EFFECT OF AlCl₃ ON THE KINETIC AND MECHANISM OF EPOXY RESIN

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ABSTRACT

Modified epoxy resins have been synthesized by reacting 1:10 mole ratio of bisphenol-A and epichlorohydrin in the presence of AlC1$_3$ epichlorohydrin complex (1:1) at 30°C. Parameters, such as epoxide equivalent weight, chlorine content, percentage crystallinity, degree of cure increase as a direct function of the concentration of AlC1$_3$ - Differential Scanning Calorimetry (D.S.C.) studies show that the values of the glass transition temperature (T$_g$) are higher for a modified epoxy resin than for a blank one. The AlC1$_3$ modifies as well, as it has autocatalytic curing properties at room temperature. The activation energy is 86 KJ/mole and order of reaction is first.

INTRODUCTION

The significance of Lewis acids in the chain polymerization has been well established in the past, (for e.g., synthesis of alternating copolymers) [1-21]. However, these have rarely been used in step growth polymerization, because most of the studies have been carried out in modifying epoxy resins by the use of metal acrylate [3-6], heterocyclic [7] etc. A search of the literature reveals that Lewis acids in the form of complexes like borontrifluoridemonoethylamine

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(BF_3-$NH_2C_2H_5$) [8] have been used as curing agent for the epoxy resins, but the use of $AlCl_3$ is still scarce. It is, therefore, worthwhile to investigate the effect of $AlCl_3$ as a complexing agent with epichlorohydrin on the properties of epoxy resin and the present work is an outcome of such efforts.

EXPERIMENTAL

Toluene, methanol, pyridine, dioxane, epichlorohydrin bisphenol-A and anhydrous aluminum chloride were used. All of them were purified (except the last two) before use. All of the experiments were carried out at 30°C.

Synthesis and Characterization of AlCl₃-Epichlorohydrin Complex

The required (Table 1) molar equivalent of aluminium chloride and 0.02 mole of epichlorohydrin in 8 ml toluene were stirred at 30°C for about 35 minutes. The excess of toluene was removed under vacuum. The complex obtained was a viscous liquid.

Solubility

The complex is soluble in methanol, dioxane, dimethy1formamide.

Viscosity

Viscosity of complex in dimethy1formamide DMF at 35±0.1°C is 0.37 poise.

IR

The IR of complex shows shifting of band due to epoxy group from 910 to 930 cm⁻¹. The composition of complex was quantified, and the assigned structure was:
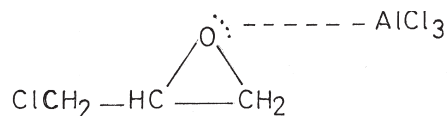
Synthesis of Epoxy Resin

The blank (A) and modified epoxy resins (B to F) have been prepared according to the method described by Lee and Neville [8].

TABLE 1.   Molar Equivalent of Epoxy Resin Containing AlCl$_3$-Epichlorohydrin Complex x 103

S.No.	Properties	ER$_A$ (O.OM)	ER$_B$ (3.2M)	ER$_C$ (7.2M)	ER$_D$ (11.2M)	ER$_E$ (15.2M)	ER$_F$ (19.2M)
1.	Epoxide equivalent (eq./100g.)	194	2080	2358	2670	2873	3142
2.	Hydroxyl content (eq./100g.)	0.12	0.032	0.037	0.045	0.058	0.072
3.	% Crystallinity	30%[13]	----	----	----	79%	87%
4.	Degree of cure (α')	0.70[13]	----	----	----	0.78	0.83
5.	Glass transition temperature (Tg)°C	130°C	----	----	----	137°C	143°C
6.	Chlorine content (%)	0.57	0.86	0.88	0.91	0.92	0.96
7.	Viscosity (at 35°C)	1.58	1.02	1.03	1.17	1.3	1.4
8.	Refractive indices	1.5695	1.4622	1.48	1.4960	1.5032	1.565
10.	Physical state	Viscous liquid	Viscous liquid	Viscous liquid	Viscous liquid	Viscous liquid	Viscous liquid
11.	Color	Whitish yellow	Light yellow	Light yellow	Yellow	Yellow	Yellowish Red.

