The first stages of an epoxy homopolymerization initiated by piperidine

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Reactions taking place in the phenyl glycidyl ether (PGE)–piperidine system were followed by size exclusion chromatography using ultra-violet detection at 254 nm. The first step was the addition of piperidine to PGE to give a tertiary amino alcohol (TAA). This reaction took place by both catalytic ($E = 50.7$ kJ mol^{-1}) and non-catalytic mechanisms. No other reaction could be detected before the piperidine concentration was depleted. The reaction of PGE with TAA was followed at 120°C. The main product was a TAA–PGE addition compound, following a pseudo-first-order kinetic rate equation. After this reaction, the PGE oligomerization takes place at room temperature.

(Keywords: epoxy homopolymerization; phenyl glycidyl ether; piperidine)

INTRODUCTION

The use of piperidine as a curing agent in epoxy formulations has been reported by several authors[1–11]. The cure cycle affects the glass transition temperature[6] and the fracture energy[11] of the resulting networks. This arises from the competition among different polymerization mechanisms when varying the cure temperature[10]. These include the secondary amine–epoxy addition reaction and the epoxy homopolymerization initiated by the resulting tertiary amino alcohol. This reaction may take place through different paths[12].

In order to get a deeper understanding of the reaction mechanism, a monoepoxy (phenyl glycidyl ether, PGE) was selected as a model system. The amount of piperidine was varied from 0.05 to 1.00 (in moles with respect to PGE). The reaction was followed by size exclusion chromatography (s.e.c.) using u.v. detection at 254 nm, which measured the distribution of phenyl rings among the different species (the piperidine cycle gave no signal with u.v. detection at 254 nm). Results concerning the first stages of this reaction will be discussed in this paper.

EXPERIMENTAL

Phenyl glycidyl ether (PGE, Aldrich) and piperidine (Carlo Erba) were used as received. Formulations in molar ratios PGE/piperidine ranging from 1:1 to 20:1 were prepared without using any solvent. A set of glass tubes containing about 1 cm^3 of a given formulation were placed in a thermostat at a selected temperature. At pre-specified times tubes were removed from the bath and quenched in dry ice. Solutions in tetrahydrofuran (THF, 2 mg ml^{-1}) were prepared and injected into a size exclusion chromatographic unit (Waters 510, u.v. detector at 254 nm, four columns of Ultrastyragel 100 (×2), 500 and 10 000 Å, flow rate = 1 cm^3 min^{-1} THF).

The tertiary amino alcohol (TAA) produced in the reaction of PGE and piperidine was characterized by differential scanning calorimetry (DuPont 990 provided with a 910 DSC cell). The polymerization of PGE initiated by TAA was studied in the same way as the PGE–piperidine reaction, using s.e.c. to quantify the reaction products.

RESULTS AND DISCUSSION

PGE–piperidine in a 1:1 molar ratio

The addition reaction of piperidine to PGE in stoichiometric amounts was studied with the following aims: (a) to assess if the epoxy homopolymerization could compete with the epoxy–amine addition reaction under these conditions; and (b) to determine the reaction kinetics.

The reaction product is a tertiary amino alcohol, TAA = 1-(*N*-piperidine)-3-phenoxy-2-propanol (*Figure 1*).

Figure 2 shows some s.e.c. chromatograms for the reaction carried out at 49°C. Only PGE and TAA were detected in the course of the reaction (the only u.v. chromophore is the phenyl ring). At full conversion only TAA was present, a fact that was corroborated for several runs carried out in the 40–120°C range. This means that the epoxy homopolymerization rate in the presence of TAA is negligible when compared to the epoxy–amine addition rate.

