Kinetics and mechanism of cationic oligomerization of styrene using poly(styrenesulphonic acid) resin as catalyst

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The cationic oligomerization of styrene in benzene using poly(styrenesulphonic acid) resin as catalyst, was carried out under nitrogen. A kinetic model involving initiation, propagation, chain transfer to monomer and spontaneous termination steps, is proposed to fit the experimental kinetic data. It is found that (1) the propagation constant decreases with increasing chain length and remains constant as $n \geq 5$; (2) the constant for chain transfer to monomer is also chain length dependent and reaches a maximum at $n=4$.

(Keywords: styrene; cationic; oligomerization; kinetics)

INTRODUCTION

The cationic oligomerization of styrene using poly(styrenesulphonic acid) resin as the catalyst, has been carried out by Aoki, Otsu and Imoto[1] and by Hasegawa and Higashimura[2]. It offers the following advantages over the homogeneous catalysis using protonic acids and metal halides: (a) separation of the spent catalyst from the reaction mixture is much easier, (b) the heterogeneous catalyst can be reused.

The present kinetic study of the oligomerization shows that the propagation constant decreases with increasing chain length and that the constant for chain transfer to monomer is also chain length dependent and reaches a maximum.

Proposed reaction mechanism

During the polymerization of a vinyl monomer, the rate constants of propagation, and chain transfer steps, k_p and k_f, are usually considered to be independent of the chain length. However for oligomerization, this is not valid due to the field effect between the anion and the first monomer unit in the propagating chain. If we consider that the concentration of sulphonyl groups in the catalyst (poly(styrenesulphonic acid) resin), is uniform in the reaction medium, the following reaction mechanism with k_p and k_f as a function of chain length can be proposed.

Initiation

$$HA + M \xrightarrow{k_i} HM^+A^-$$

Propagation

$$HM^+A^- + M \xrightarrow{k_{p1}} HM_2^+A^-$$

$$HM_2^+A^- + M \xrightarrow{k_{p2}} HM_3^+A^-$$

$$\vdots \qquad\qquad \vdots$$

$$HM_n^+A^- + M \xrightarrow{k_{pn}} HM_{n+1}^+A^-$$

Chain transfer to monomer

$$HM^+A^- + M \xrightarrow{k_{f1}} HM^+A^- + M \text{ (kinetically useless)}$$

$$HM_2^+A^- + M \xrightarrow{k_{f2}} HM^+A^- + M_2$$

$$\vdots \qquad\qquad \vdots$$

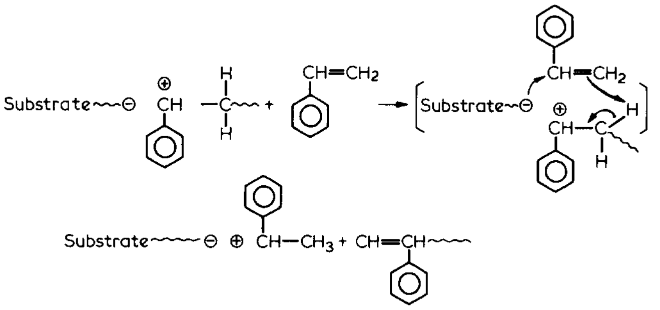
$$HM_n^+A^- + M \xrightarrow{k_t} HM^+A^- + M_n$$

Spontaneous termination

$$HM_n^+A^- \xrightarrow{k_t} HA + M_n$$

where HA (H–OSO$_2$ ~~~ substrate) is represented by C, and the propagating chain, $HM_n^+A^-$, by P_n.

In this cationic oligomerization, the chain propagation is an insertion reaction and the chain transfer can be conceived as a reaction with six member ring structure as transition state (3):



The rate of the these consecutive reactions will be affected by chain length due to steric hindrance and thus will have rate constants dependent on chain length. The transition state for spontaneous termination[4] is:

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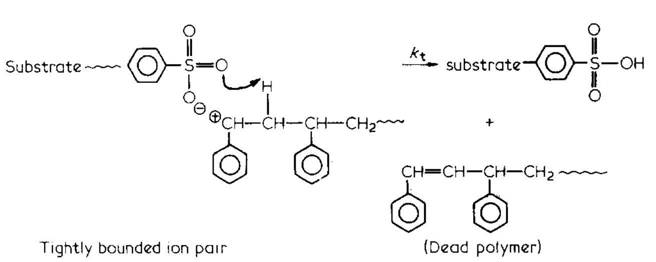

which shows that the β-hydrogen of the first monomer unit in the propagating chain is attracted by the functional group of the anion causing a separation of the chain from the substrate. Thus k_t will not be dependent on chain length. Although each separating chain contains a double bond, it will not be able to compete with monomer in the propagating reaction due to bulkiness of the chain[4,5].

