

# Butadiene–Styrene Copolymerization Initiated by *n*-BuLi/THF/*t*-AmOK

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## SYNOPSIS

In this article, the anionic copolymerization of butadiene and styrene initiated by *n*-BuLi/THF/*t*-AmOK in cyclohexane at 50°C has been studied in detail. The various ratios of the modifier (THF and *t*-AmOK) to the initiator (*n*-BuLi) influence the copolymerization rate and composition of copolymers.

It has been shown that this polymerization system is a complex one in which there exist multiple active species. By adjusting the ratio of K to Li and the ratio of THF to Li, copolymers with compositions almost identical to the ratio of initial monomers at different stages of conversion have been obtained.

The propagating regularity of various active species has been discussed qualitatively.

## INTRODUCTION

The main products formed in the anionic copolymerization of butadiene and styrene initiated by *n*-butyllithium (*n*-BuLi) in nonpolar solvent are block copolymers.<sup>1</sup> Random copolymers with 1,2-addition as the main structural feature can be obtained if a small amount of ether is added in the system.<sup>2–5</sup> It is generally believed that the distribution of butadiene and styrene units in the copolymer, which can be used as general purpose rubber, must be random, and the amount of 1,2-structure in polybutadiene chain segment should be about 10%. Although the copolymer in which styrene units are well-distributed may be obtained using *n*-BuLi/*t*-BuOK,<sup>6,7</sup> it is difficult to synthesize, because the solubility of Potassium tert-butoxide (*t*-BuOK) in nonpolar solvents is rather poor and the ratio of K to Li is difficult to adjust. This article reports a study on the copolymerization of butadiene and styrene initiated by *n*-BuLi/THF/*t*-AmOK in cyclohexane. By adjusting the ratio of *t*-AmOK to *n*-BuLi, and the ratio

of THF to *n*-BuLi, copolymers with unique randomness and composition almost identical to the ratio of initial monomers at different stages of conversion have been obtained.

## EXPERIMENTAL

### Materials

Styrene (Shanghai Gaoqiao Chemical Plant, polymerization grade) was treated with CaH<sub>2</sub> for a week and then was distilled at 35°C and 8 mmHg in the presence of fresh CaH<sub>2</sub> before use.

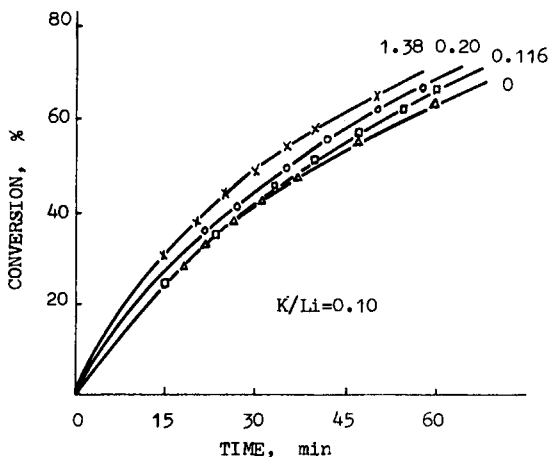
Butadiene (Shanghai Gaoqiao Chemical Plant, polymerization grade) was successively treated with 5Å molecular sieves and KOH for a week. The residual water was removed with activated 5Å molecular sieves and KOH for several days before use.

Cyclohexane (CP grade) was treated by 5Å molecular sieves for a week and then was refluxed over 4 h with dried argon in the presence of sodium before use.

Hexane (AR grade) was stirred with concentrated sulphuric acid for a week, then was washed with water. The residual acid was neutralized with 5% NaOH solution and was washed again with water until pH = 7. The residual water was successively removed with anhydrous CaCl<sub>2</sub>, 5Å molecular sieves,

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**Figure 1** Conversion plots of B-S copolymerization with different ratio of THF/Li. Reaction conditions: solvent, cyclohexane; monomer concentration, 10% (weight); butadiene/styrene, 75/25 (weight); *n*-BuLi, 0.0005 mole/100g monomer, temperature, 50°C.

and  $\text{CaH}_2$ . Hexane was refluxed over sodium with dried argon for more than 4 h, then distilled.

