

Modified Cyclohexanone–Formaldehyde and Acetophenone–Formaldehyde Resins

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SYNOPSIS

Preparation of *in situ*-modified cyclohexanone–formaldehyde and acetophenone–formaldehyde resins with compounds such as diphenols, melamine, and *p*-toluene sulfonamide were studied. Modification of acetophenone–formaldehyde resins with hydroxylamine, semicarbazide, phenylhydrazine, phthalic anhydride, and acetic anhydride was also studied. Melting points, solubilities in organic solvents, and FTIR and NMR spectra of modified resins were determined.

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INTRODUCTION

Modification of cyclohexanone–formaldehyde resin via its hydroxyl and carbonyl groups has been previously studied.¹ Hydroxyl groups were reacted with acetyl chloride, benzoyl chloride, phthalic anhydride, and carbonyl groups with hydroxylamine, semicarbazide, and phenylhydrazine.

In situ modification of acetophenone resin has been studied previously. The modifier compounds were phenol,² *p*-cumylphenol,³ and *p*-cresol.⁴ The resulting resins were used for adhesives and binders. Modified cyclohexanone/formaldehyde resins were also prepared using MEK, MIBK, methylcyclohexanone, acetaldehyde, propionaldehyde, and cinnamaldehyde. These resins were used as binders for self-hardening molds.⁵

In this work, cyclohexanone–formaldehyde and acetophenone–formaldehyde resins were modified during the preparation by the addition of a modifier compound/formaldehyde mixture to the polymerization media. Compounds that react with formaldehyde in basic media were used as modifier compounds. These were melamine, resorcinol, *p*-toluene sulfonamide, bisphenol-A, and bisphenol-C.

Modification of the acetophenone–formaldehyde resin via hydroxyl and carbonyl groups and reaction

of its hydroxyl groups with acetic anhydride, benzoyl chloride, and phthalic anhydride and of carbonyl groups with hydroxylamine and semicarbazide were also studied.

EXPERIMENTAL

IR spectra were recorded on a Jasco FTIR-5300 Fourier transform infrared spectrometer on a KBr disk. ¹H-NMR spectra were obtained for CDCl₃ or DMSO-*d*₆ solutions on a Bruker AC-(200 MHz). GPC chromatograms were obtained by using a Knauer M64 instrument equipped with a differential refractometer.

1. Preparation of Cyclohexanone–Formaldehyde Resin (CF-Resin) (10)

CF-resin was prepared according to Ref. 4. Into a three-necked flask, 98 g of cyclohexanone, 20 g of cyclohexane, and 30 g of formaline were added and heated to 60°C while stirring. Then added was 0.36 mL of 20% NaOH in equal portions. When the temperature of the mixture rose to 70–75°C, refluxing began. Then, 100 g of formaline and 3.64 mL of 20% NaOH were mixed and added continuously at a gradually increasing rate sufficient to maintain vigorous refluxing. After 2 h, the reaction was completed. The upper phase was decanted. It was then washed several times with hot water and dried at 120°C under vacuum.

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2. Preparation of Acetophenone-Formaldehyde Resin (AF-Resin) (20)

AF-resin was prepared according to Ref. 1. Into a three-necked flask, 67 g of acetophenone and 30 g of 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 resin was purified by decanting the water layer and washing several times with hot water. It was then dried at 150°C under vacuum.

3. Preparation of Bisphenol-A/Formaldehyde and Bisphenol-C/Formaldehyde Resin

The bisphenol compound, 0.03 mol, and 0.12 mol formaldehyde (37%) were mixed and 4 g of 25% NaOH was added in 5–10 min. The mixture was heated to 50°C. After stirring 8 h, the mixture was cooled to room temperature and neutralized with 5% HCl. Butanol, 12.5 mL, was added, then filtered and dried at room temperature under vacuum. A clear pale yellow product was obtained.

4. Preparation of *In Situ*-Modified Cyclohexanone-Formaldehyde Resins (11–16)

The preparation of cyclohexanone/formaldehyde resin was begun and the modifier compound/formaldehyde mixture was added after 2 h of polymerization. The stirring continued for 2 h more. Modified resin was recovered and purified as described earlier.

