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Kinetic Model for Gelation in the Diepoxide−Cyclic Anhydride Copolymerization Initiated by Tertiary Amines

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ABSTRACT: The best models available in the literature to analyze gelation in the diepoxide−cyclic anhydride copolymerization are based on the mean-field approach. A kinetic model was developed to account for the nonrandom steps of the copolymerization. Two kinetic schemes were employed with one including chain transfer steps. Predicted gel-point conversions as a function of the initiator concentration were compared with experimental results obtained for a system based on diglycidyl ether of bisphenol A, methyltetrahydrophthalic anhydride, and benzyldimethylamine, as initiator. Both kinetic schemes explained the observed first-order kinetics for monomer consumption, after an induction period. However, experimental gel-point conversions could only be fitted by assuming the presence of a chain transfer step regenerating an active species.

Introduction

A large number of studies have been devoted to different aspects of the copolymerization of epoxides with cyclic anhydrides initiated by tertiary amines.[1] The reaction proceeds through a chainwise polymerization comprising initiation, propagation, and termination or chain transfer steps. Some of the postulated reactions are shown in Figure 1.[2−12]

Initiation involves the reaction of the tertiary amine with an epoxy group giving rise to a zwitterion that contains a quaternary nitrogen atom and an alkoxide anion (1 in Figure 1a). The alkoxide reacts at a very fast rate with an anhydride group leading to a species containing a carboxylate anion as the active center (2 in Figure 1a). This species may be considered as the initiator of the chainwise copolymerization, either as such or reorganized to give 2′ (Figure 1a), as suggested by Fedtke and Domaratius.[6] In this regard, Steinmann[8] reported the presence of <1.5−3% unsaturation with respect to monomer concentration in the curing of epoxy resins with hexahydrophthalic anhydride. However, the presence of double bonds in the reaction medium could not be detected by other authors.[3] Propagation occurs through the reaction of the carboxylate anion with an epoxide to give an alkoxide anion as the active center. This, in turn, reacts at a very fast rate with an anhydride group regenerating the carboxylate anion (Figure 1b). The presence of alkoxide anions could not be detected by NMR, a fact that was explained by their fast reaction with anhydrides.[3,5] Propagation results then in an alternating chainwise copolymerization of epoxide and anhydride groups. But due to the fact that the addition of an epoxide to the growing chain is followed almost instantaneously by an anhydride addition, for modeling purposes the reaction may be regarded as the homopolymerization of a pseudocomponent (M) consisting of one epoxide and one anhydride group. In the case of the copolymerization of a diepoxide with a cyclic anhydride, the reaction may be considered as the chainwise homopolymerization of a hypothetical M_2 species.

