DMAc		BTDA		ODA		Additive	
	(mg)	(%)	(mg)	(%)	(mg)	(%)	(mg)	(%)
004	30.7716	79.84	4.7830	12.41	2.9870	7.75	—	—
012	44.5911	78.12	7.7000	13.49	4.7890	8.39	—	—
005[a]	29.8455	74.76	4.4672	11.19	2.7825	6.97	2.8265	7.08
013[a]	23.6455	65.28	3.9300	10.85	2.4486	6.76	6.1975	17.11
014[a]	21.8033	71.58	3.8349	12.59	2.3820	7.82	2.4398	8.01
006[b]	32.4691	76.02	5.0527	11.83	3.1606	7.40	2.0331	4.76
007[c]	30.6853	73.13	4.9151	11.69	3.0547	7.28	3.3148	7.90

[a] $SnCl_4 \cdot 2DMSO$
[b] $PdCl_2 \cdot 2DMSO$
[c] $PtCl_2 \cdot 2DMSO$
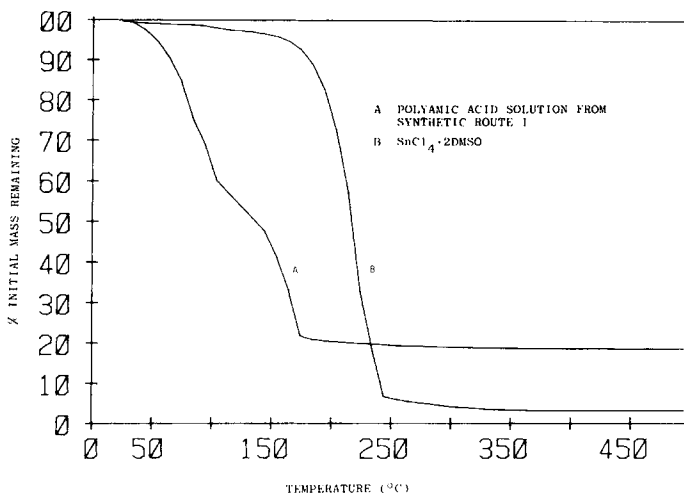
Fig. 2. TG curves of a (A) polyamic acid solution from synthetic route 1 and (B) SnCl$_4$ · 2DMSO additive.

bidentate ligands primarily to raise its boiling point. Tin (IV) chloride boils at 114.1°C. The TG curve indicates a single step mass loss occuring between 154 and 243°C with resulting residue of about 3.8% at 500°C. It is believed that the ligands are thermally removed from the additive and vaporize (dimethyl sulfoxide, bp 189°C). The tin (IV) chloride, being above its boiling point and swept by the nitrogen purge, also rapidly vaporizes. Slight hydrolysis of the tin additive, resulting in tin (IV) oxide (mp = 1127°C) may account for the residue.

By using the composition data of Table I and the digitized TG curves of Figure 2, a TG curve for the BTDA–ODA/SnCl$_4$ · 2DMSO polymer solution can be calculated, valid if procedural variables are controlled sufficiently. The TG curve was calculated using the equation:

$$A_i = W_1(M_{1i}) + W_2(M_{2i})$$

where W_1 is the weight fraction, component 1, W_2 the weight fraction, component 2, M_{1i} the fractional mass remaining at $T = i$, component 1, M_{2i} the fractional mass remaining at $T = i$, component 2, and A_i the fractional % mass remaining at $T = i$ calculated for the blend. Essentially, the calculated TG curve is the point by point addition of the absolute mass remaining for each component (i.e., polyamic acid–DMAC, additive) at each temperature.

