

AN INVESTIGATION ON KINETICS AND REACTIVE SPECIES IN ANIONIC TELOMERIZATION OF BUTADIENE INITIATED BY *n*-BUTYLLITHIUM/*N,N,N',N'*-TETRAMETHYLETHYLENE DIAMINE*

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ABSTRACT

The polymerization rate of butadiene in toluene initiated by *n*-butyllithium and tetramethyl ethylene diamine as well as the micro-structure and degree of association of polybutadiene were determined. The effect of TMEDA/*n*-BuLi (abbr. A/Li) and temperature on the polymerization rate, molecular weight, molecular weight distribution and structure of polybutadiene was investigated. Activation energy of the propagation reaction and chain transfer reaction, together with the chain transfer reaction rate constant were estimated. Kinetic parameters and contribution of different reactive species to polymerization rate were calculated by Nonlinear Least-Squares Method. A kinetic equation was proposed. The mechanism of anionic chain transfer reaction was discussed.

INTRODUCTION

A systematic kinetic study of *n*-BuLi-butadiene-toluene system was presented in the previous report^[1]. The present paper extends the system by adding TMEDA which is a highly effective additive and has been used industrially in the production of butadiene telomers^[2]. Vynogradova^[3] and Hay^[4] used TMEDA as additive in solvents of petroleum ether and hexane respectively for kinetic researches, but they came to different conclusions. The former held the view that there was only one reactive species in the system mainly while the latter assumed that di-TMEDA complexed species were responsible for the chain propagation. In this paper, toluene was used as solvent. Because of the presence of chain transfer, the reaction mechanism was more complicated. Hitherto there seems no report on the kinetic study of such a system yet. In this paper, through the determination of the polymerization rate, activation energy and polymer micro-structure, the activity of different reactive species are calculated by means of the computer. The calculated results are further confirmed by structure-kinetic method.

EXPERIMENTAL

Toluene of C. P. grade and butadiene of polymerization grade, after being treated according to Morton's method^[5], were used as solvent and monomer respectively. *n*-BuLi was prepared by reaction of *n*-butyl chloride on Li wire in cyclohexane and then distilled under high vacuum (2×10^{-6} mm Hg). TMEDA was refluxed and distilled over LiAlH₄ and then treated with sodium mirror under high vacuum and finally with *n*-BuLi.

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Polymerization rate was determined by dilatometric method under high vacuum. The polymer micro-structure was determined with an IRG-27 infrared spectrometer, the number average molecular weight with a Hitachi 115 osmometer, molecular weight distribution with a Waters-105G liquid chromatograph.

RESULTS AND DISCUSSION

1. The influence of concentration of monomer on the propagation reaction rate of polymerization

The dependence of polymerization propagation rate R_p , on monomer concentration, $[M]$, was examined at different ratios of A/Li under high vacuum. The initial concentration of the monomer, $[M_0]$, was 1.69 mol/l, the concentration of the initiator, C_0 , was 4.20×10^{-4} mol/l and the range of degree of conversion was 20–60%. By plotting $\ln [M_0]/[M_t]$ against time t , where $[M_0]$ and $[M_t]$ are the initial concentration and concentration after time t of the monomer respectively, a straight line was obtained, as shown in Fig. 1.

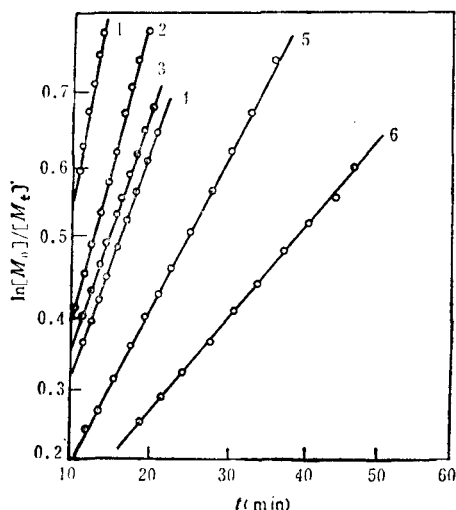


Fig. 1 The effect of monomer concentration on propagation rate

1 A/Li=0; 2 A/Li=0.88; 3 A/Li=4.07; 4 A/Li=7.44; 5 A/Li=11.2; 6 A/Li=32.5.

This indicates that the polymerization reaction rate R_p with respect to monomer concentration is of first order, which can be expressed by equation (1):

