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Synthesis of vinyl esters of cycloaliphatic epoxy resins: A kinetic study

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Abstract

Two cycloaliphatic epoxy resins C_1 and C_2 containing pendant glycidyl and epoxy cyclohexane functional groups, respectively were converted into their corresponding vinyl esters. The esterification reactions were performed using methacrylic acid in presence of triethyl amine/triphenyl phosphine as catalyst. In the present study four vinyl esters are prepared. The vinyl esters of C_1 and C_2 , synthesized in presence of triethyl amine are designated as C_1A , C_2A and triphenyl phosphine as C_1E , C_2E . Reaction advancement was assessed by monitoring the acid value as regular intervals. The kinetics of the esterification reactions were best described by a second order rate equation. The chemical structure of all the esters were verified by FTIR spectroscopy. The synthesis of all the esters was analysed by calculating various kinetic parameters, including activation energy, pre-exponential factor, entropy of activation, enthalpy of activation and Gibbs free energy of activation.

Keywords: Vinyl esters, cycloaliphatic epoxy resins, esterification, kinetic parameters

Introduction

Cycloaliphatic epoxy resins have gained widespread attention in recent years because of their lightweight nature, excellent impact strength, superior weather resistance, and outstanding thermal and electrical properties. Their outstanding properties make them highly suitable for use in outdoor electrical insulation application. However, the principal disadvantages of these resins are their high cost and brittle nature. Consequently, they required modification to enhance their performance ^[1, 2]. The reaction of epoxy resins with unsaturated monocarboxylic acid offers a practical route to improve their processing and curing behaviour, addressing their major drawbacks ^[3, 4]. The incorporation of carbon-carbon double bond in the resins provides reactive site to polymerize, enabling the development of materials with desired properties ^[5-7]. Epoxy resins are typically esterified with acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, etc to produce vinyl ester resins ^[8-10]. The present study employs methacrylic acid because it offers optimal reactivity during esterification and the cured product with enhanced chemical, thermal, and mechanical properties ^[11, 12]. Basic catalysts such as tertiary amines, phosphines, alkalis or onium salts are widely employed for the acid-epoxide reaction ^[13, 14]. Various parallel and consecutive side reactions usually occur during the esterification reaction, thereby affecting the physical and chemical properties of the cured resin ^[15, 16]. A comprehensive kinetic investigation is required to optimize the curing process and obtain resins with superior quality and performance ^[17-19].

Material and method

Cycloaliphatic epoxy resins CY 184 and CY 179 from Ciba Specialty Chemicals, Mumbai, methacrylic acid, triethyl amine, triphenylphosphine, pot. Hydroxide and acetone from Rituraj Enterprises, Kanpur, were used for the synthesis and characterization of esters.

Synthesis of vinyl esters

A three-neck round-bottom flask was used for the synthesis of vinyl ester resins. The central neck was fitted with a glass stirrer carrying a teflon blade through a stuffing box, whereas the side necks were equipped with a thermometer pocket and a reflux condenser.

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The reaction was conducted in an electrically heated oil bath regulated by a solid-state relay. Reaction advancement was assessed by monitoring the acid value as regular intervals. The chemical structure of all the prepared esters were verified by FTIR spectroscopy (Nicolet Impact 400D spectrophotometer) using KBr pellets.

Reaction Order and Rate Constant

The order of the reaction was calculated by integral method of analysis. The second order rate equation used for the reaction in which stoichiometric ratio of reactant is not unity can be written as follows [20]:

$$\ln(m-p)/m(1-p) = C_{AO}(m-p)k_T t \quad \text{----- (1)}$$

Where, p = extent of reaction at time ' t ' calculated by $p = 1 - AV_t/AV_o$

$m = C_{AO}/C_{BO}$ stoichiometric ratio,

C_{AO} and C_{BO} are initial concentration of resin and acid, respectively

The relation between C_{AO} and AV_o is expressed as

$$C_{AO} = 10^6 AV_o / 56100$$

The plot of $\ln(m-p)/m(1-p)$ versus reaction time would give a straight line with the slope $C_{AO}(m-1)k_T$. The energy of activation and frequency factor for the esterification reactions were calculated using Arrhenius equation.

