

## Active Species in Anionic Polymerization of Phenylbutadienes —Reactivity of Model Anions—

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**ABSTRACT:** The reactivity of model anions of active species in the anionic polymerization of phenylbutadienes was investigated by reactions with several electrophiles. The anions employed are generated by one-to-one addition of 1-phenyl-1,3-butadiene with *t*-BuLi, lithiation of 1-phenyl-2-butene, one-to-one addition of 2-phenyl-1,3-butadiene with *t*-BuLi, and lithiation of 3-phenyl-1-butene. The former two anions are classified as  $\pi$ -benzyl type anions and the latter two as  $\pi$ -allylphenyl type anions according to negative charge distributions. In the reactions of these anions with methanol (protonation), difference in negative charge distribution does not affect the product distribution, and the reactivity of the  $\alpha$ -position (terminal of the anion) is high. When methyl iodide is reacted,  $\alpha$ -products (products reacted at the  $\alpha$ -position) are selectively obtained (96—98%) in the case of  $\pi$ -benzyl type anions. On the other hand, the amount of  $\alpha$ -products decreased (45—85%) in the case of  $\pi$ -allylphenyl type anions. These findings can be attributed to the differences in negative charge distribution. However, in reactions with trimethylchlorosilane or trimethylchlorotin, steric effect at the  $\alpha$ - or  $\gamma$ -carbon controls the regioselectivity of the products. In reactions with acetone or ethylene oxide,  $\alpha$ -products are obtained predominantly in the case of  $\pi$ -benzyl type anions, while  $\gamma$ -products are obtained mainly in the case of  $\pi$ -allylphenyl type anions.

**KEY WORDS** 1-Phenyl-1,3-butadiene / 2-Phenyl-1,3-butadiene / *t*-BuLi / Anionic Polymerization / Model Anion / Electrophiles / Product Distribution /

Living anion chain end structures in the polymerizations of conjugated dienes have been extensively studied to elucidate the polymerization mechanism.<sup>1-14</sup> A number of discussions on the  $\pi$ -electron distribution on living oligomer chain ends and model anions has been made. However little attention has been directed to regioselectivity in the reactions of these model anions with electrophiles. Miginiac studied the reaction of 2-pentenyl-lithium with alkylketone.<sup>15</sup> Glaze *et al.* reported the reactions of neopentylallyllithium (one-to-one adduct of butadiene with *t*-BuLi) with several electrophiles.<sup>2,4</sup> However, in some cases, the regioselectivity in the reactions cannot be interpreted simply on the basis of the negative charge distributions of these anions.

In previous papers, we studied the microstructures of poly(1-phenyl-1,3-butadiene) [poly(1PB)] and poly(2-phenyl-1,3-butadiene) [poly(2PB)] pre-

pared by anionic polymerization, and elucidated the  $\pi$ -electron distributions of the living oligomer chain ends of the model anions.<sup>18,19</sup>

In this paper, we discuss the reactivity of the model anions of active species in the anionic polymerization of 1PB and 2PB by means of reactions with several electrophiles.

### EXPERIMENTAL

#### *Materials*

*trans*-1-Phenyl-1,3-butadiene (1PB),<sup>16</sup> 2-phenyl-1,3-butadiene (2PB),<sup>17</sup> 3-phenyl-1-butene (3P1B),<sup>19</sup> and *t*-BuLi<sup>16</sup> were synthesized as described in previous papers. Commercially available 1-phenyl-2-butene (1P2B), acetone, methyl iodide (MeI), trimethylchlorosilane (TMS-Cl), and trimethylchlorotin (TMT-Cl) were purified by distillations.

*Lithiation of 1P2B and 3P1B*

1P2B or 3P1B (1.0 mmol) was lithiated with *t*-BuLi (1.2 mmol) in dry THF (2.0 ml) at 5°C in an argon atmosphere. The reaction was completed after 1.5 h.

*Preparation of One-to-One Adduct of 1PB or 2PB with t-BuLi*

1PB (1.0 mmol) was added to *t*-BuLi (1.5 mmol) in THF (2.0 ml) or toluene (2.0 ml) at -78°C (in THF) or 0°C (in toluene) in an argon atmosphere. The reaction mixture was stirred for 3.0 h. The addition of 2PB (1.0 mmol) to *t*-BuLi (1.5 mmol) was carried out in THF (2.0 ml) at -78°C, and after 3.0 h the reaction was completed.

*Reaction with Several Electrophiles*

Into the anion solution thus obtained, electrophile was added under various conditions. Ethylene oxide (EO) was distilled into the anion solution directly under high vacuum. The reactions were completed within a few minutes after the addition of electrophiles, as indicated by the disappearance of red color of the anion.

*Identification of the Products*

The protonated products were identified in previous paper.<sup>18,19</sup> The other products were analyzed and fractionally isolated by a GLC (DEGA 3 mmφ × 2.25 m or SE-30 3 mmφ × 1.5 m). The isolated fractions were identified by FT <sup>1</sup>H NMR and mass spectroscopies. The <sup>1</sup>H NMR spectral data are shown in Table II. In all mass spectra, molecular ion peaks and characteristic fragment ion peaks could be observed.

*<sup>1</sup>H NMR and Mass Spectra*

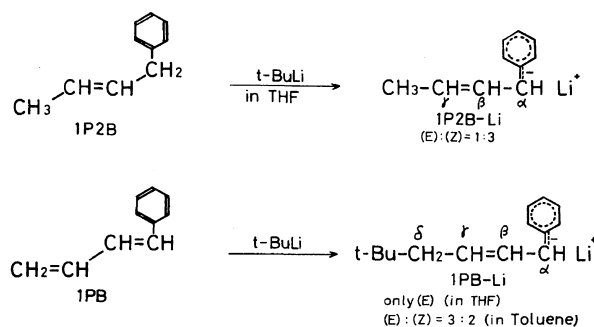
<sup>1</sup>H NMR spectra were recorded with a JEOL JNM FX 100 Fourier Transform NMR spectrometer (100 MHz). The measurements were carried out on a carbon tetrachloride solution containing a small amount of benzene-*d*<sub>6</sub> for internal lock. Typical conditions for <sup>1</sup>H FT measurements: spectral width, 1000 Hz; acquisition time, 4.10 s; data point, 16 K; pulse width 7 μs(42°); pulse repetition, 20 s; number of transients, 4–128.

