

Kinetics of Esterification of Cycloaliphatic Epoxies with Methacrylic Acid

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ABSTRACT: The esterification of cycloaliphatic epoxy resins CER I and CER II containing glycidyl and cyclohexane epoxy groups, respectively, as their reactive units was carried out using a 1:0.9 stoichiometric ratio of resin and methacrylic acid in the presence of triphenylphosphine. The reaction was performed at 80, 85, 90, 95, and 100°C and it followed second-order kinetics. The specific rate constants, calculated by regression analysis, were found to obey an Arrhenius expression. Kinetic and thermodynamic parameters, activation energy, frequency factor, entropy, enthalpy,

and free energy of the reaction, revealed that the reaction was spontaneous and irreversible and produced a highly ordered activated complex. The reactivity of CER II was found to be higher than that of CER I. The difference in the reactivity of the cycloaliphatic epoxies was explained by proposing a reaction mechanism. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3197–3204, 2002

Key words: cycloaliphatic epoxy resin; methacrylic acid; triphenylphosphine; esterification; thermodynamics

INTRODUCTION

Cycloaliphatic epoxy resins (CERs) are characterized by the presence of a saturated cycloaliphatic ring in which the active epoxy groups are either cyclohexene oxide or a pendant glycidyl group.¹ These resins display inherently lower levels of ionic impurities and viscosity and higher reactivity toward acidic than toward amine curing agents.² The cured resins show excellent weatherability and electrical properties with superior arc and tracking resistance compared to those of conventional epoxy resins based on bisphenol-A and, therefore, they are being used as replacements for porcelain in outdoor high-voltage services.^{3,4}

The unmodified cured products of CERs when cast for large complex parts are fragile and lack toughness because of their rigid multicyclic molecular structure and high crosslink density.⁵ The conventional approach to improve the impact resistance of CERs by the use of plasticizers and flexibilizers^{6,7} has not been found applicable. The increase in flexibility is reported to be accompanied with inferior thermal stability.⁸ CER prepared from octadienyl compounds have been reported^{9,10} to give improved flexural elongation and strength along with inferior water resistance and thermal stability at elevated temperatures compared to properties of conventional CERs. Many workers have modified CERs by preparing their unsaturated esters and copolymerizing them with vinyl monomers, such as styrene,¹¹ acry-

lates,¹² and methacrylates,¹³ to obtain a low-temperature and radiation-curable resin for application in coatings, printing inks, adhesives, and so forth.

The correlation between the chemical structure of CERs and that of curing agents plays a multifactorial role in the development of cured properties and it depends mainly on the type of reactive epoxy units, chemical structure of linkages and fragments between them, and kinetic characteristics of the reaction. In the present work we report the kinetics of esterification of CERs containing oxirane and cyclohexene oxide ring with ethylenically unsaturated methacrylic acid.

EXPERIMENTAL

Epoxy resins CY 184 and CY 179 (Ciba Speciality Chemicals, Buchs, Switzerland) and methacrylic acid and triphenylphosphine (Fluka A.G., Buchs, Switzerland) were used in the present study. The structures of epoxy resins are given in Figure 1.

A reaction mixture, consisting of a 1:0.9 stoichiometric ratio of cycloaliphatic epoxy resin (100 g) and methacrylic acid (42.6 mL for CER I, 54.5 mL for CER II), was charged into a three-neck flask (500 mL) equipped with a stirrer, nitrogen inlet tube, and thermometer. The flask was placed into an electrically heated oil bath ($\pm 1^\circ\text{C}$). The mixture was stirred and heated to the desired temperature followed by adding triphenylphosphine (1 phr by weight of CER) within 2 min. The esterification reaction was carried out at 80, 85, 90, 95, and 100°C and the progress of reaction was monitored by intermittently determining the acid value by the method of Ogg et al.¹⁴ The samples for

