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Mathematical Analysis of the Formation of Molecule Sizes on a Spinning Disc Reactor

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Summary: A mathematical analysis of the behaviour of the molecular weights of addition polymers during a polymerisation process is described. Spinning disc reactor (SDR) technology has been shown to yield significant improvements in terms of polymerisation rates whilst retaining close control of the molecular weights and the molecular weight distributions[1,2]. However, understanding of the kinetics of the polymerisation process on a SDR remains unresolved. One of the questions to be addressed concerns the sizes of the macromolecules preferably formed during the polymerisation process. To address this question, a mathematical analysis of the observed trends in number and weight average molecular weight, monomer concentration and polydispersity during the polymerisation process on a SDR has been undertaken. To validate the results, experimental data obtained from benzoyl peroxide initiated free radical polymerisation of styrene on a SDR[2] was used. It was concluded that most of the monomers consumed are in the growth of smaller size chains.

Keywords: addition polymerization; mathematical analysis; molecule sizes; polystyrene; spinning disc reactor

Introduction

The modelling of free-radical polymerisations is important both scientifically and industrially since the reaction mechanism is widely used for the synthesis of addition polymers. Spinning disc reactor (SDR) technology has been shown to yield significant improvements in polymerisation rates whilst maintaining tight control of the molecular weights and the molecular weight distributions[1,2]. The ability to utilise SDR technologies for free radical polymerisation would realise a new dimension in polymerisation processes. To achieve this goal, the determination of the kinetics of polymerisation processes on SDRs is a fundamental requirement. Consequently it

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is important to understand the mechanisms of rotating disc reactors and be able to explain the observed phenomena, such as significant increases in conversion occurring with no increase in molecular weights. A study is presented whereby the intervals of the molecule sizes preferably formed on the SDR are determined for specific experimental conditions. The polymerization system[2] consisted of styrene as the monomer with an initial concentration of 7.28 mol/dm^3, benzoyl peroxide as initiator with an initial concentration of $5.1 \cdot 10^{-2}$ mol/dm^3 and toluene as solvent with an initial concentration of 1.567 mol/dm^3. Polymerisation was started in a batch reactor with the product being feed to the SDR. In both reactors, the temperatures were initially set to 90°C. The results are presented in Figures 1 to 3.

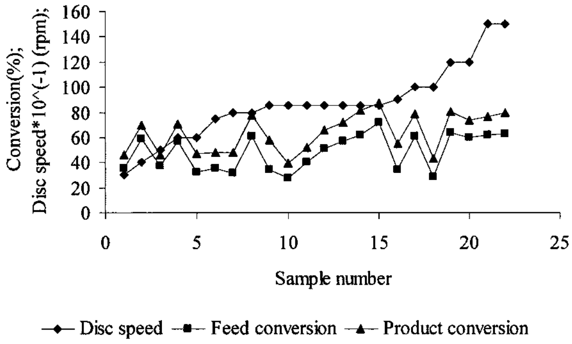

Figure1. Experimentally determined SDR feed and product conversion for different disc speeds.

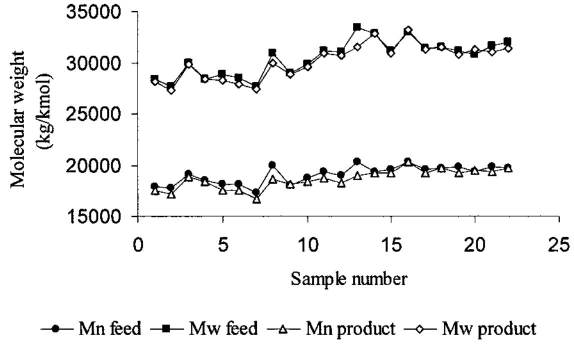

Figure 2. Molecular weights measured in the SDR feed and product.

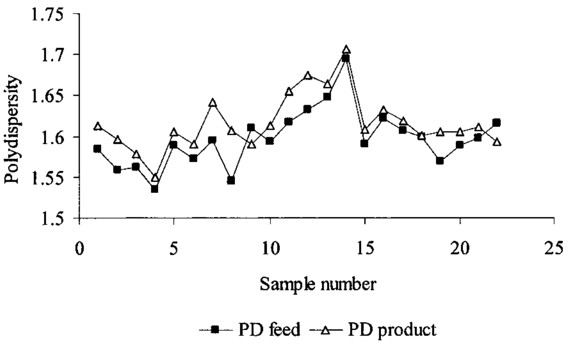

Figure 3. Polydispersity of SDR feed and product.