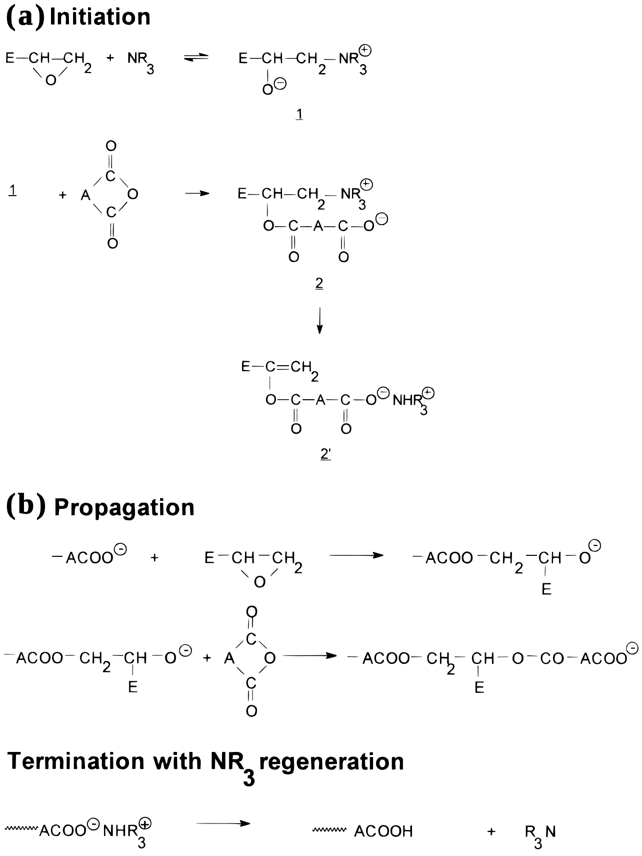

Figure 1. (a) Initiation and (b) propagation and chain termination steps in the anhydride−epoxide copolymerization initiated by tertiary amines.

The presence of termination and chain transfer steps has been suggested in the literature[1,6,8] to account for the fact that molecular weights are lower than those expected for an ideal living polymerization. A possible mechanism involving the regeneration of the tertiary amine is shown in Figure 1b. The regenerated tertiary amine becomes available to initiate a new chain.

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A simplified reaction model that includes the significant steps present in the chainwise polymerization is the following:

$$\mathrm{I} + \mathrm{M} \xrightarrow{k_i} \mathrm{I{-}M} \tag{1}$$

$$\mathrm{I{-}M}_{n-1} + \mathrm{M} \xrightarrow{k_p} \mathrm{I{-}M}_n \tag{2}$$

$$\mathrm{I{-}M}_n \xrightarrow{k_t} \mathrm{P}_n + \mathrm{I} \tag{3}$$

where M is an epoxide−anhydride group combination, I is the tertiary amine, I−M is the initiator species, and P_n is a "dead" primary chain.

When $k_i = k_p$ and $k_t = 0$, an ideal living polymerization results with a Poisson distribution of primary chains. Experimental measurements of molecular weight distributions reported for the linear polymerization of monoepoxides with cyclic anhydrides are controversial. While Matejka et al.[3,4] and Timm et al.[13,14] found narrow molecular weight distributions, several other authors[6−12] reported a relatively wide distribution of chain sizes. For example, for the bulk polymerization of hexahydrophthalic anhydride (HHPA) with phenylglycidyl ether (PGE) in the presence of benzyldimethylamine (BDMA), reported polydispersities were between 1.37 and 1.45.[8] When BDMA was replaced by 1-methylimidazole (1-MI), the range varied from 1.36 to 2.52.[8] When phthalic anhydride (PA) was polymerized in bulk with PGE in the presence of BDMA, reported polydispersities ranged from 1.22 to 1.72.[9] Replacing BDMA with 1-MI increased the polydispersity to the range comprised between 2.37 and 2.75.[9] Although high polydispersity values may be the consequence of low values of k_i/k_p,[10] termination steps have been reported even when thoroughly purified starting materials were used and extreme care was taken to avoid water.[9]

Gelation for these systems was first analyzed by Tanaka et al.[15−18] However, they incorrectly considered the reaction as a random step polyaddition of tetrafunctional (diepoxide) and bifunctional (cyclic anhydride) monomers. Dusek et al.[2] noted this fact and reanalyzed gelation assuming a living chainwise polymerization, i.e., excluding possible termination or chain transfer steps, but the use of cascade substitution instead of a kinetic method was only a rough approximation in this case.[5]

A similar approach was recently presented by Khanna and Chanda.[19] They used the statistical structural model developed by Riccardi and Williams,[20] in which the network is built up from structural fragments larger than monomer units. The fragment distribution was obtained by solving a finite number of differential equations based on chemical kinetics (initiation and propagation steps in a living polymerization scheme). Fragments were combined randomly using a Monte Carlo technique, and statistical parameters including gel-point conversions were predicted. However, as stated by these authors,[19] the procedure is not rigorous because the random combination of fragments does not lead to the true distribution of polymeric species which is determined by the polymerization kinetics.

