

# Modification of Acetophenone–Formaldehyde and Cyclohexanone–Formaldehyde Resins

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## SYNOPSIS

Cyclohexanone–formaldehyde and acetophenone–formaldehyde resin were *in situ* modified with phenol, Bisphenols, and substituted acetophenones. Furthermore, acetophenone–formaldehyde, cyclohexanone–formaldehyde, and *in situ*-modified resins were modified with anhydrides such as acetic anhydride, maleic anhydride, dodecenylsuccinic anhydride, 3,4,3',4'-biphenyltetracarboxylic dianhydride, and 4,4'-oxydiphtalic anhydride. Modification of these resins with hydroxyl amine, semicarbazide, and phenyl hydrazine were also studied. Melting points, solubilities in organic solvents, FTIR, and NMR spectrum of the modified resins were determined. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Modification of cyclohexanone–formaldehyde resin and acetophenone–formaldehyde resin have been previously studied.<sup>1,2</sup> Hydroxyl groups were reacted with acetyl chloride, benzoyl chloride, phthalic anhydride, and carbonyl groups with hydroxylamine, semicarbazide, and phenylhydrazine.

Furthermore, *in situ* modification of acetophenone–formaldehyde resin was carried out using phenol,<sup>3</sup> *p*-cumylphenol,<sup>4</sup> *p*-cresol,<sup>5</sup> and Bisphenols<sup>2</sup> as the modifier compounds. Cyclohexanone–formaldehyde resin was also *in situ* modified using methyl isobutyl ketone,<sup>6</sup> methyl ethyl ketone,<sup>6</sup> methyl cyclohexanone,<sup>6</sup> acetaldehyde,<sup>6</sup> propion–aldehyde,<sup>6</sup> cinnamaldehyde,<sup>6</sup> dicycnadiamide,<sup>7</sup> aminotriazine,<sup>7</sup> and phenol.<sup>7</sup>

In this work, cyclohexanone–formaldehyde resin (CF resin) and acetophenone–formaldehyde resin (AF resin) were modified during resin preparation by the addition of a modifier compound/formaldehyde mixture to the polymerization media. Modifier compounds were phenol, 1,1-di(4-hydroxyphenyl)cyclododecane, 1-phenyl-1,1-di(4-hydroxyphenyl)etan, 2,4-dichloroacetophenone, and 4-bromoacetophenone. AF resin, *in situ*-modified AF res-

ins, and *in situ*-modified CF resins were modified via their hydroxyl, phenolic hydroxyl, and carbonyl groups.

## EXPERIMENTAL

IR spectra were recorded on a Jasco FTIR-5300 Fourier transform infrared spectrometer. <sup>1</sup>H-NMR spectra were obtained for the CDCl<sub>3</sub> solution on a Bruker AC (200 MHz). GPC chromatograms were obtained using a Knauer M64 instrument equipped with a differential refractometer.

### Preparation of Cyclohexanone–Formaldehyde Resin (CF Resin) (10) and Preparation of Acetophenone–Formaldehyde Resin (AF Resin) (20)

The preparations of these resins were carried out as described previously.<sup>2</sup>

### Preparation of 1,1-Di(4-hydroxyphenyl)cyclododecane (Bisphenol-CD)<sup>8</sup>

A solution containing 40 g (0.42 mol) of phenol and 14.5 g (0.08 mol) of cyclododecanone was cooled to 10°C and mixed with 30 g of 96% H<sub>2</sub>SO<sub>4</sub>. Then, an exothermic reaction took place with the temperature increasing spontaneously to about 65°C. The mix-

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ture, which solidified to mass crystals after 15–20 h, was allowed to stand for 6 days. Then, the mixture was poured into water and filtrated. The organic phase was stirred with 300 mL of water at 90°C and the phases were again allowed to separate while hot. The organic layer, which was the lower one, was filtered hot and allowed to cool. It was then recrystallized from MeOH water.

#### Preparation of 1-Phenyl-1',1'-di(4-hydroxyphenyl)Etan (Bisphenol-ACP)<sup>9</sup>

A solution containing 37.6 g (0.4 mol) of phenol and 12 g (0.1 mol) of acetophenone was cooled to 10°C and mixed with 30 g of 96% H<sub>2</sub>SO<sub>4</sub>. Then, an exothermic reaction took place with the temperature increasing spontaneously to about 65°C. The mixture solidified to mass crystals after 4 h. Then, the mixture was poured into water and filtrated. The organic phase was then stirred with 300 mL of water at 90°C and again allowed to separate while hot. The organic layer, which was the lower one, was filtered hot and allowed to cool. Then, bisphenol ACP was recrystallized from toluene.

