Mathematical Modeling of 1, 3-Butadiene Polymerization Initiated by Hydrogen Peroxide

Mahmoudian, Mehdi

Nanochemistry Department, Institute of Nanotechnology, University of Urmia, Urmia, I.R. IRAN

Nosratzadegan, Keyvan

Institute of Chemical Research and Technology, Tehran, I.R. IRAN

Ghasemi kochameshki, Mahmoud

Nanochemistry Department, Institute of Nanotechnology, University of Urmia, Urmia, I.R. IRAN

Shokri, Aref*[+]

Department of Chemistry, Payame Noor University (PNU), Tehran, I.R. IRAN

ABSTRACT: *In this study, the modeling of polymerization of 1, 3-butadiene in the presence of hydrogen peroxide has been reported for the first time. For this purpose, the Method of double moments was applied. The modeling has been performed to investigate the effect of reaction condition on the properties of synthesized Polybutadiene, and the role of kinetic coefficients on the output of model i.e. sensitivity analysis. A comprehensive kinetic model was developed based on previous experimental studies. Then, the moment and population balance of the reactants were obtained. Modeling results were used to study the role of initiator concentration and the type of solvent in polymerization kinetics and final polymer properties. In addition, the sensitivity of modeling results in a transfer to the initiator, radical coupling and finally transfer to polymer reactions was investigated. This study opens a way for the engineering of manufacturing the Hydroxyl-Terminated PolyButadiene (HTPB) process to obtain the desired products with optimized reaction conditions. Results show that initiator concentration and type of solvent are important in polymerization kinetics and properties of HTPBs. A higher amount of initiator increases radical concentration and consequently rates of bimolecular termination and at the lower level, rate of propagation, and polymer double bonds reactions.*

KEYWORDS: *Hydroxyl-terminated Polybutadiene (HTPB), 1, 3-Butadiene, Radical polymerization, Molecular Weight Distribution (MWD), Initiator.*

INTRODUCTION

Hydroxyl-Terminated PolyButadiene (HTPB) is one of the most important liquid rubbers which has been used in a variety of applications especially in the production of freeze-resistant hydrolytically stable polyurethanes

as well as unsaturated polyesters [1, 2]. HTPB can be produced by both free radical [3-4] and anionic polymerization [5]. Accurate control over polymer microstructure such as molecular weight and Molecular Weight Distribution (MWD), hydroxyl functionality, and content of 1, 4-units can be accomplished by use of living anionic polymerization. On the other hand, free radical process yields polymers with less controlled over structure; however the ease of this process favors it over anionic mechanism in industrial scale.

In free radical process, HTPB can be synthesized simply by using hydrogen peroxide as initiator. This process has been widely investigated by various researchers [6-9]. Vilar and coworkers have done comprehensive Nuclear Magnetic Resonance (NMR) studies to propose a kinetic scheme [6, 10]. They analyzed NMR spectrums of commercially available and laboratory synthesized HTPBs to discuss on the possibility of different synthetic pathways. Their attempts leaded to a generally accepted mechanism for the hydrogen peroxide-initiated polymerization of 1, 3-butadiene. *Mir Mohammad Sadeghi et. al.,* have investigated the effect of initiator to monomer ratio on the HTPB properties such as number-average molecular weight (M_n), Poly Dispersity index (PDI) and hydroxyl content [2]. They correlate M_n to the initial initiator to monomer ratio with an empirical relationship. Also, the role of solvent in synthesizing HTPB has been studied by their group [11]. In their work, it was shown that the type of solvent had influence on polymerization kinetics and microstructure of product. An investigation of the reaction condition on the final polymer properties has also been carried out by Jankova and coworkers [3]. In their work, four independent variables including Mass fraction of initiator, Temperature, reaction time, and speed of stirrer were considered at first. Then, they were correlated to 5 dependent variables such as monomer conversion, M_n, weight-average molecular weight (M_w), PDI, and number-average hydroxyl functionality (f_n)) by fitting experimental data to response functions. It was demonstrated that initiator concentration and temperature are the most influential factors. With respect to this, response functions were modified and optimum values of amount of initiator and temperature were obtained by defining as an objective function.

Despite excellent and brilliant experimental works on polymerization of 1,3-butadiene in the presence of hydrogen peroxide, 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 optimum operating condition. It is also very helpful for designing new polymeric materials and novel polymerization processes [12]. These advantages have attracted many researchers in recent decades.

In light of aforementioned paragraph, we aim to study the hydrogen peroxide-initiated polymerization of 1,3-butadiene in a batch process by mathematical modeling. Method of double moments has been used to investigate the effect of different reaction factors on the kinetics, profile concentration of various reaction species, and characteristics of polymer product. In addition, the 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 free radical polymerization of 1,3-butadiene in the presence of hydrogen peroxide.

THEORITICAL SECTION
Kinetic scheme

The mechanism of the polymerization of 1,3-butadiene in the presence of hydrogen peroxide is the same as many free radical polymerization systems which is depicted in Scheme 1. First, initiator-derived radicals are formed *via* thermal decomposition of hydrogen peroxide. Then, they added to the monomer to form primary radicals. Primary radicals can further propagate by adding to more monomers and forms macro radicals. Bimolecular termination of radicals via combination and radical coupling between propagating radical and initiator and/or solvent derived radicals (small radicals) yields dead polymer which are not able to propagate further. Deactivation of radicals can also happen by transfer of radical center to other reactants in the reaction mixture e.g. solvent, initiator, monomer, and polymer. Transfer to small molecules leads to formation of radicals which may react with monomer and re-initiate polymerization. Transfer to polymer turns a dead chain to an active one. Under this circumstance, branching occurs and nonlinear polymers are formed. It is noteworthy that transfer to macro radicals is not considered in our kinetic scheme. This assumption is good since the allylic-type radicals are slow in propagation but quick in termination [13]; therefor,
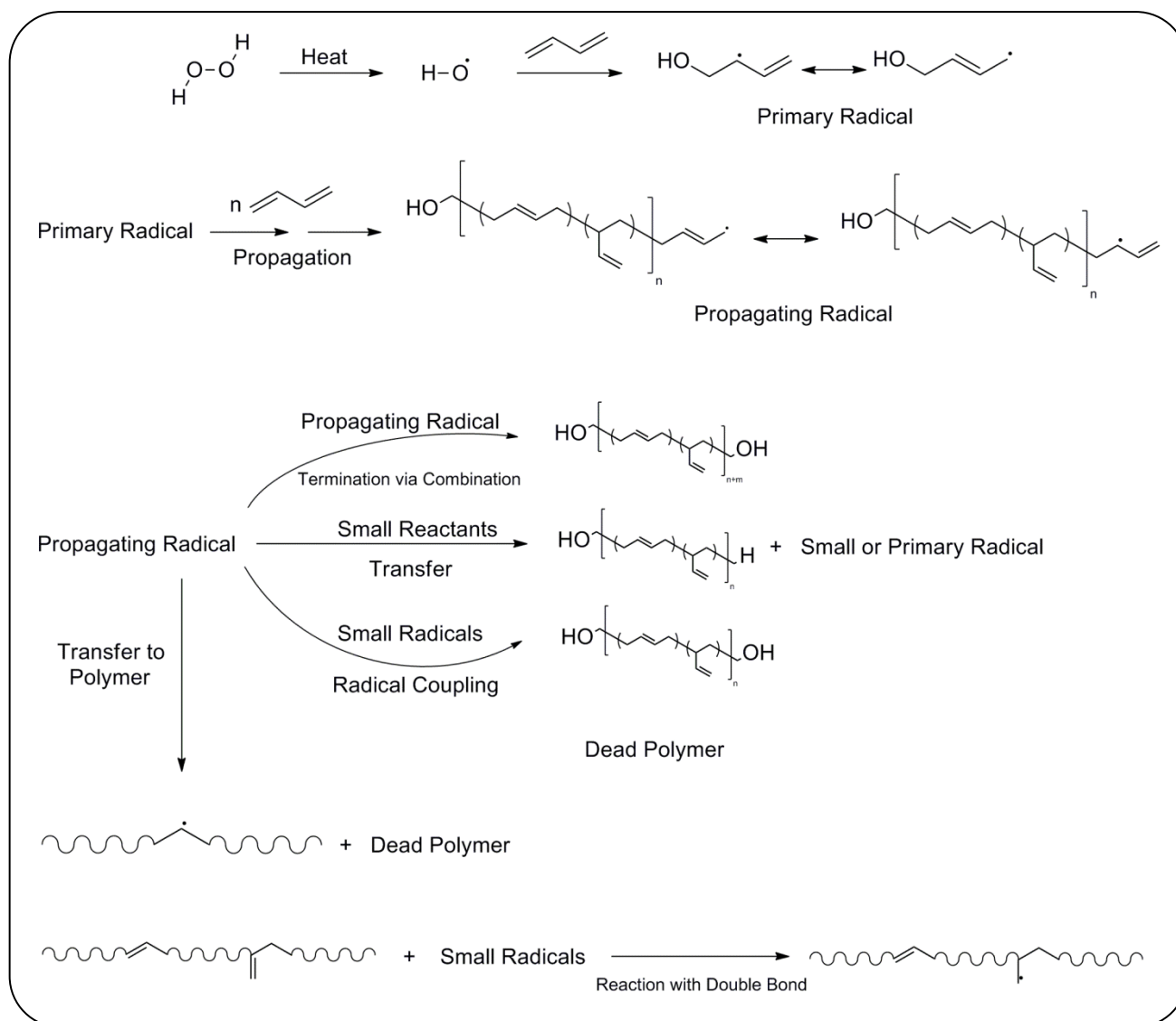
Scheme 1: Mechanism of Polymerization of 1, 3-Butadiene in the Presence of Hydrogen Peroxide.

