

MODELING OF FREE RADICAL POLYMERIZATION OF
STYRENE BY BIFUNCTIONAL INITIATORS WITH
PEROXIDE GROUPS OF UNEQUAL THERMAL STABILITIES

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Peroxide Groups of Unequal Thermal Stabilities**

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Abstract

A detailed kinetic model of the bulk styrene polymerization initiated by diperoxide bifunctional initiators is presented. When chain termination occurs via combination termination mechanism, six distinct polymeric species are identified in accordance with the nature of polymer end units. It is shown that the unequal thermal decomposition characteristics of the peroxides of the bifunctional initiator system leads to the formation of polymers having considerably higher molecular weight than those obtained by the monofunctional initiator system. It has also been found that molecular weight distribution becomes narrower as the bifunctional initiator system is used. The effect of the bifunctional initiator is more pronounced at high reaction temperatures. The new possibilities of increasing the monomer conversion and modifying the polymer molecular weight properties effectively through the use of bifunctional initiators are discussed.

Introduction

The application of multifunctional initiators to the industrial free radical polymerizations of vinyl or styrenic monomers is a relatively new area of research. In contrast to the conventional free radical polymerization initiators such as benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN) having only one labile peroxide or azo group, multifunctional initiators contain more than one labile groups (peroxide and/or azo) having different thermal decomposition characteristics. Although the use of "finishing" catalysts having high activation energies are not uncommon in many industrial free radical polymerization processes in order to enhance the monomer conversion, such mixed initiator systems or single conventional monofunctional initiator systems do not produce polymers of substantially high molecular weight, narrow molecular weight distribution (MWD) and high monomer conversion simultaneously [Kamath and Harpell, (1978)].

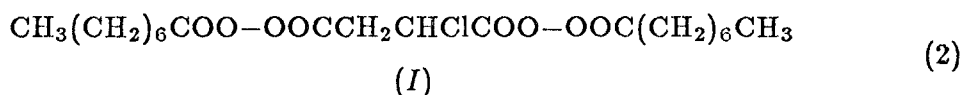
By using properly chosen multifunctional initiators and polymerization conditions, the conversion of monomers and the polymer molecular weight can be significantly increased in a well controlled manner. This has not been possible with conventional monofunctional free radical initiators. Some multifunctional initiators have also been used successfully for block copolymerizations via sequential monomer incorporation techniques [Piirma and Chou (1979), Gunesin and Piirma (1981), Waltz and Heitz (1978)]. Therefore, it is believed that the innovative application of multifunctional free radical initiators opens a new avenue for tailor making polymers or modifying polymer properties without requiring significant reactor equipment modifications. Recently O'Driscoll and Bevington (1985) analyzed the effect of multifunctional initiators on polymer molecular weight distribution in free radical polymerization using both Schultz-Flory distribution function and Monte Carlo simulation methods. They demonstrated that altering the molecular weight distribution was possible by inducing the sequential decomposition of two labile groups in a bifunctional initiator.

In this paper, we shall present a detailed kinetic model for a free radical polymerization of styrene with bifunctional initiators which contain two labile peroxide groups. The effect of unequal thermal stabilities of peroxide groups on the monomer conversion, polymer's molecular weight and MWD will be examined for various polymerization conditions.

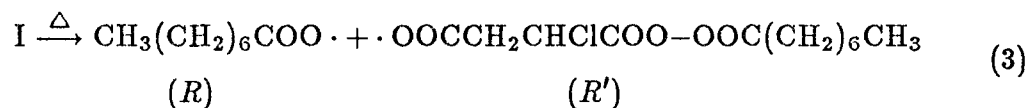
The bifunctional initiator system to be considered in the present study is the diperoxide initiator of the following general structure:



where R_1 and X represent hydrocarbon ligands. The specific initiator system chosen in our numerical simulation study is the diperoxide studied by Prisyazhnyuk and Ivanchev (1970):



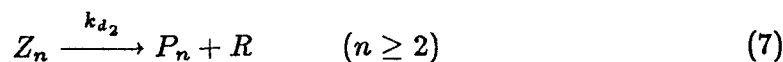
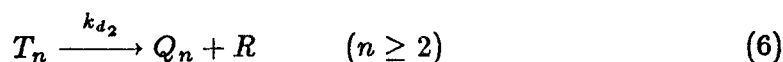
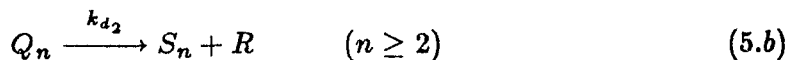
Upon heating, the initiator decomposes into two radical species as follows:



where the primary radical species R' carries an undecomposed peroxide group which may decompose further during the course of polymerization. The above authors found that the two peroxide groups in (I) have different activation energies in spite of their structural resemblance. This is generally true for many other symmetrical diperoxide initiators. When the radical species R' is involved in subsequent polymerization, polymers carrying labile peroxide end groups will be formed and such polymers are called reactive polymers. As will be shown in the following discussion, the existence of two radical species (R and R') creates quite complex reinitiation, propagation and termination reaction kinetics. As a result, the polymers produced by the bifunctional initiator will have some unique properties.

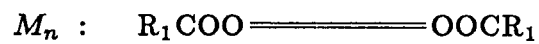
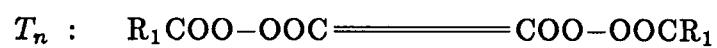
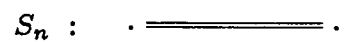
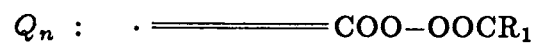
Kinetic Modeling

A mechanism of polymer formation in free radical polymerization initiated by bifunctional initiators is called poly-recombinational polymerization because reactive macromolecules formed in the early stages of polymerization participate in the reaction through re-initiation, propagation and termination. As shown in Table 1, six different polymeric species (P_n , Q_n , S_n , T_n , Z_n , and M_n) can be defined in accordance with the nature of the end units of the polymer chains. Note that P_n , Q_n , and S_n are the growing (or live) polymer radicals with n -monomer units and T_n , Z_n , and M_n are the dead polymers of n -monomer units. However, Q_n , T_n , and Z_n species carry undecomposed peroxide groups ($-\text{COO}-\text{OOCR}_1$) on the chain ends, indicating that these can be reconverted to active radical species via additional thermal decomposition reactions. Thus, the decomposition of peroxide in the bifunctional initiator system is described as following:



where k_{d_1} and k_{d_2} denote the decomposition rate constants of two peroxide groups, respectively. Here, it is assumed that β -scission reaction, induced decomposition, decarboxylation reaction and cyclization reaction do not occur. According to Ivanchev (1977), the decomposition rate constants of more stable peroxides (i.e. peroxides in Q_n , T_n , and Z_n) are independent of chain length.

Table 1. Polymeric species



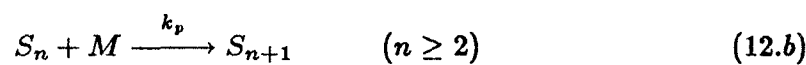
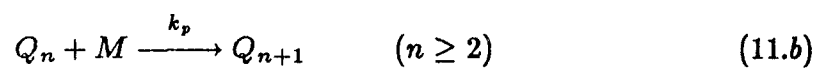
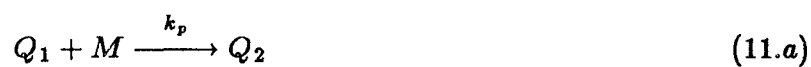
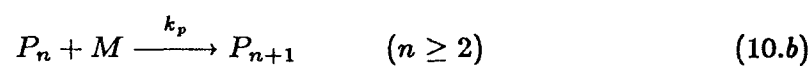
· free radical

==== polymer chain

The initiation of polymer chain propagation takes place as follows:

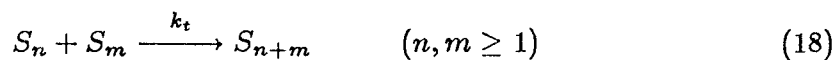
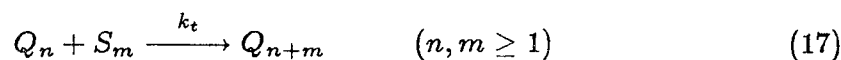
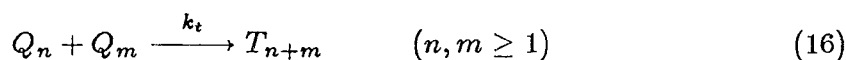
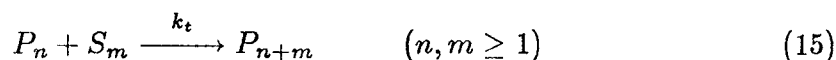
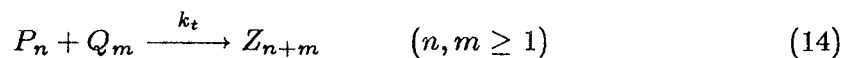
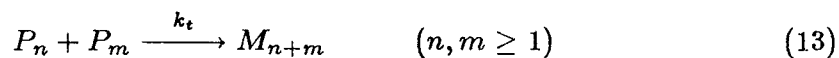


The propagation reactions are:



where the propagation rate constants are also assumed to be independent of polymer chain length.

When the termination of growing polymer chains is due to combination termination (e.g. styrene polymerization), the following reactions will take place:



Note that the main specific feature of the proposed kinetic mechanism of free radical polymerization with bifunctional initiators is a formation during the course of polymerization of macromolecules (e.g. Q_n , T_n , and Z_n) containing undecomposed peroxide groups, which subsequently lead to the formation of polymers having extended polymer chain lengths. In eqs. (13)~(18), the combination termination rate constants for the different polymeric species are assumed to be identical.

With the kinetic scheme proposed above, the rate expressions for various reaction steps take the following form:

For Initiator

$$\frac{dI}{dt} = -k_{d_1} I \quad (19)$$

$$\frac{dR}{dt} = f_1 k_{d_1} I - k_{i_1} RM + k_{d_2} (Q + T + Z) \quad (20)$$

$$\frac{dR'}{dt} = f_2 k_{d_1} I - k_{i_2} R' M \quad (21)$$

where f_1 and f_2 are the initiator efficiencies which indicate the fraction of primary radicals (R and R') being involved in chain initiation.

