European Polymer Journal. Vol. 13. pp. 137 to 139. Pergamon Press 1977 Printed in Great Britain

A THEORETICAL STUDY OF STATIONARY STATE LIVING POLYMERIZATION WITH SPONTANEOUS CHAIN TRANSFER AND TRANSFER TO MONOMER

S. C. JAIN* and V. S. NANDA†
University of Delhi, Delhi-110007, India

(*Received* 22 *April* 1976)

Abstract—In living polymers, theoretical studies so far have been concerned with the study of the effect of chain transfer to monomer or of the effect of spontaneous chain transfer on the molecular size distribution. The simultaneous effect of both types of transfer has not been considered in any detail. In this paper we discuss this problem with the stationary state approximation. The characteristics of the two chain transfer mechanisms for the stationary state and non-stationary state polymers are examined by considering some typical examples.

1. INTRODUCTION

The problem of broadening of the Poisson size distribution in living polymerization due to chain transfer to monomer has been investigated by several authors [1, 2]. The corresponding effect of spontaneous transfer presents a more difficult mathematical problem. However, in a previous communication [3], we have studied this case when initiation is infinitely fast. Exact expressions for the averages were obtained but the expression for the size distribution could be derived by the approximate continuum approach or through the stationary state solution of the problem. So far no results involving the simultaneous effect of both transfer processes have been reported. In this paper we make use of the stationary state approximation to derive the various expressions of interest for this general situation and we discuss the statistical character of the polymer formed.

2. KINETIC SCHEME AND THE RATE EQUATIONS

We consider the following kinetic scheme:

Initiation: $$I + M \xrightarrow{k_i} N_1^*$$

Propagation:

$$N_i^* + M \xrightarrow{k_2} N_{i+1}^*$$

Chain transfer:

(i) Spontaneous

$$N_i^* \xrightarrow{k_3} N_i + I$$

(ii) To monomer

$$N_i^* + M \xrightarrow{k_4} N_i + N_1^*,$$

where N_i^*, N_i, M and I denote at any instant the concentrations of the living i-mers, the dead i-mers, the monomer and the initiator respectively while k's are the rate constants.

We assume the rate of initiation to be infinitely high ($k_i \rightarrow \infty$) so that

$$\sum_i N_i^* = I_0$$

at all stages of the reaction, where I_0 is the concentration of the initiator introduced in the reaction. Further, spontaneous transfer is assumed ideally rapid so that any liberated initiator immediately starts a new chain. Also, for appreciable growth of polymer chains, it is necessary that

$$k_4 \ll k_2 \quad \text{and} \quad k_3 \ll k_2 M.$$

Based upon the above kinetic scheme, the following differential rate equations are obtained:

$$\left.\begin{aligned} \frac{dN_i^*}{dt} &= -(k_2M + k_3 + k_4M)N_i^* + (k_3 + k_4M)I_0 \\ \frac{dN_i^*}{dt} &= -(k_2M + k_3 + k_4M)N_i^* + k_2MN_{i-1}^*, i \geqslant 2 \\ \frac{dN_i}{dt} &= (k_3 + k_4M)N_i^*, i \geqslant 1. \end{aligned}\right\} \tag{1}$$

The monomer is used up not only through propagation and transfer to monomer but also in the reinitiation process following spontaneous transfer. The rate of monomer consumption is given by

$$\frac{dM}{dt} = -(k_2M + k_3 + k_4M)I_0. \tag{2}$$

On integration, Eqn. (2) leads to the expression

$$M = \{M_0' + k_3/(k_4 + k_2)\} \times [\exp\{-(k_2 + k_4)I_0t\}] - k_3/(k_4 + k_2) \tag{3}$$

where $M_0' = M_0 - I_0$. According to Eqn. (3)

$$t_m = \{(k_2 + k_4)I_0\}^{-1} \ln\{1 + (k_2 + k_4)M_0'/k_3\} \tag{4}$$

is the time at which the whole of the monomer is consumed.

---

* At Hindu College.

† At Department of Physics and Astrophysics.

3. MOLECULAR SIZE DISTRIBUTION FUNCTION AND THE AVERAGES

According to the stationary state approximation, $(\mathrm{d}N_i^*/\mathrm{d}t) = 0$ for all i-mers. Equation (1) for living chains may then be easily solved giving

$$N_i^* = I_0\{(k_3 + k_4M)/(k_2M)\} \times \{k_2M/(k_3 + k_4M + k_2M)\}^i. \qquad (5a)$$

