# Epoxy Networks with Physical Cross-Links Produced by Tail-to-Tail Associations of Alkyl Chains

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ABSTRACT: In a recent paper (Zucchi, I. A.; et al. *Macromolecules* **2008**, *41*, 4895), we showed that linear amphiphilic epoxy polymers synthesized by the polyaddition of diglycidyl ether of bisphenol A (DGEBA) with dodecylamine (DA) could undergo a physical gelation process through tail-to-tail association of dodecyl chains. The aim of the present study was to analyze in more detail conditions leading to the formation of epoxy networks with physical cross-links by the reaction of DGEBA with alkylamines of different chain lengths: octylamine (OA), dodecylamine (DA), and hexadecylamine (HA). SAXS spectra showed that tail-to-tail associations of alkyl chains were present since the beginning of polymerization and remained in the final materials. Initially, these associations correspond to micelles of the alkylamines dispersed in the solvent (DGEBA). In the course of polymerization, micelles are disaggregated as the individual alkylamine chains become part of the linear amphiphilic polymer. However, tail-to-tail associations among alkyl chains attached to the polymer backbone persisted in the final materials. Reactions were followed by rheometry at 100 °C. For every system, a significant discontinuity in the increase in the storage modulus observed at advanced conversions was assigned to a phase inversion process produced by solvent depletion. By annealing prolonged times at the reaction temperature, a crossover of storage and loss modulus was observed because of the increase in the extent of associations among alkyl chains leading to a physical gel. Times for physical gelation varied in the order OA < DA < HA. Both DGEBA–DA and DGEBA–HA polymers could be reversibly transformed from gel to liquid states by appropriate heating–cooling cycles; however, the DGEBA–OA polymer showed no thermoreversibility. Physical gels exhibited a high swelling capacity in THF (HA > DA > OA). These amphiphilic gels could be used as dispersion media for a variety of nanoparticles stabilized with alkyl chains. They can also be the basis of single-component thermally remendable epoxy networks.

## Introduction

The search for thermoreversible cross-links in polymer networks is a field of increasing interest to obtain recyclable or thermally remendable materials as well as polymers that can be processed like thermoplastics but behave like thermosets after cooling. The utilization of the thermally reversible Diels–Alder cycloaddition reaction and of the photoreversible [2 + 2] cyclo-addition reaction to generate chemically reversibly cross-links is one possible way to obtain this kind of materials.[1–6] The use of reversible noncovalent interactions such as hydrogen bonds or metal–ligand coordination has also been suggested for these purposes.[7–9] Hydrophobic interactions among alkyl chains are important in the formation of many kinds of self-assembled polymer aggregates and gels. We can find examples of the role of van der Waals interactions between long alkyl chains in the self-assembly of metal thiolates[10] and organic–inorganic hybrid materials.[11,12] The most characteristic feature of aggregates of alkyl chains is their tail-to-tail association inferred from structural characterization using XRD or SAXS. In some materials, the characteristic length of hydrophobic domains is twice the length of an extended (all-trans) alkyl chain.[11,12] In other systems this

length is reduced by the presence of trans–gauche conformations (partially coiled chains) or partial interdigitation of alkyl chains.[11]

Amphiphilic linear epoxy polymers with a hydrophilic main chain and hydrophobic pendant chains were synthesized by the polyaddition of tetra-, hexa-, and octaethylene diglycidyl ether and dodecylamine (DA) or hexadecylamine (HA).[13] The reaction was carried out in CHCl₃ solution at 45 °C to an almost complete conversion of epoxy groups. The resulting linear polymers exhibited number-average degrees of polymerization ranging from 36 to 70 repeating units. They behaved as polymeric surfactants that were organized as micelles in aqueous solution forming lyotropic liquid crystalline phases for particular concentration ranges. The lattice constant of the ordered phase corresponded to roughly twice the length of the all-trans conformation of the alkyl chain. Therefore, the self-assembly in solution was produced by tail-to-tail association of alkyl chains.

In a recent paper, we reported the synthesis of a linear amphiphilic epoxy polymer based on the polyaddition reaction of diglycidyl ether of bisphenol A (DGEBA) with dodecylamine (DA).[14] The synthesis was carried out in bulk at 100 °C using stoichiometric amounts of both monomers. No secondary reactions were observed under these conditions, and the resulting linear polymer exhibited a number-average degree of polymerization

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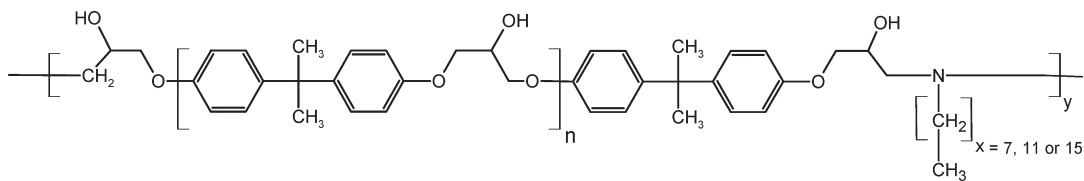
**Figure 1.** Chemical structure of the repeating unit of the linear polymer.