THF (tetrahydrofuran, AR grade) was successively treated for a week with 5Å molecular sieves and  $\text{CaH}_2$ . THF was further purified using the same method as hexane.

*n*- $\text{C}_4\text{H}_9\text{Cl}$  (CP grade) was distilled, then treated with  $\text{CaH}_2$  for several days. It was refluxed over fresh  $\text{CaH}_2$  with dried argon for 4 h.

*t*-AmOH (*t*-amyl alcohol, CP grade) was treated with 5Å molecular sieves for several days, refluxed over sodium for 4 h, distilled under dried argon to collect 101.0–103.5°C fraction ( $N_D^{25.6} = 1.4018$ ).

### Synthesis and Analysis of the Initiator

*n*-BuLi was synthesized by reacting *n*- $\text{C}_4\text{H}_9\text{Cl}$  with lithium in hexane, filtered with a 4 # sand core filter under dried argon to collect *n*-BuLi solution, then stored in the cold. *n*-BuLi was analyzed following the method of Gilman and Haubein.<sup>8</sup>

*t*-AmOK (potassium 2-methyl-2-butoxide) was synthesized by reacting *t*-AmOH with potassium<sup>9</sup> and sublimated to collect the product. The analyzing method for *t*-AmOK is the same as *n*-BuLi.

### Polymerization

Polymerization was carried out in a glove glass reactor. The reactor was successively charged with cyclohexane, styrene, butadiene, THF, and finally initiator, which was prepared by *n*-BuLi/*t*-AmOK in hexane solution. The reaction temperature was controlled at  $50 \pm 1^\circ\text{C}$ . Samples were periodically

taken and directly charged into alcohol, collected slantways, then dried in an oven at 40°C/60–70 mmHg.

### Analysis of Copolymer

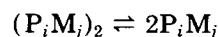
The styrene content of the copolymer was determined by a Shimadzu ultraviolet spectrophotometer. The microstructure was determined by a Nicolet infrared spectrophotometer. The sequence distribution was measured by  $^{13}\text{C}$ -NMR using a JEOL NMR spectrometer. Molecular weight was measured by an Ostward-type viscometer.

## RESULTS AND DISCUSSION

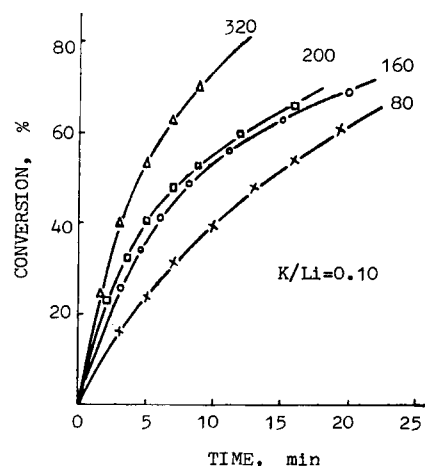
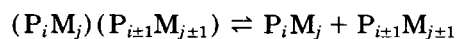
### Rate of Copolymerization

The apparent rates of butadiene–styrene copolymerization in cyclohexane at 50°C with *n*-BuLi/THF/*t*-AmOK are shown in Figures 1–3. The copolymerization rate increased slowly at low concentration of THF and increased rapidly at high THF. *t*-AmOK had the same effect on the copolymerization rate as THF.

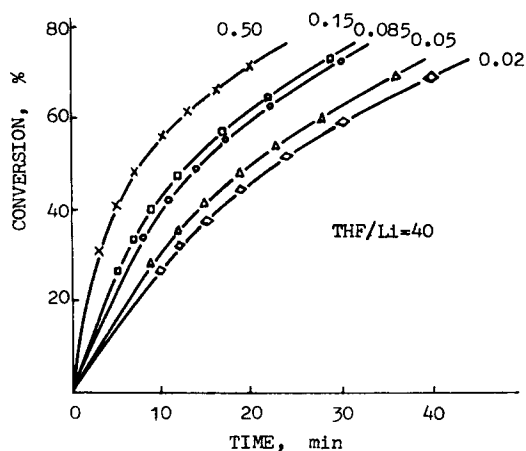
In a nonpolar solvent, the active species of Li and K as the counterion can associate not only with itself but also with each other. The equilibria between associated and monomeric species can be described as follows:



or

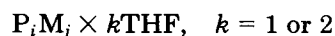


**Figure 2** Conversion plots of B-S copolymerization with different ratio of THF/Li.

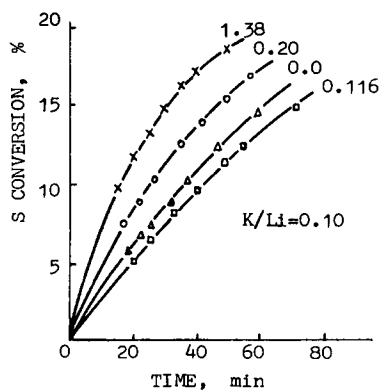


**Figure 3** Conversion plots of copolymerization with different ratio of K/Li.

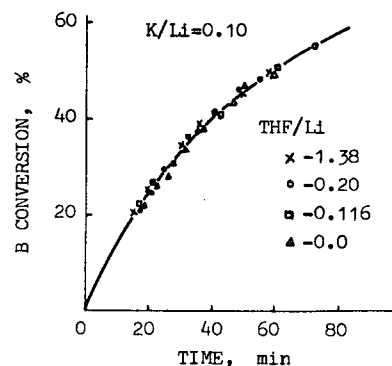
where P = polymer chain,  $i = 1$  or  $2$ ,  $i \pm 1 = 1$  or  $2$ ,  $i \neq i \pm 1$ , 1-end unit is styrene, 2-end unit is butadiene. M-alkali metal,  $j = 1$  or  $2$ ,  $j \pm 1 = 1$  or  $2$ ,  $j \neq j \pm 1$ , 1-Li, 2-K. The monomeric species can also complex THF:



The above equilibria can shift to the right with increasing THF and relative contents of species change. The rate increases because the relative contents of mono- and dicomplex, which are more reactive for propagation, increase greatly.<sup>4,5</sup> The equilibria have the same results as with *t*-AmOK since the reactivity of species with K as counterion is greater than that of Li in nonpolar solvent because the radius of  $K^+$  is bigger than that of  $Li^+$  and the



**Figure 4** Conversion of S in B-S copolymerization with different ratio of THF/Li.



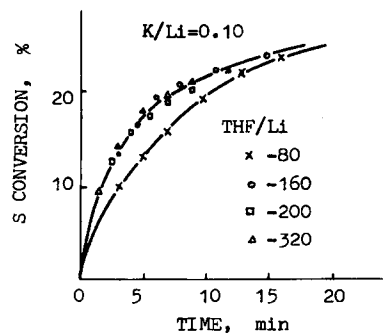
**Figure 5** Conversion of B in B-S copolymerization with different ratio of THF/Li.

polarity of the C-K bond is stronger than that of the C-Li bond.<sup>7</sup>

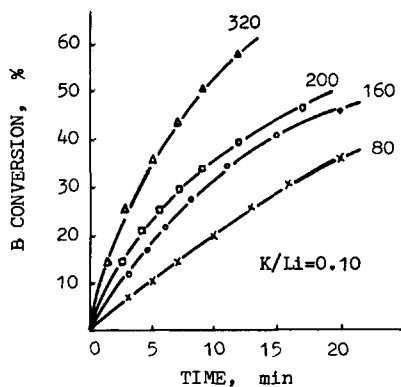
### Rate of Monomer Conversion

The rates of monomer (styrene and butadiene) conversion with K/Li or THF/Li were shown in Figures 4-9. It has been found:

1. At K/Li = 0.10, low THF/Li ratio (THF/Li = 0-1.38). The rate of styrene conversion was accelerated by THF/Li, while that of butadiene conversion did not change with THF/Li.
2. At K/Li = 0.10, high THF/Li ratio (THF/Li = 80-320). The rate of styrene conversion increased with THF/Li and when THF/Li exceeded 160 it did not change. On the contrary, the rate of butadiene conversion was accelerated greatly.
3. At THF/Li = 40, K/Li = 0.02-0.50. With an increase of *t*-AmOK, the rate of styrene conversion obviously accelerated and that of butadiene conversion accelerated slowly.