the life time of these radicals is too short. Moreover, the concentration of macro radicals is orders of magnitude lower than concentration of polymers. As a consequence, the possibility of occurrence of transfer to macro radicals is far less than transfer to dead polymer. Therefore, if this reaction happens, it will have negligible effect on the monomer conversion, M_n, PDI and f_n.

As can be seen in Scheme 1, unsaturated double bonds in the back bone and/or pendant groups of Polybutadiene are capable of reacting with radical species in the reaction mixture. When alcohols such as 2-propanol are used as solvent, it is believed that due to the low solubility of Polybutadiene, reaction mixture contain two phases.

One phase includes macro species which has low mobility and the other phase includes mostly solvent and monomer. On the basis of this, reaction of macro radicals with polymers double bonds is unlikely to happen due to diffusion limitations. It is believed that only small radicals, initiator- or solvent-derived radicals, are capable of participating in this reaction. This reaction also yields non-linear polymers.

Model development

In this work, method of double moments [14] has been applied to model the polymerization system. By utilizing this method, the number of differential equations
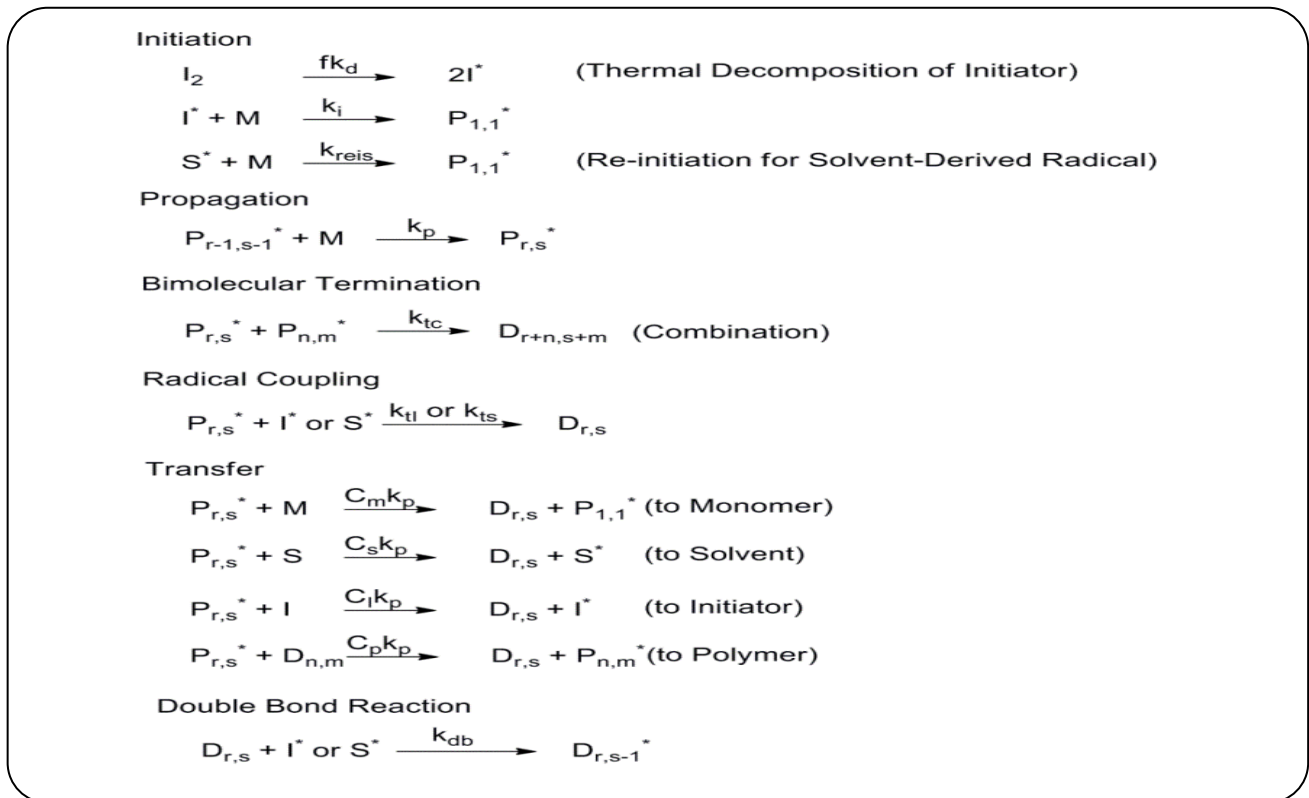
Scheme 2: Elementary Reactions involved in modeling.

is reduced considerably, but only average molecular weights can be obtained. Scheme 2 shows elementary reactions involved in modeling which are derived from previously described kinetic scheme. As can be seen in Scheme 2, each macro chain is defined with its length (first index) and number of double bonds (second index). Considering the latter makes it possible to include the reaction of double bonds in the modeling.

Definition of various chain moments and the population balance equations for different species in the reactor are presented in Tables 1 and 2, respectively. As can be seen from Table 2, the transfer to polymer and reaction with polymer double bonds terms in moment equations are functions of higher moments. Therefore the system is not closed and the closure technique for 3rd order moments is required to correlate them to the lower orders moments. In this work the method of *Hulburt* and *Katz* were used for moment closure which is easy to apply [15]. Regarding this method, 3rd order moments can be predicted via below equations:

$$\mu_{3,i} = \frac{\mu_{2,i}}{\mu_{0,i}\mu_{1,i}}\left(2\mu_{2,i}\mu_{0,i} - \mu_{1,i}^2\right) \tag{1}$$

$$\mu_{i,3} = \frac{\mu_{i,2}}{\mu_{i,0}\mu_{i,1}}\left(2\mu_{i,2}\mu_{i,0} - \mu_{i,1}^2\right) \tag{2}$$

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

$$\overline{M}_n = M_m \times \frac{\lambda_{1,0} + \mu_{1,0}}{\lambda_{0,0} + \mu_{0,0}} \tag{3}$$

$$\overline{M}_w = M_m \times \frac{\lambda_{2,0} + \mu_{2,0}}{\lambda_{1,0} + \mu_{1,0}} \tag{4}$$

$$PDI = \frac{\overline{M}_w}{\overline{M}_n} \tag{5}$$

Where M_m is the molecular weight of monomer.

Due to the fact that, the average hydroxyl functionality has a great importance since hydroxyl groups can be used in post polymerization reactions as well as incorporating with other functional groups in step polymerization. If alcohols are used as solvent, they can influence the population of hydroxyl groups [6]. As a result there are two types of hydroxyl groups: one that derived from initiator (OHI) and the other which

Table 1: Moments definition.