$$k_r = Z e^{-E_a/RT}$$

where T = absolute temperature (K),

R = gas constant (8.314 J/mol K)

Entropy, Enthalpy and Free Energy of Activation:

The entropy of activation (ΔS) was calculated using the following equation: $\neq$

$$Z = \frac{k_b T}{h} e^{-E_a/RT} e^{\Delta S/R} \quad \text{----- (2)}$$

k_b = Boltzman constant and h = Plank's constant

The enthalpy of activation (ΔH) and free energy of activation (ΔG) were calculated using the following expression.

$$\Delta H = E_a - RT \quad \text{----- (3)}$$

$$\Delta G = H - T\Delta s \quad \text{----- (4)}$$

Result and Discussions

In the present study two cycloaliphatic epoxy resins: diglycidyl hexahydrophthalate (C_1 : CY-184, Epoxide equivalent weight 180) and 3, 4-epoxy cyclohexylmethyl 3' 4'- epoxy cyclohexane carboxylate (C_2 : CY-179, Epoxide

equivalent weight 140) were used for the preparation of their esters. In practice complete esterification of epoxy resins is challenging because polymerization can simultaneously occurs with the esterification reaction, resulting a gelation before the desired low acid value is reached. Consequently, an excess of epoxy resin ratio is commonly used in the esterification reactions. In the reaction epoxy resin to methacrylic acid ratio is maintained at 1: 0.9 stoichiometric ratio to prevent gelation and obtain a product with desired molecular weight [21, 22].

Synthesis of Cycloaliphatic epoxy resins based vinyl esters in presence of triethyl amine

The temperature range selected after several trails for the esterification of C_1 and C_2 in presence of triethylamine 60-75°C. To evaluate the activation parameters the esterification of C_1 and C_2 was carried out at 60° 65° 70° and 75°C. The vinyl esters of C_1 and C_2 prepared in presence of triethyl amine catalyst were designated as C_1A and C_2A , respectively. The advancement of esterification of epoxy resins with methacrylic acid has been experimentally monitored by titrating the unreacted carboxylic groups with methanolic potassium hydroxide from which the acid value was determined. The change in acid value and extent of reaction (p) with time are given in table 1. It is apparent from the table that acid value decreases with reaction time for both the esters and it become constant at about 76% conversion indicating that the reaction did not proceed further even after carrying the reaction for extra 4 hour at 60°C. Figure 1 show plot between $\ln(m-p)/m(1-p)$ versus reaction time for the synthesis of C_1A and C_2A at 60° 65° 70° and 75°C. The plot were linear at all temperature up to ~72% conversion with highly significant correlation coefficient $r > 0.99$ which confirm that the reaction followed second order kinetics.

Table 4: Variation of acid value with time at different temperature for C_1A and C_2A

Reaction Time (min.)	60°C C_1A	60°C C_2A	65°C C_1A	65°C C_2A	70°C C_1A	70°C C_2A	75°C C_1A	75°C C_2A
0	180.2	220.9	180.2	220.9	180.2	220.9	180.2	220.9
30	144.5	165.2	138.4	154.2	126.5	135.2	110.6	126.6
60	129.6	137.6	115.5	124.1	99.6	106.7	69.1	98.9
90	115.7	116.8	97.8	112.2	84.3	88.7	58.2	75.6
120	101.5	99.8	86.3	86.6	68.8	73.8	50.3	61.4
150	91.5	88.5	76.2	73.3	65.2	61.4	45.8	53.2
180	83.6	76.3	67.4	63.8	53.5	57.0	43.6	50.3
210	77.1	71.6	63.4	59.2	49.4	55.4	43.5	50.3
240	69.7	64.5	55.5	55.6	45.6	53.9	—	—
270	63.1	60.3	51.0	53.9	43.8	51.2	—	—
300	58.2	56.1	46.2	51.7	—	51.2	—	—
330	53.7	53.7	45.2	51.7	—	—	—	—
360	50.8	53.7	45.2	—	—	—	—	—
390	49.0	—	—	—	—	—	—	—
420	47.2	—	—	—	—	—	—	—
450	45.9	—	—	—	—	—	—	—