$$R_p = k'_p [M] \quad (1)$$

where k'_p is the pseudo first order propagation rate constant which is only a function of additive concentration when the reaction temperature and initiator concentration are kept constant.

2. The effect of additive concentration on propagation rate

From the slopes of the lines in Fig. 1, the pseudo first order propagation reaction rate constants, k'_p , at different values of $[A]$ (i.e. different A/Li) can be obtained, and consequently,

the apparent propagation rate constant k_{ap} can be calculated according to the following equation:

$$k_{ap} = k'_p / C_0 \quad (2)$$

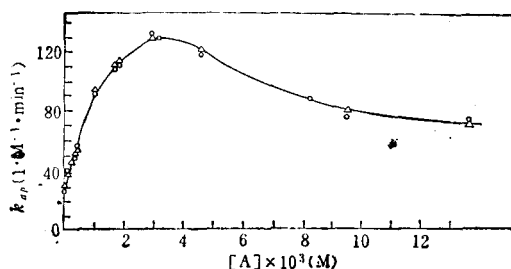


Fig. 2 The effect of $[A]$ on propagation rate
 ○ The value of experiment; △ The value of calculation.

Fig. 2 gives the plot of k_{ap} versus $[A]$. It can be seen that when $[A]$ increases from 0 to 1×10^{-3} mol/l, k_{ap} increases abruptly and attains a maximum value at $[A] = 2.92 \times 10^{-3}$ mol/l, then k_{ap} shows a gradual decrease with further increase of $[A]$, till $[A] = 8.42 \times 10^{-3}$ mol/l. Thenceforth k_{ap} becomes nearly constant. This result agrees with that of Davidjan^[6] in hexane-isoprene system.

3. The influence of additive concentration on the micro-structure of the polymer

The relationship of vinyl group content and $[A]$ can be represented by Fig. 3. The temperature of polymerization being $40 \pm 0.1^\circ\text{C}$. Within the range of $A/Li=0$ and 1, vinyl group con-

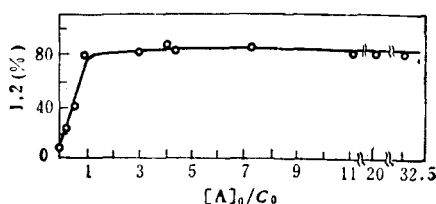


Fig. 3 The change of 1, 2% with A/Li

tent of the polymer increase quickly to 80.3% with the increase of $[A]$. Further increase of $[A]$ exerts little influence on the vinyl group content of the polymer which reaches a maximum value of 83%. This result is similar to that of Sgonnic^[3] who used petroleum ether as the solvent.

4. The relationship between propagation reaction rate and reaction temperature

In order to obtain the apparent activation energy of propagation, E_{ap} , at different values of A/Li , the pseudo first order rate constant, k'_p , at different temperatures and constant monomer and initiator concentration was first determined, and then Arrhenius equation was used to calculate E_{ap} by Non-linear Least Square Method. The results are tabulated in Table 1.