From the presented experimental data, a number of trends were identified. A slight decrease in the number average and weight average molecular weight of the SDR product was observed compared with the batch pre-polymerised SDR feed as well as a significant decrease in monomer concentration (i.e. increase in conversion) combined with a slight increase in polydispersity. These trends were mathematically analysed and solved independently. The solution of the individual analyses was a set of chains of specific length with the overall solution being the intersection of the individual solutions.

Mathematical Analysis of Trends Identified from Experimental SDR Data

Number average molecular weight is defined[3] as the total weight of all the molecules in a polymer divided by the total number of moles present:

$$M_n = \frac{\sum N_i \cdot M_i}{\sum N_i} \tag{1}$$

where the summation is over the different sizes of polymer molecules. M_n is the number average molecular weight, M_i is the weight of polymer molecule consisting of i monomer units and N_i is the number of moles whose weight is M_i. In the case of addition polymerisation, M_i can be defined as:

$$M_i = i \cdot M_{monomer} \tag{2}$$

where $i = (1,\dots,x)$ is the number of monomer units built in polymer molecule and $M_{monomer}$ is the molecular weight of the monomer unit. Combining Equations (1) and (2) gives:

$$\frac{\sum i \cdot N_i}{\sum N_i} = \frac{M_n}{M_{monomer}} \tag{3}$$

Equation (3) can then be written as:

$$\frac{1 \cdot N_1 + 2 \cdot N_2 + \dots + i \cdot N_i + \dots + x \cdot N_x}{N_1 + N_2 + \dots + N_i + \dots + N_x} = \frac{(M_n)_{feed}}{M_{monomer}} \tag{4}$$

where $(M_n)_{feed}$ is the number average molecular weight of SDR feed. From the experimental SDR data[2] presented in Figures 1 and 2, a decrease in the number average molecular weight was observed with the increase in conversion being significant. The trend of conversion is important for allowing differentiation between polymerisation and degradation. For example where the molecular weights are decreasing, it could be hypothesised that polymer degradation is occurring. However, for the case of a SDR reactor, it is evident from the data that an increase in conversion is present and therefore polymer degradation is not taking place. This observed behaviour can be included in Equation (4):

$$\frac{1 \cdot N_1 + 2 \cdot N_2 + \dots + i \cdot (N_i + \Delta_i) + \dots + x \cdot N_x}{N_1 + N_2 + \dots + (N_i + \Delta_i) + \dots + N_x} = \frac{(M_n)_{product}}{M_{monomer}} \tag{5}$$

where Δ_i is the increase in number of moles of macromolecule with i monomer units, i.e. $\Delta_i = 1,2,3,\dots$ and $(M_n)_{product}$ is the number average molecular weight of SDR product. To simplify subsequent equations, $\frac{(M_n)_{feed}}{M_{monomer}}$ is denoted by k_1 and $\frac{(M_n)_{product}}{M_{monomer}}$ by k_2. Rearranging Equation (5) gives:

$$\frac{1 \cdot N_1 + 2 \cdot N_2 + \dots + i \cdot N_i + \dots + x \cdot N_x + i \cdot \Delta_i}{N_1 + N_2 + \dots + (N_i + \Delta_i) + \dots + N_x} = k_2 \tag{6}$$

Furthermore:

$$\frac{k_1 \cdot (N_1 + N_2 + \dots + N_i + \dots + N_x) + i \cdot \Delta_i + k_1 \cdot \Delta_i - k_1 \cdot \Delta_i}{N_1 + N_2 + \dots + (N_i + \Delta_i) + \dots + N_x} = k_2 \tag{7}$$

Equation (7) can be then rewritten as:

$$\frac{k_1 \cdot (N_1 + N_2 + ... + N_i + ... + N_x + \Delta_i) + \Delta_i \cdot (i - k_1)}{N_1 + N_2 + ... + (N_i + \Delta_i) + ... + N_x} = k_2 \quad (8)$$

or:

$$k_1 + \frac{\Delta_i \cdot (i - k_1)}{N_1 + N_2 + ... + (N_i + \Delta_i) + ... + N_x} = k_2 \quad (9)$$

