

Synthesis and Characterization of Phenolic and Amino Resins Based on α, β -Unsaturated Aldehydes*

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SYNOPSIS

Phenolic and amino resins on the basis of α, β -unsaturated aldehydes were synthesized in bulk or solution. Catalysts were HCl, H_3PO_4 , or formic acid, and in some cases NaOH. The course of the reactions was followed by GPC and NMR while the structure of the reaction products was determined by one- and two-dimensional NMR. The course of the reactions is influenced by experimental conditions: the type of monomers, their molar ratio, the type and quantity of the catalyst, the reaction time and temperature, and the reaction medium. At the beginning of the reaction the addition of a nucleophile to an aldehyde takes place through parallel 1,2-addition to >C=O and 1,4-addition to >C=C< group. Oligomers with $-\text{OH}$, >C=C< , and $-\text{CHO}$ functional groups are able to add new monomer units or to react mutually to form higher molecular weight addition and condensation products. The overall rate constants for the beginning of the reactions were between 10^{-3} L/mol s for the high reactive mixtures and 10^{-7} L/mol s for the less reactive mixtures. The resins were cured by heating at temperatures above 135°C with the addition of hexamethylenetetramine.

INTRODUCTION

Phenolic and amino resins are polycondensation products of phenols, urea, or melamine with formaldehyde. They are commercial products since the beginning of this century, and as such most thoroughly investigated.^{1,2} Phenolic and amino resins on the basis of α, β -unsaturated aldehydes are the subject of more recent research³⁻¹¹ and have by now no significant practical importance. Some of them are used as additives for improvement of adhesive properties, as antioxidants, or as photosensitive compounds.¹²⁻¹⁷

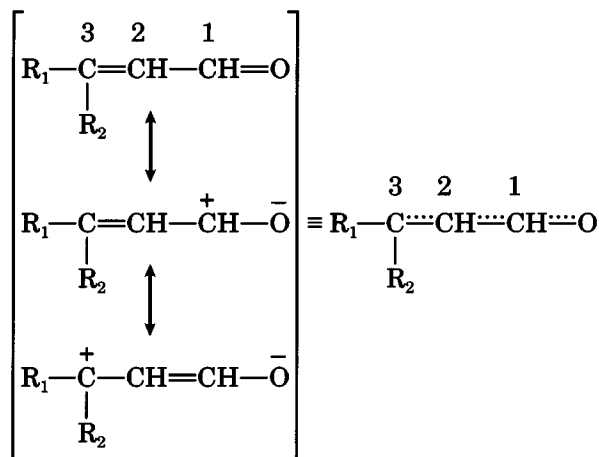
The aim of our work was the synthesis and characterization of phenolic and amino resins based on α, β -unsaturated aldehydes. Because of the propanoic units between phenolic aromatic rings, the resins were expected to be more flexible than those with formaldehyde. Another advantage compared to conventional phenolic resins should be less unreacted monomers as a consequence of the high reactivity of the unsaturated aldehydes with conjugated >C=C< and >C=O double bonds.

Because of the oxygen electron-withdrawing effect, the aldehyde's carbonyl carbon atom is electron deficient, which causes the double bond >C= C< to be polarized; as a consequence the α, β -unsaturated aldehydes are resonance hybrids of different structures with positive centers on C_1 and C_3 atoms:¹⁸

* Presented at the APTS-2 Conference—Polycondensation and Related Reactions, Gargnano, Italy, 1990.

