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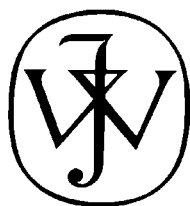
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Homopolymerization of Epoxy Monomers Initiated by 4-(Dimethylamino)pyridine

I.E. Dell'Erba, 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

The anionic epoxy homopolymerization initiated by tertiary amines, imidazoles, and ammonium salts is a complex reaction exhibiting two undesired characteristics for practical applications: (a) slow reaction rates with long induction periods, and (b) short primary chains due to the high rate of chain transfer reactions. Therefore, these systems have not found an important place in commercial applications. In this study, it is shown that using 4-(dimethylamino)pyridine (DMAP) as initiator of the polymerization of phenyl glycidyl ether (PGE) or diglycidyl ether of bisphenol A (DGEBA) enables to obtain high polymerization rates and longer primary chains than those generated using typical initiators. A critical molar ratio DMAP/epoxy groups was necessary to attain complete conversion. Networks resulting from the DMAP-initiated homopolymerization of DGEBA exhibited a high crosslink density and corresponding high values of the glass transition temperature ($T_g = 160^\circ\text{C}$) and of the rubbery elastic modulus (higher than 100 MPa). An intense brown color of reaction products, associated with an absorption band with a maximum at 360 nm, was ascribed to the presence of initiator fragments with conjugated double bonds in chain ends. These results might revalorize the anionic homopolymerization of epoxy monomers for commercial applications. *POLYM. ENG. SCI.*, 46:000–000, 2006. © 2006 Society of Plastics Engineers

INTRODUCTION

One of the possible ways of polymerizing epoxy monomers is through the use of small amounts of Lewis bases that act as initiators of the anionic polymerization [1]. Commonly used initiators (often named “catalytic” curing agents in the literature) include tertiary amines like benzyltrimethylamine, pyridine, triethylamine or 2,4,6-tris(dimethylaminomethyl)phenol, as well as imidazoles and am-

monium salts [2, 3]. There are hundreds of anionic initiators described in the patent literature [2].

Mechanisms for the anionic polymerization of epoxy monomers initiated by tertiary amines have been extensively discussed [4–13]. Unfortunately, the mechanism is so complex that there is yet no scheme universally accepted. Figure 1 shows some of the proposed reactions [4, 13].

Two types of initiation steps are often postulated. Reaction 1a is the direct attack of the tertiary amine to an epoxy group, leading to the zwitterion IP_1 . Reaction 1b consists in the formation of an alkoxide anion $\text{R}'\text{O}^-$ through a trimolecular transition state. In the absence of alcohols or any other proton-donor species, the reaction exhibits an autocatalytic behavior following a long induction period. The induction period becomes shorter, and the maximum reaction rate increases upon addition of alcohols, indicating that $\text{R}'\text{O}^-$ is much more effective than IP_1 to initiate the homopolymerization of epoxy groups. Moreover, it has been stated that IP_1 cannot initiate the polymerization at all and that proton-donors or electrophilic impurities must be present to produce the reaction [8]. Several chain-transfer steps are also present in the reaction mechanism. Reactions 3b and 3c are intramolecular chain-transfer reactions that lead to polymer chains ending in terminal vinyl and hydroxyl groups together with the regeneration of the tertiary amine or an active alkoxide (a phenoxy anion for the particular case of phenyl glycidyl ether, shown as an example in Fig. 1) [7, 10–12, 14]. Both steps 3b and 3c may involve hydrogen abstraction from any of the CH groups present in the $(n-2)$ repeating units [14], in which case a shorter active chain ending in an alkoxide group is generated. The presence of termination steps leading to inactive species is still a matter of debate. It has been reported that if a fresh amount of monomer is added to the reaction mixture after completion of the reaction, it recommences without any induction period [8]. This suggests a living character for the polymerization and the absence of termination steps.

In summary, the anionic epoxy homopolymerization is a complex reaction exhibiting two undesired characteristics for practical applications: (a) slow reaction rates with long induction periods, and (b) short primary chains due to the

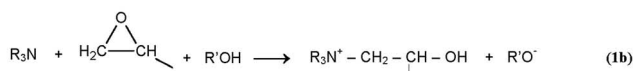
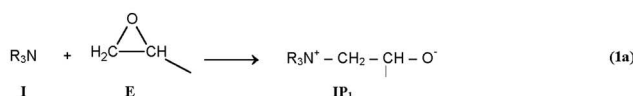
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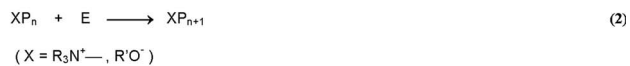
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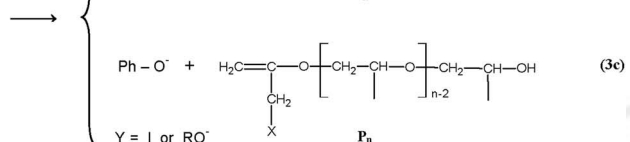
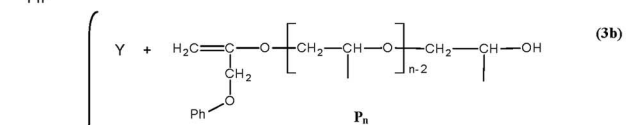
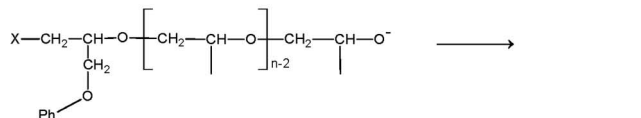
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Propagation



Chain Transfer



Termination

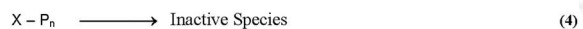


FIG. 1. Reactions taking place during the anionic polymerization of epoxy monomers initiated by tertiary amines.

high rate of chain-transfer reactions. Short primary chains are responsible for the relatively low glass transition temperatures (T_g in the order of 100°C) of polymer networks obtained by the anionic homopolymerization of diglycidyl ether of bisphenol A (DGEBA). Therefore, these systems have not found an important place in commercial applications. The use of imidazole derivatives gives better results, but does not eliminate completely the previous objections [2].

