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Molecular weight distribution and controllability in living polymerization with chain-transfer agents

Jin-Wuk Kim, Ki-Jun Lee and Hong H. Lee*
Department of Chemical Engineering, Seoul National University, Seoul 151-742, South Korea
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The same molecular weight distribution is always attained for both dead and living polymers when the living polymerization is carried out in a continuously stirred tank reactor, which cannot be achieved in a batch reactor. The average molecular weight and the yield are completely controllable to any desired values. However, the polydispersity index is determined by the average molecular weight only, its value increasing with increasing average molecular weight. The index ranges from unity to 2. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Living polymerization is one in which the average molecular weight can easily be controlled. No termination is involved in the usual sense in the polymerization but rather the termination is controlled by a chain-transfer agent and/or a catalyst, thereby leading to the controllability of the average molecular weight. More transfer agent (catalyst) is needed for lower average molecular weight. In general, the chain-transfer agent is more effective than the catalyst. In recent studies, France *et al.*[2] compared the effectiveness of various chain-transfer agents for the living polymerization and Higashimura and co-workers[3] investigated olefins for the chain-transfer activities. Polymers containing functional end groups (telechelic polymers) can be synthesized readily by the intentional addition of chain-transfer agents. Such polymers are used for the production of well-defined, sophisticated macromolecular structures, and are therefore the preferred starting materials for 'macromolecular engineering'[10].

Theoretical analyses of such living polymerization with chain-transfer agents have been made[1,6] to examine the nature of the resulting molecular weight distribution. The results are, however, mainly for the polymerization in a batch reactor. Characteristic of the molecular weight distribution resulting from a batch reactor is the existence of a bimodal molecular weight distribution[4,5], i.e., a combination of two distinct molecular weight distributions. One is due to living polymer and the other due to dead polymer or end-capped polymer.

Although batch reactors are typically used in experiments, continuous reactors, such as continuously stirred tank reactors (CSTR), are also used in practice. There are also several papers[7–9] on the use of CSTRs that are related to polymerization without transfer agents, Alassia *et al.*[7] found that a monomodal molecular weight distribution results when an impurity causes termination. Litvienko[8] studied a series of CSTRs for the purpose of maximizing the average molecular weight. Priddy[9] examined the effect of chain transfer to solvent on styrene polymerization.

In this paper, it is shown that the use of a CSTR always leads to a monomodal molecular weight distribution in living polymerization with chain-transfer agents.

It is desirable in any polymerization, including living polymerization with chain-transfer agents, that the desired average molecular weight be obtained, that the PDI be minimized, and that the conversion of monomer and thus the yield be maximized. It was revealed by Benedicto *et al.*[1] that such objectives can be realized only for a narrow range of the kinetic parameters for the living polymerization in batch reactors.

In this paper, it is shown theoretically that the average molecular weight and the yield can be completely controlled when the living polymerization is carried out in CSTRs.

LIVING POLYMERIZATION IN CSTRS

The polymerization scheme[1] can be represented as follows:

$$W_0 + M \xrightarrow{k_i} W_1 \qquad W_n + M \xrightarrow{k_p} W_{n+1},\ n \geq 1$$

$$W_n + T_0 \xrightarrow{k_{ct}} W_0 + T_n,\ n \geq 1$$

where W_0 is the initiating species (catalyst), W_n is the living polymer of chain length n, T_0 is the chain-transfer agent, T_n is the end-capped, dead polymer of chain length n, k_i is the initiating rate constant, k_p is the rate constant for the propagation, and k_{ct} is the same for the chain transfer.

