

Cardanol-Based Novolac-Type Phenolic Resins. I. A Kinetic Approach

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ABSTRACT: Novolac resins having two different mole ratios of cardanol-to-formaldehyde (1:0.6 and 1:0.8) were prepared by using aliphatic tricarboxylic acid as catalyst at four different temperatures ranging between 100 and 130°C with an interval of 10°C. The synthesized novolacs were confirmed by infrared spectroscopic analysis with the appearance of characteristic groups of the novolac resin. The reaction between cardanol (C) and formaldehyde (F) was found to follow second-order rate kinetics as determined by two different approaches. The over all rate constant (k) increased with the increase of C/F molar ratio. Based on the value of k , various other kinetic parameters such as activa-

tion energy (E_a), change in enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) of the reaction were also evaluated. The values of E_a and ΔH were found to be decreased with the increase of C/F molar ratio from 1:0.6 to 1:0.8. These values revealed the nature of the condensation reaction between cardanol and formaldehyde in presence of tricarboxylic acid catalysts. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2730–2737, 2006

Key words: polycondensation; step-growth polymerization; kinetics (polym.); activation energy; FTIR

INTRODUCTION

Cardanol, a distillate of cashew nut shell liquid (CNSL) differs in its reactivity with formaldehyde and is used for the development of substituted phenolic resins and various others valuable industrial products.^{1–4} It has been found that an intermediate pH 4–7 and 15–30% molar excess of phenol over formaldehyde results in the formation of novolac which has a disproportionately high concentration of ortho-ortho repeat units.⁵ The kinetics of the acid-catalyzed reaction of various phenols with formaldehyde has been the subject of various studies.^{6–8} Earlier workers were mainly concerned with the evaluation of the overall rate constant, first order or second order, or with the detection of various components formed during the condensation reaction of phenol and formaldehyde. Acid catalysts, particularly dicarboxylic acids where the two carboxylic groups are separated by a chain of more than five carbon atoms, have been extensively studied by several workers in the past.^{9–11} The acid strength, as measured by the first dissociated constant k_1 , of these dicarboxylic acids decreases with increase in the number of bonds between the two carbonyl groups, e.g., the values of k_1 at 25°C were found to be

6.6×10^{-5} , 4.7×10^{-5} , and 3.7×10^{-5} for succinic, glutaric, and adipic acids, respectively. The higher homolog of aliphatic dicarboxylic acid having acid strength falling between the pH range 4–7 can influence formylation and orientation of cardanol, which, finally, can influence the kinetics of formylation and this needs to be thoroughly studied. Also, the study of the formylation reaction of cardanol and formaldehyde in presence of aliphatic tricarboxylic acid is nowhere discussed up to the best of our belief. Therefore, attempt has been made to study the kinetics of condensation reaction of the formylation of cardanol catalyzed by aliphatic tricarboxylic acid, viz., citric acid in the present article.

EXPERIMENTAL

Materials

Cardanol was obtained from M/s Satya Cashew, Chennai, India. Formaldehyde (37% solution) from M/s Qualikem Industries, New Delhi, was used for formylation. Citric acid procured from M/s S.D. Fine Chemicals, Mumbai, was used as catalyst and methanol (BDH) was used to dissolve the catalyst.

Analysis of cardanol

Cardanol was subjected to extensive analysis such as determination of iodine value, viscosity, specific grav-

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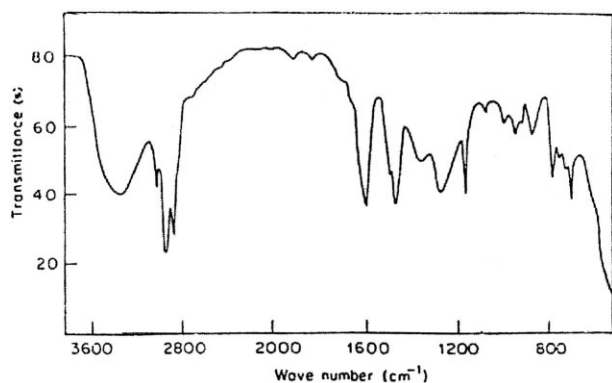


Figure 1 FTIR spectrum of cardanol.

ity as per procedures mentioned in ISI standard 840-1964.

