

# Kinetic Modeling of Esterification of Cardanol-Based Epoxy Resin in the Presence of Triphenylphosphine for Producing Vinyl Ester Resin: Mechanistic Rate Equation

Minakshi Sultania, J. S. P. Rai, Deepak Srivastava

Department of Plastic Technology, H. B. Technological Institute, Kanpur - 208 002, India

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**ABSTRACT:** In this study, cardanol-based epoxidized novolac resins and methacrylic acid were used to produce cardanol-based epoxidized novolac vinyl ester resins. The reactions were conducted under nonstoichiometric condition using triphenylphosphine as catalyst in the temperature range of 80–100°C with an interval of 5°C. The first-order rate equation and mechanism based rate equation were examined. Parameters were evaluated by least square method. A comparison of mechanism based rate equation and experimental data showed an excellent agreement. Finally, Arrhenius equation and activation energy were

presented. The specific rate constants, based on linear regression analysis, were found to obey Arrhenius equation. The values of activation energy, frequency factor, enthalpy, entropy, and free energy of the reaction revealed that the reaction was spontaneous and irreversible and produced a highly activated complex. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1979–1989, 2010

**Key words:** cardanol; vinyl ester resin; kinetics; esterification; rate equation; FT-IR

## INTRODUCTION

The use of materials from renewable resources is becoming increasingly important, as the world's leading industries and manufacturers seek to replace dwindling petrochemical-based feedstock with agricultural based materials. The quest for materials from renewable resources supports global sustainability and comes at a time when there is an excess capacity in the agricultural industry. Thus, the diversification into nonfood uses addresses both an important global environmental issue and lends stability for an important segment of our economy. The material utilization of agricultural products has to overcome many technical barriers that often resulted in products, which were either noncompetitive in price or properties compared to petroleum-based products. In this respect, cashew nut shell liquid (CNSL) holds considerable promise as a source of unsaturated hydrocarbon, an excellent monomer for thermosetting polymer production. CNSL, a phenolic based monomer, is commercially available as a natural plant-based resin precursor for surface coating, adhesives, laminates, and rubber compounding and also has several miscellane-

ous applications.<sup>1–6</sup> The CNSL can be used as starting material for organic synthesis and replaces phenol in many instances with equivalent or better results. The main constituents of CNSL are anarcadic acid, cardanol, cardol, and 2-methyl cardol. CNSL extracted by the cold-solvent method is called natural CNSL whereas hot-oil and roasting processed CNSL is called technical CNSL.<sup>7</sup> In the extraction processes involving heat, anarcadic acid is usually decarboxylated into cardanol<sup>8</sup> and, hence, cardanol is the main constituent of technical CNSL. It is a phenolic compound with a C-15 aliphatic chain in the *meta*-position having mixture of saturated and unsaturated (mono, di, and tri) compounds. As cardanol is the major component of technical CNSL, its application in resin production is of great practical interest and can be polymerized in a variety of ways.<sup>1–4</sup> In the condensation polymerization process, cardanol can be condensed with active hydrogen-containing compounds such as formaldehyde at the *ortho*- and *para*-positions of the phenolic ring under acidic or alkaline conditions to yield a series of polymers of “novolac” or “resole” type, respectively.<sup>9</sup> The cardanol-based novolac type phenolic resin may further be modified by epoxidation with epichlorohydrin to improve the performance of such phenolic type novolac in various fields.<sup>10–14</sup> The introduction of unsaturation at the end of the epoxy resin backbone by the reaction with acid functional acrylic/

Correspondence to: D. Srivastava (dsri92@gmail.com).

methacrylic monomer can produce a hybrid resin system in which the optimum properties can be derived. In this sequence an eco-friendly vinyl ester resin (VER) system could be derived from the cardanol.

VERs are one of the most important classes of thermosetting polymers that combine the chemical, mechanical, and thermal properties of epoxy resins with the rapid cure of unsaturated polyester resins (UPEs), which make them suitable product for various industrial applications such as surface coatings, adhesives, printed circuit board coatings, radiation curable inks, spherical lens materials, composite, etc.<sup>15–25</sup> From structural point of view, VERs are the addition products between different epoxy resins and unsaturated monocarboxylic acids.<sup>15–19</sup> By means of the two terminal reactive double bonds, VERs can easily form crosslinked network structures by a free-radical polymerization mechanism, with or without other comonomers.

Several research workers including Gawdzik and Matynia,<sup>26</sup> Agrawal et al.,<sup>27,28</sup> and Bajpai et al.<sup>29</sup> have studied the kinetics of the reaction of carboxyl with epoxy groups. The kinetics of addition esterification of cycloaliphatic epoxies with methacrylic acid in the presence of triphenylphosphine<sup>30</sup> and monoepoxy compounds with benzoic acid<sup>31</sup> and caproic acid<sup>32</sup> in the presence of tertiary amines have been investigated, which revealed the second-order rate kinetics. Pal et al.<sup>33,34</sup> have synthesized VERs using bisphenol-A based epoxy resin, acrylic acid, and triphenylphosphine as catalyst, in the presence and absence of monoepoxies as a reactive diluent, and found that the reaction followed first-order rate kinetics. Srivastava et al.<sup>35</sup> have studied kinetics of VER synthesis using bisphenol-A based epoxy resin and methacrylic acid, in the presence of tertiary amines (i.e., triethyl, tripropyl, and tributyl amines), in the temperature range of 80–100°C. They also found that the reactions followed first-order rate kinetics. Rafizadeh et al.<sup>36</sup> conducted the reaction between bisphenol A based epoxy resin and methacrylic acid under both stoichiometric and nonstoichiometric conditions, in the presence of triphenylphosphine as catalyst. They examined the first-order rate equation and mechanism based rate and concluded that there was deviation from the first-order rate equation. The synthesis of VER, based on cardanol, and the kinetics of esterification of such resins are still untouched by the scientific community. In this work, we have reported the results of kinetic studies of cardanol-based epoxidized novolac VER (CNEVER) synthesis via esterification of epoxy resin with methacrylic acid, in the presence of triphenylphosphine as catalyst, in the temperature range of 80–100°C. On the basis of the reaction mechanism, a rate equation was derived and rate constant was

calculated. The agreement between the experimental data and calculated data was excellent.