At steady state, the material balances around a CSTR can be written as follows:

$$Q_c W_{0i} - QW_0 - V(k_i M W_0 - k_{ct} T_0 \lambda_0) = 0 \quad \left(\lambda_0 = \sum_{n=1}^{\infty} W_n\right) \tag{1}$$

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* To whom correspondence should be addressed

$$Q_m M_i - QM - V(k_i M W_0 + k_p M \lambda_0) = 0 \tag{2}$$

$$Q_t T_{0i} - Q T_0 - V k_{ct} T_0 \lambda_0 = 0 \tag{3}$$

where Q values (s = c,m,t) are the volumetric flow rates of the catalyst (c), the monomer (m), and the chain transfer agent (t), Q is the total volumetric flow rate such that $Q = Q_c + Q_m + Q_t$, V is the volume of the reactor occupied by all the species, and the subscript i is for the rector inlet. Note that the species nomenclature was used interchangeably for the concentration. The quantities needed for the number-averaged molecular weight and the PDI are defined as follows:

$$\lambda_j \equiv \sum_{n=1}^{\infty} n^j W_n \quad (j = 0, 1, 2) \tag{4}$$

$$\lambda_j^d \equiv \sum_{n=1}^{\infty} n^j T_n \quad (j = 0, 1, 2) \tag{5}$$

where the superscript d is for the dead polymer. The material balances for these defined quantities follow from equation (1), equation (2) and equation (3) and the definitions:

$$-Q\lambda_0 + V(k_i W_0 M - k_{ct} T_0 \lambda_0) = 0 \tag{6}$$

$$-Q\lambda_0^d + V k_{ct} T_0 \lambda_0 = 0 \tag{7}$$

$$-Q\lambda_1 + V(k_i M W_0 + k_p M \lambda_0 - k_{ct} T_0 \lambda_1) = 0 \tag{8}$$

$$-Q\lambda_1^d + V k_{ct} T_0 \lambda_1 = 0 \tag{9}$$

$$-Q\lambda_2 + V[k_i M W_0 + k_p M(2\lambda_1 + \lambda_0) - k_{ct} T_0 \lambda_2] = 0 \tag{10}$$

$$-Q\lambda_2^d + V k_{ct} T_0 \lambda_2 = 0 \tag{11}$$

It then follows from the definitions that

$$\bar{X}_{n,d} = \frac{\lambda_1^d}{\lambda_0^d}, \ \bar{X}_{n,a} = \frac{\lambda_1}{\lambda_0} \tag{12}$$

$$\mathrm{PDI}_d = \frac{\lambda_0^d \lambda_2^d}{(\lambda_1^d)^2}, \ \mathrm{PDI}_a = \frac{\lambda_0 \lambda_2}{(\lambda_1)^2} \tag{13}$$

where the subscript as well as the superscript d denotes dead polymer and the subscript a represents active (living) polymer. Here, $\bar{X}_n$ is the number-average degree of polymerization. The space times for each constituent and the total, θ_i and, θ and the flow rate fractions R_i are defined as follows:

$$\theta = \frac{V}{Q}, \ \theta_i = \frac{V}{Q_i} \ (i = c, m, t) \tag{14}$$

$$R_i = \frac{Q_i}{Q} \ (i = c, m, t) \tag{15}$$

Then, equation (1) and equation (6) yield

$$\lambda_0 = R_c W_{0i} - W_0 \tag{16}$$

which in turn gives, upon inserting into equation (3)

$$T_0 = \frac{T_{0i} R_t}{1 + \theta k_{ct} \lambda_0} \tag{17}$$

The monomer concentration in the reactor, which is the concentration at the outlet of the reactor is obtained from equation (2) with the aid of equation (16):

$$M = \frac{M_i R_m}{1 + (k_i - k_p) W_0 \theta + k_p W_{0i} R_c \theta} \tag{18}$$

