

Modeling of Living Cationic Ring-Opening Polymerization of Cyclic Ethers: Active Chain End versus Activated Monomer Mechanism

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ABSTRACT: Living cationic ring-opening polymerization of cyclic ethers in the presence of diol was modeled using the method of moments. A widespread kinetic model was developed based on the previous experimental studies. Then, the moment and population balance of reactants were obtained. Modeling results were employed to study the influence of initiator and water amounts (as the impurity) as well as feeding policy in polymerization kinetics and final properties of the polymer. In addition, the sensitivity of modeling results to initiation, backbiting, and finally propagation via activated monomer reactions were investigated. Results showed the population of chains is the function of their precursors. In a typical polymerization, chains with diol functionality are the majority. Therefore, most of the polymerized monomers are incorporated into those chains. This makes the chains with diol functionality the determining group in Molecular Weight Distribution (MWD). The kinetics of polymerization and properties of the reactor's product are highly dependent on the ratio of the rate of propagation via Activated Monomer (AM) mechanism to the rate of propagation via active chain end (ACE). An increase in this ratio decreases the probability of occurrence of backbiting reaction. Therefore, cyclic dimers are less formed and MWD narrows. On the other hand, decreasing this ratio results in less diol reacted with protonated monomers. Consequently, the rate of regeneration of initiator and hence the rate of polymerization is decreased. These findings give complete facts about the ring-opening syntheses of polyethers and are valuable for evolving new grades as well as optimization current processes.

KEYWORDS: Ring-opening; Kinetic model; Cyclic ethers; Molecular weight distribution (MWD); Method of moments.

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1021-9986/2020/5/95-110

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INTRODUCTION

The significant feature in Nano composite preparation is to discover an effective way that warrants the complete exfoliation of silicate layers and, concurrently, offers more control over the polymer molecular features such as molecular weight, functionality, construction, composition and dimension. Controlled and living polymerization methods assist creation of definite polymers, which increase the intermolecular interactions as well as the exfoliation of clay layers in the nanocomposite creation. Newly, different polymerization methods like controlled radical polymerization [1–3], conventional free radical polymerization [4–6], ring-opening polymerization [7–8], living anionic polymerization [9], living cationic polymerization [10], and click reactions [11–13] have been described for the in-situ preparation of polymer/clay nano composites.

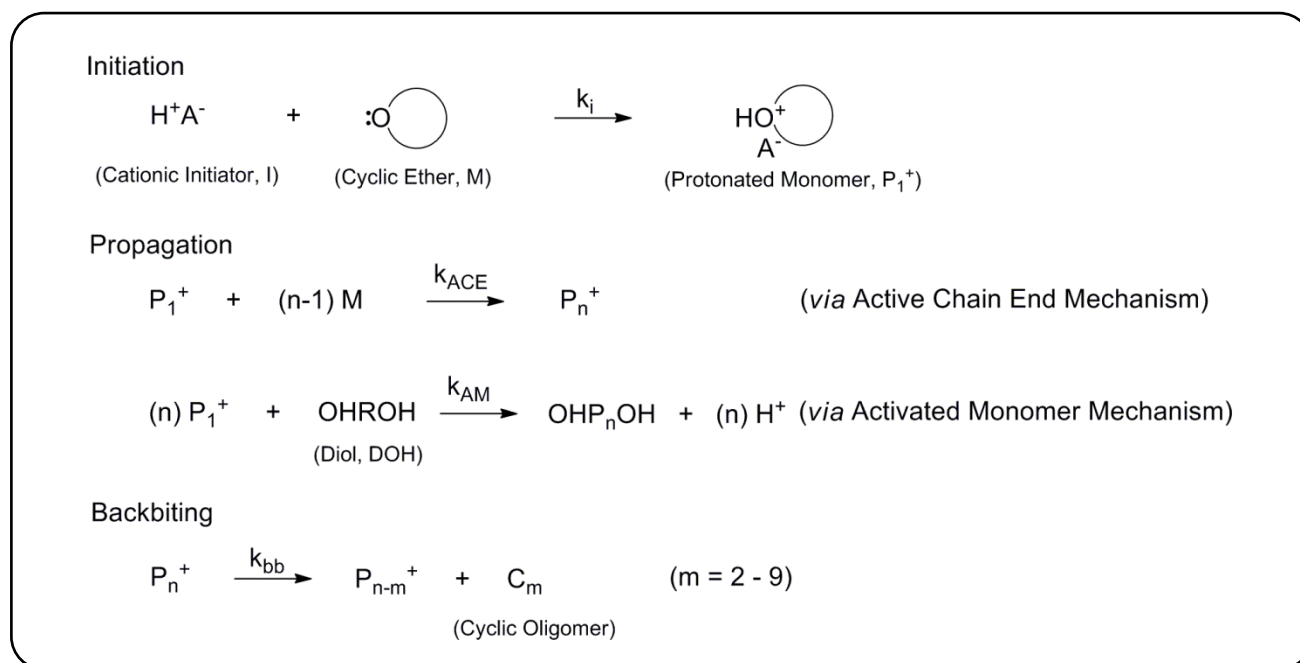
Cationic Ring-Opening Polymerization (CROP) is a facile synthetic route to polyethers. Well-defined linear polymers with narrow Molecular Weight Distribution (MWD) can be obtained if firstly, no termination or transfer of active center would occur; and secondly, cyclization would be minimized during polymerization. This is attainable by using appropriate reactants and removing impurities from reaction mixture. As shown in Scheme 1 in a conventional CROP, the polymerization is initiated by the same type of cationic initiators such as protonic acids, Lewis acids, carbocation and etc. [14]. The initiator reacts with monomer to form secondary Oxonium ion. Then, secondary Oxonium ion reacts with monomer to form tertiary Oxonium ion. This step which is so called propagation via Active Chain End (ACE) is repeated to form linear polymers. In the absence of irreversible chain-breaking reactions, CROP proceeds as living polymerization. However, intramolecular reaction i.e. backbiting which is inevitable in polymerization of cyclic ethers, results in the formation of cyclic oligomers. The formation of cyclic oligomers can be greatly inhibited if a reactant with hydroxyl group is applied. Under this condition, protonated monomers react with alcohol to form polymers with no cationic active center which is not susceptible to backbiting (Scheme 1). This reaction is called propagation *via* activated monomer mechanism (AM).

Both ACE and AM occur in the reaction mixture and compete with each other. A body of researches

has been done focusing on the kinetics of CROP of cyclic ethers when both mechanisms compete with each other [15]. *Penczek et al.* were the first to discuss the reaction of monomer with hydroxyl functionality. They studied Ethylene Oxide (EO) and Epichlorohydrin (ECH) and showed that the use of AM mechanism avoids cyclization and disproportionation of chains [16]. They further investigated the Propylene Oxide (PO) polymerization. It was demonstrated that the slow addition of monomer results in suppressing cyclic oligomers because of domination of reaction of protonated monomer with hydroxyl functionality [17]. Syntheses of telechelic oligomers and macromonomers, applying the AM mechanism with protonated monomers, have been described by *Kubisa* [18]. Their group also obtained propagation rate constant for ECH polymerization [19]. The use of diol in CROP of ECH under monomer starves condition also reported by *Penczek and Coworkers* [20]. Synthesized PECH diols were strictly bifunctional, regular head-to-tail polymers containing mainly ($\geq 95\%$) secondary hydroxyl end groups. The polymerization of other cyclic ethers such as Acrylic Acid [21], Cyclic Ketene Acetals and Vinyl Ethers [22], glycidyl phenyl ether [23, 24], 3-oxetanol [24], curable epoxy compositions [25] and etc., also has been deeply investigated by various researchers.

