Two Ways of Synthesis of Polymer Networks Based on Diglycidyl Ether of Bisphenol A, Bisphenol A, and Sulfanilamide: Kinetics Study

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ABSTRACT: The kinetics of reactions of ternary systems based on bisphenol A diglycidyl ether, bisphenol A, and a sulfanilamide curing agent were investigated using HPLC, during two different synthesis paths. The influence of tetrabutylphosphonium tetrafluoroborate as a catalyst for the epoxy–phenol reaction was studied. For the same initial composition, polymers differing by the crosslink point distribution and the chain length between crosslinks were synthesized. Different solid-state behavior is expected in these two categories of networks. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 580–591, 2001

Key words: epoxy networks; kinetics; chain extension; crosslink density

INTRODUCTION

Epoxy resins are widely used as adhesives, matrices in composite materials, or in electronic packaging applications because of their good thermomechanical properties. There is a large amount of literature available on these materials, in particular, on the structure–property relationship. It is well known that one of the most important parameters controlling the network structure are the crosslink density and the length and flexibility of linear fragments between crosslinks. Several methods are known to change these parameters: the chemical structure and molar mass of the epoxy prepolymer,[1–3] type and 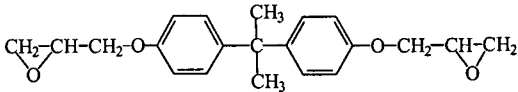functiona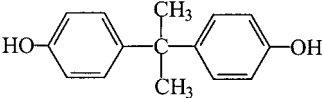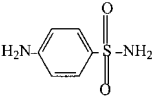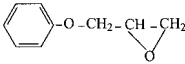lity of the curing agent,[4,5] stoichiometric ratio,[6–8] or cure times or cure schedule.[9,10] One method to modify both the crosslink density and the flexibility of the chains is to use a chain extender: It could be a primary amine with a similar structure as that of the diamine used as a hardener[11–15] or a diphenol.[16–17] The influence of the distribution of the three monomers along the chains, which means distribution of crosslinks and molar mass between crosslinks have been studied in the case of polyurethane,[18] but no study has been done in the case of epoxy networks. The purpose of the present work was to examine both the influence of the crosslink density and the monomer distribution. This first article reports results concerning the kinetics of reactions and network building; a future one will present the solid-state properties of different networks. The basic network was synthesized using diglycidyl ether of bisphenol A (DGEBA) as an epoxy prepolymer and sulfanilamide (SAA) as a curing agent. SAA is a very interesting curing agent because it has two different—NH_2 groups: The amino group is more reactive than is the amido group. So, the formation of

Table I   Characteristics of the different monomers used

Monomers	Formulae	Molecular weight $(g\ mol^{-1})$	Melting Temperature (°C)
Diglycidyl ether of bisphenol A (DGEBA)		340	40–42
Bisphenol A (BA)		228	153–156
Sulfanilamide (SA)		172	164–166
Phenyl glycidyl ether (PGE)		150	boiling point-245°C
Tetrabutylphosphonium tetrafluoroborate	$[CH_3\text{-}(CH_2)_3]_4P(BF_4)$	346	96–99

a linear prepolymer by the reaction of epoxy groups with amino groups of SAA was expected first; then, the reaction of residual epoxy groups with amido groups of SAA leads to a crosslinked material. We will use this effect to vary the network architecture.

The crosslink density has been changed using various amounts of bisphenol A (BA), used as a chain extender. The reactions of bisphenols with DGEBA have been well studied and are technologically important, because it is used commercially to prepare high molecular weight epoxy prepolymers. There are two possible types of reaction between phenol and glycidyl ether: either a direct reaction of the phenol to epoxy or a reaction of the secondary hydroxyl generated by the previous reaction with another epoxy. The selectivity of catalysts is important, that is, the ability to direct the addition of the phenolic OH group to the epoxy ring; otherwise, branched products or gelation may result if the reaction is not selective.[19] Conventional catalysts include basic organic reagents like KOH, NaOH · · ·, amine, or quaternary ammonium salts. A broad class of selective catalysts is derived from alkyl or aryl phosphonium compounds. Moreover, quaternary phosphonium salts have been found to be latent accelerators for anhydride-cured DGEBA prepolymers.[20] Tetrabutylphosphonium tetrafluoroborate was used in this work to catalyze the reaction between epoxy and phenol groups.

The network architecture, that is, the distribution of the three monomers in the network, was changed by means of the synthesis schedule. Because the initial components contain different kinds of functional groups (phenol, amino, and amido) which can react with epoxy groups, it was very interesting to study the influence of two schedules on the network synthesis, that is, opposite alternation of the basic reactions: DGEBA + SAA and DGEBA + BA + catalyst.

EXPERIMENTAL

Materials

The epoxy prepolymer used in this study was almost pure DGEBA and was supplied as DER 332 by Dow Chemicals USA. A monofunctional epoxy compound, phenyl glycidyl ether (PGE, purity 99%) from Aldrich, (Saint Quentin Fallavier, France) was also used as model of DGEBA. The curing agent was SAA (purity 98%) and the chain extender was BA (purity 97%). Tetrabutylphosphonium tetrafluoroborate[21] was used as a catalyst for the reaction between DGEBA and BA (0.005 e.e.w. DGEBA). Fluka (Saint Quentin Fallavier, France) supplied these three products. All components were used as received. The chemical structure are shown in Table 1.

SAA and BA were not soluble in the epoxy prepolymer at room temperature, and, therefore, the initial mixture of monomers was heated at 135°C and stirred until a clear solution was obtained. In all cases, the reaction between epoxy functions and

amino hydrogen groups had begun. The catalyst was added at the same time as was BA.
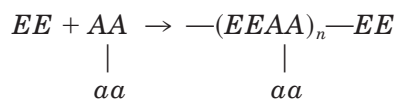
For the kinetic study, the well-mixed samples were put in glass tubes and placed in a regulated oven set at $T = 135°C$. After selected time intervals, the samples were removed, quenched in liquid nitrogen to stop the reaction, and studied by Fourier transform infrared (FTIR) spectroscopy, size-exclusion chromatography (SEC), and high-performance liquid chromatography (HPLC).

