

The Microstructure of Butadiene and Styrene Copolymers Synthesized with *n*-BuLi/THF/*t*-AmOK

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SYNOPSIS

A study of the microstructure of copolymers, synthesized by B-S anionic copolymerization, initiated with *n*-BuLi/THF/*t*-AmOK in cyclohexane at 50°C, has been performed. Moreover, the mean sequence length in the B-S copolymer chain has been determined. The result showed that the microstructure of copolymers were sharply influenced by various ratios of modifier (THF, *t*-AmOK) to initiator (*n*-BuLi). By selecting a proper ratio of K/Li and THF/Li, B-S copolymers with unique randomness, having composition almost identical to the initial monomer ratio at different stages of conversion and very low vinyl content, have been obtained.

The formation mechanism of the copolymer chain structure is discussed.

INTRODUCTION

It is generally considered that B-S copolymers used as general purpose rubber must be random (styrene content is about 25%) and vinyl content in polybutadiene chain segment should be 10%. Cheng and Ying reported that the copolymerization mechanism tends to approach zero Markov chain and that the vinyl content in copolymers increases enormously in B-S copolymerization initiated by *n*-BuLi/THF when a large amount of THF is added.^{1,2} Although the copolymer, in which styrene was distributed randomly and vinyl content was low, may be obtained by using Li-K initiator,³⁻⁵ the copolymer is difficult to synthesize because the content of incorporated styrene largely depends on the molar ratio of K/Li,⁴ due to the low solubility of *t*-BuOK in a nonpolar solvent. It has been reported that the effect of various ratios of K/Li and THF/Li on the microstructure of a copolymer has been studied and that mean sequence length has been determined in B-S copolymerization initiated by *n*-BuLi/THF/

t-AmOK in cyclohexane. The formation mechanism of copolymer chain structure has been discussed.

EXPERIMENTAL

Please refer to Ref. 6.

RESULTS AND DISCUSSION

Microstructure of Copolymers at Different Conversions

The microstructure of copolymers obtained under different ratios of modifier to initiator (K/Li = 0.10 and THF/Li = 0.20; K/Li = 0.05 and THF/Li = 40) and at different conversions has been determined and the cis, trans, and vinyl content of polybutadiene chain segment has been calculated through Shiro Anzai's method⁷ (Figs. 1-2).

From Figure 1 and Figure 2, Cis-1,4 content in copolymer is far higher than both trans-1,4 content and vinyl content at the initial stage of the reaction. Cis-1,4 content decreased gradually and trans-1,4 content increased with increasing conversion.

Cis-1,4 is the predominant structure in the polybutadiene chain obtained by anionic polymerization in nonpolar solvents. The result of the NMR study

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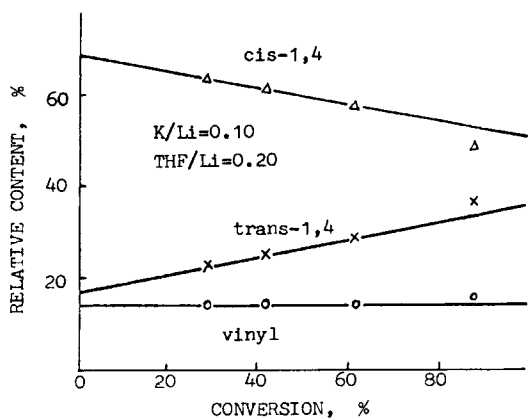
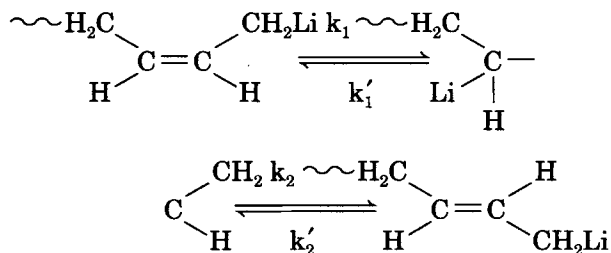


Figure 1 Relative contents of *cis*-1,4, *trans*-1,4 and vinyl unit of B-S copolymer as a function of conversion. Reaction conditions: solvent, cyclohexane; monomer concentration, 10% (weight); butadiene/styrene, 75/25 (weight); *n*-BuLi, 0.0005 mol/100g monomer; temperature, 50°C.

has shown that the species ending with *trans*-1,4 structure is more stable than that ending with *cis*-1,4 structure. Morton proposed that the reactive chain of *trans*-1,4 structure is isomerized from that of *cis*-1,4 structure through an intermediate transition state of vinyl structure^{8,9}:



If the propagation rate is far higher than that of isomerization, the *cis*-1,4 structure predominates in the copolymer. If the propagation rate is comparable to the isomerization rate, there is little vinyl structure in the copolymer in the case of $k_2 \gg k_1$ and k'_2 (the transformation rate of *trans*-1,4 is higher than that of vinyl) and vinyl structure ending has a little opportunity to propagate in the case of $k_2 \approx k_1$ and k'_2 (the transformation rate of *trans*-1,4 is comparable to that of vinyl). There would be a certain amount of vinyl structure in the final product since the segment configuration of the penultimate unit after propagating is fixed. At the initial stage of the reaction (at low conversion), the *cis*-1,4 structure will preferably be formed since the propagation rate is far higher than that of isomerization, due to high monomer concentration. At the late stage of the reaction (at high conversion), the propagation rate

decreases, due to low monomer concentration and the fact that diffusion of reactive chain is hindered due to the high viscosity of the reactive system. Therefore the *cis*-1,4 content decreases gradually and *trans*-1,4 content increases with increasing conversion since the isomerization rate would not be influenced by the diffusion process. It may be concluded that in the anionic B-S copolymerization in pure hydrocarbon solvent at $K/Li = 0.10$ and $THF/Li = 0.20$ (low THF concentration), the probability of transformation from vinyl structure into *trans*-1,4 structure is rather large because of the low propagation rate. Consequently, vinyl content increases with increasing conversion as the experimental results showed.

Relationship between Microstructure of Copolymers and Modifiers

Relationship between Microstructure of Copolymers and THF/Li at Low THF Concentration

The microstructure of B-S copolymer at $K/Li = 0.10$ and low THF concentration is shown in Figure 3. Figure 3 depicts that the percentage of vinyl structure (lower than 15%) remains almost constant as THF concentration increases. *Cis*-1,4 content increases and *trans*-1,4 content decreases with increasing THF concentration and they change slowly as THF/Li approaches 1.

Relationship between Microstructure of Copolymers and THF/Li at High THF Concentration

The microstructure of B-S copolymer at $K/Li = 0.10$ and high THF concentration is shown in Figure 4. It is found that *cis*-1,4 and *trans*-1,4 change slowly and vinyl content varies from 20% to 30%, with THF/Li ranging from 10 to 320. Yu and Ying

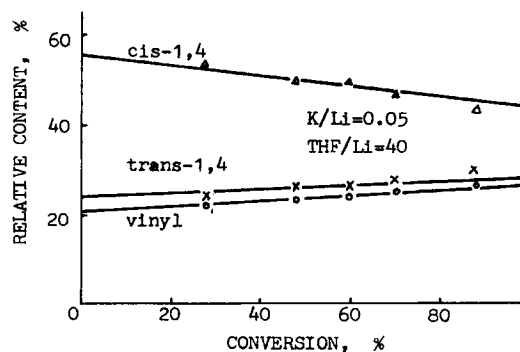


Figure 2 Relative content of *cis*-1,4, *trans*-1,4 and vinyl unit of B-S copolymer as a function of conversion.

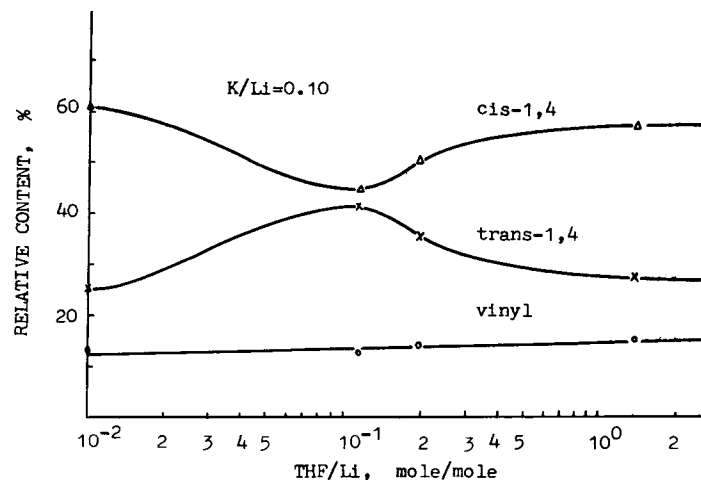


Figure 3 Effect of THF/Li on the microstructure of B-S copolymer.

reported that the vinyl content varied from 31.9% to 44.2% when THF/Li ranged between 16 and 180 in the case of B-S copolymerization initiated by *n*-BuLi/THF.¹⁰ By comparison, the vinyl content decreased sharply when *t*-AmOK was added.