### Reaction mechanism

Reaction between cardanol-based epoxidized novolac resin (CNE) and methacrylic acid can be represented as:

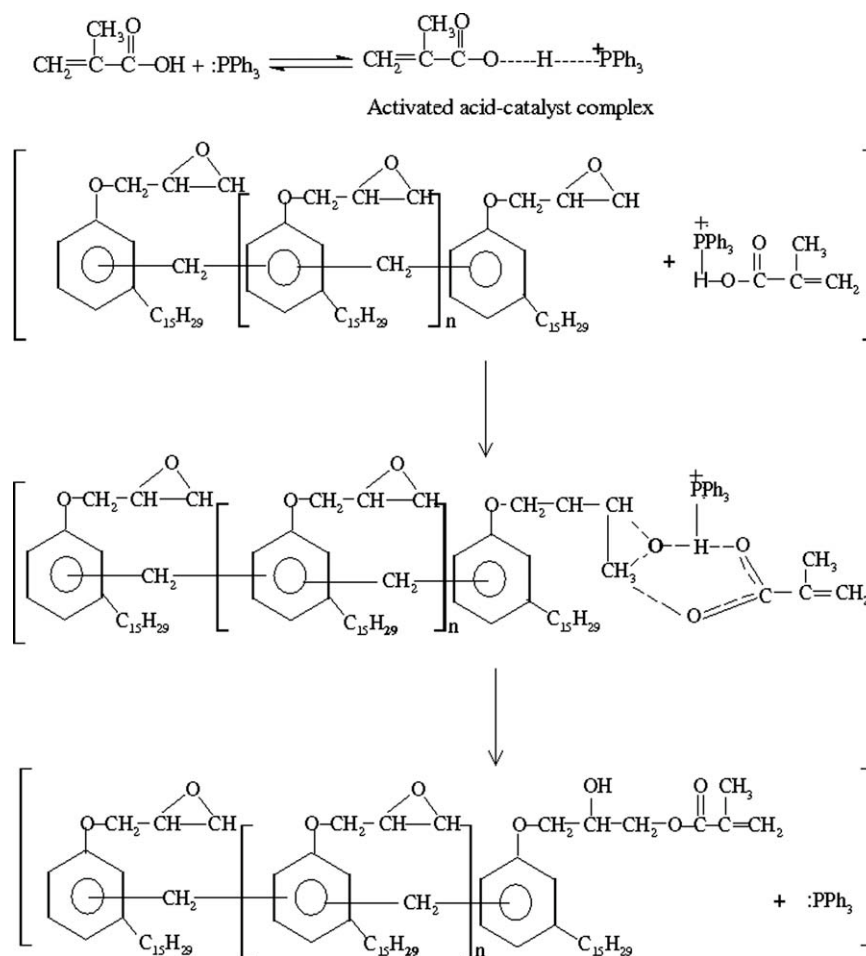


where A and B are methacrylic acid and epoxy resin, respectively. Pal et al.<sup>34</sup> conducted the reaction using 1.0 mol bisphenol-A epoxy resin and 0.9 mol acrylic acid, in the presence of triphenylphosphine catalyst, at 70–90°C. They applied a first-order rate equation, as follows:

$$-r_A = \frac{-dc_A}{dt} = kc_A \quad (2)$$

where  $c_A$  is the acid concentration and  $-r_A$  is the rate of acid consumption during the course of reaction. Their experimental data have good agreement up to 86% conversion. However, examination of  $\ln(c_{A0}/c_A)$  versus time curves, reported by Pal et al.,<sup>34</sup> revealed that all experimental data were above the first-order rate equation. Furthermore, there was increasing deviation between the experimental data and the model, by time. It was attributed to the selection of the first-order rate equation and  $k(\text{acid}) \gg 1$  assumption. Hence, the reaction mechanism should be to study present more realistic rate equation.

Scheme 1 showed the mechanism of esterification of CNE, in the presence of triphenylphosphine as catalyst. It showed that the reaction proceeded through the acid catalyst complex that worked as initiator by attacking on oxygen of the epoxy ring to form a hydroxyl group by abstracting the proton. Simultaneously, the carboxylate anion released by the activated complex attacked on the terminal carbon of the epoxy ring, forming an ester linkage with the regeneration of the catalyst. Epoxy ring might have been under severe strain and, therefore, its bond angle deviated from hybrid bond angles. Therefore, ring-opening reaction of epoxy ring and COOH acid group was dominant. Hence, there was slight chance for reaction between the produced OH group and COOH acid group. Furthermore, in this study, the acid concentration was chosen to be less than stoichiometric amount. Consequently, there was no extra acid to compete in the reaction by OH group. On the other hand, the regression coefficient of mechanistic rate equation curve fitting is too close to 1.0, as it will be shown. Hence, it was believed



Scheme 1 Mechanism of esterification of epoxy resin initiated by acid catalyst complex.

that there were no further side reactions. The mechanism has been given in the Appendix.

## EXPERIMENTAL

### Materials

Cardanol (Dheer Gramodyog, Kanpur), formaldehyde (40% solution from Qualikem Industries, New Delhi), *p*-toluene sulfonic (PTSA; E.Merck, New Delhi), methanol (BDH), epichlorohydrin (Ranbaxy Laboratories, Punjab), sodium hydroxide, methacrylic acid, and triphenylphosphine (CDH Pvt. Ltd, New Delhi), styrene, benzoyl peroxide, and hydroquinone (E.Merck, New Delhi) were used during the investigation.

### Methods

Novolac resins with mole ratio 1 : 0.5, 1 : 0.6, 1 : 0.7, and 1 : 0.8 of cardanol (C) : formaldehyde (F) were prepared using PTSA as catalyst (0.5% based on cardanol) dissolved in 2 mL methanol under

warm conditions by a method given in the past.<sup>11</sup> Half of catalyst solution was added to cardanol (about 30 g), charged in a three-necked round bottom flask fitted with a Leibig's condenser and mechanical stirrer. The remaining half of the methanolic solution of catalyst was added to the formaldehyde (40%) and this was added to the cardanol drop wise within 1 h, once the temperature of the reaction kettle was maintained to 120°C. Samples were drawn at regular intervals of 45 min from the reaction mixture, taken in a three-necked round bottom flask, for determining the free-phenol (as per ASTM standard D 1312-56) and free-formaldehyde content (as per ISO standard 9397). The reaction product was cooled and dried under vacuum at 60°C overnight before purification by column chromatography. A resin solution prepared with *n*-hexane, charged to the silica gel column chromatographic purification, was adopted mainly to remove the unreacted components, impurities etc., from the methylolated cardanol. Purification was effected using the effluent mixture of ethyl acetate-benzene (60 : 40).

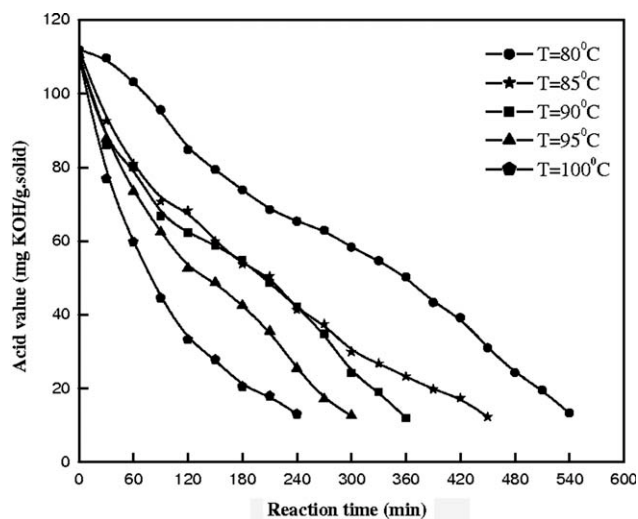


Figure 1 Acid value versus reaction time for CNEVER<sub>5</sub>.

