Polymer Bulletin 27, 9–15 (1991)

Polymer Bulletin

Macro- and microgelation in the homopolymerization of diepoxides initiated by tertiary amines

M. J. Galante, A. Vázquez, and R. J. J. Williams*

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina

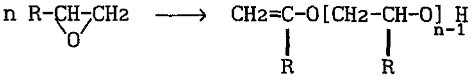
Summary

The homopolymerization of an epoxy resin based on diglycidylether of bisphenol A (DGEBA), initiated by benzyldimethylamine (BDMA), was analyzed in the 80°C - 140°C temperature range. An heterogeneous network characterized by regions of different glass transition temperature, was obtained. Microgels appeared early in the polymerization while an increase in the reactivity of the second epoxy group of a DGEBA molecule after reaction of the first one, was inferred from size exclusion chromatograms (SEC), obtained at different overall conversions. Both experimental findings were qualitatively explained through an intramolecular chain transfer step that regenerates the initiator in the proximity of pendant epoxy groups. The increase in the polymerization temperature produced an increase in the macroscopic gel conversion and a decrease in the glass transition temperature of regions of high crosslink density. This was ascribed to the increase in the ratio of intramolecular chain transfer over propagation rates, leading to shorter primary chains.

Introduction

The anionic homopolymerization of epoxides initiated by tertiary amines is a very complex reaction. Experimental work carried out on model systems, i.e. monoepoxides like phenylglycidylether or p-cresylglycidylether, led to our present knowledge of the reaction mechanism (1-4).

The main overall reaction may be written as follows (5,6):



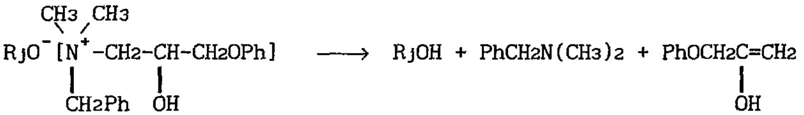
$$n\ R-\underset{\diagdown O \diagup}{CH-CH_2} \longrightarrow CH_2{=}\underset{\underset{R}{|}}{C}-O[CH_2-\underset{\underset{R}{|}}{CH}-O]_{n-1}H \qquad (1)$$

A characteristic of this reaction is that only oligomeric species are produced. Average n values, $\bar{n}$, are in the range of 2-5 (1,3). A decrease of $\bar{n}$ with polymerization temperature has also been reported (3,4).

The mechanism leading to the oligomer containing one hydroxyl and one vinylidene unsaturation per molecule, is still a controversial matter. For example, Rozenberg (1) assumes the presence of a β-elimination reaction (hydrogen abstraction by the growing alkoxy anion from the counterion). For the particular case of phenylglycidylether (PGE) initiated by benzyldimethylamine (BDMA), this reaction may be written as (1):

---

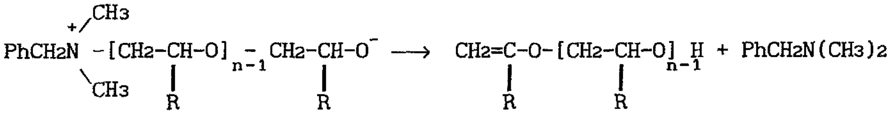
*To whom offprint requests should be sent



$$R_jO^-[\underset{CH_2Ph}{\overset{CH_3\ \ CH_3}{N^+}}-CH_2-\underset{OH}{CH}-CH_2OPh] \longrightarrow R_jOH + PhCH_2N(CH_3)_2 + PhOCH_2\underset{OH}{C}=CH_2 \qquad (2)$$

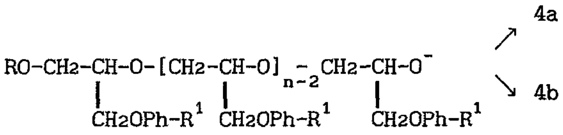
Although a tautomerization reaction of the vinyl alcohol to form a ketone could be expected, the high activity of the enol can explain its rapid transformation into an unsaturated alkoxide, with a corresponding shift in the tautomerization equilibrium (1). The polymerization initiated by the vinyl alkoxide leads to the oligomeric species shown in eq. (1).