**Figure 6** Conversion of S in B-S copolymerization with different ratio of THF/Li.



**Figure 7** Conversion of B in B-S copolymerization with different ratio of THF/Li.

In anionic polymerization, the rates of monomer conversion are represented as:

$$R_S = \frac{-d(S)}{dt} = \bar{K}_S(S)^a$$

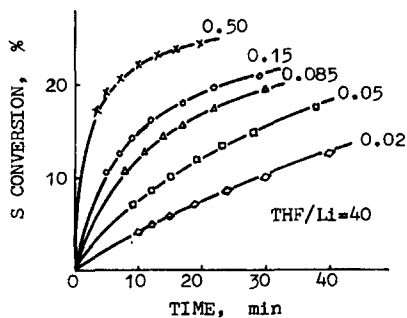
$$R_B = \frac{-d(B)}{dt} = \bar{K}_B(B)^b$$

$\bar{K}_S$  and  $\bar{K}_B$  represent the apparent rate constant of styrene and butadiene, respectively. They are functions of THF/Li, K/Li, temperature, and the proportion of monomer. S and B represent styrene and butadiene, respectively.  $a$  and  $b$  are the order of reaction. It has been derived according to first-order reaction:

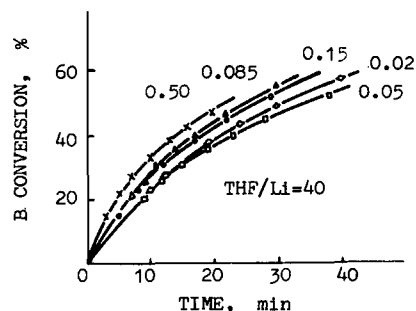
$$\text{Ln} \frac{25}{25 - X_S} = \bar{K}_S \times t$$

$$\text{Ln} \frac{75}{75 - X_B} = \bar{K}_B \times t$$

By plotting  $\text{Ln}(25/(25 - X_S))$ ,  $\text{Ln}(75/(75 - X_B))$  against  $t$ , respectively, a straight line was obtained



**Figure 8** Conversion of S in B-S copolymerization with different ratio of K/Li.



**Figure 9** Conversion of B in B-S copolymerization with different ratio of K/Li.

indicating a first-order reaction. The slopes of the plots are apparent rate constants and they are shown in Tables I-III.

From these data we have found:

1. At  $K/Li = 0.10$ , low concentration of THF,  $\bar{K}_S$  depends on THF, but  $\bar{K}_B$  does not. The increase of reaction rate is due to  $\bar{K}_S$ .
2. At  $K/Li = 0.10$ , high concentration of THF,  $\bar{K}_B$  depends on THF. The increase of reaction rate is due to  $\bar{K}_B$  and the rate depends on both  $\bar{K}_S$  and  $\bar{K}_B$  because  $\bar{K}_S \approx \bar{K}_B$ .
3. At  $THF/Li = 40$ ,  $K/Li = 0.02-0.50$ ,  $\bar{K}_S$  depends on  $t\text{-AmOK}$  and the increase of reaction rate is due to  $\bar{K}_S$ .

#### Effect of THF on Styrene Incorporated

The method by which styrene content in copolymer at different conversions has been determined is shown in Ref. 10. The results showed:

1. At  $THF/Li = 0-80$ , styrene incorporated in copolymer at the initial stage of copolymerization increased gradually with THF (Fig. 10). The relative contents of styrene incorporated in copolymer in the early stage of the reaction was less than its molar ratio in monomers when  $THF/Li$  was less than 0.20 and higher than its molar ratio in monomers when  $THF/Li$  exceeded 0.20. When  $THF/Li$  remained at 0.20, styrene entered the copolymer uniformly over the whole reaction

**Table I** Copolymerization Rate Constant

THF/Li	0	0.116	0.20	1.38
$\bar{K}_S (\text{min})^{-1}$	0.0141	0.0128	0.0173	0.0228
$\bar{K}_B (\text{min})^{-1}$	0.0183	0.0183	0.0183	0.0183

$K/Li = 0.10$ .

