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A new approach to the determination of the heat of phenolic resol synthesis

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Abstract

A new method has been developed for the determination of the heat of phenolic resol synthesis carried out in an aqueous solution. This heat is determined as the difference in the heats of syntheses of the resitol from the mixture of raw materials and from the resol studied. Heats of resitol syntheses were determined by DSC at constant heating rate using high-pressure crucibles, i.e. under isochoric conditions for the liquid–vapour sample.

The heat of synthesis of resols, obtained at formaldehyde-to-phenol molar ratio equal to 3.0 and using NaOH as catalyst, were determined. The relevant values were calculated on the basis of the chemical composition of the resols and the molar enthalpies of the aromatic ring substitution and methylene bridge formation reactions. The experimentally determined heats were consistent with the calculated ones, not when free formaldehyde (CH_2O) but its monohydrate, $CH_2O{\cdot}H_2O$ (methylene glycol, $HO–CH_2–OH$) was assumed to be the reactive form of formaldehyde in an aqueous medium (formalin). © 1998 Elsevier Science B.V.

Keywords: DSC; Heat of synthesis; Phenolic resins

1. Introduction

Increasing attention is being paid to the investigating the reaction between phenol and formaldehyde, in particular from the viewpoint of kinetics and the mechanism of the synthesis yielding resol-type, phenol–formaldehyde resins [1–5]. This situation arises from the continuing demand for plastics produced from the phenolic resins and by the development of analytical methods which make it possible to study the chemical composition and structure of these resins [6–10].

The conventional method of synthesizing phenolic resols is isothermally (usually from 50° to 80°C) heating the phenol–formalin mixture, with molar excess of formaldehyde, in the presence of alkaline metal hydroxides, salts of weak acids and strong bases [11] or amines [12,13] as catalysts. Under such conditions, strongly exothermic reactions occur, both parallel and consecutively, which give initially mono-, and then di- and trihydroxymethylphenols as well as their hemiformal derivatives (Structure I). These products then undergo the condensation reactions that yield the diphenylmethane derivatives and systems containing a higher number of aromatic rings connected by means of methylene bridges (Structure II) or dimethyl–ether bridges [12,14]. The dimethyl–ether bridges have low stability under these reaction conditions. They easily release formaldehyde and

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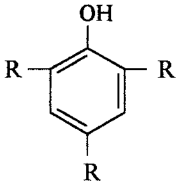
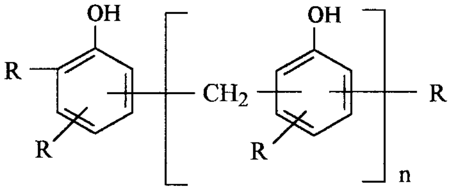
form methylene bridges [14,15]. Hence, the former can only be observed with difficulty in the reaction products.

The components of the resol-type resin, resulting from the above reactions, are reactive compounds. Their further condensation gives gradual crosslinking of resol that initially turns the material into resitol and finally into resite. The crosslinking of a resol is a spontaneous process (i.e. no catalyst is needed) when heating is provided. However, the process can also be initiated at ambient temperature when catalysed by acids.

A resol is not an explicitly defined system as regards its chemical composition. The mixtures of mono-, di- and trihydroxymethylphenols with both small and considerable amounts of hydroxymethyl derivatives of diphenylmethane and/or polycyclic systems can be called resols. The structures for the components of the phenolic resol (phenol–formaldehyde derivatives) are as follows:





where R is $CH_2(OCH_2)_j$ OH or H; j=0, 1, 2, etc; n=0, 1, 2, etc. Prokai [6–8] has shown that the compounds with the above structures are present in resols, with various isomeric versions and that, in resols at low condensation levels, the value of n is in practice limited to 0, 1 or 2, and the value of j to 0 or 1.

The chemical composition of resols is dependent on the synthesis conditions and, in particular, on the formaldehyde-to-phenol molar ratio, on the catalyst type, on the reaction time and temperature. Hence, the heat of resol synthesis does not have a constant and absolute value. This heat has to be found for an individual resol (at the defined synthesis conditions). This can be calculated, when the chemical compositions of the substrate mixture and the synthesis product(s) are known exactly, or this can be found experimentally with the use of calorimetric methods.

This paper presents a new approach to the determination of the heat of phenolic resol synthesis in an aqueous solution. DSC has been employed in the study. The purpose of the work was to demonstrate that the value of the heat, as calculated on the basis of the resin chemical composition (found by gas chromatography) and molar enthalpies for relevant reactions, complies with the experimental heat value.

