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### Identification of Thermal Degradation Products of Titanium Polyethers Using Coupled Thermogravimetric Analysis-Mass Spectroscopy: Development and Evaluation of Instrumentation

Charles E. Carraher Jr.<sup>a</sup>; H. Michael Molloy<sup>a</sup>; Thomas O. Tiernan<sup>a</sup>; Michael L. Taylor<sup>a</sup>; Jack A. Schroeder<sup>a</sup>

<sup>a</sup> Department of Chemistry and The Brehm Laboratory, Wright State University, Dayton, OH

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# Identification of Thermal Degradation Products of Titanium Polyethers Using Coupled Thermogravimetric Analysis-Mass Spectroscopy: Development and Evaluation of Instrumentation

Charles E. Carraher, Jr.  
H. Michael Molloy  
Thomas O. Tiernan  
Michael L. Taylor and  
Jack A. Schroeder

Department of Chemistry and  
The Brehm Laboratory  
Wright State University  
Dayton, OH 45435

## ABSTRACT

The construction and evaluation of a coupled Thermogravimetric Analyzer-Mass Spectrometer (TG-MS) instrument, capable of heating samples as small as one milligram to temperatures as high as 1200°C, while continuously monitoring the gaseous effluents using mass spectrometry, is described. Degradation of titanium polyethers was studied to assess the performance of the TG-MS.

## INTRODUCTION

This report describes the construction and evaluation of a coupled Thermogravimetric Analyzer-Mass Spectrometer instrument as a tool for the detection and identification of thermal degradation products arising from the combustion of polymeric materials. In the studies described, infrared spectral analysis has

been employed to obtain supplemental information on combustion residues.

The materials selected for study in evacuating the performance of the TG-MS are organometallic polymers. These polymers were chosen for several reasons. First, since degradation of these compounds typically occur by different routes in air and in inert environments, the two environments can be clearly, easily differentiated. Second, some of the organometallic polymers exhibit good high temperature stability, losing less than 20% of their initial weight to the 800-1200°C range. Identification of the degradation products from the polymer would be useful in better understanding their good stability, and in designing and synthesizing still more stable polymers. A third reason for using organometallic polymers in assessing the TG-MS is that the degradation of these materials occurs in a stepwise manner over a wide temperature range (often over a range in excess of 800 C°) with interspersed "stability plateaus" (temperature ranges where little or no weight change occurs). Continuous monitoring of the evolved chemical products, as is possible with the TG-MS described, is therefore necessary in order to understand these transitions in the degradation sequence. Finally, the organometallic polymers are good candidates for study by TG-MS because they are difficult to characterize by other techniques. Conventional C, H, N elemental analysis often yields poor results, and since many of these polymers are only sparingly soluble in most solvents, characterization by NMR or ESR is not practical. Methods such as those described herein are therefore needed for characterizing the structures of such organometallic polymer materials.

A variety of TG-MS combinations have been used previously by other investigators to evaluate the thermal properties of polymers and several publications have appeared which are concerned with the application of these techniques for studying organo-

metallic products (1-7). However, only Goldfarb, et al. (7) have reported extensive investigations of the uses of TG-MS for the study of organometallic polymers. The latter authors utilized this technique to identify thermally produced fragments of polysiloxanes.

The organometallic polymers investigated here comprise a family of titanium polyethers which are potentially useful in exterior surface coatings, owing to their excellent resistance to ultraviolet radiation (8-10).

#### INSTRUMENTATION

The TG-MS instrument constructed in the present study consists of a double-focusing duPont 21-491 Mass Spectrometer coupled through a single-stage glass jet separator to a duPont 951 Thermal Gravimetric Analyzer which is attached to a duPont 990 Thermal Analyzer Console. The MS is equipped with a Hewlett-Packard, HP-2216C computer having 24K core memory and a disc-oriented data system specially developed for the duPont 21-491 Mass Spectrometer. The MS system can be controlled by the computer system, which includes a dual 2.5M byte disc drive, a Hewlett-Packard Cathode Ray Tube terminal, a Tektronix storage scope (for display) driven by a dual 12 bit digital-to-analog (D/A) converter, and a Versatec printer/plotter. Data is acquired using a 14 bit analog-to-digital (A/D) converter (13 plus sign). This system can operate and process data at rates up to 8 KHZ. Figure 1 is a block diagram of the TG-MS combination, and the Hewlett-Packard 2116C computer and appropriate peripherals. Also shown in Figure 1 (below the dotted line), as components of this total system, are two other computer systems (HP-2100A and Data General Nova 2) which are utilized for additional data processing and for mass spectral library searches and identifications. Data from the HP-2116C is manually transferred to other

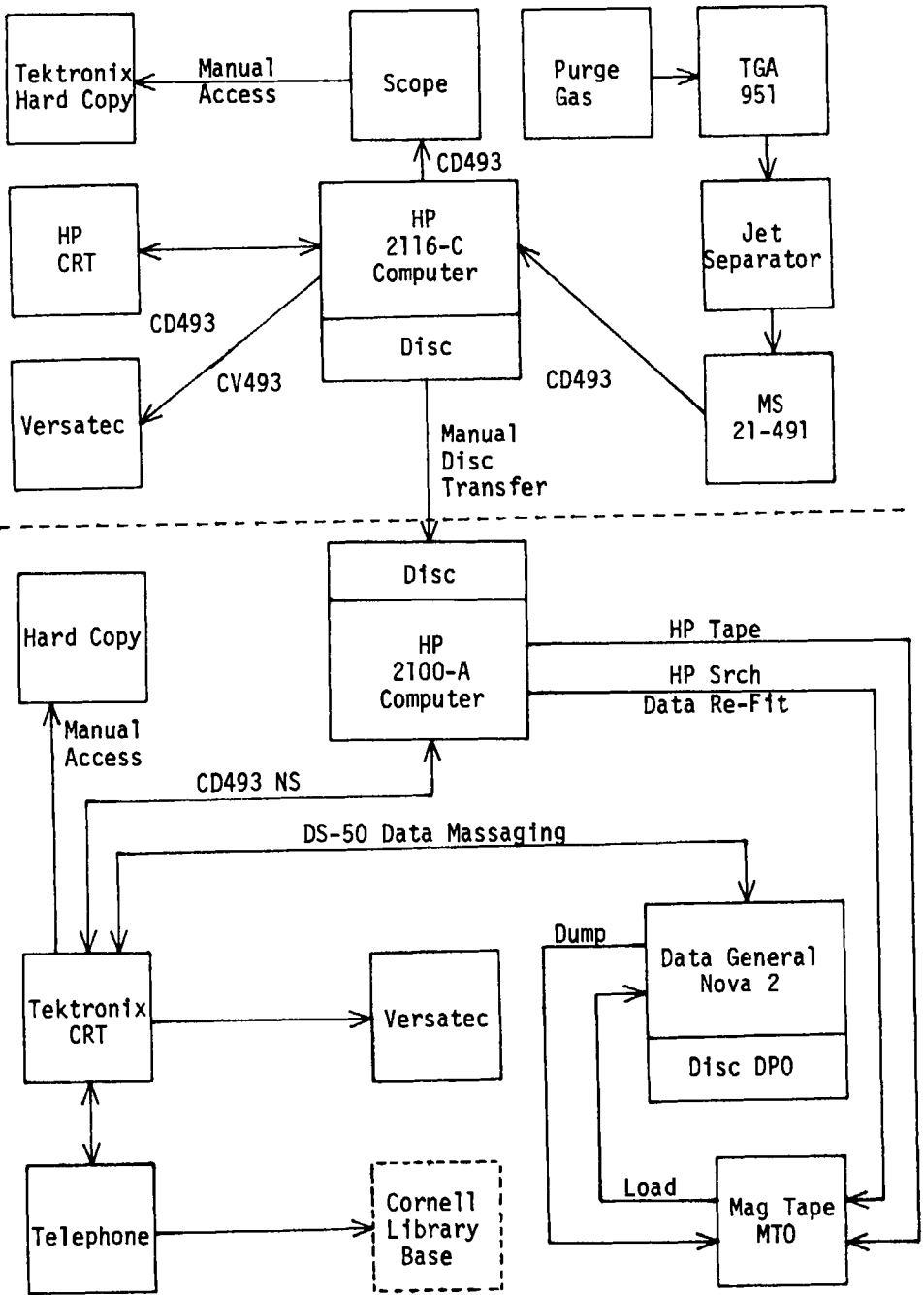


Figure 1. A Block Diagram of the TG-MS Combination Coupled with the Hewlett-Packard 2100 Series Computer and Peripherals

computer banks by moving the disc storage cartridge from one system to the other.

