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Initiator와 단량체를 여러 위치에서 공급하는 폴리에틸렌 고압식 관상반응기의 성능

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The Performance of High Pressure Polyethylene Tubular Reactors with Multiple Injections of Initiator and Monomer.

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요 약

低密度 폴리에틸렌을 生産하는데 있어서 品質管理를 爲하여 long-chain branching을 control하는 일이 대단히 중요하다. 그 理由는 long-chain branching이 生産된 低密度 폴리에틸렌의 流動學的 物性과 加工性에 큰 영향을 주기 때문이다. 高壓下에서 生産되는 폴리에틸렌 反應器의 특징은 管狀反應器를 使用하는 경우에 그 길이가 直徑의 250倍 내지 1,200倍나 된다는 點이다. 生産費의 상당한 額數가 에틸렌을 壓縮시키는데 所要되므로 傳化率을 增加시킬 수 있다면 生産費를 크게 감축시킬수 있다. 이의 한 方法으로서 initiator나 單量體 또는 兩者를 同時에 反應器의 여러 位置에서 加하여 주는 것(multiple injections)이 좋다고 文獻에 報告되어 있다. 著者들은 이러한 提示를 證明하기 爲하여 理論的인 研究를 遂行하였으며 反應器內에서의 溫度分布, 單量體 및 initiator의 傳化率, 分子量分布度等의 代表的인 結果를 報告하는 바이다.

Abstract

In the production of polyethylene under high pressure, yielding so called "low-density polyethylene," control of the long-chain branching reaction is of paramount importance to product quality. This is because the long-chain branching level influences the rheological properties and processability of the polyethylene produced. The high pressure polyethylene tubular reactor is characterized by its large length-to-diameter ratio which ranges from 250:1 to as high as 1200:1. Since a significant portion of the production cost of polyethylene in a high-pressure tubular reactor is attributed to the power consumption needed to compress the ethylene, an increase in conversion should help reduce the production cost considerably. It has been suggested in the literature that the use of multiple injections of initiator and/or monomer can increase the conversion of ethylene considerably. We have recently investigated the performance (the conversion and product quality) of a high-pressure polyethylene tubular reactor with multiple injections of initiator and monomer. As part of the investigation, temperature profiles, monomer and initiator conversion, and the number-and weight-average molecular weights were calculated along the length of the reactor. In this paper, we shall present some of the highlights of the study.

1. Introduction

The high pressure polyethylene tubular reactor is characterized by its large length-to-diameter ratio which ranges from 250:1 to as high as 12000:1. Heat is transferred from or to the reactor by the fluid circulating through the jacket that surrounds it. High jacket temperatures are used in the initial portion of the reactor to heat the cold feed to the initiation temperature. Lower jacket temperatures are used in the latter portion of the reactor in order to remove the heat of reaction generated by polymerization. It should be mentioned that poor control of reactor temperature can cause a polymer buildup on the reactor wall which, if not removed, can affect reactor performance significantly through a marked reduction in the heat transfer coefficient. As has been indicated in recent studies by Schoenemann and Thies[1,2], Agrawal and Han[3], and Chen et al.,[4] the polymerization of ethylene is a very rapid reaction, and therefore the reactor temperature rises very rapidly along the length of the reactor. Among many other parameters, the rate of increase in reactor temperature depends on the type and the amount of initiator.

Control of the polyethylene reactor, as in all polymerization reactors, has to be such that not only is the polymer production rate constant, but also the polymer properties (such as density, molecular weight and its distribution) are reproducible.

In the production of polyethylene under high pressure, yielding so called "low-density polyethylene," control of the long-chain branching reaction is of paramount importance to product quality. This is because the long-chain branching level influences the rheological properties and processability of the polyethylene produced. In the past, a number of researchers have reported relationships between the level of long-chain branching and the rheological properties of polymers, and between the molecular weight distribution and the rheological properties. For details of these relationships, the reader may consult the recent monograph by Han[5].

In their recent study of a high-pressure polyethylene tubular reactor, Agrawal and Han[3] have reported that: (1) Axial mixing affects both reactor performance and product quality (i. e., the molecular weight and its distribution), (2) The chain transfer reactions broaden the molecular weight distribution, (3) The jacket fluid (coolant) temperature, feed temperature, and the overall heat transfer coefficient, all have a profound effect on reactor performance (i. e., concentration and temperature profiles), and (4) The amount of initiator injected affects reactor performance significantly.

