

# Modified Phenol–Formaldehyde Novolac Resins: Synthesis and Thermal Oxidative Degradation

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## Synopsis

New phenolic resins containing titanium and silicon in the main polymer structure were synthesized and some of their properties were investigated. Titanium and silicon contents of the polymers ranged from 2 to 13% titanium and from 2 to 5% silicon. These polymers became insoluble and infusible as the titanium and silicon contents of the products were increased. IR spectra of these modified resins were presented. The thermal oxidative degradations of the phenolic resins modified with titanium and silicon were also investigated using thermogravimetry and differential thermal analysis. Titanium and silicon-modified polymers showed considerably lower weight changes as compared with those of unmodified or titanium-modified polymers, but the rate of the last oxidative degradation increased and the final degradation temperature decreased with increasing titanium concentration. The best results for the thermal resistance was found to be  $2\% \leq \text{Ti} \leq 6\%$  and  $\text{Si } 2\text{--}5\%$ .

## INTRODUCTION

Phenol–formaldehyde resins have been the subject of intensive investigations over the past 50 years. However, very little is known concerning titanium and silicon-modified phenol–formaldehyde resins.

In several previous articles,<sup>1–4</sup> the modification of phenol–formaldehyde polycondensates by titanium was reported. Shu and Konii<sup>1</sup> have prepared titanium-modified phenolic resins by treating novolac resin with titanium tetra-isopropoxide and heating the product with hexamethylenetetramine to obtain a heat-resistant product. Pavlova et al.<sup>2</sup> reported the preparation of titanium-containing phenol–formaldehyde resins, with novolac and resol types, by condensation of phenol–formaldehyde and orthotitanates  $[\text{Ti}(\text{OR})_4]$ , where R is alkyl or aryl]. The obtained product is a fusible, soluble resin, stable during storage.  $\text{Ti}(\text{OR})_4$  is used to ensure up to 4% titanium in the resin. Shepard and Dannels<sup>3</sup> indicated that phenol novolacs are condensed with titanium as well as germanium, zirconium, tin dihalides, diorganooxides, and similar reactive compounds. Kraitzer et al.<sup>4</sup> have prepared titanium modified phenolic resins by heating up phenyl titanate or *o*, *m*, *p*-tolyl titanates and formaldehyde in butyl alcohol under a reflux condenser and have reported that the uncured resin were compatible with usual plasticizers and could be incorporated into drying oils to form varnishes.

A survey of the available literature yielded only one paper related to phenol–formaldehyde resins modified with both titanium and silicon.

Pakhomov et al.<sup>5</sup> have modified the subject polymers with spirocyclic and cyclic titanium organosiloxanes.

There are numerous papers<sup>6-8</sup> devoted to the thermal oxidative degradation of phenol-formaldehyde resins and the effect of the modification on degradation. A literature survey has not yielded any research on the thermal oxidative degradation of phenol-formaldehyde resins modified with titanium and silicon. Pakhomov et al.<sup>5</sup> have indicated that titanium and silicon-modified phenolic resins were heat-resistant polymers.

The first part of this paper reports the synthesis of new types of phenolic resins modified with titanium and both titanium and silicon and describes some of their properties. The second part describes the effect of titanium and silicon content on modified phenol-formaldehyde resins on thermal oxidative degradation.

## EXPERIMENTAL

### Materials

Phenol (Merck, pure), formaldehyde (Merck, pure and as a 35% aqueous solution stabilized with 10% methanol), titanium tetrachloride, tetra-isopropyl titanate and diphenyldichlorosilane (Fluka, pure), tetrabutyl titanate (prepared from titanium tetrachloride and butanol<sup>9</sup> and purified), diphenylsilanediol (prepared from diphenyldichlorosilane<sup>10</sup>), the polysiloxane intermediate Z 6018 [Dow Corning Silicon product, melting point (Durrant's mercury method): 75°C, hydroxyl content (Zerewitinoff): 3.9%, volatility (480°F, 3 h): 3-6%, Si (direct H<sub>2</sub>SO<sub>4</sub>): 22.46%] were used.

IR analyses were determined by a Shimadzu 4000 IR spectrophotometer, from 4000-650 cm<sup>-1</sup> region. The samples were diluted with pure KBr (sample/KBr = 1/250, w/w) and dried at vacuum.

Linseis L 81 type combined DTA-TG thermal balance was used for the investigation of thermal oxidative degradation of the polymers. Thermogravimetric analysis (TGA) and differential thermal analyses (DTA) test conditions were sample weight, 20 mg; reference, Al<sub>2</sub>O<sub>3</sub>; atmosphere, air; sensitivity (full scale), 0.1 mv/250 mm or 0.05 mv/250 mm; heating rate, 2°C/min.

### Synthesis

High ortho novolac phenol-formaldehyde resin P with an average molecular weight of 700, mp 65-78°C, and soluble in the most common organic solvents was prepared according to the known procedure.<sup>3</sup>

Titanium-modified phenol-formaldehyde resins P<sub>2</sub>, P<sub>6</sub>, P<sub>6</sub>, P<sub>13</sub>, P<sub>3\*</sub>, P<sub>6\*</sub>, and P<sub>13\*</sub> were prepared by the reaction of high ortho novolac resin P with tetra-isopropyl titanate or titanium tetrachloride as follows: the calculated amount of tetra-isopropyl titanate or titanium tetrachloride in dry benzene were added portionwise to the calculated amount of phenol-formaldehyde resin P, at room temperature. After the addition was completed, the solvent was removed and the temperature was increased stepwise to 175°C and held there for 2 h in the case of tetra-isopropyl titanate or to 110°C, then to 130°C and held there for 2.5 and 4-5 h in the case of titanium tetrachloride, respectively, until the evolution of isopropyl alcohol or HCl were stopped.