#### Preparation of *In Situ*-modified Cyclohexanone Formaldehyde Resins (17, 18, 19)

The preparation of CF resin was begun and the modifier compound/formaldehyde mixture was added after 2 h of polymerization. The stirring continued for 4 h further. Modified resins were recovered and purified as described earlier.<sup>2</sup>

#### Preparation of *In Situ*-modified Acetophenone-Formaldehyde Resin (26, 27)

Polymerization of AF resin was begun. After about 10 h, the temperature was lowered to 60–70°C and the modified compound formaldehyde mixture was added into the reaction mixture and stirring continued for 1–4 h further. Modified resins were recovered and purified as described earlier.<sup>2</sup>

#### Preparation of *In Situ*-modified Acetophenone-Formaldehyde Resin (28, 29)

Into a three-necked flask, 58 g of acetophenone, 8 g of substituted acetophenone, and 30 g formaline were added and heated to 90°C while stirring. Ten grams of 40% KOH solution was then added slowly while stirring vigorously. The stirring was continued for 8 h at 95°C. Then, 6.5 g of 40% KOH was added

dropwise and further stirred for 7 h. The modified resins were purified by decanting the water layer and washing several times with hot water and then dried at 110°C under vacuum.

#### Reaction with Acetic Anhydride, Dodecylsuccinic Anhydride, Maleic Anhydride, BPDA, and ODP (14.1, 18.1, 23.1, 26.1, 20.7, 20.8, 20.9, 20.10)

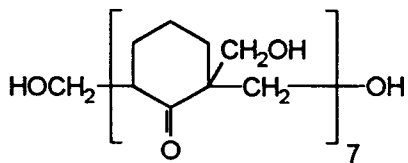
Forty milliliters of pyridine/anhydride (3 : 1) and 4 g of the resins were refluxed at 120°C for 3 h. This mixture was cooled and precipitated with cold water and then this mixture was dissolved in methanol. The mixture was poured into water. Then, the precipitate was dried at 105°C in a vacuum.

#### Benzoylation of *In Situ*-modified Cyclohexanone-Formaldehyde and *In Situ*-modified Acetophenone-Formaldehyde Resin (13.2, 14.2, 23.2)<sup>2</sup>

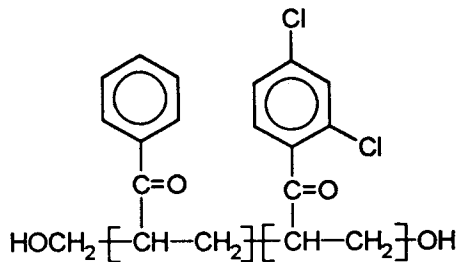
In a flange flask fitted with a multiple socked head carrying a mechanical stirrer, a dropping funnel, and a thermometer, 70 mL of dry pyridine and 50 mL of dry chloroform were placed. The flask was cooled on an ice bath, and from the dropping funnel, a previously prepared and cooled solution of 80 mL of benzoyl chloride in 80 mL of dry chloroform was added. Eight grams of dry powdered *in situ*-modified resin was added portionwise to the vigorously stirred benzoylating reagent at a rate that maintained the temperature of the reaction below 10°C. The pink-colored solution was allowed to stand at 0°C for 24 h, then was diluted with 160 mL of chloroform and transferred to a separatory funnel. It was washed successively with several portions of dilute aqueous H<sub>2</sub>SO<sub>4</sub>, water-saturated aqueous sodium hydrogen carbonate, and hot water. Eventually, chloroform was removed with an evaporator and a precipitate was obtained.

## RESULTS AND DISCUSSION

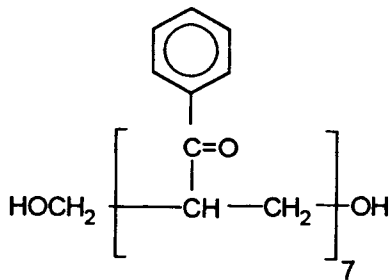
The structure of CF resin and AF resin can be represented as **10** and **20**, respectively.<sup>2</sup> *In situ*-modified resin contains a modifier compound irregularly attached to the base resin possibly via methylene groups. The structure of *in situ*-modified resins with Bisphenol-ACP, Bisphenol-CD, and acetophenone derivatives can be represented as **18**, **26**, **28**, and **29**, respectively.



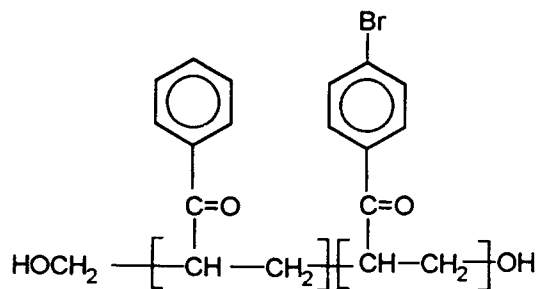
CF (10)