The use of 4-(dimethylamino)pyridine (DMAP) as an effective initiator of anionic ring-opening polymerizations has been reported in the literature [15]. We have recently used DMAP to polymerize DGEBA in the presence of different amounts of an oligomeric silsesquioxane [16], and found relatively high values of the glass transition temperature of the resulting networks. Therefore, DMAP may be considered as a potential candidate to replace typical anionic initiators used to homopolymerize epoxy monomers.

The aim of this study is to analyze the efficiency of DMAP as initiator of the anionic polymerization of epoxy monomers. The polymerization rate of phenyl glycidyl ether (PGE) initiated by DMAP will be compared with that obtained using a typical initiator like benzyldimethylamine (BDMA). The respective distribution of reaction products

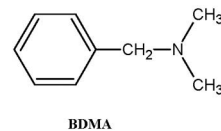
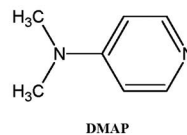
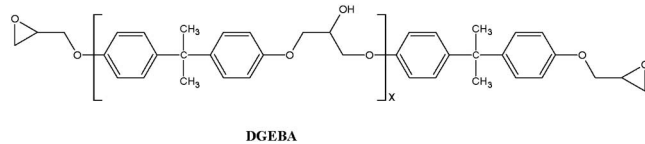
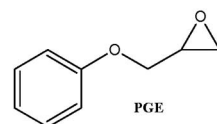


FIG. 2. Chemical structures of epoxy monomers (PGE and DGEBA) and initiators (DMAP and BDMA).

will be also compared. Then, the use of DMAP to polymerize DGEBA will be analyzed with emphasis on the effect of its initial concentration on the glass transition temperature of the resulting polymer network.

EXPERIMENTAL

Materials

Chemical structures of epoxy monomers and initiators are shown in Fig. 2. Selected epoxy monomers were phenyl glycidyl ether (PGE, Aldrich, 99% purity, 150.18 g/mol) and diglycidyl ether of bisphenol A (DGEBA, Der 332 Dow). The subscript in the chemical structure means that the product was a mixture of 97 mol% pure DGEBA and 3 mol% of the monomer with an index in the repeating unit equal to 1. PGE was heated in a vacuum oven at 80°C for 2 h to eliminate possible traces of water, while DGEBA was used as received. Selected initiators were 4-(dimethylamino)pyridine (DMAP, Fluka, 98% purity, 122.17 g/mol, m.p. 111–114°C) and benzyldimethylamine (BDMA, Aldrich, 98% purity, 135.10 g/mol). They were used as received.

Reaction Conditions

The polymerization of PGE was carried out using either DMAP or BDMA as initiators. The selected amount of

initiator was dissolved at room temperature, and solutions were submitted to the following conditions: (a) heating at 5°C/min to 180°C in a differential scanning calorimeter (DSC, mass of samples close to 10 mg), (b) polymerization at a constant temperature in the range comprised between 80 and 110°C in the cell of a differential scanning calorimeter (DSC, mass of samples in the range 5–10 mg), (c) polymerization at 80°C in a thermostatic bath (closed tubes containing about 40 mg of the initial solution were withdrawn at different times and the reaction stopped in an acetone–ice bath).

For the case of DGEBA-DMAP formulations, the selected amount of initiator was dissolved at 55°C. The polymerization was carried out in a DSC at a constant heating rate of 10°C/min so as to obtain the reaction heat. The glass transition temperature was determined in a second scan. Cured plaques were also obtained in a heated mould with the following thermal cycle: 3 h at 80°C, 3 h at 120°C, and 15 min at 165°C. These specimens were characterized by dynamic mechanical analysis and by DSC.

Techniques

Reaction heats ($-\Delta H$), overall polymerization kinetics, and glass transition temperatures (T_g) were determined by DSC. A Shimadzu DSC-50 was used for dynamic runs and a PerkinElmer DSC-Pyris 1 for isothermal runs, in both cases operating under nitrogen flow. Conversions and reaction heats were determined from partial and total areas under exothermic peaks (conversions were defined in runs where a complete conversion was attained). Glass transition temperatures were determined at the mid-point of the change in the specific heat.

Fourier-transformed infrared spectra (FTIR) were recorded with a Genesis II-Mattson device in the transmission mode. Thin coatings of samples on NaCl windows were obtained from THF solutions.

Absorption spectra in the UV–visible range were obtained using a Shimadzu UV-1601 PC device. Samples were dissolved in THF (0.06 mg/cm³) and placed in quartz cells.

Partially reacted samples of PGE-DMAP and PGE-BDMA formulations were withdrawn at various times from the thermostatic bath at 80°C and dissolved in THF to give concentrations in the order of 8 mg/cm³. Molar mass distributions were determined by size-exclusion chromatography (SEC, Knauer K-501, RI detector Knauer K-2301, and the following set of Phenomenex Phenogel 5 μ -columns: 50A, 100A, and M2). THF was used as a carrier at 1 cm³/min. Molar masses were assigned with an internal calibration procedure that will be discussed in the corresponding section.