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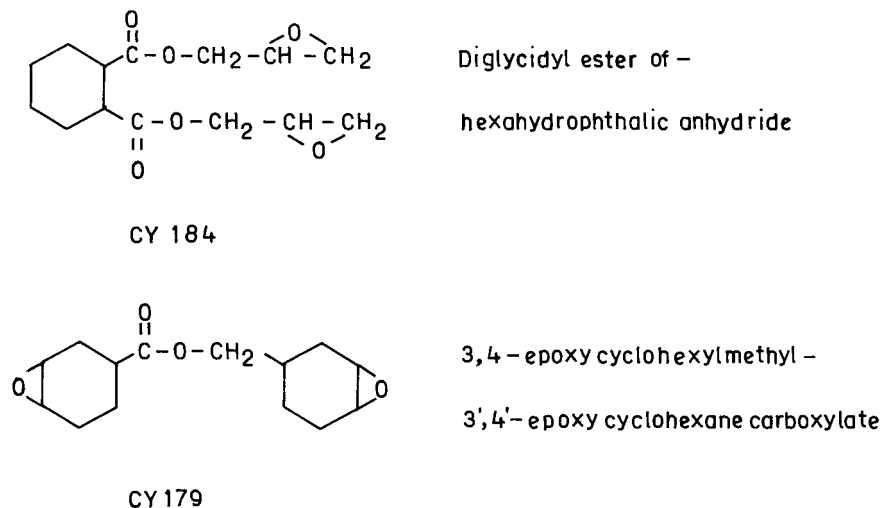


Figure 1 Structure of CER I and CER II.

the acid value were taken from the flask from the neck where the thermometer pocket was placed, with the help of a glass rod that had a spatula-like end. The extent of reaction and number-average degree of polymerization were calculated by use of Carother's equation.¹⁵

The second-order rate equation used for the reaction, in which the stoichiometric ratio of reactants is not unity, can be written as follows:¹⁶

$$\frac{\ln(m-p)}{m(1-p)} = C_{A0}(m-1)k_T t \quad (1)$$

where $p = 1 - (AV_t/AV_0)$ is the extent of reaction at any particular time t and AV_0 and AV_t are the acid values at $t = 0$ and at time t , respectively; and $M = C_{B0}/C_{A0}$ is the stoichiometric ratio, where C_{B0} and C_{A0} are the initial concentrations of resin and acid, respectively.

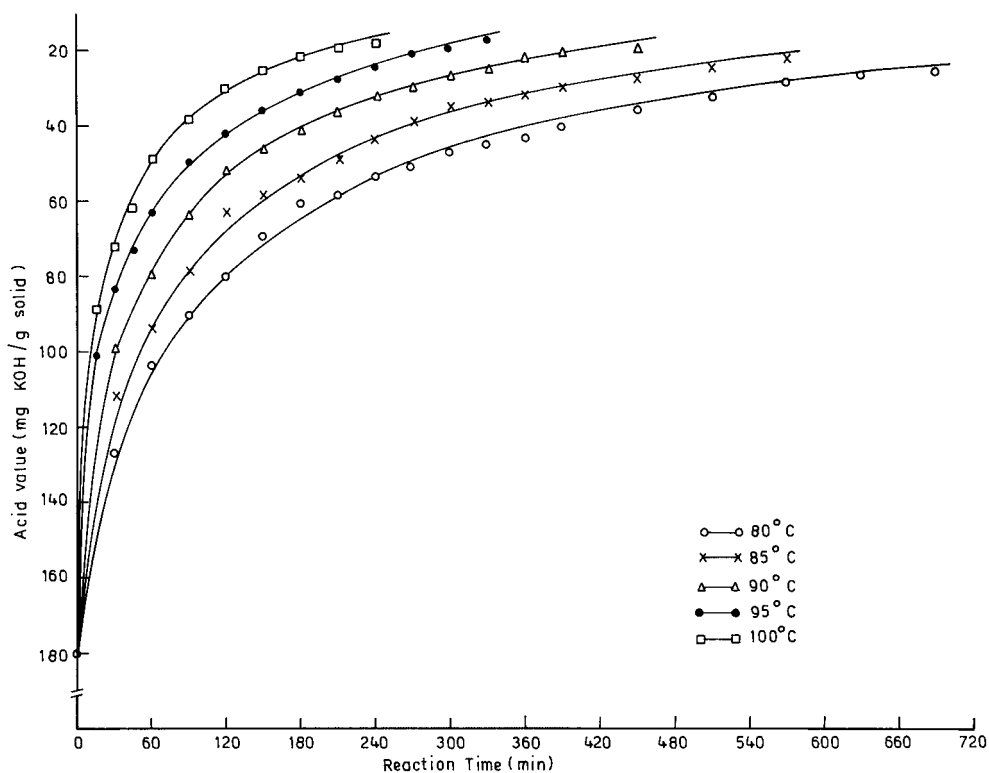


Figure 2 Acid value versus reaction time for esterification of CER I with methacrylic acid.