Type of Chains	Definition of Moments
Propagating Radical	$\lambda_{i,j} = \sum\limits_{r=1} \sum\limits_{s=0} r^i s^j \left[P_{r,s}^* \right]$
Dead Polymer	$\mu_{i,j} = \sum\limits_{r=1} \sum\limits_{s=0} r^i s^j \left[D_{r,s} \right]$

Table 2: Population Balance Equation.

	Type of Reactant	Population Balance Equations
Small Molecules	Initiator	$\dfrac{d[I]}{dt} = -k_d[I] - C_I k_p [I] \lambda_{0,0}$
	Initiator-Derived Radical	$\dfrac{d\left[I^* \right]}{dt} = 2 f k_d [I] + C_I k_p [I] \lambda_{0,0} - k_i \left[I^* \right][M] - k_{tI} \left[I^* \right] \lambda_{0,0} - k_{db} \left[I^* \right] \mu_{0,1}$
	Monomer	$\dfrac{d[M]}{dt} = -k_i \left[I^* \right][M] - k_{reis} \left[S^* \right][M] - (1 + C_M) k_p [M] \lambda_{0,0}$
	Solvent	$\dfrac{d[S]}{dt} = -C_s k_p [S] \lambda_{0,0}$
	Solvent-Derived Radical	$\dfrac{d\left[S^* \right]}{dt} = C_S k_p [S] \lambda_{0,0} - k_{reis} \left[S^* \right][M] - k_{tS} \left[S^* \right] \lambda_{0,0} - k_{db} \left[S^* \right] \mu_{0,1}$
		$A = k_i \left[I^* \right][M] + k_{reis} \left[S^* \right][M] + C_M k_p [M] \lambda_{0,0}$ $B = (1 + C_M) k_p [M] + k_{tc} \lambda_{0,0} + C_S k_p [S] + C_I k_p [I] + k_{tI} \left[I^* \right] + k_{tS} \left[S^* \right] + C_p k_p \mu_{1,0}$ $C = C_M k_p [M] + C_S k_p [S] + C_I k_p [I] + C_p k_p \mu_{1,0} + k_{tI} \left[I^* \right] + k_{tS} \left[S^* \right]$
Macro Species	Propagating Radicals' Moment	$\dfrac{d\lambda_{0,0}}{dt} = A + k_p \lambda_{0,0} [M] + C_p k_p \lambda_{0,0} \mu_{1,0} + k_{db} \left(\left[I^* \right] + \left[S^* \right] \right) \mu_{0,1} - B \lambda_{0,0}$
		$\dfrac{d\lambda_{1,0}}{dt} = A + k_p \left(\lambda_{1,0} + \lambda_{0,0} \right)[M] + C_p k_p \lambda_{0,0} \mu_{2,0} + k_{db} \left(\left[I^* \right] + \left[S^* \right] \right) \mu_{1,1} - B \lambda_{1,0}$
		$\dfrac{d\lambda_{2,0}}{dt} = A + k_p \left(\lambda_{2,0} + 2\lambda_{1,0} + \lambda_{0,0} \right)[M] + C_p k_p \lambda_{0,0} \mu_{3,0} + k_{db} \left(\left[I^* \right] + \left[S^* \right] \right) \mu_{2,1} - B \lambda_{2,0}$
		$\dfrac{d\lambda_{0,1}}{dt} = A + k_p \left(\lambda_{0,1} + \lambda_{0,0} \right)[M] + C_p k_p \lambda_{0,0} \mu_{1,1} + k_{db} \left(\left[I^* \right] + \left[S^* \right] \right) \left(\mu_{0,2} - \mu_{0,1} \right) - B \lambda_{0,1}$
		$\dfrac{d\lambda_{0,2}}{dt} = A + k_p \left(\lambda_{0,2} + 2\lambda_{0,1} + \lambda_{0,0} \right)[M] + C_p k_p \lambda_{0,0} \mu_{1,2} +$ $k_{db} \left(\left[I^* \right] + \left[S^* \right] \right) \left(\mu_{0,3} - 2\mu_{0,2} + \mu_{0,1} \right) - B \lambda_{0,2}$
		$\dfrac{d\lambda_{1,1}}{dt} = A + k_p \left(\lambda_{1,1} + \lambda_{1,0} + \lambda_{0,1} + \lambda_{0,0} \right)[M] + C_p k_p \lambda_{0,0} \mu_{2,1}$ $+ k_{db} \left(\left[I^* \right] + \left[S^* \right] \right) \left(\mu_{1,2} - \mu_{1,1} \right) - B \lambda_{1,1}$

Table 2: Population Balance Equation.

	Type of Reactant	Population Balance Equations
Macro Species	Propagating Radicals' Moment	$\frac{d\lambda_{1,2}}{dt} = A + k_p\left(\lambda_{1,2} + 2\lambda_{1,1} + \lambda_{0,2} + 2\lambda_{0,1} + \lambda_{1,0} + \lambda_{0,0}\right)[M] + C_p k_p \lambda_{0,0}\mu_{2,2}$ $+ k_{db}\left([I^*] + [S^*]\right)\left(\mu_{1,3} - 2\mu_{1,2} + \mu_{1,1}\right) - B\lambda_{1,2}$
		$\frac{d\lambda_{2,1}}{dt} = A + k_p\left(\lambda_{2,1} + 2\lambda_{1,1} + \lambda_{2,0} + \lambda_{0,1} + 2\lambda_{1,0} + \lambda_{0,0}\right)[M] + C_p k_p \lambda_{0,0}\mu_{3,1}$ $+ k_{db}\left([I^*] + [S^*]\right)\left(\mu_{2,2} - \mu_{2,1}\right) - B\lambda_{2,1}$
		$\frac{d\lambda_{2,2}}{dt} = k_p\left(\lambda_{2,2} + 2\lambda_{2,1} + \lambda_{2,0} + 2\lambda_{1,2} + 4\lambda_{1,1} + 2\lambda_{1,0} + \lambda_{0,2} + 2\lambda_{0,1} + \lambda_{0,0}\right)[M]$ $+ A + C_p k_p \lambda_{0,0}\mu_{3,2} + k_{db}\left([I^*] + [S^*]\right)\left(\mu_{2,3} - 2\mu_{2,2} + \mu_{2,1}\right) - B\lambda_{2,2}$
	Dead Polymers' Moment	$\frac{d\mu_{0,0}}{dt} = C\lambda_{0,0} + \frac{1}{2}k_{tc}\lambda_{0,0}^2 - C_p k_p \lambda_{0,0}\mu_{1,0} - k_{db}\left([I^*] + [S^*]\right)\mu_{0,1}$
		$\frac{d\mu_{1,0}}{dt} = C\lambda_{1,0} + k_{tc}\lambda_{1,0}\lambda_{0,0} - C_p k_p \lambda_{0,0}\mu_{2,0} - k_{db}\left([I^*] + [S^*]\right)\mu_{1,1}$
		$\frac{d\mu_{2,0}}{dt} = C\lambda_{2,0} + k_{tc}\left(\lambda_{1,0}^2 + \lambda_{2,0}\lambda_{0,0}\right) - C_p k_p \lambda_{0,0}\mu_{3,0} - k_{db}\left([I^*] + [S^*]\right)\mu_{2,1}$
		$\frac{d\mu_{0,1}}{dt} = C\lambda_{0,1} + k_{tc}\lambda_{0,1}\lambda_{0,0} - C_p k_p \lambda_{0,0}\mu_{1,1} - k_{db}\left([I^*] + [S^*]\right)\mu_{0,2}$
		$\frac{d\mu_{0,2}}{dt} = C\lambda_{0,2} + k_{tc}\left(\lambda_{0,1}^2 + \lambda_{0,2}\lambda_{0,0}\right) - C_p k_p \lambda_{0,0}\mu_{1,2} - k_{db}\left([I^*] + [S^*]\right)\mu_{0,3}$
		$\frac{d\mu_{1,1}}{dt} = C\lambda_{1,1} + k_{tc}\left(\lambda_{1,1}\lambda_{0,0} + \lambda_{0,1}\lambda_{1,0}\right) - C_p k_p \lambda_{0,0}\mu_{2,1} - k_{db}\left([I^*] + [S^*]\right)\mu_{1,2}$
		$\frac{d\mu_{1,2}}{dt} = C\lambda_{1,2} + k_{tc}\left(\lambda_{0,2}\lambda_{1,0} + 2\lambda_{0,1}\lambda_{1,1} + \lambda_{0,0}\lambda_{1,2}\right) - C_p k_p \lambda_{0,0}\mu_{2,2} - k_{db}\left([I^*] + [S^*]\right)\mu_{1,3}$
		$\frac{d\mu_{2,1}}{dt} = C\lambda_{2,1} + k_{tc}\left(\lambda_{2,0}\lambda_{0,1} + 2\lambda_{1,0}\lambda_{1,1} + \lambda_{0,0}\lambda_{2,1}\right) - C_p k_p \lambda_{0,0}\mu_{3,1} - k_{db}\left([I^*] + [S^*]\right)\mu_{2,2}$
		$\frac{d\mu_{2,2}}{dt} = C\lambda_{2,2} + k_{tc}\left(\lambda_{2,2}\lambda_{0,0} + 2\lambda_{1,2}\lambda_{1,0} + \lambda_{0,2}\lambda_{2,0} + 2\lambda_{2,1}\lambda_{0,1} + 2\lambda_{1,1}^2\right)$ $- C_p k_p \lambda_{0,0}\mu_{3,2} - k_{db}\left([I^*] + [S^*]\right)\mu_{2,3}$