Dynamic mechanical spectra were obtained with a PerkinElmer DMA-7 system operating at 1 Hz in the three-point bending mode at a heating rate of 10°C/min. Specimens with the following dimensions: $B = 3$ mm, $W = 2$ mm

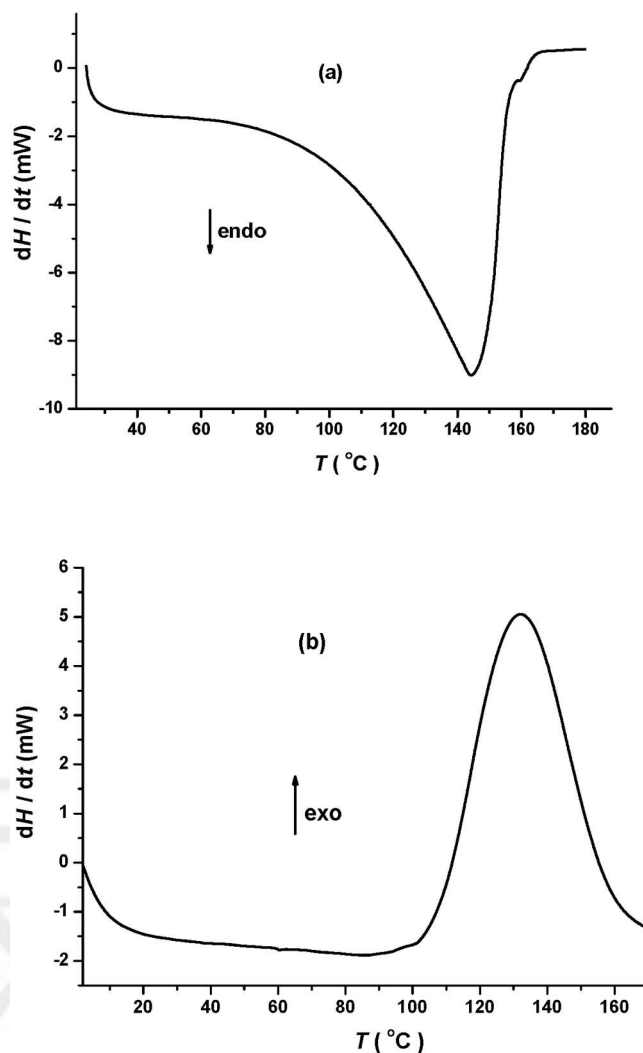


FIG. 3. Dynamic DSC runs of PGE-initiator formulations prepared with a molar ratio initiator/PGE = 0.02: (a) initiator = BDMA, (b) initiator = DMAP.

(thickness) and $L = 20$ mm (span = 15 mm) were machined from the plaques obtained in the heated mould.

RESULTS AND DISCUSSION

Polymerization of PGE

The efficiency of DMAP and BDMA to initiate the polymerization of PGE was compared from dynamic DSC runs. Figures 3 and 4 show the thermograms obtained when using a molar ratio initiator/epoxy = 0.02 (Fig. 3) or 0.08 (Fig. 4).

During the time of the scan, BDMA was not able to initiate the polymerization at the two selected concentrations. In fact, the broad endothermic peak was produced by PGE evaporation as confirmed by weighing DSC pans at the end of the runs. This behavior is characteristic of typical tertiary amines. It reveals the existence of a long induction

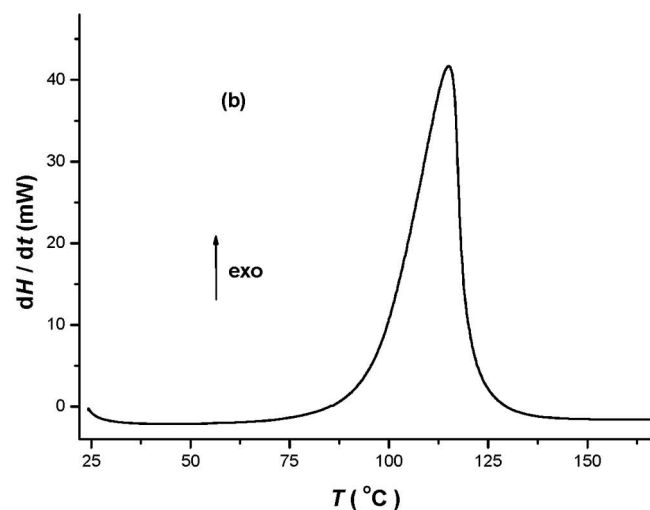
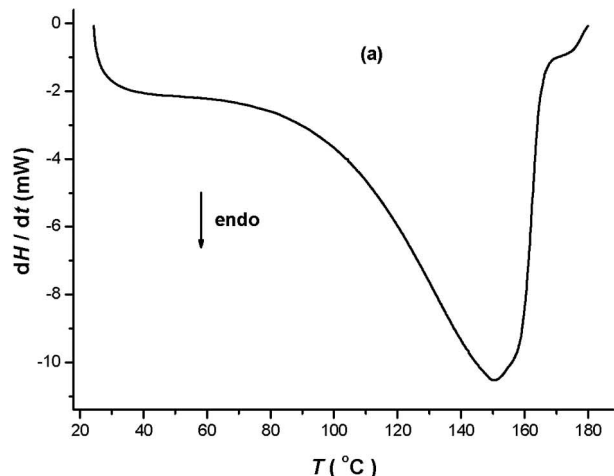


FIG. 4. Dynamic DSC runs of PGE-initiator formulations prepared with a molar ratio initiator/PGE = 0.08: (a) initiator = BDMA, (b) initiator = DMAP.

