Characterization of Living Anion Chain End of Oligomeric 2-Phenyl-1,3-butadienyllithium

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ABSTRACT: 25.0 MHz ^{13}C - and 100 MHz ^1H NMR investigations were carried out on living chain ends of oligomeric 2-phenyl-1,3-butadienyllithium (oligomeric 2PBLi) in order to reveal the anionic polymerization mechanism. The propagating species of 2PB in the anionic polymerization is considered to be the 1,4 anion. Lithiated 3-phenyl-1-butene (3P1B) was employed as a model anion of the propagating anion of 2PB. A negative charge of the chain end delocalizes to π -allyl system and to the phenyl ring over the temperature range studied (-45°C — 24°C). The conclusion was reached that the configuration of the chain end is an (E) isomer. Although the chain end is ionic (π -allyl), possibly due to the steric hindrance of γ -position, the monomer attacks the α -carbon, and consequently the in-chain units are predominantly *cis*-1,4. However, with a decrease in the sample temperature, a small amount of the charge on the α -carbon is transferred onto the γ -, β -carbon, and the phenyl ring. This leads to a considerable increase in 1,2 units in the poly(2PB) obtained at lower temperatures.

KEY WORDS 2-Phenylbutadiene / Anionic Polymerization / Living Oligomer / ^{13}C NMR / ^1H NMR / 3-Phenyl-1-butene / Metalation / Charge Distribution / Polymerization Mechanism /

We have studied the microstructures of poly(1-phenyl-1,3-butadiene) [poly(1PB)]¹ and poly(2-phenyl-1,3-butadiene) [poly(2PB)]² prepared by anionic initiators using ^{13}C - and ^1H -NMR spectroscopies. These monomers behaved in quite different ways from butadiene (B) and isoprene (I) in the anionic polymerizations. Anion chain ends of the oligomeric 1-phenyl-1,3-butadienyllithium (oligomeric 1PBLi) were investigated to show the polymerization mechanism.³ The charge distributions on the chain ends of the oligomeric 1PBLi were hardly affected by the solvating power of a solvent and the negative charge was located at the α -carbon due to the resonance effect of the phenyl ring.

2PB is the other mono-phenyl-substituted butadiene. The polymerization behavior of 2PB was considerably different from that of 1PB, as described in a previous paper.² It seems of interest to characterize a living chain end of the oligomeric 2PB and compare it with that of 1PB. Schué *et al.* studied the anion chain end of the oligomeric 2PB.⁴ However, the conclusion reported was not consistent with the microstructure of the polymer.

In this study, we have investigated a charge distribution on a living chain end of the oligomeric 2PB under various conditions by means of ^1H - and ^{13}C -NMR spectroscopies. The results are compared with those of 1PB as well as B and I, and the polymerization mechanism of 2PB is discussed.

EXPERIMENTAL

The general experimental procedures have been described in a previous paper.³

Material

2-Phenyl-1,3-butadiene(2PB) was prepared by the same method as described in a previous paper.² 3-Phenyl-1-butene(3P1B) was synthesized from methylenetriphenylphosphorane and α -phenylpropionaldehyde by a procedure described in the literature⁵ [bp 67°C (12 mmHg)].

NMR Spectra

^{13}C -NMR spectra were recorded on a JEOL JNM FX100 spectrometer (25.0 MHz). ^1H -NMR spectra

were measured by a Varian HA100 (CW) and JEOL JNM FX100 (FT) spectrometers. Typical conditions for ^1H FT measurements were: spectral width, 1000 Hz, acquisition time, 4.10 s, data point, 16 K, pulse width, $7\ \mu\text{s}$ (42°), pulse repetition, 30 s, and number of transients, 4.

