Styrene Conversion Modeling and Estimation of Polydispersity Index

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Abstract

In this study, the kinetics of free radical polymerization (FRP) of styrene, initiated by benzoyl peroxide in polar solvent, are described. A model was developed based on a set of elementary reactions by mass balance of the chemical species and method of moment analysis. The set of modeled equations was solved analytically using the Garg et al., (G-model) approach for the estimation of polystyrene average properties such as weight and number average molecular weights and polydispersity, which were found to vary with reaction conditions and styrene monomer conversion. Our earlier reported styrene monomer conversion model was improved upon by the incorporation of the Trommsdoff Norrish effect. The modified conversion model was found to give a better prediction.

Key words: Kinetics, radical polymerization, G-model, polydispersity, method of moment, Trommsdoff Norrish effect.

Introduction

Unlike the cracking process of heavy hydrocarbon, polymerization is a building up process with interesting fundamental steps. The reaction commences with the generation of radicals, followed by the initiation of monomers. The growth of the polymer via the process called propagation, gives the polymer its characteristic high molecular weight. The final step is the bimolecular termination reaction in which two radical species react to form a'dead' polymer material. It is important to realize that the aforementioned reactions take place simultaneously during the polymerization process. As a result, the end-product does not consist of polymer chains with one unique size, instead, the polymer consists of a distribution of polymer chains with a variety of different sizes [1]. Costas et al. [2] developed a kinetic model capable of predicting the evolution of polymerization rate .The free volume model was employed to account for diffusion controlled, termination, propagation and initiation reaction. Frounchi et al. [3] developed a model by modifying the assumptions made in Marten-Hamielec and Vivaldo-Lima model to achieve a better conversion prediction especially at high conversion. Cunha et al. [4] were able to analyze the influence of parameters such as agitation speed, initiator concentration etc on the final properties of high impact polystyrene (PS). Maafa et al. [5] proposed a dynamic Monte Carlo model for bifunctional initiators .The results of their model compared well with the popular method of moment when applied to the polymerization of styrene. The production of polymers with desired end-use properties is of significant financial importance to the polymer industry. One of the most important molecular properties that control the end-use characteristics of polymers is the molecular weight distribution (MWD) as it directly affects the physical, mechanical and rheological properties of the final product [6]. The molecular weight distribution of a polymer can be characterized by the number average molecular weight (Mn), weight average molecular weight (Mw), and polydispersity (PD). Molecular weight distribution (MWD)/ Polydispersity (PDI) is considered as a fundamental property that determines polymer properties and thus its applications. The development of kinetic model for the estimation of polystyrene polydispersity is a tasky component of polymerization research. Knowledge of the rate coefficients of all fundamental steps in a free-radical polymerization process is of much importance as these are invariably related to the structure and therefore to the properties of the polymer. Experimental determination of the important property i.e Polydispersity index (PDI), is not only tasking and time consuming and but also very expensive. It is on a strong debit side in terms of cost in the polymer industry. Molecular weight distributions are determined by using the HP 1090 HPLC (high performance liquid chromatography) system, equipped with the HP 1047A RI (refractive index) detector and a four-column set configuration (105, 104, 103, 102 Å 30 cm x 7.8 mm microstyragel columns) [7]. The purpose of constructing a detailed kinetic model is to be able to correlate the reaction conditions (e.g. temperature, initiator concentration, reaction time etc) with the polymer quality (e.g. Molecular Weight Distribution). This attempt has been seldomly reported until recent time, nonetheless, details of modeling technique for the estimation of PDI that have found wide acceptance and those that were recently proposed can be found in [1]. Garg et al. [8] developed an analytical method of solving polymer kinetic model that predicts much better than previous numerical solution. Their method herein referred to as Garg approach is used extensively in this work rather than numerical solution. Table 1 contains the reaction mechanism considered. Many researchers such as [3,9-10], have used various versions of reaction mechanism and recorded varied success by comparing the numerical solution with experimental. We have limited our side reactions to chain transfer to monomer and solvents only to reduce the excessively increased level of complexity in the analytical solution of the kinetic model. This side reaction limitation made our reaction scheme (Table 1) similar to that of [8]

except where they introduced transfer to chain transfer agent. As earlier mentioned, the Garg approach we rely on utilizes the method of moment analysis in the modeling approach which has been found successful in predicting statistically averaged properties of polymers, [11-13] .The method of moments transforms the original high-dimensional systems of differential equations into a low-order system of equations by introducing the leading moments of the distributions of interest. The major limitation of models based on the method of moments (MM) is that they only track average quantities. While adequate for most situations, the MM cannot examine, for example, the combined effects of chain-scission and long-chain branching on the polymer architecture, or to incorporate chain-length–dependent termination kinetics into the kinetic scheme, [14-15]. Summarily, the aim of this study is to carry out a mass balance of all the chemical species present in the set of elementary reactions considered, derive an improved kinetic model for the styrene monomer conversion prediction and estimate the polymer PDI.

Our reaction of study (Polymerization reactions) has created a lot of unsolved and complex reaction problems, [16]. A problem associated with the reaction is a unique and unified set of elementary steps for free radical vinyl monomers polymerization which is still been debated and yet to be found wholistically in open literature inspite of the continuous intensive research from polymer reaction engineering /polymer and material chemistry research group. Herein, from the report of lengthy list of researchers such as [12-31], a basic free radical styrene polymerization chain process /mechanism was considered with three essential main reaction steps (Table 1)

