

LOW DENSITY POLYETHYLENE (LDPE) POLYMERIZATION — A REVIEW

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ABSTRACT

Some important technical characteristics of LDPE manufacture are discussed and some details of the simulation of tubular, high pressure LDPE reactors are presented. The kinetic scheme used is fairly complete and includes branching reactions as well as reactions leading to vinyl and vinylidene group formation. The variation of the physical properties of the reaction mass with the change in molecular weight is also accounted for. The model predicts the monomer and initiator conversions, the temperature, and the number-average molecular weight as functions of axial position in the reactor. In addition, the model also enables the computation of the polydispersity index and the concentration of vinyl, vinylidene and methyl groups as a function of position. The latter molecular properties have important implications in terms of product properties. The effect of multiple intermediate feeds is also investigated.

INTRODUCTION

Low density polyethylene (LDPE), manufactured by the free radical polymerization of ethylene at high pressures, is a polymer of great industrial significance¹⁻⁴. Even though, linear low density polyethylene (LLDPE) is fast replacing LDPE, there are several plants in operation all over the world and simulation and optimization studies of these reactors can provide a means of maximizing the profitability of the existing plants. In addition, such studies can help placing the knowledge on the modelling of continuous polymerization reactors on a firmer footing, particularly since a considerable amount of experimental data now exist on the rates of the various reactions taking place in LDPE reactors.

POLYMERIZATION TECHNOLOGY¹⁻³

In LDPE reactors, highly purified ethylene (about 99.9% pure, with <10 ppm oxygen, controlled by IR or GC) is compressed by large ring-type piston compressors (or packed pistons, diaphragm types) in two stages with intermediate cooling, to about 1000–3000 atm. During compression, it must be ensured that ethylene always remains below 100°C. Energy requirements for the compression are very high

e.g. approximately 10500 HP for a 160 million pounds per year plant, and often constitute about a third of the total operating costs. During compression, contamination of ethylene with lubricating oils must be avoided. Considerable caution is required since a mixture of about 3% ethylene in air can explode if ignited by a 450°C source. Therefore, this requires the use of special explosion-proof electrical gear, grounding of vessels, non-sparking tools, fire-fighting equipment, continuous gas testing in critical areas, good ventilation, instrumentation and personnel being far removed, etc.

The initiator (oxygen or organic peroxides, concentrations around 10–100 ppm) is mixed before compression or in the reactor. It is usually soluble in the 'liquid' (super-critical) reaction mixture. The polymer formed is also soluble in the liquid ethylene under usual conditions employed⁵⁻⁷, since these are above the upper critical solution temperature of the ethylene/polyethylene system. Hence one has single-phase bulk polymerization taking place. The mixture is polymerized either in tubular reactors or in stirred autoclaves:

(a) *Tubular reactors:* Typical reactors are characterized by length/diameter \approx 250–

1200), diameter $\approx 1\text{--}3\text{''}$, length $\approx 750\text{--}2500\text{ ft}$, mean residence times $\approx 20\text{--}60\text{ sec}$ and mean velocity of reaction mass $\approx 50\text{--}100\text{ ft/sec}$. The first section of the reactor may be heated by Dowtherm in a jacket, but after some length, it may be necessary to cool the reaction mixture to remove the exothermic heat of reaction of about 24 kcal/mol. The temperature of the reaction mass varies from about 160°C to 300°C since above 300°C, ethylene decomposes. Pressure drops of about 100–350 atm are common, and the conversion per pass is about 10–20%. The heat transfer coefficients are low because of the thick reactor walls. If the reaction mass is not cooled, its temperature can go up to about 1000°C and then ethylene can undergo further exothermic decomposition, leading to explosions. The viscosity of the reaction mass ranges from about 4 to 30 cp (that for pure ethylene at inlet conditions is about 0.06 cp). Once in every minute, the pressure at the end of the reactor is suddenly dropped by about 100–300 atm for several seconds by partially opening a special valve. Because of this, a pressure pulse travels backwards, causing a sudden increase in the flow rate which helps in tearing off any polyethylene deposited at the walls. The effect of pressure pulsing on tearing away of the polymer is a subject of controversy since reactors without it have also been designed.

(b) *Autoclave reactors*: Typical values of the length to diameter ratios are about 4–20, and multiblade shafts are used for stirring. The mean residence times are about a few minutes. Because the *entire* reaction mass is at the same temperature and pressure, these reactors give narrower molecular weight distributions (MWDs) than do tubular reactors. However, because some fluid elements have a very high actual residence time (RTD), small amounts of very high molecular weight material (gel) are formed, making the product from such reactors unsuitable for the manufacture of films (due to haziness). However, because of this reason, the product from such reactors is good for molding since it is tougher. The polymer

formed from these reactors also has substantially higher amount of long-chain branching since the polymerization occurs in the presence of polymer (effect of backmixing).

Relief valves or rupture discs are used for safety. The pressure is controlled by a back-pressure control valve taking the signal from the discharge of the compressor. The temperature is controlled by the initiator injection rate. The product from the reactor is flashed at about 60–300 atm and at 200–250°C, with the reaction mass entering at a very high velocity and impinging on baffles. The gas leaves from the top, is cleaned of oil, wax, solvents, etc by filtration, and is recycled after recompression. The polymer stream is sent for processing.