Synthesis of cardanol formaldehyde novolac resin using citric acid as catalyst

Novolac resins with two different mole ratios, i.e., 1:0.6 (CNR-I) and 1:0.8 (CNR-II) of cardanol (C) to formaldehyde (F) were prepared using citric acid as catalyst, similar to the method adopted in our previous article.¹² One percent catalyst based on cardanol was dissolved in 2 mL of methanol under warm conditions. Cardanol was taken into a three-necked R.B. flask fitted with a Leibig's condenser and mechanical stirrer. Formaldehyde (37%) solution was added to the cardanol through a dropping funnel along with the catalyst. The reaction mixture was withdrawn after every 45 min for the determination of change in acid value (Table I), free formaldehyde and free phenol content (Table II) as per the methods published elsewhere.¹³⁻¹⁵ The reaction product was cooled and dried under vacuum at 60°C overnight before purification by column chromatography.

Analysis of resins

Fourier transform infrared (FTIR) spectra of the resins were recorded with a Bruker-Vector infrared spectrophotometer (M/s Bruker Optics Inc., Billerica, MA) (Model: 2.2) in the wavelength range of 600–4000 cm^{-1} , using a computerized recorder (Fig. 1).

Kinetic study

The over all reaction rate constant (k) was evaluated by two different approaches as given below.

Approach-I

The overall rate constant (k) of the reaction, obtained by the expression as given by Levenspiel¹⁶ for second-order rate reaction between C and F, was calculated as:

$$\ln \left[\frac{m-p}{m(1-p)} \right] = C(m-1)kt \quad (1)$$

where

$$p = 1 - \frac{A_{vt}}{A_{v0}} \quad (2)$$

A_{v0} and A_{vt} be the acid values at time $t = 0$ and at time $t = t$, respectively; p be the extent of reaction.

$$m = \frac{C}{F} \text{ (stoichiometric ratio)}$$

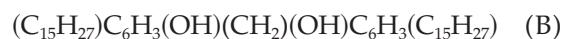
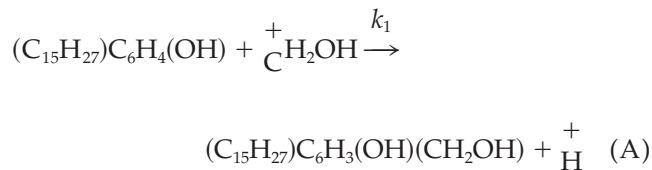
where C and F are the initial moles of cardanol and formaldehyde, respectively.

The results obtained through this approach are given in Table II.

Approach-II

The step rate constants (i.e., k_1 and k_2) and the overall rate constant (k) were obtained with C and F by a modified rate expression as given by Mishra and Pandey.¹⁷ The expression for the calculation of k_1 , k_2 , and k has been discussed as follows.

Calculation of overall rate constant (k). The reaction of cardanol (C) with formaldehyde (F) in acidic medium proceeds according to the equation

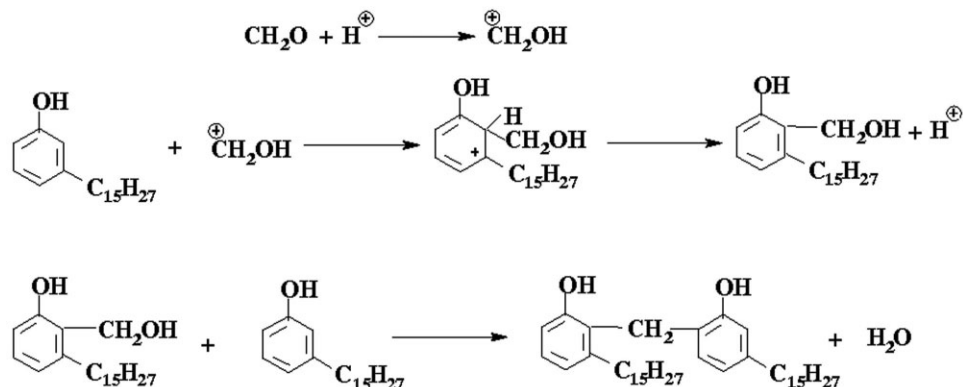


The rate expression for the formation of the product is

$$\frac{dx}{dt} = k(C-x)(F-y) \quad (3)$$

where C and F are the initial concentration of cardanol and formaldehyde, respectively, and x and y be the respective amounts of cardanol and formaldehyde reacted at time " t ".