**Table II Copolymerization Rate Constant**

THF/Li	80	160	200	320
$\bar{K}_S$ (min) <sup>-1</sup>	0.142	0.188	0.188	0.188
$\bar{K}_B$ (min) <sup>-1</sup>	0.0313	0.0526	0.0702	0.115

K/Li = 0.10.

and the styrene contents in the copolymer and monomers were the same. It is believed that the reaction reached a constant proportion copolymerization.

In a study of B-S copolymerization, initiated by *n*-BuLi/*t*-BuOK, Cheng and Ying reported that when K/Li was equal to 0.085, the copolymer having composition almost identical to that of the initial monomers at different stages of conversion had been obtained.<sup>6</sup> Both results can be considered to be identical.

- At THF/Li = 80–320, styrene incorporated in copolymer at the initial stage of the reaction surpassed its initial proportion in monomers and decreased gradually with THF (Fig. 11).

It has been proved that the above results agree well with Cheng and Ying's results.<sup>4</sup> The difference is only in that B-S copolymerization, initiated by *n*-BuLi/THF styrene, incorporated at the initial stage of the reaction, is lower than its initial composition in monomers. According to these results, it may be inferred that the addition of *t*-AmOK increased greatly the reactivity of species, which propagated the styrene monomer.

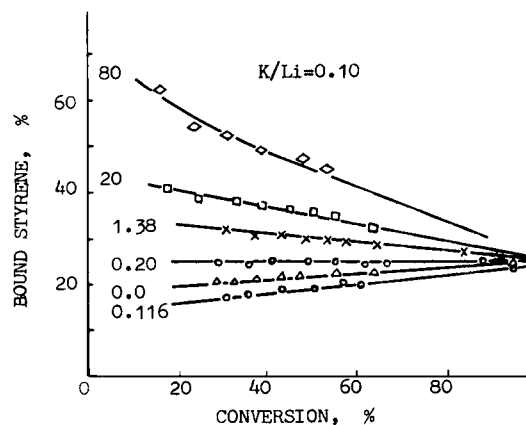
### Effect of *t*-AmOK on Styrene Incorporated Styrene

When the ratio of THF to *n*-BuLi was constant, by adjusting the concentration of *t*-AmOK, we have found that the styrene monomer entering copolymer at the initial stage of the reaction increased gradually with *t*-AmOK (Fig. 12). Especially, the styrene content in copolymer was lower than its molar ratio in monomers at K/Li < 0.05 and higher than its molar ratio in monomers at K/Li > 0.05. The com-

**Table III Copolymerization Rate Constant**

K/Li	0.02	0.05	0.085	0.15	0.50
$\bar{K}_S$ (min) <sup>-1</sup>	0.0115	0.0350	0.0470	0.0750	0.1380
$\bar{K}_B$ (min) <sup>-1</sup>	0.0338	0.0325	0.0425	0.0388	0.0500

THF/Li = 40.


**Figure 10** Styrene content in copolymer versus conversion at different ratio of THF/Li.

position of the copolymer was identical with that of monomers at different stages of conversion when K/Li was equal to 0.05.

Based on the above results, by appropriately adjusting K/Li and THF/Li, a copolymer in which styrene was well-distributed has been obtained.