For Growing Polymer

$$\frac{dP_1}{dt} = k_{i_1} RM - k_p MP_1 - k_t P_1 (P + Q + S) \quad (22)$$

$$\begin{aligned} \frac{dP_n}{dt} = & k_p M (P_{n-1} - P_n) + k_{d_2} Z_n - k_t P_n (P + Q + S) \\ & + k_t \sum_{m=1}^{n-1} P_{n-m} S_m \quad (n \geq 2) \end{aligned} \quad (23)$$

$$\frac{dQ_1}{dt} = k_{i_2} R' M - k_p MQ_1 - k_{d_2} Q_1 - k_t Q_1 (P + Q + S) \quad (24)$$

$$\begin{aligned} \frac{dQ_n}{dt} = & -k_{d_2} Q_n + k_{d_2} T_n + k_p M (Q_{n-1} - Q_n) - k_t Q_n (P + Q + S) \\ & + k_t \sum_{m=1}^{n-1} Q_{n-m} S_m \quad (n \geq 2) \end{aligned} \quad (25)$$

$$\frac{dS_1}{dt} = k_{d_2} Q_1 - k_p MS_1 - k_t S_1 (P + Q + S) \quad (26)$$

$$\begin{aligned} \frac{dS_n}{dt} = & k_{d_2} Q_n + k_p M (S_{n-1} - S_n) - k_t S_n (P + Q + S) \\ & + \frac{k_t}{2} \sum_{m=1}^{n-1} S_{n-m} S_m \quad (n \geq 2) \end{aligned} \quad (27)$$

For Temporarily Dead Polymer

$$\frac{dT_n}{dt} = -k_{d_2}T_n + \frac{k_t}{2} \sum_{m=1}^{n-1} Q_{n-m}Q_m \quad (n \geq 2) \quad (28)$$

$$\frac{dZ_n}{dt} = -k_{d_2}Z_n + k_t \sum_{m=1}^{n-1} P_{n-m}Q_m \quad (n \geq 2) \quad (29)$$

For Monomer and Dead Polymer

$$\frac{dM}{dt} = -k_{i_1}RM - k_{i_2}R'M - k_pM(P + Q + S) \quad (30)$$

$$\frac{dM_n}{dt} = \frac{k_t}{2} \sum_{m=1}^{n-1} P_{n-m}P_m \quad (n \geq 2) \quad (31)$$

where P , Q , S , T , and Z are the total concentrations of the corresponding polymeric species, i.e.,

$$\begin{aligned} P &= \sum_{n=1}^{\infty} P_n & Q &= \sum_{n=1}^{\infty} Q_n & S &= \sum_{n=1}^{\infty} S_n \\ T &= \sum_{n=2}^{\infty} T_n & Z &= \sum_{n=2}^{\infty} Z_n \end{aligned} \quad (32)$$

In order to compute the molecular weight averages of polymers, the following molecular weight moments are used:

$$\lambda_{\xi,k} \equiv \sum_{n=j}^{\infty} n^k \xi_n \quad (\xi = P, Q, S(j=1); T, Z(j=2)) \quad (33)$$

$$\lambda_k^d \equiv \sum_{n=2}^{\infty} M_n \quad (34)$$

where $\lambda_{\xi,k}$ and λ_k^d denote the k -th moment of polymeric species ξ and dead polymers, respectively.

The overall number average chain length (X_N) and weight average chain length (X_W) are defined by

$$X_N = \frac{\sum_{\xi} \lambda_{\xi,1} + \lambda_1^d}{\sum_{\xi} \lambda_{\xi,0} + \lambda_0^d} \quad (\xi = P, Q, S, T, Z) \quad (35)$$

$$X_W = \frac{\sum_{\xi} \lambda_{\xi,2} + \lambda_2^d}{\sum_{\xi} \lambda_{\xi,1} + \lambda_1^d} \quad (\xi = P, Q, S, T, Z) \quad (36)$$

The number average and weight average chain lengths of each polymeric species are also given by

$$X_{N,\xi} = \frac{\lambda_{\xi,1}}{\lambda_{\xi,0}} \quad (\xi = P, Q, S, T, Z) \quad (37)$$

$$X_{W,\xi} = \frac{\lambda_{\xi,2}}{\lambda_{\xi,1}} \quad (\xi = P, Q, S, T, Z) \quad (38)$$

The polydispersity of the polymer is a measure of molecular weight distribution broadening and is defined by

$$PD = \frac{X_W}{X_N} \quad (39)$$

The molecular weight moment equations take the following form

Polymeric species P_n :

$$\frac{d\lambda_{P,0}}{dt} \left(= \frac{dP}{dt} \right) = k_{i_1}RM + k_{d_2}Z - k_tP(P + Q) \quad (40)$$

$$\frac{d\lambda_{P,1}}{dt} = k_{i_1}RM + k_pMP + k_{d_2}\lambda_{Z,1} + k_t[P\lambda_{S,1} - (P + Q)\lambda_{P,1}] \quad (41)$$

$$\begin{aligned} \frac{d\lambda_{P,2}}{dt} = k_{i_1}RM + k_pM(2\lambda_{P,1} + P) + k_{d_2}\lambda_{Z,2} \\ + k_t[2\lambda_{S,1}\lambda_{P,1} + \lambda_{S,2}P - (P + Q)\lambda_{P,2}] \end{aligned} \quad (42)$$

Polymeric species Q_n :

$$\frac{d\lambda_{Q,0}}{dt} \left(= \frac{dQ}{dt} \right) = k_{i_2}R'M + k_{d_2}(T - Q) - k_tQ(P + Q) \quad (43)$$

$$\begin{aligned} \frac{d\lambda_{Q,1}}{dt} = k_{i_2}R'M + k_pMQ + k_{d_2}(\lambda_{T,1} - \lambda_{Q,1}) \\ + k_t[\lambda_{S,1}Q - (P + Q)\lambda_{Q,1}] \end{aligned} \quad (44)$$

$$\begin{aligned} \frac{d\lambda_{Q,2}}{dt} = k_{i_2}R'M + k_pM(2\lambda_{Q,1} + Q) + k_{d_2}(\lambda_{T,2} - \lambda_{Q,2}) \\ + k_t[2\lambda_{S,1}\lambda_{Q,1} + \lambda_{S,2}Q - (P + Q)\lambda_{Q,2}] \end{aligned} \quad (45)$$

Polymeric species S_n :

$$\frac{d\lambda_{S,0}}{dt} \left(= \frac{dS}{dt} \right) = k_{d_2}Q - k_tS(P + Q) - \frac{k_t}{2}S^2 \quad (46)$$

$$\frac{d\lambda_{S,1}}{dt} = k_{d_2}\lambda_{Q,1} + k_pMS - k_t(P + Q)\lambda_{S,1} \quad (47)$$

$$\frac{d\lambda_{S,2}}{dt} = k_{d_2}\lambda_{Q,2} + k_pM(2\lambda_{S,1} + S) + k_t[\lambda_{S,1}^2 - (P + Q)\lambda_{S,2}] \quad (48)$$

Polymeric species T_n :

$$\frac{d\lambda_{T,0}}{dt} \left(= \frac{dT}{dt} \right) = -k_{d_2}T + \frac{k_t}{2}Q^2 \quad (49)$$

$$\frac{d\lambda_{T,1}}{dt} = -k_{d_2}\lambda_{T,1} + k_t\lambda_{Q,1}Q \quad (50)$$

$$\frac{d\lambda_{T,2}}{dt} = -k_{d_2}\lambda_{T,2} + k_t(\lambda_{Q,2}Q + \lambda_{Q,1}^2) \quad (51)$$

Polymeric species Z_n :

$$\frac{d\lambda_{Z,0}}{dt} \left(= \frac{dZ}{dt} \right) = -k_{d_2}Z + k_tPQ \quad (52)$$

$$\frac{d\lambda_{Z,1}}{dt} = -k_{d_2}\lambda_{Z,1} + k_t(\lambda_{P,1}Q + \lambda_{Q,1}P) \quad (53)$$

$$\frac{d\lambda_{Z,2}}{dt} = -k_{d_2}\lambda_{Z,2} + k_t(\lambda_{P,2}Q + 2\lambda_{P,1}\lambda_{Q,1} + \lambda_{Q,2}P) \quad (54)$$

Dead Polymer :

$$\frac{d\lambda_0^d}{dt} = \frac{k_t}{2}P^2 \quad (55)$$

$$\frac{d\lambda_1^d}{dt} = k_tP\lambda_{P,1} \quad (56)$$

$$\frac{d\lambda_2^d}{dt} = k_t(P\lambda_{P,2} + \lambda_{P,1}^2) \quad (57)$$

Applying the quasi-steady state approximation to live radical species leads to the following algebraic expressions for P , Q and S (live polymeric radical species):

$$P = \frac{1}{2k_t} \left\{ -k_tQ + [(k_tQ)^2 + 4k_t(f_1k_{d_1}I + k_{d_2}(Q + T + 2Z))]^{1/2} \right\} \quad (58)$$

$$Q = \frac{1}{2k_t} \left\{ -(k_tP + k_{d_2}) + [(k_tP + k_{d_2})^2 + 4k_t(f_2k_{d_1}I + k_{d_2}T)]^{1/2} \right\} \quad (59)$$

$$S = \frac{1}{k_t} \left\{ -k_t(P + Q) + [k_t^2(P + Q)^2 + 2k_tk_{d_2}Q]^{1/2} \right\} \quad (60)$$

Table 2. Numerical Values of Kinetic Constants and Base Operating Conditions

$$\left\{ \begin{array}{l} k_{d_1} = 6.824 \times 10^{10} \exp(-22,800/RT), \text{ sec}^{-1} \\ k_{d_2} = 6.594 \times 10^{14} \exp(-30,500/RT), \text{ sec}^{-1} \end{array} \right\} \begin{array}{l} \text{Prisyazhnyuk and Ivanchev} \\ (1970) \end{array}$$

$$\left\{ \begin{array}{l} k_p = 1.051 \times 10^7 \exp(-7,060/RT), \text{ l/mol sec} \\ k_t = 1.260 \times 10^9 \exp(-1,680/RT), \text{ l/mol sec} \end{array} \right\} \begin{array}{l} \text{Brandrup and Immergut} \\ (1975) \end{array}$$

$$k_{i_1} = k_{i_2} \approx k_p$$

$$I_0 = 0.025 \text{ mol/l}$$

$$M_0 = 8.728 \text{ mol/l}$$

$$f_1 = 0.23, \quad f_2 = 0.23, \quad T = 70^\circ C$$

Model Simulations

The proposed kinetic model of the bifunctional initiator system has been used to simulate the isothermal batch bulk polymerization of styrene using the diperoxide initiator shown in eq. (2). The numerical values of kinetic constants and standard polymerization conditions are given in Table 2. Note that the decomposition activation energies of the two peroxide groups differ considerably. According to Ivanchev (1979), the thermal stability of peroxide groups is not affected by whether or not the neighboring groups have decomposed if they are separated by fairly long hydrocarbon bridges. It is also assumed that the gel effect is not strong in styrene polymerization up to relatively low monomer conversion ($\sim 60\%$). Modelling equations and moment equations derived in the previous section were solved by the fourth order Runge-Kutta method.

Figure 1 shows the fractional conversion of the initiator (species I in eq. (2)) at three different polymerization temperatures. The effects of polymerization temperature on the fractional conversion of monomers for the bifunctional initiator system and for the monofunctional system are illustrated in Figure 2(a) and 2(b), respectively. Quite clearly, a significant increase in monomer conversion is obtained when the bifunctional initiator is used, notably at high reaction temperature. When the monofunctional initiator (i.e. $k_{d_2} = 0$) is used under identical polymerization conditions, Figure 2(b) shows the monomer conversion levels off at only 23% at 100°C. This is due to the premature decomposition of the initiator as in Figure 1. This is called the dead-end polymerization. When the bifunctional initiator is used, monomer conversion is significantly increased due to the reinitiations of various polymeric species containing reactive peroxide end groups; the polymerization is first initiated by radicals formed during the breakdown of less stable peroxide group. Subsequently the polymerization is reinitiated by radicals formed during the decomposition of more stable peroxide group of the peroxide molecules on the end of longer polymer chains (cf. eqs. (5), (6), and (7)). As shown in Figure 3, the reaction mixture consists mainly of inactive polymeric species (Z_n , T_n , and M_n) and unreacted monomers at 70°C. At higher temperatures, however, the decomposition of undecomposed peroxide groups (thermally more stable) is facilitated, and the rapid generation of more radicals is resulted. Consequently, the overall monomer conversion increases considerably even after the original initiator species (I) has been completely consumed. In Figure 3, the concentration of live polymer radicals (P_n , Q_n , and S_n) are not shown because their concentrations are negligibly small.