5. Preparation of *In Situ*-Modified Acetophenone-Formaldehyde Resin (21–25)

Polymerization of the acetophenone-formaldehyde resin was begun. After about 14 h, the temperature was lowered to 60–70°C and the modifier compound-formaldehyde mixture was added into the reaction mixture and stirring continued for 1–4 h more. Modified resin was recovered and purified as described earlier.

6. Acetylation of Acetophenone-Formaldehyde Resin (20.1)

Twenty milliliters of pyridine/acetic anhydride (3 : 1) and 2 g of the AF-resin were refluxed at 120°C for 3 h. This mixture was then cooled and precipitated with cold water. The gray precipitate was dried at 105°C in vacuum.

7. Benzoylation of the Acetophenone-Formaldehyde Resin (20.2)

In a flange flask fitted with a multiple-socked head carrying a mechanical stirrer, a dropping funnel, and a thermometer, 25.7 mL of dry pyridine and 21.5 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 21.5 mL of benzoyl chloride in 21.5 mL of dry chloroform was added. Five grams of dry powdered AF-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 80 mL of chloroform and transferred to a separatory funnel. It was washed successively with several portions of dilute aqueous H₂SO₄, water-saturated aqueous sodium hydrogen carbonate, and hot water. Eventually, chloroform was removed on an evaporator and the precipitate was obtained.

8. Reaction with Phthalic Anhydride (20.3)

Two grams of AF-resin and 4.5 g of phthalic anhydride in 40 mL of pyridine were refluxed for 6 h. After evaporation of the pyridine, the resin was precipitated with water and then filtered, washed several times with water, and dried at 105°C in vacuum.

9. Reaction with Hydroxylamine (20.4)

Seven grams of AF-resin, 7 g of hydroxylamine hydrochloride, 7 mL of pyridine, and 70 mL of ethanol were mixed and refluxed for 3 h. Then, the mixture was cooled and poured into water. The precipitate was filtered, washed several times with water, and dried at 110°C in vacuum.

10. Reaction with Semicarbazide (20.5)

Two grams of semicarbazide hydrochloride and 3 g of crystallized sodium acetate were dissolved in 8 mL of water, and 1 g of AF-resin dissolved in alcohol was added. If the solution was turbid, alcohol was added until a clear solution was obtained. The mixture was warmed in a water bath for 2 h, then cooled and precipitated with cold water. The white precipitate was filtered and washed several times with water, then dried at 105°C in vacuum.

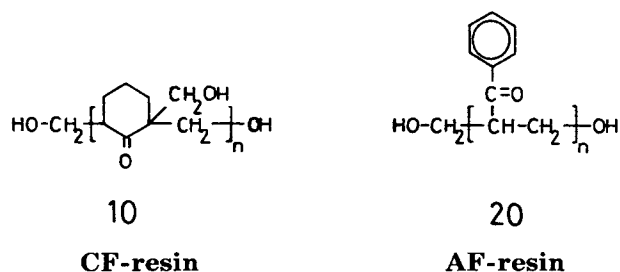
11. Reaction with Phenylhydrazine (20.6)

Four grams of AF-resin was mixed with 8.5 mL of phenylhydrazine and heated for 1 h in a water bath,

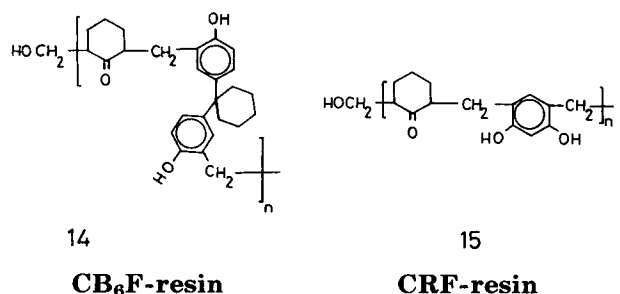
then cooled and precipitated with cold water. The red precipitate was filtered, washed several times with water, and dried at 105°C in vacuum.