Since a significant portion of the production cost of polyethylene in a high-pressure tubular reactor is attributed to the power consumption needed to compress the ethylene, an increase in conversion should help reduce the production cost considerably. It has been suggested by Albright[6], Agrawal and Han[3] and Chen et al.[4] that the use of multiple injections of initiator and/or monomer can increase the conversion of ethylene considerably. There is, however, no quantitative study reported about it in the published literature.

We have recently extended the study of Agrawal and Han[3] to investigate the performance (the conversion and product quality) of a high-pressure polyethylene tubular reactor with multiple injections of initiator and monomer. As part of the investigation, temperature profiles, monomer and initiator conversion, and the number-and-weight average molecular weights were calculated along the length of the reactor. In this paper, we shall present some of the highlights of the study.

2. System Equations For The High-Pressure Polyethylene Tubular Reactor

The steady-state mass and energy balance of the high-pressure polyethylene tubular reactor may be written as (3):

i) Mass balance for initiator:

$$\hat{D}_I\frac{d^2C_I}{dx^2}-v\frac{dC_I}{dx}-C_I\,(k_d)_0\exp\left(-\frac{\hat{E}_d}{RT}\right)=0 \qquad (1)$$

ii) Mass balance for monomer:

$$\hat{D}_M\frac{d^2C_M}{dx^2}-v\frac{dC_M}{dx}-\left\{\frac{(k_p)^2{}_0(k_d\epsilon)_0}{(k_{tc})_0}\exp\left(\frac{-\hat{E}_{pol}}{RT}\right)\right\}^{\frac{1}{2}}\times C_I^{\frac{1}{2}}C_M=0 \qquad (2)$$

iii) Energy balance:

$$\hat{K}_L\frac{d^2T}{dx^2}-\rho C_p v\frac{dT}{dx}+(-\Delta H_p)\left\{\frac{(k_p)^2{}_0(k_d\epsilon)_0}{(k_{tc})_0}\exp\left(\frac{-\hat{E}_{pol}}{RT}\right)\right\}^{\frac{1}{2}}C_I^{\frac{1}{2}}C_M+(-\Delta H_d)\,(k_d)_0C_I\exp\left(-\frac{\hat{E}_d}{RT}\right)-\frac{4U}{D}(T-T_c)=0 \qquad (3)$$

The boundary conditions are:

i) At the tube entrance ($x=0$):

$$v\Big((C_I)_0-C_I\Big)\Big]_{x=0}=-\hat{D}_I\frac{dC_I}{dx}\Big]_{x=0} \qquad (4)$$

$$v\Big((C_M)_0-C_M\Big)\Big]_{x=0}=-\hat{D}_M\frac{dC_M}{dx}\Big]_{x=0} \qquad (5)$$

$$\rho v\,C_p(T_0-T)\Big]_{x=0}=-\hat{K}_L\frac{dT}{dx}\Big]_{x=0} \qquad (6)$$

ii) At the tube exit ($x=L$):

$$\frac{dC_I}{dx}\Big]_{x=L}=0;\quad \frac{dC_M}{dx}\Big]_{x=L}=0;\quad \frac{dT}{dx}\Big]_{x=L}=0 \qquad (7)$$

The solutions of Equations (1) to (3) will yield the profiles of initiator, monomer and temperature along the length of reactor.

The polymer product consists of a mixture of similar species each having different molecular weights. It is customary tore present the molecular weight of a polymer in terms of the number-and-weight average molecular weight.

If the n^{th} moment of a polymer's molecular weight distribution is defined by the equation

$$Q_n=\sum_{r=2}^{\infty}r^nC_{Mr} \qquad (8)$$

in which C_{Mr} is the concentration of the dead polymer of chain-length r, the number-and weight-average molecular weights are given by

$$\bar{M}_n = \frac{28Q_1}{Q_0} \tag{9}$$

and

$$\bar{M}_w = \frac{28Q_2}{Q_1} \tag{10}$$

respectively, in which 28 is the molecular weight of ethylene.

