# Solution of the moment closure problem for reversible step-growth polymerization with unequal reactivity of monomer in homogeneous continuous-flow stirred tank reactors

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General reversible step-growth polymerization in homogeneous continuous-flow stirred tank reactors (HCSTRs) has been modelled by monomer having different reactivity and the moment closure problem has been solved. From dimensionless mole balance relations for all species, the generation relation has been derived. The resulting equation is a non-linear ordinary differential equation whose analytical solution yields all moments of the molecular-weight distribution to within an arbitrary constant. We have determined this constant through the molecular-weight distribution of the polymer determined in our previous paper. Sometimes high vacuum is applied in order to form polymer of high molecular weights. On doing this, the condensation product as well as the polymer leaves the reaction mass through flashing. We have examined the effect of flashing upon the molecular weight distribution of the polymer formed in HCSTRs.

**(Keywords: step-growth polymerization; molecular weight distribution; modelling)**

## INTRODUCTION

Step-growth polymerization of bifunctional monomers gives linear polymer and can be schematically represented by:

$$\mathrm{P}_m+\mathrm{P}_n \underset{k'_{p,m+n}}{\overset{k_{p,mn}}{\rightleftharpoons}} \mathrm{P}_{m+n}+\mathrm{W} \qquad m,n=1,2,\ldots \tag{1}$$

where $P_m$ and $P_n$ are polymer molecules of chain lengths $m$ and $n$ respectively. For every $m$ and $n$, equation (1) gives an elementary reaction and it is thus seen that there are infinite elementary reactions in step-growth polymerization. Above, W represents a low-molecular-weight condensation product and $k_{\mathrm{p},mn}$ and $k'_{\mathrm{p},m+n}$ are the rate constants for the forward and reverse steps.

We have already observed in the previous part of this series[1] that the polymer formed by a step-growth mechanism has a molecular-weight distribution. One defines the $k$th moment, $\lambda_k^*$, of a distribution as:

$$\lambda_k^*=\sum_{n=1}^{\infty}[\mathrm{P}_n] \qquad k=0,1,2,\ldots \tag{2}$$

where $[\mathrm{P}_n]$ represents the concentration of species $\mathrm{P}_n$ having chain length $n$. The reason for preferring moments over the molecular-weight distribution (*MWD*) is that some of these can be conveniently measured by experiments. The basic purpose of this paper is to determine analytically the moments of the distribution, which are few.

With the kinetic model for reversible step-growth polymerization, as discussed in our earlier work[1], one can establish mole balance relations for $\mathrm{P}_n$ species for all chain lengths $n$. With these *MWD* equations for homogeneous continuous-flow stirred tank reactors (HCSTRs), it is possible to derive generation relations for various moments defined by equation (1). It is found that $\lambda_1^*$ gives the total number of repeat units in the reaction mass, which is invariant. The generation relation for the zeroth moment $\lambda_0^*$ involves terms in $\lambda_0^*$ and $\lambda_1^*$. But as $\lambda_1^*$ is invariant, it can be determined analytically. However, the generation relation for $\lambda_2^*$ involves terms in $\lambda_3^*$ and lower moments, and that for $\lambda_3^*$ involves terms in $\lambda_4^*$ and lower moments, and so on. It is thus seen that $\lambda_2^*$, $\lambda_3^*$, $\lambda_4^*$, etc., cannot be determined without additional information, and this is referred to as the moment closure problem[2].

In the literature[3–5] in order to evaluate moments, workers have assumed an approximate form of the molecular-weight distribution and related $\lambda_3^*$ to $\lambda_2^*$, $\lambda_1^*$ and $\lambda_0^*$. Ideally, one would have liked to use the exact distribution, which unfortunately is not known. In the absence of this, Hulbert and Katz[6] have used Laguerre polynomials arbitrarily as the approximate *MWD* and determined $\lambda_3^*$ in terms of $\lambda_2^*$, $\lambda_1^*$ and $\lambda_0^*$. Subsequent works have assumed the *MWD* to be given by the Schulz–Zimm distribution, in this way developing the approximate moment closure relation[6–8].

In this paper, using moment-generating function $G(s\ \theta)$ defined as:

$$G(s,\theta)=\sum_{n=1}^{\infty}s^nP_n \tag{3}$$

we develop the generation relation for $G(s,\theta)$. This is found to be a Riccatti-type ordinary differential equation.