Oligomerization and Metalation Procedure

Metalation of 3P1B and oligomerization of 2PB were carried out in NMR sample tubes *in situ* under a pure argon atmosphere with *t*-BuLi. The oligomer whose spectra are shown in Figure 2 was prepared in dry diglyme at 50°C , followed by protonation with methanol; $[\text{2PB}]_0 = 0.12\ \text{M/l}^{-1}$ and $[\text{2PB}]/[\textit{t}\text{-BuLi}] = 6.0$. Lithiated 3P1B whose spectra appeared in Figure 3 and Figure 4 was prepared by metalating 3P1B in the mixture of THF and toluene (2:1 v/v) at 5°C for 1.5 h, then NMR measurements were carried out at various temperatures; $[\text{3P1B}]_0 = 0.48\ \text{M/l}^{-1}$ and $[\textit{t}\text{-BuLi}]/[\text{3P1B}] = 1.1$. The living oligomer whose spectra shown in Figure 5 and Figure 6 was prepared in the mixture of THF and toluene (2:1 v/v) at -78°C , then the temperature was raised for NMR measurements: $[\text{2PB}]_0 = 0.48\ \text{M/l}^{-1}$ and $[\textit{t}\text{-BuLi}]/[\text{2PB}] = 1.2$.

RESULTS AND DISCUSSION

Microstructure of Poly(2PB) Prepared by Anionic Initiators²

The microstructures of poly(2PB) reported in a

Table I. Microstructure of poly 2PB^{a,b}

No.	Initiator	Solvent	Temp/ $^\circ\text{C}$	Structure/%	
				<i>cis</i> -1,4	1,2
3	<i>t</i> -BuLi	Diglyme	50	97	3
7	<i>t</i> -BuLi	THF	0	90	10
8	<i>s</i> -BuLi	Toluene	0	90	10
12	<i>t</i> -BuLi	THF	-78	73	27
13	Na-Naph ^c	THF	-100	67	33

^a This is a summary of Table I in a previous paper (ref 2).

^b Polymerization time, 4.0 h. Conversions were quantitative.

^c Sodium naphthalene.

previous paper are summarized in Table I. The microstructure of the polymer depends on a polymerization temperature, hardly affected by the nature of polymerization solvents. Poly(2PB) prepared at 50°C has 97% *cis*-1,4 content. With a decrease in the polymerization temperature, 1,2 content increases. This behavior is quite different from that of 1PB as well as B and I.

Protonated One-to-One Adduct of 2PB with *t*-BuLi

Before studying the living chain end, a product distribution of one-to-one adducts of 2PB with *t*-BuLi was investigated by protonation followed by GLC analysis. As reported previously,³ a product distribution of one-to-one adducts of 1PB with *t*-BuLi after protonation was consistent with those

Table II. Product distribution of one to one adduct of 2PB with *t*-BuLi^a

Run	Solvent	Temp $^\circ\text{C}$	% of one to one adduct	% of one to one adduct ^b							
				From 1,4 anion			% of 1,4 anion	From 4,1 anion			% of 4,1 anion
				(E)- 1,4	(Z)- 1,4	1,2		(E)- 4,1	(Z)- 4,1	4,3	
1	Benzene	50	47	47	16	8	71	17	2	10	29
2	Toluene	0	79	45	13	10	68	17	4	11	32
3	THF	-78°	80	86	0	6	92	8	0	0	8
4	THF	25	81	69	1	3	73	23	0	4	27

^a For run 1, 2, and 3; $[\textit{t}\text{-BuLi}] < 0.4\ \text{M/l}^{-1}$, $[\textit{t}\text{-BuLi}]/[\text{2PB}]_0 = 2.0$, and reaction time, 1.0 h. For run 4; $[\textit{t}\text{-BuLi}] = 0.04\ \text{M/l}^{-1}$, $[\textit{t}\text{-BuLi}]/[\text{2PB}]_0 = 2.0$, and reaction time 2.0 h.

^b Product distributions are analyzed by GLC (PEG 20M) following assignments of Schué.⁴ Sum of amounts of the one to one adducts is normalized to 100%.

^c At higher temperatures over 0°C one to one adducts could not be detected. Microstructure of the oligomer obtained at a higher temperature was much more complicated than the corresponding polymer.

Scheme I.

predicted by the microstructure of the polymer. However, that of 2PB with *t*-BuLi was inconsistent with the results of the microstructure. All kinds of one-to-one adducts were detected by GLC after protonation, as reported by Schué *et al.*⁶ Among these, the adducts derived from the 4,1 anion (as mentioned later, the 4,1 anion is not the propagating anion in the polymerization of 2PB) were produced considerably at higher reaction temperatures (0–50°C) as shown in Table II. On the other hand, a one-to-one adduct prepared at –78°C contained a predominantly (E)-1,4 adduct and a small amount of a 1,2 adduct (run 3).