Mass spectra were taken on a Hitachi RMS-4 mass spectrometer.

## RESULTS AND DISCUSSION

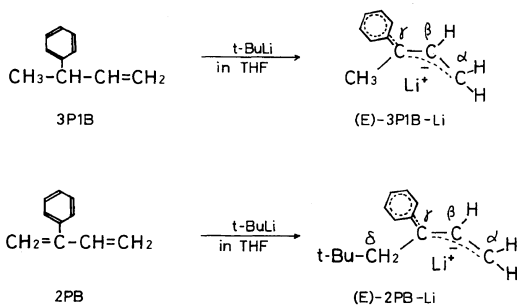
*Negative Charge Distribution of the Model Anions*

The anions employed in this study are classified into two different types on the basis of the <sup>13</sup>C and <sup>1</sup>H NMR studies presented in previous papers.<sup>18,19</sup> One type is  $\pi$ -benzyl and the other is the  $\pi$ -allyl-phenyl type. Scheme I shows the formation of  $\pi$ -benzyl type anions which are the model anions for the propagating chain end of 1PB in the polymerization. In the reaction of 1P2B with *t*-BuLi, lithiation occurs selectively at the  $\alpha$ -position, and the anion thus generated is designated as 1P2B-Li. A one-to-one addition of *t*-BuLi to 1PB was carried out as shown in Scheme I in THF and toluene. In these reactions, the *t*-butyl anions attack  $\delta$ -carbons selectively. The one-to-one adduct was obtained selectively (more than 98%) in THF, whereas higher oligomers were also obtained in toluene; the yield of the one-to-one adduct was 65%. The one-to-one adduct thus obtained is designated as 1PB-Li. These 1P2B-Li and 1PB-Li are regarded as 3-alkyl-substituted phenylallyllithiums. As was shown in a previous paper,<sup>18</sup> in both 1P2B-Li and 1PB-Li, the

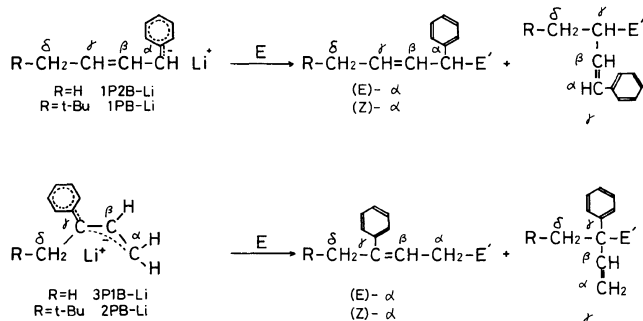


Scheme I.

## Reactivity of Phenylbutadienyllithium



Scheme II.



Scheme III.

negative charge is located at the  $\alpha$ -carbon and the phenyl ring, and delocalization to the  $\gamma$ -carbon is small. These are thus classified as  $\pi$ -benzyl type anions. Scheme II shows the formation of  $\pi$ -allylphenyl type anions. In the lithiation of 3P1B with *t*-BuLi, lithiation occurs regioselectively at the  $\gamma$ -position. The anion thus obtained is called 3P1B-Li. A one-to-one addition of *t*-BuLi to 2PB was carried out in THF, where the one-to-one adduct was obtained selectively (more than 98%). However, in this case regioselectivity of the addition is not good, and 1,4-anions (*t*-Bu anion attacks the  $\delta$ -carbon of 2PB) and 4,1-anions (*t*-Bu anion attacks the  $\alpha$ -carbon) were generated in 92 and 8% yields, respectively. The 1,4-anion, which is the propagating species in the polymerization of 2PB, is designated as 2PB-Li, as shown in Scheme II. When the reaction was carried out in toluene, a considerable amount of the 4,1-anion (35%) was formed. These 3P1B-Li and 2PB-Li are regarded as 1-alkylsubstituted phenylallyllithiums. As found in previous study,<sup>19</sup> in both 3P1B-Li and 2PB-Li, negative charges delocalize over a  $\pi$ -allyl system and the phenyl ring.

In the anionic polymerizations of 1PB and 2PB, 1,4-structures are predominant regardless of the polymerization conditions.<sup>16,17</sup> Thus, under the polymerization conditions, the reactivities of the  $\alpha$ -positions seem to be the highest in both the  $\pi$ -benzyl and  $\pi$ -allylphenyl type anions.

### Product Distribution in Reactions with Several Electrophiles

Scheme III shows products expected from the reactions of substituted phenylallyllithiums with the electrophile, *E*. For these anions, the notations of  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -position are given respectively from the anion end, as shown in the Scheme. The reaction with the electrophile, *E*, can occur either at the  $\alpha$ - or  $\gamma$ -position. The reaction products are designated as (*E*)- $\alpha$ , (*Z*)- $\alpha$ , and  $\gamma$ , depending on the reaction center.