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Under the transformation of variables, this is changed into a second-order linear ordinary differential equation, which has singularities at $s=0$ and $s=1$. We showed in the previous part of this series[1] that the solution around $s=0$ gives the *MWD* of the polymer, while in this paper we examine the solution around $s=1$, which gives the moments of the distribution. In our efforts to find the moments of the polymer, we show that it can be done to within an arbitrary constant. The latter can be determined with the solution around the singularity at $s=0$. In this paper we have in this way determined all the moments of the distribution.

## THEORETICAL DEVELOPMENTS

We have modelled the general kinetics of step-growth polymerization by assuming that the monomer reacts with itself at a different rate. This means that our kinetic model is given by:

$$\begin{aligned} k_{mn}&=k_{11} && \text{when } m=n=1 \\ k_{mn}&=2k_{\text{p}} && \text{when } m\neq n,\ \text{for } m,n=2,3.\ldots \\ k_{mn}&=k_{\text{p}} && \text{when } m=n,\ \text{for } m=n=2,3\ldots \end{aligned} \tag{4}$$

In *Figure 1* we show a schematic diagram of a HCSTR, and assume that under the reactor conditions, the polymer can flash along with the condensation product.

Assuming steady-state operation of the HCSTR and allowing for flashing, the mole balance relations for an isothermal reactor are given by:

$$(P_1-P_{10})/\theta=-2(R-1)P_1^2-2P_1\lambda_0+2\beta W\sum_{r=2}^{\infty}P_r+(\rho_{\text{W}}/\rho\theta_{\text{W}})P_1 \tag{5a}$$

$$(P_2-P_{20})/\theta=RP_1^2-2P_2\lambda_0-\beta WP_2+2\beta W\sum_{r=3}^{\infty}P_r+(\rho_{\text{W}}/\rho\theta_{\text{W}})P_2 \tag{5b}$$

$$(P_n-P_{n0})/\theta=\sum_{r=1}^{n-1}P_rP_{n-r}-2P_n\lambda_0-\beta W(n-1)P_n+2\beta W\sum_{r=n+1}^{\infty}P_r+(\rho_{\text{W}}/\rho\theta_{\text{W}})P_n \tag{5c}$$

$$(W-W_0)/\theta=(R-1)P_1^2+\lambda_0^2-\beta W(\lambda_1-\lambda_0)+(\rho_{\text{W}}/\rho\theta_{\text{W}})W-(\rho_{\text{W}}/M_{\text{W}}\lambda_{10}^*\theta_{\text{W}}) \tag{5d}$$

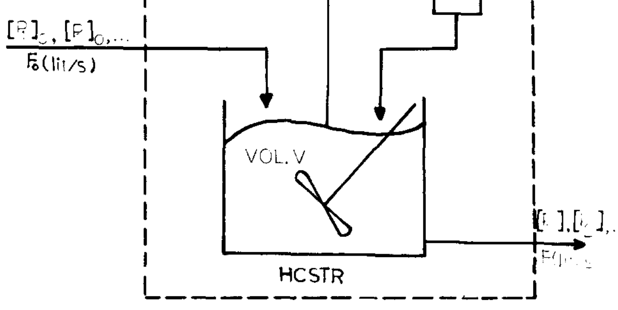

**Figure 1** Schematic diagram of HCSTR

where

$$R=k_{11}/k_{\text{p}} \tag{6a}$$

$$\beta=k'_{\text{p}}/k_{\text{p}} \tag{6b}$$

$$\theta=k_{\text{p}}\lambda_{10}^*V/F_0 \tag{6c}$$

$$P_n=[\text{P}_n]/\lambda_{10}^* \tag{6d}$$

$$\theta_{\text{W}}=k_{\text{p}}\lambda_{10}^*V/F_{\text{W}} \tag{6e}$$

The above kinetic equations can be combined into one single equation using the moment-generating function $G$ defined as:

$$G=\sum_{n=1}^{\infty}s^nP_n \tag{7}$$

The resulting equation is

$$\frac{\partial G}{\partial s}=\frac{1}{\beta Ws}G^2-\frac{1}{\beta Ws}\left(2\lambda_0+\frac{(1+s)\beta W}{(1-s)}+\frac{1}{\theta}-\frac{\rho_{\text{W}}}{\rho\theta_{\text{W}}}\right)G+\frac{1}{\beta Ws}\left(\frac{G_0}{\theta}+P_1^2(R-1)(s^2-2s)+2\beta W\frac{s\lambda_0}{1-s}\right) \tag{8}$$