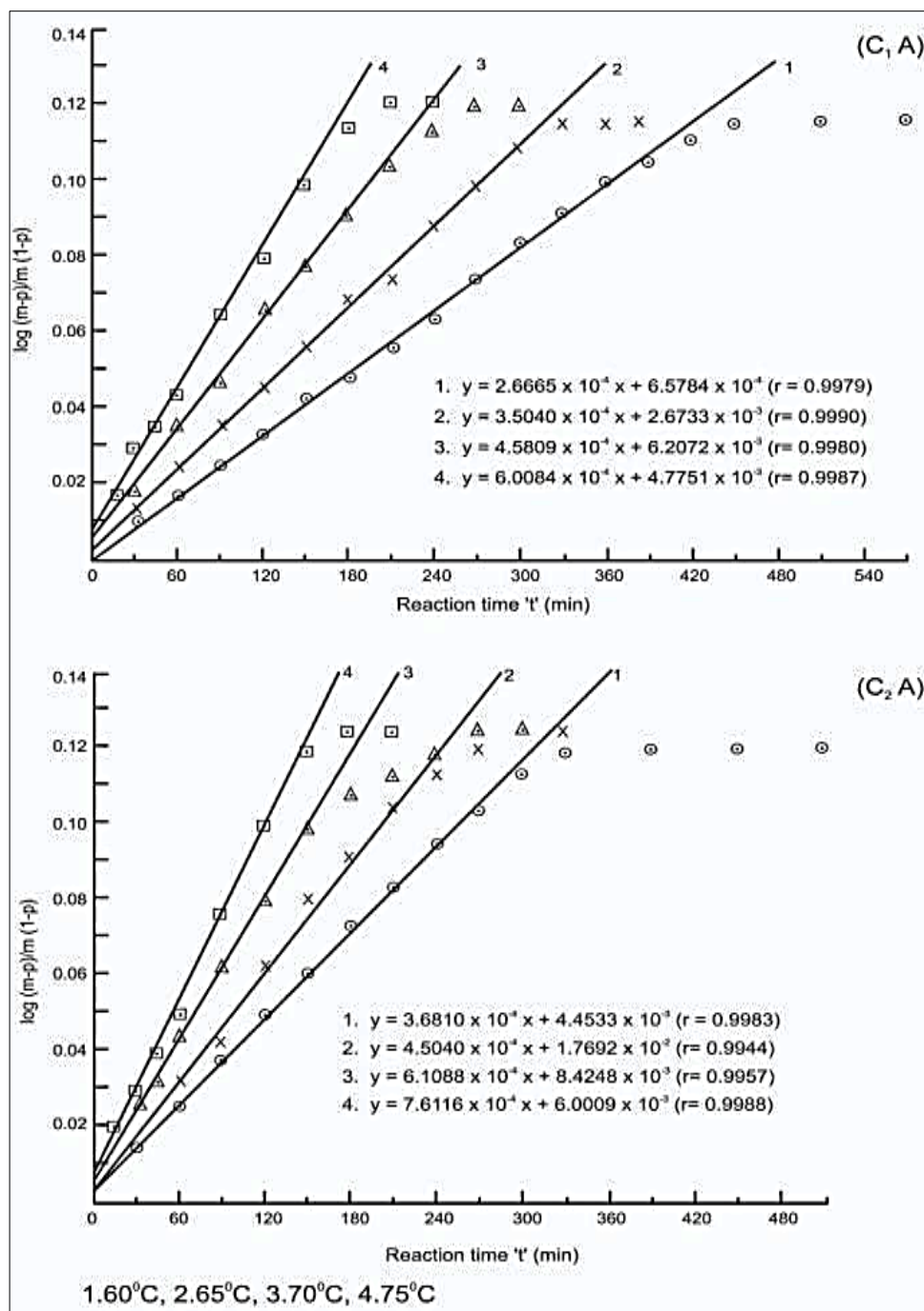


Fig 1: $\ln(m-p)/m(1-p)$ versus reaction time for the synthesis of C_1A and C_2A