The <sup>1</sup>H NMR spectra of the products showed well-defined patterns and assignments could be made partly on the basis of a comparison with the spectra of the corresponding polymers.<sup>16,17</sup>

We examined the  $\alpha$ - to  $\gamma$ -product ratio and made a comparison of the results with the regioselectivity

Table I. Product distribution in the reactions of substituted phenyllithiums

E	-E'	Solvent	Temp °C	$\pi$ -Benzyl type anions						$\pi$ -Allylphenyl type anions								
				1P2B-Li/%		1PB-Li/%		3P1B-Li/%		2PB-Li/% <sup>a</sup>								
				(E)- $\alpha$	(Z)- $\alpha$	(E)- $\alpha$	(Z)- $\alpha$	(E)- $\alpha$	(Z)- $\alpha$	(E)- $\alpha$	(Z)- $\alpha$	(E)- $\alpha$	(Z)- $\alpha$	(E)- $\alpha$	(Z)- $\alpha$	(E)- $\alpha$	(Z)- $\alpha$	
CH <sub>3</sub> OH	-H	THF	0	19	35	46	(3)	70	8	22	(6)	61	0	39	(8)	81	0	11
CH <sub>3</sub> OH	-H	THF	-78	42	32	26	(4)	71	11	18	(7)	78	0	22	(9)	86	0	6
CH <sub>3</sub> OH	-H	Toluene	0	—	—	—	(5)	65	23	12	—	—	—	—	—	—	—	—
CH <sub>3</sub> I	-CH <sub>3</sub>	THF	0	82	14	4	(12)	85	11	4	(15)	45	0	55	(17)	78	0	15
CH <sub>3</sub> I	-CH <sub>3</sub>	THF	-78	94	3	3	(13)	88	11	1	(16)	45	0	55	(18)	78	0	15
CH <sub>3</sub> I	-CH <sub>3</sub>	Toluene	0	—	—	—	(14)	72	26	2	—	—	—	—	—	—	—	—
TMS-Cl <sup>e</sup>	-Si(CH <sub>3</sub> ) <sub>3</sub>	THF	0	56	11	33	(21)	91	4	5	(24)	100	0	0	(26)	91	0	0
TMS-Cl	-Si(CH <sub>3</sub> ) <sub>3</sub>	THF	-78	59	13	28	(22)	92	3	5	(25)	100	0	0	(27)	91	0	0
TMS-Cl	-Si(CH <sub>3</sub> ) <sub>3</sub>	Toluene	0	—	—	—	(23)	61	21	18	—	—	—	—	—	—	—	—
TMT-Cl <sup>d</sup>	-Sn(CH <sub>3</sub> ) <sub>3</sub>	THF	0	8	4	88	(30)	68	12	20	(33)	100	0	0	(35)	61	18	13
TMT-Cl	-Sn(CH <sub>3</sub> ) <sub>3</sub>	THF	-30	6	5	89	(31)	75	11	14	(34)	100	0	0	(36)	65	23	4
TMT-Cl	-Sn(CH <sub>3</sub> ) <sub>3</sub>	Toluene	0	—	—	—	(32)	61	24	15	—	—	—	—	—	—	—	—
Acetone	-C(CH <sub>3</sub> ) <sub>2</sub> OH	THF	0	30	25	45	(39)	58	4	38	(42)	0	0	100	(44)	93	0	0
Acetone	-C(CH <sub>3</sub> ) <sub>2</sub> OH	THF	-78	59	27	14	(40)	75	0	25	(43)	9	0	91	(45)	46	0	47 <sup>f</sup>
Acetone	-C(CH <sub>3</sub> ) <sub>2</sub> OH	Toluene	0	—	—	—	(41)	40	31	29	—	—	—	—	—	—	—	—
EO <sup>e</sup>	-(CH <sub>2</sub> ) <sub>2</sub> OH	THF	-78	43	57	0	(48)	100	0	0	(50)	0	0	100	(51)	12	10	71
EO	-(CH <sub>2</sub> ) <sub>2</sub> OH	Toluene	-78	—	—	—	(49)	100	0	0	—	—	—	—	—	—	—	—

<sup>a</sup> 7–9% of the 4,1-anion was formed. <sup>b</sup> In parentheses run numbers are shown. <sup>c</sup> Trimethylchlorosilane. <sup>d</sup> Trimethylchlorotin. <sup>e</sup> Ethylene oxide. <sup>f</sup> *n*-BuLi was used in place of *t*-BuLi.

Table II. <sup>1</sup>H NMR spectral data of products

Run No.	Anion	-E'	Structure	Data <sup>a</sup> (δ)
(10)	1P2B-Li	-CH <sub>3</sub>	(E)-α	1.30 (3H, d, -CH <sub>3</sub> ), 1.63 (3H, d, -CH <sub>3</sub> ), 3.31 (1H, qui, -CH-), 5.44 (2H, m, -CH=CH-), 7.08 (5H, m, ph)
(11)	1P2B-Li	-CH <sub>3</sub>	(Z)-α	1.30 (3H, d, -CH <sub>3</sub> ), 1.63 (3H, d, -CH <sub>3</sub> ), 3.70 (1H, qui, -CH-), 5.44 (2H, m, -CH=CH <sub>2</sub> -), 7.08 (5H, m, ph)
(12)	1P2B-Li	-CH <sub>3</sub>	γ	0.74 (6H, d, -CH <sub>3</sub> ), 1.88 (1H, m, -CH-), 5.36 (2H, m, -CH=CH-), 7.08 (5H, m, ph)
(13)	1PB-Li	-CH <sub>3</sub>	(E)-α	0.87 (9H, s, -CH <sub>3</sub> ), 1.33 (3H, d, -CH <sub>3</sub> ), 1.88 (2H, d, -CH <sub>2</sub> -), 3.36 (1H, qui, -CH-), 5.43 (2H, m, -CH=CH-), 7.12 (5H, m, ph)
(14)	1PB-Li	-CH <sub>3</sub>	(Z)-α	0.90 (9H, s, -CH <sub>3</sub> ), 1.30 (3H, d, -CH <sub>3</sub> ), 1.98 (2H, d, -CH <sub>2</sub> -), 3.71 (1H, qui, -CH-), 5.43 (2H, m, -CH=CH-), 7.12 (5H, m, ph)
(15)	3P1B-Li	-CH <sub>3</sub>	(E)-α	1.06 (3H, t, -CH <sub>3</sub> ), 1.98 (3H, s, -CH <sub>3</sub> ), 2.16 (2H, qui, -CH <sub>2</sub> -), 5.66 (1H, t of q, =CH-), 7.16 (5H, m, ph)
(16)	3P1B-Li	-CH <sub>3</sub>	γ	1.36 (6H, s, -CH <sub>3</sub> ), 4.97 (2H, d of m, =CH <sub>2</sub> ), 5.94 (1H, d of d, -CH=), 7.17 (5H, m, ph)
(17)	2PB-Li	-CH <sub>3</sub>	(E)-α	0.77 (9H, s, -CH <sub>3</sub> ), 1.01 (3H, t, -CH <sub>3</sub> ), 2.15 (2H, qui, -CH <sub>2</sub> -), 2.43 (2H, s, -CH <sub>2</sub> -), 5.50 (1H, t, -CH=), 7.13 (5H, m, ph)
(18)	2PB-Li	-CH <sub>3</sub>	γ	0.79 (9H, s, -CH <sub>3</sub> ), 1.44 (3H, s, -CH <sub>3</sub> ), 1.82 (2H, s of d, -CH <sub>2</sub> -), 4.92 (1H, d of d, =CH <sub>2</sub> ), 4.97 (1H, d of d, =CH <sub>2</sub> ), 6.11 (1H, d of d, -CH=), 7.19 (5H, m, ph)