The non-linearity in (8) is eliminated by using the transformation:

$$G=-\beta Ws(\partial y/\partial s)/y \tag{9}$$

The variation of $y$ is the following second-order hypergeometric differential equation:

$$s(1-s)\,\mathrm{d}^2y/\mathrm{d}s^2+[\alpha'(1-s)+2]\,\mathrm{d}y/\mathrm{d}s+[\alpha_0^2\theta(1-s)R(s)+(\alpha-\alpha_0)]y=0 \tag{10}$$

where

$$\alpha_0=1/\beta W\theta \tag{11a}$$

$$\alpha=\alpha_0+2\lambda_0/\beta \text{W} \tag{11b}$$

$$\alpha'=\alpha-\rho_{\text{W}}/\rho\theta_{\text{W}}\beta W \tag{11c}$$

$$R(s)=R_0+R_1s+R_2s^2+R_3s^3+\ldots \tag{11d}$$

$$R_0=P_{10}-2P_1^2(R-1)\theta \tag{11e}$$

$$R_1=P_{20}+P_1^2(R-1)\theta \tag{11f}$$

$$R_n=P_{n+1,0}\qquad n\geqslant 2 \tag{11f}$$

On examination of equation (10), it is observed that it has two singularities, one at $s=0$ and the other at $s=1$. The solution around the former gives the *MWD* of the polymer, which has been examined in the previous part of the study[1] and is summarized in *Table 1*. The solution around $s=1$ gives the moments of the distribution in a natural way, which is shown as follows.

On examining the defining equation (7) for the moment-generating function $G$, it is seen that the coefficient of $s^n$ represents the molar concentration of species $\text{P}_n$. If we substitute:

$$s=1-u \tag{12}$$

and expand term by term, equation (7) becomes:

$$G=\lambda_0-\lambda_1u+\tfrac{1}{2}(\lambda_2-\lambda_1)u^2+\ldots+(-1)^k\left(\sum_{n=1}^{\infty}\frac{n(n-1)(n-2)\ldots(n-k+1)}{k!}P_n\right)\times u^k+\ldots. \tag{13}$$

It is thus seen that the solution of equation (10) around

**Table 1** Solution around singularity $s=0$

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Series solution[9]

$$y=\sum_{m=0} C_m s^{m+\sigma} \tag{1}$$

Indicial equation

$$\sigma[(\sigma-1)+(\alpha'+2)]=0 \tag{1.2}$$

Roots of indicial equation

$$\sigma_1=0 \qquad \sigma_2=-(1+\alpha) \tag{1.3}$$

$\sigma_2$ leads to infeasible solution

General solution for $y$

$$y=C_0\sum_{m=0}^{\infty} r_m s^m \qquad r_0=1,\ r_m=C_m/C_0 \tag{1.4}$$

Recursive relation for $r_m$

$$r_{m+1}=\{[m(m-1+\alpha')-(\alpha-\alpha_0)]r_m+\alpha_0^2\theta(\Sigma_{m-1}-\Sigma_m)\}/(m+1)(m+\alpha'+2) \tag{1.5a}$$

where

$$\Sigma_m=\sum_{j=0}^{m} \mathrm{R}_j \mathrm{r}_{m-j} \tag{1.5b}$$

$$G=-\beta W r_1 s\frac{1+a_1 s+a_2 s^2+\ldots}{1+b_1 s+b_2 s^2+\ldots}=-\beta W r_1 s(1+c_1 s+c_2 s^2\ \ldots) \tag{1.6}$$

$$a_m=(m+1)r_{m+1}/r_1 \qquad b_m=r_m \qquad c_m=a_m-b_m-\sum_{j=1}^{m-1} b_j c_{m-j} \tag{1.7}$$