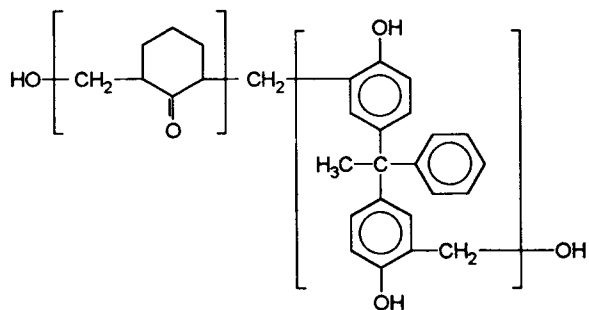
2,4-ClAF(28)



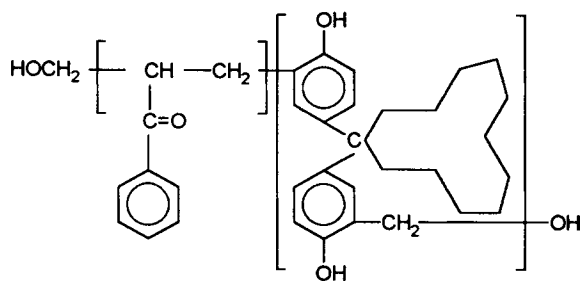
AF (20)



4-Br-AF(29)



CB<sub>ACP</sub>F (18)



AB<sub>CD</sub>F (26)

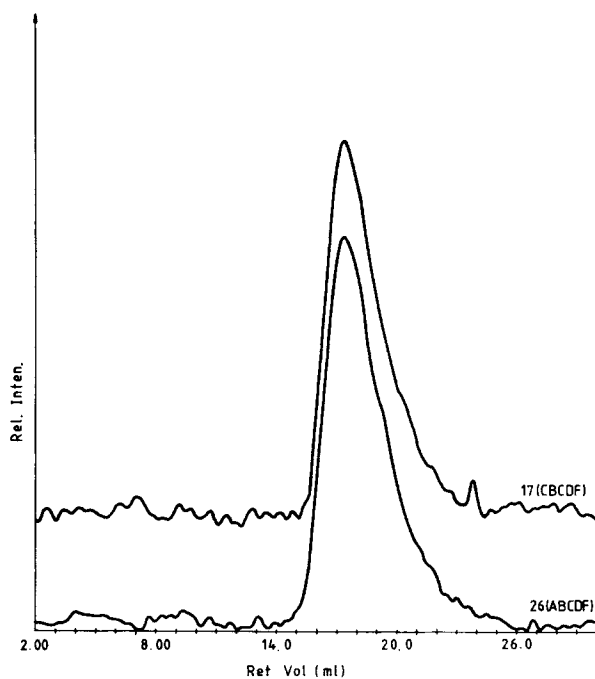


Figure 1 GPC of modified resins.  $M_w$  determined by GPC: CB<sub>CD</sub>F (17),  $M_w = 1163$ ; AB<sub>CD</sub>F (26),  $M_w = 1543$ .

Table I Physical Properties of the Resins

No.	Resins	Mp (°C)	DMF	DMSO	CHCl <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CO	CCl <sub>4</sub>	MeOH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	Ether
10	Cyclohexanone-formaldehyde <sup>a</sup> (CF)	110	sl	s	s	sl	hsl	sl	sl	sl	sl
17	Cyclohexanone-Bisphenol-CD- formaldehyde (CB <sub>CD</sub> F)	92	s	s	s	hs	hs	sl	hsl	hs	s
18	Cyclohexanone-Bisphenol- ACP-formaldehyde (CB <sub>ACP</sub> F)	130	s	s	s	s	s	s	sl	hs	sl
19	Cyclohexanone-phenol- formaldehyde (CFF)	160	s	s	s	sl	sl	hsl	hsl	s	i
20	Acetophenone-formaldehyde <sup>a</sup> (AF)	65	s	s	s	sl	hs	hs	hs	hsl	s
26	Acetophenone-Bisphenol CD- formaldehyde (AB <sub>CD</sub> F)	56	s	sl	s	s	hs	s	hs	hs	s
27	Acetophenone-Bisphenol ACP-formaldehyde (AB <sub>ACP</sub> F)	85	s	s	s	s	sl	sl	hs	hsl	hsl
28	Acetophenone-2,4- dichloroacetophenone- formaldehyde	63	s	s	s	s	sl	hs	sl	s	hs
29	Acetophenone-4-bromo- acetophenone-formaldehyde	88	s	s	s	s	sl	s	sl	s	hsl
13.0	Cyclohexanone-Bisphenol-A- formaldehyde (CBF)	90	s	s	s	s	hs	hs	s	s	sl
13.2	Benzoylated	145	s	sl	s	s	s	sl	sl	s	sl
13.4	Oxime	165	s	hsl	s	s	hs	s	s	sl	hsl
13.5	Semicarbazone	155	s	sl	s	sl	sl	hsl	hsl	hs	i
13.6	Reaction with phenyl hydrazine	51	s	s	s	s	s	s	s	s	s
14.0	Cyclohexanone-Bisphenol-C- formaldehyde <sup>a</sup> (CB <sub>6</sub> F)	115	sl	hs	s	s	sl	hs	hs	hs	hs
14.1	Acetylated	110	s	hs	s	s	s	sl	sl	s	sl
14.2	Benzoylated	88	s	s	s	s	sl	sl	s	s	hs
18.1	Acetylated cyclohexanone- Bisphenol-ACP- formaldehyde	130	s	hsl	s	s	sl	hs	hs	s	i