Now, the mass balance equation for dead polymer $M_r (r=2, \infty)$ can be expressed by

$$\hat{D}_{Mr}\frac{d^2C_{Mr}}{dx^2} - v\frac{dC_{Mr}}{dx} + R_{Mr} = 0 \tag{11}$$

together with the boundary conditions,

$$v\left((C_{Mr})_0 - C_{Mr}\right)\Big]_{x=0} = -\hat{D}_{Mr}\frac{dC_{Mr}}{dx}\Big]_{x=0} \tag{12}$$

$$\frac{dC_{Mr}}{dx}\Big]_{x=L} = 0 \tag{13}$$

If Equations (11) to (13) are multiplied by r^n and summed from $r=2$ to $r=\infty$, one has

$$\hat{D}_{Mr}\frac{d^2Q_n}{dx^2} - v\frac{dQ_n}{dx} + \sum_{r=2}^{\infty} r^n R_{Mr} = 0 \tag{14}$$

together with the boundary condition,

$$\left(\sum_{r=2}^{\infty} r^n (C_{Mr})_0 - Q_n\right)\Big|_{x=0} = -\hat{D}_{Mr}\frac{dQ_n}{dx}\Big|_{x=0} \tag{15}$$

$$\frac{dQ_n}{dx}\Big|_{x=L} = 0 \tag{16}$$

The solution of Equation (14) will yield the desired moments Q_n for $n=0, 1$ and 2. The computation of the average molecular weights, $\bar{M}_n$ and $\bar{M}_w$, is now possible using Equations (9) and (10).

For the notations used in Equations (1) to (16), the reader may consult the paper of Agrawal and Han[3].

In the derivation of Equations (1) to (3), we have assumed a constant pressure in the reactor. However, it is reported in the literature [6] that the pressure drop in a typical commercial reactor may range from 100 to 350 atm. Note that the polymerization rate is strongly dependent on pressure[3]. The large pressure drop in the polyethylene tubular reactor comes primarily from the formation of very viscous polyethylene, whose viscosity increases as the conversion of ethylene (and consequenty the molecular weight of polyethylene) are increased downstream of the feed location. The pressure profiles along the length of the reactor, when available, can easily be incorporated, with little effort, into the system equations. Unfortunately, however, no information is available on this point in the published literature.

3. Results and Discussion

System Equations (1) to (3), with boundary conditions (4) to (7), were first transformed into integral equations, and were then analyzed in the square-integrable function space to derive both a uniqueness criterion and algorithms for numerical computations. In the present study, we used the computer program developed by Agrawal and Han[3]

Fig. 1 shows a schematic of the three reactor systems investigated: (a) a reference reactor (a single injection of initiatior and monomer), 5.08cm in diameter (D) and 610m in length (L); (b) a reactor with multiple injections of initiator; (c) a reactor with multiple injections of initiator and monomer (i. e., ethylene feed). It should be pointed out that, when monomer is fed at more than one location along the length of the reactor (see, for instance, *Fig.* 1c), one has to increase the reactor diameter after each addition of monomer in order to have the same linear velocity along the entire length of the reactor.

Throughout the study, we have considered an ethylene throughput of 68,040kg/hr and a reactor pressure of 2,500 atm. The numerical values of other system parameters used are given

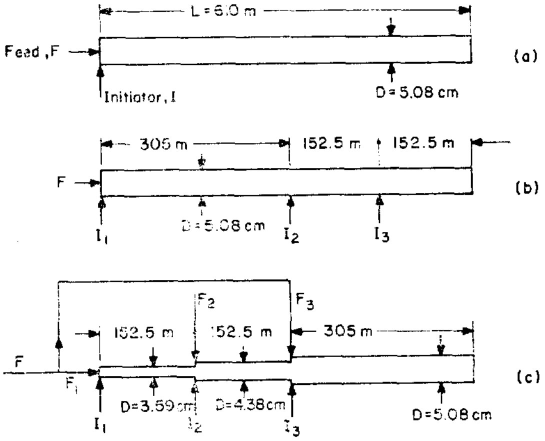

Fig. 1. Schematic of the tubular reactor systems investigated; (a) A reference reactor with a single injection of initiator and monomer; (b) A reactor with multiple injections of initiator; (c) A reactor with multiple injections of initiator and monomer.

in *Table* 1.