*MWD* of the polymer

$$P_1=\beta W r_1 \qquad P_n=\beta W r_1 c_{n-1} \qquad n\geqslant 2 \tag{1.8}$$

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the singularity at $s=1$ gives various moments of the distribution. We rewrite equation (10) in terms of $u$ to obtain:

$$u(u-1)\,\mathrm{d}^2y/\mathrm{d}u^2-(\alpha'u+2)\,\mathrm{d}y/\mathrm{d}u+[\alpha_0^2\theta u R^*(u)+(\alpha-\alpha_0)]y=0 \tag{14}$$

Here, $\alpha_0$, $\alpha$ and $\alpha'$ remain unchanged in definition but:

$$R^*(u)=R_0^*+R^*u+R_2^*u^2+\ \ldots \tag{15a}$$

$$R_0^*=\lambda_{00}-P_1^2(R-1)\theta \tag{15b}$$

$$R_1^*=-(\lambda_{10}-\lambda_{00})-P_1^2(R-1)\theta \tag{15c}$$

$$R_k^*=(-1)^k\left(\sum_{n=k}^{\infty}\frac{(n-1)(n-2)\ldots(n-k)}{k!}\right)P_{n0} \qquad k\geqslant 2 \tag{15d}$$

In order to determine an analytical solution of equation (14), one can propose a series solution of the form:

$$y=C_0\sum_{m=0}^{\infty} r_m u^{m+\sigma} \tag{16}$$

For this the roots of $\sigma$ are 3 and 0. Therefore, the general solution must have a logarithmic term because of the integral difference between the roots. The two solutions corresponding to $\sigma_1=3$ and $\sigma_2=0$ are then written as:

$$y_1(u)=C_0\sum_{m=0}^{\infty} r_m u^{m+3} \tag{17a}$$

and

$$y_2(u)=C_0^*\sum_{m=0}^{\infty} r_m^* u^m+k_3 y_1(u)\ln u \tag{17b}$$

Substituting the second solution in the differential equation for $y$ reveals that the logarithmic term drops out because the product $k_3C_0$ should be identically zero in order to keep $\lambda_1$ invariant. Therefore the overall series solution can be written as:

$$y=C_0^*\sum_{m=0}^{\infty} r_m^* u^m \tag{18}$$

where

$$r_0^*=1 \tag{19a}$$

and the coefficient series $r^*$ is obtained recursively from:

$$(i+1)(i-2)r_{i+1}^*=[i(i-1+\alpha')-(\alpha-\alpha_0)]r_1^*-\alpha_0^2\theta\Sigma_{i-1}^* \tag{19b}$$

$$\Sigma_i^*=\sum_{j=0}^{i} R_j^*\,\mathrm{r}_{i-j}^* \tag{19c}$$

Using the transformation:

$$G=\beta W(1-u)(\partial y/\partial u)/y \tag{20}$$

we revert back to $G$:

$$G=\beta W\frac{r_1^*}{r_0^*}\frac{1+a_1^*u+a_2^*u^2+\ \ldots}{1+b_1^*+b_2^*u^2+\ \ldots} \tag{21a}$$

$$=\beta W\frac{r_1^*}{r_0^*}(1+c_1^*u+c_2^*u^2+\ \ldots) \tag{21b}$$

where

$$a_i^*=[(i+1)r_{i+1}^*-ir_i^*]/r_1^* \tag{22a}$$

$$b_i^*=r_i^* \tag{22b}$$

and

$$c_i^*=a_i^*-b_i^*-\sum_{j}^{i-1} c_j^* b_{i-j}^* \tag{22c}$$

Comparing the above series solution of $G$ with equation (13) gives the algebraic relationship for the moments:

$$\lambda_0=\beta W r_1^* \tag{23}$$

$$\lambda_1=-\beta W r_1^* c_1^* \tag{24}$$

$$\tfrac{1}{2}(\lambda_2-\lambda_1)=\beta W r_1^* c_2^* \tag{25}$$

$$\tfrac{1}{6}(\lambda_3-3\lambda_2+2\lambda_1)-\beta W r_1^* c_3^* \tag{26}$$

$$\tfrac{1}{24}(\lambda_4-6\lambda_3+11\lambda_2-6\lambda_1)=\beta W r_1^* c_4^* \tag{27}$$

and so on.

