Cis/Trans Reactivity: Epoxy−Amine Systems

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ABSTRACT: The reactivities of cis and trans isomers of 1,2-diaminocyclohexane (1,2-DCH)/epoxy resin were studied separately. We found that the primary amine hydrogen disappears in both isomers at a similar rate when they react with an epoxy resin. However, the formation of tertiary amines differs considerably. The reactivity of the second amine hydrogen for the trans isomer is greater than that for the cis isomer, and this difference is observed as the reaction proceeds. The main reason for the slower disappearance of the cis secondary amine is steric hindrance and this fact is observed in the preexponential factors, glass transition temperatures (T_g), and ratio of rate constants of secondary to primary amine (R). The reaction was followed by Fourier transform infrared spectroscopy in the near-infrared range. The values of T_g were obtained by differential scanning calorimetry.

Introduction

Cycloaliphatic diamines are very common curing agents for epoxy resins used in different fields such as electric/electronic components, prepregs, civil engineering, coatings, adhesives, etc. The final properties of the epoxy systems depend mainly on the cross-linked network, which is directly related to the chemical structure of the starting monomers and the cure program. Many kinetic studies of epoxy−amine reactions can be found in the literature,[1−6] but to our knowledge there are not any where the reactivity of the isomers of cycloaliphatic diamines have been studied separately. However, we consider this type of study would be very important because most of these amines, if not all, are a mixture of isomers. Prince et al.[7,8] working on synthesis of polyamides derived from 1,4-diaminocyclohexane found a great difference in the glass transition temperature (T_g) and melting point (mp) of polyamides obtained from *cis*-1,4-diaminocyclohexane and *trans*-1,4-diaminocyclohexane and different diacids.

Very few studies of epoxy/cycloaliphatic diamines are found in the literature. Verchère et al.[9] studied the reaction of epoxy resin with 4,4'-diamino-3,3'-dimethyldicyclohexyl methane (3-DCM). This system was also studied by Jordan et al.[10] Chen et al.[11] investigated the evolution of the reaction of an epoxy resin with several cycloaliphatic diamines: isophorone diamine (IPD), 3-DCM, and 4-amino-α,α,4-trimethyl-cyclohexanemethanamine (MNDA). Palmese and McCullough[12] studied the properties of an epoxy resin/bis-*p*-aminocyclohexylmethane (PACM-20). Recently, Vyazovkin and Sbirrazzuoli[13] used an epoxy system based on isophorone diamine (IPD) to study the mechanism of the reaction, however the possibility of different isomer reactivities had not been taken into account. We previously mentioned this possibility, but the reaction was globally considered.[14]

Experimental Section

Materials. The epoxy monomer used was a pure diglycidyl ether of bisphenol A (DGEBA) from Aldrich with an epoxy equivalent equal to 174 g equiv^{-1}. The curing agents used were two isomers of 1,2-diaminocyclohexane (1,2-DCH), *cis*-1,2-DCH and *trans*-1,2-DCH (from Fluka with a purity of ≥98% and a molecular weight of 114 g mol^{-1}). The purity of both amines was tested by gas chromatography−mass spectrometry (GC−MS) and wet analysis; a value of ≈99.1% for both was found.

Sample Preparation. Stoichiometric amounts of DGEBA and each isomer of 1,2-DCH were used. DGEBA was previously melted, and both weighing and mixing took place in an N_2 atmosphere.

Techniques. Fourier transform infrared spectroscopy (FTIR) has long been known[15−17] as a versatile method for both qualitative and quantitative analysis of epoxy/amine systems. Several studies[18−21] have been carried out in the near-IR region because in this region the spectrum is less complex compared with the usual mid-IR range. The details of the experimental FTIR method have been described in a previous paper.[22] Infrared measurements were carried out on a Perkin-Elmer Spectrum 2000, equipped with a Dynascam Interferometer, cooled IR source, KBr beam splitter, and DTGS detector. Each spectrum from 7000 to 4000 cm^{-1} was averaged over 20 scans at 8 cm^{-1} resolution with a scanning rate (OPD) of 4 cm^{-1}. Measurements were carried out at different temperatures (60, 70, 80, and 90 °C) using a temperature controller, a Specac 20140 equipped with a circular NaCl cell, and a Teflon spacer (path length 1 mm). The thermal equilibrium was optimized with an external thermostatic bath, pumping water (flow: 500 mL min^{-1} at 10 °C) through the cell. When the controller showed the programmed temperature, the reactive mixture was injected into the NaCl cell with a syringe. A series of spectra was recorded and obtained versus time at each cure temperature using software for kinetic determinations (Perkin-Elmer). The peaks at 4931 cm^{-1} (for cis isomer) and 4923 cm^{-1} (for trans isomer) were used to follow the primary amine, whereas the peak at 4530 cm^{-1} was used to monitor the epoxy group.