## Derivatives of AF

<b>20.7</b>	Reaction with maleic anhydride	255	s	s	s	hs	hs	s	hs
<b>20.8</b>	Reaction with dodecenylic succinic anhydride	70	s	s	s	s	s	s	s
<b>20.9</b>	Reaction with biphenyl tetracarboxylic dianhydride	130	s	s	s	s	sl	s	sl
<b>20.10</b>	Reaction with oxydiphtalic anhydride	85	s	s	s	s	sl	s	sl
<b>23.0</b>	Acetophenone-Bisphenol-C-formaldehyde <sup>a</sup> (AB <sub>6</sub> F)	50	sl	hsl	hsl	hsl	hsl	hs	s
<b>23.1</b>	Acetylated	64	s	s	s	s	sl	s	s
<b>23.2</b>	Benzoylated	70	s	s	s	s	sl	s	s
<b>23.4</b>	Oxime	140	s	s	s	s	s	sl	sl
<b>23.5</b>	Semicarbazone	180	s	sl	s	s	sl	sl	i
<b>26.1</b>	Acetylated acetophenone bisphenol-CD-formaldehyde	70	s	s	s	sl	hsl	s	hsl

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

<sup>a</sup> Ref. 2.

*In situ*-modified ketonic resins were examined with TLC and GPC. The modified resins were found to have a co-condensation-type structure as observed earlier.<sup>2</sup> There was no segregation of ketonic resin and the resin of the modifier compound with formaldehyde. This was clearly proved by TLC and GPC (Fig. 1) as described earlier.<sup>2</sup>

### *In Situ*-modified Cyclohexanone-Formaldehyde and Acetophenone-Formaldehyde Resin

Physical properties such as softening point and solubility are shown in Table I. The solubilities of the modified resins were considerably different. The modified CF resin (**17**, **18**) and AF resin (**26–29**) had better solubilities than did the corresponding ketonic resins. Bisphenol-modified CF resin (**18**) and AF resin (**27**, **29**) had higher softening points of about 20°C. Phenol-modified CF resin (**19**) had a higher softening point of about 50°C than that of CF resin and better solubility. This method could be considered a convenient way of producing CF resin with a high softening point. On the other hand, the modified resin (**17**, **26**, **28**) had a lower softening point.

FTIR spectra of *in situ*-modified resins are shown in Figure 2. Peaks due to modifier compounds were clearly seen as well as were peaks due to CF and AF resins. Phenol- and Bisphenol-modified CF resins (**17–19**) showed peak at 1600, due to aromatic rings and at 1700–1720 cm<sup>-1</sup> due to the carbonyl groups. Bisphenol-modified AF resins (**26**, **27**) showed peaks at 1600 and 700 cm<sup>-1</sup> due to aromatic rings and at 1680 cm<sup>-1</sup> due to carbonyl groups. Both Bisphenol-C and Bisphenol CD-modified AF resins showed a stronger signal due to aliphatic C—H groups at about 2900–2950 cm<sup>-1</sup> compared to AF resin and ACP-modified AF resin. Substituted acetophenone-modified AF resin (**28**, **29**) showed peaks at 1600 and 700 cm<sup>-1</sup> due to aromatic rings, at 820 cm<sup>-1</sup> due to aromatic C—Cl, at 1680 cm<sup>-1</sup> due to the carbonyl groups, and at 840 cm<sup>-1</sup> due to aromatic C—Br groups.

### Modification of Modified Cyclohexanone-Formaldehyde and Acetophenone-Formaldehyde Resins

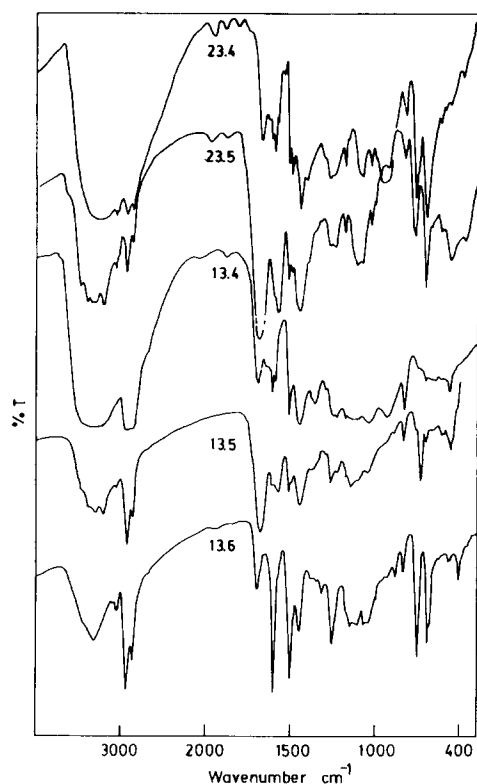
*In situ*-modified resins, such as cyclohexanone-Bisphenol-A-formaldehyde (**13**), cyclohexanone-Bisphenol-C-formaldehyde (**14**), cyclohexanone Bisphenol ACP-formaldehyde (**18**), acetophenone-Bisphenol-C-formaldehyde (**23**), and acetophenone-Bisphenol-CD-formaldehyde resin