### Propagation Regularity of Species

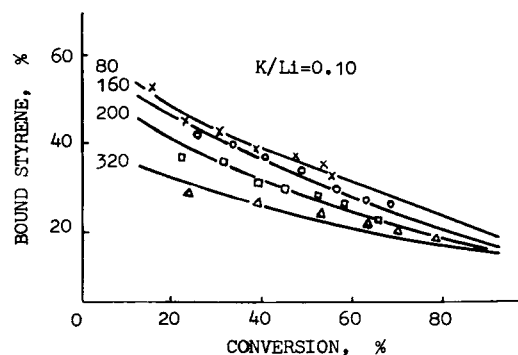
The B-S copolymerization system is a complex one in which multiple active species coexist. Referring to the literature<sup>4-7</sup> it can be believed that at least the following active species exist in the system in which B-S copolymerization is initiated with *n*-BuLi/THF/*t*-AmOK:

Associated species  $(P_iM_j)_2$

Cross associated species  $(P_iM_j)(P_{i\pm 1}M_{j\pm 1})$

Monomeric species  $P_iM_j$

Complex species  $P_iM_j \times kF$


**Figure 11** Styrene content in copolymer versus conversion at different ratio of THF/Li.

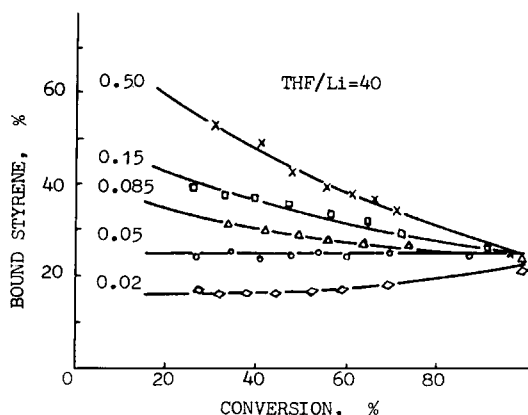
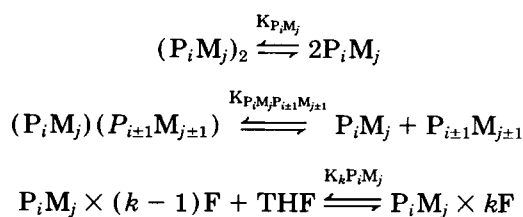


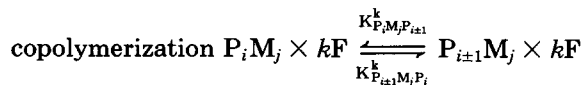
Figure 12 Styrene content in copolymer versus conversion at different ratio of K/Li.

The equilibria between these species can be described as follows:



where P is propagating chain,  $i = 1$  or  $2$ ,  $i \pm 1 = 1$  or  $2$ ,  $i \neq i \pm 1$ , 1-end unit is styrene (S), 2-end unit is butadiene (B). M is alkali metal,  $j = 1$  or  $2$ ,  $j \pm 1 = 1$  or  $2$ ,  $j \neq j \pm 1$ , 1-Li, 2-K. F is tetrahydrofuran (THF),  $k$  is complex number,  $k = 1$  or  $2$ .  $K$  is equilibrium constant.

Because of the rather low reactivity of associated species<sup>11</sup> and the high ratio of THF to *n*-BuLi in this research, the propagation reaction of associated species could be neglected and we only considered the propagation reaction of other species. The polymerization can be described in term of twenty-four reactions:



$K$  indicates the propagation rate constant,  $k$  is complex number,  $k = 0, 1, 2$ , subscript denotes species end and the type of propagating monomer. The propagating reactions of styrene and butadiene are in accord with a first-order reaction.

$$\frac{-d(S)}{dt} = \bar{K}_S \times (S) \quad \frac{-d(B)}{dt} = \bar{K}_B \times (B)$$

$$\bar{K}_S = \sum K_{SM_j S}^k (SM_j \times kF) + \sum K_{BM_j S}^k (BM_j \times kF)$$

$$\bar{K}_B = \sum K_{BM_j B}^k (BM_j \times kF) + \sum K_{SM_j B}^k (SM_j \times kF)$$

$\bar{K}_S$  and  $\bar{K}_B$  represent apparent rate constant of styrene and butadiene, respectively.