2. Experimental

2.1. Materials

- Phenol ('Petrochemia' S.A., Płock, Poland) after atmospheric distillation; fraction with boiling range of 182.0–182.5°C.
- Formalin (Zakłady Azotowe 'Kędzierzyn S.A., Kędzierzyn-Koźle, Poland) containing ca. 40% w/w formaldehyde, stabilised with methanol (ca. 5%).
- Sodium hydroxide, analytically pure ('Polskie Odczynniki Chemiczne', Gliwice, Poland).

2.2. Synthesis of resols

The resin syntheses were carried out in a laboratory glass reactor equipped with a stirrer, thermometer and reflux condenser. The mixture of phenol, formalin and water was heated up to a temperature of 60°C and then the catalyst (40% sodium hydroxide solution) was added. The phenol : formaldehyde : water : catalyst molar ratio was 1 : 3 : 12 : 0.15 (W-1 resin) or 1 : 3 : 8.5 : 0.15 (W-2 resin). The synthesis was continued at 60°C. The reaction mixture was sampled for DSC measurements after homogenisation (before the catalyst was added), and then for DSC and GC analyses after the synthesis had been run for 1 and 8 h.

2.3. Differential scanning calorimetry

The DSC measurements used ca. 100 mg samples which were weighed to ±0.001 mg. The weighed amount of catalyst was added to the reaction mixture (before the reaction was initiated), directly to the crucible. Measurements were performed in high-pressure steel crucibles, i.e. under isochoric conditions for the liquid–vapour system, at a heating rate of β=2°C min^{-1}, within the temperature range of 25° to 250°C. The Mettler DSC-30 differential scanning calorimeter coupled to a TA-4000 thermal analysis system was used. The temperature calibration of the calorimeter was carried out as per recommendations of the manufacturer, while the heat calibration involved indium (ΔH_f=28.5 J g^{-1}) with a suitable admixture of water [16,17].

2.4. Gas chromatography

The products obtained from the reaction of phenol and formalin components were analysed (in the form of trimethylsilyl ethers) by capillary gas chromatography. A MXT-1 column from Restek, with poly (dimethylsiloxane) stationary phase, was used to separate the mixtures studied. The column length was 15 m, the internal diameter was 0.28 mm and the thickness of the stationary-phase film was 0.2 μm. The column temperature was programmed from 60° to 320°C at the rate of 10°C min^{-1}. The samples were injected with the 'on-column' method at 60°C. The detector (FID) temperature was 320°C. The instrument employed was a Perkin–Elmer, model 9700. The chromatograms were interpreted on the basis of the investigations of Prokai [6–8].

3. Results and discussion

The DSC curves for the mixture of raw materials and catalyst as well as for samples of the reaction mixture which were taken after 1 and 8 h of synthesizing the W-2 resin are presented in Fig. 1; the corresponding DSC curves for the W-1 resin presented the same profiles. The contents of the phenol–formaldehyde components in the mixtures studied are shown in Table 1. When the mixtures of phenol, formalin and sodium hydroxide were heated under isochoric conditions, DSC curves were recorded with two distinct separated exothermic effects – 0 curve in Fig. 1. The first effect occurs within the temperature range of 40° to 150°C, while another can be met within 160 and ~200°C. The low-temperature effect is composed of three overlapping sub-effects that can be explained by the kinetics of the parallel-consecutive reactions which make up the phenolic resol synthesis. Two analogous exothermic effects were observed when the samples of the reaction mixtures (in fact resols) were heated, curves 1 and 8 in Fig. 1. The value of the low-temperature effect was reduced with the progress of the synthesis, while the value of the high-temperature effect equals that of the effect obtained when the corresponding mixture of the raw materials was heated. It was, moreover, found that for resitol, obtained under conditions applicable for determination of the resin gelation time [18], the low-temperature effect was hardly observed, while the high-temperature effect remained unchanged. Hence, the low-temperature stage corresponded to the synthesis of resitol, and the high-temperature stage to the conversion of resitol into resite. Therefore, it is possible to assume that the difference in the values of thermal effects of the resitol synthesis (under the DSC conditions applied) from the mixture of substrates and a suitable resolic resin is the heat that was released from the synthesis of the resin in the laboratory reactor. In Table 2, the heats are collected for resitol syntheses from raw materials and resol samples studied (column 3) and the resulting heats for the syntheses of corresponding resols (column 4) in aqueous solutions of phenol and formaldehyde, under atmospheric pressure laboratory reactor, for the resins discussed in this paper.