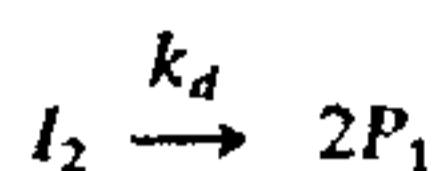
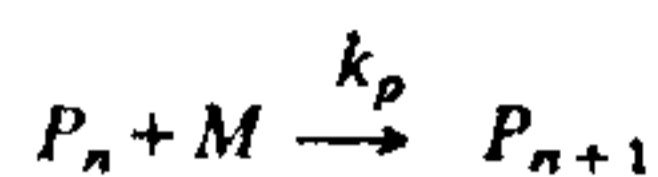
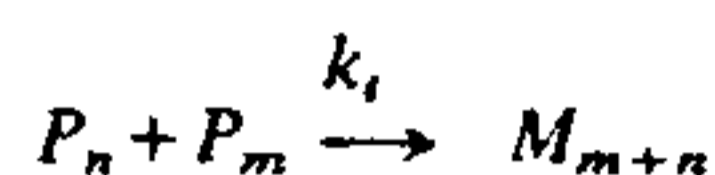
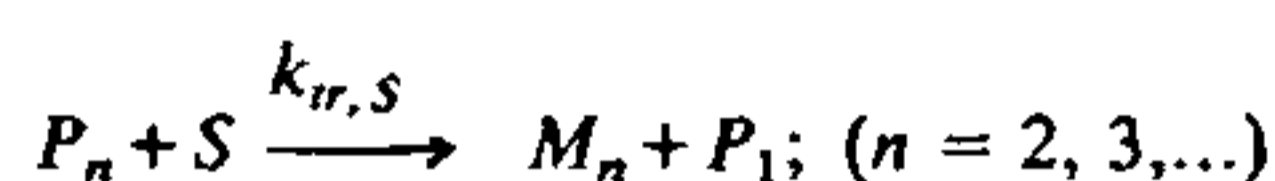
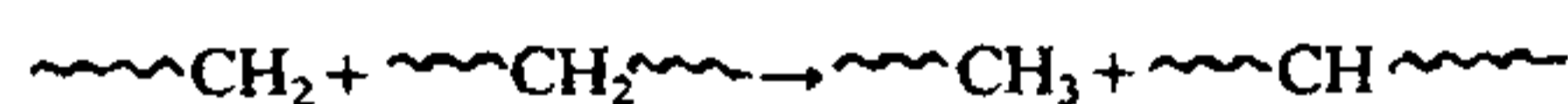
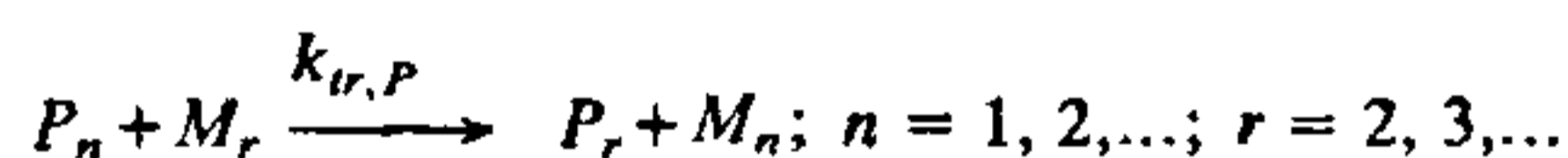
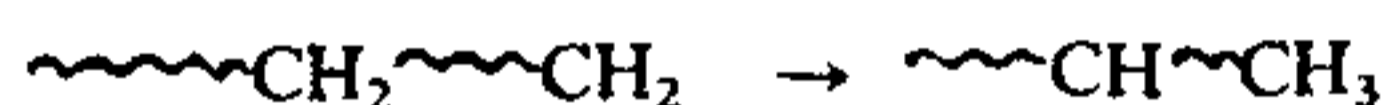
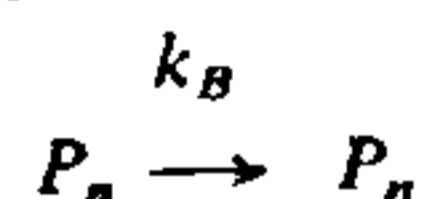
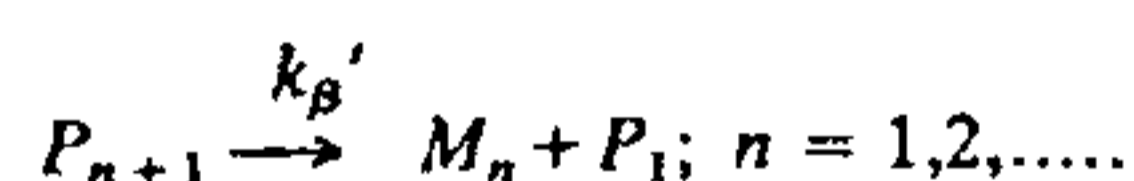
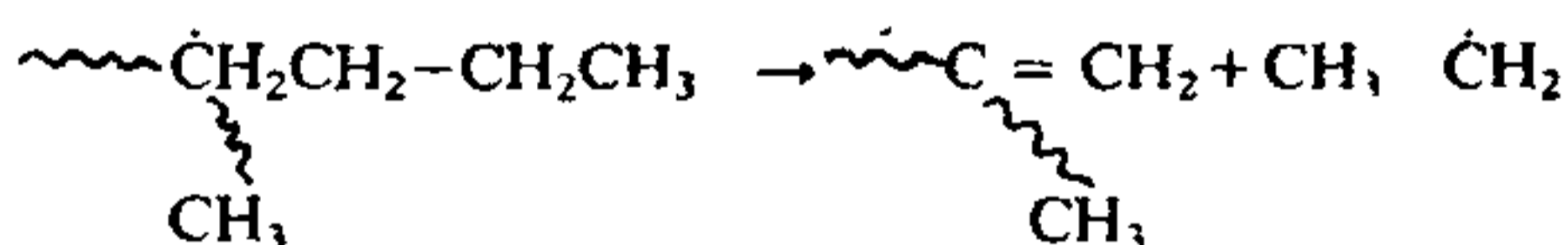
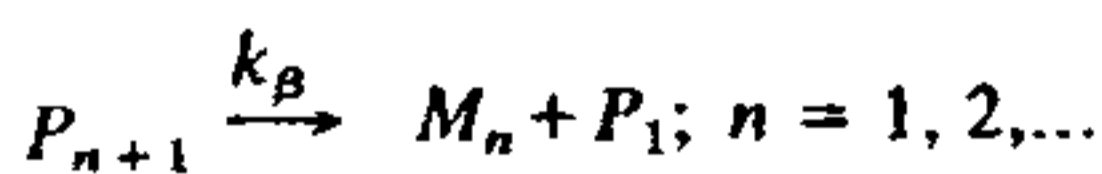
Typical characteristics of the commercial polymer are: polydispersity index $\approx 10\text{--}50$; number of butyl and ethyl (no propyl) branches per 1000 methylene groups of the polymer $\approx 15\text{--}40$; density of the solid polymer $\approx 0.915\text{--}0.925\text{ g/cm}^3$; amount of $\text{R}_1\text{HC}=\text{CH}_2$ (vinyl groups) per 1000 methylene groups of the polymer ≈ 0.05 ; amount of $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$ (vinylidene groups) per 1000 methylene groups $\approx 0.2\text{--}0.8$; number of $\text{R}_1\text{HC}=\text{CHR}_2$ groups per 1000 methylene groups $\approx 0.01\text{--}0.06$. At these double bond locations, oxidative attack can occur, and hence these molecular characteristics of the polymer are of immense importance.

