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DIFFERENTIAL SCANNING CALORIMETRY STUDY OF REACTIONS OF EPOXIDES WITH POLYAMINES

F. SEVERINI*, R. GALLO and R. MARULLO

Istituto di Chimica Industriale dell'Università-Messina, Italy

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The reactions of 1,2,3,4-diepoxybutane (DEPB), 1,2,7,8-diepoxyoctane (DEPO), the diglycidyl ether of 1,4-butanediol (DGEBU) and the diglycidyl ether of bisphenol A (DGEBA) with ethylenediamine (EDA), diethylenetriamine (DETA) and tetraethylene-pentamine (TEPA) have been studied with DSC only. The epoxide reactivity decreases according to the sequence:

DEPO > DEPB > DGEBU > DGEBA

At low amine concentration the conversion of epoxy groups increases as the active hydrogen concentration increases, no matter which polyamine is used.

From DSC dynamic measurements, according to Freeman and Carroll's treatment, the reaction activation energy is about 98 kJ/E.M.M. for a large range of polyamine/epoxy ratios, while as calculated from isothermal experiments using Barton's equation, it is 38–42 kJ/E.M.M.

The reaction of epoxides with crosslinking agents such as amines is of great practical importance and has been the subject of several studies concerning mixtures containing nearly one active hydrogen atom to one epoxidic group [1–5]. Largerly DSC has been employed to study the kinetics of these reactions and to determine some important parameters such as activation energy and reaction order [1, 2, 5].

The present study considers the reactions of four different epoxides with aliphatic polyamines in amounts corresponding to active hydrogen concentrations between 0.1 and 7 g atoms per E.M.M.; the activation energy has also been determined.

The reactions have been investigated mainly in DSC dynamic experiments; a few tests have been performed isothermally, using only DGEBA and DGEBU to determine the activation energy.

Experimental

The following reactants were used:

Bisphenol A diglicydil ether (DGEBA); E.M.M. = 201, Epikote 828 (Shell Chem.).

* To whom correspondence should be addressed.

1,4-Butanediol diglicydil ether (DGEBU); E.M.M. = 131, Heloxy WC 67 (Wihlington Chem.).

1,2,3,4-Diepoxybutane (DEPB); E.M.M. = 41, Fluka reagent.

1,2,7,8-Diepoxyoctane (DEPO); E.M.M. = 80, Fluka reagent.

Ethylenediamine (EDA); Fluka, analytical grade. Diethylenetriamine (DETA) and tetraethylenepentamine (TEPA); Fluka, technical grade.

Beside each epoxide is reported the weight which contains 1 g equivalent of epoxy group (E.M.M.) and the trade name. Products were used without further purification.

DSC curves were obtained on a DSC 2 Perkin–Elmer instrument. Samples of 10–15 mg epoxide were weighed in aluminium pans and the polyamine then added from a microsyringe.

The instrument was preset at 308 or 323 K and the sample was either heated to 493–503 K at 20 degree/min (dynamic tests) or rapidly heated (160 deg/min) to a predetermined temperature (isothermal test).

Indium was used as the standard for calibrating the temperature axis and the enthalpy output. All experiments were carried out in nitrogen atmosphere.

Results and discussion

The obtained data were analysed assuming that the evolved heat is directly proportional to the extent of reaction.

The average heat of reaction of one epoxy group with an amine was taken as 108.8 kJ/E.M.M., i.e. the heat of reaction of the model system phenylglycidyl ether/*n*-butylamine [6].

DGEBU–DGEBA

Polyamine/epoxide ratios from 0.0036 to 1.07 mol amine/E.M.M. were used.

For TEPA, at concentrations lower than 0.8 mol/E.M.M. regular DSC curves characterized by only one peak were obtained (Fig. 1A), while at higher amine concentrations the DSC curves show a main peak followed by several secondary endothermic and exothermic peaks which are not completely reproducible and may in some cases represent up to 20–25% of the total evolved heat.

Figure 1B shows a typical example of a DSC curve affording small exothermic peaks, due to the reaction of residual epoxidic groups, following the initial endothermic signal.