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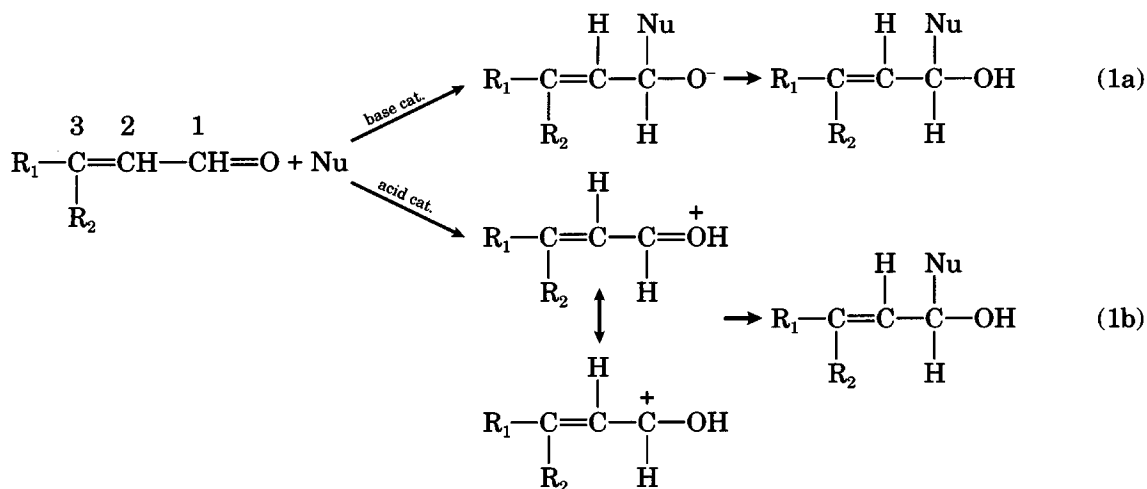
Journal of Applied Polymer Science, Vol. 45, 597-606 (1992)
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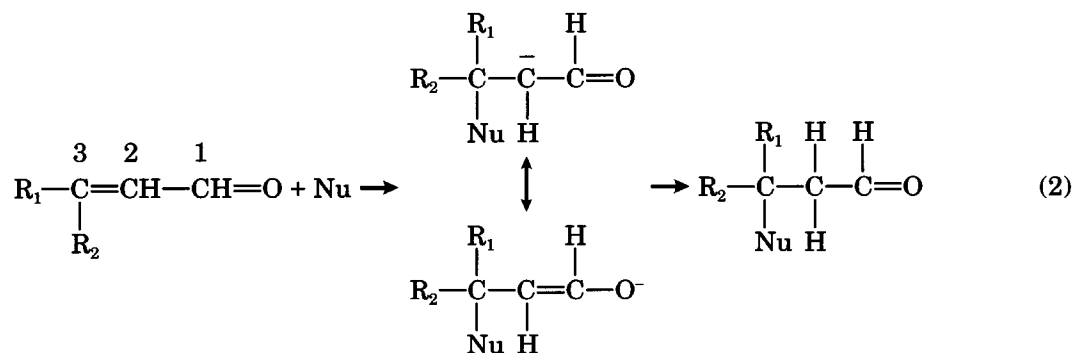
Actual functionality of α,β -unsaturated aldehydes is two-, but they can be regarded as three-functional compounds because of the reactive hydroxyl group formed with the addition of a nucleophile to the aldehyde's C_1 atom. Phenols and amino compounds have a functionality of two or more. The reactivity of phenols depends on electron density of the aromatic ring, which is strongly influenced by the type of substituents.

The addition of a nucleophile to an α,β -unsaturated aldehyde takes place on both electropositive C_1 and C_3 atoms: 1,2-addition or direct addition to the C_1 of carbonyl bond $\text{>C}=\text{O}$, and 1,4-addition or conjugated addition to the C_3 of the double bond $\text{>C}=\text{C}<$ as follows:¹⁸

1,2-addition:



1,4-addition:



Addition products with reactive functional groups $-\text{CHO}$, $\text{>C}=\text{C}<$, and $-\text{OH}$ are formed. The addition of the phenolic hydroxyl group to the al-

dehyde double bond $\text{>C}=\text{C}<$ is possible as well, preferably in alkaline medium. The addition prod-

ucts react further with monomers or between themselves to form products of higher molecular weight.

EXPERIMENTAL

Materials

The used nucleophilic compounds (Nu) were various phenols such as phenol (P), cresols (C), *p*-ethylphenol (EP), dimethylphenols (DMP), and resorcinol (R); the amino compounds were urea (U), melamine (M), and guanamines (G), while the α,β -unsaturated aldehydes (Ua) were acrolein (A), crotonaldehyde (CR), methylcrotonaldehyde (MC), and cinnamaldehyde (CA). Phenols and aldehydes were products of Merck, urea of INA, melamine of

Aldrich, and guanamines of SKW. The aldehydes were distilled before use.

Inorganic acids HCl and H₃PO₄, organic acid HCOOH and in some cases Na hydroxide were used as catalysts and hexamethylenetetramine as curing agent.

The solvents were of a *pro analysi* grade.

Synthesis

In table I a survey of the used monomers, of their molar ratios, of catalysts, and of synthesis conditions is given. The resins were synthesized in bulk and in solution with or without catalyst. The reaction rates were influenced by the type of monomers, their molar ratios, the type and quantity of catalysts and

Table I Survey of Monomers, Their Molar Ratios, Catalysts, and Synthesis Conditions

Synthesis	
In Bulk	In Solution
<i>High Reactive Mixtures</i>	
Without or With Basic Catalyst	With Acid Catalyst; MeOH, EtOH, Acetone, MEK
P-A DMP-A, CR C-A, CR R-CR, MC, CA (NaOH)	R-CR, CA (HCl; 30%)
<i>Less Reactive Mixtures</i>	
With Acid Catalyst	With Acid Catalyst; DMSO
C-A, CR, CA (HCl) DMP-A, CR (HCl) EP-CA (HCl)	U-A (HCl, HCOOH; 50%) U-CA (HCl, H ₃ PO ₄ , HCOOH; 70%) M-A, CR, CA (HCOOH, H ₃ PO ₄ , HCl; 40%) G-A, CR, CA (H ₃ PO ₄ ; 50%)
<i>Molar Ratio (Nu/Ua/Cat)</i>	
Without cat.: 1 : 1 to 1 : 2 Basic cat.: 1 : 1 : (0.01-0.05) Acid cat.: 1 : 1 to 2 : 1: (0.01-0.08)	Resorcinol resins: 1 : 1 to 2 : 1: (0.001 to 0.01) Amino resins: 1 : 1 to 1 : 3: (0.005 to 0.2)
<i>Reaction Temperatures</i>	
High reactive mixtures Room temp. Less reactive mixtures Over 70°C	Resorcinol resins and amino resins with A: 50-55°C Amino resins with CR and CA: over 70°C