An important finding was the constancy of the total area per unit mass under the s.e.c. chromatogram, for different conversion levels. This implies that partial areas under the PGE and TAA peaks were proportional to their molar concentrations. Therefore, the conversion could be estimated as:

$$x = A_{TAA}/(A_{TAA} + A_{PGE}) \quad (1)$$

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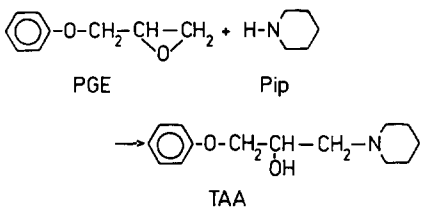

Figure 1 Addition of piperidine (Pip) to phenyl glycidyl ether (PGE) to give a tertiary amino alcohol (TAA)

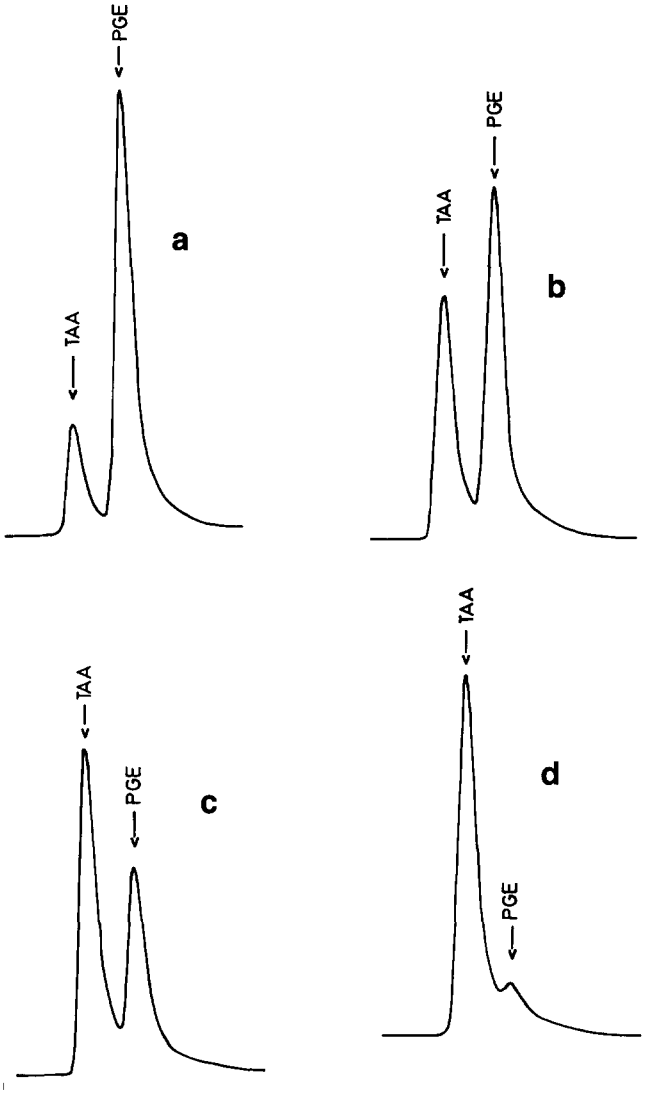

Figure 2 S.e.c. chromatograms of the PGE–piperidine reaction products (1:1 molar ratio). Reaction carried out at 49°C for various reaction times: (a) 6 min, (b) 11 min, (c) 21 min and (d) 76 min

Figure 3 shows the fractional conversion vs. time curves in the temperature range 40–60°C. Autocatalytic behaviour is observed, consistent with kinetic studies reported for epoxy–amine addition reactions[13–15]. The kinetic rate equation can be written as[14]:

$$dx/dt = (k'e_0 + ke_0^2x)(1-x)^2 \qquad (2)$$

where k is the catalytic rate constant (catalysis by OH groups), k' is the non-catalytic rate constant and e_0 is the initial molar concentration of epoxy groups.