The effect of bifunctional initiator concentration on the monomer conversion is illustrated in Figure 4. As expected, the use of high initiator concentration leads to high monomer conversion. The experimental data of monomer conversion shown in Figures 2(a) and 4 are from Prisyazhnyuk and Ivanchev (1970). Note that the prediction of the proposed kinetic model agrees quite well with experimentally observed monomer conversion data.

Figure 5 shows the ratios of total primary radical concentrations in the bifunctional initiator system to that in the monofunctional initiator system. Apparently, at low temperatures (e.g. 70°C) no significant increase in radical concentration is observed during the course of polymerization. However, the ratio increases very sharply at higher temperatures due to the rapid depletion of primary radicals when monofunctional initiator is used. Similar phenomenon is also observed for total live polymer radical concentrations in two different initiator systems as shown in Figure 6.

The dramatic effect of bifunctional initiators on the polymer molecular weight properties is illustrated in Figure 7(a). When compared with the number average chain length (NACL) of polystyrene produced by the monofunctional initiator (Figure 7(b)), the NACL obtained by the bifunctional initiator is considerably higher, particularly at high polymerization temperatures. Figure 7(a) also illustrates that although the NACL is lower at higher reaction temperature during the early reaction stage, the polymer molecular weight increases continuously with reaction time, notably at higher polymerization temperatures. Clearly, this is due to the continuous reinitiation of polymeric species Q_n , T_n , and Z_n which contain undecomposed peroxide groups. During the early reaction period, polymer formation is primarily due to the decomposition of less stable peroxides; however as monomer conversion increases more stable peroxides (mostly residing in active polymer chains) decompose, resulting in a significant increase in the overall degree of polymerization. Clearly, this molecular weight enhancement with the bifunctional initiator system is due to the combination termination mode which allows the formation of reactive polymer chain ends. From practical point of view, the use of high polymerization temperatures in order to produce polymers of high molecular weight is advantageous in that batch polymerization time can be reduced significantly without sacrificing the molecular weight of polymers. It has also been found that the MWD of polystyrene obtained with the bifunctional initiator is narrower than that obtained with the monofunctional initiator. Figure 8 shows this point. The MWD narrowing effect is especially noticeable for high temperature polymerizations. Figure 7 and 8 sug-

gest that the molecular weight and MWD control of polystyrene can be achieved effectively by using the bifunctional initiators having more than one labile groups differing in their thermal decomposition rates.

The number average chain lengths of various polymeric species have also been computed and they are shown in Figure 9 for three different polymerization temperatures. Note that the NACLs of live polymers (e.g. P_n , Q_n , and S_n) tend to be higher at higher reaction temperature; however, their contribution to the NACL of final polymer is negligibly small because of their low concentrations (c.f. Figure 3). Unfortunately, the complete comparison of our model simulations with experimental data is not made due to the lack of reported experimental molecular weight measurements for the bifunctional initiator system in Prisyazhnyuk and Ivanchev (1970).

Concluding Remarks

In this paper, we have presented a detailed kinetic model of the bulk styrene polymerization initiated by diperoxide bifunctional initiators. When chain termination occurs via combination termination mechanism, six distinct polymeric species are identified in accordance with the nature of polymer end units. The overall number average chain length and the number average chain lengths of each polymeric species were computed by solving the molecular weight moment equations. It has been illustrated that the unequal thermal decomposition characteristics of the peroxides of the bifunctional initiator system leads to the formation of polymers having substantially higher molecular weight than those obtained by the monofunctional initiator system. The effect of the bifunctional initiator is more pronounced at high reaction temperatures. Such polymer chain extension phenomenon is a consequence of extended radical lifetime and increased radical concentration via sequential decomposition of peroxides. It has also been found that MWD becomes narrower as the bifunctional initiator system is employed. The proposed model prediction was compared with the experimental data reported in the literature and the agreement was quite satisfactory. Through our model simulation, it has been demonstrated that the use of bifunctional initiators offers polymerization reaction engineers a new opportunity for increasing the monomer conversion and modifying the polymer molecular weight properties more effectively.

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Notation

E_1	Activation energy of decomposition of less stable peroxide
E_2	Activation energy of decomposition of more stable peroxide
f_i	Initiator efficiency ($i = 1, 2$)
I	Initiator concentration
I_0	Initial initiator concentration
k_{d_i}	Initiator decomposition rate constant ($i = 1, 2$)
k_{i_j}	Initiation rate constant ($j = 1, 2$)
k_p	Propagation rate constant
M	Monomer concentration
M_0	Initial monomer concentration
PD	Polydispersity
X_N	Number average chain length of polymer
X_W	Weight average chain length of polymer
$\lambda_{\xi, k}$	k-th moment of species ξ
λ_k^d	k-th moment of dead polymer

Figure Captions

- Figure 1 Initiator conversion profiles for different reaction temperatures.
- Figure 2(a) Effect of polymerization temperature on monomer conversion with diperoxide bifunctional initiator, $I_0=0.025$ mol/l; ●, experimental data [Prisyazhnyuk and Ivanchev (1970), 70°C, $I_0=0.025$ mol/l].
- Figure 2(b) Effect of polymerization temperature on monomer conversion with monofunctional initiator, $I_0=0.025$ mol/l.
- Figure 3 Effect of temperature on the composition distribution of polymeric species for bifunctional initiator system, $I_0=0.025$ mol/l; (a) 70°C, (b) 85°C, (c) 100°C.
- Figure 4 Effect of bifunctional initiator concentration on monomer conversion at 70°C [Experimental data by Prisyazhnyuk and Ivanchev (1970), 70°C; ●, $I_0=0.025$ mol/l; ○, $I_0=0.050$ mol/l; ■, $I_0=0.075$ mol/l].
- Figure 5 Primary radical concentration ratios at different polymerization temperatures.
- Figure 6 Growing polymer radical concentration ratios at different polymerization temperatures.
- Figure 7(a) Effect of polymerization temperature on number average polymer chain length for bifunctional initiator system, $I_0=0.025$ mol/l.
- Figure 7(b) Effect of polymerization temperature on number average polymer chain length for monofunctional initiator system, $I_0=0.025$ mol/l.
- Figure 8(a) Effect of temperature on polydispersity for bifunctional initiator system, $I_0=0.025$ mol/l.
- Figure 8(b) Effect of temperature on polydispersity for monofunctional initiator system, $I_0=0.025$ mol/l.

Figure 9 Effect of temperature on the number average chain length of polymeric species, $I_0=0.025$ mol/l; (a) 70°C, (b) 85°C, (c) 100°C.