Use of equation (16), equation (17) and equation (18) in equation (1) leads to a third-order algebraic equation for the concentration of the catalyst (that is, initiator concentration, W_0) as follows:

$$a_1 W_0^3 + a_2 W_0^2 + a_3 W_0 + a_4 = 0 \tag{19}$$

where

$$a_1 = k_{ct}(k_i - k_p)\theta^2$$

$$\begin{aligned} a_2 = & -2k_{ct}(k_i - k_p) W_{0i} R_c \theta^2 - k_{ct}(k_i - k_p) T_{0i} R_t \theta^2 \\ & + k_p k_{ct} W_{0i} R_c \theta^2 + k_i k_{ct} M_i R_m \theta^2 + (k_p + k_{ct} - k_i)\theta \end{aligned}$$

$$\begin{aligned} a_3 = & -k_{ct}(2W_{0i} R_c \theta + T_{0i} R_t \theta) + (k_i - k_p) W_{0i} R_c \theta \\ & + k_{ct}(k_i - k_p)[(W_{0i} R_c \theta)^2 + T_{0i} W_{0i} R_t R_c \theta^2] \\ & - k_p k_{ct}[T_{0i} W_{0i} R_t R_c \theta^2 + 2(W_{0i} R_c \theta)^2] \\ & - k_i k_{ct} M_i W_{0i} R_c R_m \theta^2 - k_p W_{0i} R_c \theta - k_i M_i R_m \theta - 1 \end{aligned}$$

$$\begin{aligned} a_4 = & \, k_p k_{ct}[(W_{0i} R_c)^3 + (W_{0i} R_c)^2 T_{0i} R_t] + k_{ct} T_{0i} W_{0i} R_c R_t \theta \\ & + (k_p + k_{ct})(W_{0i} R_c)^2 \theta + W_{0i} R_c \end{aligned}$$

Since the coefficients a_1 through a_4 consist of the space times, the kinetic parameters and the inlet conditions, the solution of equation (19) yields the value of W_0. This value can in turn be used in equation (17) and equation (18) to obtain the values of the concentrations T_0 and M, respectively.

MOLECULAR WEIGHT DISTRIBUTION AND PDI

The equations for the moments, i.e., equations (7)–(11), are solved to yield

$$\lambda_0^d = k_{ct} T_0 \lambda_0 \theta \tag{20}$$

$$\lambda_1 = \frac{M(k_i W_0 + k_p \lambda_0)}{1/\theta + k_{ct} T_0} \tag{21}$$

$$\lambda_1^d = k_{ct} T_0 \lambda_1 \theta \tag{22}$$

$$\lambda_1 = \frac{M[k_i W_0 + k_p(2\lambda_1 + \lambda_0)]}{1/\theta + k_{ct} T_0} \tag{23}$$

$$\lambda_2^d = k_{ct} T_0 \lambda_2 \theta \tag{24}$$

To show that the number-average molecular weight is the same for both the dead and the living polymer, it is sufficient that

$$\lambda_0 \lambda_1^d = \lambda_1 \lambda_0^d \tag{25}$$

which follows from the definitions in equation (12). Use of equation (20) and equation (22) in equation (25) should reveal that $\lambda_0 \lambda_1^d$ is equal to $\lambda_1 \lambda_0^d$, that is $\bar{X}_{n,d} = \bar{X}_{n,a}$. Thus, the number-average molecular weight distribution is monomodal.

Likewise, it is sufficient to show for the monomodal PDI that

$$\lambda_0^d \lambda_2^d (\lambda_1)^2 = \lambda_0 \lambda_2 (\lambda_1^d)^2 \tag{26}$$

which follows from equation (13). Again, use of equation (20), equation (22) and equation (24) for λ_0^d, λ_1^d and λ_2^d, respectively, in equation (26) should show that $\lambda_0^d \lambda_2^d (\lambda_1)^2$ is equal to $\lambda_0 \lambda_2 (\lambda_1^d)^2$.