In our former work^[1] the values of E_{ap} obtained in a system without TMEDA is similar to those obtained by Shatalov^[7]. In the absence of TMEDA association takes place in the

Table 1 Values of apparent activation energy at different A/Li ratios

A/Li	$k_{ap} \times 10^2 \text{ (min}^{-1}\text{)}$			E_{ap} (kcal/l)	$A \times 10^{10}$	r
	40°C	50°C	60°C			
0	1.080	2.645	—	17.5	3.14×10^{14}	1.00
0.88	2.033	3.423	3.548	5.83	15.9×10^2	0.95
20.0	2.845	3.150	4.670	6.63	26.9×10	0.93
51.4	3.048	4.191	—	6.39		1.00
100	2.296	3.200	4.783	7.56	19.8	0.96

A: Frequency factor

r: Correlation coefficient

Table 2 Degree association at different A/Li ratios
(at temperature $40 \pm 0.1^\circ\text{C}$, $[M]=1.66 \text{ mol/l}$)

A/Li	$C_0 \times 10^4$	A	t_a (min)	t_d (min)	N
3.00	4.12	1.23	916.0	875.0	1.047
97.5	4.21	41.0	158.7	150.8	1.052

 t_a : Time of flow of active chains of polymers t_d : Time of flow of polymers after termination

N: Degree of association

system. The associator requires a higher activation energy for dissociation than that for polymer chain propagation (E_{ap}). This results in a higher value of E_{ap} . In contrast, E_{ap} becomes smaller in the presence of TMEDA.

Our experimental values of E_{ap} are close to those obtained by Morton^[8] (6.00—7.20) in a n-BuLi-THF system with mainly monomeric species. This points to the fact that there are practically non-associated active species in our case. The degree of association was determined^[9] according to Morton's viscosity method. The results are tabulated in Table 2.

From the above table it can be seen that in the presence of the additive (A/Li=3.00 and 97.5) the degree of association approached 1. This indicates that the propagation reaction of initiator was practically of the first order, and at the same time the polymer active chain was monomeric in the presence of TMEDA.

In n-BuLi-TMEDA-butadiene system, Hay^[4] determined E_{ap} to be 3.47 kcal/mol. The author considers that loose ionic pair of polybutadiene group Li was present in that system. While Alest^[10] reported that E_{ap} of system with loose ionic pair was zero or even negative. So E_{ap} =6—7 kcal/mol in the present paper shows that the active centers were practically tight ion pairs.

5. The effect of temperature on the micro-structure of polymers

The amount of vinyl group in the polymer at different temperatures was determined by

Table 3 The effect of temperature on the vinyl group content (1, 2%) of the polymer

Temp. (°C)	A/Li		
	0.91	20	596
40	87.6 (5°C)	81.0	78.0
50	80.5 (40°C)	82.6	79.5
60	43.7	82.0	79.0

means of an infrared spectrometer. The results are tabulated in Table 3.

From Table 3, it can be seen that when $A/Li \neq 1$, the amount of vinyl group content decreases considerably with the increase in polymerization temperature. The explanation for this phenomenon was a problem of great controversy among scientists in the field of high polymers. Some consider that the independence of vinyl group content indicates that the complex formed from the polymer lithium active chain and TMEDA is stable, while others hold the opposite opinion. The present work was done under the condition of substantial variation of A/Li . It seems to be that when A/Li is low there exists in the system mostly solvated or monomeric TMEDA complexed active chain, which is unstable. Therefore the degree of solvolysis decreases as the temperature is raised. The dissociation of the monomeric complex leads to the reduction of vinyl group content. When A/Li is increased, a rather stable species of dimeric ligand complex is present. The result is the independence of vinyl group content with temperature.

6. The effect of amount of additive on the number average molecular weight ($\bar{M}_n$) and molecular weight distribution (MWD) of the polymer

Fig. 4 gives the effect of the additive concentration on $\bar{M}_n$ and $\bar{M}_k/\bar{M}_n$ of the polymer. It can be seen from Fig. 4 that chain transfer does not exist in the absence of TMEDA. This fact agrees with the result of Hsieh^[11]. It is also seen that there is a sharp decrease of $\bar{M}_n$ and increase of $\bar{M}_k/\bar{M}_n$ for small ratios of A/Li . As A/Li approximately approaches 1, the changes of $\bar{M}_n$ become gradual. Up to A/Li is as high as 30, $\bar{M}_k/\bar{M}_n$ attains a