Network Synthesis

Two ways of synthesis were investigated. They are summarized below and are called schedule 1 and schedule 2.
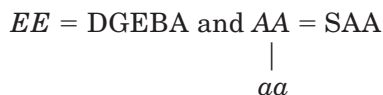
Schedule 1

Stage 1: Reaction of epoxy groups (E) from DGEBA with amino groups (A) of SAA at 135°C:

$$EE + AA \rightarrow \underset{\underset{aa}{|}}{-}(EEAA)_n\underset{\underset{aa}{|}}{-}EE$$

$$(\mathbf{I})$$

where

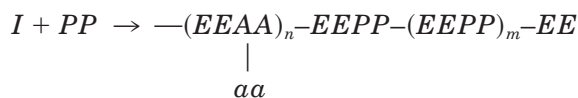$$EE = \text{DGEBA and } AA = \underset{\underset{aa}{|}}{\text{SAA}}$$

There is always an excess of epoxy functions in this stage, as compared to aminohydrogen functions.

Stage 2: Addition of BA and catalyst. Catalyzed reaction of epoxy-containing products of stage 1 with phenol groups (P) of BA at 135°C:

$$I + PP \rightarrow \underset{\underset{aa}{|}}{-}(EEAA)_n–EEPP–(EEPP)_m–EE$$
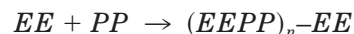
$$(\mathbf{II})$$

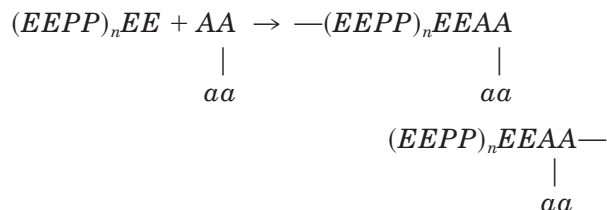(or *EEPP* chain end)

where $PP = \text{BA}$.

Stage 3: Catalyzed reaction between the residual epoxy groups and amidohydrogen groups (a) of SAA at 200°C.

Schedule 2

Stage 1: Catalyzed reaction of epoxy groups from DGEBA with BA at 135°C; epoxy groups are in excess:

$$EE + PP \rightarrow (EEPP)_n–EE$$

Stage 2: Addition of SAA. Reaction of epoxy-containing products of stage 1 with aminohydrogen groups of SAA at 135°C:

$$(EEPP)_nEE + AA \rightarrow \underset{\underset{aa}{|}}{-}(EEPP)_n\underset{\underset{aa}{|}}{EEAA}$$

$$(EEPP)_n\underset{\underset{aa}{|}}{EEAA}{-}$$

$$(\mathbf{III})$$

Stage 3: Catalyzed reaction between the residual epoxy groups and amidohydrogen groups (a) of SAA at 200°C.

One can see that the chemical reactions of stage 1 of schedule 1 and stage 2 of schedule 2 are the same (epoxy + SAA), except that the second one is catalyzed. Also, the reactions of stage 2 of schedule 1 and stage 1 of schedule 2 are exactly the same (epoxy + BA). For the same initial formulation, networks obtained at the end of the two schedules must have the same theoretical crosslink density (same concentration of $AAaa$) and average molecular mass between crosslinks. But in looking at the products of the reactions which are schemed above, we expect that the network architecture produced at the end of the two schedules will be different. The network obtained by schedule 1 is expected to have parts with a high concentration of crosslinks, connected by long linear fragments resulting from chain extension due to the epoxy–phenol reaction. On the contrary, the network synthesized by schedule 2 is expected to have a more regular distribution of crosslinks and linear chains.

Instrumentation

Fourier transform infrared (FTIR) spectroscopy was performed via a Nicolet 550 spectrometer. Samples were either sandwiched between two potassium bromide (KBr) discs or finely grounded and mixed with the KBr powder. The methyl band at 2962 cm^{-1} was used as a reference; the disappearance of the epoxy function was followed
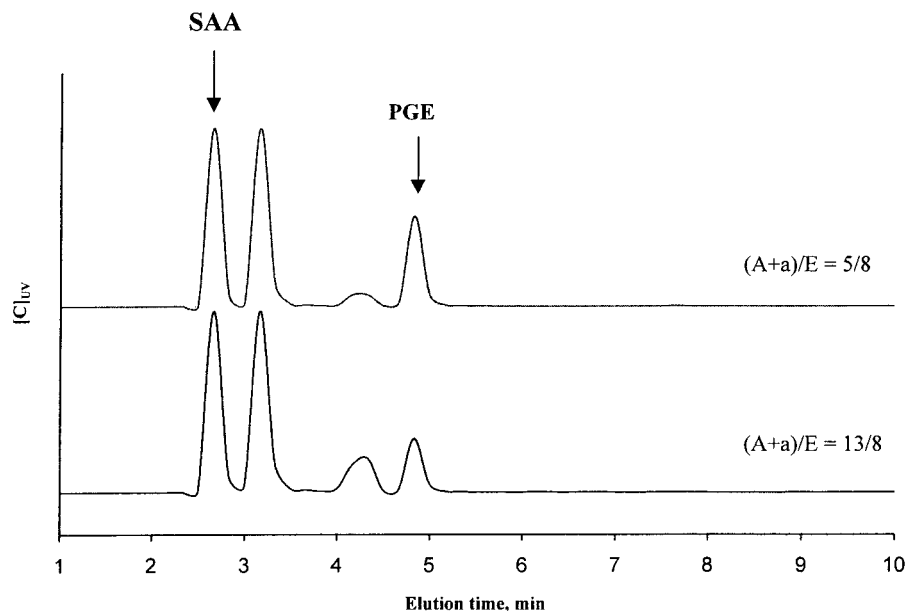
Figure 1   HPLC chromatograms of PGE:SAA reaction products after 20 min at 135°C.

with the height of the epoxy band at 915 cm^{-1} with respect to the methyl band height.