Though not explicitly indicated by the equation, it was found that the absolute mass of each component individually analyzed should match as closely as possible the mass of each component present in the blend. That this is true is demonstrated in Figure 3. For example, no y-axis scaling of curve B will accurately reproduce curve C since curve B contains no data points in the range 95–130°C, but curve C does. In addition to controlling sample mass for analytical reasons, it is also important to control the experimental conditions for chemical reasons. For example, Sazanov studied
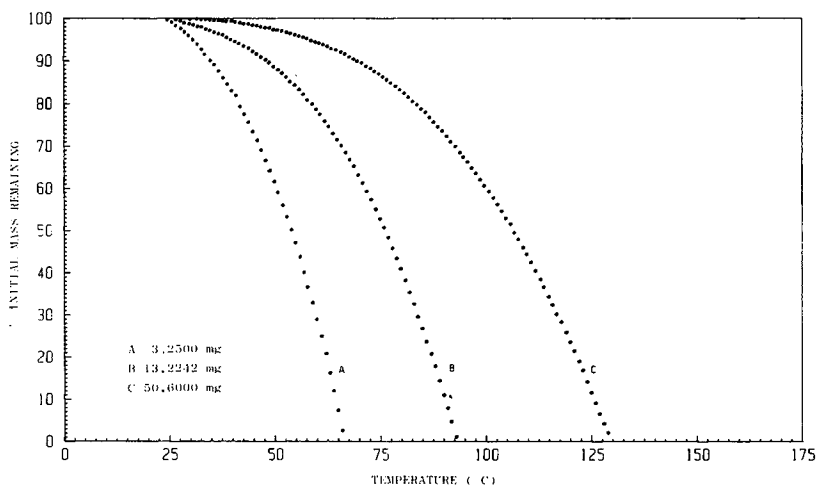
Fig. 3.   The effect of initial sample mass on the TG curve: (A) 3.2500 mg; (B) 13.2242 mg; (C) 50.600 mg.

the influence of heating rate, atmosphere control, and sample holder geometry on the kinetics of the thermal degradation of polyimides.[13] Though the TG behavior of a particular component can be mathematically modeled using kinetic methods, the better technique is to control the absolute sample mass.

A comparison of the calculated TG curve with the actual TG curve resulting from the analysis of sample 013 is shown in Figure 4. Significant differences between the two curves are evident above 100°C. It appears that polymer/additive interactions are occuring in this system. To amplify the apparent interactions, the difference between the actual and calculated TG curves was obtained and the results of this subtraction are shown in Figure 5. Above 175°C there is more mass remaining in the polymer system than
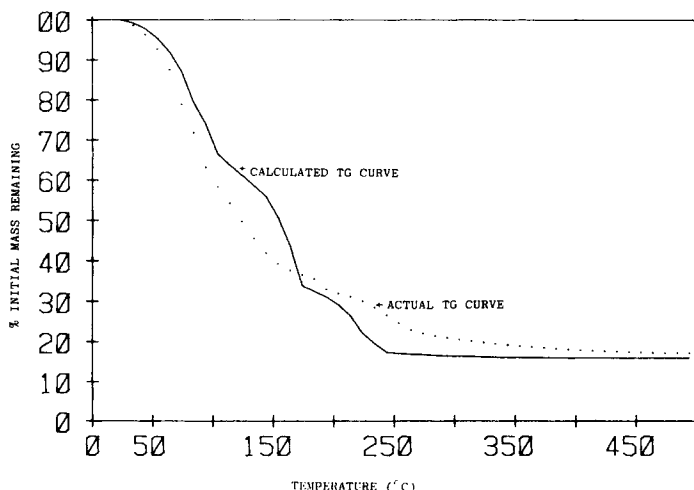

Fig. 4.   The actual and calculated TG curves for a BTDA/ODA polymer solution containing SnCl$_4$ · 2DMSO.
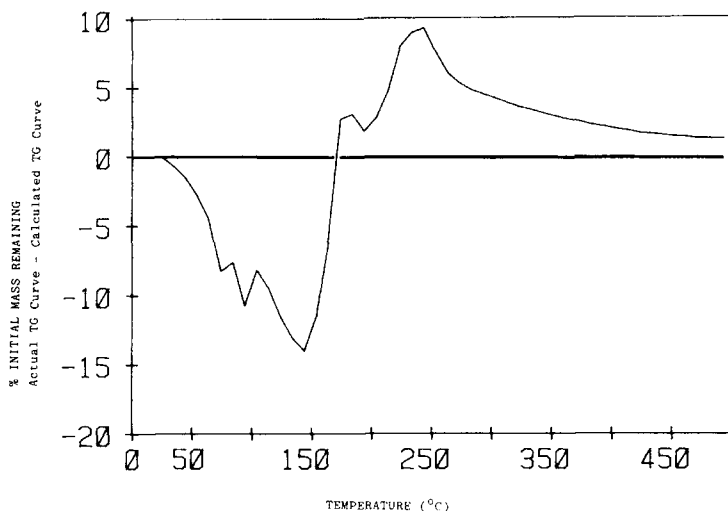
Fig. 5. The difference TG curve for a BTDA/ODA polymer solution containing $SnCl_4 \cdot$ 2DMSO.