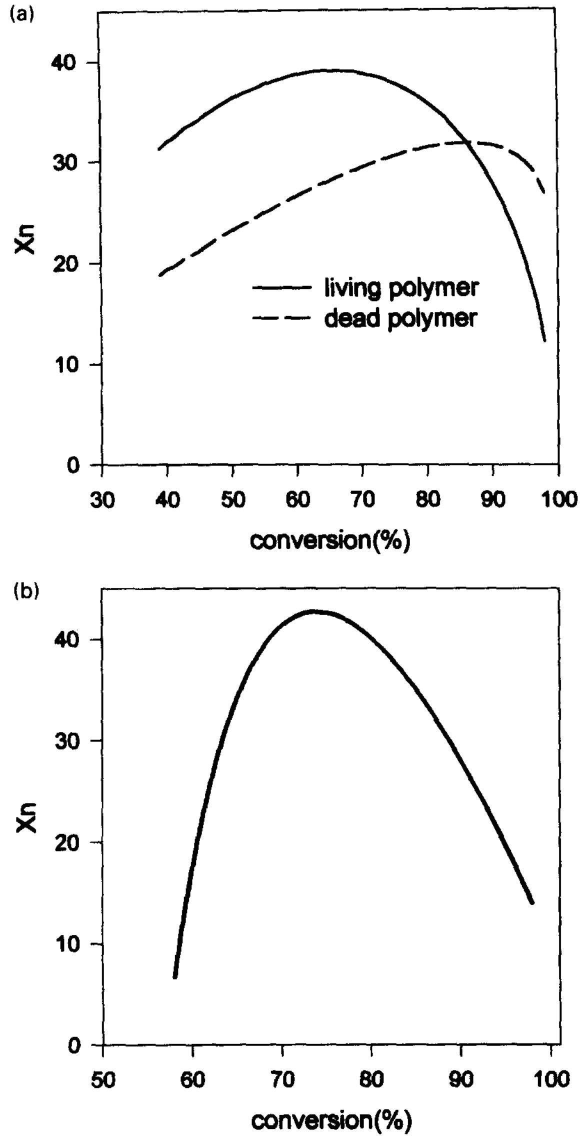

Figure 1 (a) Variation of the number-average degree of polymerization with conversion. The reactor is batch system. k_i:k_p:k_{ct} = 1:1:0.1 (l mol^{-1} h^{-1}). Concentration of catalyst:monomer:chain-transfer agent = 1:100:10 (mol l^{-1}). (b) Variation of the number-average degree of polymerization with conversion. The reactor is continuous system. k_i:k_p:k_{ct} = 1:1:0.1 (l mol^{-1} h^{-1}). Concentration of catalyst:monomer:chain-transfer agent = 1:100:10 (mol l^{-1}) (Q_c:Q_m:Q_t = 1:3:3 (l h^{-1}))

Figure 1 shows the number-average degrees of polymerization resulting from a batch system (*Figure 1a*) and from a CSTR (*Figure 1b*) for the identical living polymerization. The number-average degrees of polymerization in *Figure 1a* is that obtained by Benedicto *et al.*[1] and it is indeed bimodal. That is, the $\bar{X}_n$ distribution of the living polymer is different from that for the dead polymer. The $\bar{X}_n$ distribution in *Figure 1b* for a CSTR is monomodal as expected since the $\bar{X}_n$ values are identical for both the living and the dead polymer.

It is noted in this regard that the average molecular weight and the polydispersity index will be the same for living and dead polymers irrespective of what the total flow rate and the fractional flow rates for each component are.

The difference in *Figure 1* between the batch reactor and the CSTR lies in higher utilization of the transfer agent present in the CSTR than in the batch reactor. *Figure 2* shows the percent consumption of the chain-transfer agent as a function of monomer conversion or as space time is varied for both the batch reactor and the CSTR. It is seen that a higher percentage of the chain-transfer agent is used in the CSTR than in the batch reactor at the same conversion. Note in this regard that the initial concentration of the chain-transfer agent in the batch reactor is the same as the inlet concentration in the CSTR and that only the total flow rate, and not the individual component flow rates, is varied in the simulation.