Determination of k_i, k_t *and total concentration of propagating chains.* The propagating chains are adsorbed on the resin surface through electrostatic attraction forces. By adding highly polar liquid as quenching agent the propagating chains will be terminated and their positions in contact with the catalyst will be substituted by the quenching agent. Using NaOH as the quenching agent, the reactions are

$$P_n^+A^- + NaOH \xrightarrow{\text{step 1}} P_nOH + Na^+A^-$$

$$\xrightarrow[\text{step 2}]{+NaOH} P_nO^-Na^+ + H_2O$$

$$HA(\text{unreacted}) + NaOH \xrightarrow{\text{step 3}} Na + A^- + H_2O$$

The NaOH consumed in steps 1 and 3 is the initial catalytic group concentration $[C]_0$, that consumed in step 2 is the concentration of the propagating chains. If an excess NaOH is used to terminate the reaction, then the total concentration of propagating chains, $P_T(=\sum_{n=1}^{\infty}[P_n])$, and the concentration of catalytic group, $[C]$, can be determined by back-titration with HCl.

By making material balance for the concentration of catalytic group, we have

$$\frac{d[C]}{dt} = -k_i[C][M] + k_t[P_T] \tag{1}$$

from which k_i and k_t can be determined using the experimental data of $[C]$, $[M]$ and $[P_T]$ *versus* time.

Determination of k_{fn}/k_{pn} *and* k_{pn}/k_t. Using the method of Mayo[5], we have

$$\frac{[M_n]_q}{\left(\sum\limits_{k=n+1}^{\infty}[M_k]_q\right)} = \frac{k_{fn}[M][P_n] + k_t[P_n]}{k_{Pn}[M][Pn]}$$

$$= \frac{k_{fn}}{k_{pn}} + \frac{k_t}{k_{Pn}} \cdot \frac{1}{[M]} \tag{2}$$

where the subscript q refers to the product after quenching. Plotting the left side of the above equation *versus* $1/[M]$, the slope is k_t/k_{pn} and intercept k_{fn}/k_{pn}. If k_t is known, k_{pn} and then k_{fn} can be calculated for $n=2$, and k_{p1} can be calculated by extrapolation of k_{pn} *versus n* curve. k_{f1} is kinetically useless and will not be determined.

Calculation of MWD *and conversion.* According to the proposed mechanism, the rate equations for $[C]$, $[P_n]$'s and $[M_n]$'s can be formulated as follows.

$$\frac{d[C]}{dt} = k_t[P_T] - k_i[C][M]$$

$$= k_t[P_T] - k_i([C]_0 - [P_T])[M] \tag{3}$$

$$\frac{d[P_1]}{dt} = k_i([C]_0 - [P_T])[M]$$

$$-(k_{p1}[M] + k_t)[P_1] + \sum_{2}^{N} k_{fn}[P_n][M] \tag{4}$$

$$\frac{d[P_2]}{dt} = k_{p1}[P_1][M]$$

$$-[P_2](k_{p2}[M] + k_{f2}[M] + k_t) \tag{5}$$

$$\vdots$$

$$\frac{d[P_N]}{dt} k_{pN-1}[P_{N-1}][M]$$

$$-[P_N](k_{pN}[M] + k_{fN}[M] + k_t) \tag{6}$$

$$\frac{d[P_T]}{dt} = k_i[C][M] - k_{pN}[M][P_N] - \sum_{1}^{N} k_t P_n$$

$$= k_i[C]_0[M]$$

$$-(k_t + k_i[M])[P_T] - k_{pN}[P_N][M] \tag{7}$$

$$\frac{d[M_n]}{dt} = k_{fn}[P_n][M] + k_t[P_n], \quad 2 \leqslant n \leqslant N \tag{8}$$

$$-\frac{d[M]}{dt} = k_i[C][M]$$

$$+\sum_{1}^{N} k_{pn}[P_n][M] - k_t[P_1] \tag{9}$$

Using the above relationships $[P_n]$ and $[M_n]$ can be calculated.