High-performance liquid chromatography (HPLC) was performed with a Waters equipment including a 600E controller, an analytical UV/vis detector set at 254 nm, and a U6K injector. The separation was done on a Novapak C18 column, and the mobile phase was a mixture of acetonitrile and water. An elution gradient running from 60% CH_3CN + 40% H_2O to 100% CH_3CN during 15 min was used. The identification of some reaction products was possible using a mass spectroscopy detector. The epoxy conversion, x_e, can be calculated from the height (h_t) of the DGEBA peak after a given time t of the reaction as follows, assuming equireactivity of all epoxy groups[22]:

$$x_e = 1 - \sqrt{\frac{h_t}{h_0}} \quad (1)$$

where h_0 is the initial height of the DGEBA peak. x_e is related to the monomer conversion X by $X = 1 - (1 - x)^2$.

Molar mass determination by SEC was conducted on a Waters chromatograph equipped with a 510 pump, an U6K injector, a refractive index detector, and a UV/vis absorbance detector set at 254 nm, a precolumn, and two Macherey–Nagel columns (Nucleogel 100-5 + 500-5). The mobile phase was tetrahydrofuran. A molar mass calibration curve was constructed from standards of monodisperse polystyrene.

RESULTS AND DISCUSSION

This study was conducted mainly on a stoichiometric system based on 4 mol DGEBA (EE)/1.25 mol of SAA ($AAaa$)/1.5 mol of BA (PP), and the ratio of functional groups is 8/5/3. The stoichiometric ratio was defined as

$$r = \frac{[NH] + [OH]}{[E]} \text{ or } r = \frac{[A] + [a] + [P]}{[E]} \quad (2)$$

First, the results of the preliminary studies on the reaction between SAA and the epoxy are reported, then the results concerning the reactions between epoxy and phenol. Finally, the kinetics of reactions during the different stages of schedule 1 and schedule 2 are compared.

SAA and Epoxy Reaction

SAA/PGE

The reaction was followed first using a monofunctional compound (PGE) in order to avoid gelation and to have low molecular weight products. Two stoichiometric ratios $(A + a)/e$ were used: 5/8 and 13/8. The reaction temperature was 135°C. Chromatograms obtained by HPLC are plotted in Figure 1. The elution times are 2.7 and 4.8 min for SAA and PGE, respectively. After 20 min of reaction at t_e = 3.17 min and t_e = 4.33 min, two reaction products are
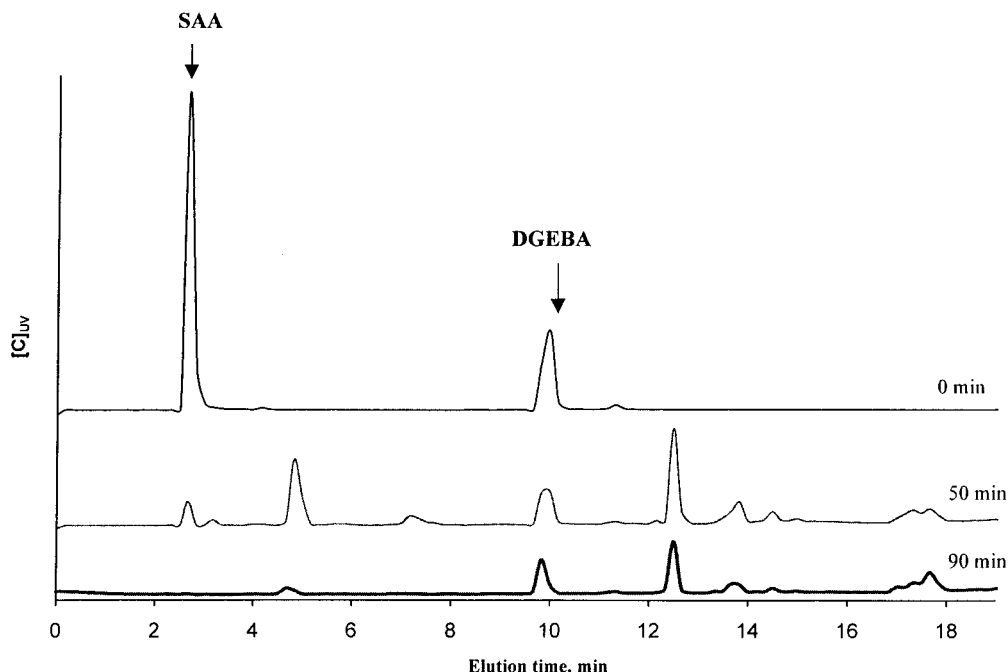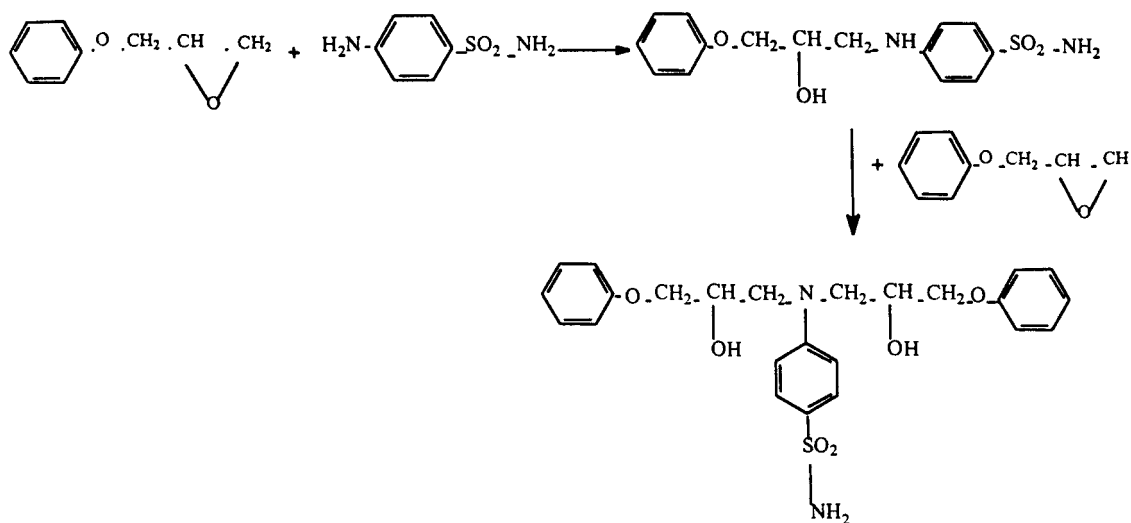
Figure 2 HPLC chromatograms of DGEBA : SAA (4.0 : 1.25) reaction products after different reaction times at 135°C.