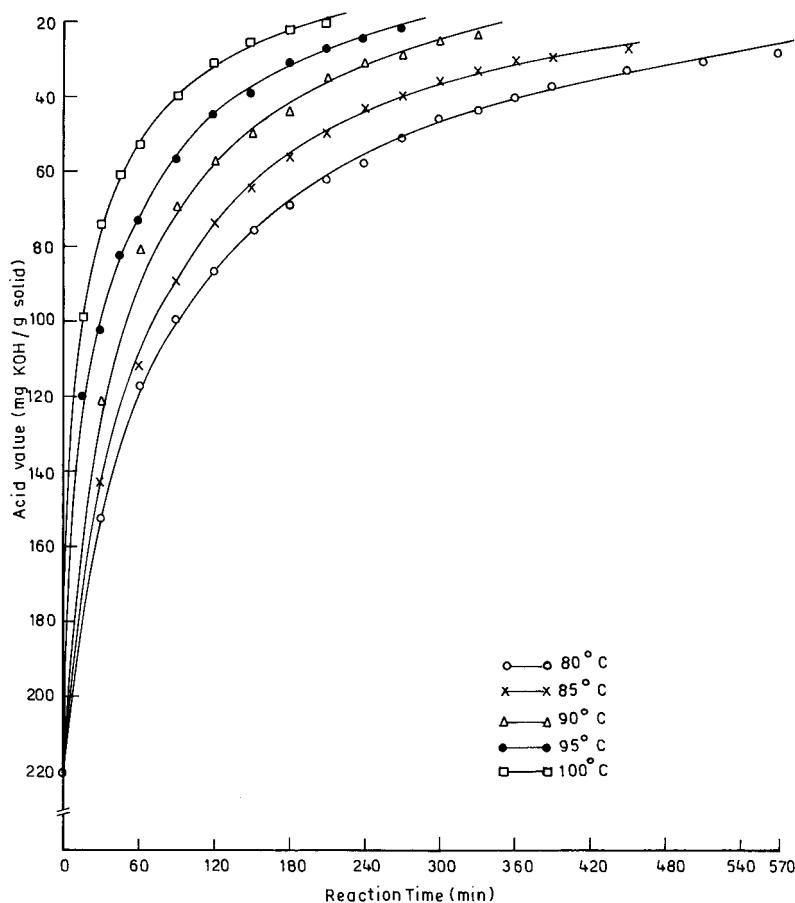


Figure 3 Acid value versus reaction time for esterification of CER II with methacrylic acid.

The relation between C_{A0} and AV_0 is expressed as

$$C_{A0} = \frac{10^6 \times AV_0}{56,100}$$

k_T = rate constant

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

$$k_T = Z e^{-E_a/RT} \quad (2)$$

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

The entropy of activation ΔS^\ddagger was calculated using the following equation:

$$k_T = \frac{k_b T}{h} e^{-E_a/RT} e^{\Delta S^\ddagger/R} \quad (3)$$

where k_b is the Boltzmann constant and h is Planck's constant.

The enthalpy of activation ΔH^\ddagger and free energy of activation ΔG^\ddagger were calculated using the following expressions:

$$\Delta H^\ddagger = E_a - RT \quad (4)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (5)$$

RESULTS AND DISCUSSION

The esterification of CER I and CER II was carried out at 80, 85, 90, 95, and 100°C in the presence of triphenylphosphine. Figures 2 and 3 show the results of esterification of CERs with methacrylic acid catalyzed by triphenylphosphine. The results are typical of the behavior generally observed for polyesterification reactions. It is apparent from the figures that the acid value decreases with increase in reaction time and is not linear in the initial stages of the reaction. This is 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 (45–80%) reveals that the reactivity of the functional group is independent of molecular size, which is a characteristic of the polyesterification reactions.