EXPERIMENTAL

Materials

Styrene monomer was purified by washing three times with 10 wt% aqueous NaOH solution, followed by washing three or more times with distilled water until the monomer become neutral. It was dried overnight in a refrigerator with calcium chloride; distilled under vacuum of about 35 mm Hg at about 56°C, stored in a refrigerator and used with two days.

The catalyst poly(stryrenesulphonic acid) resin, Amberlyst 15 (A-15) from Rohm and Hass Co., had a total ion exchange capacity of 4.9 meq $[H^+]$/g of dried resin, surface area 55 m^2/g and an average pore diameter of 200–600 Å[6]. The resin was pretreated by the method of Magnotta and Gates[7] to remove the moisture, *viz*: (a) washed with deionized water and methanol sucessively; (b) immersed in 4 wt% NaOH aqueous solution and then in 10 wt% HCl aqueous solution for cationic exchange; and (c) dried at 1–4 mm Hg at 120°C for three days.

Benzene of LC grade was washed with concentrated sulphonic acid to remove thiopene, neutralized by 10% Na_2CO_3 aqueous solution and then washed with distilled

Table 1 Rate constants for oligomerization of styrene catalysed by A-15 in benzene at 50°C: $[M] = 0.1M$, $[C]_0 = 10mM$

Chain length n	1	2	3	4	5	6	7 to ∞
k_{pn}/k_t = 1/slope, 1 mole^{-1}	1000.0*	7268.0	3605.4	1581.4	186.4	36.77	34.20
$k_{fn}/k_{pn} = C_n$ = Intercept	–	0.003	0.061	0.34	0.44	0.45	0.48
k_{pn}, l mole^{-1} s^{-1}	239.0	173.70	86.17	35.41	4.46	0.88	0.82
k_{fn} l mole^{-1} s^{-1}	†	0.52	5.26	12.85	1.92	0.396	0.392
k_i l mole^{-1} s^{-1}				3.705 x 10^{-3}			
k_t s^{-1}				2.39 x 10^{-2}			

* Estimated from k_{pn} *versus* n plot

† Kinetically useless

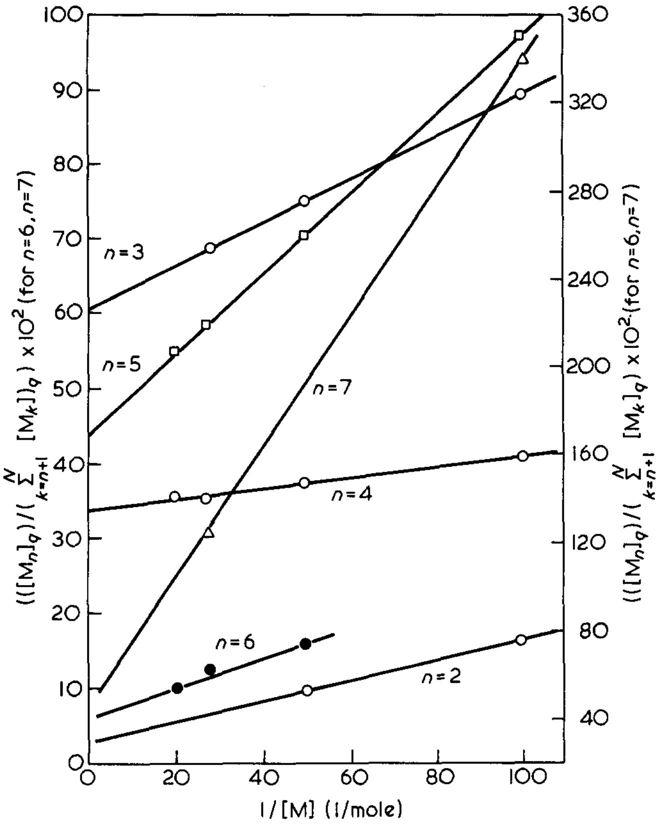

Figure 1 Plot of data according to equation (2) for $n=2$ to $n=7$

water until it became neutral. It was then dried with calcium chloride for one day, filtered, refluxed under normal pressure with calcium hydride for two to three days and distilled. The benzene treated in this way had a moisture concentration of less than 60 ppm. Bromobenzene of SSG grade was refluxed under normal pressure with calcium hydride for two to three days and then distilled. Methanol of LC grade was used as quenching agent. The NaOH used as quenching agent was 0.0487 N, and the HCl 0.0066 N.