Another way to explain the formation of oligomers containing one hydroxyl and one vinylidene unsaturation per molecule, is to assume an intramolecular hydrogen abstraction in the growing alkoxy anion. Vázquez et. al. considered the following reaction (4):

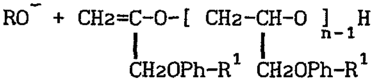


$$PhCH_2\underset{CH_3}{\overset{+\ CH_3}{N}}-[CH_2-\underset{R}{CH}-O]_{n-1}-CH_2-\underset{R}{CH}-O^- \longrightarrow CH_2=\underset{R}{C}-O-[CH_2-\underset{R}{CH}-O]_{n-1}H + PhCH_2N(CH_3)_2 \qquad (3)$$

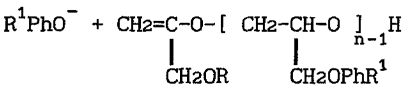
We recently suggested the following possibilities for the intramolecular hydrogen abstraction (7):



$$RO-CH_2-\underset{CH_2OPh-R^1}{CH}-O-[CH_2-\underset{CH_2OPh-R^1}{CH}-O]_{n-2}-CH_2-\underset{CH_2OPh-R^1}{CH}-O^- \begin{matrix} \nearrow 4a \\ \searrow 4b \end{matrix}$$



$$RO^- + CH_2=\underset{CH_2OPh-R^1}{C}-O-[\ CH_2-\underset{CH_2OPh-R^1}{CH}-O\ ]_{n-1}H \qquad (4a)$$



$$R^1PhO^- + CH_2=\underset{CH_2OR}{C}-O-[\ CH_2-\underset{CH_2OPhR^1}{CH}-O\ ]_{n-1}H \qquad (4b)$$

Steps 4a and 4b may also involve an hydrogen abstraction from any of the CH groups present in the (n-2) repeating units. In particular, step 4b explains the presence of phenol (or substituted phenol) in the reaction mixture, in agreement with experimental findings (3,4).

The homopolymerization of a diepoxide like diglycidylether of bisphenol A (DGEBA) with a tertiary amine leads to a network. For the particular case of a DGEBA resin-BDMA system in the 80°C - 150°C temperature range, the kinetics showed a first order behavior with respect to both epoxy and tertiary amine concentrations and a non-Arrhenius dependence on temperature (7). The aim of this paper is to report experimental results on the macroscopic gelation of a DGEBA-BDMA system and the appearance of a microgel phase at early stages of the polymerization, i.e. well before the macroscopic gelation. A qualitative explanation of the observed findings, based on the suggested mechanism for the intramolecular chain transfer, will be provided.

Experimental

The DGEBA-based epoxy resin (Araldit GY250, Ciba-Geigy) had a weight per epoxy equivalent, WPE = 190 g/eq. It was carefully dehydrated at 85°C, under vacuum, before use. BDMA (Sigma) was used in a proportion equal to 0.06 moles BDMA/eq. epoxy. The polymerization was carried out at temperatures comprised in the range 80°C to 140°C. The epoxy conversion at every temperature was calculated from conversion vs time curves obtained using differential scanning calorimetry (DSC) (7).

The concentration of DGEBA (M=340 g/mol), was followed along the polymerization up to the macroscopic gelation, using size exclusion chromatography (SEC). A set of tubes, each one containing 16 mg. of the DGEBA-BDMA solution, was placed in an oil bath kept at constant temperature. After predetermined time intervals, tubes were extracted from the oil bath and rapidly cooled in a water-ice bath. Then, THF (Tetrahydrofuran) was added to make a 0.2% solution (weight by volume). SEC chromatograms were obtained using a Waters 510 device (R.I detector, set of ultrastyragel columns 100, 100, 500 and 10000 Å, and a 1 ml/min flow rate of THF). Macroscopic gelation was associated to the reaction time at which the THF addition led to a swelling of the polymer instead of its complete dissolution.

Glass transition temperatures (Tg) of partially cured sample were determined using both DSC and TMA (thermal mechanical analysis). A Dupont 910 thermal analyzer was used, with a scanning rate of 10°C/min. Tg values were taken as the onset of the base line deflection.

Results and Discussion

Figure 1 shows the macroscopic gel conversion observed for different cure temperatures.

