

Reaction Kinetics in Anionic Copolymerization: A Revisit on Mayo-Lewis Equation^{*}

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Abstract Reactivity ratio is a traditional parameter quantifying the reaction kinetics in copolymerization, which is important for potentially controlling microstructures of polymers and guiding the copolymerization process. Our recent experiments using tube-NMR technique enable us to *in situ* monitor the concentration profiles of the co-monomers during the anionic copolymerization process. This motivates us to revisit the Mayo-Lewis (ML) equation, which is the basis for derivation of reactivity ratio and has been extensively utilized in addition copolymerization. We found that although an explicit ML expression is desirable for ease of calculation and correlation with experimental data, it fails in our anionic copolymerization experiment as well as some data available in the literature. The origin is ascribed to the validity of the steady state assumption which is essential in the ML equation. This assumption can be released in anionic copolymerization and replaced by the fact that the overall concentration of the living chain ends keeps constant throughout the copolymerization. Alternative numerical method has been utilized to obtain the rate constants and consequently the reactivity ratios. Our work suggests that the ML equation should be applied with caution.

Keywords: Anionic copolymerization; Polyether; Reactivity ratio; Mayo-Lewis equation; Steady state assumption.

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INTRODUCTION

In recent years, living copolymerization has attracted a lot of attention^[1–12]. In contrast to the conventional free radical copolymerization in which heterogeneous chain-to-chain composition and uncontrolled microstructure are anticipated, all chains are initiated simultaneously and grow at approximately the same rate in living or pseudo-living copolymerization. This crucial difference from the free radical copolymerization can potentially lead to a sequence-controlled process, which is expected to precede the current state of the art in polymer synthesis and approach the goal of precision in molecular array on single polymer chains^[13, 14]. In our group, we are specifically interested in oxyanionic polymerization, including liquid crystalline polyethers and their copolymers^[15–18]. Herein, we utilized *in situ* NMR technique to monitor the concentration profiles of the co-monomers simultaneously at any point of the anionic copolymerization process^[19–22]. The on-line technique as well as the relatively “clean” polymerization process enable us to investigate the copolymerization kinetics to a higher degree of precision; more important, the knowledge of reactivity of co-monomers is critical to provide guidance for designing and tailoring of the microstructures of polymers.

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In a perfect living anionic polymerization, the initiation step is instantaneous at the beginning of the polymerization. No chain transfer and termination reaction occur. Polymer chains grow with constant number of chains and constant concentration of living reactant. In contrast, in free radical polymerization, initiation, chain growth and termination occur throughout the period of polymerization. The number of the chains keeps increasing with reaction time, accompanying with birth, growth, transfer and termination processes at any time interval. For such a complicated process, it is actually extremely difficult to derive the reaction kinetics of copolymerization analytically. A steady state hypothesis has been commonly adapted to facilitate the study of copolymerization kinetics, as in the well-known Mayo-Lewis (ML) equation^[23]. The ML equation has seemed so successful and applicable for decades. It has been widely treated and transformed into various formalisms with certain approximations in order to correlate experimental data, such as Fineman-Ross^[24], Yezrielev, Brokhina and Roskin^[25], Tosi^[26], Braun, Brendlein and Mott^[27], Joshi and Joshi^[28], Kelen-Tudos and its extension^[29, 30] as well as nonlinear least-squares method through statistical data processing^[31, 32].

In this work, we investigated the copolymers composed of liquid crystalline polyether and poly(butylene oxide) through anionic copolymerization. Taking advantage of tube-NMR on-line technique, we are able to analyze the copolymerization kinetics without assuming the steady-state, which is the key assumption in the ML equation. Starting from the differential kinetic equations of a binary system, we demonstrate the numerical solution to determine the rate constants and consequently the reactivity ratios of the monomers in anionic copolymerization. This approach has been further compared with the general methods based on the ML equation, and the limitations are discussed.

EXPERIMENTAL

Materials

Toluene was stirred with sodium over 24 h and distilled into a high-vacuum flask which was freeze-thawed three times in a vacuum line. Potassium *tert*-butoxide (Acros Organics) in a concentration of 1 mol/L in tetrahydrofuran (THF), 18-crown-6 and dibutylmagnesium (Acros Organics) were used as received. Liquid crystalline monomer EO-Azo was synthesized in our laboratory following the similar procedure as previously described^[15]. Its ¹H-NMR spectrum is shown in the Supporting Information (Fig. S1).