derived from solvent (OHS). The population balance for both types of hydroxyl functionalities which attached to the polymer chains can be written as follows:

$$\frac{d[OHI]}{dt} = k_i\left[I^*\right][M] + C_I k_p[I]\lambda_{0,0} + \tag{6}$$

$$k_{tI}\left[I^*\right]\lambda_{0,0} + k_{db}\left[I^*\right]\mu_{0,1}$$

$$\frac{d[OHS]}{dt} = k_{reis}\left[S^*\right][M] + \tag{7}$$

$$k_{tS}\left[S^*\right]\lambda_{0,0} + k_{db}\left[S^*\right]\mu_{0,1}$$

Number-average hydroxyl functionality, f_n and also molar fraction of hydroxyl groups derived from solvent can be obtained via following equations:

Table 3: Kinetic Coefficients used in the modeling of 1,3-Butadiene Polymerizations in the Presence of hydrogen peroxide at T=110 °C.

Rate Constant	Value	Reference
k_d	$1.02\times10^{16}\exp(-17982/T)$	[16]
f	0.35	[16]
k_p	$8.05\times10^{17}\exp(-4295/T)$	[17]
k_{db}	K_p	[18]
k_i, k_{reis}	$5\times k_p$	[19]
C_M	3.02×10^{-4}	[18]
C_I	10^{-4}	----
C_S	10^{-3}	----
C_P	5×10^{-3}	[20]
k_{tc}	$1.13\times10^{10}\exp(-711/T)$	[20]
k_{tI}, k_{tS}	10^{10}	----

$$\overline{f_n} = \frac{[OHI]+[OHS]}{\mu_{0,0}} \tag{8}$$

$$X_{OHS} = \frac{[OHS]}{[OHI]+[OHS]} \tag{9}$$

Kinetic rate constants are given in Table 3. Some rate constants have been roughly approximated. As it will be discussed in next section, this approximation has not a dramatic effect in modeling results therefore their usage is not flawed. By knowing kinetic rate constants, set of differential equations (Table 2 and Equations (6) and (7)) can be solved via a commercial ODE solver (ode15s or ode23tb in MATLAB R2009a.

RESULTS AND DISCUSSION

In this work modeling has been conducted for two main purposes: first, investigation the effect of reaction condition on the properties of synthesized Polybutadienes; and second, understanding the role of kinetic coefficients on the output of model i.e. sensitivity analysis. Initial molar ratio of monomer: solvent: hydrogen peroxide = 10:5:1 was used for base level. Initial molar concentration of monomer and reaction time were 6 Molar and 6 hours, respectively. These values are in the range of real processes for HTPB production. The modeling results for basic level were presented in Figs. 1 to 4. As can be seen in Fig. 1, M_n decreases over reaction time. This is due to the fact that monomer concentration decreased while more active chains are produced. Therefore, less monomer consumed per chain and hence kinetic chain length decreases which yields to decline in M_n.

It should be noted that branching and cross linking which may occur in this system have more effect on the M_w than M_n. This influence clearly can be seen in rapid increment of PDI which presented in Fig. 2. PDI starts with values close to 1.5; the expected value when termination only occurs via combination based on the most probable distribution. However, production of dead chains through reaction time, transfer to polymer, and reaction of polymer double bonds result in fast increase of PDI.

The f_n has been depicted in Fig. 3. In the absence of branching reactions, if termination only occurs *via* combination, it is expected that f_n possess a constant value of 2. However, as it has been shown in Fig. 3, f_n starts from near 1.9 at the onset of reaction and reach 2.5 at the end of polymerization. This trend can be described as follows: at the beginning of reaction, transfer to small molecules (see Scheme 1) yields dead polymers with only one terminal hydroxyl group. Therefore, f_n drops to value less than 2. This reduction is not significant since termination via combination is dominant. As the time passes, concentration of dead polymers increases and therefore, the probability of transfer to polymer and reaction of polymer double
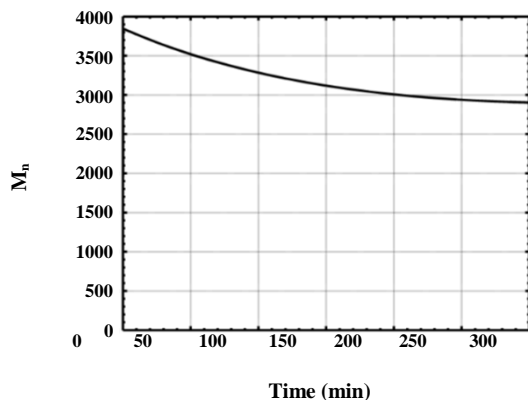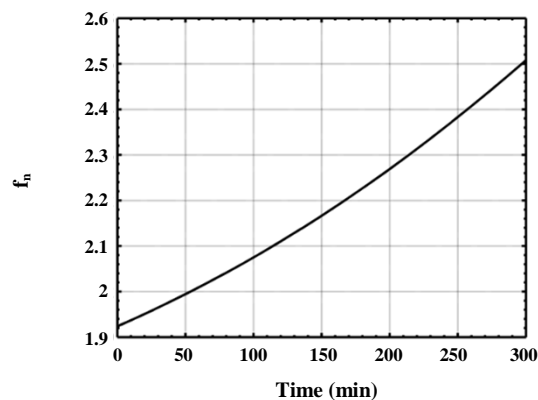
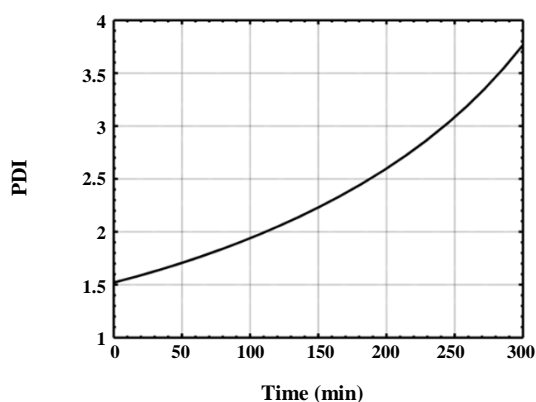*Fig. 1: Evolution of M_n with time for base level.*

Fig. 2: Changes of PDI during polymerization.