Because of the high boiling points of the reagents the endothermic peak is not attributable to evaporation processes and may possibly be due to a rearrangement of the initially formed crosslinked structure. The enthalpy of reaction between DGEBU or DGEBA and TEPA increases as the amine concentration rises and reaches an asymptotic value beginning at an active hydrogen atom concentration

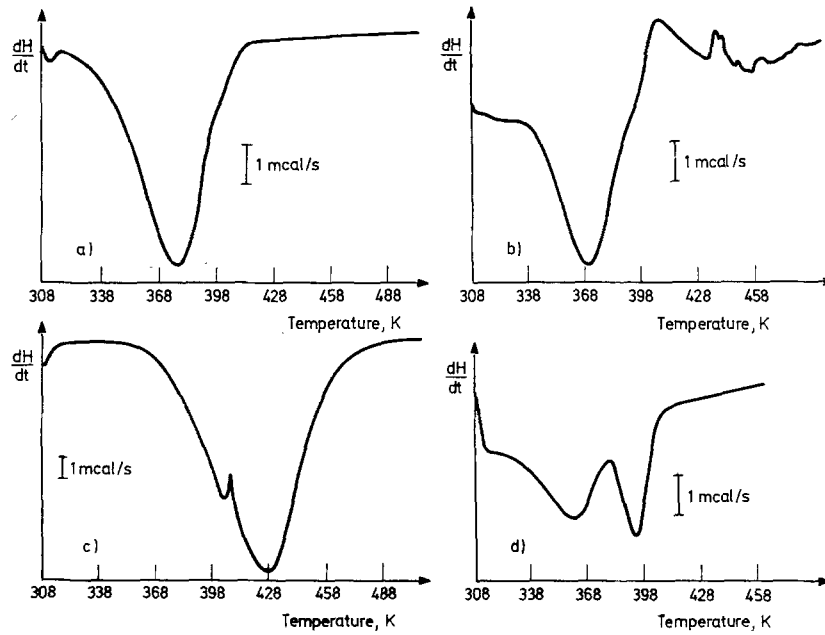

Fig. 1. Typical DSC curves: a) DGEBU + TEPA (0.5 moles TEPA/E.M.M.); b) DGEBU + TEPA (1 mol TEPA/E.M.M.); c) DEPO + TEPA (0.16 moles TEPA/E.M.M.); d) DEPB + DETA (0.09 moles DETA/E.M.M.)

of 5 to 6, corresponding to a strong excess calculated on a basis of 1 active hydrogen atom to 1 epoxy group (Figs 2 and 3). Figure 4 shows the conversion α vs. temperature plots for the reactions of DGEBA and DGEBU with TEPA (0.5 mol TEPA/E.M.M.). The fraction reacted α was calculated as the fraction of the total measured enthalpy of the reaction.

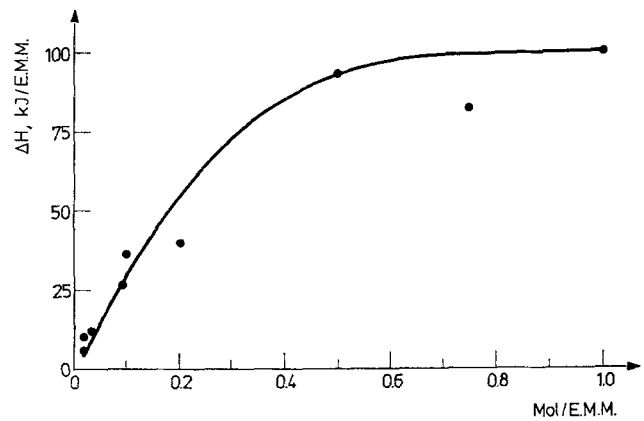

Fig. 2. DGEBU + TEPA; heat of reaction vs. moles TEPA/E.M.M

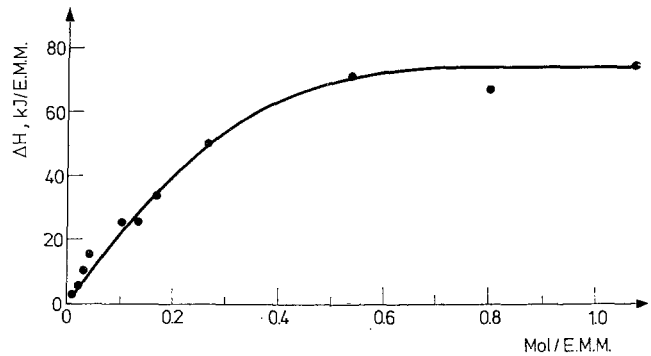

Fig. 3. DGEBA + TEPA; heat of reaction vs. moles TEPA/E.M.M.