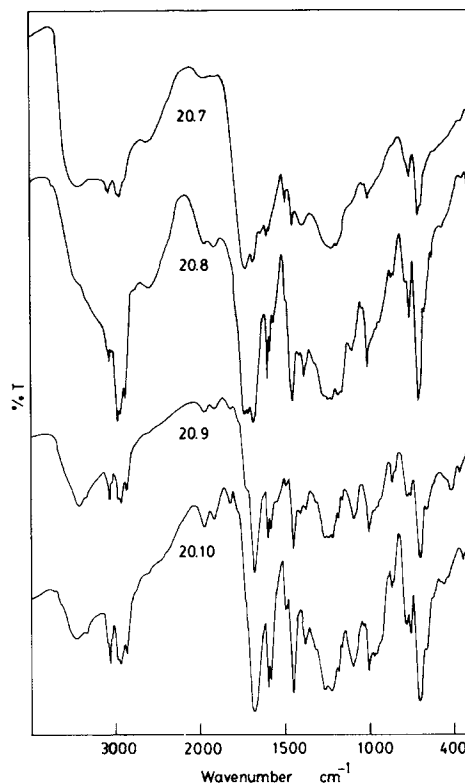
(26), contain both aliphatic hydroxyl and phenolic hydroxyl groups. These resins were acetylated and benzoylated by acetic anhydride and benzoyl chloride, respectively. Both methylol and phenolic hydroxyl groups of the resins should be acetylated and benzoylated. The solubility and softening point of these derivatives increased (Table I). The effect of Bisphenol-C<sub>6</sub> on the properties of *in situ*-modified ketonic resin may be regulated by changing the amount of Bisphenol-C<sub>6</sub>. Increasing the amount of Bisphenol-C<sub>6</sub> resulted in a resin with a higher melting point and lower solubilities (Table II).

The FTIR spectrum of acetylated and benzoylated *in situ*-modified CF resin and AF resin, i.e., (13.2, 14.1, 14.2, 18.1, 23.1, 23.2, 26.1) showed peaks at 1740 cm<sup>-1</sup> due to the carbonyl of both ester and ketone groups. The peak at 3500 cm<sup>-1</sup> due to hydroxyl groups almost disappeared (Fig. 3).

The FTIR spectrum of acetylated *in situ*-modified AF resin (13.1, 26.1) showed peaks at 1740 cm<sup>-1</sup> due to carbonyl of the ester and at 1680 cm<sup>-1</sup> due



**Figure 4** FTIR spectra of derivatives of *in situ*-modified resins: (13.4) oxime of CBF; (13.5) semicarbazone of CBF; (13.6) phenyl hydrazone of CBF; (23.4) oxime of AB<sub>6</sub>F; (23.5) semicarbazone of AB<sub>6</sub>F.



**Figure 5** FTIR spectra of derivatives of AF resins: (20.7) reaction with maleic anhydride; (20.8) reaction with dodecyl succinic anhydride; (20.9) reaction with 3,3,3',4'-biphenyl tetracarboxylic dianhydride; (20.10) reaction with 4,4'-oxydiphtalic anhydride.

to ketone groups of the resins (Fig. 3). Benzoylated resin (23.2) showed a single carbonyl peak at 1690 cm<sup>-1</sup>.

The oxime derivative of the cyclohexanone-Bisphenol-A-formaldehyde (13.4) and acetophenone-Bisphenol-C<sub>6</sub>-formaldehyde (23.4) showed typical peaks due to the oxime groups. The peak at 3300 cm<sup>-1</sup> was due to both hydrogen-bonded hydroxyl groups of oxime and methylol groups of modified CF and AF resins. Peaks at 1650 and 915 cm<sup>-1</sup> and at 1675 and 950 cm<sup>-1</sup> were due to C=N and N—O groups, respectively (Fig. 4).

The semicarbazone derivative of the resin (13.5, 23.5) showed a peak at 1580 cm<sup>-1</sup> due to N—H groups and a peak at 1695 cm<sup>-1</sup> due to both carbonyl and C=N groups. The phenyl hydrazone of the CBF resin (13.6) showed peaks at 3320 and 1500 cm<sup>-1</sup> due to N—H groups (Fig. 4). This product (13.6) had good solubility in all solvents (Table I).