Integrating equation (2) with $K = ke_0^2$ and $\theta = k'/(ke_0)$, we obtain:

$$\frac{1}{(1+\theta)}\left[\frac{x}{(1-x)} + \frac{1}{(1+\theta)}\ln\left(\frac{(x+\theta)}{\theta(1-x)}\right)\right] = F(x,\theta) = Kt \qquad (3)$$

Figure 4 shows the fitting of equation (3) to the three fractional conversion vs. time plots in *Figure 3*. An Arrhenius plot of the catalytic rate constant K is shown in *Figure 5*. The resulting activation energy is $E = 50.7$ kJ mol^{-1} (12.1 kcal mol^{-1}), in good agreement with most of the results reported for the epoxy–amine catalysed reaction. The non-catalytic mechanism is of significance at the beginning of the reaction.

An increase in the θ value with temperature may be inferred from the fitting shown in *Figure 4*. However, a precise quantification was not possible owing to the small contribution of the non-catalytic mechanism and the narrow temperature range investigated.

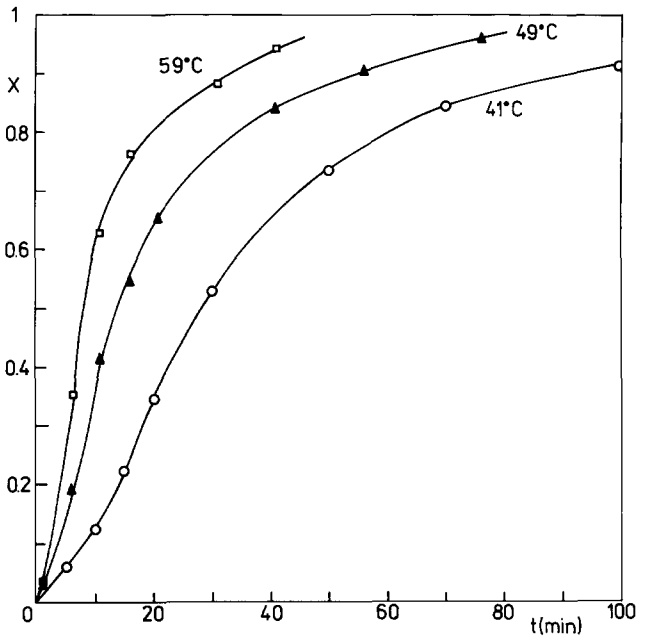

Figure 3 Fractional conversion as a function of time for the PGE–piperidine reaction (1:1 molar ratio), at 41, 49 and 59°C