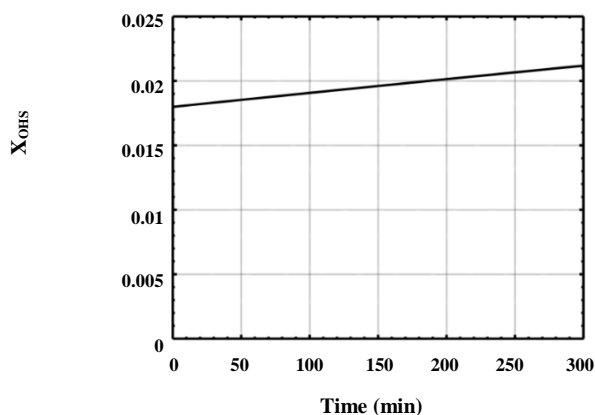*Fig. 3: f_n as a function of time.*

Fig. 4: Molar fraction of hydroxyl functionalities which have been derived from the solvent i.e. an alcohol.

bonds increases. Consequently, non-linear polymers with branches are formed which are capable of having more than two hydroxyl functionalities. As a result, an increase in f_n values observes.

As previously described, when alcohols such as ethanol or 2-propanol are used as solvent, radicals which derived from them (see Scheme 2), have the potential for both re-initiation and radical coupling reaction. The fraction of this type of functionality was showed in Fig. 4. However, It is not considerable because of low concentration of S^* in comparison with I^*. It is gratifying to note that these values are comparable to values that have been obtained via NMR studies [6, 12].

Good agreement between these results with previously reported experimental data [2, 3] suggests that modeling output is reliable enough for kinetic investigation.

Influence of Reaction Conditions on the properties of HTPBs

Effect of Initiator Concentration

To investigate the impact of initiator on the kinetics and polymer properties, modeling was carried out with three different concentration of hydrogen peroxide. In all experiments the initial molar concentration of monomer and solvent was kept constant (same as base level) while the initial concentration of hydrogen peroxide varied.

Decreasing molar ratio of monomer to hydrogen peroxide i.e. increasing initiator concentration, yields rise in concentration of radicals in the reaction mixture. As a result, rate of monomer consumption (rate of polymerization) increases (see Fig. 5 (A) and monomer population balance in Table 2). Also the rate of radical-radical termination increases. The rate of former reaction depends on first power of radical concentration while the latter reaction depends on the second power of radical concentration. Therefore, the kinetic chain length
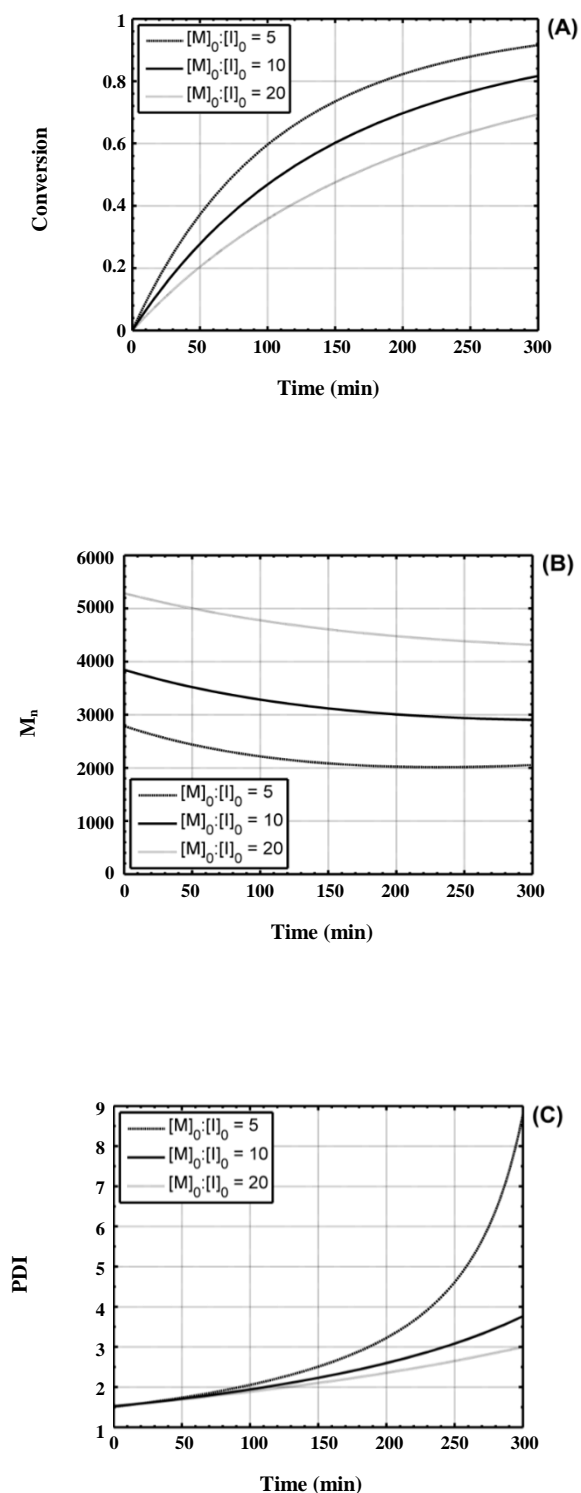
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Fig. 5: Effect of initiator concentration on the (A) monomer conversion, (B) M_n, and (C) PDI.

which is defined as the ratio of the rate of polymerization to the rate of termination [21] decreases. Hence M_n is the lowest for the experiment with highest content of initiator (Fig. 5 (B)).

As it has been shown in Fig. 5 (C), increase of radical concentration leads to a sharp rise in PDI value. This is due to the fact that radical-radical termination reaction, reaction with polymer double bonds, and transfer to polymer is amplified because of higher radical content. These can increase the number of dead chains and more importantly number of branched polymers. Therefore, MWD is broadened.

According to the mechanism of reaction (Scheme 1 and Equations (6)-(8)), it is expected that f_n increases whit increase in initiator concentration (Fig. 6 (A)). Since this functionality comes from initiator-derived radicals, the fraction of hydroxyl groups which derived from solvent declines (Fig. 6 (B)).

Effect of Type of Solvent

Changing the solvent directly affects the transfer to solvent and re-initiation reactions as well as radical coupling reaction and reaction of polymer double bonds. However as reported by *Mir Mohammad Sadeghi* and *Coworkers*, rate of polymerization may change dramatically due to the changes of initiator decomposition rate and initiator efficiency [13]. Only the former effect has been investigated in our work by changing the values for C_S, k_{reis}, k_{ts} and k_{dbs} (only for terms which contains S^*). Two limits have been considered and compared with base level: first, no production of S^*, i.e. $C_s = 0$ and second, no consumption of S^*, i.e. $C_s = 10^{-3}$ and $k_{reis} = k_{ts} = k_{dbs} = 0$. Also results have been obtained and compared when transfer occurs two orders of magnitude faster than base level, i.e. $C_s = 10^{-1}$. It should be noted that in all experiments the concentration of reactants have been the same as base level [22].

Fig. 7 depicts how changing the solvent may affect kinetics as well as polymer properties. In case of monomer conversion (Fig. 7 (A)) no significant change is observed. Considering monomer population balance (Table 2), it is believed that the dominant term would be propagation term. Since the concentration of monomer has been the same for all experiments, therefore the propagating radicals' concentration may be influenced by change of solvent. As can be seen in Fig. 7 (C), this concentration is almost equal for all experiments, thanks to values of kinetic coefficients. When transfer occurs, one propagating radical
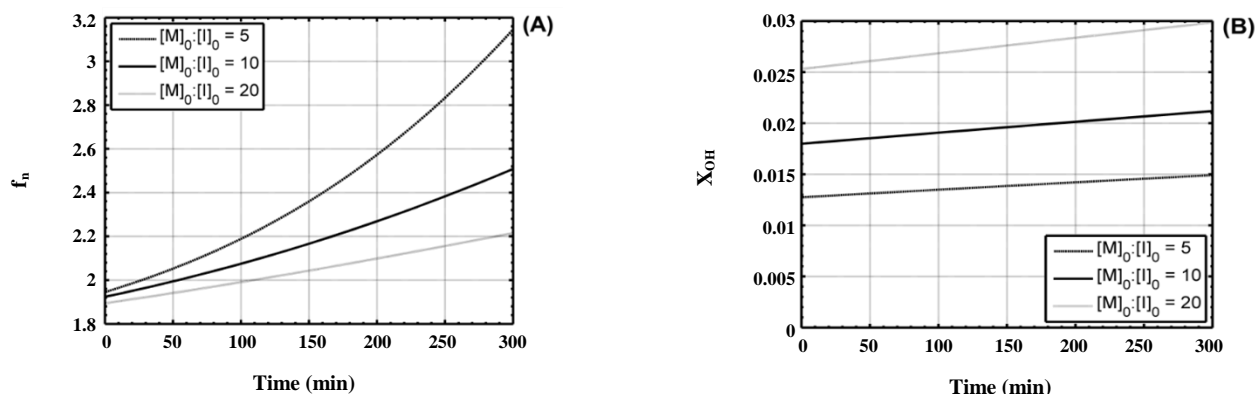
Fig. 6: Effect of Initiator concentration on the (A) f_n and (B) X_{OHS}.