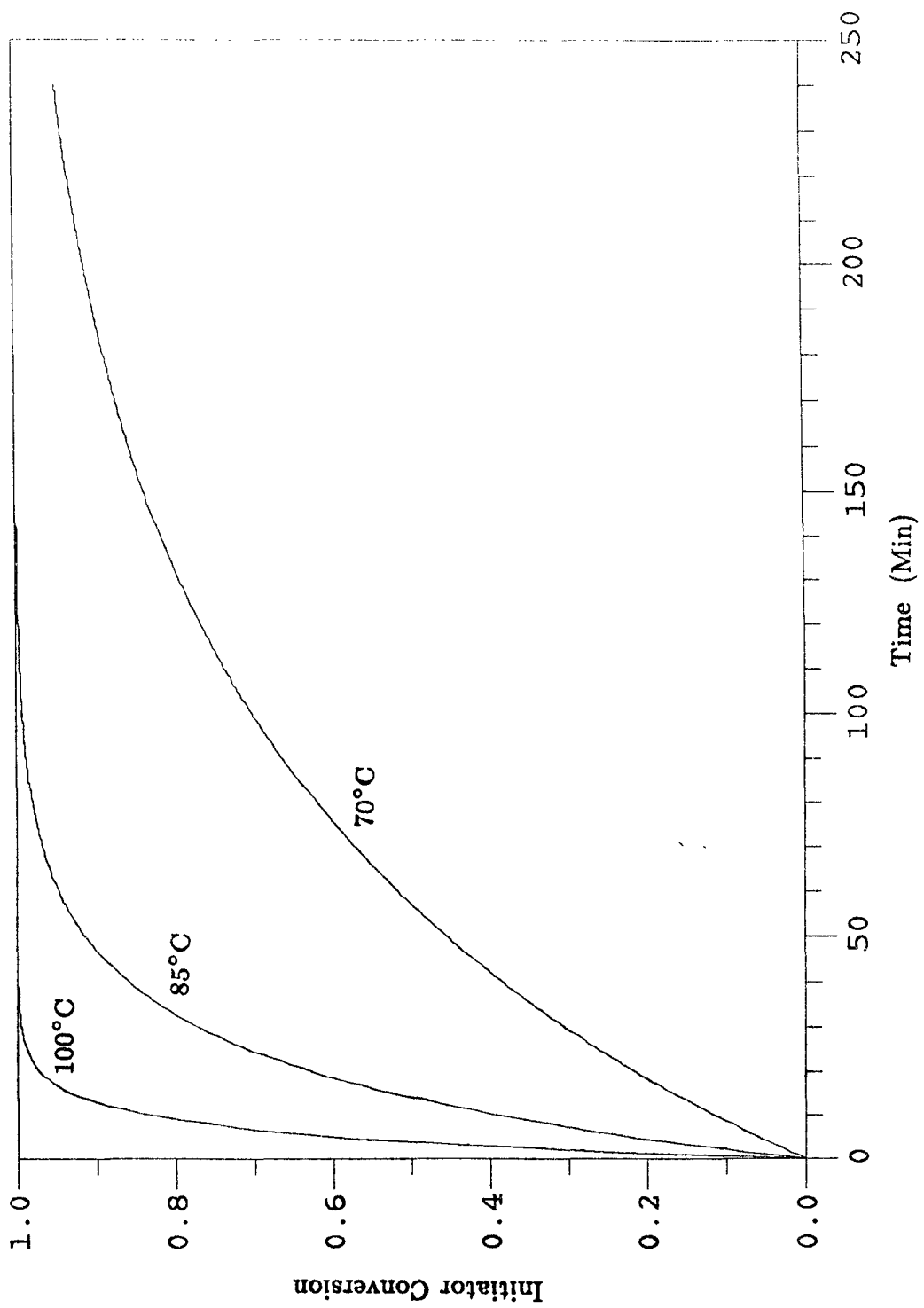


Figure 1

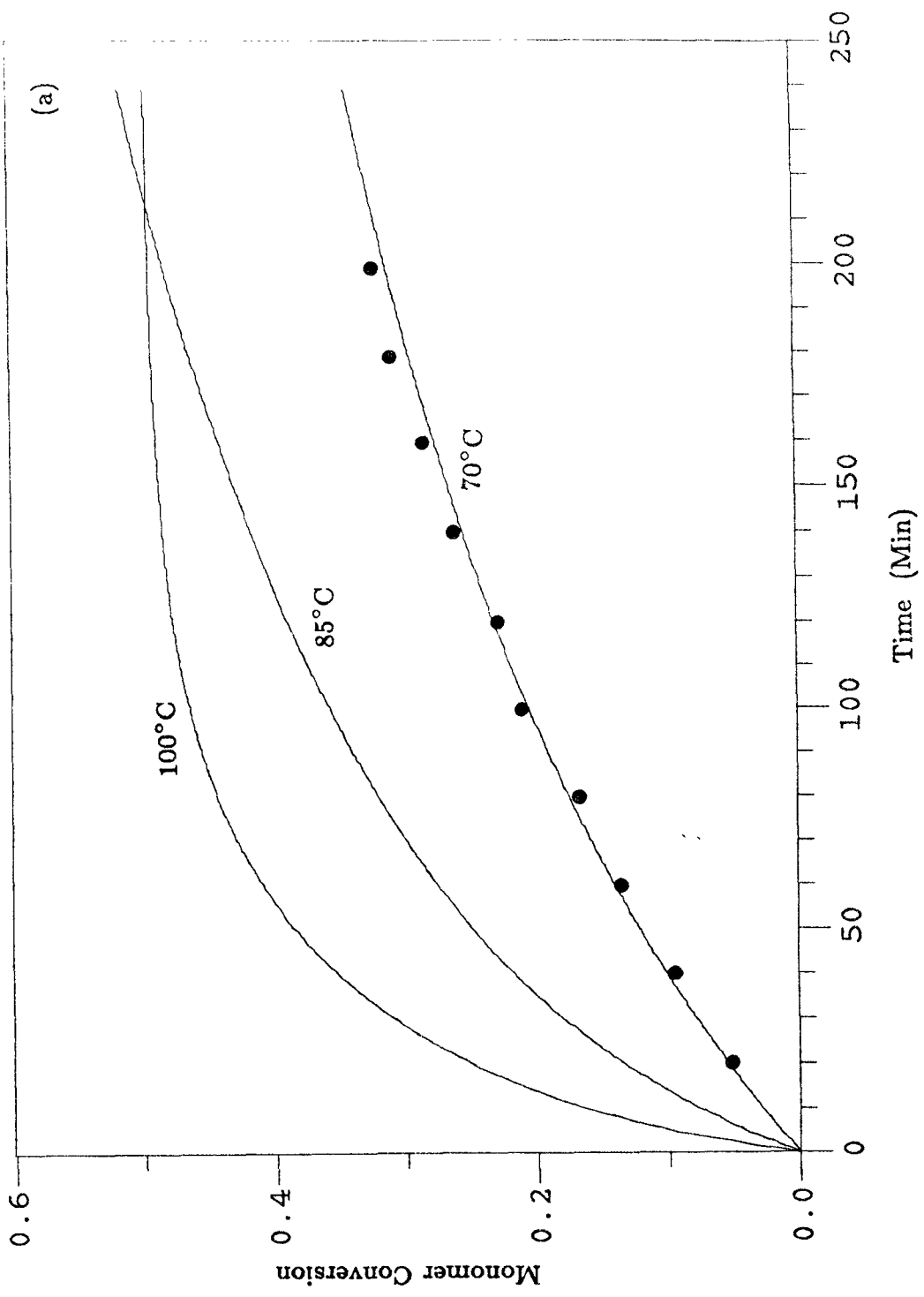


Figure 2(a)

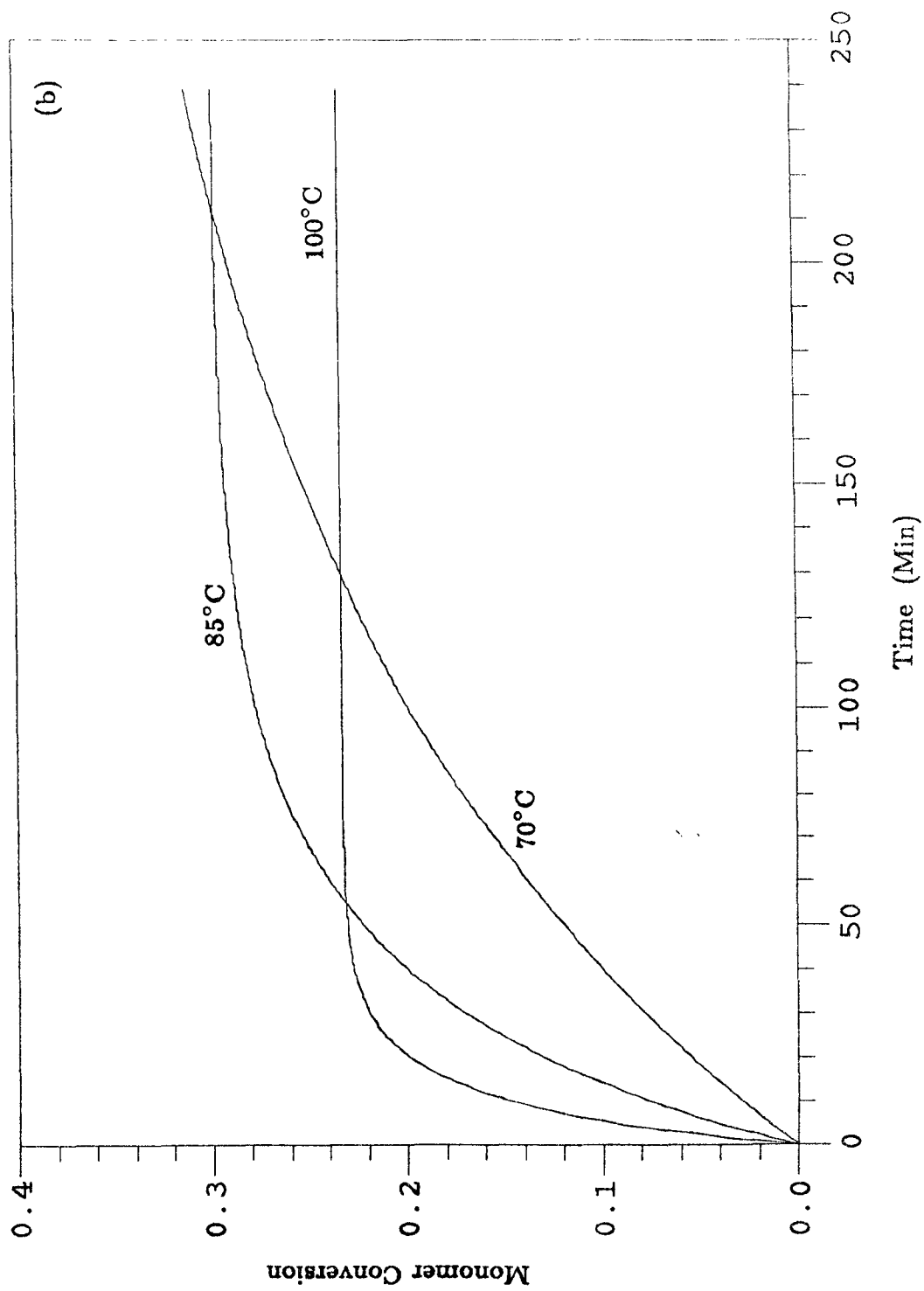


Figure 2(b)

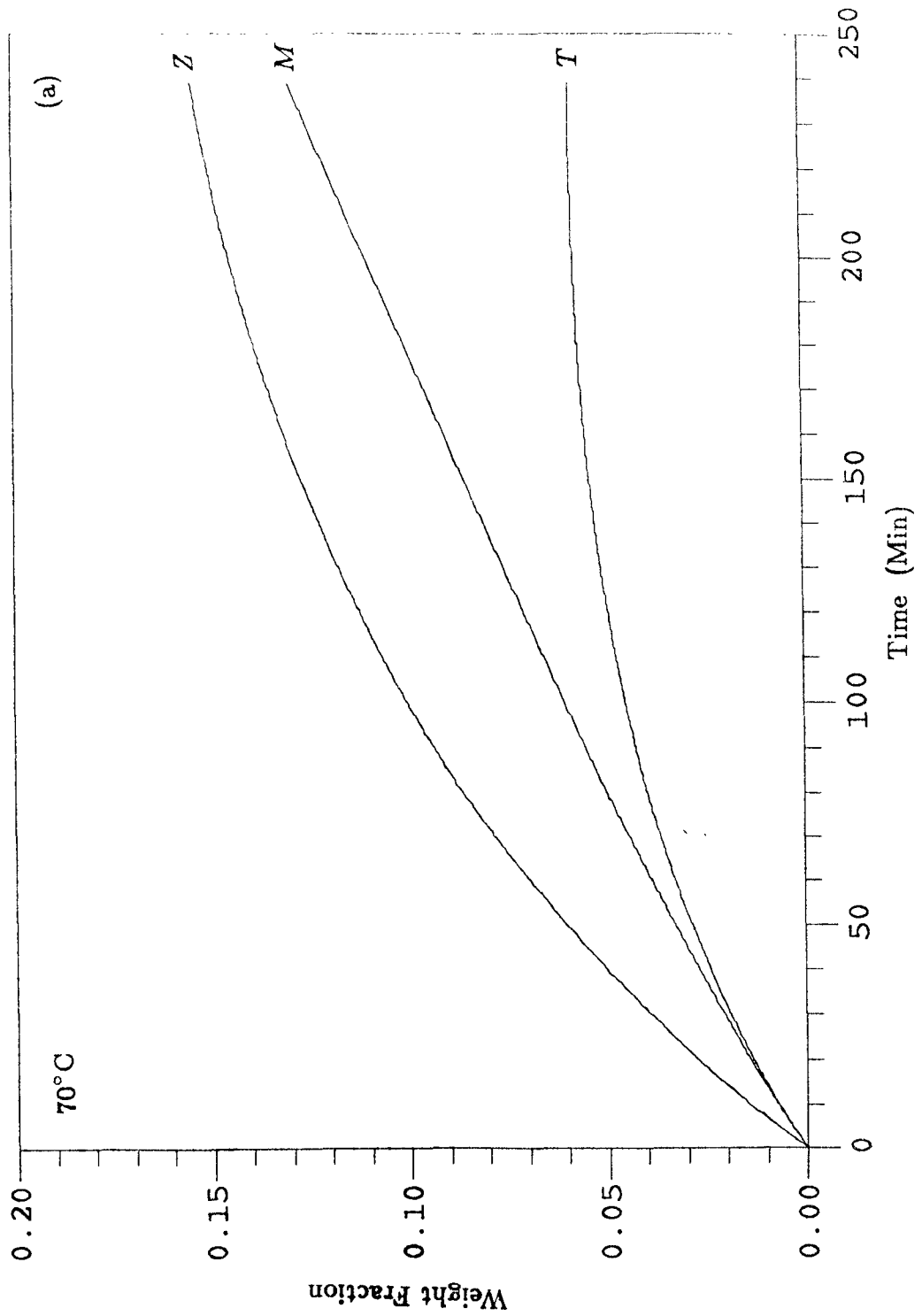


Figure 3(a)

