Characterization of Living Anion Chain End of Oligomeric 1-Phenyl-1,3-butadienyllithium

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ABSTRACT: 25.0 MHz ^{13}C and 220 MHz ^1H NMR investigations were carried out on living anion chain ends of oligomeric 1-phenyl-1,3-butadiene (1PB) in order to reveal the anionic polymerization mechanism. The propagating species of 1PB can be concluded to be the 4,1 anion. Lithiated 1-phenyl-2-butene (1P2B) was employed as a model anion of the propagating species of 1PB. A negative charge on the chain end delocalizes at α -carbon and phenyl ring, and delocalization to γ -carbon is small regardless of the polymerization solvent. Therefore, the monomer attacks α -carbon and consequently the in-chain 1,4 unit is predominant even in THF solvent. These behaviors are quite different from those observed in oligomeric butadiene and/or isoprene chain ends. In THF the living chain end is regarded as only *trans*-4,1, whereas in hydrocarbon media it is an almost equal mixture of *trans*- and *cis*-4,1 structures.

KEY WORDS 1-Phenylbutadiene / Anionic Polymerization / Living Oligomer / ^{13}C NMR / ^1H NMR / 1-Phenyl-2-butene / Metalation / Charge Distribution / Polymerization Mechanism /

We have recently elucidated microstructures of poly(1-phenyl-1,3-butadiene) [poly(1PB)] and poly(2-phenyl-1,3-butadiene) [poly(2PB)] prepared by anionic initiators.^{1,2} These results lead to the conclusion that 1PB and 2PB behave in quite different ways from butadiene (B) and isoprene (I) in anionic polymerization.

A large number of investigations have been carried out on the adducts of alkylolithium and B or I, using NMR spectroscopic results to account for the polymerization mechanism.³⁻¹⁴ These results clearly revealed the structures of the living chain ends and suggested the mechanism of the polymerizations. Recently Bywater *et al.* have studied benzylic alkali metal compounds by ^{13}C NMR spectroscopy in order to discuss the charge distribution of benzylic anions corresponding to the propagating species of styrene derivatives in anionic polymerization.¹⁵ On the other hand, several NMR studies have been reported on phenyl allyl anions.^{16,17} Living anion chain ends of polymeric and oligomeric 1PB are considered to be quite similar to the phenyl allyl anion.¹⁸

In this study we have investigated ^{13}C and ^1H NMR spectra of living anions of oligomeric 1PB under various conditions. It is of interest to see how the charge distributes in the anion chain end (covalent or ionic) and how the microstructure of poly(1PB) is controlled in a homogeneous polymerization system.

EXPERIMENTAL

Materials

trans-1-Phenyl-1,3-butadiene (1PB) was synthesized by the method described in a previous paper¹.

1-Phenyl-2-butene (1P2B) was obtained from Tokyo Kasei Co. and purified by distillation over LiAlH_4 . The 1P2B thus obtained was the pure *trans* isomer, according to its IR and ^{13}C NMR spectra.

t-BuLi was prepared from *t*-butyl chloride and lithium dispersion (Alfa) in pentane by the method reported by Smith.¹⁹ *t*-BuLi was used as benzene- d_6 solution. *t*-BuLi benzene- d_6 solution was prepared by displacing pentane with benzene- d_6 under high vacuum.

Solvents were carefully purified by distillation in the presence of suitable drying reagents.

Oligomerization and Metalation Procedure

Oligomerization of 1PB and metalation of 1P2B were carried out in NMR sample tubes *in situ* under a pure argon atmosphere with *t*-BuLi at 5°C. Concentrations of the anion chain end of oligomeric 1PB were 0.06–0.30 mol dm⁻³.

¹H and ¹³C NMR Spectra

¹H NMR spectra were recorded on a Varian HR 220 (220 MHz), and ¹³C NMR spectra were measured with a JEOL JNM FX 100 spectrometer (25.0 MHz). In some cases THF was used in the place of THF-*d*₈ to eliminate the appearance of multiplet solvent peaks due to ¹³C–D coupling. Very strong absorptions of solvent peaks compared with sample signals were carefully recorded within the dynamic range of the AD converter of the instrument (12 bits). Typical conditions for the ¹³C measurements were: spectral width, 5 kHz; acquisition time, 0.812s; data points, 8192; pulse width, 7 μs (42°); pulse repetition, 2.0s; number of transients (80 ~ 128) × 12.