Relationship between Microstructure of Copolymers and K/Li

The microstructure of B-S copolymer at THF/Li = 40 and K/Li ranging from 0.02 to 0.50 is shown in Figure 5. The results show the *trans*-1,4 and vinyl content increase gradually and *cis*-1,4 content decreases when K/Li was less than 0.10; the change in the three kinds of structure tends to be little with K/Li when K/Li exceeds 0.10. The vinyl content varies only from 23% to 30% with the K/Li ranging from 0.02 to 0.50, however, in reactions initiated by

n-BuLi/*t*-BuOK without THF, vinyl content varies from about 8% to 40%.³ From the above results, it can be suggested that the complex species of K has low reactivity to increase vinyl content.

Mean Sequence Length

In our previous research,⁶ when K/Li = 0.10 and THF/Li = 0.20 or K/Li = 0.05 and THF/Li = 40, copolymers having compositions almost identical to that of the initial monomer ratio at different conversions have been obtained. The sequential distribution and mean sequence length of the copolymers have been determined by using ¹³C-NMR technique. The total conversion was about 30%. Each peak in the NMR spectra has been established using Alen Roy Katritzky's results.¹¹ The relative content of each peak has been calculated according to peak height. The content of the diad group and mean se-

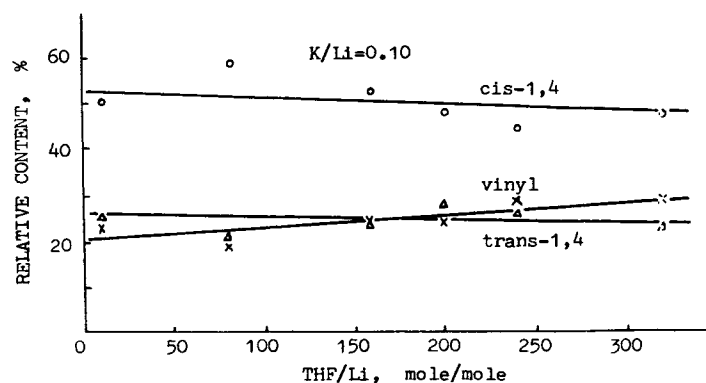


Figure 4 Effect of THF/Li on the microstructure of B-S copolymer.

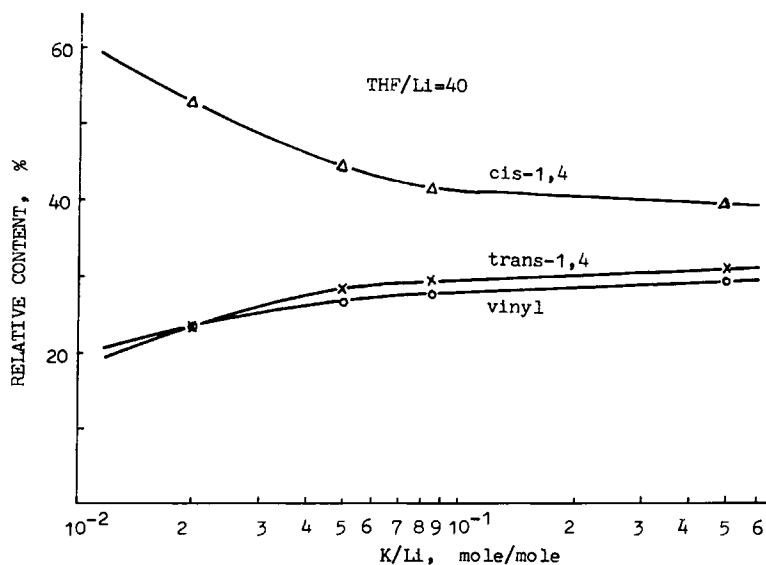


Figure 5 Effect of K/Li on the microstructure of B-S copolymer.

quence length have been determined according to the literature.¹² The results obtained are shown in Tables I-III.

The results show that the content of styrene diad (SS) in both copolymers is relatively low. The content of vinyl diad (VV) in copolymer No. I is higher than that in copolymer No. II and it agrees well with the result obtained by using an IR technique.⁶ From the above results the copolymers obtained have unique randomness and do not have long styrene blocks.