corresponding to ~31 repeating units. The main difference with respect to the family of polymers synthesized by Weiss and Finkelmann[13] is the lower hydrophilicity and the higher rigidity of the main polymer chain. In this case, the tail-to-tail association of alkyl chains must be restricted to pairs of chains or to clusters composed of a few alkyl chains because of conformational restrictions of the main polymer backbone. However, these associations were slowly produced when annealing the polymer several hours at the reaction temperature, leading to a thermoreversible physical gel.[14]

The aim of the present study was to compare the ability to form thermoreversible physical gels of amphiphilic linear epoxies obtained by reaction of DGEBA with alkylamines of different chain lengths: octylamine (OA), dodecylamine (DA), and hexadecylamine (HA). Corresponding hydrophobic/hydrophilic balances, expressed as mass ratios, are 24:76 (OA), 32:68 (DA), and 38:62 (HA). The thermoreversibility and swelling characteristics of the physical gels will be discussed in relation to possible practical applications.

**Experimental Section**

**Materials.** The diepoxy monomer was based on diglycidyl ether of bisphenol A (DGEBA, DER 332, Aldrich) with a mass per mole of epoxy groups equal to 174.3 g/mol ($n = 0.03$ in the chemical structure shown in Figure 1). The alkylamines were octylamine (OA, 99 wt % Aldrich, liquid at room temperature), dodecylamine (DA, 98 wt %, Fluka, melting temperature in the range 27−29 °C), and hexadecylamine (HA, 98 wt % Aldrich, melting temperature in the range 43−46 °C).

**Synthesis of the Epoxy−Amine Linear Polymers.** Stoichiometric amounts of DGEBA and the corresponding alkylamine were mixed by vigorous stirring at ~100 °C. The polymerization was carried out in bulk at 100 °C for variable periods of time. Figure 1 shows the chemical structure of the repeating unit of the linear polymers. To arrest structuration processes, polymers were stored at −5 °C, a temperature that is below their glass transition temperatures.

**Techniques.** Polarized optical microscopy (POM) was used to assess the optical isotropy of the mixture of monomers at 100 °C before polymerization. A Leica DMLB microscope provided with a hot stage (Linkam THMS 600) and crossed-polarizers was used.

Small-angle X-ray scattering (SAXS) measurements were performed in an S3 MICRO instrument (Hecus X-ray Systems, Graz, Austria) with point focalization, equipped with a GENIX microfocus X-ray source operating at 50 kV and 1 mA and a FOX 2D point-focusing element (both from Xenocs, Grenoble). The scattered intensity was recorded using position-sensitive detectors (Hecus). For the measurements, gelled samples were sandwiched between Kallebrat films, whereas fluid samples (as those for time-resolved experiments) were placed in flame-sealed glass capillaries (diameter = 2 mm).

The evolution of the storage ($G'$) and loss modulus ($G''$) was followed using an Anton Paar rheometer (model Physica MCR-301) provided with a CTD 600 thermo chamber. Isothermal scans were performed at 100 °C, and dynamic scans were performed at 1 °C/min. A parallel-plate configuration (diameter $D = 25$ mm, gap $H \approx 1$ mm) was used in oscillatory mode with a 1% amplitude at a frequency of 1 Hz.

The molar mass distribution of the linear epoxy polymers obtained after 3 h reaction at 100 °C was analyzed by size exclusion chromatography (SEC, Knauer K-501, RI detector Knauer K-2301). A set of three Phenomenex Phenogel 5 μm columns, 50A, 100A, and M2, was used. THF was employed as a carrier with a flow rate of 1 mL/min.

Glass transition temperatures ($T_g$) were determined by differential scanning calorimetry (DSC, Perkin-Elmer Pyris 1) from scans performed at 10 °C/min. $T_g$ was obtained from onset values of the change in specific heat during heating scans.

Gel fractions (GF = weight of insoluble dried sample/initial sample weight) and degrees of swelling (DS % = 100 × weight of swollen sample/weight of insoluble dried sample) of physical gels were determined gravimetrically from samples cut in squared pieces of approximately 1 × 1 × 0.2 cm³. The GF content was estimated by weighing the insoluble portion obtained after extraction in tetrahydrofuran (THF) for 24 h at room temperature. The degree of swelling was determined by weighing the swollen sample.

Middle-infrared spectroscopy (Nicolet 6700 FTIR) was employed to characterize the physical gels after 90 h annealing at 100 °C. Measurements were carried out in the attenuated total reflectance mode (smart Orbit ATR accessory).