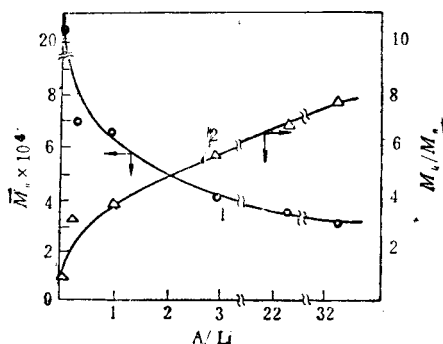


Fig. 4. 1, The effect of $[A]$ on $\bar{M}_n$; 2, The effect of $[A]$ on $\bar{M}_k/\bar{M}_n$

value of about 7. This result indicates that TMEDA is an important factor causing chain transfer. Even in the presence of a chain transfer agent (i.e. toluene), no change in molecular weight occurs without the presence of TMEDA in the system. This indicates that active species of chain transfer mainly is complex. Furthermore the degree of telomerization, which is represented by $\bar{M}_k/\bar{M}_n$, is dependent on [A].

In the absence of additive, the molecular weight distribution index, I , is approximately equal to 1.03, the distribution is narrow. In the presence of additive, the distribution becomes wide (Fig. 5). I increases with A/Li and reaches to about 2.4 as A/Li increases to about 20. Thence forward further increase of A/Li I will become constant, up to A/Li is about 600. This result agrees with that of Morton^[5]. The reason for the widening of molecular weight dis-

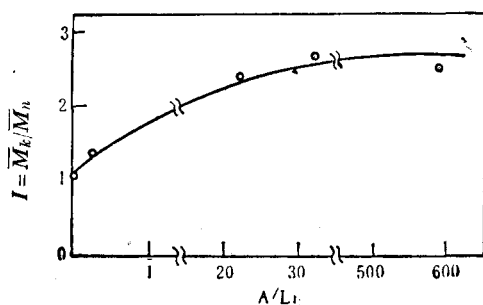


Fig. 5 The effect of [A] on I

tribution is due to the randomizing effect of the chain transfer reaction caused by TMEDA. This also explains the fact that initiation by Li substituted toluene (i.e. benzyl lithium) is a very quick process, which points further to the important role of TMEDA in producing chain transfer reaction.

7. The effect of temperature on the chain transfer reaction

In order to determine chain transfer constant (C_{tr}) and chain transfer reaction rate constant (k_{tr}) at $C_0 = 4.20 \times 10^{-4}$ mol/l, $[M] = 1.78$ mol/l, A/Li = 0.91, first the number average molecular weights at 5°C, 40°C, 60°C were determined under constant degree of conversion by varying the molar ratios of solvent to monomer, then by applying Gehrke formula^[12]:

$$\frac{1}{\bar{P}_n} - \frac{1}{\bar{P}_{n0}} = C_{tr} \cdot \frac{[S]}{[M_0] - [M]_t} \frac{\ln [M]_t}{[M]_0} \quad (3)$$

where $\bar{P}_n$ is the experimental number average polymerization degree of polymer; $\bar{P}_{n0}$ is the designed number average polymerization degree; [S] is the initial concentration of toluene. And solving by means of Linear Least Squares Method, C_{tr} and K_{tr} were obtained and listed in Table 4.