These results are inconsistent with the polymerization behavior of 2PB, where the microstructure of poly(2PB) prepared at higher temperatures is mainly *cis*-1,4, and that prepared at –78°C contains a significant amount of 1,2 structures (see Table I). This discrepancy may arise from the difference in the anion concentration or the difference between the initiation and the propagation reaction. The one-to-one adduct was formed by the addition of 2PB to *t*-BuLi, whereas in the polymerization, addition of monomer to phenyllallyl anion, the propagating anion, must be considered.

In the course of the reaction between *t*-BuLi and 2PB in THF at higher concentration (0.2 M l^{–1}), at room temperature, one-to-one adducts were hardly obtained. On the other hand, when the reaction was carried out in dilute condition (0.02 M l^{–1}) one-to-one adducts were obtained in good yields as shown in run 4 in Table II.

Propagating Species in Anionic Polymerization of 2PB

Two isomeric anions, 1,4 anion(I) or 4,1 anion(II), can be considered for the propagating species in the polymerization (see Figure 1). Here, the 1,4 anion(I) is intended to include σ -1,4, π -1,4, or σ -1,2 chain

Figure 1. Two possible isomeric structures of propagating species in the anionic polymerization of 2PB.

ends, which are converted to each other through an allylic equilibrium. Similarly, the 4,1 anion(II) will include σ -4,1, π -4,1, or σ -4,3. The 1,4 anion(I) and the 4,1 anion(II) cannot be converted to each other.

The propagating anion of 2PB in the polymerization is concluded to be 1,4 anion(I), not 4,1 anion(II). The 1,4 propagating anion(I) can be proposed by the result that a terminal methyl proton resonance of the protonated oligomeric 2PB appeared as a doublet at δ 1.8 ppm, not a singlet as shown in Figure 2.*¹ This is also supported by the microstructure of the polymers, which contain 1,4

*¹ A terminal methyl resonance of a protonated 4,1 anion(II) is expected to appear as a singlet at δ 2 ppm, from the ¹H NMR spectrum of (E)-2-phenyl-2-butene. The molecular weight of the oligomer estimated from a relative intensity of the doublet resonance at δ 1.8 ppm is substantially consistent with the M_n measured by VPO.

Figure 2. The 100 MHz ^1H NMR spectrum of oligomeric 2PB protonated with methanol; M_n of oligomer = 1400; $M_w/M_n = 1.6$.

and 1,2 units but no 3,4 units. Poly(2PB) obtained in the previous study did not contain detectable amounts of head to head or tail to tail linkages and had single narrow molecular weight distributions according to gel-permeation chromatograms. Therefore, a living poly(2PB) anion must have a single propagating species. Thus, these results indicate that the only propagating species in the polymerization is the 1,4 anion(I).

Characterization of Metalated 3P1B

In the previous study a model 1,4 propagating anion in the polymerization of 1PB could be prepared by the lithiation of 1-phenyl-2-butene. A model 1,4 propagating anion in the polymerization of 2PB is difficult to generate by the lithiation of a corresponding hydrocarbon such as 3-phenyl-2-butene. However, a similar model anion was easily prepared by lithiating 3P1B as shown in Scheme II.

Figure 3 shows the ^1H -NMR spectrum of lithiated 3P1B(III) in $\text{THF}-d_8$. Symbols of signals correspond to those used in the above Scheme II (see (III-c)). Absence of olefin proton resonances belonging to the original 3P1B at δ 4.8–5.2 ppm indicates the completion of the metalation reaction. The phenyl proton resonances appear more upfield than those of the original 3P1B, indicating that a substantial amount of the negative charge delocalizes to the phenyl ring as observed in the case of 1PB³ and other benzyll^{7–10} or phenyl allyl^{11,12} anions. Especially a upfield shift of the para proton resonance is noticeable. Since the microstructures of poly(2PB) depend on polymerization temperatures, a variable tempera-

Scheme II.

ture study was carried out for this sample. The spectra are readily interpreted as the first order splitting. A_2X spin system at room temperature (24°C) changed into ABX spin system at -40°C . The spectrum at -40°C shows a typical ^1H -NMR spectrum pattern of phenyl- π -allyl system,¹¹ indicating that the anion center delocalized to the π -allyl system as (III-b) and/or (III-c) in Scheme II.