Despite excellent and clear experimental works on CROP of cyclic ethers, no comprehensive mechanistic study by mathematical modeling has been reported yet. Modeling is a powerful tool for kinetic and mechanistic studies; it gives lots of information which may be hard and costly to obtain by experiment. Moreover, results of modeling can be used for determination of kinetic coefficients as well as optimum operating condition. It is also very helpful for designing new polymeric materials and novel polymerization processes [26]. These advantages have attracted many researchers in recent decades.

According to the above paragraph, we aim to study the CROP of cyclic ethers in the presence of a diol in a semi-batch process by mathematical modeling. Method of moments has been used to investigate the effect of different reaction factors on the kinetics, profile concentration of various reaction species, characteristics of polymer product and more importantly conditions which make AM as a dominant pathway of propagation.



Scheme 1: Mechanism of living CROP of cyclic ethers in the presence of diol [27].

In addition, sensitivity of modeling results to the kinetic coefficients has been analyzed. To the best of our knowledge this is the first report of modeling of living CROP of cyclic ethers in the presence of difunctional alcohol.

THEORITICAL SECTION

Model development

In this work, method of moments [28] has been applied to model the polymerization system. By utilizing this method, the number of differential equations is reduced considerably, but only average molecular weights can be obtained. Model has been developed based on kinetic scheme which is presented in Scheme 1. Since our goal is to model living CROP [27] therefore no termination of active center was considered in mechanism. Also, some initiating systems consist of initiator and co-initiator. These two components react with each other to form initiator-co-initiator complex which may reacts with monomer to form protonated monomer [29]. In our modeling, for simplicity only the formation of protonated monomer has been considered as initiation reaction step.

Another assumption that has been made in modeling is that only the formation of cyclic dimer has been included. According to the literature, variety of cyclic oligomers from dimer thorough nonamer can be formed in polymerization of cyclic ethers [30]. For a certain type of

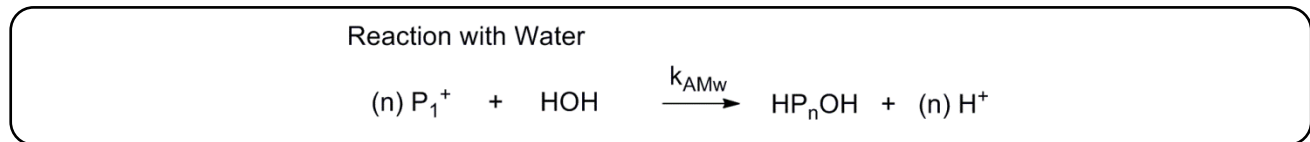
monomer, however, a specific cyclic oligomer is dominant. For example, 1,4-dioxane is the major cyclic product in polymerization of ethylene oxide [30]. In the polymerization of epichlorohydrin only cyclic dimers are formed due to the backbiting [31]. The cyclic tetramer is the most abundant cyclic oligomer in the polymerization of Oxetane [30]. As a consequence our model has been limited to the formation of cyclic dimers. This is due to fact that, when method of moments has been applied, no chain length distribution of species is obtainable. Moreover, knowing the concentration of cyclic products is of greater importance than average chain length of them. Therefore, it is pretty rational to include one type of cyclic oligomer (dimer in this paper) as the representative of cyclic products in the modeling.

It has been reported that hydroxyl group of water is capable of participating in reaction with protonated monomer. As a result, if it presents at the reaction mixture as an impurity, it directly affects the MWD and final polymer properties. Therefore, the reaction of water has been included in the kinetic scheme as shown in Scheme 2. It is gratifying to note that the effect of other impurities with hydroxyl functionality on the kinetics is analogous to water.

Definition of various chain moments and the population balance equations for different species in the reactor

Table 1: Moments Definition.

Type of Chains	Definition of Moments
Polymer with Cationic Active Center	$\lambda_i = \sum_{n=1} n^i V [P_n^+]$
Polymer with diol functionality	$\mu_i = \sum_{n=1} n^i V [OHP_nOH]$
Polymer derived from reaction of protonated monomer with water	$\delta_i = \sum_{n=1} n^i V [HP_nOH]$



Scheme 2: Reaction of protonated monomer with water as an impurity in the reaction mixture.

are presented in Table 1 and Table 2, respectively. As can be seen in Table 2, the rate of reactions of diols or polymers with diol functionality is multiplied by a factor of 2 due to the fact that each of those molecules contains two hydroxyl groups.

It should be noted that the volume changes during polymerization due to the feeding of monomer into the reactor. As a consequence, for any type of reactant the population balance can be formulated as follows:

$$\frac{dn_i}{dt} = \frac{\dot{m}_i}{M_{w,i}} + R_i V \quad (1)$$

Where n_i , \dot{m}_i , $M_{w,i}$, and R_i , are the mole, mass flow rate, molecular weight and rate of reaction of reactant "i". V is the reaction volume. In this system, only monomer enters the reactor and mass flow rate for other species is zero.

Change in volume due to the feeding of monomer is:

$$\frac{dV}{dt} = \frac{\dot{m}_m}{\rho_m} \quad (2)$$

Where ρ_m is the density of monomer. The monomer conversion can be calculated via the following equation:

$$P = \frac{n_{MP}}{n_{Mt}} \quad (3)$$

n_{MP} is the total mole of polymerized monomers which is obtained by integrating of below equation from time zero to desired time, t :

$$\frac{dn_{MP}}{dt} = k_i \frac{n_I n_M}{V} + k_{ACE} \frac{n_M \lambda_0}{V} \quad (4)$$

n_{Mt} is the total amount of monomer which is the sum of initial moles of monomer which are presented in the reactor, n_{M0} , and overall moles of monomer which are fed to the reactor, n_{Mf} .

Regarding moment equations, properties of reactor product can be obtained via following equations:

$$\bar{X}_n = \frac{\lambda_1 + \mu_1 + \delta_1 + 2n_{c_2}}{\lambda_0 + \mu_0 + \delta_0 + n_{c_2}} \quad (5)$$

(Number-average degree of polymerization)

$$\bar{X}_w = \frac{\lambda_2 + \mu_2 + \delta_2 + 4n_{c_2}}{\lambda_1 + \mu_1 + \delta_1 + 2n_{c_2}} \quad (6)$$

(Weight-average degree of polymerization)

$$PDI = \frac{\bar{X}_w}{\bar{X}_n} \quad (5)$$

(Polydispersity index)

$$\bar{f}_n = \frac{\lambda_0 + 2\mu_0 + \delta_0}{\lambda_0 + \mu_0 + \delta_0 + n_{c_2}} \quad (6)$$

(Number-average hydroxyl functionality)

A difficulty in modeling of the CROP process is the lack of reliable kinetic parameters. The literature data are often very scattered even for the initiation and propagation rate constants of the best known systems. In this work, we use the set of typical parameters for simulation purposes (Table 3). By knowing kinetic rate constants, set of differential equations (Table 2 and Equations (2) and (4)) can be solved via a commercial ODE solver (ode15s or ode23tb in MATLAB R2009a).

Table 2: Population Balance Equations.