As seen from the reactions (A) and (B), cardanol is being used up in both the steps. Therefore, at any stage in the reaction, the cardanol consumed will be more than formaldehyde consumed. This could be



Scheme 1 Reaction mechanism for the synthesis of cardanol-based novolac resin.

seen from Table III. The average proportion of cardanol and formaldehyde reacted was actually found to be

$$x = 1.60y \quad (\text{for CNR-I}) \quad (4)$$

$$x = 1.45y \quad (\text{for CNR-II}) \quad (5)$$

Substituting the value of x from eqs. (4) and (5) in eq. (1) and integrating, we get

$$k = \frac{2.303 \times 1.67}{t(1.67F - C)} \log \frac{C(F - y)}{F(C - 1.67y)} \quad (\text{for CNR - I}) \quad (6)$$

$$k = \frac{2.303 \times 1.45}{t(1.45F - C)} \log \frac{C(F - y)}{F(C - 1.45y)} \quad (\text{for CNR - II}) \quad (7)$$

Calculations of step rate constants (k_1 and k_2). From reactions A and B, the rate of formation of monomethylol cardanol might be given as

$$\frac{dy}{dt} = k_1(nC - y - r)(F - y) \quad (8)$$

The concentration of cardanol, formaldehyde, and monomethylol cardanol would be $(C - \omega)$, $(F - y)$, and $(y - r)$, respectively, at any time interval 't' where x , y , and r are the respective amounts of cardanol, formaldehyde, and monomethylol cardanol reacted at time t and n ($= 1$) be the functionality of cardanol.

The rate of formation of dihydroxydicardanyl methane was

$$\frac{dr}{dt} = k_2(nC - y - r)(y - r) \quad (9)$$

where $(nC - y - r)$ was the concentration of cardanol at any time t .

The amount of cardanol reacted at any stage of the reaction was equal to the sum of the formaldehyde and monomethylol cardanol reacted at any time t , i.e.,

$$-\frac{dx}{dt} = -\frac{dy}{dt} - \frac{dr}{dt} \quad (10)$$

Therefore, from eqs. (8), (9), and (10)

$$-\frac{dx}{dt} = -nk_1(C - x)(F - y) - nk_2(C - x)(y - r) \quad (11)$$

It follows from eqs. (3) and (11) that

$$k(C - x)(F - y) = nk_1(C - x)(F - y) + nk_2(C - x)(y - r) \quad (12)$$

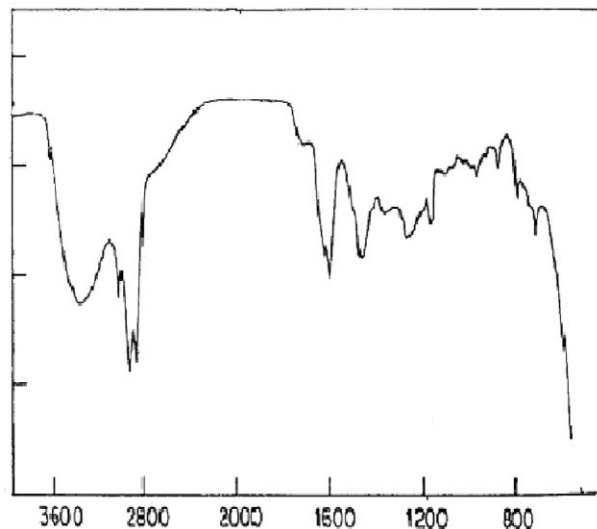


Figure 2 FTIR of cardanol-based novolac-type resin (CNR-I).