Table 1: Kinetic mechanism of styrene polymerization adopted in this study

S/N	Polymerization stage	Polymerization mechanism	Reaction Rates (This Study)
		Main Reactions	
1.	Initiator Decomposition	$I \xrightarrow{k_d} 2R^\bullet$	$r_I = -k_d C_I$ $r_{R^\bullet} = 2fk_d C_I$
2.	Chain Initiation	$R^\bullet + M \xrightarrow{k_I} P_1$	$r_{R^\bullet} = -k_I C_M C_{R^\bullet}$ $r_M = -k_I C_M C_{R^\bullet}$ $r_{P_1} = k_I C_M C_{R^\bullet}$
3.	Thermal Initiation	$3M \xrightarrow{k_{thmi}} P_1$	$r_M = -k_{thmi} C_M^3$ $r_{P1} = k_{thmi} C_M^3$
4.	Propagation	$P_i + M \xrightarrow{k_P} P_{i+1}$	$r_{P_i} = -k_p C_{P_i} C_M$ $r_{P_i} = k_p C_{P_{i-1}} C_M$ $r_M = -k_p C_M \sum\limits_{i=1}^{\infty} C_{P_i}$
5.	Termination by combination	$P_i + P_j \xrightarrow{k_{tc}} D_{i+j}$	$r_{P_i} = -k_{tc} C_{P_i} \sum\limits_{j=1}^{\infty} C_{P_j}$ $r_{P_j} = -k_{tc} C_{P_j} \sum\limits_{i=1}^{\infty} C_{P_i}$ $r_{D_i} = \frac{1}{2} k_{tc} C_{p-j} \sum_{j=1}^{i-1} C_{P_j}$ [12]
		Side Reactions	
6.	Chain transfer to monomer	$P_i + M \xrightarrow{k_{trm}} P_1 + D_i$	$r_{P_i} = -k_{trm} C_{P_i} C_M$ $r_M = -k_{trm} C_M \sum\limits_{i=1}^{\infty} C_{P_i}$ $r_{D_i} = k_{trm} C_{p_i} C_M$ $r_{P_1} = k_{trm} C_{P_i} C_M$
7.	Chain transfer to polymer	$P_i + D_j \xrightarrow{k_{trp}} D_i + P_j$	$r_{P_i} = -k_{trp} C_{P_i} \sum\limits_{j=1}^{\infty} j\, C_{D_j}$ $r_{P_i} = k_{trp}\, i\, C_{D_i} \sum\limits_{i=1}^{\infty} C_{P_j}$ $r_{D_i} = -k_{trp}\, i\, C_{D_i} \sum\limits_{j=1}^{\infty} C_{P_j}$ $r_{D_i} = k_{trp} C_{P_i} \sum\limits_{j=1}^{\infty} j\, C_{D_j}$ $r_{LCB} = k_{trp} \sum_{i=1}^{\infty} C_{P_i} \sum_{j=1}^{\infty} j C_{D_j}$ [20]
8.	Chain transfer to Solvent	$P_i + S \xrightarrow{k_{trs}} D_i + P_1$	$r_{P_i} = -k_{trs} C_{P_i} C_S$

Where I= initiator , R* = generated radical , M = monomer ,Pi = growing polymer of lenght i , Dj= dead polymer of lenght j ,S = solvent

Garg et al. [8] reported the inclusion of f term in the reaction rate 1.When the radicals are formed upon initiator decomposition, they need to reach monomer molecules to form the primary radicals. However, due to several mechanisms induced by impurities and chemical species like solvent present in the reaction mixture, many radicals are destroyed or consumed before reacting with monomer. Thus, only a fraction (f) of radicals formed is able to form these primary radicals. Kiparissides et al. [32] in his report observed that one of the most important problems in simulating the operation of industrial high pressure polymer reactors is the selection of appropriate values of the various rate constants.

Kinetic Model Development

For easy expression of the kinetic rate equation using the above kinetic scheme, the following assumptions on modeling of free radical polymerization were made;

Modeling and Computational Assumptions

I. Steady state approximation for radicals.

II. The reaction rate constants are independent of chain lengths.

III. All the reactions are irreversible and elementary

IV. The reactor contents are perfectly mixed

V. Radicals generated are of equal reactivity (Flory's principle)

VI. Constant reactor pressure.

VII. Constant initiator efficiency.

VIII. Rate constants are independent of viscosity

Mass and Molar Balances for all Species Present (Monomer, Initiator, Solvent, Live radical and Dead Polymer):

Rate equation was established for each of the reaction steps (Table 1).The Garg approach was later employed in this aspect of the research. The mass balance of the chemical species in an ideal batch reactor was carried out. Details of the resulting chemical mass balances in terms of moment equation (Eq. 6-11) can be found in Appendix A of the supporting information materials of [8]. The method of moments is based on the statistical representation of the molecular properties of interest e.g weight- average molecular weight (Mw), number-average molecular weight (Mn) in terms of the leading moments of the respective distributions, [33]. Accordingly, the leading moments of the total number chain length distributions (TNCLDs) of live and dead polymer chains are defined as;

$$Live: \qquad \lambda_k = \sum_{i=1}^{\infty} i^k \, [P_i] \qquad (1)$$

$$Dead: \qquad \mu_k = \sum_{j=1}^{\infty} j^k \, [D_i] \qquad (2)$$

Number(M_n) and weight average molecular weights (M_w);

$$M_n = M_w \frac{\lambda_1 + \mu_1}{\lambda_0 + \mu_0} \qquad (3)$$

$$M_w = M_w \frac{\lambda_2 + \mu_2}{\lambda_1 + \mu_1} \qquad (4)$$

Polydispersity index (PDI) $= \frac{M_w}{M_n} = \frac{(\lambda_2 + \mu_2)(\lambda_0 + \mu_0)}{((\lambda_1 + \mu_1)^2} \qquad (5)$

There is need to generate six equations (Eq. 12-17) from the chemical mass balances to calculate the six moments ($\lambda_1, \lambda_2, \lambda_3, \mu_1, \mu_2, \mu_2$)for the determination of molecular weight distribution (Eq. 3-5).

