

# Chain Extended Cyclohexanone-Formaldehyde and Acetophenone-Formaldehyde Resins

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**ABSTRACT:** The preparation of chain extended cyclohexanone-formaldehyde and acetophenone-formaldehyde resins and their physical properties were studied. The chain extension was regulated by the ratio of the hydroxyl groups of the ketonic resin/reactive reagents. Both resins were chain extended with dimethyl dichlorosilane, phosphorus oxychloride, phenylphosphonic dichloride, toluene-2,4-diisocyanate, prepolymers (prepared from trimethylolpropane and toluene-2,4-diisocyanate), phthalic anhydride, tetrahydrophthalic anhydride, trimellitic anhydride, 4,4'-oxydiphthalic anhydride, and maleic anhydride. Solubilities, melting point, molecular weight, and flammability of the chain extended resins were affected by the extender reagent. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 655–663, 1998

**Key words:** ketonic resins; chain extension; anhydrides; phosphorous oxychloride; dimethyl dichlorosilane; toluene-2,4-diisocyanate

## INTRODUCTION

Cyclohexanone-formaldehyde (CF, **10**) and acetophenone-formaldehyde (AF, **20**) resins (Scheme 1) were modified via their hydroxyl and carbonyl groups in earlier studies.<sup>1–3</sup> The type of modifying compound had a marked affect on the melting point and solubilities of the modified resins. The molecular weights of the ketonic resins were not increased considerably by the modification reactions.

Copolymers of CF resin with polystyrene<sup>4–6</sup> and polyacrylonitrile<sup>7</sup> were produced by radical polymerization of vinyl monomers by activated CF resin. Furthermore, the reaction of the hydroxyl groups of the ketonic resins with phthalic anhydride<sup>3</sup> were also studied. A variety of modified ketonic resins were produced by changing the ratio of the hydroxyl groups of the resin to the modifying reagent.<sup>1–3</sup> For example, when the molar ratio of hydroxyl to anhydride was about 1, all

the hydroxyl groups of the ketonic resin reacted with phthalic anhydride to give a modified ketonic resin containing free carboxylic acid groups in place of the hydroxyl groups. If this ratio was 9 : 1, a dimeric chain extended CF resin was produced<sup>3</sup> because each CF-resin molecule contained approximately nine hydroxyl groups. Chain extensions of ketonic resins with an extender reagent such as anhydrides, dimethyl dichlorosilane, phosphorus oxychloride, or toluene-2,4-diisocyanate (TDI) were achieved and preliminary results were obtained.<sup>8</sup> Further studies on the preparation and characterization of chain extended CF and AF resin were carried out in this work. The reagents used for the chain extension reactions were anhydrides, dimethyl dichlorosilane, phosphorus oxychloride, phenylphosphonic dichloride, TDI, and prepolymer prepared from TDI and trimethylol propane. For achieving chain extension, the molar ratio of hydroxyl to reagent used was above 1. The molecular weights, solubilities, and melting points of the extended ketonic resins were determined.

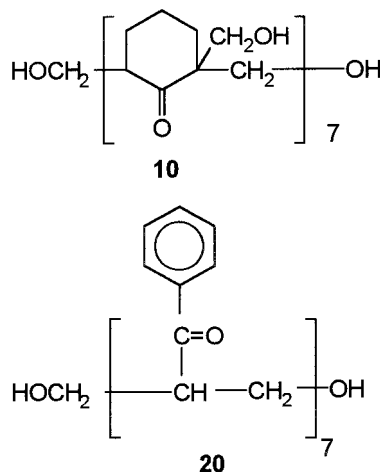
By introducing silicon and phosphorus into the resin structure, some improvements in such prop-

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**Scheme 1** Formulas for resins **10** and **20**.

erties as inflammability and water desorption were found.

## EXPERIMENTAL

IR spectra were recorded on an A.T.I. UNICAM Mattson 1000 series FTIR spectrometer.  $^1\text{H-NMR}$  and  $^{31}\text{P-NMR}$  spectra were obtained for  $\text{CDCl}_3$  and DMSO solution on a Bruker AC (200 MHz).

The number ( $M_n$ ) and weight average ( $M_w$ ) molecular weight values were calculated from GPC chromatograms according to standard polystyrene calibration using a Knauer M64 Instrument and THF as the eluent at a flow rate of 1 mL/min.

Contact angle measurements of the copolymer films were done on a Kernco model G III contact angle meter at room temperature using distilled water.

The flame-retardant properties of chain extended ketonic resins when dimethyl dichlorosilane, phosphorus oxychloride, and phenylphosphonic dichloride were used as chain extenders were further tested according to UL-94.

Preparation of the CF resin (**10**) and the AF resin (**20**) was carried out as described previously.<sup>2</sup> The resins were dried at 110°C under a vacuum. The CF and AF resins were further dried by refluxing with xylene using a Dean–Stark apparatus.