TABLE I
Variation of Extent of Reaction (p) and Degree of Polymerization (X_n) with Reaction Time at Different Temperatures of CNR-I and CNR-II Novolac Resins

Temperature (°C)	Time (s)	CNR-I		CNR-II	
		p	X_n	p	X_n
100	2700	0.51	1.61	0.38	1.51
	5400	0.56	1.73	0.54	1.93
	8100	0.62	1.88	0.61	2.91
	10,800	0.66	2.00	0.65	2.36
	13,500	0.74	2.24	0.69	2.60
110	2700	0.55	1.70	0.47	1.71
	5400	0.59	1.79	0.56	2.00
	8100	0.65	1.95	0.62	2.25
	10,800	0.72	2.19	0.68	2.53
	13,500	0.75	2.28	0.71	2.92
120	2700	0.60	1.18	0.48	1.74
	5400	0.65	1.95	0.57	2.04
	8100	0.71	2.16	0.64	2.33
	10,800	0.76	2.35	0.69	2.60
	13,500	0.79	2.45	0.74	2.95
130	2700	0.62	1.88	0.57	2.02
	400	0.66	2.00	0.65	2.36
	8100	0.72	2.19	0.70	2.72
	10,800	0.78	2.42	0.74	2.95
	13,500	0.80	2.68	0.78	3.26

$$k = nk_1 + nk_2 \frac{y-r}{F-y} \quad (13)$$

Now $(y+r) = x$ or $r = x - y$ and the functionality of phenol (n) = 1

$$k = k_1 + k_2 \frac{2y-x}{F-y} \quad (14)$$

Substituting the values of x , y , and k (from Tables III and V) at two different time intervals, two simultaneous equations for k_1 and k_2 at a given temperature were obtained. Utilizing the values of stepwise rate

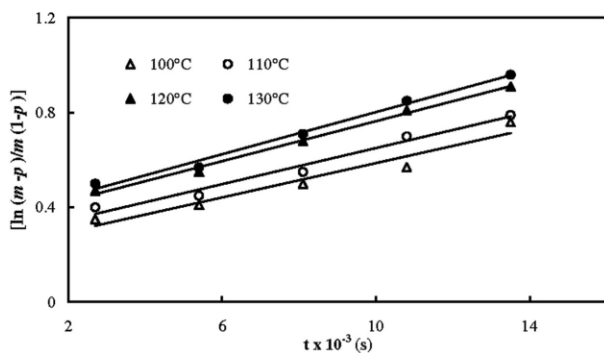


Figure 3 Plot between $[\ln(m-p)/m(1-p)]$ and time for CNR-I novolac resin.

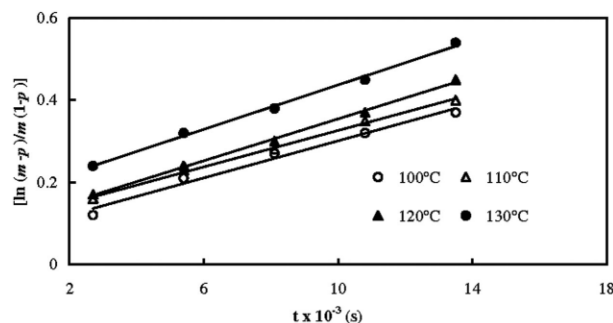


Figure 4 Plot between $[\ln(m-p)/m(1-p)]$ and time for CNR-II novolac resin.

constants, k_1 and k_2 , the overall rate constant k was calculated at different temperatures (Table IV).

Based on the calculated value of " k " by two different approaches, the activation energy (E_a) was calculated from the slope of the plot between $\ln k$ versus $1/T$. Using this value of E_a , change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated using the following equations and the results are given in Table VI.

$$\Delta G = -RT \ln k \quad (15)$$

$$\Delta H = E_a - RT, \quad (16)$$

$$\Delta S = \frac{\Delta G - \Delta H}{T} \quad (17)$$

where R is constant ($8.314 \text{ J K}^{-1} \text{ mole}^{-1}$) and T is absolute temperature (Kelvin).