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Table II.  $^1\text{H}$  NMR spectral data of products (continued)

Run No.	Anion	$-E'$	Structure	Data ( $\delta$ )
(19)	1P2B-Li	$-\text{Si}(\text{CH}_3)_3$	(E)- $\alpha$	0.12 (9H, s, $-\text{CH}_3$ ), 1.83 (3H, d of m, $-\text{CH}_3$ ), 2.92 (1H, d, $-\dot{\text{C}}\text{H}-$ ), 5.63 (2H, m, $-\text{CH}=\text{CH}-$ ), 7.14 (5H, m, ph)
(20)	1P2B-Li	$-\text{Si}(\text{CH}_3)_3$	(Z)- $\alpha$	0.12 (9H, s, $-\text{CH}_3$ ), 1.83 (3H, d of m, $-\text{CH}_3$ ), 3.42 (1H, d, $-\dot{\text{C}}\text{H}-$ ), 5.67 (2H, m, $-\text{CH}=\text{CH}-$ ), 7.14 (5H, m, ph)
	1P2B-Li	$-\text{Si}(\text{CH}_3)_3$	$\gamma$	0.06 (9H, s, $-\text{CH}_3$ ), 1.21 (3H, d, $-\text{CH}_3$ ), 1.77 (1H, m, $-\text{CH}-$ ), 6.16 (2H, m, $-\text{CH}=\text{CH}-$ ), 7.20 (5H, m, ph)
(21)	1PB-Li	$-\text{Si}(\text{CH}_3)_3$	(E)- $\alpha$	0.09 (9H, s, $-\text{CH}_3$ ), 1.02 (9H, s, $-\text{CH}_3$ ), 2.03 (2H, d, $-\text{CH}_2-$ ), 2.96 (1H, d, $-\dot{\text{C}}\text{H}-$ ), 5.60 (2H, m, $-\text{CH}=\text{CH}-$ ), 7.16 (5H, m, ph)
(22)	1PB-Li	$-\text{Si}(\text{CH}_3)_3$	(Z)- $\alpha$	0.09 (9H, s, $-\text{CH}_3$ ), 1.00 (9H, s, $-\text{CH}_3$ ), 2.03 (2H, d, $-\text{CH}_2-$ ), 3.29 (1H, d, $-\dot{\text{C}}\text{H}-$ ), 5.60 (2H, m, $-\text{CH}=\text{CH}-$ ), 7.16 (5H, m, ph)
(23)	1PB-Li	$-\text{Si}(\text{CH}_3)_3$	$\gamma$	0.08 (9H, s, $-\text{CH}_3$ ), 1.00 (9H, s, $-\text{CH}_3$ ), 1.50 (2H, m, $-\text{CH}_2-$ ), 1.87 (1H, m, $-\dot{\text{C}}\text{H}-$ ), 6.15 (2H, m, $-\text{CH}=\text{CH}-$ ), 7.25 (5H, m, ph)
(24), (25)	3P1B-Li	$-\text{Si}(\text{CH}_3)_3$	(E)- $\alpha$	0.08 (9H, s, $-\text{CH}_3$ ), 1.63 (2H, d, $-\text{CH}_2-$ ), 1.97 (3H, s, $-\text{CH}_3$ ), 5.57 (1H, t of q, $-\text{CH}=\text{CH}-$ ), 7.18 (5H, m, ph)
(26), (27)	2PB-Li	$-\text{Si}(\text{CH}_3)_3$	(E)- $\alpha$	0.10 (9H, s, $-\text{CH}_3$ ), 0.91 (9H, s, $-\text{CH}_3$ ), 1.61 (2H, d, $-\text{CH}_2-$ ), 2.46 (2H, s, $-\text{CH}_2-$ ), 5.56 (1H, t, $=\text{CH}-$ ), 7.30 (5H, m, ph)

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Table II. <sup>1</sup>H NMR spectral data of products (continued)

