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ANIONIC POLYMERIZATION OF PHENYL BUTADIENES
—MICROSTRUCTURE AND CHARACTERIZATION
OF ACTIVE SPECIES

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DEPARTMENT OF HYDROCARBON CHEMISTRY

FACULTY OF ENGINEERING

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GENERAL INTRODUCTION

The microstructure of a polymer and the characterization of the propagating chain end offer ^{the} great ^{many} many informations on the investigation of polymerization mechanism. The characterization of the active species was rather difficult since it is usually unstable and its concentration is quite low. However, the much industrial interest in the physical properties and microstructures of polymers gave a strong impetus toward the research in this area. Furthermore, the new and improved techniques such as superconducting high field ^1H NMR and pulsed Fourier transform ^{13}C NMR spectroscopies have been extensively developed in the last decade. It could be demonstrated that it is quite possible to analyze the microstructures of various polymers and characterize the active species in certain anionic polymerizations. Up to now, many data have been collected for the relationship between the microstructure of a polymer and the nature of the active species in various anionic polymerization systems.

Polydienes constitute an extremely significant group in synthetic polymers. The importance of the polydienes lies in the fact they contain the bulk of the commercial elastomers currently in use. The most common dienes used as the materials for commercially available polymers are butadiene and isoprene. Since the polybutadiene and polyisoprene which have high cis-1,4 content show good physical properties as a synthetic elastomer, a large number of **researches** were made from the industrial point of view upon the polymerization

catalysts which can polymerize butadiene or isoprene to high 1,4-polymer¹. The diene polymers show different physical properties according to the fraction of each structural unit, that is, trans-1,4, cis-1,4, 1,2, and 3,4 units. Therefore, many methods for the determination of the microstructure have been established²⁻⁵. In the last decade especially ¹H and ¹³C NMR spectroscopic techniques were developed remarkably and they can estimate the fraction of each structural unit directly without any correction factors. The NMR spectroscopic techniques can reveal the dyad and triad sequence distribution of each structural unit as well as the monoad microstructure, and accordingly relationship between the microstructure and the physical property can be precisely discussed⁶⁻⁷. The anionic polymerizations of these diene monomers have been investigated intensively and the propagating species are studied directly by the NMR spectroscopies⁹⁻¹². Some of the important results are shown below. The ¹H NMR spectra of the chain end of living oligomeric butadiene indicated that the terminal chain unit has a 1,4 structure (1,2 chain end was not detected), whereas the in-chain units show about 9% 1,2 structure¹⁰. The proton resonance spectrum of the chain-end unit in the case of isoprene also indicates an exclusive 4,1 structure, showing no 4,3 or 1,2 structures, despite the fact that the in-chain units contain approximately 10% 3,4 structure¹¹. Similarly, the spectrum of the living oligomeric 2,3-dimethylbutadiene chain end shows an exclusively 1,4 structure, despite the presence of 15-20% in-chain 1,2

units ¹¹. The interesting and unexpected finding was that the spectrum of the living oligomeric 2,4-hexadiene showed a delocalized structure even in the hydrocarbon media although the in-chain units consist of mainly 1,4 structure ¹². In this way these studies shed light on the nature of the living chain ends of several diene monomers. However, several problems remain unsolved as mentioned above in connection with the microstructures of the in-chain units.

1-Phenyl-1,3-butadiene(1PB) and 2-phenyl-1,3-butadiene (2PB) are not commercially available and the resulting polymer may not show specific physical properties. 1PB and 2PB, however, have phenyl substituents, which are expected to stabilize the anions on the propagating chain ends. In the cases of butadiene and isoprene the stabilization of the anions are caused only by the allylic conjugation, whereas the stabilization caused by the allylic and benzylic conjugation are expected for 1PB and 2PB. From the mechanistic view of the anionic polymerization of diene monomers, 1PB and 2PB have special interest when the microstructures of poly1PB and poly2PB are investigated and the propagating chain ends are characterized. The stabilized anion chain ends of 1PB and 2PB possibly give solutions to the unsolved problems in that area.

1PB can be polymerized by the cationic initiators as reported by Asami et al. ¹³ and Masuda et al. ¹⁴. They concluded that the resulting polymers mainly have 3,4 unit and about half of the 3,4 double bonds are consumed by intramolecular cyclizations. Since various types of cyclization

occurred, the polymers contain much complicated microstructures. On the other hand, 1PB is polymerized by anionic initiators without any cyclizations to give a high molecular weight linear polymer. Asami et al. investigated the anionic polymerization of 1PB and reported the resulting polymers contain 95% trans-1,4 unit from the results of IR and 60 MHz ^1H NMR spectra ¹⁵. However, in their paper detailed informations on the microstructure of the polymer and the mechanism of the polymerization were not discussed sufficiently.

2PB, the other mono-phenylsubstituted butadiene, can be polymerized by various kinds of initiators. $i\text{-Bu}_3\text{Al-TiCl}_4$ ¹⁶ or $\text{AlHCl}_2\text{-OEt}_2\text{-AlI}_3\text{-TiCl}_4$ ¹⁷ catalyst system polymerizes 2PB to give the polymer having mainly cis-1,4 structure. By the cationic initiators 2PB is polymerized to the polymer containing 1,4 structure ^{18, 19}. However, in these cases about a half of the double bonds of the 1,4 structure were consumed by cyclizations. Asami et al. ²⁰ and Ambrose et al ²¹ investigated the anionic polymerization of 2PB, and both of them concluded the resulting polymer contains mainly 1,4 structure. However, detailed information on the microstructure of the polymer and the mechanism of the polymerization cannot be presented by their studies.

Although several studies on the polymerizations of 1PB and 2PB were thus carried out, the microstructures of the polymers could not be revealed explicitly. The hydrogenation of the double bond of 1,4-poly1PB or 1,4-poly2PB leads to the copolymer having the same structural unit of styrene-ethylene alternating copolymer. The synthesis of the styrene-

ethylene alternating copolymer is not known at present and is considered to be difficult using styrene-ethylene monomer pair. From this point of view, it is important to elucidate the microstructure of these polymers and to find the catalyst system leading to highly 1,4 polymerization of LPB and 2PB.

Characterization of active species in a polymerization is much interesting in many aspects. The characterizations of the active species of short life time have been carried out for the cationic polymerization by means of the stopped flow technique ^{22, 23} and for the radical polymerization by the ESR spectroscopy ²⁴. In the anionic polymerization the propagating chain end is sometimes living for a long time under appropriate conditions. This was first pointed out by Szwarc and colleagues ^{25,26} in the anionic polymerization of styrene using sodium naphtharene as an initiator. They called this "living polymerization", which means the absence of the terminations and/or transfer reaction. Under such conditions the living anion chain ends can be directly investigated by various methods. The anionic polymerizations of butadiene, isoprene, and styrene demonstrate the typical living polymerization system. A large number of studies on the living anion chain ends in such cases were carried out extensively ²⁷⁻³¹. The chemical shifts of the NMR spectroscopies are mainly reflected by the electron density at the carbon under consideration. Therefore, the NMR spectroscopies seem to be one of the most powerful methods for the investigation of the nature of the propagating chain ends. Morton and his colleagues first succeeded in observing

^1H NMR spectra of oligomeric butadienyllithium chain end applying sophisticated "transparent butadiene- d_6 " ⁹⁻¹², which solubilizes oligomeric butadienyllithium and minimize the occasional 1,2 in-chain unit. They concluded that in hydrocarbon solvents σ -allyl chain end leads to in-chain 1,4 unit. Recently Bywater et al. 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 ³².

It is of significance to synthesize new copolymers under the concept of "molecular design". There have accumulated a large number of knowledges about the reactivities and relative reactivities of various monomers in polymerizations. Many kinds of useful polymers should be prepared by making the best of such results and application of organic chemistry. The hydrogenations of 1,4-polydienes give unique copolymers, such as alternating copolymer ³³⁻³⁵ or head to head and tail to tail vinyl polymers ^{36, 37}. As mentioned previously the hydrogenations of 1,4-poly1PB and 1,4-poly2PB gives the polymers which have the same structure as styrene-ethylene alternating copolymer. In the anionic copolymerization of butadiene with styrene ^{38, 39}, the relative reactivity of butadiene is much higher than that of styrene, and 80% of styrene charged remains unreacted when 90% of butadiene is consumed. Therefore such copolymerization gives almost styrene-butadiene block copolymer and the random copolymer of these two monomers can hardly be obtained. 1PB and 2PB

can be said to have intermediate structure between styrene and butadiene. The anionic copolymerizations of 1PB and 2PB with butadiene or styrene will lead to new copolymers which have special properties.

This thesis summarizes the results of a series of the investigations of the anionic polymerizations of 1PB and 2PB.

This thesis is divided into three parts. Part I (chapter 1 and 2) describes the studies of the microstructures of poly1PB and poly2PB prepared by the anionic polymerizations using the NMR spectroscopies. In part II (chapter 3, 4, 5, and 6) the active species in the anionic polymerizations of 1PB and 2PB are characterized. Part III (chapter 7 and 8) is concerned with the syntheses of the new type of copolymers as the applications of the results obtained in part I and part II.

The out line of each chapter is given as follows.

In chapter 1 1PB is polymerized by the anionic and coordinated catalysts. The microstructure of the resulting polymer was investigated by ^1H and ^{13}C NMR spectra. The polymers obtained contain trans-1,4 unit mainly. The microstructure of the polymer predominantly depends on the nature of solvents.

Chapter 2 describes the microstructure of poly2PB prepared by anionic initiators. The investigation of the microstructure is achieved with the aid of the polymerization of 2-phenyl-1,3-butadiene-1,1- d_2 by ^1H and ^{13}C NMR spectro-

scopies. The resulting polymer contains cis-1,4 structure predominantly. The microstructure of the polymer is affected principally by the polymerization temperature.

Since the microstructures of poly1PB and poly2PB are revealed explicitly in the chapter 1 and 2, in the following chapters (chapter 3, 4, 5, and 6) the characterizations of the propagating chain ends and the model anions of them are carried out.

Chapter 3 describes the characterization of living anion chain end of oligomeric 1-phenyl-1,3-butadienyllithium and the model anion of it. The resonance effect of the phenyl ring at the chain end on the stabilization of the anion is prevailing in this case. ^{13}C and ^1H NMR spectroscopic methods reveal that the anion chain end is classified as π -benzyl type anion where the negative charge is located at the α -carbon and the phenyl ring. The effect on the microstructure caused by the polymerization solvent is successfully interpreted by the negative charge distribution on the chain end.

Chapter 4 describes the characterization of living anion chain end of oligomeric 2-phenyl-1,3-butadienyllithium and the model anion of it. The anion chain end is classified as π -allylphenyl type anion where the negative charge is delocalized over π -allyl system and the phenyl ring. The negative charge distribution on the chain end can interpret the effect on the microstructure caused by the polymerization temperature.

Although there have been large number of discussions

on the π -electron distributions of living oligomer chain ends or model anions of them, regioselectivity in the reaction of such model anion with electrophilic reagent was paid little attention. In previous two chapters the π -electron distributions on the living oligomer chain ends of 1PB and 2PB and on the model anions are elucidated. It will be of interest to discuss the product distributions in the reactions with electrophiles and to compare them with the regioselectivity expected from the negative charge distributions.

In chapter 5 1- or 3-alkylsubstituted phenylallyl-lithiums, the model anions of the propagating species in the anionic polymerizations of 1PB and 2PB, are reacted with several electrophiles such as methyl iodide or ethylene oxide. The factors controlling the regioselectivity in the reactions are discussed by the product distributions in the reactions.

The resonance effect of the phenyl ring is prevailing on the living chain end in the case of 1PB. Therefore, in chapter 6, 1-(2-methoxyphenyl)-1,3-butadiene (o-MeO1PB) and 1-(4-methoxyphenyl)-1,3-butadiene (p-MeO1PB) are synthesized and polymerized by the anionic initiators. Since the methoxy substituent at para position is known as the electron releasing group, such group is expected to push the negative charge out of the phenyl ring of the chain end. On the other hand, as to o-MeO1PB the influence of the MeO substituent at the ortho position may be complicated due to the so-called "ortho effect".

The microstructures of poly1PB and poly2PB and the

nature of the active species in the polymerizations are revealed in chapters 1 to 6. As the application of these results, new copolymers which have specific sequence distributions are prepared as discussed in the following chapters.

Chapter 7 describes preparation and high resolution NMR spectra of styrene-ethylene alternating copolymer and poly(4-phenyl-1-butene), which are obtained by hydrogenating poly1PB and poly2PB. The styrene-ethylene alternating copolymer are hardly prepared by a simple polymerization process using styrene and ethylene as monomers.

Styrene-butadiene copolymers have been prepared commercially in various ways. 1PB and 2PB can be said to have intermediate structure between styrene and butadiene. It must be of interest to prepare the copolymer of 1PB or 2PB with styrene or butadiene. In chapter 8 such copolymerizations are carried out and the influence of the nature of the living chain ends are investigated.

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PART I Microstructures of Poly(phenylbutadiene)'s
Prepared by Anionic Initiators

ABSTRACT: The 220-MHz ^1H and 25.05-MHz ^{13}C NMR spectra of poly(1-phenyl-1,3-butadiene) (poly1PB) samples prepared by anionic and coordinated catalysts were investigated. Assignments of ^1H and ^{13}C NMR spectra were made for the various poly1PB's. Poly1PB samples initiated by alkyl lithium in hydrocarbon solvents contain 50–60% trans-1,4, 24–28% cis-1,4, and 8–24% 3,4 structures. On the other hand, poly1PB samples prepared by sodium naphthalene or alkyl lithium in THF had microstructures of 78–84% trans 1,4, 8–13% cis-1,4, and 8–10% 3,4 units. From the ^{13}C NMR spectra, dyad sequence distributions of t-t, t-c, c-t, c-c, and t-3,4 were estimated. Observed dyad sequence distributions were in good agreement with those calculated from Bernoullian statistics.

A large number of studies on the microstructure of polybutadiene and polyisoprene have been carried out by NMR spectroscopy.^{1–5} Polymerization mechanisms were discussed based on the sequence distributions of each unit (1,2, 3,4, trans-1,4, and cis-1,4). On the other hand, the microstructure of poly(phenylbutadiene)'s has been paid little attention. Since 1-phenylbutadiene (1PB) may be regarded as either a β -substituted styrene or phenyl-substituted butadiene, it is of interest to elucidate the microstructure of poly1PB prepared under various polymerization conditions.

Recently the cationic polymerization of 1PB was reported by Masuda et al.⁶ and Asami et al.⁷ Both concluded that 1PB was polymerized mostly to a 3,4 structure and that about half of the 3,4 double bonds were cyclized intramolecularly during the polymerization. The polymer had a very complicated microstructure due to cyclization. On the other hand, 1PB is polymerized by anionic initiators to a high molecular weight linear polymer without cyclization. Asami et al. studied the anionic polymerization of 1PB.⁸ They concluded poly1PB prepared in anionic polymerization had 95% trans-1,4 configuration from the results of an IR and 60-MHz NMR spectra. However, 60-MHz ^1H NMR spectra of poly1PB were not sufficient to resolve the microstructure in detail of poly1PB prepared at various conditions.

In this paper, we have studied high-resolution ^1H and ^{13}C NMR spectra of poly1PB's prepared by anionic or coordinated polymerization and obtained detailed information on the microstructure of poly1PB and on the mechanism of the polymerizations.

Experimental Section

Materials. *trans*-1-Phenyl-1,3-butadiene was prepared from *trans*-cinnamaldehyde and methylmagnesium bromide followed by dehydration with 30% sulfuric acid,⁹ purification by distillation over LiAlH_4 , and storage under argon at -15°C . The monomer is the *trans* isomer (bp $79\text{--}81^\circ\text{C}$ (8 mmHg)).

Solvents were carefully purified by distillation in the presence of suitable drying reagents. Alkyl lithium and sodium naphthalene were prepared by the usual method, in which *tert*-butyllithium was obtained according to the method reported by Smith¹⁰ and 1,1-diphenylhexyllithium (1,1-DPHLi) was prepared from *n*-BuLi and 1,1-diphenylethylene.¹¹

Polymerization Procedure. Polymerization was carried out in a three-necked flask under a pure argon atmosphere. When the initiator was added to the monomer solution, the reaction mixture turned red, showing that propagation species were generated. After a certain reaction time the polymer was precipitated by pouring it into a large amount of methanol, filtering, and drying in vacuo.

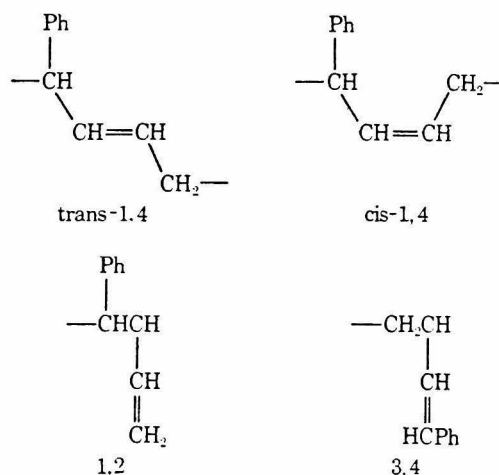
Trans-Cis Isomerization: A benzene solution of polymer (0.1–0.2 w/v %) was irradiated with a high-pressure mercury lamp. The irradiation was carried out in the presence of thiobenzoic acid (2–4 w/v % of the polymer) as a sensitizer at 20°C . The isomerized polymer was purified by repeated reprecipitations from benzene solution with methanol.

^1H and ^{13}C NMR Spectra. ^1H NMR spectra were obtained using a Varian HR 220 on 10–15 w/v % CDCl_3 solutions of polymer. ^{13}C NMR spectra were measured with a JEOL FX 100 spectrometer (25.05 MHz) on 20–40 w/v % CDCl_3 solutions of polymers. Both ^1H and ^{13}C NMR measurements were carried out at probe temperature with tetramethylsilane as an internal standard. Typical conditions for the ^{13}C measurement were: spectral width 5 kHz, acquisition time 0.812 s, data points 8192, pulse width $7\ \mu\text{s}$ (42°), pulse interval 1.5 s, and number of transients 1000–2000.

Gel-Permeation Chromatogram. Gel-permeation chromatograms were recorded on a Waters ALC/GPC 244 equipped with four columns ($10^5 + 10^4 + 10^3 + 500\ \text{\AA}$). The solvent was tetrahydrofuran and the flow rate was 1.5 mL/min. The molecular weight of poly1PB was determined according to calibration curves obtained with standard polystyrenes.

Results and Discussion

The following four structural units are contained in poly1PB. Infrared spectra of poly1PB prepared in this study were essentially the same regardless of the reaction conditions. No 1,2 units were found in the polymers, as evidenced by the absence of the absorptions at 990 and 910 cm^{-1} . The strong absorption at 965 cm^{-1} indicated that the double bonds in 1,4 and 3,4 units have mainly the *trans* configuration.



220-MHz ^1H Spectra of Poly1PB. ^1H NMR spectra (220 MHz) of polymers no. 17 and 16 are shown in Figure 1 with assignment of resonances. Polymer no. 16 had the highest 1,4 content and polymer no. 17 had the highest 3,4 content in this study. The chemical shifts and assignments are listed in Table I. Olefin proton resonances of 1,4 units appeared at δ 5.11 and 5.30 ppm. Lower field olefin proton resonances at δ 5.68 and 6.00 ppm were attributed to 3,4 units. The fraction of 1,4 and 3,4 units was estimated from relative intensities of the olefin proton resonances and checked by the methine proton resonances of 1,4 units at δ 3.05 and 3.39 ppm and phenyl proton

Table I
¹H Chemical Shift of Poly1PB

Unit	Proton	Chemical shift, ppm
1,4	Phenyl	6.98, 6.82
	Olefin	5.30, 5.11
	Methine	3.39, 3.05
	Methylene	2.20, 1.97
3,4	Phenyl	6.97
	Olefin	6.00, 5.68
	Methine	2.20
	Methylene	1.36 (sh), 1.23

resonances. The 1,4 and 3,4 content in various poly1PB's are listed in Table II together with the polymerization conditions. The presence of cis-1,4 units will be discussed later. A highly 3,4 polymer of poly1PB was obtained for the first time using a Ziegler type catalyst. The methine proton resonance of 3,4 units overlapped completely the methylene proton resonances of trans-1,4 units at δ 2.20 ppm. Phenyl proton resonances of 1,4 units were split into two peaks at δ 6.82 and 6.98 ppm when the 1,4 content was high. The higher field peak was assigned to ortho protons and the lower field peak was assigned to meta and para protons. This kind of splitting was observed in NMR spectra of polystyrene.¹² Regardless of the mode of addition (except 1,2 addition) relative intensities of phenyl, olefin, and aliphatic proton resonances should be 5 to 2 to 3 if reactions such as cyclization did not occur. In contrast to poly1PB prepared by cationic polymerization,^{6,7} this relation held in all the polymers prepared in this study.