**Results and Discussion**

**Polymerization, Phase Inversion, and Physical Gelation.** Stoichiometric mixtures of DGEBA and the different alkylamines were isotropic solutions at 100 °C as inferred from the black field observed in POM. At the beginning of polymerization, alkylamines must be organized as micellar structures dispersed in DGEBA, in a similar way as is observed in dispersions of the alkylamines in aqueous solutions.[15] At the end of polymerization, the system consists of chains of the linear amphiphilic polymer. Therefore, during polymerization, micelles must disaggregate as the individual alkylamine chains become part of the linear amphiphilic polymer. At some point during the polymerization, the consumption of the reactive solvent must produce a kind of phase inversion where the amphiphilic polymer becomes the majority phase.

The tail-to-tail association of alkyl chains in the course of polymerization was investigated by SAXS spectra taken at the polymerization temperature (100 °C). The DGEBA−DA formulation was selected for this study because its polymerization kinetics at 100 °C had already been reported.[14] The conversion is >90% after 30 min of reaction, and the polymerization is almost complete after 2 h of reaction. Figure 2 shows the evolution of SAXS spectra for the DGEBA−DA blend during polymerization at 100 °C, taken with acquisition times of 20 min starting from the beginning of polymerization. A broad scattering peak with a maximum at $q = 0.269$ Å$^{-1}$, corresponding to a characteristic length $d = 2\pi/q = 2.33$ nm, was present from the start to the end of polymerization. It might be argued that there is no proof that the self-organization took place during the 20 min acquisition time of the first spectrum. This argument cannot be reconciled with the following facts: (a) the intensity of SAXS spectra did not exhibit significant changes from the first to
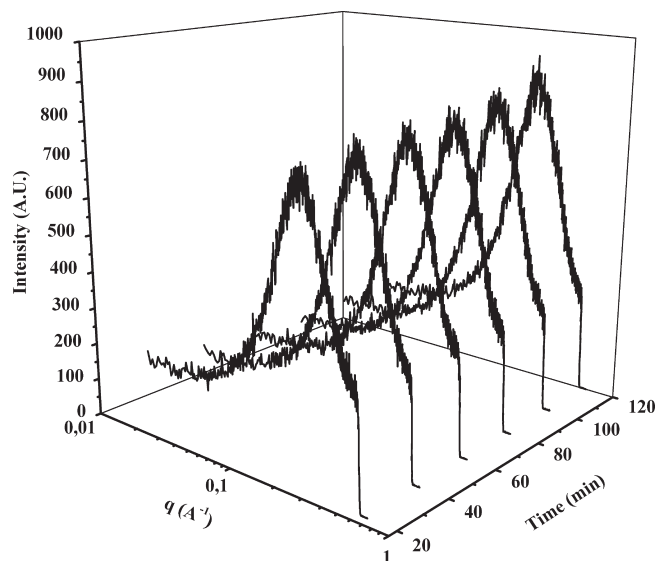
**Figure 2.** Evolution of SAXS spectra for the DGEBA−DA blend during polymerization at 100 °C.



**Figure 3.** SAXS spectra obtained at 25 °C for the three different DGEBA−alkylamine linear polymers after a 180 h annealing period at 100 °C.

the final spectra plotted in Figure 2, covering most of the conversion range and (b) phase diagrams of alkylamines in water show the presence of a micellar dispersion at high temperatures;[15] similar diagrams are expected in other polar solvents like DGEBA. Therefore, we can conclude that a micellar dispersion was present in the initial solution at the reaction temperature.

The characteristic distance observed in the SAXS spectra of Figure 2 corresponds to tail-to-tail associations of partially coiled or interdigitated dodecyl chains (an extended dodecyl chain with all-trans conformation has a length close to 1.5 nm;[11] the measured distance must correspond to the tail-to-tail association of two chains). There was no significant variation in the location of the scattering peak during polymerization. Only a slight increase in intensity was observed with reaction time.

X-ray scattering is predominantly produced by structures with higher electronic density. In our case, the hydrophilic backbone should be the main scattering structure; the presence of a scattering peak suggests that portions of the hydrophilic backbone are separated by a characteristic distance equal to the tail-to-tail association of dodecyl chains from the start up to the end of polymerization.

Figure 3 shows SAXS spectra obtained at 25 °C for the three different DGEBA−alkylamine linear polymers after a 180 h annealing period at 100 °C. Defined scattering peaks are present for every one of the amphiphilic polymers with maxima at 1.64 nm for OA, 2.33 nm for DA, and 2.72 nm for HA. These distances correspond to the tail-to-tail association of two partially coiled (or interdigitated) alkyl chains. Therefore, SAXS provides evidence of the nanostructuration of the systems during polymerization and after a prolonged annealing at the reaction temperature. The broadness of the scattering peaks indicates that the alkyl chains are in a liquid-like state. Moreover, strong scattering observed at low $q$ values suggests the possible presence of structures on a different (larger) scale, but this needs further study.