$$\frac{1}{V_R}\frac{d(\lambda_0 V_R)}{dt} = 2fk_dI - (k_{tc} + k_{td})\lambda_0^2 = 2fk_dI - k_t\lambda_0^2 \qquad (6)$$

$$\frac{1}{V_R}\frac{d(\lambda_1 V_R)}{dt} = 2fk_dI + (1+R_{SM})k_{pr}M\lambda_0 - k_t\lambda_0\lambda_1 - (R_{MM}+R_{SM})k_{pr}M\lambda_1 \qquad (7)$$

$$\frac{1}{V_R}\frac{d(\lambda_2 V_R)}{dt} = 2fk_dI + (1+R_{SM})k_{pr}M\lambda_0 + 2k_{pr}M\lambda_1 - k_t\lambda_0\lambda_1 - (R_{MM}+R_{SM})k_{pr}M\lambda_2 \qquad (8)$$

$$\frac{1}{V_R}\frac{d(\mu_0 V_R)}{dt} = (R_M M + R_S S)\,k_{pr}\lambda_0 + (1 - \frac{R_T}{2})k_t\lambda_0^2 \qquad (9)$$

$$\frac{1}{V_R}\frac{d(\mu_1 V_R)}{dt} = (R_M M + R_S S)\,k_{pr}\lambda_1 + k_t\lambda_0\lambda_1 \qquad (10)$$

$$\frac{1}{V_R}\frac{d(\mu_2 V_R)}{dt} = (R_M M + R_S S)\,k_{pr}\lambda_2 + k_t\lambda_0\lambda_2 + R_T k_t\lambda_1^2 \qquad (11)$$

Where V_R = Volume of solution at any time t, L

I(Initiator concentration , mol/L) $= I_0 e^{-k_d t}$

M (Monomer concentration, mol/L) $= M_0 \exp[-B_0(1 - e^{-k_d t})]$

S (Solvent concentration,mol/L $= S_0 \exp[-R_S B_0(1 - e^{-k_d t})]$

$$B_0 = \sqrt{\frac{8fk_{pr}^2 I_0}{k_d k_t}} \qquad (11a)$$

$$k_{pr} = k_p + k_{fm} \qquad (11b)$$

$$R_{SM} = \frac{C_S}{(1+C_M)}\frac{M}{S} \approx \frac{C_S}{(1+C_M)}\frac{M_0}{S_0} \qquad (11c)$$

$$R_{MM} = \frac{k_{fm}}{k_{pr}} = R_M \qquad (11d)$$

$$C_S = \frac{k_{fs}}{k_p} \qquad (11e)$$

$$C_M = \frac{k_{fm}}{k_p} \qquad (11f)$$

$$R_S = \frac{k_{fs}}{k_{pr}} \qquad (11g)$$

In conjunction with Eq. 3-5, the values of λ0, λ1, λ2, μ0, μ1, μ2 for each of the reaction conditions (2a-15d) can be calculated.

2a.	t = 10 mins ,	C_I = 0.0825 mol/L	T = 363 K
2b.	t = 10 mins ,	C_I = 0.0620 mol/L	T = 363 K
2c.	t = 10 mins ,	C_I = 0.0413 mol/L	T = 363 K
2d.	t = 10 mins ,	C_I = 0.0206 mol/L	T = 363 K
3a.	t = 10 mins ,	C_I = 0.0825 mol/L	T = 333 K
3b.	t = 10 mins ,	C_I = 0.0620 mol/L	T = 333 K
3c.	t = 10 mins ,	C_I = 0.0413 mol/L	T = 333 K
3d.	t = 10 mins ,	C_I = 0.0206 mol/L	T = 333 K
5a.	t = 20 mins ,	C_I = 0.0825 mol/L	T = 363 K
5b.	t = 20 mins ,	C_I = 0.0620 mol/L	T = 363 K
5c.	t = 20 mins ,	C_I = 0.0413 mol/L	T = 363 K
5d.	t = 20 mins ,	C_I = 0.0206 mol/L	T = 363 K
6a.	t = 20 mins ,	C_I = 0.0825 mol/L	T = 333 K
6b.	t = 20 mins ,	C_I = 0.0620 mol/L	T = 333 K
6c.	t = 20 mins ,	C_I = 0.0413 mol/L	T = 333 K
6d.	t = 20 mins ,	C_I = 0.0206 mol/L	T = 333 K
8a.	t = 30 mins ,	C_I = 0.0825 mol/L	T = 363 K
8b.	t = 30 mins ,	C_I = 0.0620 mol/L	T = 363 K
8c.	t = 30 mins ,	C_I = 0.0413 mol/L	T = 363 K
8d.	t = 30 mins ,	C_I = 0.0206 mol/L	T = 363 K
9a.	t = 30 mins ,	C_I = 0.0825 mol/L	T = 333 K
9b.	t = 30 mins ,	C_I = 0.0620 mol/L	T = 333 K
9c.	t = 30 mins ,	C_I = 0.0413 mol/L	T = 333 K
9d.	t = 30 mins ,	C_I = 0.0206 mol/L	T = 333 K
11a.	t = 40 mins ,	C_I = 0.0825 mol/L	T = 363 K
11b.	t = 40 mins ,	C_I = 0.0620 mol/L	T = 363 K
11c.	t = 40 mins ,	C_I = 0.0413 mol/L	T = 363 K
11d.	t = 40 mins ,	C_I = 0.0206 mol/L	T = 363 K
12a	t = 40 mins ,	C_I = 0.0825 mol/L	T = 333 K
12b.	t = 40 mins ,	C_I = 0.0620 mol/L	T = 333 K
12c.	t = 40 mins ,	C_I = 0.0413 mol/L	T = 333 K
12d.	t = 40 mins ,	C_I = 0.0206 mol/L	T = 333 K
14a.	t = 50 mins ,	C_I = 0.0825 mol/L	T = 363 K
14b.	t = 50 mins ,	C_I = 0.0620 mol/L	T = 363 K
14c.	t = 50 mins ,	C_I = 0.0413 mol/L	T = 363 K
14d.	t = 50 mins ,	C_I = 0.0206 mol/L	T = 363 K
15a.	t = 50 mins ,	C_I = 0.0825 mol/L	T = 333 K
15b.	t = 50 mins ,	C_I = 0.0620 mol/L	T = 333 K
15c.	t = 50 mins ,	C_I = 0.0413 mol/L	T = 333 K
15d.	t = 50 mins ,	C_I = 0.0206 mol/L	T = 333 K