According to gel permeation chromatography, the polymers in this study generally had narrow molecular weight distributions ($M_w/M_n = 1.1-1.2$) and the molecular weight was proportional to a feed ratio of monomer to initiator, that is, this polymerization was of the so-called living type. Polymer samples no. 17 and 18 prepared with Ziegler-type catalysts had broader molecular weight distributions ($M_w/M_n = 1.7-2.5$) and they were symmetrical. The molecular weights of poly1PB samples prepared in this study were 6500-15000, and therefore the influence of end groups was considered to be negligible.

In the course of anionic polymerization of butadiene and isoprene, the presence of a polar solvent drastically increased

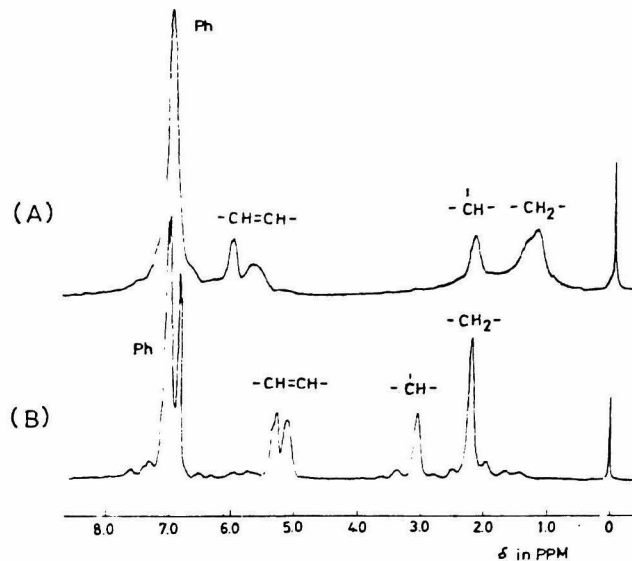


Figure 1. 220-MHz ¹H NMR spectra of (A) polymer no. 17 (3,4 unit, more than 98%) and (B) polymer no. 16 (1,4 unit, 92%).

the vinyl content in the resulting polymer on account of the electron-delocalized structure of the living chain end.^{13,14} It is of particular interest that in anionic polymerization of 1PB higher 1,4 content could be obtained when polar solvents such as THF or diglyme were used. Nonpolar solvents lead to higher 3,4 content. As shown in Table II (no. 8 and 9), however, addition of a small amount of polar solvent into toluene increased the 3,4 content about 2.5 times (42-44%). This phenomenon was observed in the polymerization of butadiene and isoprene initiated by alkyl lithium in hydrocarbon solvents.^{15,16} However, when polymerization was carried out in a polar solvent (no. 10), the 3,4 content was much lower (10%). This is quite different from the case of butadiene and isoprene. No simple explanation for this can be offered at present. When polymerization was initiated by *t*-BuLi in benzene, the 3,4 content was exceptionally low (8%). On the other hand, when polymerizations of 1PB were carried out by *t*-BuLi in toluene (no. 11) or by *n*-BuLi in benzene (no. 4), the 3,4 content increased to 16%. The reason for this also cannot be given. Asami

Table II
 Polymerization Conditions and Microstructure of Poly(1-phenylbutadiene)^a

No.	Catalyst	Solvent	Polymerization		Conv, %	1,4, %		3,4, %	Cis-1,4/trans-1,4	
			Temp, °C	Time, h		Trans	Cis		¹ H NMR	¹³ C NMR
1	Na-Naph ^a	THF	0	3.5	98	78	12	10	0.15	0.16
2	Na-Naph	THF	-78	3.5	98	79	12	9	0.15	0.16
3	<i>n</i> -BuLi ^b	Toluene	20	4.0	100	59	24	17	0.41	0.39
4		Benzene	20	4.0	100	59	25	16	0.42	
5		THF	0	3.5	99	78	12	10	0.15	0.13
6		Hexane	0	4.0	89	48	28	24	0.58	0.58
7	<i>s</i> -BuLi	Toluene	20	4.0	99	58	25	17	0.43	
8		Toluene ^f	20	4.0	99	45	11	44	0.24	
9		Toluene ^g	20	4.0	100	46	12	42	0.26	
10		THF	0	3.5	99	77	13	10	0.17	0.17
11	<i>t</i> -BuLi	Toluene	20	3.5	100	56	28	16	0.50	
12		Benzene	20	3.5	100	66	26	8	0.39	0.40
13		THF ^h	-78	4.0	100	79	11	10	0.14	0.13
14		Hexane	20	4.0	95	49	28	23	0.57	0.59
15	1,1-DPHLi ^c	Toluene	20	4.0	99	58	25	17	0.52	
16		Diglyme	-78	4.0	99	84	8	8	0.09	0.09
17	Co(AA) ₂ ^d	Toluene	30	24.0	92			98		
18	VCl ₄ ^e	Toluene	-78	24.0	62	33	0	67	0	0

^a Na-Naphthalene [Na-Naph] = 2.0×10^{-2} mol/L. ^b [RLi] = 2.0×10^{-2} mol/L. ^c 1,1-Diphenylhexyllithium [1,1-DPHLi] = 2.0×10^{-2} mol/L. ^d Co(AcAc)₂-AlEt₂Cl, Al/Co = 3.0, Co = 0.5×10^{-2} mol/L. ^e VCl₄-Anisole-AlEt₂Cl, Al/Anisole/V = 3/5/1, [VCl₄] = 2.5×10^{-2} mol/L. ^f THF/*s*-BuLi = 5.0. ^g THF/*s*-BuLi = 10.0. ^h [M]₀ = 1.0 mol/L.

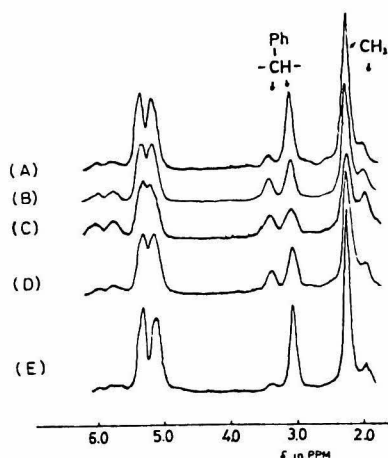


Figure 2. Partial 220-MHz ^1H NMR spectra of poly1PB: (A) no. 2 (B) no. 3, (C) no. 14, (D) no. 15, and (E) no. 16.

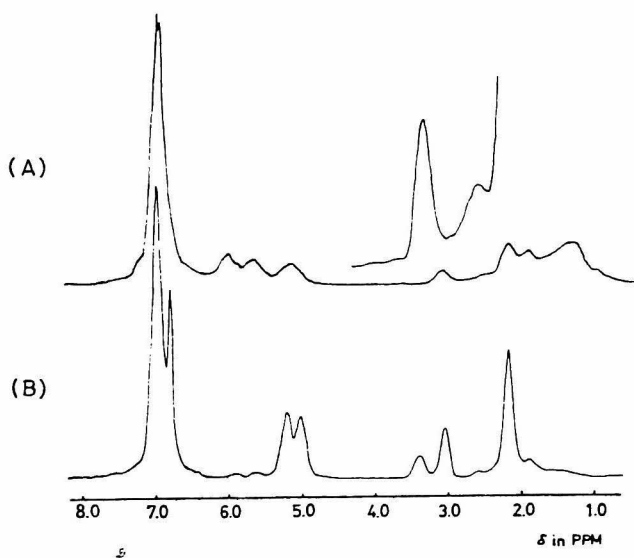


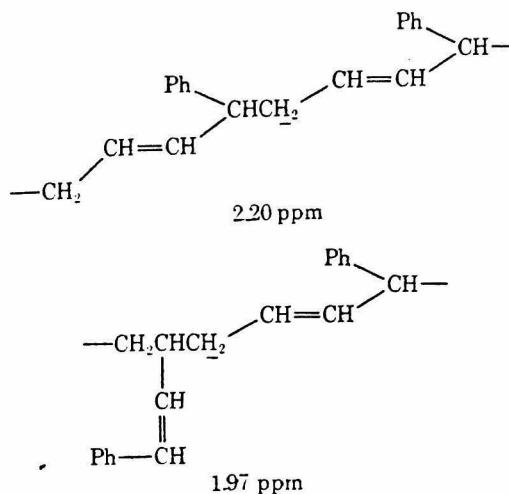
Figure 3. 220-MHz ^1H NMR spectra of (A) no. 18 (1,4 33%, 3,4 67%) and (B) no. 12 (1,4 92%, 3,4 8%).

reported that poly1PB prepared in benzene by alkyl lithium contained 75% 3,4 units.¹⁷ We cannot reproduce this, and the 3,4 content in this polymer should be less than 20% as mentioned above.

Another characteristic feature of these polymers is as described above that the methine proton resonances of 1,4 unit were split into two signals at δ 3.05 and 3.39 ppm. Partial ^1H NMR spectra of poly1PB prepared at various conditions were shown in Figure 2. The relative areas of the two methine proton resonances depended mostly on the polymerization solvent. Generally the relative intensity of the lower field resonance was increased together with the 3,4 content when the polymerization was carried out in a hydrocarbon solvent. This splitting could be attributed to one of the following differences in microstructure: (a) methine proton resonance of occasional cis-1,4 configuration, (b) effect of flanking the 3,4 unit to the trans-1,4 configuration, and (c) heterogeneous linkages such as head-to-head and tail-to-tail linkages of the trans-1,4 unit.

Since the lower field resonance at δ 3.39 ppm generally increased with an increase of 3,4 content, the effect of a flanking 3,4 unit to a trans-1,4 unit will be discussed. Figure 3 shows 220-MHz ^1H NMR spectra of (A) no. 18 and (B) no. 12. In the spectrum of A, methine proton resonance of a 1,4 unit appeared only at δ 3.05 ppm and no observable signal was seen

at δ 3.39 ppm in spite of the higher 3,4 content (67%). On the other hand, in the spectrum of B, sample no. 12 containing a small amount of 3,4 units (8%), the methine proton resonances of 1,4 units appeared at δ 3.05 and 3.39 ppm. These results show that the splitting of methine proton resonance of 1,4 units is not attributed to the effect of flanking 3,4 units. The methylene proton resonance of the trans-1,4 unit was also split into two signals at δ 1.97 and 2.20 ppm in the spectra shown



in Figure 3. The effect of a flanking 3,4 unit to the trans-1,4 unit seems to appear in this splitting. These two resonances were assigned as follows: It is not satisfactory to obtain the fraction of 3,4-trans-1,4 linkage from these two resonances because of strong overlapping due to other sequences. This fraction can be obtained from the ^{13}C spectra discussed later.

^{13}C NMR Spectra of Poly1PB. Further studies on the splitting of methine proton resonances of the 1,4 unit into δ 3.05 and 3.39 ppm will be discussed combined with ^{13}C NMR spectra of polymers. In Figure 4 25.0-MHz ^{13}C NMR spectra of poly1PB are compared. Tentative assignments of some resonances were made with the aid of proton coupled spectra. As described previously, polymer sample no. 17 is essentially a 3,4 polymer. In the ^{13}C NMR spectrum of A all signals were assignable to the 3,4 structure. The signal at M is attributed to the aromatic C-1 carbon and the signal at O is attributed to the olefin carbon attached to the phenyl group. The signal at H was attributed to the methylene carbon and the signal at F is attributed to the methine carbon of a 3,4 unit. The spectrum of poly1PB having the highest 1,4 structure (no. 16, 92%) is presented in Figure 4B. The signal at L is ascribed to the aromatic C-1 carbon and the signal at O is assigned to one of the olefin carbons of a trans-1,4 unit. The signal at A is attributed to the methine carbon and the signal at H is assigned to the methylene carbon of a trans-1,4 unit. Small peaks of the carbon belonging to 3,4 units were observed in the spectrum. The methylene carbon resonance of 3,4 units completely overlapped that of trans-1,4 units. One of the olefin carbon resonances of trans-1,4 units also overlapped that of the 3,4 units at O. In Figure 4C the ^{13}C NMR spectrum of polymer no. 18 is shown. The methine proton resonance of this polymer showed only one absorption at δ 3.05 ppm. Four broad peaks appeared in the aliphatic carbon region in the ^{13}C NMR spectrum. The signal designated C is not observed in Figures 4A and 4B and may be assigned to the methine carbon in trans-1,4 units flanked by 3,4 units. The broad nature of absorptions in this spectrum is attributed to trans-1,4-3,4 sequence distribution and 3,4-3,4 stereosequence distribution. The aliphatic carbon regions of the spectra are expanded in Figures 5A and 5B.

Polymer sample no. 12 had low 3,4 content (8%) and poly-

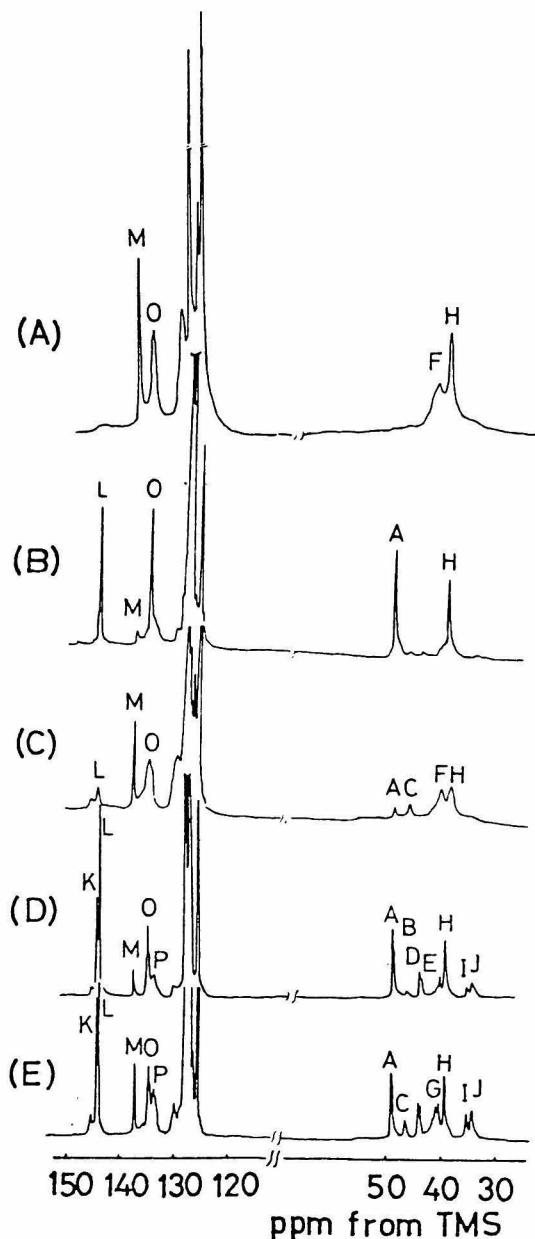


Figure 4. 25.0-MHz ^{13}C NMR spectra of (A) no. 17, (B) no. 16, (C) no. 18, (D) no. 12, and (E) no. 14

mer no. 14 had high 3,4 content, but in both samples relative intensities of the methine proton resonances at δ 3.39 to 3.05 ppm were large. As the relative intensity of the methine proton resonance at δ 3.39 ppm was increased, the relative intensities of the carbon resonances at B, D, E, G, I, and J were increased, as shown in Figures 4 and 5. The same origin is considered in regard to these absorptions.

In the ^{13}C NMR spectra of polybutadiene or polyisoprene, resonances of methylene carbons in cis-1,4 units appear at approximately 5–7 ppm higher field than those of trans-1,4 units.¹⁸ The peaks at I and J appeared at about 5 ppm higher field than those at G and H. The resonances designated D and E appeared also at about 5 ppm higher field than those at A and B. Therefore, the resonances at D, E, I, and J may be attributed to methine and methylene carbons in cis-1,4 units, respectively. Since a polymer containing a high cis-1,4 content could not be obtained in this study, cis-1,4 units were generated by isomerizing trans-1,4 units.

Trans-Cis Isomerization. It is reported that cis and trans double bonds in poly-1,4-isoprene and butadiene can be isomerized readily without significant side reactions by irra-

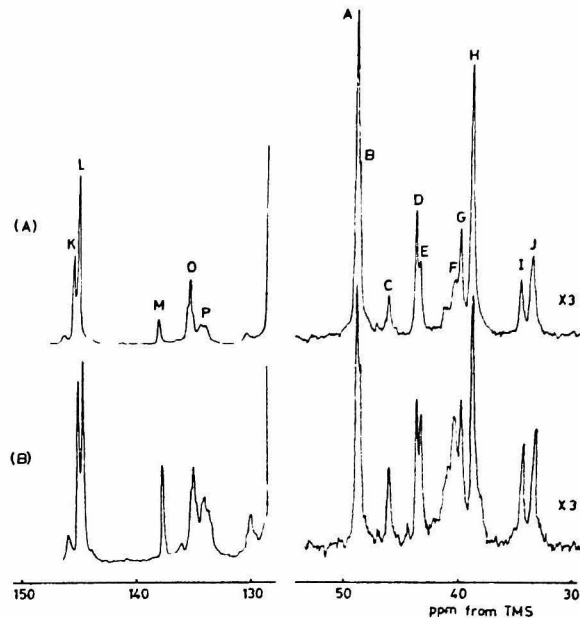


Figure 5. Expanded ^{13}C NMR spectra of (A) no. 12 and (B) no. 14.

diation with ultraviolet light.^{19,20} The dyad or triad sequence distributions of trans-1,4, cis-1,4, and vinyl units in such polymers were studied in detail.^{4,5} In these studies about 2% (w/v) polymer solutions in benzene were employed for the UV irradiation in the presence of photosensitizer. When poly1PB was isomerized at such concentrations, gelation took place immediately. Poly1PB is considered to be more sensitive to UV light than polybutadiene or polyisoprene. The isomerization of poly1PB was successfully carried out on the more dilute solution (0.1–0.2 w/v %). The sensitizer, thiobenzoic acid, was used at the same ratio to polymer (2–4 w/w % of polymer) as in the case of polybutadiene and polyisoprene.