The chain transfer activation energy E_{tr} is calculated by Arrhenius equation. E_{tr} obtained is higher than E_p by 5 kcal/mol, i.e. $\Delta E = E_{tr} - E_p \doteq 4.5$ kcal/mol, the correlation coefficient r being 0.99. From this result it follows that in anionic telomerization, $E_{tr} > E_p$, therefore arise in temperature is favorable to the proceeding of chain transfer reaction

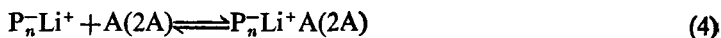
Table 4 Values of C_{tr} and k_{tr} at different temperatures

Temp. (°C)	C_{tr} $\times 10^5$	k_{tr} $\times 10^3$	Correlation coefficient r
5	1.76	6.9	1.00
40	3.62	90.9	0.99
60	7.26	922	0.93

8. Discussion on the mechanism of chain transfer reaction

It is known that chain transfer can only take place in the presence of coordinated active species. Since Li atom possesses empty orbitals and there is a lone pair of electron on each of the N atoms of TMEDA, it can be imagined that mono-TMEDA-complex (PLiA) and di-TMEDA-complex (PLi₂A), can be formed. According to Hay^[4] a coordinated complex of tetrahedron structure exists in n -BuLi-TMEDA-hexane system. If there were only monomeric and monocoordinated active species in the system, there would have been no turning point on the graph of Fig 2, the fall of the line after maximum indicates the presence of a third component which we assume to be the di-TMEDA-complexed active species. Accordingly we postulate the following mechanism:

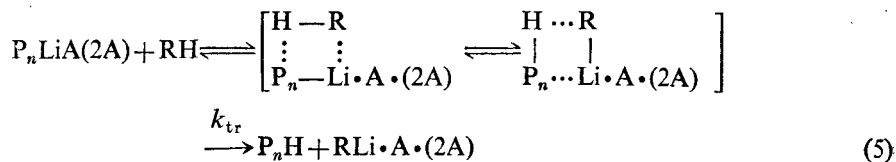
At first, the following reaction takes place:



where P_n^- is the polybutadiene carbon anion.

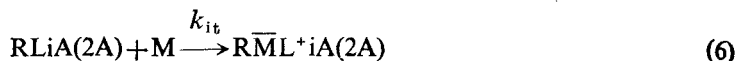
The filling of empty orbitals of Li through coordinating with lone pair of electrons of N lowers the bonding strength between Li and C of polybutadiene, thus chain transfer reaction is made liable to happen through the substitution of α -H of toluene by Li complex. The process of chain transfer can be pictured as follows:

The first step is the coordination of toluene with polybutadiene-Li and then the unstable coordinated compound rapidly dissociates (eq. (5))

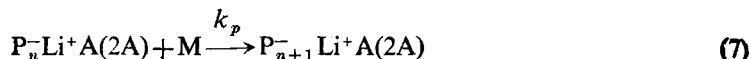


where R stands for benzyl group.

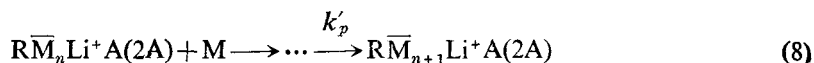
In general benzyl-Li is less active than BuLi, but due to the electron donating property of TMEDA, its activity is greatly enhanced. This makes a new initiation process likely to take place, Kume^[18] found by IR spectroscopy that there was benzyl group at one end of the telomer. In our experiment $\bar{M}_k/\bar{M}_n$ has been determined to be 3-7. This indicates that benzyl-Li after chain transfer still possesses enough activity to start further initiation (eq. (6)).



But in our experiment as an average, the number of times of chain transfer is about 3—7 which amounts to about 0.08—0.18% of that of chain propagation (eq. (7)).



The number of times of re-initiation is the same as that of chain transfer. As the number of chain transfer and re-initiation is small compared with that of chain propagation, so we can assume that the effect of both chain transfer and re-initiation on the rate of chain propagation can be neglected. Chain propagation can be represented by the following equation:



Neglecting the effect of terminal group, we can put $k_p' \doteq k_p$.

The validity of our assumption that chain transfer reaction has little effect on the rate of chain propagation can be verified by our following calculations.