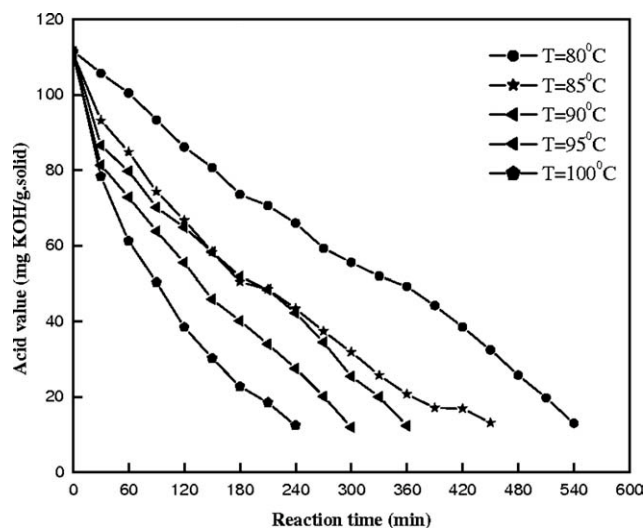


Figure 3 Acid value versus reaction time for CNEVER<sub>7</sub>.

The novolac resins (CFN), thus formed, were treated with molar excess of epichlorohydrin and 40% solution of sodium hydroxide at 120°C for about 10 h. The formed products were vacuum distilled for the removal of excess of epichlorohydrin. The epoxide equivalent weights (EEW) of CNE resin were found to be 414 eq g<sup>-1</sup>, 454 eq g<sup>-1</sup>, 320 eq g<sup>-1</sup>, and 439 eq g<sup>-1</sup>, respectively, as determined by pyridinium chloride method.<sup>37</sup>

CNEVERs were prepared by using the mole ratio 1 : 0.9 of CNE and methacrylic acid. The reaction was carried out in the presence of triphenylphosphine (TPP) catalyst (1 phr by weight of the resin) and hydroquinone (200 ppm as inhibitor) at 80°, 85°, 90°, 95°, and 100°C in nitrogen atmosphere, and the progress of the reaction was monitored by determining the acid value intermittently by the method of

Ogg et al.<sup>38</sup> The extent of the reaction and number average degree of polymerization was calculated using Carothers' equation.<sup>39</sup> To remove the free methacrylic acid, the prepared resin was dissolved in benzene and treated with potassium carbonate, stirring for 2 h at 30°C. The acid, in the form of an acid salt, was extracted by water and benzene was evaporated using a Rotovap<sup>TM</sup> evaporator under vacuum.<sup>40</sup> These resins were designated as CNEVER<sub>5</sub>, CNEVER<sub>6</sub>, CNEVER<sub>7</sub>, and CNEVER<sub>8</sub>, respectively. The resins were characterized for their structures by FT-IR spectroscopy (Perkin-Elmer FT-IR, RX-1 spectrophotometer).

The activation energy ( $E_a$ ) and frequency factor ( $Z$ ) were calculated using the Arrhenius equation.

$$k_T = Ze^{-E_a/RT} \quad (3)$$

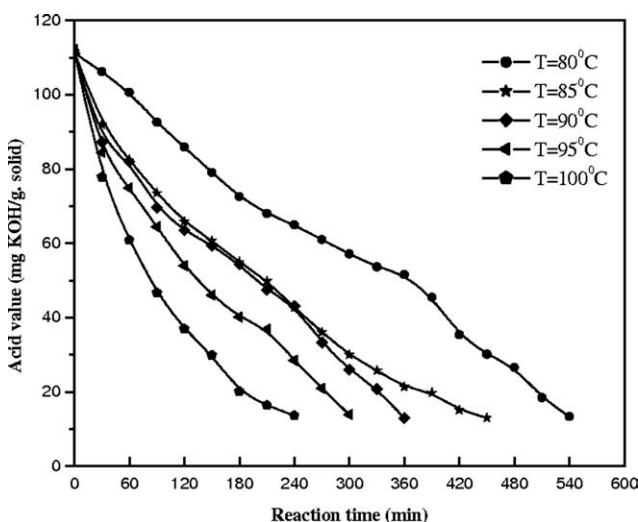


Figure 2 Acid value versus reaction time for CNEVER<sub>6</sub>.

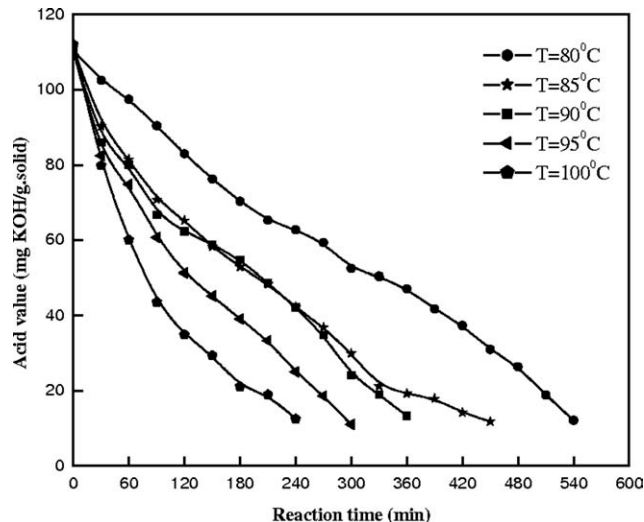


Figure 4 Acid value versus reaction time for CNEVER<sub>8</sub>.