RESULTS AND DISCUSSION

Analysis of cardanol

The analysis of cardanol is a necessary requirement for the preparation of phenolic resin. The analytical data of cardanol are compared with standard technical CNSL. The relatively lesser viscosity (40.2 cp) of the cardanol in comparison with that of standard technical CNSL (550 cp) indicated lesser ash content and nonself-polymerized fractions. The specific gravity of cardanol (0.9 g/cc) was also relatively lower in comparison with standard CNSL (0.960 g/cc) due to lower ash content and self-polymerized fraction. The iodine value represented the degree of unsaturation in cardanol (280.4 wjjs). This indicated relatively higher degree of unsaturation in the aliphatic side chain in comparison to the standard CNSL (250 wjjs).

Synthesis of novolac resins

The polymerization of cardanol can be accomplished either by formaldehyde condensation or through the

TABLE II
Variation of k and R^2 with Temperature of CNR-I and CNR-II Novolac Resins by Approach I

S. no.	Temperature (°C)	$k \times 10^5$ (CNR-I) ((mol L ⁻¹) ⁻¹ s ⁻¹)	$k \times 10^4$ (CNR-II) ((mol L ⁻¹) ⁻¹ s ⁻¹)	R^2
1.	100	2.98	0.80	0.9895
2.	110	3.43	1.00	0.9864
3.	120	4.47	1.24	0.9853
4.	130	5.07	1.44	0.9698

unsaturation in the side chain. The degree of unsaturation in final product before and after the reaction has been found to be same (280.4 wjjs). Hence, there will be no reaction at the alkyl chain of the cardanol. The polymerization of the resins proceeds with a complicated step growth polymerization reaction mechanism.¹⁵ In the first step, the formation of a hydroxy-methylene carbonium ion from methylene glycol might occur, which could be the hydroxyl-alkylating agent. The methylol group might be a transient intermediate under acidic condition. Cardanyl carbonium ion might result under these conditions, which reacted very fast with cardanol, yielding dihydroxy-dicardanyl methane. The proposed mechanism for this has been shown in Scheme 1.

Analysis of novolac resins

Figures 1 and 2 show the appearance of different characteristic peaks related to cardanol and cardanol-based novolac type resin (CNR-I), respectively. The positions of peaks in the spectrum (Fig. 2) resembled the peaks of novolac resins prepared in our previous study.¹²

The presence of the most important functional group, i.e., methylene group (—CH₂—), linked between two benzene rings was revealed by the peak appearance at about 1350 cm⁻¹ (Fig. 2) and this peak

appeared comparatively broader than the peak that appeared in Figure 1 for pure cardanol.

Kinetic parameters

Approach-I

Table I shows the variation of extent of reaction (p) and degree of polymerization (X_n) with reaction time periods and temperatures for CNR-I and CNR-II novolac resins. It is clear from the data that at particular temperature, the degree of polymerization (X_n) was found to be higher for CNR-II than for CNR-I at the same reaction time. This indicated that CNR-II novolac resin was more reactive than CNR-I. This also indicated that CNR-II enabled relatively higher degree of methylation in comparison with that for CNR-I. The result resembled the concept explained by Little¹⁸, where he correlated the rate of reaction with the

TABLE III
Variation of Reacted Moles of Cardanol (x) and Formaldehyde (y) at Different Temperatures and Times

Temperature (°C)	Time (s)	CNR-I		CNR-II	
		x	y	x	y
100	2700	0.052	0.026	0.068	0.054
	5400	0.19	0.05	0.20	0.16
	8100	0.24	0.12	0.37	0.29
	10,800	0.40	0.2	0.55	0.44
	13,500	0.63	0.31	0.61	0.48
110	2700	0.057	0.028	0.070	0.57
	5400	0.21	0.12	0.21	0.17
	8100	0.25	0.16	0.39	0.31
	10,800	0.42	0.20	0.52	0.45
	13,500	0.64	0.32	0.63	0.50
120	2700	0.073	0.36	0.070	0.062
	5400	0.25	0.12	0.23	0.18
	8100	0.30	0.15	0.414	0.33
	10,800	0.43	0.21	0.60	0.47
	13,500	0.65	0.32	0.65	0.52
130	2700	0.083	0.40	0.18	0.087
	5400	0.26	0.13	0.30	0.24
	8100	0.33	0.16	0.43	0.34
	10,800	0.44	0.22	0.61	0.49
	13,500	0.66	0.32	0.67	0.53