TABLE I  
Reaction Conditions and the Solubility of the Modified Polymers

Symbols used for modified polymers	Feed amount of Ti and Si (%)		Ti and Si compds. and polymers used in reaction	Polymerization temperature (°C)	Polymerization period (h)	Solubility <sup>a</sup>		
	Ti	Si				Alcohol	Acetone	Benzene
P	—	—	—	160	3.5	+	+	+
P <sub>2</sub>	2.0	—	P, Ti(i-OPr) <sub>4</sub>	175	2.0	+	+	—
P <sub>6</sub>	6.6	—	P, Ti(i-OPr) <sub>4</sub>	175	2.0	—	—	—
P <sub>6</sub>	6.6	—	P, Ti(i-OPr) <sub>4</sub>	175	—	—	+	—
P <sub>1,3</sub>	13.2	—	P, Ti(i-OPr) <sub>4</sub>	175	2.0	—	—	—
P <sub>3*</sub>	3.3	—	P, TiCl <sub>4</sub>	130	5.0	+	+	+
P <sub>6*</sub>	6.6	—	P, TiCl <sub>4</sub>	130	4.0	±	+	+
P <sub>1,3*</sub>	13.2	—	P, TiCl <sub>4</sub>	130	4.0	t	t	t
P <sub>2,2</sub>	1.8	2.0	P <sub>2</sub> , Ph <sub>2</sub> Si(OH) <sub>2</sub>	150	3.0	t	±	±
P <sub>6,2</sub>	5.7	2.0	P <sub>6</sub> , Ph <sub>2</sub> Si(OH) <sub>2</sub>	150	3.0	t	t	t
P <sub>6*,3<sup>z</sup></sub>	5.8	3.0	P <sub>6*</sub> , Z 6018	140	4.0	—	±	±
P <sub>3*,3*</sub>	3.0	3.0	P, TiCl <sub>4</sub> , Ph <sub>2</sub> SiCl <sub>2</sub>	110, 190	3.0 + 4.0	—	+	+
P <sub>5*,5*</sub>	5.0	5.0	P, TiCl <sub>4</sub> , Ph <sub>2</sub> SiCl <sub>2</sub>	110, 190	3.0 + 4.0	—	—	—
P <sub>0,2*</sub>	—	2.0	P, Ph <sub>2</sub> SiCl <sub>2</sub>	190	8.0	+	+	—
P <sub>0,5*</sub>	—	5.0	P, Ph <sub>2</sub> SiCl <sub>2</sub>	190	3.5	+	+	±
P <sub>0,2<sup>z</sup></sub>	—	2.0	P, Z 6018	140	4.0	±	+	±

<sup>a</sup> + = soluble; ± = partly soluble; — = insoluble; t = trace.

In order to obtain the intermediate polymer  $P_6$  used in the preparation of titanium and silicon-modified polymer  $P_{6,2}$ , the condensation reaction between phenol-formaldehyde resin and tetra-isopropyl titanate was stopped by cooling the intermediate as the temperature reached to 175°C.

Titanium and silicon-modified phenol-formaldehyde resins  $P_{2,2}$ ,  $P_{6,2}$ ,  $P_{3^*,3^*}$ ,  $P_{5^*,5^*}$ ,  $P_{6^*,3Z}$  were prepared as follows: The calculated amount of the powder mixture of the polymer  $P_2$  or  $P_6$  and diphenylsilanediol was heated at 150°C for 3 h and the polymers  $P_{2,2}$  or  $P_{6,2}$  were obtained, respectively, or the powder mixture of the polymer  $P_{6^*}$  and Z 6018 was heated at 140°C for 4 h and the polymer  $P_{6^*,3Z}$  was obtained.

The polymers  $P_{3^*,3^*}$  and  $P_{5^*,5^*}$  were prepared from phenol-formaldehyde resin P, titanium tetrachloride, and diphenyldichlorosilane by a similar method used in the preparation of the polymers  $P_{3^*}$ ,  $P_{6^*}$ , and  $P_{13^*}$ . After the addition of titanium tetrachloride was completed, the reaction temperature was increased to 110°C and held there for 3 h; then diphenyldichlorosilane was added at the same temperature. The temperature was increased from 110 to 190°C and held there for 4 h until the evolution of HCl was stopped.

Silicon-modified phenol-formaldehyde resins  $P_{0,2^*}$ ,  $P_{0,5^*}$ ,  $P_{0,2Z}$  were prepared by the reaction of polymer P and diphenyldichlorosilane or Z 6018, respectively, by a similar method used in the preparation of titanium and silicon-modified polymers mentioned above.

The analyses performed according to the known methods<sup>11-13</sup> showed that the differences between Ti, Si contents of the polymers and the feeding amounts are 0.1–0.3%. The purification of the subject-modified phenolic resins has been performed by dissolving the polymer in a convenient solvent and then precipitating from solution by a miscible nonsolvent. The symbols, the reaction conditions, and the solubilities of the modified phenolic resins synthesized in this work are presented in Table I.

## RESULTS AND DISCUSSION

### Modified Phenolic Resins

In this work, titanium-modified phenolic resins were synthesized by the reaction of high ortho novolac phenol-formaldehyde resin with either tetra-isopropyl titanate or titanium tetrachloride. Those containing both titanium and silicon were synthesized in two ways: one is the reaction of phenol-formaldehyde resin with titanium tetrachloride and diphenyldichlorosilane; the other is the reaction of titanium-modified phenol-formaldehyde resin or one of its intermediate  $P_6$  with diphenylsilanediol or an intermediate silicon polymer Z 6018. The titanium and silicon contents of these polymers, depending on modification, varied between 2 and 13% for titanium and 2 and 5% for silicon.

Titanium-modified and both titanium- and silicon-modified phenol-formaldehyde resins synthesized in this work were generally obtained as hard brittle solids or powders of different shades of brown. They were soluble, partly soluble, or insoluble in alcohol, acetone, and benzene (Table I). These polymers became insoluble and infusible as the titanium and silicon contents of the products were increased (e.g.,  $P_6$ ,  $P_{13^*}$ ,  $P_{5^*,5^*}$ ). The similar state was

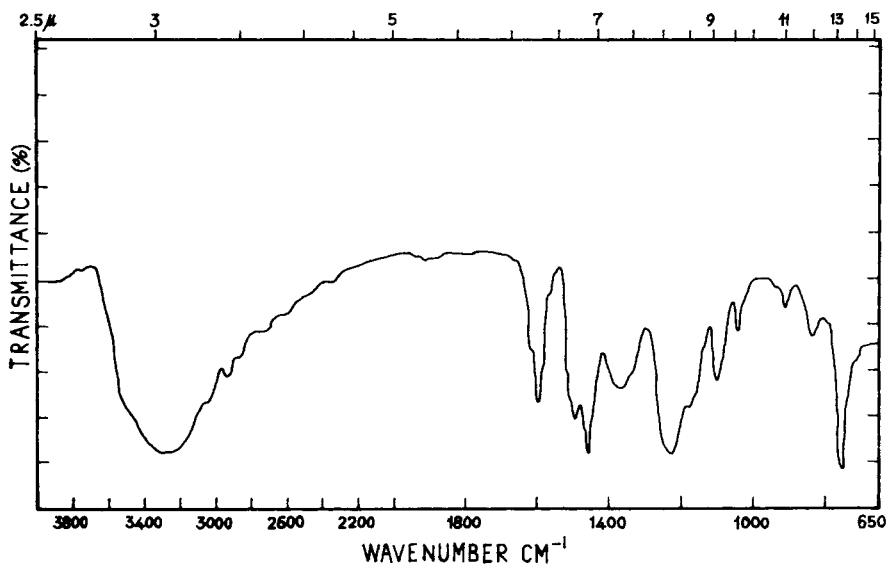


Fig. 1. IR spectrum of phenol-formaldehyde resin P.

observed when some of the titanium modified polymers (e.g.,  $P_2$ ,  $P_{6*}$ ) were heated at about 125–175°C for about 1–2 h. It seems that in order to obtain a thermosetting-titanium-modified phenol-formaldehyde resin, it is sufficient to heat them at an appropriate temperature and period.

The overall changes, in the structure of phenol-formaldehyde resin, depending on modification by various titanium and silicon compounds, were investigated by IR analysis in the 4000–650  $\text{cm}^{-1}$  region.