Measurements as a function of temperature on annealed samples (not shown) revealed that the characteristic peaks shown in Figure 3 are still detectable at temperatures above the glass−rubber transition. (See the following sections.)

Additional experimental evidence of the structuration occurring in these systems can be obtained by rheometry.
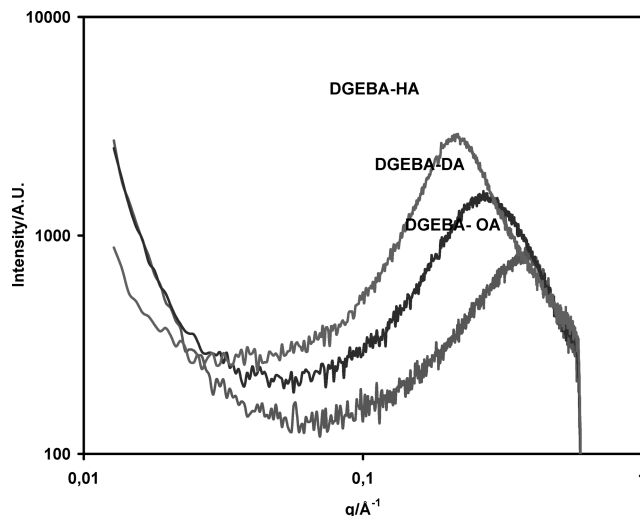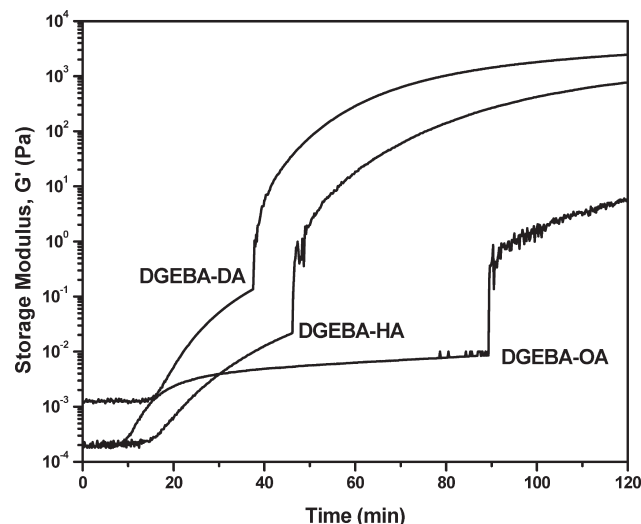


**Figure 4.** Evolution of the storage modulus for the three DGEBA−alkylamine systems during the first 2 h of reaction at 100 °C.

Figure 4 shows the evolution of the storage modulus for the three DGEBA−alkylamine systems during the first 2 h of reaction at 100 °C. A sharp discontinuity in the derivate of the storage modulus was observed for the three systems at particular reaction times: 37.5 min for DA, 46.5 min for HA, and 90 min for OA. Abrupt changes in the rheological response of multiphase materials are usually ascribed to a phase inversion process. In our case, this phase inversion is expected because the solvent (DGEBA) is continuously depleted, whereas the polymer-rich disperse domains increase in size. At a particular overall conversion, the polymer-rich phase becomes the continuous phase, a fact that can be associated with the sudden increase in the storage modulus. During this period, the loss modulus (not shown) lies several decades above the storage modulus for the three systems. This means that phase inversion occurred in the liquid state.

Phase inversion times increased in the sequence DA < HA < OA. In principle, this order could follow the respective polymerization rates in the micellar systems. This means that DGEBA−OA should be the least reactive of the three
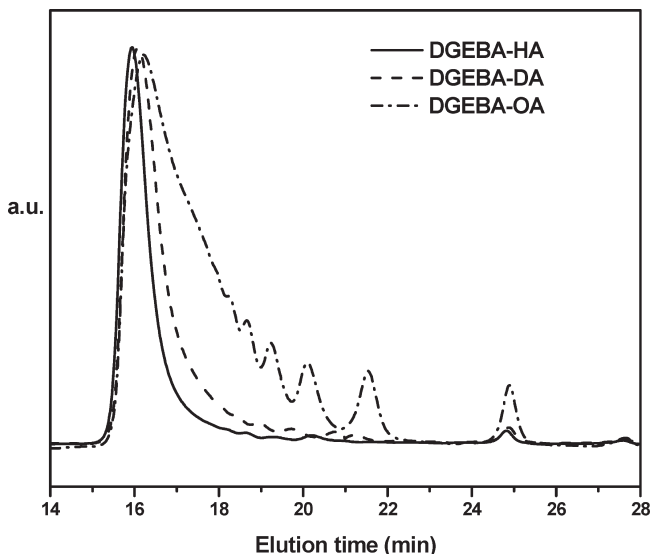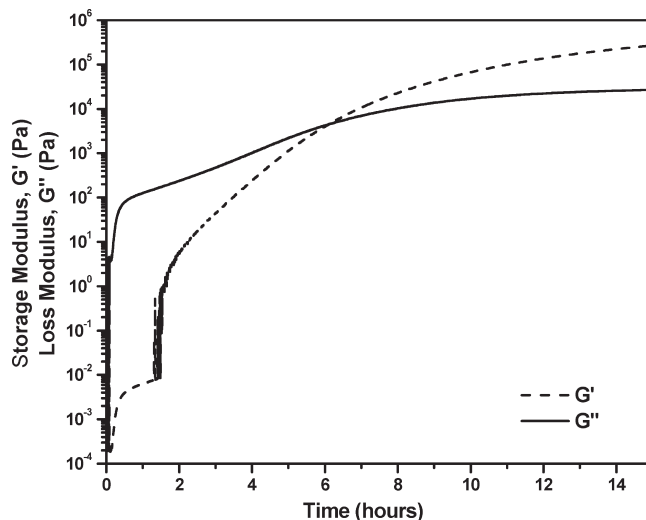
**Figure 5.** SEC chromatograms of DGEBA−alkylamine systems after 3 h of polymerization at 100 °C.