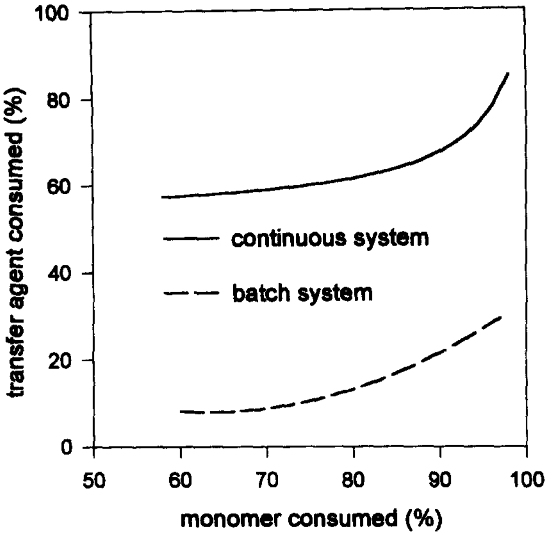

Figure 2 Percent of transfer agent consumed versus percent of monomer consumed when k_i:k_p:k_{ct} = 1:1:0.1 (l mol^{-1} h^{-1}). Concentration of catalyst: monomer:chain-transfer agent = 1:100:10 (mol l^{-1}). (Q_c:Q_m:Q_t = 1:3:3 (l h^{-1}) in CSTR system)

CONTROLLABILITY OF AVERAGE MOLECULAR WEIGHT AND CONVERSION

It is shown in this section that the number-average degree of polymerization $\bar{X}_n$ and the conversion x can be completely controlled to any desired values. This complete controllability in a CSTR contrasts the controllability attainable in a batch reactor that is possible only for a window of rate constants. It is also shown that the PDI is completely determined by the average molecular weight.

In proceeding, it is recognized first that both PDI and $\bar{X}_n$ for the living polymer are the same as those for the dead polymer, such that only those equations for the living polymer are sufficient for further development.

Define B as follows:

$$B \equiv \frac{W_0}{\lambda_0} \tag{27}$$

It then follows from the definition and equation (16) that

$$\lambda_0 = \frac{R_c W_{0i}}{1+B} \tag{28}$$

Use of the above in equation (16) gives

$$W_0 = \frac{B R_c W_{0i}}{1+B} \tag{29}$$

The PDI given by equation (13) can be rewritten as follows:

$$\mathrm{PDI} = \frac{\lambda_0 \lambda_2}{(\lambda_1)^2} = \frac{\lambda_2}{\lambda_1} \frac{1}{\bar{X}_n} \tag{30}$$

The ratio λ_2/λ_1, according to equation (21) and equation (23), is

$$\frac{\lambda_2}{\lambda_1} = 1 + \frac{2k_p}{k_p + k_i B}\bar{X}_n \tag{31}$$

where the definition of B and equation (12) for $\bar{X}_n$ have been used. Use of equation (31) in equation (30) yields the expression for the defined quantity B in terms of PDI and the number-average degree of polymerization:

$$B = \frac{k_p}{k_i}\left[\frac{2}{\mathrm{PDI} - 1/\bar{X}_n} - 1\right] \tag{32}$$

It follows from equation (6) that

$$B = \frac{W_0}{\lambda_0} = \frac{1 + k_{ct}\theta T_0}{k_i \theta M} \tag{33}$$

equation (8) yields λ_1 and, when it is divided by λ_0 for $\bar{X}_n$, the result is

$$\bar{X}_n = \frac{M\theta(k_i B + k_p)}{1 + k_{ct}\theta T_0} \tag{34}$$

where equation (27) was used. When equation (33) is multiplied by equation (34), there results upon rearrangement

$$B(\bar{X}_n - 1) = \frac{k_p}{k_i} \tag{35}$$

Combining equation (32) with equation (35) yields

$$\mathrm{PDI} = \frac{1}{\bar{X}_n} + \frac{2}{1 + 1/(\bar{X}_n - 1)} \tag{36}$$

It is seen that the PDI (the polydispersity index) is uniquely determined by $\bar{X}_n$ (the number-average degree of polymerization) alone.