	Type of Reactant	Population Balance Equations
Small Molecules	Initiator	$\frac{dn_I}{dt} = -k_i \frac{n_I n_M}{V} + \frac{n_{P_i^+}}{V} (2k_{AM} (n_{DOH} + \mu_0) + k_{AMw} (n_{H_2O} + \delta_0))$
	Diol	$\frac{dn_{DOH}}{dt} = -2k_{AM} \frac{n_{P_i^+} n_{DOH}}{V}$
	Monomer	$\frac{dn_M}{dt} = -k_i \frac{n_I n_M}{V} - k_{ACE} \frac{n_M \lambda_0}{V} + \frac{\dot{m}_M}{M_{w,M}}$
	Water	$\frac{dn_{H_2O}}{dt} = -k_{AMw} \frac{n_{P_i^+} n_{H_2O}}{V}$
	Protonated Monomer	$\frac{dn_{P_i^+}}{dt} = k_i \frac{n_I n_M}{V} - k_{ACE} \frac{n_M n_{P_i^+}}{V} - \frac{n_{P_i^+}}{V} (2k_{AM} (n_{DOH} + \mu_0) + k_{AMw} (n_{H_2O} + \delta_0))$
	Cyclic Dimer	$\frac{dn_{C_2}}{dt} = k_{bb} \lambda_0$
		$A = k_i \frac{n_I n_M}{V} - \frac{n_{P_i^+}}{V} (2k_{AM} (n_{DOH} + \mu_0) + k_{AMw} (n_{H_2O} + \delta_0))$
		$B = 2k_{AM} \frac{n_{P_i^+} n_{DOH}}{V}$
	$C = k_{AMw} \frac{n_{P_i^+} n_{H_2O}}{V}$	
Macro Species	Moments of Polymers with Cationic Active Center	$\frac{d\lambda_0}{dt} = A$
		$\frac{d\lambda_1}{dt} = A + k_{ACE} \frac{n_M \lambda_0}{V} - 2k_{bb} \lambda_0$
		$\frac{d\lambda_2}{dt} = A + k_{ACE} \frac{n_M (2\lambda_1 + \lambda_0)}{V} - 4k_{bb} (\lambda_1 - \lambda_0)$
	Moments of Polymers with diol functionality	$\frac{d\mu_0}{dt} = B$
		$\frac{d\mu_1}{dt} = B + 2k_{AM} \frac{n_{P_i^+}}{V} \mu_0$
		$\frac{d\mu_2}{dt} = B + 2k_{AM} \frac{n_{P_i^+}}{V} (2\mu_1 + \mu_0)$
	Moments of Polymers derived from reaction of protonated monomer with water	$\frac{d\delta_0}{dt} = C$
		$\frac{d\delta_1}{dt} = C + k_{AMw} \frac{n_{P_i^+}}{V} \delta_0$
		$\frac{d\delta_2}{dt} = C + k_{AMw} \frac{n_{P_i^+}}{V} (2\delta_1 + \delta_0)$

Table 3. Kinetic parameters used in modeling of CROP of Cyclic Ethers in the presence of Diol (Reaction time is 90 min).

Parameter	Value	Dimension
k_i	5	L/mol.s
k_{ACE}	10^{-3}	L/mol.s
k_{AM}	0.5	L/mol.s
k_{AMw}	0.5	L/mol.s
k_{bb}	10^{-4}	1/s
n_{Mf}	2.5	mol
Feeding Time, t_f	1800	s
\dot{m}	$n_{Mf} \times M_{w,M} / t_f$	g/s
n_{M0}	0	mol
n_{I0}	3.2×10^{-3}	mol
n_{DOH0}	0.08	mol
n_{S0}	0.6	mol
n_{H_2O0}	2.5×10^{-2}	mol
V_0	53	mL
$M_{w,M}$	100	g/mol
ρ_M	1200	g/L

RESULTS AND DISCUSSION

Moments and molecular weights of different types of chains

Fig. 1 (A–C) shows the development of the zero, first, and second moments during the CROP polymerization in the presence of a diol. The zeroth moments shown in Fig. 1(A) are moles of macro species. The value of zeroth moments directly is defined by their precursors. Macroocations are derived from initiator molecules while polymers with di and mono hydroxyl functionality are derived from diol and water, respectively. Therefore, at any time of polymerization a correlation between moles of chains and their precursors can be made as follows:

$$\lambda_0 = n_{I0} - n_I \quad (7)$$

$$\mu_0 = n_{DOH0} - n_{DOH} \quad (8)$$

$$\delta_0 = n_{H_2O0} - n_{H_2O} \quad (9)$$

Fig. 1(B) shows the incorporation of monomeric units into chains. It is obvious that most of monomers are consumed in reaction of propagation via AM mechanism. Out of 2.5 moles of monomer, total number of polymerized monomers for chains with diol functionality is 2.152

at the end of the reaction, while this value is 0.34 and 8×10^{-3} for chains with mono hydroxyl functionality and chains with cationic active center, respectively. The same trend is observable for development of second moments as shown in Fig. 1(C).

Evolution of X_n and PDI with time is shown in Fig. 2. There are three types of chain in this system: chains with cationic active center, chains with diol functionality, and chains which derived from reaction of water. Chains with diol functionality have the greatest values of X_n . This is due to the fact that most of monomers are incorporated into these chains (Fig. 1(B)). Polymers with active center, however, are very short chains. In addition to the low 1st order moment, the backbiting is another factor that prevents chain growth. X_n is under 5 during polymerization for these chains. Backbiting also broadens MWD and therefore, increases the PDI value (Fig. 2(B)). Fig. 2 proves the advantage of AM over ACE and implies that higher molecular weight polymers with narrower dispersity are obtainable via AM.

Each type of chain has its own MWD and has an impact on overall MWD (Equation (5)-(7)) which is depending

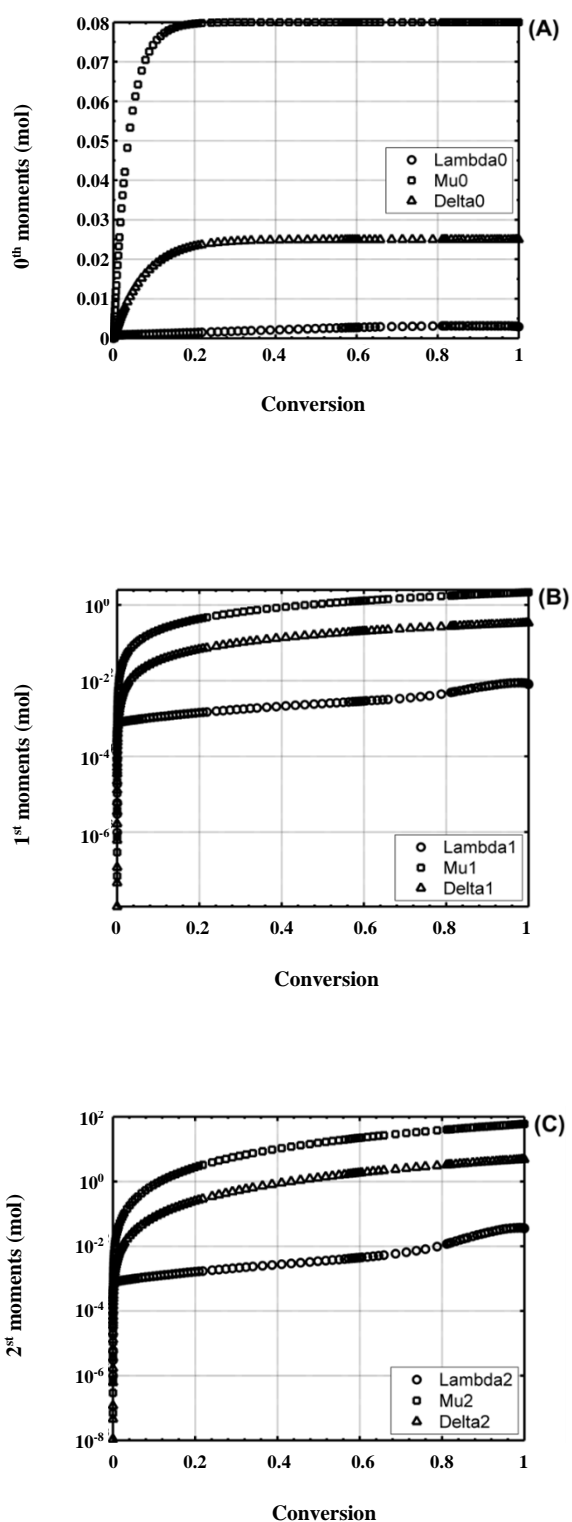


Fig. 1: Development of (A) zeroth, (B) first, and (C) second moments of various types of chains in living CROP.

on its population. As expected, polymers with diol functionality which are in majority (Fig. 1(A)) are the most influential term in the development of overall X_n and PDI. Therefore, the values of overall X_n and PDI are close to polymers with diol functionality as well as their evolution with conversion. It is gratifying to note that the linear increase of X_n and decreasing of PDI with conversion is the typical behavior of living systems.