## RESULTS AND DISCUSSION

On careful examination of the recursive relation in equation (19) it is seen that $r_3^*$ is indeterminate. This arbitrary constant can be determined only through knowledge of the *MWD* of the polymer. Algebraic manipulation of equation (22) (at $m=2$) and equation (25) yields the desired result:

$$\frac{3r_3^*-2r_2^*}{r_1^*}=r_2^*+r_1^*\left(\frac{2r_2^*}{r_1^*}-1-r_1^*\right)+\frac{\lambda_2-\lambda_1}{2\beta W r_1^*} \tag{28}$$

or

$$r_3^*=\frac{2}{3}r_2^*+r_1^*r_2^*-\frac{1}{3}r_1^{*2}(1+r_1^*)+\frac{1}{6}r_1\left(\sum_{n=1} n^2c_{n-1}-\lambda_1\right) \tag{29}$$

Flashing of the condensation product occurs when a vacuum is applied to the rector. This is done in order to push the overall polymerization in the forward direction and to obtain polymer of high molecular weight. Without flashing (i.e. $F_W = 0$) we have the case of closed reactor operation in which stoichiometry is satisfied and the concentration of condensation product in the reactor is given by:

$$W = W_0 + \lambda_{00} - \lambda_0 \tag{30a}$$

Above $W_0$ and $\lambda_{00}$ are the condensation product and polymer in the feed. When vacuum is applied, two situations may arise: W alone leaves the reactor or W leaves along with the polymer. In the first case, W is determined by assuming vapour–liquid equilibrium (assumed to be governed by Raoult's law) between the reaction mass and escaping vapour. Here:

$$P_W^0 W/(\lambda_0 + W) = P_T \tag{30b}$$

and

$$W = \frac{(W_0 + \lambda_{00})}{(1 - \rho_W\theta/\rho\theta_W)} - \lambda_0 - \frac{\rho\rho_W\theta}{M_W\lambda_{10}^*(\rho\theta_W - \rho_W\theta)} \tag{30c}$$

where $P_T$ is the total pressure of the system and $P_W^0$ is the vapour pressure of the condensation product. Above $F_W$ is the rate at which condensation product is escaping from the HCSTR.

In the situation when both condensation product and polymer evaporate, it is assumed that higher oligomers have a lower relative volatility and hence remain in the reaction mass. Only monomer $P_1$ is assumed to leave the reactor, which we recycle after separation. In this case, the vapour–liquid equilibrium is given by:

$$P_{P_1}^0 P_1/(\lambda_0 + W) + P_W^0 W/(\lambda_0 + W) = P_T \tag{30d}$$

and equation (30c) remains valid.

It is now an easy matter to obtain the moments of the polymer formed in HCSTRs. For given kinetic parameters ($\beta$ and $R$), feed conditions (specified $R(s)$ in equation (11)) and reaction conditions (reactor pressure $P_T$ and temperature $T$), it is possible to determine if there is flashing. If there is no flashing, $W$ is given by equation (30a) and is substituted in equations (5a) and (31) for $P_1$ and $\lambda_0$. The net polymer balance is obtained by adding equations (5a, b, c) for all $n$:

$$(\lambda_0 - \lambda_{00})/\theta = -(R-1)P_1^2 - \lambda_0^2 + \beta W(\lambda_1 - \lambda_0) + (\rho_W/\rho\theta_W)\lambda_0 \tag{31}$$

We further observe that in equation (5a):

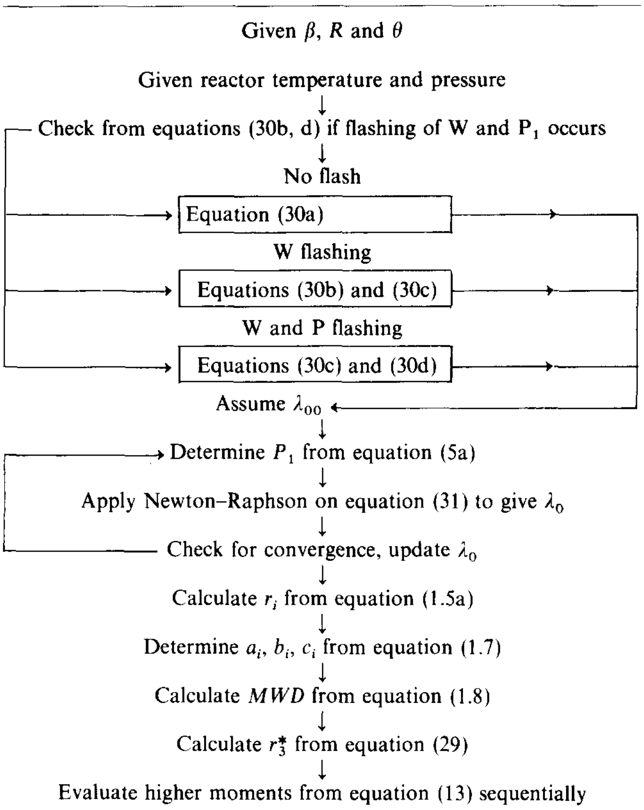
$$\sum_{n=2}^{\infty} P_n = \lambda_0 - P_1 \tag{32}$$