Monomer Conversion Model

Considering the elementary steps shown below, we have;

Initiation:

$$I \xrightarrow{k_d} nR^\bullet \tag{12}$$

$$r_{R^\bullet} = 2fk_dC_I \tag{13}$$

Chain Initiation:

$$R^\bullet + M \xrightarrow{k_{CI}} P^\bullet \tag{14}$$

$$r_{R^\bullet} = -k_{CI}C_MC_{R^\bullet} \tag{15}$$

Propagation:

$$P_1^\bullet + M \xrightarrow{k_P} P_{1+i}^\bullet \tag{16}$$

Termination by combination:

$$P_i^\bullet + P_j^\bullet \xrightarrow{k_{tc}} D_{i+j} \tag{17}$$

Termination by disproportionation:

$$P_i^\bullet + P_j^\bullet \xrightarrow{k_{td}} D_i + D_j \tag{18}$$
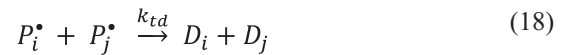
The following assumptions were made;

   I.   Steady state approximation for radical concentration.

   II.   Rate of initiation is equal to the rate of termination.

Mass balance on the generated radicals gives

$$r_{R^\bullet} = 2fk_dC_I - k_{CI}C_MC_{R^\bullet} \approx 0 \tag{19}$$

$$C_{R^\bullet} = \frac{2fk_dC_I}{k_{CI}C_M} \tag{20}$$

From Eq. (16), $\quad R_P = -\dfrac{dC_M}{dt} = k_pC_P^\bullet C_M \tag{21}$

Considering $\quad R_I = R_t \tag{22}$

$$2fk_dC_I = 2k_tC_P^{\bullet 2} \tag{23}$$

The factor 2 arises from the fact that at each incidence of termination reaction, two radicals disappear.

$$C^{2 \bullet}_{P} = \frac{2fk_d C_I}{2k_t} \tag{24}$$

$$C^{\bullet}_P = \sqrt{\frac{fk_d C_I}{k_t}} \tag{25}$$

Put Eq. (25) in Eq. (21), we have

$$R_P = -\frac{dC_M}{dt} = k_p \left(\frac{fk_d}{k_t}\right)^{\frac{1}{2}} C_I^{\frac{1}{2}} C_M \tag{26}$$

From (13),

$$\frac{dc_I}{dt} = -k_d C_I \tag{27}$$

Separating the variables and integrating both sides, we have

$$\frac{dc_I}{C_I} = -k_d dt \tag{28}$$

$$\ln C_I = -k_d t, \text{ putting limit from } C_{I_O} \text{ to } C_I \tag{29}$$

$$\frac{C_I}{C_{I_O}} = e^{-k_d t} \tag{30}$$

$$C_I = C_{I_O} e^{-k_d t} \tag{31}$$

Put Eq.(31) in Eq.(26),

$$-\frac{dC_M}{dt} = k_p \left(\frac{fk_d}{k_t}\right)^{\frac{1}{2}} \left(C_{I_O} e^{-k_I t}\right)^{\frac{1}{2}} C_M \tag{32}$$

Assume $k_\alpha = k_p \left(\frac{fk_d}{k_t}\right)^{\frac{1}{2}}$ \qquad (33)

$$-\frac{dC_M}{dt} = k_\alpha \left(C_{I_O}\right)^{\frac{1}{2}} e^{-\frac{k_d t}{2}} C_M \tag{34}$$

$$-\frac{dC_M}{C_M} = k_\alpha \left(C_{I_O}\right)^{\frac{1}{2}} e^{-\frac{k_d t}{2}} dt \tag{35}$$

Initial conditions:

$$C_M = C_{M_0} \qquad : t = 0 \text{ and defining}$$

$$x = \frac{M_0 - M}{M_0} = \left[1 - \frac{M}{M_0}\right] \tag{36}$$

For the Left hand side (L.H.S) of (35) :

$-\ln C_M$ taking limit from C_{M_0} to C_M , we have

$$-\ln C_M - -\ln C_{M_0} \tag{37}$$

$$-\ln C_M + \ln C_{M_0} \tag{38}$$

$$\ln C_{M_0} - \ln C_M = \ln \frac{C_{M_0}}{C_M} \tag{39}$$

But $x = 1 - \frac{C_M}{C_{M_0}}$ \qquad (40)

i.e $\frac{C_M}{C_{M_0}} = 1 - x$ \qquad (41)

$$\ln \frac{C_M}{C_{M_0}} = -\ln \frac{C_{M_0}}{C_M} = -\ln(1-x) \tag{42}$$

Integrating R.H.S of Eq. (40) , we have

$$\frac{k_\alpha \left(C_{I_O}\right)^{\frac{1}{2}} e^{-\frac{k_d t}{2}}}{\frac{-k_d}{2}} \tag{43}$$

$$\frac{-2}{k_d} k_\alpha \left(C_{I_O}\right)^{\frac{1}{2}} e^{-\frac{k_d t}{2}} \tag{44}$$

Putting limits from $t = 0$ to $t = t$

$$\frac{-2}{k_d} k_\alpha \left(C_{I_O}\right)^{\frac{1}{2}} e^{-\frac{k_d t}{2}} - \frac{-2}{k_d} k_\alpha \left(C_{I_O}\right)^{\frac{1}{2}} \tag{45}$$

$$\frac{2}{k_d} k_\alpha \left(C_{I_O}\right)^{\frac{1}{2}} - \frac{2}{k_d} k_\alpha \left(C_{I_O}\right)^{\frac{1}{2}} e^{-\frac{k_d t}{2}} \tag{46}$$

$$\frac{2}{k_d} k_\alpha \left(C_{I_O}\right)^{\frac{1}{2}} \left[1 - e^{-\frac{k_d t}{2}}\right] \tag{47}$$

Now equating Eq. (44) and Eq. (42),

$$-\ln(1-x) = \frac{2}{k_d} k_\alpha \left(C_{I_O}\right)^{\frac{1}{2}} \left[1 - e^{-\frac{k_d t}{2}}\right] \tag{48}$$

$$-\ln(1-x) = k_\beta \left[1 - e^{-\frac{k_d t}{2}}\right] \tag{49}$$

OR

$$\ln(1-x) = k_\beta \left[e^{-\frac{k_d t}{2}} - 1\right] \tag{50}$$

Where $k_\beta = \frac{2}{k_d} k_\alpha \left(C_{I_O}\right)^{\frac{1}{2}}$

The value of the unknown conversion (x) is to be calculated for each of the earlier stated conditions (2a-15d).