In each reactor system considered (see *Fig* 1), the reactor length is divided into two parts: the first half (305m) is the preheating zone which is assumed to be at 163°C, and the other half (305m) is the cooling zone which is assumed to be at 50°C. In all cases investigated, the temperature of the monomer and initiator is assumed to be at 80°C at the reactor inlet. When multiple injections of initiator and/or monomer are used, the feed at a point other than the reactor inlet is assumed to be heated to the reactor temperature at that point.

Fig. 2 shows temperature profiles, and monomer and initiator conversions, along the length of the reactor for a single injection (i. e., the reference case) and for multiple injections of initiator. The initiator concentration used at each injection point is given in *Table* 2. *Table* 2 also gives monomer and initiator conversions, average molecular weight and its distribution for a single injection and multiple injections of initiator. It is seen that injections of the initiator at three different locations along the length of the reactor can give rise to an increase in the conversion of monomer and initiator. Note however that, as the initiator concentration is increased, the peak temperature moves toward the reactor exit. This indicates that there is insufficient cooling in the reactor before additional initiator is injected downstream. One way of avoiding too high a peak temperature at the exit of the reactor is to use a longer reactor. This will be discussed below.

Of course, one could increase monomer conversion further by increasing the initiator concentration more. However, the use of too high an initiator concentration at one injection point can raise the reactor temperature higher than the maximum temperature allowed. Too high a reactor temperature will cause decomposition of ethylene, giving rise to carbon deposits on the wall. This can cause fouling of the inner tube surface by high molecular weight polymer, and also, possibly, an explosion. Therefore one should not increase the initiator concentration solely for increasing the conversion.

Fig. 3 shows temperature profiles, and monomer and initiator conversion, for multiple injections of initiator along a reactor whose length is 1830m, 3 times the length of the reference reactor (610m). In this reactor system, initiator was injected at three equally spaced points. The first injection was at the reactor inlet, the second at 610m from the reactor inlet, and the third at 1220m from the reactor inlet. In effect, three tubuar reactors, each 610m long, are connected in series. In each section (610m long) of the reactor system, the first half (305m) is the preheating zone whose temperature is kept at 163°C, and the other half is the cooling zone whose temperature is kept at 50°C. *Table* 3. gives the initiator concentration at different locations along the

Table 1. Summary of the values of physical constants used in computations of polymerization reactors

Physical properties of ethylene:

Heat capacity, C_p: 0.85 cal/g°C Density of fiuid,, ρ: 0.72g/cc

Engineering constants:

Overall heat transfer coefficient, U: 98.25 cal/hr. cm^2 °C

Peclet number, Pe: 100 (for both heat and mass transfer)

Reaction rate constants:

Initiator rate constant, $(k_d)_0$: 8.2×10^{11}(1/sec)

Rate constant of propagation, $(k_p)_0$: 1.25×10^8 (1/sec)

Rate constant of chain transfer reaction to dead polymer, $(k_{tr,p})_0$: 0.46

Table 2. Effect of multiple injections of initiator on average molecular weight and conversion

Run No. identification	Initiator I_1	Concentration I_2	(gm-moles/cc) I_3	Initiator conversion (%)	Monomer conversion (%)	$\bar{M}_n\times10^{-4}$	$\bar{M}_w/\bar{M}_n$
1[(a)]	1.150×10^{-6}	0.0	0.0	45.0	10.10	0.68	1.73
2	1.080×10^{-6}	0.192×10^{-6}	0.096×10^{-6}	39.9	10.06	0.64	1.65
3	1.096×10^{-6}	0.192×10^{-6}	0.096×10^{-6}	47.3	11.51	0.59	1.66
4	1.110×10^{-6}	0.192×10^{-6}	0.096×10^{-6}	68.1	15.12	0.50	1.73

(a) A single injection of initiator to be used for comparison purposes.