The IR spectra of the polymers  $P$ ,  $P_2$ ,  $P_6$ ,  $P_{3*}$ ,  $P_{6*}$ ,  $P_{13*}$ ,  $P_{0.2*}$ ,  $P_{0.5*}$ ,  $P_{0.2Z}$ ,  $P_{2.2}$ ,  $P_{3*,3*}$ ,  $P_{5*,5*}$ , and  $P_{6*,3Z}$  are presented in Figures 1–7.

A careful comparison of the spectra indicates definite differences mainly in the absorption bands, appearing at 3620–3030, 1720–1615, 1612–1585, 1520–1430, 1409–1315, 1180–1100, 900–940, and 920–850  $\text{cm}^{-1}$  regions.

From the IR spectra of the titanium-modified polymers  $P_2$ ,  $P_6$ ,  $P_{3*}$ ,  $P_{6*}$ , and  $P_{13*}$  (Figs. 2–4) one sees that the intensity of phenolic and methylol hydroxyl vibration band at 3620–3030  $\text{cm}^{-1}$ <sup>14</sup> has been significantly reduced. The same IR spectra also indicate the disappearance or the reduction of the intensity of the band observed at 1409–1315  $\text{cm}^{-1}$ <sup>15</sup> due to the hydroxyl groups (especially methylol hydroxyl), depending on the type and amount of the modification compounds. The changes in the above-mentioned bands can be attributed to the change in the hydroxyl groups, especially in the methylol content of phenol-formaldehyde resin due to the modification reactions. In the case of modification by titanium tetrachloride, the changes in the above-mentioned bands and in the intensities are different, because the reaction mechanism between titanium tetrachloride and novolac polymer is considerably different from those of tetra-isopropyl titanate and, consequently, the structure of the obtained polymer is also different.

Titanium tetrachloride is a very reactive compound. It reacts very strongly with phenolic hydrogen at the para position as well as with phenolic hydroxyl groups.<sup>16–18</sup> A structural similarity between this polymer and coordination

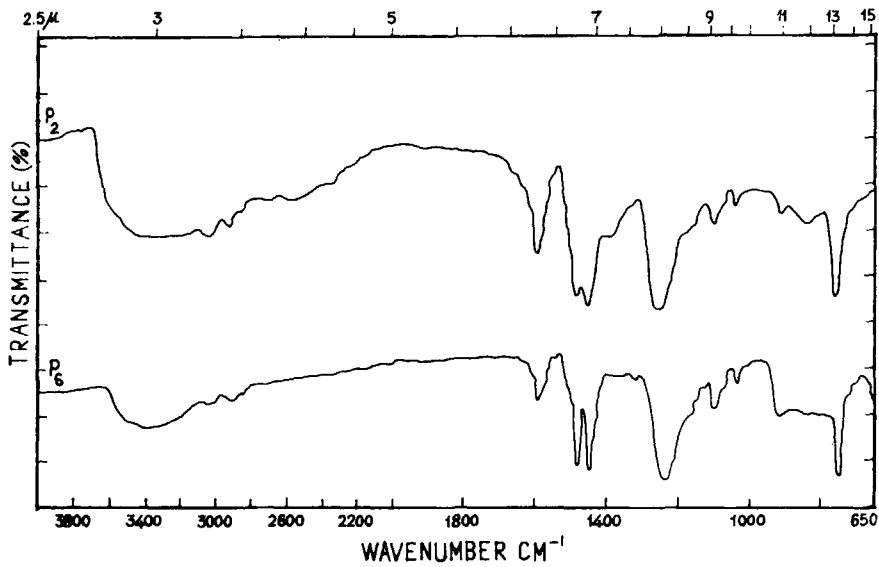


Fig. 2. IR spectra of the polymers  $P_2$  and  $P_6$ .

(complex) polymers of titanium<sup>19,20</sup> is also possible. The absorption band at  $1612\text{--}1585\text{ cm}^{-1}$  was observed as a broad band at  $1720\text{--}1615\text{ cm}^{-1}$ , that is, a new absorption band appeared at  $1720\text{--}1615\text{ cm}^{-1}$  for polymers  $P_{6^*}$  and  $P_{13^*}$  (Fig. 3). The ingrowth of the band may be considered as an indication of an arrangement of quinoid-type structure.<sup>21</sup> Also, the appearance of a new broad band at  $920\text{--}850\text{ cm}^{-1}$ <sup>22,23</sup> is due to the formation of Ti—O bond in the main polymer structure after the modification by titanium compounds (Figs. 2–4).

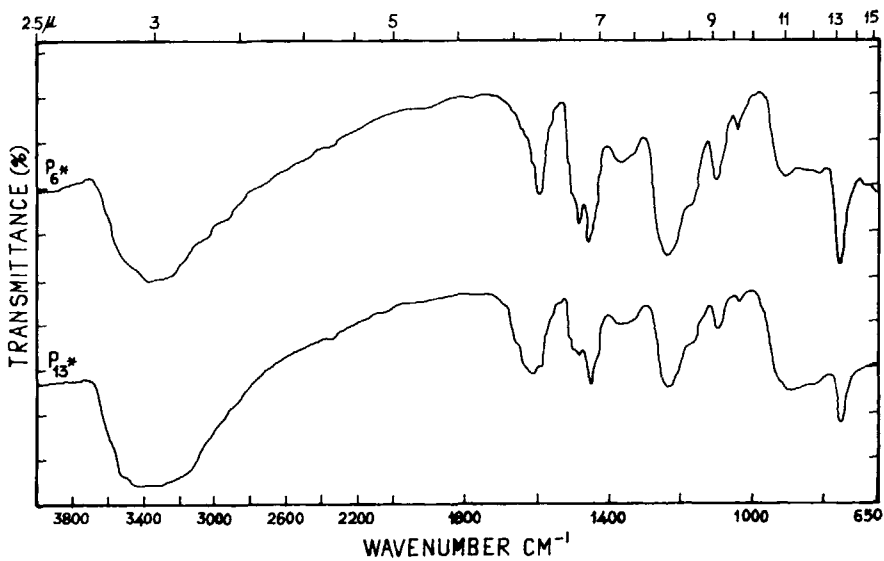


Fig. 3. IR spectra of the polymers  $P_{6^*}$  and  $P_{13^*}$ .

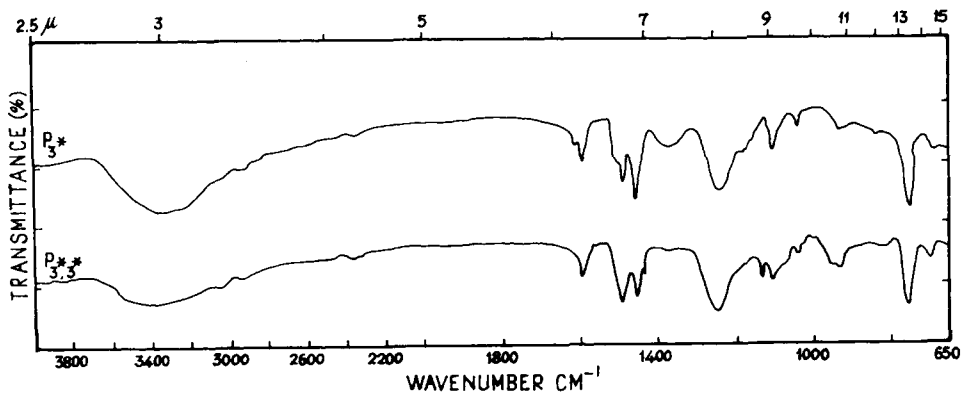


Fig. 4. IR spectra of the polymers  $P_{3^*}$  and  $P_{3^*,3^*}$ .