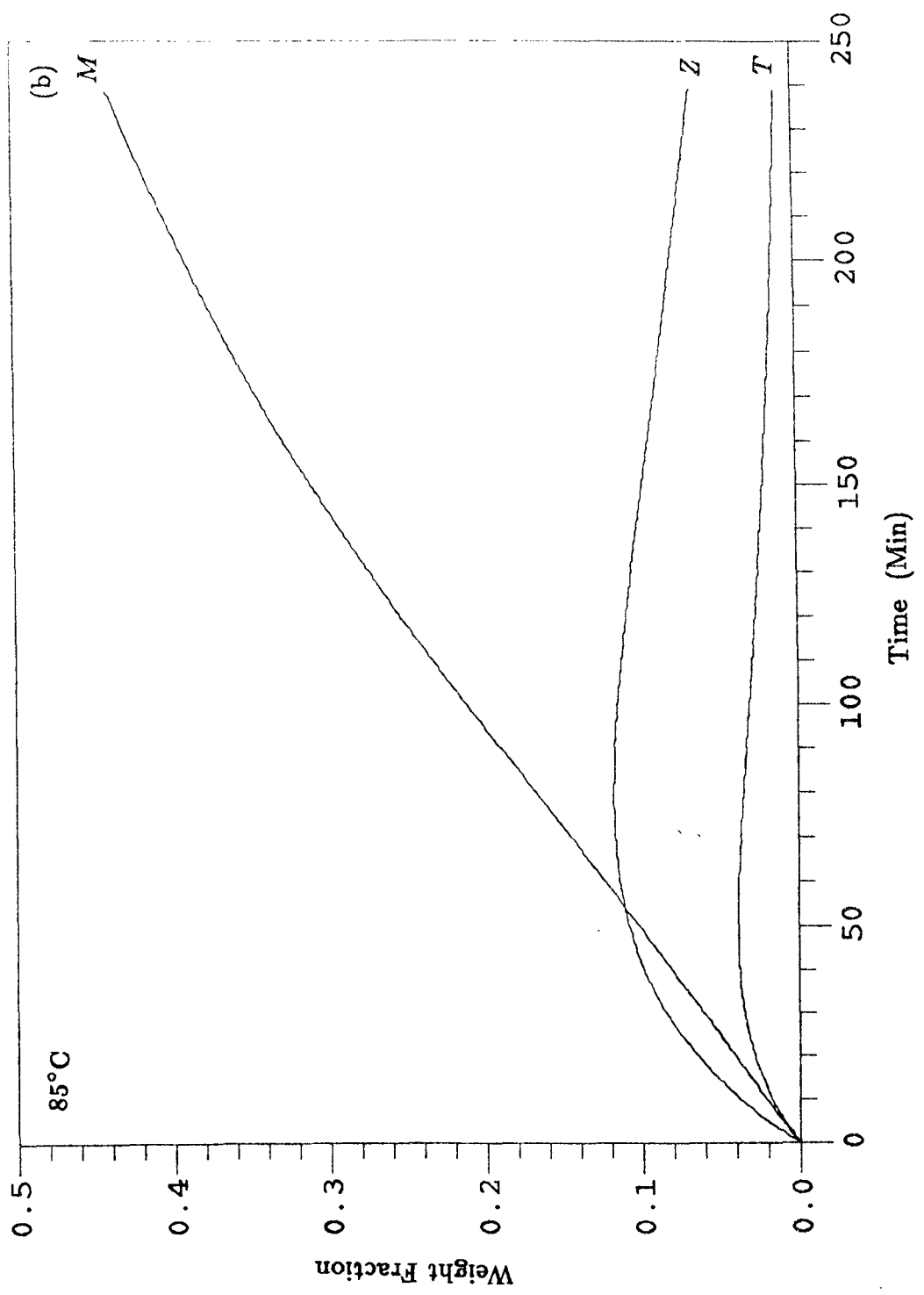


Figure 3 (b)

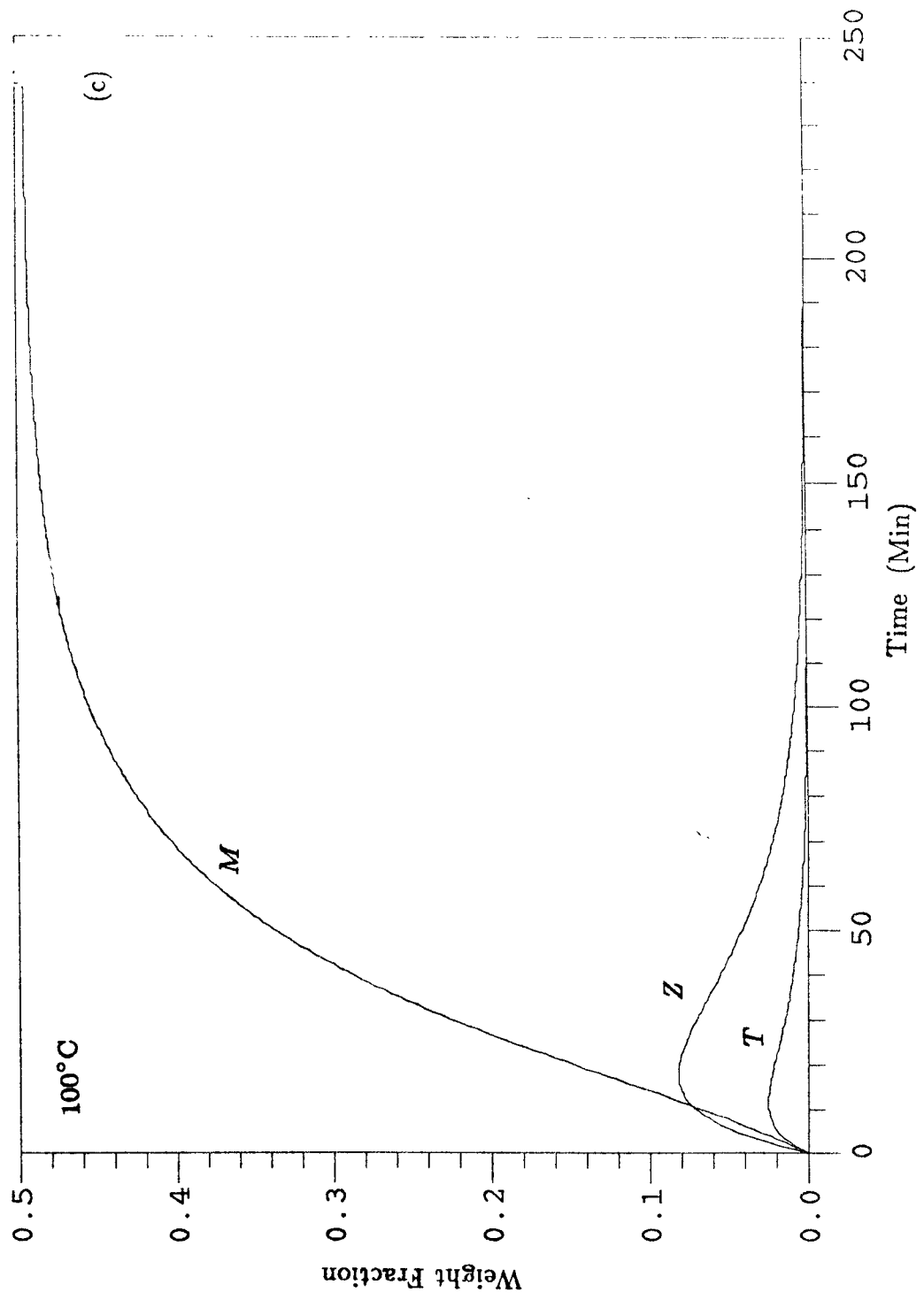


Figure 3(c)