Run No.	Anion	-E'	Structure	Data (δ)
(28)	1P2B-Li	-Sn(CH <sub>3</sub> ) <sub>3</sub>	(E)-α	0.29 (9H, s, -CH <sub>3</sub> ), 1.13 (3H, d, -CH <sub>3</sub> ), 3.56 (1H, d, -CH-), 6.00 (2H, m, -CH=CH-), 7.20 (5H, m, ph)
(29)	1P2B-Li	-Sn(CH <sub>3</sub> ) <sub>3</sub>	(Z)-α	0.29 (9H, s, -CH <sub>3</sub> ), 1.13 (3H, d, -CH <sub>3</sub> ), 3.92 (1H, d, -CH-), 6.00 (2H, m, -CH=CH-), 7.20 (5H, m, ph)
	1P2B-Li	-Sn(CH <sub>3</sub> ) <sub>3</sub>	γ	0.27 (9H, s, -CH <sub>3</sub> ), 1.53 (3H, d, -CH <sub>3</sub> ), 2.40 (1H, qui, -CH-), 5.40 (2H, m, -CH=CH-), 7.20 (5H, m, ph)
(30)	1PB-Li	-Sn(CH <sub>3</sub> ) <sub>3</sub>	(E)-α	0.26 (9H, s, -CH <sub>3</sub> ), 1.13 (9H, s, -CH <sub>3</sub> ), 2.16 (2H, d, -CH <sub>2</sub> -), 2.60 (1H, d, -CH-), 6.00 (2H, m, -CH=CH-), 7.20 (5H, m, ph)
(31)	1PB-Li	-Sn(CH <sub>3</sub> ) <sub>3</sub>	(Z)-α	0.25 (9H, s, -CH <sub>3</sub> ), 1.15 (9H, s, -CH <sub>3</sub> ), 2.16 (2H, d, -CH <sub>2</sub> -), 2.92 (1H, d, -CH-), 6.00 (2H, m, -CH=CH-), 7.20 (5H, m, ph)
(32)	1PB-Li	-Sn(CH <sub>3</sub> ) <sub>3</sub>	γ	0.35 (9H, s, -CH <sub>3</sub> ), 0.90 (9H, s, -CH <sub>3</sub> ), 1.49 (2H, m, -CH <sub>2</sub> -), 1.91 (1H, m, -CH-), 6.23 (2H, m, -CH=CH-), 7.21 (5H, m, ph)
(33), (34)	3P1B-Li	-Sn(CH <sub>3</sub> ) <sub>3</sub>	(E)-α	0.28 (9H, s, -CH <sub>3</sub> ), 2.01 (2H, d, -CH <sub>2</sub> -), 2.08 (3H, s, -CH <sub>3</sub> ), 6.17 (1H, t, -CH=), 7.14 (5H, m, ph)
(35)	2PB-Li	-Sn(CH <sub>3</sub> ) <sub>3</sub>	(E)-α	0.27 (9H, s, -CH <sub>3</sub> ), 0.96 (9H, s, -CH <sub>3</sub> ), 2.04 (2H, d, -CH <sub>2</sub> -), 2.56 (2H, s, -CH <sub>2</sub> -), 5.91 (1H, t, -CH=), 7.26 (5H, m, ph)
(36)	2PB-Li	-Sn(CH <sub>3</sub> ) <sub>3</sub>	(Z)-α	0.19 (9H, s, -CH <sub>3</sub> ), 0.91 (9H, s, -CH <sub>3</sub> ), 1.89 (2H, d, -CH <sub>2</sub> -), 2.45 (2H, s, -CH <sub>2</sub> -), 5.91 (1H, t, -CH=), 7.26 (5H, m, ph)

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Table II.  $^1\text{H}$  NMR spectral data of products (continued)

Run No.	Antion	$-E'$	Structure	Data ( $\delta$ )
	2PB-Li	$-\text{Sn}(\text{CH}_3)_3$	$\gamma$	0.16 (9H, s, $-\text{CH}_3$ ), 1.15 (9H, s, $-\text{CH}_3$ ), 2.11 (2H, s, $-\text{CH}_2-$ ), 5.60 (2H, m, $=\text{CH}_2$ ), 5.88 (1H, m, $-\text{CH}=\text{}$ ), 7.24 (5H, m, ph)
(37)	1P2B-Li	$-\text{C}(\text{CH}_3)_2\text{OH}$	(E)- $\alpha$	1.04 (3H, s, $-\text{CH}_3$ ), 1.10 (3H, s, $-\text{CH}_3$ ), 1.57 (3H, d, $-\text{CH}_3$ ), 3.08 (1H, d, $-\text{CH}-$ ), 5.64 (2H, m, $-\text{CH}=\text{CH}-$ ), 7.14 (5H, m, ph)
(38)	1P2B-Li	$-\text{C}(\text{CH}_3)_2\text{OH}$	(Z)- $\alpha$	1.04 (3H, s, $-\text{CH}_3$ ), 1.10 (3H, s, $-\text{CH}_3$ ), 1.48 (3H, d, $-\text{CH}_3$ ), 3.48 (1H, d, $-\text{CH}-$ ), 5.64 (2H, m, $-\text{CH}=\text{CH}-$ ), 7.14 (5H, m, ph)
	1P2B-Li	$-\text{C}(\text{CH}_3)_2\text{OH}$	$\gamma$	1.12 (3H, d, $-\text{CH}_3$ ), 1.15 (6H, s, $-\text{CH}_3$ ), 2.26 (1H, qui, $-\text{CH}-$ ), 6.07 (1H, d of d, $=\text{CH}-$ ), 6.17 (1H, d, $=\text{CH}-$ ), 7.22 (5H, m, ph)
(39)	1PB-Li	$-\text{C}(\text{CH}_3)_2\text{OH}$	(E)- $\alpha$	0.85 (9H, s, $-\text{CH}_3$ ), 1.07 (6H, s, $-\text{CH}_3$ ), 1.90 (2H, d, $-\text{CH}_2-$ ), 3.14 (1H, d, $-\text{CH}-$ ), 5.74 (2H, m, $-\text{CH}=\text{CH}-$ ), 7.16 (5H, m, ph)
(40)	1PB-Li	$-\text{C}(\text{CH}_3)_2\text{OH}$	(Z)- $\alpha$	0.80 (9H, s, $-\text{CH}_3$ ), 1.12 (6H, s, $-\text{CH}_3$ ), 1.90 (2H, d, $-\text{CH}_2-$ ), 3.48 (1H, d, $-\text{CH}-$ ), 5.44 (2H, m, $-\text{CH}=\text{CH}-$ ), 7.16 (5H, m, ph)
(41)	1PB-Li	$-\text{C}(\text{CH}_3)_2\text{OH}$	$\gamma$	0.92 (9H, s, $-\text{CH}_3$ ), 1.11 (3H, s, $-\text{CH}_3$ ), 1.15 (3H, s, $-\text{CH}_3$ ), 1.52 (2H, m, $-\text{CH}_2-$ ), 2.20 (1H, m, $-\text{CH}-$ ), 5.94 (1H, d of d, $-\text{CH}=\text{}$ ), 6.22 (1H, d, $-\text{CH}=\text{}$ ), 7.22 (5H, m, ph)
(42), (43)	3P1B-Li	$-\text{C}(\text{CH}_3)_2\text{OH}$	$\gamma$	1.03 (3H, s, $-\text{CH}_3$ ), 1.07 (3H, s, $-\text{CH}_3$ ), 1.44 (3H, s, $-\text{CH}_3$ ), 5.03 (1H, d of d, $=\text{CH}_2$ ), 5.14 (1H, d of d, $=\text{CH}_2$ ), 6.63 (1H, d of d, $-\text{CH}=\text{}$ ), 7.20 (5H, m, ph)
(44), (46)	2PB-Li	$-\text{C}(\text{CH}_3)_2\text{OH}$	(E)- $\alpha$	0.76 (9H, s, $-\text{CH}_3$ ), 1.16 (6H, s, $-\text{CH}_3$ ), 2.28 (2H, d, $-\text{CH}_2-$ ), 2.42 (2H, s, $-\text{CH}_2-$ ), 5.64 (1H, t, $=\text{CH}-$ ), 7.20 (5H, m, ph)