eluted. Because of the higher reactivity of aminohydrogen groups compared to amidohydrogen groups,[17] the following reactions are expected:

For formulation with an excess of epoxy, that is, $(A + a)/e = 5/8$, after 80 min of reaction, three new reaction products are also eluted at $t_e = 6.28$ min, $t_e = 6.81$ min, and $t_e = 7.70$ min. They can be attributed to the reaction products of residual epoxy groups with amido groups of SAA.

SAA/DGEBA

The same study is now repeated for a formulation based on 4 mol of DGEBA and 1.25 mol of SAA without any catalyst. The stoichiometric ratio is therefore $(A + a)/e = 5/8$, that is, we have a large excess of epoxy functions. Chromatograms obtained by HPLC are presented in Figure 2. The
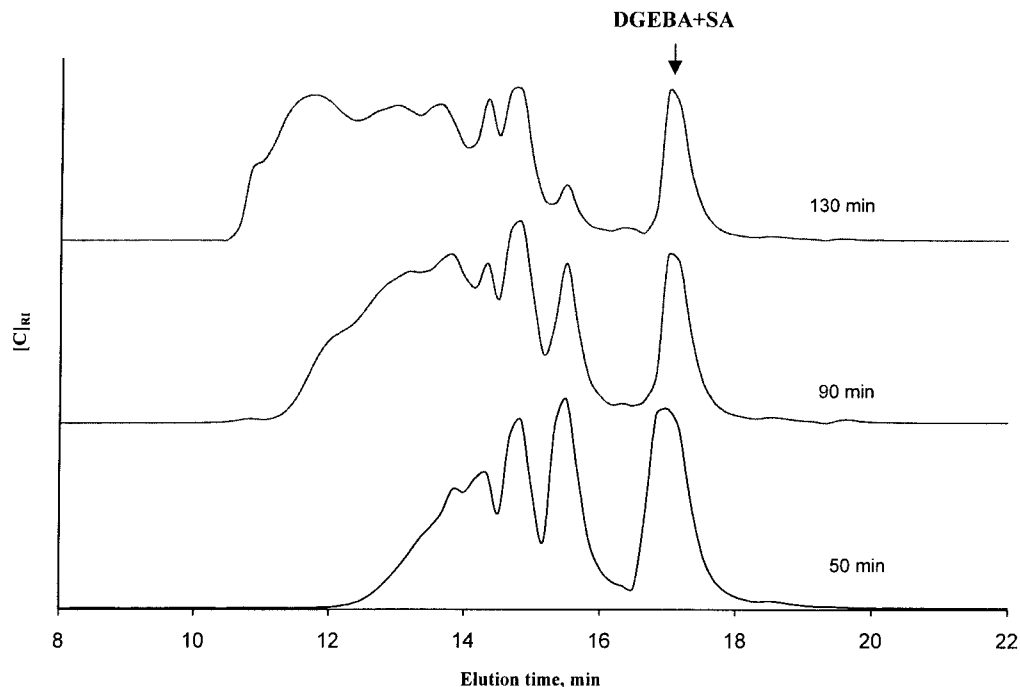
Figure 3 SEC chromatograms of DGEBA : SAA (4.0 : 1.25) reaction products after different reaction times at 135°C.

elution times for DGEBA and SAA are 10.5 and 2.7 min, respectively. The first reaction peak appears at t_e = 4.85 min and the second one at t_e = 12.5 min. However, when the reaction time is increased, other reaction products are eluted at 7.2 and 13.8 and between 17 and 18 min. SEC chromatograms after different reaction times at 135°C are given in Figure 3. SAA and DGEBA are eluted at the same time. The conversion of monomers, calculated from HPLC data and the evolution of the mass-average molecular mass, calculated from SEC data, are shown in Figure 4.