The duPont 951 Thermal Gravimetric Analyzer, supported by four flexible legs, was placed in a 22x16x3 inch deep sand bed to reduce vibrations generated by other instruments in the laboratory and by personnel movements.

The line which transmits the purge gas to the TG is  $\frac{1}{4}$ -inch o.d. stainless steel with a Swagelok quick disconnect which is used during sample loading and preliminary adjustment of the system. Also incorporated in the purge gas line were a drying tube and a shut-off valve to regulate the helium flow. The pressure of the second-stage purge gas regulator was set at 40 P.S.I. to reduce the possibility of a large volume of air entering and subsequently damaging the TG-MS system in the event of a leak in the gas line.

The TG quartz-furnace tube was attached to the MS as shown in Figure 2. The quartz furnace tube was extended by adding  $2\frac{1}{2}$  inches of  $\frac{1}{4}$ -inch o.d. quartz tubing in order to facilitate connection with the jet separator. Connection was made by means of a Swagelok union with a  $\frac{1}{4}$ -inch ceramic-teflon front ferrule and a stainless steel back ferrule to reduce the probability of breaking the tip of the quartz tube.

A 2-inch section of  $\frac{1}{4}$ -inch o.d. glass tubing was connected, also using Swagelok unions, between the jet separator and quartz tube and the entire interface assembly was placed in a specially constructed heated oven. This arrangement permits the jet separator to be easily disconnected and cleaned by simply loosening the connections on the Swagelok fitting which secure the 2-inch glass tube (Figure 2). A glass-lined stainless steel transfer line is used to connect the MS to the jet separator oven. This line is thirty inches in length and  $\frac{1}{8}$ -inch o.d. glass lined stainless steel tubing is employed.

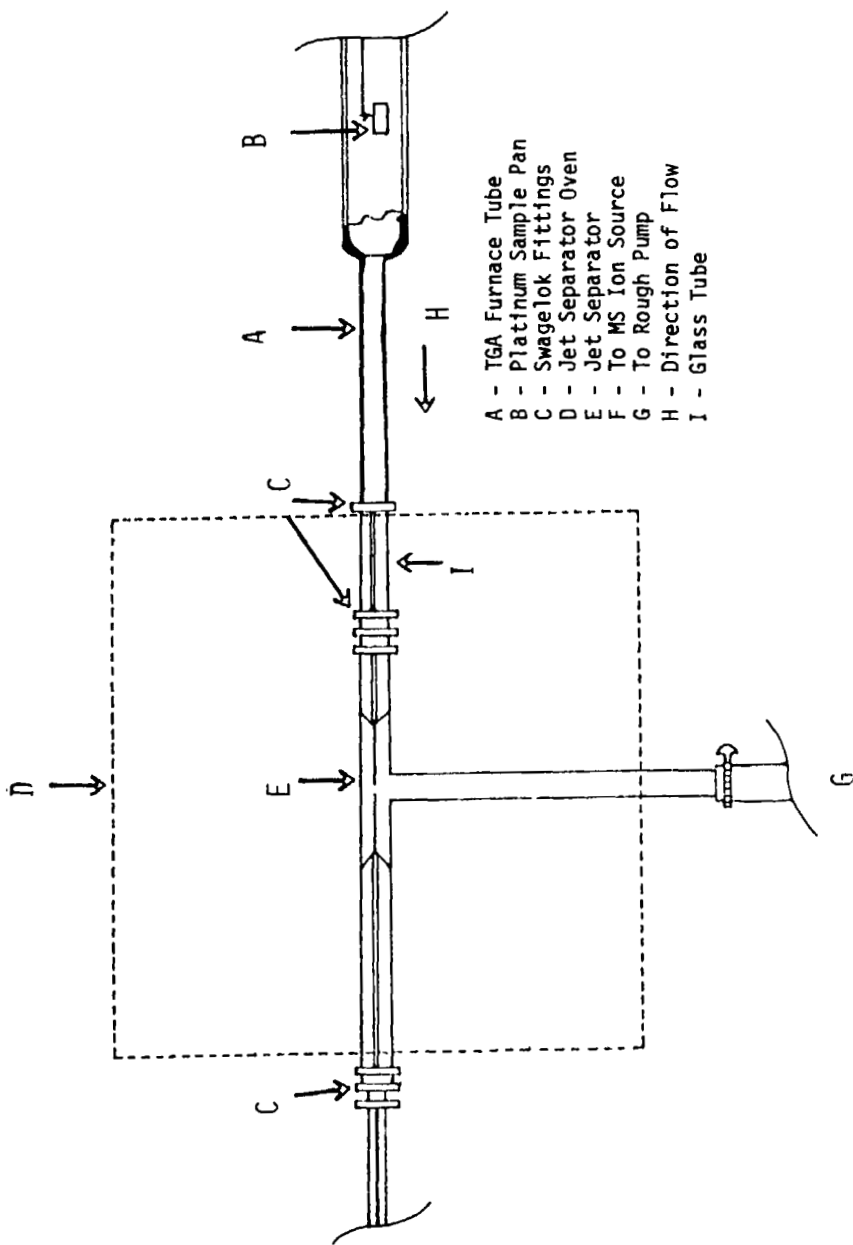


FIGURE 2. DIAGRAM OF THE TG-MS INTERFACE SHOWING THE COUPLING OF THE JET SEPARATOR TO THE TG QUARTZ FURNACE TUBE

A thermocouple, interfaced with the Hewlett-Packard 2116C computer, was employed to sense the temperature during the course of the thermogravimetric analysis. This probe was attached to the TG in order to monitor the actual temperature of the sample during each run (Figure 1). During sample analysis, the TG-jet separator connection was wrapped with heating tape and maintained at a temperature of 125°C while the jet separator oven was maintained at 135°C. The MS-jet separator transfer line was also wrapped with heat tape and maintained at 165°C while the source temperature was held at 230°C.

The mass spectral data acquired using the TG-MS combination can also be compared with standard mass spectral files utilizing a low cost library search system which currently contains some 41,000 mass spectra. This time-sharing computer data system is located at Cornell University and is frequently capable of providing useful identification data even when the unknown spectra results from a mixture of sample components (11,12). The HP 2100A computer system is interfaced directly to this search system via an acoustic coupler, using normal telephone lines. (Figure 1). This mass spectral data system was used in the present study to facilitate analysis of the data obtained for several samples from the TG-MS system.

The infrared spectral data gathered on the original samples and degradation residues were obtained utilizing KBr pellets and Perkin-Elmer 237B, 457 and 621 Grating Infrared Spectrophotometers.

#### Instrument Calibration Procedures

The mass scale from m/e 12 to m/e 1000 of the dePont 21-491 Mass Spectrometer was calibrated over the range from m/e 12-1000 by introducing perfluorokerosene (PFK) into the MS system and then following the steps indicated in the block diagram given in Figure 3. PFK was used as a mass calibration standard since it is