The number-average degree of polymerization (X_n) for the esters of CER I and CER II prepared at 80, 85, 90, 95, and 100°C, calculated using Carother's equa-

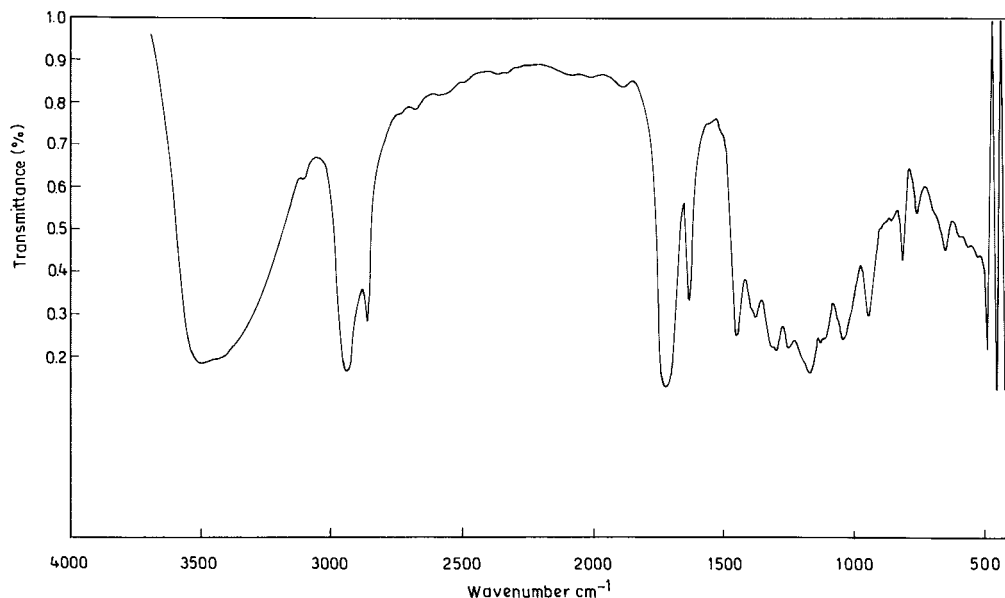


Figure 4 FTIR spectra of esterified CER I.

This confirms the esterification of both CERs by methacrylic acid.

Figures 6 and 7 show the plots between $[\ln(m - p)/m(1 - p)]$ and reaction time for the esterification of CER I and CER II, respectively, at 80, 85, 90, 95, and 100°C. The plots were linear at all temperatures up to about 88% conversion, with a highly significant correlation coefficient ($r > 0.99$), which confirms that the reaction follows second-order kinetics. It is apparent from the figures that there is a deviation from the linear behavior in the higher conversion region ($>88\%$), probably attributable to the change in reaction kinetics. The specific rate constants k_T at 80, 85, 90,

95, and 100°C for the esterification of CER I and CER II were calculated from the slope of the plots shown in Figures 6 and 7, respectively. The values of k_T for CER II at all temperatures were higher than those obtained for CER I, which again indicates that the resin with the cyclohexane epoxy group is more reactive than the other.

Figure 8 shows the plots between $\ln k_T$ and the reciprocal of the temperature for CER I and CER II. It is apparent from the figure that they obey 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.

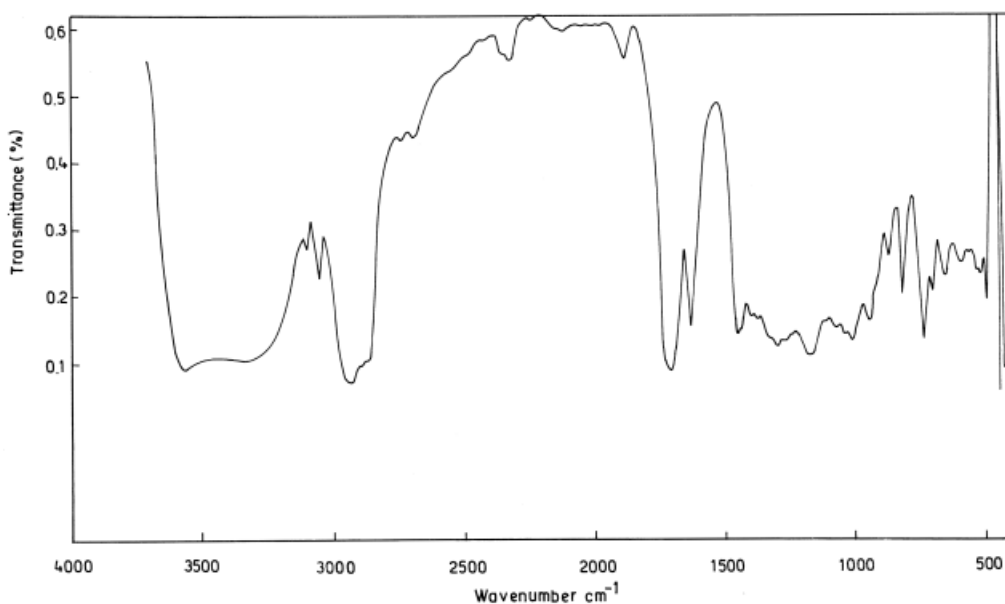


Figure 5 FTIR spectra of esterified CER II.