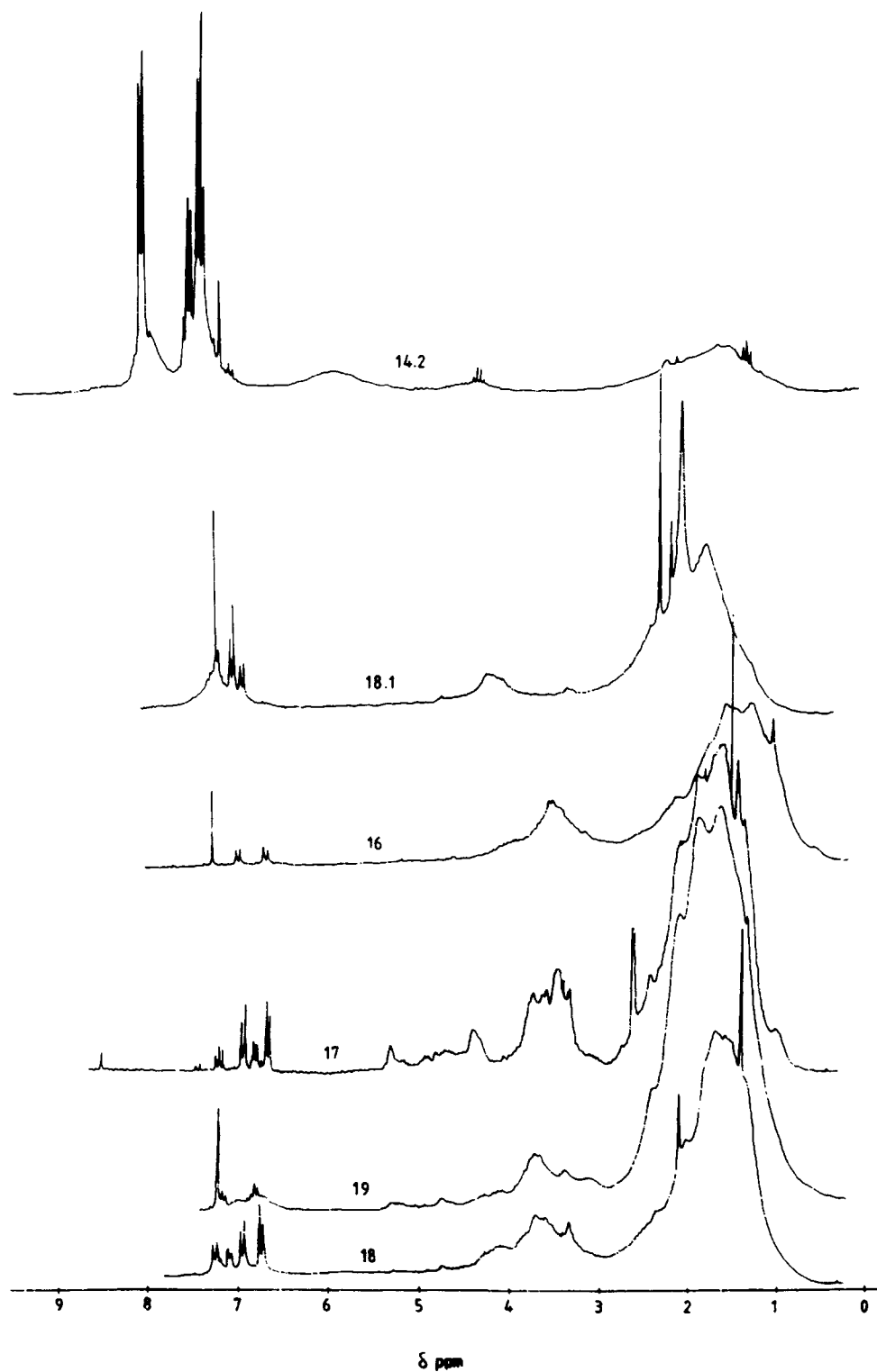


Figure 6 <sup>1</sup>H-NMR spectra of modified CF resins: 16 and 17 in DMSO-*d*<sub>6</sub>.