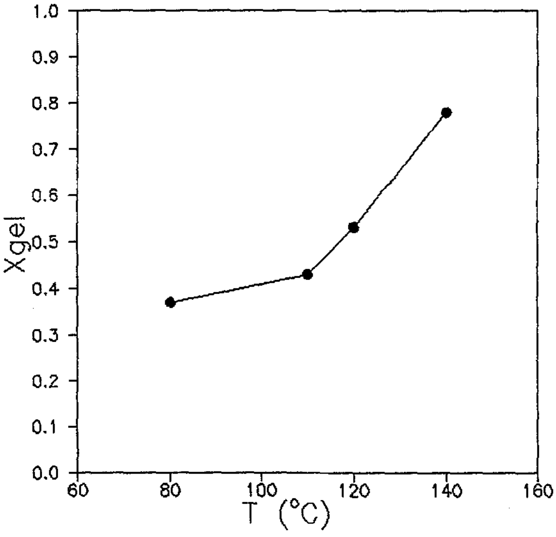


Fig. 1 Macroscopic gel conversion as a function of the polymerization temperature.

The significant increase in the gel conversion with reaction temperature is consistent with the corresponding decrease in the average length of oligomeric chains observed when increasing temperature in model systems (3). This may be ascribed to the increase in the rate of intramolecular chain transfer with respect to chain propagation. An unexpected finding was the difficulty in the filtration of the THF solutions previous to the injection in the SEC device. Although solutions were optically homogeneous, a microgel phase which could be recovered from the filter when working on a preparative scale, was present from the early stages of the reaction. However, the DGEBA monomer was assumed to be present in the filtered solution. Figure 2 shows the decrease of the height of the DGEBA peak in the SEC chromatogram, as a function of conversion, for polymerizations carried out at different temperatures.

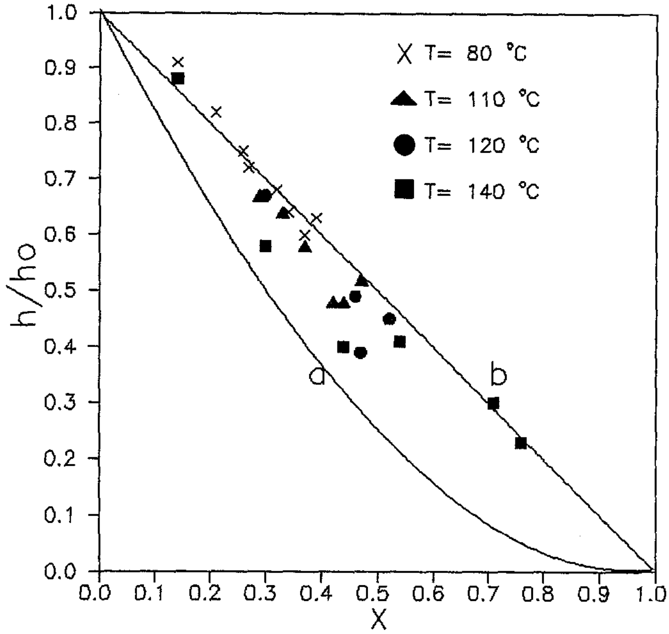


Fig.2 Height of DGEBA peak (M=340 g/mol) in SEC chromatograms as a function of conversion, for polymerizations carried out at various temperatures:
a) theoretical prediction for a reaction without substitution effects;
b) theoretical prediction for an infinite substitution effect.

Assuming that both epoxy groups of the DGEBA molecule react independently (no substitution effect) the probability that a DGEBA monomer has not reacted when the overall conversion is X, is given by the simultaneous probability that both epoxy groups remain unreacted. Thus,

$$C/C_o = h/h_o = (1-X)^2 \qquad (5)$$

Eq.(1) is plotted as curve a. in Fig.2. Several DGEBA-diamine polymerizations follow this curve up to gelation (8,9), proving that in ordinary step-growth polymerizations epoxy groups of DGEBA react independently. However, this is not the case for the chain polymerization initiated by a tertiary amine.

On the other hand, we may assume the other limiting case, i.e. that once an epoxy group of a DGEBA monomer enters reaction, the other group, that becomes a pendant reactive site of the oligomeric chain, reacts at a very fast rate. In the limit of an infinite reactivity of the pendant group, only unreacted or bireacted DGEBA molecules could be distinguished. Therefore, the concentration of DGEBA monomer will be a linear function of the overall epoxy conversion,

$$C/C_o = h/h_o = (1-X) \qquad (6)$$

This situation is depicted as curve b. in Fig.2. Experimental points are close to this limit.