Synthesis of epoxy resin A was carried out by refluxing bisphenol-A (0.075 mol) and epichlorohydrin (0.75 mol) in a three-necked flask followed by a gradual addition of sodium hydroxide (0.15 mol) over a period of 3.5 hours. Heating was continued for an additional 15 minutes, after which the content was dissolved in toluene (80 ml), and the solution was filtered to remove the salt. The excess of epichlorohydrin and toluene was removed by distillation under reduced pressure (400 mm). The resulting viscous product was stored in an air-tight container. Epoxy resin B was prepared by reacting bisphenol-A (0.075 mol) and epichlorohydrin (0.75 mol) in the presence of 3.2×10^{-3} molar equivalent $AlCl_3$-epichlorohydrin complex and was prepared in a similar manner as was epoxy resin A. Epoxy resin C, D, E, and F were also prepared the same way as was epoxy resin B, but the quantity of $AlCl_3$-epichlorohydrin complex was increased to 7.2×10^{-3}, 11.2×10^{-3} 10^{-3} molar equivalent, respectively.

Characterization

Epoxide equivalent, hydroxyl and hydrolyzable chlorine content were determined by wet analysis. (epoxide equivalent in pyridinium chloride method) [8].

Viscosity

Viscosity of the resins was determined in toluene at various temperature (35-80°C) using an Ubbelohde viscometer.

Infrared Analysis

The infrared spectra were recorded using a Perkin-Elmer spectrophophotometer (model 377).

Thermal Analysis

Differential Scanning Calorimetry

The measurements of heat reaction were conducted using the Dupont 2100 Differential Scanning Calorimetry with nitrogen as purge as, 40ml/min. All the experiments were carried out under typical scan conditions (at 156°C and 419°C) to obtain the heat flow curve. The weight of the sample were between 1-8 mg. The glass transition temperature (T_g) of the cured sample after the typical scan runs was determined in dynamic region at 10°C/min.

RESULTS AND DISCUSSION

Table 1 shows that the epoxide equivalent weight, chlorine content are a direct function of the complex concentration. However, other parameters such as hydroxyl content, refractive indices, viscosity, decrease as a function of concentration of the complex.

The hydroxyl value of the modified resins are in the range of 0.032-0.064 eq/100g, which is less than for blank epoxy resin (A). The presence of hydrolyzable chlorine which may be due to side reactions, partial dehydrohalogenation, abnormal addition of epichlorohydrin and formation of bond chlorine, ranges from 0.86- 0.96.

Spectral Analysis

The infrared spectrum of an epoxy resin (Figure 1) shows absorbance in the region of 1380-1360 cm^{-1} as a result of ring breathing or symmetric stretching vibration, and around 910 cm^{-1} due to symmetric stretching of the epoxy group. The band around 2900 cm^{-1} is due to -CH and -CH$_2$ groups in the ring and confirms the presence of the epoxy ring in the resins. The broadened band around 3400 cm^{-1} indicates the presence of -OH group. There are two bands, one at 930 cm^{-1} and other at 910 cm^{-1} which belong to complex and residual epichlorohydrin, respectively.

The D.S.C. curve has been used to obtain residual heat reaction [9] with the help of following formula [10, 11].

$$(\alpha') \quad = \quad \text{H/Hult, Hult = Ht +Hr} \tag{1}$$

Where H $\quad$ = $\quad$ An instantaneous heat of reaction

$\quad$ Ht $\quad$ = $\quad$ Total heat of reaction

$\quad$ Hr $\quad$ = $\quad$ Residual heat of reaction

$\quad$ (α') $\quad$ = $\quad$ Degree of cure

It is clear (Table 1) that the value of degree of cure (α') is higher for modified epoxy resins (B to F) in comparison to that of blank sample A.