The quantification of epoxy and amine was carried out by considering the ratio of absorbances at different times with respect to the absorbance at $t = 0$. Because a fixed path length was used, a reference band was not necessary (the thickness fluctuations during the cure can be considered to be negligible, because the density varies from 1110 kg m^{-3} for the uncured

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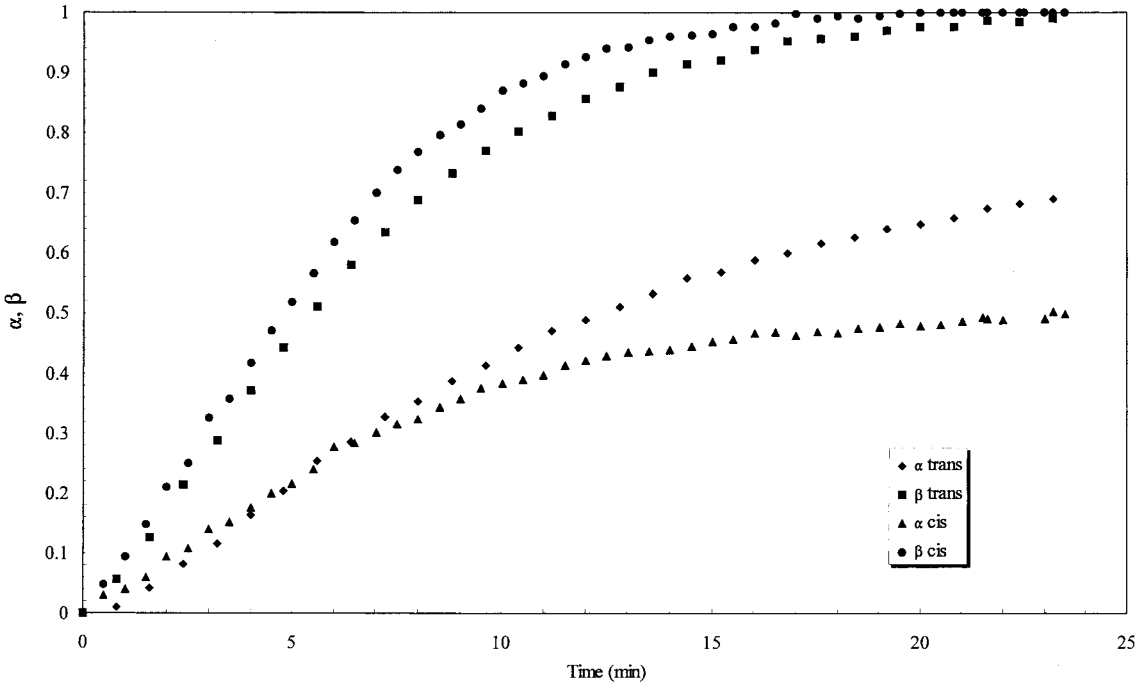

Figure 1. Degree of conversion for epoxy (α) and primary amine (*β*) as a function of reaction time for 1,2-diaminocyclohexane (cis and trans isomers) at 80 °C.

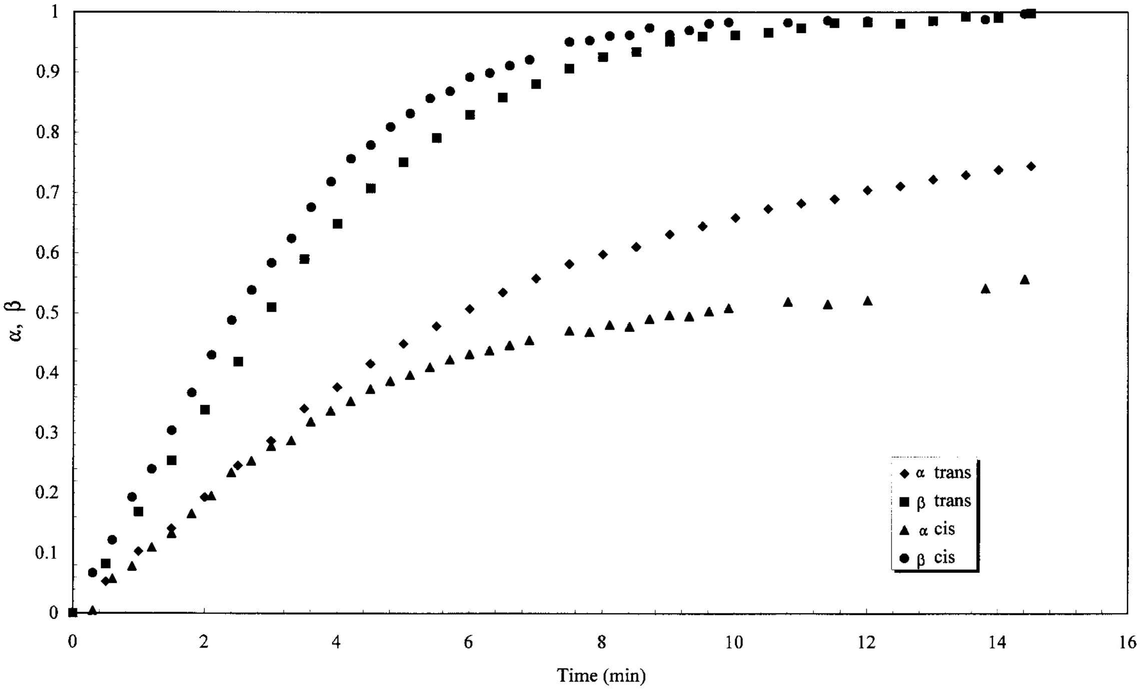

Figure 2. Degree of conversion for epoxy (α) and primary amine (*β*) as a function of reaction time for 1,2-diaminocyclohexane (cis and trans isomers) at 90 °C.

mixtures to 1140 kg m^{-3} after cure at 90 °C). We found more reproducible results taking the peak height instead of the band area, probably because of the overlapping of the amine and the hydroxyl formed bands. Different concentrations of epoxy and amine were used to verify the dependence of the absorbance (height) on the concentration. The plots obtained show that Beer's law is obeyed for both wavenumbers used.