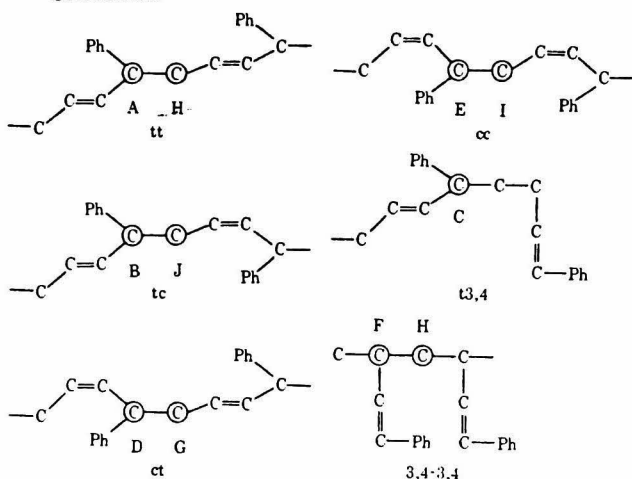
^{13}C NMR spectra and gel permeation chromatograms of sample no. 13 irradiated with UV light for 30, 120, and 240 min are shown in Figure 6. The resonances at B, D, E, G, I, and J in the aliphatic carbon region and K and P in the olefin carbon region increased in proportion to the irradiation time. On the other hand peaks at C, F, and M disappeared immediately after the irradiation. In the ^1H spectrum of the isomerized polymer the olefin proton resonance of 3,4-units disappeared and the lower field methine proton resonance at δ 3.39 ppm increased. This indicates that during the isomerization of trans internal double bond to cis, 3,4 double bonds were cyclized intramolecularly. Small changes in gel-permeation chromatograms in Figure 6 were attributed to intermolecular reaction during long irradiation. However, these side reaction did not interfere with the investigation on the isomerization of the trans-1,4 units. Since the effect of the side reaction was negligible and trans-cis isomerization was considered to occur predominantly, increases in the intensities of the absorptions at B, D, E, G, I, J, K, and P in proportion to the irradiation are due to the resonances of cis-1,4 unit isomerized from a trans-1,4 unit. These absorptions are attributed to the methine and methylene carbons of the trans-1,4-cis-1,4, cis-1,4-trans-1,4, or cis-1,4-cis-1,4 linkages. The assignments of these peaks in the aliphatic carbon region were made in dyad sequences in Table III.

Conti et al. reported additive parameters in order to calculate ^{13}C chemical shifts of styrene-butadiene copolymers and recently revised them.^{21,22} The additive parameters proposed by Conti²² can be applied to calculate the ^{13}C chemical shift of poly1PB. The results are listed in Table III. The calculated chemical shifts were in good agreement with the observed values. These facts also support the validity of

Table III
Assignment of Aliphatic Carbon Resonances in ^{13}C NMR Spectra^a

Peak	Chemical shift, ppm		Diff
	Obsd	Calcd	
A	48.7	48.2	0.5
B	48.6	48.2	0.4
C	46.1	45.8	0.3
D	43.7	42.7	1.0
E	43.5	42.7	0.8
F	40.5		
G	40.0	40.2	-0.2
H	39.0	40.2	-1.2
I	34.8	34.7	0.1
J	33.8	34.7	-0.9

^a Structures:



the assignments in Table III. Here, the peaks at A, E, H, and I were predicted to have the same chemical shifts as the peaks at B, D, G, and J, respectively. The sequence distributions of trans-1,4 and cis-1,4 were not reflected in the aliphatic carbon region of the ^{13}C NMR spectra according to the parameters. In the ^{13}C NMR spectra of polybutadiene sequence distributions of trans-1,4 and cis-1,4 were hardly observed in the aliphatic carbon region.^{1,2,23} However, from the relative intensities of peaks A to B, D to E, G to H, and I to J, it is obvious that these pairs of absorptions reflected the sequence distributions of trans-1,4 and cis-1,4 units in poly1PB. From the ^{13}C NMR spectra of poly1PB, it is confirmed that poly1PB has cis-1,4 unit as well as trans-1,4 and 3,4 units. The splitting of the methine proton resonances into peaks at 3.05 and 3.39 ppm is ascribed to trans-1,4 and cis-1,4 units, respectively. The fractions of trans-1,4-cis-1,4 and 3,4 units determined by ^1H

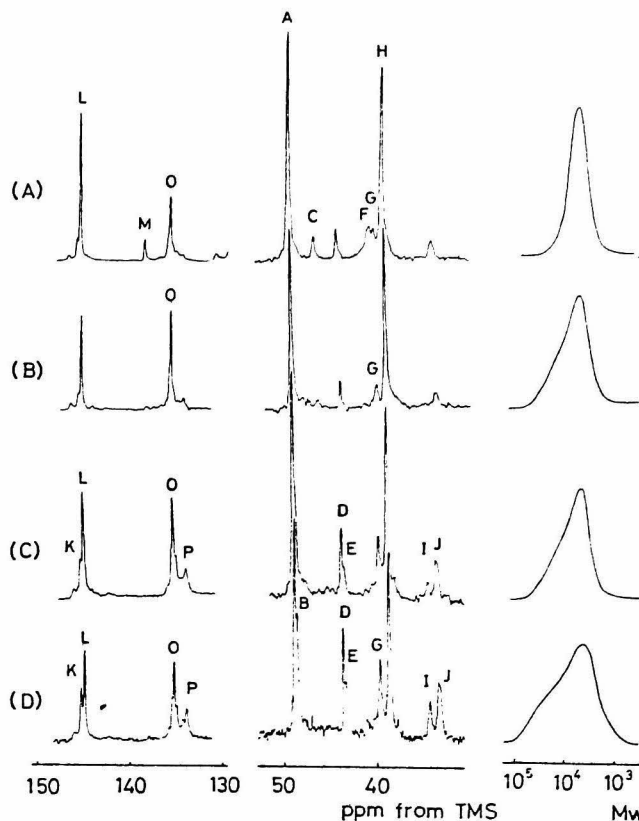


Figure 6. ^{13}C NMR spectra and gel-permeation chromatograms of trans-cis isomerized poly1PB: (A) original polymer (no. 13), (B) UV irradiation for 30 min, (C) UV irradiation for 120 min, and (D) UV irradiation for 240 min.

NMR spectra are listed in Table II. From the ^{13}C spectra the ratio of cis-1,4 units to trans-1,4 units can be estimated using the following equation.

$$\text{cis-1,4/trans-1,4} = \frac{I(D) + I(E)}{I(A) + I(B) + I(C)}$$

The results are listed in the last column in Table II compared with the values obtained from the ^1H NMR spectra. They are in good agreement. Since spin-lattice relaxation times (T_1) of aliphatic carbons of poly1PB in CDCl_3 were estimated to be shorter than 300 ms, the pulse interval of 3.5 s was sufficient for eliminating the effects of differences in T_1 for the different carbon atoms. Gated decoupling during sampling of the free induction decay suppressed the nuclear Overhauser effect almost completely.

The fractions of the dyad sequence distribution of trans-

Table IV
Sequence Distribution of Trans-1,4, Cis-1,4, and 3,4 Unit in Poly1PB^c

Sequence	Polymer								Peak ^b
	No. 16		No. 12		No. 14		UV irradi.		
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	
tt	0.69	0.70	0.42	0.41	0.25	0.24	0.47	0.48	A
tc	0.07	0.07	0.19	0.18	0.20 ^a	0.14	0.20	0.21	J
ct	0.06	0.07	0.18	0.18	0.16 ^a	0.14	0.21	0.21	G
	0.07	0.07	0.17	0.18	0.16	0.14	0.21	0.21	D
cc	0.01	0.01	0.08	0.08	0.11 ^a	0.08	0.10	0.10	E
	0.02	0.01	0.08	0.08	0.15 ^a	0.08	0.11	0.10	I
Trans-3,4	0.08	0.07	0.05	0.05	0.11	0.11			C

^a A part of c-3,4 resonance will be included in this region. ^b The fraction of each sequence was obtained from the peak intensity to total intensities of aliphatic carbon resonances. ^c Calculated values are based on the assumption of a random distribution of each unit.

1,4-trans-1,4 (tt), cis-1,4-cis-1,4 (cc), trans-1,4-cis 1,4 (tc), cis-1,4-trans-1,4 (ct), and trans-1,4-3,4 (t-3,4) were obtained from the ^{13}C spectra based on the assignment in Table III. The results are summarized in Table IV. The fractions of these dyad sequences were calculated assuming Bernoullian statistics. The observed and calculated dyad fractions are in good agreement, indicating that trans-1,4, cis-1,4, and 3,4 units are distributed randomly in poly1PB. In the case of sample no. 14 containing higher 3,4 units, however, the observed fractions of tc, ct, and cc sequences were larger than those calculated. This is due to the contribution of c-3,4-, 3,4-c, and 3,4-t sequences which were not negligible when the 3,4 content increased. The absorptions of carbons in such sequences may have appeared in the region overlapped with peaks E, I, and J.

As to head-to-head or tail-to-tail linkages, the methine carbon resonance in a head-to-head linkage is predicted to have a peak at δ 55.5 ppm according to calculations using the parameters proposed by Conti.²² There was no observable signal in that region in the ^{13}C NMR spectra of poly1PB. Therefore, poly1PB prepared by anionic polymerization could be considered to have very few head-to-head and consequently tail-to-tail linkages. This shows that the arrangement of head-to-tail linkages is controlled by the living end, and the microstructure of the terminal monomer unit is little affected by the structure of the penultimate unit.

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ABSTRACT: The 220-MHz ^1H and 25.05-MHz ^{13}C NMR spectra of poly(2-phenyl-1,3-butadiene) (poly2PB) samples prepared by anionic initiators were investigated. The resonances in the ^{13}C -NMR spectra were assigned by comparing them with the ^{13}C NMR spectra of poly(2-phenylbutadiene-1,1- d_2) and those of cis-trans isomerized poly2PB. The microstructure of the polymer depends on the polymerization temperature and is hardly affected by the polymerization solvent. Poly2PB polymerized at 57 °C has 98% cis-1,4 content. With a decrease in the polymerization temperature, the 1,2 content increases. The polymer prepared at -100 °C has 67% cis-1,4 and 33% 1,2 content. Dyad and triad sequence distributions of cis-1,4 and 1,2 units were estimated from the ^{13}C -NMR spectra. Observed sequence distributions were in good agreement with those calculated from the first-order Markov chain model.

In a previous paper, the microstructure of poly(1-phenylbutadiene) (poly1PB) prepared by anionic initiators was studied by means of ^1H - and ^{13}C -NMR spectra.¹ 2-Phenyl-1,3-butadiene (2PB) is the other monophenyl-substituted butadiene. The polymerizations of 2PB have been carried out by various kinds of initiators or catalysts. In the polymerization of 2PB with *i*-Bu₃Al-TiCl₄² or AlHCl₂-OEt₂-AlI₃-TiCl₄,³ the resulting polymers were reported to have mainly the cis-1,4 structure. In the cationic polymerization,^{4,5} it was reported that the polymer had mainly the 1,4 structure and that about half of the double bonds in the polymers were consumed by a cyclization. This kind of cyclization was shown in the cationic polymerization of 1PB. Asami et al.⁶ and Ambrose et al.⁷ studied the anionic polymerization of 2PB. Asami et al. reported that 2PB was polymerized to a high molecular weight polymer by sodium naphthalene or cumyl potassium in THF following living polymerization and that the resulting polymer had a high cis-1,4 content over a wide range of polymerization temperature (-78-60 °C). On the other hand, Ambrose reported that the polymer prepared in a nonpolar solvent had 93% 1,4 content and that the polymerization in polar media increased the vinyl content to 50% in a manner similar to that shown in the anionic polymerization of butadiene and isoprene. As shown in the previous paper, 1PB behaved in a quite different way in the anionic polymerization compared with butadiene or isoprene.¹ Therefore, it is interesting to determine the microstructure of poly2PB and to compare it with that of poly1PB.

In this paper, we have studied high-resolution ^1H - and ^{13}C -NMR spectra of poly2PB prepared by anionic initiators at various polymerization conditions and obtained detailed information concerning the microstructure of poly2PB and the mechanism of the polymerization.

Experimental Section

The general experimental procedures have been described in the previous paper.¹

Materials. 2-Phenyl-1,3-butadiene (2PB) was synthesized from acetophenone and vinylmagnesium bromide followed by dehydration over potassium hydrogen sulfate.⁸ Since 2PB thus obtained was contaminated with a small amount of acetophenone and undehydrated alcohol, the monomer was purified by column chromatography using activated alumina (200 mesh, Wako) as absorbent and *n*-hexane as eluent. The first fraction was collected

and distilled over LiAlH₄ (85 °C (37 mmHg)). The monomer was stored under argon at -15 °C.

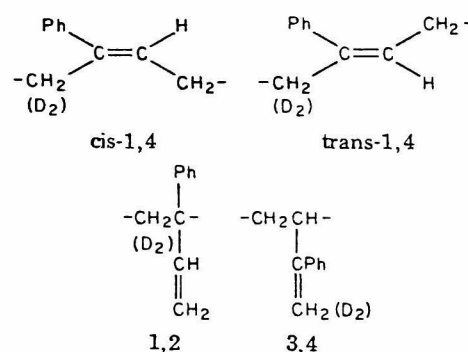
2-Phenyl-1,3-butadiene-1,1- d_2 (2PB-1,1- d_2) was prepared from acetophenone- d_3 by the same procedure as the preparation of 2PB. The acetophenone- d_3 was obtained by the repeated deuterium exchange reaction of acetophenone with D₂O in the presence of NaOD at 60 °C. The deuteration degree of 2PB-1,1- d_2 was 96%.

^1H - and ^{13}C -NMR Spectra. ^1H -NMR spectra were recorded using Varian HR-220 and HR-300 spectrometers. ^{13}C -NMR spectra were measured on a JEOL JNM FX 100 spectrometer (25.05 MHz). Both ^1H - and ^{13}C -NMR measurements were carried out at ambient probe temperature on CDCl₃ solutions of polymer with tetramethylsilane as an internal standard.

Typical conditions for the quantitative ^{13}C measurement were: spectral width 5 kHz, acquisition time 0.812 s, data points 8192, pulse width 7 μs (42°), pulse repetition 15 s, number of transients 1000-2000. Gated decoupling was employed during the sampling of the free induction decay.

Results and Discussion

The following four structural units can be contained in poly2PB. Polymerization conditions and microstructures



of the polymers are listed in Table I. The microstructures in Table I will be discussed later. According to gel permeation chromatography, the polymers in this study have narrow molecular weight distributions ($M_w/M_n = 1.2-1.3$). The molecular weight is proportional to the feed ratio of monomer to initiator, that is, this polymerization as well as that of poly1PB is of the so-called living type.

220- and 300-MHz ^1H -NMR Spectra of Poly2PB. Figure 1 shows ^1H -NMR spectra (220 MHz) of typical polymers. In contrast to poly1PB, in the case of poly2PB relative intensities of olefin to phenyl proton resonances depend entirely on the microstructure of the polymer. The

Table I
Polymerization Conditions and Microstructure of Poly2PB^a

no.	initiator	solvent	temp, °C	microstructure, ^b %		olefin H/aromatic H	
				cis-1,4	1,2	obsd ^d	calcd
1	Na-Naph ^c	THF	57	98		0.20	0.20
2	Na-Naph	THF	50	97	3	0.21	0.21
3	<i>t</i> -BuLi	diglyme	50	97	3	0.20	0.21
4	Na-Naph	THF	30	95	5	0.21	0.22
5	<i>s</i> -BuLi	toluene	30	92	8	0.21	0.23
6	Na-Naph	THF	0	90	10	0.23	0.24
7	<i>t</i> -BuLi	THF	0	90	10	0.23	0.24
8	<i>s</i> -BuLi	toluene	0	90	10	0.22	0.24
9	Na-Naph	THF	-30	80	20	0.28	0.28
10	Na-Naph	THF	-78	72	28	0.31	0.31
11	<i>s</i> -BuLi	THF	-78	74	26	0.31	0.30
12	<i>t</i> -BuLi	THF	-78	73	27	0.30	0.31
13	Na-Naph	THF	-100	67	33	0.33	0.33

^a Polymerization time 4.0 h; conversions are quantitative; [2PB]₀ = 1.0 mol/L, [initiator] = 1.4 × 10⁻² mol/L. ^b Estimated from ¹³C-NMR spectra. ^c Sodium naphthalene. ^d Estimated from ¹H-NMR spectra.

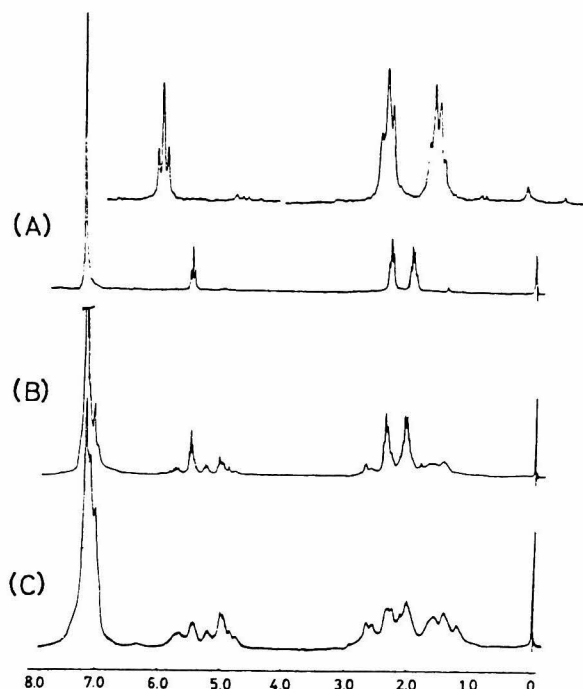


Figure 1. 220-MHz ¹H-NMR spectra of poly2PB: (A) no. 1; (B) no. 8; and (C) no. 11.

polymers prepared at 57 °C (polymer 1) and 0 °C (polymer 8) are essentially 1,4 polymer, as evidenced by the ratio of olefin to phenyl proton resonances, one to five. In addition, in the spectrum of polymer 1 sharp peaks and spin-spin couplings can be seen, showing high structural regularity of the polymer. In the case of poly1PB, all the resonances are broader and spin-spin couplings are hardly observed due to the presence of 3,4 and cis-1,4 unit along with the predominant trans-1,4 unit.

As the polymerization temperature decreases, the ¹H-NMR spectra show complicated patterns. This indicates that a structure other than 1,4 units increases in the polymer chain with a decrease in the polymerization temperature. Figure 2B shows the 300-MHz ¹H-NMR spectrum of polymer 11. The resolution of the spectrum is improved and the absorptions in the olefinic and aliphatic regions are separated into several sets of resonances, which are designated as in Figure 2B. Tentative assignments of these resonances are discussed later.

25.0-MHz ¹³C-NMR Spectra of Poly2PB. Further studies of the microstructure of the polymer are discussed as revealed by ¹³C-NMR spectra. Figure 3 shows the

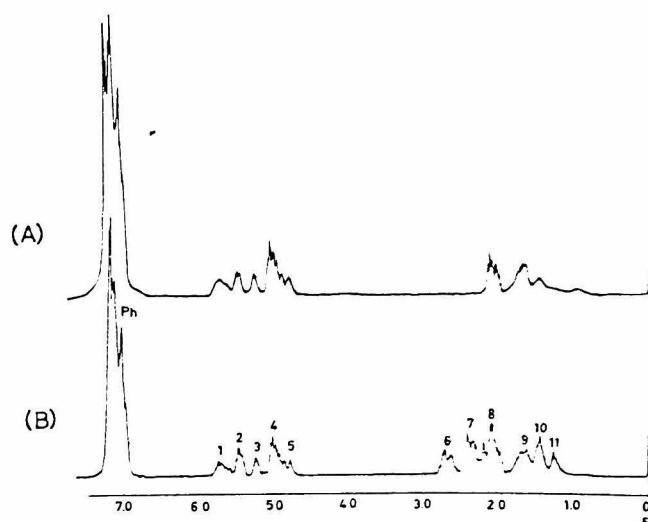


Figure 2. 300-MHz ¹H-NMR spectra of (A) poly2PB-1,1-d₂ and (B) poly2PB no. 11.

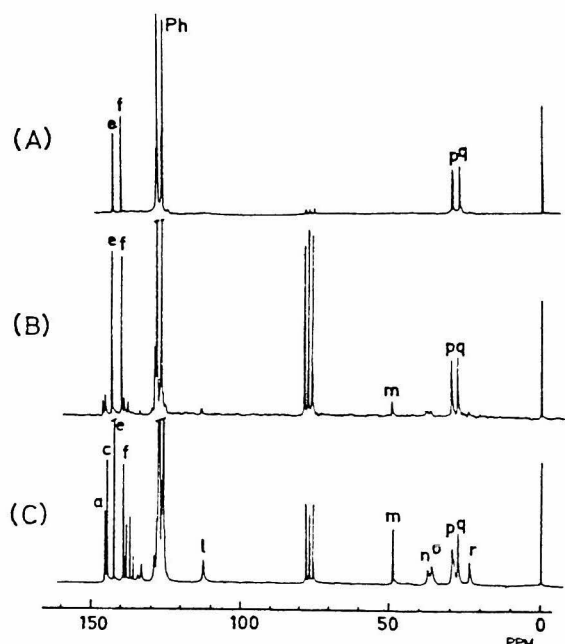


Figure 3. 25.05-MHz ¹³C-NMR spectra of poly2PB: (A) no. 1; (B) no. 8; and (C) no. 11.

