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Molecular-mass distributions resulting from the homopolymerization of monoepoxides initiated by tertiary amines

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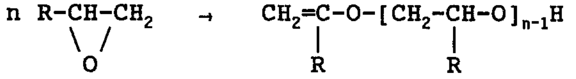
Summary

A reaction scheme based on propagation and intramolecular chain transfer steps is proposed for the anionic homopolymerization of epoxides initiated by tertiary amines. Chain transfer regenerates a living chain and gives a dead chain with terminal vinilydene unsaturations and hydroxy groups. The possibility of generating phenols or substituted phenols is also considered. Molecular-mass distributions were predicted as a function of conversion by both kinetic and Monte Carlo methods. Predictions were compared with experimental results reported in the literature. The evolution of the number-average degree of polymerization could be reasonably predicted.

Introduction

The anionic homopolymerization of monopoxides initiated by tertiary amines may be described by the following overall reaction (1,2):

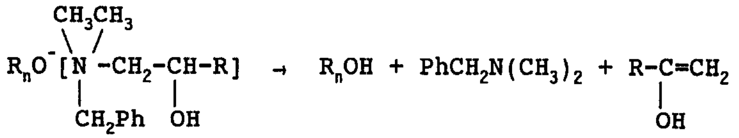


$$n\ \underset{\diagdown\ O\ \diagup}{R\text{-}CH\text{-}CH_2} \rightarrow CH_2\text{=}\underset{R}{C}\text{-}O\text{-}[CH_2\text{-}\underset{R}{CH}\text{-}O]_{n-1}H$$

(1)

The reaction mechanism shows a distinct living character, but the high rate of chain transfer leads to a distribution of oligomeric species (3-6). Average n values are in the range of 2-5 (3,5).

The mechanism leading to the presence of one terminal hydroxy group and one terminal vinylidene unsaturation per molecule, is still a controversial matter. Rozenberg (3) assumes the presence of a β-elimination reaction (hydrogen abstraction by the growing alkoxy anion from the counterion). For example, when using benzyldimethylamine (BDMA) as initiator, the proposed chain transfer reaction may be written as (3):



$$R_nO^-[\overset{CH_3CH_3}{\underset{CH_2Ph}{N}}\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}R] \rightarrow R_nOH + PhCH_2N(CH_3)_2 + R\text{-}\underset{OH}{C}\text{=}CH_2$$

(2)

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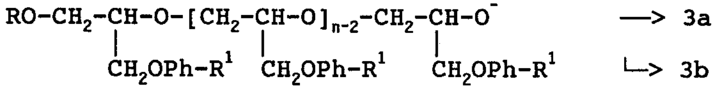
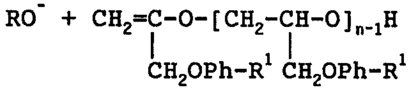
Although a tautomerization reaction of the vinyl alcohol to form a ketone could be expected, the high activity of the enol can explain its rapid transformation into an unsaturated alkoxide, with a corresponding shift in the tautomerization equilibrium (3). The polymerization initiated by the vinyl alkoxide leads to chains containing terminal vinylidene unsaturations and hydroxy groups.

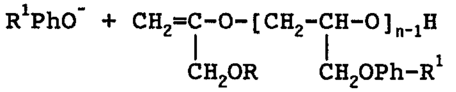
We recently suggested that an intramolecular chain transfer could also explain the resulting structures (7,8).



$$RO\text{-}CH_2\text{-}\underset{CH_2OPh\text{-}R^1}{\underset{|}{CH}}\text{-}O\text{-}[CH_2\text{-}\underset{CH_2OPh\text{-}R^1}{\underset{|}{CH}}\text{-}O]_{n-2}\text{-}CH_2\text{-}\underset{CH_2OPh\text{-}R^1}{\underset{|}{CH}}\text{-}O^- \quad \longrightarrow 3a,\ \hookrightarrow 3b$$



$$RO^- + CH_2{=}\underset{CH_2OPh\text{-}R^1}{\underset{|}{C}}\text{-}O\text{-}[CH_2\text{-}\underset{CH_2OPh\text{-}R^1}{\underset{|}{CH}}\text{-}O]_{n-1}H \tag{3a}$$



$$R^1PhO^- + CH_2{=}\underset{CH_2OR}{\underset{|}{C}}\text{-}O\text{-}[CH_2\text{-}\underset{CH_2OPh\text{-}R^1}{\underset{|}{CH}}\text{-}O]_{n-1}H \tag{3b}$$

Step (3b) explains the presence of phenol (or a substituted phenol) in the reaction mixture particularly when operating at high temperatures (5,6). Due to the high flexibility of polyether chains, both steps (3a) and (3b) may involve hydrogen abstraction from any of the CH groups present in the (n-2) repeating units, although with different probabilities as will be discussed in what follows. The regenerated initiator may be thus an oligomeric species.