TABLE I  
Extent of Reaction ( $p$ ) and Degree of Polymerization ( $X_n$ ) with Time for CNEVER<sub>5</sub>

Time (min)	80°C		85°C		90°C		95°C		100°C	
	$p$	$X_n$	$p$	$X_n$	$p$	$X_n$	$p$	$X_n$	$p$	$X_n$
30	0.02	1.02	0.17	1.20	0.22	1.27	0.21	1.24	0.30	1.40
60	0.08	1.08	0.28	1.36	0.27	1.35	0.34	1.47	0.46	1.77
90	0.15	1.16	0.37	1.53	0.40	1.60	0.43	1.70	0.60	2.30
120	0.24	1.30	0.39	1.59	0.44	1.70	0.52	1.99	0.70	2.96
150	0.29	1.38	0.46	1.79	0.47	1.79	0.56	2.13	0.75	3.43
180	0.34	1.48	0.52	1.97	0.50	1.91	0.62	2.40	0.81	4.37
210	0.39	1.58	0.55	2.09	0.56	2.13	0.68	2.80	0.84	4.84
240	0.42	1.65	0.63	2.48	0.62	2.41	0.77	3.70	0.88	6.07
270	0.44	1.71	0.67	2.70	0.68	2.84	0.85	5.02		
300	0.48	1.83	0.73	3.27	0.78	3.84	0.89	6.24		
330	0.51	1.94	0.76	3.59	0.83	4.64				
360	0.55	2.09	0.79	4.01	0.89	6.42				
390	0.61	2.38	0.82	4.56						
420	0.65	2.60	0.85	5.02						
450	0.72	3.18	0.89	6.40						
480	0.78	3.87								
510	0.83	4.59								
540	0.88	6.05								

where  $T$  is temperature (K) and  $R$  is the gas constant.

The entropy of activation ( $\Delta S$ ) was calculated using following equation:

$$k_T = \frac{k_b T}{h} e^{-E_a/RT} e^{\Delta S/R} \quad (4)$$

where  $K_b$  is Boltzmann's constant and  $h$  is Planck's constant.

The enthalpy of activation ( $\Delta H$ ) and free energy of activation ( $\Delta G$ ) were calculated using the following expressions.

$$\Delta H = E_a - RT \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

## RESULTS AND DISCUSSION

The esterification of CNE<sub>5</sub>, CNE<sub>6</sub>, CNE<sub>7</sub>, and CNE<sub>8</sub> was carried out at 80°, 85°, 90°, 95°, and 100°C, in the presence of triphenylphosphine as catalyst. Figures 1–4 showed the esterification of CNE and methacrylic acid, in the presence of triphenylphosphine. The results were typical of the behavior generally observed for polyesterification reactions. It was apparent from the figures that the acid value

TABLE II  
Extent of Reaction ( $p$ ) and Degree of Polymerization ( $X_n$ ) with Time for CNEVER<sub>6</sub>

Time (min)	80°C		85°C		90°C		95°C		100°C	
	$p$	$X_n$	$p$	$X_n$	$p$	$X_n$	$p$	$X_n$	$p$	$X_n$
30	0.05	1.04	0.17	1.20	0.21	1.25	0.25	1.31	0.30	1.40
60	0.09	1.10	0.26	1.33	0.26	1.33	0.33	1.46	0.46	1.76
90	0.17	1.19	0.34	1.48	0.37	1.55	0.43	1.68	0.58	2.23
120	0.23	1.28	0.41	1.63	0.43	1.68	0.52	1.97	0.67	2.73
150	0.29	1.38	0.46	1.76	0.47	1.79	0.59	2.26	0.73	3.27
180	0.35	1.49	0.51	1.92	0.51	1.94	0.64	2.55	0.82	4.48
210	0.39	1.58	0.55	2.10	0.57	2.18	0.67	2.75	0.85	5.21
240	0.42	1.65	0.62	2.41	0.61	2.38	0.75	3.41	0.89	5.95
270	0.45	1.75	0.68	2.78	0.70	2.97	0.81	4.36		
300	0.49	1.85	0.73	3.25	0.77	3.64	0.88	5.88		
330	0.52	1.96	0.77	3.69	0.81	4.35				
360	0.54	2.03	0.81	4.27	0.88	6.11				
390	0.59	2.27	0.82	4.53						
420	0.68	2.83	0.86	5.51						
450	0.73	3.23	0.87	6.12						
480	0.76	3.58								
510	0.83	4.76								
540	0.88	6.02								

**TABLE III**  
Extent of Reaction ( $p$ ) and Degree of Polymerization ( $X_n$ ) with Time for CNEVER<sub>7</sub>

Time (min)	80°C		85°C		90°C		95°C		100°C	
	$p$	$X_n$	$p$	$X_n$	$p$	$X_n$	$p$	$X_n$	$p$	$X_n$
30	0.05	1.05	0.16	1.18	0.22	1.27	0.26	1.33	0.30	1.39
60	0.10	1.11	0.24	1.29	0.28	1.37	0.34	1.48	0.45	1.75
90	0.16	1.18	0.33	1.45	0.37	1.54	0.42	1.67	0.55	2.08
120	0.23	1.28	0.40	1.61	0.42	1.66	0.50	1.89	0.65	2.63
150	0.28	1.36	0.47	1.82	0.48	1.82	0.59	2.24	0.73	3.23
180	0.34	1.48	0.54	2.07	0.53	2.03	0.64	2.52	0.80	4.07
210	0.37	1.54	0.56	2.14	0.57	2.16	0.69	2.90	0.83	4.77
240	0.41	1.63	0.61	2.37	0.62	2.43	0.75	3.47	0.89	6.34
270	0.47	1.80	0.66	2.69	0.69	2.89	0.82	4.44		
300	0.50	1.91	0.71	3.08	0.77	3.72	0.89	6.45		
330	0.53	2.03	0.77	3.67	0.82	4.50				
360	0.56	2.13	0.81	4.36	0.89	6.36				
390	0.60	2.34	0.85	5.06						
420	0.66	2.64	0.85	5.08						
450	0.71	3.05	0.88	6.08						
480	0.77	3.69								
510	0.82	4.55								
540	0.88	6.16								

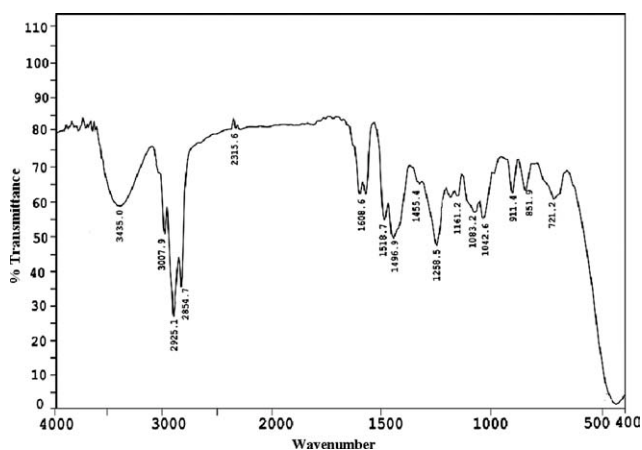
decreased with increase in reaction time and was not linear in the initial stages of the reaction. This was attributed to the high concentration of the reactive sites and the greater possibility of association of acid and epoxide groups. The linearity of the plots in the conversion region (>74%) revealed that the reactivity of the functional group was independent of molecular size, which was a characteristic of the polyesterification reactions. The number-average degree of polymerization ( $X_n$ ) for the esters of CNE<sub>5</sub>, CNE<sub>6</sub>, CNE<sub>7</sub>, and CNE<sub>8</sub> prepared at 80°, 85°, 90°, 95°, and 100°C, calculated using Carother's equation, are given in Tables I, II, III, and IV, respec-

tively. At all temperatures the  $X_n$  of all esters increased with reaction time. With the increase in reaction temperature by 10°C, the reaction time for a particular extent of reaction in the conversion region (>50% and <88%) reduced by half for all the esters. The plot of  $X_n$  versus reaction time showed nonlinearity in the initial stages (<50% conversion) and higher conversion region (>88%), which again was a characteristic of the catalyzed esterification reaction.<sup>39</sup>