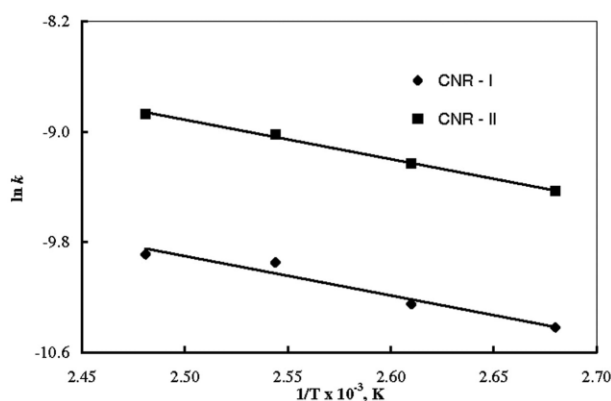


Figure 5 Plot between $\ln k$ versus $1/T$ for CNR-I and CNR-II novolac resins (approach-I).

TABLE IV
Variation of Step Rate Constants (k_1, k_2) and Overall Rate Constant (k) at Different Temperatures and Times of CNR-I and CNR-II Novolac Resins

Temperature (°C)	$k_1 \times 10^6$ ((mol L ⁻¹) ⁻¹ s ⁻¹)		$k_2 \times 10^4$ ((mol L ⁻¹) ⁻¹ s ⁻¹)		$k_{\text{exp}} \times 10^6$ ((mol L ⁻¹) ⁻¹ s ⁻¹)		$k_{\text{calc}} \times 10^6$ ((mol L ⁻¹) ⁻¹ s ⁻¹)	
	CNR-I	CNR-II	CNR-I	CNR-II	CNR-I	CNR-II	CNR-I	CNR-II
100	0.19847	3.855	0.99848	0.2896	0.28587	0.054404	0.22817	0.05439
	0.54633	7.817	0.18088	0.1017	0.47028	0.0990691	0.47028	0.09906
	0.4385	0.87531	0.31392	0.1245	0.41364	0.150488	0.4130	0.150
	0.8764	8.8595	0.18611	0.1237	0.61857	0.25696	0.6188	0.25694
110	0.4124	4.0122	0.1921	0.2410	0.57351	0.0573519	0.2469	0.05725
	0.5313	1.8729	0.6325	0.3859	0.53111	0.103297	0.5311	0.10329
	0.6598	9.8020	0.1446	0.1193	0.43145	0.164899	0.4314	0.16489
	0.1661	9.8026	0.5745	0.1194	0.65732	0.282146	0.6572	0.28213
120	0.3425	4.3456	8.9555	0.3333	0.32226	0.0633183	0.3294	0.06329
	0.8302	5.3070	0.2992	0.2894	0.64732	0.11648	0.6472	0.11647
	0.6944	1.0877	0.1569	0.1175	0.54451	0.183167	0.5445	0.18316
	0.8526	2.7166	0.0885	0.2205	0.68746	0.31051	0.6874	0.311130
130	0.5646	6.4713	0.7646	0.2805	0.36069	0.091397	0.3606	0.09139
	0.7619	1.3262	0.1067	0.9372	0.68795	0.166679	0.6878	0.16667
	0.8406	1.2316	0.1642	0.10742	0.61635	0.197295	0.6163	0.197222
	0.1242	2.48874	0.2637	0.22052	0.71858	0.331517	0.7185	0.331507

k_{exp} : Experimental values of k ; k_{calc} : calculated values of k .

change of acidity of the reaction medium. The change of acidity ultimately decides the extent of reaction.

The plot between $[\ln(m-p)/m(1-p)]$ and reaction time (t) at different reaction temperatures (T) of CNR-I and CNR-II novolac resins has been shown in Figures 3 and 4, respectively. The plots were found to be almost linear at all temperatures, with highly significant correlation coefficient ($R^2 > 0.98$) and hence the reaction followed second-order reaction kinetics. It is evident from Figures 3 and 4 that the data deviated from its linear behavior in higher conversion region, which might be due to change in the reaction kinetics. The rate constant k , at all temperatures, for the condensation reaction resulting in CNR-I and CNR-II novolac resins were calculated from the slope (refer Table II) of the plots shown in Figures 3 and 4, respec-

tively. The values of k for CNR-II novolac resin at all temperatures were found to be higher than that obtained for CNR-I novolac resin. This behavior again indicated that CNR-II novolac resin was more reactive than CNR-I novolac resin.