In this paper a reaction scheme based on step (3a), will be stated and numerically solved using both kinetic and Monte Carlo methods. A fitting with experimental results for the evolution of the number-average degree of polymerization as a function of conversion (5), will be shown.

Reaction Model

The model is stated from the time at which the initiator concentration may be considered constant, i.e. after the induction period (3,7). From this time on, only propagation and chain transfer steps are considered. It is assumed that eq.(3a) describes the most significant chain transfer step. The reaction of chain transfer to alcohol and proton-donor compounds is not taken into account in the analysis.

The following reactions may be written:

$$I+M \xrightarrow{k_p} I\text{-}M \tag{4}$$

$$I\text{-}M+M \xrightarrow{k_p} I\text{-}M_2 \tag{5}$$

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$$I\text{-}M_n + M \xrightarrow{k_p} I\text{-}M_{n+1} \tag{6}$$

For n≥2,

$$I\text{-}M_n \xrightarrow{k_t.f(j)} I\text{-}M_{n-j} + P_j \quad (n \geq j \geq 2) \tag{7}$$

Step (6) is the generic propagation step of the anionic polymerization. Step (7) represents the generic intramolecular chain transfer step (eq. 3a), leading to a P_j ($j \geq 2$) dead chain. It is assumed that the intramolecular hydrogen abstraction requires that the O^- anion approaches a CH group of the oligomeric chain. P_1 cannot be produced due to steric reasons; P_2 is produced with the maximum probability and, in general, the probability of obtaining a P_j decreases with $(j-1)^{3/2}$. This arises from a comparison of the formation of larger cycles, i.e. involving i times the units necessary to build up the smallest cycle (i=2,3,...). Its probability decreases as $i^{3/2}$, as discussed by Stepto (9). Therefore, the chain transfer rate is fixed as proportional to k_t $(j-1)^{-3/2}$.

Kinetic Method

The following kinetic reactions arise from the reaction model:

$$-d[M]/dt = k_p[M]\left\{[I]+\sum_{n=1}^{\infty}[I\text{-}M_n]\right\} = k_p[M][I_o] \tag{8}$$

$$-d[I]/dt = k_p[M][I]-k_t\sum_{n=2}^{\infty}(n-1)^{-3/2}[I\text{-}M_n] \tag{9}$$

$$d[I\text{-}M]/dt = k_p[M]\left([I]-[I\text{-}M]\right)+k_t\sum_{n=3}^{\infty}(n-2)^{-3/2}[I\text{-}M_n] \tag{10}$$

$$n \geq 2;\ d[I\text{-}M_n]/dt = k_p[M]\left([I\text{-}M_{n-1}]-[I\text{-}M_n]\right) + k_t\sum_{j=n+2}^{\infty}(j-n-1)^{-3/2}[I\text{-}M_j] - k_t[I\text{-}M_n]\sum_{j=1}^{n-1}(n-j)^{-3/2} \tag{11}$$

$$n \geq 2;\ d[P_n]/dt = k_t(n-1)^{-3/2}\sum_{j=n}^{\infty}[I\text{-}M_j] \tag{12}$$

The assumption of a constant concentration of initiator leads to a first order kinetic equation for the monomer consumption (eq.8). This was the observed behaviour for the homopolymerization of a diepoxide based on diglycidyl ether of bisphenol A initiated with BDMA (7).

Equation (8) was solved analytically and the set of eqs.(9) to (12) was solved numerically using a Runge-Kutta 4th order method and truncating the set of species at I-M_{100} and P_{100}. The solution depends on two dimensionless parameters: $[I_0]/[M_0]$ and $k_t/(kp[M_0])$.