predicted as seen by the positive peak in Figure 5. The more rapid mass loss in the low temperature region results in a negative peak. Also, note that the high temperature asymtotic approach to a positive difference value due to the increased amount of residue. The enhanced rate of low temperature mass loss and the increased amount of high temperature residue is consistent with hydrolysis of the tin additive yielding HCl as a volatile byproduct and SnO_2 as residue. The low temperature mass loss may also be due to a lowering of the imidization temperature. Analysis of sample 014 which contained 8% additive showed similar results.

Because the samples contained about 70% solvent on an initial sample mass basis additional information was obtained by heating the sample to 90°C at 5°C/min and holding isothermally for more than 60 min. It was hoped that removal of the solvent during this time would allow subsequent thermal events to be observed with greater sensitivity. Actually, only about 70% of the solvent vaporized with this experimental condition. It was also verified in this study that the polymer additives did not lose significant mass during the 90°C isotherm. The procedure described here was followed with only the platinum and palladium additive systems. However, due to the incomplete volatilization of the solvent under these conditions, data interpretation was nevertheless not simplified.

The TG analysis of the $PtCl_2 \cdot$ 2DMSO additive is shown in Figure 6. The mass loss expected due to loss of each dimethyl sulfoxide ligand (18.50%) followed by loss of each chloride (8.40%) is indicated on the TG curve. It is important to note that the TG curve contains a region (above 350°C) where the sample mass plateaus. This indicates the residue, under the conditions of the analysis, is stable above 350°C. The composition of the residue is not known, but it probably does not result simply from the loss of each ligand because if it did 46.2% (not 55.9%) residue would result. Perhaps initially one dimethyl sulfoxide ligand is lost followed by loss of two equivalents of
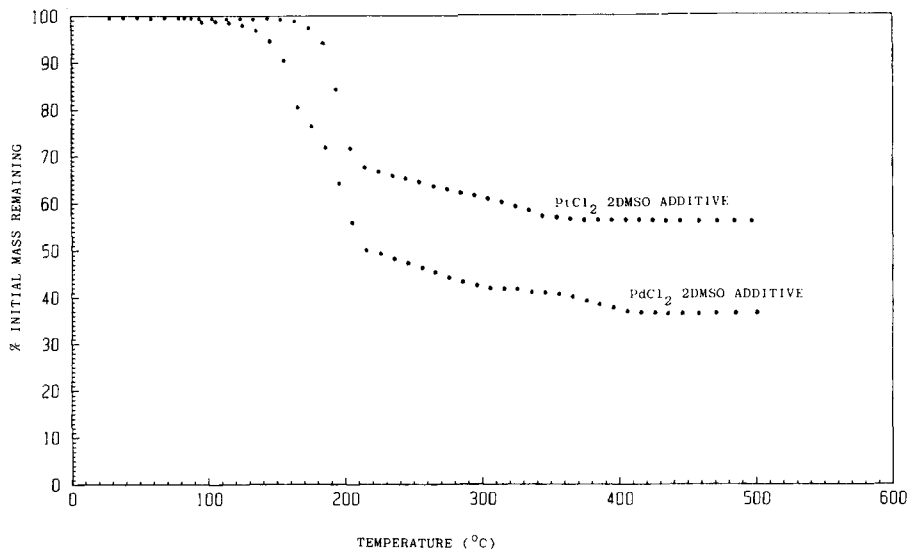
Fig. 6.   The TG curves for the $PtCl_2 \cdot 2DMSO$ and $PdCl_2 \cdot 2DMSO$ additives.

methyl chloride thereby resulting in a mixture of PtS and PtO. The cal-
culated residual mass for an equimolar PtS and PtO mixture is 57.6%.