Copolymerization

The monomers for copolymerization are 1,2-butylene oxide (BO) and EO-Azo. The anionic ring-opening polymerization conditions of these monomers have been readily established to obtain well-defined, monodispersed homopolymers^[15]. For the copolymerization, we followed the procedure as described previously^[18]. Briefly, a specially designed NMR-tube reactor was placed in a high-vacuum line and flame-dried three times. EO-Azo monomers (10.2 mg, 26.5 μmol) were added into the tube reactor and degassed at 40 °C. The initiator potassium *tert*-butoxide (~2 μL, 1 mol/L in THF) and a trace amount of 18-crown-6 were then added into the reactor under the nitrogen atmosphere, and freeze-thawed three times. BO monomers were stirred with dibutylmagnesium over 24 h and distilled into the tube reactor. A moderate amount of deuterium toluene was then distilled into the tube and frozen immediately. Finally, the NMR-tube reactor was removed from the vacuum line and flame-sealed. The reactor was warmed to 25 °C immediately before the NMR measurements started.

In situ NMR

¹H-NMR spectra were recorded on a Varian MERCURY spectrometer (400 MHz) using deuterium toluene as the solvent. *In situ* NMR was used to track the process of polymerization reaction. The spectrum was acquired every 10 min or longer. The characteristic resonances of the monomers are well-separated in the spectra. The polymerization time and the period of data collection lasted over 1 day.

RESULTS AND DISCUSSION

Anionic Copolymerization and Its Characterization

A typical series of ^1H -NMR spectra for the copolymerization of EO-Azo monomers and BO monomers are shown in Fig. 1. The well-separated chemical shifts of protons on oxirane group of EO-Azo monomers ($\delta = 2.83\text{--}2.85$) and that of BO monomers ($\delta = 2.49\text{--}2.53$) can be identified, as illustrated in the zoom-in spectra in Fig. 1. They were used to determine the consumption of the monomer EO-Azo and the monomer BO. It shows that the intensities of these monomers decay with time of copolymerization. By following the integrals of the characteristic resonances of these two monomers, the concentration profiles of the monomers with reaction time can be obtained, which will be further utilized to extract the kinetic parameters of the copolymerization.

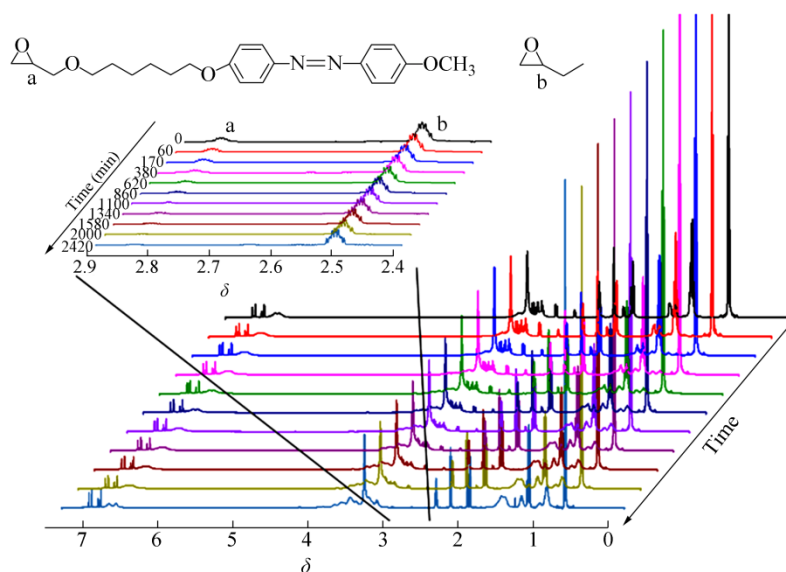


Fig. 1 Real-time ^1H -NMR spectra overlay (the bottom); the zoom-in spectral region (the top) used to determine the consumption of the EO-Azo monomers and the BO monomers

Monomer incorporation has been demonstrated as a function of total conversion as shown in Fig. 2, where M represents the residual monomer concentration, M_0 is the initial monomer concentration, determined from the real-time NMR spectra. This plot illustrates the evolution of monomer feed composition during the copolymerization and reveal the concurrent incorporation of EO-Azo and BO monomers into the growing polymer chain. As seen in the figure, concentration of EO-Azo monomers decreases much more rapidly than that

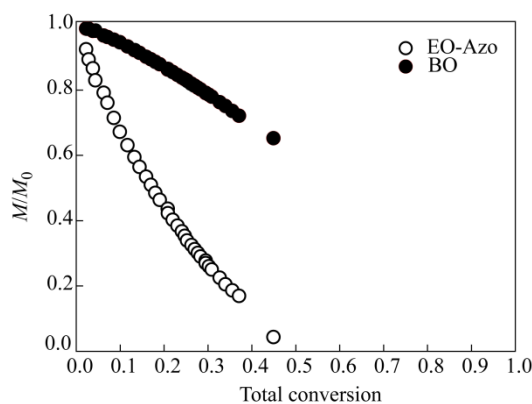


Fig. 2 Percentage of monomer concentration versus total conversion for copolymerization of EO-Azo and BO determined from the real-time ^1H -NMR spectra

of BO monomers in the reaction mixture, indicating that EO-Azo is incorporated considerably faster compared to BO and has a higher reactivity. The rate constants and the reactivity ratios of these two monomers will be derived in the following numerical method.