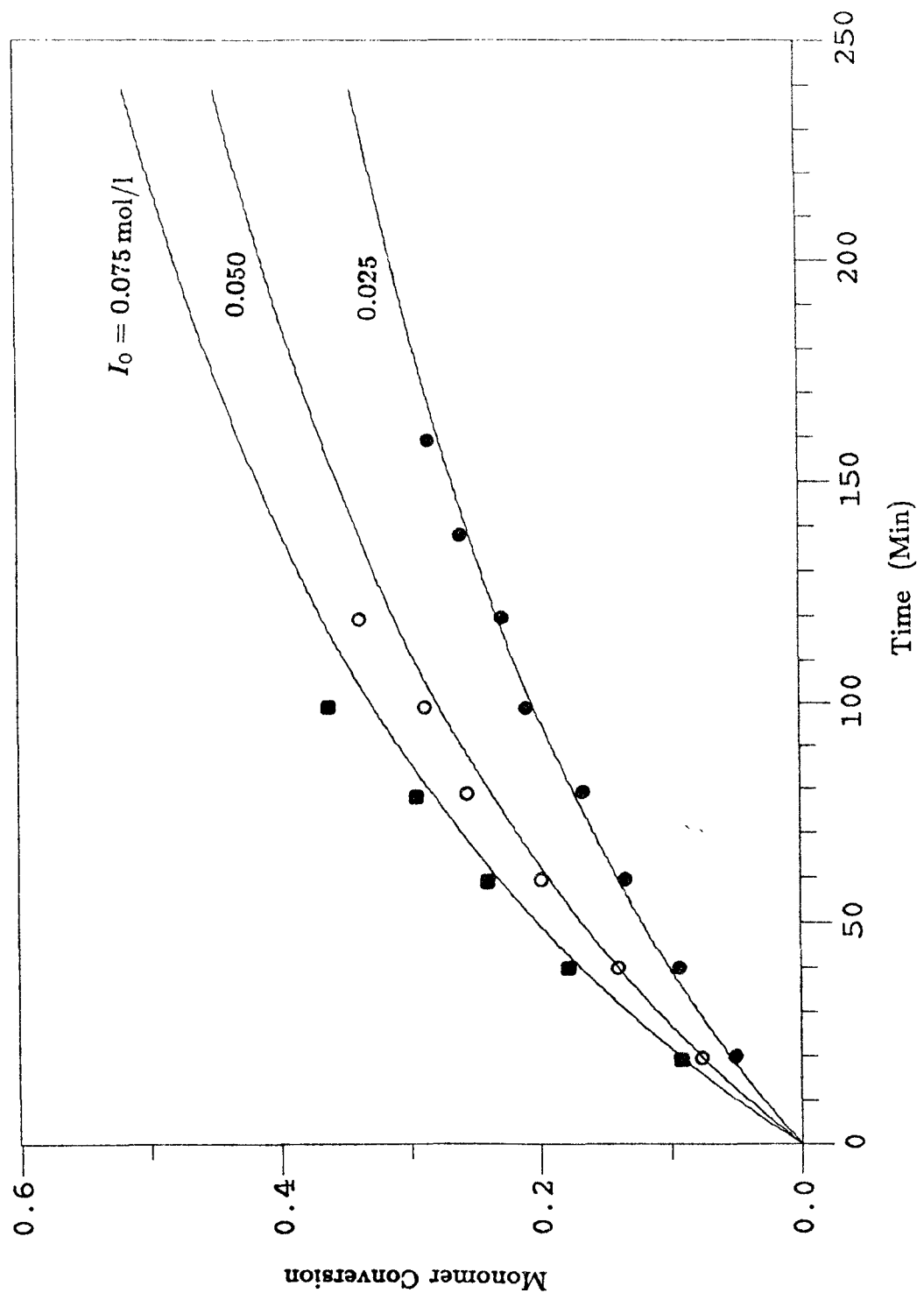


Figure 4

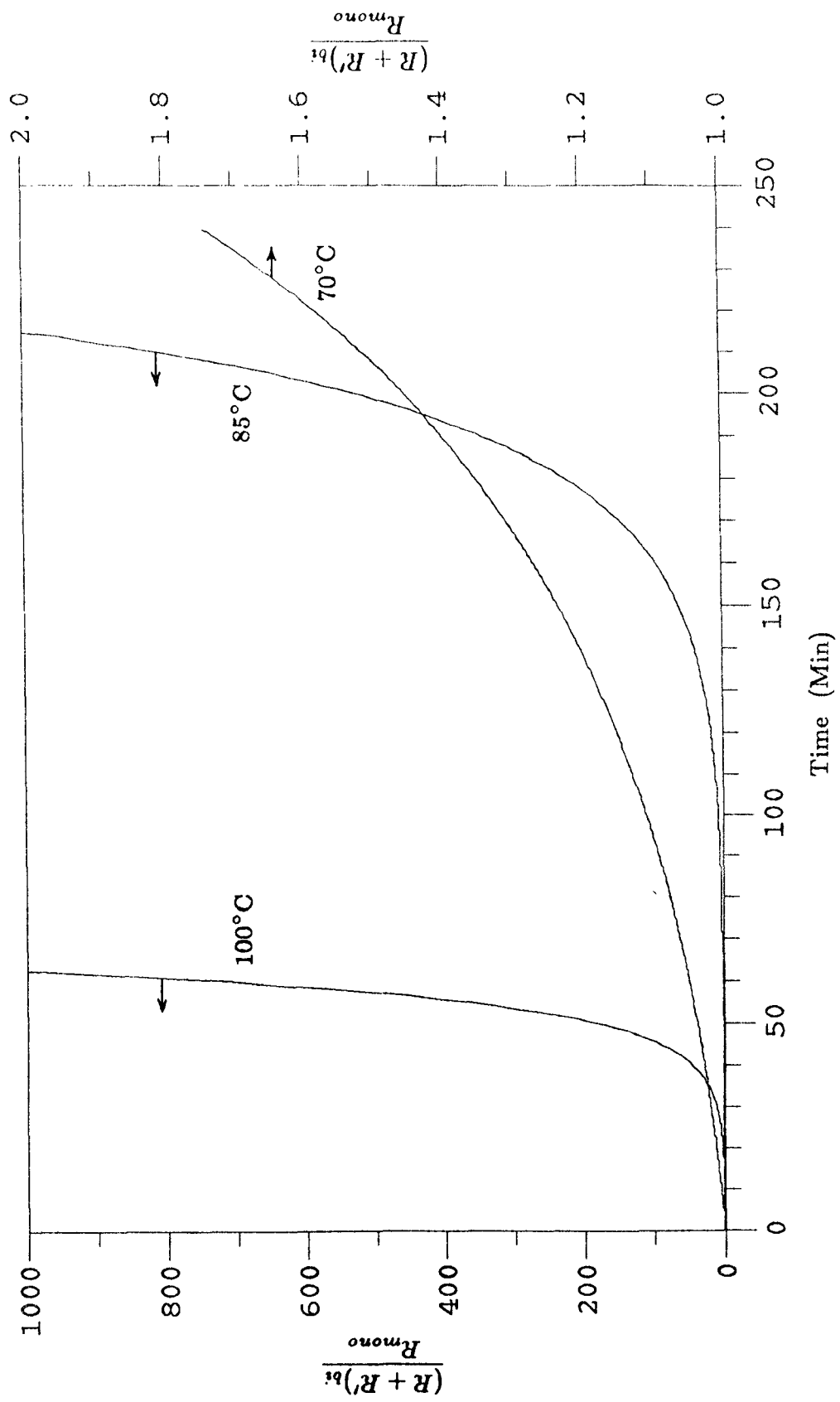


Figure 5

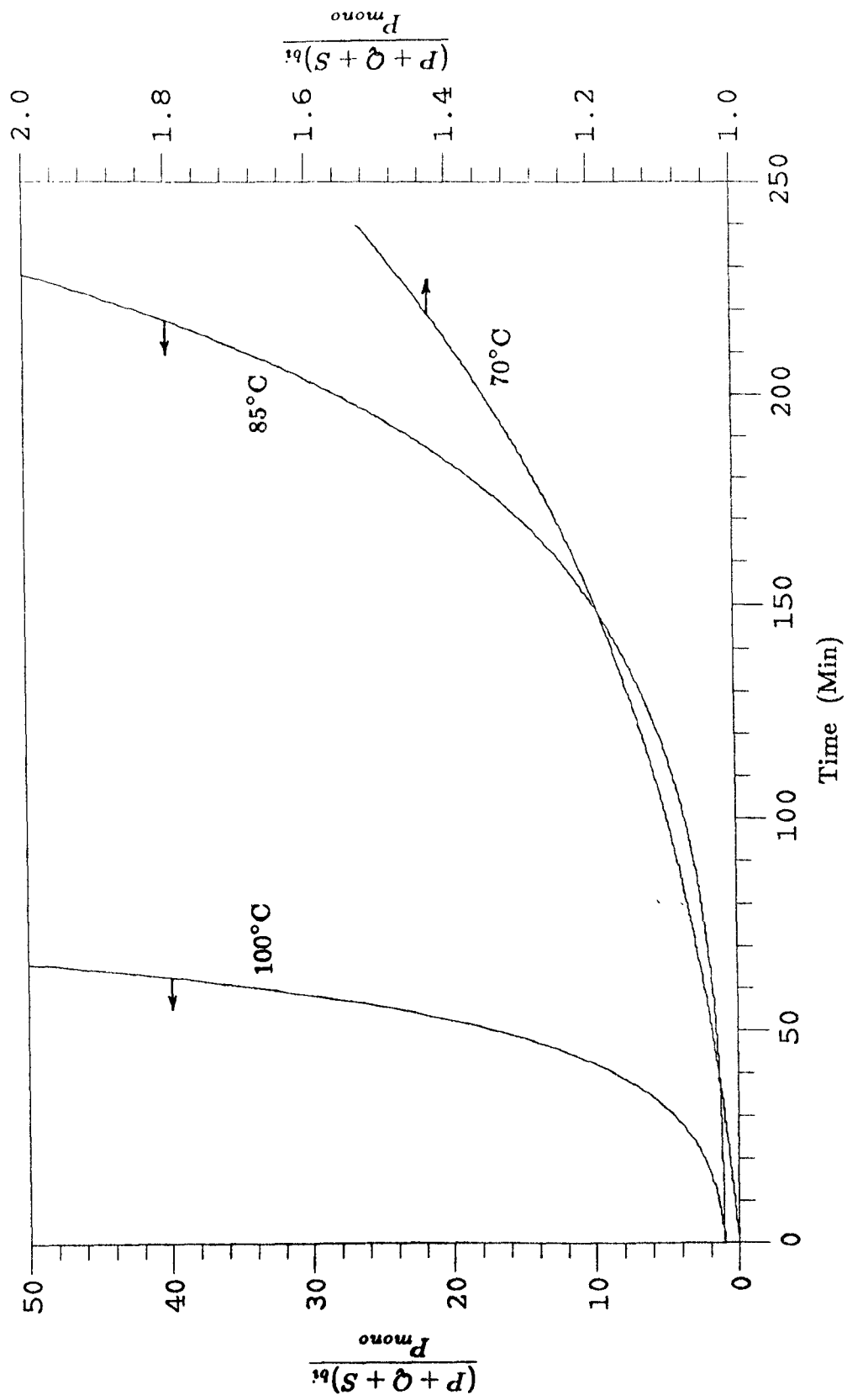


Figure 6

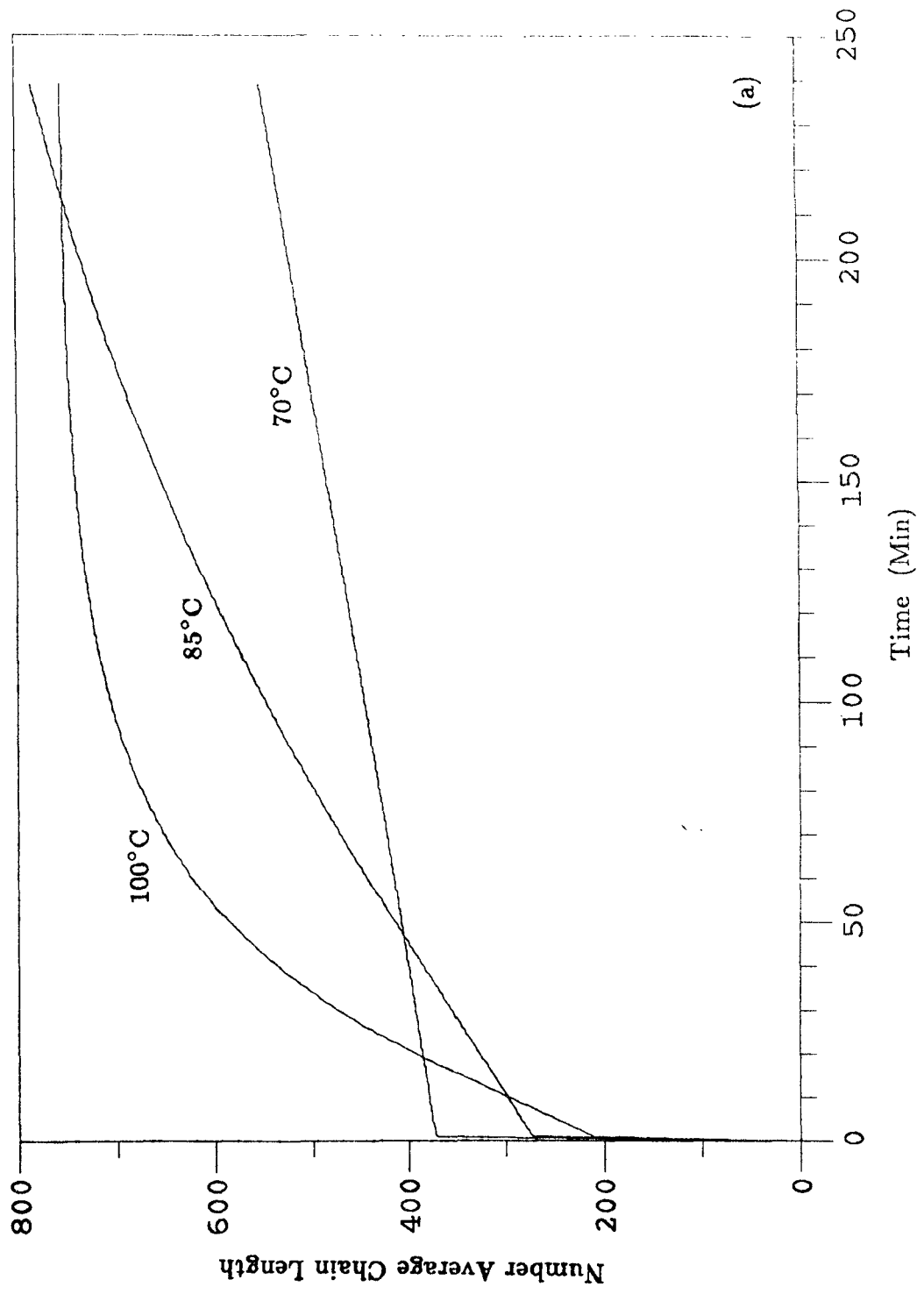


Figure 7(a)

