

Properties of Trialkylamines as Catalysts of Resoles Synthesis

B. KAŁĘDKOWSKI,¹ J. HETPER,² M. GRZYTA¹

¹ Institute of Heavy Organic Synthesis, 47-225 Kędzierzyn-Koźle, Poland

² Institute of Chemistry, University of Opole, Oleska Str. 48, 45-052 Opole, Poland

Received 23 June 1999; accepted 18 October 1999

ABSTRACT: A series of the syntheses of phenol–formaldehyde resoles was carried out in the presence of trimethyl-, triethyl-, tripropyl-, and tributylamines and sodium hydroxide as catalysts for this process. The rate constants were calculated for the partial reactions identified in the synthesis. Also, the performance properties of the resins obtained and the hardened resin samples were estimated in simple tests. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 898–902, 2000

Key words: resin synthesis; phenol-formaldehyde resoles; condensation reaction, trialkylamines; GC

INTRODUCTION

The resole resins are obtained from the reactions of phenol and formaldehyde in the presence of strongly alkaline compounds like hydroxides of alkaline metals (Li, Na, K) or hydroxides of alkaline earth metals (Ca, Sr, Ba).¹ Tertiary amines have also been suggested recently as catalysts for the resole synthesis, with triethylamine (TEA) especially preferred.^{2,3} The catalytic activity of TEA is only slightly lower than that of sodium hydroxide but the resins obtained in the presence of TEA offer different properties which sometimes are advantageous from the viewpoint of the applicability of the resins themselves or the products obtained from the resin(s). Apart from some patent claims, there are no detailed articles published on the resole synthesis which involves the presence of trialkylamines. Also, there is not much information available on the properties of the resins obtained with the use of tertiary amines.

The catalytic properties of four tertiary amines were investigated in this work and they were referred to those for sodium hydroxide. The physical–chemical and performance properties of the resoles obtained are discussed as well.

EXPERIMENTAL

Raw Materials, Products, and Chemicals

Phenol, pure, was from Petrochemia S.A. (Płock, Poland); the product was additionally purified by distillation (fraction with boiling point of 182–182.5°C was used). Formalin, pure, containing 35% of reactive formaldehyde, was from ZA Kędzierzyn S.A. (Kędzierzyn-Koźle, Poland). The catalysts used were trimethylamine (TMA), 45% aqueous solution, from Aldrich-Chemie (Steinheim, Germany); TEA, tripropylamine (TPA), and tributylamine (TBA), all 99% pure, from Merck-Schuchardt (Hohenbrunn bei München, Germany), and sodium hydroxide (SH), analytically pure, was from POCh (Gliwice, Poland). Notation for the resoles synthesised is Resole + catalyst symbol, for example, Resole TMA, Resole SH, etc.

Correspondence to: J. Hetper.

Journal of Applied Polymer Science, Vol. 77, 898–902 (2000)
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Analytical Methods

Potentiometric titration as per ISO⁴ was employed to determine the reactive formaldehyde content in the reaction mixtures. The method was based on the condensation reaction between formaldehyde and hydroxylamine hydrochloride.

Thin-layer chromatography was used to estimate the free phenol content in the reaction mixture. The procedure utilized a Camag analytical set, Nanomat III, equipped with the computer-controlled Scanner 3 densitometer.

Gas chromatography was a method for the determination of the compositions of the reaction mixtures. The analyses were performed with a Carlo Erba Mega 2 gas chromatograph equipped with the flame-ionization detector. The samples were injected "on-column" and separated in a capillary column (RTX-1, Restek). The column temperature was programmed to be linearly increased within the range of 60–290°C at the rate of 10°C/min. The analytical parameters were selected and the results were construed on the basis of the work by Prókai.⁵

Determination of Physicochemical Properties of Resoles and of Hardened Products Obtained Therefrom

The *density of resin(s)* was determined according to the Polish Standard.⁶ The *outflow time of the resin(s)* was found as provided for in the Polish Standard.⁷ The time was measured which was needed for 100 cm³ of liquid resin to flow out of an orifice in the bottom of a metal cup.

The *gelation time of the resole(s)* was evaluated by measuring the time after which gelation was observed in a resin sample being heated up. The sample was placed on a metal plate, in a depression in its central part. The plate was heated up to the temperature of 150°C and the resin was mixed all the time with a thin glass rod. The time was measured when the resin material could not flow down the glass rod.

The *nitrogen content in the hardened resin(s)* was determined by means of an EA 1108 CHN-O analyzer from Fisons Instruments.

The *ash content after incineration of the hardened resin(s)* was determined according to the Polish Standard.⁸ The resin was heated at 900°C during 4 h and the residue was weighed.

The *environmental pollution factor* was found as specified in ref. 9. The method is based on the resin sample weight drop (in percent) when the material is heated at 135°C and then at 230°C.