Our aim is to develop a kinetic model to predict the gel-point conversion in these systems. Analysis of the buildup of the polymer network will be based on a two-stage procedure. In one of the stages, the kinetic equations are solved to account for the nonrandom steps, i.e., the distribution of primary chains produced by the alternating copolymerization of epoxy groups and cyclic anhydrides. In another stage, statistical techniques are employed to account for random combinations of the distribution of primary chains. To perform the calculations it was necessary to develop a kinetic scheme fitting experimental results. The analysis led to two possible kinetic schemes. The first one was based on eqs 1 and 2, i.e., a living chainwise polymerization. The second kinetic scheme included eq 3 with the active species regenerated. The analysis of gelation provided insight to decide which of the schemes better decribed the formation of the polymer network.

There is an antecedent in the literature of a kinetic method used to describe the molecular weight distribution in the pregel stage for a particular diepoxide−anhydride copolymerization.[12] However, in order to account for the experimental observed polydispersity, an exponential distribution of molecules containing different numbers of chains in the structure was arbitrarily assumed at some initial extent of the reaction. This was used to fit the evolution of the weight-average molecular weight as a function of conversion for a particular system, but it cannot be used as a general procedure to predict gelation in a diepoxide−cyclic anhydride system.

Experimental Section

Materials. The diepoxide was based on diglycidyl ether of bisphenol A (DGEBA; MY790, Ciba-Geigy), with a weight per epoxy group, WPE = 173.8 g, as determined by acid titration and dried under vacuum at 80 °C before use. The cyclic anhydride was methyltetrahydrophthalic anhydride (MTHPA; HY918, Ciba-Geigy). It was mixed with the diepoxide in a ratio of anhydride groups/epoxy groups = 1.1, i.e., using a 10% excess of anhydride over the stoichiometric formulation. This is the same ratio used by other authors[7,10] to prevent epoxy homopolymerization that occurs in formulations containing an epoxy excess.[21] The initiator was benzyldimethylamine (BDMA; Sigma). It was used in a molar ratio with respect to epoxy groups (i_o/e_o), ranging from about 0.01 to 0.10.

Calorimetry. A differential scanning calorimeter (Shimadzu DSC-50) was used to carry out the polymerization in the isothermal mode, under nitrogen, in the temperature range between 80 and 180 °C and to determine the residual heat of reaction in samples prereacted in an oil bath kept at constant temperature (in the 80−120 °C range).

Conversion (x) was defined as the ratio of the partial reaction heat over the maximum reaction heat obtained for a fully reacted sample:

$$x = (\Delta H)/(\Delta H)_{\max} \tag{4}$$

Conversion was also calculated from the residual reaction heat, $(\Delta H)_{\mathrm{res}}$, as:

$$x = 1 - (\Delta H)_{\mathrm{res}}/(\Delta H)_{\max} \tag{5}$$

Gelation. A set of tubes containing about 100 mg of sample each was placed in an oil bath at 80 °C. Tubes were extracted from the bath at different times and chilled in ice to stop the reaction. Gelation was determined from solubility tests in tetrahydrofuran (THF). The corresponding gel-point conversion was determined from the measurement of the residual reaction heat by DSC and using eq 5.

Results and Discussion

Kinetics. The polymerization kinetics were studied for formulations containing a constant initiator concentration, $i_o/e_o = 0.04$. Isothermal DSC runs were carried out at temperatures between 80 and 180 °C. Addition-