On the other hand, the anion at 24°C cannot simply be concluded as σ -allyl, even if the two α -protons are magnetically equal. The two α -protons of the π -allyl system can become magnetically equal

Figure 3. The 100 MHz ^1H NMR spectra of lithiated 3P1B(III) at various temperatures; (A) -40°C and (B) 24°C .

when rotation around the α -carbon- β -carbon bond is fast.¹³ In order to determine whether the lithiated 3P1B(III) at 24°C is a σ -allyl or π -allyl, a γ -proton or -carbon resonance must be examined.

However, since lithiated 3P1B(III) has no γ -proton whose chemical shift gives the best information about the distribution of the charge,^{14,15} ^{13}C -NMR spectra will be studied in order to discuss the charge distribution at 24°C . Figure 4 shows the ^{13}C -NMR spectra of the lithiated 3P1B(III) at 24°C and -40°C . Chemical shifts of the carbon resonances are listed in Table III together with their assignments. The chemical shift of a γ -carbon resonance strongly depends on the charge distribution. In the case of 5,5-dimethylhexene-2-yl lithium, produced by 1,4 addition of *t*-BuLi and B, the chemical shift difference of the γ -carbons was estimated 21–24 ppm between σ -(covalent) and π -(ionic) allyl structures.¹⁶ In Figure 4, however, the γ -carbons appear almost at the same position at 24°C and -40°C ; the difference in the chemical shifts is 2.1 ppm. Therefore, the charge distribution must be essentially the same at 24°C and -40°C . As shown by ^1H -NMR spectra, at -40°C the charge can be considered to delocalize to the π -allyl system as shown in (III-b) and/or (III-c). At 24°C the charge also delocalizes to the phenyl ring and to π -allyl

system.*² The rotation around the α -carbon- β -carbon bond is fast enough at 24°C to equalize two α -protons magnetically.

While the charge distribution can be regarded as being the same essentially with variation in temperature, with a decrease in the sample temperature, α -carbon resonance slightly shows a downfield shift and γ -, *para*-, *ortho*-, β -, and aromatic C-1 carbon resonance respectively shift slightly upfield. The trend of such shifts are also shown above in the ^1H -NMR spectra (Figure 3). These shifts indicate that a small amount of the charge on the α -carbon is transferred onto γ -, β -carbon, and the phenyl ring at lower temperatures. O'Brien proposed eq 1 for the linear ^{13}C shift (δ)- π -electron density (ρ) relationship.¹⁷ The variation of the charge distribution is shown in terms of π -electron densities estimated from ^{13}C chemical shifts using eq 1 and listed in Table III.

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

Two configurations can be considered for the lithiated 3P1B(III) as shown in Scheme II; (Z)-(III-b) and (E)-(III-c). In Figure 4 each resonance appeared as a sharp single signal. Therefore, lithiated

*² In the case of phenylallyllithium¹² the charge also delocalizes to the π -allyl system at 21°C .

Table III. ^{13}C chemical shift^a and π -electron density for lithiated 3P1B

Position	Chemical shift, δ		π -Electron density, ρ		$\Delta\rho$
	-40°C	24°C	-40°C	24°C	
α	60.6	56.3	1.46	1.49	-0.03
β	136.3	137.3	0.98	0.97	0.01
γ	82.5	83.5	1.32	1.32	0
Aromatic C-1	146.5	147.3	0.91	0.91	0
<i>ortho</i>	114.7	115.9	1.12	1.11	0.01
<i>para</i>	109.5	110.6	1.15	1.14	0.01

^a Shifts are listed in ppm downfield from TMS using a solvent peak (THF, 67.0 ppm) as a standard.

Figure 4. The 25.0 MHz ^{13}C -NMR spectra of lithiated 3P1B(III) at various temperatures; (A) 24°C and (B) -40°C .