Differential scanning calorimetry (DSC) analysis was performed with a DSC-7 Series Perkin-Elmer equipped with a Digital Celebris 466 computer, TAC 7/7 controller, and both dynamic and isothermal software. Details on calibration and general conditions can be found elsewhere.[23]

Results and Discussion

Degree of Conversion. Figures 1 and 2 show the variation of the conversion versus time for epoxy (α) and primary amine (*β*) for both isomers at two chosen temperatures (80 and 90 °C), as

$$\alpha = ([E_0] - [E])/[E_0] \qquad \beta = ([A_1]_0 - [A_1])/[A_1]_0$$

where $[E_0]$ and $[A_1]_0$ are the initial concentrations of the epoxy and the primary amine, respectively, and [E] and $[A_1]$ are the concentrations of the epoxy and the primary amine at any time.

It can be observed that although β is very similar for both isomers, α begins to differ as the reaction proceeds. As β represents the consumption of the primary amine or the opening of the epoxy ring by the first amine hydrogen, the reactivity of the first cis hydrogen is similar, or even a little higher than that of the trans.

Figures 1 and 2 show that the α curves are very similar for both isomers up to α values of 0.24−0.28. Above these values, α diverges, being higher for trans than cis (this behavior is observed at other temperatures). This fact is directly related to the reactivity of the secondary amine hydrogens on both isomers. If these hydrogens were not reactive, the possibility of reaction would only be primary amine hydrogens/epoxy groups. If the reactivity were the same, α would have the same values for the cis and trans isomers. Consequently and according to the experimental data (see Figures 1 and 2), the reactivity of the secondary amine hydrogens of the trans isomer are higher than those of the cis isomer.

If we assume that the reaction takes place only between the primary amine hydrogens and the epoxy groups and by considering, as stated, that the mixture is stoichiometric (2 mol DGEBA/1 mol 1,2-DCH) then $\beta = 2\alpha$. Figures 1 and 2 show that in fact $\beta \cong 2\alpha$ up to α values of 0.24−0.28. This result indicates that there is practically no reaction between the secondary amine hydrogens and epoxy groups for $\alpha < 0.28$.

It can be observed that the maximum value reached for α_{cis} is $\sim$0.5, whereas $\alpha_{trans} > 0.7$ (90 °C). These differences in the final degree of conversion for both isomers cannot be explained in terms of cure temperature (T_c). There is a relationship between T_c/conversion and conversion/T_g (glass transition temperature). When T_c and the maximum value of the T_g (T_g^{∞}) for a given system are close, the value of conversion tends to be maximum. However, the experimental values obtained by DSC at 10 K min^{-1} are $(T_g^{\infty})_{cis} = 95$ °C and $(T_g^{\infty})_{trans} = 166$ °C. Therefore, there must be another reason to explain why the final conversion of the cis isomer is much lower than that for the trans isomer. The reason may be related to the differences in reactivities of the secondary hydrogens, as already indicated.

Evaluation of Rate Constants. A parameter directly related to the cross-linked network is the ratio of the rate constants (R) for the hydrogens on secondary and primary amino groups. This parameter represents the effect of the substitution of the primary amine hydrogen by an epoxy group on the secondary amino hydrogen. If $R \to 0$, the structure would not be cross-linked. We have shown[22] that when the mechanism of cure proceeds according to an OH-catalyzed/noncatalyzed simultaneous path, (eqs 1, 2 and 3, 4, respectively), R (k_2/k_1 or k_2^{I}/k_1^{I}) can be directly obtained through the rate equation for the formation of secondary amine (d[A$_2$]/dt) and evaluated by a simple ratio of concentrations primary/secondary amine; that is, $R = [A_1]/[A_2]$.

It is important, however, to consider that some authors[24,25] have taken into account the possible influence of other products on the reaction rate, these being either present or generated during the course of reaction (such as primary, secondary, or tertiary amines). A general multipath mechanism catalyzed by hydroxyl (eqs 1 and 2), primary amine (eqs 5 and 6), secondary amine (eqs 7 and 8), tertiary amine (eqs 9 and 10), and noncatalyzed path (eqs 3 and 4) can be proposed:

$$A_1 + E \xrightarrow[OH]{k_1} A_2 \qquad A_2 + E \xrightarrow[OH]{k_2} A_3 \qquad (1),(2)$$

$$A_1 + E \xrightarrow{k_1^{I}} A_2 \qquad A_2 + E \xrightarrow{k_2^{I}} A_3 \qquad (3),(4)$$

$$A_1 + E \xrightarrow[A_1]{k_1^{II}} A_2 \qquad A_2 + E \xrightarrow[A_1]{k_2^{II}} A_3 \qquad (5),(6)$$

$$A_1 + E \xrightarrow[A_2]{k_1^{III}} A_2 \qquad A_2 + E \xrightarrow[A_2]{k_2^{III}} A_3 \qquad (7),(8)$$

$$A_1 + E \xrightarrow[A_3]{k_1^{IV}} A_2 \qquad A_2 + E \xrightarrow[A_3]{k_2^{IV}} A_3 \qquad (9),(10)$$

where E, OH, A$_1$, A$_2$, and A$_3$ are the epoxy, hydroxyl, primary, secondary, and tertiary amines, respectively. By considering eqs 1−10, the reaction rate for the formation of the secondary amine is given by the following equation:

$$\frac{d[A_2]}{dt} = k_1[OH][A_1][E] - k_2[OH][A_2][E] + k_1^{I}[A_1][E] - k_2^{I}[A_2][E] + k_1^{II}[A_1]^2[E] - k_2^{II}[A_1][A_2][E] + k_1^{III}[A_1][A_2][E] - k_2^{III}[A_2]^2[E] + k_1^{IV}[A_1][A_3][E] - k_2^{IV}[A_2][A_3][E] \qquad (11)$$

Assuming that the ratio of rate constants (R) is independent of the path,[1−3,5,6,13,14,26] then: $k_2/k_1 = k_2^{I}/k_1^{I} = k_2^{II}/k_1^{II} = k_2^{III}/k_1^{III} = k_2^{IV}/k_1^{IV} = R$. When [A$_2$] attains its maximum value, (d[A$_2$]/dt)$_{max}$ = 0. It can be seen that after some algebraic manipulations, the resultant equation is the same as previously obtained when only eqs 1, 2 and 3, 4 were considered; that is, $R = [A_1]/[A_2]$.