Westerhout et al. [34] in their report concluded that all published polymerization models are limited to narrow conversion ranges. One common trend observed which may further support their opinion in modeling polymerization processes is that the tasking direct determination of kinetic parameters have made researchers to rely frequently on kinetic parameters taken from literature values in which experimental conditions may be considerably different. Wu et al. [25], in their intensive report on batch polymerization of styrene stated a feature of free radical polymerization in bulk called the gel or trommsdorff Norish effect where the rate of reaction increases with an increase in conversion instead of decreasing as monomer is consumed. They attributed the gel effect to a decrease in the rate of termination and consequently an increase in the macro-radical concentration. They further related the decrease in termination rate to the restricted diffusion of macro-radicals in the polymerizing system of

high viscosity. Kee and Kyu [22] observed that the gel effect in styrene polymerization is not as strong as in other vinyl monomer polymerization especially methylmethacrylate (MMA) polymerization. Still, the gel effect is not quite negligible at high conversion or low solvent volume fraction.The approach of [22] was adopted in this study to correct our earlier monomer conversion model. Herein, the gel effect (g(t))correlation suggested by Friis and Hamielec [27] for bulk styrene polymerization is used and modified for solution polymerization as demonstrated by Hamer et al. [35].

$$g(t) = \frac{k_t}{k_{to}} = \exp[-2(B\,x + C\,x^2 + Dx^3)] \qquad (51)$$

where x and k_{to} denote the monomer conversion and the terminal rate constants at zero monomer conversion.

$$B = 2.57 - 5.05 \times 10\text{-}3\ T(K) \qquad (52)$$

$$C = 9.56 - 1.76 \times 10\text{-}2\ T(K) \qquad (53)$$

$$D = -3.03 - 7.85 \times 10\text{-}3\ T(K) \qquad (54)$$

The constants A, B and C were the work of Hui and Hamielec [28] over four decades ago to correct the gel effect and are used till today in majority of studies of vinyl monomer polymerization.

Incorporating the gel effect into the earlier model, we have

$$-\ln(1-x) = k_\beta[e^{\frac{-k_d t}{2}}\text{-}1] + g(t) \qquad (55)$$

The incorporation of the gel effect is intended to improve the model accuracy though also increases the model complexity.

$$ln\frac{1}{1-x} = k_\beta[e^{\frac{-k_d t}{2}}\text{-}1] + e^{-2(B\,x + C\,x^2 + Dx^3)} \qquad (56)$$

$$ln\frac{1}{1-x} = k_\beta e^{\frac{-k_d t}{2}}\text{-}k_\beta + e^{-2(B\,x + C\,x^2 + Dx^3)} \qquad (57)$$

Take the arc ln of both sides

$$\frac{1}{1-x} = -k_\beta\frac{-k_d t}{2} - ln^{-1}k_\beta - 2(B\,x + C\,x^2 + Dx^3) \qquad (58)$$

$$\frac{1}{1-x} + 2(B\,x + C\,x^2 + Dx^3) = -[k_\beta\frac{-k_d t}{2} + ln^{-1}k_\beta] \qquad (59)$$

Eq. 50 presented our earlier model which was able to predict lower styrene conversion especially when poor polar solvents such as toluene is used but failed completely to predict high styrene conversion. The model was improved upon and modified by the introduction of the Trommsdorf Norrish (gel) effect (Eq. 51) to obtain modified model (Eq. 59).The modified model which is a polynomial of order four was solved using Maple17.1 environment. Complex and negative roots obtained for the conversion were rejected.

Examination of compilation of literature values of rate parameters often reveals a very wide range of reported values in spite of the great number of papers published on the modeling of polymer reactors , Gupta et al. [36], Ehrlich and Mortimer [29], Goto et al. [24], Lee and Marano ([37], Takahashl and Ehrlich [38], Thies and Schoenemann [39], . Kiparissides et al. [32] in their review attributed the inconsistency of published set of rate constants to the complexity of the reaction, the large number of kinetic

parameters to be determined experimentally and the wide range of experimental conditions over which the kinetic parameters were estimated. To overcome the wide divergence in literature values of kinetic parameters for free radical polymerizations under ostensibly the same conditions, agreed values were given to some fundamental kinetic parameters for simple monomers. The work of Hui and Hamielec [28] and host of others (Table 3.1) had for long and up till date remained a point of reference. From their previous study of styrene homo-polymerization, rate-constants for the various elementary steps are given as shown (Table 2.0).

Table 2: Rate-constants for the various elementary steps

S/N	Kinetic Model Parameters	Reference
1.	k_p (L mol^{-1}min^{-1}) = 6.54×10^8 exp(-7051/RT)	
2.	k_{fm} (L mol^{-1}min^{-1}) = 1.38×10^8 exp(-12670/RT)	
3.	k_t (L mol^{-1}min^{-1}) = 7.53×10^{14} exp(-1677/RT)	[8]
4.	k_d (min^{-1}) = 1.69×10^{14} exp(-25383/RT)	
5.	k_{fs} (L mol^{-1}min^{-1}) = 9.95×10^{10} exp(-11,000/T)	
6.	k_{tc} (L mol^{-1}min^{-1}) = 2.67×10^8 exp(-2.084/RT)	
7.	f = 0.5	[40]
8.	M_0 (Styrene) = 8.612 mol/L	
9.	Molecular Weight of Styrene (Mw) =104.15	
10.	Temperature = 393,363 and 333K	
11.	S_0 (Acetone) = 13.38 mol/L	This study
12.	I_0 (Initiator) = 0.0825 mol/L, 0.0620mol/L, 0.0413 mol/L, 0.0206 mol/L	
13.	R = 1.987 cal/mol.K	