RESULTS AND DISCUSSION

Propagating Species in Anionic Polymerization of 1PB

The microstructure of poly(1PB) reported in a previous paper¹ is summarized in Table I. Poly(1PB) has predominantly a *trans*-1, 4 structure even if the polymerization was carried out in THF. *Cis*-1, 4 and 3, 4 units increase with a decrease in the polarity of the polymerization solvent. This behavior is quite different from that of B and I in the anionic polymerization. In the polymerization of those monomers the presence of polar solvents increases

the vinyl unit drastically.²⁰ The origin of this difference in the behavior will be traced later.

The propagating species of 1PB in the anionic polymerization can be concluded to be the 4,1 anion (I), not the 1,4 anion (II), since the resulting polymers

4,1 anion (I)

1,4 anion (II)

contain only 1,4 and 3,4 units. The presence of the 4,1 propagating anion is supported by the result that the one to one adduct of *t*-BuLi and 1PB terminated with methanol consists of *trans*-4,1 *cis*-4,1, and 4,3 adducts as shown below.

trans-4,1 65%

cis-4,1 23%

4,3 12%

The product distribution of the one to one adduct was estimated by gas chromatography and their sum was normalized to 100%. The amount of one to one adduct in the oligomeric species can be estimated as 65% of all the adducts from gel-permeation

Table I. Microstructure of poly(1-phenylbutadiene)^a

No.	Initiator	Solvent	Polymerization		Conversion %	Structure/%		
			Temp/°C	Time/h		<i>trans</i> -1,4	<i>cis</i> -1,4	3,4
13	<i>t</i> -BuLi	THF	-78	4.0	100	79	11	10
12	<i>t</i> -BuLi	Benzene	20	3.5	100	66	26	8
11	<i>t</i> -BuLi	Toluene	20	3.5	100	56	28	16
14	<i>t</i> -BuLi	Hexane	20	4.0	95	49	28	23

^a This is a summary of Table II in the previous paper (ref 1).

chromatography.

Characterization of Metalated 1P2B

As it is difficult to obtain a pure n' mer chain end, a model compound of the chain end was employed for the NMR investigations. The model anion for the 4,1 propagating anion in the polymerization of 1PB is prepared by metalating 1P2B with t -BuLi as shown in Scheme I. The reaction did not proceed in pure hydrocarbon solvent.

Figure 1 shows the 25.0 MHz ^{13}C NMR spectra of lithiated 1P2B (III) in THF. Chemical shifts of the carbon resonances are listed in Table II. Small resonances at 17.8 and 39.0 ppm show the presence of a small quantity of unreacted 1P2B. ^{13}C chemical shifts and ^{13}C -H coupling constants of phenyllithium compounds were first reported by van Dongen *et al.*¹⁶ The assignments were carried out by comparing the observed spectra with those reported in the literature, with the aid of the off-resonance spectra. In Figure 1 *ortho* and *para* carbon resonances of the phenyl ring appear at higher field than

Figure 1. 25.0 MHz ^{13}C NMR spectra of lithiated 1P2B (III) at various temperatures: (A) 0°C , (B) -45°C , and (C) 24°C ; 1P2B 2.37 mmol, THF 1.5 cm^3 , and 3.00 mol dm^{-3} t -BuLi benzene- d_6 solution, 0.87 cm^3 .

ordinary phenyl carbon resonances such as toluene. The high-field shift of the *para* carbon resonance is particularly noteworthy. This result indicates that the negative charge delocalizes to the phenyl ring and that the electron density increases especially at *para* position. The result is almost identical to those reported in phenyllithium,¹⁷ 1,3,3-trimethyl-1-phenylbutyllithium,²¹ 1,1-diphenylhexyllithium,²² 1,1-diphenylbutyllithium,²³ and 1,3-diphenylallyllithium.²⁴ At 24°C the *ortho* carbon resonance at 115.0 ppm is much broader than the other resonances. Upon cooling, the broader resonance collapses at 0°C , then splits into two sets of peaks (111.4 and 118.6 ppm) at -45°C . This phenomenon is explained by the presence of the rotational barrier of the α -carbon-phenyl partial double bond. At -45°C the rotation about this α -carbon-phenyl bond is slow enough to distinguish two *ortho* carbons which are magnetically non-equivalent. By simulating the *ortho* carbon resonance at various temperatures using the equation proposed,²⁵ the activation parameters $\Delta H^\ddagger = 9.5 \text{ kcal mol}^{-1}$ (39.7 kJ mol^{-1}) and $\Delta S^\ddagger = -12 \text{ cal mol}^{-1} \text{ deg}^{-1}$ ($-50.2 \text{ J K}^{-1} \text{ mol}^{-1}$) could be obtained for the rotation.