¹³C-NMR spectra of poly2PBs. ¹³C-NMR spectra of poly2PB polymerized at 57 °C (polymer 1) or 0 °C

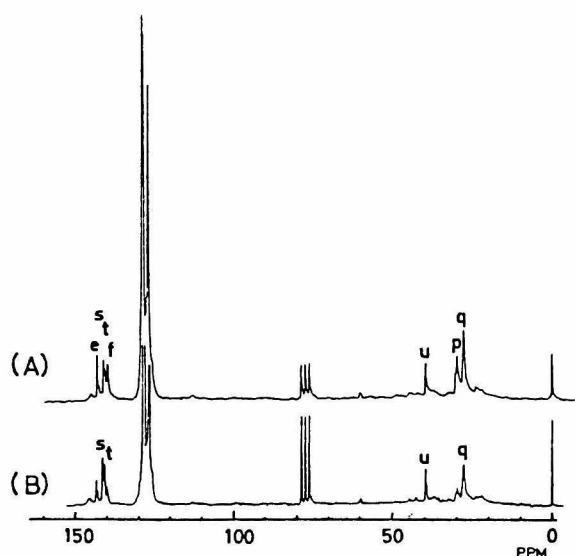


Figure 4. 25.05-MHz ^{13}C -NMR spectra of cis-trans isomerized poly2PB; UV irradiation for (A) 30 min and (B) 60 min.

(polymer 8) are simple and the principal resonances are assigned to carbons in 1,4 units. Two peaks at p and q are attributed to the methylene carbons in 1,4 units. The methylene carbon resonances appear at about 10 ppm higher field than those of *trans*-1,4-poly1PB. Generally, methylene carbons flanked by cis olefin double bonds appear at higher field than those flanked by *trans*.⁹ Therefore, the double bond in the 1,4 unit of the polymer can be assumed to be cis. Ultraviolet spectra of *cis*-2-phenyl-2-butene (λ_{max} 245 nm) and *trans*-2-phenyl-2-butene (λ_{max} 235 nm) were investigated by Stille et al.² as model compounds to elucidate the microstructure of poly2PB. The polymers in this study have an absorption maximum at 247 nm (in THF, $\log \epsilon = 4$). This result also suggests that the double bond in the 1,4 units is cis. Polymer 1 is considered to have more than 98% cis-1,4 linkages. The *trans*-1,4 structure may be disfavored due to the steric hindrance of the phenyl group and the monomer adds selectively to the cis-1,4 structure at higher polymerization temperatures.

On the other hand, poly2PB prepared at lower temperature shows complicated ^{13}C -NMR spectra. This indicates that the microstructure of poly2PB is controlled by the polymerization temperature and that a structure other than cis-1,4 units increases with decreasing polymerization temperature, as suggested by the ^1H -NMR spectra. The microstructure of poly2PB prepared at lower temperature will be discussed subsequently.

Cis-Trans Isomerization. In order to determine the presence of *trans*-1,4 units in poly2PB, cis-trans isomerization was carried out. It is reported that cis and *trans* double bonds in poly-1,4-isoprene and butadiene can be isomerized readily with each other without significant side reaction by irradiation with ultraviolet light.¹⁰ As shown in the previous paper, the *trans*-cis isomerization of poly1PB with UV irradiation was successfully carried out employing dilute solutions (0.1–0.2 wt/vol % in benzene).¹ The cis-trans isomerization of poly2PB was also carried out under the same conditions. ^{13}C -NMR spectra of UV irradiated polymer 1 are shown in Figure 4. In the aliphatic carbon region of the spectra the relative intensity of a new peak at u (39.5 ppm) increases and that of the peak at p decreases in proportion to the irradiation time. The sum of the intensities of the peaks at u and p are equal to that of the peak at q. Gel permeation chromatograms of the polymers did not show any significant change during

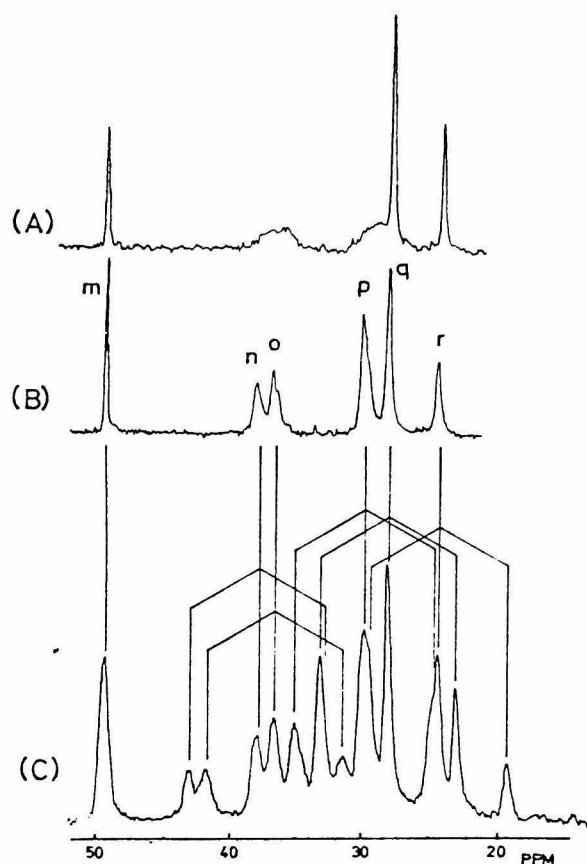


Figure 5. 25.05-MHz ^{13}C -NMR spectra of (A) poly2PB-1,1- d_2 , (B) no. 11, and (C) proton coupled spectra of no. 11.

the irradiation and in the ^1H -NMR spectra of the isomerized polymers relative intensities of phenyl to olefin proton resonances are 5. These results indicate that side reactions such as cyclization and main chain scission are negligible and cis-trans isomerization is considered to be the principal reaction caused by the irradiation. The peak at u is attributed to the methylene carbon in *trans*-1,4 units isomerized from cis-1,4 units. The other methylene carbon resonance of the *trans*-1,4 unit may appear overlapped completely with the peak at q. The peaks which appear at s and t are attributed to the aromatic C-1 and the olefin carbon in *trans*-1,4 units, respectively. In the ^{13}C -NMR spectra of the polymer prepared at -78°C (Figure 3C), no observable peaks can be seen at s, t, and u. The absence of these peaks indicates that the poly2PB prepared in this study has too small quantities of *trans*-1,4 units to be detected by ^{13}C -NMR spectra (less than 1%).

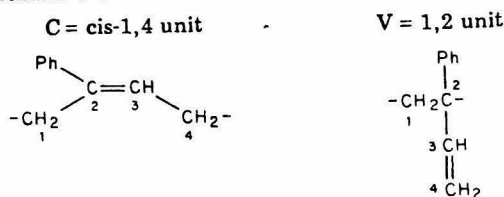
The presence of 3,4 units will now be discussed. Figure 5C shows the proton-coupled ^{13}C -NMR spectrum of the aliphatic region of polymer 11. The peak at m appears as a singlet. This peak, therefore, is attributed to the quaternary carbon in 1,2 units. On the other hand, the peaks at n, o, p, q, and r all appear as triplets with a coupling constant of 128 Hz. This indicates that these peaks are all to be attributed to methylene carbons. If the polymer contains 3,4 units, a doublet resonance due to C-H coupling of the methine carbon should appear. As such a resonance cannot be found in the spectrum, poly2PB's in this study contain almost no 3,4 units.

^1H - and ^{13}C -NMR Spectra of Poly2PB-1,1- d_2 . In order to discuss the microstructure of the polymer more precisely, 2PB-1,1- d_2 was synthesized and polymerized. The microstructure of poly2PB-1,1- d_2 is shown above (positions of deuteriums are shown in parentheses). Figure 2A shows a ^1H -NMR spectrum of poly2PB-1,1- d_2 prepared

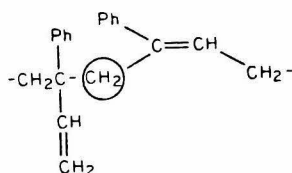
Table II
Assignments of Peaks in ^{13}C -NMR Spectra of Poly2PB

peak	chemical shift	assignment ^a	peak	chemical shift	assignment
a	145.8	V(Ph-1)	j	134.7	VCV(3)
b	145.6	V $\overline{\text{C}}\text{V}(\text{Ph-1})$	k	133.3	V $\overline{\text{C}}\overline{\text{C}}(3)$
c	145.2	V(3)	l	112.5	V(4)
d	145.0	V $\overline{\text{C}}\overline{\text{C}}(\text{Ph-1})$	m	49.2	V(2)
e	142.9	C $\overline{\text{C}}\overline{\text{C}}(\text{Ph-1}) + \text{C}\overline{\text{C}}\text{V}(\text{Ph-1})$	n	37.7	V $\overline{\text{C}}(1)$
f	139.6	C $\overline{\text{C}}\overline{\text{C}}(2)$	o	36.4	V(1)
g	138.6	C $\overline{\text{C}}\text{V}(2)$	p	29.7	C $\overline{\text{C}}(1)$
h	137.1	V $\overline{\text{C}}\overline{\text{C}}(2)$	q	27.7	C $\overline{\text{C}}(4)$
i	136.2	V $\overline{\text{C}}\text{V}(2)$	r	23.9	C $\overline{\text{V}}(4)$

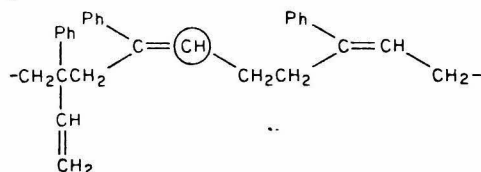
^a Each carbon atom is designated as follows: Ph-1 = aromatic C-1 carbon



for example, V $\overline{\text{C}}(1)$ means



V $\overline{\text{C}}\overline{\text{C}}(3)$ means



under the same conditions as polymer 11. If the polymer contains 3,4 units, relative intensities of olefin to phenyl proton resonances must decrease in the spectrum of the poly2PB-1,1-d₂. This is almost the same within an experimental error in both spectra (0.31 and 0.30), showing that poly2PB in this study has almost no 3,4 units.

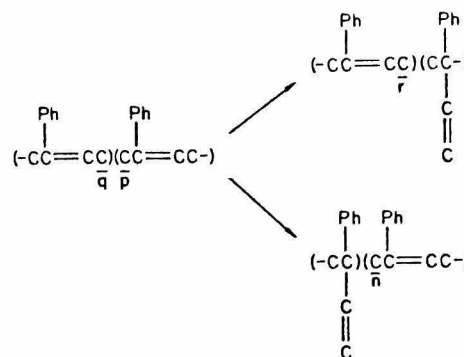
Figure 5A shows the ^{13}C -NMR spectrum of poly2PB-1,1-d₂. The resonances of the carbons attached to deuteriums are broadened due to ^{13}C -D couplings and quadrupole broadening. The peaks at n, o, and p are broadened in Figure 5A, indicating that the peaks at n, o, and p are attributed to the carbons attached to the deuteriums, that is, the carbons in one position (C-1).

The assignments of the peaks in the aliphatic region of ^{13}C -NMR spectra are made in dyad sequence distributions of cis-1,4 (C) and 1,2 unit (V) and are shown in Table II. The assignments of the peaks at n and o are made by the aid of their relative intensities, that is, $I(o)$ is larger than $I(n)$ by $f(vv)$ as follows:

$$I(o) \propto f(v) = f(vv) + f(cv) = f(vv) + f(vc)$$

$$I(n) \propto f(vc)$$

where, for example, $I(o)$ means the relative intensity of the peak at o and $f(vv)$ means the fraction of the sequence of VV. The resonances of C-1 and C-4 in 1,4 units are shifted to n and r by a flanking 1,2 unit as shown below:



On the other hand, aliphatic carbon resonances of 1,2 units remain unshifted even if a flanking unit changes. The peaks at o and p are observed as envelopes of partially separated resonances, showing triad sequence distributions which appear more explicitly in the olefin and aromatic C-1 regions.

The fractions of cis-1,4 and 1,2 units are calculated using the following equations from the ^{13}C -NMR spectra measured with suppressed NOE and the longer pulse repetition (listed in Table I)

$$f(c) = \frac{I(n) + I(p) + I(q) + I(r)}{I(m) + I(n) + I(o) + I(p) + I(q) + I(r)} \times 100$$

$$f(v) = \frac{I(m) + I(o)}{I(m) + I(n) + I(o) + I(p) + I(q) + I(r)} \times 100$$

where $f(c)$ and $f(v)$ mean the fraction of cis-1,4 and 1,2 unit, respectively. Since the longest spin-lattice relaxation times (T_1) of carbons of poly2PB in CDCl_3 were estimated to be shorter than 3.0 s, the pulse repetition of 15 s was sufficient for eliminating the effects of differences in T_1 . The gated decoupling during sampling of the free induction decay suppressed NOE almost completely. The ratio of the olefin to phenyl proton resonances varies with the microstructure of the polymer. The ratios observed in the ^1H -NMR spectra are in good agreement with the values calculated from $f(c)$ and $f(v)$ thus obtained. This fact shows that the cyclization reported by Ambrose et al. is negligible in the anionic poly2PB.

2PB behaves in a quite different way in the anionic polymerization compared with butadiene or isoprene. The microstructure of poly2PB is hardly affected by the nature of the polymerization solvent, while it is the dominant factor determining the microstructure of polybutadiene and polyisoprene. The nature of the counterion, sodium or lithium, also does not affect the microstructure. The microstructure of poly2PB depends on the polymerization temperature. An effect of the solvent, however, appears in a few cases. 2PB did not polymerize in toluene at -78 °C with butyllithium. Addition of tenfold quantities of THF to butyllithium initiates polymerization even at -78 °C. The microstructure of the resulting polymer is almost the same as that of polymer 11. The microstructure becomes complicated when the polymerization is carried out in benzenes at elevated temperature. In this case, the polymer may contain 3,4 units and cyclization reactions appear to occur.

The assignment of the peaks in the olefinic and aromatic carbon regions of the ^{13}C -NMR spectra is carried out as follows. In a partial spectrum with increased computer resolution (0.24 Hz) (Figure 6C), a peak at c can be observed to be overlapped with a peak at d. As the T_1 values of these two peaks are sufficiently different, the double pulse technique (WEFT) was applied to separate these peaks.¹¹ Figure 6A and 6B shows off-resonance and noise decoupled spectra, respectively, which were obtained by

Table III
Sequence Distribution of Cis-1,4 and 1,2 Units in Poly2PB

sequence	polymer 6			polymer 12			polymer 13			peak ^a
	obsd	calcd ^c	calcd ^d	obsd	calcd ^c	calcd ^e	obsd	calcd ^c	calcd ^f	
Dyad										
CC	0.79	0.81		0.51	0.53		0.40	0.45		q
VC	0.10	0.09		0.23	0.20		0.28	0.22		n
CV	0.10	0.09		0.23	0.20		0.27	0.22		r
VV ^b	0.01	0.01		0.03	0.07		0.05	0.11		
Triad										
CCC	0.70	0.73	0.70	0.36	0.39	0.36	0.22	0.30	0.23	f
CCV	0.09	0.08	0.09	0.15	0.14	0.15	0.16	0.15	0.16	g
VCC	0.10	0.08	0.09	0.16	0.14	0.16	0.17	0.15	0.17	h
VCV	0.01	0.001	0.01	0.07	0.05	0.07	0.12	0.07	0.11	i

^a The observed fraction of each sequence was obtained from intensity of this peak. ^b This observed fraction was obtained by subtracting the sum of the fractions of CC, VC, and CV from 1.00. ^c Calculated assuming Bernoullian statistics. ^d Calculated assuming first-order Markov chain model: $P_{c/c} = 0.88$, $P_{c/v} = 1.00$, $P_{v/c} = 0.12$, and $P_{v/v} = 0$. ^e $P_{c/c} = 0.70$, $P_{c/v} = 0.85$, $P_{v/c} = 0.30$, and $P_{v/v} = 0.11$. ^f $P_{c/c} = 0.59$, $P_{c/v} = 0.85$, $P_{v/c} = 0.40$, and $P_{v/v} = 0.15$.

Table IV
Assignments of Resonances in ¹H-NMR Spectra of Poly2PB

peak	δ from Me ₄ Si	assignment ^a	intensities ^b	
			obsd	calcd
1	5.75	V(3)	0.27	0.27
2	5.49	CCC(3)	0.35	0.36
3	5.24	CCV(3)	0.16	0.16
4	5.02	V(4)	0.51	0.54
5	4.76	VCC(3) + VCV(3)	0.22	0.23
6	2.70	VCC(1) + VCV(1)	0.47	0.46
7	2.38	CCC(1)	0.69	0.72
8	2.09	CCV(4) + CCV(1)	0.98	1.02
9	1.67	CCV(4) + VCC(4)	0.56	0.62
10, 11	1.42, 1.19	V(1) + VCV(4)	0.76	0.68

^a These notations of protons are the same that are in Table II. ^b These are expressed as relative intensities to that of phenyl proton resonances which are always 5.00.

applying a 3.0 s–180°–0.6 s–90° pulse sequence. The pulse interval of 0.6 s gave the partially relaxed spectra; peaks except c, j, and k are not recovered due to the longer T_1 of these carbons. The spectra in Figure 6 show the following results: (a) The peaks at c and d are attributed to the different kind of carbons, that is, the peak at c, having shorter T_1 , is assigned to –CH= and the peak at d, showing longer T_1 , is attributed to the carbon α to phenyl in cis-1,4 units respectively. (b) The peaks at j and k are attributed to –CH= carbons. The assignments of the peaks are carried out by comparing the observed intensities of the peaks and the sequence distributions calculated assuming Bernoullian or first-order Markov statistics with the aid of the results of the off-resonance spectra. The results of the assignments are shown in Table II.¹² The peaks attributed to carbons in the central unit of CCC(3) and CCV(3) may be overlapped with ortho, meta, and para carbon resonances. No carbon resonances of 1,2 units are shifted by changing a flanking unit in all regions of the ¹³C-NMR spectra.

Sequence Distribution in Poly2PB. The fractions of dyad and triad sequence distributions are obtained from ¹³C-NMR spectra recorded with suppressed NOE and longer pulse repetition times and are summarized in Table III. Four probabilities characterizing the first-order Markov chain model are calculated from the following equations.

$$P_{c/c} = f(cc)/f(c) \quad P_{c/v} = f(vc)/f(v)$$

$$P_{v/c} = f(cv)/f(c) \quad P_{v/v} = f(vv)/f(v)$$

The designation $P_{c/v}$, for example, means the probability that the monomer adds in cis-1,4 fashion to a 1,2 chain end.