The *miscibility of the resin(s) with water* was determined according to the ISO Standard.¹⁰ The *binding strength (or binding ability) of the resole(s)* was tested according to refs. 11 and 12. The resole resin was mixed with glass beads and it was hardened at 230°C. A test specimen (rod) made from this material was subjected to the bend test (σ_a) with use of an Instron 1112 instrument. The test was repeated after the rod was treated with steam, σ_b (the maintaining of specimen during 72 h in the atmosphere of saturated steam at 20°C). The high value of σ indicates that resin adheres strongly to the glass surface, which is an important application property of resin.

Synthesis of Resoles

The resoles were synthesised in a 1-dm³ reactor equipped with a stirrer, thermometer, and reflux condenser. The molar ratio of the reactants was the same for all the resole syntheses: phenol : formaldehyde : water : catalyst = 1 : 3 : 11.58 : 0.15. The reaction temperature was 60°C. Each synthesis took 8 h to complete. The reaction mixtures were sampled in regular intervals. The physicochemical properties were determined for the reaction products and after the resoles were hardened at 230°C.

RESULTS AND DISCUSSION

Compositions of the Reaction Mixtures

The molar concentrations for the components present in the reaction mixtures after 2 and 8 h are presented in Table I for all the resoles studied. The results obtained were utilized in kinetic calculations which were needed to compare the activity and selectivity specifications for the catalysts investigated.

Kinetic Calculations

The rate constants for the reactions occurring in the synthesis processes were estimated according to the model suggested by Zavitsas et al.¹³ A set of parallel and successive addition reactions between phenol and formaldehyde was mentioned in this model (Fig. 1). Additionally, phenol was assumed to react in the form of the phenolate anion and the concentration of this form is limited by the dissociation constant of phenol. On the other hand, methylene glycol was assumed as a reactive form of formaldehyde. The equilibrium

Table I Composition of the Reaction Mixtures (mol/dm³)

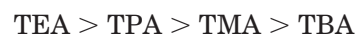
Component Name	Resole TMA		Resole TEA		Resole TPA		Resole TBA		Resole SH	
	2 h	8 h	2 h	8 h	2 h	8 h	2 h	8 h	2 h	8 h
2-Hydroxymethylphenol	0.49	0.18	0.37	0.12	0.47	0.16	0.63	0.40	0.30	0.06
4-Hydroxymethylphenol	0.38	0.22	0.34	0.17	0.30	0.15	0.34	0.31	0.27	0.11
2,6-Dihydroxymethylphenol	0.17	0.07	0.15	0.05	0.20	0.16	0.12	0.14	0.12	0.02
2,4-Dihydroxymethylphenol	0.36	0.45	0.53	0.41	0.42	0.42	0.20	0.42	0.48	0.30
2,4,6-Trihydroxymethylphenol	0.53	1.00	0.54	0.99	0.49	0.92	0.13	0.55	0.97	1.07
Two-ring condensation products	0.03	0.27	0.07	0.29	0.05	0.29	0.01	0.14	0.12	0.42
Three-ring condensation products	0.00	0.03	0.01	0.06	0.01	0.05	0.00	0.02	0.01	0.13

conditions among ethylene glycol, free formaldehyde, and its oligomers were taken into consideration for the calculations. According to the model by Zavitsas, a set of linear kinetic equations should be arranged with the use of the concentration values determined for all the components. That gives the values of rate constants for the seven reactions considered.

It should be remembered that the model by Zavitsas gives good results only for the early stage of the resin synthesis, that is, some 1–2 h. The condensation reactions between the phenol–formaldehyde adducts yield two- and three-ring structures which make the system more complicated then. The calculations should therefore be carried out for the data obtained at the initial stage of the synthesis.

Table II provides the rate constant values calculated with the use of the Zavitsas method. The

results characterize the activity of the catalyst used as well as its ability to direct the substituent group(s) to the active position(s) at the phenol nucleus. The k_1 and k_2 values refer to the reaction of the first molecule of formaldehyde with the unsubstituted phenol molecule. These constants are therefore the best way to determine the general catalyst activity. The data from Table II make it possible to arrange the catalysts used as per their activities, which decrease in the following sequence:



This sequence follows the increasing number of carbon atoms in the alkyl radical of these amines, except for TMA, which offers lower activity than

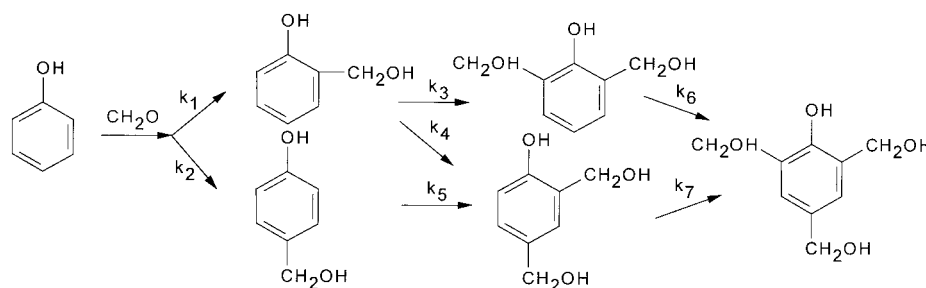


Figure 1 Scheme of addition reactions of formaldehyde and phenol according to Zavitsas et al.¹¹