### Reaction with Phthalic Anhydride

Ketonic resin, phthalic anhydride, and xylene were added into the Dean–Stark system and refluxed for 1 h. Two drops of tetraisopropyl titan-

ate was then added slowly while stirring vigorously. The stirring was continued for 3 h at 95°C. After evaporation of the xylene, the resin was dissolved in acetone and precipitated with water, filtered, washed several times with water, and dried at 105°C in a vacuum for 5 h.

### Reaction with Tetrahydrophthalic Anhydride

#### Method I

Five grams of CF resin and 2 g of tetrahydrophthalic anhydride in 30 mL of pyridine were refluxed for 3 h while stirring vigorously. After evaporation of the pyridine, the resin was precipitated with water, filtered, washed several times with water, and dried at 105°C in a vacuum.

#### Method II

Five grams of CF resin, 2 g of tetrahydrophthalic anhydride, and 0.2 mL of  $\text{H}_2\text{SO}_4$  in 30 mL of chloroform were refluxed for 3 h while stirring vigorously. The mixture was cooled to room temperature, neutralized with  $\text{NaHCO}_3$  solution, and washed with water several times. After the evaporation of the chloroform, the resin was washed several times with hot water and dried at 105°C in a vacuum.

### Reaction with Maleic Anhydride

Ten grams of CF resin was dissolved in 100 mL xylene and 0.5 grams of maleic anhydride was added and refluxed for 1 h under nitrogen into the Dean–Stark system. Two drops of tetraisopropyl titanate were then added slowly while stirring vigorously. The stirring was continued for 3 h at 100°C. The product was precipitated with hexane, dissolved in acetone, and poured into water. The precipitate was filtered and dried at 105°C in a vacuum.

### Reaction with Trimellitic Anhydride

Five grams of CF resin was dissolved in 100 mL of xylene and 0.32 g of trimellitic anhydride was added and refluxed for 1 h. Two drops of tetraisopropyl titanate were then added slowly while stirring vigorously. The stirring was continued for 3 h at 100°C. The product was precipitated with hexane, then filtered and dried at 105°C in a vacuum.

**Reaction with 4,4'-Oxydiphthalic Anhydride (ODPA)**

Into the Dean–Stark system were added 5 g of AF resin, 0.38 g of ODPA, and 50 mL xylene; they were refluxed for 1 h. Two drops of tetraisopropyl titanate were then added slowly while stirring vigorously. The stirring was continued for 3 h at 100°C. The product was precipitated with hexane and then filtered and dried at 105°C in a vacuum.

**Reaction with Phenylphosphonic Dichloride (C<sub>6</sub>H<sub>5</sub>POCl<sub>2</sub>)**

Ten grams of ketonic resin was dissolved in 100 mL xylene, and one gram of phenylphosphonic dichloride (C<sub>6</sub>H<sub>5</sub>POCl<sub>2</sub>) was added and refluxed for 4 h. The product was precipitated with hexane, filtered, and dried at 105°C in a vacuum.

**Reaction with Phosphorus Oxychloride (POCl<sub>3</sub>)**

Ten grams of ketonic resin was dissolved in 25 mL of pyridine, and 0.3 mL of POCl<sub>3</sub> was added slowly while stirring vigorously at 5°C. Then the temperature was increased to 40°C, and the mixture was stirred for 8 h. After evaporation of the pyridine, the precipitate was dissolved in acetone and poured into water. The resin was filtered and dried at 50°C in a vacuum.

**Reaction with Dimethyl Dichlorosilane [(CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>]**

Ten grams of ketonic resin was dissolved in 20 mL of pyridine, and 0.65 g of dimethyl dichlorosilane was then added slowly while stirring vigorously at 5°C. The temperature was then increased to 40°C and stirring was continued for 8 h. The resin was precipitated with water, filtered, washed several times with hot water, and dried at 70°C in a vacuum.

**Reaction with TDI**

Into a four-necked flask, 10 g of ketonic resin, 1.5 g of TDI, and 50 mL of xylene were added under nitrogen. The temperature of the mixture was allowed to increase to 40°C, and 1 drop of dibutyltin dilaurate (T12) was added. The temperature increased to 85°C with the effect of the exothermic reaction. The reaction was continued for 6 h at 85°C. The product was precipitated during the reaction. The resin was purified by decanting the xylene and washing several times

with hot water and acetone. It was then dried at 105°C under a vacuum.

**Reaction with Prepolymer Prepared from Trimethylol Propane and TDI**

Ten grams of ketonic resin was dissolved in 20 mL of isobutyl acetate, and then 3.2 g of prepolymer solution in isobutyl acetate was added at room temperature while stirring vigorously under the nitrogen atmosphere. Then 1 drop of T12 catalyst was added and the stirring continued for 8 h at 25°C. The mixture was poured into ether, and the white precipitate was filtered and dried at 60°C in a vacuum.