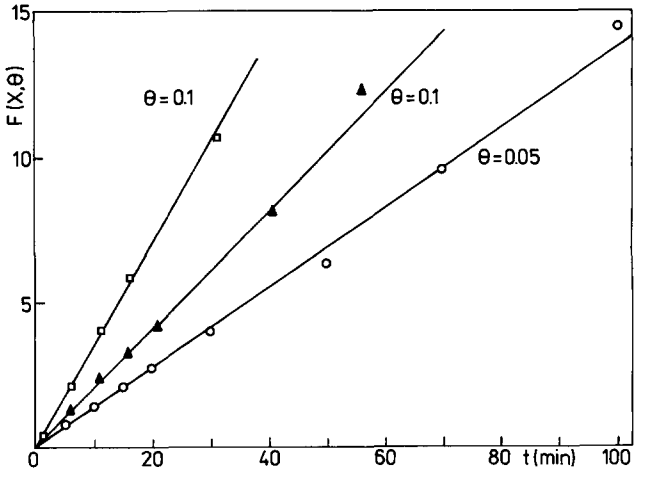

Figure 4 Fitting of experimental data to the proposed kinetic model

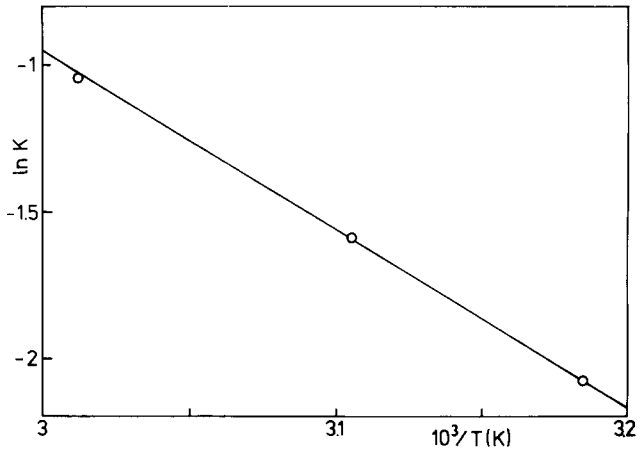

Figure 5 Arrhenius plot of the catalytic rate constant

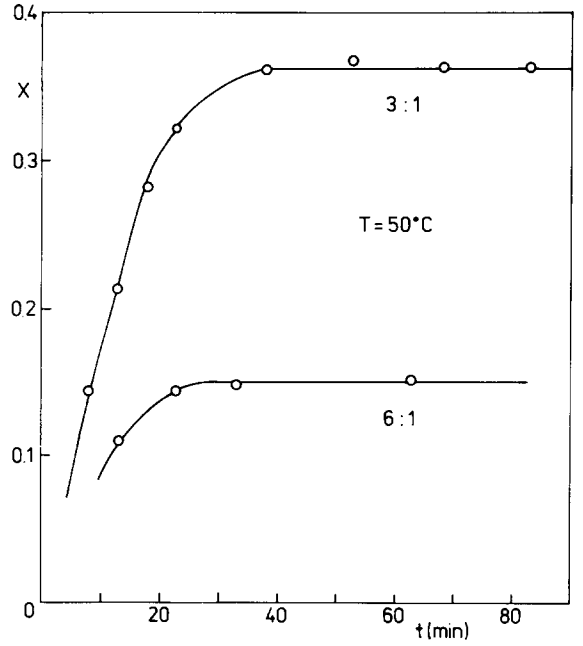

Figure 6 PGE conversion as a function of time for formulations containing excess epoxy (PGE/piperidine equal to 3:1 and 6:1 in molar ratios), reacted at 50°C

PGE–piperidine in an epoxy excess

The PGE–piperidine system containing epoxy in excess was studied with the aim of following the first reaction products formed in the course of the homopolymerization reaction. *Figure 6* shows PGE conversion as a function of time for two runs carried out at 50°C. The PGE–piperidine molar ratio was close to 3:1 in one case and 6:1 in the other. Only TAA and the residual PGE peaks appeared in the s.e.c. chromatograms. The asymptotic conversions were close to the expected values (assuming that TAA formation was the only product): 0.36 (exp.) vs. 0.33 (theor.) for the 3:1 ratio and 0.15 (exp.) vs. 0.17 (theor.) for the 6:1 ratio. Again, it was found that the epoxy–amine addition was the only reaction occurring up to piperidine exhaustion. The action of TAA as an initiator of the PGE homopolymerization was very low at 50°C (after 7 h at 50°C a very small peak of a product with a higher molar mass could be detected in s.e.c. chromatograms).

To start the homopolymerization mechanism, a formulation prepared with a 6:1 molar ratio of PGE/piperidine was heated at 120°C for 4 h. The resulting s.e.c. chromatogram is shown in *Figure 7*. Both PGE and TAA reacted further and two reaction products in the region of lower elution volumes (higher molar masses) appeared. *Table 1* shows the areas of the different peaks, as a percentage of the total. The only u.v. chromophore is the phenyl ring, and the results represent the distribution of phenyl rings among the different species.