The reaction mechanism of anionic copolymerization with Li as counterion and THF as modifier has been studied in detail. Lacking data on the active species with K as counterion and THF as modifier, the above constants have not been obtained at this time and we only could give a qualitative analysis according to the composition and structure of the copolymer.

- At K/Li = 0.10, low concentration of THF. Most associated species dissociated into monomeric species and partial monomeric species complex into monocomplex with increasing THF. The main species were monomeric species and monocomplex with Li or K as counterion in the system ( $P_i M_j$ ,  $P_i M_j \times F$ ). Due to the increase of the reaction rate with THF it can be shown that the propagating reactivity of the monocomplex is greater than that of the monomeric species (Fig. 1, Table I). From the literature,<sup>4,5</sup> it is well known that the monomeric species of Li mainly propagate the butadiene monomer, the monocomplex of Li mainly propagate butadiene monomer and a little styrene monomer. The monomeric species of K mainly propagate styrene monomer.<sup>6,7</sup> It can also be found that the monocomplex of K also propagates styrene monomer predominantly (Fig. 10). Although the monocomplex of Li also propagates styrene monomer, the propagating ability is less than for the former. In addition, since  $\bar{K}_S$  increases gradually and  $\bar{K}_B$  is almost constant with THF, this shows that THF preferably complexes K in the coexistence of Li and K.
- At K/Li = 0.10, high concentration of THF. Nearly all monomeric species turned into monocomplex and a portion of monocomplex into dicomplex at a high concentration of THF. There existed active species of both mono- and dicomplex of Li and K ( $P_i M_j \times F$ ,  $P_j M_j \times 2F$ ).

The propagating reactivity of dicomplex is greater than that of monocomplex because the

reaction rate increases with THF (Fig. 2, Table II). Cheng and Ying reported that in B-S copolymerization, initiated by *n*-BuLi/THF when concentrations of THF is very high, there exists mainly a dicomplex of Li and the reactivity ratios for both monomers approach unity.<sup>5</sup> Because styrene content in the copolymer at the beginning of reaction decreased with THF and  $\bar{K}_B$  increased gradually,  $\bar{K}_S$  is almost constant and it may be considered that the dicomplex of K mainly propagates butadiene monomer and has greater reactivity to combine butadiene monomer than that of Li.

- At THF/Li = 40, K/Li = 0.02–0.50. The results are identical to the above corollaries from Figure 3, Figure 12, and Table III. There exist monomeric species, mono- and dicomplex of Li, K in the system, but at such high concentration of THF and the monocomplex species is overwhelming. Since THF preferably complexed K, the amount of monocomplex of K increased sharply with addition of *t*-AmOK, the reaction rate increase gradually, and styrene content in the copolymer at the beginning of reaction increased gradually, too. The increase of  $\bar{K}_S$  was faster than that of  $\bar{K}_B$ .

## CONCLUSION

- It can be illustrated that this system is a complex one in which there exist multiple active species since there are different propagating characteristics and kinetic behaviors at different ratios of modifier to *n*-BuLi in copolymerization of butadiene and styrene initiated by *n*-BuLi/THF/*t*-AmOK in cyclohexane at 50°C.
- Addition of THF and *t*-AmOK can accelerate the reaction of B-S copolymerization initiated by *n*-BuLi in cyclohexane.
- Addition of THF and *t*-AmOK can increase styrene content incorporated in the copolymer at the initial stage of the reaction in anionic

B-S copolymerization initiated by *n*-BuLi in cyclohexane.

- By adjusting the ratio of *t*-AmOK to *n*-BuLi, and the ratio of THF to *n*-BuLi, copolymers, having compositions almost identical to that of the initial monomer ratio at different stages of conversion, have been obtained,
- The propagation regularity of each species in sufficient monomers at the initial stage of the copolymerization has been obtained through qualitative analysis.

The monomeric species of Li mainly propagate butadiene, the monocomplex of Li mainly propagate butadiene and a little styrene, and the dicomplex of Li propagate both styrene and butadiene in comparable quantity. The monomeric species of K mainly propagate styrene, the monocomplex of K mainly propagate styrene, the dicomplex of K mainly propagate butadiene.

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