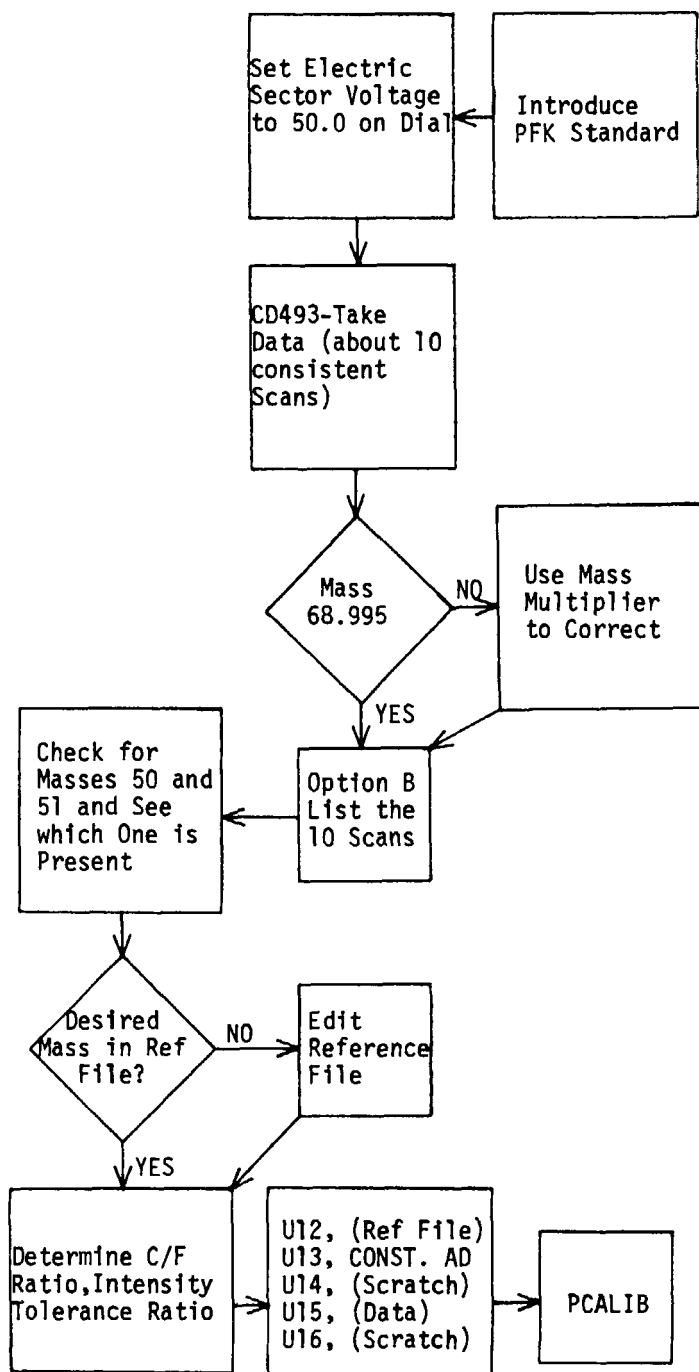


FIGURE 3. CALIBRATION FLOW CHART FOR THE DuPONT 21-491 MS

a widely utilized and well characterized reference standard which exhibits a large number of fragment ions (13). The MS is equipped with a Hall probe to measure the magnetic field strength. The computer monitors the Hall probe voltage (as an indicator of the magnetic field, and, upon calibration, the mass scale, the ion beam intensity and the thermocouple output simultaneously. The positions of ion peaks on the mass scale are determined by on-line centroiding of that portion of each peak with intensity greater than 50% of the maximum of that peak, which yields typical scan to scan reproducibility in mass assignments of 200 to 500 PPM. The Hall probe voltage centroids are converted to mass using a polynomial equation, typically eighth order. Repetitive scans of the PFK standard are acquired until ten consistent scans are obtained. The Hall probe voltages corresponding to the mass peaks detected in each scan are then averaged and displayed or printed out. A check of the print out is made to eliminate possible errors which may occur at this stage such as peaks of adjacent mass being averaged together, or one or more obviously erroneous values being included in the average. The peaks are then compared one by one with the reference spectrum stored on the disc. At this point, a nominal mass for each experimental peak is computed by using an approximate polynomial. The nominal mass is used only as an initial step in the identification of the masses and therefore does not need to be accurate. The poorer the approximate polynomial is, however, the greater will be the need to edit the calculated results. Next, each nominal mass in the unknown spectrum is compared (with specific tolerance limits) to a peak in the reference spectrum file and this list is displayed. At this point the operator can change or delete any of the matches made by the computer, as well as add any apparent matches which were missed. These data, consisting of a list of the Hall probe voltages, masses assigned, and weighting factors, determined from the mass

of each peak, and the number of spectra in which it occurred, are recorded on the disc.

The data are then processed by a least squares curve fitting program which determines accurately the polynomial expression which best fits the data. A table is then displayed showing the coefficients of all the terms for polynomials ranging in order from two to eight, and indicating the accuracy of the fit for each. Finally, the desired order of smoothing is chosen, the computer automatically records the information on the disc and the mass multiplier is set to a predetermined value (for more information on this procedure see references 14-16). The calibration procedure typically requires thirty to sixty minutes, and yields accurate mass assignments. The mass spectrometer, when properly tuned, provides unit mass spectral resolution up to mass 1000. However, for the present study, only the mass range from  $m/e$  12 to  $m/e$  400 was utilized.

Calibration of the TG-MS instrument was accomplished using 2.5 to 3.5 milligrams of a standard calcium oxalate monohydrate, and entailed correlating the TG thermogram with the mass spectral data. Calcium oxalate monohydrate was used for calibration since it is the standard commonly used to calibrate the apparatuses. In addition, the degradation products are well known, with water, carbon monoxide and carbon dioxide being the three principle degradation products (17). Figure 4 illustrates the correlation between weight loss as indicated by the TG profile and the appearance of identifiable ions in the mass spectra. In Figure 4, the plot labelled T is a plot of the total ion current as a function of temperature, A is a plot of  $m/e$  18 (indicative of water) as a function of temperature, B is a plot of  $m/e$  28 (indicative of carbon monoxide) as a function of temperature, C is a plot of  $m/e$  44 (indicative of carbon dioxide) as a function of temperature and G is a plot of per cent weight loss as a function of tempera-

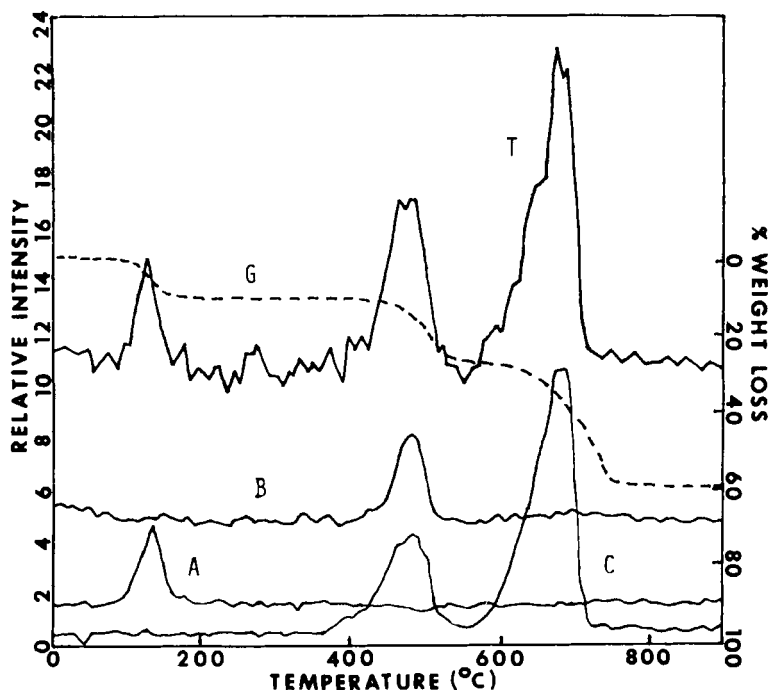


FIGURE 4. TG(---) AND MS(—) PLOTS FOR CALCIUM OXALATE MONA-HYDRATE DECOMPOSITION. THE MS IONIZING VOLTAGE WAS 70eV, THE FLOW RATE OF HELIUM WAS 55mL/MIN AND THE HEATING RATE WAS 20°C/MIN. THE SAMPLING FREQUENCY OF THE DATA ACQUISITION SYSTEM WAS 41 KC. T = TOTAL ION CURRENT A = PLOT OF m/e 18 B = PLOT OF m/e 28 C = PLOT OF m/e 44 G = TG

ture. The TG-MS calibration is normally valid for several weeks, if the system is used regularly and if no instrument malfunctions occur.

During a typical TG-MS analysis requiring 45 minutes the TG temperature was programmed to increase at a constant heating rate of 20°C per minute, over the range from ambient temperature to 900°C, while volatile degradation products formed from degradation of the organometallic polymer were continuously swept from the TG tube by the helium carrier gas (flowing through the furnace

tube at 55 milliliters per minute), then through the helium jet separator, and finally into the mass spectrometer ion source where ionization occurred and a characteristic mass spectrum was produced. The typical MS ion source temperature was 230°C and the ionizing voltage was 70eV.

The TG-MS system was monitored periodically to ensure that sample "carry over" or "memory effects" did not occur. This was accomplished by conducting a run with no sample in the TG pan. The data gathered from such blank runs were checked and in all instances, indicated no sample residues from previous analyses.

### RESULTS AND DISCUSSION

Titanium polyethers are of the general form I. As previously noted, these compounds have been suggested as ultraviolet stabilizers for exterior coatings (8-10). Also, titanium polyethers have been shown to be semiconductors, exhibiting specific resistivity in the range of  $10^5$  to  $10^7$  ohm-cm (18,19). It is particularly interesting that the titanium polyethers, as a family, exhibit poor low temperature stability (below 200°C) but moderate to good high temperature stability (retaining up to 80% weight at temperatures up to 900°C) (8,10). It was hoped that TG-MS analysis of these compounds would provide information on the decomposition mechanism, including identification of the major evolved degradation fragments and the sequence of bond breakage, to (potentially) identify the site of least stability, eventually enabling the design of more thermally stable polyethers and would reveal the weakest bond in the compounds. Results obtained from these degradation studies are summarized below.