**RESULTS AND DISCUSSION**

Chain extensions of the CF (**10**) and AF resins (**20**) were achieved by the reaction of their hydroxyl groups with the di- and trifunctional compounds phthalic anhydride, tetrahydrophthalic anhydride, maleic anhydride, trimellitic anhydride, ODPA, dimethyl dichlorosilane, phosphorus oxychloride, phenylphosphonic dichloride, TDI, and prepolymer that was prepared from trimethylol propane and TDI. An appropriate ratio of hydroxyl to reagent was used to achieve chain extension without crosslinking because the hydroxyl functionalities of the CF and AF resins are about 9 and slightly over 2, respectively.

Chain extended ketonic resins were examined with TLC. Both ketonic resins were successfully converted into a chain extended structure.

**Chain Extension with Anhydrides**

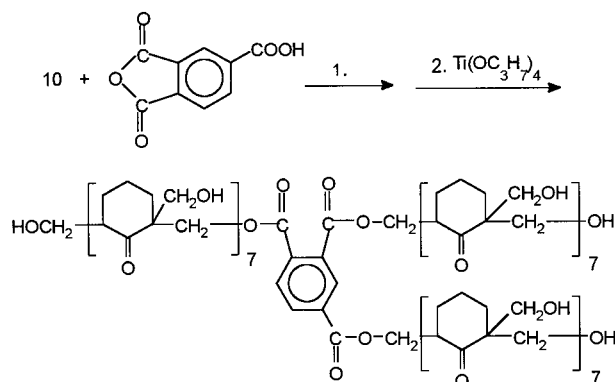
Chain extensions of the CF (**10**) and AF (**20**) resins were carried out by their reactions with the anhydrides phthalic anhydride, tetrahydrophthalic anhydride, trimellitic anhydride, maleic anhydride, and ODPA. The ratio of the hydroxyl groups of the resin to the anhydrides had a considerable effect on the melting point and  $M_n$  and  $M_w$  of the extended resin as seen in Table I.

At the beginning of the chain extension reaction, the hydroxyl group of the ketonic resin with the anhydride group reacted to yield an ester and free carboxylic acid that condensed with a hydroxyl group of another ketonic resin molecule to produce a chain extended resin. As an example, the reaction between the CF resin and trimellitic anhydride is shown in Scheme 2. The condensation reaction between carboxylic acid and the hy-

**Table I Physical Properties of Resins 10 and 20 and Chain Extended Ketonic Resins**

Basic and Chain Extended Resins	Chain Extender	Molar Ratio	mp (°C)	$M_n$	$M_w$	Solubilities						
						DMF	CHCl <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CO	CCl <sub>4</sub>	MeOH	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	THF
<b>10</b>	—		110	1500	1600	s	s	sl	hsl	sl	sl	s
<b>10.1E</b>	Phthalic anhydride	1/1	210	3500	3700	s	s	s	sl	hsl	s	sl
<b>10.2E</b>	Tetrahydrophthalic anhydride	1/2	205	—	—	s	s	sl	hs	s	s	s
<b>10.3E</b>	Maleic anhydride	2/1	220	—	—	s	s	hsl	hsl	hsl	sl	s
<b>10.4E</b>	Trimellitic anhydride	3/1	180	—	—	s	sl	sl	i	hs	hs	sl
<b>10.5E</b>	C <sub>6</sub> H <sub>5</sub> POCl <sub>2</sub>	2/1	280	—	—	sl	sl	hsl	i	hsl	i	hsl
<b>10.6E</b>	POCl <sub>3</sub>	3/1	160	—	—	s	s	sl	sl	hs	s	s
<b>10.7E</b>	(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	2/1	150	2000	3000	s	s	sl	hs	sl	sl	s
<b>10.7E2</b>	Excess (CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	1/9	155	5400	8900	s	s	sl	s	hsl	s	s
<b>10.8E</b>	TDI	1/1	215	3400	3750	s	sl	sl	sl	hsl	sl	sl
<b>10.9E</b>	Prepolymer	3/1	175	—	—	sl	hs	hsl	sl	i	hs	i
<b>20</b>	—		65	1000	1000	s	s	sl	hs	hs	hs	s
<b>20.1E</b>	Phthalic anhydride	2/1	148	6100	10500	sl	s	sl	i	i	hs	s
<b>20.2E</b>	Maleic anhydride	2/1	165	—	—	s	sl	sl	i	i	hs	hs
<b>20.3E</b>	ODPA	4/1	205	—	—	hsl	hsl	hsl	i	i	hs	hsl
<b>20.4E</b>	C <sub>6</sub> H <sub>5</sub> POCl <sub>2</sub>	2/1	105	—	—	s	sl	s	hs	hsl	hs	s
<b>20.5E</b>	POCl <sub>3</sub>	3/1	85	—	—	s	sl	s	hsl	hsl	s	s
<b>20.6E</b>	(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	2/1	100	—	—	s	s	s	hs	hs	s	s
<b>20.7E</b>	TDI	1/1	185	—	—	sl	hsl	hsl	i	hsl	hsl	sl
<b>20.8E</b>	Prepolymer	3/1	195	—	—	hs	hsl	i	i	i	hsl	i