Analysis of the DSC curves for the reaction of DGEBA or DGEBU with TEPA shows that the temperature of the DSC peak decreases as the TEPA concentration increases; this is also true for 1,2,7,8-diepoxyoctane (Fig. 5).

DEPB – DEPO

Results on the reactions of DEPO with TEPA and DETA are listed in Table 1. Table 2 contains results on the reactions of DEPB with TEPA, DETA and EDA at the same concentration of 0.09 mol/E.M.M.

All the data show that the epoxide conversion increases as the active hydrogen concentration increases.

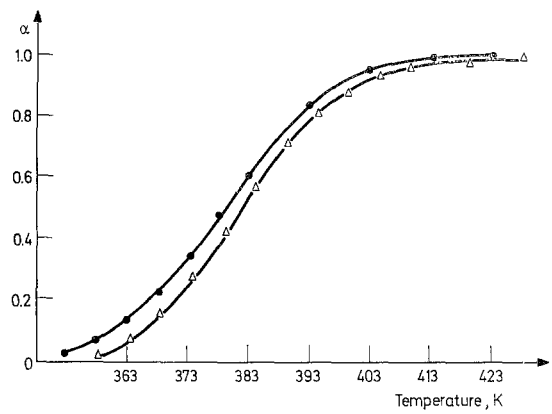

Fig. 4. Fraction (α) of epoxy groups reacted vs. temperature. α was estimated as the ratio of the heat evolved at each temperature and the total measured heat evolved. DGEBA + TEPA △; DGEBU + TEPA ●; 0.5 moles TEPA/E.M.M.

Table 1

Results from DSC analysis of reactions between DEPO and amines. Temperature range ● 308–493 K; □ 308–573 K. Heating rate 20 degree/min

Amine	Active H g atoms per E.M.M.	ΔH kJ/E.M.M.	Epoxy group conversion %, α
DETA ●	0.45	31.0	0.28
TEPA ●	0.63	41.8	0.38
TEPA □	1.10	62.8	0.57

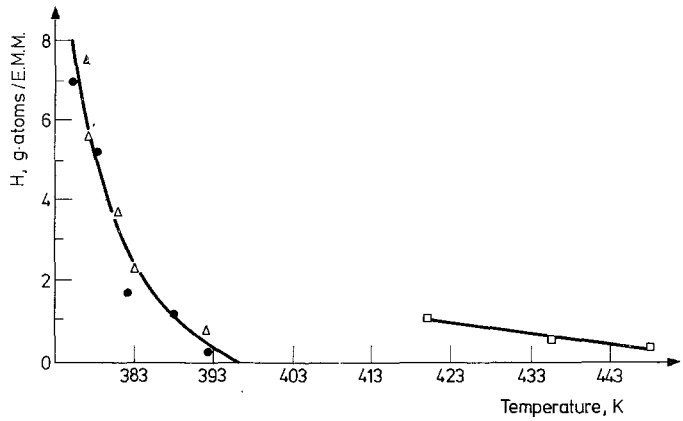

Fig. 5. Temperature of DSC peak vs. active hydrogen atom number/E.M.M. Reaction of TEPA with: DGEBU ●; DGEBA △; DEPO □

The DEPO DSC curves show a shoulder preceding the maximum, whereas for DEPB two peaks appear, the second one giving the main contribution to the total area (Figs 1C and 1D).

The presence of two peaks could mean that the reaction proceeds with a different mechanism from that in the case of the other epoxides.