#### $Cp_2TiCl_2$ and Hydroquinone

The polyether derived from the condensation of dicyclopentadienyl titanium dichloride,  $Cp_2TiCl_2$ , with hydroquinone exhibited

an initial weight loss at a temperature of 89°C, with the most rapid weight loss (about 8%) occurring between 100 and 180°C, followed by an almost constant-slope weight loss of 20% over the next 600 C° range (Figure 5). The comparatively rapid degradation

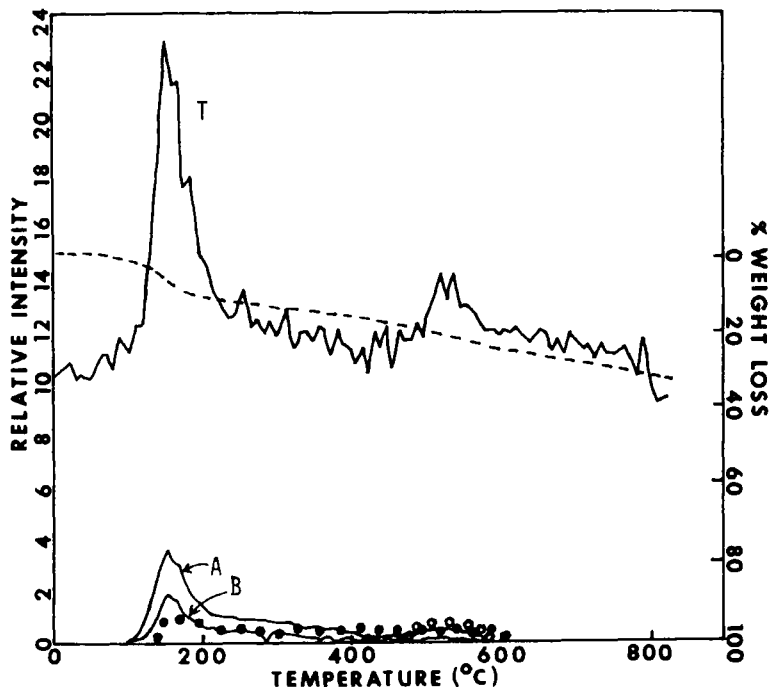
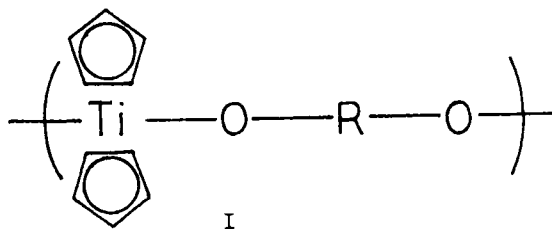


FIGURE 5. TG(---) AND MS (—) PLOTS FOR THE CONDENSATION PRODUCT FROM DICYCLOPENTADIENYL TITANIUM DICHLORIDE AND HYDROQUINONE DECOMPOSITION. THE MS IONIZING VOLTAGE WAS 70eV, THE FLOW RATE OF HELIUM WAS 55 mL/MIN AND THE HEATING RATE WAS 20 C°/MIN. THE SAMPLING FREQUENCY OF 41 KC WAS USED. T = TOTAL ION CURRENT A = PLOT OF m/e 66—, B = PLOT OF m/e 65— C = PLOT OF m/e 108.... D = PLOT OF m/e 78 ○○○○ E = PLOT OF m/e 94 ●●●●●

occurring between 100 and 180°C gives rise to volatile degradation products which exhibit 15 major (normalized intensities greater than 1%) mass peaks (Table 1). Peaks are observed at m/e 66, 65, 39, 40, 26, 63, 64, 31, 62, 67, 41 and 51 and these ions and their respective intensities correspond to those which are characteristic of the standard spectrum of cyclopentadiene as listed in the John Wiley compilation by McLafferty, et al. (Table 2). In addition, at temperatures between 120 and 180°C three additional major mass peaks appeared in the mass spectrum of the degradation products (m/e = 108, 54 and 82). Thus peaks at m/e 108, 54, 82, 26, 51, 41 and their respective intensities are consistent with the standard spectrum of p-benzoquinone (Table 2). Over this temperature range, however, the ions characteristic of cyclopentadiene are greater in intensity than those attributable to p-benzoquinone. Thus, degradation apparently occurs at moderate

Table 1

Major Ions in the Mass Spectra of the Degradation Products from the Pyrolysis of the Condensation Product of Dicyclopentadienyl Titanium Dichloride,  $Cp_2TiCl_2$ , and Hydroquinone, HQ, at 143°C

<u>m/e</u>	<u>Apparent Degradation Product</u>	<u>Normalized Intensity</u>	<u>m/e</u>	<u>Apparent Degradation Product</u>	<u>Normalized Intensity</u>
66	Cp	52.129	31	Cp	3.852
65	Cp	23.439	51 <sup>a</sup>	HQ,Cp	1.257
39	Cp	17.985	26 <sup>a</sup>	HQ,Cp	4.704
40	Cp	16.991	41 <sup>a</sup>	HQ,cp	2.656
63	CP	4.217	108	HQ	7.117
64	Cp	3.427	54	HQ	4.542
67	Cp	3.021	82	HQ	2.595
62	Cp	3.183			

a. these fragment ions can be derived from Cp and HQ

Table 2

Comparison of Mass Spectral Data for Cyclopentadiene, p-Benzoquinone, Phenol and Benzene Compared with the TG-MS Spectra of the Condensation Product of Dicyclopentadienyl Titanium Dichloride and Hydroquinone

		<u>Cyclopentadiene</u>								
m/e		66	65	39	40	48	64	67	63	31
		<u>Relative Intensity</u>								
John Wiley Atlas Mass Spectrum	1000	473	316	273	82	82	63	58	49	
TG-MS Degradation Product Spectrum	1000	450	345	326	-	81	58	61	74	
		<u>p-Benzoquinone</u>								
m/e		108	54	82	26	50	51			
		<u>Relative Intensity</u>								
John Wiley Atlas Mass Spectrum	1000	790	357	298	54	43				
TG-MS Degradation Product Spectrum	1000	638	365	661	68	43				
		<u>Phenol Mass</u>								
m/e		94	39	66	65	40	55			
		<u>Relative Intensity</u>								
John Wiley Atlas Mass Spectrum	1000	531	467	395	219	151				
TG-MS Degradation Product Spectrum	1000	430	-	319	612	665				
		<u>Benzene Mass</u>								
m/e		78	51	52	50	39				
		<u>Relative Intensity</u>								
John Wiley Atlas Mass Spectrum	1000	205	196	179	141					
TG-MS Degradation Product Spectrum	1000	240	481	-	100					



temperatures mainly through evolution of the cyclopentadiene moiety, and less so, but still to a significant extent, through the evolution of p-benzoquinone. At the temperature of 227°C ions at m/e of 141-142 appear, which are characteristic of the product resulting from coupling of phenylene and cyclopentadiene was (Table 3).

At temperatures above 388°C, the mode of degradation has changed and 13 additional major mass peaks appear in the mass spectra of the degradation products (Table 3). Between 388°C and 588°C, peaks are observed at m/e 78, 51, 52, 50, 39 and 27 and the respective intensities of these ions match those which are reported in standard spectrum of phenol (Table 2). Ions were observed at m/e 154, above 488°C, presumably indicative of the phenylene dimer (Table 3). Therefore, higher temperatures apparently result in greater fragmentation of the oxyphenylene, -O-O, moiety.

Table 3

Major Ions in the Mass Spectra of the Degradation Products from the Pyrolysis of the Condensation Product of Dicyclopentadienyl Titanium Dichloride,  $Cp_2TiCl_2$ , and Hydroquinone, HQ, at 503°C

m/e	Apparent Degradation Product	Normalized Intensity	m/e	Apparent Degradation Product	Normalized Intensity
78	Benzene	8.816	55	Phenol	2.497
52	Benzene	4.238	40	Phenol	2.299
27	Benzene	0.860	43	Phenol	2.239
142	Benzene,Cp	1.857	41	Phenol	1.859
51	Benzene,Phenol	2.599	65	Phenol	1.200
39	Benzene,Phenol	2.479	154 <sup>a</sup>	Benzene	2.039
94	Phenol	3.758			

a. mass 154 represents the coupling of benzene

The mass spectral ions characteristic of the cyclopentadiene and p-benzoquinone moieties reached maximum intensities at a degradation temperature of 151°C and then decreased steadily, becoming insignificant at temperatures above 480°C (Table 4). Ions indicative of benzene reached an intensity maximum at 511°C, decreased markedly at temperatures above 588°C, and fell off gradually in intensity to a temperature of 749°C (Table 4). The ion indicative of phenylene dimerization reached a maximum at 557°C, and was detectable to temperatures of 618°C (Table 4).