**Figure 6.** Evolution of the storage ($G'$) and loss modulus ($G''$) of the DGEBA−OA system during a prolonged heating at 100 °C.

systems. To prove this assumption, samples after 3 h of polymerization were analyzed by SEC. Figure 5 shows the corresponding SEC chromatograms. Both DGEBA−DA and DGEBA−HA reactions were practically completed at this time leading to linear polymers with number-average degrees of polymerization close to 30 based on PS standards. A very small residual peak of DGEBA at an elution time close to 25 min was observed for both systems. On the other hand, the DGEBA−OA polymerization was the slowest one; after 3 h of reaction, residual monomer and small oligomers were still present in significant amounts. Therefore, the sequence of phase inversion times appears to be correlated with the sequence of polymerization rates. The reaction rate depends on the size and shape of micelles and on the steric availability of amine groups as conversion increases (disaggregation of micelles). The striking feature was the very slow rate of polymerization of DGEBA−OA. As will be shown later, the strength of tail-to-tail associations of alkyl chains is greater than the one of DA or HA chains. This can possibly affect the incorporation of individual OA molecules present in the initial micelles to the polymer chains. However, after a prolonged time at 100 °C the DGEBA−OA reaction was also completed, as will be discussed below.
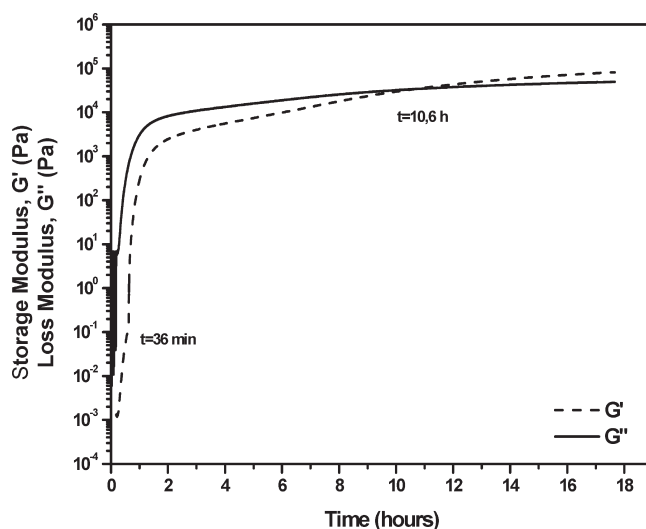
Figures 6−8 show the evolution of the storage ($G'$) and loss modulus ($G''$) of the three systems during a prolonged heating at 100 °C. A crossover of both moduli was observed after 6.1 (OA), 10.6 (DA), and 26.2 h (HA), indicating the formation of physical gels with cross-links produced by tail-to-tail association of alkyl chains. The shortest alkyl chains exhibit the faster gelation rate.

The association among alkyl chains also produced an increase in the glass transition temperature of the materials. After 3 h reaction at 100 °C, $T_g$ values were 7, 10, and 20 °C for DGEBA−HA, DGEBA−DA, and DGEBA−OA, respectively. After 180 h of annealing at 100 °C, these values increased to 12, 19, and 40 °C, respectively.