The assignment of the two new peaks was made from the molar balance of piperidine residues. The initial formulation had a molar ratio of piperidine to PGE equal to 0.17. As no free piperidine should be present after prolonged heating at 120°C in excess epoxy, the 0.17 mol of piperidine must be distributed among the three peaks (i.e. every peak except the one of PGE). These 0.17 mol must be associated with the fraction of PGE consumed in the reaction, i.e. 0.355 mol (*Table 1*). TAA is composed of 1 mol of PGE and 1 mol of piperidine. By assuming that the two peaks of higher molar masses are TAA–PGE (a species containing 2 mol of PGE per mole of piperidine) and TAA–$(PGE)_2$ (a species containing 3 mol of PGE per mole of piperidine), the total amount of piperidine residues may be calculated as:

$$\text{fraction of piperidine residues} = [\text{TAA}] + \frac{[\text{TAA–PGE}]}{2} + \frac{[\text{TAA–(PGE)}_2]}{3}$$

Using the experimental values reported in *Table 1*, we get a fraction of piperidine residues equal to 0.179, in excellent agreement with the expected value. A duplicate run was carried out under the same conditions and values were repeated within experimental error.

The probable structures of the reaction products generated during the first stages of the homopolymerization are shown in *Figure 8*. Although the proposed structures may be formally obtained through the epoxide ring

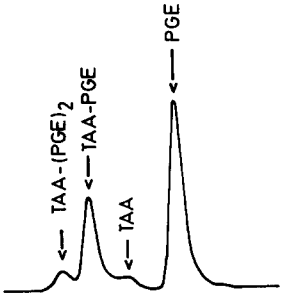

Figure 7 S.e.c. chromatogram for a PGE/piperidine formulation (6:1 molar ratio), reacted for 4 h at 120°C (see text for the assignment of peaks)

Table 1 Percentage of phenyl rings in the different species present in a formulation containing 6:1 molar ratio of PGE/piperidine after 4 h at 120°C

Species	Phenyl rings (%)
PGE	64.5
TAA	2.0
TAA–PGE	28.5
TAA–$(PGE)_2$	5.0

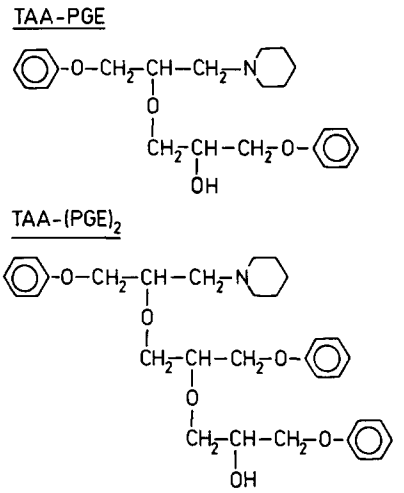

Figure 8 Probable structures of the reaction products generated during the first stages of the homopolymerization

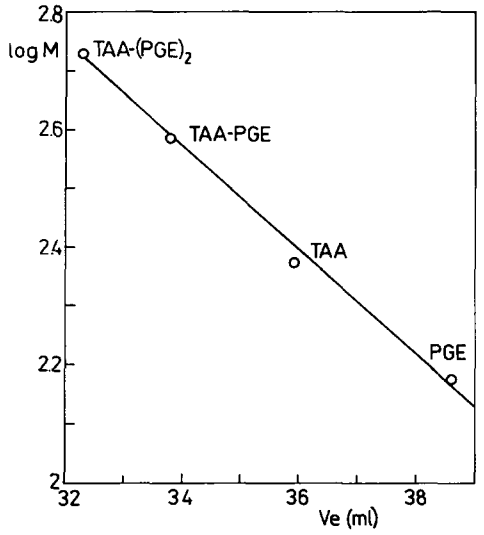

Figure 9 Calibration curve obtained by using the four peaks present in the s.e.c. chromatogram of *Figure 7*

opening by a secondary OH, a complex anionic mechanism is probably present[10,12,16]. (The addition of PGE to TAA to form a zwitterion[10] would lead to a species having the same molar mass as the proposed structure. However, it does not seem plausible that this species constitutes the main reaction product during the first stages of epoxy homopolymerization[16].)