Thus, we observe a very fast reaction between SAA and DGEBA during the first 50 min. SAA molecules react almost completely. The conversion of SAA increases faster than that of DGEBA
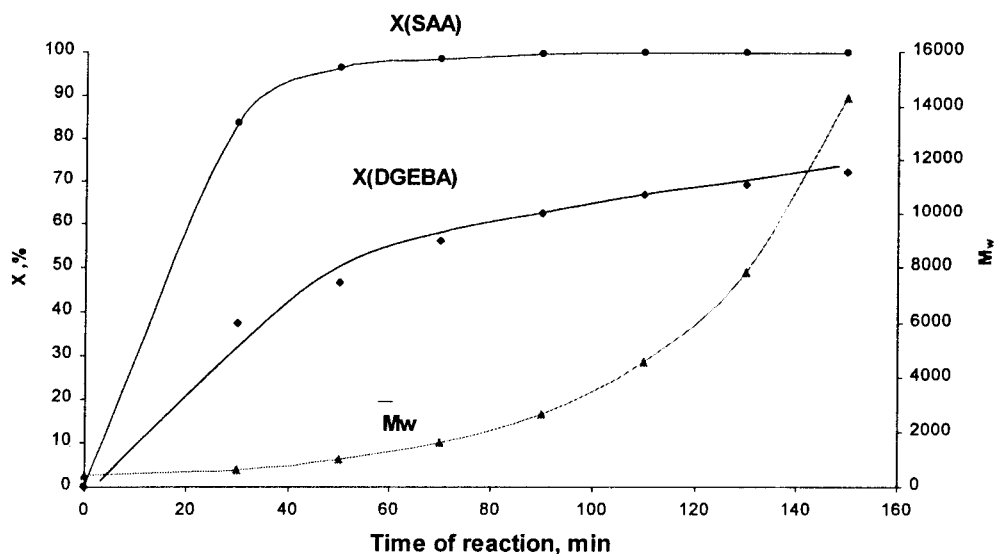
Figure 4 Monomer conversion and mass-average molar mass (PS calibration) as a function of reaction time at 135°C for DGEBA : SAA system.
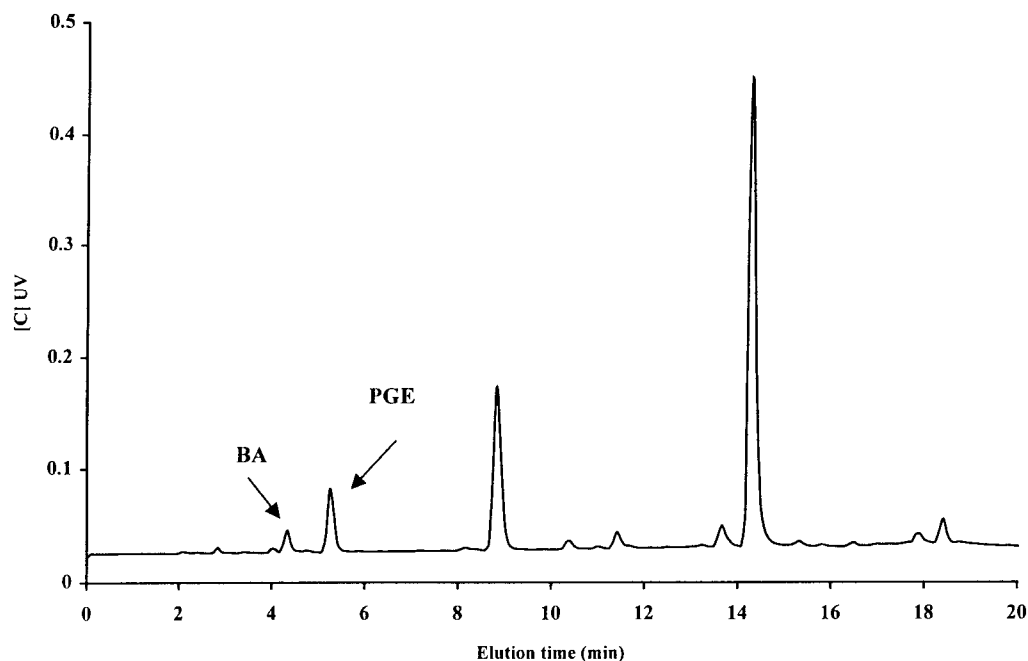
Figure 5   HPLC chromatograms of PGE : BA (4.0 : 1.25) reaction products after 210 min at 135°C.

because we have an excess of DGEBA. Some low molar mass products are formed as can be seen on the chromatograms. As previously, they result from the epoxy–amine reaction. At this stage, assuming that there is no (or little) reaction of the amide groups, SAA could be considered as a difunctional monomer and the mass-average molar mass can be calculated using the treatment of Miller and Macosko[23,24] with the usual assumptions of equal reactivity of functional groups of the same type and the absence of an intramolecular reaction. M_w may be expressed as

$$\overline{M_w} = \frac{(1 + r_{x_A^2})(rM_{AA}^2 + M_{EE}^2) + 4r_{x_A}M_{AA}M_{EE}}{(rM_{AA} + M_{EE})(1 - r_{x_A^2})} \quad (3)$$

where M_{AA} is the molar mass of SAA, and M_{EE}, the molar mass of DGEBA; $r = A/E$ with the assumption that a groups do not react; and x_A is the extent of reaction of A groups (=aminohydrogen groups).

The mass-average molecular mass derived from eq. (3) for $x_A = 1$ (or $x_E = 0.312$, and $X = 0.53$), that is, the complete reaction of amine groups, is equal to 828 g/mol. This value is closed to the experimental value obtained by SEC (Fig. 4) for the same epoxy conversion.

When the reaction time is increased, low-rate reactions between DGEBA and some reaction products take place. Epoxy groups, which are in excess, are able to react with amidohydrogen groups and high molar mass products are produced. For such a formulation, gelation should occur for an epoxy conversion, x_E, given by

$$x_A x_E = \frac{1}{(f_A - 1)(f_E - 1)} \quad (4)$$

where f_A and f_E are the functionalities of SAA and DGEBA, respectively.

With $r = x_E/x_A$, gelation should be reached for an epoxy conversion equal to 0.456 (or $X = 0.70$). The experimental value is found in this range (Fig. 4).

