ELSEVIER

Polymer 43 (2002) 1631–1639

polymer

www.elsevier.com/locate/polymer

Modelling of phenolic resin polymerisation

C.C. Riccardi[a,*], G. Astarloa Aierbe[b], J.M. Echeverría[b], I. Mondragon[c]

[a]*Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), Av. J.B. Justo 4302, B7608FDQ Mar del Plata, Argentina*
[b]*Bakelite-Ibérica, Ctra. A Navarra, Epele, 39, 20120 Hernani, Spain*
[c]*Dpto. Ingeniería Química y Medio Ambiente, Escuela Ingeniería Técnica Industrial, Universidad del País Vasco/Euskal Herriko Unibertsitatea, Av. Felipe IV 1-B, 20011 Donostia-San Sebastián, Spain*

Received 30 July 2001; received in revised form 18 October 2001; accepted 19 October 2001

Abstract

The kinetics of the polymerisation of resol-type phenolic resins has been modelled taking into account the phenol and formaldehyde equilibria. The kinetic parameters were obtained by adjusting the experimental evolution of phenol, formaldehyde and initial addition products during synthesis. The influence of the type and amount of catalyst, the initial pH, the initial formaldehyde-to-phenol molar ratio and the condensation temperature, on the kinetics rate constants was quantified. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Phenolic resin; Kinetics; Modelling

---

1. Introduction

As phenolic resins are the oldest thermosetting polymers the influence of many synthesis parameters has been studied for different resols by lot of authors using several analytical techniques [1–12]. Previously the influence of the type of catalyst [13–15], the amount of catalyst and initial pH [16], the initial formaldehyde-to-phenol molar ratio [17] and the condensation temperature [18], on the formation of phenolic resol resins were studied by our group.

The modelling of novolak phenolic resin was done by Drumm and Le Blanc [19] and Kumar et al. [20]. However, little work has been reported on the mathematical modelling of resol-type phenolic resins due to the complexity of the kinetic scheme. Pal et al. [21,22] have developed a theoretical model for the branching reactions were conversions of phenol and formaldehyde, number-average chain length, degree of branching, and the internal and external *ortho*- and *para*-H atoms concentration were simulated as a function of time for several values of five rate constants. However, kinetic parameters were taken from the novolak chemistry, which differs widely in the nature of the reactions, reactivity ratios and substitution effects. Recently, Manfredi et al. [23] have presented the modellisation of the synthesis of a resol-type phenolic resin including the effects of formaldehyde and phenol equilibrium. They have adjusted kinetic constants by comparing the evolution of phenol and formaldehyde concentrations of resols catalysed with sodium hydroxide at constant temperature with different formaldehyde-to-phenol molar ratios.

The aim of this paper is to apply the model previously described [23] to study also the influence of the others synthesis parameters on the kinetic schema.

2. Experimental

2.1. Synthesis of resols

Fourteen pre-polymers were synthesized by varying the type or amount of catalyst, the initial formaldehyde-to-phenol (F/Ph) molar ratio, the condensation temperature, or the initial pH. Table 1 shows the name, formulation and synthesized conditions for each resol.

Phenol (>99%) and alkaline catalyst were commercial products used without further purification. Formaldehyde (37% aqueous solution) was prepared from a 50% commercial solution adding distilled water; the pH of the solution was then adjusted to 7.0 with sodium hydroxide (1 M) except for the three resols marked with (*) on Table 1.

Pre-polymers were prepared in the Bakelite-Ibérica factory by mixing phenol and formaldehyde aqueous solution, with the desired molar ratio, in a three necked flask equipped with a thermometer, stirred, and refrigeration

---

[*] Corresponding author. Tel.: +54-0223-481-6600; fax: +54-0223-481-0046.

E-mail address: criccard@fi.mdp.edu.ar (C.C. Riccardi).

0032-3861/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00736-4

Table 1
Formulations and synthesized conditions for each pre-polymer

Name	Catalyst	Temperature (°C)	F/Ph	Amount of catalyst (g/500 g of phenol)	pH
Rna *	Na(OH)	80	1.8	5.7	8
RZn	$Zn(CH_3COO)_2 \cdot H_2O$	80	1.8	11.7	8
RBa *	$Ba(OH)_2$	80	1.8	3.75	8
RT60	$(CH_3CH_2)_3N$	60	1.8	8.6	8
RT95	$(CH_3CH_2)_3N$	95	1.8	5.7	8
RT43	$(CH_3CH_2)_3N$	80	1.8	4.3	8
RT84	$(CH_3CH_2)_3N$	80	1.8	8.4	8
RT20 *	$(CH_3CH_2)_3N$	80	1.8	20.0	8
RT10	$(CH_3CH_2)_3N$	80	1.0	13.0	8
RT14	$(CH_3CH_2)_3N$	80	1.4	8.5	8
RT22	$(CH_3CH_2)_3N$	80	2.2	7.8	8
RT26	$(CH_3CH_2)_3N$	80	2.6	5.4	8
RT823	$(CH_3CH_2)_3N$	80	1.8	20.0	8.23
RT836	$(CH_3CH_2)_3N$	80	1.8	20.0	8.36

column. The pH was then adjusted with the necessary amount of the corresponding alkaline catalyst. The mixture was heated to the selected condensation temperature (heating rate: 2.5–3.5 °C/min) and stirred during reaction. Samples were taken during synthesis. Zero time was defined as time to the mixtures reached the condensation temperature. The reaction was stopped putting the reactor in a cold-water bath, when the resin showed a 1/1 g/g dilutability in water. Samples were kept at 4 °C.

2.2. High performance liquid chromatography

Analyses were conducted with a Waters 510 chromatograph equipped with a Waters 486 UV detector, set at 280 nm. The columns were Spherisorb ODS-2 (5 μm). In order to decrease the viscosity of the solvents, the columns were thermostated to 35 °C. A mobile phase of methanol–water was used with an elution gradient of 20–80% of methanol in 180 min, and 80–100% in 5 min.