The number-average and weight-average degrees of polymerization, based on dead species, were defined as

$$\overline{DP}_n = \sum_{n=2}^{\infty} n[P_n] \ / \ \sum_{n=2}^{\infty}[P_n] \qquad (13)$$

$$\overline{DP}_w = \sum_{n=2}^{\infty} n^2[P_n] \ / \ \sum_{n=2}^{\infty} n[P_n] \qquad (14)$$

Monte Carlo Method

The reaction scheme, eqs (4) to (7), was also solved numerically with the Monte Carlo approach. The simulation was started with the desired ratio $[I_0]/[M_0]$, and the different events that a living chain (including the pure initiator) could undergo, were computed through the corresponding probabilities, i.e. $k_t(j-1)^{-3/2}/(k_p[M_0])$. Every run was repeated 50 times to obtain a narrow dispersion of results.

Results and Discussion

Berger and Lohse (5) reported experimental results of $\overline{DP}_n$ as a function of conversion for the homopolymerization of p-cresyl glycidyl ether initiated by benzyldimethylamine. Figure 1 shows a comparison with theoretical predictions of results obtained at 80°C and different BDMA concentrations (from 2 to 8 mol %). Both the kinetic and Monte Carlo simulations gave the same results shown by the full curve. A good agreement is observed for $[I_0]/[M_0] = 0.02$ and $k_t/(k_p[M_0]) = 0.035$. At high conversions, the simulation predicts a decrease of $\overline{DP}_n$. This arises from the fact that when the monomer is present at low concentrations, the cutting of chains prevails over their growth. Rozenberg (3) presented experimental results for the dependence of $\overline{DP}_n$ on conversion for the homopolymerization of phenyl glycidyl ether initiated by BDMA. He showed a decrease in the number average molecular weight from 785, at a conversion equal to 0.76 to 750 at full conversion. Then, the model seems to be able to reproduce experimental trends.

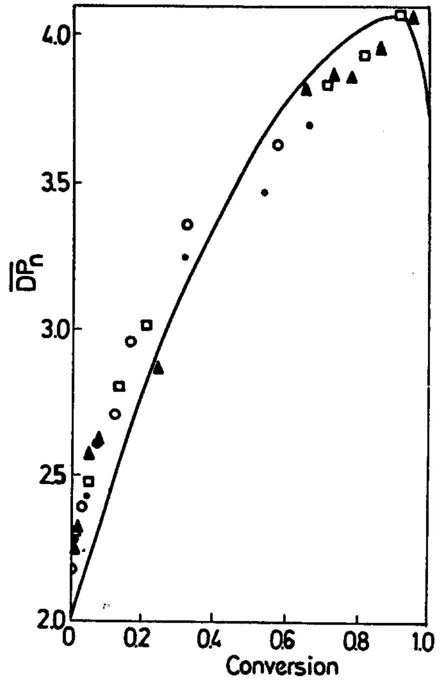

Fig.1 Comparison of theoretical simulation (full curve) with experimental results of $\overline{DP}_n$ vs conversion for the polymerization of p-cresyl glycidyl ether at 80°C initiated by BDMA at various concentrations (in mol %): (○)2; (●)4; (■)6; (□)8. Fitting parameters were $[I_0]/[M_0] = 0.02$ and $k_t/(k_p[M_0]) = 0.035$.

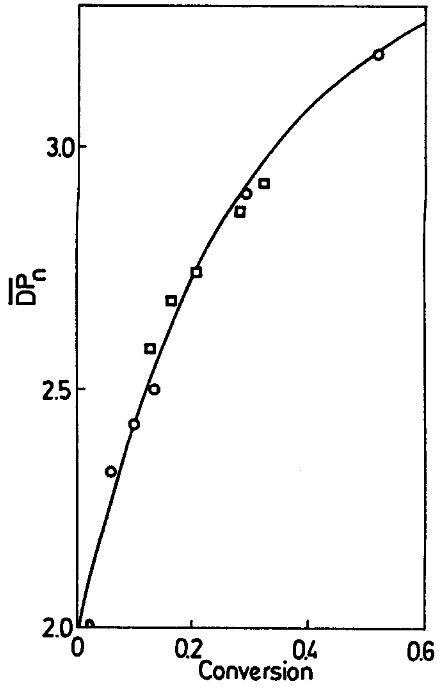

Fig.2 Comparison of theoretical simulations (full curve) with experimental results of $\overline{DP}_n$ vs conversion for the polymerization of p-cresyl glycidyl ether initiated by 2 mol % BDMA, at 100°C (○) and 150°C (□). Fitting parameters were $[I_0]/[M_0] = 0.02$ and $k_t/(k_p[M_0]) = 0.085$.