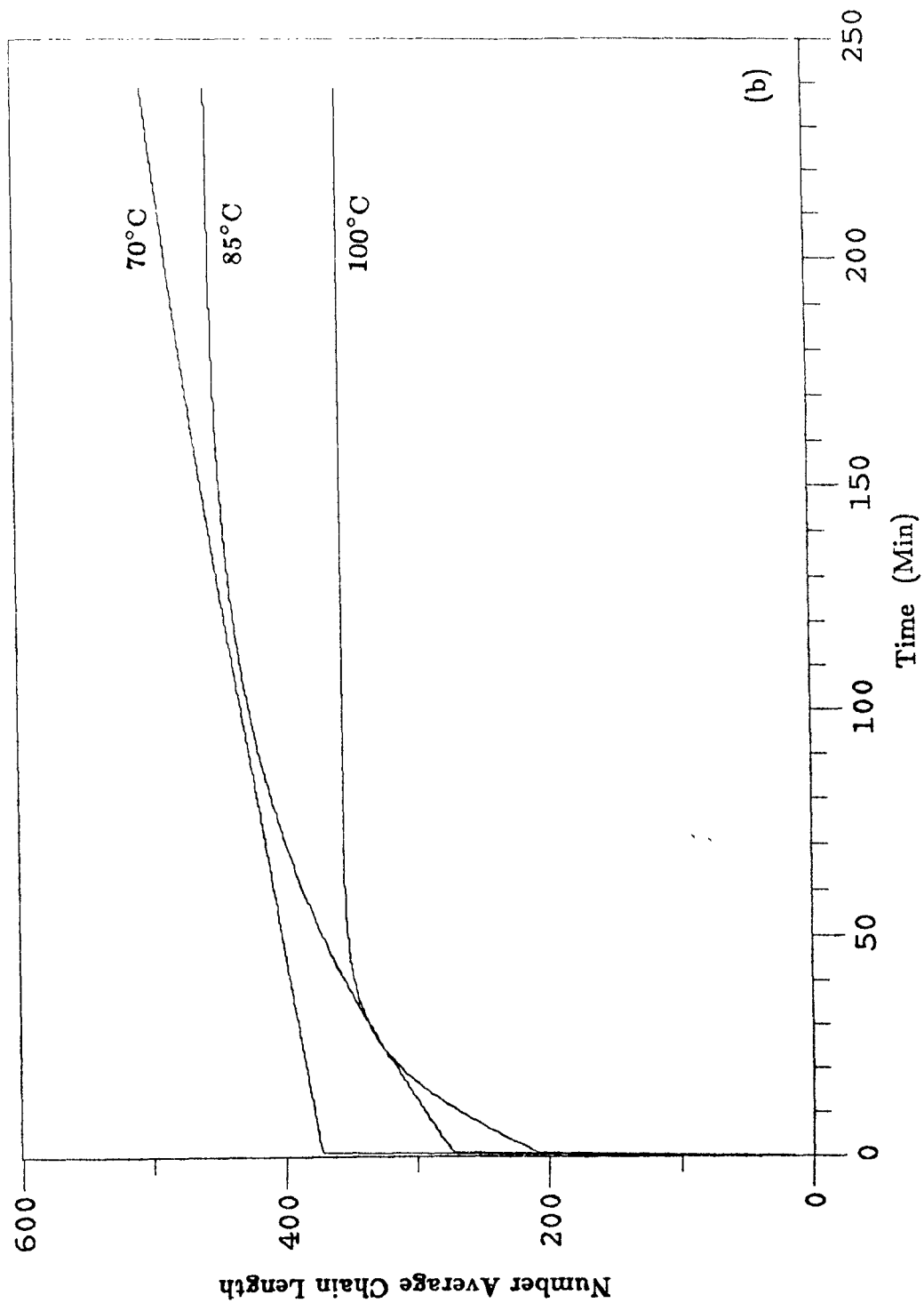


Figure 7 (b)

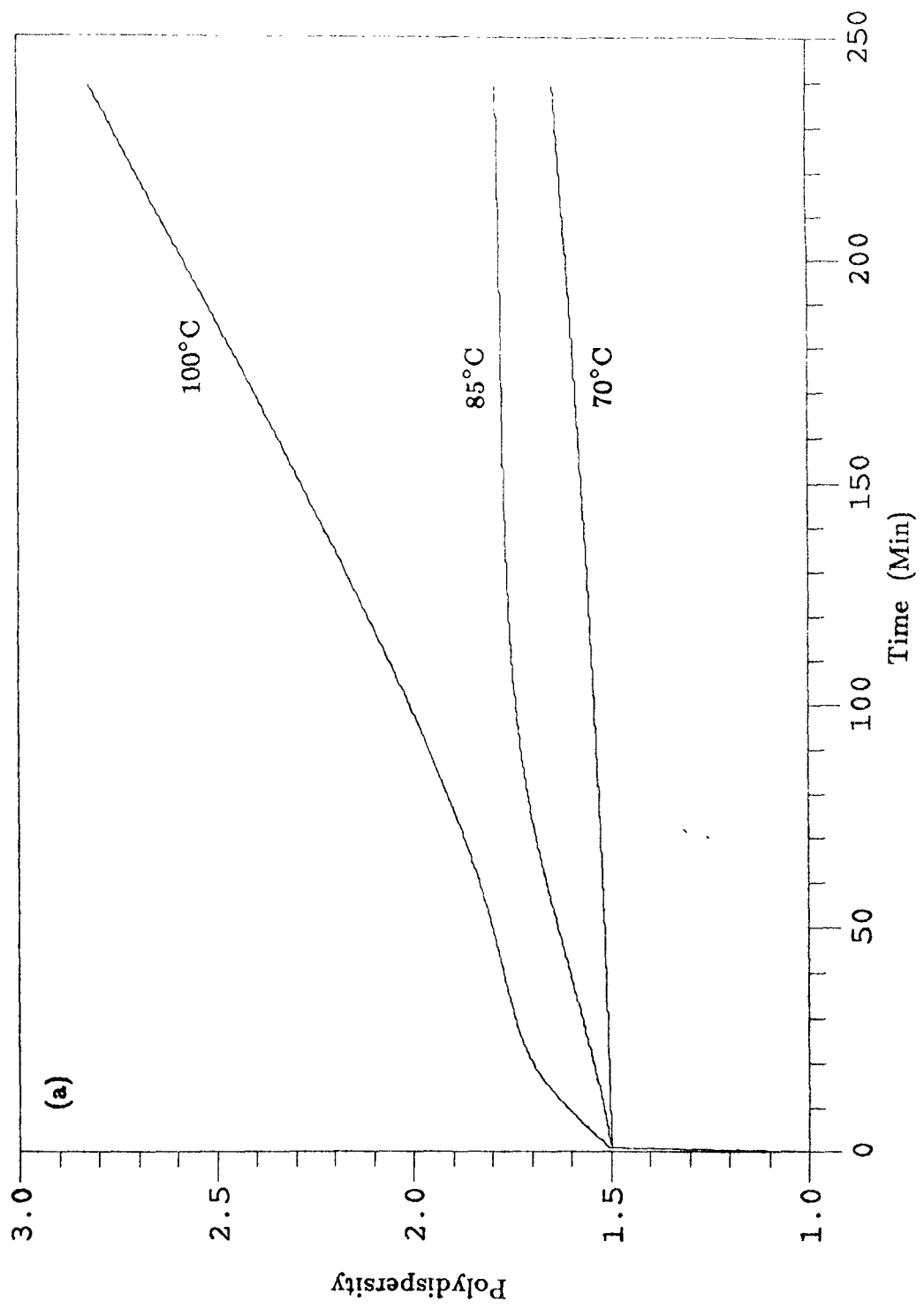


Figure 8(a)

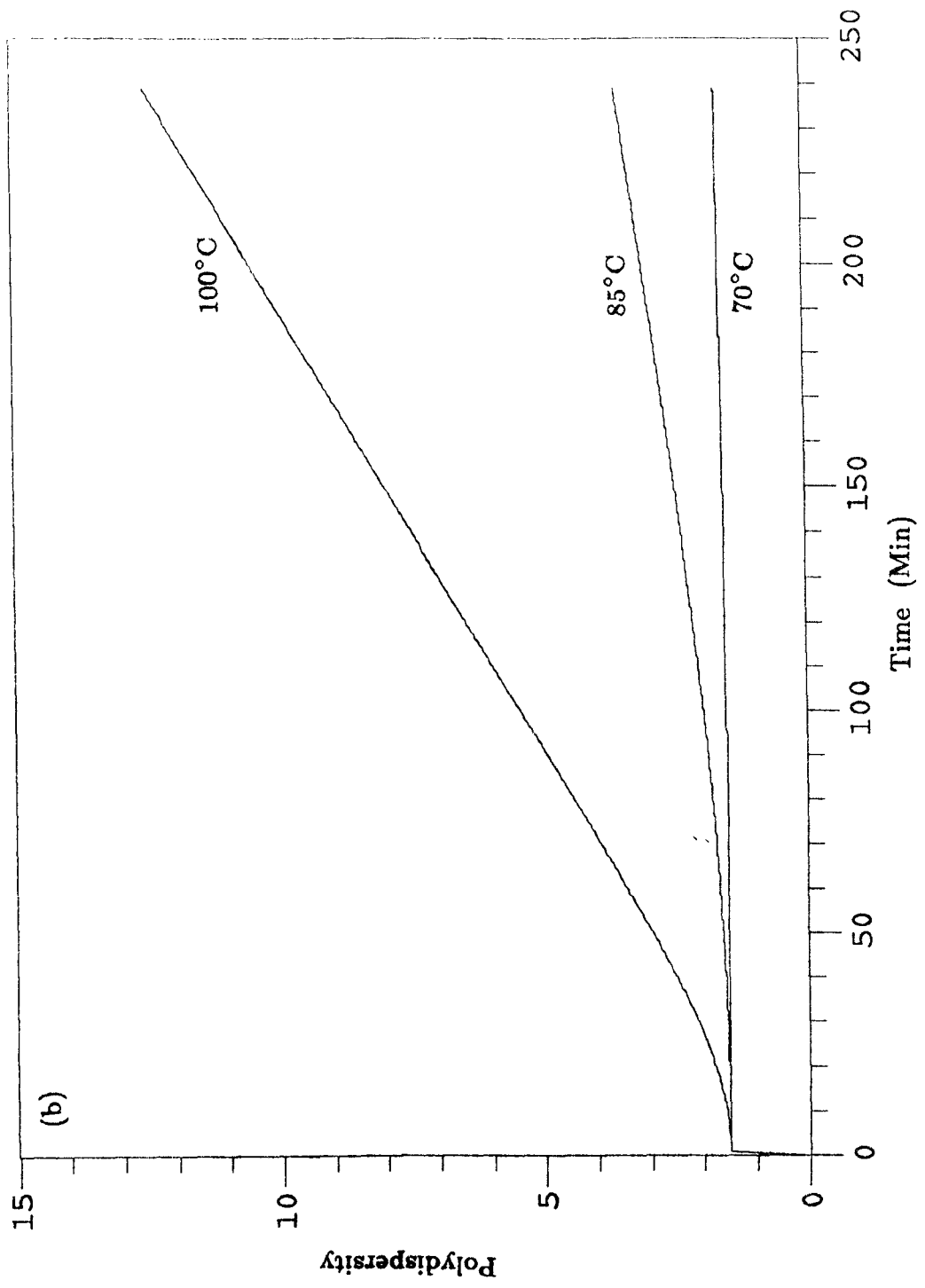


Figure 8(b)