period necessary to form the active species that initiates the polymerization. In contrast, DMAP was able to polymerize PGE in the course of dynamic scans. The reaction heat per mole of epoxy groups was estimated as 33.9 kJ/mol for the sample with DMAP/PGE = 0.02 (the reaction was still taking place at 170°C), and 95.3 kJ/mol for the sample with DMAP/PGE = 0.08. The last value is close to the reaction heat reported for an epoxy homopolymerization (92 kJ/mol) [17], meaning that the reaction can attain complete conversion when using an appropriate amount of DMAP. Solutions prepared with DMAP/PGE = 0.02 attained a conversion of about 36% during the dynamic scan. Second and third scans did not show exothermic peaks implying that no active species were present in the system. Therefore, from the results obtained with dynamic DSC runs, we may conclude that: (a) DMAP is a much better initiator than BDMA; (b) there is a critical DMAP/epoxy molar ratio comprised between 0.02 and 0.08, above which complete conversion of epoxy groups is attained; (c) a termination reaction

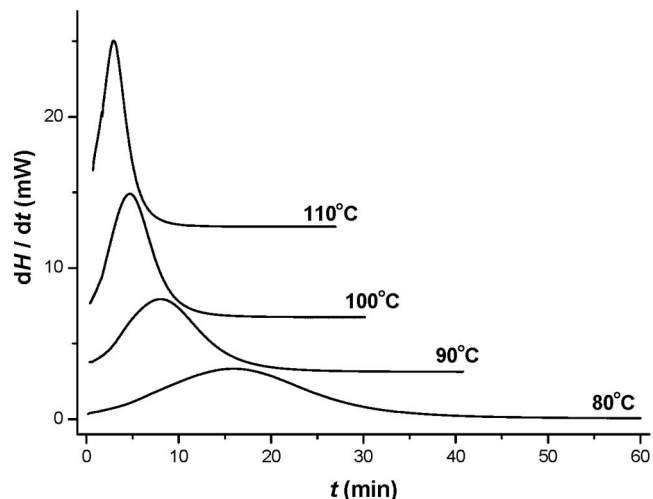


FIG. 5. Isothermal DSC runs of PGE-DMAP formulations with a molar ratio DMAP/PGE = 0.08 ($T = 80, 90, 100,$ and 110°C).

consuming the active species in an irreversible way is present in the reaction mechanism.

Isothermal DSC runs were performed for solutions with a molar ratio DMAP/PGE = 0.08. Thermograms for 80, 90, 100, and 110°C are shown in Fig. 5. The polymerization takes place at a fast rate comparable to the rate of epoxy-aliphatic amine formulations. The reaction heat for the four temperatures was equal to 95.1 ± 3.2 kJ/mol, a value similar to that obtained in dynamic DSC runs for the same composition. It is concluded that the reaction may be carried out to complete conversion in about 60 min at 80°C and 10 min at 110°C. These results prove that DMAP is in fact an excellent initiator for the anionic polymerization of epoxy groups.

The shape of isothermal DSC runs indicates that the kinetics follows an autocatalytic path. The initiation is not instantaneous, but must proceed at a finite rate leading to a continuous increase in the concentration of active species. As inferred from the results of dynamic DSC runs, a termination step accounting for the consumption of active species must be also present in the reaction mechanism.

To quantify the effect of temperature on the overall polymerization rate, we postulate that the consumption of epoxy groups may be expressed by the following phenomenological equation:

$$dx/dt = kf(x) = A \exp(-E/RT)f(x) \quad (1)$$

where x is the conversion of epoxy groups, t is time, and k is an overall kinetic constant exhibiting an Arrhenius dependence on temperature with an overall activation energy symbolized by E . This is in fact a strong hypothesis because it is not obvious that a complex reaction scheme can be reduced to such a simple kinetic equation [3]. The validity of this hypothesis may be corroborated applying an isoconversional method. The time necessary to attain a particular

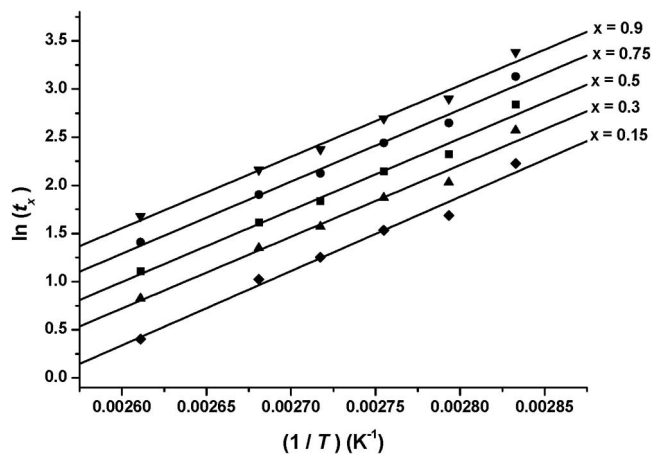


FIG. 6. Application of the isoconversional method for the anionic polymerization of PGE initiated by DMAP.

conversion x at a given temperature T may be obtained from Eq. 1.

$$\ln t_x = \ln A^{-1} + \ln F(x) + E/RT \quad (2)$$

where the unknown function $F(x)$ depends only on the particular conversion (it is the integral between 0 and x of $f(x)^{-1}dx$). Therefore, if Eq. 1 is valid, then plots of $\ln t_x$ vs. $1/T$ at different conversions should be a set of parallel straight lines. Figure 6 shows such a plot using data of DSC runs performed at 80, 85, 90, 95, 100, and 110°C. This confirms the validity of the phenomenological rate equation given by Eq. 1 for the PGE-DMAP system. The overall activation energy calculated from the slope of the straight lines of Figure 6 is $E = 62.4 \pm 0.5$ kJ/mol.