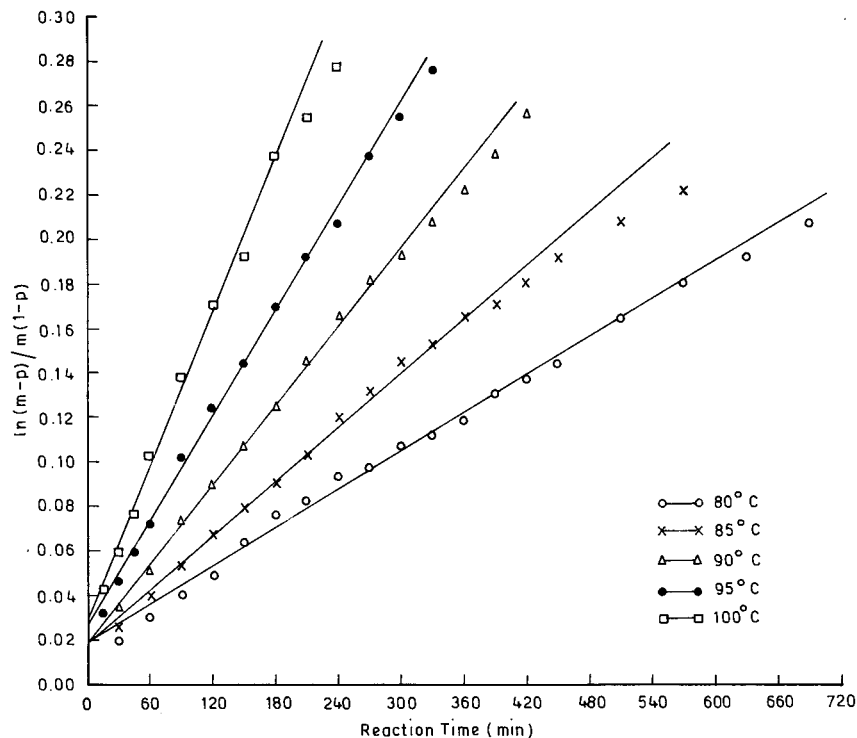


Figure 6 $[\ln(m-p)/m(1-p)]$ versus reaction time for the esterification of CER I: 80°C, $y = 0.2845 \times 10^{-3}x + 0.0189$ ($r = 0.9863$); 85°C, $y = 0.3989 \times 10^{-3}x + 0.0187$ ($r = 0.9967$); 90°C, $y = 0.5752 \times 10^{-3}x + 0.0208$ ($r = 0.9939$); 95°C, $y = 0.7873 \times 10^{-3}x + 0.0259$ ($r = 0.9985$); 100°C, $y = 1.1649 \times 10^{-3}x + 0.0270$ ($r = 0.9972$).