Procedure

The oligomerization was carried out as follows. 0.01 M (0.0313 g) of the catalyst A-15 was placed in a flask equipped with a three-way tap and a magnetic stirrer, and 15 ml of the benzene and bromobenzene (equal moles to styrene monomer to be added) (0.1 M, 0.16 ml) added. The mixture was heated at 50°C for at least 1 h under dry nitrogen to allow solvent swelling of the catalyst beads.

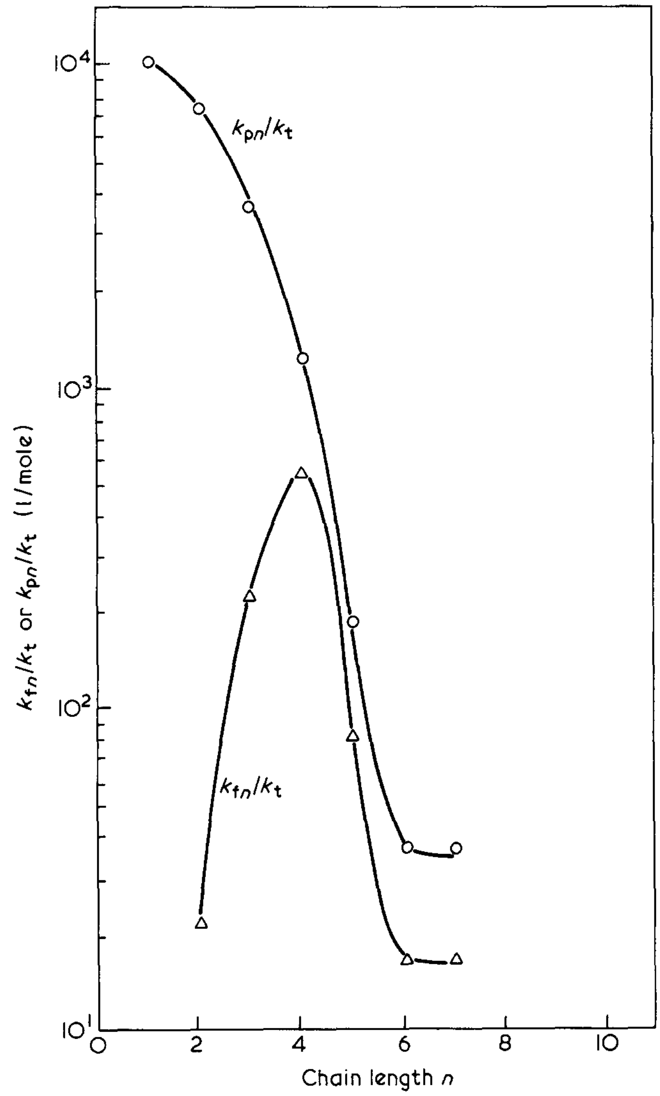

Figure 2 Plot of log(k_{pn}/k_t) *versus* n and log(k_{fn}/k_t) *versus* n, for the oligomerization of styrene catalysed by A-15 in benzene at 50°C: $[C]_0$=10 mM $[M]_0$=0.1 M

(The bromobenzene was used as an internal standard for determination of monomer conversion using gas chromatography). The styrene monomer (0.1 M, 0.18 ml) was then added and 0.01 ml sample was taken every 7.5 to 15 min for determination of the conversion using gas chromatography. The gas chromatograph, Shimadzu GC-6A, had a 6 ft column packed with 5% SP-12-0/1.75% bentone 34 on 100/120 supelcoprt. The temperature of injection port was 270°C and the column temperature