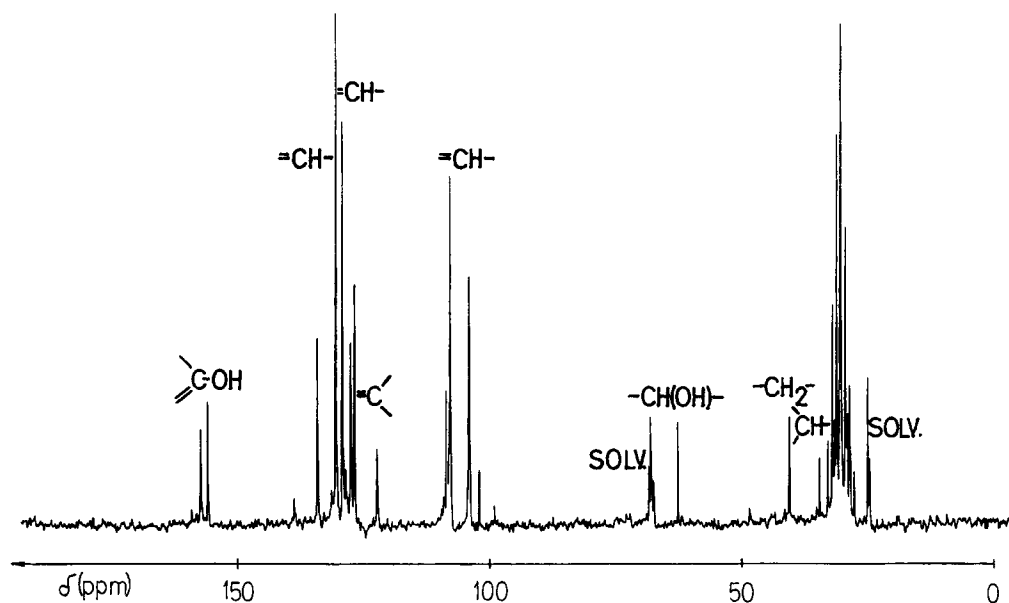


Figure 1 ^{13}C -NMR spectrum of the isolated reaction product of resorcinol and cinnamaldehyde (100°C, 12 h, molar ratio 1 : 1, 1 mol % NaOH).