3. Model formulation

In water alkaline medium, phenol and formaldehyde are present in the form of phenolate [9] and methylene glycol [24], respectively. The phenol equilibrium constant will be called ke_1 and the formaldehyde one as ke_2. Fig. 1 shows both equilibrium reactions.

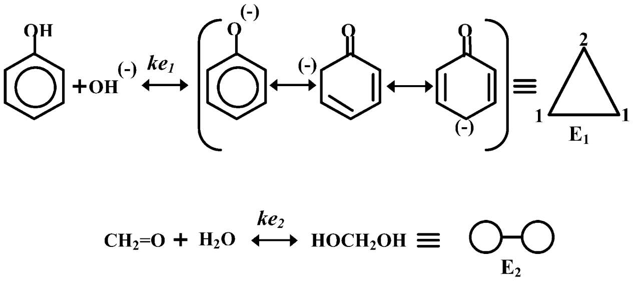

Fig. 1. Formation of the reactive compounds from phenol and formaldehyde.

Phenol, represented by E_1, has three sites, two *ortho* (namely 1) and one *para* (namely 2), that can undergo chemical reactions with different reactivities [25]. Formaldehyde as methylene glycol is considered with two reactive positions and it is represented by E_2. The initial addition reaction of formaldehyde with phenol is faster than the subsequent condensation reaction between substituted phenol rings; consequently, methylolphenols are initially the predominant intermediate compounds. These reactions and corresponding representation for methylolphenols compounds are summarised in Fig. 2. Methylol groups are represented by Me_1 and Me_2 and free *ortho* and *para* positions in methylolphenols are namely $1'$ and $2'$, respectively, to take into account the different reactivity of the same positions in phenol. These methylolphenols condense either with other methylol groups to form ether linkages or, more generally, with the available reactive unsubstituted positions in the phenol ring (*ortho* or *para* to the phenol's hydroxyl group) to form methylene bridges. As consequence, the reactions to be taken into account are: (i) formaldehyde addition to a free reactive position (*ortho* or *para*), (ii) condensation of two methylols giving an ether bridge or a methylene bridge (with formaldehyde and water evolution), and condensation of a methylol with a free position in the phenol ring giving a methylene bridge. These reactions are summarised in Fig. 3, where formaldehyde is liberated from the dimethylene ether linkage. The molecular fragments that can be distinguished are shown in Fig. 4 where the methylene bridges are represented by ΛΛΛ and the *i* in a position name means that in the other two positions there are internal methylene bridges.

The entire course of the resol polymerisation can be represented in terms of reactions between the 19 basic entities defined from E_1 to E_{19} [21]. Each reaction's rate constant is related to that of the reaction between the methylene glycol and the *ortho* free phenol's position by

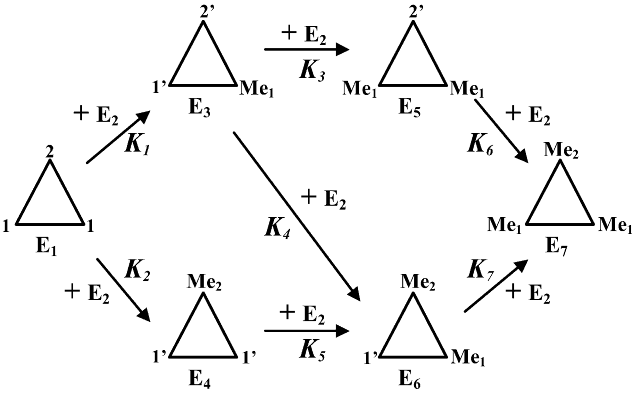

Fig. 2. Addition reactions.

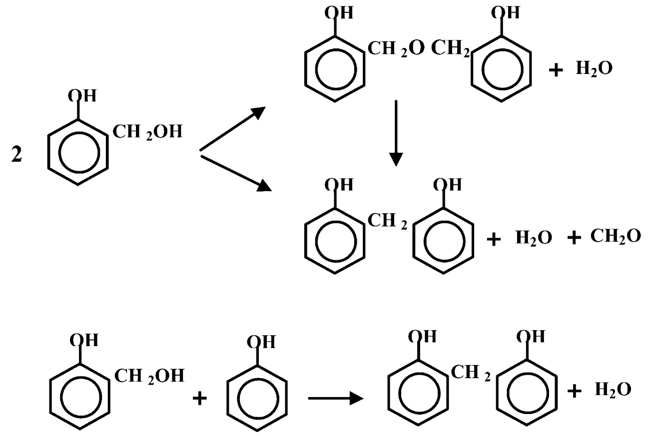

Fig. 3. Examples of possible condensation reactions.

combination of reactivities ratios of each position to the *ortho* phenol one.

For the reaction:

$$E_1 + E_2 \rightarrow E_3 \qquad (1)$$

as the concentration of phenolate and methylene glycol are defined as ke_1 [E_1] and ke_2 [E_2], respectively, and the entity E_1 has two *ortho* positions and the entity E_2 is bi-functional, the obtained kinetic expression is the following:

$$-\frac{d[E_1]}{dt} = 4k_{10}ke_1[E_1]ke_2[E_2] \qquad (2)$$

where k_{10} is the constant reaction value of the methylene glycol addition to the *ortho* phenol position. The kinetic expression can be written in terms of dimensionless concentrations defined as $E_i = [E_i]/[E_1]_0$:

$$-\frac{dE_1}{dt} = 4kc\ ke_1E_1ke_2E_2 \qquad (3)$$

where kc is defined as

$$kc = k_{10}[E_1]_0 \qquad (4)$$

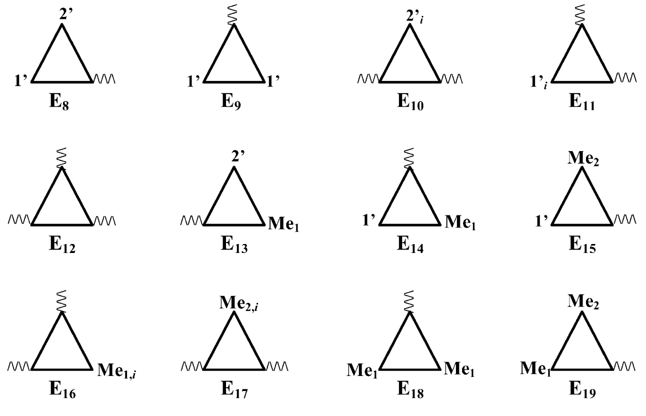

Fig. 4. Fragments of molecules that can be distinguished after condensation reactions.

In the following part of the text, all the concentrations are used in the dimensionless form.

Each reactivity ratios is defined as follows:

(i) The reactivity of a *para* phenol position to an *ortho* phenol position is r_2.

(ii) The reactivity ratio for the addition reaction of a methylolphenol free position with respect to the same phenol site is defined with r_{ijk}, where i is the reacting position and j or j and k are methylol groups, i.e. r_{11} means the reactivity of a free *ortho* position when there is a methylol in the *ortho* position, with respect to the reactivity of the same site when there is no substitution in *ortho*.

(iii) The condensation–addition ratio when the methylol reacts with a free position of the phenol is called r. However, when the methylol reacts with a free methylolphenol position, the reactivity ratio is fc × r, where fc is the relationship between the free *ortho* or *para* positon of a methylolphenol and the same position in the phenol. These parameters take into account the substitution effect.

(iv) The substitution effects of methylol groups in the condensation reaction are taken into account by defining m_{ijk} reactivity ratios, where i is the reacting position and j and k are methylol groups, i.e. m_{121} means the reactivity ratio between a methylol group in *ortho* position in the E_7 entity with respect to the same position in the E_3 one.

(v) It is assumed that the reactivity of external sites is not affected by the formation of a methylene bridge, except by the possible change in the substitution effect. However, when two methylene bridges are joined to a ring the reactivity ratio of the remaining internal site is defined as r_{ie}.

As an example, the corresponding rate constant of the reaction of the entity E_{19} with E_{15} can be calculated by $kc \times r \times fc \times m_2 \times m_{21} \times r_{12}$. A set of 19 simultaneous non-linear algebraic differential equations was thus obtained.

4. Results and discussion

The evolution of free formaldehyde during synthesis was followed by chemical assay [26], while the disappearance of phenol and formation of the mono-substituted phenols, E_3 and E_4, were quantitatively followed by liquid chromatography. The evolution of di- and tri- substituted phenols can be followed qualitatively by high performance liquid chromatography (HPLC) and the E_6 and E_7 peaks cannot be separated. Experimental results were reported previously [13–18].

To obtain the reactivity ratios a numerical solution was performed with a multiple parameter regression method used to fit the mass concentrations of entities E_1 to E_4. The constancy in the total number of phenolic rings from

Table 2
Equilibrium and kc constants

Resol	$kc \times 10^4$ (s^{-1})	ke_1	ke_2	ke_1ke_2
RNA	0.530	0.923	0.637	0.592
RZN	0.122	1.072	0.792	0.848
RBA	0.254	0.931	0.882	0.821
RT60	0.069	1.025	0.937	0.960
RT95	0.842	1.133	1.006	1.140
RT43	0.315	1.021	0.655	0.669
RT84	0.392	0.983	0.947	0.931
RT20	0.837	1.310	0.807	1.057
RT10	0.113	1.024	1.019	1.043
RT14	0.632	1.015	0.920	0.934
RT22	0.332	1.008	0.961	0.969
RT26	0.440	1.082	0.471	0.510
RT823	0.812	1.095	0.908	0.993
RT836	1.060	1.083	0.946	1.024

the computed concentrations of the various basic entities and the total concentration of CH_2 groups (as $-CH_2$ linkages, CH_2OH or in unreacted formaldehyde) was checked. The other verification of the calculation was the constancy in molar balances for initial formaldehyde and initial phenol, respectively. Fig. 5 shows fitting results for resol RT10 expressed as mass fractions, W, of entities E_1 to E_4 vs. reaction time. Similar good results can be obtained for all resols. Tables 2–4 show the fitting parameters of the model.

The product ke_1ke_2 is comparable to the constant m_0 defined by Zavitsas et al. [27], notwithstanding our model does not take into account the equilibrium change due to the variation in water concentration. They had found values between 0.25 and 1, with m_0 tending to one for dilute systems, more or less constant with temperature and diminishing slowly with the increased of the F/Ph ratio. Our results have the same tendency (see Table 2) and pH values do not show influence.

Table 3 shows r_{ijk} reactivity ratios. Francis and Yeddanapalli [28] reported that the condensation–addition ratio (r) was 0.0625 for free sites of phenol, in the same order of results. Minami and Ando [29] suggested a higher reactivity ($r \times$ fc) for free sites of methylolphenols but that is only the case of the synthesis of RZn resol. The $r \times$ fc values decrease if the F/Ph molar ratio is increased, the results of Manfredi et al. [23] has the same tendency. Except for the resol catalysed with zinc acetate, reactivities ratios r_2 are in the same order of those reported values [23,27,30–32]. This is in accord with the fact that in the synthesis of resol RZn the addition of formaldehyde onto phenol is almost exclusively *ortho* directed [15]. When an *ortho* position have reacted the reactivity of the free *ortho* position is decreased while the reactivity of the *para* position is substantially increased, i.e. $r_{11} < 1$ and $r_{12} > 1$; the reactivity of free positions is increased when the *para* position have reacted, i.e. r_{21} and r_{121} are greater than one.