Figure 7 shows a comparison of FTIR spectra of the initial solution of PGE with DMAP (molar ratio DMAP/PGE = 0.08), and the product obtained after polymerization at 80°C for 2 h to complete conversion (disappearance of the epoxy peaks at 863 and 916 cm^{-1}). The ring-opening of the epoxy group generated a strong band at about 1130 assigned to the asymmetric C—O—C stretching vibration, the disappearance of a band at 3000 cm^{-1} assigned to the CH and CH₂ groups in the oxirane ring, and the increase in the intensity of peaks at 2868 and 2922 cm^{-1} assigned to the symmetric and asymmetric stretch of the (R—O)—CH₂—bonds [18]. Peaks at 1642 and 3430 cm^{-1} assigned to terminal vinylidene groups and terminal OH groups of polyether chains produced by chain-transfer reactions (reactions 3b and 3c in Fig. 1) appeared in the FTIR spectrum of the reaction products.

One significant characteristic of an epoxy homopolymerization initiated by DMAP is the intense brown color that is developed from the beginning of the polymerization (the initiation with BDMA does not lead to colored products). Figure 8 shows absorption spectra in the UV–visible region for THF-solutions of PGE-DMAP (molar ratio DMAP/PGE = 0.08) before polymerization (a), and after complete con-

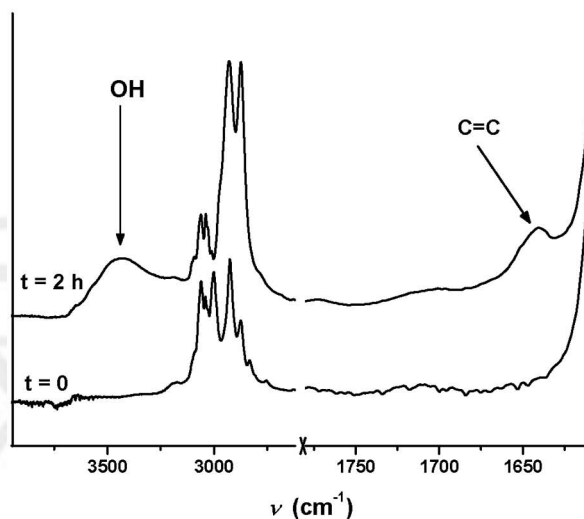
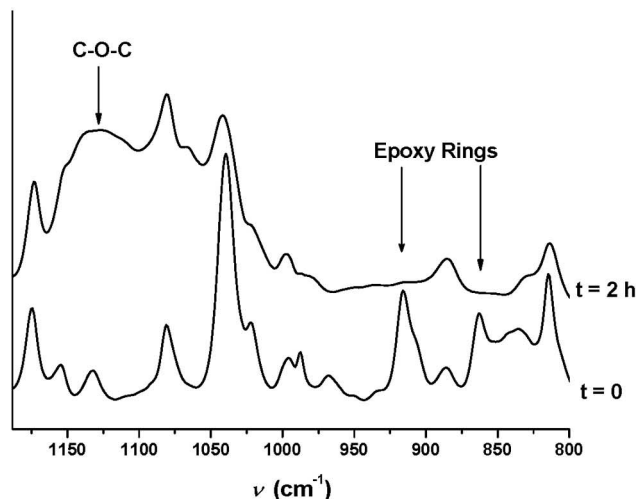


FIG. 7. Comparison of FTIR spectra of the initial solution of PGE with DMAP (molar ratio DMAP/PGE = 0.08), and the product obtained after polymerization at 80°C for 2 h to complete conversion.

version of PGE at 80°C (b). Apart from the broadening of the band located in the UV region, a new band with a maximum at 360 nm and with a tail extending toward the visible part of the spectrum is observed. In the undiluted system, this is a very intense band that gives a characteristic dark-brown color to the final products. As this coloration starts from the beginning of the polymerization, it can be related to a change in the chemical structure of DMAP in the initiation step.

Figure 9 shows the mechanism proposed for the initiation step (reaction 1a in Fig. 1). The effectiveness of DMAP to initiate the epoxy polymerization is ascribed to the presence of a resonance structure with a negative charge placed on the N of the pyridine cycle and a positive charge placed on the tertiary amine nitrogen. This structure is responsible for the fast nucleophilic attack of the epoxy ring. The double-bond conjugation is probably responsible for the appearance of the broad absorption band at 360 nm in the

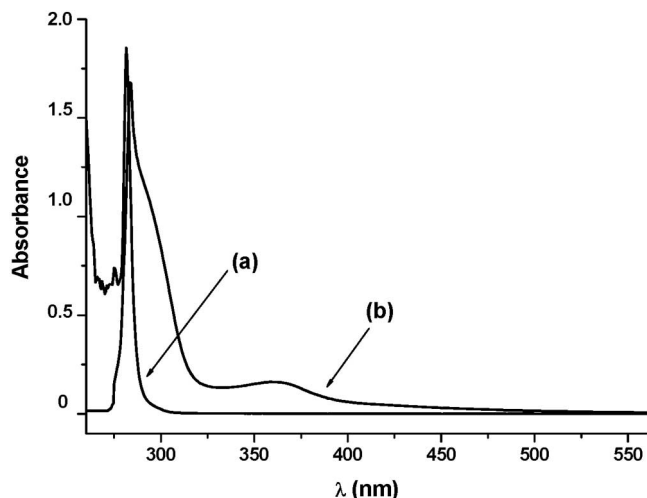


FIG. 8. Absorption spectra in the UV–visible region for THF-solutions of PGE-DMAP (molar ratio DMAP/PGE = 0.08): (a) before polymerization, (b) after complete conversion of PGE at 80°C.

UV–visible spectrum. The characteristic coloration to the final material may be explained assuming that a fraction of the population of polyether chains has the initiator attached to one of the chain ends. The resonance stabilization of the positive charge (partially shared by both nitrogen atoms) after the initiation step and the fact that there is not a mobile positive counterion in close vicinity to the alkoxide group, as in the case of the initiation by typical tertiary amines, can explain the high value of the propagation rate.