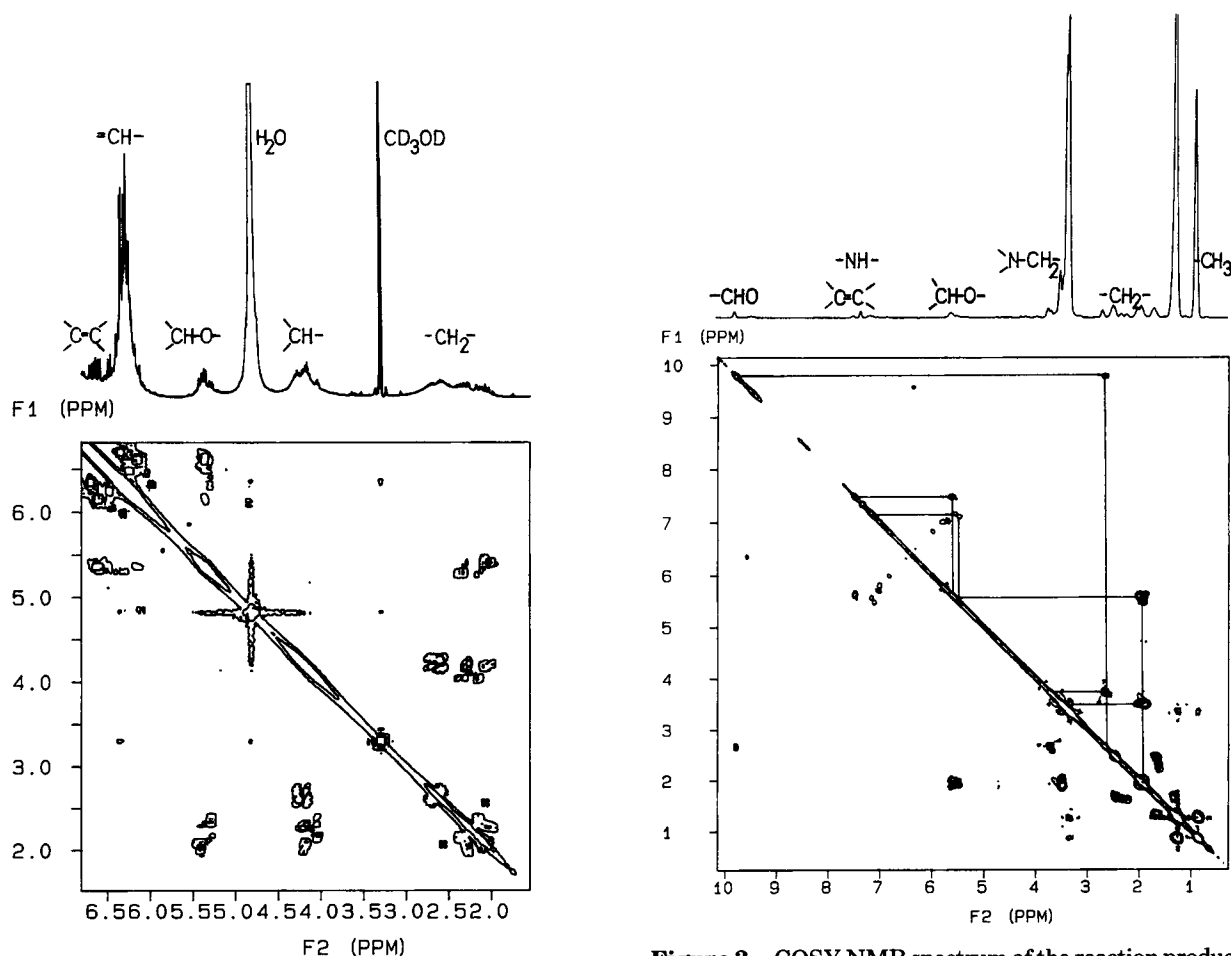


Figure 2 COSY NMR spectrum of the reaction products of resorcinol and cinnamaldehyde (55°C, 2 h, molar ratio 2 : 1, 1 mol % HCl, methanol).

Figure 3 COSY NMR spectrum of the reaction products of caprinoguanamine and acrolein (55°C, 12 h, molar ratio 1 : 2, 2 mol % H_3PO_4 , methanol). (Reprinted with permission granted from Ref. 29).

solvents, and the reaction conditions. Experimental conditions were chosen mostly in regard to the reactivity of the specific reaction mixtures.

Compared to conventional phenolic resins, the molar ratio between the nucleophiles and the α,β -unsaturated aldehydes corresponded to novolac formulations (1 : 0.5–0.85) when phenols were used and to resol formulations (1 : 1.5–3.0) when amino compounds were used. These differences were needed since resol formulations for the phenol types of nucleophiles led to gelation.

All the resins were red to dark-brown colored and soluble in polar organic solvents. The resins from guanamines and alkyl-substituted phenols were also soluble in nonpolar solvents like toluene or chlorinated solvents.

The syntheses were performed in a glass vessel at the chosen temperature with the reaction time varying according to the type of the monomers and to the type and quantity of catalyst. The reaction was stopped by neutralization and subsequently by cooling the mixture.

For structure determination fractions of R—CA resin were isolated by adsorption HPLC; the other resins' products were purified by precipitation and washing with a nonsolvent, followed by drying or freeze drying at vacuum.

Methods

One- and two-dimensional nuclear magnetic resonance (NMR) spectroscopy was used for structure determination, gel permeation chromatography (GPC) to follow the course of reactions, and standard laboratory methods for resins characterization: determination of solid content, viscosity, gel time, molecular weight distribution, amount of unreacted monomers, and determination of the acetone or methanol extractables after curing with 10% of hexamethylenetetramine for 2 h at 160°C or for 3 h at 135°C.

For NMR measurements a Jeol FX 90Q spectrometer at 22.5 MHz frequency, and a Varian VXR 300 spectrometer at 75 MHz for ^{13}C nucleus were