Bisphenol A and Epoxy Reactions

BA/PGE/Catalyst

The reaction between phenol and epoxy groups was followed at 135°C on a stoichiometric mixture of BA and PGE, in the presence of the catalyst. The HPLC chromatogram is shown in Figure 5: Two main reaction products are observed at elution times equal to 8.9 and 14.5 min, respectively. They correspond to the addition products of BA with one and two PGE. Secondary reaction products are also evidenced on the chromatogram and we supposed that the side-reaction addition of epoxy to the secondary
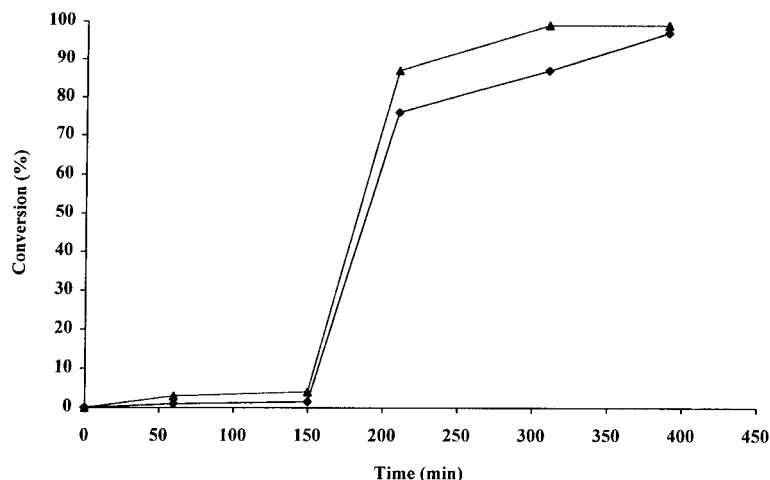
Figure 6 Monomer conversion as a function of reaction time at 135°C for PGE : BA system: (◆) BA; (▲) PGE.

hydroxyl produced by the BA–PGE reaction occurs. The epoxy and phenol conversion are plotted in Figure 6. During the first 2 h, the reaction rate is low and then increases. This low initial reaction rate can be explained by the fact that the catalyst used in this work can quickly associate with hydroxyl and epoxyde groups (and also with amino or amido groups, if they are present) at room temperature[25] and the reactivities of these intermediates have different temperature dependencies. Nearly full conversion of the monomers is reached after 5 h at 135°C.

BA/DGEBA/Catalyst

Next, a formulation based on 4 mol of DGEBA and 1.5 mol of bisphenol A was studied; the catalyst was 0.005 e.e.w. DGEBA. Once again, the reaction is followed at 135°C, using chromatography and IR spectroscopy. The conversion of epoxy and phenol groups and a change in the mass-average molar mass as function of the reaction time are given in Figure 7. HPLC and IR results show a good agreement. Three zones can be observed:

- During the first 20 min of the reaction, 10% of epoxy groups react;
- Then, an induction (or latent) period of about 150 min is observed; there are no visible changes in epoxy conversion and molar mass during 180 min of reaction at 135°C. Equation (3) can also be used to calculate the M_w of this epoxy prepolymer: M_{AA} is replaced by M_{PP}, the molar mass of BA; x_A is replaced by x_P; and r is now equal to the ratio of phenol groups to epoxy

groups, $r = 3/8$. For a full conversion of phenol groups, $x_P = 1$, $x_E = 0.375$, and $X_{EE} = 0.61$; the M_w should be equal to 1135 g/mol. This value is the same range as is the experimental one, for the same monomer conversion, which is reached after 210 min of the reaction.

- If the reaction time is increased, then the residual epoxy groups are able to react with the secondary hydroxy, as was observed above with the model compound PGE.

Ternary Systems

Reaction Between the Three Monomers DGEBA, SAA, and BA, Without Catalyst

The reaction of DGEBA and SAA was studied in the presence of BA. BA was expected to act as a catalyst.[4] The monomer conversion and change in the mass-average molar mass as a function of the reaction time at 135°C are shown in Figure 8 and can be compared to the results in Figure 4.

- One can see that SAA really reacts faster than without BA, but, surprisingly, it is observed that BA also reacts: The conversion of the BA monomer is equal to 20% after 50 min at 135°C. SAA or some of the products formed during its reaction with DGEBA (tertiary amino groups) can perhaps catalyze[17] the reaction of BA with DGEBA at this temperature.
- In each case, the monomer conversion goes to a plateau value which is quite similar in both formulations. The conversions are 100 and
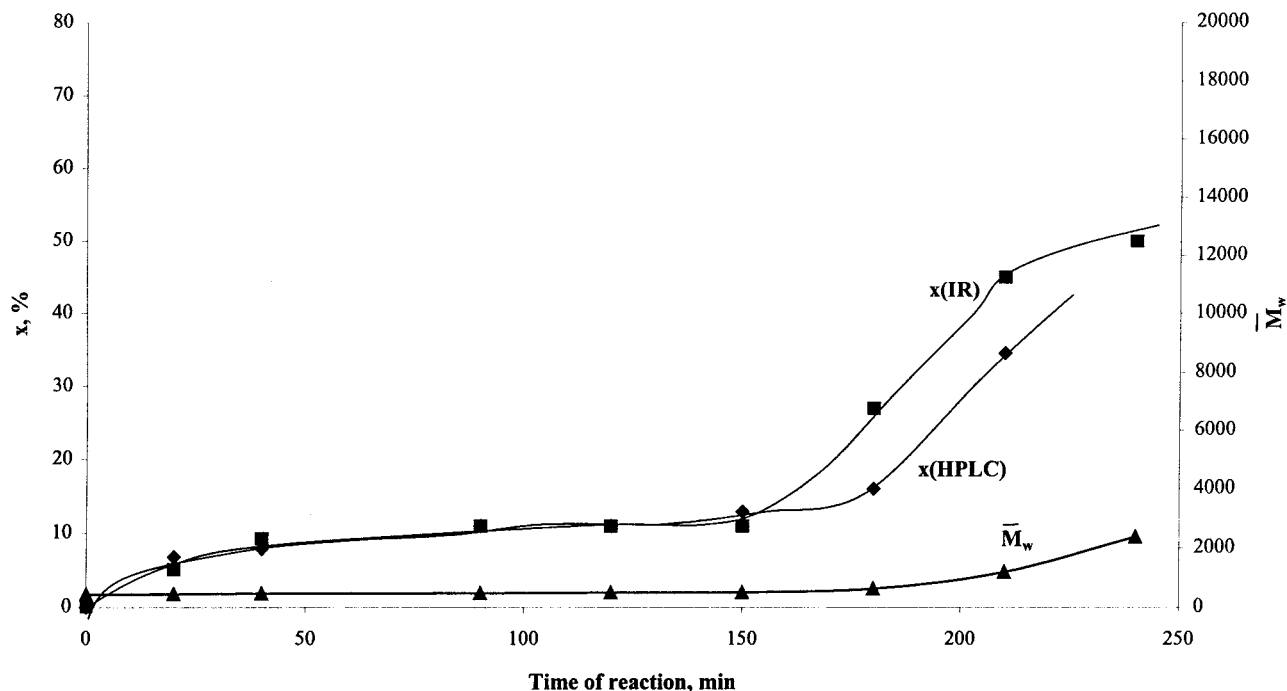
Figure 7   Monomer conversion and mass-average molar mass as a function of reaction time at 135°C for DGEBA : BA system.