continued on next page



Table II. <sup>1</sup>H NMR spectral data of products (continued)

Run No.	Anion	-E'	Structure	Data (δ)
(47)	1P2B-Li	-(CH <sub>2</sub> ) <sub>2</sub> OH	(E)-α	1.66 (3H, d, -CH <sub>3</sub> ), 1.79 (2H, q, -CH <sub>2</sub> -), 3.41 (2H, t, -CH <sub>2</sub> -), 3.36 (1H, q, -CH-), 5.44 (2H, m, -CH=CH-), 7.11 (5H, m, ph)
	1P2B-Li	-(CH <sub>2</sub> ) <sub>2</sub> OH	(Z)-α	1.64 (3H, d, -CH <sub>3</sub> ), 1.76 (2H, q, -CH <sub>2</sub> -), 3.41 (2H, q, -CH <sub>2</sub> -), 3.74 (1H, q, -CH-), 5.44 (2H, m, -CH=CH-), 7.11 (5H, m, ph)
(48), (49)	1PB-Li	-(CH <sub>2</sub> ) <sub>2</sub> OH	(E)-α	0.86 (9H, s, -CH <sub>3</sub> ), 1.88 (4H, m, -CH <sub>2</sub> -), 3.38 (1H, m, -CH-), 3.44 (2H, t, -CH <sub>2</sub> -), 5.47 (2H, m, -CH=CH-), 7.08 (5H, m, ph)
	3P1B-Li	-(CH <sub>2</sub> ) <sub>2</sub> OH	γ	1.34 (3H, s, -CH <sub>3</sub> ), 1.94 (2H, t of d, -CH <sub>2</sub> -), 3.39 (2H, t, -CH <sub>2</sub> -), 4.98 (1H, d of d, =CH <sub>2</sub> ), 5.04 (1H, d of d, =CH <sub>2</sub> ), 4.95 (1H, d of d, -CH=), 7.12 (5H, m, ph)
(51)	2PB-Li	-(CH <sub>2</sub> ) <sub>2</sub> OH	(E)-α	0.68 (9H, s, -CH <sub>3</sub> ), 1.18 (2H, s, -CH <sub>2</sub> -), 1.30 (2H, m, -CH <sub>2</sub> -), 1.97 (2H, m, -CH <sub>2</sub> -), 3.28 (2H, t, -CH <sub>2</sub> -), 5.40 (1H, t, =CH-), 7.00 (5H, m, ph)
	2PB-Li	-(CH <sub>2</sub> ) <sub>2</sub> OH	(Z)-α	0.87 (9H, s, -CH <sub>3</sub> ), 1.20 (2H, s, -CH <sub>2</sub> -), 1.35 (2H, m, -CH <sub>2</sub> -), 2.01 (2H, m, -CH <sub>2</sub> -), 3.37 (2H, t, -CH <sub>2</sub> -), 5.55 (1H, t, =CH-), 7.00 (5H, m, ph)
	2PB-Li	-(CH <sub>2</sub> ) <sub>2</sub> OH	γ	0.76 (9H, s, -CH <sub>3</sub> ), 1.82 (2H, s of q, -CH <sub>2</sub> -), 2.10 (2H, m, -CH <sub>2</sub> -), 3.29 (2H, m, -CH <sub>2</sub> -), 5.08 (1H, d of d, =CH <sub>2</sub> ), 5.12 (1H, d of d, =CH <sub>2</sub> ), 6.09 (1H, d of d, =CH-), 7.21 (5H, m, ph)

<sup>a</sup> TMS as internal standard: s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet.

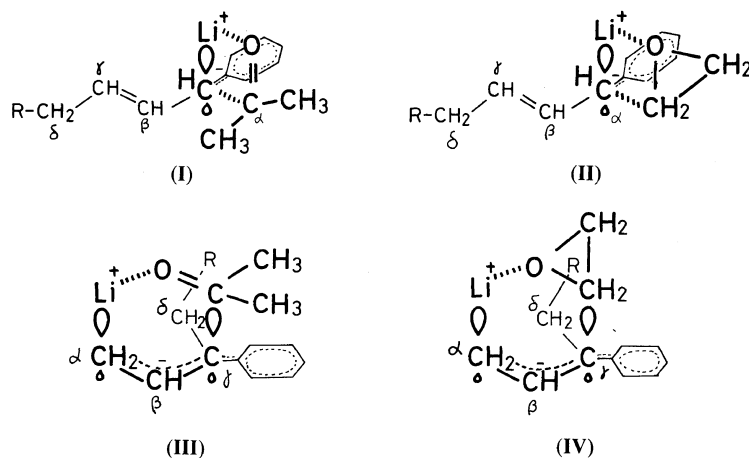
expected from the negative charge distribution.