The analysis of the polymer system containing $PtCl_2 \cdot 2DMSO$ (sample
007) is shown in Figure 7. A difference between the actual and theoretical
TG curve is seen in the 150–300°C region. The more rapid mass loss seen
in the actual TG curve results in the negative difference peak of Figure 8.
From 250 to about 450°C the two curves are nearly identical. However, the
residual mass above 300°C, being lower than that predicted on the basis of
the individual components, results in the negative valued horizontal on the
difference curve. Above 450°C there is a marked difference between the
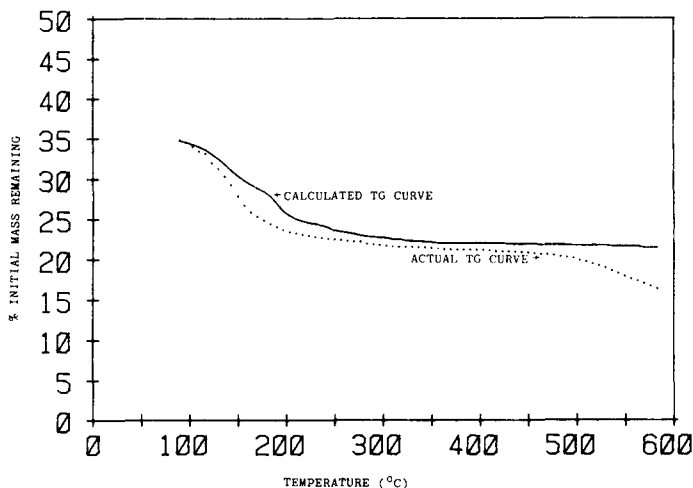actual and calculated TG curve. The actual system has less high temper-

Fig. 7.   The actual and calculated TG curves for a BTDA/ODA polymer solution containing
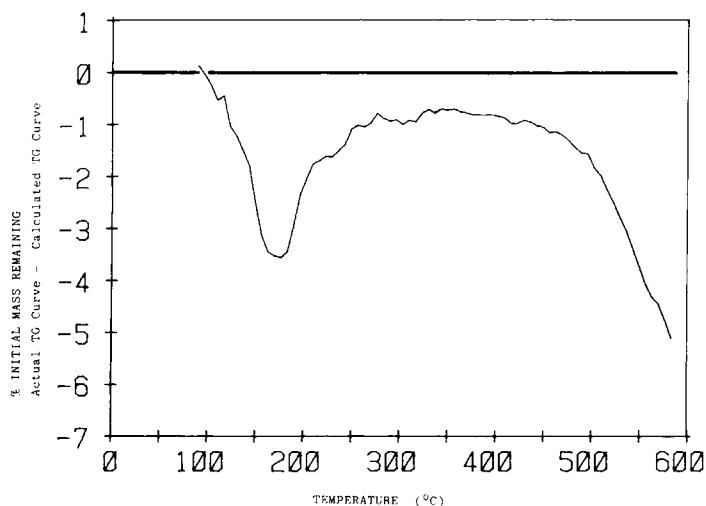$PtCl_2 \cdot 2DMSO$.

Fig. 8.   The difference TG curve for a BTDA/ODA polymer solution containing PtCl₂ ·
2DMSO.

ature thermal stability than would be predicted based on the thermal be-
havior of individual components. These results are supportive of the
platinum additive lowering the imidization temperature and a synergism
leading to decomposition of the polymer. The decomposition is very evident
above 450°C.

The TG curve for the PdCl$_2$ · 2DMSO additive is shown in Figure 6. Again,
the mass loss, expected due to each dimethyl sulfoxide ligand (23.42%)
followed by loss of each chloride (10.63%) is indicated on the TG curve. The
residue expected, Pd metal, upon loss of all ligands is 31.9%, whereas the
TG curve indicates 36.0% residue. Above 400°C the residue is stable under
the experimental conditions.