Table II Reaction Rate Constants

Symbol of Constant	Values of Reaction Rate Constants (dm ³ mol ⁻¹ h ⁻¹)				
	Resole TMA	Resole TEA	Resole TPA	Resole TBA	Resole SH
k_1	1.792	2.128	1.984	0.933	3.018
k_2	0.773	1.059	0.729	0.429	1.381
k_3	1.560	1.975	1.658	0.684	2.274
k_4	1.234	1.668	1.472	0.544	2.299
k_5	1.013	1.510	1.303	0.587	1.994
k_6	3.009	4.169	2.609	1.961	3.884
k_7	1.074	1.204	0.916	0.778	1.358

that of TEA and TPA. This deviation from the rule is accompanied by the similar deviation of the dissociation constant for TMA from the rule adhered to by the remaining amines. The constant for TMA is 0.63×10^{-4} , while the values for TEA, TPA, and TBA are 7.4×10^{-4} , 5.5×10^{-4} , and 2.1×10^{-4} , respectively.¹⁴ The relatively low rank of TBA among these amine catalysts can be explained by the low solubility of TBA in water.

The k_1/k_2 ratio indicates the ability of a catalyst to direct the substituent group(s) to the active 2 and 4 position(s) at the phenol ring. Similarly, the k_3/k_4 ratio refers to the mono-substituted phenol. The analysis of the data in Table II suggests that the so-defined selectivity of the amines investigated is similar.

Trialkylamines are less active catalysts than is NaOH, although the difference is not very high for TEA. Also, the amines offer a selectivity which is similar to that of NaOH. The differences can be observed for the k_3/k_4 ratios which are slightly higher for amines. This may suggest that amines, unlike NaOH, will direct more substituents to position 2 than to position 4 at the phenol ring.

Properties of Resins and Hardened Products

The physicochemical and performance properties of the synthesized resoles and the products obtained by setting the resoles are collected in Table III. Serious differences can be observed between the properties of amine-catalyzed resins and those for the resins obtained in the presence of sodium hydroxide. It is obvious that inorganic catalysts remain in the resin after synthesis and resin setting, which is responsible for the ash content after incineration. In the case of trialkylamines, the whole amount of the catalyst is released to the atmosphere. This is confirmed by the analysis of the nitrogen content in the hardened resins.

This emission is disadvantageous for environmental protection. However, the performance properties of resoles are improved since there are no inorganic components in the resoles synthesized in the presence of amine catalysts. The binding ability test was performed for Resole TEA in comparing to Resin SH. Results of the measurements indicate that the σ_a value for the first

Table III Physicochemical and Application Properties of Synthesized Resoles

	Resole TMA	Resole TEA	Resole TPA	Resole TBA	Resole SH
Density (g/cm ³)	1.119	1.117	1.109	1.099	1.138
Outflow time (s)	11.8	12.0	12.2	11.2	12.0
Gelation time (s)	156	180	215	265	62
Mass loss of catalyst after of setting of resin (%)	89.0	91.8	97.6	97.9	0
Ash concentration (%)	0	0	0	0	1.13
Environment pollution factor (%)	4.90	5.62	4.91	4.33	4.71
Mixability of with water (1 : x), x =	∞	∞	∞	∞	∞

Resole is about 10% higher than for second one (4.61 against 4.1 MPa). However, after steaming, the respective values of σ_b were 0.64 and 0.14 MPa. So, the products obtained from Resole TEA are expected to be more resistant on the hydrolysis agents than are conventional hardened resins. The lower binding strength of Resole SH probably results from the presence of an alkaline inorganic catalyst residue in the hardened resin.

The same can also be the cause for the gelation time for Resole SH to be a few times shorter than those for other resoles (see Table III, row 3). This observation seems to correspond to the well-known fact that the catalysts which are active in the resole synthesis will also be active in the resin-setting process. The amine catalysts are released from the resin(s) at the initial stage of the setting process, so any further reaction will proceed much more slowly. The long gelation time of a resin is advantageous from the viewpoint of its transport and storage.

SUMMARY

The results of this work indicate that the simple tertiary amines with C_1 — C_4 alkyl substituents are good catalysts for the resole synthesis reactions, although their activities are not as high as that for sodium hydroxide. TEA and TPA were found to offer the highest catalytic activities in that synthesis among the amines studied. It was observed that the selectivity of the amine catalyst—understood as the preferred substitution on the phenol ring—was not dependent on the num-

ber of carbon atoms in the amine alkyl groups. The properties of amine catalysts in this field differ insignificantly from those of NaOH.

The advantages of the resoles obtained in the presence of trialkylamines, as compared to conventional resins, are longer gelation time, no ash after incineration, and improved hydrolysis resistance. The drawback for these catalysts is their emission from resins in the setting process.

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