Runs 1 to 9 in Table I show product distributions in protonation reactions with methanol. The ratios of the  $\alpha$ -products, combined yield of (*E*)- $\alpha$  and (*Z*)- $\alpha$ , to the  $\gamma$ -products are nearly the same as those for the products from 1P2B-Li and those from 3P1B-Li (in both R=H as shown in Scheme III) where the negative charge distributions of the respective anions are quite different from each other as mentioned above. The ratios of the  $\alpha$ -products to  $\gamma$ -products are also comparable to those of the products from 1PB-Li and those from 2PB-Li (in both R=*t*-Bu) whose negative charge distributions are also quite different. Thus, it may safely be said that product distributions with protonation are not affected by the negative charge anion distributions, but slightly affected by the steric effect of the R groups of these anions.

Runs 10 to 36 in Table I show product distributions in substitution reactions with MeI, TMS-Cl, and TMT-Cl. In the reactions of the  $\pi$ -benzyl type anions with MeI (runs 10 to 14), the amount of  $\alpha$ -product was more than 96%. This means that the reactions occurred at the more sterically hindered  $\alpha$ -position with high regioselectivity. As the electron rich  $\alpha$ -position was attacked, the negative charge distribution rather than the steric effect is considered to determine the reaction center in these cases. However, when more bulky substrates (TMS-Cl and TMT-Cl) are used, the amount of  $\gamma$ -product increase as compared with the corresponding products formed by the reaction with MeI because of the steric hindrance between the phenyl substituent at the  $\alpha$ -position and the reactants (runs 19 to 23 and runs 28 to 32). In the reactions of 1PB-Li with TMS-Cl and TMT-Cl, the amount of  $\gamma$ -product did not exceed 20% (runs 21 to 23 and runs 30 to 32). The bulkiness of the R (*t*-Butyl) group also participates in these reactions. On the other hand, when the  $\pi$ -allylphenyl type anions react with MeI (runs 15 to 18), the  $\gamma$ -product increases, compared with the  $\gamma$ -product from the  $\pi$ -benzyl type anions. The  $\gamma$ -positions of the  $\pi$ -allylphenyl type anions are more sterically hindered than those of the  $\pi$ -benzyl type anions. In the  $\pi$ -allylphenyl type anions, however, the negative charge delocalizes throughout the  $\pi$ -allyl system and this may increase the reactivity of the  $\gamma$ -position. The steric effect of the R group could be observed in the reactions of 2PB-Li with MeI (runs 17 and 18) where the amount of the  $\gamma$ -product

decreased compared with 3P1B-Li (runs 15 and 16). When more bulky substrates, TMS-Cl and TMT-Cl, are reacted, no  $\gamma$ -product could be obtained because of the steric hindrance between the phenyl substituent and the substrates (runs 24 to 27, 33 and 34). Exceptional results were obtained in the reactions of 2PB-Li with TMT-Cl (runs 35 and 36) where considerable amounts of the  $\gamma$ -product were formed. The reason for this behavior is not understood. In this manner, the product distribution is controlled by the negative charge distribution when the effective bulkiness of the reactant is small. On the other hand, the steric effect may be operative on product distributions when bulky substrates are reacted. Runs 37 to 51 in Table I show the results of reactions with acetone or EO. In general, allylic organometallic compounds react with these oxygen-containing substrates predominantly to give the  $\gamma$ -product.<sup>20</sup> For these reactions six-center cyclic ( $S_Ei'$ ) or non-cyclic ( $S_E2'$ ) mechanisms have been proposed.<sup>21-24</sup> In the present study,  $\pi$ -benzyl type anions were reacted with acetone (runs 37 to 41) to give 55–86%  $\alpha$ -products in spite of the phenyl substituent at the  $\alpha$ -position. These results contrast with the fact that neopentylallyllithium gives 22–45%  $\alpha$ -products in reactions with ketones which encounter less steric hindrance.<sup>2,4</sup> In the reactions of the  $\pi$ -benzyl type anions with EO only  $\alpha$ -products are formed (runs 47 to 49). Consequently  $\pi$ -benzyl type anions are liable to form  $\alpha$ -products in reactions with acetone or EO. On the other hand, except for the reactions of 2PB-Li with acetone (runs 44 and 46),  $\pi$ -allylphenyl anions react with either acetone (runs 42 and 43) or EO (runs 50 and 51) to give predominantly  $\gamma$ -products. In the reactions of 3P1B-Li with acetone or EO,  $\gamma$ -products are formed exclusively (runs 42, 43, and 50). In the reactions of 2PB-Li with acetone (runs 44 and 46) the  $\gamma$ -product, which is the main product in the former cases, could not be obtained due to the steric hindrance of the R (*t*-Bu) group. When the *n*-Bu group is used instead of *t*-Bu as R, that is, as a one-to-one adduct of *n*-BuLi and 2PB, the steric hindrance of the R group toward acetone is reduced and the  $\gamma$ -product is obtained in a 47% yield (run 45). In this manner, the  $\pi$ -allylphenyl type anions are liable to give  $\gamma$ -products in the reaction with acetone or EO. These differences in the behavior of  $\pi$ -benzyl and  $\pi$ -allylphenyl type anions are attributed to the difference in the transition states in the

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**Figure 1.** Transition states in the reactions of substituted phenylallyllithiums with acetone or ethylene oxide.

reactions. When  $\pi$ -benzyl type anions react with acetone or EO, the four center transition states as shown (I) and (II) in Figure 1 can be assumed ( $S_{Ei}$ ), since the negative charge is located at the  $\alpha$ -carbon and phenyl ring. Therefore, the reactions take place at the  $\alpha$ -carbon to give  $\alpha$ -products. Since the steric hindrance against the phenyl ring is larger in (I) than in (II), the transition state of (I) gives a considerable amount of  $\gamma$ -product (14–45%, runs 37 to 41), whereas that of (II) gives the  $\alpha$ -product exclusively (runs 47 to 49). In contrast to this, in the reactions of  $\pi$ -allylphenyl type anions, the transition states are regarded as the six-center cyclic structures as shown in (III) and (IV) in Figure 1, since the negative charge delocalizes throughout the  $\pi$ -allyl system and the phenyl ring. These transition states lead to  $\gamma$ -products ( $S_{Ei'}$ ). However, in the reaction of 2PB-Li with acetone (R = *t*-Bu in (III) in Figure 1), a transition state such as (III) cannot be formed because of the steric repulsion of the *t*-Butyl group toward acetone. When R changes to *n*-Butyl, a considerable amount of  $\gamma$ -product is obtained *via* a transition state such as (III) due to the reduction of the steric repulsion (run 45). This steric effect can slightly be observed in the reaction of 2PB-Li with EO where a 22%  $\alpha$ -product is obtained (run 51). However, in the reaction of 3P1B-Li with EO, no  $\alpha$ -product is formed (run 50). In this manner, in reactions with acetone or EO, the product distribution can be explained on basis of the steric requirement in the transition

state.