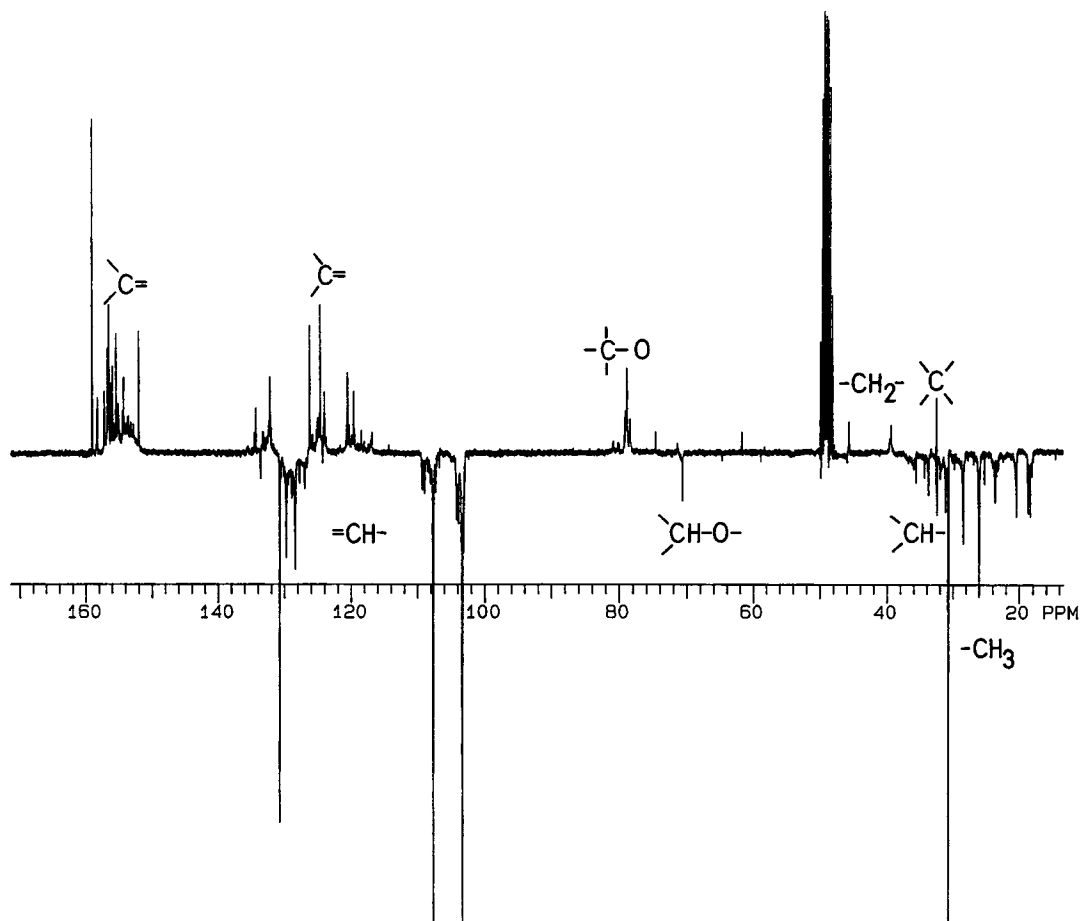


Figure 4 APT spectrum ($\tau = 7.7$ ms) of the reaction products of resorcinol and methacrolein (55°C, 2 h, molar ratio 1.5 : 1, 1 mol % HCl, methanol).

used. All spectra were quoted on TMS as internal standard using the reference resonances of the deuterated solvents CDCl_3 , CD_3OD , acetone- d_6 or $\text{DMSO}-d_6$.

The molecular weight distribution of the resins was measured by GPC using an UV detector at wavelength 254 nm, μ -Styragel columns with pore sizes 10 and 50 nm, and THF as eluent. The calibration standards were polystyrenes, phenols, amino compounds, and unsaturated aldehydes used in the work.

RESULTS AND DISCUSSION

Since all the work was very extensive with a large number of experimental data, we are demonstrating the results of the structure investigations on some examples only. Details for some systems were published elsewhere.¹⁹⁻³⁰

The individual resins differed in molecular weight distribution and in types of structural units. On the NMR spectra of the resins, regardless of the type of monomers, there were new signals of $\text{Nu}-\text{C}(\text{R}_1, \text{R}_2)-$, $-\text{CH}_2-$, and $-\text{CH}(\text{OH})-$ groups of

addition products and $\text{Nu}-\text{CH}(\text{Nu})-$ and $\text{>CH}-\text{O}-\text{CH}<$ groups of condensation products. An example is the ^{13}C -NMR spectrum of the isolated fraction of $\text{R}-\text{CA}$ resin (Fig. 1). Below 100 ppm there are signals of aliphatic C atoms with $J_{\text{CH}} \approx 130$ Hz ($20-50$ ppm $-\text{CH}_2-$ and $\text{>CH}-$ groups, $60-80$ ppm $-\text{CH}_2-\text{OH}$, and $\text{>CH}-\text{OH}$ groups); above 100 ppm there are signals of aromatic C atoms and atoms of unreacted $\text{>C}=\text{C}<$ double bonds with $J_{\text{CH}} \approx 160$ Hz. The observed chemical shifts were in good agreement with the predicted values ($\text{>CH}-$ 37.1 ppm, $-\text{CH}_2-$ 40.0 ppm, $\text{>CH}-\text{OH}$ 67.6 ppm).³¹

The signals in ^1H -NMR spectra were assigned on the basis of two-dimensional homonuclear chemical shift correlated NMR measurements (COSY, Fig. 2): the couplings between individual protons are seen as out-of-diagonal signals. The addition prod-