The population of cyclic dimer is depicted in Fig. 3. In comparison with Fig. 1(A) cyclic dimers constitute less than 2 percent of the product. However this percentage may vary according to the reaction condition.

The influence of reactant amounts on the product

Fig. 4 depicts the effect of initiator on the conversion, X_n , and PDI. Increase in the initial amount of initiator raises the concentration of cationic active centers (Eq. (9)). Therefore, both terms in the equation for rate of monomer consumption (Eq. (4)) increases the system reaches conversion of 1 more rapidly. In Fig. 4 A when the amount of initiator doubles, whole monomers are consumed at feeding time.

The amount of initiator may have no considerable effect on the development of X_n and PDI as shown in Figs 4(B-C). This is due to the fact that in this system the dominant mechanism for chain growth is AM. As a result, a great portion of chains are those derived from diol (Fig. 1A). Greater number of chains increases the probability of incorporation of monomers into them (Fig. 1B). Therefore, moments of polymers with diol functionality is much higher than polymers with cationic active center. Under this circumstance, change of initiator concentration has a little effect on the MWD since it only changes the population of polymers with cationic active center.

The effect of the presence of water as an impurity in the reaction system has been shown in Figs. 5 and 6. Fig 5(A) reveals that by an increase in the amount of water the rate of polymerization increases. This can be explained by considering Scheme 2. When water is introduced to the system, it reacts with protonated monomer via AM mechanism (Scheme 2). Initiator molecules are regenerated by this reaction. As a result, the concentration of initiator increases in the system (Fig 5(B)) which is a key factor in the polymerization rate (Eq. (4)).

Moreover, new type of chains is derived from reaction of activated monomer with water. These chains increase

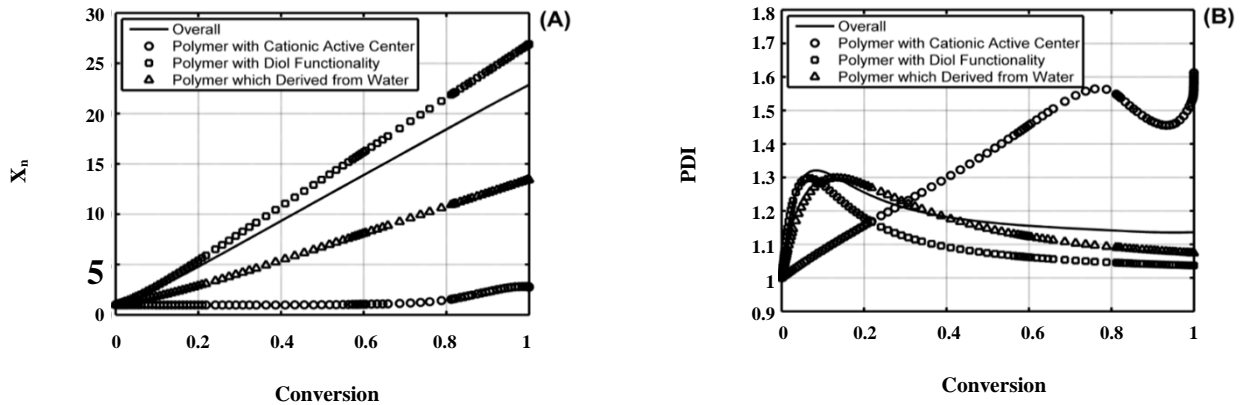


Fig. 2: (A) Number-average degree of polymerization and (B) Polydispersity index for different types of chains (symbols) and overall polymeric product (line).

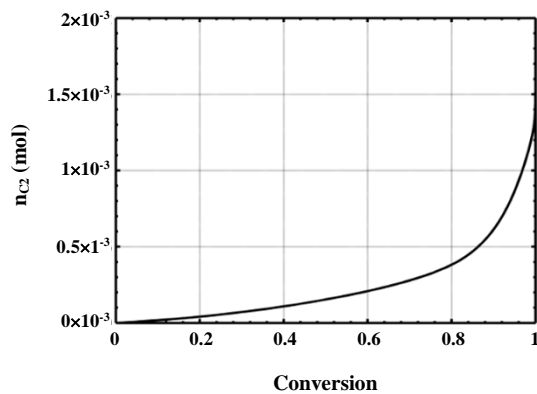


Fig. 3: Population of cyclic dimer.

overall population of polymers, i.e. 0th moment, while the number of polymerized monomers, i.e. 1st moment is raised slightly. As a consequence X_n decreases (Fig. 5(C)). Also, since new chains grow differently from other macro species the PDI increases (Fig. 5(D)). It is noteworthy that in this work the kinetic rate constant for reaction of protonated monomer with water is assumed as equal to the reaction of diol with protonated monomer. The difference between these two kinetic parameters amplifies the broadening of MWD.

The presence of water has a noticeable effect on the average functionality of polymers as shown in Fig. 6. The chains which are derived from water are monofunctional, therefore a raise in amount of water yields a drop in the average functionality. It should be noted that these results can be extended to other monofunctional impurities which are capable of getting involved in AM mechanism.

An effective parameter that is dominant in the determination of the propagation mechanism is the ratio of monomer to Diol. The ACE propagation yields polymers which are susceptible to cyclization. Amount of cyclic oligomers can be suppressed if AM mechanism is the main propagation mechanism. The rate of propagation via ACE and AM mechanisms can be formulated as follows:

$$R_{ACE} = k_{ACE} \frac{n_M \lambda_0}{V^2} \quad (10)$$

$$R_{AM} = 2k_{AM} \frac{n_{P_1^+} (n_{DOH} + \mu_0)}{V^2} \quad (11)$$

The ratio of two propagation mechanisms is:

$$\frac{R_{AM}}{R_{ACE}} = \frac{2k_{AM}}{k_{ACE}} \frac{n_{P_1^+} (n_{DOH} + \mu_0)}{\lambda_0 n_M} \quad (12)$$

Substituting Eq. (10) into Eq. (14) yields:

$$\frac{R_{AM}}{R_{ACE}} = \frac{2k_{AM}}{k_{ACE}} \frac{n_{P_1^+} n_{DOH}}{\lambda_0 n_M} \quad (13)$$

From Eq. (15) it can be concluded that the ratio of AM to ACE is tuned by changing the monomer to diol concentration. However, this may not be applicable when a process runs under a fixed amount of reactants. A simple way to change the concentration during polymerization is the use of feeding policy. In this work, three feeding policies are investigated which shown in Fig. 7. All experiments are identical in formulation but varied in feeding policy.