The IR spectra of the silicon-modified polymers  $P_{0.2^*}$ ,  $P_{0.5^*}$ ,  $P_{0.2z}$  are presented in Figure 5. The appearances of the new bands at 1180–1100, 1130–1120, and 990–940  $\text{cm}^{-1}$ <sup>14,24-26</sup> are associated with Si—O and Si—Ph bonds in the polymer structure, depending on modification by silicon compounds.

The IR spectra of both titanium- and silicon-modified polymers  $P_{2.2}$ ,  $P_{3^*,3^*}$ ,  $P_{5^*,5^*}$ , and  $P_{6^*,3z}$  are presented in Figures 4, 6, and 7. These spectra have the characteristic bands of phenol-formaldehyde resin, titanium-modified polymers, and silicon-modified polymers.

The most notable other differences are the changes in the intensities of the absorption bands at 1520–1430, 835, 755<sup>14,15,23</sup> and 940–900  $\text{cm}^{-1}$ <sup>14</sup> that are related with the  $0-0'$  and  $p$ -substituted aromatic rings of high ortho novolac resin, respectively.

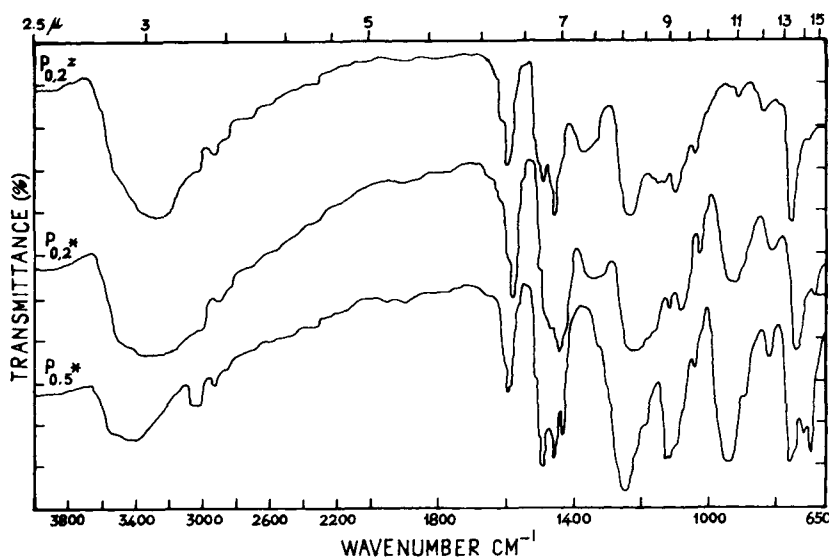
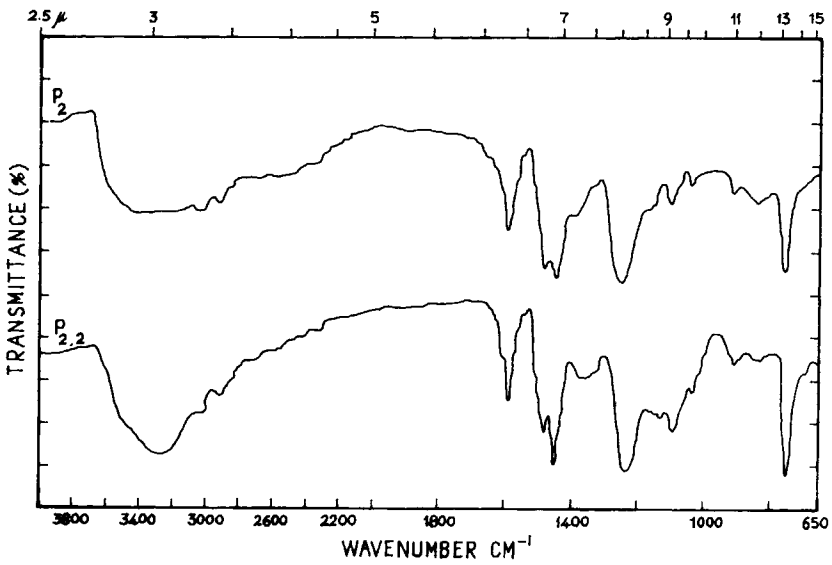
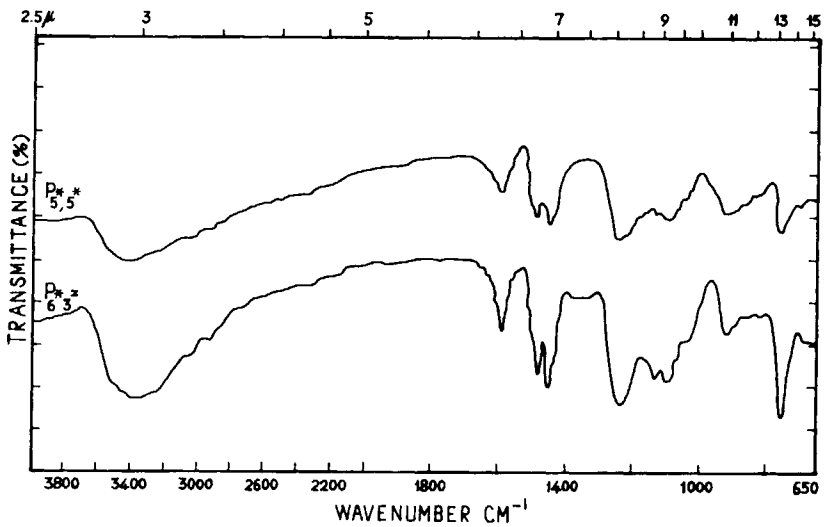


Fig. 5. IR spectra of the polymers  $P_{0.2^*}$ ,  $P_{0.5^*}$ , and  $P_{0.2z}$ .

Fig. 6. IR spectra of the polymers  $P_2$  and  $P_{2,2}$ .Fig. 7. IR spectra of the polymers  $P_{5^*,5^*}$ , and  $P_{6^*,3z}$ .

### Thermal Oxidative Degradation

In several previous articles,<sup>6-8</sup> the thermal oxidative degradation of phenol-formaldehyde polycondensates was reported and it was mentioned that the phenolic resins mainly degrade in three recognizable steps: preliminary, middle, and a final oxidative degradation.