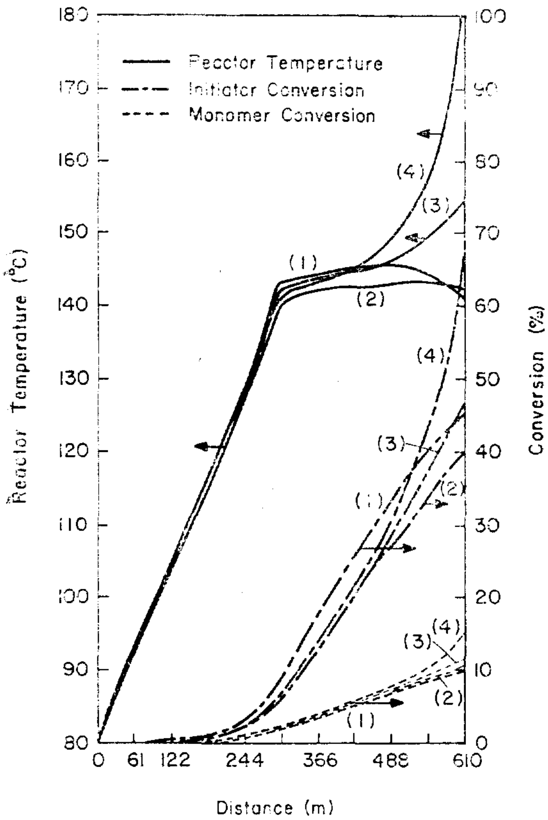

Fig. 2. Profile of reactor temperature, initiator and monomer concentrations in a tubular reactor: (1) Single injections of initiator and monomer; (2), (3), and (4) Multiple injections of initiator at different initiator concentrations. See *Table* 2. for the initiator concentration used.

reactor, and monomer and initiator conversions, average molecular weight and its distribution. Note that the initiator concentration used in this case (see *Table* 3) is quite low compared to that in the reference reactor (see *Table* 2), and yet the levels of monomer and initiator conversion are quite comparable in the two cases. In carrying out the computation reported in this paper, we used the computed values of temperature, and monomer and initiator concentrations at the outlet of one injection for the inlet conditions of the subsequent injection. In other words, possible mixing effects at the respective injection points were neglected. This can be improved by applying the boundary conditions, Equations (4) to (7), at each injection points.

It is of particular interest to note in *Fig.* 3 that there are three peaks in the reactor temperature. It can be said from *Fig.* 3 that

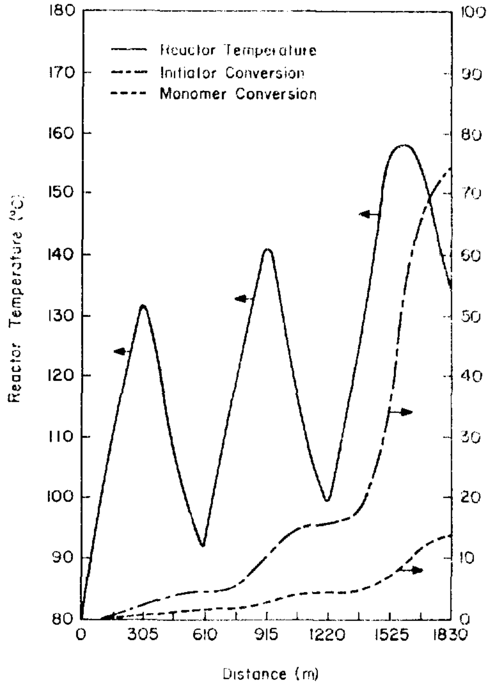

Fig. 3. Profile of reactor temperature, initiator and monome rconcentrations in a long tubular reactor (1830m) with multiple injections of initiator. See *Table* 3. for the initiator concentration used.

when the initiator is first injected at the reactor inlet, the polymerization reaction is initiated and rapidly accelerates to a high rate (hence reaching a peak temperature). It then gradually slows down, and, when all the initiator is consumed, the reactor temperature falls with the aid of external cooling. At this point, additional initiator is introduced and the reaction continues for another stage. In this manner the total desired conversion is spread over three stages, and high conversion of initiator and monomer is consequently achieved.