To define a decrease in number average molecular weight, the following condition requires to be satisfied:

$$(M_n)_{product} < (M_n)_{feed} \quad (10)$$

This can be represented as:

$$k_1 + \frac{\Delta_i \cdot (i - k_1)}{N_1 + N_2 + ... + (N_i + \Delta_i) + ... + N_x} < k_1 \quad (11)$$

Since $\Delta_i > 0$ and $N_1 + N_2 + ... + (N_i + \Delta_i) + ... + N_x > 0$, the solution of Equation (11) is:

$$i < k_1, \text{ or after substitution } i < \frac{(M_n)_{feed}}{M_{monomer}} \quad (12)$$

However if the trend observed indicated that the number average molecular weight increases with time, alongside an increase in conversion, the condition to be satisfied becomes:

$$i > \frac{(M_n)_{feed}}{M_{monomer}} \quad (13)$$

To maintain a constant number average molecular weight over time whilst increasing conversion, an increase in the number of chains is necessary hence the following condition requires to be satisfied:

$$i = \frac{(M_n)_{feed}}{M_{monomer}} \quad (14)$$

A second analysis considered weight average molecular weight (M_w)[3]:

$$M_w = \frac{\sum N_i \cdot M_i^2}{\sum N_i \cdot M_i} \quad (15)$$

Substituting Equation (2) into Equation (15) gives:

$$\frac{\sum i^2 \cdot N_i}{\sum i \cdot N_i} = \frac{M_w}{M_{monomer}} \tag{16}$$

In expanded form, Equation (16) can be presented as:

$$\frac{1^2 \cdot N_1 + 2^2 \cdot N_2 + \ldots + i^2 \cdot N_i + \ldots + x^2 \cdot N_x}{1 \cdot N_1 + 2 \cdot N_2 + \ldots + i \cdot N_i + \ldots + x \cdot N_x} = \frac{(M_w)_{feed}}{M_{monomer}} \tag{17}$$

where $(M_w)_{feed}$ is the weight average molecular weight of the SDR feed. From the experimental SDR data[2] presented in Figures 1 and 2, a decrease in weight average molecular weight was detected, alongside a significant increase in conversion. This behaviour can be incorporated within Equation (17):

$$\frac{1^2 \cdot N_1 + 2^2 \cdot N_2 + \ldots + i^2 \cdot (N_i + \Delta_i) + \ldots + x^2 \cdot N_x}{1 \cdot N_1 + 2 \cdot N_2 + \ldots + i \cdot (N_i + \Delta_i) + \ldots + x \cdot N_x} = \frac{(M_w)_{product}}{M_{monomer}} \tag{18}$$

where $(M_w)_{product}$ is the weight average molecular weight of SDR product. Again, to simplify the subsequent equations, $\frac{(M_w)_{feed}}{M_{monomer}}$ is denoted as k_3 and $\frac{(M_w)_{product}}{M_{monomer}}$ as k_4. Rearranging Equation (18) gives:

$$\frac{1^2 \cdot N_1 + 2^2 \cdot N_2 + \ldots + i^2 \cdot N_i + \ldots + x^2 \cdot N_x + i^2 \Delta_i}{1 \cdot N_1 + 2 \cdot N_2 + \ldots + i \cdot (N_i + \Delta_i) + \ldots + x \cdot N_x} = k_4 \tag{19}$$

Furthermore:

$$\frac{k_3 \cdot (1 \cdot N_1 + 2 \cdot N_2 + \ldots + i \cdot N_i + \ldots + x \cdot N_x) + i^2 \Delta_i + k_3 \cdot i \cdot \Delta_i - k_3 \cdot i \cdot \Delta_i}{1 \cdot N_1 + 2 \cdot N_2 + \ldots + i \cdot (N_i + \Delta_i) + \ldots + x \cdot N_x} = k_4 \tag{20}$$

After rearranging, Equation (20) becomes:

$$\frac{k_3 (1 \cdot N_1 + 2 \cdot N_2 + \ldots + i \cdot N_i + \ldots + x \cdot N_x + i \cdot \Delta_i) + i \cdot \Delta_i \cdot (i - k_3)}{1 \cdot N_1 + 2 \cdot N_2 + \ldots + i \cdot (N_i + \Delta_i) + \ldots + x \cdot N_x} = k_4 \tag{21}$$

or:

$$k_3 + \frac{i \cdot \Delta_i \cdot (i - k_3)}{1 \cdot N_1 + 2 \cdot N_2 + \ldots + i \cdot (N_i + \Delta_i) + \ldots + x \cdot N_x} = k_4 \tag{22}$$