Figures 3 and 4 show that the variation of concentration of primary, secondary, and tertiary amines against time for both isomers (at 90 °C). The value of [A$_1$] was directly obtained from the experiments, and [A$_2$] and [A$_3$] from the following mass balances:

$$[A_1]_0 = [A_1] + [A_2] + [A_3] \qquad (12)$$

$$[E_0] = [E] + [A_2] + 2[A_3] \qquad (13)$$

where [E$_0$] and [A$_1$]$_0$ are the initial concentrations of epoxy and primary amine, respectively, and [A$_1$], [A$_2$], and [A$_3$] are the concentrations of primary, secondary, and tertiary amines at any time, respectively. By combining eqs 12 and 13, [A$_2$] and [A$_3$] are evaluated:

$$[A_2] = [E_0]\,(B^*\beta - \alpha) \qquad (14)$$

$$[A_3] = [E_0](\alpha - \beta^* B/2) \qquad (15)$$

where $B = 2\,[A_1]_0/[E_0]$ ($B = 1$ for stoichiometric mixtures used in our case).

If we consider, in agreement with several authors,[3,9,13,14,27−29] that the mechanisms catalyzed by OH groups and noncatalyzed are predominant over the mechanisms catalyzed by primary, secondary, and tertiary amines and no evaporation of monomers takes place (using a closed cell), the rate constants can

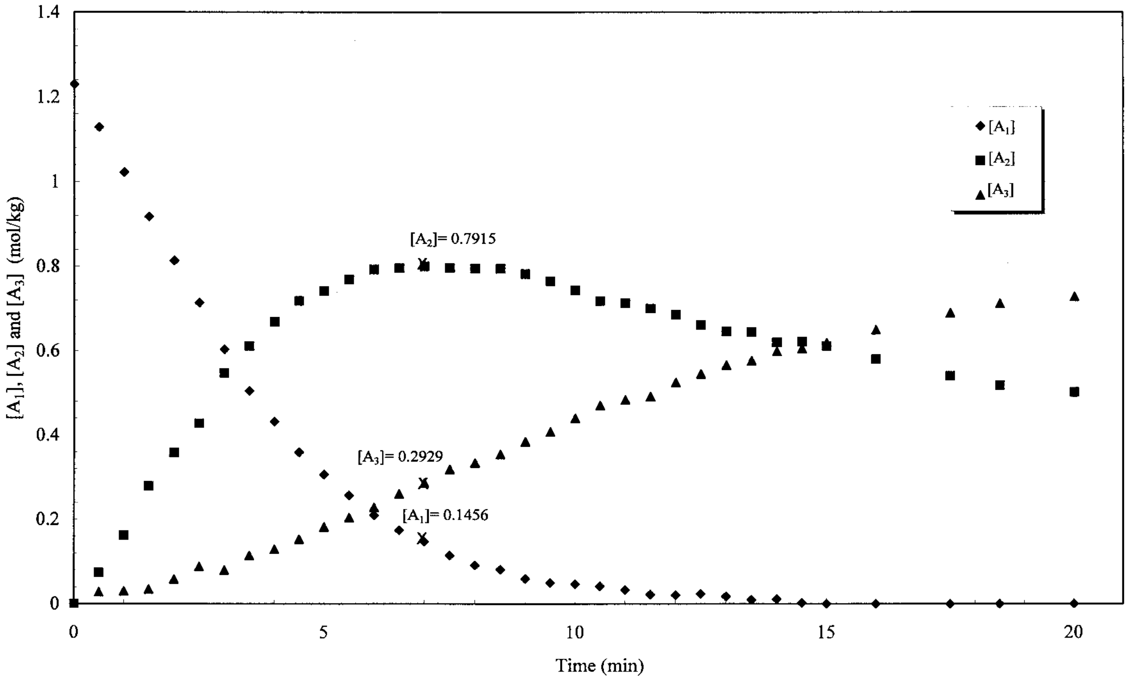

Figure 3. Variation of the concentrations of primary, secondary and tertiary amines ([A$_1$], [A$_2$], and [A$_3$], respectively) as a function of reaction time for *trans*-1,2-diaminocyclohexane at 90 °C.