The course of the initial stage of the oxidative degradation taking place at lower temperature range was found to cover post-curing, thermal reforming, additional reactions, and preliminary oxidation. The middle stage mainly depends on the chain scission, ring stripping, secondary oxidation processes,



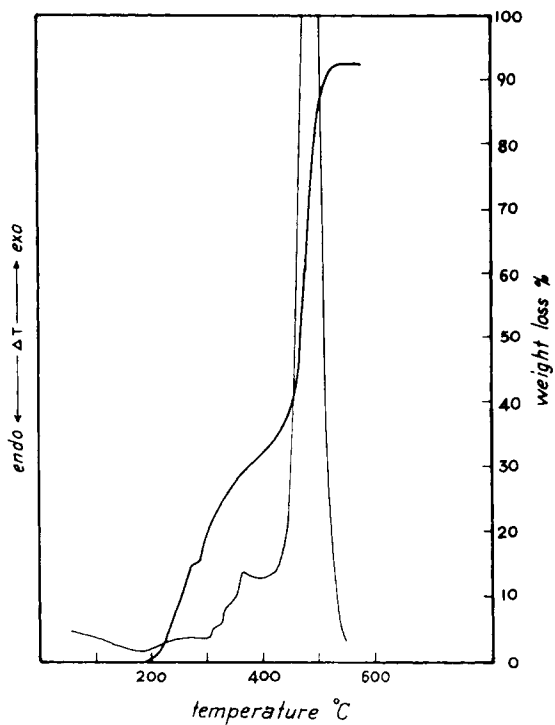


Fig. 8. TG and DTA curves of phenol-formaldehyde resin P.

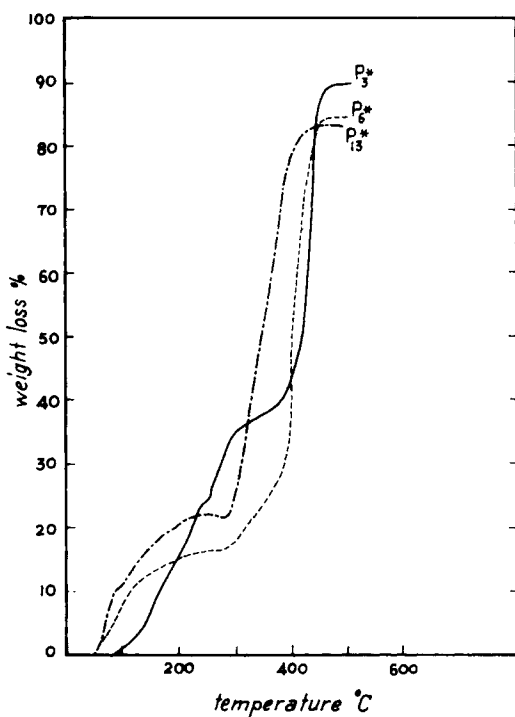


Fig. 9. TG curves of the polymers  $P_{3^*}$ ,  $P_{6^*}$ , and  $P_{13^*}$ .

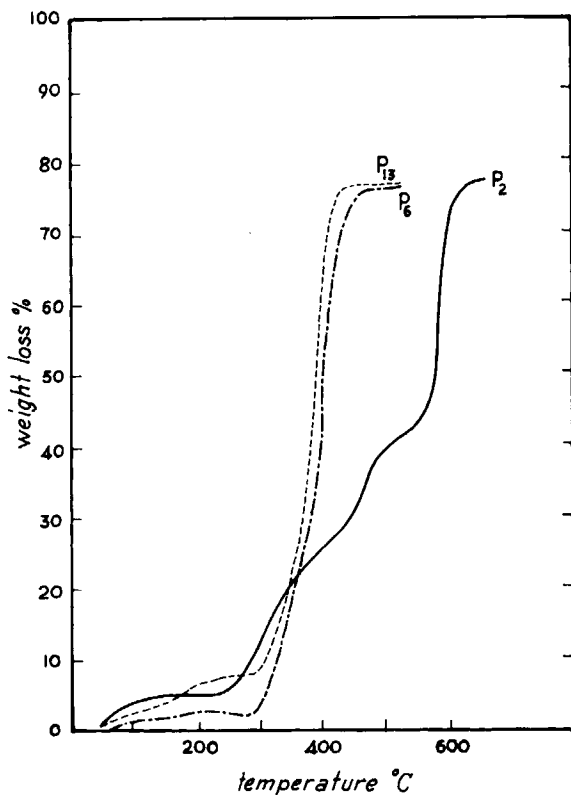


Fig. 10. TG curves of the polymers P<sub>2</sub>, P<sub>6</sub>, and P<sub>13</sub>.

and the formation of volatile fractions resulting from the oxidative degradation and takes place at markedly high temperature intervals during oxidation. The first stage is obviously controlled by the proportion of unreacted methylol and the other functional groups, the middle and the last stages are controlled by the elemental composition of the polymer.

Although DTA in combination with TGA is a valuable tool for the study of the thermal oxidative degradation, TGA and DTA methods alone do not give a full picture of thermal oxidative degradation of phenolic resins and they usually are used as comparative tools. Pyrolysis technique combined with gas chromatography and spectroscopic analysis are also needed for evaluation of the oxidative degradation products. For this reason, instead of a detailed discussion of the experimental results related to the reactions, the overall processes of oxidative degradation as determined by DTA and TGA are presented in this paper. TGA and DTA curves are presented in Figures 8–18 and the data obtained from these curves are given in Table II.

The overall oxidative degradation processes of the titanium- and silicon-modified polymers are not essentially identical; the type and the amount of the compounds [Ti(i-OPr)<sub>4</sub>, TiCl<sub>4</sub>, Ph<sub>2</sub>Si(OH)<sub>2</sub>, or Ph<sub>2</sub>SiCl<sub>2</sub>] used in the synthesis of these polymers significantly effect the reactions covering the thermal oxidative degradation.

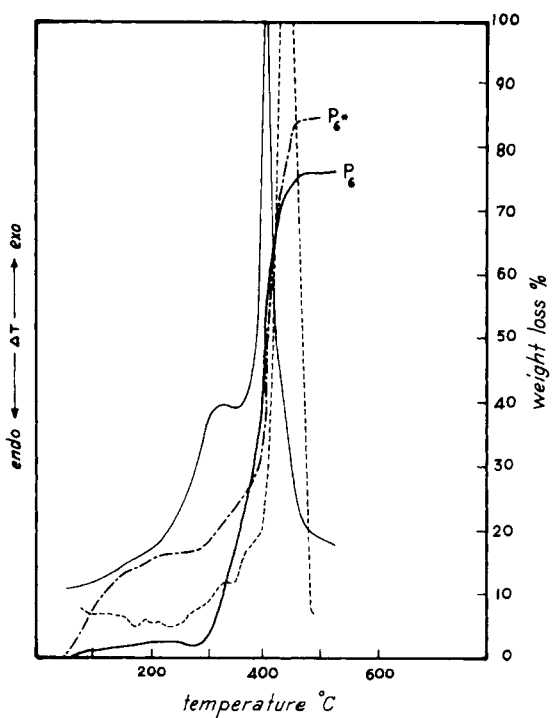


Fig. 11. TG and DTA curves of the polymers  $P_6^*$  and  $P_6$ .