The exact monomer ratio in the reactant mixture was determined based on the ^1H -NMR spectrum of the mixture prior to the initiation of the polymerization, as shown in the Fig. 3. By comparing the integrals of the proton on oxirane group of monomer EO-Azo (c: $\delta = 2.8$) and monomer BO (d: $\delta = 2.5$), we can get the feed molar ratio of EO-Azo and BO monomers equal to 1:5. As the initial feed weight of EO-Azo monomer is exactly known, the amount of BO monomer is thus obtained. The initial concentrations of EO-Azo and BO are 1.343 mmol/g and 6.714 mmol/g, respectively. The concentration of the initiator potassium *tert*-butoxide or the active reactant was calculated on a basis of the ^1H -NMR spectrum of the final copolymer. In the ^1H -NMR spectrum (the top in Fig. 3), the resonances of *tert*-butyl end group (a: $\delta = 1.1$) and the protons on the benzene rings of Azo group (b: $\delta = 7.9$) can be identified. Since EO-Azo monomers are completely consumed at the end, the concentration of the anionic reactants can be deduced based on this integral ratio (a:b) and the initial amount of EO-Azo monomers.

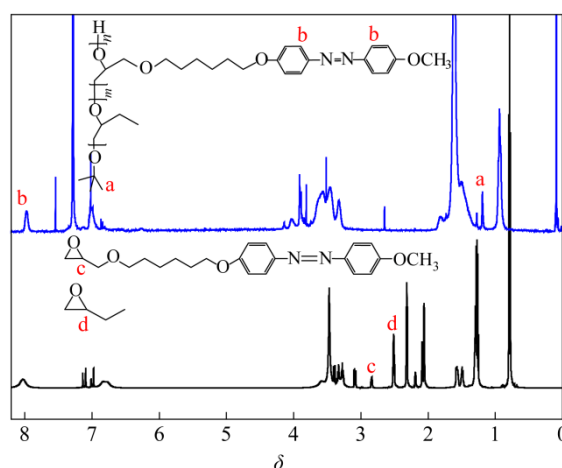
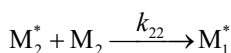
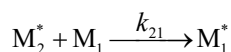
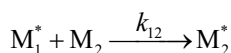
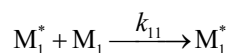


Fig. 3 ^1H -NMR spectra of the initial reactant mixture before reaction in deuterated toluene (the bottom) and the final copolymer in CDCl_3 (the top)

The Numerical Method for Derivation of Copolymerization Kinetics

The copolymerization of two types of monomers M_1 and M_2 involves four chain growth processes on assuming that the reactivity of the reactants depends only on the terminal unit, that is, no penultimate effect:



The rates of the concentration changes of the monomers and active species are coupled in four differential kinetic equations as shown below, under the assumption that the influences of initiation and termination reactions are neglected:

$$\frac{d[M_1]}{dt} = -k_{11}[M_1^*][M_1] - k_{21}[M_2^*][M_1] \quad (1)$$

$$\frac{d[M_2]}{dt} = -k_{12}[M_1^*][M_2] - k_{22}[M_2^*][M_2] \quad (2)$$

$$\frac{d[M_1^*]}{dt} = -k_{12}[M_1^*][M_2] + k_{21}[M_2^*][M_1] \quad (3)$$

$$\frac{d[M_2^*]}{dt} = -k_{21}[M_2^*][M_1] + k_{12}[M_1^*][M_2] \quad (4)$$

where the reactivity ratios are defined as $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$. Once the values of the four reaction rate constants k_{11} , k_{12} , k_{22} , k_{21} are known, the reactivity ratios can be calculated accordingly. For anionic living polymerization, the total concentration of the active reactants is constant, that is, $[M_1^*] + [M_2^*] = \text{constant}$. As such, we use 4th order Runge-Kutta method to derive the solutions of the differential equations^[33]. Firstly, initial values of $[M_1]_{t=0}$, $[M_2]_{t=0}$, $[M_1^*]_{t=0}$, $[M_2^*]_{t=0}$ and the most likely k_{11} , k_{12} , k_{22} , k_{21} are input and the numerically calculated results of $[M_1]$, $[M_2]$, $[M_1^*]$, $[M_2^*]$ are generated. These numerical results are then compared with the experimental data to yield an error. The program checks the error until it is less than that we preset (10^{-2}). If the error is out of the range, the program will use Newton Method and Backtracking Line Search to find the next set of estimations of k_{11} , k_{12} , k_{22} , k_{21} ^[34]. Each time when the program yields a most probable value, this value will be returned back to the differential kinetic equations to verify the valuation case and check whether it fits the experiment data or not. Until the final fitting precision is small enough ($< 10^{-2}$), the numerical results can be considered as the closest values to the real ones. All of these steps are automatically run by the program written by C++ language. In the end, the four reaction rate constants and the concentration changes of the active reactants are obtained, consequently, the reactivity ratios of the monomers can be calculated.

Figure 4 shows the concentration profiles of monomers obtained by real-time NMR measurements and their fits with the kinetic model as mentioned previously. The time-dependent concentrations of the two anionic species are thus derived. The starting conditions were $[EO-Azo]_{(t=0)} = [EO-Azo]_0$, $[BO]_{(t=0)} = [BO]_0$, $[EO-Azo]_{(t=0)} = [EO-Azo]_0$ and $[BO]_{(t=0)} = 0$. $[EO-Azo]_0$ and $[BO]_0$ were treated as fitting parameters, similar to the recent numerical method^[21]. For $[EO-Azo]_0$, the initiator concentration was taken assuming that the initiator behaves as an active EO-Azo end in a simplified scenario. Especially, $[M_{EO-Azo}^-] + [M_{BO}^-] = \text{constant}$ is utilized, which value (0.179 mmol/g) has been obtained according to the NMR results in Fig. 3. The concentration profiles of the monomers fit well with the original experimental data as shown in Fig. 4. The rate constants are shown in Table 1. Based on the rate constants, the reactivity ratios can be calculated as $r_{EO-Azo} = k_{AA}/k_{AB} = 5.88$, $r_{BO} = k_{BB}/k_{BA} = 0.17$. The values of r_{EO-Azo} and $1/r_{BO}$ indicate that addition of EO monomers to the chain ends is 5.88 times faster than that of BO monomers. The value of $r_{EO-Azo} \times r_{BO} \approx 1$ suggests an ideal copolymerization process, which is common in anionic copolymerization.

Table 1. The derived rate constants

Rate constant	Value (g·mmol ⁻¹ ·min ⁻¹)
k_{AA}	1.158×10^{-2}
k_{AB}	1.971×10^{-3}
k_{BA}	5.188×10^{-3}
k_{BB}	8.806×10^{-4}

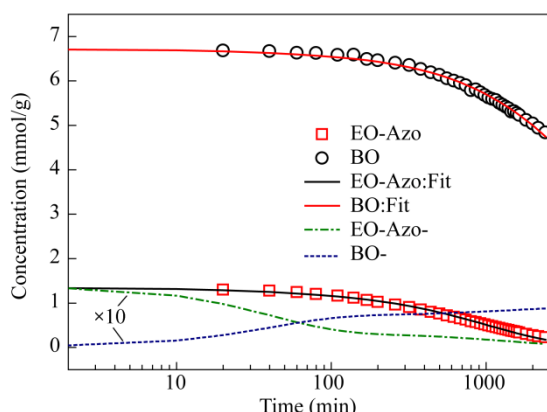


Fig. 4 Time-dependent concentrations of monomers obtained by real-time NMR and their fits with the kinetic model

Empty symbols represent experimental concentrations, the solid lines are the fitting curves. The anionic reactants of [EO-Azo-] and [BO-] derived from the numerical method are multiplied by 10 to make them visible on the same scale.

The Mayo-Lewis Equation and Reaction Kinetics in Anionic Copolymerization

Based on the four copolymerization kinetic Eqs. (1–4), the relative changes of the monomer concentrations at any instant follow the formula:

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]} \quad (5)$$

By making a steady-state assumption, that is, $d[M_1^*]/dt = 0$ and $d[M_2^*]/dt = 0$, then $k_{12}[M_1^*][M_2] = k_{21}[M_2^*][M_1]$ is thus obtained on the basis of Eqs. (3) or (4). Substituting this relationship into Eq. (5), the explicit expression of Mayo-Lewis equation can be finally obtained:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}$$

In a chemical reaction composed of two or more step reactions, analytic solution to the differential kinetic equations can be hardly obtained. The steady-state assumption makes the differential equations algebraic so that they could be mathematically tractable. The steady-state assumption has a long history and was proposed in treating chain reaction polymerization regardless of whether the mechanism is anionic, cationic, radical or organometallic^[23]. Tang has proposed a statistical theory to treat free radical polymerization without applying the steady state assumption^[35]. He derived the molecular distribution functions related to the chemical kinetic equations and obtained the analytic expressions for $\Sigma[M^*]$ under certain conditions, which are the same as those obtained by assuming a constant overall concentration of all radicals generated in the reacting system, however, the molecular distribution functions are rather unsound under the steady state assumption. Although the ML equation is utilized extensively, indeed, evaluation of the validity of the basic steady state assumption still deserves enough attention.