Physical gels were examined by solubility tests in THF. Samples were kept at 100 °C for different periods of time, cooled to room temperature, and immersed in THF for 24 h. Figures 9 and 10 show the evolution of the gel fraction and the degree of swelling of the physical gels with annealing time at 100 °C. Although times at which physical gels were first observed follow the same sequence as in Figures 6−8, their
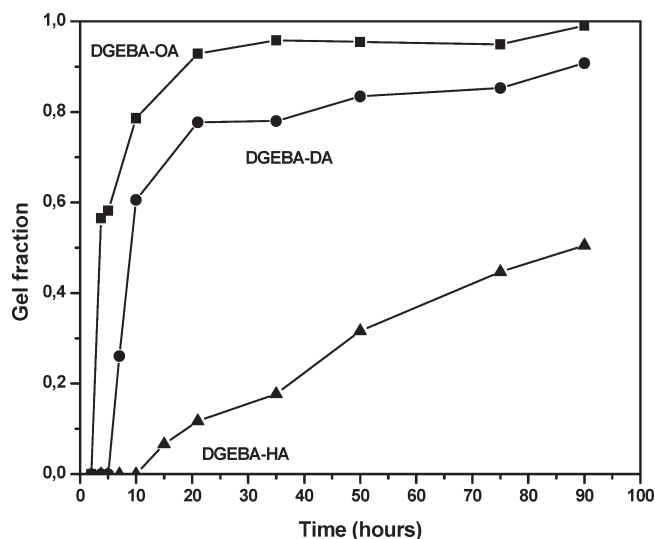


**Figure 7.** Evolution of the storage ($G'$) and loss modulus ($G''$) of the DGEBA−DA system during a prolonged heating at 100 °C.
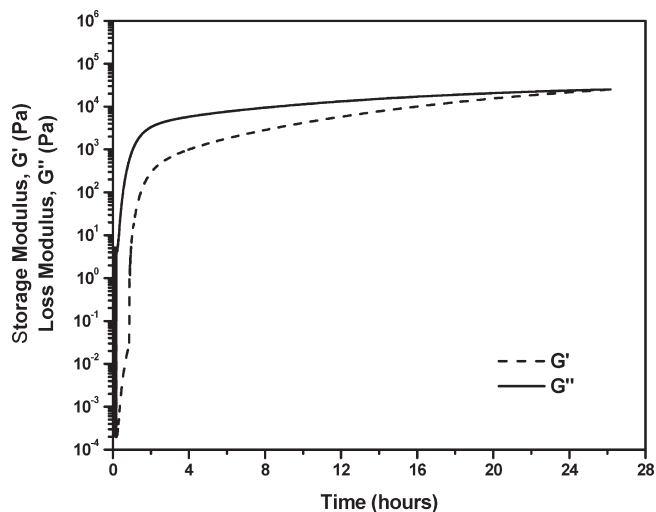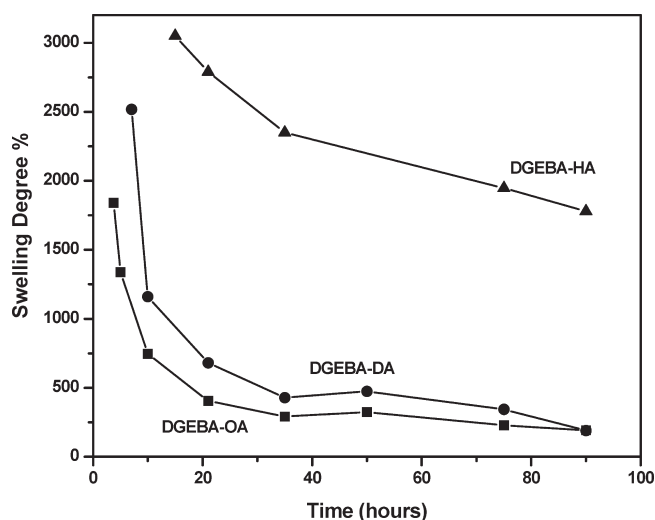


**Figure 8.** Evolution of the storage ($G'$) and loss modulus ($G''$) of the DGEBA−HA system during a prolonged heating at 100 °C.

**Figure 9.** Gel fractions of DGEBA−alkylamine physical gels after annealing for different times at 100 °C.



**Figure 10.** Swelling degrees of DGEBA−alkylamine physical gels after annealing for different times at 100 °C.

values are lower than those determined at 100 °C. This is the consequence of the continuation in the association of alkyl chains during the cooling step and the storage period at room temperature (for samples with $T_g$ located below room temperature). After gelation, DGEBA−OA polymers exhibit a very fast increase in the gel fraction attaining values > 90%. Alkyl chain associations in DGEBA−HA polymers took place slowly leading to a continuous increase in the gel fraction and a corresponding decrease in the swelling degree. DGEBA−DA systems exhibit an intermediate behavior. Sol fractions of the different DGEBA−alkylamine polymers were analyzed by SEC after 90 h of annealing at 100 °C. Only a high-molar-mass peak was observed, located at the same elution time for the three samples, with only traces of low molar mass products. This proves that the DGEBA−OA reaction was completed during this period.