s, soluble; sl, slightly soluble; hs, hot soluble; hsl, hot slightly soluble; i, insoluble.



10.4E

**Scheme 2** The reaction between the CF resin and trimellitic anhydride.

droxyl groups needed to be catalyzed. This was achieved by the addition of tetraisopropyl titanate catalyst. However, the chain extension reaction only occurred if a proper hydroxyl/anhydride ratio was used (Table I). The CF and AF resins contained approximately 9 and 2 hydroxyl groups, respectively. A dimeric chain extended CF resin was obtained by using a 9/1 hydroxyl/anhydride ratio. If the ratio was 1/1, a modified CF resin containing carboxylic acid groups was produced.<sup>2,3</sup>

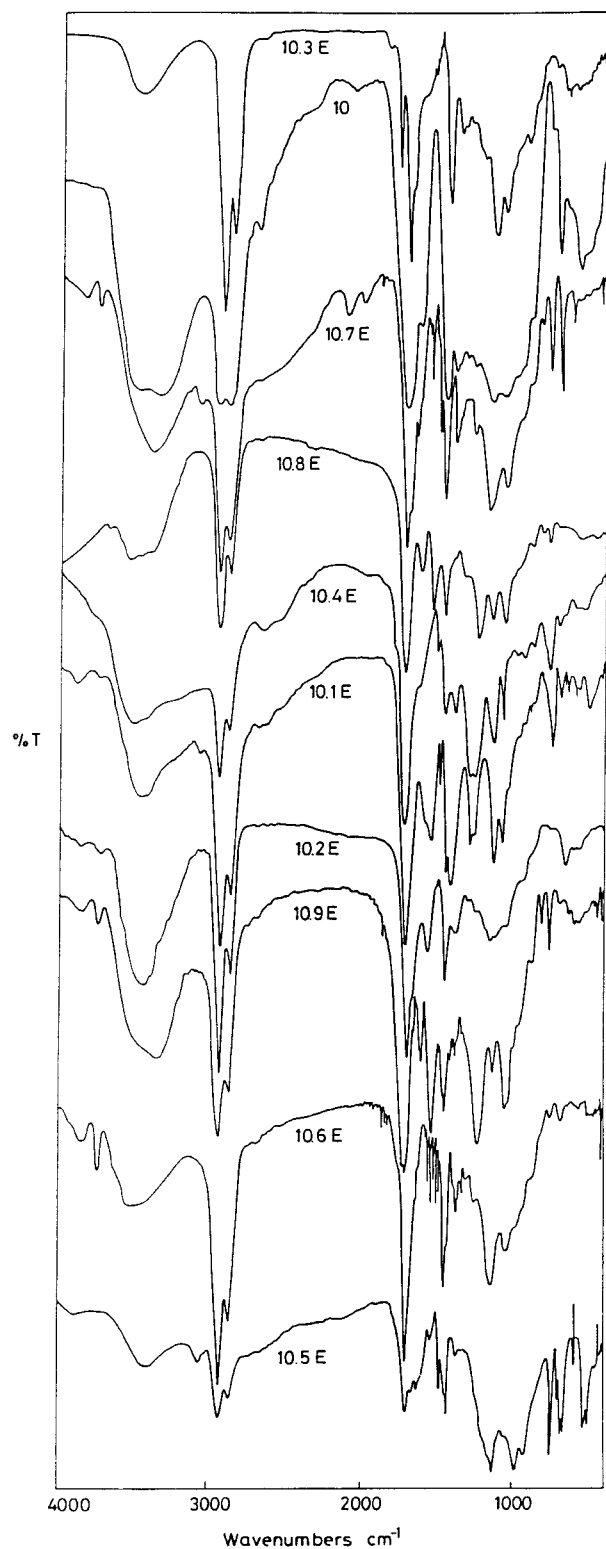
The FTIR spectrum of these resins showed peaks due to both the ketonic resin and the anhydride reagents. Chain extended resins **10.1E**, **10.2E**, **10.3E**, **10.4E**, **20.1E**, **20.2E**, and **20.3E** showed peaks at 1730 and 1700–1680  $\text{cm}^{-1}$  due to the carbonyl of the formed ester groups and the carbonyl group of the ketonic resins, respectively. The FTIR spectra of ketonic resins that were chain extended with anhydrides showed a considerably lower ratio of the hydroxyl peak at 3400  $\text{cm}^{-1}$  to the C—H peak at about 2870–2950  $\text{cm}^{-1}$  compared to the ketonic resin (Figs. 1, 2). The proton NMR spectra of the chain extended ketonic resins are summarized in Table II. The signals due to the carboxylic ester and the protons of the ketonic resin were both observed. Besides, the signal due to the free carboxylic acid group was observed at 12.6 ppm (**10.3E** and **10.4E**). The reaction of the ketonic resins with phthalic anhydride, maleic anhydride, and ODPa without chain extensions were studied before.<sup>1–3</sup> The solubilities and melting points of ketonic resins that were chain extended with phthalic anhydride, maleic anhydride, and ODPa were considerably different from those modified CF and AF resins.