D.S.C. heat flow curve has also been used to percent crystallinity with the help of formula [14].

$$\% \text{ Crystallinity} \quad = \quad \text{Ha - H / Ha - Hc} \tag{2}$$

$\quad$ Ha $\quad$ = $\quad$ Amorphous enthalpy

$\quad$ Hc $\quad$ = $\quad$ Crystalline enthalpy

$\quad$ H $\quad$ = $\quad$ Sample enthalpy
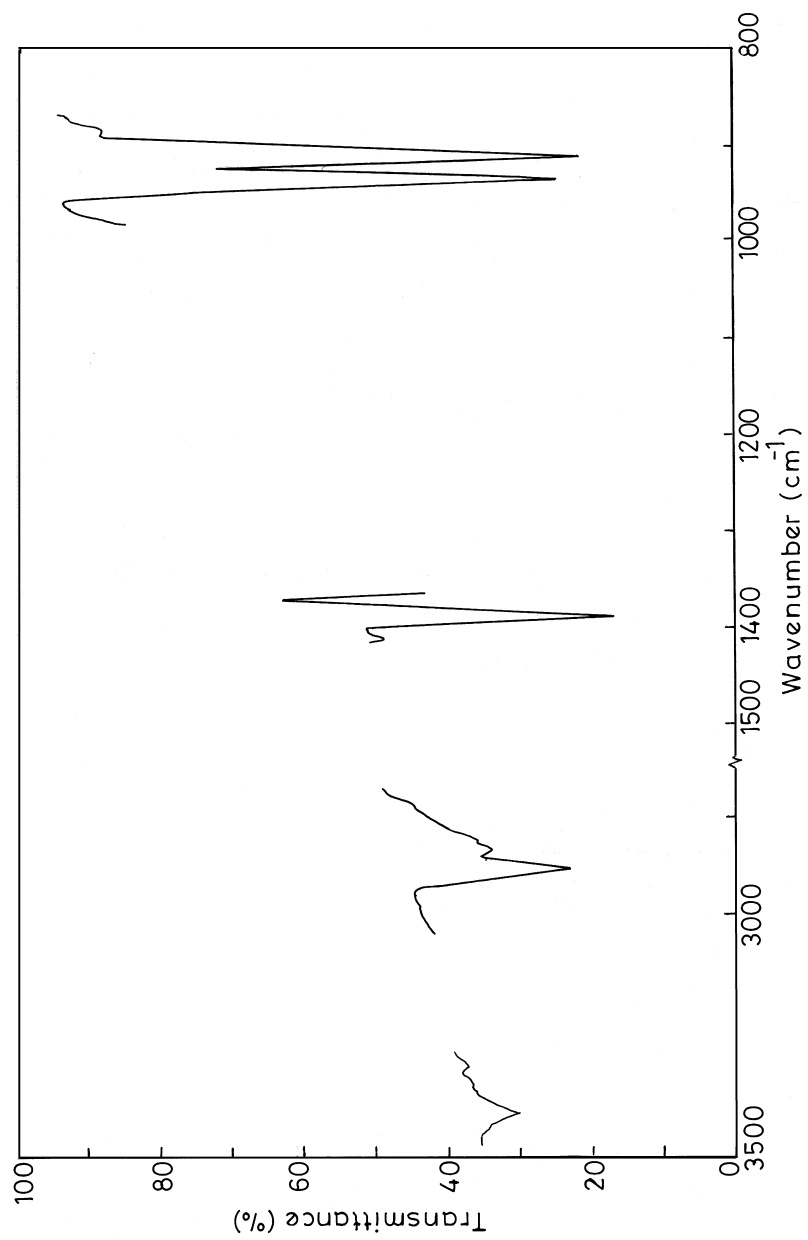
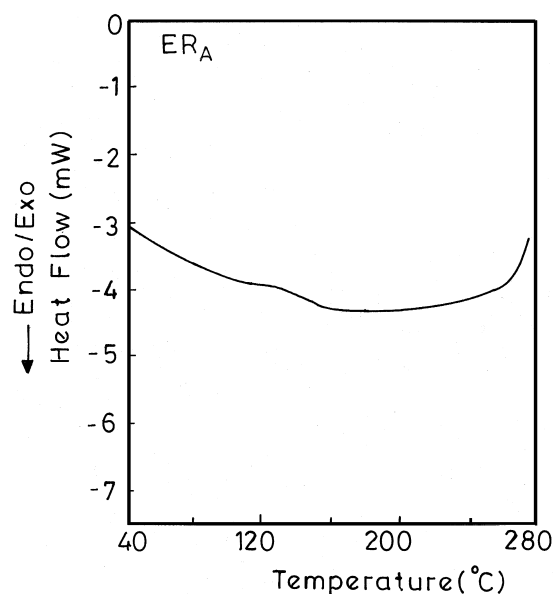**Figure 1.** IR spectrum of ER_B.