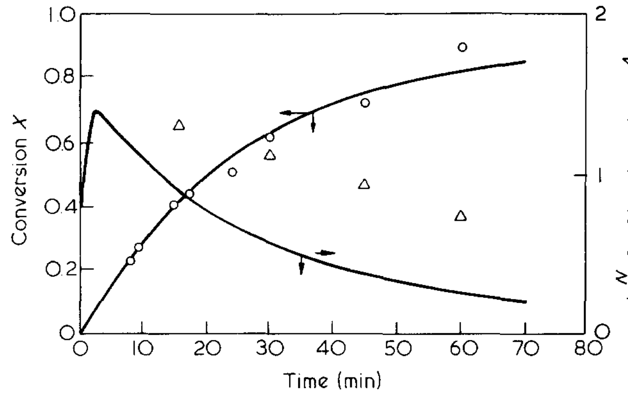

Figure 3 Plot of oligomerization of styrene catalysed by A-15 in benzene at 50°C: $[M]_0=0.1$ M, $[C]_0=10$ mM. (——) theoretical curve, (○) conversion, (△) total active polymer

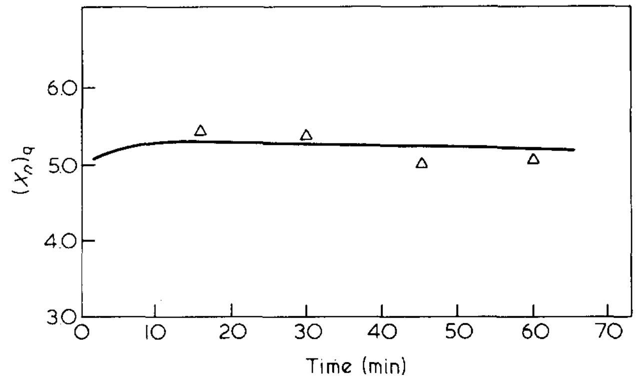

Figure 4 Number average chain length $(X_n)_g$ *versus* time curve for polystyrene oligomers synthesized by A-15 in benzene at 50°C, $[M]_0=0.1$ M and $[C]_0=10$ mM. (△) experimental data, (——) theoretical curve

100°C. The nitrogen gas flow rate was 40 ml/min. At the end of the reaction, the quenching agent was added at 0°C in an amount equivalent to 5–10 times the catalyst concentration. After 1 h, a 10 ml sample was taken from the benzene layer. It was then filtered, and the filtrate evaporated at 50°C under 5 mm Hg to give the residual oligomers. If the quenching agent used was aq. NaOH, a sample was taken from the water layer and titrated with HCl (0.0066 N) to determine its concentration. The oligomer so obtained was then determined for its *MWD* using the g.p.c., Waters model 210, with RI detector and two shodex GPC A-802 column of 50 cm in series.

RESULTS AND DISCUSSION

Determination of k_i *and* k_t

Since $[C]=[C]_0-[P_T]$, by use of the experimental data for $[P_T]$ we can derive $\Delta[P_T]/\Delta t$, $[C]$ and $[M]$ *versus* time and, thus k_i and k_t (*Table 1*).

Determination of k_{p_n} *and* k_{fn}

Plotting the left side of equation (2) (in which $[M_n]_q$ and $\sum_{k=n+1}^{\infty}[M_k]_q$ were determined experimentally *versus* $1/[M]$ for n from 2 to 7, the slope (k_t/k_{p_n}) and intercept (k_{fn}/k_{p_n}) can be obtained and are listed in *Table 1*. These linear plots are shown in *Figure 1*. Variations of k_{p_n}/k_t and k_{fn}/k_t with n are plotted in *Figure 2*.

The values of k_{p_n}/k_t, decreases with n and level off as $n \geqslant 6$. The value of k_{fn}/k_t increases at first, then decreases with n and reaches a maximum at $n=4$. This can be explained as follows; during chain propagation, the monomer molecule is inserted between the positive and negative ions one at a time, but as the chain length increases, chain coiling around the ion-pair reduces the chance for monomer moving toward the active site. Thus k_{p_n} decreases with n.

The ratio k_{fn}/k_t increases initially and then decreases with n. This may be attributed to the fact that the frequency of chain vibration around the point of contact between the positive and negative ions decreases as the chain length increases due to the increased momentum. This frequency lowering increases the chance of exposure of the β hydrogen, which can be abstracted by the functional group of the active site, and thus increases the rate of chain transfer. However as $n \geqslant 5$, chain coiling reduces the chance of monomer moving toward the β hydrogen and thus decreases the chain transfer rate.