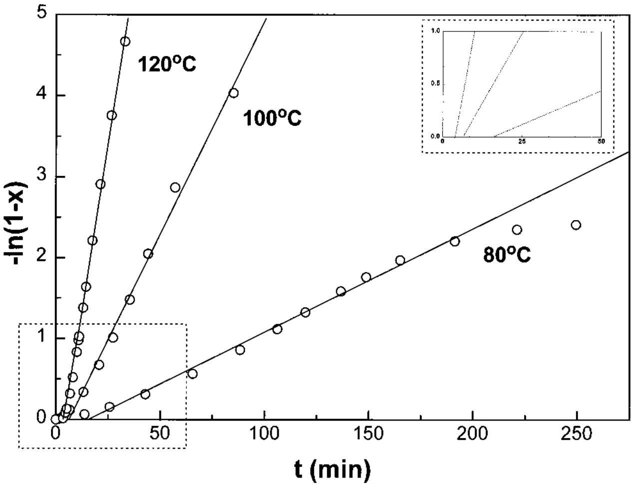

Figure 2. Regression of isothermal DSC runs with first-order kinetics.

ally, conversion vs time curves were obtained by measuring the residual reaction heat of samples prereacted in an oil bath at constant temperature (in the 80−120 °C range). An excellent first-order regression was obtained for both types of experimental approaches. As an example, Figure 2 shows the regression of isothermal DSC runs for three different temperatures. After an induction period (amplified in the right upper corner of Figure 2), first-order kinetics are observed. At 80 °C, deviation from the straight line at high conversions is the consequence of vitrification ($T_g > 80$ °C at $t > 200$ min).

Figure 3 shows an Arrhenius plot leading to an activation energy, $E = 69.3$ kJ/mol. Results obtained using both experimental methods are practically coincident. A similar observation was reported by Fava[22] for a DGEBA−HHPA formulation initiated by 2,4,6-tris[(dimethylamino)methyl]phenol. First-order kinetics are also typical of uncatalyzed epoxy−anhydride systems.[7]

Kinetic results may be analyzed in the frame of the simple kinetic model given by eqs 1−3. It may be assumed that during the induction period a constant concentration of active species is reached, i.e. $(\mathrm{i}-\mathrm{m}) = Ki_o$ (eventually $K = 1$, meaning that all the initiator is converted into active species), so that after this period, the monomer consumption is given by:

$$\mathrm{d}m/\mathrm{d}t = -k_p m \sum (i - m_n) \tag{6}$$

However, in order to fit the experimental first-order kinetic behavior, it is necessary to assume that the concentration of active species remains constant, after the induction period. This may be accomplished by assuming that a living polymerization is taking place ($k_t = 0$) or by replacing the termination step (eq 3) by an equation leading to the regeneration of an active species (instead of the tertiary amine). A possible termination step is the following one:

$$\mathrm{I{-}M}_n \xrightarrow{k_t} \mathrm{P}_{n-1} + \mathrm{I{-}M}, \text{ for } n = 2, 3, ... \tag{7}$$

Then, as $\sum(i - m_n) = Ki_o$ for both possibilities, the rate equation after the induction period follows a first-order kinetic equation:

$$\mathrm{d}m/\mathrm{d}t = -k_p K i_o m \tag{8}$$

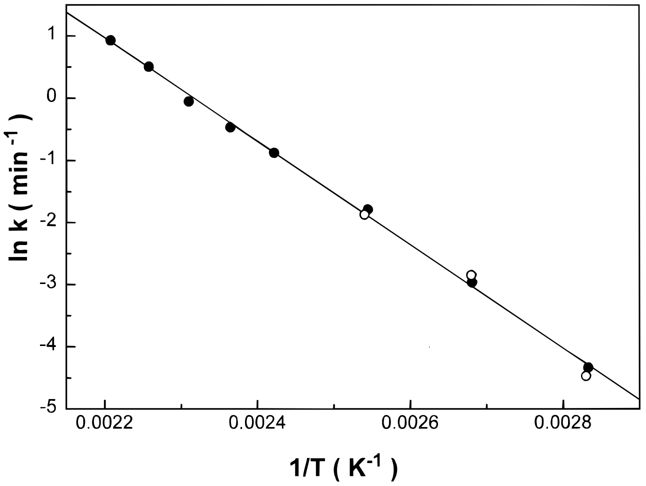

Figure 3. Arrhenius plot (specific rate constants obtained by (●) DSC in the isothermal mode and (○) the residual reaction heat vs time).