Fig. 4. gives temperature profiles, and monomer and initiator conversions along the length of the reactor when the feed (i.e., monomer) stream is split and injected at three different locations along the length of the reactor (see *Fig.* 1c for the reactor dimensions). The initiator concentration and the mass flow rate of monomer at each injection point are given in *Table* 4. Note that the inner diameters of the reactor at different sections, as given in *Fig.* 1c, are determined on the basis of the assumptions, that the density of the fluid is uniform throughout the reactor and that the mass flow rate is proportional to the cross sectional area of the tubular reactor.

Table 4. gives monomer and initiator conversions, molecular weight and its distribution for multiple injections of initiator and monomer. Note that the initiator concentration in *Table* 4. is based on the individual feed (i.e., monomer) stream at the respective injection points, whereas the initiator concentrations in *Tables* 2. and 3 are based on the total feed stream. In the case of multiple injections of monomer, the feed rate at the reactor inlet (F_1) is one half of the total, and those at the second (F_2) and third (F_3) injection points are each one fourth of the total (see the footnote of *Table* 4). Thus, the initiator concentration on the basis of the total feed rate is (Run No. 4 of *Table* 4, for instance) $(5.77\times10^{-7}\times1/2)+(5.77\times10^{-7}\times1/4)+(5.77\times10^{-7}\times1/4)=5.77\times10^{-7}$ (gm-moles/cc). On the other hand, the initiator concentration for Run No. 4 of *Table* 2. is $(1.110\times10^{-6}+0.192\times10^{-6}+0.096\times10^{-6})=1.398\times10^{-6}$ (gm-moles/cc). It is seen that, using much less initiator than is needed for multiple injections of initiator alone, multiple injections of monomer and initiator along the length of the reactor give rise to high conversions of both monomer and initiator without impairing product quality. Comparison of *Table* 4 with *Table* 2. indicates further that the poyethylene produced with multiple injections of both initiator and monomer has a higher average molecular weight than that produced with either a single injection or multiple injections of initiator alone. In the

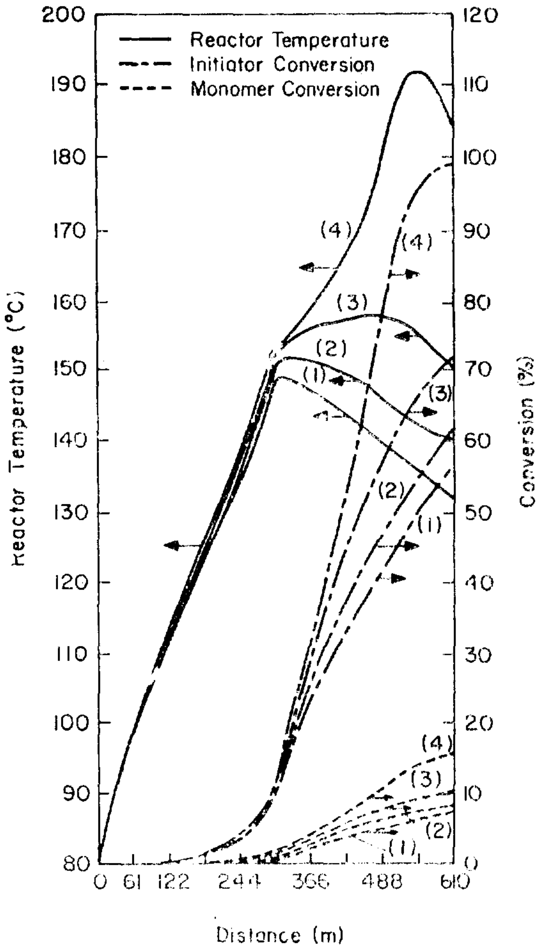

Fig. 4. Profiles of reactor temperature, initiator and monomer concentrations in a tubular reactor for multiple injections of monomer and initiator. See *Table* 4 for the feed rate of monomer and initiator concentration used.

computational results given in *Table*4, we have used a single value of axial diffusion coefficient ($\hat{D}_I$ and $\hat{D}_M$) throughout the entire reactor.