turns into a dead polymer and the small radical (S^*) is produced (See Scheme 2). This reduces population of propagating radicals. If the newly formed S^* re-initiates polymerization at comparable rate with propagation, new propagating radical is produced and therefore no retardation in monomer consumption would happen. In other words, in case of fast re-initiation, population of propagating radicals almost identical to "No Transfer to Solvent" experiment as can be seen in Fig. 7 (C). In our experiments it is obvious that even at high values of transfer constant $(C_s = 10^{-1})$ no retardation is detectable due to the fast re-initiation. On the hand, when no re-initiation is assumed, no change in conversion and macro radicals' concentration is observed. This can be explained by low C_S in this experiment [18]. A glance at solvent concentration profile (Fig. 7(C)) reveals that only very small amounts of solvents are consumed due to the transfer to solvent reaction. Therefore, this reaction has little effect on the kinetics and is not determining. However if value of transfer to solvent constant were much bigger than 10^{-3}, then its relevant reactions would have significant role in kinetics of polymerization.

High values of C_s remarkably increases population of dead chains and make transfer to solvent reaction as a dominant pathway to production of dead polymers as it is shown in Fig. 7 (D). Since the monomer conversion is almost identical for all experiments, M_n mainly influenced by concentration of dead chains. From Fig. 7 (E) it is clear that for all experiments except one with $C_s = 10^{-1}$ in which concentration of dead chains is far above other experiments, M_n values is comparable. PDI graphs (Fig. 7 (F)) also demonstrate that dominant mode of termination determines the evolution of PDI through reaction time. When transfer to solvent does not occur or happens at very low rates,

termination via combination and branching reactions mainly affect PDI values. Inversely, PDI values are influenced predominantly by transfer to solvent at high C_S values.

Change of solvent may also have drastic impact on the functionality of HTPB if it changes the dominant mode of termination as well as population of dead chains (Equation (8)). As it has shown in Fig. 8 (A), when transfer is absent or limited, number of dead chains is defined by other modes of termination (Fig. 7 (D)) while increasing C_s, amplifies unimolecular termination i.e. transfer to solvent. As a result number of dead chains raises and therefore, number average functionality declines. Moreover, under this circumstance, solvent-derived radicals are responsible for most of hydroxyl functionality which is observable in Fig. 8 (B).

From Figs. 7 and 8, it can be concluded that changing the solvent may have considerable effect on kinetics and polymer properties if it turns transfer to solvent reaction as a dominant synthetic pathway.

Sensitivity analysis

Sensitivity analysis has been done with two main purposes: first, estimation of error which may be caused by rough estimation of kinetic coefficients; and second, investigation the importance of some reactions which have been included in the kinetic scheme. It can be found from Table 2 that kinetic rate constants for transfer to initiator and radical coupling reactions were roughly estimated. Therefore, sensitivity of modeling results on these values has been investigated. In addition, the influence of transfer to polymer reaction on the final modeling results has been studied [19].