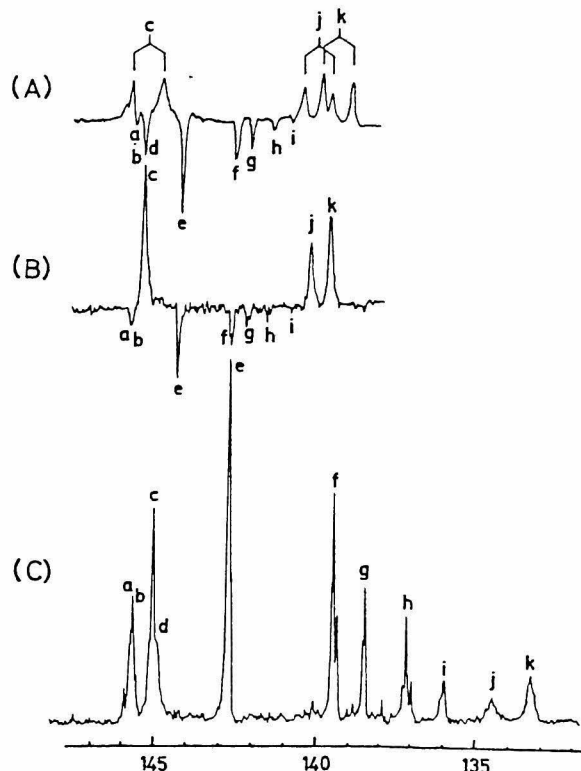


Figure 6. 25.05-MHz ¹³C-NMR spectra of No. 13. Partially relaxed spectra by applying a 3.0 s–180°–0.6 s–90° pulse sequence: (A) off-resonance and; (B) noise decoupled spectra; (C) partial spectrum with an increase in computer resolution (0.24 Hz).

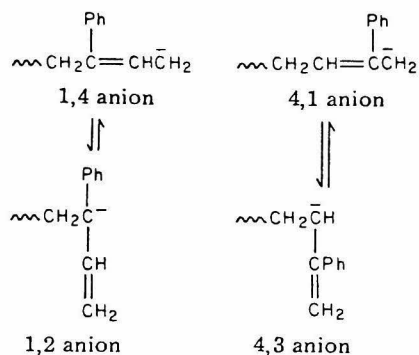
No carbon resonances of 1,2 units are observably split by triad sequence distributions. The observed and calculated

sequence distributions are in good agreement when the 1,2 content is low in both of the statistics. However, the sequence distributions calculated from Bernoullian statistics deviated from the observed ones with an increase in 1,2 content, while those calculated from the first-order Markov chain model are still in good agreement. The steric hindrance may arise when the monomer adds in 1,2 fashion to a 1,2 chain end. This may cause the deviation from the random distribution and make the polymer follow the first-order Markov chain model. Pentad sequence distributions can be seen in the peaks at f, g, h, and i. However, as the splitting of the peaks is insufficient, fractions of them cannot be obtained.

The assignment of proton resonances in Figure 2B are carried out with the aid of the relative intensities of the resonances and the spectrum of poly2PB-1,1-d₂. The results are listed in Table IV.¹² The observed intensities of the resonances and those calculated assuming a first-order Markov chain model are in good agreement in the olefinic proton region. In the aliphatic region, however, the assignments are difficult due to strongly overlapping resonances, and only tentative assignments are made.

According to the conclusions of this and the previous paper, differences in the behavior of 1PB and 2PB in the anionic polymerization may be summarized as follows: (a) The microstructure of poly2PB depends on the polymerization temperature, while that of poly1PB is independent of it. (b) The nature of solvent hardly influences the microstructure of poly2PB. The microstructure of poly1PB, however, is affected by it. (c) Both 2PB and 1PB are polymerized predominantly to the 1,4 polymer. The 1,4 double bond is entirely cis in poly2PB, whereas the trans-1,4 units are mixed with a small amount of cis-1,4 in poly1PB. (d) Pure 1,4 polymer is obtained in the case of poly2PB. 1,4-Polymer is contaminated by 3,4 units in the case of 1PB. (e) The sequence distributions in poly2PB are expressed by the first-order Markov chain model, while that in poly1PB conforms to Bernoullian statistics.

Schué et al. studied a living oligomer of poly2PB prepared with *t*-BuLi-d₉ in benzene-d₆ and reported that the ratio of 1,4 to 4,1 anion was 1.7.^{13,14} The polymers in our study contain only cis-1,4 and 1,2 units, and do not contain head-to-head and/or tail-to-tail linkages. Therefore, the anionic propagating species at high temperature is considered to be the 1,4 anion, not the 4,1, whereas that of isoprene is reported to be the 4,1 anion.¹⁵ This is further



confirmed by the ¹H-NMR spectrum of 2PB oligomer prepared at 60 °C. In this spectrum methyl protons of the chain end can be seen at δ 1.75 as a doublet (*J* = 7 Hz),

not as a singlet, after termination by methanol, indicating the 1,4 chain end of the oligomer. At high temperature the 1,2 chain end may be unstable due to a low ceiling temperature such as shown in the anionic polymerization of α -methylstyrene, and the monomer adds to the 1,4 chain end selectively. The chain end was shown above as σ allyl. However, the π -allyl type chain end can be considered. Further studies on the living chain end are in progress.

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Appendix. Infrared Spectra of Poly2PB.

In the spectra of poly2PB distinctive absorption appeared at 840, 865, 909, and 1005 cm⁻¹. Relative intensities of the absorption at 909 and 1005 cm⁻¹ to 865 cm⁻¹ increased when the polymerization temperature decreased regardless of the nature of the polymerization solvents. These absorptions were assigned by several authors using model compounds. Stille² ascribed the absorption at 840 cm⁻¹ to the double bond of a cis-1,4 unit. This absorption, however, does not change after hydrogenating the polymer, while the absorption at 865 cm⁻¹ disappears. Asami⁶ ascribed the absorption at 865 cm⁻¹ to cis-1,4 units and the absorption at 909 and 1005 cm⁻¹ to 1,2 units. On the other hand, Ambrose⁷ ascribed the absorption at 865 cm⁻¹ to 3,4 units and the absorption at 1005 cm⁻¹ to 1,2 units. According to our results for the microstructure of poly2PB, our assignments are consistent with Asami's.

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PART II Characterizations of Active Species in
 Anionic Polymerizations of Phenylbutadienes

Chapter 3

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

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.

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 alkyllithium 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 paper.¹

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*₆ 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.

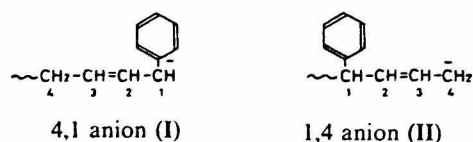
RESULTS AND DISCUSSION

Propagating Species in Anionic Polymerization of 1PB

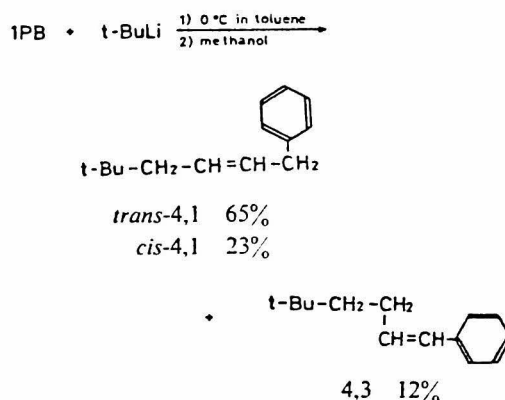
The microstructure of poly(1PB) reported in a previous paper¹ is summarized in Table I. Poly(1PB) has predominantly a *trans*-1,4 structure even if the polymerization was carried out in THF. *Cis*-1,4 and 3,4 units increase with a decrease in the polarity of the polymerization solvent. This behavior 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



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.



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)*

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

* 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 1. The reaction did not proceed in pure hydrocarbon solvent.

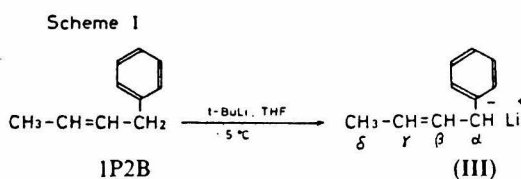


Figure 1 shows the 25.0 MHz ^{13}C NMR spectra of lithiated 1P2B (III) in THF. Chemical shifts of the carbon resonances are listed in Table II. Small resonances at 17.8 and 39.0 ppm show the presence of a small quantity of unreacted 1P2B. ^{13}C chemical shifts and ^{13}C -H coupling constants of phenylallyllithium 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

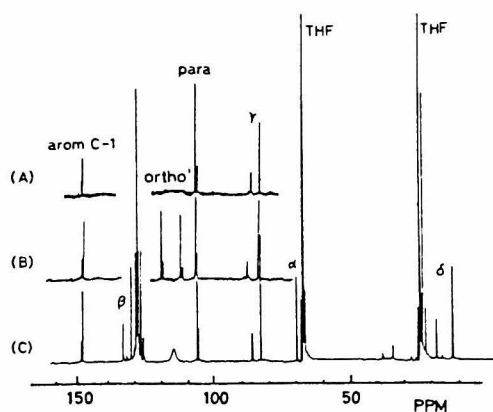


Figure 1. 25.0 MHz ^{13}C NMR spectra of lithiated 1P2B (III) at various temperatures: (A) 0°C, (B) -45°C, and (C) 24°C; 1P2B 2.37 mmol, THF 1.5 cm³, and 3.00 mol dm⁻³ *t*-BuLi benzene-*d*₆ solution, 0.87 cm³.

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 phenylallyllithium,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 $\Delta H^\ddagger = 9.5$ kcal mol⁻¹ (39.7 kJ mol⁻¹) and $\Delta S^\ddagger = -12$ cal mol⁻¹ deg⁻¹ (-50.2 J K⁻¹ 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 IP2B and living oligomeric IPBLi

Position	Lithiated IP2B		Living oligomeric IPBLi			
	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 IP2B (III) contains *cis* and *trans* isomers in the ratio of 3:1.^{*1} Although the meta-

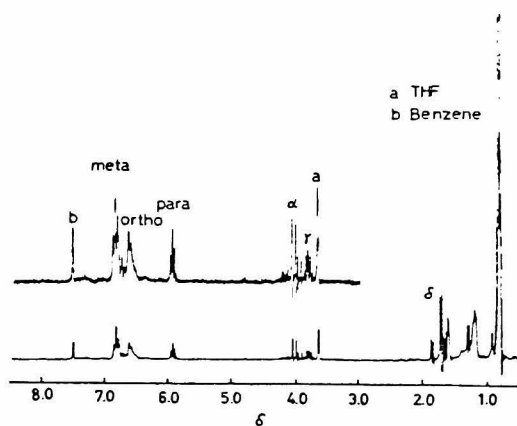


Figure 2. 220 MHz ^1H NMR spectrum of lithiated IP2B (III): IP2B 0.08 mmol, THF- d_6 0.3 cm^3 , and 1.36 mol dm^{-3} *t*-BuLi benzene- d_6 solution, 0.15 cm^3 .

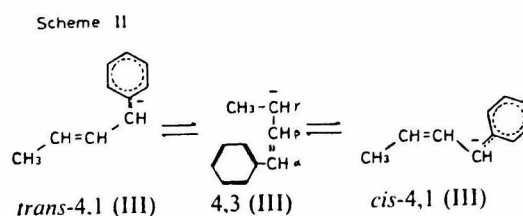
^{*1} H. Kloosterziel reported a *cis*-4,1 tendency for a potassium salt of IP2B in ref 28.

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 ¹³C 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

*² Although this result is inconsistent with the microstructure of poly(1PB) obtained in THF, the product distributions after protonation of phenylallyl 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 ¹³C chemical-shift data obtained for lithiated 1P2B can be safely used to understand the ¹³C 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.



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 ¹³C 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

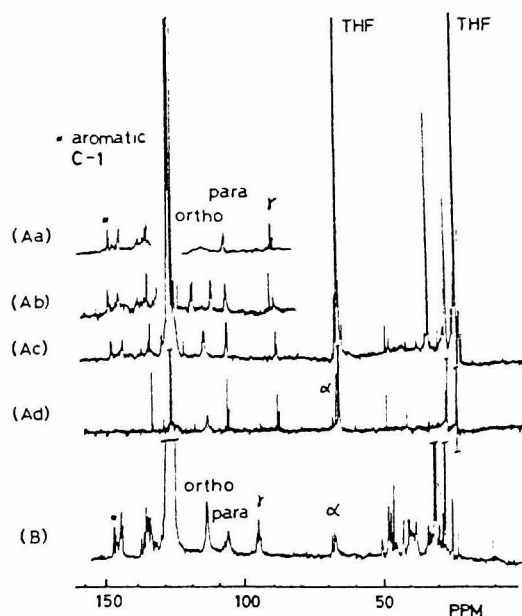


Figure 3. 25.0 MHz ¹³C NMR spectra of living oligomeric 1PB at various temperatures: (Aa) 6°C, (Ab) -40°C, and (Ac) 24°C in THF; (Ad) spectrum recorded at 24°C by applying a 180°-5.0s-90°-20s pulse sequence; (B) 24°C in benzene-*d*₆. (Aa-c) \overline{DP} = 5.8, (Ad), \overline{DP} = 3.6, and (B) \overline{DP}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

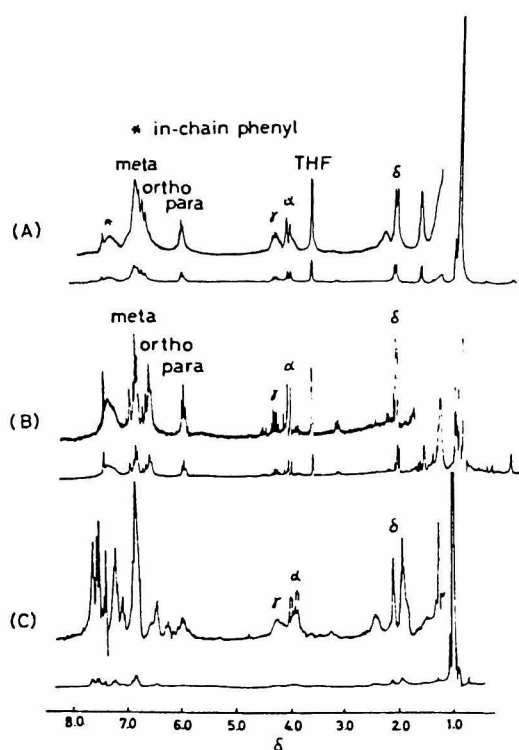
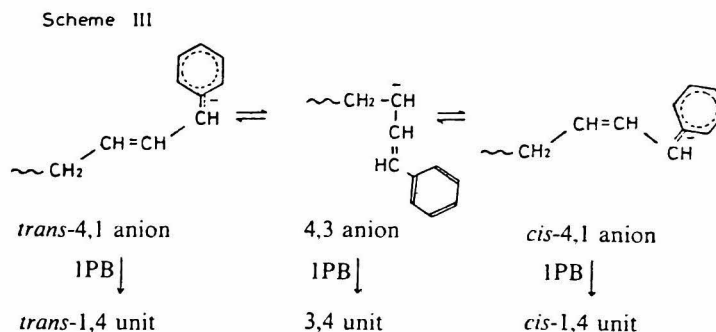
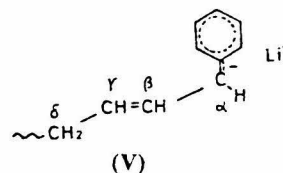


Figure 4. 220 MHz ^1H NMR spectra of living oligomeric 1PB: (A) $\overline{\text{DP}}=1.2$ in $\text{THF-}d_8$, (B) $\overline{\text{DP}}=3.2$ in $\text{THF-}d_8$, and (C) $\overline{\text{DP}}=3.5$ in $\text{toluene-}d_8$.

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).



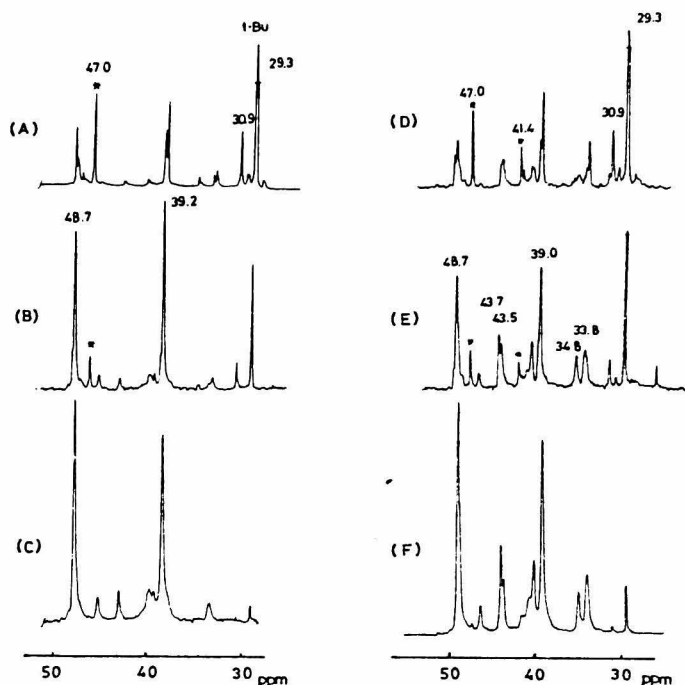


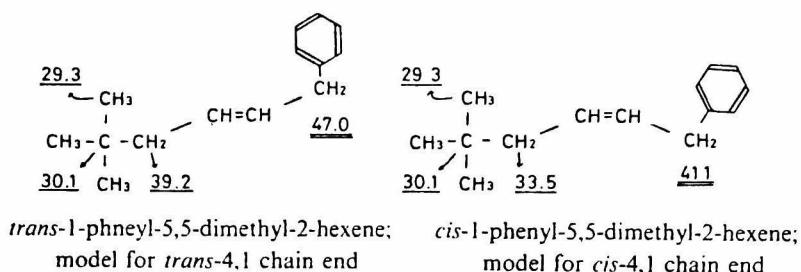
Figure 5. ^{13}C NMR spectra of methanol terminated oligomeric IPB: (A) $\text{DP}=2.5$, (B) $\text{DP}=20$, and (C) $\overline{\text{DP}}=90$ prepared in THF; (D) $\overline{\text{DP}}=2.4$, (E) $\overline{\text{DP}}=15$, and (F) $\overline{\text{DP}}=75$ prepared in benzene. * shows the terminal methylene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

Geometry of Double Bond in the Chain End of Oligomeric IPB

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 IPB clearly supported the above results. As shown in Figures 5A, B, and C, the methanol

terminated oligomeric IPB 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 6/4^{*4}). 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 IPB were fractionally collected from the adducts of *t*-BuLi and IPB by gas chromatography on a column DEGA 2.25 m. The ^{13}C chemical shifts of the model compounds are shown below.

*4 *Cis*-4,1 isomer was predominant in the case of lithiated IP2B(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.

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

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 (3PIB) 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.

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(3PIB) was synthesized from methylenetriphenylphosphorane and α -phenyl-propionaldehyde 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; $[2\text{PB}]_0 = 0.12\ \text{M/l}^{-1}$ and $[2\text{PB}]/[t\text{-BuLi}] = 6.0$. 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; $[3\text{P1B}]_0 = 0.48\ \text{M/l}^{-1}$ and $[t\text{-BuLi}]/[3\text{P1B}] = 1.1$. 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: $[2\text{PB}]_0 = 0.48\ \text{M/l}^{-1}$ and $[t\text{-BuLi}]/[2\text{PB}] = 1.2$.

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

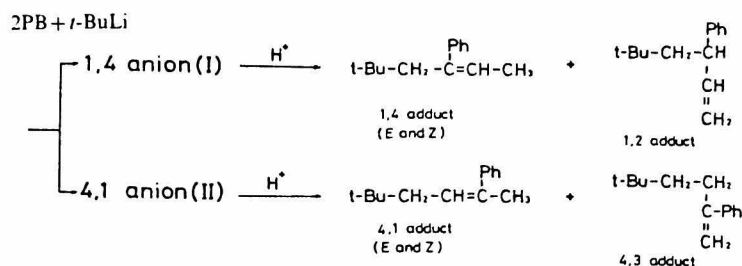
Table II. Product distribution of one to one adduct of 2PB with *t*-BuLi^a

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

^b Product distributions are analyzed by GLC (PEG 20M) following assignments of Schuë.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 Schuë *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

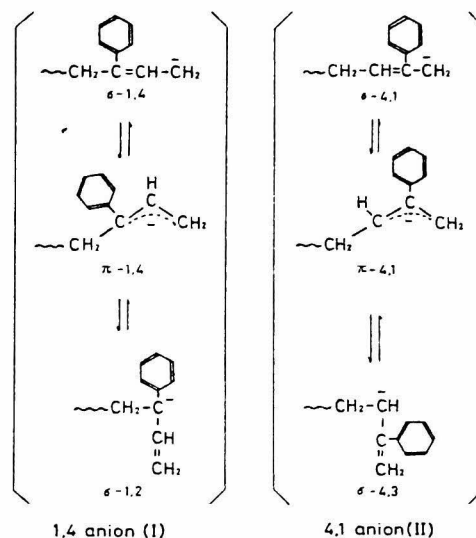


Figure 1. Two possible isomeric structures of propagating species in the anionic polymerization of 2PB.