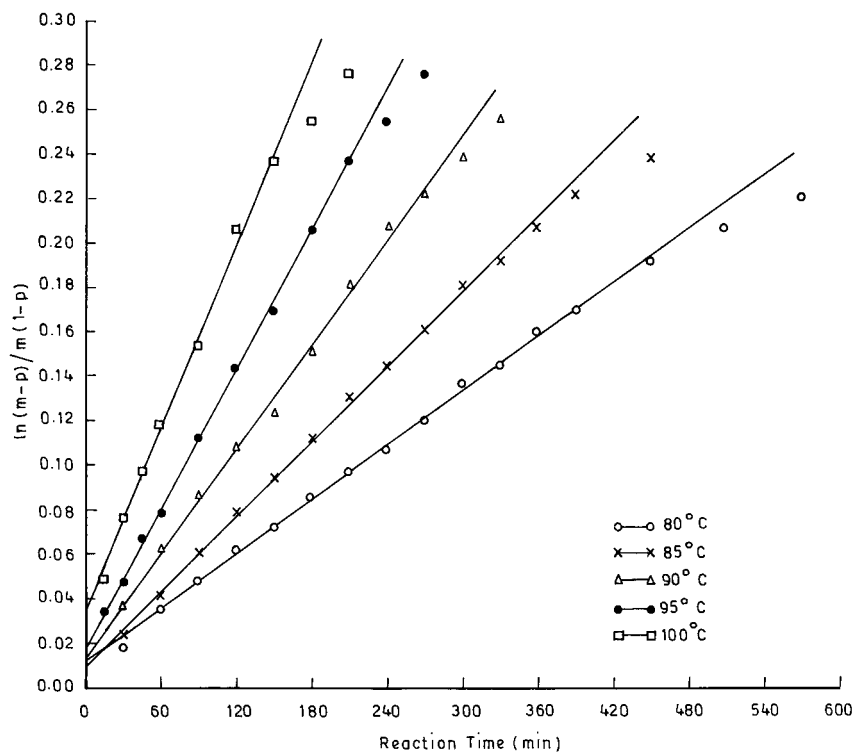


Figure 7 $[\ln(m-p)/m(1-p)]$ versus reaction time for the esterification of CER II: 80°C, $y = 0.4055 \times 10^{-3}x + 0.0117$ ($r = 0.9990$); 85°C, $y = 0.5681 \times 10^{-3}x + 0.0088$ ($r = 0.9992$); 90°C, $y = 0.7814 \times 10^{-3}x + 0.0139$ ($r = 0.9975$); 95°C, $y = 1.0433 \times 10^{-3}x + 0.0183$ ($r = 0.9996$); 100°C, $y = 1.3987 \times 10^{-3}x + 0.0331$ ($r = 0.9951$).

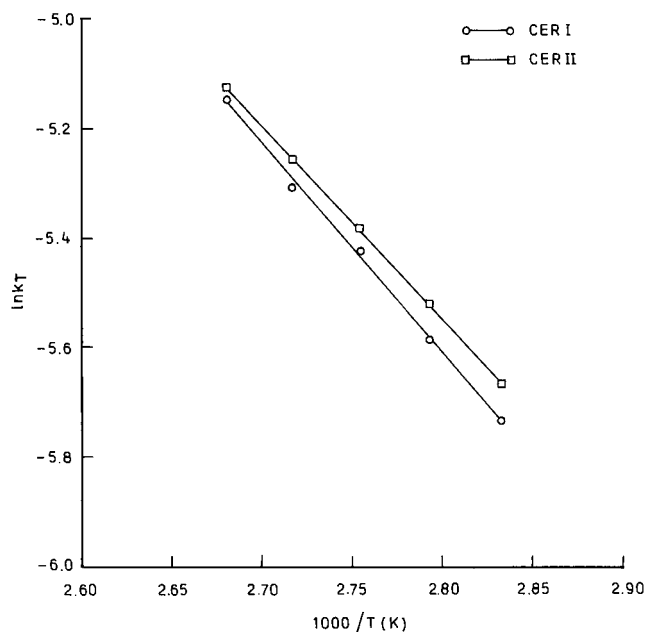
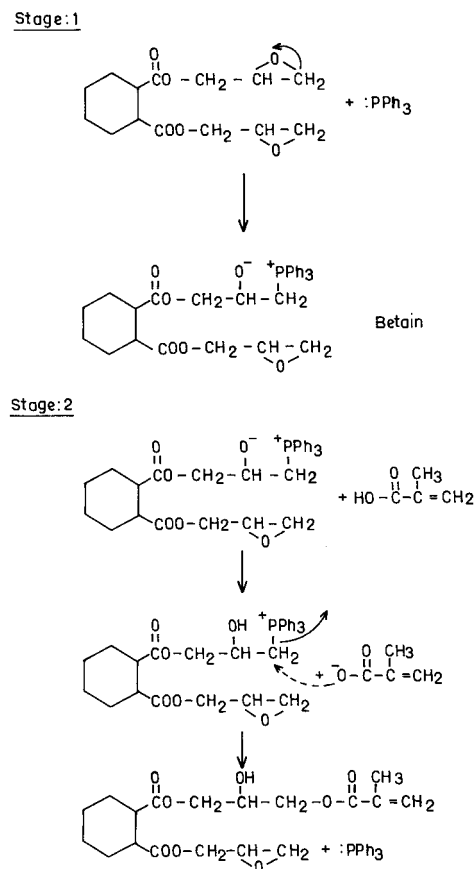