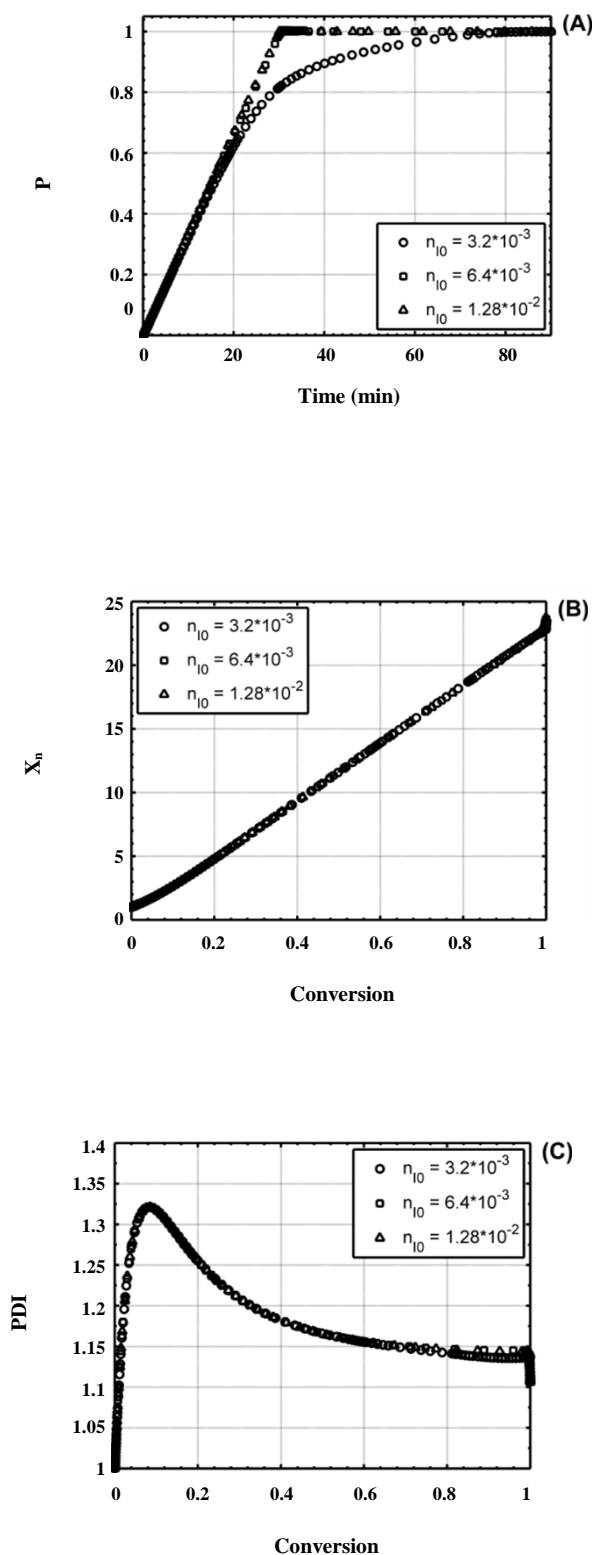


Fig. 4: Effect of the initial amount of initiator on (A) the conversion, (B) X_n , and (C) PDI.

In Fig. 7, results for batch experiment (no feeding monomer) has been shown with circles while results for semi-batch experiments have been shown with squares for one that feeding time is equal to the reaction time and dashed line for one that feeding time is third of reaction time. When the polymerization is carried out in batch mode, all monomers are introduced to the system at the onset of reaction. This increases the probability of reaction of protonated monomer with monomer. As a result, protonated monomers are consumed rapidly and converted to polymers with cationic active center. In Fig. 7(A) it can be seen that applying semi-batch process prolongs the presence of protonated monomer in reaction mixture. Therefore, diol molecules have more opportunity to react with them. As shown in Fig. 7(B) about 25% of diol molecules remain unreacted in batch process. In other words rate of propagation via AM mechanism is suppressed because of rapid consumption of protonated monomers. Drop in rate of propagation via AM yields an overall reduction in the rate of polymerization. That is why the batch experiment has the lowest conversion. It should be noted that rate of propagation via ACE is dependent to the total amount of cations in the system. As a result, it does not change when all protonated monomers converted to macro cations. Fig. 7 (A-C) also reveals that the rate of polymerization is faster when the monomer's mass flow rate is higher. Higher mass flow rate have two consequences: first, rise in the instantaneous monomer concentration and second rise in population of protonated monomers. This increases the rate of propagation via both AM and ACE mechanism and hence overall rate of polymerization.

At any given conversion X_n is higher for batch experiment as depicted in Fig. 7(D). Also, no significant variation is observable when monomer's mass flow rate changes. This is a consequence of reduction in the number of chains (0 th moment) due to the unreacted diols. Average functionality is the only polymer property which is not influenced considerably by variation in feeding policy. According to Eq. (8) the population of polymers is determining in the value of \bar{f}_n . In these experiments only the population of polymers with diol functionality changes because of variation in yield of diols. However as shown in Fig. 7(E) this effect is negligible.

Fig. 7(F) is the graphical presentation of Eq. (15). As expected the ratio of the rate of AM to ACE is less than

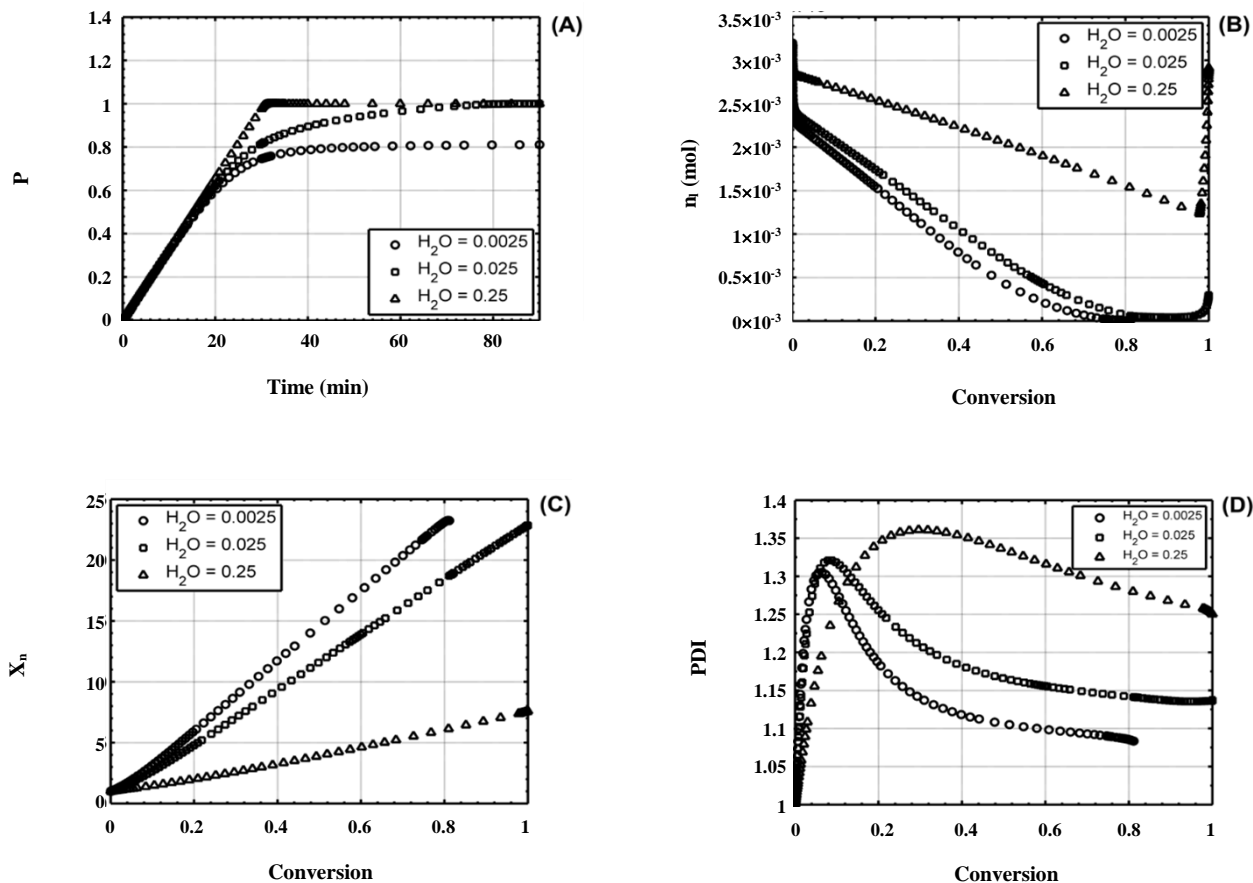


Fig. 5: Effect of the amount of water (in mol) on (A) the conversion, (B) population of initiator (C) X_n , and (D) PDI.