Figures 5 and 6 showed the FT-IR spectra of synthesized CNE and CNEVER, respectively. It was evident from the figure (Fig. 5) that there was a broad

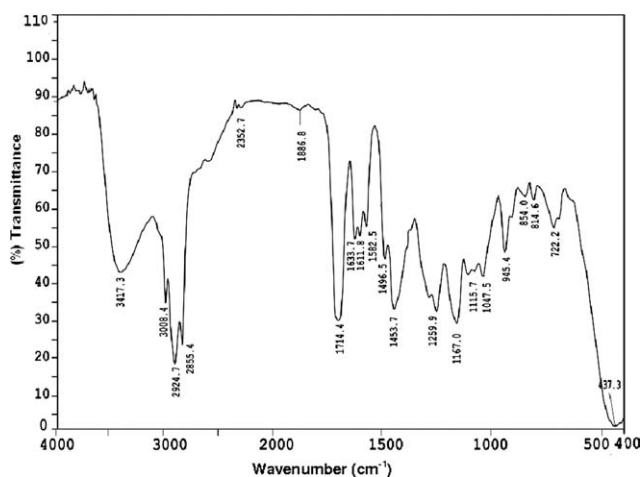
**TABLE IV**  
Extent of Reaction ( $p$ ) and Degree of Polymerization ( $X_n$ ) with Time for CNEVER<sub>8</sub>

Time (min)	80°C		85°C		90°C		95°C		100°C	
	$P$	$X_n$	$p$	$X_n$	$p$	$X_n$	$p$	$X_n$	$p$	$X_n$
30	0.07	1.07	0.19	1.22	0.22	1.27	0.25	1.31	0.29	1.37
60	0.12	1.13	0.27	1.34	0.27	1.35	0.32	1.44	0.46	1.78
90	0.18	1.21	0.36	1.53	0.40	1.60	0.45	1.74	0.61	2.37
120	0.25	1.31	0.41	1.64	0.44	1.70	0.53	2.03	0.69	2.87
150	0.31	1.42	0.48	1.82	0.47	1.79	0.59	2.27	0.74	3.32
180	0.36	1.53	0.52	1.99	0.50	1.91	0.65	2.57	0.81	4.33
210	0.41	1.63	0.56	2.15	0.56	2.13	0.70	2.95	0.83	4.70
240	0.43	1.69	0.62	2.42	0.62	2.41	0.77	3.74	0.89	6.31
270	0.46	1.78	0.67	2.73	0.68	2.84	0.83	4.71		
300	0.53	1.99	0.73	3.25	0.78	3.84	0.90	6.80		
330	0.54	2.06	0.81	4.29	0.83	4.64				
360	0.57	2.19	0.83	4.61	0.88	6.00				
390	0.62	2.43	0.84	4.87						
420	0.66	2.68	0.87	5.74						
450	0.72	3.14	0.89	6.53						
480	0.76	3.59								
510	0.83	4.66								
540	0.89	6.38								

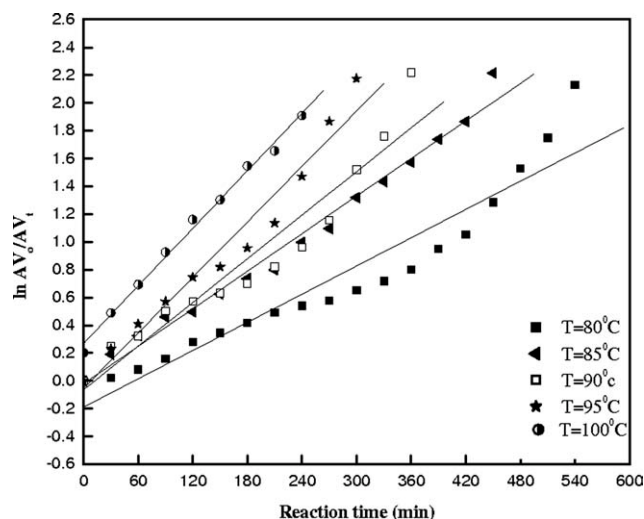


**Figure 5** FT-IR spectrum of cardanol-based epoxidized novolac resin, CNE<sub>7</sub>.

band near 3200–3600  $\text{cm}^{-1}$ , due to the hydroxyl stretching vibration of the phenolic hydroxyl group. The absorption band for the methylene group ( $-\text{CH}_2-$ ) was clearly visible near 2854  $\text{cm}^{-1}$  in the spectrum of the epoxidized novolac. Absorption bands near 1496 and 1582  $\text{cm}^{-1}$  and small peak near 1042  $\text{cm}^{-1}$  appeared in the spectrum. These could be possibly due to the semicircle stretching vibration of the substituted aromatics, giving an indication of the presence of a substituted benzene nucleus in all of the polymer samples. The plane C–H deformation associated with aromatic hydrogen atoms was seen in the spectrum by the peak appearance near 1161  $\text{cm}^{-1}$ . The shifting of peak related to the phenolic hydroxyl indicated the reaction of the oxirane group of the epoxy and hydroxyl group of the novolacs. This was further confirmed by the peak appearance near 1258  $\text{cm}^{-1}$ . The absorption bands near 911  $\text{cm}^{-1}$  and 851  $\text{cm}^{-1}$  was due to the ring deformation of the terminal epoxy group, which confirmed the presence of the epoxy groups in the



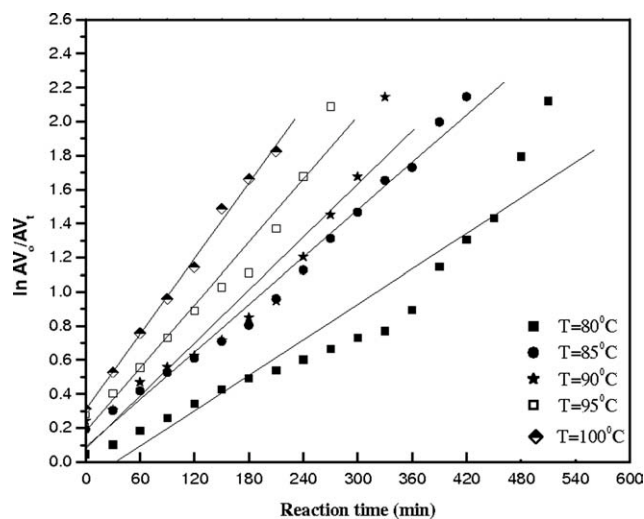
**Figure 6** FT-IR spectrum of CNEVER<sub>7</sub> sample.