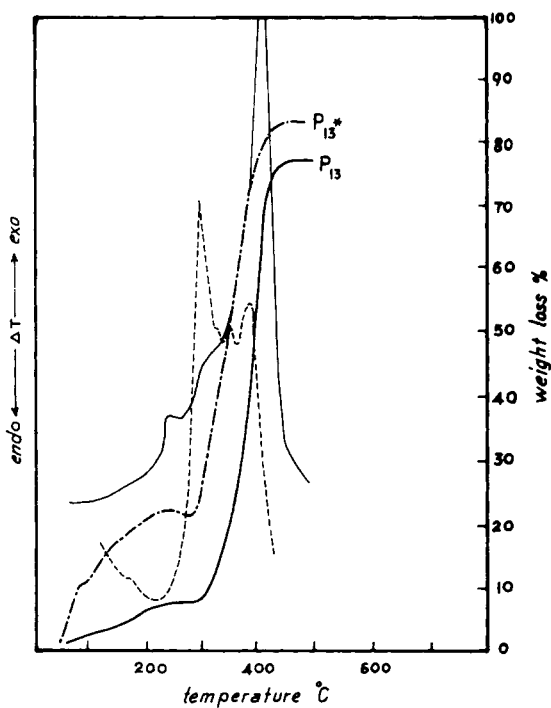


Fig. 12. TG and DTA curves of the polymers  $P_{13}^*$  and  $P_{13}$ .

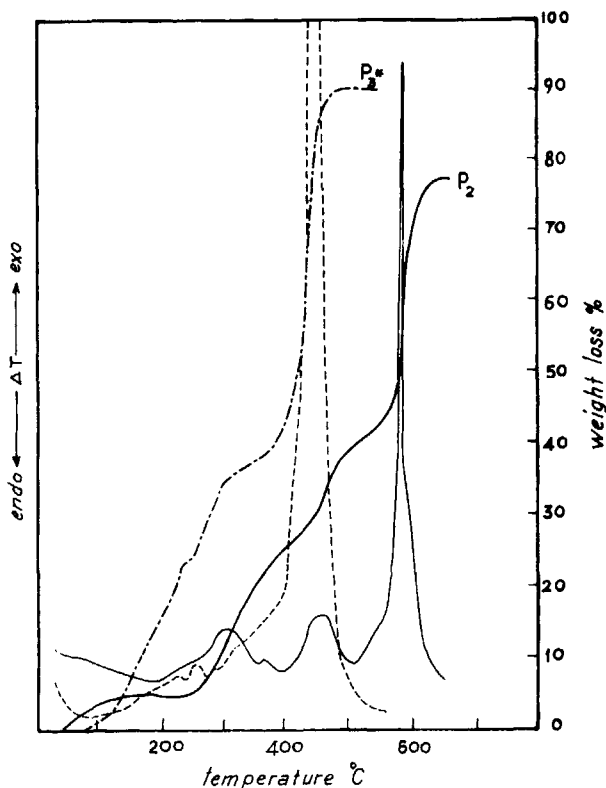


Fig. 13. TG and DTA curves of the polymers P<sub>3\*</sub> and P<sub>2</sub>.

TGA and DTA curves of high ortho resin used in the synthesis of titanium- and silicon-modified phenol-formaldehyde resins are given in Figure 8. These curves show the presence of three quite clearly defined degradation stages. Between the 200 and 300°C interval, corresponding to the initial stage, a distinct weight loss of 19.5% was observed owing to the volatilization of water and other low-molecular-weight components. The volatile products should be expected from the final condensation of residual methylol groups together with the products expected from the initial stage of degradation. The middle stage takes place in the 300–400°C temperature range with a weight loss of about 30%. The final oxidative degradation is observed after 400°C and completed at about 520°C. DTA of this polymer is entirely in the exothermic area. Between 175 and 300°C there is a broad exotherm which is associated with the initial stage. The exotherms with three very small peaks are observed at 310, 330, and 360°C related to the middle step oxidation. A strong sharp peak at 470°C corresponds to the last oxidative degradation.

TGA curves given in Figures 9 and 10 show that the titanium-modified phenol-formaldehyde resins P<sub>3\*</sub>, P<sub>6\*</sub>, P<sub>13\*</sub>, P<sub>2</sub>, P<sub>6</sub>, and P<sub>13</sub> degrade somewhat more rapidly as the titanium level in the polymer structure increases. If titanium tetrachloride is the modification compound, the increase in the