RESULTS AND DISCUSSION

The overall structure of cyclohexanone-formaldehyde resin (CF-resin) and acetophenone-formaldehyde resin (AF-resin) can be represented as follows¹:



In situ-modified CF-resin and AF-resin contain modifier compounds irregularly attached to the base resin, probably via methylene groups. As an example, the structure of *in situ* bisphenol-C and resorcinol-modified CF-resin can be represented as **14** and **15**, respectively.



In situ-modified ketonic resin was examined with TLC and GPC, and the modified resins were found to have a cocondensation-type structure. There was no segregation of the ketonic resin and the resin of the modified compound with formaldehyde. This is clearly seen from GPC in Figure 1.

1. *In Situ* Modified Cyclohexanone-Formaldehyde Resin (CF-Resin)

Physical properties such as softening point and solubility are shown in Table I. Solubility of the modified resins depended on the type of modifier compound, e.g., melamine and bisphenol-A-modified CF-

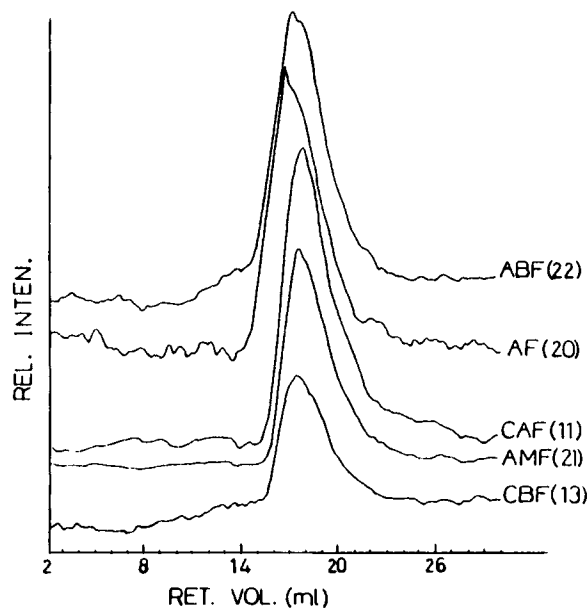


Figure 1 GPC of modified resins. \bar{M}_w determined by GPC: ABF (**22**): 2656; AF (**20**): 3389; CAF (**11**): 1215; AMF (**21**): 2531; CBF (**13**): 1365.

resin (**12** and **13**, respectively) had better solubility in ethanol and acetone than did CF-resin (**10**). Bisphenol-C-modified resin (**14**) had lower solubility in most of the solvents including in strong solvents such as DMSO.

FTIR spectra of modified resins are shown in Figure 2. Peaks due to modifier compounds were clearly seen as well as peaks due to CF-resin. Acetophenone-modified CF-resin (**11**) showed peaks at 1610 and 700 cm^{-1} due to the aromatic ring and at 1700 cm^{-1} due to the carbonyl group of acetophenone. Melamine-modified CF-resin (**12**) showed peaks at 1510 and 1570 cm^{-1} due to melamine groups. The modified resin of (**13**), (**14**), (**15**), and (**16**) showed a peak at 1610 cm^{-1} due to the C—C stretching vibration of the aromatic ring of bisphenol-A, bisphenol-C, resorcinol, and *p*-toluene sulfonamide.

2. *In Situ*-Modified Acetophenone-Formaldehyde Resin (AF-Resin)

Melamine, resorcinol, and *p*-toluene sulfonamide-modified AF-resin (**21**, **24**, and **25**, respectively) were soluble in toluene and acetone but only slightly soluble in ether. Bisphenol-C-modified resin (**23**) had poorer solubility than that of AF-resin (**20**) in strong solvents such as DMF and DMSO.