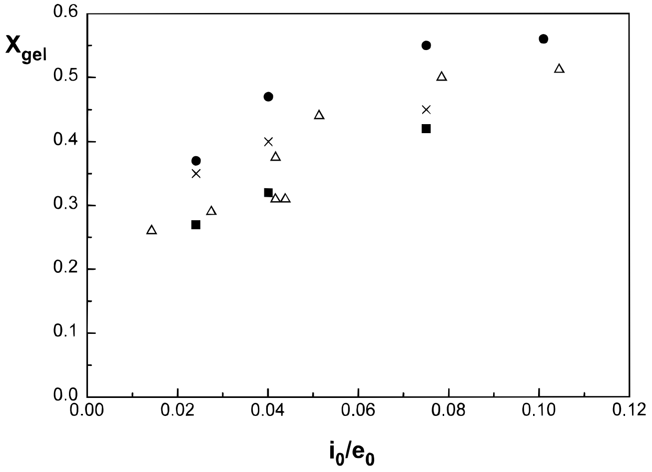

Figure 4. Gel-point conversions as a function of the initial molar ratio of initiator (BDMA) to epoxy groups, for DGEBA−cyclic anhydride systems: (△) MTHPA, 80 °C, bulk, this work; (●) HHPA, 80 °C, bulk, ref 2; (×) HHPA, 110 °C, 50% xylene, ref 2; (■) HHPA, 110 °C, bulk, ref 2.

The activation energy is the result of the dependence of the product k_pK on temperature.

Gelation. Figure 4 shows experimental values of the gel-point conversion as a function of the initiator concentration, expressed in mol of initiator/mol of epoxy groups, i_o/e_o. Values obtained in this work lie in the same range as those reported by Dusek et al.[2] using a different cyclic anhydride (HHPA instead of THPA). A similar trend is observed, i.e., the gel-point conversion increases with the initiator concentration, a fact which is typical of chainwise polymerizations.

As discussed in the Introduction, the epoxide−anhydride copolymerization may be simulated by the homopolymerization of a hypothetical M_2 species (each M is the combination of one anhydride group and one epoxy group). The gel-point conversion for a chainwise homopolymerization of an f-functional monomer when the $(f/2)$ polymerizable groups are equally reactive and react independently, and no intramolecular reactions occur in finite species, may be obtained from the following equation derived by Stockmayer:[23]

$$x_{\mathrm{gel}} = 2/[(f-2)(P_w - 1)] \tag{9}$$

where P_w is the mass-average degree of polymerization of primary chains.

In our case, $f = 4$ (i.e., the diepoxide has two polymerizable groups), so:

$$x_{gel} = 1/(P_w - 1) \quad (10)$$

Alternative derivations of eq 10 were performed by Dusek and Somvársky[24] and by Macosko and Miller.[25] In fact, eq 10 constitutes one of the stages of the kinetic method, i.e., the expression for the gel-point conversion has its origin in the use of statistical techniques accounting for random combinations of primary chains. It is now necessary to calculate P_w from a kinetic scheme (the other stage of the kinetic method).

First, the case of a living chainwise polymerization will be considered, i.e., the reaction will be represented by eqs 1 and 2, and it will be assumed that chain transfer does not take place. The system is described by the following kinetic equations:

$$di/dt = -k_i m i \quad (11)$$

$$d(i-m)/dt = k_i m i - k_p m(i-m) \quad (12)$$

$$d(i-m_n)/dt = k_p m[(i-m_{n-1}) - (i-m_n)], \quad \text{for } n = 2, 3, ... \quad (13)$$

At $t = 0$, $m = e_o$, $i = i_o$, and $(i-m_n) = 0$ ($n = 1, 2, ...$).