Once the assignment of molar masses to the different peaks appearing in the s.e.c. chromatogram is performed, it is possible to produce a calibration curve. Such a plot is shown in *Figure 9*.

The progress of the homopolymerization reaction was followed at a constant temperature. Although no reaction of the PGE/TAA mixture was observed after 10 days at room temperature, once the initiator was generated at 120°C (possibly the alkoxide derived from the TAA[10,16]), the homopolymerization took place to completion at room temperature. *Figure 10* shows s.e.c. chromatograms for a PGE–piperidine formulation (6:1 molar ratio), reacted for 4 h at 120°C and then (a) 8 days at 20°C or (b) 13 days at 20°C. After 13 days the PGE conversion was 84%, the concentration of the first member of the series (TAA–PGE) was half of the starting value (i.e. fraction shown in *Table 1*), and a significant increase in the concentration of larger oligomers was observed. A small fraction of TAA was still present.

Using the calibration curve shown in *Figure 9*, the maximum of the peaks assigned to the oligomers is located in the region of 600–700 g mol^{-1}, but a balance of piperidine residues would require a larger average size of the oligomer distribution (for 100% conversion the average size—including the first member of the series—would be given by the TAA–(PGE)$_5$ with a molar mass of 985 g mol^{-1}). The explanation is given by the regeneration of the initiator during the oligomerization[12,17–19]. Then, one initiator (i.e. the alkoxide derived from the TAA) generates more than one oligomeric chain.

Intramolecular chain transfer may be a possible mechanism leading to the regeneration of the initiator[17–19], as is shown in *Figure 11*. If the proton is abstracted from the CH belonging to the TAA residue, a phenoxide would be generated. After a propagation step and a chain transfer to an alcohol, the species shown in *Figure 12* would appear. This product (and the series starting from it) was identified when the homopolymerization was initiated by 1-(*N*-methylanilino)-3-phenoxy-2-propanol[12]. However, it was not present in our s.e.c. chromatograms, at least in significant quantities (a peak very close to the

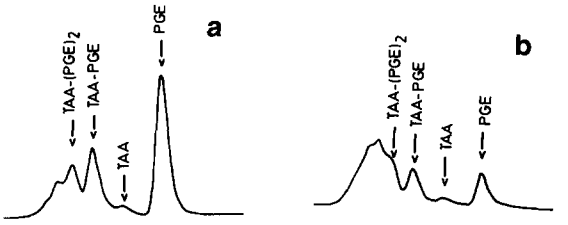

Figure 10 S.e.c. chromatograms for a PGE/piperidine formulation (6:1 molar ratio), reacted for 4 h at 120°C and (a) 8 days at 20°C or (b) 13 days at 20°C

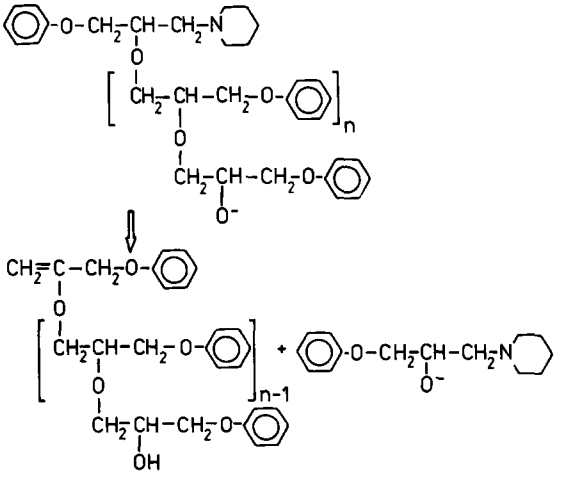

Figure 11 Intramolecular chain transfer leading to the regeneration of the initiator

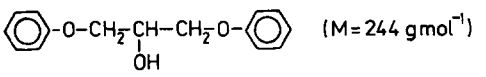

Figure 12 Species found with the use of other initiators (see text) but not present in significant quantities in the system described in this paper