SIMULATIONS OF LDPE REACTORS

Several workers^{8–20} have attempted to simulate industrial LDPE reactors. A detailed discussion is given by Gupta *et al*²¹. Some results from two recent comprehensive studies^{20,21} are presented here.

The tubular reactor is modelled as an ideal plug-flow reactor with no axial mixing. It is assumed that periodic pressure pulsation in actual reactors does not lead to significant axial mixing, as inferred from pilot plant studies¹⁵. Further, because of turbulence, it can be assumed that there are no radial variations in the concentrations of the different species and in the temperature. Since the pressure drops are usually $< 10\%$ of the mean value, it can be

Table 1 Kinetic scheme

1. Initiation2. Propagation3. Termination4. Chain transfer to modifier or solvent (n-hexane)5. Chain transfer to polymer (intermolecular long chain branching)6. Backbiting (intramolecular chain transfer)7. β -Scission of secondary radical (vinyl group formation)8. β -Scission of tertiary radical (vinylidene group formation)

assumed as constant throughout²⁰. Equations are available for various physical properties of the reaction mass viz density (ρ), specific heat (C_p), viscosity (η), and thermal conductivity (k). Laurence²⁰ and Gupta *et al*²¹ differ essentially in the use of different physical property correlations, but the final results are quite similar.

The kinetic scheme used in these studies^{20,21} is given in table 1. This incorporates most of the important main and side reactions. The values for the rate constants used are given in table 2. It has been found²⁰⁻²² that there is a considerable disagreement on the rate constants used by different workers in this area. In fact the rate of polymerization under typical conditions has been computed to vary from²⁰ 0.498×10^6 to 9.156×10^5 mol/lit-sec. The values given in table 1 are probably the best available and represent a combination of the constants of Chen *et al*¹² and Goto *et al*¹³. Other workers have given the activation energy E as a function of the pressure, P , and for more accurate results, one must use this more detailed information. The value of the initiator efficiency is assumed to be unity.

Mole balance equations for the different species as well as for the moments of the chain length distribution, and an energy balance equation for the plug-flow reactor with the physical properties varying with position are given²⁰⁻²². These can be solved using an adaptation of the Runge-Kutta²¹ or Gear's²⁰ method.