3P1B(III) must contain only one of the above two species. After protonation of the lithiated 3P1B(III) with methanol at 10°C , 3P1B and (E)-2-phenyl-2-butene((E)-2P2B)^{*3} were obtained in 42% and 58% yield respectively as shown in Scheme III according to GLC analysis. On the other hand, (Z)-2P2B could not be detected. Assuming that (E)-(Z) isomerization does not occur in the π -allyl system,¹⁹ the lithiated 3P1B(III) will contain only the (E)-

^{*3} (E)-2P2B was fractionally collected by the GLC on a column DEGA 2.25m and identified by ^1H NMR and ultraviolet spectra. The chemical shift and the coupling constants are as follows. H_{phenyl} , δ 7.2 ppm, H_a , δ 2.0 ppm, H_b , δ 5.8 ppm, and H_c , δ 1.8 ppm; J_{a-b} = 1.4 Hz, J_{a-c} = 1.1 Hz and J_{b-c} = 6.8 Hz. The ultraviolet spectrum of this sample has an absorption maximum at 245 nm (in cyclohexane), indicating (E)-isomer according to the literature.¹⁸

Scheme III.

configuration, that is, (III-c). In contrast with the lithiated 3P1B, lithiated 1-phenyl-2-butene in a previous paper had *cis* and *trans* configurations in the ratio of 3:1.

Characterization of Living Chain End of Liogomeric 2PB

Characterization of a living chain end of oligomeric 2PB will be subsequently carried out based on the knowledge obtained above. Figure 5 shows the ^1H -NMR spectrum of the oligomeric 2PBLi measured at -47°C . Each resonance is broader due to in-chain units. In the spectrum two α -protons (H_a

Figure 5. The 100 MHz ^1H NMR spectrum of oligomeric 2PBLi; measured at -47°C ; $\overline{DP}$ = 2.1.

Table IV. ^{13}C chemical shift^a and π -electron density for oligomeric 2PBLi

Position	Chemical shift, δ		π -Electron density, ρ		$\Delta\rho$
	-45°C	24°C	-45°C	24°C	
α	67.0	58.9	1.42	1.47	-0.05
β	137.5	139.1	0.97	0.96	0.01
γ	85.8	87.9	1.30	1.29	0.01
Aromatic C-1	146.6	147.6	0.91	0.91	0
<i>ortho</i>	113.7	115.9	1.12	1.11	0.01
<i>para</i>	105.3	108.6	1.18	1.16	0.02

^a Shifts are listed in ppm downfield from TMS using a solvent peak (THF, 67.0 ppm) as a standard.

Figure 6. The 25.0 MHz ^{13}C NMR spectra of oligomeric 2PBLi at various temperatures: (A) 24°C , (B) 0°C , (C) -20°C , and (D) -45°C ; $\overline{DP}=1.7$.

and H_b ; for the notation, see (IV-a)) are magnetically non-equivalent and have different coupling constants with β -proton (H_c) whose resonance is overlapped completely with the in-chain phenyl proton resonances at δ 7.2 ppm. Further, phenyl proton resonances of the chain end shift upfield. These results show that the charge also delocalizes to a π -allyl system and the phenyl ring in the same manner as the lithiated 3P1B at -45°C . On the other hand, at 24°C the α -proton resonances of this sample collapsed. When the sample temperature was raised

to 45°C , the collapsed resonance became complex due to the decomposition of the sample. Hence, the charge delocalization at the higher temperature could not be determined by the ^1H -NMR spectra.

The ^{13}C -NMR spectra of the oligomeric 2PBLi at various temperatures are studied (Figure 6). Chemical shifts of the carbon resonances are listed in Table IV together with the assignments. Several characteristic resonances of the living chain end in Figure 6 have almost the same chemical shifts as those in Figure 4, indicating that the charge distribution in the oligomeric 2PBLi is essentially the same as lithiated 3P1B(III). In Figure 6 the γ -carbons at various temperatures have almost the same chemical shifts. Therefore, the charge distributions will not vary essentially with the variation of the sample temperature. The charge delocalizes to the π -allyl system and the phenyl ring at higher temperatures (-20 – 24°C) as well as at -47°C in the same manner as lithiated 3P1B(III).

Scheme IV.