The phthalic anhydride chain extended CF resin had a much higher softening point than the phthalic anhydride modified CF resin. However, the ODPa chain extended AF resin (**20.10E**) had a higher softening point and poorer solubility than the modified AF resin (**20.10**).

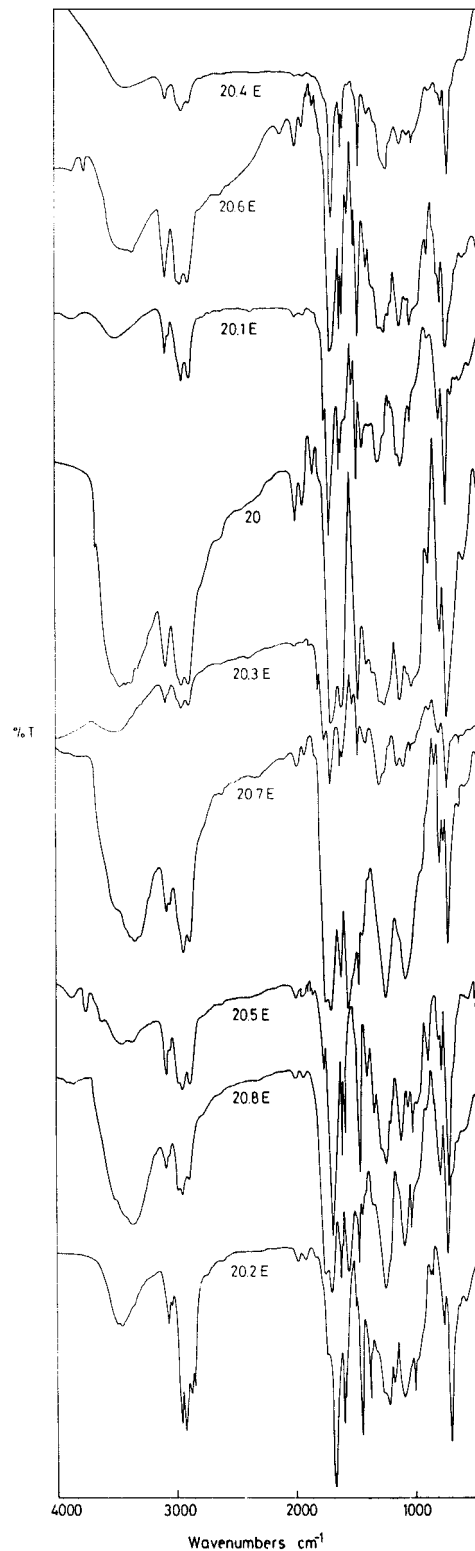
### Chain Extension with Phosphorus Oxychloride and Phenylphosphonic Dichloride

Chain extension of ketonic resins with phosphorus oxychloride was achieved by using a ratio of 3 mol of ketonic resin to 1 mol of phosphorus oxychloride (Scheme 3). The extended resins (**10.6E**, **20.5E**) had higher melting points and better solubilities in organic solvents (Table I). This ratio was about 2 when phenylphosphonic dichloride was used as a chain extender, and the chain extended resins (**10.5E**, **20.4E**) had much higher melting points and less solubility in organic solvents. The ketonic resins that were chain extended with both phosphorus oxychloride (**10.6E**, **20.5E**) and phenylphosphonic dichloride (**10.5E**, **20.4E**) generated less smoke than ketonic resins and exhibited flame-retardant properties. Flame-retardant tests were made on the filter papers that were soaked in the dichloromethane solution of the extended resins. The chain extended resins (**10.5E**, **10.6E**, **20.4E**, **20.5E**) had considerably less smoke and exhibited self-extinguishing properties.