Table 2 Rate constants²¹ in table 1 (at $p = 2000$ atm.)
 $k = k_0 \exp(-E/RT)^*$

Reaction	k_0	E
Initiation, k_d (DTBP)	1.6×10^{16}	38400
Propagation, k_p	2.95×10^7	7091
Termination, k_t	1.6×10^9	2400
Chain transfer to modifier or solvent (hexane), $k_{tr,S}$	6.445×10^6	9400
Chain transfer to polymer (intermolecular long chain branching) $k_{tr,P}$	9×10^5	9000
Backbiting (intramolecular chain transfer), k_B	2.95×10^8	9417
β -Scission of secondary radicals, $k_{\beta'}$	**	**
β -Scission of tertiary radicals, k_{β}	**	**

* k_0 in 1/s or lit/mole-s, E in cal/mole; ** $k_{\beta'}$ = $2.315 \times 10^{22} \exp(-33,576/RT) / \{8.51 \times 10^{10} \exp(-13,576/RT) + 5.82 \times 10^{11} \exp(-14,665.4/RT)\}$; k_{β} = $1.583 \times 10^{23} \exp(-34,665.4/RT) / \{8.51 \times 10^{10} \exp(-13,576/RT) + 5.82 \times 10^{11} \exp(-14,665.4/RT)\}$.

Table 3 Operating conditions for reactor simulations

Reaction pressure $P = 2000$ atmosphere (assumed constant)
 Feed temperature $T = 110^\circ\text{C}$
 Feed monomer concentration $[M]_0 = 19.41$ mol/liter
 Feed initiator concentration $[I_2]_0 = 2 \times 10^{-3}$ mol/liter
 Feed solvent concentration $[S]_0 = 0.0$
 Feed velocity $v = 900$ cm/sec.
 Reactor diameter $D = 5.08$ cm
 Jacket temperature $T_j = 180^\circ\text{C}$ (assumed constant)
 Wall heat transfer coefficient $h_w = 0.025$ cal/cm²-sec K
 ρ , C_p , etc of feed are computed using correlations²¹.

Feed concentrations:

$[P_1] = 0.0$; $[P_2] = 0.0$; $\mu_0^* = 0.0$; $\mu_1^* = 0.0$; $\mu_2^* = 0.0$

$\mu_0 = 0.0$; $\mu_1 = 0.0$; $\mu_2 = 0.0$.

μ_i , μ_i^* are the i th moment of the dead and live species respectively.

Table 3 shows values for a typical industrial reactor for which some results are presented. The performance of single-feed reactors is considered first. Figure 1 shows^{21,22} how the temperature of the reaction mass as well as the initiator conversion and the monomer conversion vary with position. The temperature is observed to shoot up very rapidly to about 280°C (parametric sensitivity), and at this position in the reactor, all the initiator is depleted. There is no polymerization beyond this point, and the reactor behaves purely as a heat exchanger. It is interesting to observe how sharply the conversions increase near the temperature peak, and emphasizes the necessity of using small values of Δx to get numerically stable solutions. Recently, generalized conditions leading to parametrically sensitive reactor operation have been obtained²³.

Figure 2 shows the variation of the number average molecular weight (\bar{M}_n), and the polydispersity index (PDI), as a function of position in the reactor, while figure 3 shows similar variations of the number of methyl, vinyl and vinylidene groups per 1000 methylene groups. The value of $[\text{Me}]$ of about 30 per 1000 CH_2 groups lies in the range of 20–35 given by Anson¹ and Goto *et al*¹³ and the value of $[\text{Vinyl}] + [\text{Vinylidene}]$ is about 1 per 1000 CH_2 units, which is also close to the value usually encountered^{1,13}. The computed values of the