The polydispersity index is shown in *Figure 3*. It is seen that the PDI increases with increasing $\bar{X}_n$, approaching the maximum possible value of 2 as the number-average degree of polymerization approaches infinity. The unrealistic minimum PDI value of unity is reached when approaches unity. Thus, the range of PDI is from unity to 2. The PDI rises rather quickly with increasing $\bar{X}_n$ when $\bar{X}_n$ is relatively small. For instance, an $\bar{X}_n$ of 10 corresponds to a PDI of 1.9 and an $\bar{X}_n$ of 50 to a PDI of 1.98. High-molecular weight polymer with a PDI near unity cannot be produced using CSTRs.

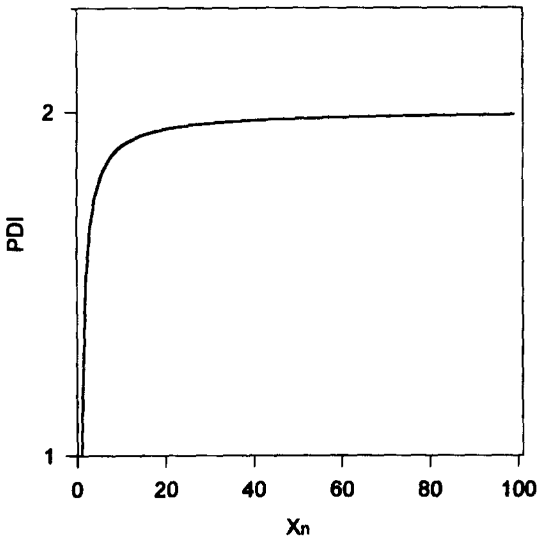

Figure 3 Variation of the polydispersity index with number-average degree of polymerization

Since the PDI is determined by $\bar{X}_n$, only the number-average degree of polymerization and the conversion could possibly be controlled. To show complete controllability of these two quantities, it is sufficient that there exist two independent equations that contain more than two manipulating variables such as inlet conditions. These two equations are those for $\bar{X}_n$ and x since these are to be set at the desired values.

The expression for the number-average degree of polymerization $\bar{X}_n$, given as λ_1/λ_0, can now be obtained in terms only of the inlet conditions and rate constants as follows:

$$\bar{X}_n = \frac{z_m(1 - x)(k_i B + k_p)}{1 + \dfrac{k_{ct}(1 + B)z_t}{1 + B + k_{ct}z_c}} \tag{37}$$

$$z_m = \theta M_i,\ z_t = \theta R_t T_{0i},\ z_c = \theta R_c W_{0i} \tag{38}$$

where equation (16), equation (17), equation (21), equation (28) and equation (29) have been used. The conversion x is given by $(M_i - M)/M_i$ so that $M = M_i(1 - x)$, which has also been used to arrive at equation (37). The definition of conversion and equation (18) for M are used with the aid of equation (28) and equation (29) to express the conversion as follows:

$$x = \frac{(1 - R_m)(1 + B) + z_c(k_i B + k_p)}{1 + B + z_c(k_i B + k_p)} \tag{39}$$

when the desired values of $\bar{X}_n$ and x are set, the value of B is fixed through equation (35). Given a polymerization reaction, the corresponding rate constants are also fixed. Therefore, only R_m, z_m, z_c and z_t in equation (37) and equation (39) are free to be chosen to satisfy the set values of $\bar{X}_n$ and x through the two equations. These four variables represent the operating conditions (inlet conditions) that can be manipulated. The fraction of monomer in the feed, R_m, may be selected arbitrarily as long as $R_m < 1$. Equation (39) then contains only one unknown, namely z_c. The solution of equation (39) for z_c is such that the following should be satisfied:

$$R_m + x > 1 \tag{40}$$

so that the calculated value of z_c be positive. Now that z_c is known, equation (37) can be solved for z_m for an arbitrarily chosen value of z_t. It can easily be shown that the value of z_m thus calculated is always positive. Some examples of the calculation are given in *Table 1* for a set of rate constants used by Benedicto *et al.*[1] The conversion is fixed at the highest level of 0.99 and the degree of polymerization is varied from 5 to 100. For the set values of R_m and z_t, the