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.

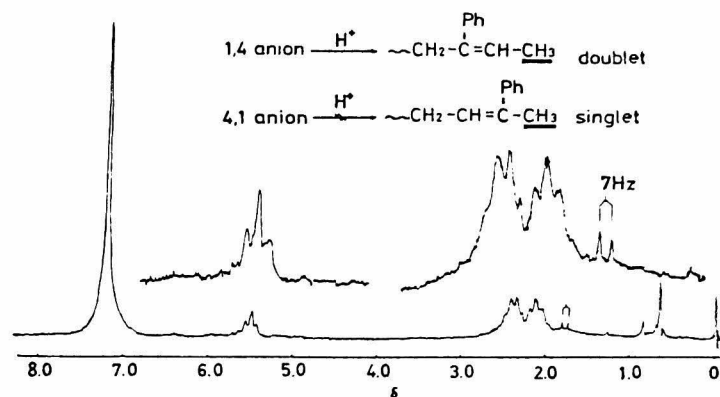


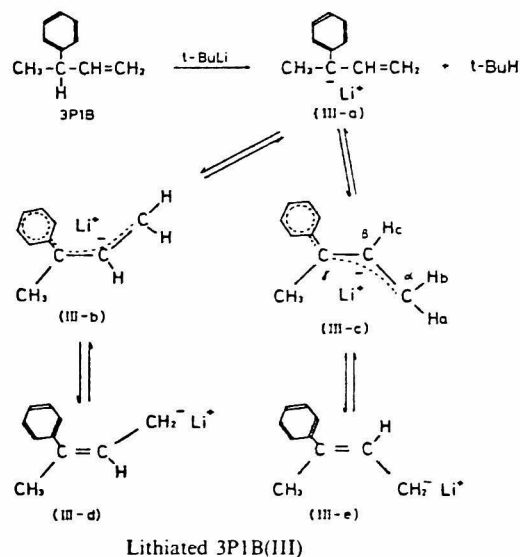
Figure 2. The 100 MHz ^1H NMR spectrum of oligomeric 2PB protonated with methanol; M_n of oligomer = 1400; $M_w/M_n = 1.6$.

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 $\text{THF-}d_6$. 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 benzyl^{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

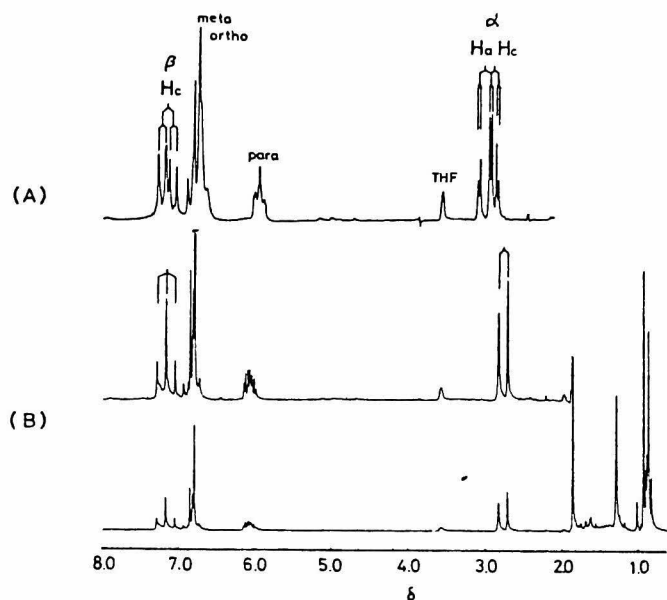


Figure 3. The 100 MHz ^1H NMR spectra of lithiated 3P1B(III) at various temperatures; (A) -40°C and (B) 24°C .

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.

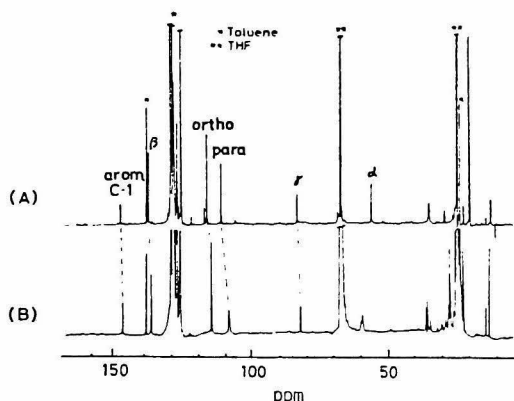
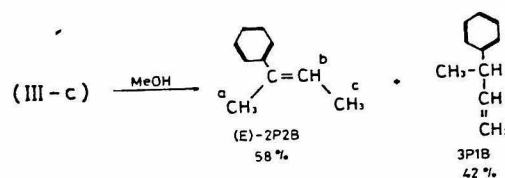


Figure 4. The 25.0 MHz ^{13}C -NMR spectra of lithiated 3P1B(III) at various temperatures: (A) 24°C and (B) -40°C .

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 2.25 m 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 Oligomeric 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

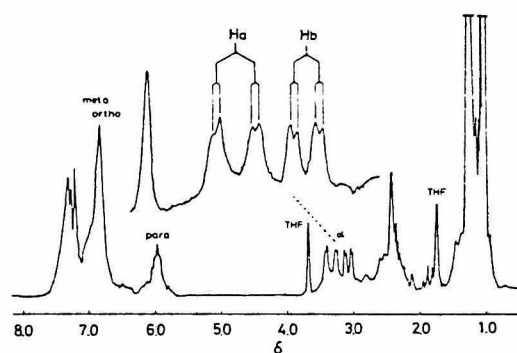


Figure 5. The 100 MHz ^1H NMR spectrum of oligomeric 2PBLi; measured at -47°C ; $DP=2.1$.

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.

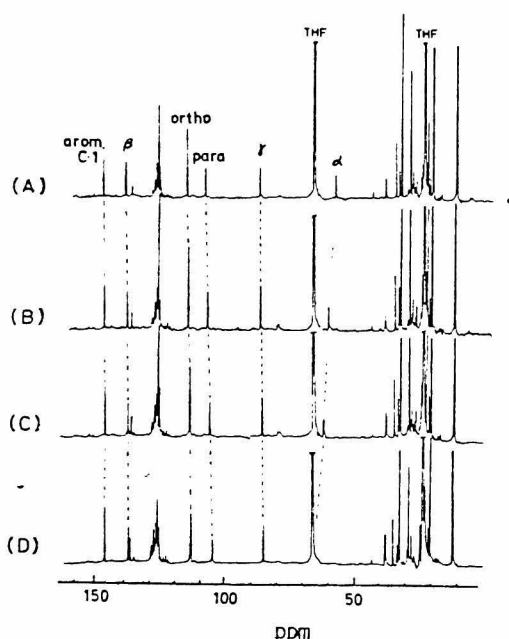
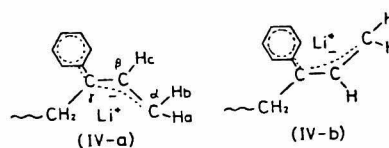


Figure 6. The 25.0 MHz ^{13}C NMR spectra of oligomeric 2PBLi at various temperatures: (A) 24°C, (B) 0°C, (C) -20°C, and (D) -45°C; $\overline{DP} = 1.7$.

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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Chapter 5

Reactivity of **Substituted** Phenylallyllithiums

— Regioselectivity in the Reaction with Several Electrophiles

ABSTRACT

The reactivities of several substituted phenylallyllithiums have been investigated in the 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 π -benzyl type anions and the latter two as π -allylphenyl type anions according to negative charge distributions. In the reactions of these substituted phenylallyllithiums with methanol (protonation) the difference in the negative charge distribution does not affect the product distribution, and reactivity of the α -position (terminal of the anion) is high (54 ~ 94%). When methyl iodide is reacted, α -products (products reacted at the α -position) are selectively obtained (96 ~ 98%) in the case of the π -benzyl type anions, whereas the amount of the α -products decreased (45 ~ 85%) in the case of the π -allylphenyl type anions. These behavioral differences can be attributed to

the differences in the negative charge distributions. However, in the reaction with trimethylchlorosilane or trimethylchlorotin, steric effect at the α - or γ -carbon controls the regioselectivity of the product. In the reaction with acetone or ethylene oxide, α -products are obtained predominantly in the case of the π -benzyl type anions, whereas γ -products are obtained in the case of π -allylphenyl type anions. These differences are interpreted by the steric requirements in the transition states.

INTRODUCTION

Structures of living anion chain ends in the polymerizations of conjugated dienes have been extensively studied to elucidate the polymerization mechanisms¹⁻¹⁴. Numbers of discussions on the π -electron distribution of living oligomer chain ends or model anions of them were developed. On the other hand, regioselectivity in the reaction of such model anion with electrophile was paid little attention. Miginiac studied the reaction of 2-pentenyllithium with alkylketones¹⁵. Glaze et al. reported the reaction of neopentylallyllithium with several electrophiles^{2, 4}. However, in some cases the regioselectivity in the reactions cannot be interpreted simply by the negative charge distributions of the anions^{2, 4}.

In previous papers, we have studied microstructures of poly(1-phenyl-1,3-butadiene)¹⁶ and poly(2-phenyl-1,3-butadiene)¹⁷ prepared by anionic polymerization, and elucidated π -electron distributions of the living oligomer chain ends of the model anions^{18, 19}.

In this paper we will study the reactions of 1- or 3-alkylsubstituted phenylallyllithiums with several electrophiles, and discuss the factors controlling the regioselectivity in the reactions.

EXPERIMENTAL

Materials

trans-1-Phenyl-1,3-butadiene (1PB)¹⁶, 2-phenyl-1,3-butadiene (2PB)¹⁷, 3-phenyl-1-butene (3P1B)¹⁹, and *t*-BuLi¹⁶ 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 under 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) under argon atmosphere. The reaction mixture was stirred for 3.0 h. Addition of *t*-BuLi (1.5 mmol) to 2PB (1.0 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 at various conditions. Ethylene oxide (EO) was distilled into the anion solution directly under high vacuum. The reactions were completed disappearing red color instantaneously by the addition of the electrophiles.

Identification of the product

The protonated products were identified in previous papers ¹⁸, ¹⁹. The other products were analyzed and fractionally collected by a GLC (DEGA 3 mm ϕ \times 2.25 m or SE-30 3 mm ϕ \times 1.5 m). The collected fractions were identified by a FT ¹H NMR spectroscopy. The spectral data are shown in Table II.

¹H NMR spectra

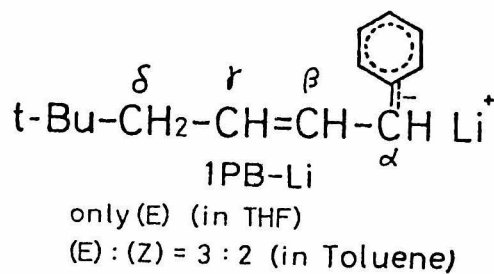
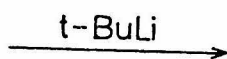
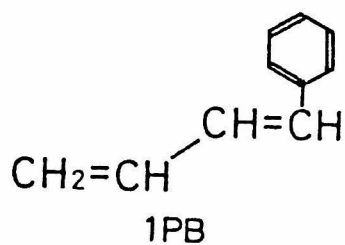
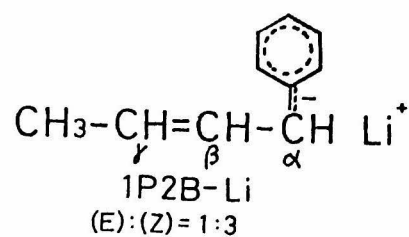
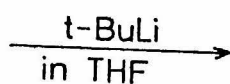
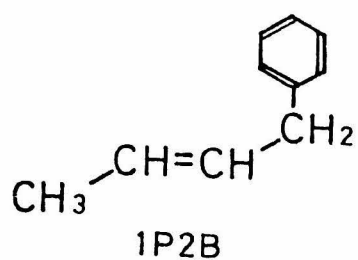
¹H NMR spectra were recorded with a JEOL JNM FX 100 Fourier Transform (FT) NMR spectrometer (100 MHz). The measurements were carried out on carbon tetrachloride solution with a small amount of d₆-benzene for internal lock. Typical conditions for the ¹H FT measurements were: spectral width, 1000 Hz; acquisition time, 4.10 s; data point, 16 K; pulse width, 7 μ s (42 $^\circ$); pulse repetition, 20 s; number of transients, 4 \sim 128.

RESULTS AND DISCUSSION

Negative charge distributions of the substituted phenylallyllithiums

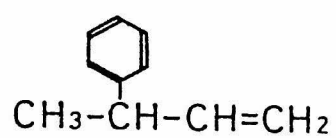
The anions employed in this study are classified into two different types according to the ¹³C and ¹H NMR studies as discussed in previous papers ¹⁸, ¹⁹. One is π -benzyl type and the other is π -allylphenyl type. Scheme I shows formation

Scheme I

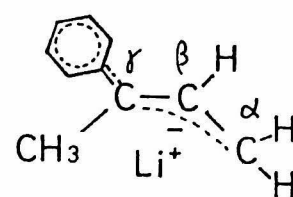
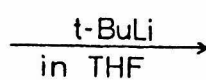


of the π -benzyl type anions, which are the model anions for propagating chain end of 1PB in polymerization. In the reaction of 1P2B with t-BuLi, the lithiation occurs selectively at the α -position, and the anion thus generated was designated as 1P2B-Li. One-to-one addition of t-BuLi to 1PB is carried out as shown in Scheme I in THF and toluene. In the reactions the t-Bu anion attacks the δ -carbon selectively. The one-to-one adduct was obtained selectively (more than 98%) in THF, whereas higher oligomers were also obtained in toluene; 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-alkylsubstituted phenylallyllithiums. As shown in a previous paper¹⁸, in both 1P2B-Li and 1PB-Li negative charge is located at the α -carbon and the phenyl ring, and delocalization to the γ -carbon is small. Therefore, these are classified as the π -benzyl type anions. In Scheme II formation of the π -allylphenyl type anions are illustrated. In the lithiation of 3P1B with t-BuLi, the lithiation occurs regioselectively at the γ -position. The anion thus obtained is called 3P1B-Li. One-to-one addition of t-BuLi to 2PB is 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-anion (t-Bu anion attacks the δ -carbon of 2PB) and 4,1-anion (t-Bu anion attacks the α -carbon) were generated in 92 and 8 % yield respectively. The 1,4-anion, 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, considerable amount of the 4,1-

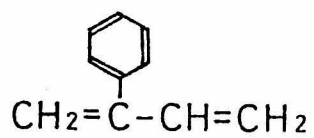
Scheme II



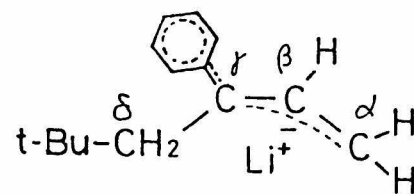
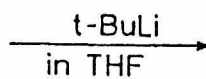
3P1B



(E)-3P1B-Li



2PB



(E)-2PB-Li

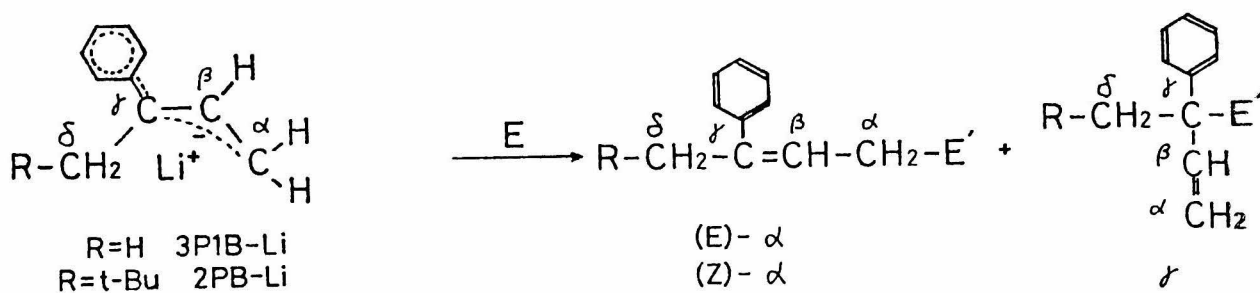
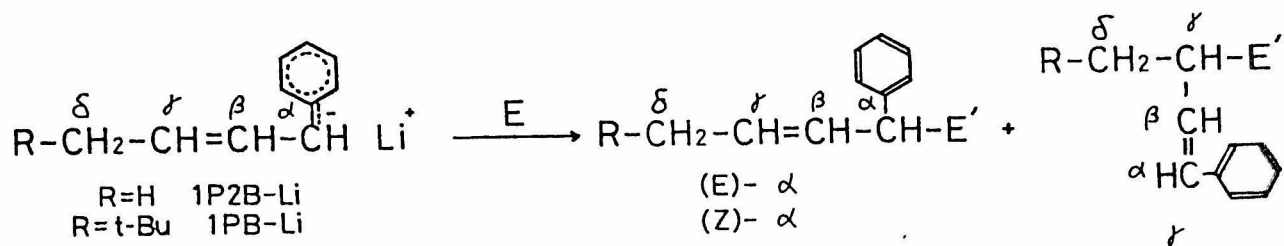
anion (35%) was formed. These 3PlB-Li and 2PB-Li are regarded as 1-alkylsubstituted phenylallyllithiums. As revealed in previous study ¹⁹, in both 3PlB-Li and 2PB-Li negative charge delocalizes over a π -allyl system and the phenyl ring.

In the anionic polymerizations of 1PB and 2PB, 1,4-structures are predominant regardless of the polymerization conditions ^{16, 17}. Therefore, in the polymerization conditions the reactivities of the α -positions seem to be the highest in both the π -benzyl and π -allylphenyl type anions.

Product distribution in reactions with several electrophiles

Scheme III shows products expected in the reactions of the substituted phenylallyllithiums with electrophile, E. For these anions, the notations of α -, β -, γ - and δ -position are given respectively from the anion end as shown in the Scheme. The reaction with the electrophile, E, can occur either at α - or γ - position. The reaction products are designated as (E)- α , (Z)- α , and γ depending on the reaction center. In the case of the π -benzyl type anions (1P2B-Li and 1PB-Li), the α -products are expected to be major products, considering the higher electron density at the α -position shown by the ¹³C NMR spectroscopic results ¹⁸. On the other hand, in the case of the π -allylphenyl type anions (3PlB-Li and 2PB-Li) increases in the proportions of the γ -products will be expected as the negative charge delocalizes over the π -allyl system and the electron density at the γ -position increases ¹⁹. We will discuss the α - to γ -product ratio and compare the results with

Scheme III



the regioselectivity expected from the negative charge distribution.

Runs 1 to 9 in Table I show the product distributions in the protonation reactions with methanol. The ratios of the α -products, combined yield of (E)- α and (Z)- α , to the γ -products are almost the same between the products from 1P2B-Li and those from 3P1B-Li (in both R=H in Scheme III) where the negative charge distributions are quite different each other as mentioned above. The ratios of the α -products to γ -products are also comparable between the products from 1PB-Li and those from 2PB-Li (in both R=t-Bu) whose negative charge distributions are also quite different. Thus, the product distributions with protonation are not affected by the negative charge distributions of the anion, but slightly affected by the steric effect of the R groups of the anions.