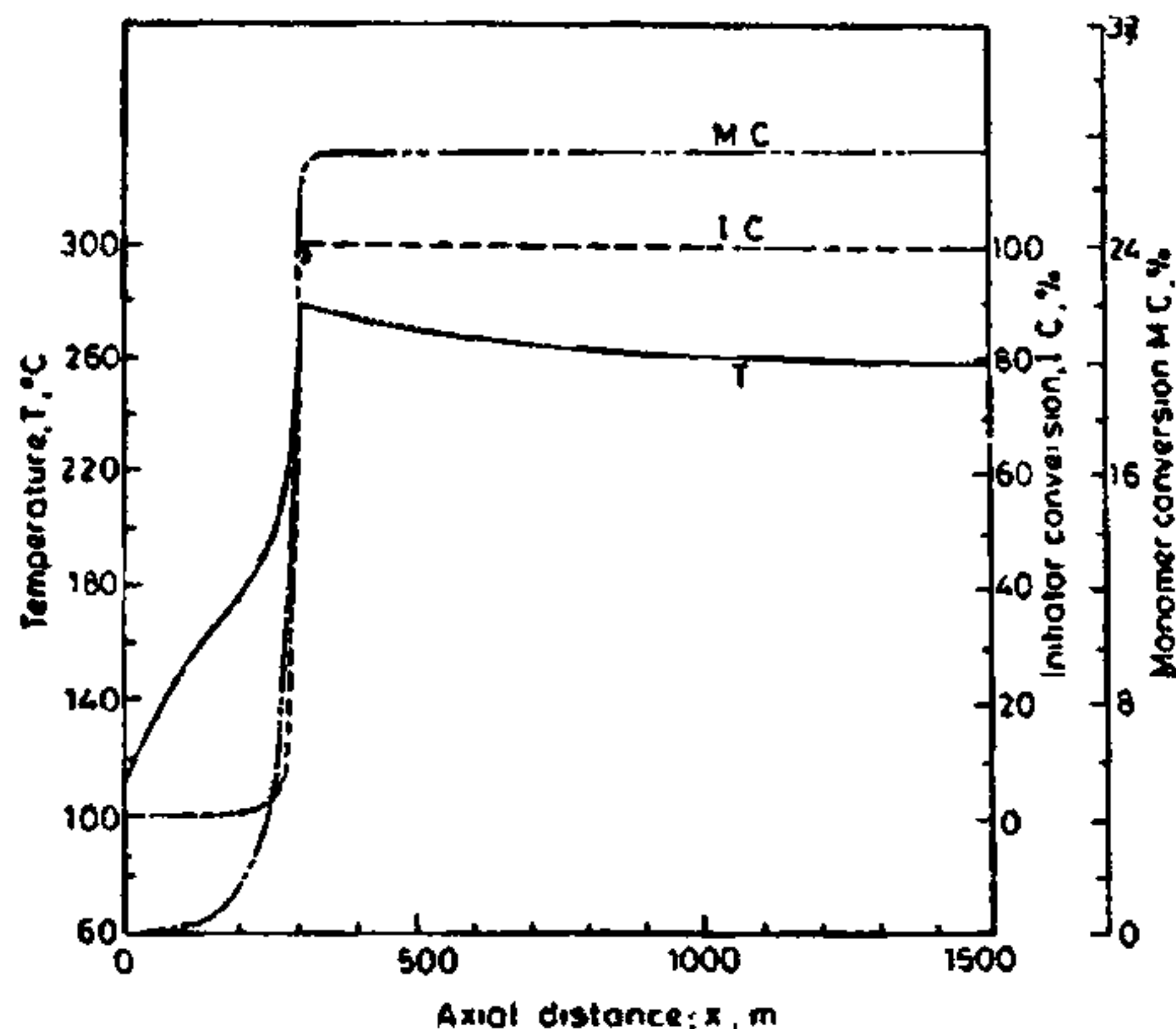


Figure 1. Variation of temperature, initiator conversion and monomer conversion with axial position for a single-feed reactor²¹. Conditions given in table 3.

PDI are within the range of 4–6 encountered in industrial reactors while the value of \bar{M}_n is near typical values reported by earlier workers^{12,13}.

The effect of varying the different reactor parameters as for example, D , $[I_2]_0$, T_0 , T_w , etc have also been studied^{21–22}, but detailed results are not presented here. Similar results have recently been reported by Shirodkar and Tsien²⁴, who have curve-fitted the rate constants to match their results with industrial data.