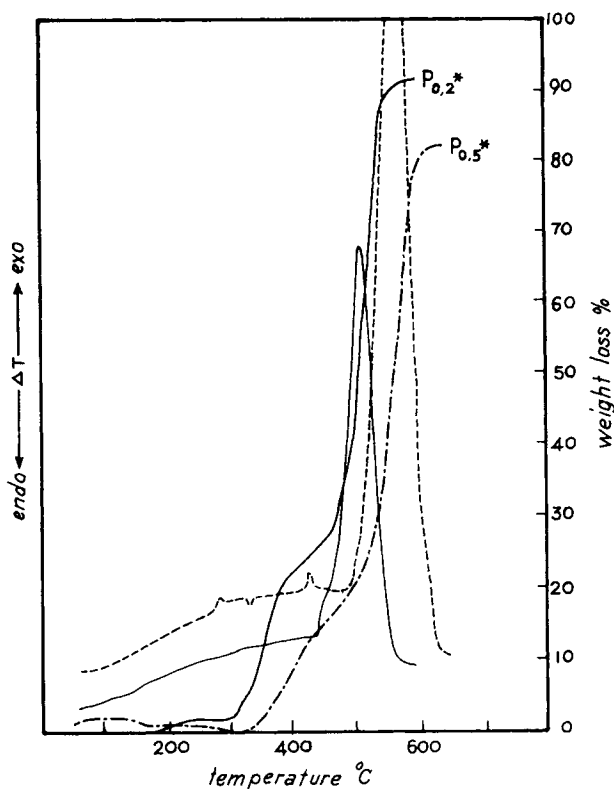


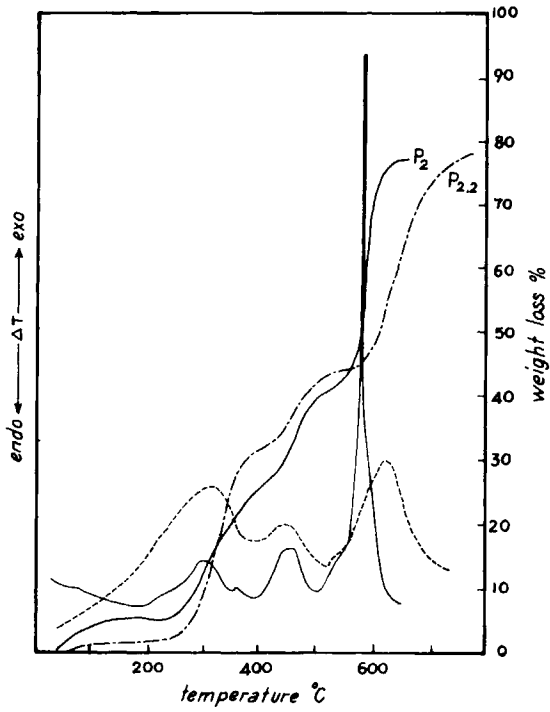
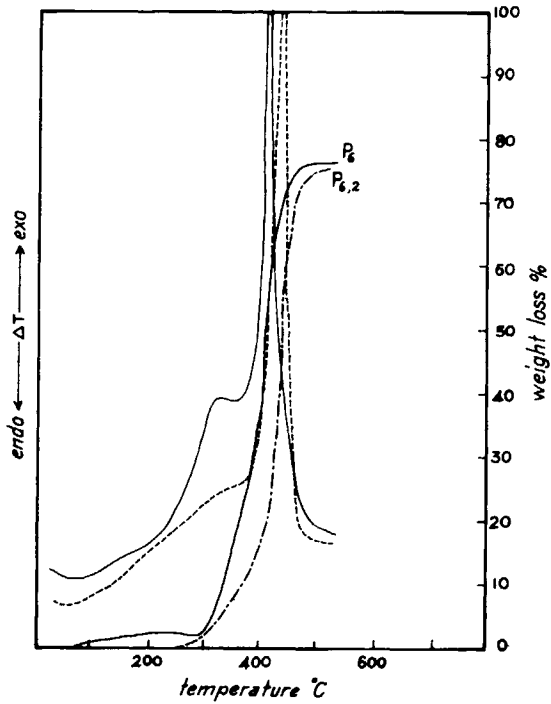
Fig. 14. TG and DTA curves of the polymers  $P_{0.2}^*$  and  $P_{0.5}^*$ .

oxidative degradation rate is higher than the case of the modification compound tetra-isopropyl titanate usage. Generally, the rate of the last oxidative degradation increases and the final degradation temperature decreases with increasing titanium concentration of polymers (Table II). DTA curves of the polymers  $P_6^*$  and  $P_{13}^*$  show a new broad endothermic peak not previously observed at about 100–300°C (Figs. 11 and 12). One can also observe from DTA curves of the polymers  $P_6$ ,  $P_{13}$ ,  $P_3^*$ , and  $P_{13}^*$  (Figs. 11–13) that the exothermic peaks corresponding to the middle stage oxidative degradation almost disappear or are overshadowed by the exothermic peaks of their last oxidative degradation.

The thermograms of silicon-modified polymers have almost similar characteristics with those of phenol-formaldehyde resin and titanium-modified polymers (Fig. 14). The oxidative thermal degradation decreases, and, as a result of this, the final degradation temperature increases as the silicon content of the polymer is increased (Table II).

The weight losses of the polymers  $P_{0.2}^*$  and  $P_{0.5}^*$  up to 400°C are smaller than those of titanium-modified polymers  $P_2$  and  $P_6$  (Table II).

The DTA curve of polymer  $P_2$  (Fig. 13) clearly indicates the three stages of oxidative degradation taking place one after another but with different speeds and at higher temperature intervals. The first step is between 200 and 400°C,

Fig. 15. TG and DTA curves of the polymers  $P_2$  and  $P_{2,2}$ .Fig. 16. TG and DTA curves of the polymers  $P_6$  and  $P_{6,2}$ .

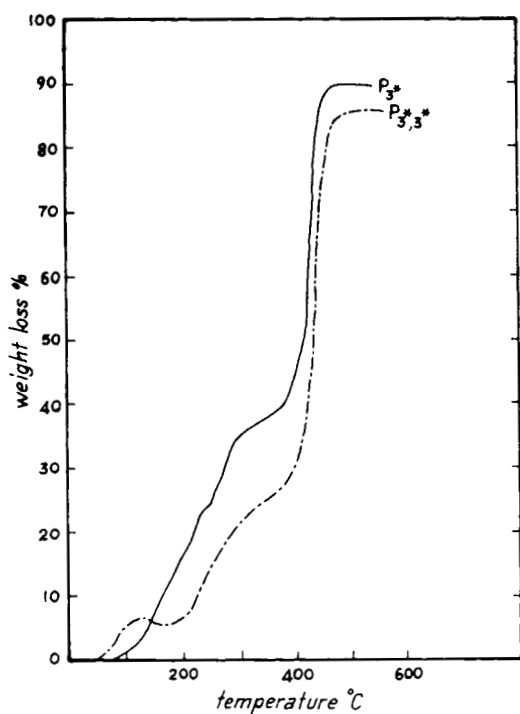


Fig. 17. TG curves of the polymers P<sub>3\*</sub> and P<sub>3\*,3\*</sub>.

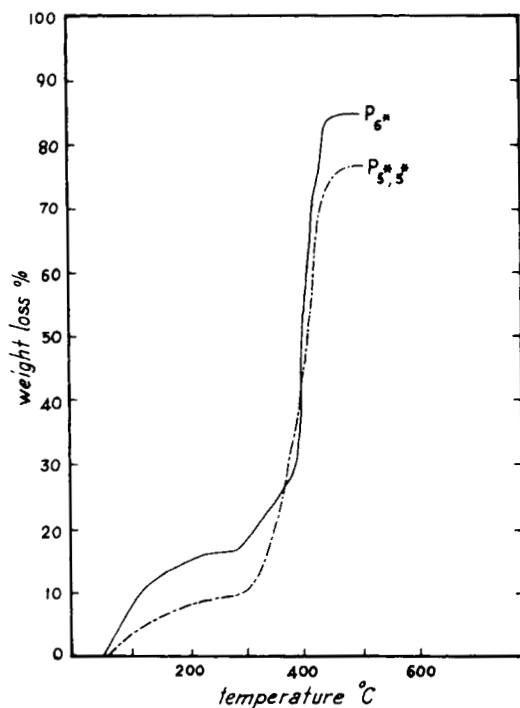


Fig. 18. TG curves of the polymers P<sub>6\*</sub> and P<sub>5\*,5\*</sub>.

TABLE II  
Weight Losses (%) at Various Temperatures and the Final Degradation Temperature Determined from the  
TGA Curves of the Modified Polymers