Intramolecular chain transfer leading to the regeneration of the initiator, i.e. step (4a), may be invoked to explain the experimental findings. Thus, the generated RO^- will most probably attack a pendant epoxy belonging to its original chain. If this situation is repeated, combined with some propagation steps, a local network (a microgel) will be produced. This constitutes a similar explanation as the one commonly accepted to acquaint for the presence of microgels in free-radical polymerizations of polyfunctional monomers (10). In this case, at the beginning of reaction there is a high probability that the free radical at the end of a growing chain attacks a pendant unsaturation of its own chain. Repetition of this mechanism leads to a high rate of intramolecular cyclization and the appearance of microgels.

The presence of two Tg's in partially cured samples was inferred from DSC scans and clearly confirmed in TMA scans. As an example, Fig.3 shows the TMA scan of a sample cured at 80°C up to a conversion X=0.6

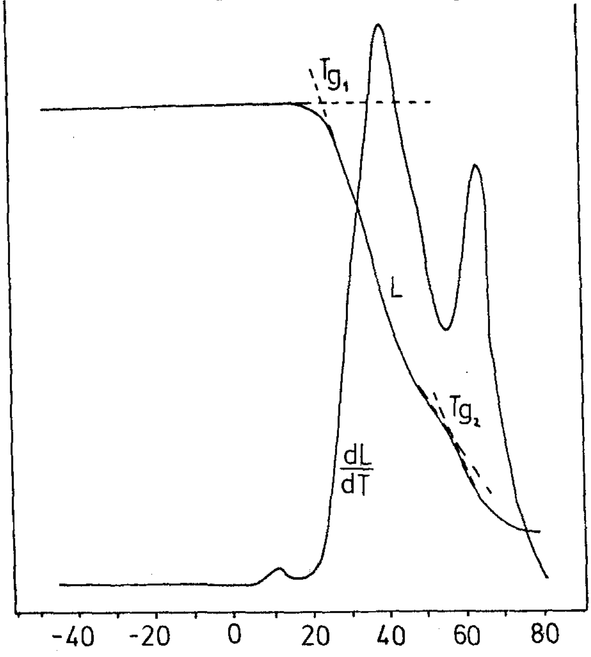


Fig.3 TMA scan of a DGEBA-BDMA sample cured at 80°C to a conversion X=0.6

Figure 4 shows the evolution of both Tg's as a function of conversion for specimens cured at 80°C and 140°C.

DSC was only used at temperatures above 30°C. In these conditions the relevant Tg was the higher one while the presence of the other could only be inferred at high conversions. Networks built up at lower temperatures (80°C) showed a higher Tg than those produced at higher temperatures (140°C), as previously reported (7). This may be explained with the same arguments used to analyze the increase in the gel conversion with temperature, i.e. an increase in the ratio of intramolecular chain transfer over propagation leading to shorter primary chains.

The use of TMA made it possible to distinguish the presence of two Tg's. The higher one varied with the cure temperature while the lower one did not show such a variation, within the experimental error of the determination.

Microgels were filtered from a specimen cured at 140°C up to a conversion

X=0.69. The glass transition temperature determined with DSC, was Tg=45°C. This value, which is represented by an asterisk in Fig. 4, lies in the curve representing the highest Tg for samples cured at 140°C. As expected microgels constitute the regions of high crosslink density.