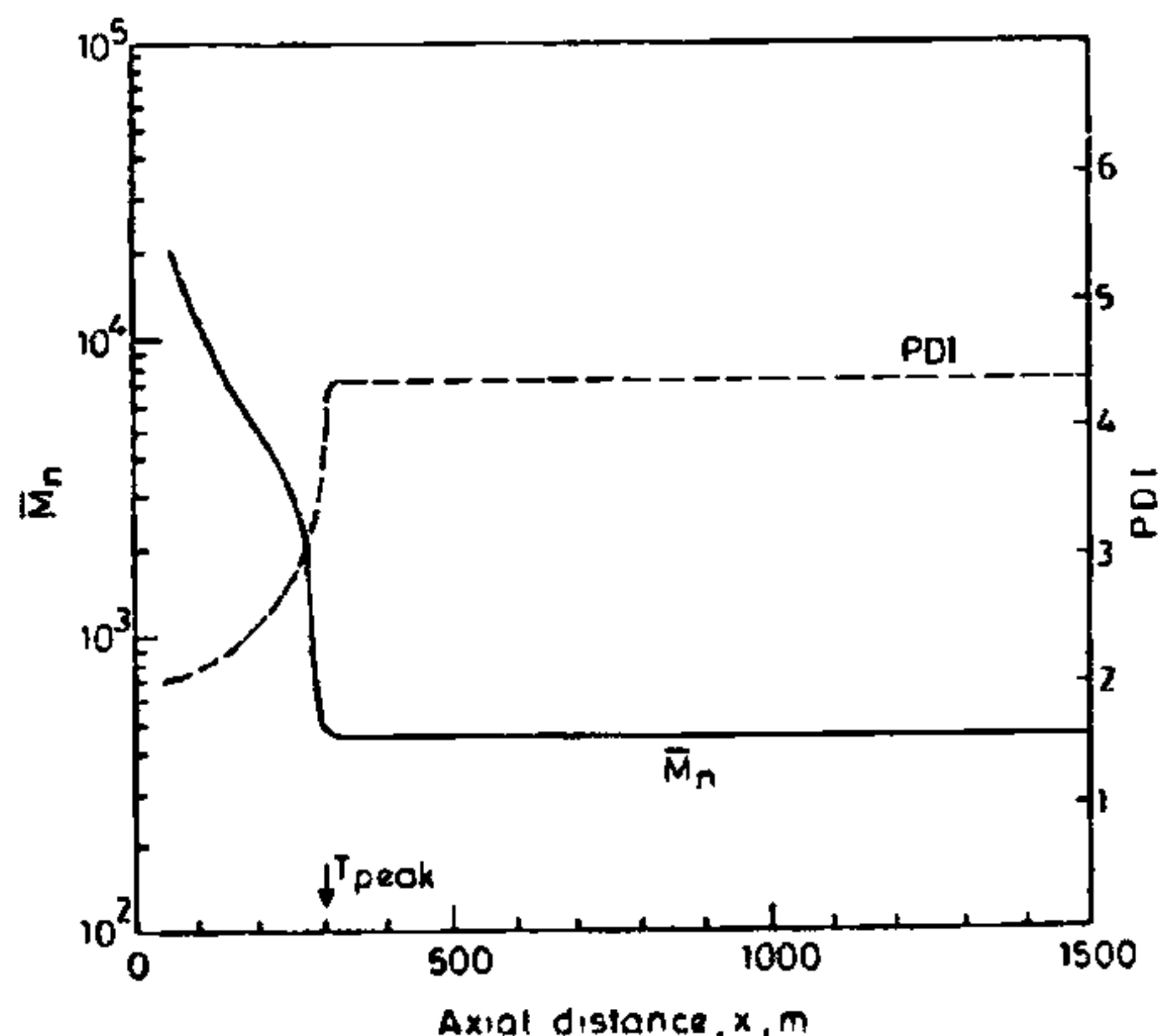


Figure 2. Axial variation of \bar{M}_n and PDI²¹. Conditions as in figure 1.

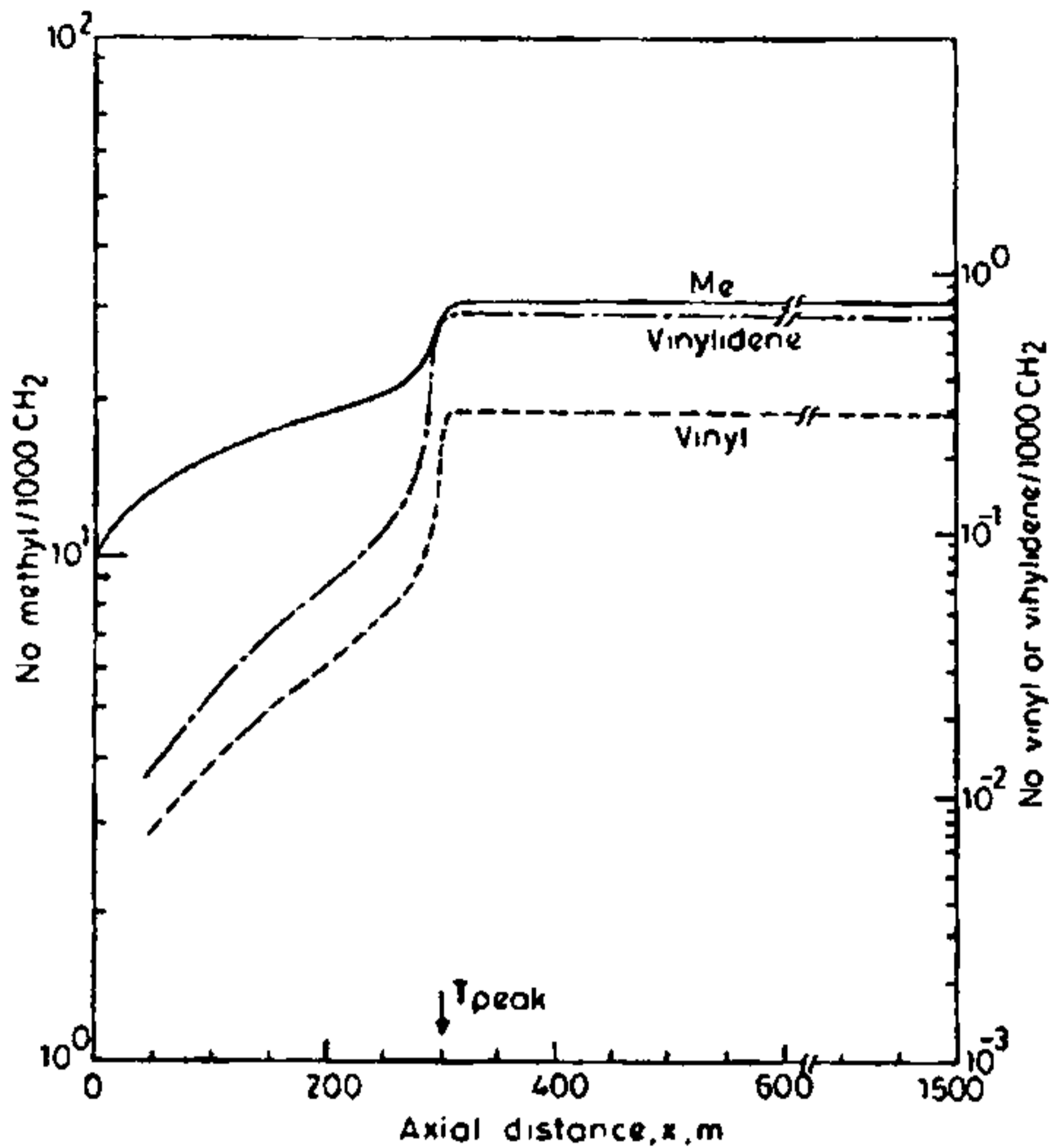


Figure 3. Axial variation of methyl, vinyl and vinylidene group concentrations²¹. Conditions as in figure 1.