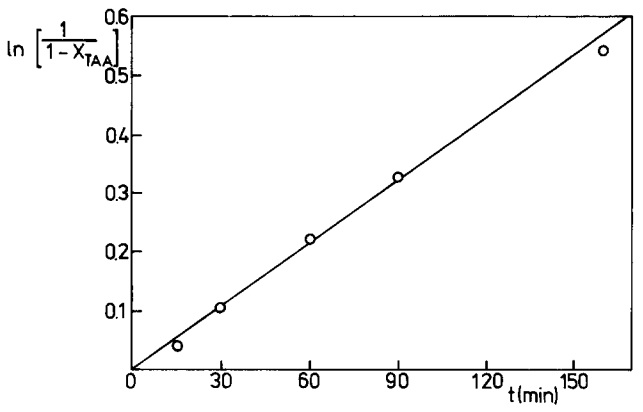

Figure 13 Fitting of experimental data to the pseudo-first-order kinetic model for the reaction of TAA with excess PGE

one of TAA should have appeared in the course of polymerization).

PGE–tertiary amino alcohol

In order to quantify the slow transformation of TAA into the first member of the oligomeric series (TAA–PGE), the reaction of PGE with TAA was followed at 120°C. TAA was prepared by completely reacting a formulation of PGE and piperidine in a stoichiometric ratio, at 60°C. The reaction product, 1-(*N*-piperidine)-3-phenoxy-2-propanol, was characterized by differential scanning calorimetry, giving a melting point of 55°C. The crystalline powder could be rapidly dissolved in PGE.

A formulation of PGE/TAA in a 20:1 molar ratio was reacted at 120°C. Up to 50% conversion of TAA, only one reaction product, i.e. TAA–PGE, could be detected by s.e.c. So, TAA conversion was calculated as:

$$x_{TAA} = \frac{0.5A_{TAA-PGE}}{A_{TAA} + 0.5(A_{TAA-PGE})}$$

The formula is based on the fact that there are two phenyl rings per mole of TAA–PGE.

As PGE is present in large excess, its concentration may be taken as constant. So, a pseudo-first-order kinetic equation may be proposed:

$$dx_{TAA}/dt = k_1(1 - x_{TAA}) \quad (4)$$

Equation (4) may be integrated to give

$$\ln[1/(1 - x_{TAA})] = k_1 t \quad (5)$$

Figure 13 shows a very good fit of the kinetic model to experimental results. The resulting pseudo-first-order kinetic constant was $k_1 = 3.57 \times 10^{-3}\ min^{-1}$.

The transformation of TAA into TAA–PGE must be associated with a very high activation energy barrier, as no reaction was detected after 10 days at room temperature. The elementary step with a high activation energy is possibly one forming the anionic initiator[10,16].

CONCLUSIONS

The study of the PGE homopolymerization initiated by piperidine revealed the following features:

The first step was the addition of piperidine to PGE to give a tertiary amino alcohol (TAA). No other reaction could be detected before the piperidine concentration was depleted. The amine–epoxy addition reaction took place by the usual mechanisms (catalysis by OH groups with an activation energy $E = 50.7\ kJ\ mol^{-1}$, and a non-catalytic mechanism predominating at low conversions).

The first step of the epoxy homopolymerization was the reaction of PGE with TAA to give TAA–PGE, i.e. the product arising from the epoxide addition to the secondary OH of TAA (possibly through an anionic mechanism). This step required a high activation energy (no reaction was detected after 10 days at room temperature), and followed a first-order kinetic law when operating in a large PGE excess.

After the generation of TAA–PGE, the reaction could take place at room temperature, giving oligomers of the type TAA–$(PGE)_n$ but also of the type $(PGE)_n$, as inferred from an overall balance of piperidine residues. Oligomers devoid of TAA are produced by a chain-transfer step that regenerates the initiator.

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