A graph has been plotted between $\ln k$ and $1/T$ for CNR-I and CNR-II novolac resins and shown in Figure 5. The nearly straight-line behavior indicated that the reaction proceeded as per Arrhenius reaction rate concept.¹⁹

Approach-II

The reacted moles of cardanol (x) formaldehyde (y) at different temperatures (T) and reaction time periods (t) are given in Table III. The values of step rate constants k_1 and k_2 and overall rate constant k for ap-

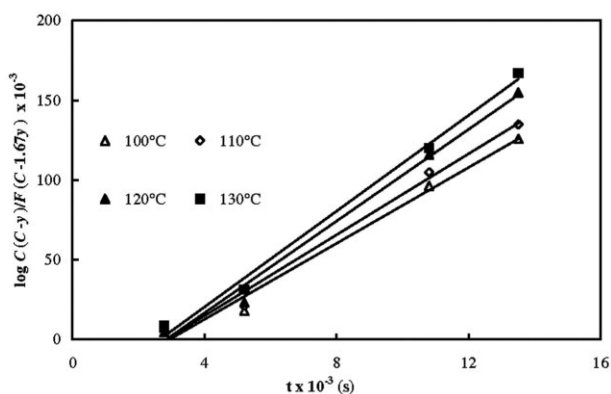


Figure 6 Plot between $\log C(C-y)/F(C-1.67y)$ and time (t) at different temperatures for CNR-I novolac resin.

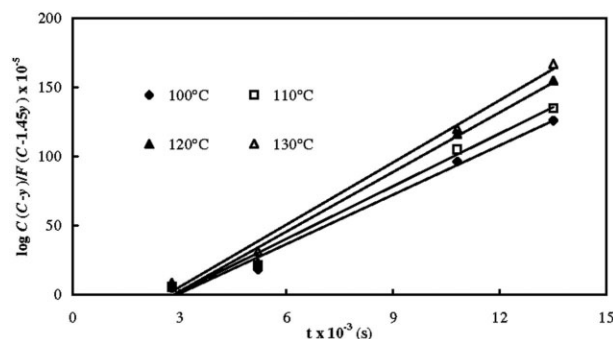


Figure 7 Plot between $\log C(C-y)/F(C-1.45y)$ and time (t) at different temperatures for CNR-II novolac resin.

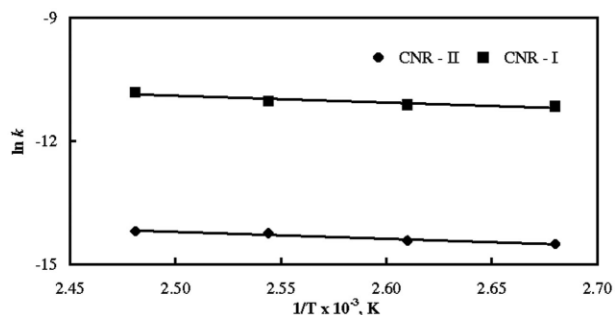


Figure 8 Plot between $\ln k$ versus $1/T$ for CNR-I and CNR-II novolac resins (approach-II).

proach-II are presented in Table IV. It is clear from the table that the values of k_1 were lower than that of k_2 at all temperatures for the condensation reaction under acidic medium. Therefore, k_1 may be considered to be the rate determining step. The values of k_1 , k_2 , and k of the reaction of cardanol and formaldehyde (Scheme 1) were found to obey a second-order rate law with a high correlation coefficient ($R^2 > 0.98$). A linear dependence of $\log \frac{C(C-Y)}{F(C-1.67Y)}$ versus time (Fig. 6) for

CNR-I and $\log \frac{C(C-Y)}{F(C-1.45Y)}$ versus time (Fig. 7) further confirmed the second-order rate law. From the plot between $\ln k$ and $1/T$ (Fig. 8 for CNR-I and CNR-II), the value of the E_a for the overall reaction was calculated from the slope of the plot.