Calculation of conversion, $[P_T]$, X_n, $[M_n]$, $[P_n]$ *and* MWD. Using the RKG method to solve the simultaneous equations (3)–(9) (with $n=8$, $[M]_0=0.1$ M, $[C]_0=10$ mM at 50°C), we obtained the time curves of conversion, $[P_T]$, number average chain length X_n, $[M_n]$, $[P_n]$ and MWD as shown in *Figures 3–7*.

Figure 3 shows that the calculated conversion curve is in agreement with the results obtained. The total active oligomer concentrations, so calculated, are shown to have

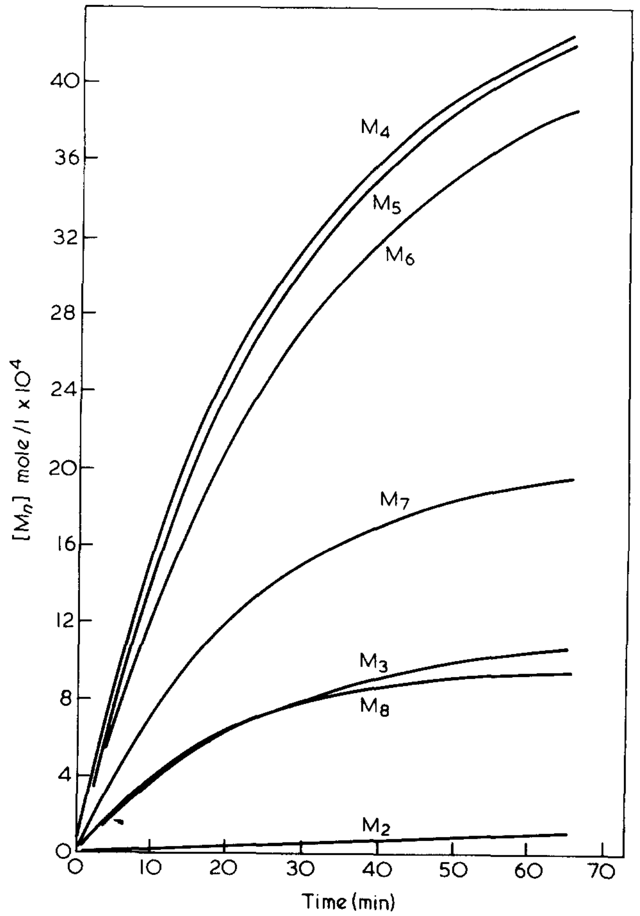

Figure 5 Theoretical time curves of formation of all dead end polymers at same reaction conditions as *Figure 2*, for $n=2$ to $n=8$