Fig. 9 shows the modeling results for three different values of transfer to initiator, C_I. Based on the kinetic
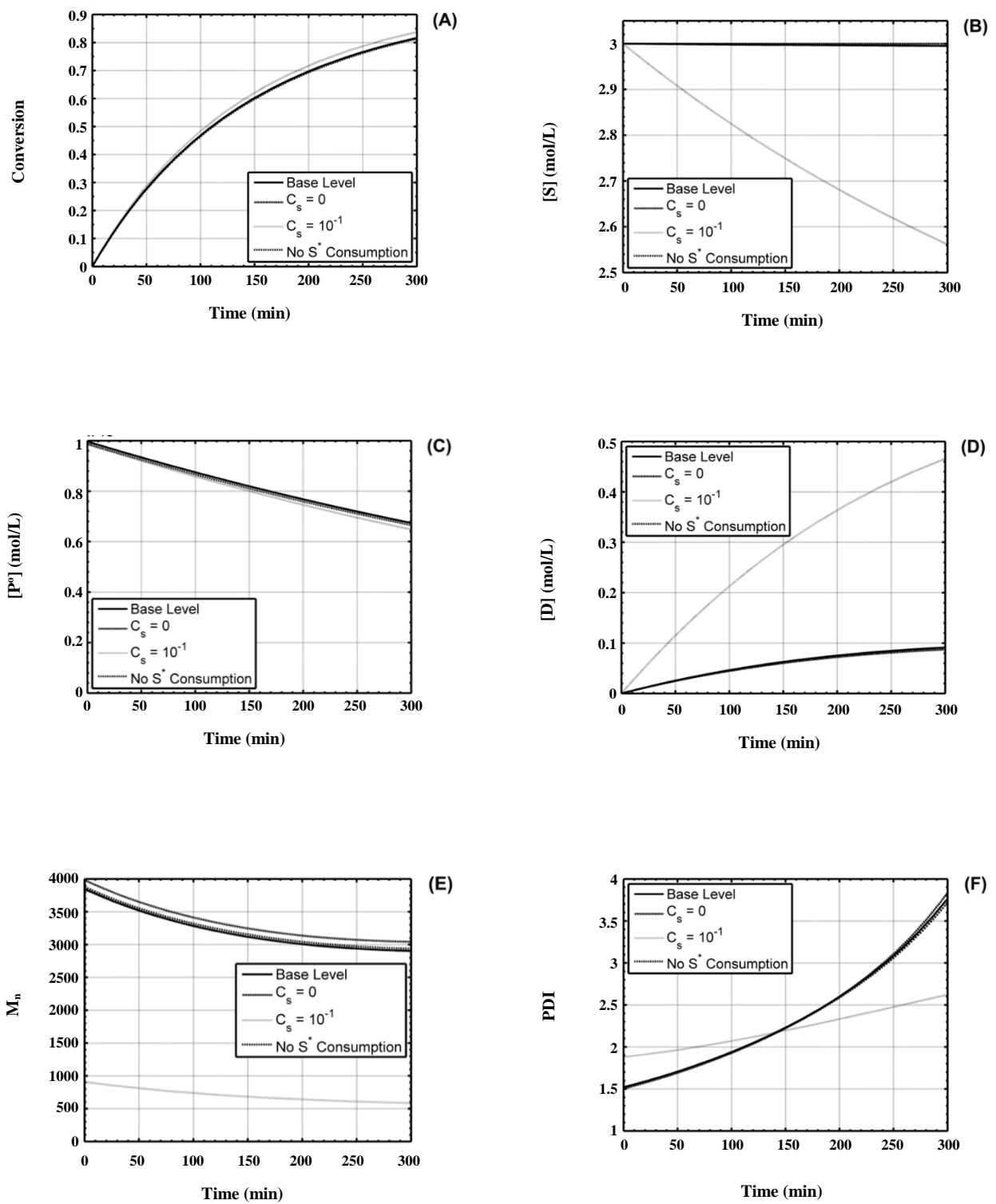
Fig. 7: Influence of applying various hypothetical solvents on (A) monomer conversion, (B) solvent concentration profile, (C) propagating radical concentration, (D) polymer concentration, (E) M̄n, and (F) PDI.
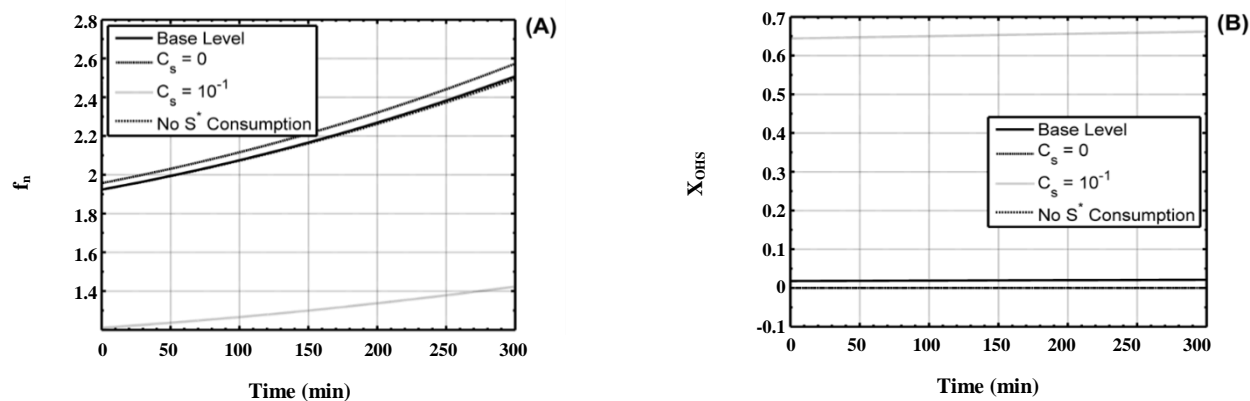
Fig. 8: Influence of applying various hypothetical solvents on functionality of HTPBs.
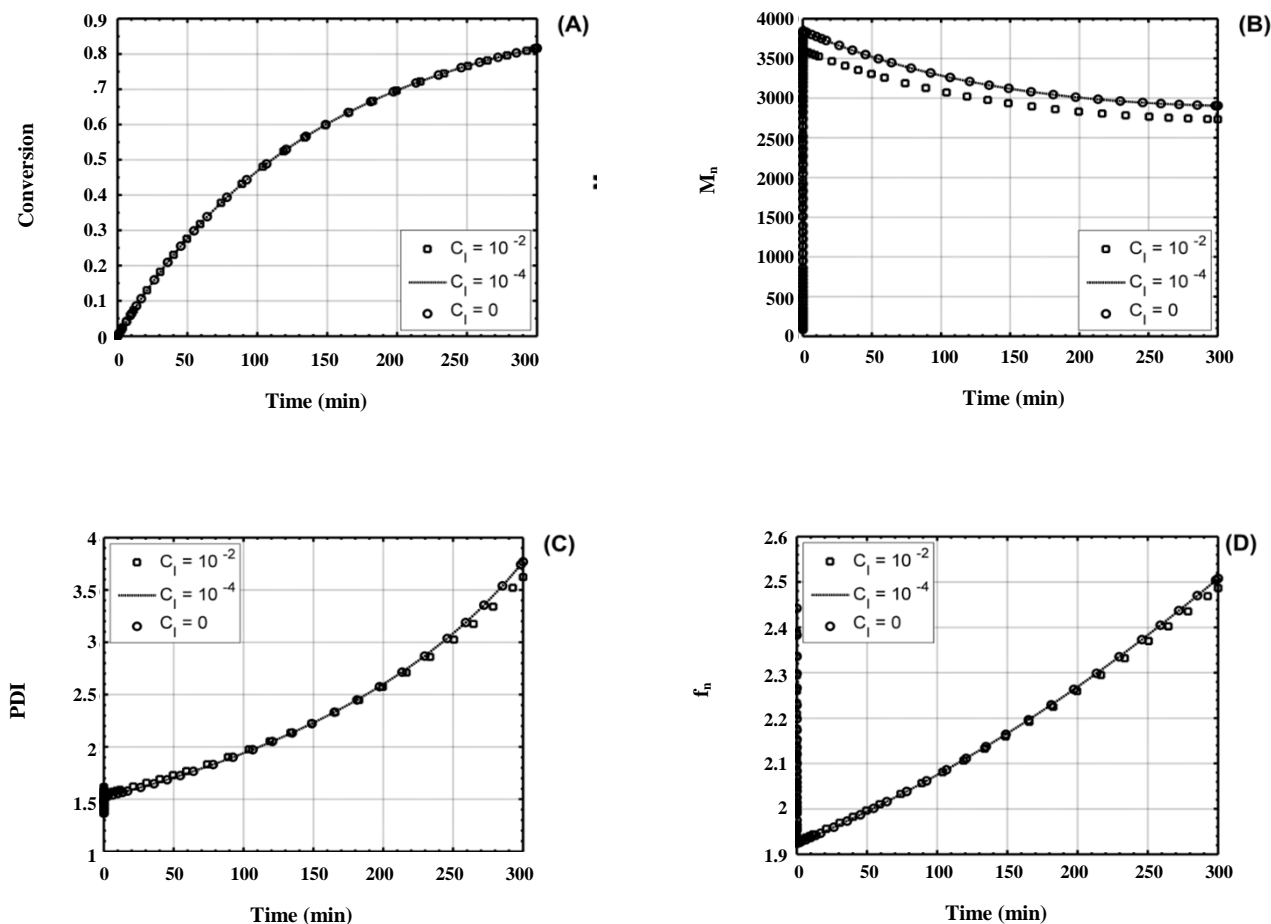

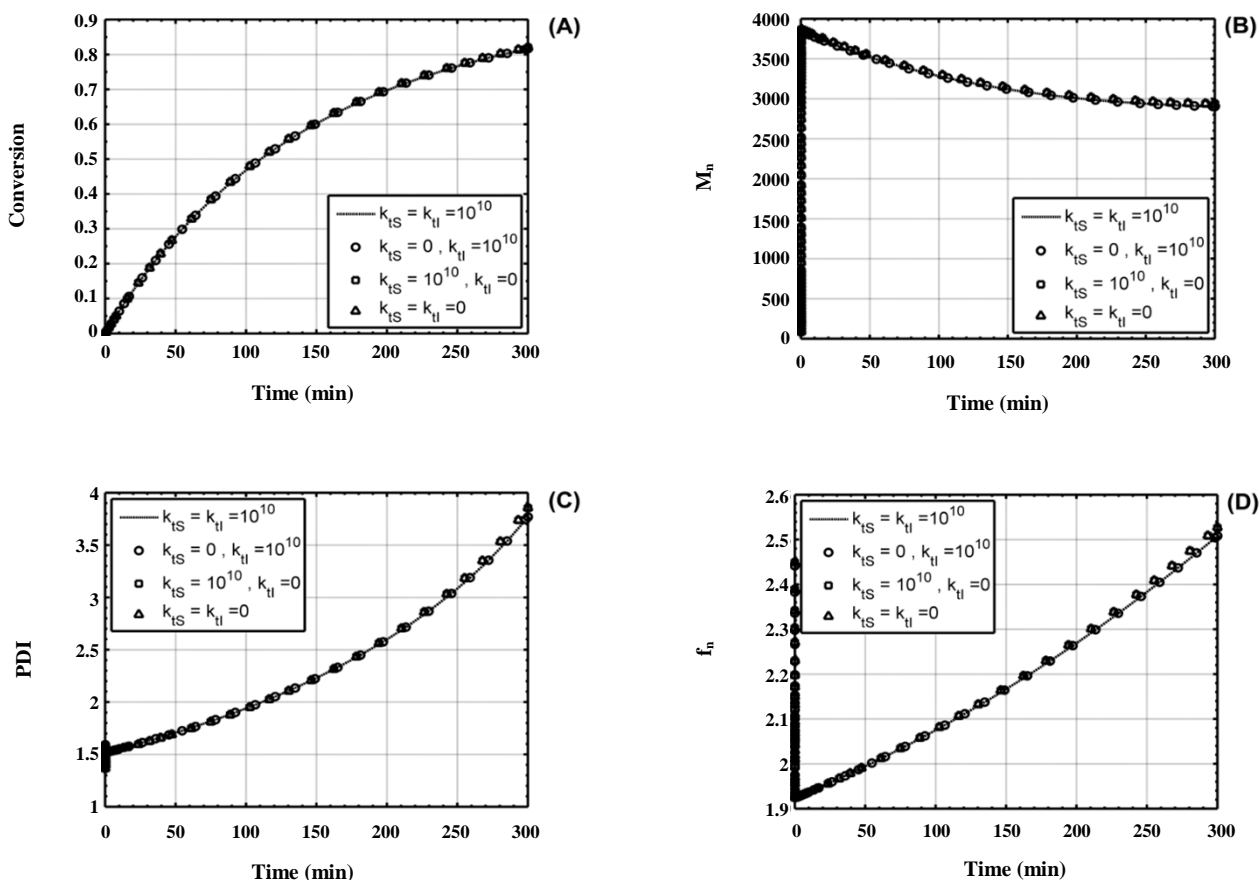*Fig. 9: Sensitivity of modeling results to changes in transfer to initiator constant, C_I.*