To represent a decrease in weight average molecular weight, the following condition must be satisfied:

$$(M_w)_{product} < (M_w)_{feed} \tag{23}$$

This can be represented as:

$$k_3 + \frac{i \cdot \Delta_i \cdot (i - k_3)}{1 \cdot N_1 + 2 \cdot N_2 + ... + i \cdot (N_i + \Delta_i) + ... + x \cdot N_x} < k_3 \tag{24}$$

Since $\Delta_i, i > 0$ and $N_1 + 2 \cdot N_2 + ... + i \cdot (N_i + \Delta_i) + ... + x \cdot N_x > 0$ the solution of Equation (24) is:

$$i < k_3\text{, or after substitution } i < \frac{(M_w)_{feed}}{M_{monomer}} \tag{25}$$

Alternatively if the weight average molecular weight increases with time, the condition to be satisfied is:

$$i > \frac{(M_w)_{feed}}{M_{monomer}} \tag{26}$$

To achieve a constant weight average molecular weight over time and an increase in conversion, an increase in number of chains must be achieved hence the following condition must be satisfied:

$$i = \frac{(M_w)_{feed}}{M_{monomer}} \tag{27}$$

Now considering polydispersity (PD):

$$PD = \frac{M_w}{M_n} = \frac{\sum N_i \cdot M_i^2 \cdot \sum N_i}{(\sum N_i \cdot M_i)^2} \tag{28}$$

According to Equations (9) and (22), the polydispersity of the SDR product ($(PD)_{product}$)) is given by:

$$(PD)_{product} = \frac{k_3 + \frac{i \cdot \Delta_i \cdot (i - k_3)}{1 \cdot N_1 + 2 \cdot N_2 + ... + i \cdot (N_i + \Delta_i) + ... + x \cdot N_x}}{k_1 + \frac{\Delta_i \cdot (i - k_1)}{N_1 + N_2 + ... + (N_i + \Delta_i) + ... + N_x}} \tag{29}$$

From the experimental data[2] presented in Figure 3, a slight increase in polydispersity of the SDR product compared with the polydispersity of the disc feed was observed. This can be represented as:

$$\frac{k_3-\dfrac{i\cdot\Delta_i\cdot(k_3-i)}{1\cdot N_1+2\cdot N_2+\ldots+i\cdot(N_i+\Delta_i)+\ldots+x\cdot N_x}}{k_1-\dfrac{\Delta_i\cdot(k_1-i)}{N_1+N_2+\ldots+(N_i+\Delta_i)+\ldots+N_x}}>\frac{k_3}{k_1} \tag{30}$$

Furthermore:

$$\frac{k_3\cdot(1-\dfrac{i\cdot\Delta_i\cdot(k_3-i)}{k_3\cdot(1\cdot N_1+2\cdot N_2+\ldots+i\cdot(N_i+\Delta_i)+\ldots+x\cdot N_x)})}{k_1\cdot(1-\dfrac{\Delta_i\cdot(k_1-i)}{k_1\cdot(N_1+N_2+\ldots+(N_i+\Delta_i)+\ldots+N_x)})}>\frac{k_3}{k_1} \tag{31}$$

$$\frac{1-\dfrac{i\cdot\Delta_i\cdot(k_3-i)}{k_3\cdot(1\cdot N_1+2\cdot N_2+\ldots+i\cdot(N_i+\Delta_i)+\ldots+x\cdot N_x)}}{1-\dfrac{\Delta_i\cdot(k_1-i)}{k_1\cdot(N_1+N_2+\ldots+(N_i+\Delta_i)+\ldots+N_x)}}>\frac{1}{1} \tag{32}$$

$$(1-\frac{i\cdot\Delta_i\cdot(k_3-i)}{k_3\cdot(1\cdot N_1+2\cdot N_2+\ldots+i\cdot(N_i+\Delta_i)+\ldots+x\cdot N_x)})>(1-\frac{\Delta_i\cdot(k_1-i)}{k_1\cdot(N_1+N_2+\ldots+(N_i+\Delta_i)+\ldots+N_x)} \tag{33}$$