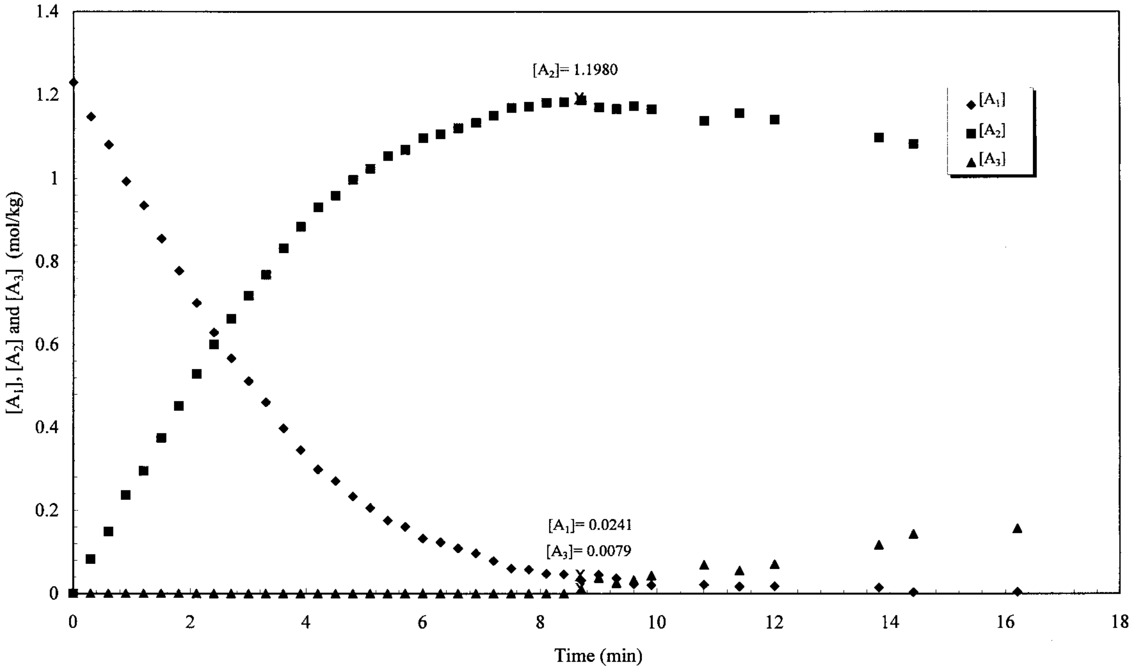

Figure 4. Variation of the concentrations of primary, secondary and tertiary amines ([A$_1$], [A$_2$], and [A$_3$], respectively) as a function of reaction time for *cis*-1,2-diaminocyclohexane at 90 °C.

be evaluated from the following equation:[14]

$$\frac{-(\mathrm{d}[A_1]/\mathrm{d}t/[A_1])}{(1-\alpha)} = K_1^{\mathrm{I}} + K_1\alpha \qquad (16)$$

The values of K_1 and K_1^{I} are obtained directly by plotting the first term of the eq 16 versus α ([A$_1$] and α are taken from the experiment). The parameters K_1 and K_1^{I} represent the global rate constants related to the elemental rate constants (k_1 and k_1^{I}) and initial epoxy concentration: $K_1 = k_1\,[E_0]^2$ and $K_1^{\mathrm{I}} = k_1^{\mathrm{I}}\,[E_0]$. The ratio of rate constants (R) is calculated, as stated, at $[A_2]_{\max}$ (see marks in Figures 3 and 4).

Table 1 shows the values of rate constants, activation energies, preexponential factors, R and T_g^{∞} for both isomers. It is worth pointing out that although the parameters involved in k_1^{I} and k_1 (preexponential factors and activation energies) are very similar for both isomers, they strongly differ for k_2^{I} and k_2 (calculated from the definition of R; $k_2 = k_1R$ and $k_2^{\mathrm{I}} = k_1^{\mathrm{I}}\,R$). We also found important differences for the concentration of tertiary amines (cross-linked units), T_g^{∞}, and R. At $[A_2]_{\max}$, the values of [A$_3$] are (at 90 °C) 0.2929 and 0.0079 mol kg^{-1} for trans and cis isomers, respectively (see Figures 3 and 4), and the glass transition temperatures are $(T_g^{\infty})_{\mathrm{trans}} = 166$ °C and $(T_g^{\infty})_{\mathrm{cis}} = 95$ °C; a great

Table 1. Kinetic Parameters for *trans*- and *cis*-1,2-Diaminocyclohexane Isomers

	trans (T_g^∞ = 166 °C)						cis (T_g^∞ = 95 °C)					
parameter	60 °C	70 °C	80 °C	90 °C	E_a (kJ mol^{-1})^a	A^b	60 °C	70 °C	80 °C	90 °C	E_a (kJ mol^{-1})^a	A^b
R	0.2350	0.2155	0.1987	0.1840			0.0381	0.0304	0.0245	0.0201		
K_1 (s^{-1})	1.31×10^{-3}	2.14×10^{-3}	4.21×10^{-3}	6.95×10^{-3}	56.8	1.1×10^{6}	1.47×10^{-3}	2.64×10^{-3}	4.44×10^{-3}	7.81×10^{-3}	55.3	7.6×10^{5}
K_1^{I} (s^{-1})	4.65×10^{-4}	1.36×10^{-3}	2.08×10^{-3}	3.80×10^{-3}	67.6	2.3×10^{7}	6.82×10^{-4}	1.29×10^{-3}	2.34×10^{-3}	4.53×10^{-3}	62.8	5.2×10^{6}
k_1 (kg^2 mol^{-2} s^{-1})	2.17×10^{-4}	3.53×10^{-4}	6.95×10^{-4}	1.15×10^{-3}	56.8	2.3×10^{5}	2.43×10^{-4}	4.35×10^{-4}	7.35×10^{-4}	1.29×10^{-3}	55.3	1.3×10^{5}
k_1^{I} (kg mol^{-1} s^{-1})	1.88×10^{-4}	5.52×10^{-4}	8.45×10^{-4}	1.55×10^{-3}	67.8	1.0×10^{7}	2.77×10^{-4}	5.23×10^{-4}	9.52×10^{-4}	1.84×10^{-3}	62.8	2.1×10^{6}
k_2 (kg^2 mol^{-2} s^{-1})	5.13×10^{-5}	7.58×10^{-5}	1.36×10^{-4}	2.13×10^{-4}	48.5	2.2×10^{3}	8.60×10^{-6}	1.50×10^{-5}	1.77×10^{-5}	2.52×10^{-5}	34.0	2.1
k_2^{I} (kg^2 mol^{-2} s^{-1})	4.47×10^{-5}	1.19×10^{-4}	1.65×10^{-4}	2.88×10^{-4}	59.4	1.2×10^{5}	9.77×10^{-6}	1.80×10^{-5}	2.88×10^{-5}	3.58×10^{-5}	41.4	34.7