For $i/i_n^2 \ll 1$ (i_n being the average chain length), this result can be put in a more convenient form

$$N_i^* = I_0\phi \exp(-i\phi), \qquad (5b)$$

where $\phi = [\{\alpha_1/(1 - Y)\} + \alpha_2]$, $\alpha_1 = k_3/(k_4M_0')$, $\alpha_2 = k_4/k_2$ and $Y = 1 - (M/M_0')$. Using Eqns. (1) and (5b), the expression for dead chains is obtained in the form

$$\begin{aligned} N_i = {} & \{I_0(\alpha_1\beta)\exp(-i\alpha_2)\} \\ & \times \left[\left\{\left(\frac{1}{2} + \frac{\alpha_2^2}{\alpha_1}\right)\exp(-i\alpha_1)\right\}\right. \\ & - \{(1/i) + (\alpha_2^2/\mu)\}\exp(-i\mu) \\ & \left. + \left\{(2 - i\alpha_2)\alpha_2 \int_{i\alpha_1}^{i\mu} (\mathrm{e}^{-\lambda}/\lambda)\,\mathrm{d}\lambda\right\}\right], \end{aligned} \qquad (6)$$

where

$$\beta = M_0'/I_0, \mu = \alpha_1/(1 - Y).$$

The number-average chain length i_n and the weight-average chain length i_w are defined by the relations

$$i_n = \sum_i i(N_i^* + N_i) \Big/ \sum_i (N_i^* + N_i) \qquad (7)$$

$$i_w = \sum_i i^2(N_i^* + N_i) \Big/ \sum_i i(N_i^* + N_i). \qquad (8)$$

In principle the values of sums in Eqn. (7) and (8) may be obtained directly from the size distribution Eqn. (5) and (6). However, in the present case, to avoid the assumption made in obtaining the size distribution, we proceed directly from the differential rate Eqn. (1). For living chains we readily find

$$\sum_i N_i^* = I_0 \qquad (9)$$

$$\sum_i i N_i^* = I_0\{(1/\phi) + 1\} \qquad (10)$$

$$\sum_i i^2 N_i^* = I_0\{(2/\phi^2) + (3/\phi) + 1\}. \qquad (11)$$

The corresponding results for dead chains are

$$\sum_i N_i = \alpha_2 Y M_0' - \{\alpha_1 M_0'/(1 + \alpha_2)\} \times \ln\left(1 - \frac{Y(1 + \alpha_2)}{1 + \alpha_1 + \alpha_2}\right) \qquad (12)$$

$$\sum_i iN_i = M_0' Y \qquad (13)$$

$$\sum_i i^2 N_2 = \{(2/\alpha_2) + 1\}(M_0' Y) + 2(\alpha_1 \alpha_2^2)M_0' \times \ln\left\{1 - \frac{Y}{(1 + \alpha_1/\alpha_2)}\right\}. \qquad (14)$$

Substituting the values of the summations in Eqns. (7) and (8), we obtain

$$i_n = \frac{(1/\phi) + \beta Y + 1}{\alpha_2\beta Y - \alpha_1\beta\ln(1 - \eta Y) + 1} \qquad (15)$$

$$\begin{aligned} i_w = {} & \{(1/\phi) + \beta Y + 1\}^{-1}[\{(2/\alpha_2) + 1\}\beta Y \\ & + 2(\alpha_1\beta/\alpha_2^2)\ln(1 - \eta Y) + \{(2/\phi^2) + (3/\phi) + 1\}], \end{aligned} \qquad (16)$$

where

$$\eta = \left\{1 \Big/ \left(1 + \frac{\alpha_1}{1 + \alpha_2}\right)\right\}.$$

By putting $\alpha_2 = 0$ and $\alpha_1 = 0$ in Eqns. (5), (6), (15) and (16) in turn we obtain respectively the results for spontaneous chain transfer [3] and for chain transfer to monomer [4].

DISCUSSION OF RESULTS

In the earlier sections, making use of the stationary state approximation, we derived expressions for the size distribution and various averages of interest. It can be verified through the procedure followed in Ref. [3] that the conditions for the validity of the stationary state for the living and the overall polymers are respectively $t \gg (1/\gamma)\ln\{\gamma/(k_3 + k_4M_0')\}$ and $(\alpha_1 + \alpha_2)\beta Y \gg 1$, where $\gamma = k_3 + (k_2 + k_4)M_0'$.