The order of degradation was deduced by noting the TG temperature at which selected ion fragments initially appeared (Table 4). The first significant ion detected in the mass spectrum of the degradation products was  $m/e$  66, corresponding to cyclopentadiene (see A in Form II), followed shortly by  $m/e$  108 corresponding to p-benzoquinone (see B in Form II). The ion next observed was  $m/e$  141, derived from the coupling of the phenylene and cyclopentadiene moieties. At 388°C, benzene was detected as indicated by the appearance of  $m/e$  of 78 (see C in Form II), followed by observation of  $m/e$  of 94 attributable to phenol (see D in Form II). Finally,  $m/e$  154, representing the product from coupling of phenylene,  $\theta$ - $\theta$ , was detected. The fragmentations leading to the observed moieties which are described above are illustrated in form II, below, with their sequence of occurrence indicated by the alphabetical designations

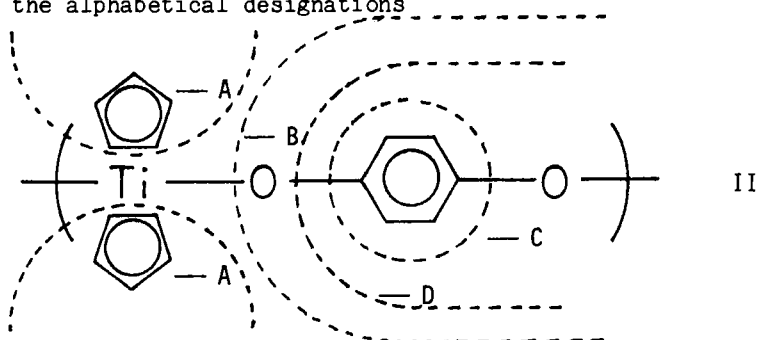


Table 4

Major Ions in the Mass Spectra of the Degradation Products from the Pyrolysis of the Condensation Product of Dicyclopentadienyl Titanium Dichloride,  $\text{Cp}_2\text{TiCl}_2$ , and Hydroquinone as a Function of Temperature.

m/e	Degradation Product	Initial Appearance		Maximum Intensity		Final Appearance	
		Temp. °C	Normalized Intensity	Temp. °C	Normalized Intensity	Temp. °C	Normalized Intensity
66	Cp <sup>a</sup>	89	.523	151	55.122	480	2.298
108	HQ <sup>b</sup>	120	1.127	151	7.988	726	1.055
142	Cp- $\emptyset$ <sup>c</sup>	227	.307	503	1.859	634	.574
78	$\emptyset$	388	.272	511	9.632	588	1.227
94	Phenol	457	1.831	503	3.758	749	.899
154	$\emptyset$ - $\emptyset$ <sup>d</sup>	488	.424	557	2.323	618	.530

a. Cp represents cyclopentadiene

b. HQ represents hydroquinone

c.  $\emptyset$  represents benzene

d.  $\emptyset$ - $\emptyset$  represents the product from the dimerization of phenylene

The absence of ions with significant intensities at  $m/e$  47 (Ti),  $m/e$  79 ( $TiO_2$ ) and  $m/e$  170-180 (Ti- $\emptyset$ ) indicate that titanium-containing, volatile species were not formed, which is consistent with the metal remaining within the TG residue.

In summary, the order of appearance of degradation products from the degradation of the condensation products of dicyclopentadiene titanium dichloride with p-benzoquinone are: A-cyclopentadiene, B-p-benzoquinone, C-benzene and D-phenol.

The infrared spectrum of the degradation residue of the product derived from the titanium polyether shows identifiable bands only at wave numbers below  $800\text{ cm}^{-1}$ , and the observed spectrum is identical to that of titanium dioxide,  $TiO_2$  (Figure 6).  $TiO_2$  is white whereas the solid residue derived from the titanium polyether was light brown in color. If the resulting residue contained only Ti or  $TiO_2$ , then the weight of the residue would be 17 or 28% respectively of the initial sample. The observed residue weight from the TG was 56% of the original sample, however consistent with the inclusion of materials other than titanium (Figure 6). Polymeric "tars" typically yield spectra which exhibit broad bands having little if any definition. Therefore, such tars

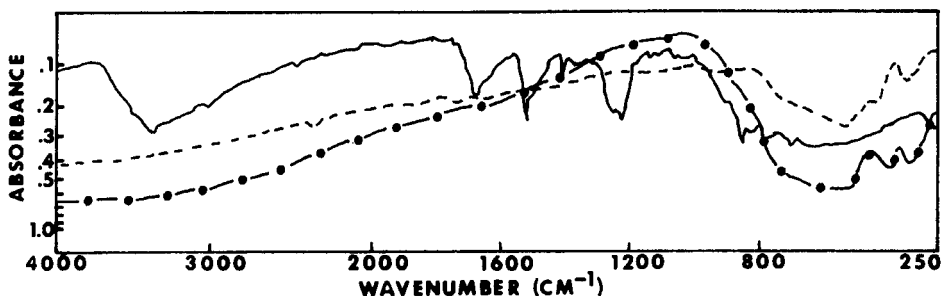


FIGURE 6. INFRARED SPECTRA OF THE CONDENSATION PRODUCT OF DICYCLOPENTADIENYL TITANIUM DICHLORIDE AND HYDROQUINONE (—) OF THE RESIDUE AFTER HEATING TO  $900^{\circ}\text{C}$  IN HELIUM AT A RATE OF  $20\text{ C}^{\circ}/\text{MIN}$  (---), AND OF TITANIUM DIOXIDE (-●-●-).

yield essentially only background contributions to the infrared spectra of the residue. It is likely that the formation of  $\text{TiO}_2$  occurs subsequent to the removal of the helium environment since oxygen is needed to form  $\text{TiO}_2$  and several oxygen-containing moieties were detected in the evolved degradation products. Quantitative elemental analysis of the amount of titanium present in the residue as Ti or  $\text{TiO}_2$  would have to be completed to satisfactorily resolve the question of whether or not the oxygen was derived from the sample itself, the surrounding atmosphere, or both.

#### $\text{Cp}_2\text{TiCl}_2$ and Bisphenol A

The polyether derived from the condensation of dicyclopentadienyl titanium dichloride,  $\text{Cp}_2\text{TiCl}_2$ , with bisphenol A, exhibited major weight loss in two temperature ranges (Figure 7). In the first range between 105 and 400°C the products evolved initially (at 105°C) yield ions characteristic of the cyclopentadiene moiety (m/e 66) (Figure 6). Ions characteristic of the propyl moiety (m/e 44) began to appear in significant (>1%) intensities at around 204°C and continue to be detected until the heating cycle is completed. Two maxima in the m/e 44 intensity are observed at 342 and 420°C. The second temperature range in which significant weight loss occurs is coincident with the observation of ions in the mass spectrum of the degradation product which are characteristic of the phenol moiety (m/e 94). There are initially observed at about 273°C, reach a maximum at around 419°C, and become insignificant at about 641°C. The probable origin of the moieties just mentioned are indicated in Form III where the sequence of elimination of these fragments is indicated by the alphabetical designations. Table 5 summarizes the order of appearance of the degradation products.

As in the case with the products from the condensation with hydroquinone, a significant quantity of nonmetallic residue was