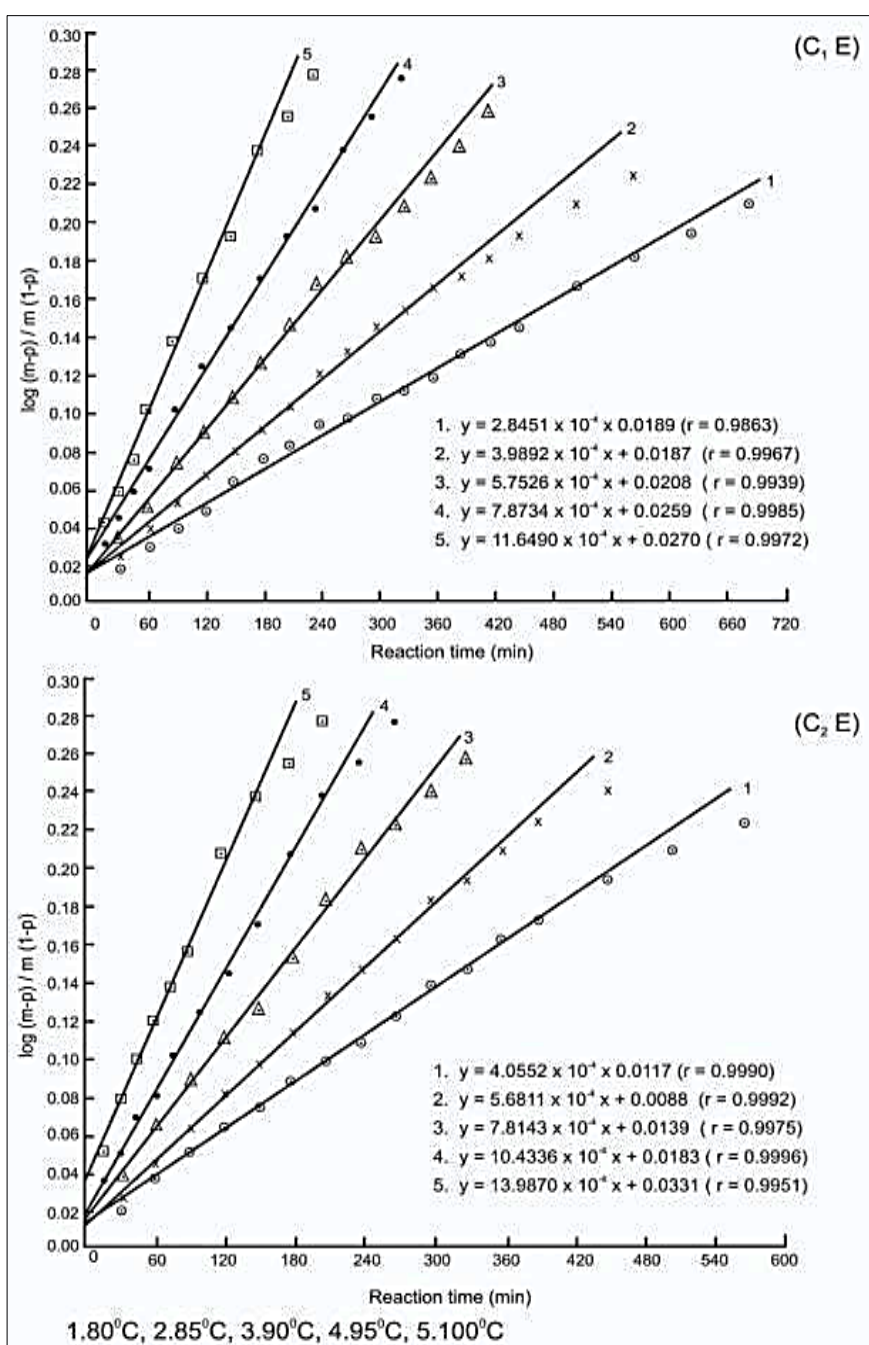
Synthesis of cycloaliphatic epoxy resin based vinyl esters in presence of triphenyl phosphine