Table I Physical Properties of the Resins

No.	Resins	MP (°C)	Solubilities										
			DMF	DMSO	CHCl ₃	(CH ₃) ₂ CO	CCl ₄	MeOH	C ₂ H ₅ OH	C ₆ H ₆ CH ₃	Ether		
10	Cyclohexanone-formaldehyde	110	sl	s	s	sl	hsl	sl	sl	sl	sl	sl	sl
11	Cyclohexanone-acetophenone-formaldehyde	98	s	s	s	hs	sl	hs	sl	sl	sl	sl	sl
12	Cyclohexanone-melamine-formaldehyde	102	s	s	s	s	hs	sl	s	hs	hs	hs	hs
13	Cyclohexanone-bisphenol-A-formaldehyde	90	s	s	s	s	hs	hs	s	s	s	sl	sl
14	Cyclohexanone-bisphenol-C-formaldehyde	115	sl	hs	s	s	sl	hs	hs	hs	hs	hs	hs
15	Cyclohexanone-resorcinol-formaldehyde	88	s	s	s	s	hsl	s	sl	hs	hs	hsl	hsl
16	Cyclohexanone- <i>p</i> -toluene-sulfonamide-formaldehyde	90	s	s	s	s	sl	hs	hs	sl	sl	hsl	hsl
20	Acetophenone-formaldehyde	65	s	s	s	sl	hs	hs	hs	hs	hs	hsl	s
21	Acetophenone-melamine-formaldehyde	73	s	sl	s	s	hs	hsl	hsl	hs	hs	hsl	hsl
22	Acetophenone-bisphenol-A-formaldehyde	66	s	s	s	s	hs	hsl	hs	hs	hs	hsl	hsl
23	Acetophenone-bisphenol-C-formaldehyde	50	sl	hsl	s	hsl	hsl	hsl	hs	hs	hs	hs	s
24	Acetophenone-resorcinol-formaldehyde	63	s	s	s	s	hs	hsl	i	hs	s	hsl	hsl
25	Acetophenone- <i>p</i> -Toluene-sulfonamide-formaldehyde	63	s	s	s	s	sl	hs	hs	hs	s	hs	hs
20.0	Derivatives of acetophenone formaldehyde												
20.1	Acetylated	72	s	s	s	s	s	hs	hs	hs	s	hs	hs
20.2	Benzoylated	60	s	s	s	s	s	s	s	s	s	s	s
20.3	Reaction with phthalic anhydride	98	—	s	s	s	hs	hs	hs	hs	s	hs	hs
20.4	Oxime	133	s	s	s	s	hsl	s	hs	hs	hsl	hsl	i
20.5	Semicarbazone	115	s	s	s	s	hsl	hsl	hs	hs	hsl	hsl	i
20.6	Reaction with phenylhydrazine	74	s	s	s	s	s	sl	s	s	s	s	s

s: soluble; sl: slightly soluble; i: insoluble; hs: soluble (hot); hsl: slightly soluble (hot).