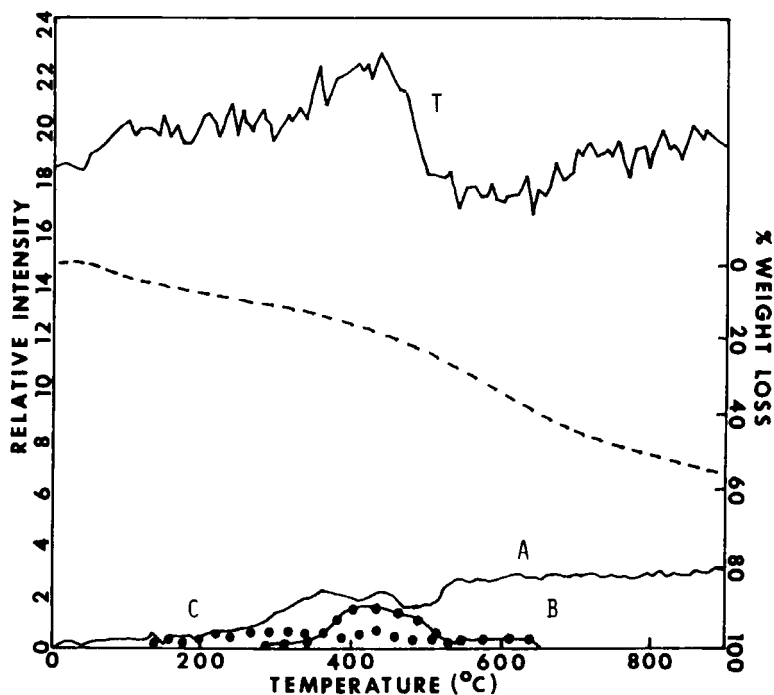
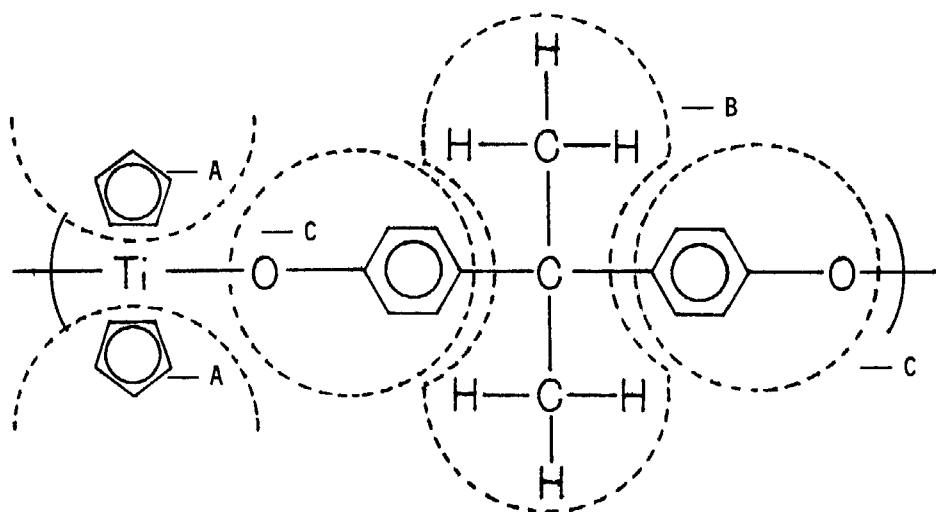


FIGURE 7. TG (---) AND MS(—) PLOTS FROM THERMAL DEGRADATION OF THE CONDENSATION PRODUCT FROM DICYCLOPENTADIENYL TITANIUM DICHLORIDE AND BISPHENOL A OBTAINED AT A MS IONIZING VOLTAGE OF 70 eV, TG FLOW RATE OF HELIUM AT 55 mL/MIN FOR A HEATING RATE OF 20 C°/MIN AND A DATA SAMPLING FREQUENCY OF 41 KC.

T = TOTAL ION CURRENT    A = PLOT OF  $m/e$  44 (—)  
 B = PLOT OF  $m/e$  94 (●)    C = PLOT OF  $m/e$  66 (...)

observed from the degradation of the  $Cp_2TiCl_2$ /bisphenol A condensation product at temperatures up to 900°C. The residue constituted 44% of the initial sample (see Figure 6) (Ti-12%;  $TiO_2$ =20%).

In summary, the order of appearance of the degradation products from the pyrolysis of the condensation products of dicyclopentadienyl titanium dichloride with bisphenol A was: A-cyclopentadiene, B-propyl and C-phenol.



III

Degradation occurs through several kinetically controlled stability plateaus. Again, a stability plateau is a temperature range in which little or no weight loss occurs, and a kinetically controlled stability plateau is a region where weight loss occurs independently of heating rate, which is evident experimentally, because the plateau is not parallel to the temperature axis but exhibits a low pitch.

#### $\text{Cp}_2\text{TiCl}_2$ and Di-tert-butyl-p-hydroquinone

The order of appearance of degradation products from the pyrolysis of the condensation product of dicyclopentadienyl titanium dichloride and di-tert-butyl-p-hydroquinone is shown in Table 6 and illustrated schematically in Form IV, where the degradation sequence is indicated by the alphabetical designations.

Table 5

Major Ions in the Mass Spectra of Degradation Products from the Pyrolysis of the Condensation Product of Dicyclopentadienyl Titanium Dichloride,  $\text{Cp}_2\text{TiCl}_2$ , and Bisphenol A as a Function of Temperature

m/e	Degradation Product	Initial Appearance		Maximum Intensity		Final Appearance	
		Temp. °C	Normalized Intensity	Temp. °C	Normalized Intensity	Temp. °C	Normalized Intensity
66	Cp <sup>a</sup>	105	.668	335	5.364	488	.830
44	Propane	204	4.760	342	18.382	> 900	-
94	Phenol	273	.387	419	20.453	641	.243

a. Cp represents cyclopentadiene



Table 6

Major Ions in the Mass Spectra of the Degradation Products from Pyrolysis of the Condensation Product of Dicyclopentadienyl Titanium Dichloride,  $\text{Cp}_2\text{TiCl}_2$ , and Di-tert-butyl-p-benzoquinone as a Function of Temperature

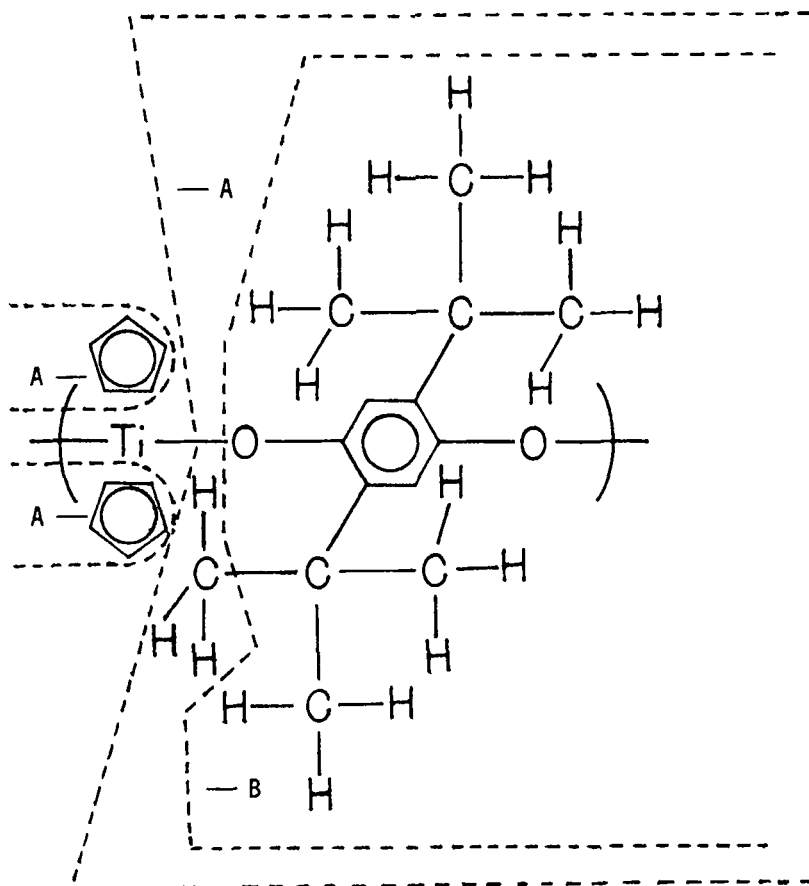
m/e	Degradation Product	Initial Appearance		Maximum Intensity		Final Appearance	
		Temp. °C	Normalized Intensity	Temp. °C	Normalized Intensity	Temp. °C	Normalized Intensity
66	Cp <sup>a</sup>	74	.947	434	3.404	848	.293
220	DTHQ <sup>b</sup>	74	1.375	258	27.479	> 900	-
205	THQ <sup>c</sup>	82	1.542	258	27.479	> 900	-
108	HQ <sup>d</sup>	89	.719	243	7.153	533	.435
94	Phenol	135	2.570	243	4.238	503	.771
44	Propane	404	12.473	572	21.595	787	5.212

a. Cp represents cyclopentadiene

b. DTHQ represents di-tert-p-benzoquinone moiety

c. THQ represents di-tert-p-benzoquinone moiety minus a methyl group

d. HQ represents p-hydroquinone minus two protons



## IV

Ions characteristic of the cyclopentadiene moiety were again the first to appear in the mass spectrum of the degradation products, initially at a temperature of  $74^{\circ}\text{C}$ . Unlike the two compounds discussed above, degradation in this case occurs rapidly largely over a narrow  $50^{\circ}\text{C}$  temperature range (from  $130$  to  $180^{\circ}\text{C}$ ), with about 80% weight loss from the sample (see Figure 8). Evolution of cyclopentadiene ( $m/e$  66) and appearance of the  $m/e$  220