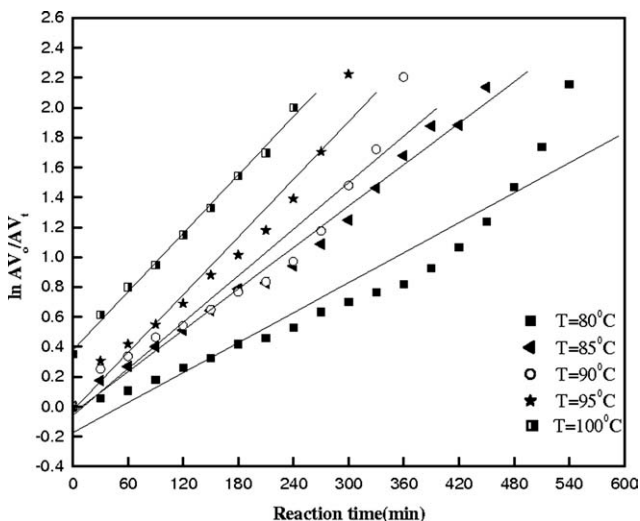
**Figure 7**  $\ln AV_0/AV_t$  versus time for CNEVER<sub>5</sub>, 80°C,  $y = 3.39 \times 10^{-3} \times (r = 0.9541)$ ; 85°C,  $y = 4.5 \times 10^{-3} \times (r = 0.9922)$ ; 90°C,  $y = 5.23 \times 10^{-3} \times (r = 0.9593)$ ; 95°C,  $y = 6.65 \times 10^{-3} \times (r = 0.9796)$ ; 100°C,  $y = 8.62 \times 10^{-3} \times (r = 0.9969)$ .

polymer. The band at 1582  $\text{cm}^{-1}$ , assigned to phenolic rings, confirmed this observation.

The disappearance of peak near 911  $\text{cm}^{-1}$  due to oxirane group of epoxide linkage and appearance of a new peak near 1714  $\text{cm}^{-1}$  (Fig. 6), due to ester functional group of VER, confirmed the formation of CNEVER. Further, there appeared a peak near 1633  $\text{cm}^{-1}$  which might be attributed to the formation of double bond during the synthesis of VER. The occurrence of the band near 1167  $\text{cm}^{-1}$  was probably due to the C–O–C stretching and the peak at 945  $\text{cm}^{-1}$  depicted the out-of-plane bending



**Figure 8**  $\ln AV_0/AV_t$  versus time for CNEVER<sub>6</sub>, 80°C,  $y = 3.47 \times 10^{-3} \times (r = 0.9516)$ ; 85°C,  $y = 4.65 \times 10^{-3} \times (r = 0.9926)$ ; 90°C,  $y = 5.19 \times 10^{-3} \times (r = 0.9617)$ ; 95°C,  $y = 6.14 \times 10^{-3} \times (r = 0.9791)$ ; 100°C,  $y = 8.53 \times 10^{-3} \times (r = 0.9977)$ .

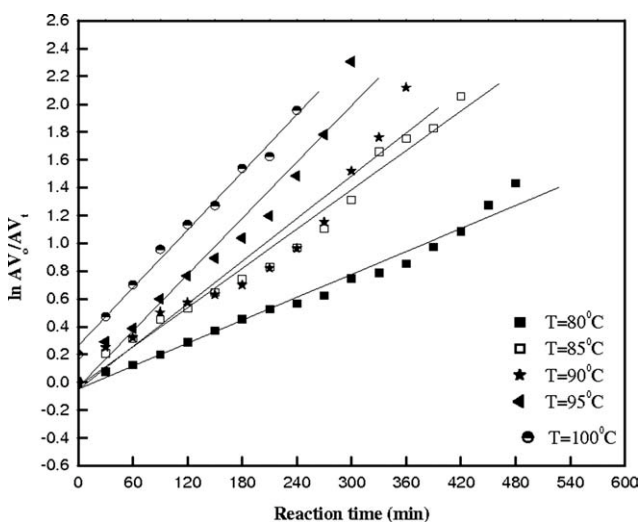


**Figure 9**  $\ln AV_o/AV_t$  versus time for CNEVER<sub>7</sub>, 80°C,  $y = 3.34 \times 10^{-3} \times (r = 0.9541)$ ; 85°C,  $y = 4.61 \times 10^{-3} \times (r = 0.9934)$ ; 90°C,  $y = 5.18 \times 10^{-3} \times (r = 0.964717)$ ; 95°C,  $y = 6.43 \times 10^{-3} \times (r = 0.9782)$ ; 100°C,  $y = 8.68 \times 10^{-3} \times (r = 0.9978)$ .

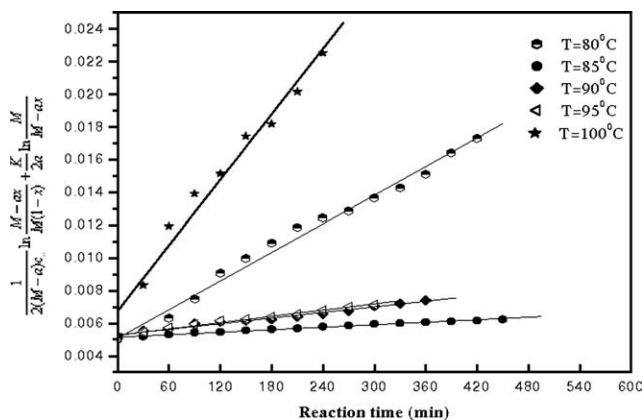
of vinyl ester monomer. These findings were consistent with the previous work by Rodriguez.<sup>41</sup> This confirmed the formation of VER.

In the first step, the first-order rate equation, which was previously suggested by Pal et al.,<sup>33</sup> was fitted on the experimental data. Rate constants were calculated using the well-established least square method.<sup>42</sup> Relationship for the first-order rate equation is:

$$\ln \frac{AV_t}{AV_o} = -k_T t \Rightarrow k_T = - \frac{\sum_{i=1}^n t_i \ln \left( \frac{AV_t}{AV_o} \right)}{\sum_{i=1}^n t_i^2} \quad (7)$$



**Figure 10**  $\ln AV_o/AV_t$  versus time for CNEVER<sub>8</sub>, 80°C,  $y = 2.75 \times 10^{-3} \times (r = 0.9891)$ ; 85°C,  $y = 4.71 \times 10^{-3} \times (r = 0.9896)$ ; 90°C,  $y = 5.12 \times 10^{-3} \times (r = 0.9612)$ ; 95°C,  $y = 6.74 \times 10^{-3} \times (r = 0.9795)$ ; 100°C,  $y = 8.65 \times 10^{-3} \times (r = 0.9957)$ .