Fig. 10: Sensitivity of modeling results to variation in rate of radical coupling reaction.

scheme (Schemes 1 and 2), transfer to initiator turn an active radical into a dead chain. The newly formed I^* reacts fast with monomer, therefore it can be said that total concentration of propagating radicals remains unchanged. Therefore, its effect on the rate of polymerization is not noticeable as shown in Fig. 9 (A). On the other hand, more dead chains produce when this reaction occurs. As a result, the number of polymerized monomers per chain, say M_n, is reduced (Fig. 9 (B)). However this reduction is not significant due to the low rate of this reaction in comparison with other reactions such as bimolecular termination. Figs. 9 (C) and (D) support the aforementioned statement. Low sensitivity of PDI and f_n to values of C_I implies that it is not a dominant term in the population of polymeric chains. As a consequence, it can be concluded that the error of estimating C_I is negligible and even this reaction can be omitted from kinetic scheme [20–21].

The same conclusion can be made about radical coupling reactions. As shown in Fig. 10, results of modeling remain constant while input kinetic coefficients have been varied significantly. This insensitivity can be explained by low concentration of both initiator- and solvent- derived radicals in the reaction mixture and hence, low rate of radical coupling reactions [22-23].

Fig. 11 depicts the impact of transfer to polymer constant, C_P, on the kinetics of polymerization and properties of reactor product. As it has shown in Scheme 2, the population of both polymers and propagating radicals remain unchanged by transfer to polymer. Therefore, the rate of polymerization, M_n and f_n are independent from this reaction. But this reaction directly effects on MWD by producing nonlinear polymers. It is clear that PDI are influenced by C_P values. A glance at a population balance for moments of polymeric chains (Table 2) reveals that the rate of transfer to polymer
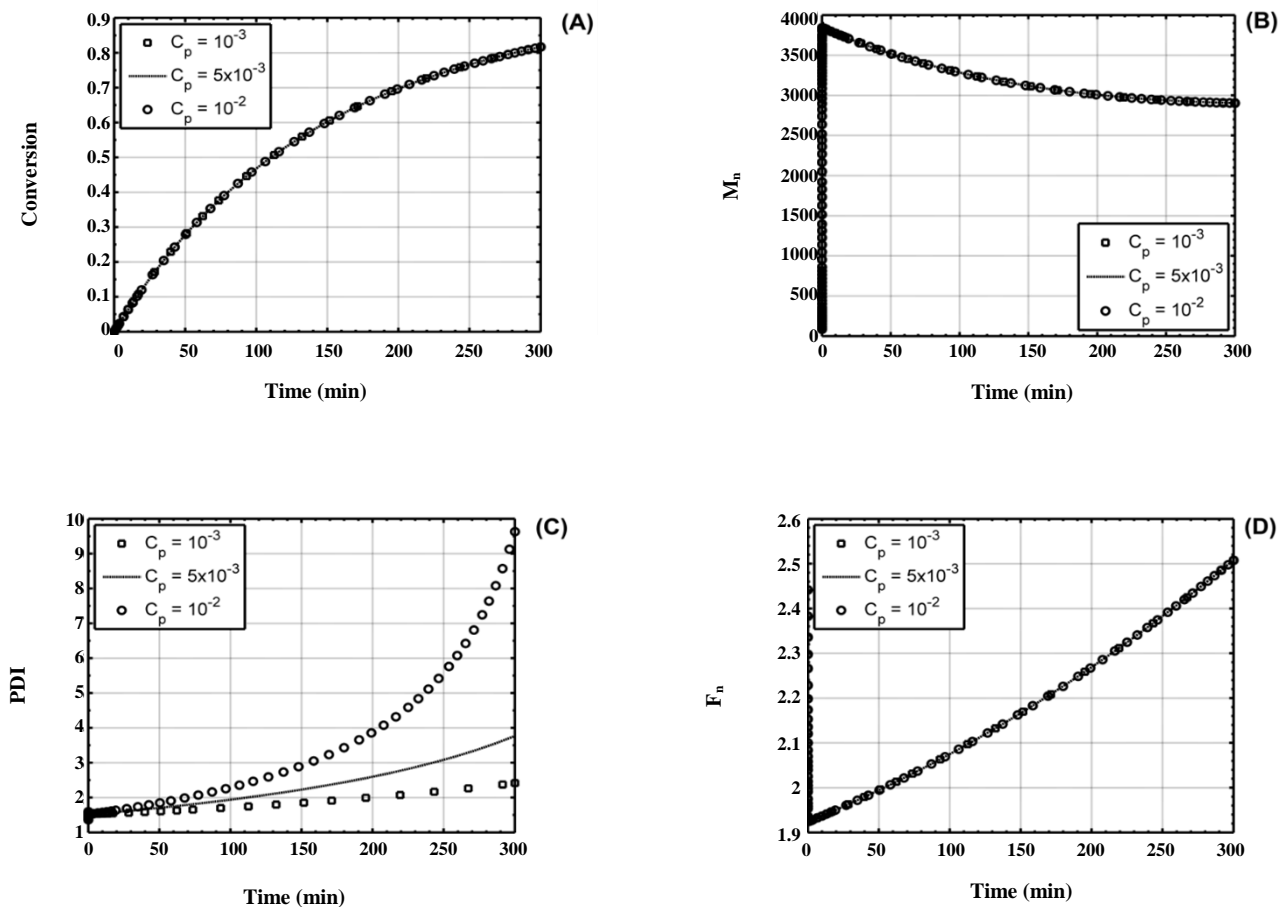
Fig. 11: Influence of values of transfer to polymer constant on the modeling results.

is dependent on the size of the polymeric chain. Polymer with greater chain length is more probable to undergo transfer to polymer reaction. Therefore, big chains get bigger while smaller chains may have less chance to react with macro radicals. In addition, when transfer to polymer occurs long branches are formed. These branched radicals may be terminated with another branched radical via combination and produce cross-linked polymers. All the above broaden MWD and hence an increment in PDI [24-25].

CONCLUSIONS

The modeling of 1,3-butadiene polymerization in the presence of hydrogen peroxide have been reported for the first time and Method of double moments has been used to investigate the effect of different reaction factors on the kinetics, profile concentration of various reaction species, and characteristics of polymer product. The modeling has been performed for two main purposes: studying the effect

of reaction condition on the properties of synthesized Polybutadienes and understanding the role of kinetic coefficients on the output of model i.e. sensitivity analysis.

Modeling results are in good agreement with previously reported experimental data which indicates on the validity of model. Results show that initiator concentration and type of solvent are influential in kinetics of polymerization and properties of HTPBs. Higher amount of initiator increases radical concentration and consequently rates of bimolecular termination and at lower level, rate of propagation and polymer double bonds reactions. Therefore, higher conversion and shorter chains with broad dispersity and higher functionality is obtained. Moreover, results show that type of solvent may affect polymerization kinetics and polymer properties if rate of transfer to solvent is comparable with rate of propagation. Based on sensitivity analysis, it can be demonstrated that including transfer to initiator and radical coupling reactions in kinetic

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scheme is not essential. Analysis also suggests that transfer to polymer mainly effect on the MWD and PDI. These results give comprehensive information about the radical syntheses of HTPB and are useful for developing new grades as well as optimization current processes.

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