Figures 4 and 5 show some results^{21,22} for a reactor with a single *intermediate* feed, the latter consisting of monomer and initiator only. The use of monomer in the intermediate feed leads to cold shot cooling of the reaction mass

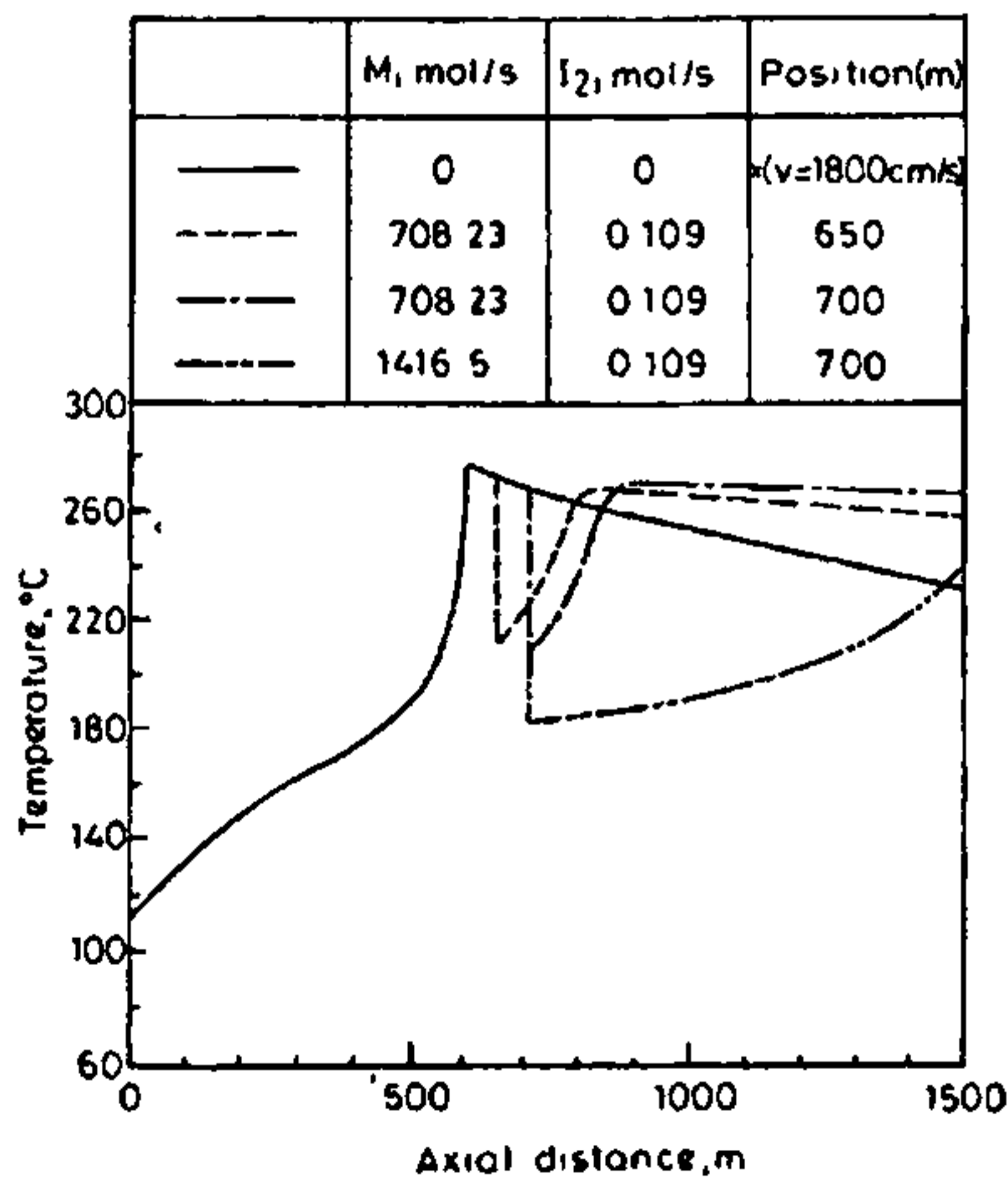


Figure 4. Axial temperature profile with a single intermediate feed²¹. Feed position and characteristics are as indicated.