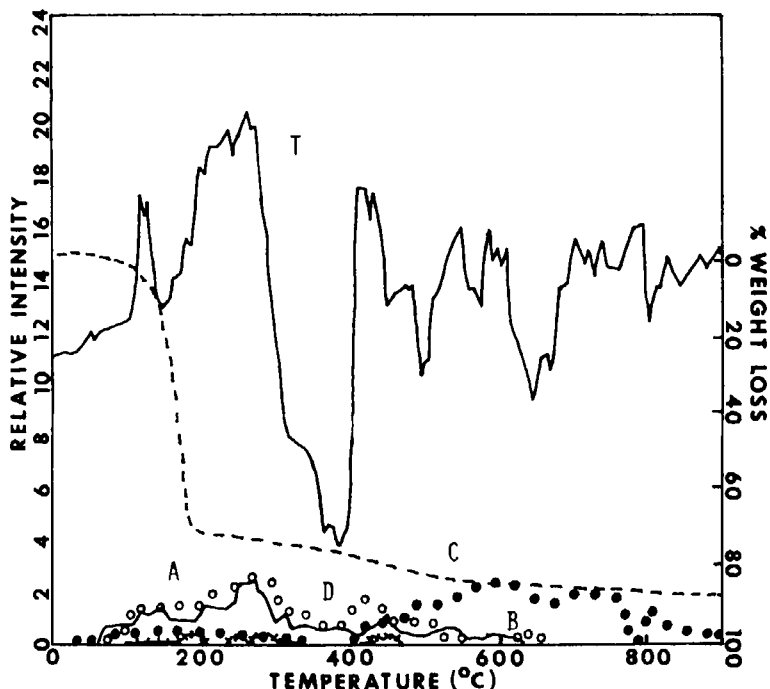


FIGURE 8. TG(---) AND MS(—) PLOTS FROM THERMAL DEGRADATION OF THE CONDENSATION PRODUCT FROM DICYCLOPENTADIENYL TITANIUM DICHLORIDE AND DI-TERT-BUTYL-P-HYDROQUINONE OBTAINED AT A MS IONIZING VOLTAGE OF 70eV, TG FLOW RATE OF HELIUM AT 55 mL/MIN FOR A HEATING RATE OF 20 C°/MIN AND A DATA SAMPLING FREQUENCY OF 41 KC. T = TOTAL ION CURRENT A = PLOT OF m/e 66 (○) B = PLOT OF m/e 220 (—) C = PLOT OF m/e 44 (●) D = PLOT OF m/e 205 (◻)

ion, which corresponds to the entire di-tert-butyl-p-hydroquinone moiety (less 2 protons), began at 74°C (see A in Form IV). The mass spectral ion at m/e 205 corresponds to the di-tert-butyl-p-hydroquinone moiety (less a methyl group) and appeared initially at a temperature of 82°C. As expected, evolution of this product closely parallels that which is indicated by the mass 220 moiety. Other major ions observed in the mass spectra of the degradation products of this compound were m/e 44 probably indicative of

propane,  $m/e$  94 which apparently results from the phenol product, and  $m/e$  108 which corresponds to the *p*-hydroquinone product.

At  $97^{\circ}\text{C}$  ion masses were detected in the degradation product spectra, 14 being greater than 1% in normalized intensity. The number of ion masses detected in the mass spectra maximized at a pyrolysis temperature of  $235^{\circ}\text{C}$ , and 50 of the 67 ions observed were greater than 1% in normalized intensity. The number and intensity of mass spectral peaks then decreased steadily, as the temperature increased to  $400^{\circ}\text{C}$ . It is clear, therefore, that degradation of this compound occurred abruptly with the generation of a large number of fragments. These fragments appear to be largely derived from the di-*tert*-butyl-*p*-hydroquinone moiety, and the mass spectra are in good agreement with tabulated mass spectral data for the 12 most abundant fragments.

The residue resulting from degradation of the  $\text{Cp}_2\text{TiCl}_2$ /di-*tert*-butyl-*p*-hydroquinone condensation products, in contrast to the previously discussed compounds, consists entirely of titanium (% residue = 12, % Ti = 13, %  $\text{TiO}_2$  = 22) without organic content.

#### $\text{Cp}_2\text{TiCl}_2$ and Tetrachloro-*p*-hydroquinone

Degradation of the condensation product from dicyclopentadienyl titanium dichloride,  $\text{Cp}_2\text{TiCl}_2$ , with tetrachloro-*p*-hydroquinone began at a temperature of  $105^{\circ}\text{C}$ , as indicated by the observation of  $m/e$  246-249 in the mass spectra of evolved products. These ions are indicative of the tetrachloro-*p*-hydroquinone moiety ( $m/e$  246)(Table 7). The evolution of cyclopentadiene followed, initially at about  $143^{\circ}\text{C}$ , and continued to  $404^{\circ}\text{C}$  (Figure 9, Table 7). Degradation was rapid (similar to that of the condensation product of dicyclopentadienyl titanium dichloride with di-*tert*-butyl-*p*-hydroquinone) with 70% weight loss occurring in the range from 170 to  $230^{\circ}\text{C}$ . This was followed by a gradual weight loss of an additional 10% from 420 to  $520^{\circ}\text{C}$ . In

Table 7

Major Ions in the Mass Spectra of the Degradation Products from Pyrolysis of the Condensation Product of Dicyclopentadienyl Titanium Dichloride,  $\text{Cp}_2\text{TiCl}_2$ , and Tetrachloro-p-hydroquinone as a Function of Temperature

$m/e$	Degradation Product	Initial Appearance		Maximum Intensity		Final Appearance	
		Temp. °C	Normalized Intensity	Temp. °C	Normalized Intensity	Temp. °C	Normalized Intensity
246	TCHQ <sup>a</sup>	105	.549	741	1.331	>900	-
66	Cp <sup>b</sup>	143	4.616	166	6.064	404	1.032
36	Cl or HCl	618	.464	772	2.240	>900	-

a. TCHQ represents tetrachloro-p-hydroquinone moiety

b. Cp represents cyclopentadiene

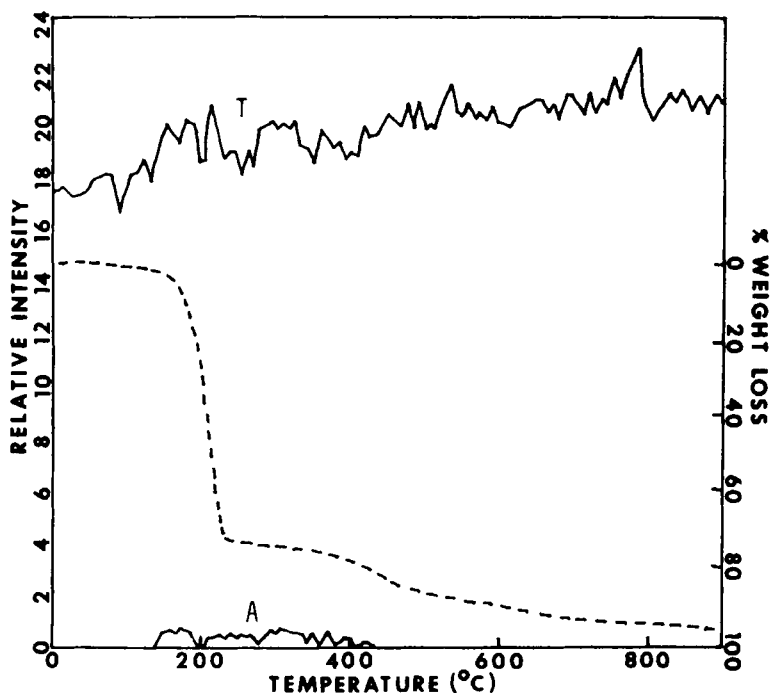
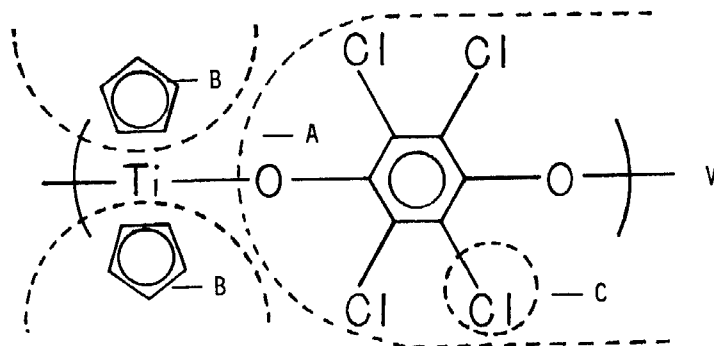


FIGURE 9. TG(---) AND MS(—) PLOTS FROM THERMAL DEGRADATION OF THE CONDENSATION PRODUCT FROM DICYCLOPENTADIENYL TITANIUM DICHLORIDE AND TETRACHLORO-P-HYDROQUINONE OBTAINED AT A IONIZING VOLTAGE OF 70eV, TG FLOW RATE OF HELIUM AT 55 mL/MIN FOR A HEATING RATE OF 20 C<sup>o</sup>/MIN AND A DATA SAMPLING FREQUENCY OF 41 IC. T = TOTAL ION CURRENT A = PLOT OF m/e 66

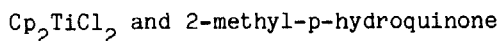
contrast to the previously discussed compound ( $Cp_2TiCl_2$  with di-tert-butyl-p-hydroquinone) excessive fragmentation did not occur either during or after the rapid weight loss (only 29 ion masses were detected in the degradation product spectra and only 7 exceeded 1% in normalized intensity. Furthermore there did not appear to be any significant change in the observed total ion current over the entire temperature range. Trace quantities of ions indicative of tetrachloro-p-hydroquinone (less one or two chlorine atoms)(m/e 175 and 210) were detected at temperatures

near 300°C and 700°C. Traces of hydrogen chloride and chlorine m/e 36 were detected from 600 to 900°C.