An interesting finding was the combination of high gel fractions and relatively high swelling ratios of DGEBA−DA physical gels. These gels provide an amphiphilic environment to incorporate different types of salts and nanoparticles. These properties will be analyzed in another publication.
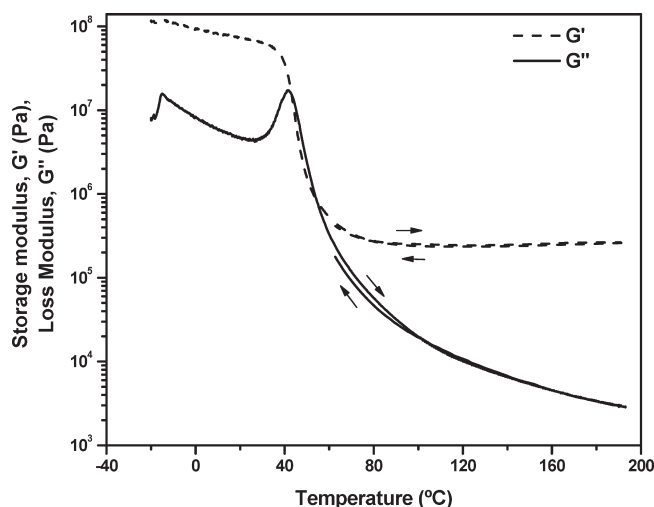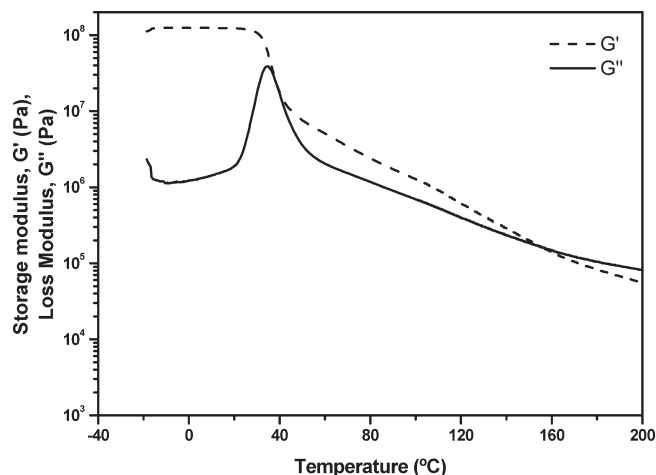


**Figure 11.** Storage ($G'$) and loss modulus ($G''$) of the DGEBA−OA polymer as a function of temperature.

**Thermoreversibility of the Physical Gels.** After 15 h of annealing at 100 °C, the DGEBA−OA polymer was cooled to −20 °C and scanned in the rheometer at 1 °C/min. The variation of $G'$ and $G''$ with temperature is shown in Figure 11. The material behaves like a chemically cross-linked polymer. After the glass−rubber transition, at ∼40 °C, an almost constant value of the rubbery modulus increasing slightly with temperature was observed. A cooling cycle at 1 °C/min following the heating scan reproduced the same curves. Therefore, DGEBA−OA polymer exhibited no thermoreversibility up to 200 °C. The explanation of this behavior is possibly related to the high strength of the associations among alkyl chains observed in the process of formation of the physical gel. Thermoreversibility would require heating to temperatures located above the polymer decomposition temperature. It might be argued, however, that an epoxy−OH polyetherification reaction can compete with the slow DGEBA−OA reaction, leading to a chemically cross-linked network. The following experimental evidence allows us to discard this assumption: (i) thermoreversibility was indeed found for the two other systems excluding the presence of a polyetherification reaction in these cases and (ii) FTIR spectra of the three systems were exactly the same (except for the relative intensity of methylene peaks); no evidence of a new band at 1130 cm$^{-1}$ (asymmetric C−O−C stretching vibration) that is characteristic of polyetherification reactions[16] was observed for the DGEBA−OA polymer.

Figure 12 shows the thermoreversibility observed for the DGEBA−DA polymer after 18 h of annealing at 100 °C, cooling to −20 °C, and scanning at 1 °C/min. After devitrification, a crossover between $G'$ and $G''$ curves is observed at 156 °C, where the polymer undergoes a gel−liquid transition. However, before getting to this point, there is continuous decrease in the storage modulus in the rubbery state that can be related to the continuous decrease in the fraction of associated dodecyl chains. The possibility of varying the association of alkyl chains with temperature can be of interest for the application of this polymer as a single-component thermally remendable epoxy network.