Runs 10 to 18 in Table I show the product distributions in the substitution reactions with MeI, TMS-Cl, and TMT-Cl. In the reactions of the π -benzyl type anions with MeI (runs 10 to 14), the amount of the α -product reached more than 96%. This means the reactions occurred at more sterically hindered α -position with high regioselectivity. As the electron rich α -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 or TMT-Cl) are reacted, the amounts of the γ -products increase due to the steric hindrance between the phenyl substituent at the α -position and the reactants (runs 19 to 23 and runs 28 to 32). In the reactions of 1PB-Li with

Table I Product distribution in reactions of substituted phenyllithiums

E	-E'	solvent	temp. /°C	n-benzyl type anions			π-allylphenyl type anions		
				IP2B-Li(%) (E)-α (Z)-α γ	IPB-Li(%) (E)-α (Z)-α γ	3PIB-Li(%) (E)-α (Z)-α γ	2PB-Li(%) (E)-α (Z)-α γ		
CH ₃ OH	-H	THF	0	(1) ^{b)} 19 35 46	(3) 70 8 22	(6) 61 0 39	(8) 81 0 11		
CH ₃ OH	-H	THF	-78	(2) 42 32 26	(4) 71 11 18	(7) 78 0 22	(9) 86 0 6		
CH ₃ OH	-H	toluene	0	- - -	(5) 65 23 12	- - -	- - -		
CH ₃ I	-CH ₃	THF	0	(10) 82 14 4	(12) 85 11 4	(15) 45 0 55	(17) 78 0 15		
CH ₃ I	-CH ₃	THF	-78	(11) 94 3 3	(13) 88 11 1	(16) 45 0 55	(18) 78 0 15		
CH ₃ I	-CH ₃	toluene	0	- - -	(14) 72 26 2	- - -	- - -		
TMS-Cl ^{c)}	-Si(CH ₃) ₃	THF	0	(19) 56 11 33	(21) 91 4 5	(24) 100 0 0	(26) 91 0 0		
TMS-Cl	-Si(CH ₃) ₃	THF	-78	(20) 59 13 28	(22) 92 3 5	(25) 100 0 0	(27) 91 0 0		
TMS-Cl	-Si(CH ₃) ₃	toluene	0	- - -	(23) 61 21 18	- - -	- - -		
TMT-Cl ^{d)}	-Sn(CH ₃) ₃	THF	0	(28) 8 4 88	(30) 68 12 20	(33) 100 0 0	(35) 61 18 13		
TMT-Cl	-Sn(CH ₃) ₃	THF	-30	(29) 6 5 89	(31) 75 11 14	(34) 100 0 0	(36) 65 23 4		
TMT-Cl	-Sn(CH ₃) ₃	toluene	0	- - -	(32) 61 24 15	- - -	- - -		
acetone	-C(CH ₃) ₂ OH	THF	0	(37) 30 25 45	(39) 58 4 38	(42) 0 0 100	(44) 93 0 0 (45) (46 0 47)		
acetone	-C(CH ₃) ₂ OH	THF	-78	(38) 59 27 14	(40) 75 0 25	(43) 9 0 91	(46) 93 0 0		
acetone	-C(CH ₃) ₂ OH	toluene	0	- - -	(41) 40 31 29	- - -	- - -		
EO ^{e)}	-(CH ₂) ₂ OH	THF	-78	(47) 43 57 0	(48) 100 0 0	(50) 0 0 100	(51) 12 10 71		
EO	-(CH ₂) ₂ OH	toluene	-78	- - -	(49) 100 0 0	- - -	- - -		

a) 7 ~ 9 % of the 4,1-anion was formed.

b) In parentheses run numbers are shown

c) trimethylchlorosilane

d) trimethylchlorotin

e) ethylene oxide

TMS-Cl and TMT-Cl, the amount of the γ -products did not exceed 20% (runs 21 to 23 and runs 30 to 32). The bulkiness of the R (t-Bu) group will also participate in the reactions. On the other hand, when the π -allylphenyl type anions are reacted with MeI (runs 15 to 18), the γ -products increase as compared with the γ -products from the π -benzyl type anions. The γ -positions of the π -allylphenyl type anions are more sterically hindered than those of the π -benzyl type anions. In the π -allylphenyl type anions, however, the negative charge delocalizes over π -allyl system. Therefore, the electron density on the γ -position becomes higher and the reactivity of that position increases as compared with that of the π -benzyl type anion. The steric effect of the R group is observed in the reactions of 2PB-Li with MeI (runs 17 and 18) where the amount of the γ -product is smaller than that from 3PlB-Li (runs 15 and 16). When more bulky substrates, TMS-Cl or TMT-Cl, are reacted, any γ -products cannot 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 γ -products were formed. This behavior cannot be accounted for. In this manner, the product distribution is affected by the negative charge distribution when the size of substrate is small. On the other hand, it is determined by the steric effect when the bulky substrates are reacted.

Runs 37 to 51 in Table I show the results of the reactions with acetone or EO. In general, allylic organometallic

compounds react with these oxygen-containing substrates predominantly to give γ -products²⁰. For these reactions six-center cyclic ($S_E i'$) or non-cyclic ($S_E 2'$) mechanisms have been proposed²¹⁻²⁴. In the present study the π -benzyl type anions are reacted with acetone (runs 37 to 41) to give 55 ~ 86% α -products in spite of the phenyl substituent at the α -position. These results are in contrast to the results that neopentylallyllithium gives 22 ~ 45% α -products in the reactions with ketones having less steric hindrance^{2, 4}. In the reactions of the π -benzyl type anions with EO only α -products are formed (runs 47 to 49). In this way the π -benzyl type anions are liable to give the α -products in the reactions with acetone or EO. On the other hand, except the reactions of 2PB-Li with acetone (runs 44 and 46), the π -allylphenyl anions are reacted with acetone (runs 42 and 43) or EO (runs 50 and 51) to give predominantly γ -products. In the reactions of 3PlB-Li with acetone or EO the γ -products are formed exclusively (runs 42, 43, and 50). In the reactions of 2PB-Li with acetone (runs 44 and 46) the γ -product, which is main product in the former cases, could not be obtained due to the steric hindrance of R (t-Bu) group. When n-Bu group is used instead of t-Bu as R, that is, one-to-one adduct of n-BuLi and 2PB, the steric hindrance of R group against acetone is reduced and the γ -product is obtained in 47 % yield (run 45). In this manner, the π -allylphenyl type anions are liable to give the γ -products in the reaction with acetone or EO. These different behaviors between the π -benzyl and the π -allylphenyl type anions are attributed to the

difference in the transition states in the reactions. When the π -benzyl type anions are reacted with acetone or EO, the four center transition states as shown in (I) and (II) in Figure 1 can be assumed ($S_E i$), since the negative charge is located at the α -carbon and phenyl ring. Therefore, the reactions take place at the α -carbon to give the α -products. Since the steric hindrance against the phenyl ring is larger in (I) than (II), the transition state of (I) gives partially the γ -product (14 ~ 45%, runs 37 to 41), whereas that of (II) gives the α -product exclusively (runs 47 to 49). In contrast, in the reactions of the π -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 delocalize over π -allyl system and the phenyl ring. These transition states will lead to the γ -products ($S_E i'$). However, in the reaction of 2PB-Li with acetone (R=t-Bu in (III) in Figure 1), the transition state like (III) cannot be formed because of the steric repulsion of the t-Bu group against acetone. When R is changed to n-Bu, considerable amount of the γ -product is obtained *via* the transition state like (III) due to the reduction of the steric repulsion (run 45). Such steric effect is slightly observed in the reaction of 2PB-Li with EO where 22 % α -product is obtained (run 51), whereas in the reaction of 3PlB-Li with EO no α -product is formed (run 50). In this manner, in the reactions with acetone or EO the product distribution can be interpreted by the steric requirement in the transition state.

Throughout the α -products in this study configurations

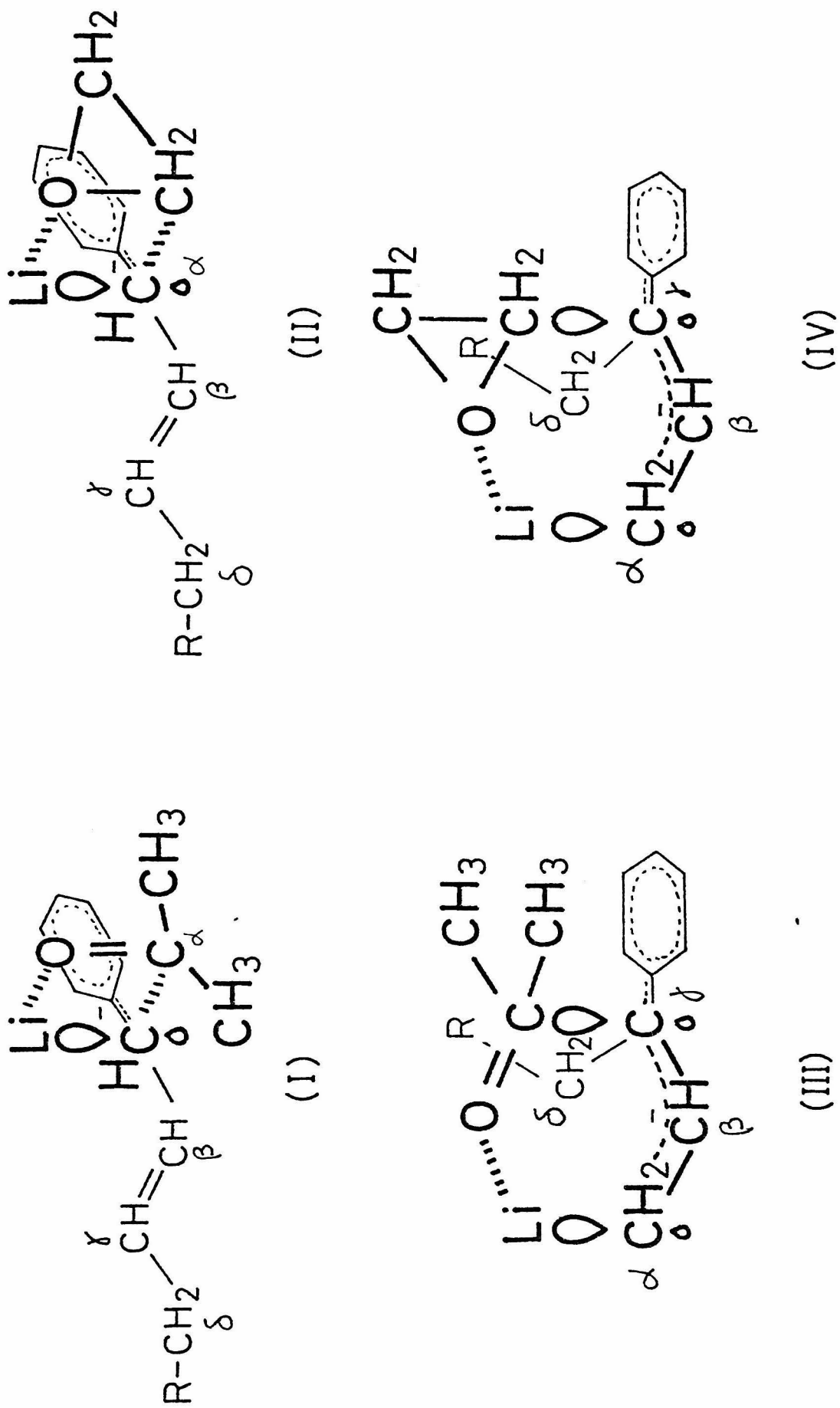


Figure 1 Transition states in reactions of substituted phenylallyllithiums with acetone or ethylene oxide

Table II ^1H NMR spectral data of products

run No.	anion	-E' structure	data δ (6)
(10)	1P2B-L1	-CH ₃ (E)- α	1.30(3H, d, -CH ₃), 1.63(3H, d, -CH ₃), 3.31(1H, qui, -CH-), 5.44(2H, m, -CH=CH-), 7.08(5H, m, ph)
(11)	1P2B-L1	-CH ₃ (Z)- α	1.30(3H, d, -CH ₃), 1.63(3H, d, -CH ₃), 3.70(1H, qui, -CH-), 5.44(2H, m, -CH=CH-), 7.08(5H, m, ph)
	1P2B-L1	-CH ₃ γ	0.74(6H, d, -CH ₃), 1.88(1H, m, -CH-), 5.36(2H, m, -CH=CH-), 7.08(5H, m, ph)
(12)	1P2B-L1	-CH ₃ (E)- α	0.87(9H, s, -CH ₃), 1.33(3H, d, -CH ₃), 1.88(2H, d, -CH ₂ -), 3.36(1H, qui, -CH-),
(13)			5.43(2H, m, -CH=CH-), 7.12(5H, m, ph)
(14)	1P2B-L1	-CH ₃ (Z)- α	0.90(9H, s, -CH ₃), 1.30(3H, d, -CH ₃), 1.98(2H, d, -CH ₂ -), 3.71(1H, qui, -CH-),
			5.43(2H, m, -CH=CH-), 7.12(5H, m, ph)
(15)	3P1B-L1	-CH ₃ (E)- α	1.06(3H, t, -CH ₃), 1.98(3H, s, -CH ₃), 2.16(2H, qui, -CH ₂ -), 5.66(1H, t of q, =CH-),
(16)	3P1B-L1	-CH ₃ γ	7.16(5H, m, ph) 1.36(6H, s, -CH ₃), 4.97(2H, d of m, =CH ₂), 5.94(1H, d of d, -CH=), 7.17(5H, m, ph)
(17)	2P2B-L1	-CH ₃ (E)- α	0.77(9H, s, -CH ₃), 1.01(3H, t, -CH ₃), 2.15(2H, qui, -CH ₂ -), 2.43(2H, s, -CH ₂ -),
(18)	2P2B-L1	-CH ₃ γ	5.50(1H, t, -CH=), 7.13(5H, m, ph) 0.79(9H, s, -CH ₃), 1.44(3H, s, -CH ₃), 1.82(2H, s of d, -CH ₂ -), 4.92(1H, d of d, =CH ₂), 4.97(1H, d of d, =CH ₂), 6.11(1H, d of d, -CH=), 7.19(5H, m, ph)

continued on next page

Table II ¹H NMR spectral data of products (continued)

run No.	anion structure	data (δ)
(19)	1P2B-L1 -Si(CH ₃) ₃	(E)-α 0.12(9H, s, -CH ₃), 1.83(3H, d of m, -CH ₃), 2.92(1H, d, -CH-), 5.63(2H, m, -CH=CH-), 7.14(5H, m, ph)
(20)		(Z)-α 0.12(9H, s, -CH ₃), 1.83(3H, d of m, -CH ₃), 3.42(1H, d, -CH-), 5.67(2H, m, -CH=CH-), 7.14(5H, m, ph)
	1P2B-L1 -Si(CH ₃) ₃	γ 0.06(9H, s, -CH ₃), 1.21(3H, d, -CH ₃), 1.77(1H, m, -CH-), 6.16(2H, m, -CH=CH-), 7.20(5H, m, ph)
	1PB-L1 -Si(CH ₃) ₃	(E)-α 0.09(9H, s, -CH ₃), 1.02(9H, s, -CH ₃), 2.03(2H, d, -CH ₂ -), 2.96(1H, d, -CH-), 5.60(2H, m, -CH=CH-), 7.16(5H, m, ph)
(21)	1PB-L1 -Si(CH ₃) ₃	(Z)-α 0.09(9H, s, -CH ₃), 1.00(9H, s, -CH ₃), 2.03(2H, d, -CH ₂ -), 3.29(1H, d, -CH-), 5.60(2H, m, -CH=CH-), 7.16(5H, m, ph)
(22)		γ 0.08(9H, s, -CH ₃), 1.00(9H, s, -CH ₃), 1.50(2H, m, -CH ₂ -), 1.87(1H, m, -CH-), 6.15(2H, m, -CH=CH-), 7.25(5H, m, ph)
(23)		(E)-α 0.08(9H, s, -CH ₃), 1.63(2H, d, -CH ₂ -), 1.97(3H, s, -CH ₃), 5.57(1H, t of q, -CH=), 7.18(5H, m, ph)
(24), (25)	3P1B-L1 -Si(CH ₃) ₃	(E)-α 0.10(9H, s, -CH ₃), 0.91(9H, s, -CH ₃), 1.61(2H, d, -CH ₂ -), 2.46(2H, s, -CH ₂ -), 5.56(1H, t, =CH-), 7.30(5H, m, ph)
(26), (27)	2PB-L1 -Si(CH ₃) ₃	(E)-α 0.10(9H, s, -CH ₃), 0.91(9H, s, -CH ₃), 1.61(2H, d, -CH ₂ -), 2.46(2H, s, -CH ₂ -), 5.56(1H, t, =CH-), 7.30(5H, m, ph)

Table II ^1H NMR spectral data of products (continued)

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

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Table II ^1H NMR spectral data of products (continued)

run No.	anion	-E' structure	data (δ)
	2PB-L1	-Sn(CH ₃) ₃	0.16(9H, s, -CH ₃), 1.15(9H, s, -CH ₃), 2.11(2H, s, -CH ₂ -), 5.60(2H, m, =CH ₂), 5.88(1H, m, -CH=), 7.24(5H, m, ph)
(37)	1P2B-L1	-C(CH ₃) ₂ OH	(E)- α 1.04(3H, s, -CH ₃), 1.10(3H, s, -CH ₃), 1.57(3H, d, -CH ₃), 3.08(1H, d, -CH-), 5.64(2H, m, -CH=CH-), 7.14(5H, m, ph)
(38)	1P2B-L1	-C(CH ₃) ₂ OH	(Z)- α 1.04(3H, s, -CH ₃), 1.10(3H, s, -CH ₃), 1.48(3H, d, -CH ₃), 3.48(1H, d, -CH-), 5.64(2H, m, -CH=CH-), 7.14(5H, m, ph)
	1P2B-L1	-C(CH ₃) ₂ OH	γ 1.12(3H, d, -CH ₃); 1.15(6H, s, -CH ₃), 2.26(1H, qui, -CH-), 6.07(1H, d of d, =CH-), 6.17(1H, d, =CH-), 7.22(5H, m, ph)
(39)	1PB-L1	-C(CH ₃) ₂ OH	(E)- α 0.85(9H, s, -CH ₃), 1.07(6H, s, -CH ₃), 1.90(2H, d, -CH ₂ -), 3.14(1H, d, -CH-), 5.74(2H, m, -CH=CH-), 7.16(5H, m, ph)
(40)	1PB-L1	-C(CH ₃) ₂ OH	(Z)- α 0.80(9H, s, -CH ₃), 1.12(6H, s, -CH ₃), 1.90(2H, d, -CH ₂ -), 3.48(1H, d, -CH-), 5.44(2H, m, -CH=CH-), 7.16(5H, m, ph)
(41)	1PB-L1	-C(CH ₃) ₂ OH	γ 0.92(9H, s, -CH ₃), 1.11(3H, s, -CH ₃), 1.15(3H, s, -CH ₃), 1.52(2H, m, -CH ₂ -), 2.20(1H, m, -CH-), 5.94(1H, d of d, -CH=), 6.22(1H, d, -CH=), 7.22(5H, m, ph)
(42), (43)	3P1B-L1	-C(CH ₃) ₂ OH	γ 1.03(3H, s, -CH ₃), 1.07(3H, s, -CH ₃), 1.44(3H, s, -CH ₃), 5.03(1H, d of d, =CH ₂), 5.14(1H, d of d, =CH ₂), 6.63(1H, d of d, -CH=), 7.20(5H, m, ph)
(44), (46)	2PB-L1	-C(CH ₃) ₂ OH	(E)- α 0.76(9H, s, -CH ₃), 1.16(6H, s, -CH ₃), 2.28(2H, d, -CH ₂ -), 2.42(2H, s, -CH ₂ -), 5.64(1H, t, =CH-), 7.20(5H, m, ph)

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Table II ¹H NMR spectral data of products (continued)

run No.	anion	-E' structure	data (6)
(47)	1P2B-L1	(E)-α	1.66(3H, d, -CH ₃), 1.79(2H, q, -CH ₂), 3.41(2H, t, -CH ₂ -), 3.36(1H, q, -CH-), 5.44(2H, m, -CH=CH-), 7.11(5H, m, ph)
		(Z)-α	1.64(3H, d, -CH ₃), 1.76(2H, q, -CH ₂ -), 3.41(2H, t, -CH ₂ -), 3.74(1H, q, -CH-), 5.44(2H, m, -CH=CH-), 7.11(5H, m, ph)
(48), (49)	1PB-L1	(E)-α	0.86(9H, s, -CH ₃), 1.88(4H, m, -CH ₂ -), 3.38(1H, m, -CH-), 3.44(2H, t, -CH ₂ -), 5.47(2H, m, -CH=CH-), 7.08(5H, m, ph)
(50)	3P1B-L1	γ	1.34(3H, s, -CH ₃), 1.94(2H, t of d, -CH ₂ -), 3.39(2H, t, -CH ₂ -), 4.98(1H, d of d, =CH ₂), 5.04(1H, d of d, =CH ₂), 4.95(1H, d of d, -CH=), 7.12(5H, m, ph)
(51)	2PB-L1	(E)-α	0.68(9H, s, -CH ₃), 1.18(2H, s, -CH ₂ -), 1.30(2H, m, -CH-), 1.97(2H, m, -CH ₂ -), 3.28(2H, t, -CH ₂ -), 5.40(1H, t, =CH-), 7.00(5H, m, ph)
		(Z)-α	0.87(9H, s, -CH ₃), 1.20(2H, s, -CH ₂ -), 1.35(2H, m, -CH ₂ -), 2.01(2H, m, -CH ₂ -), 3.37(2H, t, -CH ₂ -), 5.55(1H, t, =CH-), 7.00(5H, m, ph)
	2PB-L1	γ	0.76(9H, s, -CH ₃), 1.82(2H, s of q, -CH ₂ -), 2.10(2H, m, -CH ₂ -), 3.29(2H, m, -CH ₂ -), 5.08(1H, d of d, =CH ₂), 5.12(1H, d of d, =CH ₂), 6.09(1H, d of d, =CH-), 7.21(5H, m, ph)

a) TMS as internal standard; s:singlet, d: doublet, t: triplet, q:quartet, qui: quintet

of the double bonds generally reflect those of the anions employed (see Scheme I and II). The α -products from 1PB-Li contain more quantities of (E) configurations than (Z). (Z) configurations generally increase in the products from 1P2B-Li than 1PB-Li. As the anions of 3P1B-Li or 2PB-Li are considered to be (E) configurations, the α -products obtained from these lithium compounds have predominantly (E) configurations.