The temperature range selected after several trails for the esterification of C_1 and C_2 in presence of triphenyl phosphine 70-90°C To evaluate the activation parameters the esterification of C_1 and C_2 was carried out at 80°, 85°, 90°, 95° and 100°C. The vinyl esters of C_1 and C_2 prepared in presence of triphenyl phosphine catalyst were designated as C_1E and C_2E , respectively. The change in acid value and extent of reaction with time are given in table 2. It is

apparent from the table that the acid value decreases with time fastly up to 70% conversion, then slow down but reaction continued even after 90% conversion. Figure 2 show plot between $\ln(m-p)/m(1-p)$ versus reaction time for the synthesis of C_1E and C_2E at 80°, 85°, 90°, 95° and 100°C. The plot were linear at all temperature up to ~88% conversion with highly significant correlation coefficient $r > 0.99$ which confirm that the reaction followed second order kinetics.

Table 2: Variation of acid value with time at different temperature for C₁E and C₂E

Reaction Time (min.)	80°C C ₁ E	80°C C ₂ E	85°C C ₁ E	85°C C ₂ E	90°C C ₁ E	90°C C ₂ E	95°C C ₁ E	95°C C ₂ E	100°C C ₁ E	100°C C ₂ E
0	180.2	220.9	180.2	220.9	180.2	220.9	180.2	220.9	180.2	220.9
30	126.9	152.4	111.5	142.2	97.8	120.7	82.5	102.1	71.7	74.4
60	102.7	117.1	84.1	111.2	79.1	81.2	63.4	73.2	48.3	53.0
90	90.1	99.4	77.8	88.9	63.4	68.0	49.0	55.6	38.2	39.4
120	80.4	86.1	67.0	73.3	53.1	57.1	41.9	44.4	30.9	31.5
150	69.0	74.6	58.4	64.3	46.2	50.5	36.4	37.7	25.3	26.2
180	61.1	68.9	53.7	55.6	40.7	43.9	30.9	31.2	21.9	23.5
210	58.1	61.8	49.1	48.9	35.8	35.1	26.8	26.5	19.3	21.2
240	52.6	56.9	43.6	43.4	32.9	31.4	25.5	24.4	18.1	—
270	50.8	50.8	39.3	40.1	29.6	28.5	21.7	22.1	—	—
300	46.9	46.4	35.3	35.5	26.7	26.3	19.5	—	—	—
330	45.4	44.2	33.2	33.2	25.1	24.4	17.3	—	—	—
360	43.1	39.8	31.9	30.1	22.9	—	—	—	—	—
390	40.4	37.6	29.3	28.9	21.3	—	—	—	—	—
450	35.5	33.1	27.4	26.7	20.1	—	—	—	—	—
510	32.6	30.9	25.0	—	—	—	—	—	—	—
570	28.3	28.7	23.4	—	—	—	—	—	—	—
630	26.4	—	—	—	—	—	—	—	—	—