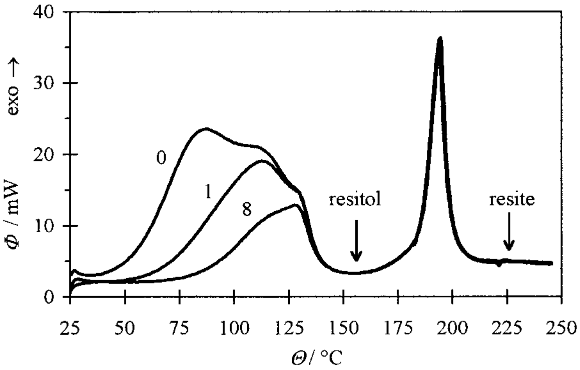


Fig. 1. DSC curves for the mixture of raw materials and catalyst, and for the reaction mixture samples taken after 1 and 8 h of the synthesis of the W-2 resin in the laboratory reactor.

In order to estimate the heat of synthesis for phenolic resols on the basis of their chemical composition, it was taken into account that it was not

Table 1
Contents of phenol–formaldehyde components in reaction mixtures samples taken after 1 and 8 h of W-1 and W-2 resins syntheses in laboratory reactor

i	Component [a]	M_i/(g mol^{-1})	x_i	y_i	Component content, w_i/% w/w			
					W-1 (1 h)	W-1 (8 h)	W-2 (1 h)	W-2(8 h)
W-1 0	Phenol	94.11	0	0	3.98	0.20	4.02	0.17
1	2-HMP	124.1	1	0	4.18	0.14	3.64	0.62
2	4-HMP	124.1	1	0	2.96	0.00	2.22	0.87
3	2-HMP hem.	154.1	1	0	0.00	0.00	2.36	0.24
4	4-HMP hem.	154.1	1	0	0.00	0.00	2.06	0.25
5	2,6-DHMP	154.1	2	0	1.76	0.10	1.45	0.24
6	2,4-DHMP	154.1	2	0	7.84	2.18	3.87	3.09
7	DHMP hem.	184.2	2	0	1.64	0.74	5.28	1.58
8	DHMP dihem.	214.2	2	0	0.00	0.00	2.22	0.14
9	2,4,6-THMP	184.2	3	0	10.30	11.56	7.48	14.05
10	THMP hem.	214.2	3	0	0.09	3.05	4.40	7.09
11	THMP dihem.	244.3	3	0	0.00	0.47	2.77	1.65
12	THMP trihem.	274.3	3	0	0.21	0.26	0.97	0.00
13	DPM deriv.	320.3	4	1	2.00	14.10	2.60	13.40
14	BzDPM deriv.	456.4	5	2	0.40	8.10	0.40	6.00
	$\sum_i(w_ix_iM_i^{-1})/(\mathrm{mol\,kg^{-}1})$				4.006	5.432	4.879	6.584
	$\sum_i(w_iy_iM_i^{-1})/(\mathrm{mol\,kg^{-}1})$				0.0800	0.7952	0.0987	0.6813

[a] HMP=hydroxymethylphenol, DHMP=dihydroxymethylphenol, THMP=trihydroxymethylphenol, DPM=diphenylmethane, hem.=hemiformal, Bz=benzyl, deriv.=hydroxymethyl derivative; w_i is a weight fraction for the 'i' component, x_i the number of its hydroxyl groups, y_i the number of methylene bridges in the component, and M_i its molecular weight.

formaldehyde but the hydrated forms of monomeric and/or oligomeric formaldehyde – methylene glycol, HO–CH$_2$–OH and polyoxymethylene glycols, HO–(CH$_2$O)$_n$–H, respectively, that are the principal components of formalin and that they remain in balance with each other [14,19,20]. It was thus assumed that a substrate which reacts with phenol is not formaldehyde but methylene glycol. This assumption is clear when one takes into consideration that the equilibrium constant of the reaction

$$\mathrm{CH_2O + H_2O \leftrightarrow HO{-}CH_2{-}OH}$$

is of the order of 2×10^{-3}, at a temperature of 60°C. Hence, the concentration of free formaldehyde in the reaction medium can be as low as a few tenths of a percent [14].

Moreover, the resol synthesis thermal effect was assumed to be due, under experimental conditions, to contributions from the reactions of hydrated forms of formaldehyde with phenol which yield in succession:

Table 2
Experimental heat of resitol and resol syntheses and calculated one of resol syntheses

Symbol of resin	Duration of the resol synthesis in lab reactor	Heat of the resitol synthesis by DSC	Heat of the resitol synthesis in lab reactor by DSC and calculated from composition analysis by GC	
	$t_{\mathrm{synth.}}$/h	$-Q^{\mathrm{DSC}}_{\mathrm{resol}}$/(J g^{-1})	$-Q^{\mathrm{DSC}}_{\mathrm{resol}}$/(J g^{-1})	$-Q^{\mathrm{GC}}_{\mathrm{resol}}$/(J g^{-1})
	0	389	—	—
W-1	1	229	160	151
	8	112	277	277
	0	460	—	—
W-2	1	267	193	184
	8	131	329	306

mono-, di- and trihydroxymethylphenols and the contributions of further condensation of these products giving methylene bridges between aromatic rings. The difference in heat effects resulting from the substitution locations at the aromatic ring was neglected. Also, no consideration was given to the thermal effects from the formation and decomposition of hemiformals (HO–Ph–CH_2O–CH_2OH) which are in equilibrium with components of formalin and with hydroxymethyl derivatives of phenol (HO–Ph–CH_2OH) [21]. The latter effects in part compensate with each other.