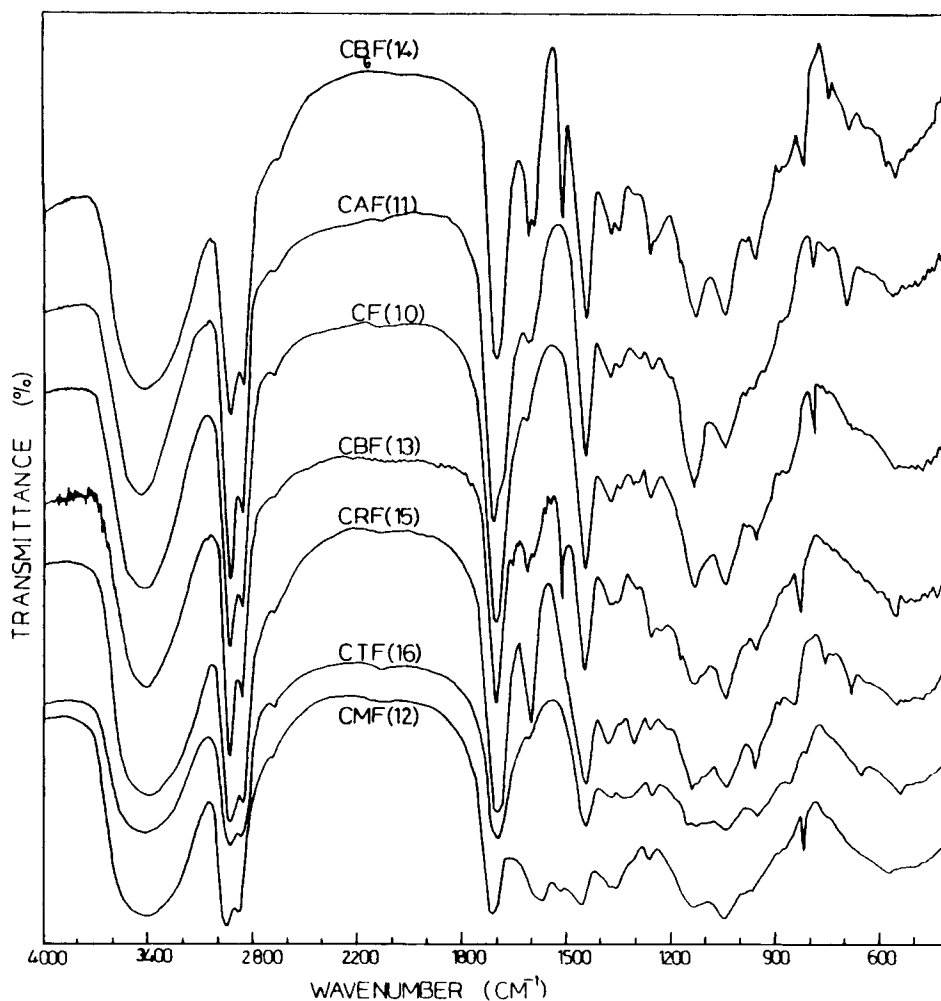


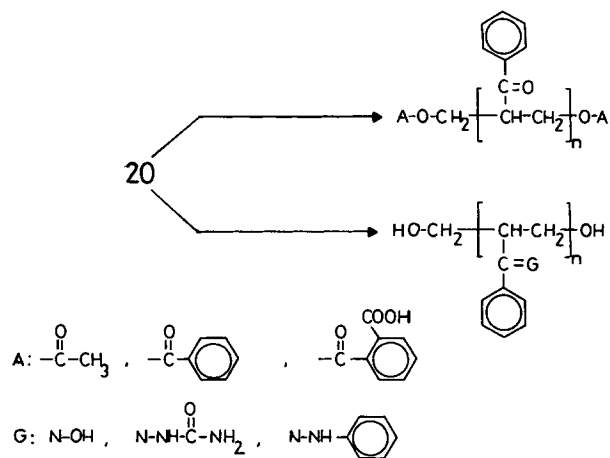
Figure 2 FTIR spectra of *in situ*-modified cyclohexanone-formaldehyde resins.

FTIR spectra of modified resins of (22), (23), (24), and (25) showed peaks at 1600 cm^{-1} as a doublet and at 700 cm^{-1} due to aromatic rings of both acetophenone and the modifier compound and at 1680 cm^{-1} due to the carbonyl group of acetophenone. Melamine-modified AF-resin (21) showed peaks at 1500 and 1550 cm^{-1} due to the melamine group (Fig. 3.).

3. NMR Study of *In Situ*-Modified Resins

Proton NMR spectra of CF-resin (10), modified CF-resins (11–14), AF-resin (20), and modified AF-resins (21–24) are shown in Figure 4. Observed signals due to corresponding nuclei are summarized in Table II. The intensity of the signals due to the modifier compounds was about $\frac{1}{10}$ of signals due to

the base resin. This result was expected since the amount of modifier compound was about $\frac{1}{10}$ of cyclohexanone or acetophenone.