The last analysis is that of the polymer containing PdCl$_2$ · 2DMSO (sample
006) (Fig. 9). From 100 to 500°C there is no qualitative difference between
the actual and calculated TG curves. This is in sharp contrast to the
SnCl$_4$ · 2DMSO and PtCl$_2$ · 2DMSO systems, which both showed negative
low temperature difference peaks. At about 510°C a large difference between
the calculated and actual TG curve resulted due to the sample exploding.
The difference TG curve is shown in Figure 10. Though an envelope of
response is seen, it is very small relative to the two previous analyses. The
presence of the palladium additive does not seem to affect the imidization
temperature or cause low temperature decomposition. However, under the
experimental conditions rapid sample mass loss occurs at high temperature.
This analysis was interesting in that if procedural variables including sam-
ple mass are carefully controlled and no interactions are present, the dif-
ference technique is faithful in portraying none.

CONCLUSIONS

The comparison of a calculated TG curve, assuming no chemical or phys-
ical interactions between components, with the actual TG curve of the
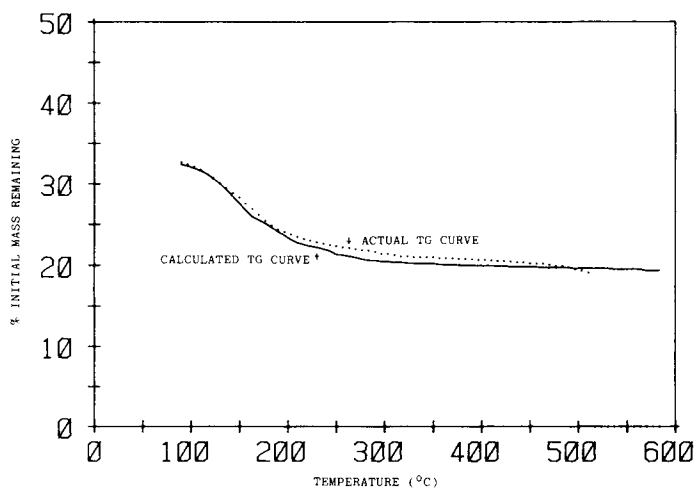mixture can be very interesting. The change in rate of solvent mass loss

Fig. 9. The actual and calculated TG curves for a BTDA/ODA polymer solution containing PdCl$_2 \cdot$ 2DMSO.

due to the onset of imidization was shown. Thermal stability characteristics can be determined by comparison of the actual TG curve with the calculated TG curve. To assign the difference TG behavior to real chemical or physical interactions and not to experimental artifacts requires very careful control of procedural variables. Analysis has proved that the absolute mass of each component must be carefully controlled to obtain valid calculated and difference TG curves. The comparison of differential scanning calorimetric analysis with the difference TG curve, though difficult due to the high solvent content of the samples, is being pursued. The difference TG technique may indicate specific regions on the TG cure for subsequent analysis by combined techniques. Further, this technique may be a powerful aid in establishing temperature and atmosphere programming[14] protocols which
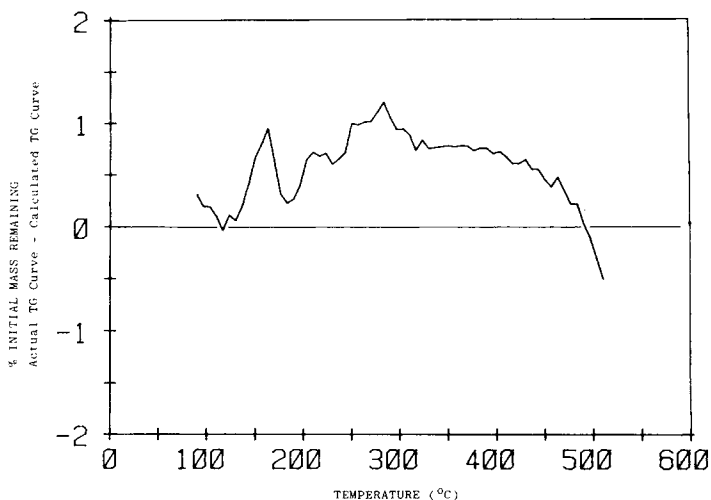

Fig. 10. The difference TG curve for a BTDA/ODA polymer solution containing PdCl$_2 \cdot$ 2DMSO.

yield regions of minimum interaction between components for optimization of blend analysis.

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