[a] E_a = activation energy. [b] A = preexponential factor.

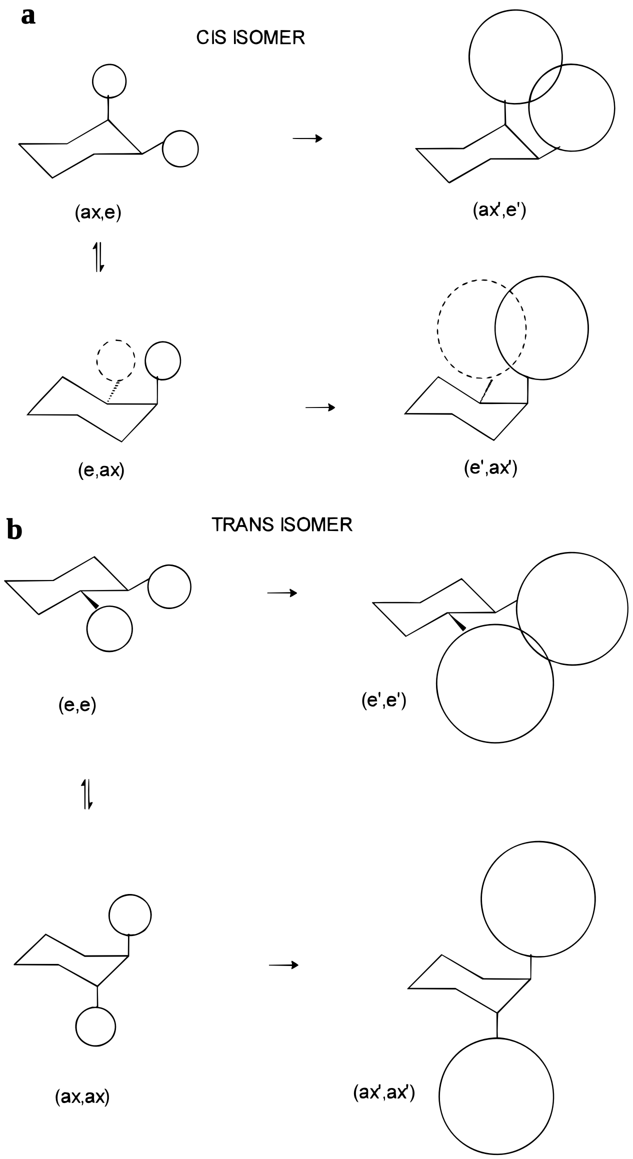

Figure 5. Schematic pictures showing the steric hindrance of the different conformers for both isomers: (a) cis, (b) trans.

difference for such similar products. Also, *R* shows an "anomalous" behavior again. Both isomers exhibit similar tendency with the cure temperature; *R* decreases as the temperature increases. However the value of *R* for the trans isomer is up to nine times greater (90 °C) than the value for the cis isomer.

Conformers of Cis/Trans Isomers. Figure 5 (not drawn to scale and is only for illustrative purposes) represents both isomers and their conformers. Small circumferences show the primary amino groups (left side) and large circumferences the secondary amino groups (right side). The cis isomer of the monomer (Figure 5a) has two energetically identical chair conformations (ax, e) and (e, ax). Each of these conformers has one amino substituent in the axial position and another in the equatorial. The trans isomer of the monomer (Figure 5b) shows two energetically different chair conformations (e, e) and (ax, ax). One of the conformations locates the amino group in an equatorial position (e, e) and the other one in an axial position (ax, ax). The diequatorial monomer is ≈2 kcal mol^{-1} more stable than the diaxial one[30] and, because of the energy difference between both conformations, the equilibrium is displaced toward the diequatorial conformer. The relative population of the diequatorial conformation is ≈29 times higher than in the diaxial one ($K = e^{-\Delta G/RT}$, and if $T \cong 298$ K, and $\Delta G° \cong 2$ kcal mol^{-1}, then $K \cong 0.035$ and $1/K \cong 29$).

To elucidate the different pathways, many reactions must be considered and Figure 5 is only an overall representation, but there exists other possibilities.