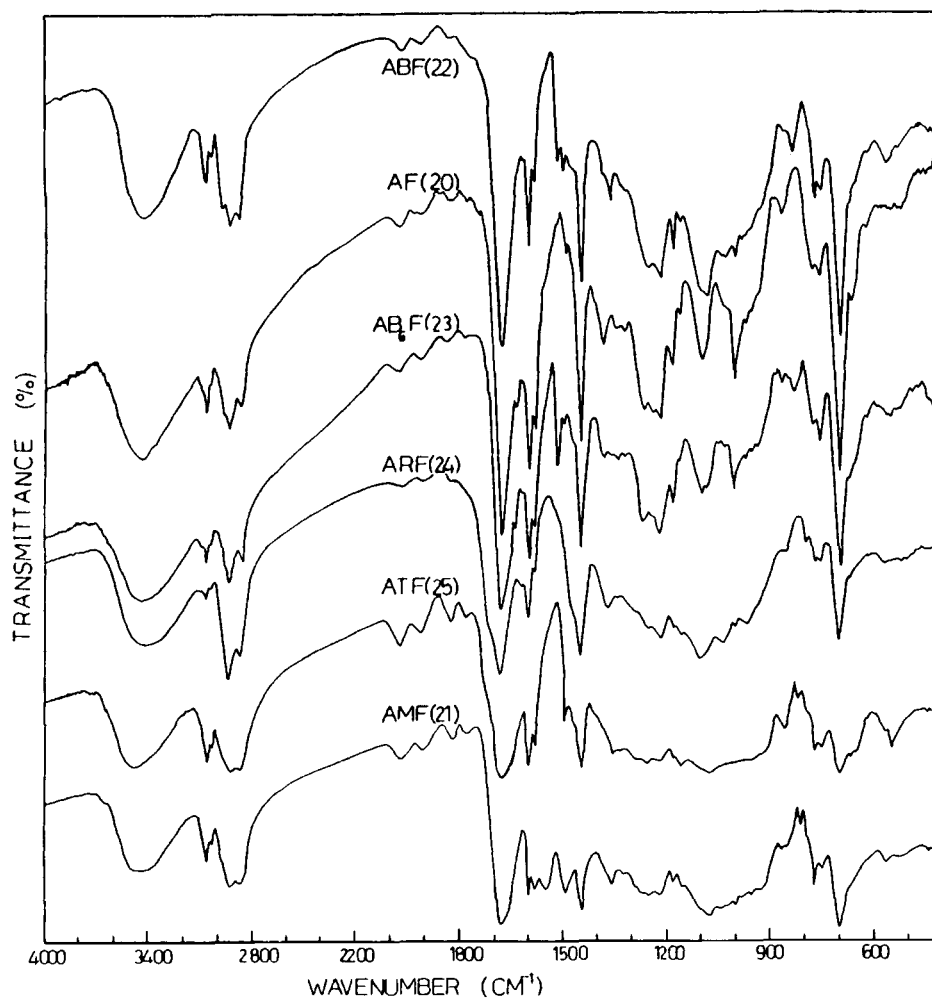


Figure 3 FTIR spectra of *in situ*-modified acetophenone-formaldehyde resins.

4. Modification of Acetophenone-Formaldehyde Resin (AF-Resin)

AF-resin (**20**) was acetylated with acetic anhydride and benzoylated with benzoyl chloride in the presence of pyridine to mask its hydroxyl groups. The solubility range of both acetylated and benzoylated AF-resin (**20.1** and **20.2**) was increased considerably (Table I). The modified product derived from AF-resin by reaction with phthalic anhydride (**20.3**) had also good solubility properties. The solubilities of other derivatives such as oxime, semicarbazone, and phenylhydrazone of the AF-resin (**20.4**, **20.5**, and **20.6**, respectively) are summarized in the Table I.

The FTIR spectrum of acetylated AF-resin (**20.1**) showed peaks at 1740 cm^{-1} due to the car-

bonyl of ester groups and at 1680 cm^{-1} due to carbonyl groups of AF-resin (Fig. 5) and the peak at 3500 cm^{-1} had nearly disappeared. However, benzoylated AF-resin (**20.2**) showed a single peak at 1680 cm^{-1} due to both the carbonyl of the ester groups and the carbonyl groups of AF-resin. The product (**20.3**) showed peaks at 2675 and 2342 cm^{-1} due to the carboxylic groups and a broader peak at 1680 cm^{-1} due to the carbonyl groups. The peak at 3400 cm^{-1} due to the methylol groups of the AF-resin almost disappeared.

The oxime derivative of the AF-resin (**20.4**) showed typical peaks due to the oxime groups. The peak at 3314 cm^{-1} was due to both hydrogen-bonded hydroxyl groups of oxime and methylol groups of AF-resin. Peaks at 1668 and 951 cm^{-1} were due to $\text{C}=\text{N}$ and $\text{N}-\text{O}$ groups of oxime.