Two configurations [(E)-isomer; (IV-a) and (Z)-isomer; (IV-b)] can also be considered for the anion chain end of the oligomeric 2PBLi. Since all the carbon resonances of the chain end appear as a single peak, the chain end of the oligomeric 2PBLi will contain only one of two configurations. Considering that the one-to-one adduct listed in run 3 in Table II has predominantly a (E)-1,4 structure and that the lithiated 3P1B(III-c) has only the (E)-isomer, the

chain end of the oligomeric 2PBLi must also have only the (E)-configuration. (Z)-configuration may be disadvantageous due to the bulkiness of the phenyl ring. This result presents a striking contrast to the oligomeric 1PBLi where the chain end contains the *trans*-4,1 and *cis*-4,1 ends in almost equal amounts.

Furthermore, similar to the spectra of the lithiated 3P1B, with a decrease in the sample temperature, the α -carbon resonance shifts downfield and β -, γ -, *ortho*, *para*, and aromatic C-1 carbon resonances slightly move upfield. These downfield and upfield shifts indicate that a small amount of the charge on the α -carbon is transferred onto the γ -, β -carbon, and the phenyl ring. The variation in the charge distribution is shown in terms of the π -electron densities estimated from ^{13}C chemical shifts using eq 1 as listed in Table IV.

In the case of the lithiated 1-phenyl-2-butene and the oligomeric 1PBLi,³ *ortho* carbon resonances at 24°C were extremely broader than the other resonances. Upon cooling, the broader resonances collapsed at 0°C, then splitted into two peaks of equal intensity. This phenomenon is explained by the presence of a rotational barrier of the α -carbon-phenyl partial double bond. However, in the present case of lithiated 3P1B and the oligomeric 2PBLi, the *ortho* carbon resonances is a sharp peak even at -45°C, indicating that rotation of the phenyl ring is fast enough at -45°C and the partial double bond character of γ -carbon-phenyl bond is weaker than the lithiated 1P2B and the oligomeric 1PBLi. The charge is located at the α -carbon and the phenyl ring in the case of lithiated 1P2B and oligomeric 1PBLi, but delocalizes widely to the π -allyl system and the phenyl ring in the present case. Therefore, the bond order of the γ -carbon-phenyl bond in the present case may be smaller than that of the α -carbon-phenyl bond in the lithiated 1P2B and the oligomeric 1PBLi. The difference in the bond order will affect the phenyl rotation.

An attempt was made to investigate the charge distribution at the chain end in a hydrocarbon solvent as well as in THF. However, in the hydrocarbon solvent an initiation reaction could not occur at a low temperature (-40 ~ -78°C), and at higher temperatures (higher than 0°C) the 4,1 anion which is not the propagating species was generated. Therefore, the 1,4 propagating chain end of the oligomeric 2PBLi could not be investigated in a pure hydrocarbon solvent. However, since the micro-

structure did not change according to the polarity of the solvent, the charge distribution is believed to be the same as in a hydrocarbon solvent.

Polymerization Mechanism of 2PB in Anionic Polymerization

The propagating species in the polymerization of 2PB can be described as shown in the structure of (IV-a). The chain end is ionic, that is, the charge delocalizes widely over the π -allyl system and the phenyl ring. The configuration of the chain end is (E). In the case of B and I, such ionic (π -allyl) chain ends lead mainly to in-chain 1,2 units after the monomer addition since the monomers are liable to attack the more electronegative γ -carbons. However, in the case of poly(2PB) the polymers prepared at higher temperatures have high *cis*-1,4 content although the chain ends are π -allyl lithium. The monomer will not be able to attack the γ -carbon due to the steric hindrance of the bulkier phenyl group. The monomer adds to the α -carbon selectively at higher temperatures, and consequently the resulting polymer contains the high 1,4 content. A low ceiling temperature for a σ -1,2 anion such as shown in the anionic polymerization of α -methylstyrene may be expected, and this may be a disadvantage in making an addition to the γ -carbon. Moreover, since the configuration of the chain end is exclusively (E) and (E)-(Z) isomerization will not occur in the π -allyl system, the configuration of the in-chain 1,4 unit is only *cis*. On the other hand, with a decrease in the polymerization temperature, a small amount of the charge on the α -carbon is transferred onto the γ -, and β -carbon, and the phenyl ring. Consequently the α -carbon is less electronegative, and the monomer is added more to the γ -carbon. This leads to the considerable formation of in-chain 1,2 units.

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