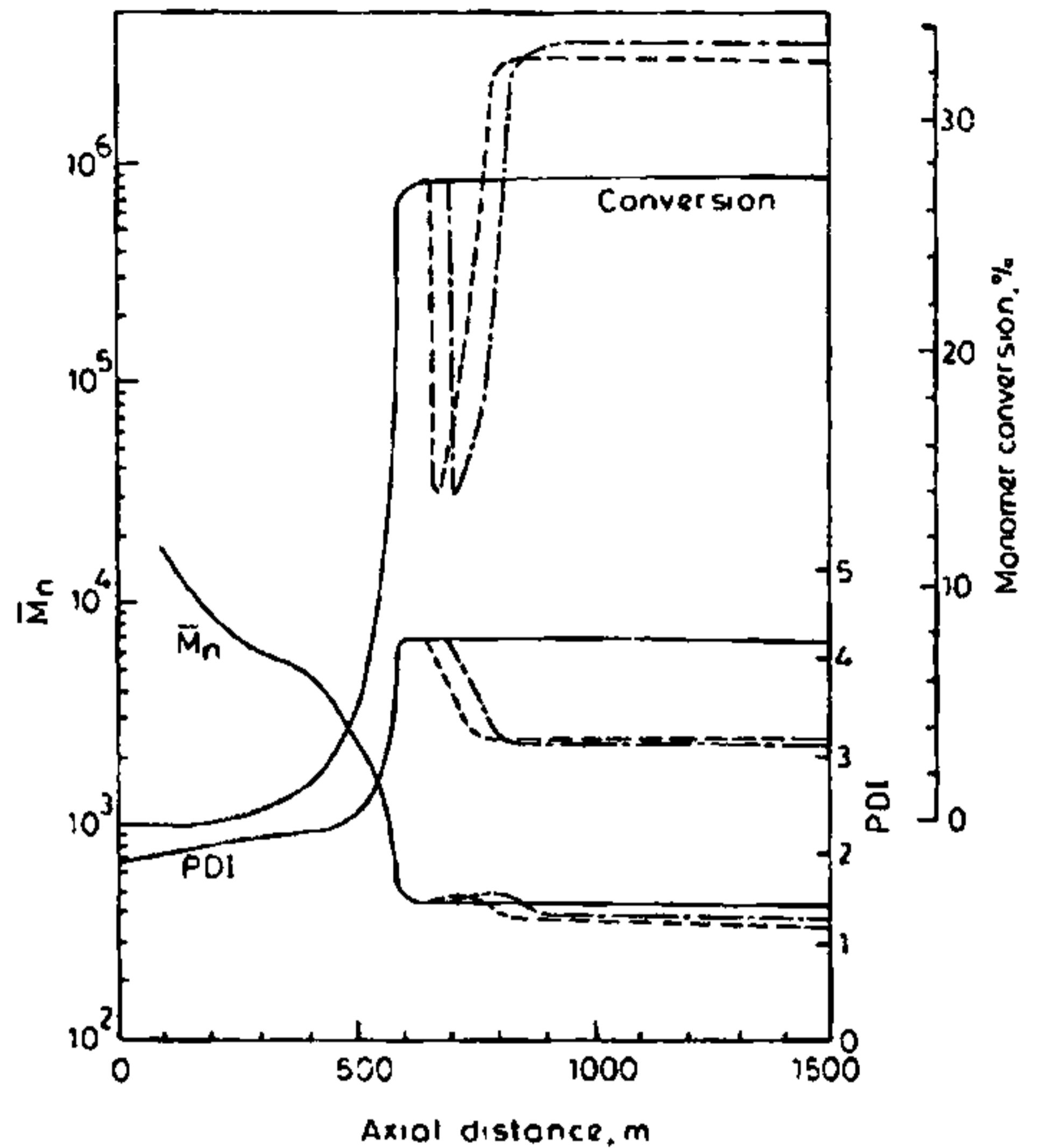


Figure 5. M_n , PDI and overall monomer conversion for an LDPE tubular reactor with a single intermediate feed²¹. Conditions same as in figure 4.

and enables further polymerization. The solid lines correspond to operating conditions as given in table 3, except for the feed velocity which is now 1800 cm/sec. The monomer conversion at any position (figure 5) was defined in terms of the total monomer fed to the reactor *up to that point*. The conversion of the monomer is found to increase slightly by the use of an intermediate feed without affecting the value of M_n significantly. However, the PDI is found to be *lowered* in such reactors. This is probably because a considerable amount of low molecular weight polymer is produced after the intermediate feed point and this reduces the weight average molecular weight substantially. It is possible that by choosing intermediate feed conditions appropriately, the polymer formed after this point has high molecular weight, and the PDI is increased thereafter, as reported by Goto *et al*¹³.

There have been attempts to optimize the performance of LDPE reactors. Yoon and Rhee²⁵ determine the optimal temperature profile required for maximum conversion, using the maximum principle. Their results sug-

gest an increasing temperature profile (first gradually and later, abruptly). However, more comprehensive optimization studies are needed incorporating constraints, and possibly, multiple objective functions.

Epilogue

An attempt was made to present some important quantitative features of the polymerization of LDPE. Several workers claim that their simulation studies match with industrial data, but details are missing for proprietary reasons. The most severe problem is the lack of 'correct' rate constants—several sets are available in the literature, differing from each other by several orders of magnitude, and the high pressures necessary almost prohibit more fundamental laboratory studies to resolve this controversy.

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