The existence of a critical DMAP concentration to get complete conversion of epoxy groups was related to the presence of a termination reaction consuming the active species. This reaction might be the formation of cyclic ethers (Fig. 10), a possibility postulated in the literature for reactions of pyridine and poly(vinyl pyridine) with epoxy compounds [19, 20].

The average size of polyether chains produced using either BDMA or DMAP may be compared following the

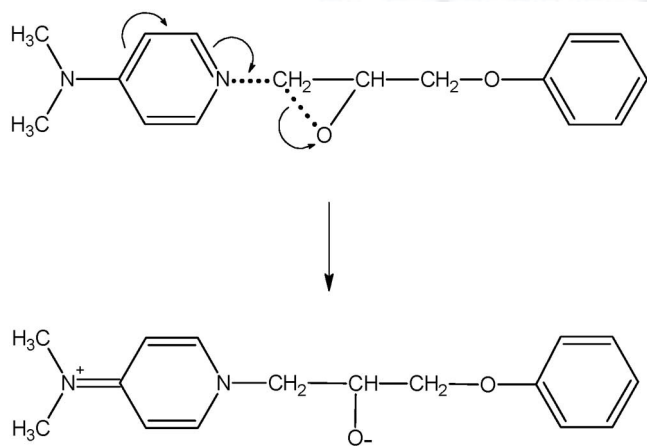


FIG. 9. Mechanism proposed for the initiation step in the homopolymerization of PGE initiated by DMAP.

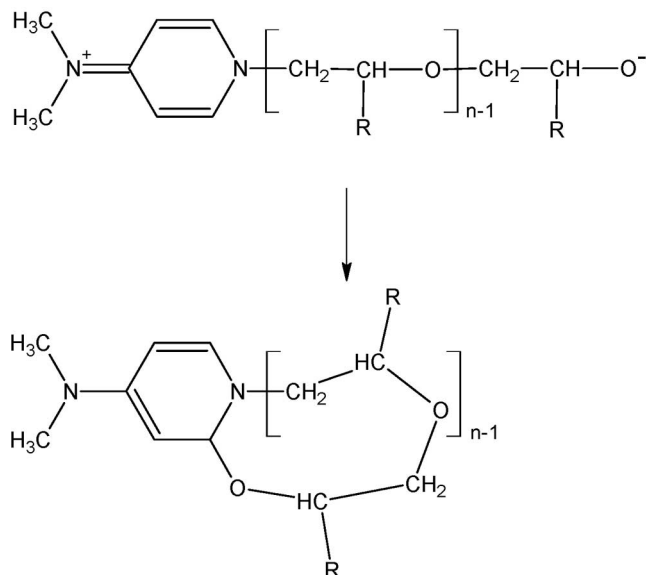


FIG. 10. Mechanism proposed for the termination step in the homopolymerization of PGE initiated by DMAP.

distribution of reaction products by SEC. Figure 11 shows the distribution of oligomers produced in the polymerization of PGE at 80°C initiated by BDMA. The reaction was very slow; after 7 h, there was still a small amount of residual PGE. Peaks were assigned to the family of P_n oligomers (as the molar mass of BDMA is very close to the one of PGE, it is not possible to distinguish an IP_{n-1} from a P_n oligomer). A calibration curve was built up with the usual assumption that the logarithm of the molar mass (M) is linearly related with elution times.

$$\log M = \alpha - \beta t \quad (3)$$

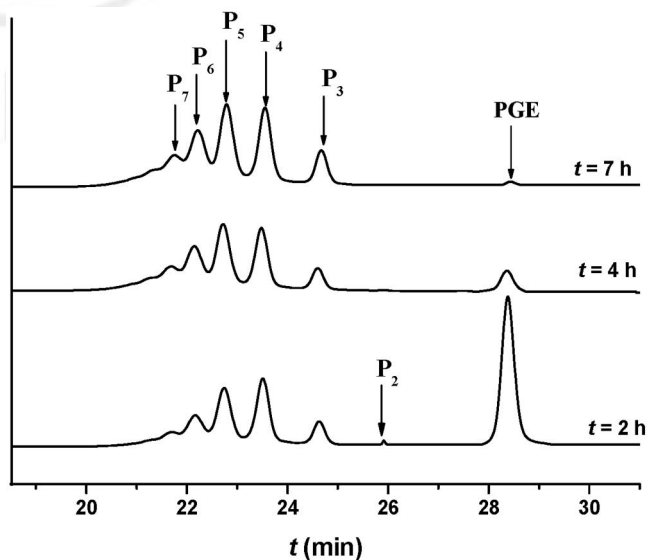


FIG. 11. SEC chromatograms showing the distribution of reaction products in the BDMA-initiated polymerization of PGE at 80°C (molar ratio BDMA/PGE = 0.08).

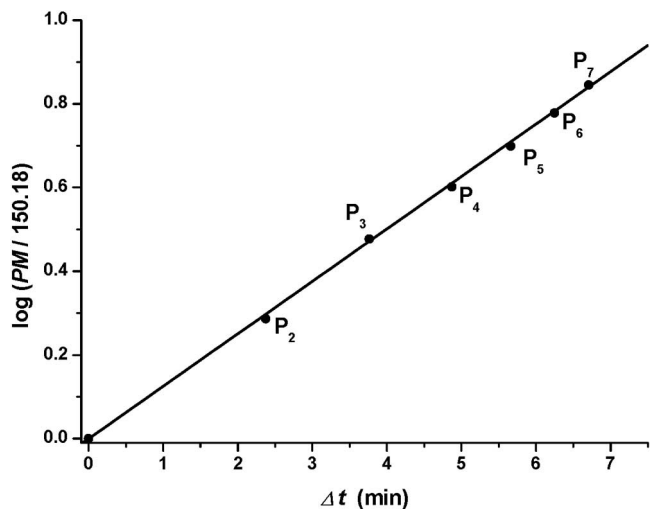


FIG. 12. Calibration curve of the SEC columns using the oligomers produced in the BDMA-initiated polymerization of PGE as internal standards.