The semicarbazone derivative of the resin (**20.5**)

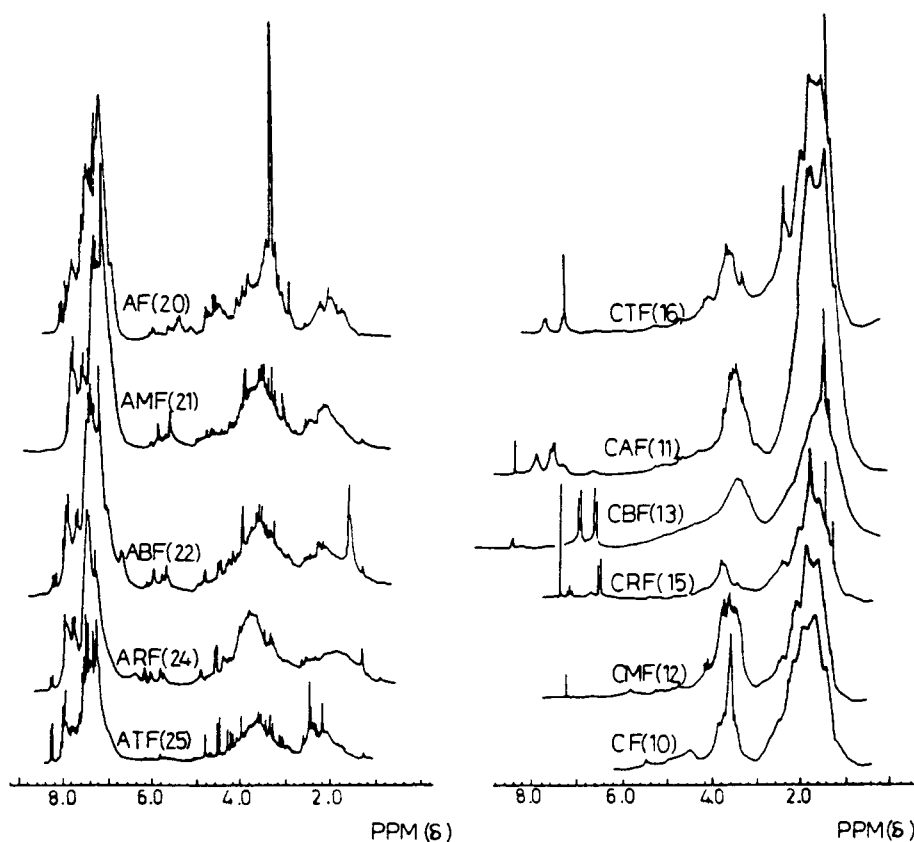


Figure 4 $^1\text{H-NMR}$ spectra of *in situ*-modified cyclohexanone-formaldehyde and acetophenone-formaldehyde resins.

showed sharp peaks at 3475 and 1577 cm^{-1} due to N-H groups and a peak at 1698 cm^{-1} due to both carbonyl and C=N groups. The phenylhydrazone

of the AF-resin (**20.6**) showed peaks at 3350 and 1500 cm^{-1} due to N-H groups. The product (**20.6**) had good solubility in all solvents.

Table II $^1\text{H-NMR}$ Spectral Data of the Resins: δ ppm (CDCl_3)

Resins	$-\text{CH}_3$	$-\text{CH}-$ 	$-\text{CH}_2-$	$-\text{CH}_2\text{OH}$	$-\text{N}-\text{CH}_2$ 	Arom. CH	Phenolic OH	$-\text{N}-\text{H}$
CF (10)	—	(1.2-2.3)		(3.2-4.2)	—	—	—	—
CAF (11)	—	(1.5-2.5)		(2.9-4.7)	—	(7.5-8.4)	—	—
CMF (12)	—	(1.3-2.8)		(3.3-3.9)	—	—	—	(7.3)
CBF (13)	—	(1.3-2.0)		(3.4-3.5)	—	(6.7-7.0)	(8.5)	—
CRF (15)	—	—	(1.3-2.5)	(3.6-3.7)	—	(6.3-7.1)	(7.3)	—
CTF (16)	—	(1.3-2.6)		(3.0-4.2)	—	(7.2-7.8)	—	—
AF (20)	—	(1.7-2.6)	(3.0-3.5)	(3.7-4.9)	—	(7.0-8.2)	—	—
AMF (21)	—	(1.4-2.6)		(2.7-4.0)	—	(7.1-7.8)	—	(7.3)
ABF (22)	(1.6)	(2.1-2.6)		(2.9-4.5)	—	(6.7-8.3)	—	—
ARF (24)	—	—	(1.3-3.0)	(3.0-4.5)	—	(7.3-8.3)	—	—
ATF (25)		(1.6-2.7)		(2.8-4.8)	—	(7.3-8.3)	—	—