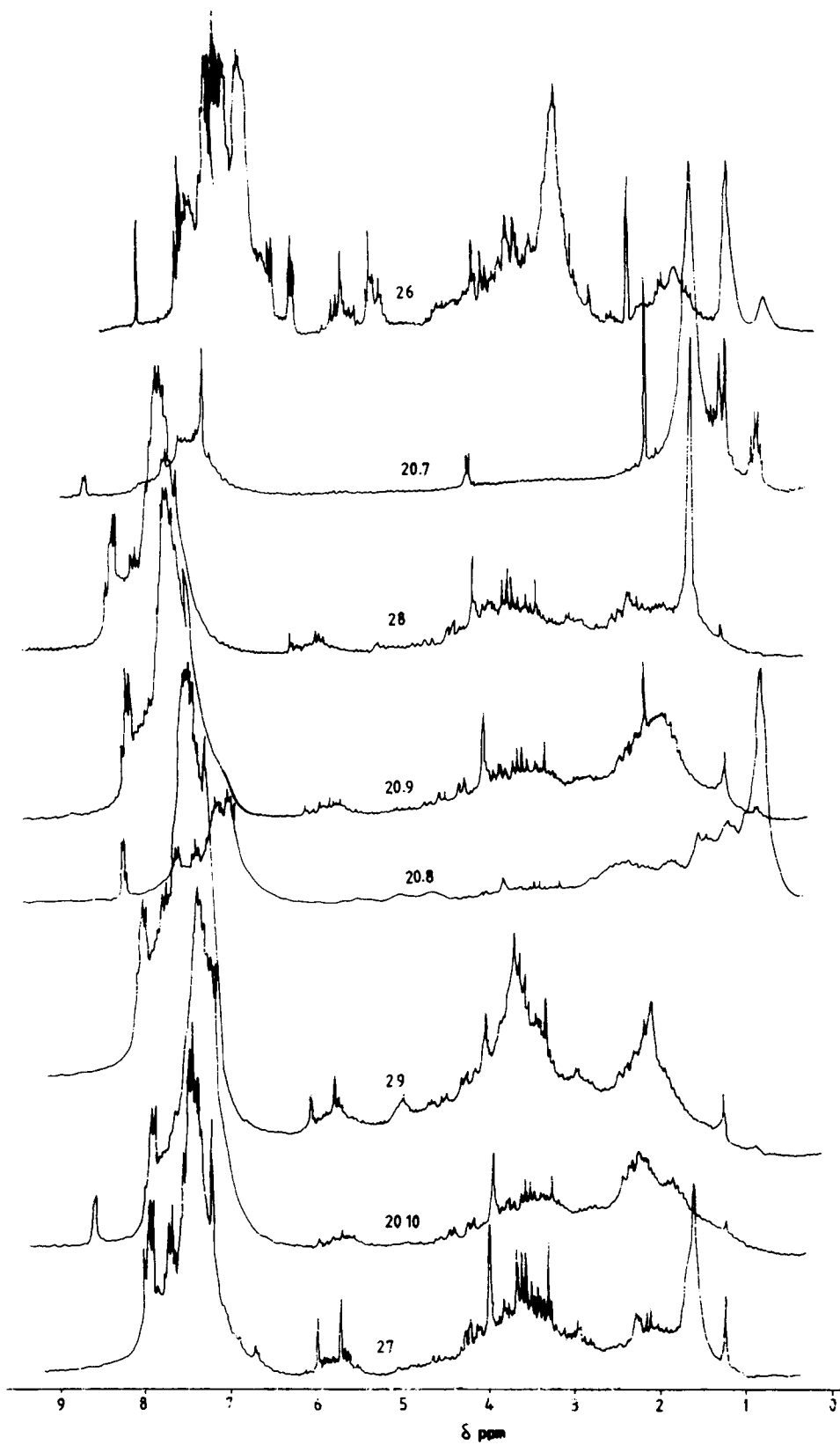
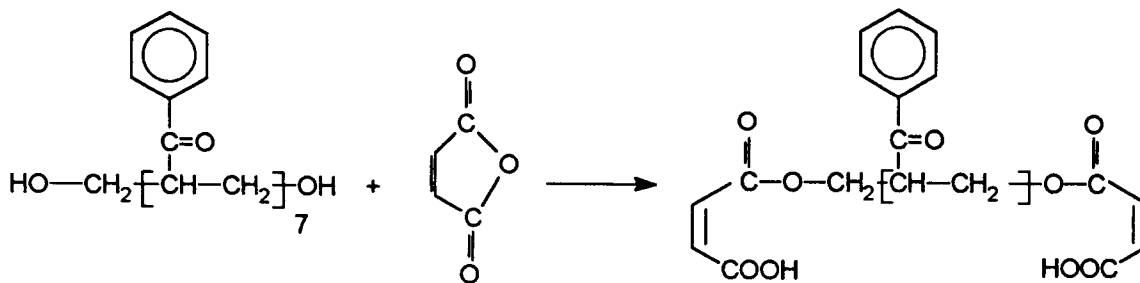


Figure 7 <sup>1</sup>H-NMR spectra of modified AF resins: 26 in DMSO-*d*<sub>6</sub>.

Table III <sup>1</sup>H-NMR Spectral Data of the Resins: δ ppm (in CDCl<sub>3</sub>)