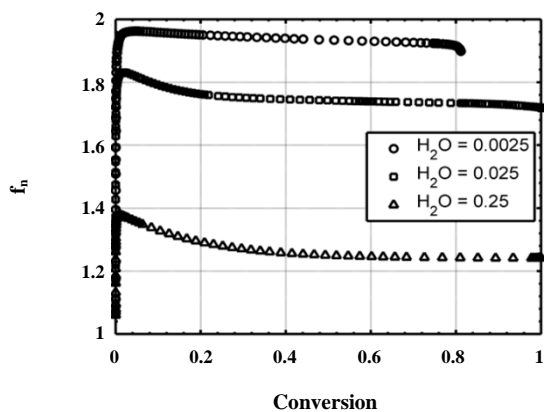


Fig. 6: Effect of the amount of water (in mol) on number-average hydroxyl functionality.

unit when polymerization is carried out under batch condition. Decreasing monomer concentration by reducing its mass flow rate makes AM mechanism as the dominant propagation reaction step. This results in suppression of

undesired cyclic dimers as depicted in Fig. 7(G) which has a considerable effect on the MWD and PDI values (Fig. 7(H)).

Effect of rate constants on the kinetics

The effects of various rate constants on the CROP kinetics were examined. Fig.8 depicts the influence of initiation rate constant on the kinetics. Higher initiation rate constant increases the rate of production of activated monomer (Fig. 8(A)). As a result, rate of propagation via both AM and ACE increases. As it has shown in Fig. 8(B), higher polymerization rate is obtained when the initiation rate constant rises. Change in population of protonated monomer has more effect on the rate of propagation via AM than ACE (Fig. 8(C)). The fraction of cyclic dimer is depicted in Fig. 8(D). An increment in the initiation rate constant reduces the fraction of the cyclic dimers due to the increase in the ratio of the rate of propagation via AM to ACE.

The impact of the backbiting on the polymerization has shown in Fig. 9. According to kinetic scheme (Scheme 2),

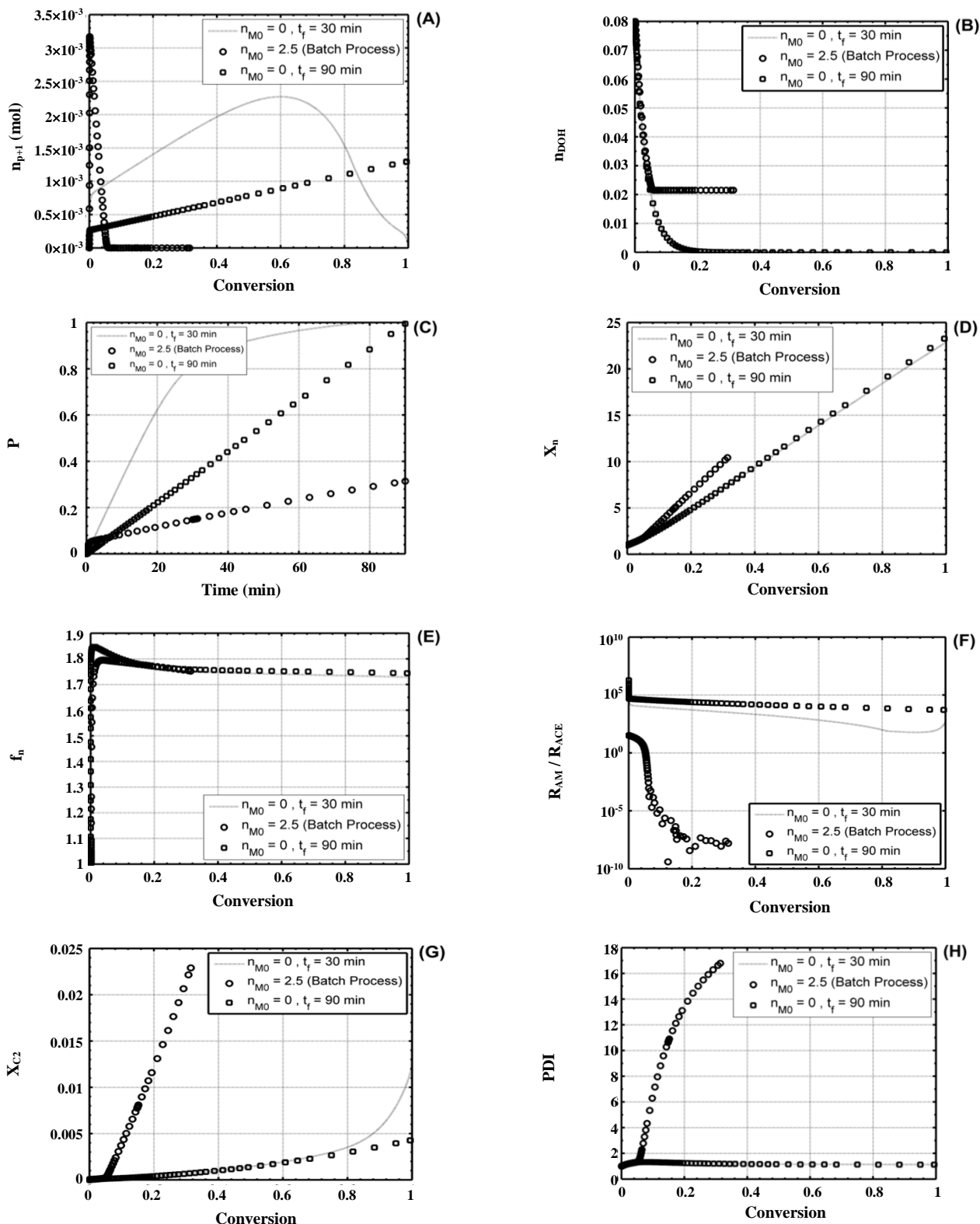


Fig. 7: Influence of feeding policy on the (A) population of protonated monomer, (B) amount of diol, (C) conversion, (D) X_n , (E) f_n , (F) Ratio of the rate of propagation via AM to ACE, (G) molar fraction of cyclic dimer, and (H) PDI.