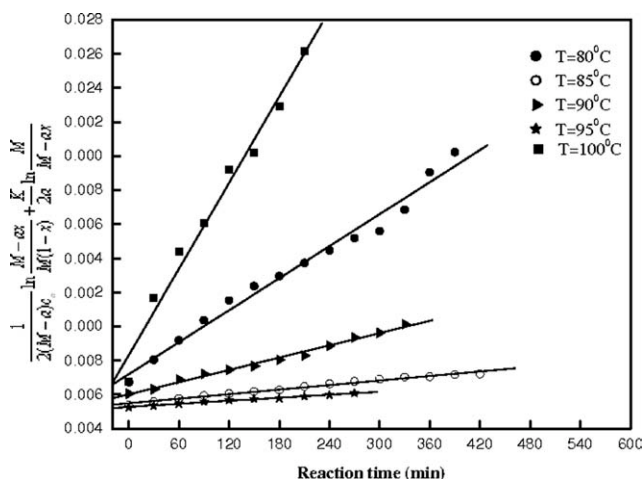


**Figure 11** Results of mechanism based equation of CNEVER<sub>5</sub>.

Figures 7–10 showed plots between  $[\ln(AV_o/AV_t)]$  and reaction time ( $t$ ) for CNEVER<sub>5</sub>, CNEVER<sub>6</sub>, CNEVER<sub>7</sub>, and CNEVER<sub>8</sub>, respectively. These plots showed the results of the first-order rate equation curve fitting on the data. In general, this result was acceptable. However, the trend of the experimental data showed that there was some systematic deviation from the first-order rate equation. This sort of trend could be observed from the work of Pal et al.,<sup>34</sup> although they used acrylic acid instead of methacrylic acid. Therefore, it was obvious that the first-order rate equation was not necessarily adequate. Consequently, in the next step, the mechanistic rate equation was tried. Relationship of least square method application for the mechanistic based rate equation is:

$$\frac{1}{2(M-a)AV_o} \ln \frac{M-ap}{M(1-p)} = K't - KA \quad (8)$$

where  $A = \frac{1}{2a} \ln \frac{M}{M-ap}$ .



**Figure 12** Results of mechanism based equation of CNEVER<sub>6</sub>.



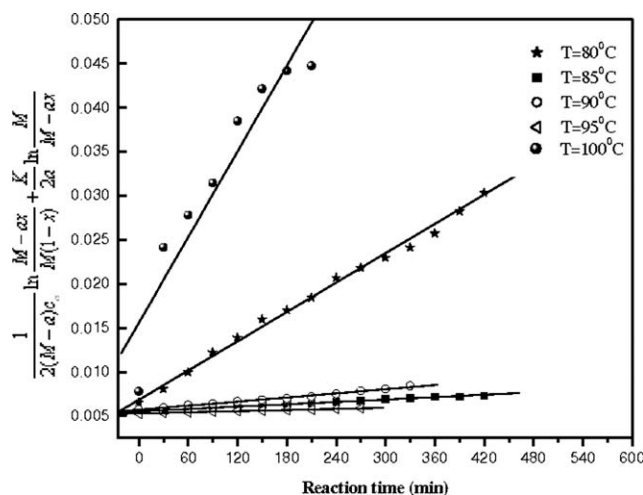


Figure 13 Results of mechanism based equation of CNEVER<sub>7</sub>.

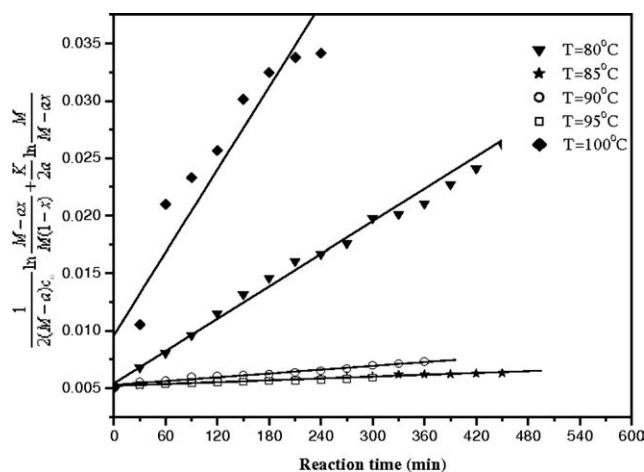


Figure 14 Results of mechanism based equation of CNEVER<sub>8</sub>.

$$\Rightarrow \begin{bmatrix} K \\ K' \end{bmatrix} = \text{inv} \left( \begin{bmatrix} \sum_{i=1}^n t_i^2 & -\sum_{i=1}^n A_i t_i \\ \sum_{i=1}^n A_i t_i & -\sum_{i=1}^n A_i^2 \end{bmatrix} \right) \times \begin{bmatrix} \sum_{i=1}^n \left( \frac{1}{2(M-a)AV_o} \ln \frac{M-ap}{M(1-p)} \right) t_i \\ \sum_{i=1}^n \left( \frac{1}{2(M-a)AV_o} \ln \frac{M-ap}{M(1-p)} \right) A_i \end{bmatrix} \quad (9)$$

Figures 11–14 showed the results of the mechanism based rate equation curve fitting for CNEVER<sub>5</sub>, CNEVER<sub>6</sub>, CNEVER<sub>7</sub>, and CNEVER<sub>8</sub>, respectively. The experimental data was randomly distributed around the theoretical concentrations. This distribu-

tion could be attributed to the random errors in measurements. Table V presented the numerical values of rate constant for nonstoichiometric condition at different temperatures along with their regression coefficients. The regression coefficient *R* showed the superiority of the first-order rate equation. Thus the first-order rate equation was more realistic.