Bywater *et al.*¹⁴ and Glaze *et al.*^{3,5} studied 5,5-dimethyl-2-hexenyllithium (IV), produced by 1,4 addition of t -BuLi and B, using ^1H and ^{13}C NMR spectrometry. The ^{13}C and ^1H NMR data of (IV) previously reported are summarized in Table III. As is well known, (IV) exists as covalent species (σ -allyl) in hydrocarbon solvents. On the other hand, in the presence of a donating solvent, the lithium cation was strongly coordinated by the solvent, and charge would thus be transferred to the organic moiety of (IV): ionic species (π -allyl). The increase in charge would be expected to concentrate on γ - and α -carbon atoms.

The α -carbon resonance of lithiated 1P2B (III) appears at 70.2 ppm. This value is 40–50 ppm lower field than that for the α -carbon of (IV), indicating its substantial sp^2 hybridization. The same results were obtained in other phenyl alkali metal salts.^{15,17,21} The γ -carbon resonance of lithiated 1P2B (III) appears at lower field than that of π -allyl (IV), showing smaller delocalization of charge to the γ -carbon.

Many experimental and theoretical results indicate that the ^{13}C chemical shift is an effective measure of the hybridization and charge density on the observing carbon. O'Brien proposed eq 1 for

Table II. ^{13}C chemical shift^a and π -electron density for lithiated 1P2B and living oligomeric 1PBLi

Position	Lithiated 1P2B		Living oligomeric 1PBLi			
			δ in ppm		ρ^c	
	δ in ppm	ρ^c	In THF	In benzene ^e	In THF	In benzene
α	70.2	1.40	68.0	69.0	1.42	1.41
β	130.6 ^b	1.02	— ^d	—	—	—
	133.5	1.00				
γ	83.3	1.32	89.8	95.5	1.28	1.24
	86.4	1.30				
δ	11.9	—	— ^d	—	—	—
	18.5	—				
arom. C-1	148.4	0.90	148.8	147.7	0.90	0.91
	148.7	0.90				
<i>ortho</i>	115.0	1.12	115.6	114.3	1.11	1.12
<i>meta</i>	128.5	1.03	—	—	—	—
<i>para</i>	106.7	1.17	107.4	106.5	1.17	1.17
	106.4					

^a Shifts are recorded in ppm downfield from TMS using the following solvent peaks as standards: C_6D_6 128.4 and THF 67.0.

^b A set of data shows *cis* isomer above, and *trans* isomer below.

^c π -electron density calculated with eq 1.

^d Cannot be identified as distinct resonances.

^e In benzene- d_6 .

the linear ^{13}C shift (δ)– π -electron density (ρ) relationship.²⁶

$$\delta = 289.5 - 156.3 \rho \quad (1)$$

π -Electron densities estimated from the ^{13}C chemical shift using eq 1 are listed in Table II.

The resonances of β , γ , δ , arom.C-1, *ortho* (only at -45°C), and *para* carbons consist of two sets of peaks. Generally a carbon flanked by a *cis* olefin double bond appears at higher field than that flanked by a *trans* one.²⁷ Therefore, judging from the intensities of the two resonances the predominant isomer would be the *cis* isomer. In the ^1H NMR spectrum (Figure 2), as will be discussed later, the δ proton resonance appears as two sets of doublet. This shows lithiated 1P2B (III) contains *cis* and *trans* isomers in the ratio of 3:1.*¹ Although the meta-

Figure 2. 220 MHz ^1H NMR spectrum of lithiated 1P2B (III): 1P2B 0.08 mmol, $\text{THF-}d_8$ 0.3 cm^3 , and 1.36 mol dm^{-3} *t*-BuLi benzene- d_6 solution, 0.15 cm^3 .