From the values of k obtained from approach-I and approach-II (Table V), it can be concluded that the rate constant increased with the increase of C/F molar ratio. Vetoshkine²⁰ drew a similar conclusion while studying the kinetics of formation of water-soluble phenol-formaldehyde resins. The difference in the reactivity of the CNR-I and CNR-II, under acidic condition, might be due to the reaction of citric acid with formaldehyde and might form an active intermediate. According to Caser,²¹ these active intermediate then attacked the cardanol molecule. The driving force for the reaction was derived from the electrophilic nature of the formaldehyde-proton complex and appeared to be proportional to the concentration of acid catalyst. Kagawa and Shirai²² explained that water had a

strong influence on the activity of acid catalyst. The rate of reaction was increased with the increase in dilution.²³

The activation energy (E_a), change in enthalpy (ΔH), free energy (ΔG), and entropy (ΔS) were calculated from approach-I and approach-II for CNR-I and CNR-II and are given in Table VI. From the table, it is clear that E_a and ΔH values were higher for CNR-I than that for CNR-II that confirmed that the CNR-II resin was more reactive. As $\Delta G > 0$ and $\Delta S > 0$ for the reaction, it could be said that the process is spontaneous and irreversible.²⁴

The data of Table VI also revealed that the energies needed to overcome the condensation reaction were found to be lower for the higher concentration of formaldehyde used in the reaction. This could possibly be due to higher contact frequency between cardanol and formaldehyde. Both the approaches showed the same tendency for all the activation parameters, which indicated that both the methods may be suitable for the kinetic investigation. However, the second approach might be most suitable method to study the reaction kinetics as, in this approach, the step rate constants were easily calculated in presence of weak catalyst such as tricarboxylic acid. The acid value approach (i.e., approach-I) might result some inaccuracy in measurements, as this was calculated by a titration method.

CONCLUSIONS

The step growth polymerization of cardanol and formaldehyde proceeded with second-order rate kinetics with tricarboxylic acid such as citric acid. The value of step rate constant k_1 was lower than k_2 for both the novolac resins, CNR-I and CNR-II, and hence k_1 may be considered as the rate determining constant. The value of overall rate constant, k , was found to be higher for CNR-II than that for CNR-I novolac resin. The higher values of activation energy, E_a , in CNR-I novolac resin than that in CNR-II novolac resin at a given temperature indicated that reaction started earlier in CNR-II novolac resin at that temperature. Therefore, the higher the molar ratio is, the lower E_a is for the reaction. This might be due to the presence of

TABLE V
Comparison of Overall Rate Constant (k) Obtained from Approach-I and Approach-II

S. no.	Temperature (°C)	Approach-I		Approach-II	
		CNR-I, $k \times 10^5$ ((mol L ⁻¹) ⁻¹ s ⁻¹)	CNR-II, $k \times 10^4$ ((mol L ⁻¹) ⁻¹ s ⁻¹)	CNR-I, $k \times 10^7$ ((mol L ⁻¹) ⁻¹ s ⁻¹)	CNR-II, $k \times 10^5$ ((mol L ⁻¹) ⁻¹ s ⁻¹)
1.	100	2.98	0.800	4.90	1.42
2.	110	3.63	1.00	5.40	1.79
3.	120	4.77	1.20	6.47	2.01
4.	130	5.07	1.40	6.80	2.28

TABLE VI
Thermodynamic Parameters of CNR-I and CNR-II Novolac Resins Calculated from Approach-I and Approach-II

Thermodynamic parameters	Approach-I		Approach-II	
	CNR-I	CNR-II	CNR-I	CNR-II
E_a (kJ mol ⁻¹)	54.53	54.44	31.98	31.68
ΔH (kJ mol ⁻¹)	51.26	51.17	28.71	28.41
ΔG (kJ mol ⁻¹)	34.05	30.81	47.41	36.46
ΔS (J K ⁻¹ mol)	43.81	51.79	47.58	20.48

water in the resins. The positive values of change in entropy (ΔS) and change in free energy (ΔG) indicated that the reaction is spontaneous, irreversible, and producing disordered complex compounds.

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