The reactivity ratios of m_{ij} shown on Table 4, do not seem to depend on the corresponding F/Ph molar ratio. The reactivity of a methylol group in an *ortho* position increases if there is a methylol group in the other *ortho* position ($m_{12} > 1$) while decreases if the methylol is in the *para* position ($m_{12} < 1$), except for resols RNa and RT95.

Table 5 shows the calculated constant reaction values for addition reactions, expressed in l mol^{-1} per s; for the reaction between the methylene glycol and the *ortho* phenol position dimensionless value (K_1^* and the value expressed by mass of catalyst ($K_{1,w}$) are also shown.

As each reaction's rate constant is related to that of the reaction between the methylene glycol and the *ortho* free phenol's position, it is possible to define a dimensionless time, t^*, by multiplying the reaction time by K_1^*. The experimental mass fractions of E_3 and E_4 (i.e. W_3 and W_4) and the HPLC areas for E_5 and E_6 plus E_7 (i.e. A_5 and $A_6 + A_7$) can be represented as a function of t^* for comparison purposes.

To study the influence of the catalyst used on the prepolymer synthesis, resols RNa, RZn, RBa, RT84 and RT20 were compared. The $K_{1,w}$ constants are in the same order except for RZn which synthesis is the slowest one. Fig. 6 shows the comparison of addition product distributions of this resols versus dimensionless time. The mass fraction of

Table 3
Reactivity ratios for the addition reaction

Resol	r	fc	fc(r)	r_2	r_{11}	r_{12}	r_{21}	r_{121}	r_{211}	r_{ie}
RNA	0.062	0.44	0.027	0.912	0.082	2.57	17.67	6.98	1.978	0.001
RZN	0.024	10.30	0.247	0.090	0.001	1.29	4.58	8.43	13.820	0.874
RBA	0.040	0.74	0.029	0.754	0.021	1.54	12.00	7.00	0.781	2.581
RT60	0.046	0.54	0.025	0.879	0.183	2.51	12.99	6.46	2.329	2.140
RT95	0.046	0.70	0.032	0.865	0.172	2.55	11.75	6.32	2.340	2.037
RT43	0.054	0.92	0.050	1.087	0.228	2.74	5.93	2.80	1.091	0.153
RT84	0.045	0.78	0.035	1.653	0.395	4.25	3.83	5.43	0.001	1.524
RT20	0.046	0.86	0.040	1.375	0.478	4.82	3.13	4.07	0.633	1.766
RT10	0.053	0.61	0.032	0.940	0.105	3.15	11.78	6.17	2.226	2.685
RT14	0.046	0.53	0.024	0.885	0.179	2.51	13.18	6.50	2.323	2.154
RT22	0.015	0.65	0.010	0.880	0.095	2.77	11.12	6.86	2.205	0.240
RT26	0.012	0.92	0.011	1.126	1.477	2.54	4.80	7.39	1.258	0.227
RT823	0.028	0.66	0.018	0.905	0.113	2.48	13.40	7.27	1.758	0.652
RT836	0.046	0.58	0.027	0.850	0.155	2.76	13.43	6.54	2.173	2.112

Table 4
Reactivity ratios taking into account the substitution effects of methylol groups in the condensation reaction

Resol	m_2	m_{11}	m_{12}	m_{21}	m_{121}	m_{212}
RNA	0.001	6.865	1.361	0.053	0.055	0.410
RZN	8.679	2.645	0.024	0.659	2.874	4.532
RBA	0.170	2.688	0.710	1.607	0.024	0.487
RT60	0.243	2.601	0.883	1.578	0.026	0.218
RT95	0.127	2.433	1.028	1.115	0.059	0.104
RT43	0.963	6.340	0.456	0.502	0.741	3.268
RT84	0.634	3.777	0.437	0.881	1.012	3.705
RT20	0.886	4.077	0.519	0.542	1.304	4.151
RT10	0.209	2.710	0.552	1.249	0.005	0.010
RT14	0.259	2.655	0.856	1.662	0.018	0.238
RT22	0.349	2.846	0.700	1.276	0.108	6.567
RT26	0.246	0.602	0.185	0.721	0.434	1.273
RT823	0.235	0.709	1.031	1.579	0.602	1.273
RT836	0.232	2 0.354	0.946	1.348	0.032	0.0910

E_3 is higher in resols RZn and RT20 because in these cases, the addition of formaldehyde onto phenol is *ortho* directed [15]. While the synthesis of RZn is characterised with a low value of the reactivity ratio of a *para* phenol to an *ortho* phenol position (r_2), the synthesis of RT20 has a high value for the product ke_1ke_2, meaning that the equilibrium position favoured this reaction. The difference in the prepolymerisation conditions of RT20, the absence of OH groups coming from Na(OH) used to adjust the pH in RT84, explained the change in the equilibrium conditions because OH groups could form phenolate ions [16]. The mass fraction of E_4 is insignificant for RZn due to the low value of r_2. The highest mass fraction of E_4 in the synthesis of RNa is denoted for the highest value in the ratio of the reactivity of a free *ortho* position when there is a methylol in the *para* position, with respect to the reactivity of the same site when there is no substitution in *para*(r_{21}). As a result of the slow addition of formaldehyde onto phenolic rings during RZn synthesis, condensation reactions were delayed and condensation

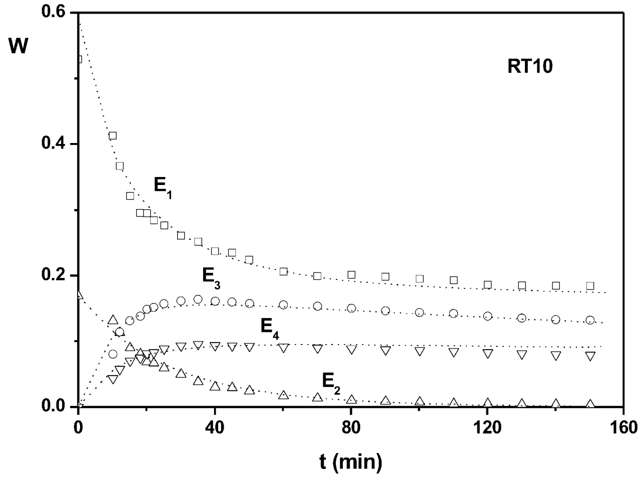

Fig. 5. Mass fraction of entities E_1 to E_4 vs. reaction time. Dot lines represent the model prediction.