Table 1 Examples of calculation results for various values of the desired conversion and number-average degree of polymerization when k_i:k_p:k_{ct} = 1:1:0.1 ($\mathrm{l\ mol^{-1}\ h^{-1}}$)

$\bar{X}_n$	x	PDI	R_m	z_t ($\mathrm{mol\ h\ l^{-1}}$)	z_m ($\mathrm{mol\ h\ l^{-1}}$)	z_c ($\mathrm{mol\ h\ l^{-1}}$)
50	0.99	1.98	0.50	100	13 345.40	49
5	0.99	1.80	0.50	100	1213.01	49
100	0.99	1.99	0.50	100	26 820.20	49
50	0.99	1.98	0.10	100	30 936.10	9
50	0.99	1.98	0.99	100	9520.90	98
50	0.99	1.98	0.50	10	5744.54	49

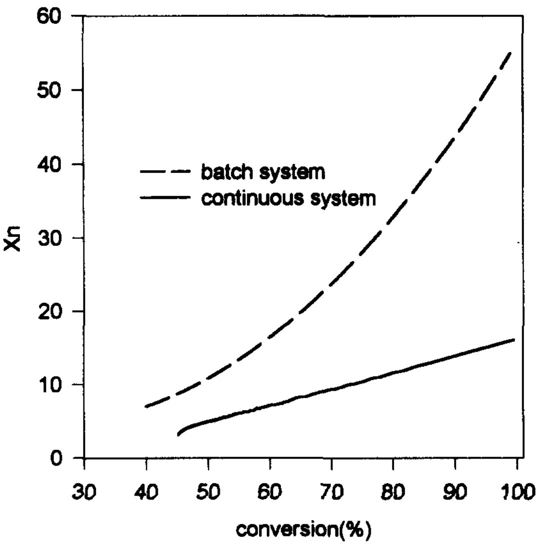

Figure 4 Variation of the number-average degree of polymerizatin with conversion k_i:k_p:k_{ct} = 1.25:1:5 (l mol^{-1} h^{-1}). Concentration of catalyst:-monomer:chain-transfer agent = 1:100:10 (mol l^{-1}) (Q_c:Q_m:Q_t = 1:3:3 (l h^{-1}) in CSTR system)

values of z_m and z_c that lead to the desired conversion and $\bar{X}_n$ are tabulated in the last two columns in *Table 1*. It is seen that for a given set of $x = 0.99$ and $\bar{X}_n = 50$, ranges of the inlet and operating conditions exist that are contained in R_m, z_c, z_m and z_t.

As pointed out by Benedicto *et al.*[1], use of an efficient transfer agent, i.e. $k_{ct} \gg k_p$, does not lead to an efficient yield of short-chain polymers (oligomers) in a batch reactor. On the other hand, use of an efficient transfer agent in a CSTR leads to an efficient yield of oligomers. This fact is illustrated in *Figure 4* for the same rate constants. It is seen that short-chain polymers are readily produced at the highest possible conversion when a CSTR is used.

It is difficult to compare the theory with the experimental results in the literature since either the data are not available or, even in few cases where available, they do not give all the information required. However, a qualitative comparison can be made regarding the dependence of the degree of polymerization on the initiator concentration. Priddy[9] showed that the degree of polymerization decreases with increasing initiator concentration, which the theory predicts.

To summarize, the number-average degree of polymerization and the yield can always be controlled to the desired values. These desired values are attained when z_c and z_m are manipulated to the values determined by equation (37) and equation (39) for a set of R_m and z_t that can be chosen arbitrarily, which means that R_m and z_t are still free for other purposes.

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