A copolymerization process could be very complicated, for instance, the free radical copolymerization as we mentioned previously. The ML equation and the further treatments can certainly facilitate the study of the copolymerization kinetics, especially when several copolymerization processes at different feeds of the monomers are terminated at low conversions, in that case the copolymer compositions can be deduced with minimal changes of monomer feeds and further incorporated into the ML equation. Considering the complexity of the free radical polymerization process which is involved with initiation, chain growth, chain transfer and termination all the time throughout the period of polymerization, it often lacks direct experimental evidence on

fulfilling the steady state assumption to our knowledge. The conventional argument that the concentration of active reactant $[M^*]$ is much smaller than the concentration of the monomers cannot necessarily result in $d[M^*]/dt = 0$ in logic, as seen in Eqs. (3) or (4). In the ML equation, the net influence of initiation and termination is neglected or assumed to be cancelled each other. Anyhow, constant concentration of each active reactant is assumed. The ML equation is found to work in numerous free radical copolymerization processes, and the derived reactivity ratios seem applicable^[2, 36]. In our opinion, the complicated copolymerization process may happen to make a stationary state to fulfill the steady state hypothesis. Additionally, there exist many uncertainties in experiments, even deficiencies in different analysis methods, which have been already recognized widely^[36].

Judging from the derivation of the ML equation, it seems more applicable to living anionic copolymerization when the initiation only occurs instantaneously at the beginning of the polymerization, and no termination and chain transfer during the chain growth. The “living” nature of the anionic copolymerization implies a constant overall concentration of the active reactants, that is, $d([M_1^-] + [M_2^-])/dt = 0$. However, this doesn't necessarily result in $d[M_1^-]/dt = 0$, $d[M_2^-]/dt = 0$ as adapted in the steady state assumption. In fact, our experiment data depicted in Fig. 4 demonstrate continuous changing of the concentrations of the anionic species as the copolymerization proceeding. This phenomenon has been also observed in other anionic copolymerization systems^[21]. The real-time technique together with the numerical method seem powerful and illustrative since the changes of concentrations of the active reactant can be followed in this “living” system. Four rate constants which cannot be acquired in the traditional methods can be directly derived^[24, 29], and the reactivity ratios of the co-monomers can be obtained consequently. This also encouraged us to apply the ML equation based methods to analyze the data for comparison, as elucidated in the Supporting Information. Unfortunately, the derived results by using F-R method or K-T method cannot give meaningful results, which are in contradiction with the experiments.

This method can be uniquely applied to the living anionic copolymerization with non-termination and a simple initiation process, where the concentration of the active reactants is explicitly known, and the steady state assumption is avoided. We expect the numerical method a promising step forward to acquire deep understanding of the copolymerization kinetics^[21, 37], although the living anionic polymerization process itself might be complicated in many cases^[1, 2]. From the four reaction rate constants, we can have a quantitative knowledge of the monomer reactivity in the process of copolymerization. Besides, the *in situ* experiment combined with the numerical method can follow up the whole copolymerization process and all the data are in real time. Tedious experiments at low conversions with a series of different feed ratios can be excused, which might also lead to erroneous and misleading information^[36]. The numerical method is anticipated to provide a genuine avenue to in-depth study of the reaction kinetics of anionic copolymerization.

CONCLUSIONS

Anionic copolymerization of epoxy monomers has been conducted by employing *in situ* tube-NMR technique, which allows to follow the concentration profiles of the co-monomers during the polymerization process in real time. The unique nature of the living copolymerization enables to obtain the numerical solutions to the differential kinetic equations without steady state assumption. The rate constants of the chain growth and the reactivity ratios of the co-monomers have been derived consequently, which have been further compared with the conventional methods on the basis of Mayo-Lewis equation. The origin of the discrepancy has been discussed and the cautious application with Mayo-Lewis equation has been pointed out.

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SUPPORTING INFORMATION

¹H-NMR spectrum of EO-Azo monomer; F-R and K-T fitting of the experimental data.

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