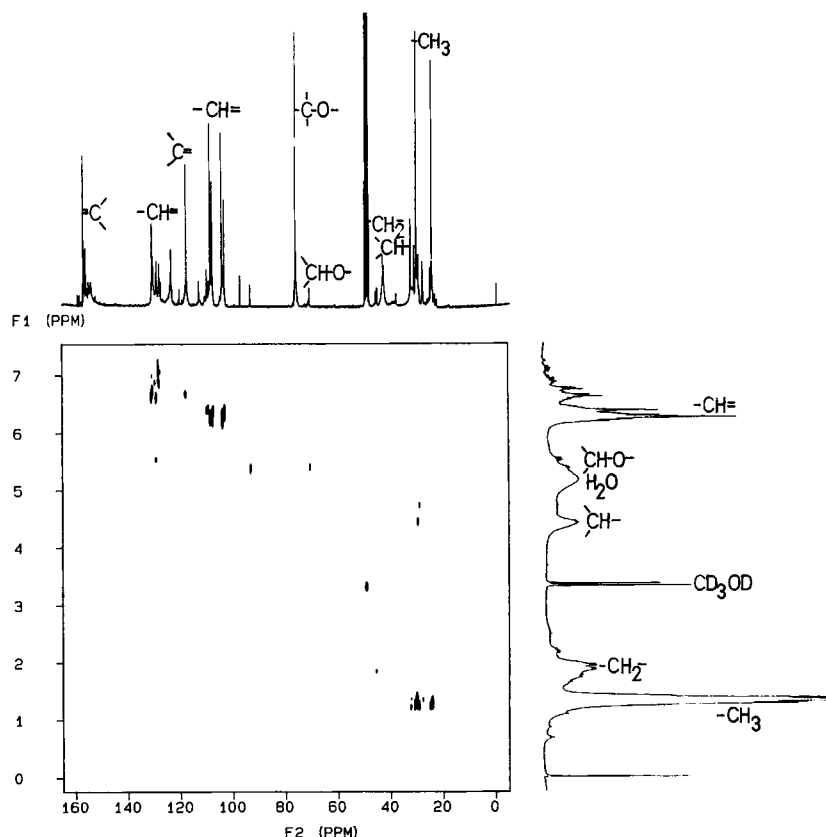
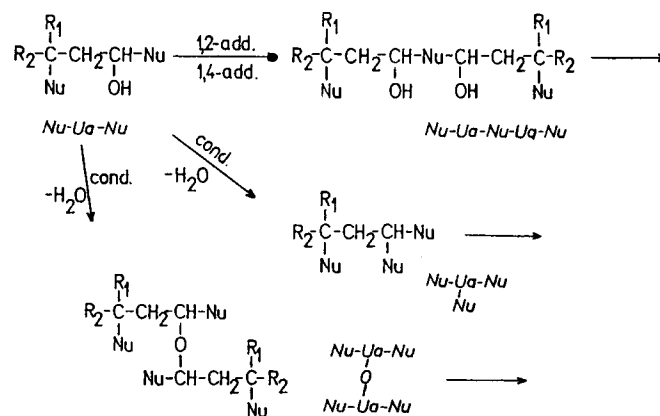
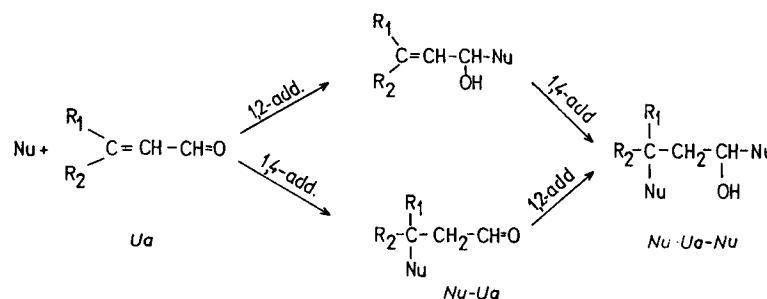


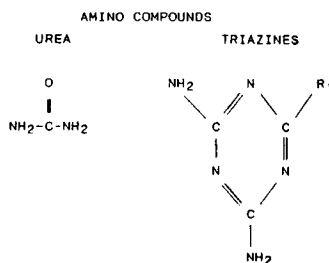
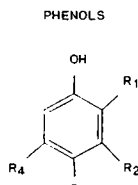
Figure 5 HETCOR NMR spectrum of the reaction products of resorcinol and methylcrotonaldehyde (110°C, 5 h, molar ratio 2 : 1, 5 mol % NaOH).

ucts of the type Nu-Ua, reaction (1b), have couplings between >CH-OH (5.4 ppm) and $-\text{CH}=\text{CH}-$ groups (around 6.5 ppm); the addition products of the type Nu-Ua-Nu, reactions (1) and (2), have couplings between $-\text{CH}_2-$ (2.1

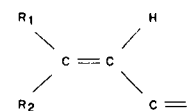
ppm), $\text{>CH}-$ (4.1 ppm), and >CH-OH groups (5.4 ppm); partially condensed products have couplings between $-\text{CH}_2-$ (2.2 ppm), $\text{>CH}-$ (4.1 ppm), >CH-OH (5.45 ppm), and $\text{>CH-O}-$



NUCLEOPHILES (Nu)



α,β -UNSATURATED ALDEHYDES (Ua)



Phenols	Substituents				Triazines	Substituent R ₁
	R ₁	R ₂	R ₃	R ₄		
Phenol (P)	-H	-H	-H	-H	Melamine (M)	-NH ₂
o-Cresol (oC)	-CH ₃	-H	-H	-H	Acetoguanamine (AG)	-CH ₃
m-Cresol (mC)	-H	-CH ₃	-H	-H	Caprinoguanamine (CG)	-C ₉ H ₁₉
p-Cresol (pC)	-H	-H	-CH ₃	-H	Benzoguanamine (BG)	-C ₆ H ₅
4-Ethylphenol (EP)	-H	-H	-C ₂ H ₅	-H		
2,5-Dimethylphenol (2,5-DMP)	-CH ₃	-H	-H	-CH ₃		
3,5-Dimethylphenol (3,5-DMP)	-H	-CH ₃	-H	-CH ₃		
Resorcinol (R)	-H	-OH	-H	-OH		

Aldehydes	Substituents	
	R ₁	R ₂
Acrolein (A)	-H	-H
Crotonaldehyde (CR)	-CH ₃	-H
Methylcrotonaldehyde (MC)	-CH ₃	-CH ₃
Cinnamaldehyde (CA)	-C ₆ H ₅	-H

Figure 6 Reaction scheme for the reactions between phenols or amino compounds (Nu) and α,β -unsaturated aldehydes (Ua).

ether groups (5.3 ppm); the condensation products with methine groups have couplings between $-\text{CH}_2-$ (2.6–2.7 ppm) and $\text{>CH}-$ groups (4.2–4.3 ppm).