9. Calculation and discussion of activity of different active species in the system

(1) The calculation of rate constants of different active species

According to the literature and the above discussion, there exist the following dynamic equilibria in the system:



where K_1 and K_2 are the mono-TMEDA and di-TMEDA complex equilibrium constant respectively.

TMEDA, being a strong electron donating agent, causes the association basically all into the dissociation (eq. (9)). Furthermore the association possesses very low activity. So the chain propagation can be assumed practically to the contribution of monomeric, mono-TMEDA and di-TMEDA complexes.



From the above reasoning, the following can be formulated:

$$k_{ap} = \frac{k_1 + k_2 K_1 [\text{A}] + k_3 K_1 K_2 [\text{A}]^2}{1 + K_1 \text{A} + K_1 K_2 [\text{A}]^2} \quad (15)$$

where $k_{ap} = k_p'/C_0$ is the experimental apparent propagation rate constant, k_1 , k_2 , k_3 , are

the absolute rate constants of monomeric, mono-TMEDA complex, and di-TMEDA complex respectively.

Solving by means of Non-linear Least Squares Method, the following results are obtained:

$$f \left\{ \frac{k_1 + k_2 K_1 [A] + k_3 K_1 K_2 [A]^2}{1 + K_1 [A] + K_1 K_2 [A]^2} - k_{ap} \right\}^2 = 0 \quad (16)$$

$k_1 = 0.507 \text{ (L} \cdot \text{M}^{-1} \cdot \text{S}^{-1}\text{)}, k_2 = 33.3 \text{ (L} \cdot \text{M}^{-1} \cdot \text{S}^{-1}\text{)}, k_3 = 0.267 \text{ (L} \cdot \text{M} \cdot \text{S}^{-1}\text{)} K_1 = 32.2, K_2 = 2508,$

Correlation index: $R^2 = 0.9997$.

S. T. (Subject to) $k_1 > 0,$

$k_2 > 0,$

$k_3 > 0,$

$K_1 > 0,$

$K_2 \geq 0.$

Put the five kinetic parameters into equation (15), we obtain:

$$k_{ap} = \frac{(30.4 + 645 \times 10^2 [A] + 129 \times 10^4 [A]^2)}{(1 + 32.2 [A] + 807 \times 10^2 [A]^2)} \quad (17)$$

Within the range of $[A] = 0-13 \times 10^{-3}$, by using equation (17) the calculated k_{ap} values are plotted against $[A]$, the results are expressed in Fig. 2, from which it can be seen that the curve obtained from calculated values coincides fairly well with that obtained experimentally. This is a strong proof of our assumptions on the mechanism of chain transfer and chain propagation are through the presence and action of different active species. At the same time that the propagation rate is independent of anionic chain transfer is also verified.

k_{ap} practically remains constant after $[A]$ increases to a value of 12×10^{-3} .

$$k_{ap} \doteq 72 \text{ (L} \cdot \text{M}^{-1} \cdot \text{S}^{-1}\text{)}$$

Within the region of the curve, the kinetic equation is to be:

$$R_p = k_{ap} C_0 [M] \quad (k_{ap} \text{ is from formula (17)}) \quad (18)$$

By means of equation (18), the quantities of different active species can be calculated. Table 5 gives the plotting of quantity of each active species against A/Li. When A/Li exceeds 30, the degree of complex of the active centers approaches 94% (i.e. $A/Li \doteq 7$). The amount of mono-TMEDA complex, which has the highest activity ($k_2 > k_1 > k_3$), becomes maximum. Therefore there is a turning point in the plot of Fig. 2, where $[A] \doteq 3$, which corresponds to $A/Li \doteq 7$.

The contributions of different active species can be visualized by analyzing Table 5. When A/Li exceeds 1.3, the mono-TMEDA complex has a contribution of above 50%, then its contribution rapidly rises to more than 80%. So the main active center for chain propagation in the system is mono-TMEDA complex, especially within the range A/Li between of 3 and 7. When A/Li is less than 1, it is polybutadiene-Li chain which is responsible for chain propagation. After $A/Li > 20$, though the concentration of di-TMEDA-complex is increased, its contribution to the rate of chain propagation is still less important.