Symbols used for modified polymers	Feed amount of Ti and Si (%)		Ti and Si compds. and polymers used in reaction	From TGA data													Final degrad. temp (°C)
	Ti	Si		Weight loss (%) at various temperatures (°C)													
P	—	—	—	100	150	200	225	250	275	300	325	350	375	400	425	450	520
P <sub>2</sub>	2.0	—	P, Ti(i-OPr) <sub>4</sub>	—	—	1.0	4.0	10.0	15.5	19.5	24.2	27.9	30.9	32.5	35.5	41.0	520
P <sub>6</sub>	6.6	—	P, Ti(i-OPr) <sub>4</sub>	3.7	5.0	5.0	5.0	5.5	8.0	10.5	16.0	20.0	23.0	25.5	27.5	31.5	625
P <sub>13</sub>	13.2	—	P, Ti(i-OPr) <sub>4</sub>	1.5	2.0	3.0	2.8	2.5	2.0	4.0	10.5	18.0	28.5	47.0	69.5	75.0	460
P <sub>3*</sub>	3.3	—	P, TiCl <sub>4</sub>	2.5	4.0	6.5	7.3	7.5	7.5	9.0	13.8	20.5	34.0	59.5	75.5	76.2	450
P <sub>6*</sub>	6.6	—	P, TiCl <sub>4</sub>	1.5	8.0	17.5	22.8	24.9	30.8	35.5	37.0	38.2	39.8	44.5	58.0	85.0	475
P <sub>13*</sub>	13.2	—	P, TiCl <sub>4</sub>	8.5	10.8	15.4	16.4	16.5	16.5	18.5	21.5	24.5	27.5	35.5	69.5	83.5	460
P <sub>3*,3*</sub>	2.7	2.7	P, TiCl <sub>4</sub> , Ph <sub>2</sub> SiCl <sub>2</sub>	11.2	17.5	20.5	22.2	22.2	21.5	25.5	36.0	51.5	65.0	78.0	82.0	83.0	450
P <sub>5*,5*</sub>	4.9	4.9	P, TiCl <sub>4</sub> , Ph <sub>2</sub> SiCl <sub>2</sub>	5.0	6.0	6.5	8.5	13.5	17.0	20.0	22.5	24.5	26.5	30.0	38.5	60.0	500
P <sub>2,2</sub>	1.8	2.0	P <sub>2</sub> , Ph <sub>2</sub> Si(OH) <sub>2</sub>	4.0	6.5	7.5	9.5	9.5	9.5	11.0	13.8	20.5	31.0	44.0	59.5	75.5	470
P <sub>6,2</sub>	5.7	2.0	P <sub>6*</sub> , Ph <sub>2</sub> Si(OH) <sub>2</sub>	—	0.2	1.0	1.0	1.2	2.0	8.0	14.0	24.5	29.5	31.0	33.0	35.5	720
P <sub>0,2*</sub>	—	—	P, Ph <sub>2</sub> SiCl <sub>2</sub>	0.5	0.2	1.5	2.0	2.0	2.0	2.2	5.5	11.0	19.5	23.0	25.0	27.5	500
P <sub>0,5*</sub>	—	5.0	P, Ph <sub>2</sub> SiCl <sub>2</sub>	2.0	1.5	1.0	1.0	1.0	0.8	0.2	0.2	2.0	4.5	10.0	13.0	15.5	610

\*P<sub>6</sub> = An intermediate polymer prepared from polymer P and *tetra*-isopropyl titanate.



corresponding exotherm peaks at 300°C with a small one at 360°C. The second region is between 400 and 500°C temperature interval, corresponding exotherm peaks at 460°C. The third region has a temperature range between 500 and 620°C and a strong and sharp peak at about 575°C.

The shape of this DTA curve suggests that numerous reactions take place concurrently during the three stages of oxidative degradations. In the first stages, the heating of the polymer results in polycondensation and crosslinking and consequently the heat resistance and final degradation temperature increases.

The fact is most probably caused by the formation of Ti—O—Ti bonds between linear polymer chains as mentioned by Nesmeyanov et al.<sup>27</sup> and Adrianov.<sup>19</sup> The rate of the last oxidative degradation is increased as the titanium level in the polymer is increased (Fig. 10 and Table II), in spite of the formation of Ti—O—Ti bonds among the linear chains, because, in that case, the weak bonds in the polymer structure are also increased.

True to expectation, the polymer P<sub>3\*</sub> prepared from titanium tetrachloride containing about 3% titanium does not show any increase in the final oxidative degradation temperature, whereas, in the case that tetra-isopropyl titanate is the modification compound, the final oxidative degradation temperature increases from 475 to 625°C (Fig. 13, Table II).

From the TGA and DTA curves of titanium- and silicon-modified polymers P<sub>2,2</sub> and P<sub>6,2</sub> (Figs. 15 and 16, Table II) that the weight changes below 300°C are less than 5% and are significantly smaller than those recorded for phenol-formaldehyde resin and titanium-modified polymers P<sub>3\*</sub>, P<sub>6\*</sub>, and P<sub>13\*</sub> prepared from titanium tetrachloride (Table II). The decrease in the weight changes of these polymers at 100–300°C seems to depend upon the type of modified polymer, the content of titanium and silicon in the polymer structure. It is also related to the increase in the stability of the subject polymers.

As noted from the TGA curves of modified polymers P<sub>3\*</sub>, P<sub>6\*</sub>, P<sub>13\*</sub>, P<sub>6</sub>, P<sub>13</sub>, P<sub>3\*,3\*</sub>, P<sub>5\*,5\*</sub> (Figs. 9, 10, 17, and 18 and Table II), the major weight losses were observed at 400–460°C and the oxidative degradation rates in this temperature region are remarkably similar, regardless of the type of the

TABLE III  
Heat Resistance of the Modified Polymers

Symbols used for modified polymers	From TGA data		Final degradation temp (°C)	Loss of wt (polymers heated 10 h at 250°C) (%)
	Limit of temp (°C) for loss of wt			
	≤ 5%	10%		
P <sub>2</sub>	225	300	625	15.4
P <sub>2,2</sub>	290	300	720	5.6
P <sub>6</sub>	300	325	460	5.8
P <sub>6,2</sub>	325	375	500	2.4
P <sub>6*</sub>	85	150	460	30.0
P <sub>5*,5*</sub>	100	275	470	9.5
P <sub>3*</sub>	100	150	475	36.0
P <sub>3*,3*</sub>	100	225	500	23.8
P <sub>0,2*</sub>	300	340	575	1.7

modification compounds or the content of titanium and silicon except for the polymers  $P_2$ ,  $P_{2,2}$ ,  $P_{6,2}$ ,  $P_{0,2^*}$ , and  $P_{0,5^*}$  (Table II).

The polymers  $P_{2,2}$ ,  $P_{6,2}$ , and  $P_{5^*,5^*}$  containing both titanium  $\leq 6$  and silicon 2–5% showed considerably lower weight change, especially up to 300 and 400°C, when compared with those of the unmodified or titanium modified polymers (Figs. 15, 16, and 18 and Tables II and III). The temperatures at which the weight losses are less than or equal to 5 or 10% determined from the TGA curves are given in Table III. From values of weight losses obtained by heating polymers at 250°C for 10 h, polymers  $P_{2,2}$ ,  $P_{6,2}$ ,  $P_6$ , and  $P_{0,2^*}$  are the most stable polymers.

## CONCLUSIONS

Titanium-modified polymers can be prepared by the reaction of high ortho novolac resin P with either tetra-isopropyl titanate or titanium tetrachloride. Those containing both titanium and silicon can be synthesized in two ways: one is the reaction of P with titanium tetrachloride and diphenyldichlorosilane; the other is the reaction of titanium-modified novolac resin  $P_2$  or  $P_6$  with diphenylsilanediol.

The thermal resistance of phenol–formaldehyde resins can be improved by modification with both titanium and silicon producing thermally stable polymers. The optimum level of titanium and silicon concentration giving the best improvement, i.e., the best results for the thermal resistance, was found to be  $2\% \leq \text{Ti} \leq 6\%$  and Si 2–5%.

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