*¹ H. Kloosterziel reported a *cis*-4,1 tendency for a potassium salt of 1P2B in ref 28.

lation was carried out with pure *trans*-1P2B, the *cis* isomer was obtained. This indicates the configuration of β - γ bond is isomerized through a 4,3 anion as shown in Scheme II. In addition to *cis*-1P2B and *trans*-1P2B, 1-phenyl-1-butene was identified after protonation of lithiated 1P2B (III) with methanol by gas chromatography. The ratio of *cis*-1P2B, *trans*-1P2B, and 1-phenyl-1-butene was 35 : 19 : 46.^{*2} It is surprising that 1-phenyl-1-butene was obtained as a main isomer after the protonation of the anion. However, no carbon resonances assignable to the 4,3 anion could be observed in Figure 1. The resonance effect of the phenyl ring will lead to the 4,1 anion. In the case of living oligomeric B and I, neither 1,2 nor 4,3 anion chain ends could be detected, even in THF medium, by NMR spectroscopies.²⁰

Figure 2 shows the 220 MHz ^1H NMR spectra of lithiated 1P2B (III). The spectra show the same features as were observed in ^{13}C NMR spectra. Phenyl proton resonances show a high-field shift. α -Proton resonances appear as a doublet at considerably lower field (δ 4.1) as compared with the α -proton resonance of (IV). The changes in chemical shifts indicate a substantial amount of charge delocalization into the phenyl ring and the presence of a partial double bond between the α -carbon and phenyl ring. The γ -proton resonance of lithiated 1P2B (III) appears at δ 3.8–4.2 as a complicated multiplet. This value is almost midway between σ - and π -allyl (IV) in *cis* isomer.^{*3} It is difficult to compare the chemical shift of lithiated 1P2B (III) with that of (IV). However, it is safe to say that the delocalization of the negative charge to γ -carbon in lithiated 1P2B (III) is smaller than in π -allyl (IV). The

Scheme II

negative charge of lithiated 1P2B (III) must delocalize at α -carbons and phenyl rings and the delocalization to γ -carbon is small.

Characterization of Living Chain End of Oligomeric 1PB

Unlike the metalation of 1P2B, the oligomerization of 1PB can be carried out in pure hydrocarbon solvents. Figure 3 shows the ^{13}C NMR spectra of the living oligomeric 1PB. Although resonances are broader and more complicated due to in-chain units, they are essentially the same as that of

Figure 3. 25.0 MHz ^{13}C NMR spectra of living oligomeric 1PB at various temperatures: (Aa) 6°C, (Ab) -40°C, and (Ac) 24°C in THF; (Ad) spectrum recorded at 24°C by applying a 180°-5.0s-90°-20s pulse sequence; (B) 24°C in benzene- d_6 . (Aa-c) $\overline{\text{DP}} = 5.8$, (Ad), $\overline{\text{DP}} = 3.6$, and (B) $\overline{\text{DP}} = 6.0$.

^{*2} Although this result is inconsistent with the microstructure of poly(1PB) obtained in THF, the product distributions after protonation of phenyllallyl anions are quite sensitive to the structures of organic moieties.^{29,30} Lithiated 1P2B, therefore, cannot strictly be a model compound of the propagating chain end of 1PB. However, comparing the results obtained here and those in the literature,¹⁶ the ^{13}C chemical-shift data obtained for lithiated 1P2B can be safely used to understand the ^{13}C NMR spectra of the living oligomeric 1PB. The larger amount of 1-phenyl-1-butene is suggested by the higher-field shift of γ -proton and carbon resonances of the lithiated 1P2B, compared with those of the oligomeric 1PB anion.

^{*3} Lithiated 1P2B(III) contains predominantly *cis* isomer. Therefore, we adopt the results of *cis*-(IV) for the comparison.

lithiated 1P2B (III) in Figure 1. Chemical shifts of the resonances and π -electron densities estimated by eq 1 are listed in Table II. The spectrum shows a high-field shift for the *ortho* and *para* carbons, and a down-field shift for the aromatic C-1 carbon, as compared with the corresponding shifts of 1P2B. Similar chemical-shift trends were seen for lithiated 1P2B (III). The changes in chemical shifts of the aromatic carbons indicate a substantial amount of charge delocalization into the phenyl ring. As observed in the ^{13}C NMR spectra of lithiated 1P2B (III), the shape of the *ortho* carbon resonance depends on the sample temperature. At 24°C the *ortho* carbon resonance is a singlet. Upon cooling, the singlet collapses at 6°C, then splits into two distinct peaks at -40°C. This is also explained by the decrease in the rotation of the α -carbon-phenyl partial double bond. The activating parameters $\Delta H^\ddagger = 7.7 \text{ kcal mol}^{-1}$ (32.2 kJ mol^{-1}), $\Delta S^\ddagger = -19 \text{ cal mol}^{-1} \text{ deg}^{-1}$ ($-79.5 \text{ J K}^{-1} \text{ mol}^{-1}$) are obtained for the rotation. The α -carbon resonance