(2) The calculation of the contributions of different active species

In the absence of TMEDA, the polymer obtained contains 11.8% of vinyl group structure. So it can be assumed that it is wholly ascribed to the contribution of monomeric species.

Table 5 The effect of A/Li on each active species

A/Li	PLi	PLiA	PLi2A
0	0.9999	8.065×10^{-1}	3.223×10^{-4}
0.88	0.9786	0.0113	0.0101
0.91	0.9762	0.0121	0.01169
3.00	0.8805	0.3417	0.1053
4.07	0.7637	0.04355	0.1927
7.203	0.6606	0.0528	0.3866
22.54	0.1162	0.03563	0.8482
32.5	0.0607	0.02677	0.9125
51.4	0.0241	0.0173	0.9587
596	2.078×10^{-4}	1.635×10^{-3}	0.9992

By correlating the equation for propagation rate (equation (15)) with the microstructure of the polymer, the following kinetic equation can be obtained^[14]:

$$1, 2\% = \frac{\alpha k_2[\text{PLi}] + \beta k_2 K_1[\text{PLi}][\text{A}] + \gamma k_3 K_1 K_2 [\text{PLi}][\text{A}]^2}{k_1[\text{PLi}] + k_2 K_2[\text{A}] + k_3 K_1 K_2 + k_3 K_1 K_2 [\text{A}]^2} \\ = \frac{\alpha k_1 + \beta k_2 K_1[\text{A}] + \gamma k_3 K_1 K_2 [\text{A}]^2}{k_1 + k_2 K_1[\text{A}] + k_3 K_1 K_2 [\text{A}]^2} \quad (19)$$

where α , β and γ are the contribution of monomeric species, mono-TMEDA complex and di-TMEDA complex toward the formation of 1, 2%-structure respectively.

Fig. 6 indicates that when A/Li is below 7, the contribution of di-TMEDA complex to chain propagation approaches zero, that is $\gamma=0$. Then equation (19) becomes:

$$1, 2\% = \frac{0.118k_1 + \beta k_2 K_1[\text{A}]}{k_1 + k_2 K_1[\text{A}] + k_3 K_1 K_2 [\text{A}]^2}$$

i.e.

$$\beta = \frac{1, 2\% (k_1 + k_2 K_1[\text{A}] + k_3 K_1 K_2 [\text{A}]^2) - 0.118k_1}{k_2 K_1[\text{A}]} \quad (20)$$

At different values of $[\text{A}]$ β can be obtained by substituting experimental values of 1, 2%

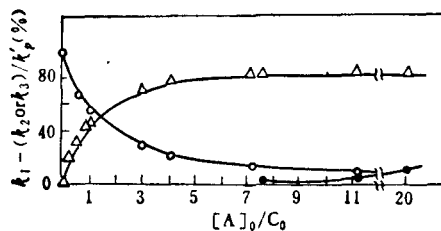


Fig. 6 The contribution of active species on propagation rate

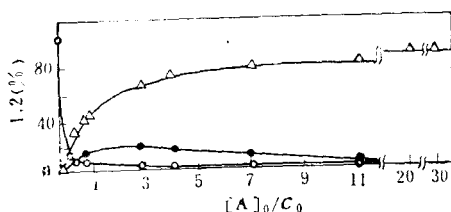


Fig. 7 The contribution of active species on 1, 2 structure

with their corresponding values of $[A]$ into equation (20).

When A/Li exceed 30, the contribution of monomeric species approaches zero. Then equation (19) becomes:

$$\gamma = \frac{1, 2\%(k_1 + k_2 K_1 [A] + k_3 K_1 K_2 [A]^2 - \beta k_3 K_1 [A])}{k_3 K_1 K_2 [A]^2} \quad (21)$$

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