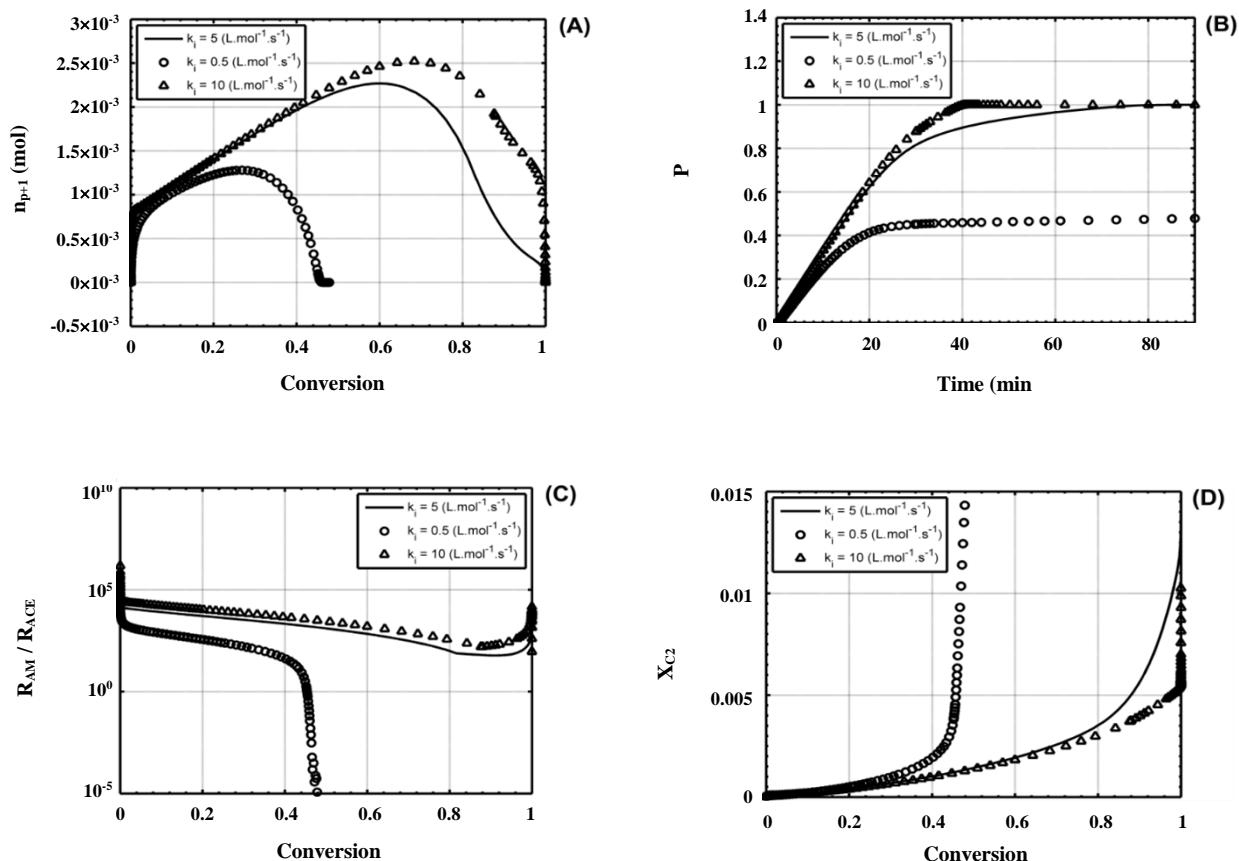


Fig. 8: Influence of the initiation rate constant on the (A) population of protonated monomer, (B) conversion, (C) ratio of the rate of propagation via AM to ACE and (D) molar fraction of cyclic dimer.

the backbiting reaction does not change the population of macrocations therefore it is expected that the rate of polymerization is independent of this reaction. However, it yields cyclic dimers. In Fig. 9(A) the fraction of cyclic dimers has been presented. This fraction is about 1.4×10^{-3} when k_{bb} is 10^{-5} (s^{-1}) and will be about ten times greater if k_{bb} increases an order of magnitude. The higher fraction of cyclic products broadens MWD. When the more cyclic products are produced, the PDI value rises (Fig. 9(B)). Presence of cyclic dimers in the final product also reduces number-average degree of polymerization as shown in Fig. 9(C). This is due to the fact that few monomeric units are incorporated in each cyclic product which results in more increment of 0^{th} moment than 1^{st} moment (Equation (5)). As a consequence, values of X_n drop. In addition to X_n , f_n reduces by increasing rate constant of backbiting. Since cyclic dimers have no hydroxyl functionality, their production only increases the denominator of the Eq. (8) and hence reduces f_n .

In Fig. 10 the influence of kinetic rate constant for the propagation via AM mechanism (k_{AM}) has been shown. The variation of k_{AM} directly affects the population of protonated monomer. As shown in Scheme 2, higher k_{AM} increases the probability of the reaction of a protonated monomer with a diol (or polymer with diol functionality). Therefore, maximum population of protonated monomers is decreased (Fig. 10(A)). On the other hand, faster propagation via AM mechanism, means faster production of initiator (See Table 2) and hence production of protonated monomer. These species are present in reaction mixture at any time of reaction when $k_{AM} = 5$ and 0.5 ($L/mol.s$).

In experiment with the lowest k_{AM} (0.05 ($L/mol.s$)), activated monomers are produced only at the initial stages of reaction and then react with monomers to form macrocations. This yields some diols remain unreacted (Fig. 10(B)) and consequently overall rate of polymerization decreases (Fig. 10(C)).

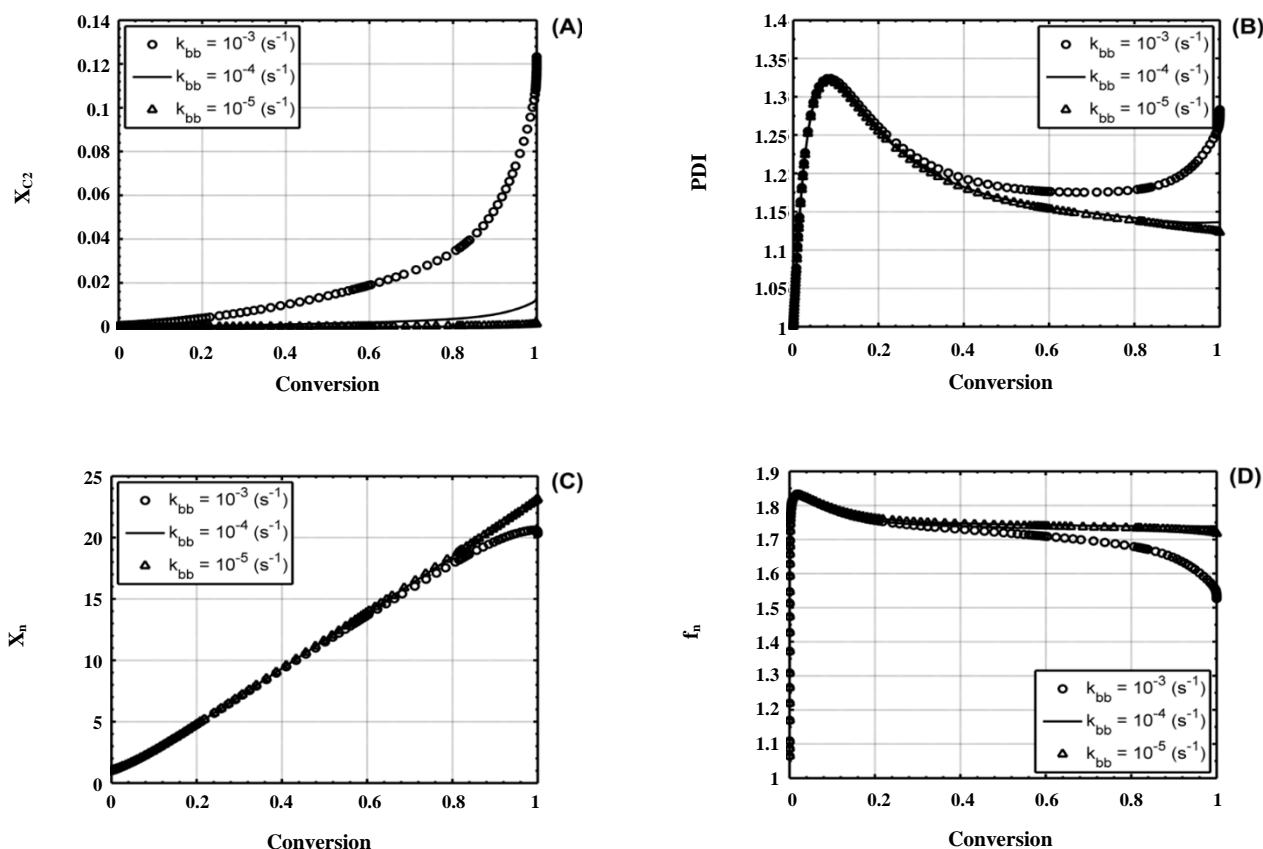


Fig. 9: Influence of the backbiting rate constant on the (A) molar fraction of cyclic dimer, (B) PDI, (C) X_n , and (D) f_n .