Where kd = Initiator dissociation rate constant

    kfm = Chain transfer to monomer

    kt = Termination rate constant

    kp = Propagation rate constant

    kfs = Chain transfer to solvent

    M0 = Initial monomer concentration

    R = Universal gas constant

    S0 = Initial solvent concentration

    I0 = Initial initiator concentration

RESULTS AND DISCUSSION

The experimental procedure and styrene monomer conversion results obtained are as reported in our earlier study [41].Herein contains the discussion of every aspect of the study and their corresponding graphs and tables.
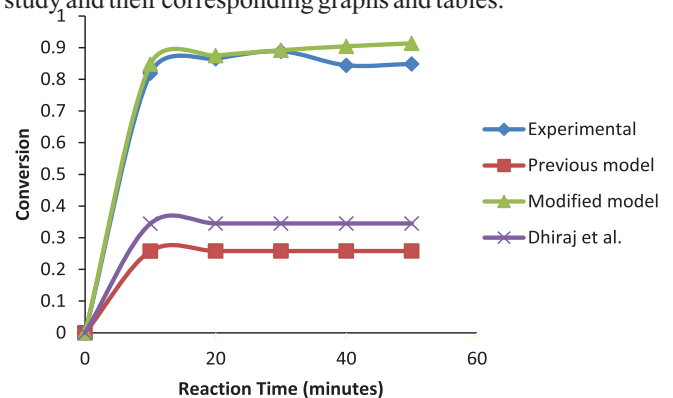
Fig. 1: Experimental data versus model data

The earlier model (Eq. 50) was improved upon and modified by the introduction of the Trommsdorf Norrish (gel) effect (Eq. 55) to obtain modified model (Eq. 59).The modified model which is a polynomial of order four was solved using Maple17.1 environment. In Fig. 1, the improved model similarly mimicked the experimental data up to the 30 minutes reaction time after which a very slight deviation was observed. Our previous conversion model exhibited same behaviour with that of Garg et al. The exclusion of the gel effect in the Garg et al. [8] conversion model may likely be responsible for its poor predicting potentials.

Eq. 12-17 as earlier mentioned were solved analytically as carried out by [8] for the calculation of the live moments of radicals and dead moments of polymers (Eq. 60-66) and the subsequent average properties (Mn, Mw, PDI) of the polymer. The details can be found in the supporting information of their paper. We however present herein a summary of the analytical solution.

$$\lambda_0 = \sqrt{\frac{2fk_d I_0}{k_t}} \qquad (60)$$

$$\lambda_1 = \lambda_0 \left[\frac{1+L}{1+R_P L} \right] \qquad (61)$$

$$\lambda_2 = \lambda_0 \left\{ \frac{1+(3-R_P)L+(2-R_P)L^2}{(1+R_P L)^2} \right\} \qquad (62)$$

$$\mu_0 = R_M\{M_0 - M\} + \{S_0 - S\} + \left(1 - \frac{R_T}{2}\right).2f.\{I_0 - I\} \qquad (63)$$

$$\mu_1 = \{M_0 - M\} + \{S_0 - S\} + 2f\{I_0 - I\} \qquad (64)$$

When $R_L < 0.1$, $P \approx 2 + R_T$

$$\mu_2 = P.(1 + R_{SM})^2.D_0.\left[\sum_{m=1}^{\infty}\left(\frac{C_0^m}{m.m!} - \frac{(C_0 y)^m}{m.m!}\right) - lny\right] + (2p - 1).(1 + R_{SM}).\{M_0 - M\} + (P - 1).2f.\{I_0 - I\} \qquad (65)$$

When $10 > R_L \geq 0.1$, $P = \frac{2}{R_L+1} + \frac{R_T}{(R_L+1)^2}$

$$\mu_2 = P.(1 + R_{SM})^2.D_0.\left[\sum_{m=1}^{\infty}\left(\frac{C_0^m}{m.m!} - \frac{(C_0 y)^m}{m.m!}\right) - lny\right] + (2p - 1).(1 + R_{SM}).\{M_0 - M\} + (P - 1).2f.\{I_0 - I\} \qquad (66)$$

When $R_L \geq 10$

$$\mu_2 = \left(\frac{2}{R_P}(1 + R_{SM})^2 - (1 + R_{SM}).\{M_0 - M\} + \left(\frac{R_T}{R_P^2}(1 + R_{SM})^2 + \frac{4}{R_P}(1 + R_{SM}) - 1\right).2f.\{I_0 - I\}\right) \qquad (74)$$

$$L = \frac{k_{pr}M\lambda_0}{2fk_d I} \qquad (66a)$$

$$R_P L = \frac{k_{fm}M + k_{fs}S}{k_t \lambda_0} = R_L \qquad (66b)$$

$$R_p = \frac{k_{fm}}{k_{pr}} + R_{SM} \qquad (66c)$$

$$R_T = \frac{k_{tc}}{k_t} \qquad (66d)$$

$$D_0 = \frac{2(k_{pr}M_0)^2}{k_t \lambda_0}e^{-C_0} \qquad (66e)$$

$$C_0 = 2B_0 \qquad (66f)$$

$$y = e^{\frac{-k_d t}{2}} \qquad (66g)$$

The PDI sometimes called heterogeneity ratio, dispersion ratio or non-uniformity coefficient is commonly used for the description of the polymer molecular weight distribution (MWD). Similarly, the values of the live moments are infinitesimally small compared to their corresponding dead moments (Table 3.0).The reports of many researchers such as [42-44] further confirmed the extremely low value of the live moments by modifying eq.19 as PDI $= \frac{M_w}{M_n} \approx \frac{\mu_2 \mu_0}{\mu_1^2}$

The PDI is a measure of the heterogeneity of sizes of molecules in the synthesized PS. Polymers of nature are typically monodispersed with PDI value of 1.00, [45]. This value indicates perfect uniformity, in which all molecules about (6.02×10^{23}) have exactly the same molecular weight. Rogosic et al. [46] in their research concluded that higher polydispersity index indeed implies wider MWD. However, contrary to the widely accepted belief, the reverse is not true. Similarly, as against the widely believed physical significance of PDI, Mencer [47] debunked that the ratio is an absolute measure of the molecular weight distribution of polymers. In the light of these, the main molecular weight of polymers remains a key parameter to characterize polymers especially in terms of physical property-processability relationship. Pinto et al.[48] further stated that temperature variation may affect negatively the quality of the polymer produced since changes in the polymerization temperature cause increase in PDI.