Figure 8 Plots of $\ln k_T$ versus reciprocal of temperatures for CER I, $y = 3.8149x + 5.0747$ ($r = 0.9988$); CER II, $y = 3.4924x + 4.2352$ ($r = 0.9998$).

fication reactions. Using these values of E and Z , the thermodynamic parameters entropy, enthalpy, and free energy of the activation were calculated using eqs. (3), (4), and (5), respectively, and the values are given in Table III. It is clear from the table that the E , Z , and ΔH^\ddagger values are higher for CER I than those for CER II, which again indicates that the latter resin is more reactive. The difference in the reactivity of the two cycloaliphatic epoxy resins lies in the ring size, which affects their basicity. The proposed mechanisms for the esterification of CER I and CER II with methacrylic acid in the presence of triphenylphosphine are given in **Scheme 1** and **Scheme 2**, respectively.

In **Scheme 1**, the reaction starts by the nucleophilic attack of triphenylphosphine, which opens the epoxide ring, producing a betaine (stage 1) followed by the formation of a carboxylate anion (stage 2) by proton abstraction from the methacrylic acid. This carboxylate anion attacks the electrophilic carbon attached to the phosphorus, forming an ester linkage and regenerating the catalyst. In **Scheme 2**, the reaction starts by electrophilic attack of the proton, obtained from

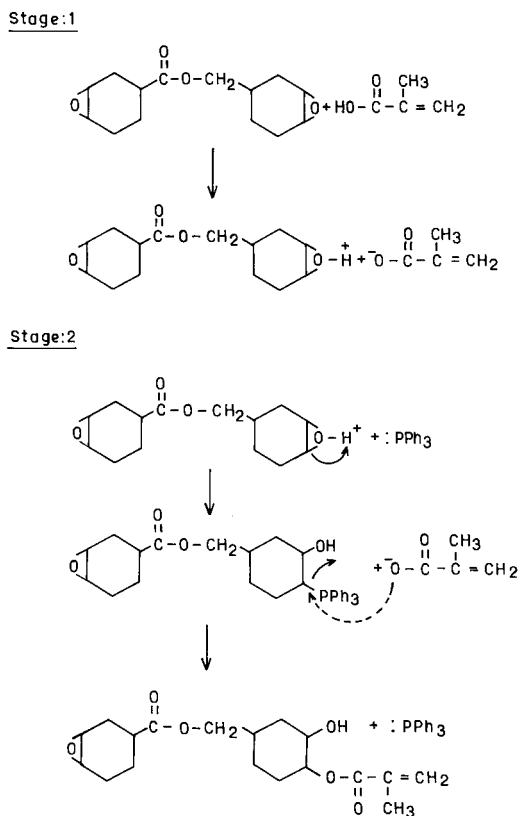


Scheme 1 Mechanism of esterification of CER I with methacrylic acid in the presence of triphenylphosphine.

methacrylic acid, on the epoxide ring (stage 1) and the carboxylate anion is formed. At stage 2 the ring is opened by the reaction of triphenylphosphine at the electron-deficient carbon atom. The carboxylate anion then attacks to form an ester linkage and releases the catalyst. The addition esterification in both cases (**Schemes 1** and **2**) is accompanied by the condensation esterification (reaction between the hydroxyl group of hydroxy ester formed and acid) and etherification (reaction between hydroxyl and epoxy groups). These reactions play an important role in the chain extension, branching, and crosslinking of the molecules formed in the reaction system, which finally result in the network formation.^{18,19} The difference in mechanism is attributed to the higher electron density

TABLE III
Thermodynamic Parameters of Esterification of CER I and CER II with Methacrylic Acid in the Presence of Triphenylphosphine

Resin	Activation energy, E_a (kJ/mol)	Frequency factor, Z (mol/L ⁻¹ /min ⁻¹)	Entropy, $-\Delta S^\ddagger$ (J/K ⁻¹ /mol ⁻¹)	Enthalpy, ΔH^\ddagger (kJ/mol)	Free energy, ΔG^\ddagger (kJ/mol)
CER I	73.0095	1.1877×10^5	183.5 ± 0.5	70.0 ± 0.2	136.5 ± 2.0
CER II	66.8767	1.7186×10^4	199.4 ± 0.5	63.8 ± 0.2	136.0 ± 2.0