Table 5
Constant rates for addition reactions

Resol	$K_{1,w}$ (10^5 l mol^{-1} s^{-1} g)	K_1^* (10^4 s)	K_1 (10^4 l mol^{-1} s^{-1})	K_2 (10^5 l mol^{-1} s^{-1})	K_3 (10^5 l mol^{-1} s^{-1})	K_4 (10^4 l mol^{-1} s^{-1})	K_5 (10^4 l mol^{-1} s^{-1})	K_6 (10^5 l mol^{-1} s^{-1})	K_7 (10^4 l mol^{-1} s^{-1})
RNA	0.116	1.254	0.066	0.301	0.013	0.254	0.081	0.285	0.110
RZN	0.019	0.416	0.022	0.0099	0.0012	0.044	0.273	1.321	0.893
RBA	0.117	0.835	0.044	0.165	0.0037	0.158	0.054	0.103	0.122
RT60	0.016	0.265	0.014	0.062	0.007	0.042	0.019	0.076	0.024
RT95	0.354	3.837	0.202	0.873	0.108	0.636	0.319	1.267	0.395
RT43	0.103	0.842	0.044	0.241	0.046	0.129	0.110	0.238	0.056
RT84	0.092	1.457	0.076	0.635	0.120	0.193	0.259	0.00046	0.167
RT20	0.095	3.537	0.189	1.297	0.296	0.266	0.595	0.538	0.252
RT10	0.103	4.693	0.134	0.631	0.042	0.443	0.252	0.838	0.247
RT14	0.110	2.357	0.093	0.414	0.043	0.283	0.122	0.499	0.158
RT22	0.112	1.289	0.088	0.387	0.027	0.275	0.156	0.546	0.193
RT26	0.140	0.897	0.076	0.333	0.481	0.176	0.567	0.165	0.241
RT823	0.087	3.228	0.174	0.786	0.256	0.059	0.261	0.836	0.382
RT836	0.117	4.342	0.234	0.994	0.097	0.715	0.345	1.156	0.409

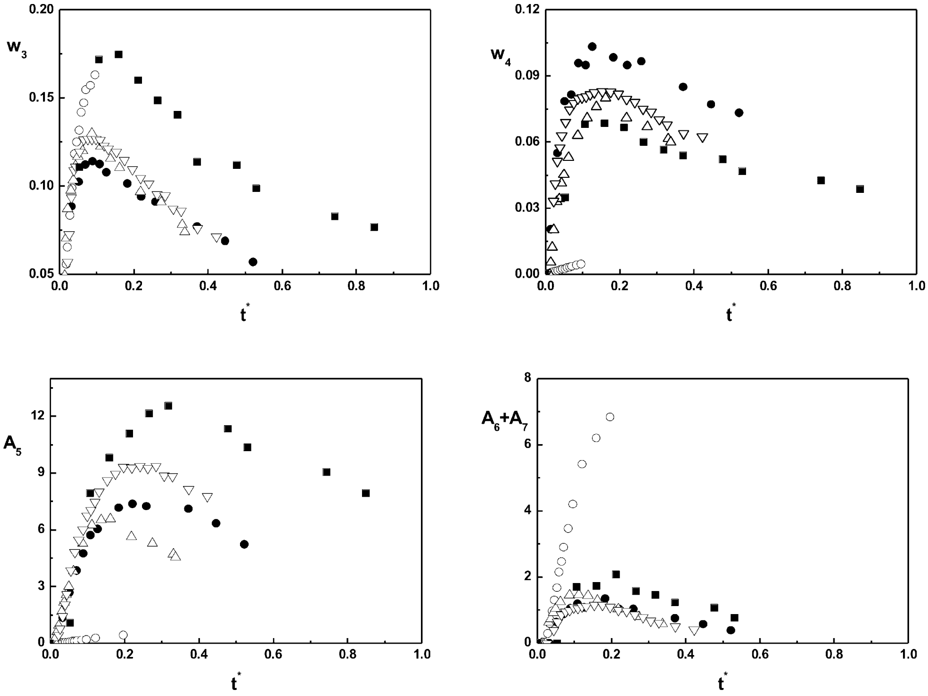

Fig. 6. Effect of catalyst type on the mass fraction of E_3 and E_4 and on the HPLC area of E_5 and $E_6 + E_7$. Symbols: (●) RNa, (○) RZn, (△) RBa, (▽) RT84, (■) RT20.

products were very slightly detected at the final point [15] and that can explain the highest concentration of $E_6 + E_7$ products for this resol.

To study the influence of polymerisation conditions, the effect of the amount of catalyst, the operating temperature, the ratio F/Ph and the pH on the constant of the reaction between the methylene glycol and the *ortho* phenol position is analysed in synthesis of resols catalysed with triethylamine.

Fig. 7 shows the plot of constant K_1 as function of the amount of catalyst expressed as w (grams of catalyst for each 500 g of phenol). The resulting linear expression is:

$$K_1\ (10^7\ l\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}) = 1.55 + 9.36w \tag{5}$$

Yeddanapalli and Gopalakrishna [33] found a linear relationship too, for a resol catalysed with NaOH at 80 °C with F/Ph equal to 0.2 and different pH values and Manfredi et al. [23] found that the kinetic constant increased with the quantity of alkaline catalyst.