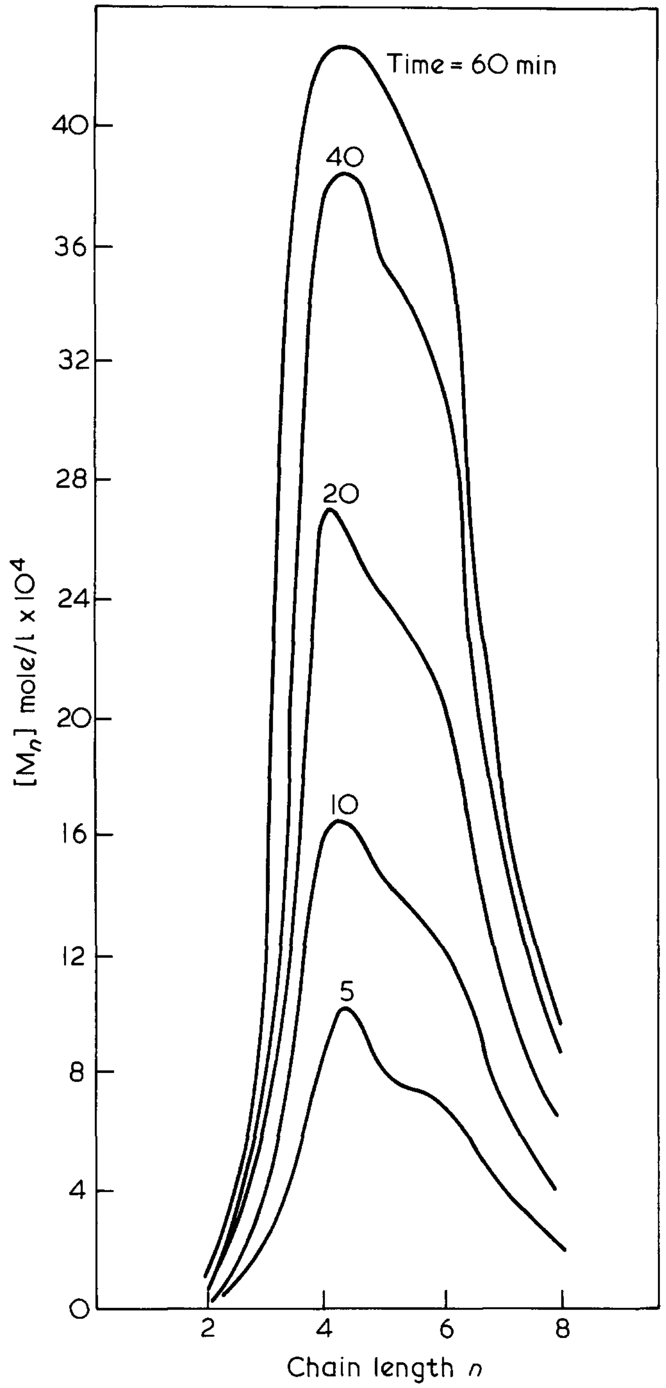

Figure 6 Theoretical growth pattern for the dead polymers of all chain length according to *Figure 2*

values lower than those obtained, but both show the same trend of variation with time. The calculated [P_T] shows an initial increase and then a significant decrease, indicating that the [P_n]'s do not follow a steady state.

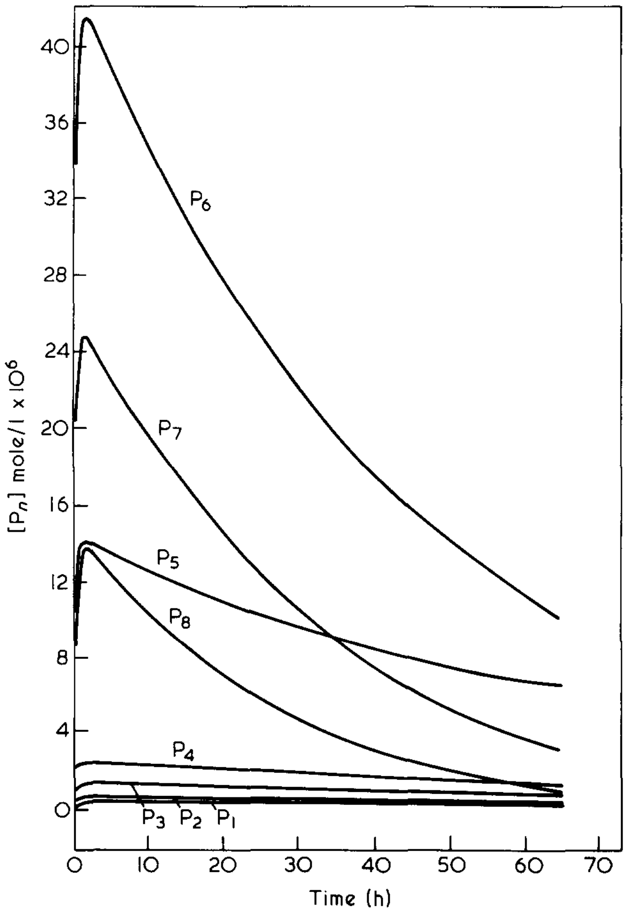

Figure 7 Theoretical time curves for formation of all active polymers at same reaction conditions as *Figure 2*, for $n=1$ to $n=8$

Figures 5–7 show that the dead oligomers (with $n=4$ and 5) always reach higher values during the reaction and that the active oligomers with $n=4$ and 5 almost reach at steady value. The active oligomers with $n=6$, 7 and 8 are in high concentration at the early stage due to higher monomer concentration but then decrease rapidly with time due to chain transfer and spontaneous termination.

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