Solution of Equation (33) then requires the following equation to be solved:

$$\frac{k_3}{k_1}>\frac{\dfrac{i\cdot\Delta_i\cdot(k_3-i)}{1\cdot N_1+2\cdot N_2+\ldots+i\cdot(N_i+\Delta_i)+\ldots+x\cdot N_x}}{\dfrac{\Delta_i\cdot(k_1-i)}{N_1+N_2+\ldots+(N_i+\Delta_i)+\ldots+N_x}} \tag{34}$$

After rearranging Equation (34) and including the constraint $\Delta_i>0$, Equation (34) can be rewritten as:

$$k_1\cdot i^2-(k_1\cdot k_3+k_3\cdot k_2)\cdot i+k_1\cdot k_3\cdot k_2>0 \tag{35}$$

The solution of the Equation (35) which represents a quadratic trinomial depends on the sign of its discriminant (D). If:

$$(k_1 \cdot k_3 + k_3 \cdot k_2)^2 - 4 \cdot (k_1)^2 \cdot k_3 \cdot k_2 < 0 \tag{36}$$

Then for every i, Equation (35) has the same sign as the i^2 coefficient. Else if:

$$(k_1 \cdot k_3 + k_3 \cdot k_2)^2 - 4 \cdot (k_1)^2 \cdot k_3 \cdot k_2 \geq 0 \tag{37}$$

The interval in which the set of solutions lies will depend on the coefficient of i^2. For the experimental SDR data, Equation (37) is satisfied and the coefficient of i^2 is positive at all times, $k_1 > 0$ i.e. $\frac{(M_n)_{feed}}{M_{monomer}} > 0$. Therefore the quadratic trinomial presented in Equation (35) will be satisfied for all i outside the interval given by the solutions, $i_{1,2}$, of the trinomial represented as the quadratic equation:

$$i_{1,2} = \frac{(k_1 \cdot k_3 + k_3 \cdot k_2) \pm \sqrt{(k_1 \cdot k_3 + k_3 \cdot k_2)^2 - 4 \cdot (k_1)^2 \cdot k_3 \cdot k_2)}}{2 \cdot k_1} \tag{38}$$

or after substitution:

$$i_{1,2} = \frac{(\frac{(M_n)_{feed}}{M_{monomer}} \cdot \frac{(M_w)_{feed}}{M_{monomer}} + \frac{(M_w)_{feed}}{M_{monomer}} \cdot \frac{(M_n)_{product}}{M_{monomer}})}{2 \cdot \frac{(M_n)_{feed}}{M_{monomer}}} \pm$$

$$\pm \frac{\sqrt{(\frac{(M_n)_{feed}}{M_{monomer}} \cdot \frac{(M_w)_{feed}}{M_{monomer}} + \frac{(M_w)_{feed}}{M_{monomer}} \cdot \frac{(M_n)_{product}}{M_{monomer}})^2 - 4 \cdot (\frac{(M_n)_{feed}}{M_{monomer}})^2 \cdot \frac{(M_w)_{feed}}{M_{monomer}} \cdot \frac{(M_n)_{product}}{M_{monomer}})}}{2 \cdot \frac{(M_n)_{feed}}{M_{monomer}}} \tag{39}$$

To increase polydispersity:

$$i = (0, i_1) \text{ or } i = (i_2, \infty) \text{ and } i_1 < i_2 \tag{40}$$

It should be noted that $i > 0$ for all i. Furthermore if polydispersity was observed to be decreasing over time, the condition to be satisfied becomes:

$$i = (i_1, i_2) \tag{41}$$

To ensure polydispersity is constant over time whilst increasing conversion, an increase in the number of chains would be required and hence the following condition needs to be satisfied:

$$i = i_1 \text{ or } i = i_2 \tag{42}$$

The overall solution of the system of trends analysed is the intersection of the individual solutions with the molecule sizes preferably formed on the spinning disc reactor being determined as the intersection of the solutions of equations (12), (25) and (40).

Results and Discussion of the Analysis

The reaction system analysed on a spinning disc reactor was benzoyl peroxide initiated free radical polymerisation of styrene[2]. The temperature of the SDR was controlled to within 84-91°C, and the rotational speed applied was between 300 and 1500rpm. The SDR feed was pre-polymerised in a batch rector. Pre-polymerisation time was between 40 and 120 minutes. Data from twenty two runs on the SDR was made available. Two to four measurements were acquired for each run and the average value was considered. These results were obtained through standard laboratory experimentation procedures and did not utilise design of experiments.