Table 4: Changes in Polymer average properties and PDI with Reaction parameters

Reaction time (min)	Mw	Mn	Polydispersity
	363 k, I_0 =0.0825 mol/L		
10	330.65	159.30	2.076
20	390.04	168.19	2.319
30	453.36	175.63	2.581
40	519.41	181.41	2.863
50	587 36	1.85 65	3.164
	363k, I_0=0.0620 mol/L		
10	378.54	167.80	2.256
20	450.72	178.07	2.531
30	527.94	186.66	2.828
40	608.76	193.33	3.149
50	692.20	198.24	3.492
	363k, I_0=0.0413 mol/L		
10	464.08	182.18	2.547
20	558.83	194.79	2.869
30	660.54	205.32	3.217
40	767.47	213.51	3.595
50	878.39	219.53	4.001
	363k, I_0=0.0206 mol/L		
10	673.17	214.74	3.135
20	821.56	232.61	3.532
30	981.62	247.55	3.965
40	1150.96	259.17	4.440
50	1327.80	267.70	4.960

There are many parameters that control molecular weight of the synthesized PS .The tables below (4-5) show a clearer trend of how some of these parameters such as reaction time, temperature and initiator concentration affects polymer

Table 3.0: PS Average properties at different reaction conditions

| Samples/	Live moments			Dead moments			Average properties		
Time(min)	λ_0 x10^9	λ_1 x10^9	λ_2 x10^9	μ_0	μ_1	μ_2	Mw	Mn	PDI
2a/10	9.9	0.204	0.632	0.04828	0.07394	0.23510	330.65	159.30	2.076
2b/10	8.6	0.191	0.653	0.03628	0.05854	0.21306	378.54	167.80	2.256
2c/10	7.0	0.175	0.695	0.02417	0.04234	0.18892	464.08	182.18	2.547
2d/10	5.0	0.154	0.805	0.01205	0.02489	0.16111	673.17	214.74	3.135
3a/10	2.3	4.6	0.139	0.00299	0.00596	0.03481	607.46	207.18	2.932
3b/10	2.0	4.3	0.143	0.00225	0.00482	0.03297	711.14	223.03	3.189
3c/10	1.6	3.9	0.152	0.00150	0.00360	0.03091	893.26	249.84	3.575
3d/10	1.1	3.4	0.174	0.00075	0.00223	0.02844	1325.99	310.50	4.270
5a/20	9.9	0.351	0.021	0.06830	0.11046	0.41430	390.04	168.19	2.319
5b/20	8.6	0.376	0.023	0.05133	0.08789	0.38092	450.72	178.07	2.531
5c/20	7.0	0.321	0.026	0.03419	0.06404	0.34414	558.83	194.79	2.869
5d/20	4.96	0.302	0.034	0.01706	0.03815	0.30137	821.56	232.61	3.532
6a/20	2.26	4.65	1.45	0.00588	0.01176	0.06935	613.46	208.11	2.948
6b/20	1.95	4.35	0.149	0.00442	0.00951	0.06572	718.31	224.10	3.205
6c/20	1.60	3.99	0.159	0.00294	0.00710	0.06164	902.44	251.15	3.59
6d/20	1.13	3.52	0.184	0.00147	0.00441	0.05677	1339.76	312.37	4.289
8a/30	9.9	0.704	0.093	0.07661	0.12938	0.56400	453.36	175.63	2.581
8b/30	8.6	6.92	0.00104	0.05758	0.10334	0.52458	527.94	186.66	2.828
8c/30	7.0	0.676	0.00123	0.03835	0.07572	0.48093	660.54	205.32	3.217
8d/30	5.0	0.656	0.00167	0.01913	0.04554	0.42982	981.62	247.55	3.965
9a/30	2.3	4.7	0.151	0.00866	0.01740	0.10362	619.49	209.03	2.964
9b/30	2.0	4.4	0.157	0.00650	0.01408	0.09824	725.52	225.17	3.222
9c/30	1.6	4.1	0.167	0.00433	0.01052	0.09220	911.67	252.47	3.611
9d/30	1.1	3.6	0.195	0.00216	0.00653	0.08499	1353.60	314.24	4.308
11a/40	9.9	0.157	0.00472	0.08006	0.13965	0.69748	519.41	181.41	2.863
11b/40	8.6	0.016	0.00538	0.06017	0.11184	0.65470	608.76	193.33	3.149
11c/40	7.0	0.153	0.00651	0.04008	0.08228	0.60722	767.47	213.51	3.595
11d/40	5.0	0.015	0.00906	0.01999	0.04982	0.55136	1150.96	259.17	4.44
12a/40	2.3	4.8	0.158	0.01133	0.02288	0.13762	625.56	209.96	2.979
12b/40	2.0	4.5	0.164	0.00851	0.01852	0.13054	732.77	226.24	3.239
12c/40	1.6	4.2	0.176	0.00567	0.01384	0.12259	920.95	253.79	3.629
12d/40	1.1	3.7	0.206	0.00283	0.00860	0.11310	1367.52	316.11	4.326
14a/50	9.9	0.0361	0.00026	0.08149	0.14547	0.82157	587.36	185.65	3.164
14b/50	8.6	0.0360	0.00029	0.06124	0.11674	0.77700	692.20	198.24	3.492
14c/50	7.0	0.3588	0.00036	0.04080	0.08611	0.72730	878.39	219.53	4.001
14d/50	5.0	0.0357	0.00051	0.02035	0.05238	0.66871	1327.80	267.70	4.960
15a/50	2.3	4.9	0.166	0.01391	0.02821	0.17136	631.67	210.89	2.995
15b/50	2.0	4.6	0.172	0.01046	0.02285	0.16263	740.07	227.31	3.256
15c/50	1.6	4.3	0.185	0.00697	0.01709	0.15283	930.29	255.10	3.647
15d/50	1.1	3.8	0.218	0.00347	0.01062	0.14111	1381.52	317.98	4.345

average properties such as Mw. Mn and the estimated PDI.