appears at 69.0 ppm in benzene- d_6 (Figure 3B). However, it seems to be overlapped with a strong solvent resonance in THF (Figure 3Ac). When a 180°-5.0 s—90°-20 s pulse sequence was employed to this sample, intensities of the solvent resonances decreased and the α -carbon resonance appeared at 68.0 ppm, as shown in Figure 3Ad. These α -carbons appear at considerably lower field than that of (IV). In addition, the $J_{^{13}\text{C}-^1\text{H}}$ of the α -carbon in benzene- d_6 is 149 Hz. The substantial sp^2 hybridization of the α -carbon is established by these results. The γ -carbon resonances appear at lower field than that of π -allyl (IV), showing a limited distribution of the negative charge at γ position. The γ -carbon resonance appears at a slightly higher field in THF than in benzene- d_6 . The negative charge seems to delocalize to γ position in THF more than in benzene- d_6 . However, the difference is smaller than the difference observed between σ - and π -allyl (IV) chain ends, which is estimated to be 21—24 ppm according to Table III.

Figure 4 shows ^1H NMR spectra of the living

Table III. ^1H and ^{13}C chemical shift of 5,5-dimethylhexene-2-ylolithium

	Position	$^{13}\text{C}^a$	$^1\text{H}^b$
$\begin{array}{c} \delta \quad \gamma \quad \beta \quad \alpha \\ \text{t-Bu}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 \quad \text{Li}^+ \\ \sigma\text{-allyl (IV)} \end{array}$	α	20.0 ^c 20.7	0.80 ^c 0.78
	β	140.3 144.3	6.11 6.06
	γ	103.0 103.3	4.50 4.64
	δ	41.3 48.2	1.89 1.94
	α	31.0 —	1.19 1.29
	β	142.5 146.0	6.10 5.98
	γ	81.9 79.6	3.35 3.63
	δ	43.7 50.7	1.88 1.85
$\begin{array}{c} \delta \quad \gamma \quad \beta \quad \alpha \\ \text{t-Bu}-\text{CH}_2-\text{CH}-\text{C}=\text{CH}_2 \\ \quad \quad \quad \quad \quad \text{H} \\ \quad \quad \quad \quad \quad \text{Li}^+ \\ \pi\text{-allyl (IV)} \end{array}$			

^a Data in ref 14.

^b δ from TMS; data in ref 3 and 5.

^c A set of data shows *cis* isomer above, and *trans* isomer below.

Figure 4. 220 MHz ^1H NMR spectra of living oligomeric 1PB: (A) $\overline{\text{DP}}=1.2$ in $\text{THF}-d_8$, (B) $\overline{\text{DP}}=3.2$ in $\text{THF}-d_8$, and (C) $\overline{\text{DP}}=3.5$ in $\text{toluene}-d_8$.

oligomeric 1PB. The higher-field shift of phenyl proton resonances and the lower-field shift of α -proton resonance indicate the delocalization of charge to the phenyl ring and the presence of a partial double bond between the phenyl ring and the α -carbon, which were suggested by the ^{13}C NMR spectra. A γ -proton of the oligomeric 1PB chain end appears at δ 4.3 as a complicated multiplet in both

$\text{THF}-d_8$ and $\text{toluene}-d_8$, indicating that the nature of the solvent has almost no effect on the distribution of the negative charge. Furthermore, the chemical shift of the γ -proton is closer to that of σ -allyl (IV) than that of π -allyl (IV). This shows that the delocalization of the charge to γ -carbon is small regardless of the nature of a solvent. These results are quite different from those observed in oligomeric B and I chain ends. In those cases the distribution of charge is strongly affected by the nature of the solvent. In hydrocarbon media the chain end is reported to be σ -allyl (covalent), in which the charge localizes at α -carbon; this chain end is believed to form an in-chain 1,4 unit when the next monomer adds to it. But, in polar media such as THF the chain end is regarded as π -allyl (ionic) where the charge delocalizes from α to γ -carbon, and this chain end is considered to form an in-chain vinyl unit preferentially.¹⁷

The negative charge, when considered with the information as far obtained, distributes in the chain end of oligomeric 1PB as follows: (a) The negative charge delocalizes at the α -carbon and the phenyl ring. (b) The α -carbon is substantially sp^2 hybridized due to the delocalization. The lithium atom must be interacting with π -electrons. (c) The delocalization to the γ -carbon is small. (d) The distribution of the charge is hardly affected by the nature of the solvent. From these results we could describe the living chain end of the oligomeric 1PB as shown in (V).