Cis Isomer. Because both conformers are energetically identical, only one pathway will be considered:

$$\begin{tikzcd}
 & & (\mathrm{ax}',\mathrm{e}') \arrow[dr, "k_{\mathrm{ax}'',\mathrm{e}'}"] & & \\
(\mathrm{ax},\mathrm{e}) \arrow[r, "k_{\mathrm{ax}',\mathrm{e}}"] & (\mathrm{ax}',\mathrm{e}) \arrow[ur, "k_{\mathrm{ax}',\mathrm{e}'}"] \arrow[dr, "k_{\mathrm{ax}'',\mathrm{e}}"'] & & (\mathrm{ax}'',\mathrm{e}') \arrow[r, "k_{\mathrm{ax}'',\mathrm{e}''}"] & (\mathrm{ax}'',\mathrm{e}'') \\
 & & (\mathrm{ax}'',\mathrm{e}) \arrow[ur, "k^*_{\mathrm{ax}'',\mathrm{e}'}"'] & &
\end{tikzcd} \qquad (17)$$

Trans Isomer. Because both conformers are energetically different, there are two pathways:

$$\begin{tikzcd}
 & & (\mathrm{e}',\mathrm{e}') \arrow[dr, "k_{\mathrm{e}'',\mathrm{e}'}"] & & \\
(\mathrm{e},\mathrm{e}) \arrow[r, "k_{\mathrm{e}',\mathrm{e}}"] & (\mathrm{e}',\mathrm{e}) \arrow[ur, "k_{\mathrm{e}',\mathrm{e}'}"] \arrow[dr, "k_{\mathrm{e}'',\mathrm{e}}"'] & & (\mathrm{e}'',\mathrm{e}') \arrow[r, "k_{\mathrm{e}'',\mathrm{e}''}"] & (\mathrm{e}'',\mathrm{e}'') \\
 & & (\mathrm{e}'',\mathrm{e}) \arrow[ur, "k^*_{\mathrm{e}'',\mathrm{e}'}"'] & &
\end{tikzcd} \qquad (18)$$

$$\begin{tikzcd}
(\mathrm{ax},\mathrm{ax}) \arrow[r, "k_{\mathrm{ax}',\mathrm{ax}}"] & (\mathrm{ax}',\mathrm{ax}) \arrow[r, "k_{\mathrm{ax}',\mathrm{ax}'}"] \arrow[dr, "k_{\mathrm{ax}'',\mathrm{ax}}"'] & (\mathrm{ax}',\mathrm{ax}') \arrow[r, "k_{\mathrm{ax}'',\mathrm{ax}'}"] & (\mathrm{ax}'',\mathrm{ax}') \arrow[r, "k_{\mathrm{ax}'',\mathrm{ax}''}"] & (\mathrm{ax}'',\mathrm{ax}'') \\
 & & (\mathrm{ax}'',\mathrm{ax}) \arrow[ur, "k^*_{\mathrm{ax}'',\mathrm{ax}'}"'] & &
\end{tikzcd} \qquad (19)$$

where a simple prime indicates the first hydrogen substitution by the epoxy group and double prime corresponds to the disubstitution, and $k_{\mathrm{ax}',\mathrm{e}}$, $k_{\mathrm{ax}',\mathrm{e}'}$, ...; $k_{\mathrm{e}',\mathrm{e}}$, $k_{\mathrm{e}',\mathrm{e}'}$, ..., $k_{\mathrm{ax}',\mathrm{ax}}$, $k_{\mathrm{ax}',\mathrm{ax}'}$,... are the rate constants involved in the different steps of the cure process.

Whereas k_1 and k_1^{I} for both isomers are similar (Table 1), the activation energies corresponding to k_2 and k_2^{I} are lower than for k_1 and k_1^{I}. This fact was already observed for other epoxy/amine systems; one of them based on a cycloaliphatic amine, isomer mixture (1,3 bisaminomethyl cyclohexane)[14] and the other one based on *meta*-xylenediamine.[31] These results can be due to the stabilization of the activated complex through the OH group formed after the first hydrogen substitution.[32] If we also consider that the activation energies (for k_1 and k_1^{I}) are slightly lower for the cis isomer than for the trans isomer, the transition state energies ($\Delta E^{\ddagger}$) of the conformers probably follow the sequence: $\Delta E^{\ddagger}_{\mathrm{ax}',\mathrm{ax}} > \Delta E^{\ddagger}_{\mathrm{e}',\mathrm{e}} \cong \Delta E^{\ddagger}_{\mathrm{ax}',\mathrm{e}} > \Delta E^{\ddagger}_{\mathrm{ax}',\mathrm{ax}'} > \Delta E^{\ddagger}_{\mathrm{e}',\mathrm{e}'} \cong \Delta E^{\ddagger}_{\mathrm{ax}',\mathrm{e}'}$. The substituted conformers of both isomers (ax′, e′), (e′, e′), and (ax′, ax′), have two OH groups and in (ax′, e′) and (e′, e′), these groups are very close to each other and to the nitrogen atom. The closeness of the OH groups may increase the catalytic effect lowering the activation energy to form the tertiary amines: (ax″, e′), (ax″, e″); (e″, e′), (e″, e″); and (ax″, ax′), (ax″, ax″). The transition state energies of the conformers going to tertiary amines could then be: $\Delta E^{\ddagger}_{\mathrm{ax}',\mathrm{ax}'} > \Delta E^{\ddagger}_{\mathrm{ax}',\mathrm{e}'} \cong \Delta E^{\ddagger}_{\mathrm{e}',\mathrm{e}'} > \Delta E^{\ddagger}_{\mathrm{ax}'',\mathrm{ax}'} \gg \Delta E^{\ddagger}_{\mathrm{ax}'',\mathrm{e}'} \cong \Delta E^{\ddagger}_{\mathrm{e}'',\mathrm{e}'}$. The low values of activation energies (E_{a}) found for the cis isomer agree with this tendency. In fact, 34.0 kJ mol^{-1} is the lowest value of activation energy that we have found in the technical literature for bisphenol A/epoxy amine systems. If we also consider that the values of E_{a} for the catalyzed path (with the presence of one OH group as catalyst) are lower than the noncatalyzed one, the previous discussion on the role of the OH group seems to be consistent. The alternative path represented by the rate constants $k_{\mathrm{ax}'',\mathrm{e}}$, $k^*_{\mathrm{ax}'',\mathrm{e}'}$ (eq 17); $k_{\mathrm{e}'',\mathrm{e}}$, $k^*_{\mathrm{e}'',\mathrm{e}'}$ (eq 18), and $k_{\mathrm{ax}'',\mathrm{e}}$, $k^*_{\mathrm{ax}'',\mathrm{e}'}$ (eq 19) can be neglected because the second hydrogen substitution (on the same amino group) is less important than the first one (as the values of R reflect). This fact is specially significant for the cis isomer.