For every set of data, the interval of chain lengths preferably formed was calculated. For a few runs the observed trend differed to that for the majority of runs. For example for some runs a slight decrease in polydispersity or slight increase in molecular weights was noted. These runs were also analysed and the results are presented. The monomer in system analysed was styrene:

$$M_{\text{monomer}} = M_{\text{styrene}} = 104 \text{ g/mol} \tag{43}$$

After undertaking the trend analysis for the twenty two experimental runs presented in Table 1, the majority (18 of the 22) lay within three intervals presented in Equation (44), (46) and (47). The largest group of experimental results (16 of the 22) fitted chain length interval of:

$$(0, i_1) \tag{44}$$

And with two of the individual runs (samples 9 and 22) lying within the following two intervals respectively:

$$\left(\frac{(M_n)_{feed}}{M_{monomer}}, \frac{(M_w)_{feed}}{M_{monomer}}\right) \tag{45}$$

$$\left(i_1, \frac{(M_n)_{feed}}{M_{monomer}}\right) \tag{46}$$

where:

$$i_1 = \frac{\left(\frac{(M_n)_{feed}}{M_{monomer}} \cdot \frac{(M_w)_{feed}}{M_{monomer}} + \frac{(M_w)_{feed}}{M_{monomer}} \cdot \frac{(M_n)_{product}}{M_{monomer}}\right)}{2 \cdot \frac{(M_n)_{feed}}{M_{monomer}}} - \frac{\sqrt{\left(\frac{(M_n)_{feed}}{M_{monomer}} \cdot \frac{(M_w)_{feed}}{M_{monomer}} + \frac{(M_w)_{feed}}{M_{monomer}} \cdot \frac{(M_n)_{product}}{M_{monomer}}\right)^2 - 4 \cdot \left(\frac{(M_n)_{feed}}{M_{monomer}}\right)^2 \cdot \frac{(M_w)_{feed}}{M_{monomer}} \cdot \frac{(M_n)_{product}}{M_{monomer}}}}{2 \cdot \frac{(M_n)_{feed}}{M_{monomer}}} \tag{47}$$

Less than 5% of the data analysed (sample number 20) showed that chains that increased in number lay in the interval:

$$(i_2, \infty) \tag{48}$$

i.e. they favoured the production of bigger chains, where:

$$i_2 = \frac{\left(\frac{(M_n)_{feed}}{M_{monomer}} \cdot \frac{(M_w)_{feed}}{M_{monomer}} + \frac{(M_w)_{feed}}{M_{monomer}} \cdot \frac{(M_n)_{product}}{M_{monomer}}\right)}{2 \cdot \frac{(M_n)_{feed}}{M_{monomer}}} + \frac{\sqrt{\left(\frac{(M_n)_{feed}}{M_{monomer}} \cdot \frac{(M_w)_{feed}}{M_{monomer}} + \frac{(M_w)_{feed}}{M_{monomer}} \cdot \frac{(M_n)_{product}}{M_{monomer}}\right)^2 - 4 \cdot \left(\frac{(M_n)_{feed}}{M_{monomer}}\right)^2 \cdot \frac{(M_w)_{feed}}{M_{monomer}} \cdot \frac{(M_n)_{product}}{M_{monomer}}}}{2 \cdot \frac{(M_n)_{feed}}{M_{monomer}}} \tag{49}$$

These results are presented in Table 1 and Figure 4.

Table 1. Experimentally measured molecular weights and results from the analysis.