**Fig 2:** In (m-p)/m(1-p) versus reaction time for the synthesis of C₁E and C₂E

Characterization of synthesized vinyl esters

The formation of cycloaliphatic epoxy resin esters was confirmed by FTIR spectroscopy through the presence of characteristic absorption bands corresponding to hydroxyl (-OH), carbonyl (C=O), and carbon-carbon double bond (C=C) functional groups. The FTIR spectra of C₁A, C₂A, C₁E, and C₂E are presented in Figure 3. All spectra exhibit a broad absorption band around 3510 cm⁻¹, which is assigned to the hydroxyl (-OH) group formed as a result of the ring

opening of glycidyl and cycloaliphatic epoxy groups during the esterification reaction. A characteristic absorption band at 1635 cm⁻¹ is observed in all spectra, indicating the presence of the acryloyl (C=C) double bond. In addition, absorption bands at approximately 2935 cm⁻¹ and 3050 cm⁻¹ correspond to methyl and methylene stretching vibrations, respectively. These characteristic absorption bands collectively confirm the successful synthesis of vinyl esters from cycloaliphatic epoxy resins.

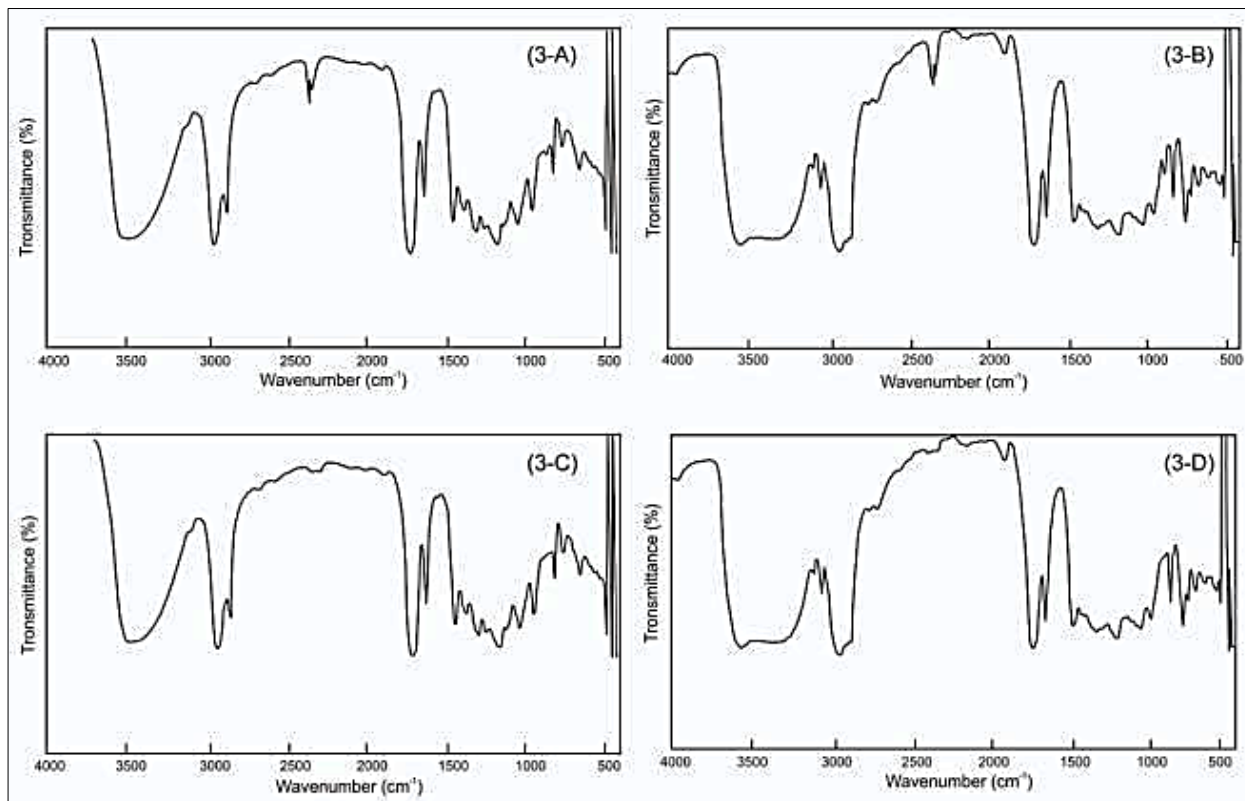


Fig 3: FTIR Spectra of C₁A, C₂A, C₁E and C₂E

Kinetic parameters of the esterification reactions:

The second order rate constant k_T 60° 65° 70° and 75°C for the synthesis of C₁A and C₂A were calculated from slope of plots of figure 1 and are given in Table 3. For the esters C₁E and C₂E

rate constant at 80°, 85°, 90°, 95° and 100°C were calculated from figure 2 and written also in table 3. Figure 4 shows the plot between $\ln k_T$ and the reciprocal of temperature for C₁A, C₂A, C₁E and C₂E.

Table 3: Specific rate constant with temperature for all the esters.

	C ₁ A	C ₂ A
333	1.7381	1.9575
338	2.2840	2.5328
343	2.2986	3.2486
348	3.9164	4.0478
	C ₁ E	C ₂ E
353	1.8545	2.1566
358	2.6001	3.0213
363	3.7495	4.1557
368	5.1316	5.5486
373	7.2566	7.4384

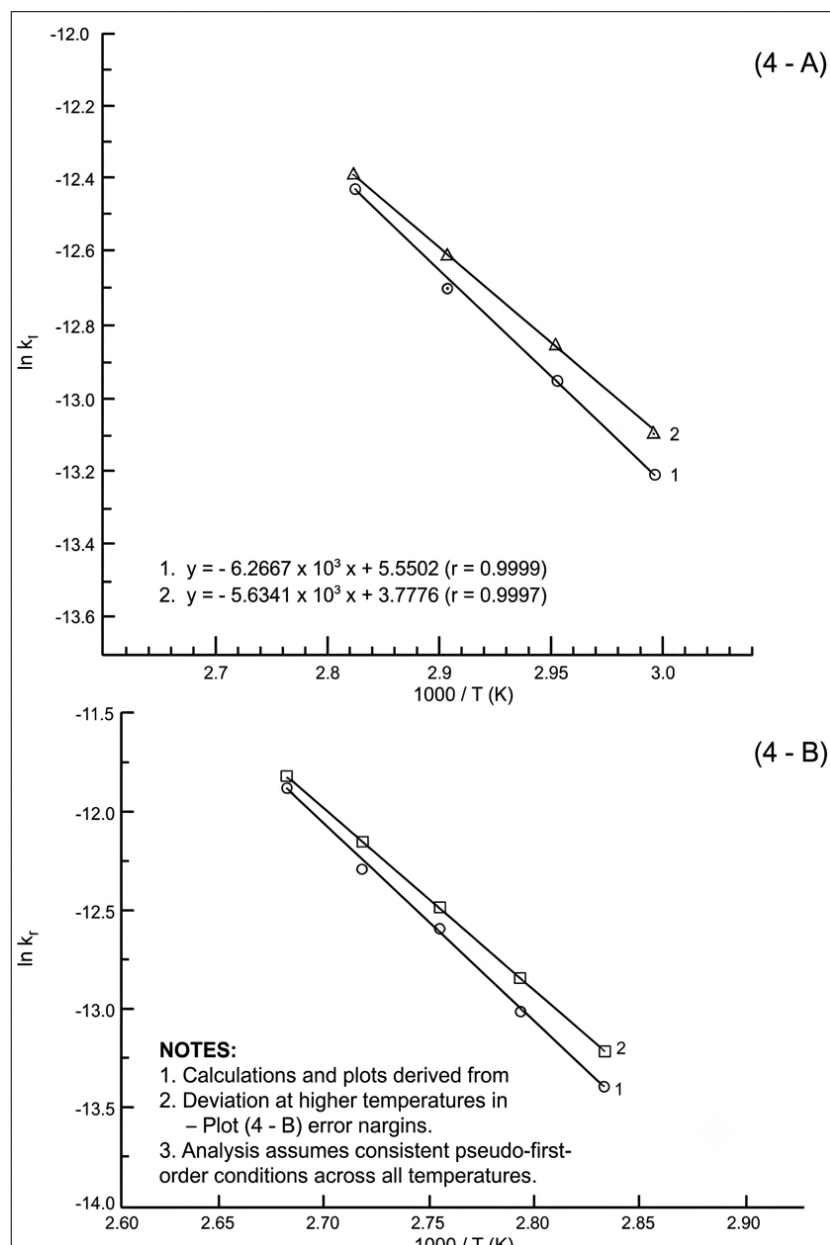


Fig 4: $\ln k_T$ vs. $1000/T$ for C_1A , C_2A , C_1E and C_2E .

The Arrhenius plots obtained by regression analysis were linear, confirming that the reactions followed Arrhenius kinetics. The activation energy (E_a) and pre-exponential factor (Z) were calculated from the slope and intercept of the plots, respectively. Subsequently, the activation

parameters, namely enthalpy of activation (ΔH^*), entropy of activation (ΔS^*), and Gibbs free energy of activation (ΔG^*), were evaluated. The corresponding values are presented in Table 4.

Table 4: Activation parameters for all the esters.

Activation parameters	Vinyl esters			
	C_1A	C_2A	C_1E	C_2E
E_a KJ/mol	52.0756	46.8196	73.1922	66.2533
Z (mol/lit) $^{-1}$ min $^{-1}$	2.570×10^2	0.4369×10^2	4.7018×10^5	2.4767×10^5
$-\Delta S^*$ J/K mol	227.3 ± 0.2	248.6 ± 0.2	171.5 ± 0.3	190.6 ± 0.3
ΔH^* kJ/mol	49.3 ± 0.2	44.2 ± 0.2	70.3 ± 0.2	63.4 ± 0.2
ΔG^* kJ/mol	126.7 ± 2.0	128.4 ± 2.0	128.2 ± 2.0	128.7 ± 2.0

As shown in Table 4, the values of activation energy (E_a), pre-exponential factor (Z), and enthalpy of activation (ΔH^*) for C_1A and C_1E are higher than those for C_2A and C_2E , respectively. These results indicate that the resin containing the epoxycyclohexane group is more reactive than the resin containing the pendant glycidyl group. The positive values