FTIR spectra of chain extended resins (**10.5E**, **10.6E**, **20.4E**, **20.5E**) showed peaks at 1700  $\text{cm}^{-1}$  due to the ketone groups of the resins, at 1240–1310  $\text{cm}^{-1}$  due to the P=O groups, at 1100  $\text{cm}^{-1}$  due to —P—O— groups, and at 850–950  $\text{cm}^{-1}$  due to the  $\text{C}_6\text{H}_5\text{O—P—}$  groups. The peak at 3450  $\text{cm}^{-1}$  due to the hydroxyl groups decreased (Figs. 1, 2). <sup>1</sup>H-NMR spectra of these resins are summarized in Table II. The <sup>31</sup>P-NMR of the resins are shown in Figure 3. The extended CF resin (**10.6E**) contains P—O—C bonds with two different types of environments in which one has two stereoisomers. This appears as a doublet at about –5 ppm in Figure 1. This is probably due to the different type of alkyl hydroxyl groups of the CF resin. Similarly chain extended AF resin contains two different types of hydroxyl groups reacted with phosphorus oxychloride (**20.5E**). The presence of a doublet peak at about –5 ppm suggests that two of the three P—O—C bonds were stereoisomers and all of the phosphorus chlorine bonds were replaced by phosphorus oxygen bonds. The signal due to the P—OH type phosphorus was not observed. An unexpected signal at 19 ppm was also observed in the spectrum of **10.6E**.



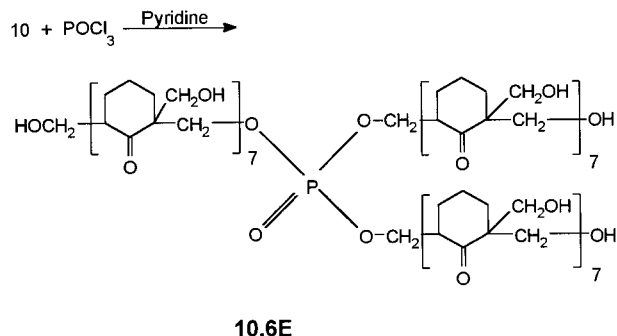
**Figure 1** FTIR spectra of CF resin **10** and chain extended CF resins **10.1E**, phthalic anhydride; **10.2E**, tetrahydrophthalic anhydride; **10.3E**, maleic anhydride; **10.4E**, trimellitic anhydride; **10.5E**,  $C_6H_5POCl_2$ ; **10.6E**,  $POCl_3$ ; **10.7E**,  $(CH_3)_2SiCl_2$ ; **10.8E**, TDI; and **10.9E**, prepolymer prepared from trimethylol propane.



**Figure 2** FTIR spectra of AF resin **20** and a chain extended AF resins **20.1E**, phthalic anhydride; **20.2E**, maleic anhydride; **20.3E**, ODPA; **20.4E**  $C_6H_5POCl_2$ ; **20.5E**,  $POCl_3$ ; **20.6E**,  $(CH_3)_2SiCl_2$ ; **20.7E**, TDI; and **20.8E**, prepolymer prepared from trimethylol propane.

Table II  $^1\text{H-NMR}$  Spectral Data of Resins,  $\delta$  (ppm)

Resin No.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{---O---Si---O---} \\   \\ \text{CH}_3 \end{array}$							
	$\text{---CH}_3\text{---}$	$\text{---}\overset{ }{\text{C}}\text{H---}, \text{---CH}_2\text{---}$	$\text{---CH}_2\text{OH}$	Arom. CH	$\text{---CH=CH---}$	$\text{---COOH}$	$\text{---CH}_2\text{O---}$	
<b>10</b>	—	1.2–2.3	3.2–4.2	—	—	—	—	
<b>10.1E</b>	—	1–2.6	3.2–4	7–8	—	—	4–5.3	
<b>10.2E</b>	—	1.2–3	3.2–4	—	—	12.6	4.1	
<b>10.3E</b>	—	1–2.8	3.4–3.8	—	5.3	12.6	4.2–4.7	
<b>10.4E</b>	—	1–3	3.4–4.2	6.8–8.7	—	—	5.2	
<b>10.5E</b>	—	1.4–3	3.5–4.4	7.2–8.8	—	—	5.3	
<b>10.6E</b>	—	1.2–2.8	3.2–4	—	—	—	—	
<b>10.7E</b>	—	1.05–2.4	3.5–4.2	—	—	—	0.09	
<b>10.7E2</b>	—	1–2.2	—	—	—	—	0.02–0.09, 0.15	
<b>10.8E</b>	2.2	1–2.4	3.2–4	6.95, 7.05, 7.15	—	—	—	
<b>20</b>	—	1.7–3.5	3.7–4.9	7–8.2	—	—	—	
<b>20.1E</b>	—	1.2–3.5	3.5–4	7.2–8	—	—	4.1–5.2	
<b>20.2E</b>	—	1–2.2	3.2–4.6	7.2–8	5.3	—	4–4.6	
<b>20.3E</b>	—	1–3.2	3.4–5.4	7–7.5, 7.7–8.4	—	—	4–5.3	
<b>20.5E</b>	—	0.85–3.6	3.8–4.6	7.2–8.1	—	—	—	
<b>20.6E</b>	—	1.7–3.5	3.7–4.9	7–8.2	—	—	0.12, 0.09, 0.1	