Writing Eq. 3 for PGE and subtracting the resulting equation from Eq. 3 leads to:

$$\log(M/150.18) = \beta(t_{\text{PGE}} - t) \quad (4)$$

Figure 12 shows the resulting calibration curve ($\beta = 0.1253 \text{ min}^{-1}$) that enables to obtain average molar masses. The number-average molar mass of the final product (after 7 h reaction) was $M_n = 706 \text{ g/mol}$. This corresponds to an average of 4.7 PGE units incorporated to a polyether chain, which lies in the range of values reported in the literature [7, 8].

The distribution of reaction products in the DMAP-initiated polymerization of PGE, carried out at 80°C, is shown in Fig. 13. The reaction is much faster than with BDMA. At 70 min, there was no residual PGE in the system. The number-average molar mass of the product distribution at the end of the polymerization was $M_n = 1095 \text{ g/mol}$, equivalent to an average of 6.5 PGE units and one DMAP fragment or to 7.3 PGE units. Therefore, the use of DMAP, instead of a typical tertiary amine, leads to longer polyether chains, a fact explained by the higher value of the propagation rate.

Polymerization of DGEBA

DMAP was also an efficient initiator for the anionic polymerization of DGEBA. Figure 14 shows a DSC thermogram for a formulation prepared with a molar ratio DMAP/epoxy groups = 0.08. The reaction heat per mole of epoxy groups was 90.7 kJ/mol indicating an almost complete conversion of epoxy groups. The glass transition temperature of the polymer network was determined in a second scan (Fig. 15), giving a $T_g = 159.4^\circ\text{C}$. This value is significantly higher than those obtained with typical tertiary amines (values close to 100°C). This may be ascribed to the

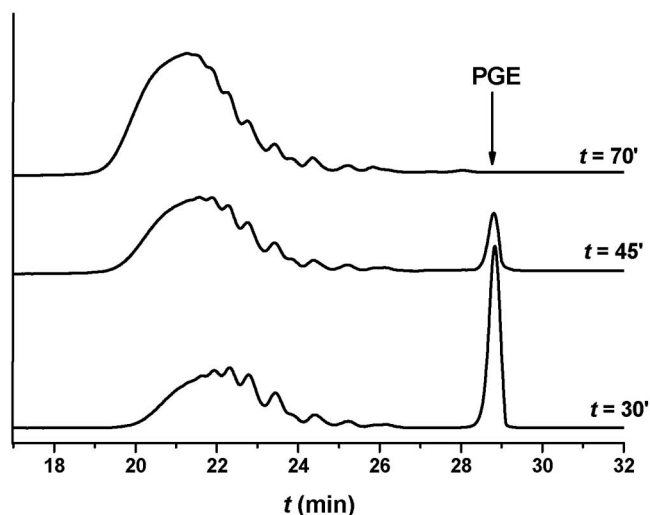


FIG. 13. SEC chromatograms showing the distribution of reaction products in the DMAP-initiated polymerization of PGE at 80°C (molar ratio DMAP/PGE = 0.08).

longer primary chains resulting from the DMAP-initiated polymerization that leads to higher crosslink densities.

To confirm the high-crosslink density obtained when using DMAP as initiator, cured samples were characterized by DMA. Figure 16 shows the storage modulus as a function of temperature for the sample obtained with a molar ratio DMAP/epoxy groups = 0.08. The decrease of the storage modulus occurs at about the same temperature as the glass transition temperature recorded by DSC. But, what is remarkable is the relatively high value of the rubbery modulus, $E_R = 106 \text{ MPa}$ at 225°C, when compared with values reported for materials obtained using typical tertiary amines as initiators. For example, using BDMA as initiator in a molar ratio BDMA/epoxy groups = 0.06 led to a network with a $T_g = 100^\circ\text{C}$ and a rubbery modulus, $E_R = 48 \text{ MPa}$ at 160°C [21]. As $E_R \sim \nu(RT)$, where ν is the concentration

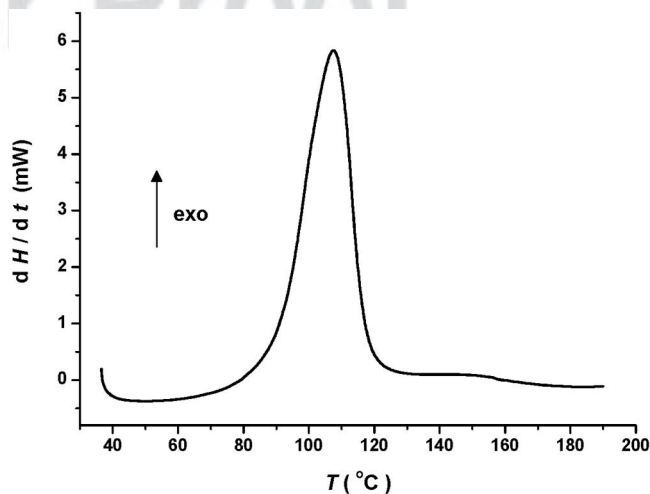


FIG. 14. DSC thermogram of a DGEBA-DMAP solution with a molar ratio DMAP/epoxy groups = 0.08.