70% for SAA and DGEBA, respectively. In both cases, the plateau is reached more rapidly for SAA than for DGEBA.

- The values of the mass-average molar mass (M_w) are different in each case. A lower value is obtained when the three components are mixed together at the beginning of the

synthesis and there is no evolution of molar mass after 150 min at 135°C.

Kinetics of the Reactions During Schedule 1

Stage 1. The first stage is the reaction between DGEBA and SAA. It was stopped after 50 min at 135°C because we wanted to limit the reaction of
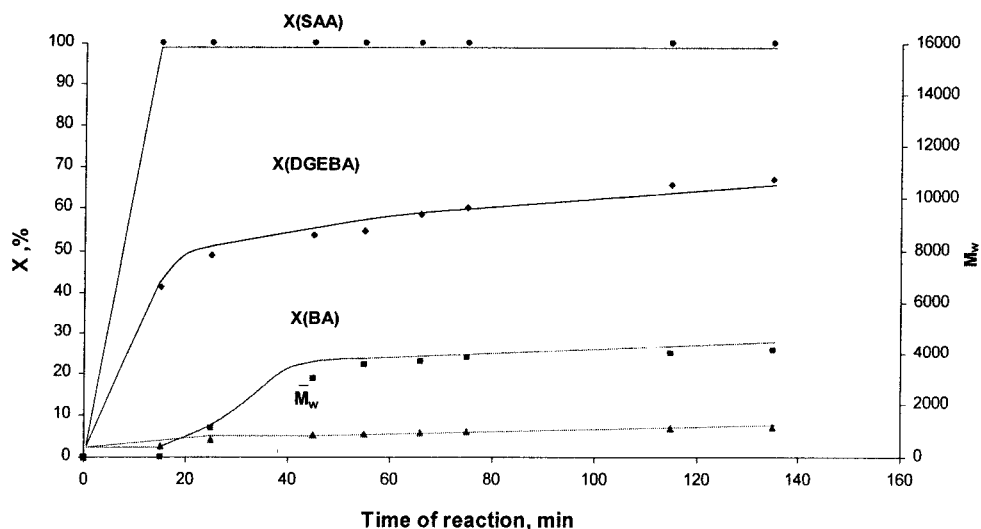

Figure 8   Monomer conversion and mass-average molar mass as a function of reaction time at 135°C for the ternary DGEBA : BA : SAA (4.0 : 1.25 : 1.5) blend without catalyst.
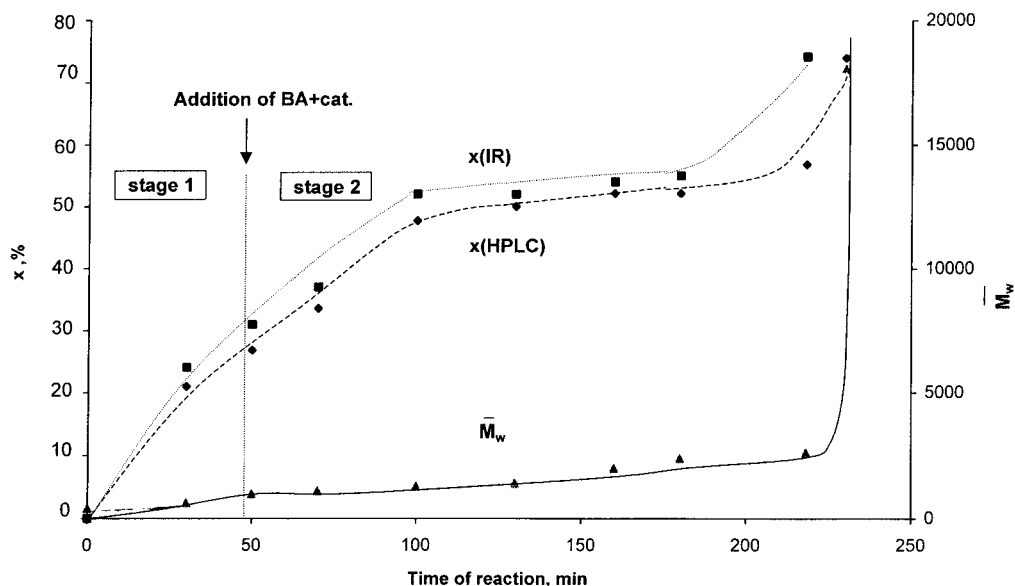
Figure 9   Epoxy conversion and mass-average molar mass as a function of reaction time at 135°C during schedule 1 for DGEBA : BA : SAA system.

the amido groups. The conversion of epoxy groups, measured by HPLC, is 30%, which corresponds to the conversion calculated theoretically, $x_{th} = (2.5/8) \times 100 = 31.2\%$, for reactions of both hydrogen atoms of the amino groups of SAA. The mass-average molar mass, M_w, of the prepolymer is equal to 1000. It is low because of the large excess of epoxy used.