Figure 2(i).   DSC curve of ER$_A$.

Glass transition temperature (T$_g$) for blank epoxy resin A (130°C) (Figure 2(i)) is less then for epoxy resins E and F (Figure 2 (ii), (iii)) as 137 and 143°C, respectively.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried on a TGAV5 1A Dupont 2100 at a heating rate of 10°C/min, under nitrogen atmosphere.

The effect of AlC1$_3$ on the thermal stability of the epoxy resin was studied by thermogravimetric analysis (Figure 3). A resin sample containing AlC1$_3$ was stable up to 265°C and started losing weight above this temperature. However, the blank epoxy resin was stable up to 130°C.

In modified epoxy resin containing AlC1$_3$, rapid decomposition was observed at 300-400°C, and almost total volatilization of the polymer occurs at 430°C. It may be attributed to the incorporation of AlC1$_3$ in the resin.

Kinetics

The apparent activation energy (Ea) corresponding to the decomposi-tion process and order of reaction, was calculated from Coats and Redfern [12] equation from the dynamic experiment;
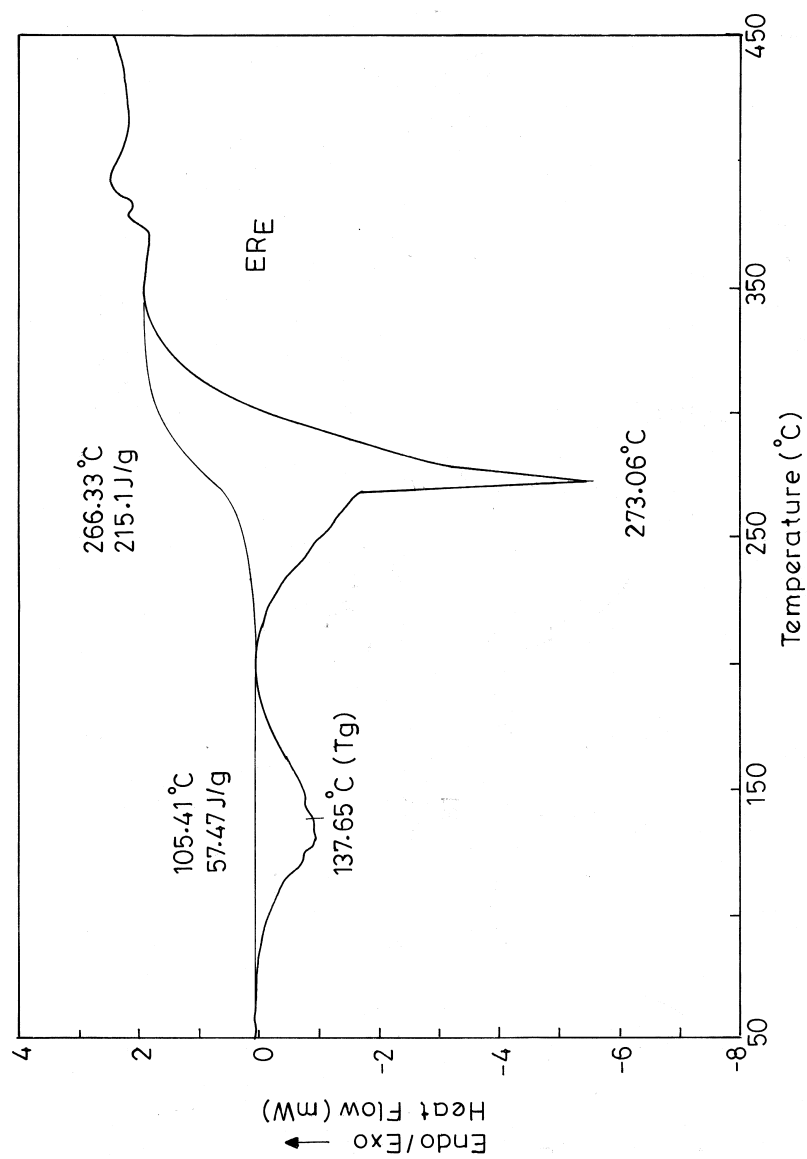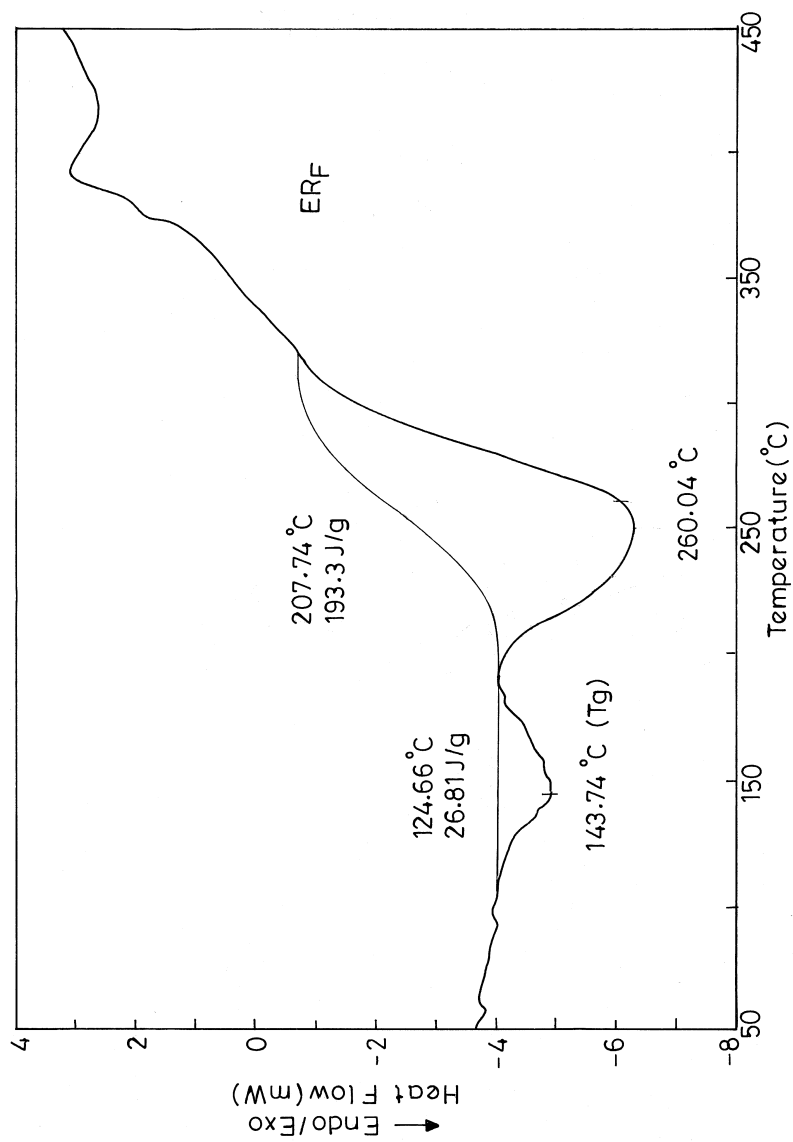
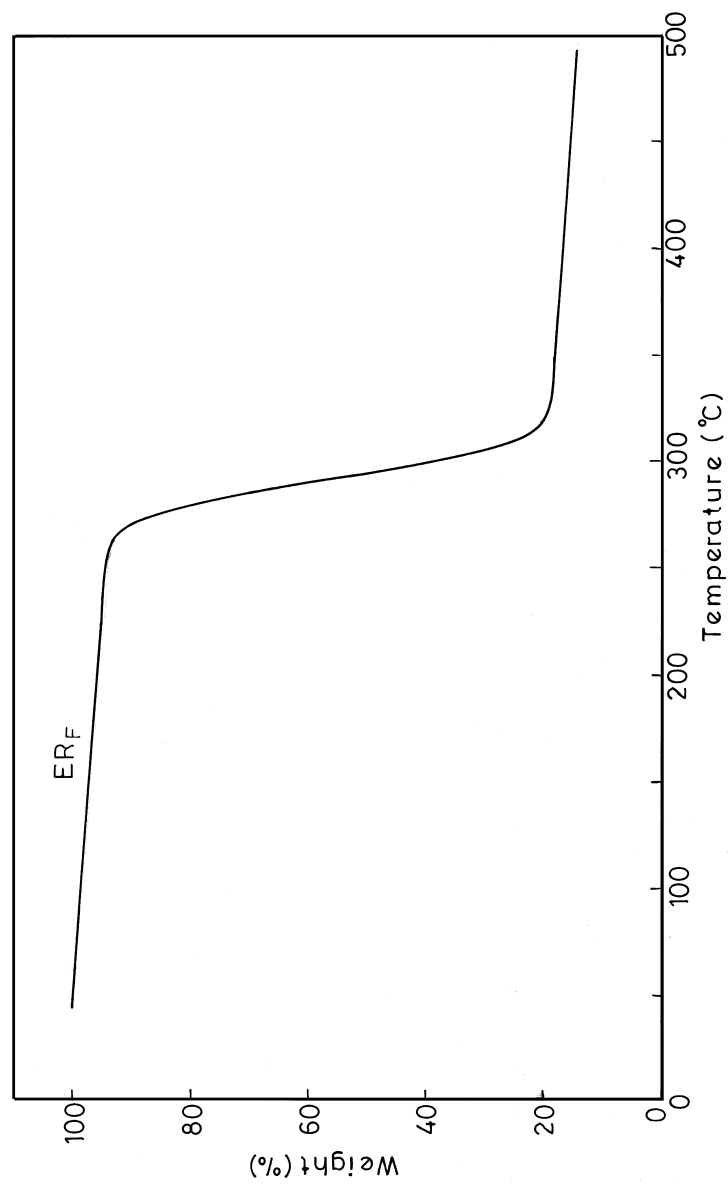**Figure 2(ii).** DSC curve of ER_A.