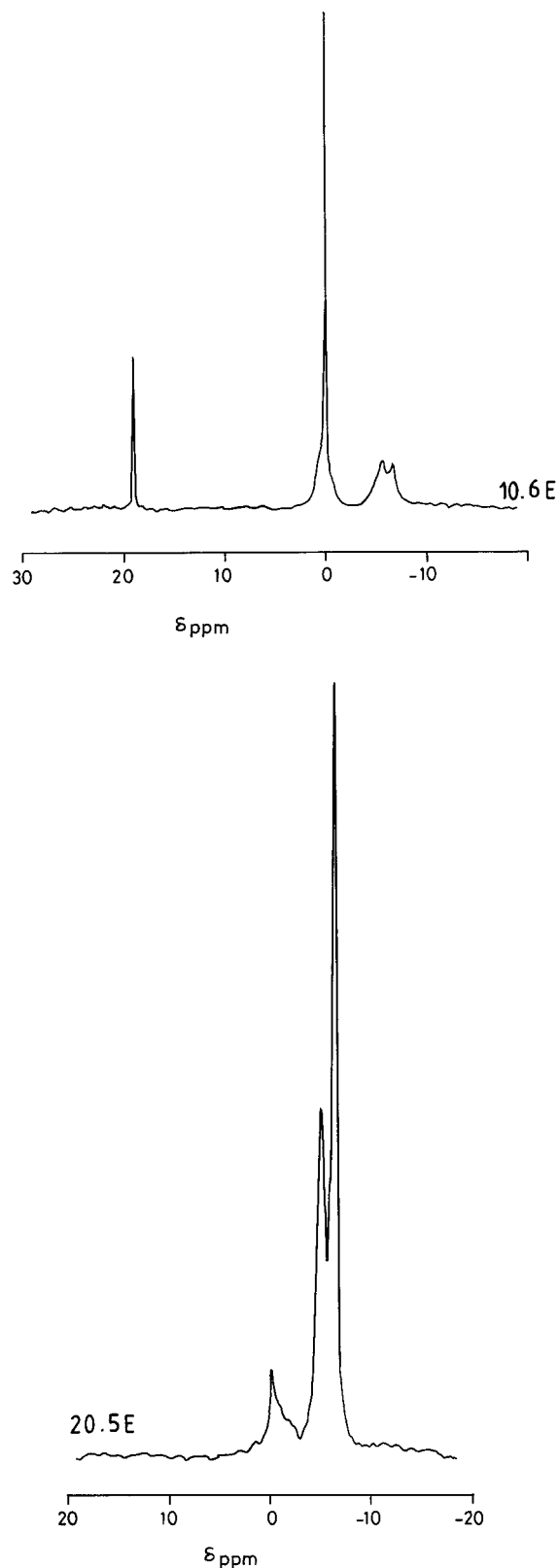
**Scheme 3** The chain extension of Ketonic resins with phosphorus oxychloride.

### Chain Extension with Dimethyl Dichlorosilane

Dimethyl dichlorosilane reacted with the hydroxyl groups of the ketonic resin to give the chain extended resins **10.7E**, **10.7E2** (Scheme 4), and **20.6E**. When the ratio of ketonic resin to dimethyl dichlorosilane was 2/1, a dimeric chain extended CF resin was formed and its molecular weight was twice that of the CF resin. The FTIR spectra of **10.7E**, **10.7E2**, and **20.6E** showed much smaller peaks at  $3450\text{--}3500\text{ cm}^{-1}$  due to the residual hydroxyl groups and at  $1700$  and  $1680\text{ cm}^{-1}$  due to the carbonyl groups of the ketonic resins (Figs. 1, 2). The peaks at  $940\text{--}970$  and  $1080\text{ cm}^{-1}$  due to the Si—O bonds of —Si—O—CH<sub>2</sub>— and at  $1250$  and  $850\text{--}750\text{ cm}^{-1}$  due to the Si—CH<sub>3</sub> groups were present. <sup>1</sup>H-NMR spectra were recorded from the CDCl<sub>3</sub> solution without tetramethylsilane. A signal at about 0.1 ppm due to Si—CH<sub>3</sub> protons could be clearly seen. A further chain extension was achieved by using a CF resin/(CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> ratio of 1/9. In this case, the molecular weight of the extended resin (**10.7E2**) was 4 times higher than the CF resin (Table I) and linear and branched chain extension reactions were both in progress. In addition, the excess (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> reacted with all the hydroxyl groups of the ketonic resin and internal cyclic structures were probably formed. The FTIR spectrum of **10.7E2** showed no hydroxyl peak at about  $3400\text{ cm}^{-1}$ , and the peaks due to Si—O and Si—O—CH<sub>2</sub> were much more intense (Fig. 4).