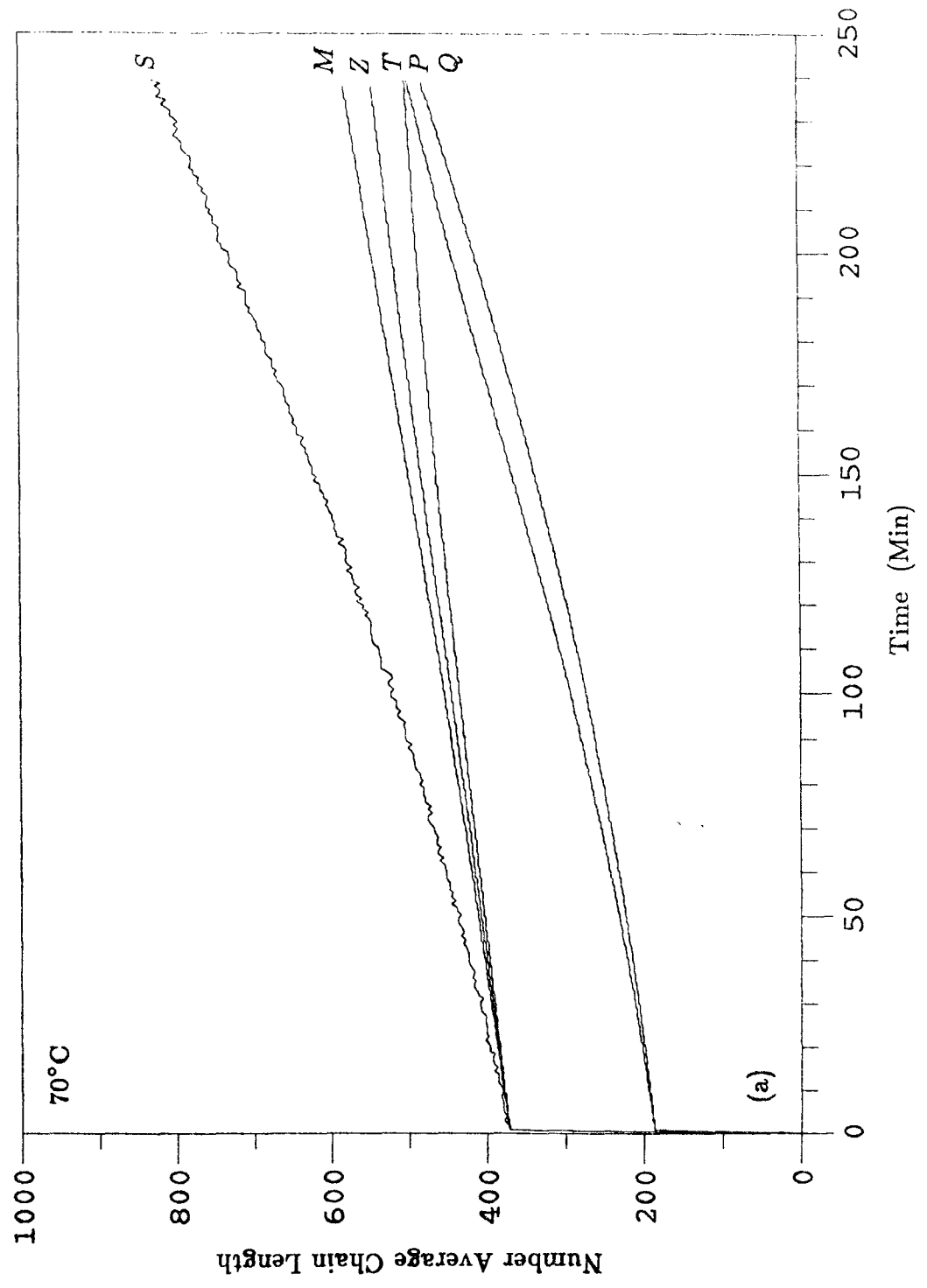


Figure 9 (a)

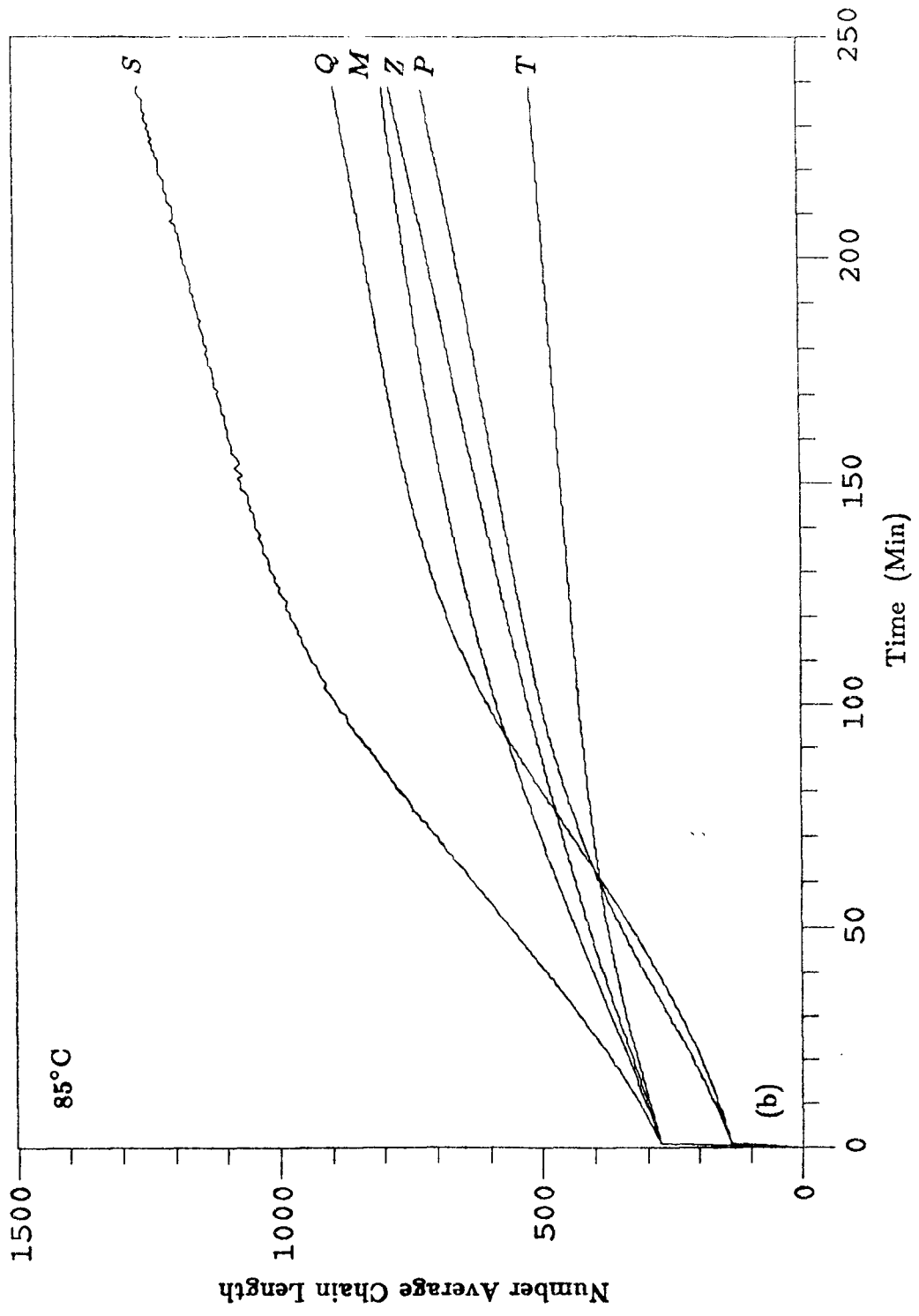


Figure 9 (b)

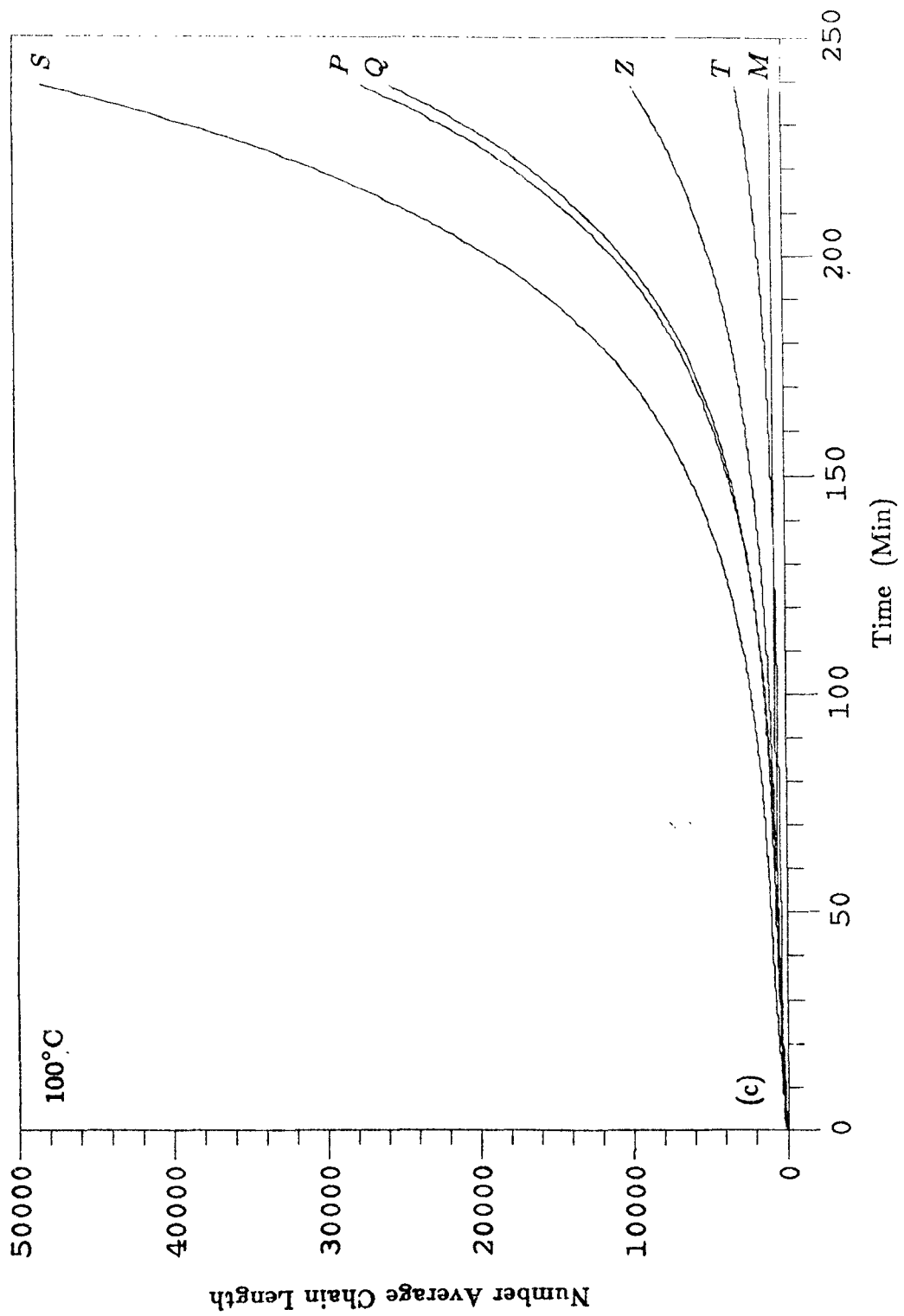


Figure 9 (c)

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