S[a]	Mn[b] g/mol	Mw[b] g/mol	PD[b]	Mn[c] g/mol	Mw[c] g/mol	PD[c]	D	i_1	i_2	Interval solution
1	17923	28402	1.585	17475	28192	1.613	3.19E+9	105.8	433.5	0,105
2	17732	27637	1.558	17118	27342	1.597	2.84E+9	104.8	417.5	0,105
3	19149	29888	1.561	18891	29824	1.579	3.97E+9	114.3	456.6	0,114
4	18529	28423	1.534	18318	28402	1.55	3.26E+9	111.4	432.1	0,111
5	18139	28814	1.589	17580	28220	1.605	3.36E+9	106.7	438.9	0,106
6	18106	28489	1.573	17544	27907	1.591	3.21E+9	106.8	432.5	0,106
7	17325	27631	1.595	16729	27465	1.642	2.82E+9	101.6	420.6	0,101
8	19993	30894	1.545	18647	29960	1.607	4.31E+9	116.3	457.8	0,116
9	17969	28923	1.61	18142	28861	1.591	3.53E+9	107.5	451.4	173,278
10	18703	29786	1.593	18365	29625	1.613	3.88E+9	110.7	456.9	0,110
11	19282	31185	1.617	18678	30907	1.655	4.57E+9	112.8	477.5	0,112
12	18997	31023	1.633	18307	30649	1.674	4.44E+9	110.5	475.3	0,110
13	20259	33392	1.648	18919	31486	1.664	5.76E+9	115.6	505.3	0,115
14	19338	32785	1.695	19246	32827	1.706	5.61E+9	113.1	515.9	NS[d]
15	19591	31165	1.591	19221	30905	1.608	4.65E+9	115.9	477.7	0,115
16	20332	32987	1.622	20300	33144	1.633	5.89E+9	120.6	513.2	NS[d]
17	19519	31359	1.607	19241	31275	1.619	4.77E+9	115.4	483.3	0,115
18	19698	31502	1.599	19675	31505	1.601	4.93E+9	117.4	488.0	NS[d]
19	19860	31168	1.569	19188	30823	1.606	4.6E+9	117.1	472.1	0,117
20	19353	30744	1.589	19446	31219	1.605	4.51E+9	115.9	476.7	477,∞
21	19816	31673	1.598	19291	31083	1.611	4.91E+9	116.6	484.4	0,116
22	19755	31933	1.616	19701	31385	1.593	5.17E+9	117.3	496.0	117,189

[a] Sample number.
[b] SDR feed.
[c] SDR product.
[d] No solution.

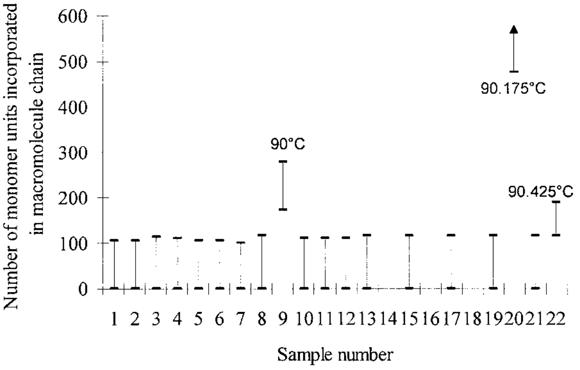

Figure 4. Calculated length of chains preferably increasing during the polymerisation process on the spinning disc reactor.

A small number of the experimental runs (samples 14, 16 and 18) had no mathematical solution as there was no intersection between the solutions of the individual analysis. After examining the data in more detail it was observed that the difference between the average molecular weight of product and feed was small and of opposite sign to that expected (i.e. for sample number 18 $(M_w)_{product}$-$(M_w)_{feed}$=3). This is most likely due to experimental error in the measurement of molecular weights. The difference in molecular weights could be of different sign in which case the results from the analysis would be feasible.

Conclusions

A mathematical methodology for the analysis of the trends for the addition polymer qualities of number average and weight average molecular weights and their calculated ratio, polydispersity, is proposed. The approach was developed for benzoyl peroxide initiated free radical polymerisation of styrene on a spinning disc reactor. From Table 1 and Figure 4 it was observed that for the majority of the experimental data, the results of the mathematical analysis for a polymerisation process performed on a spinning disc reactor, the number of smaller polymer chains increases. This is in agreement with the known theory of polymers and is confirmed mathematically. Further work is planned to determine the relationship between the variable(s) influencing the chain lengths preferably formed and the chain length itself since as it is possible to calculate chain length, this can be incorporated into the design and ultimately the control of the polymerisation process.

As a result of the number of runs being limited, it was not possible to draw any firm conclusions. However, one tentative observation that could be made with respect to the SDR temperature was that for those chains whose increase lay within a specific interval, or exceeded a specific value, the disc temperature was equal to, or above, 90°C whilst for the remaining runs it was below 90°C. The variables expected to have an effect on the products macromolecule chain length are disc rotation speed and SDR polymerisation time. For the data available no conclusive findings could be drawn and further experimental work is required.

Although the methodology is developed for polymerisation processes carried out on a spinning disc reactor (SDR), the approach is applicable to other reactor systems. Furthermore general rules can be determined so that for specific data, collected over time, on number and weight average molecular weight, for addition polymerisations undertaken in any rector system, intervals for polymer chain sizes preferably formed during the process can be calculated.

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