Figure 2(iii). DSC curve of ER$_F$.

Figure 3. TGA curve of ER_F.
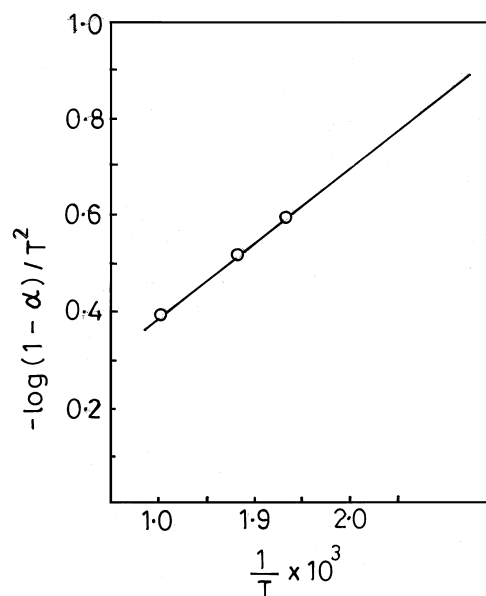
Figure 4.   A graph between - log (log
(1-α)/ T2 vs. l/T x10 (ER$_F$).

$$\log g\,(\alpha)/T^2 = -\,E_a/2.3\ RT \quad + \ \log ZA/BE\ (1\text{-}2RT/E_a)\text{-}(3)$$

Z = pre exponential factor
T = temperature
R = gas constant
B = linear heating rate

The activation energy, calculated from the slope of linear graph, between log g (α) vs (1/T)x10^3 is 86 KJ/mole which is higher as compared to blank epoxy resin (34 KJ/mole). The overall order of reaction follows a firstorder kinetics, because the value of (α) is low (0.090.10).

Mechanism

Lewis acids are the compounds containing empty orbital position in the outer shell of one of the atoms. The Lewis acid form a complex with epichloro-hydrin but not with bisphenol-A, according to the following structure.
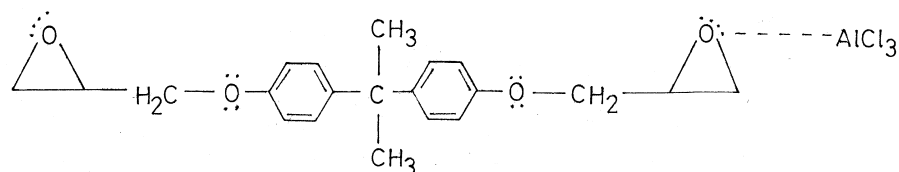
ACKNOWLEDGEMENT

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