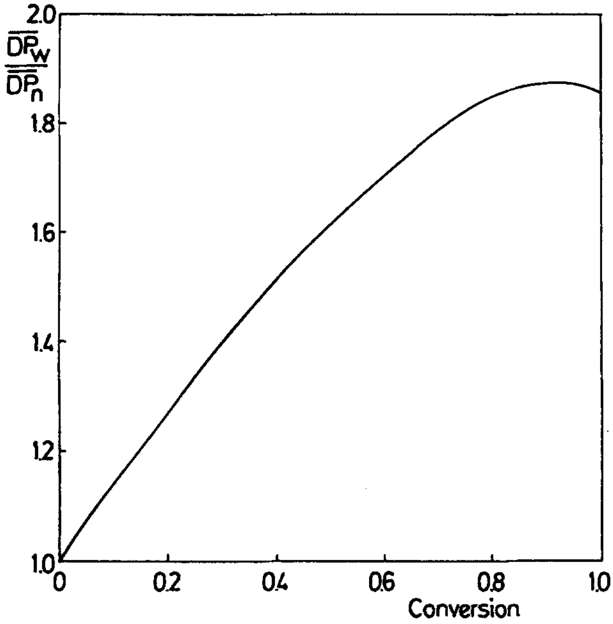

Fig.3 Polydispersity index as a function of conversion arising from the model for $[I_0]/[M_0]=0.02$ and $k_t/(k_p[M_0])=0.035$

Figure 2 show the fitting of the model to experimental results arising from polymerizations carried out at 100°C and 150°C (5). $\overline{DP}_n$ values were lower than those for the previous case (80°C), but no difference was found between values obtained at 100°C and 150°C. The polymerization kinetic showed a very small temperature dependence in this range (5,7). The fitting was now obtained by keeping the same value of $[I_0]/[M_0]$ but increasing $k_t/(k_p[M_0]$ to 0.085, i.e. increasing temperature leads to an increase in the relative rate of chain transfer.

Figure 3 shows the polydispersity index, $\overline{DP}_w/\overline{DP}_n$, as a function of conversion, arising from the model for $[I_0]/[M_0]$ = 0.02 and $k_t/(k_p[M_0])$ = 0.035. The polydispersity increases during almost all the polymerization period, goes through a small maximum and reaches a value of 1.85 at full conversion. According to Rozenberg (3), the homopolymerization of epoxides initiated by tertiary amines leads to a very narrow molecular-mass distribution, with polydispersity indexes in the range of 1.04 to 1.07 practically not varing with conversion. Our model could only simulate this range of results for very low DP_n values, i.e. in the 2-2.5 range. It was not possible to obtain low polydispersity indexes at $\overline{DP}_n$ values close to 4 or 5, i.e. in the range of values reported by Rozenberg (3). It is indeed very difficult to imagine a mechanism leading to practically monodisperse chains,with 5 monomer units or so, with a size varying very little with conversion in the 0.4-1 range. Even a pure living polymerization (without chain transfer) has a higher polydispersity, i.e. close to $1+1/\overline{DP}_n$. Therefore, it is necessary to obtain reliable experimental information concerning the polydispersity of the oligomeric fraction before attempting to improve the kinetic description.

Conclusions

A kinetic scheme has been proposed to account for most of the experimental trends observed in the homopolymerization of epoxides initiated by tertiary amines. It is based on the presence of an intramolecular chain transfer step that leads to a shorter living chain (including the regeneration of the initiator as a possibility) and a dead chain. This step explain both the chemical structure of the polymer and the possibility of producing phenols or substituted phenols during the polymerization. Theoretical simulations based on the kinetic scheme enabled us to fit experimental results of $\overline{DP}_n$ as a function of conversion reported in the literature (5). However, the model did not predict the low values of polydispersity indexes reported by some authors (3).

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