Equations (5a) and (31) are solved simultaneously. A convenient method of solving these is to use the Newton–Raphson technique. A trial value of $\lambda_0$ is assumed and the quadratic equation (5a) gives $P_1$. The feasible value of $P_1$ is substituted in the following rearranged form of equation (31):

$$F_P = (\lambda_0 - \lambda_{00})/\theta - (R-1)P_1^2 - \lambda_0^2 + \beta W(\lambda_1 - \lambda_0) + (\rho_W/\rho\theta_W)\lambda_0 \tag{33}$$

For the correct value of $\lambda_0$, $F_P$ reduces to zero. Otherwise one updates the previous trial value of $\lambda_0$ by moving along the gradient (keeping $\lambda_0 \leqslant 1$). The value of $F_P$ is checked and iteration is continued till convergence is achieved.

**Table 2** Algorithm for computation of moments of polymer formed in HCSTRs


Given $\beta$, $R$ and $\theta$

Given reactor temperature and pressure

Check from equations (30b, d) if flashing of W and $P_1$ occurs

No flash

Equation (30a)

W flashing

Equations (30b) and (30c)

W and P flashing

Equations (30c) and (30d)

Assume $\lambda_{00}$

Determine $P_1$ from equation (5a)

Apply Newton–Raphson on equation (31) to give $\lambda_0$

Check for convergence, update $\lambda_0$

Calculate $r_i$ from equation (1.5a)

Determine $a_i$, $b_i$, $c_i$ from equation (1.7)

Calculate *MWD* from equation (1.8)

Calculate $r_3^*$ from equation (29)

Evaluate higher moments from equation (13) sequentially

When there is flashing one substitutes either equation (30b) or equation (30d) into (5a) and (31) and repeats the procedure for determining $\lambda_0$ and $P_1$.

A flowchart for the computation is presented in *Table 2*. Once $\lambda_0$ and $P_1$ are evaluated it is an easy matter to determine the *MWD* and consequently the constant $r_3^*$. Higher moments are calculated sequentially from equation (13) as shown in the chart.

## CONCLUSIONS

We have solved analytically the moment closure problem in reversible step-growth polymerization carried out in HCSTRs with unequal reactivity of the monomer. The dimensionless mole balance equations for all species were first written down and then, with the use of the moment-generating function $G(s, \theta)$, they were combined appropriately to give its generation relation. This is a non-linear ordinary differential equation, which under transformation becomes a second-order linear differential equation. The latter has singularities at $s=0$ and $s=1$. The extended power series solution of Frobenius has been proposed around both singularities[9]. We show that the series solution around $s=0$ gives the *MWD* and the one around $s=1$ gives the moments of the distribution.

The series solution around singularity $s=1$ has an arbitrary constant $r_3^*$, which, once evaluated, gives all moments of the distribution. It has been shown that $r_3^*$ can be calculated only from knowledge of the *MWD*.

In order to get high-molecular-weight polymer in HCSTRs a high vacuum is applied to push the overall polymerization in the forward direction. Depending on the vapour pressure of the oligomers, sometimes low-molecular-weight polymer also escapes along with the condensation product. We have modelled all possibilities of flashing from the reactor. The limiting situation $\theta \rightarrow \infty$ represents the polymer at equilibrium. The *MWD* for various flashing possibilities, and for equilibrium, have also been presented. We further show that whether we are considering vacuum application or equilibrium, the moment closure problem remains unaltered. Finally a computer algorithm has been presented which identifies whether there is flashing under the reactor conditions, then appropriately calculates $\lambda_0$, $P_1$ and $W$, which ultimately gives all moments of the polymer formed in HCSTRs.

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