Stage 2. To increase the molar mass of the prepolymer obtained after stage 1, the BA (1.5 mol of BA to initial 4 mol DGEBA) and the catalyst (0.005 e.e.w. DGEBA) were added at the same time for chain extension of this prepolymer. Stage 2 begins by the introduction of the new components and the time of mixing was 20 min at 135°C. Conversion of the monomers, determined by HPLC and M_w evolution, are plotted in Figure 9.

Once again, three zones are observed:

- The first one from 0 to 50 min (from the start of stage 2) shows the reaction of about 45% of DGEBA and 20% of BA initially present at the beginning of stage 2.
- Then, the second zone from 50 to 110 min shows that there is no appreciable evolution in the monomer conversion and molar mass; this 1-h induction period is shorter than is the 2.5-h induction time that was observed in the binary DGEBA/BA/catalyst system. This fact can be explained by the superposition of the reaction between epoxy and amido functions, but also by a lower number of functions able to associ-

ate with the catalyst. At this temperature, it has been shown that the catalyst has no influence on the kinetics of the reaction between epoxy and amino or epoxy and amido functions.[25]

- The third zone corresponds to a sharp increase of both the monomer conversion and molar mass which lead to gelation. The gel point for this formulation was found at 240 min of the total reaction time and for an epoxy conversion equal to $x_E = 0.80$.

Kinetics of the Reactions During Schedule 2

Stage 1. In this case, it is the reaction between DGEBA and BA in the presence of a catalyst. Following the results expressed in Figure 7, the first stage of the synthesis was stopped after 195 min at 135°C because a linear prepolymer without or with little branching is expected. At this time, the epoxy conversion is equal to 37%, which agrees with the calculated conversion for the complete reaction of BA ($x_{th} = 0.375$). The mass-average molar mass is again near 1000.

Stage 2. Sulfanilamide is added to the DGEBA/BA/catalyst mixture after 195 min of reaction at 135°C. The reaction of SAA and the epoxy prepolymer is followed by HPLC, SEC, and FTIR methods. The summarized epoxy conversion for schedule 2 is given in Figure 10.

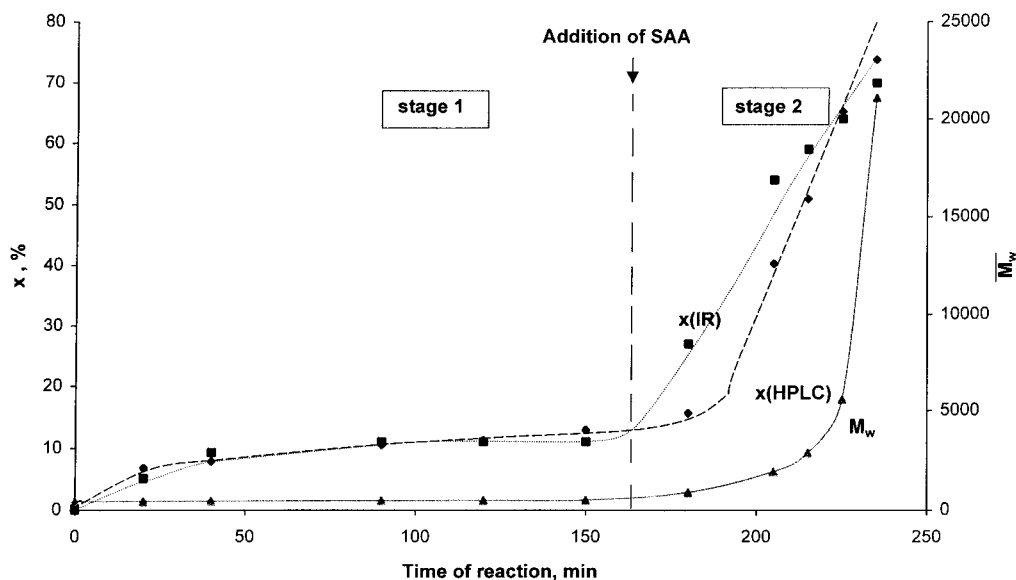Sharp increases of the epoxy conversion and of

Figure 10 Epoxy conversion and mass-average molar mass as a function of reaction time at 135°C during schedule 2 for DGEBA : BA : SAA system.

the M_w are noticed. It is explained by the fast reaction of SAA with epoxy at the beginning of stage 2 and then after 45 min by the superposition of the catalyzed reaction between BA and epoxy after the induction period. Gelation is reached after 300 min for an epoxy conversion equal to 0.80.

Comparison Between the Two Schedules

The epoxy conversion and evolution of molar mass for the two schedules can be compared using Figure 9 and Figure 10. The gel point was reached for schedule 1 after 240 min and for schedule 2 after 300 min of total process at a similar conversion of epoxy groups about 80%. It can be seen that, although two schedules have different kinetics, both prepolymers obtained at the end of schedule 1 and schedule 2 show the same epoxy conversion. From the comparison of the two schedules, one can also expect different evolution of the viscosity during the network synthesis. This fact could be interesting for in processing these networks.

CONCLUSIONS

The synthesis of prepolymers based on DGEBA, SAA (as the curing agent), and BA (as the chain extender) were studied. The epoxy conversion of two basic reactions (DGEBA + SAA and DGEBA + BA + catalyst) was described. Two schedules were used by changing the order of the component mixing and of the reactions. For formulation

DGEBA : SAA : BA = 4.0 : 1.25 : 1.5, mol (cat., 0.005 e.e.w.), it was shown that, although the schedules have different kinetics, the prepolymers with equal conversion of epoxy groups and mass-average molar mass were obtained by both schedules. Further work has to be done to characterize the structure–properties relationships for networks obtained by the two schedules.

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