Scheme 2 Mechanism of esterification of CER II with methacrylic acid in the presence of triphenylphosphine.

on oxygen of the epoxy cyclohexane ring than that of the oxirane ring because the basicity of oxygen attached to the cycloaliphatic ring increases with the ring size.^{20,21}

The thermodynamic parameters ΔG^\ddagger for the esterification of CER I and CER II were 136.5 and 136.0 (± 2.0) kJ/mol, respectively, whereas the values of ΔS^\ddagger were found to be negative [-183.5 (± 0.5) kJ/mol for CER I and -199.4 (± 0.5) kJ/mol for CER II]. Given that $\Delta G^\ddagger > 0$ and $\Delta S^\ddagger < 0$ for the reaction, it could be said that the process is spontaneous and irreversible.²² The high negative value of ΔS^\ddagger indicates the formation of an ordered activated complex in the esterification of CERs.

CONCLUSIONS

The esterification of cycloaliphatic epoxy resins (CY 184 and CY 179) with methacrylic acid catalyzed by

triphenylphosphine follows second-order reaction kinetics. The reactivity of the cyclohexane epoxy group toward methacrylic acid was found to be higher than that of the glycidyl epoxy group because of the difference in their ring size. The reaction is spontaneous and irreversible and produces a highly ordered activated complex.

References

1. Mark, H. F.; et al., Eds. *Encyclopedia of Chemical Technology*, Vol. 9; Wiley-Interscience: New York, 1978; p 272.
2. Mark, H. F.; et al., Eds. *Encyclopedia of Polymer Science*, Vol. 6; Wiley-Interscience: New York, 1986; p 322.
3. Stevens, J. J. In: *Epoxy Resin Technology*; Bruin, P. F., Ed.; Wiley-Interscience: New York, 1968; p 11.
4. Lee, S. M. In: *Epoxy Resins: Chemistry and Technology*; May, C. A., Ed.; Marcel Dekker: New York, 1988; p 861.
5. Burhans, A. S. SPE 33rd ANTEC 1975, 331.
6. Suzuki, T.; Katayama, S.; Yamamoto, H. Jpn. Pat. 62128161, 1987; Chem Abstr 1987, 107, 199967b.
7. Hamahura, T.; Nishizawa, T.; Okyokoka, M.; Yamamoto, R. Jpn. Pat. 0859790, 1996; Chem Abstr 1996, 125, 60129h.
8. Batog, A. E.; Pet'ko, I. P.; Penczek, P. Adv Polym Sci 1999, 144, 49.
9. Tokizawa, M.; Okada, H.; Wakabayashi, N.; Kimura, T.; Fukutani, H. J Appl Polym Sci 1993, 50, 627.
10. Tokizawa, M.; Okada, H.; Wakabayashi, N. J Appl Polym Sci 1993, 50, 875.
11. Ootsuka, Y. Jpn. Pat. 05295197, 1993; Chem Abstr 1994, 120, 219567v.
12. Kageishi, I.; Osanai, Y.; Ando, Y. PCT Int. Appl. WO 9954417, 1999; Chem Abstr 1999, 131, 311777p.
13. Okumura, K.; Endo, T. Jpn. Pat. 0841150, 1996; Chem Abstr 1996, 124, 356228g.
14. Ogg, C. L.; Porter, W. L.; Willitis, C. O. Ind Eng Chem Anal Ed 1945, 17, 394.
15. Odian, G., Ed. *Principles of Polymerization*, 2nd ed.; Wiley-Interscience: New York, 1981; p 40.
16. Levenspiel, O., Ed. *Chemical Reaction Engineering*, 2nd ed.; Wiley-Interscience: New York, 1972; p 41.
17. Lee, H.; Neville, K., Eds. *Handbook of Epoxy Resins*; McGraw-Hill: New York, 1967; Chapter 4-3.
18. Matejka, L.; Pokorny, S.; Dusek, K. Polym Bull 1982, 7, 123.
19. Le Blainvaux, F.; Madec, P. J.; Marechal, E. Polym Bull 1985, 13, 237.
20. Levy, G.; Deloth, P. C R Acad Sci 1974, C279, 331.
21. Haines, A. H. In: *Comprehensive Organic Chemistry*; Sammes, P. G., Ed.; Pergamon: Elmsford, NY, 1979; p 853.
22. Atkins, P. W., Ed. *Physical Chemistry*; Oxford University Press: London, 1994; p 927.