Another example is the COSY NMR spectrum of caprinoguanamine-acrolein resin (Fig. 3). In the case of resorcinol-methylcrotonaldehyde resin attached proton test (APT) spectrum shows products with $-\text{O}-\text{C}(\text{CH}_3)_2-$ groups, which can be attributed to phenolic hydroxyl group addition products (Fig. 4). This is supported also by the absence of C-H couplings of the chemical shifts around 79 ppm in two-dimensional heteronuclear chemical shift correlation (HETCOR) spectrum (Fig. 5).

On the basis of the experimental data the general proposed reaction scheme is given in Figure 6.

In general, structure units with ether and hydroxymethylene groups are characteristic for the phenolic resins with basic catalyst; the condensation by formation of methine groups prevails in phenolic and amino resins with acid catalysts.

The course of the reactions was followed by measuring the changes of molecular weight distribution in dependence of reaction time by GPC. At the beginning of the reactions, all of them followed a statistical combination of monomers, though differences in the rate of formation and consumption of

individual species were observed. The number of monomer units for individual peaks in chromatograms was estimated on the basis of calculated molecular weight, taking into account the solvation effect, i.e., the interactions between THF and polar hydroxyl groups.^{32,33} In mixtures with lower reactivities, the oligomers with up to five monomer units were observed, while in mixtures with higher reactivities products with more than eight units prevailed.

On the basis of GPC measurements the experimental kinetic curves were constructed. An example is the reaction between resorcinol and CA at molar ratio 2 : 1 in methanol with 0.5 mol % HCl heated for 2 h at 55°C (Fig. 7).

The kinetic parameters were calculated for the beginning of the reactions, when the addition of nucleophile to the unsaturated aldehyde was the prevailing reaction. The reactions were of about second order. The overall rate constants were calculated as the sum of rate constants of 1,2- and 1,4-additions. Since the experimental conditions for the individual reactions differed in regard to the monomer reactivities, the rate constants for all the investigated systems could not be directly compared. The calculated values were between 10^{-3} L/mol s for the high reactive mixtures and 10^{-7} L/mol s for the less reactive mixtures.

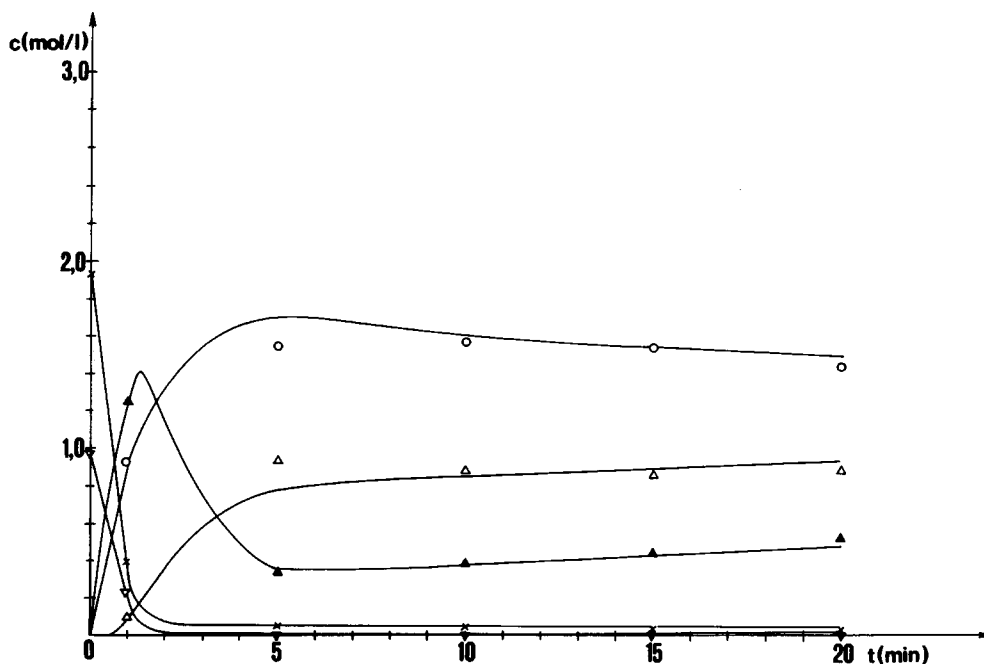


Figure 7 Experimental kinetic curve for the reaction of resorcinol and cinnamaldehyde (55°C, 2 h, molar ratio 2 : 1, 0.5 mol % HCl, methanol): ○ MW 2000–10,000 (above 5 monomer units), Δ MW 700–1000 (4–5 monomer units), ▲ MW 400–500 (2–3 monomer units), MW relative to polystyrene standards, ∇ cinnamaldehyde, × resorcinol.