The configuration of a double bond of an  $\alpha$ -product cannot be explained simply. As shown in Scheme I, 1P2B-Li has (*E*)- and (*Z*)-isomer in 1 to 3 ratio. However, in general,  $\alpha$ -products obtained from 1P2B-Li contain a considerable (*E*)-configurations. On the other hand, 1PB-Li gives more (*E*)-isomer than 1P2B-Li. Thus, in the  $\alpha$ -product obtained from 1PB-Li, the (*E*)-configuration was generally found as the preferable isomer compared to the  $\alpha$ -product obtained from 1P2B-Li. Furthermore, as shown in Scheme II, 3P1B-Li and 2PB-Li contain only (*E*)-configurations. Therefore,  $\alpha$ -products obtained from these anions have predominantly (*E*)-configuration.

Thus, the reactivities of the model anions are determined by various factor, such as negative charge distribution, steric effect, and the nature of the transition state according to the type of reaction. These results could not be obtained in the characterization of the living chain ends by means of the NMR spectroscopic method used in previous studies.<sup>18,19</sup> In the polymerization of 1PB and 2PB, since these monomers contain no oxygen atoms which can interact with counter cations, the steric requirement in the transition state is not a key step, in contrast to the reaction with acetone and EO. Poly(1PB) prepared by the anionic polymerization has mainly a 1,4 structure (76–92%).<sup>16</sup> Therefore, taking the negative charge distribution into ac-

count, the microstructures are considered to be determined by the negative charge distribution as in the case of the reaction with methanol and MeI. On the other hand, poly(2PB) obtained by the anionic polymerization also has a 1,4 structure (67—92%)<sup>17</sup> although the chain end is the  $\pi$ -allylphenyl type<sup>19</sup> which generally leads to an in-chain vinyl unit. The present study indicates that the reaction is governed by the steric effect when the substrates are bulky. In the anionic polymerization of 2PB the microstructure is considered to be determined by the steric effect as observed in the reaction with TMS-Cl and TMT-Cl, since the monomer (2PB) is a rather bulky substrate, and the 1,4 unit predominates.

## REFERENCES

1. W. H. Glaze, J. E. Hanicak, M. L. Moore, and J. Chaudhuri, *J. Organometal. Chem.*, **44**, 39 (1972).
2. W. H. Glaze, J. E. Hanicak, D. J. Berry, and D. P. Duncan, *J. Organometal. Chem.*, **44**, 49 (1972).
3. W. H. Glaze, J. E. Hanicak, J. Chandhuri, M. L. Moore, and D. P. Duncan, *J. Organometal. Chem.*, **51**, 13 (1973).
4. W. H. Glaze, D. J. Berry, and D. P. Duncan, *J. Organometal. Chem.*, **52**, 233 (1973).
5. J. Sledz, F. Schuë, B. K. Kaempf, and S. Libs, *Eur. Polym. J.*, **10**, 1207 (1974).
6. S. Brownstein, S. Bywater, and D. J. Worsfold, *Macromolecules*, **6**, 715 (1973).
7. S. Bywater, D. J. Worsfold, and G. Hollingsworth, *Macromolecules*, **5**, 389 (1972).
8. F. Schuë, D. J. Worthfold, and S. Bywater, *Macromolecules*, **3**, 509 (1970).
9. M. Morton, R. D. Sanderson, R. Sakata, and L. A. Falvo, *Macromolecules*, **6**, 186 (1973).
10. M. Morton, R. D. Sanderson, and R. Sakata, *J. Polym. Sci., Polym. Lett. Ed.*, **9**, 61 (1971).
11. M. Morton, R. D. Sanderson, and R. Sakata, *Macromolecules*, **6**, 181 (1973).
12. R. Salle and J. Gole, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 1199 (1977).
13. S. Bywater and D. J. Worsfold, *J. Organometal. Chem.*, **159**, 229 (1978).
14. S. Bywater, P. Lachance, and D. J. Worsfold, *J. Phys. Chem.*, **79**, 2148 (1978).
15. P. Miginiac, *Bull. Soc. Chim. Fr.*, 1077 (1970).
16. T. Suzuki, Y. Tsuji, and Y. Takegami, *Macromolecules*, **11**, 639 (1978).
17. T. Suzuki, Y. Tsuji, Y. Takegami, and H. J. Harwood, *Macromolecules*, **12**, 234 (1979).
18. T. Suzuki, Y. Tsuji, Y. Watanabe, and Y. Takegami, *Polym. J.*, **11**, 651 (1979).
19. T. Suzuki, Y. Tsuji, Y. Watanabe, and Y. Takegami, *Polym. J.*, **11**, 937 (1979).
20. G. Courtois and L. Miginiac, *J. Organometal. Chem.*, **69**, 1 (1974).
21. M. Gaudemar, *Bull. Soc. Chim. Fr.*, 974 (1962).
22. L. Miginiac, Ph. Miginiac, and Ch. Prevost, *Bull. Soc. Chim. Fr.*, 3560 (1965).
23. H. Felkin and C. Frajerman, *Tetrahedron Lett.*, 1045 (1970).
24. M. Cherest, H. Felkin, and C. Frajerman, *Tetrahedron Lett.*, 379 (1971).