Fig. 10(D) reveals that k_{AM} is not a determining factor for X_n because the population of chains is mainly influenced by initial amounts of diol, initiator and water. In these experiments, initial amounts are identical, but the instantaneous concentrations are not the same because of different kinetics. However, this is not so considerable that can change population of macro species dramatically.

Fig. 10(E) depicts f_n which is calculated via Eq. (8). Reduction in the number of chains with diol functionality which is a consequence of low k_{AM} decrease f_n . Also, high k_{AM} value reduces the number of macrocations by increase the rate of reaction of diol with protonated monomer. Therefore, f_n reaches the values close to 2.

As expected, propagation via AM mechanism is amplified when k_{AM} increases (Fig. 10(F)). This reduces the occurrence of cyclization and hence fraction of cyclic dimers Fig. 10(G). Cyclic dimers have a noticeable effect on the PDI as shown in Fig. 10(H). Their small length broadens the MWD. Especially at higher conversions

when most of chains have high degree of polymerization. It should be noted that PDI values for experiment with $k_{AM} = 5$ (L/mol.s) is higher than those for experiment with $k_{AM} = 0.5$ (L/mol.s). This is owing to the high rate of propagation via AM. Under this circumstance, most of monomers are incorporated in chains with diol functionality. Therefore the difference between chain length of macrocations and those which are derived from water with polymer with diol functionality increases. This nonuniform distribution of polymerized monomers raises PDI.

CONCLUSIONS

The modeling of CROP of cyclic ethers in the presence of diol has been investigated for the first time and the method of moments was used for this purpose. Results show that the population of chains is the function of their precursors. In a typical polymerization, chains with diol functionality are the majority. Therefore, most of polymerized monomers are incorporated into those chains.

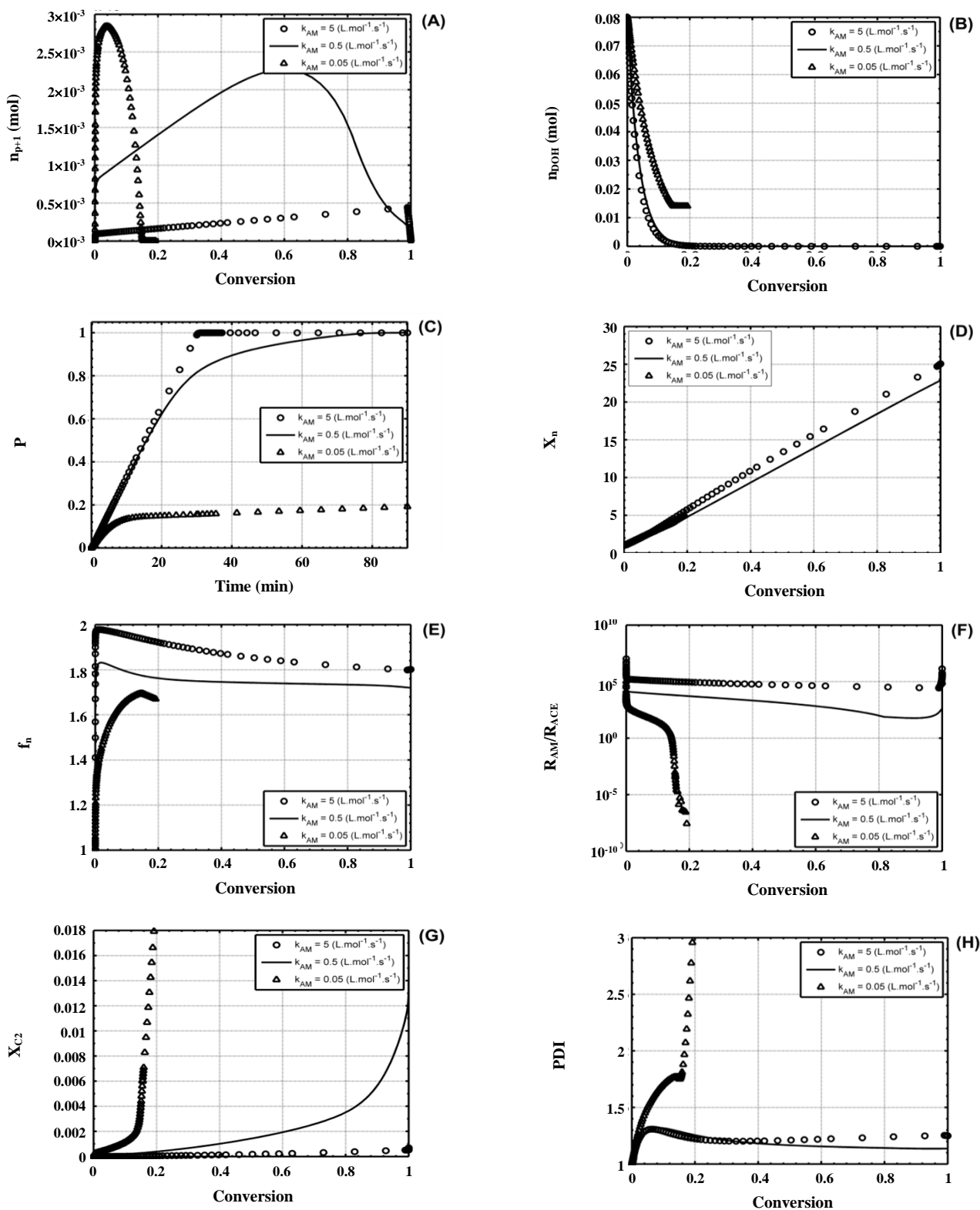


Fig. 10: Influence of the propagation via AM rate constant on the (A) population of protonated monomer, (B) amount of diol, (C) conversion, (D) X_n , (E) f_n , (F) Ratio of the rate of propagation via AM to ACE, (G) molar fraction of cyclic dimer, and (H) PDI.

This makes the chains with diol functionality as the determining group in MWD. That is why the change of initial amount of initiator has little effect on X_n and PDI. The kinetics of polymerization and properties of reactor product are highly dependent on the ratio of the propagation rate via AM mechanism to the rate of propagation via ACE. Increase of this ratio, for example by operating polymerization in semi-batch, decreasing of monomer mass flow rate, increasing of k_i and/or k_{AM} reduce the possibility of incident of backbiting reaction. Therefore, cyclic dimers are less formed and MWD narrows. On the other hand, decreasing this ratio results in less diol reacted with protonated monomers. Subsequently, the rate of regeneration of initiator and hence the rate of polymerization is reduced.

These results give complete information about the ring-opening syntheses of polyethers and are valuable for developing new grades as well as optimization of present processes.

Received : Feb. 7, 2019 ; Accepted : Jun. 10, 2019

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