Contact angle measurements were made on extended resin films prepared by casting from dichloromethane solution on a glass slide. Ketonic resins that were extended with dimethyl dichlorosilane had considerably higher contact angles than corresponding ketonic resins.

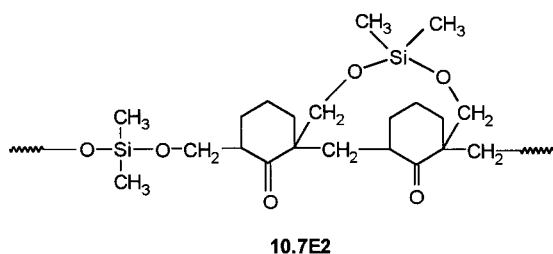
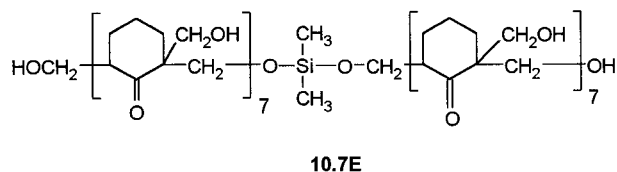
The ketonic resins that were chain extended with dimethyl dichlorosilane (**10.7E**, **20.6E**)



**Figure 3** <sup>31</sup>P-NMR chain extended resins **10.6E** (CF-POCl<sub>3</sub>) and **20.5E** (AF-POCl<sub>3</sub>).



generated less smoke than ketonic resins and exhibited flame-retardant properties. Flame-retardant tests were made on the filter papers that were soaked in the dichloromethane solution of the resins.



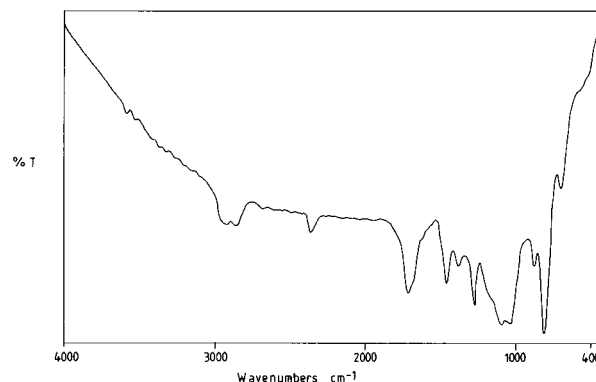
**Scheme 4** Formulas for chain extended resins **10.7E** and **10.7E2**.

#### Chain Extension with TDI and Prepolymer Prepared from Trimethylol Propane and TDI

Chain extension reactions of ketonic resins were achieved with TDI and prepolymer (**10.8E**, **10.9E**, **20.7E**, **20.8E**). These extended resins had much higher melting points. The solubilities of these resins decreased considerably (Table I). The FTIR spectra of these extended resins showed peaks due to TDI or prepolymer and peaks due to ketonic resins. The peaks at 3350 and 1595  $\text{cm}^{-1}$  were due to the  $\text{—NH}$  of the urethane group and at 3050, 970, 720, and 520  $\text{cm}^{-1}$  due to the aromatic ring of TDI. The broadened peak at 1700  $\text{cm}^{-1}$  was due to the carbonyl groups of both the ketonic resin and the urethane group (Figs. 1, 2).

#### CONCLUSION

Chain extension of CF and AF resins were successfully achieved by reacting their hydroxyl groups with extender reagents containing two or more functional groups. The proper choice of resin/reagent ratio was necessary to produce an extended ketonic resin without crosslinking. The increase in the molecular weight and physical properties of the extended resins was regulated



**Figure 4** FTIR spectra of **10.7E2**, a CF resin with excess dimethyl dichlorosilane.

by the hydroxyl group/reagent ratio. The type of reagent had a marked affect on the extended resin physical properties such as the melting point and solubilities in organic solvents. Proper extension of the resins with  $(\text{CH}_3)_2\text{SiCl}_2$  and  $\text{POCl}_3$  resulted in an extended CF resin and an AF resin with better solubilities, higher melting points, and self-extinguishing properties. Phenylphosphonic dichloride, TDI, prepolymer, and anhydride extenders were used to produce extended resins with lower solubilities and higher melting points. The chain extended CF resin and AF resin were considered to be completely new resins; they may be used in a number of different areas, especially where higher molecular weight resin is desired, as well as in the existing applications of ketonic resins.

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