One of the most important characteristics of the high pressure polymerization of ethylene is the long-chain branching reaction. It is well known today that chain transfer from free radicals to dead polymer chains gives rise to long-chain branching, affecting the molecular weight and its distribution. *Table* 5. shows predicted values of molecular weight and its distribution, for different values of the long-chain branching rate constant, when multiple injections of initiator are employed (see *Fig.* 1b for the reactor system studied). It should be pointed out that, since accurate numerical values of the long-chain branching rate constants are not available in the published literature, we have assigned values so that the computed values of average molecular weight are typical of low-density polyethylenes commercially available. Note in *Table* 5. that the long-chain transfer reaction does not affect the conversion or monomer, but changes the molecular weight and its distribution. This predicted trend is in good agreement with the experimental observations given in *Table* 6. of some commercial low-density poly ethylenes.

Table 3. Multiple injections of initiator in a long reactor (1830)m

Initiator I_1	Concentration I_2	(gm-moles/cc) I_3	Initiator conversion (%)	Monomer conversion (%)	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
2.88×10^{-7}	0.64×10^{-7}	2.24×10^{-7}	73.8	13.44	0.82	1.81

Table4. Effect of multiple injections of monomer(a) and initiator on average molecular weight and conversion

Run No. identification	Initiator I_1	Concentration I_2	(gm-moles/cc) I_3	Initiator conversion (%)	Monomer conversion (%)	$M_n\times10^{-4}$	M_w/M_n
1	4.33×10^{-7}	4.33×10^{-7}	4.33×10^{-7}	56.7	7.5	0.98	1.75
2	5.05×10^{-7}	5.05×10^{-7}	5.05×10^{-7}	61.7	8.7	0.87	1.74
3	5.48×10^{-7}	5.48×10^{-7}	5.48×10^{-7}	72.0	10.5	0.79	1.75
4	5.77×10^{-7}	5.77×10^{-7}	5.77×10^{-7}	99.2	15.7	0.72	1.85

(a) Throughput of monomer at three injection points (see *Fig.* 1c for the locations of injection) are : $F_1=3.4\times10^4$ kg/hr; $F_2=1.7\times10^4$ kg/hr; $F_3=1.7\times10^4$ kg/hr.

Table 5. Effect of varing long-chain branching rate(a) on average molecular weight and its distribution

$k_{tr,p}/k_p$	$\bar{M}_n\times10^{-4}$	$\bar{M}_w/\bar{M}_n$
1.83×10^1	2.15	2.61
9.09×10^1	7.34	4.29
1.83×10^2	13.91	7.60

(a) Instead of varying $k_{tr,p}$, the rate constant for chain transfer reaction to dead polymer, the ratio of $k_{tr,p}$ to k_p was varied. Here k_p is the rate constant for chain propagation. $k_{tr,p}/k_p$ may be considered to be varying little with temperature

Table 6. Average molecular weight of some commercially available low-density polyethylenes[7]

Manufacturer	Sample code	$\bar{M}_n\times 10^{-4}$	$\bar{M}_w\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
Chemplex*	CX 3032	1.82	5.6	3.08
	CX 1005	2.07	15.9	7.65
	CX 1016	2.03	15.9	7.85
U.S. Industrial	NA 279	2.00	8.59	4.3
Chemicals Co.**	NA 144	1.78	9.26	5.2
	NA 244	1.74	15.30	8.8
	NA 205	1.89	28.20	14.9

* Long-chain branching level (LCB) is substantially less in CX 3032 than in either CX 1016 and CX 1005, and LCB level between CX 1005 and CX 1016 is not very different.

** Long-chain branching level increase in the order: NA 279, NA 144, NA 244, and NA 205.

References

1. K. Schoenemann and J. Thies, First Intern. Symp. Chem. React. Eng., Carnegie Innst., Washington, D.C., 1970.
2. K. Schoenemann, Tenth Annual Meeting, European High Pressure Research Group, Strasbourg, 1972.
3. S. Agrawal and C.D. Han, *AIChE J.*, **21** (1975), 449.
4. C.H. Chen, J.G. Vermeychuk, J.A. Howell and P. Ehrlich, *AIChEJ.*, **22** (1976) 463.
5. C.D. Han. "Rheology in Polymer Processing", Academic Press, New York, 1976.
6. L.F. Albright, "Processes for Major Addition Type Plastics and Their Monomers," McGraw-Hill, New York, 1974.
7. C.D. Han and C.A. Villamizar, *J. Appl. Polym. Sci.*, in press.