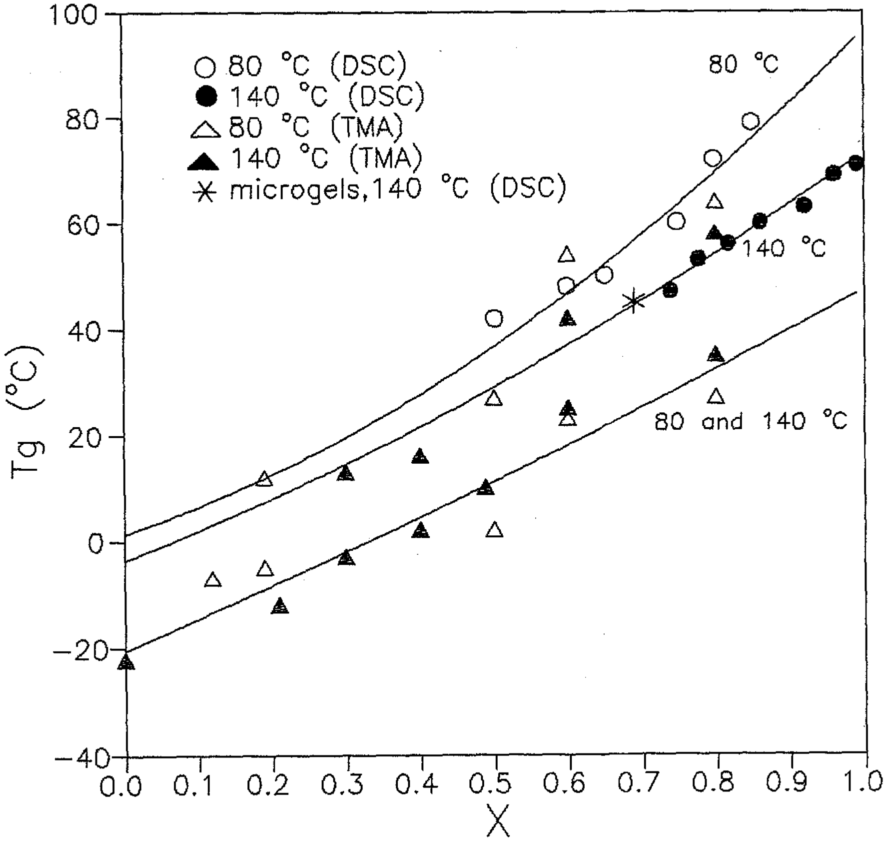


Fig. 4 Evolution of both Tg's as a function of conversion for specimens cured at 80°C and 140°C. Results from both DSC and TMA techniques are plotted.

Conclusions

The anionic homopolymerization of DGEBA-based epoxy resins, initiated by BDMA, leads to an heterogeneous network characterized by regions of different glass transition temperature. Microgels with a higher crosslink density than the average, appear early in the polymerization. At the same time, there is an increase in the reactivity of the second epoxy group of a DGEBA after reaction of the first one. Both experimental findings are qualitatively explained by assuming the presence of an intramolecular chain transfer in the reaction mechanism (step 4a), that liberates the initiator, RO^- in the proximity of pendant epoxy groups, i.e. the unreacted end of a DGEBA molecule. A fast reinitiation involving pendant epoxides, explains both the substitution effect and the formation of microgels, i.e. through a repetition of propagation and intramolecular chain transfer steps.

The increase in the polymerization temperature leads to an increase in the macroscopic gel conversion and a decrease in the glass transition temperature of the regions of high crosslink density. This is explained through the increase in the ratio of intramolecular chain transfer over propagation rates, an effect that leads to shorter primary chains.

References

1. Rozenberg B A (1986) Kinetics, thermodynamics and mechanism of reactions of epoxy oligomers with amines. In: Dušek K (ed.) **Epoxy resins and composites II**. Springer, Berlin Heildelberg New York (Advances in Polymer Science, vol 75, pp 113-165)
2. Fedtke M (1987) **Makromol Chem Macromol Symp** 7:153
3. Berger J, Lohse F (1985) **Eur Polym J** 21:435
4. Vázquez A, Matějka L, Špaček P, Dušek K (1990) **J Polym Sci A: Polym Chem** 28:2305
5. Fedtke M, Sorokin V I, Tänzer W (1987) **Vysokomol Soed** A29:1275
6. Tänzer W, Szestay M, László-Hedvig Z, Fedtke M (1988) **Acta Polymerica** 39:696
7. Vázquez A, Bentaleb D, Williams R J J **J Appl Polym Sci**, in press
8. Verchère D, Sautereau H, Pascault J P, Riccardi C C, Moschiar S M, Williams R J J (1990) **Macromolecules** 23:725
9. Grillet A C, Galy J, Pascault J P, Bardin I (1989) **Polymer** 30:2094
10. Dušek K (1982) Network formation by chain crosslinking (co) polymerisation. In: Haward R N (ed.) **Developments in Polymerisation-3.** Applied Science, London, Ch.4 pp. 143-206

Accepted July 23, 1991 C