Figure 5. ^{13}C NMR spectra of methanol terminated oligomeric 1PB: (A) DP=2.5, (B) DP=20, and (C) DP=90 prepared in THF; (D) DP=2.4, (E) DP=15, and (F) DP=75 prepared in benzene. * shows the terminal methylene carbon.

Geometry of Double Bond in the Chain End of Oligomeric 1PB

In Figure 4C the α -proton resonance consists of two sets of doublets in toluene- d_8 , while it is a single doublet in THF- d_8 (Figure 4A, B). δ -Proton resonance also appears at δ 1.9 and δ 2.1 in toluene- d_8 , whereas it appears only at δ 2.1 in THF- d_8 . In hydrocarbon solvents *trans*- and *cis*-4,1 chain ends must coexist at an equilibrium through the 4,3 anion, as shown in Scheme III. The effect of association of the living end could not be established by means of NMR spectra. However, the initiation and propagation rates are much slower in hydrocarbon solvents than in THF. This must be due to the association of the alkyllithium and the living chain end. On the other hand, in THF- d_8 the living chain end seems to be preferentially *trans*-4,1. The effect of such a *trans*-*cis* isomerization on the microstructure of polyisoprene was recently investigated by Bywater *et al.*²⁹ ^{13}C NMR spectra of methanol terminated oligomeric 1PB clearly supported the above results. As shown in Figures 5A, B, and C, the methanol

terminated oligomeric 1PB prepared in THF have only *trans*-4,1 chain ends (47.0 ppm), which is the same as that of a model *trans*-4,1 end (47.0 ppm). On the other hand, as shown in Figures 5D, E, and F, samples prepared in benzene have both *trans*-4,1 (47.0 ppm) and *cis*-4,1 (41.4 ppm) chain ends (relative intensity is *trans*/*cis* $\approx$ 6/4³⁴). The chemical shift of the *cis*-4,1 chain end is close to that of a model *cis*-4,1 end (41.1 ppm). The model compounds, *trans*- and *cis*-1-phenyl-5,5-dimethyl-2-hexene, for the chain end of terminated oligomeric 1PB were fractionally collected from the adducts of *t*-BuLi and 1PB by gas chromatography on a column DEGA 2.25 m. The ^{13}C chemical shifts of the model compounds are shown below.

³⁴ *Cis*-4,1 isomer was predominant in the case of lithiated 1P2B(III). The configuration of 1,4 double bonds seems to depend on the structure, as reported in ref 30.

Polymerization Mechanism of IPB in the Anionic Polymerization

The behavior of IPB in the anionic polymerization is described as follows. Since the negative charge delocalizes at the α -carbon and the phenyl ring, and the delocalization to γ -carbon is limited regardless of the polymerization solvent, the monomer adds to the α -carbon, and consequently 1,4 units are predominant in in-chain units. Since the resonance effect of the phenyl ring on the stabilization of the anion is prevailing in the case, the distribution of the negative charge was hardly affected by the solvation of the lithium cation.^{*5} The configuration of the in-chain 1,4 unit is determined by that of the anion 4,1 chain end. In THF the anion chain end is regarded as only *trans*-4,1, whereas in hydrocarbon media there is an almost equimolar mixture of *trans*- and *cis*-4,1 chain ends. They must be in equilibrium through 4,3 anions. By the addition of the monomer to the *cis*-4,1 and 4,3 anion in the equilibrium, *cis*-1,4 and 3,4 units can increase in the polymers prepared in hydrocarbon media.

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^{*5} *trans*-1-(4-methoxyphenyl)-1,3-butadiene was prepared with *p*-anisaldehyde and triphenylallylphosphonium bromide, followed by repeated recrystallizations from a hexane solution at -30°C , and polymerized with *t*-BuLi in THF. It was expected from the Hammett's substituent constant that the charge was transferred to γ -carbon from a phenyl ring due to the *p*-methoxy group in the propagating chain end and that the number of 3,4 units would increase in the resulting polymer. However, the microstructure of the polymer was exactly the same as that of poly(IPB) prepared under the same conditions. The electron donating power of the *p*-methoxy group might be too weak to affect the distribution of the negative charge in the chain end.

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