Results obtained for this sample preclude the postulation of a well-defined degradation sequence. During the heating cycle, (at about 100°C) a cloud of gaseous material was visually evident and a yellow deposit appeared on the inside tip of the TG quartz tube. Thus, mass spectral ions detected at higher temperatures may be due in part to the evolution and/or degradation of this yellow solid, rather than arising solely directly from the condensation product. A tentative sequence of degradation is indicated by the date in Table 7 and illustrated schematically in Form V, where the order of fragmentation is again designated by the alphabetical notation.

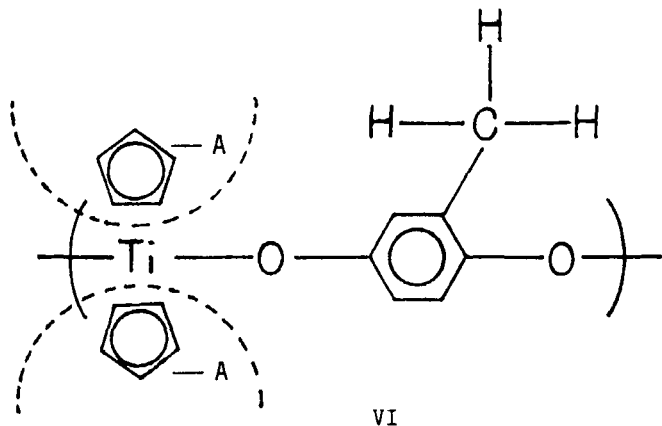


The final weight of the residue at 900°C was approximately 12% of the initial sample which corresponds to the value expected if the residue consists only of titanium without any organic residue (% Ti = 14, % TiO<sub>2</sub> = 24).



The last titanium polyether studied was that derived from the condensation of dicyclopentadienyl titanium dichloride, Cp<sub>2</sub>TiCl<sub>2</sub>, and 2-methyl-p-hydroquinone. The postulated degrada-

tion sequence for this compound is indicated by the data shown in Table 8 and is illustrated schematically in Form VI.



The mass spectral ions observed initially from the degradation products were  $m/e$  18 and  $m/e$  17 which were detectable in the temperature range from 51 to 160°C, reaching a maximum at about 97°C. This particular sample exhibited a strong infrared band at about 3300 to 3000  $\text{cm}^{-1}$ , which is probably indicative of the presence of water. Therefore, the initial weight loss apparently resulted from the elimination of water from the hydrated sample. The initial evolved ions and associated fragments from the polymer chain itself which corresponded to the cyclopentadiene moiety began at about 105°C and continue to around 450°C. There were no other major ion masses detected in the degradation product mass spectra although trace intensities of  $m/e$  78 (benzene),  $m/e$  109 (*p*-hydroquinone), in the degradation product mass spectra, and  $m/e$  123 (methyl-*p*-hydroquinone) were observed. No major change in the total ion current was evident and the total weight loss amounted to only 30%, which occurred gradually over an 800 C° temperature range (Figure 10). The major weight loss was largely due to cyclopentadiene elimination (see A in Form VI) (one cyclo-



Table 8

Major Ions in the Mass Spectra of the Degradation Products from Pyrolysis of the Condensation Product of Dicyclopentadienyl Titanium Dichloride, Cp<sub>2</sub>, and 2-Methyl-p-hydroquinone as a Function of Temperature

m/e	Degradation Product	Initial Appearance		Maximum Intensity		Final Appearance	
		Temp. °C	Normalized Intensity	Temp. °C	Normalized Intensity	Temp. °C	Normalized Intensity
18	H <sub>2</sub> O	51	14.475	97	26.638	212	16.188
66	Cp <sup>a</sup>	105	.467	289	4.220	457	.310

a. Cp represents cyclopentadiene

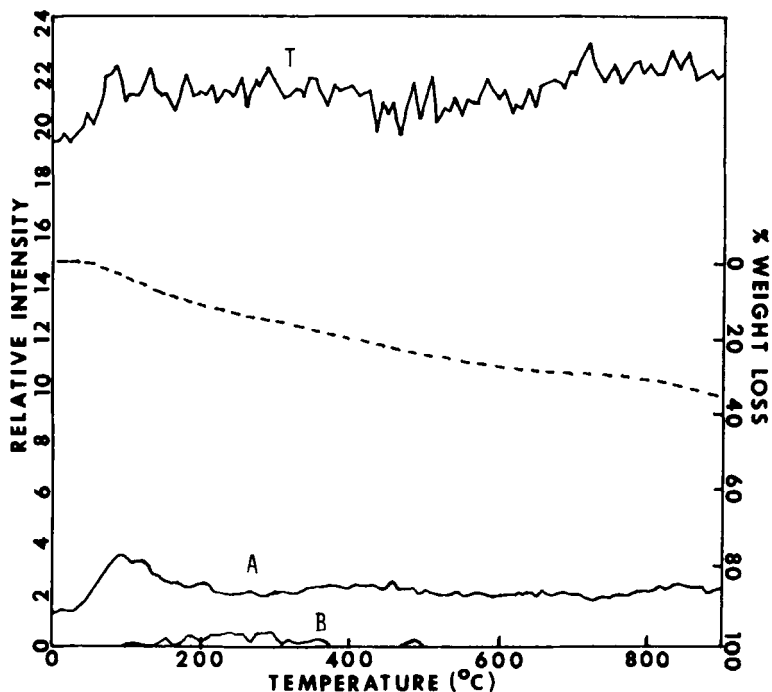


FIGURE 10. TG(---) and MS(—) PLOTS FROM THERMAL DEGRADATION OF THE CONDENSATION PRODUCT FROM DICYCLOPENTADIENYL TITANIUM DICHLORIDE AND 2-METHYL-P-HYDROQUINONE OBTAINED AT A IONIZING VOLTAGE OF 70eV, TG FLOW RATE OF HELIUM AT 55 mL/MIN FOR A HEATING RATE OF 20 C<sup>o</sup>/MIN AND A DATA SAMPLING FREQUENCY OF 41 KC. T = TOTAL ION CURRENT A = PLOT OF m/e 18 B = PLOT OF m/e 66

pentadiene = 22% and two cyclopentadienes = 44% of the residue). Therefore, the residue contained a substantial quantity of organic material (% Ti = 16, % TiO<sub>2</sub> = 26).

#### CONCLUSIONS

The results of the present study show that the coupled TG-MS instrument can provide much useful data relevant to determining the composition of polymeric materials of the type studied here.

Table 9  
 Temperature Range in which Cyclopentadiene was Observed  
 for the Titanium Polyethers

Associated Diol	Initial Temperature of Appearance	Temperature at which Product Observation Maximized	Final Temperature at which Product was Observed
p-hydroquinone	89°	151°C	480°C
bisphenol A	105°C	335°C	488°C
di-tert-butyl-p-hydroquinone	74°C	258°C	848°C
tetrachloro-p-hydroquinone	143°C	166°C	404°C
2-methyl-p-hydroquinone	105°C	289°C	457°C

The data obtained here suggest structures for the titanium polyether which are consistent with those previously proposed (8-10). Furthermore, this technique often permits detection of major trends in the sample degradation sequence. Two general phenomena could be tentatively identified for the titanium polyethers investigated in the present study. First, the initially evolved degradation product has cyclopentadione, which typically appeared at a temperature in the neighborhood of 100°C (Table 9). Secondly, this was generally followed by the evolution of the p-hydroquinone-containing moiety, along with the associated oxygen(s). A great deal of variation was observed, however, with respect to the extent and rate of degradation of the hydroquinone-containing moiety from the several polymers studied, and the quantities of organic components in the final residues from degradation also varied markedly.

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