Table 2

Results from DSC analysis in the range 308–473 K of the reactions between DEPB and amines Heating rate 20 degree/min

Amine	Active H g atoms per E.M.M.	ΔH kJ/E.M.M.	Epoxy group conversion %, α
EDA	0.36	15.5	0.14
DETA	0.45	24.7	0.22
TEPA	0.63	36.4	0.33

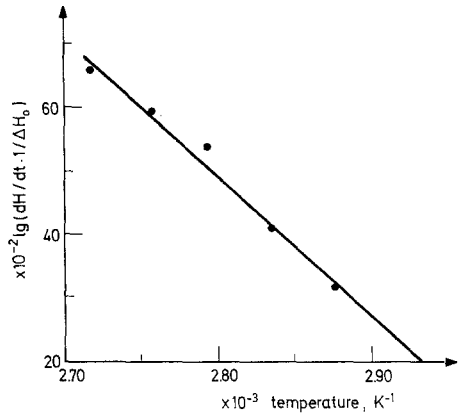

Fig. 6. Arrhenius plot according to Barton's equation for the reaction DGEBU + TEPA (1 mole TEPA/E.M.M.)

Activation energy evaluation

The reactions of DGEBA and DGEBU with TEPA (1 mol TEPA/E.M.M.) were carried out isothermally at 353, 358 and 363 K and at 343, 353 and 368 K, respectively. Reproducible regular DSC curves were obtained, and the activation energy was calculated using Barton's equation [1]:

$$\ln r_\alpha = \ln [A f(\alpha)] - \frac{E}{RT}.$$

Figure 6 shows the $\lg r_\alpha$ vs. $\frac{1}{T}$ plot for the reaction of DGEBU with TEPA.

Table 3 lists activation energy values calculated from DSC dynamic experiments using Freeman and Carroll's equation [7]. Figure 7 shows the

$$\frac{\Delta \lg \frac{d\alpha}{dt}}{\Delta \lg (1-\alpha)} \text{ vs. } \frac{\Delta \frac{1}{T}}{\Delta \lg (1-\alpha)} \quad \text{plot}$$

Table 3

Activation energy data from DSC analysis of the reactions between TEPA and epoxides. Heating rate 20 degree/min

Epoxide	Active H g atoms per E.M.M.	*E*, kJ/E.M.M.	Range of scanned temperature, K
DGEBA	0.30	97.9	323—473
DGEBA	0.74	99.2	323—473
DGEBU	3.50	99.2	323—473
DEPO	1.10	98.3	308—573

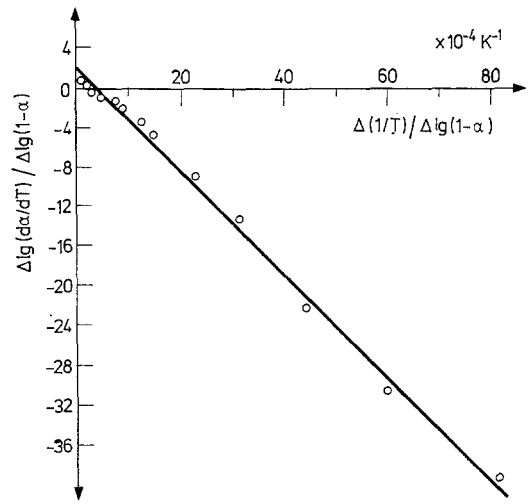

Fig. 7. Activation energy calculation according to Freeman and Carroll for the reaction DEPO + TEPA (0.16 moles TEPA/E.M.M.)

for the reaction of DEPO with TEPA (0.16 mol TEPA/E.M.M.). No matter which epoxide and amine are used and regardless of their ratio in the mixture, the activation energy obtained from DSC dynamic measurements is about 98 kJ/E.M.M. This value is higher than those obtained isothermally (41.4 and 42.7 kJ/E.M.M.) for DGEBA and DGEBU respectively. This difference agrees with other data reported in the literature [2].

Epoxide and amine reactivities

Table 4 contains results on the reactions of the four studied epoxides with the same amine concentration (0.09 mol TEPA/E.M.M.), corresponding to 0.63 active hydrogen atoms/E.M.M.