P_w arises from:

$$P_w = \sum n^2(i-m_n) \Big/ \sum n(i-m_n) \quad (14)$$

The general solution of the kinetic equations was obtained by Gold[26,27] and by Dusek and Somvársky.[24] Two particular cases of interest are (i) $k_i = k_p$ (Poisson distribution). Replacing in eq 12 gives:

$$x_{gel} = (i_o/e_o)^{1/2} \quad (15)$$

(ii) $k_i/k_p \rightarrow \infty$ (instantaneous initiation):

$$x_{gel} = [(i_o/e_o) + (i_o/e_o)^2]^{1/2} \quad (16)$$

The solution of the general case is given by:[24]

$$x_{gel} = (i_o/e_o)(k_p/k_i)[\ln(i_o/i) + (k_i/k_p - 1)(1 - i/i_o)] \quad (17)$$

with

$$\ln^2(i/i_o) - 2(k_i/k_p - 1)[\ln(i/i_o) + 1 - (i/i_o)] = (k_i/k_p)^2(e_o/i_o) \quad (18)$$

Figure 5 shows a comparison of theoretical predictions for $k_i/k_p = 0.1$, 1, and ∞, with our experimental values. Clearly, the living polymerization model does not fit the experimental behavior. Different explanations may be invoked to account for this difference.

First, it has been stated that a small amount of free acid present in the system has to be included in the calculations thus increasing the effective amount of initiator.[2,5] This will produce a horizontal shift of experimental points to the right, eventually providing a good fit with the theoretical prediction. However, taking into account that the model assumes that all the tertiary amine may be activated, it is not possible to increase the concentration of the active species further (the tertiary amine acts as a coinitiator of the free acid). Therefore, this does not seem to be a good argument for the observed difference between theoretical predictions and the experimental behavior.

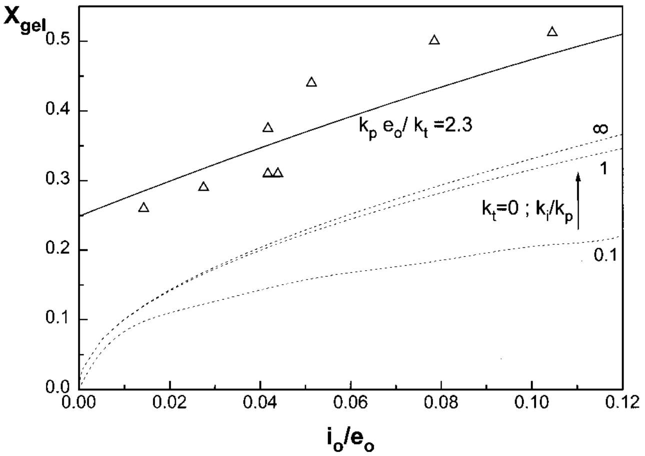

Figure 5. Comparison of experimental values of gel-point conversions with predicted values for (a) living chainwise polymerization (dashed curves are plotted for different values of the ratio k_i/k_p) and (b) kinetic model including chain termination with regeneration of the active species ($k_p e_o/k_t = 2.3$).

A second argument is to question the assumptions involved in the derivation of Stockmayer's criterion for gelation (eq 10). Of these, the fact that both epoxy groups of a DGEBA molecule react independently of one another (i.e., equal reactivities and no substitution effects) has to be accepted by the experimental evidence arising from its reaction with diamines.[5] However, the occurrence of intramolecular cyclization cannot be discarded a priori. Experimental evidence of the presence of intramolecular cyclization arises from studies of gelation in solution. Diluting the system with a solvent will increase the amount of intramolecular cycles and shift gelation to higher conversions. From experimental data plotted in Figure 4, a slight increase in x_{gel} is observed when the reaction is performed in a 50% xylene solution. However, when these data were replotted as a function of the reciprocal of the monomer concentration,[28] intercepts at infinite concentration gave x_{gel} values much higher than theoretical predictions arising from the living polymerization model. Although there are insufficient data to draw strong conclusions, these results indicate that intramolecular cyclization may not be invoked as the only reason to explain the departure of experimental gel-point conversions from theoretical predictions. The presence of a significant amount of intramolecular cyclization may lead to the formation of microgels at an early stage of the polymerization, as in the case of free-radical polymerizations.[29] Some indirect evidence of their presence was reported by Antoon and Koenig,[30] using ^{13}C-NMR measurements on a DGEBA−NMA (nadic methyl anhydride)−BDMA system. A smooth decrease in the intensity for all carbons in the system was observed, implying that the polyester segments generated were not well solvated.