To independence of the amount of catalyst, K_1 is expressed by mass of catalyst (see $K_{1,w}$ in Table 5). The Arrhenius plot, shown in Fig. 8, leads to the following

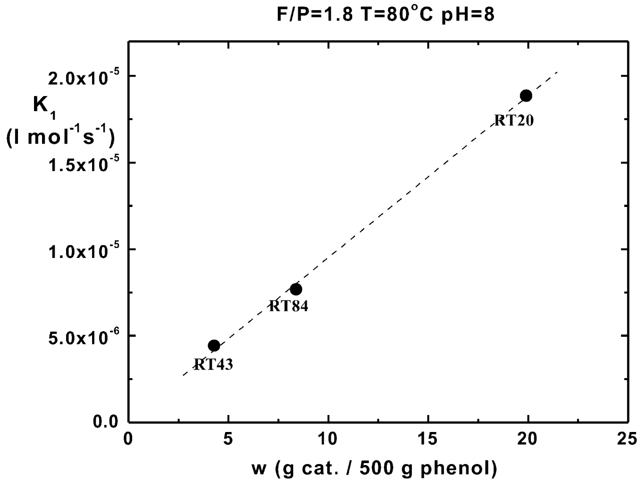

Fig. 7. Constant rate for the reaction of methylene glycol and the *ortho* phenol as function of the mass of catalyst.

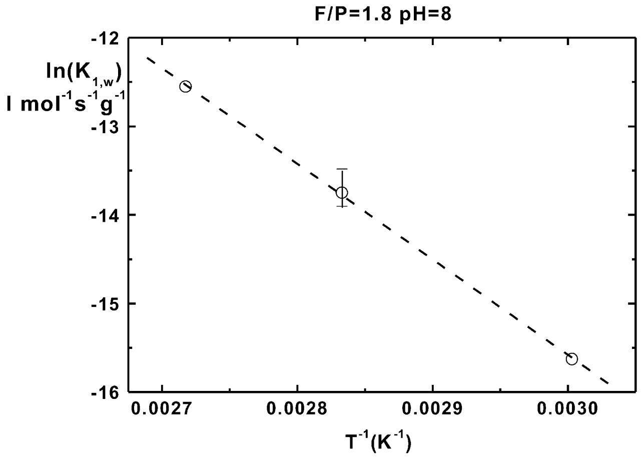

Fig. 8. Arrhenius plot of $K_{1,w}$.

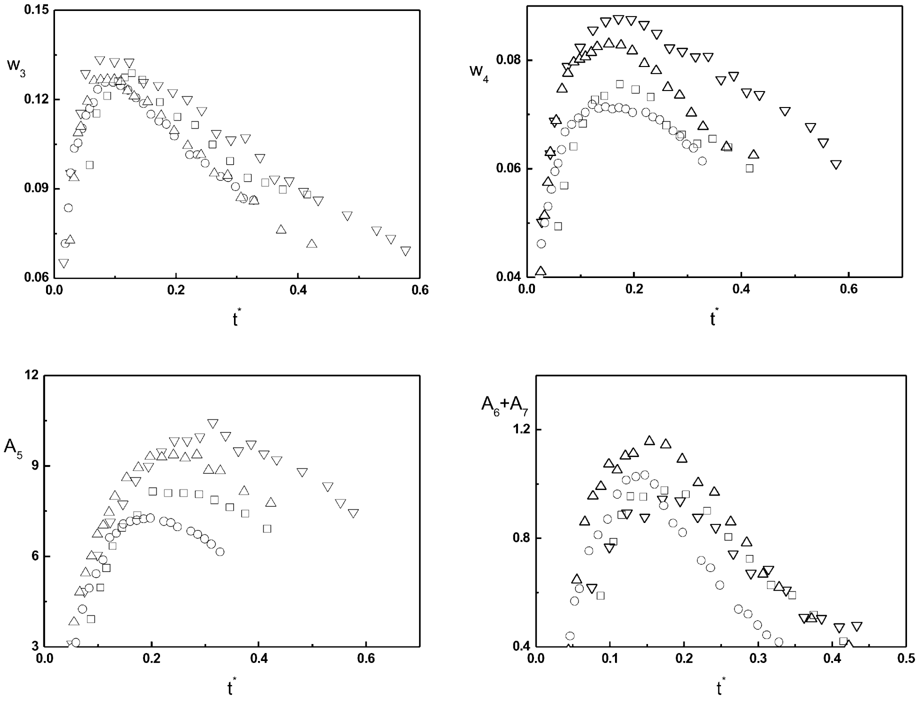

Fig. 9. Mass fraction of E_3 and E_4 and HPLC area of E_5 and $E_6 + E_7$ for resols catalysed with triethylamine. Symbols: (○) RT43, (□) RT95, (△) RT84, (▽) RT60.

expression:

$$K_{1,w}\ (l\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}\ \mathrm{g}^{-1}) = 1.5\times 10^{7}\ \exp(-10719.22/T\ (\mathrm{K})) \tag{6}$$

with an activation energy of 89.11 kJ/mol. The plotted point at 80 °C is the mean value of all RT resols prepared at pH 8, the corresponding error bars are also shown. Table 6 shows activation energy values for all the addition reactions together with bibliography results reported for resols catalysed with sodium hydroxide. Values obtained in this work are in the same order of that previously reported [31,33,34].

In Fig. 9 addition product distributions of resols polymerised with triethylamine varying the amount of catalyst at different temperature are plotted versus t^* to be independent of the kinetic influence of the reaction between the methylene glycol and the *ortho* free phenol's position. Concentrations of entities E_4 and E_5 are increasing with the amount of catalyst used, independently of the synthesis temperature. On concentration of entities $E_6 + E_7$ the two factors have opposite effects increased by the amount of catalyst and decreased by temperature rise [18].