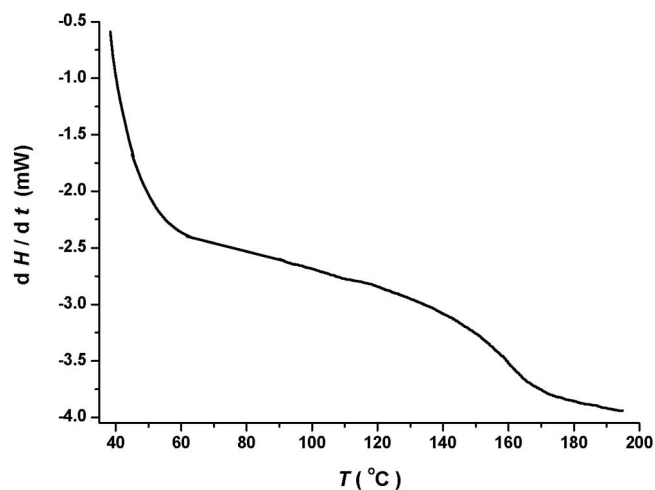


FIG. 15. DSC thermogram obtained in a second scan following the run shown in Fig. 14.

of elastic chains, this means that the use of DMAP as initiator increases the crosslink density by a factor close to 2 with respect to the use of a typical tertiary amine as initiator.

Reaction heats for DGEBA polymerized using different DMAP/epoxy molar ratios were determined by DSC, while glass transition temperatures of resulting products were determined using the prolonged cure cycle described in the Experimental section to give enough time for a complete polymerization in samples containing low amounts of initiator. Values of reaction heats and glass transition temperatures are plotted in Fig. 17 as a function of the DMAP/epoxy molar ratio. The critical amount of initiator necessary to obtain an almost complete conversion is close to 0.08 moles of DMAP per mole of epoxy groups. Lower amounts of DMAP did not allow obtaining complete conversion because of the presence of termination reactions consuming

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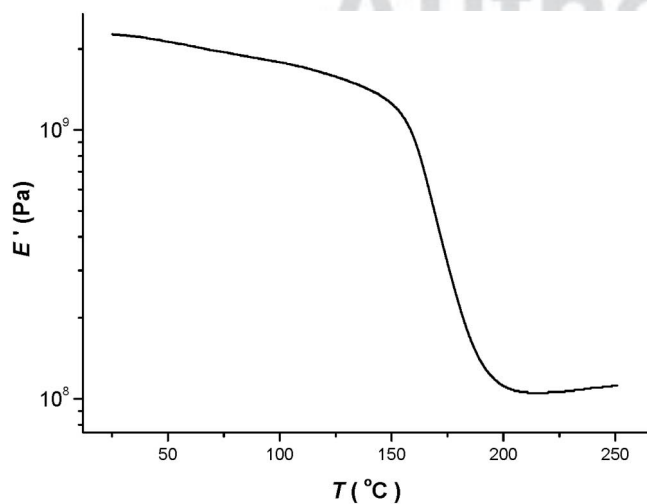


FIG. 16. Storage modulus as a function of temperature for DGEBA polymerized using a molar ratio DMAP/epoxy groups = 0.08.

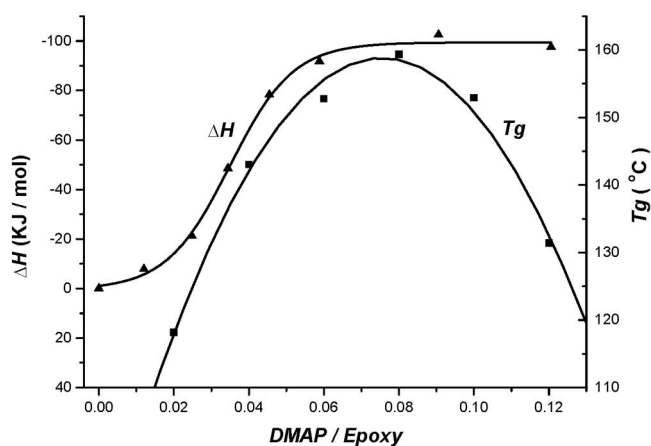


FIG. 17. Reaction heats and glass transition temperatures for DGEBA polymerized using different molar ratios of DMAP/epoxy groups.

the active species. The glass transition temperature presents a definite maximum for formulations prepared with DMAP/epoxy groups = 0.08. The crosslink density decreases both for lower DMAP amounts due to an incomplete reaction, and for higher DMAP amounts due to the generation of shorter primary chains (larger number of active chains competing for the epoxy groups). Therefore, there is an optimum DMAP concentration for the anionic polymerization of DGEBA.

CONCLUSIONS

The efficiency of DMAP as an initiator of the anionic polymerization of epoxy monomers was tested with PGE and DGEBA. In both cases, the polymerization could be carried out at much faster rates than those observed when using typical tertiary amines as initiators. A critical molar ratio DMAP/epoxy groups = 0.08 was necessary to attain complete conversion. This indicates the presence of termination reactions consuming the active species. Performing the polymerization with the critical DMAP/epoxy ratio led to a maximum T_g close to 160°C for polymer networks based on DGEBA. This value of T_g is significantly higher than those obtained with typical tertiary amines. This was ascribed to the higher crosslink density associated with the longer primary polyether chains resulting from the use of DMAP as initiator. SEC analysis of reaction products of the anionic polymerization of PGE initiated either by BDMA or by DMAP confirmed that the latter produced longer chains. The intense brown color of reaction products, associated with an absorption band with a maximum at 360 nm, was ascribed to the presence of initiator fragments with conjugated double bonds in chain ends.

In summary, DMAP is an excellent initiator for the anionic polymerization of epoxy groups provided it is used in a critical molar ratio DMAP/epoxy groups = 0.08 (for DGEBA-based epoxy monomers), and that the dark coloration of reaction products is acceptable for the intended applications.

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