On the other hand, a strong argument to explain experimental gel-point conversions is to assume that chain termination with simultaneous regeneration of active species takes place in the system (eq 7). This effect will increase the concentration of primary chains in agreement with experimental observations for linear polymers.[13,14] For illustration purposes, it will be assumed that after the induction period at constant temperature, the concentration of active species equals the initial amount of tertiary amine. Then, the kinetic model after the induction period is described by the following set of differential equations:

$$d(i-m)/dt = -k_p m(i-m) + k_t \sum_{n=2} (i-m_n) \quad (19)$$

$$d(i-m_n)/dt = k_p m[(i-m_{n-1}) - (i-m_n)] - k_t(i-m_n), \text{ for } n = 2, 3, ... \quad (20)$$

$$d(p_n)/dt = k_t(i-m_{n+1}), \text{ for } n = 1, 2, ... \quad (21)$$

$$dm/dt = -k_p i_o m \quad (22)$$

At $t = 0$ (time counted after the induction period in the isothermal polymerization), $(i-m) = i_o$, $m/m_o = 1 - i_o/e_o$, and $p_n = (i-m_2) = (i-m_3) = ... = 0$.

The concentration of chains (living and dead) of length n is given by:

$$c_n = p_n + (i-m_n) \quad (23)$$

The mass-average degree of polymerization of primary chains arises from:

$$P_w = \sum n^2 c_n / \sum n c_n \quad (24)$$

The evolution of the concentration of primary chains was obtained from the numerical solution of the set of eqs 19−22, fixing the value of the dimensionless parameters: i_o/e_o and $k_p e_o/k_t$. Gelation was defined as the particular conversion at which P_w calculated from eq 24 was the same as the one arising from eq 10 (gel-point condition).

Figure 5 shows a reasonable fitting for $k_p e_o/k_t = 2.3$. This means that the presence of chain termination with simultaneous regeneration of the active species provides a reasonable explanation of the experimental gelation results. Moreover, as the gel condition depends on the concentration of epoxy groups (e_o) present in the dimensionless group ($k_p e_o/k_t$), dilution with a solvent will shift the gelation curve upward in qualitative agreement with experimental results plotted in Figure 4. This dependence follows from the consideration of propagation as a second-order reaction and termination as a first-order one. To improve the description it should be necessary to determine (a)the fraction of tertiary amine that is effectively activated after the induction period at constant temperature, (b) the exact description of the termination step, and (c) the role played by intramolecular cyclization.

Conclusions

A statistical kinetic model was developed to analyze gelation in the chainwise copolymerization of diepoxides with cyclic anhydrides, relaxing the mean-field approximation present in the best studies available in the literature. Two different kinetic schemes were used as follows: (a) an alternating chainwise copolymerization without chain transfer steps, i.e., a living polymerization, and (b) an alternating chainwise copolymerization including a chain transfer step regenerating the active species. Both schemes explained the observed first-order kinetic behavior for monomer consumption, after an induction period. They were both employed to fit an experimental curve of gel-point conversions as a function of the initiator concentration. While scheme a failed, scheme b could fit the experimental results. Therefore, this study provides evidence for the presence of chain transfer steps in this complex copolymerization. However, the exact role played by intramolecular cyclization has yet to be more fully elucidated.

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