of Gibbs free energy of activation (ΔG^*) for all the esters suggest that the esterification reaction proceeds through an energy-demanding activated state. In contrast, the large negative values of entropy of activation (ΔS^*) indicates the formation of a highly ordered activated complex during the esterification process.

Conclusions

The present study demonstrates that the esterification of cycloaliphatic epoxy resins with methacrylic acid in the presence of triethylamine/triphenyl phosphine as catalysts follows second-order reaction kinetics. The reactivity of the cycloaliphatic epoxy resins (CERs) was found to depend on the nature of the epoxy functional group. The CER containing an epoxycyclohexane group exhibited higher reactivity than the resin containing a pendant glycidyl group, as evidenced by its lower activation energy, confirming the significant influence of ring structure on the reaction rate. The calculated kinetic parameters, including activation energy (E_a), pre-exponential factor (Z), enthalpy of activation ($\Delta H^\ddagger$), entropy of activation ($\Delta S^\ddagger$), and Gibbs free energy of activation ($\Delta G^\ddagger$), provided valuable insights into the reaction mechanism. The positive values of $\Delta G^\ddagger$ indicate that the esterification proceeds through an energy-demanding activated state, whereas the negative values of $\Delta S^\ddagger$ suggest the formation of a highly ordered activated complex during the reaction. Overall, the kinetic analysis provides a better understanding of the esterification process and offers useful information for optimizing the synthesis and curing behavior of cycloaliphatic vinyl ester resins.

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