Figure 15 showed plots between  $\ln k_T$  versus reciprocal of the temperature, which indicated that they obeyed the Arrhenius law. The slope and intercept of the plots obtained by regression analysis were used to calculate the energy of activation and frequency factor for the esterification reaction. Using these values of  $E_a$  and  $Z$ , the thermodynamic parameters, entropy, enthalpy, and free energy, of the activation were calculated and the values have been tabulated in Table VI. It was clear from Table VI

TABLE V  
Rate Constants and Regression Constants

Results based on the first-order rate equation, eq. 2												
<i>T</i> (°C)	CNEVER <sub>5</sub>		CNEVER <sub>6</sub>		CNEVER <sub>7</sub>		CNEVER <sub>8</sub>					
	<i>k</i>	<i>R</i>	<i>k</i>	<i>R</i>	<i>k</i>	<i>R</i>	<i>k</i>	<i>R</i>	<i>k</i>	<i>R</i>		
80	0.042	0.937	0.044	0.987	0.044	0.924	0.047	0.915				
85	0.068	0.962	0.068	0.911	0.067	0.959	0.071	0.925				
90	0.061	0.991	0.059	0.987	0.061	0.940	0.061	0.910				
95	0.063	0.905	0.064	0.919	0.066	0.917	0.067	0.956				
100	0.078	0.994	0.077	0.927	0.075	0.959	0.078	0.994				
Results based on the mechanism based rate equation, eqs. (9) and (10)												
<i>T</i> (°C)	CNEVER <sub>5</sub>			CNEVER <sub>6</sub>			CNEVER <sub>7</sub>			CNEVER <sub>8</sub>		
	<i>k</i>	<i>K</i>	<i>R</i>	<i>k</i>	<i>K</i>	<i>R</i>	<i>k</i>	<i>K</i>	<i>R</i>	<i>k</i>	<i>K</i>	<i>R</i>
80	0.001	0.043	0.994	0.001	0.045	0.993	0.001	0.073	0.996	0.001	0.061	0.995
85	0.001	0.009	0.989	0.001	0.012	0.989	0.001	0.012	0.990	0.001	0.009	0.989
90	0.002	0.012	0.988	0.002	0.017	0.992	0.002	0.014	0.992	0.002	0.012	0.988
95	0.002	0.012	0.991	0.002	0.009	0.986	0.002	0.009	0.989	0.002	0.009	0.989
100	0.003	0.004	0.958	0.003	0.005	0.969	0.003	0.005	0.973	0.003	0.004	0.959

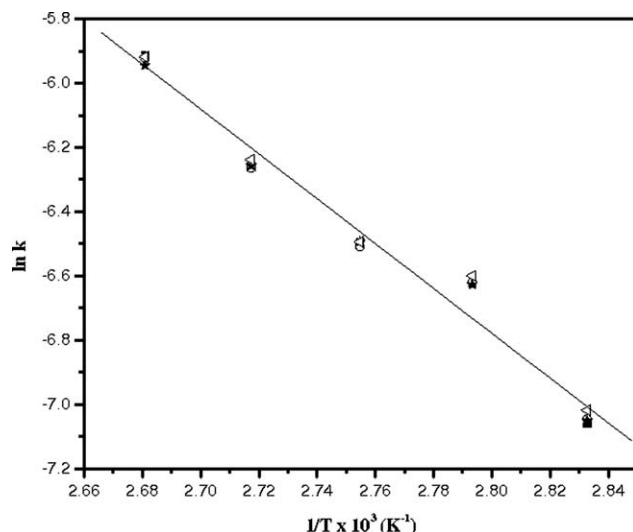


Figure 15 Arrhenius rate constant plot.

that  $E_a$ ,  $Z$ , and  $\Delta H$  values were almost the same for all the vinyl esters, which confirmed that the reactivity of the CNEs toward methacrylic acid, in the presence of triphenylphosphine, was almost the same. The thermodynamic parameters  $\Delta G$  and  $\Delta S$  were positive and negative, respectively, for CNEVER<sub>5</sub>, CNEVER<sub>6</sub>, CNEVER<sub>7</sub>, and CNEVER<sub>8</sub> (Table VI). As  $\Delta G > 0$  and  $\Delta S < 0$  for the reaction, it could be said that the process was spontaneous and irreversible. The high negative value of  $\Delta S$  indicated the formation of ordered activated complex in the synthesis of VERs.

### CONCLUSIONS

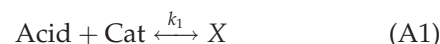
1. The esterification of CNE with methacrylic acid, in the presence of triphenylphosphine as catalyst, followed first-order reaction kinetics. The first-order rate equation and mechanism based rate equation were fitted on the experimental data by the least square method. A comparison of mechanism based rate equation and experimental data shows an excellent agreement.
2. The reaction proceeded through the transitory interaction of acid and triphenylphosphine by forming an acid catalyst complex.

3. The reaction was spontaneous, irreversible, and produced a highly ordered activated complex.

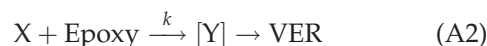
Authors are thankful to the Director, Defense Materials Stores Research and Development Establishment (DMSRDE, a unit of Defense Ministry, Government of India) Kanpur, India, who had permitted to do the work in the organization. The authors thank S. B. Yadaw, Head Composite material Division. Special thanks to Kamal Dheer for providing cardanol well in time.

### APPENDIX

#### Mechanism of esterification of cardanol-based epoxidized novolac resin



$k_{-1}$  (activated acid catalyst complex)



According to the above steps, the rate of disappearance of acid may be obtained as:

$$\frac{d[\text{acid}]}{dt} = k[X][\text{epoxy}] \quad (\text{A3})$$

where,

$$[X] = \frac{k_1[\text{acid}][\text{cat}]}{k_{-1} + k[\text{epoxy}]} \quad (\text{A4})$$

Therefore, the rate of disappearance of acid is obtained as:

$$-\frac{d[\text{acid}]}{dt} = \frac{kk_1[\text{acid}][\text{cat}][\text{epoxy}]}{k_{-1} + k[\text{epoxy}]} \quad (\text{A5})$$

As step (3) is fast and considering  $k_{-1}$  is  $\gg k[\text{epoxy}]$ , the above rate law reduces to,

$$-\frac{d[\text{acid}]}{dt} = \frac{kk_1[\text{acid}][\text{cat}][\text{epoxy}]}{1 + k[\text{epoxy}]} \quad (\text{A6})$$

or

$$-\frac{dc_A}{dt} = \frac{K'c_{ACB}}{1 + Kc_B} \quad \text{where } K' = kK^1[\text{cat}] \quad (\text{A7})$$

TABLE VI  
Thermodynamic Parameters

Sample Code	Activation Energy, $E_a$ (kJmol <sup>-1</sup> )	Entropy, $\Delta S$ (kJmol <sup>-1</sup> )	Enthalpy, $\Delta H$ (kJmol <sup>-1</sup> )	Free Energy, $\Delta G$ (kJmol <sup>-1</sup> )
CNEVER <sub>5</sub>	133.66	-313.91	3.15	110.79
CNEVER <sub>6</sub>	131.44	-313.81	3.15	110.76
CNEVER <sub>7</sub>	130.33	-313.85	3.15	110.78
CNEVER <sub>8</sub>	129.24	-313.57	3.16	110.68

Integration of eq. (A7), under nonstoichiometric conditions, gives:

$$\frac{1}{2(M-a)AV_0} \ln \frac{M-ap}{M(1-p)} + \frac{K}{2a} \ln \frac{M}{M-ap} = K't \quad (\text{A8})$$

where  $M = 1/0.9$ ,  $a = 1/2$ , and  $p$  is the extent of reaction.

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