Table 5: Changes in Polymer average properties and PDI with Reaction parameters.

Reaction time (min)	Mw	Mn	Polydispersity
	333 k, I_0 =0.0825 mol/L		
10	607.46	207.18	2.932
20	613.46	208.11	2.948
30	619.49	209.03	2.964
40	625.56	209.96	2.979
50	631.67	210.89	2.995
	333k, I_0=0.0620 mol/L		
10	711.14	223.03	3.189
20	718.31	224.10	3.205
30	725.52	225.17	3.222
40	732.77	226.24	3.239
50	740.07	227.31	3.256
	333k, I_0=0.0413 mol/L		
10	893.26	249.84	3.575
20	902.44	251.15	3.590
30	911.67	252.47	3.611
40	920.95	253.79	3.629
50	930.29	255.10	3.647
	333k, I_0=0.0206 mol/L		
10	1325.99	310.50	4.270
20	1339.76	312.37	4.289
30	1353.60	314.24	4.308
40	1367.52	316.11	4.326
50	1381 52	317 98	4 345

Average polymer properties contained in Tables 4.0-5.0 when compared with other various reports such as [49-51] ,one can conclude that the choice of polymerization agents , nature of solvent, initiator and polymerization temperature, as well as the ratio of dose of reagents introduced during reaction have an impact on the final PS and its corresponding PDI. We noticed a reduced value of Mn and Mw at high temperature. Teferal et al. [52] similarly reported same trend but failed to adduce reason for such inspite of the detailed work done.

The weight average and number average molecular weight history with time are in Fig. 2 and 3 at different reaction temperature. The respective polydispersity histories are simultaeneously shown on the two figures. With increase in reaction time, a noticeable increase in Mw and Mn is observed accompanied by small increase in PDI. Similar trend was observed by [53-54].
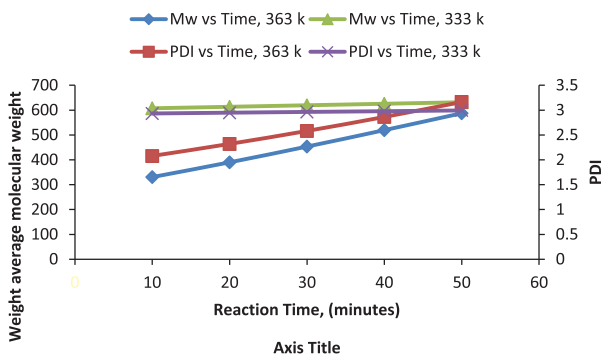

Fig 2: Plot of Mw / PDI vs Time at constant initiator concentration.
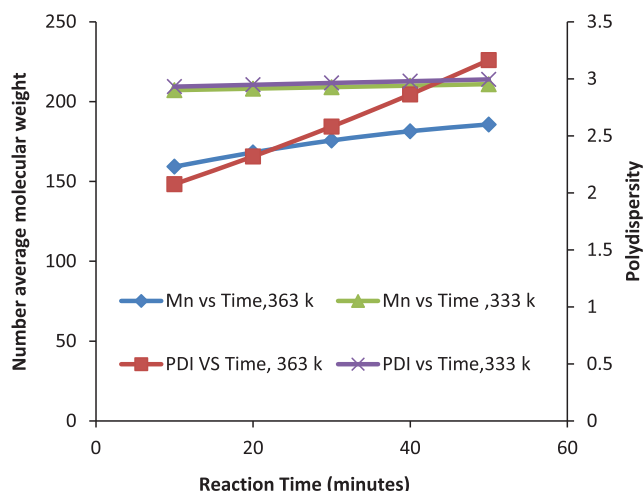
Fig 3: Plot of Mn / PDI vs Time at constant initiator concentration

In all, for a maximum reaction time, the PDI values range between 2.076 – 4.345 at temperature histories considered. Both Mn and Mw as depicted by Fig. 4 increase with reaction time presumably due to the free radical process, [54].The figures depict that PDI increases slightly with time with a more linear increase at higher temperature. This trend was similarly observed in the data published by Ivanchev et al. [55].
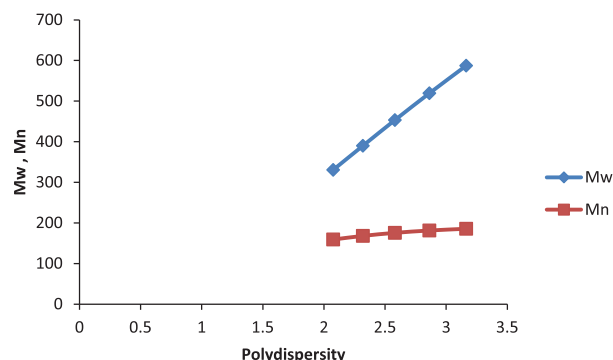
Fig. 4: Plot of Mw / Mn versus Polydispersity

Conclusion:

Elementary reactions typical of radical polymerization of vinyl monomers derived from literature were adopted in this study to model the polymerization process by mass balance of the chemical the species. The Garg approach to polymer kinetic modeling using method of moment and its subsequent analytical solution for the determination of PDI, Mw and Mn were also adopted. The earlier styrene monomer conversion model was improved upon by the inclusion of the trommsdorf Norrish affects, though complicated the conversion model but improved the model predictive potentials. The models arrived at are valuable tools in the design, simulation and optimization of PS reactors.

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