The kinetic constant $K_{1,w}$ increases with the F/Ph molar ratio, as it is shown in Fig. 10. The same influence of the F/Ph ratio was found for the resol catalysed with sodium hydroxide by Manfredi et al. [23]. Fig. 11 shows addition product distributions versus t^* of resols polymerised with

Table 6
Activation energies of addition reaction

Constant	E_{act} (kJ mol^{-1})			
	This work	Ref. [31]	Ref. [34]	Ref. [33]
K_1	89.1	88.3	87.9	82.7[a]
K_2	91.7	85.8	89.5	
K_3	98.5	85.4	86.6	105.0
K_4	88.2	79.5	80.3	97.8
K_5	99.0	87.9	90.4	100.2
K_6	91.5	80.8	97.1	114.9[a]
K_7	92.2	80.3	90.4	

[a] Mean value of the two reactions.

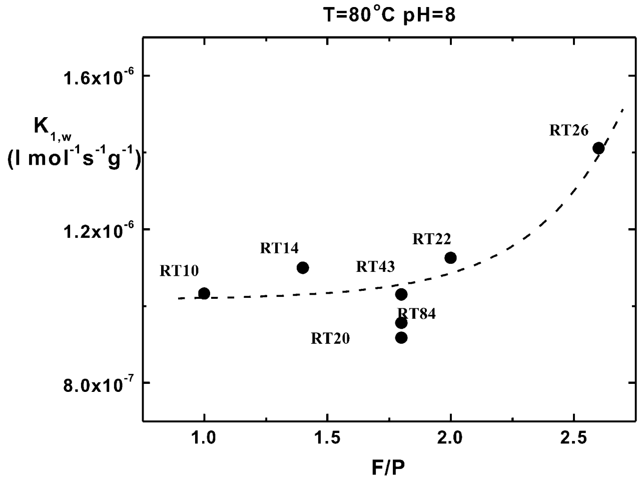

Fig. 10. Effect of the F/Ph molar ratio on $K_{1,w}$.

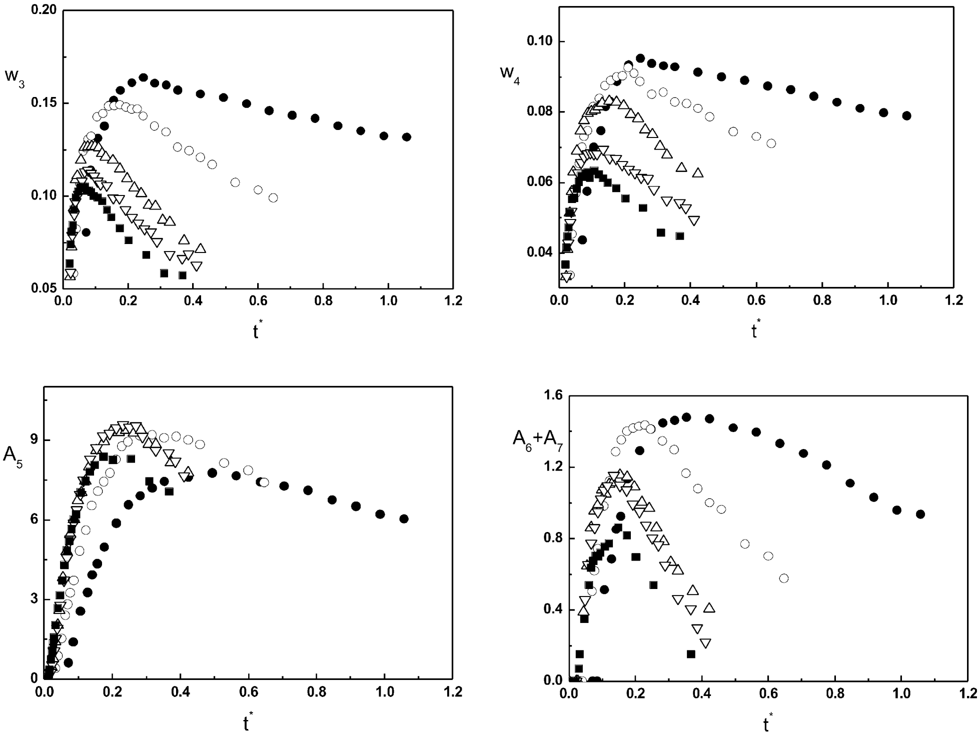

Fig. 11. Effect of the F/Ph molar ratio on mass fraction of E_3 and E_4 and on HPLC area of E_5 and $E_6 + E_7$ for resols catalysed with triethylamine. Symbols: (●) RT10, (○) RT14, (△) RT84, (▽) RT22, (■) RT26.

different F/Ph molar ratio. The concentration, and the position of the maximum, of entities E_3 and E_4 diminish while the ratio F/P is increased. The concentration of entity E_5 does not show great difference except for resol RT14. The concentration and the position of the maximum for entities $E_6 + E_7$ looks as F/Ph = 1.8 is a limiting ratio below which condensation reactions occur at lesser extent.

Although the pH range analysed is narrow, from Fig. 12 it seems that there is a minimum in the graph of the kinetic constant $K_{1,w}$ versus the pH value. De Jong and De Jonge [35] studied the formaldehyde–phenol reaction catalysed with sulphuric acid in the pH range of 2.65–5.80 and found a minimum of the kinetic constant for pH 4.3.