Table 4

Reactions between epoxides and TEPA. Heating rate 20 deg/min, 0.09 mol TEPA/E.M.M. Range of scanned temperature: DGEBA, 323–473 K; DGEBU, 323–473 K; DEPB, 308–473 K; DEPO, 308–573 K

Epoxide	ΔH, kJ/E.M.M.	Epoxy group conversion %, α
DGEBA	20.9	0.19
DGEBU	26.6	0.24
DEPB	34.7	0.32
DEPO	42.3	0.39

According to the heat evolved, the quantity of each reacting epoxide decreases as follows:

$$DEPO > DEPB > DGEBU > DGEBA .$$

This sequence may be regarded as an indicator of epoxide reactivity.

Given the DSC curve complexity, the value reported for DEPB has been estimated with some approximation.

The heat of reaction vs. active hydrogen concentration plot (Fig. 8) shows that the evolved heat increases as the active hydrogen concentration increases, no matter which amine is used and regardless of the ratio of primary to secondary hydrogen atoms present.

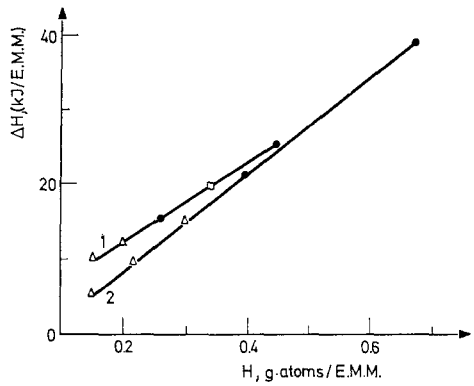

Fig. 8. Heat of reaction vs. active hydrogen g atoms/E.M.M. Curve 1: DGEBU + amines; Curve 2: DGEBA + amines; □ EDA; ● DETA; △ TEPA

In the described experiments, characterized by short reaction times, the heat evolved from the reacting E.M.M. was always lower than 108.8 kJ, the heat of reaction of one epoxy group with an amine [6]. The features of the crosslinked system that are formed during the reaction between epoxide and amine probably influence the diffusion of the reagents and, as a consequence, the further development of the reaction [8] and the temperature of the DSC curve peak (Fig. 5) corresponding to the maximum reaction rate.

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ZUSAMMENFASSUNG — Die Reaktion von 1.2.3.4-Diepoxybutan (DEPB), 1.2.7.8-Diepoxyoctan (DEPO) und der Diglycidyläther von 1.4-Butandiol (DGEBU) und Bisphenol A (DGEBA) mit Äthylendiamin (EDA), Diäthylentriamin (DETA) und Tetraäthylenpentamin (TEPA) wurde ausschließlich mit DSC untersucht. Die Reaktivität der Epoxide nimmt in der Reihenfolge

DEPO > DEPB > DGEBU > DGEBA

ab. Die Konversion der Epoxygruppen steigt mit zunehmender Konzentration an aktivem Wasserstoff an, gleich welches Polyamin benutzt wird. Dynamische DSC-Messungen, ausgewertet nach Freeman und Caroll, ergeben für einen weiten Bereich des Polyamin/Epoxy-Verhältnisses eine Aktivierungsenergie von 98 kJ/E.M.M., während aus isothermen Experimenten nach Barton's Gleichung Werte von 38—42 kJ/E.M.M. berechnet werden.

Резюме — С помощью ДСК изучена реакция взаимодействия 1,2,3,4-диэпоксибутана (ДЭПБ), 1,2,7,8-диэпоксиоктана (ДЭПО), диглицидного эфира 1,4-бутандиола (ДГЭБУ), диглицидного эфира бисфенола А (ДГЭБА) с этилендиа мином, диэтилентриамином и тетраэтиленпентамином. Реакционная способность эпоксидов уменьшается в последовательности: ДЭПО > ДЭПБ > ДГЭБУ > ДГЭБА. При низкой концентрации амина превращение эпоксигрупп увеличивается, поскольку увеличивается концентрация активного водорода независимо от того какой полиамин был исполсзован. Обработкой данных ДСК динамических измерений по методу Фримэна—Каррола была вычислена для широкой области соотношений полиамин-эпоксид энергия активации равная 98 кдж/Э. М. М. Энергия активация, вычисленная на основе уравнения Бэртона из данных изотермических измерений, была равной 38—42 кдж/Э. М. М.