Table II Results of Characterization of Resorcinol Crotonaldehyde and Cinnamaldehyde Resins' Solutions ($T = 55^{\circ}\text{C}$, $t = 2$ h, 1 mol % HCl)

Molar Ratio Nu/Ua	Solvent	Solid Contents (%)	Viscosity 10^{-6} m ² /s	Gel time (129°C)	Resid. Resorc. (%)	Resid. Ald. (%)	Acetone Extractables After Cure ^a (%)
Resorcinol-Crotonaldehyde Resins							
1 : 1	MeOH	30.0	1.25	25 s	1.1	<0.01	1.7
1.5 : 1	MeOH	27.9	0.48	26 s	4.2	<0.01	1.7
2 : 1	MeOH	24.6	0.35	>15 min	7.1	<0.01	1.7
1 : 1	EtOH	28.0	1.10	>15 min	3.9	0.8	1.9
1.5 : 1	EtOH	25.6	0.87	>20 min	6.9	0.01	5.6
1 : 1	Acetone	29.3	0.75	35 s	2.3	0.01	1.8
1.5 : 1	Acetone	30.2	0.56	2 min	3.7	0.32	0.8
1 : 1	MEK	31.1	0.90	3 min 13 s	4.4	0.65	2.8
1.5 : 1	MEK	29.7	0.61	5 min 55 s	6.8	0.02	6.9
Resorcinol-Cinnamaldehyde Resins							
1.5 : 1	EtOH	18.3	—	3 min	1.3	<0.1	6.8
1.5 : 1	Acetone	35.2	12.35	40 s	0.9	0.8	21.2
1.5 : 1	MeOH	19.2	2.66	17 s	1.0	<0.1	3.8
1.5 : 1	MeOH	38.1	—	34 s	0.5	0.1	0.9

^a Curing with 10% hexamethylenetetramine at 160°C for 2 h.

In Tables II and III the results of the determination of some resorcinol, urea, and guanamine resins' properties are given. Curing the resorcinol resins with hexamethylenetetramine gives resins with good stability against solvents. The less reactive urea and guanamine resins have at the used curing conditions more amounts of extractables as compared to resorcinol resins. As expected, the concentration of

unreacted aldehydes was, regardless of the type of the resin, quite low. The resins showed excellent adhesive properties to glass and metal substrates.

CONCLUSION

The reactions of phenols or amino compounds with α,β -unsaturated aldehydes show a similarity to those

Table III Characterization of Some Urea and Guanamine Resins Synthesized in Organic Solvents

Type of Resin	Catalyst	Molar Ratio Nu/Ua/Cat	Solvent	Reaction Temp. (°C)	Reaction Time (min)	Solid Contents (%)	Resid. Nu (mol %)	Resid. Ua (mol %)	Extractables After Cure (%)	
									at 135°C	at 160°C
U-CA	HCl	1 : 1 : 0.05	DMSO	100	160	70.7	14.0	4.3	24.6 ^a	12.8 ^a
U-CA	HCl	1 : 1 : 0.01	DMSO	100	240	71.0	11.3	0.5	18.6 ^a	10.1 ^a
U-CA	HCl	1 : 2 : 0.01	DMSO	90	240	77.0	1.4	4.8	22.2 ^a	7.2 ^a
U-CA	HCOOH	1 : 2 : 0.01	DMSO	90	240	77.7	3.2	5.0	21.2 ^a	6.3 ^a
U-CA	H ₃ PO ₄	1 : 2 : 0.01	DMSO	90	240	77.6	2.0	4.5	24.0 ^a	8.1 ^a
CG-A	H ₃ PO ₄	1 : 2 : 0.02	MeOH	55	720	48.7	0.7	1.0	14.2 ^b	—
CG-CR	H ₃ PO ₄	1 : 2 : 0.05	Toluene	98	320	48.0	1.2	1.8	23.7 ^b	—
CG-CA	H ₃ PO ₄	1 : 2 : 0.05	Toluene	100	430	47.3	1.4	2.0	21.8 ^b	—
BG-A	H ₃ PO ₄	1 : 2 : 0.02	DMF	50	280	28.7	0.9	1.2	1.7 ^b	—
BG-CR	H ₃ PO ₄	1 : 2 : 0.05	DMF	85	345	28.8	1.0	2.1	59.4 ^b	—
BG-CA	H ₃ PO ₄	1 : 2 : 0.05	DMF	70	490	28.7	1.2	1.5	73.4 ^b	—

^a Methanol extractables.

^b Acetone extractables.

with formaldehyde. Besides the addition to the carbonyl carbon atom also the addition to the double bond takes place. Both the course and the rate of the reactions depend on the monomer and catalyst choice. So far, no final conclusions can be made in order to evaluate the practical advantage of resins based on α,β -unsaturated aldehydes compared to conventional resins.

The financial support of the work from the Research Community of Slovenia is gratefully acknowledged.

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Received May 21, 1991

Accepted August 1, 1991