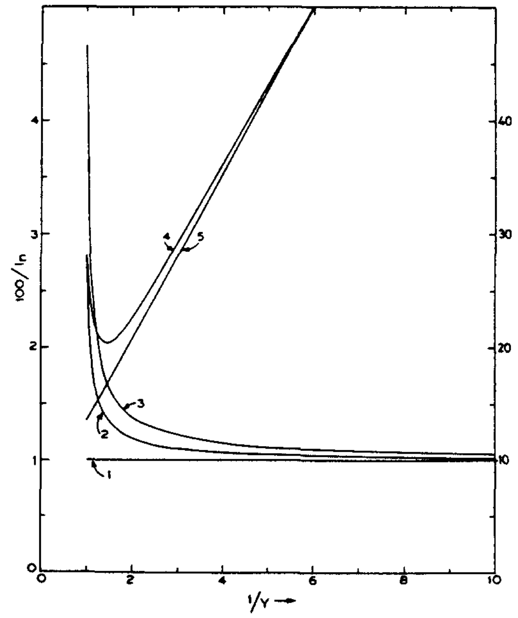

Fig. 1. Variation of $(100/i_n)$ with $1/Y$. Curve 1: $\alpha_1 = 0$, $\alpha_2 = 10^{-2}$; curve 2: $\alpha_1 = 5 \times 10^{-3}$, $\alpha_2 = 5 \times 10^{-3}$; curve 3: $\alpha_1 = 10^{-2}$, $\alpha_2 = 0$; curve 4: $\alpha_1 = 6 \times 10^{-4}$, $\alpha_2 = 0$; curve 5: $\alpha_1 = 0$, $\alpha_2 = 6 \times 10^{-4}$. For curves 1, 2 and 3, $\beta = 10^5$ and for 4 and 5, $\beta = 1.37 \times 10^3$. The ordinate scale on the right is for curves 4 and 5.

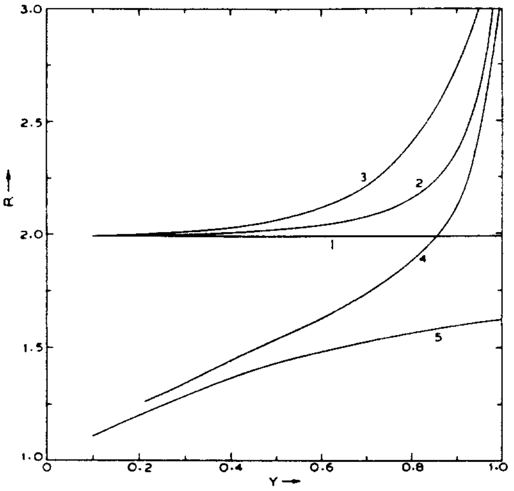

Fig. 2. Variation of R $(= i_w/i_n)$ with Y. Curves 1, 2 and 3 as in Fig. 1. Curve 4: $\alpha_1 = 6 \times 10^{-4}$, $\alpha_2 = 0$; curve 5: $\alpha_1 = 0$, $\alpha_2 = 6 \times 10^{-4}$. For both these curves $\beta = 174$.

We now discuss some important characteristics of the polymer formed with the two chain transfer mechanisms in the stationary state approximation. Comparisons with the results in the non-stationary cases would also be made.

In Fig. 1 a number of plots of $(1/i_n)$ vs $1/Y$ $(= M_0'/M_0' - M)$ are shown. Here curves 1, 2 and 3 represent the stationary state polymer as the condition $(\alpha_1 + \alpha_2)\beta Y \gg 1$ is satisfied even at very low conversions. For $\alpha_1 = 0$ (transfer only to monomer), as is clear from curve 1, $(1/i_n)$ does not vary with conversion. On the other hand, when spontaneous transfer is present, it is noticed from curves 2 and 3 that $(1/i_n)$ increases rapidly at high values of conversion. The value of $(1/i_n)$ at very low conversions is the same in all three cases because of the same β value and the choice of the values of rate constants which makes $\alpha_1 + \alpha_2 =$ constant. Curves 4 and 5, taken from Ref. [3], represent the behaviour of the non-stationary polymer because the condition $(\alpha_1 + \alpha_2)\beta Y \gg 1$ is not satisfied even in the closing stages of the reaction. It could be concluded that the decrease of $1/i_n$ with increasing conversion up to moderate conversions is a characteristic of fast initiated non-stationary living polymer.

In Fig. 2, the plots of $R(= i_w/i_n)$ as a function of conversion bring out how the inhomogeneity changes in the various situations. As in Fig. 1, curves 1, 2 and 3 are for stationary state polymer. For curve 1, where transfer is only to monomer, R is independent of Y as expected for a Flory distribution; for curve 3, only spontaneous chain transfer is present and R increases slowly at first but at higher conversions the increase is more rapid. In the mixed case depicted by curve 2, the increase is comparatively less pronounced. Curves 4 and 5 are for the non-stationary case, the former showing the behaviour for the case of spontaneous transfer while the latter for transfer to monomer. The appropriate formulae in these cases have been given in our earlier work [2, 3]. It may be noted from the various curves that for low conversions the polymer formed in the non-stationary case is more homogenous. When only transfer to monomer is operative (curve 5), R is always below the Flory distribution value; with spontaneous transfer alone (curve 4), R crosses this value at high conversions and increases rather rapidly thereafter. In the mixed case, intermediate behaviour is expected.

It is clear from these discussions that for living polymerization construction of plots (as in Figs. 1 and 2) from experimental data can lead to important information about the reaction mechanism.

REFERENCES

1. W. T. Kyner, J. R. M. Radok and M. Wales, *J. chem. Phys.* **30**, 363 (1959).
2. V. S. Nanda, *Trans. Faraday Soc.* **60**, 949 (1964).
3. V. S. Nanda and S. C. Jain, *Europ. Polym. J.* **6**, 1605 (1970).
4. S. C. Jain and V. S. Nanda, *Indian J. Chem.* **13**, 314 (1975).