Because of the slow rate of physical gelation of DGEBA−HA polymer at 100 °C, the following thermal cycle was used to analyze its thermoreversibility. First, the system was heated at 100 °C for 3 h. Then, it was cooled to 60 °C and kept at this temperature for 17 h. Figure 13 shows the evolution of

**Figure 12.** Storage ($G'$) and loss modulus ($G''$) of the DGEBA−DA polymer as a function of temperature.
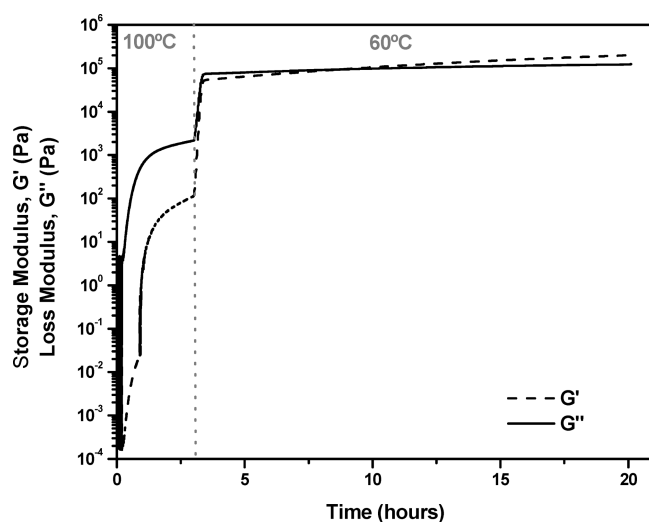


**Figure 13.** Evolution of the storage ($G'$) and loss modulus ($G''$) of the DGEBA−HA system during 3 h at 100 °C and 17 h at 60 °C.
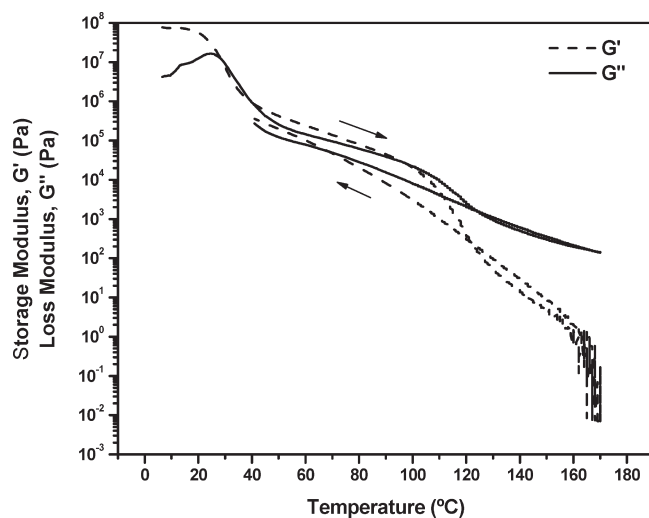


**Figure 14.** Storage ($G'$) and loss modulus ($G''$) of the DGEBA−HA polymer during heating and cooling scans at 1 °C/min.

the storage and loss moduli during this thermal cycle. Physical gelation was observed after 8.7 h, indicating the

faster rate of association of hexadecyl chains at 60 °C compared with 100 °C. After this period, the polymer was cooled to 0 °C, heated at 1 °C/min to 170 °C, and cooled again at the same rate to 0 °C. Figure 14 shows the evolution of storage and loss moduli during this thermal cycle. A clear thermoreversible behavior was observed; a gel−liquid transition occurred at 98 °C in the heating scan, followed by a liquid−gel transition at 68 °C in the cooling scan. The relatively high rate of reassociation of hexadecyl chains during a cooling scan might also be useful for considering possible applications of this polymer as a thermally remendable epoxy network.

## Conclusions

Linear amphiphilic epoxy polymers were synthesized by the bulk polyaddition reaction of stoichiometric amounts of DGEBA with alkylamines of different length: OA, DA, and HA. At the reaction temperature (100 °C), the initial systems were characterized as isotropic solutions containing aggregates (micelles) produced by tail-to-tail association of alkyl chains dispersed in the solvent (DGEBA). During polymerization, two main events were observed: (a) phase inversion process characterized by a sharp discontinuity in the derivative of the storage modulus versus time curve and (b) physical gelation defined by the crossover between the storage and loss moduli. The SAXS scattering peak assigned to tail-to-tail associations of alkyl chains remained present during the whole process. The rate of the physical gelation process could be varied with the annealing temperature (e.g., for the DGEBA−HA polymer physical gelation was accelerated by annealing the polymer at 60 °C instead of 100 °C). The physical gels exhibited a variable amount of sol fraction and a significant degree of swelling in THF. The strength of associations of alkyl chains varied in the order OA > DA > HA. This produced a faster physical gelation for the DGEBA−OA polymer, but, as a counterpart, physical associations did not show thermal reversibility up to 200 °C. For DGEBA−DA and DGEBA−HA polymers, a reversible transition from a physical gel to a liquid was evidenced in heating−cooling cycles. The thermoreversibility of the physical cross-links among dodecyl or hexadecyl chains may be used to design recyclable epoxy polymers or thermally remendable epoxy networks. The high swelling capacity of the physical gels in THF may be used to trap different salts or nanoparticles from THF solutions taking the advantage of the amphiphilic character of the material. This interesting property will be discussed in a future publication.

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