The total thermal effect (enthalpy) for the synthesis process of a given resol was evaluated from the formula:

$$Q_{\mathrm{resol}} = \delta \mathrm{H}_x \sum_{i=1}^{n} \frac{w_i x_i}{M_i} + \delta \mathrm{H}_y \sum_{i=1}^{n} \frac{w_i y_i}{M_i}, \qquad (1)$$

where w_i is a weight fraction for the 'i' component and x_i the number of its hydroxyl groups, y_i the number of methylene bridges in the component, M_i its molecular weight, and δH_x the molar enthalpy for the condensation of phenol and methylene glycol which creates the hydroxymethylene group:

$$\begin{aligned}&\mathrm{OH{-}Ph + HO{-}CH_2{-}OH \rightarrow}\\ &\quad \mathrm{HO{-}Ph{-}CH_2OH + H_2O,}\end{aligned} \qquad (2)$$

and δH_y is the sum of molar enthalpies in the reaction of phenol and methylene glycol (δH_x) and in the subsequent condensation reaction of hydroxymethylphenol and phenol yielding the methylene bridge between the aromatic rings:

$$\begin{aligned}&\mathrm{OH{-}Ph + HO{-}Ph{-}CH_2OH \rightarrow}\\ &\quad \mathrm{HO{-}Ph{-}CH_2{-}Ph{-}OH + H_2O}\end{aligned} \qquad (3)$$

The standard molar enthalpies for the reactions (2) and (3) were calculated from standard molar enthalpies (heats of formation) for the following compounds: phenol (-151.56 kJ mol^{-1} [15]), methylene glycol (-454.77 kJ mol^{-1} [22]), 4-hydroxymethylphenol (-355.88 kJ mol^{-1} [15]), 4,4′-dihydroxyphenylmethane (-290.98 kJ mol^{-1} [15]) and water (-286.03 kJ mol^{-1} [23]; -285.9 kJ mol^{-1} [24]). The following values were obtained for the standard molar enthalpies:

- for the reaction (2), which creates the hydroxymethyl group (substitution of the aromatic ring) from phenol and methylene glycol: $\delta H_x^{\ominus} = -35.59\,\mathrm{kJ\,mol^{-1}}(\mathrm{-CH_2OH})$.
- for the reactions (2)+(3), which create the methylene bridge from the substrates (methylene glycol and phenol): $\delta H_y^{\ominus} = -105.16\,\mathrm{kJ\,mol^{-1}}(\mathrm{-CH_2-})$.

Assuming the above standard molar enthalpies for the reactions to be their molar enthalpies at the temperature of synthesis, the total heat values were evaluated for the synthesis of resols. The contributions resulting from the contents of individual components (Table 1) were summarised as per Eq. (1). The obtained results are given in the last column of Table 2. Despite the simplifications assumed, the calculated heats for the synthesis of resols were, in all cases, close to the values determined experimentally as the difference in the synthesis heats for the corresponding resitols under DSC conditions. Hence, these results confirm the initial assumption in this study, that not formaldehyde but methylene glycol has to be treated as the substrate reacting with phenol (and its derivatives) in aqueous solutions. So, irrespective of the actual reaction mechanism (transient ion forms of hydrated forms of formaldehyde are usually assumed to exist [14]), in thermal calculations for the reactions proceeding in aqueous solutions, in alkaline media, methylene glycol has to be understood to be the reactive parent substance. There is no doubt that the molar enthalpy of the reaction between phenol and free formaldehyde ($\delta H^{\ominus}=-20.1$ kJ mol^{-1} [15,25]) is not applicable in the thermal (caloric) calculations connected with this syntheses since the results are too low, by some 40%. The above agreement for the calculated and experimental results proves that the location for the substitution of the hydroxymethyl group in phenol and reversible reactions of various formaldehyde forms present in aqueous solutions (methylene glycol, polyoxymethylene glycols, hemiformals) have little effect on the total heat of the process. Hence, these can be neglected in engineering calculations.

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