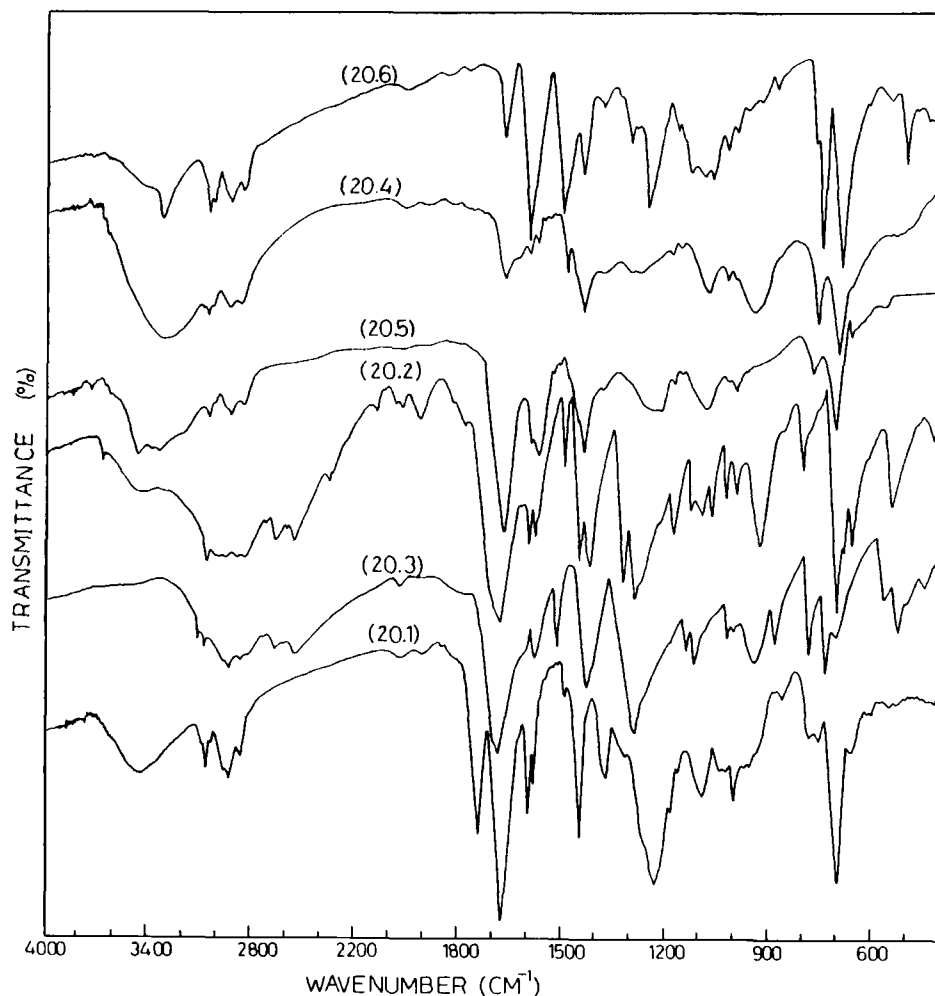


Figure 5 FTIR spectra of derivatives of acetophenone-formaldehyde resin: (20.1) acetylated; (20.2) benzoylated; (20.3) reaction with phthalic anhydride; (20.4) oxime; (20.5) semicarbazone; (20.6) reaction with phenylhydrazine.

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