Microstructure Formation in the Presence of Modifier

In nonpolar solvents, there exist multiple active species in the anionic copolymerization system with *n*-BuLi/THF/*t*-AmOK. All active species (including associated species, monomeric species, monocomplex and dicomplex species) are subjected to dynamic equilibria. Increasing THF concentration would make the equilibria shift gradually from associated, monomeric to monocomplex, dicomplex species. R. Ohlinger considered that the possibility

of forming the multicomplex species with complex number exceeding 2 at extremely high THF concentration cannot be ruled out, nevertheless the multicomplex species would have no ability to propagate.¹³ If Li and K were coordinated with THF to form tricomplex, it could be inferred that tricomplex would have little propagating reactivity.¹ Thus it can be reasonably considered the active species are monomeric, mono- and dicomplex species under the experimental conditions in this article.

Due to the different radii of Li and K, Li and K coordinate with THF and monomers to form transition complex in different manners and to form different microstructures.

Without THF

There exist associated and monomeric species of Li and K as counterions in the system. The propagation of associated species can be neglected⁶ and the monomeric species plays a major role in propagation.

There is a large amount of Li species at low *t*-AmOK concentration. It mainly grows cis-1,4 and trans-1,4 structure, but only has a little tendency to grow styrene and vinyl structure. Styrene content

Table I Diad Content of B-S Copolymer Microstructure

No.	SC	ST	VC	CT	CS	TS	CV	TV	SV	VS	VV	SS	TT	CC	CT	TC
I	0	6.28	2.56	11.01	0	3.17	7.66	4.55	3.38	2.02	10.60	2.67	17.67	6.68	7.20	14.54
II	0	0.40	1.70	4.37	0	1.39	6.55	2.58	0.78	3.84	4.60	0	21.38	15.74	16.93	19.75

Experiment No. I, K/Li = 0.05 and THF/Li = 40; No. II, K/Li = 0.10 and THF/Li = 0.20

Table II Mean Sequence Length of B-S Copolymer Chain

No.	n_s	n_v	n_t	n_c	n_{sc}	n_{st}	n_{vc}	n_{vt}	n_{vs}	n_{vt}
I	1.40	1.68	1.76	1.42	1.40	2.40	2.29	2.88	2.08	3.66
II	1.00	1.46	1.94	1.70	1.61	1.96	2.05	2.28	2.15	10.21

Table III Mean Block Number of B-S Copolymer Chain

No.	N_s	N_v	N_t	N_c	N_{sc}	N_{st}	N_{vc}	N_{vt}	N_{vs}	N_{vt}
I	7.2	15.6	23.4	16.0	23.4	21.3	21.4	23.4	17.5	17.4
II	3.21	9.93	22.7	22.5	25.7	24.1	25.7	25.7	8.24	8.24

and vinyl content increase rapidly with increasing *t*-AmOK.³

At $K/Li = 0.10$, Low THF Concentration

There mainly exist monomeric and monocomplex species of Li and K in the system. At low THF concentration, the monocomplex of Li mainly propagates cis-1,4 and trans-1,4 structure, the monocomplex of K mainly propagates styrene monomer. Therefore, styrene content increases very quickly, but vinyl structure increases slowly (Fig. 3 and Ref. 6).

At $K/Li = 0.10$, High THF Concentration

There exist few monomeric species, a few monocomplex and mainly dicomplex, of Li and K in the system. The dicomplex of Li propagates both styrene and butadiene in comparable quantity, the dicomplex of K mainly propagates butadiene. Vinyl content increases gradually and styrene content decreases with increasing THF (Fig. 4 and Ref. 6).

At $THF/Li = 40$, K/Li Ranging from 0.02 to 0.50

There mainly exist mono-, dicomplex of Li and K when THF concentration is not very high. According to the above explanation, the total content of cis-1,4 and trans-1,4 structure in copolymers decreases and that of styrene unit and vinyl structure increases with increasing *t*-AmOK (the relative content of Li species decreases at the same time). The increase of styrene unit is faster than that of vinyl structure (Fig. 5 and Ref. 6).

CONCLUSIONS

1. In butadiene-styrene copolymerization, initiated by *n*-BuLi/THF/*t*-AmOK in cyclo-

hexane, the vinyl content of copolymers is from 10% to 20%. Even at very high THF concentration (THF/Li = 320) the vinyl content does not exceed 30%.

2. By selecting the proper ratio of K/Li and THF/Li, the copolymers, in which styrene unit distributed randomly and vinyl content was relatively low, have been obtained. At $K/Li = 0.10$ and $THF/Li = 0.20$, the vinyl content is about 15%. At $K/Li = 0.05$ and $THF/Li = 40$, the vinyl content does not exceed 24%.

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