No.	Resins	—CH <sub>3</sub>	—CH <sub>2</sub> —, —CH—	—CH <sub>2</sub> OH	—CH=CH—	Arom. CH	Phenolic OH	—CH <sub>2</sub> OOC—	—COOH
(10)	CF <sup>2</sup>	—	(1.2-2.3)	(3.2-4.2)	—	—	—	—	—
(16)	CB <sub>6</sub> F	—	(1.2-2.4)	(3.2-4.2)	—	(6.75-7)	—	—	—
(17)	CB <sub>CD</sub> F	—	(1.2-2.4)	(3.2-5)	—	(6.6-7.4)	8.5	—	—
(18)	CB <sub>ACP</sub> F	2.1	(1.2-2.3)	(3.2-4.4)	—	(6.65-7.25)	—	—	—
(19)	CFF	—	(1.2-2.3)	(3.2-5.3)	—	(6.7-7.4)	—	—	—
(14.2)	Benzoylated of CB <sub>6</sub> F	—	(1.4-2.4)	—	—	(7.2-8.2)	—	4.2	—
(18.1)	Acetylated of CB <sub>ACP</sub> F	2.1	(1.8-2.4)	—	—	(6.9-7.2)	—	4-4.2	—
(20)	AF <sup>2</sup>	—	(1.7-3.5)	(3.7-4.9)	—	(7-8.2)	—	—	—
(26)	AB <sub>CD</sub> F	—	(2-3), (1-1.5)	(3.2-5)	—	(6.2-7.2)	8.45	—	—
(27)	AB <sub>ACP</sub> F	2	(1.2-3)	(5.4-6.2)	—	(6.7-8.2)	—	—	—
(28)	2,4-Cl AF	—	(1.7-3.5)	(5.4-6.2)	—	(7-8)	—	—	—
(29)	4-Br AF	—	(1.7-3.5)	(3-5)	—	(7.2-8)	—	—	—
<u>Derivatives of AF</u>									
(20.7)	Reaction with maleic anhydride	—	(1-2)	—	8.6	—	—	4.2	—
(20.8)	Reaction with DDSA	—	(0.8-2.6)	(3.2-4)	—	(7.2-8.5)	—	—	12.6
(20.9)	Reaction with BPDA	—	(2-3)	(3.2-4)	—	(7.4-8)	—	(4.2-4.5)	—
(20.10)	Reaction with ODPA	—	(2-2.6)	(3.2-4)	—	(7.3-8.6)	—	4.4	—



Scheme 1

### Modification of Acetophenone-Formaldehyde Resin

AF resin (**20**) was modified with a cyclic anhydride such as maleic anhydride (**20.7**), dodecyl succinic anhydride (**20.8**), and dianhydride such as BPDA (**20.9**) and ODPA (**20.10**). The reaction of hydroxyl groups of the resins with anhydrides was carried out in such a way that one hydroxyl would react with one anhydride group to form an ester and a free carboxylic acid group. As an example, the reaction between AF resin and maleic anhydride can be shown in Scheme 1.

Maleic anhydride-modified AF resin (**20.7**) showed the typical peaks of AF resin as well as a peak at  $1730\text{ cm}^{-1}$  due to ester groups and broad peaks at about  $3400$  and  $2550\text{ cm}^{-1}$  due to carboxylic groups (Fig. 5).

Dodecyl succinic anhydride-modified AF resin (**20.8**) showed peaks at  $1730$  and  $2550\text{ cm}^{-1}$  due to ester and free carboxylic groups, respectively. Besides, the ratio of the aliphatic C—H peaks at about  $2870$ – $2950\text{ cm}^{-1}$  to the aromatic C—H peak at about  $3050\text{ cm}^{-1}$  was considerably higher (Fig. 5). Long alkyl groups caused the modified resin (**20.8**) to be soluble in almost all common organic solvents (Table I).

### NMR Study of Modified Resins

Proton NMR spectra of modified CF resin (**17**, **18**, **19**, **14.2**, **18.1**) and modified AF resin (**26**, **27**, **20.7**–**20.10**) are shown in Figures 6 and 7, respectively. The observed signals due to corresponding protons are summarized in Table III.

Phenol- and Bisphenol-modified CF resins showed signals at 6.7 and 7.2 ppm due to aromatic protons. The signal due to phenolic hydroxyls was not always observed. However, signals due to phenolic hydroxyls of  $\text{CB}_{\text{CD}}\text{F}$  and  $\text{AB}_{\text{CD}}\text{F}$  resin were observed at 8.5

ppm. Bisphenol-modified AF resin showed signals due to both aliphatic and aromatic protons.

### CONCLUSIONS

Acetophenone-formaldehyde and cyclohexanone-formaldehyde resins have been used mainly as additives in hundreds of applications in the industry. In this work, *in situ*-modified acetophenone-formaldehyde and cyclohexanone-formaldehyde resins and their modification via functional groups were achieved. This may open up new areas of applications where ketonic resins have limited use due to their solubilities and melting points. The modified resins have a variety of solubilities, melting points, and functional groups such as phenolic hydroxyl, carboxylic acid, oxime, and ester and they could be used as ketonic resins with higher/less solubility in a particular solvent and higher/lower melting points. Besides, the modified resins with carboxylic acid groups may also promote the adhesive strength of a coating to metal surfaces. Oxime derivatives may be used in the paints as additives. In this case, they may act both as an anti-skinning additive due to oxime groups and as a adhesive/gloss promoter due to the ketonic resin structure. Modified ketonic resin with high mp may be used in the ink industry where a binder with a high melting point is desired.

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