Although pathways for the cis isomer are, from a purely energetically point of view, more favorable than for the trans isomer, the values obtained of T_{g}, R, and [A_3] are much higher for the trans isomer than for the cis isomer. Figures 5a and 5b show that there is another important factor to be considered. The structures (ax′, e′)/(e′, ax′) and (e′, e′) are clearly more steric hindered than (ax′, ax′). The preexponential factors (A) for the cis isomer corresponding to k_2 and k_2^{I} are so low (Table 1) that we repeated all calculations several times before accepting them. The preexponential factors reflect the probability of effective collisions between active sites and they are up to 10^4 times higher for the trans than for the cis isomer. Because of this fact, and although the activation energies favor the cis mechanism, the rate constants k_2 and k_2^{I} are lower for the cis than for the trans isomer. It is clear that the population of conformers does not play an important role. In fact, as stated, the concentration of diequatorial conformer of the monomer for the trans isomer is [e, e] = 29 [ax, ax], however the reaction proceeds via the (ax,ax) conformer.

The conformer (ax′, ax′) plays a crucial role on R and T_{g}. R is directly related to the network morphology and with the degree of cross-linking,[14,22,24,25] which has a strong effect on T_{g}. According to the proposed mechanism, the ideal value of R to attain the maximum value of cross-linking is 0.5.[1,14,22,31] The values observed (Table 1) are always lower than such an ideal value, which indicates that the reaction to form tertiary amines is more difficult than the one to form secondary amines. For the cis isomer, this fact is probably due to the steric effect, whereas for the "almost" hindrance-free conformer (ax′, ax′), this is mainly due to the energetic factor.

To compare these results we have tried to find other commercial cis/trans isomers without success. However, very low values of R were obtained[22] (from 0.16 at 25 °C to 0.075 at 100 °C) for a very popular cycloaliphatic diamine as isophorone diamine (IPD), which is a mixture of two stereoisomers (cis/trans, ≈75/25). We have also found very low values of R for another cycloaliphatic diamine, 4,4′-diamino-3,3′-dimethyldicyclohexyl methane (3-DCM). For this amine (mixture of five stereoisomers), R varies from 0.170 at 60 °C to 0.100 at 100 °C (unpublished data). It has been observed[22] that R is much greater for a pure aliphatic diamine (ethylenediamine) and for an aliphatic diamine with aromatic substituent (*meta*-xylenediamine) than for the cycloliphatic ones. The values of R for these aliphatic amines are comprised between 0.42 (at 25 °C) and 0.38 (being constant above 60 °C). Neither amines are isomer mixtures, which strongly suggests that the effect of the substitution is markedly important in cycloaliphatic amines where the presence of conformers with different values of transition state energies and/or steric hindrance determine the pathways of the reaction. As a consequence of this steric hindrance effect, the difference of reactivity of the second hydrogen on the same amino group between the cis and trans substituted isomers probably diminishes according to the positions of the nitrogen atoms on the cyclohexane ring according to the following sequence: $(N-N)_{1,2} > (N-N)_{1,3} > (N-N)_{1,4}$.

To conclude, we would say that the kinetic studies of epoxy formulations based on epoxy resin cured with multiring polycyclic amines can be very complicated as these amines have four or more isomers with probably different reactivities in primary and secondary hydrogens.

Conclusions

According to the results presented in this work there is a very important difference between the reactivities of cis and trans isomers when they react with a bisphenol A epoxy resin. Although both primary diamines disappear at almost the same rate, the formation of the tertiary amines strongly differs. These facts are related to the activation energies and to the steric hindrance of the secondary amines when they react with the epoxy group to form the tertiary amine.

We have found a great difference between the preexponential factors corresponding to the second substitution hydrogen/epoxy. The probability of effective collision to form the tertiary amine is up to 10^4 times greater in the trans isomer than in the cis one.

The thermal analysis also shows a great difference in the values obtained for the T_g^∞ values. Most cycloaliphatic diamines cured with bisphenol A epoxy resins show between 135 and 160 °C. For the *trans*-1,2-DCH we obtained a value of T_g^∞ that lies slightly above this range (166 °C). Conversely, the value of T_g^∞ measured for cis-1,2-DCH is clearly below the range (95 °C), indicating that the value of the final (maximum) conversion obtained must be much lower than in the case of the trans isomer. Another parameter directly related to the structure formation is the ratio of rate constants secondary amine/primary amine (R), which shows the same differences again. The value of R is greater for trans isomer than for the cis one, which may be directly related to the network morphology and the degree of cross-linking. Accordingly, the expected degree of cross-linking of the cis isomer must be lower than that of the trans isomer. The degree of conversion and cross-linking have a deep effect on T_g^∞ as well as on mechanical and chemical properties. These effects should be taken into account when cycloaliphatic amines (usually isomer mixtures) are used for industrial purposes.

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