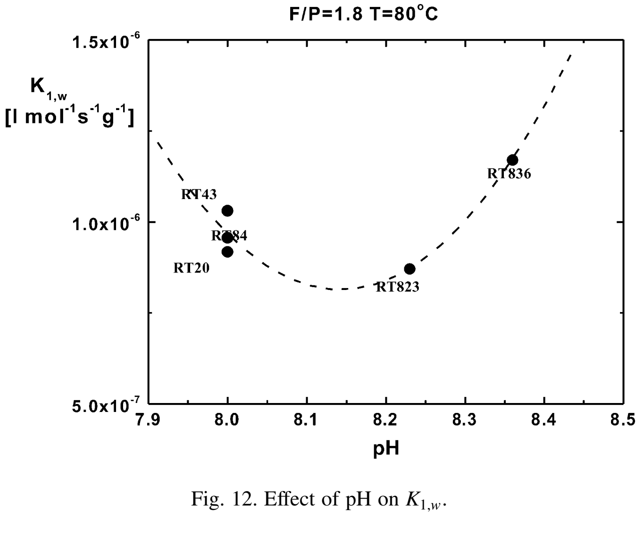

Fig. 12. Effect of pH on $K_{1,w}$.

5. Conclusions

The model previously reported [23], can explain the influence of synthesis parameters on the distribution of products in polymerisation of phenolic resins. The model, in according to with bibliographic results, predicts that:

- The synthesis of a resol catalysed with zinc acetate is characterised with a low value of the reactivity ratio of a *para* phenol to an *ortho* phenol position.
- The absence of OH in a resol catalysed with triethylamine favours the addition of formaldehyde onto the *ortho* position of phenol and accelerates the synthesis.
- The kinetic constant for the reaction of methylene glycol and the *ortho* phenol is linearly increased with the amount of catalyst
- Activation energy values for addition reactions obtained in this work are in the same order of that previously reported.
- While addition rate constants increased with the F/Ph molar ratio, F/Ph = 1.8 seems to be a limiting ratio below which condensation reactions occur at lesser extent.
- Although the pH range analysed is narrow it seems that there is a minimum in the graph of the kinetic constant $K_{1,w}$ versus the pH value.

Acknowledgements

One of the authors wishes to thank the Ministerio de Educación y Ciencia for the grant IN92-DI5376286 supplied for this project which was carried out with the collaboration of Bakelite Ibérica.

References

[1] Knop A, Pilato LA. Phenolic resins. Berlin: Springer, 1985.
[2] King PW, Mitchell RH, Westwood AR. J Appl Polym Sci 1974;18:1117.
[3] Méchin B, Hanton D, Le Goff J, Tanneur JP. Eur Polym J 1984;20:333.
[4] Méchin B, Hanton D, Le Goff J, Tanneur JP. Eur Polym J 1986;22:115.
[5] So S, Rudin A. J Appl Polym Sci 1990;41:205.
[6] Kim MG, Wu Y, Amos LW. J Polym Sci, Part A: Polym Chem Ed 1997;35:3275.
[7] Holopainen T, Alvilla L, Rainio J, Pakkanen TT. J Appl Polym Sci 1997;66:1183.
[8] Grenier-Loustalot MF, Larroque S, Grenier P, Leca JP, Bedel D. Polymer 1994;35:3046.
[9] Grenier-Loustalot MF, Larroque S, Grande D, Grenier P, Bedel D. Polymer 1996;37:1363.
[10] Grenier-Loustalot MF, Larroque S, Grenier P, Bedel D. Polymer 1996;37:939.
[11] Grenier-Loustalot MF, Larroque S, Grenier P. Polymer 1996;37:639.
[12] Grenier-Loustalot MF, Larroque S, Grenier P, Bedel D. Polymer 1996;37:955.
[13] Astarloa-Aierbe G, Echeverría JM, Egiburu JL, Ormaetxea M, Mondragon I. Polymer 1998;39:3147.
[14] Astarloa-Aierbe G, Echeverría JM, Martín MD, Mondragon I. Polymer 1998;39:3467.
[15] Astarloa-Aierbe G, Echeverría JM, Mondragon I. Polymer 1999;40:5873.
[16] Astarloa-Aierbe G, Echeverría JM, Vázquez A, Mondragon I. Polymer 2000;41:3311.
[17] Astarloa-Aierbe G, Echeverría JM, Martín MD, Etxeberria AM, Mondragon I. Polymer 2000;41:6797.
[18] Astarloa-Aierbe G, Echeverría JM, Riccardi CC, Mondragon I. Polymer 2002, in press.
[19] Drumm MF, Le Blanc JR. In: Solomon DH, editor. Step growth polymerisation, 1st ed. New York: Wiley, 1972.
[20] Kumar A, Gupta SK, Kumar B. Polymer 1982;23:1929.
[21] Pal PK, Kumar A, Gupta SK. Br Polym J 1980;12:121.
[22] Pal PK, Kumar A, Gupta SK. Polymer 1981;22:1699.
[23] Manfredi LB, Riccardi CC, De la Osa O, Vázquez OA. Polym Int 2001;50:1.
[24] Kumar A, Kulshreshtha AK, Gupta SK. Polymer 1980;21:317.
[25] Zavitsas AA. J Polym Sci, Part A1 1968;6:2533.
[26] ISO 9397 Standard, 1987.
[27] Zavitsas AA, Beaulieu RD, Leblanc JR. J Polym Sci, Part A1 1968;6:2541.
[28] Francis DJ, Yeddapanalli LM. Makromol Chem 1969;125:119.
[29] Minami T, Ando T. Kogyo Kagaku Zasshi 1956;59:668.
[30] Eapen KC, Yeddanapalli LM. Die Makrom Chem 1968;119:4.
[31] Zavitsas AA, Beaulieu RD. ACS Div Org Coat Plast Prep 1967;27:100.
[32] Freeman JH, Lewis C. J Am Chem Soc 1954;76:2080.
[33] Yeddanapalli LM, Gopalakrishna VV. Makromol Chem 1959;32:112.
[34] Zavitzas AA. ACS Div. Org Coat Plast Prep 1967;26:93.
[35] De Jong JI, De Jonge J. Rec Trav Chim 1953;72:497.