CONCLUSION

In the reactions of substituted phenylallyllithiums with methanol the differences in the negative charge distributions do not affect the product distributions and reactivities of the α -positions are high. When MeI is reacted, the products are reflected by the negative charge distribution. However, in the reactions with TMS-Cl or TMT-Cl, steric effects at α or γ -carbons rules regioselectivities of the products. The steric requirement in the transition state is the key step in the reactions with acetone or EO.

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Chapter 6

Anionic Polymerization of 1-(2-Methoxyphenyl)-1,3-butadiene and 1-(4-Methoxyphenyl)-1,3-butadiene — Microstructures of Polymers and Characterizations of Living Anion Chain End

ABSTRACT: Anionic polymerizations of 1-(2-methoxyphenyl)-1,3-butadiene (o-MeO-1PB) and 1-(4-methoxyphenyl)-1,3-butadiene (p-MeO-1PB) were carried out with t-BuLi. Poly(p-MeO-1PB) polymerized in THF has the same microstructure as poly(1-phenyl-1,3-butadiene) prepared under the same condition: trans-1,4 78-79%, cis-1,4 11-12%, and 3,4 10%. Whereas poly(p-MeO-1PB) polymerized in toluene or benzene has 3,4 structure (more than 98%) with cyclization. On the other hand, poly(o-MeO-1PB) polymerized in THF or toluene has 3,4 structure (more than 98%). Poly(o-MeO-1PB) prepared in toluene, however, has cyclized structures considerably.

The characterization of the living anion chain ends of oligomeric p-MeO-1PB and o-MeO-1PB shows that the electron releasing effect of the methoxy substituents could not affect the microstructures of the resulting polymers. The microstructures are determined by the aggregated structures of the chain ends or the steric hindrance caused by the ortho methoxy group.

We have recently investigated the microstructures of poly(1-phenyl-1,3-butadiene) (poly1PB)¹ and poly(2-phenyl-1,3-butadiene) (poly2PB)² prepared by the anionic polymerization, and further characterized the living anion chain ends of the oligomers^{3,4}. These two monomers behaved in quite different way from butadiene or isoprene in the anionic polymerization, and the structures of the living anion chain ends of 1PB and 2PB had essential features.

Poly1PB obtained in THF with anionic initiators contains mainly trans-1,4 structure (73-84%), whereas in the polymers prepared in hydrocarbon solvents cis-1,4 and 3,4 structures increased (cis-1,4, 26-23% and 3,4 8-23%)¹. On the living anion chain end of 1PB, a negative charge is localized at the α -carbon and the phenyl ring, and the delocalization to the γ -carbon is small³. We have attributed this negative charge distribution to the electron withdrawing caused by the resonance effect of the phenyl group of 1PB.

In this paper effects of the methoxy groups introduced at para or ortho position of the phenyl ring of 1PB are investigated. There have been many studies on o-, m-, or p-methoxystyrenes⁵⁻⁸. The anionic polymerization of o-methoxystyrene is reported to give high isotactic polymer⁸. In this study trans-1-(4-methoxyphenyl)-1,3-butadiene (p-MeO-1PB) and trans-1-(2-methoxyphenyl)-1,3-butadiene (o-MeO-1PB) are synthesized and polymerized with t-BuLi. The microstructures of the resulting polymers and the negative charge distributions on the living anion chain ends are investigated by NMR spectroscopies.

EXPERIMENTAL

The general experimental procedures have been described in previous papers^{1,3}.

Material

trans-1-(4-Methoxyphenyl)-1,3-butadiene (p-MeO-1PB) and trans-1-(2-methoxyphenyl)-1,3-butadiene (o-MeO-1PB) were prepared from trans-4-methoxycinnamaldehyde and trans-2-methoxycinnamaldehyde respectively by the procedure described in the literature⁹, and purified by distillation over LiAlH_4 . trans-4-Methoxycinnamaldehyde and trans-2-methoxycinnamaldehyde were synthesized from p- and o-anisaldehyde by the method in the literature¹⁰.

Polymerization Procedure

Polymerization was carried out in a three-necked flask under a pure argon atmosphere.

Oligomerization Procedure

The oligomerization of p-MeO-1PB and o-MeO-1PB were carried out in ^{13}C NMR sample tube (10 mm ϕ) *in situ* under argon atmosphere with t-BuLi at 5 °C for 1.5 h; [monomer]= 0.59 mol dm^{-3} , [t-BuLi]/[monomer] = 1.5. p-MeO-1PB and o-MeO-1PB were used as toluene solutions (50% w/w).

NMR spectra

^{13}C and ^1H NMR spectra were recorded by a JEOL JNM FX 100 spectrometer (25.0 MHz for ^{13}C and 99.6 MHz for ^1H). Conditions for the measurements were described in the previous paper³.

RESULTS AND DISCUSSION

In Table I the results of the polymerization of p-MeO-lPB are summarized. The typical ^{13}C NMR spectra of the polymer No 2 and No 6 are shown in Figure 1A and 1B. The spectrum appeared in Figure 1A is almost identical to that of 1,4-poly-lPB prepared under the same condition as that of the sample No 2, except that a resonance of methoxy carbon appears (at 55.1 ppm) and the resonances of para and meta carbons are shifted to lower and higher field respectively. Assignments of the resonances were carried out following that of 1,4-poly-lPB previously reported¹. The microstructures of the polymers are estimated from the relative intensities of the aliphatic carbon resonances and listed in Table I. The dyad sequence distributions in the samples No 1, No 2, and No 3 estimated from the aliphatic carbon resonances are identical to that of poly-lPB prepared under the same conditions. Figure 1B shows the spectrum of the sample No 6 which was polymerized in benzene as a solvent. Poly-lPB polymerized under the same condition as sample No 6 have predominantly 1,4 structure and gives the ^{13}C NMR spectra similar to Figure 1A. Whereas the spectrum of Figure 1B is quite different from it and very similar to that of 3,4-poly-lPB which can be obtained with Ziegler type catalyst¹, except the methoxy carbon resonance appears and the resonances of para and meta carbons are shifted to lower and higher field respectively. In the spectrum the resonances of the aliphatic region have humps, indicating that the 3,4 structure is contaminated with some irregular portions. The ^1H NMR

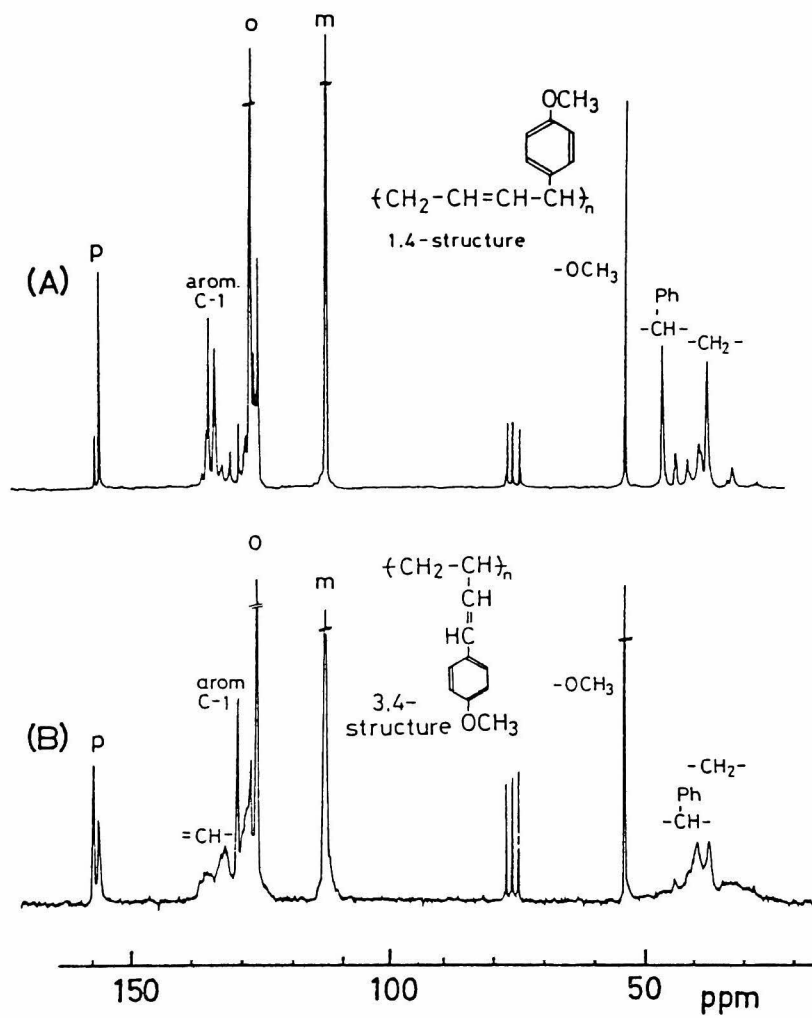


Figure 1 ^{13}C NMR spectra of poly(p-MeO-lPB); (A) sample No 2 and (B) No 6

spectrum of this sample clearly indicates the ratio of the olefin protons to the phenyl protons is significantly short of two to five. The broader nature of the ^{13}C NMR spectrum thus can be due to the cyclization of 3,4 double bond.

The microstructure of poly(p-MeO-lPB) revealed by the ^{13}C and ^1H NMR spectra are listed in Table I. The polymer samples polymerized in THF have mainly trans-1,4 structure and have almost the identical structures with poly(lPB) prepared under the same condition. On the other hand, the polymer samples polymerized in toluene or benzene have quite different structures from poly(lPB) polymerized under the same condition, and contain more than 98% 3,4 structure with the cyclization. Thus the microstructure of poly(p-MeO-lPB) strongly depends on the polymerization solvent although that of poly(lPB) is slightly affected by it.

The results of the polymerizations of o-MeO-lPB are summarized in Table II and the typical ^{13}C NMR spectra of the polymers are shown in Figure 2. In Figure 2A the spectrum of the sample No 8 which is polymerized in THF is shown. The aliphatic region of this spectrum is quite different from 1,4-poly(lPB) polymerized under the same condition and almost identical with that of 3,4-poly(lPB). Figure 2B shows the spectrum of the sample No 10. This spectrum is much complicated and shows the double bond of the 3,4 unit is cyclized to a considerable extent. The proportion of the cyclization is estimated from the ^1H NMR spectrum.

The microstructures of poly(o-Me-lPB) estimated by ^{13}C and ^1H NMR spectra are listed in Table II. The polymer samples

Table III ^{13}C chemical shift and π -electron density for living oligomeric p-MeO-lPB and o-MeO-lPB

position	p-MeO-lPB		o-MeO-lPB		
	δ ^a	ρ ^b	δ	ρ	
α	65.6	1.43	62.6	1.45	
	66.3	1.43			
β	135.9	0.98	135.2	0.99	
γ	84.6 ^c	1.31	92.0	1.26	
	85.2	1.31			
δ	51.0	-	50.7	-	
arom. {	C-1	144.6	0.93	139.3	0.96
		144.5	0.93		
	C-2	116.2	1.11	148.4	0.90
		115.8	1.11		
	C-3	116.7	1.11	112.5	1.13
		116.2	1.11		
	C-4	147.5	0.91	104.4	1.18
	C-5	same as C-3		123.4	1.06
	C-6	same as C-4		111.8	1.14

a) Chemical shift in ppm downfield from TMS using the solvent peak as standard; THF 67.0

b) π -electron density calculated by the following equation¹¹;
 $\delta = 289.5 - 156.3\rho$

c) A set of data shows cis isomer above and trans isomer below.

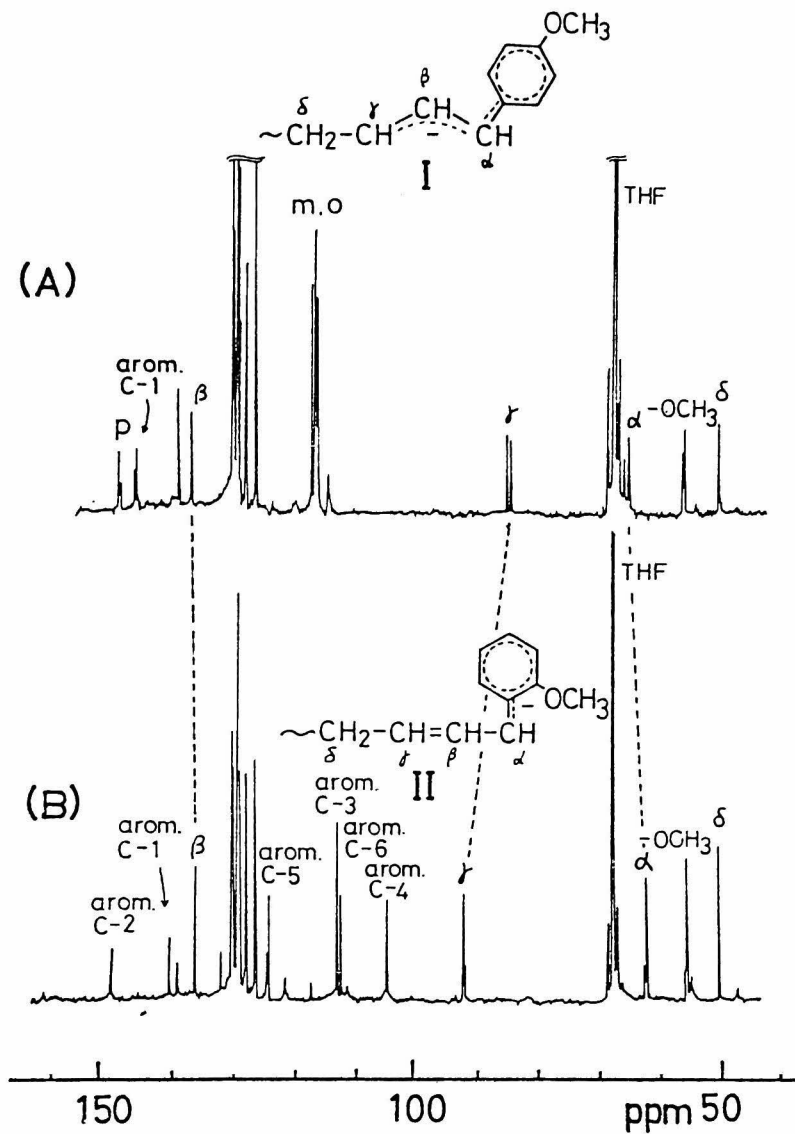


Figure 3 ^{13}C NMR spectra of living anion chain ends of (A) oligomeric p-MeO-lPB ($\overline{DP} = 1.4$) and (B) oligomeric o-MeO-lPB ($\overline{DP} = 1.1$)

polymerized in THF have more than 98% 3,4 structure regardless of a counter cation and polymerization temperature. On the other hand, polymer samples polymerized in toluene also have 3,4 structure, whereas in these cases considerable amounts of the 3,4 unit are consumed by the cyclization. The substitution of the methoxy group at ortho position of LPB drastically changes the microstructure of the polymer prepared by anionic initiators. The cyclizations of the 3,4-polymer were observed when polymerizations were carried out in hydrocarbon media.

In order to study the effect of the substitution of the methoxy group further, ^{13}C NMR spectra of the living anion chain ends of oligomeric p-MeO-LPB and o-MeO-LPB are investigated. Figure 3A shows the ^{13}C NMR spectrum of the living anion chain ends of oligomeric p-MeO-LPB in THF. In the spectrum, the resonances designated as α , β , γ , ortho(o), meta(m), para(p), and the aromatic C-1 (arom. C-1) of the living chain end appear. The chemical shifts of the resonances are listed in Table III with the π -electron densities calculated by O'Brien's equation with the ^{13}C chemical shifts¹¹. Among them the resonances of the γ and α carbons shifted by 5 and 2 ppm to higher field respectively as compared with the corresponding carbon resonances of oligomeric living LPB chain end. These shifts are attributed to change in the negative charge distribution caused by the methoxy group at the para position. The electron releasing methoxy group pushes some part of the negative charge out of the phenyl ring onto the α and γ carbons in the living anion chain end. Since the amount of the high

field shift of the γ -carbon is larger than that of the α -carbon, the chain end rather approximates to the π -allyl-phenyl type chain end which is shown in I in Figure 3. Such a charge delocalized chain end favors in-chain 3,4 unit since the monomer is liable to attack the γ -carbon. However, polymer samples prepared in THF have low 3,4 content as shown above. Such small change in the negative charge distribution may not affect the microstructure of the resulting polymer. The resonances of the γ , α , and methoxy carbons consist of two peaks of almost equal intensity, indicating the chain end is the mixture of almost equal amount of trans-4,1 and cis-4,1 chain ends. However, the in-chain unit is predominantly trans-1,4 structure as shown above. On the other hand, when the polymerization was carried out in toluene or benzene, the polymer has 3,4 structure although it has been cyclized. Unfortunately the living anion chain end could not be observed by the NMR spectroscopies in hydrocarbon media due to the poor solubility of the living oligomer. The living oligomeric p-MeO-lPB could be solubilized in hydrocarbon media (benzene or toluene) when the \overline{DP} (degree of polymerization) of the oligomer is extended up to 5. However, any resonances of the anion chain end could not be observed by the NMR spectroscopies, although the in-chain resonances were appeared. The anion chain end is considered highly aggregated. The drastic change in the microstructure observed with poly(p-MeO-lPB) polymerized in hydrocarbon media is possibly attributed to the highly aggregated chain end structure caused by the intermolecular coordination of

the methoxy oxygen to the lithium cation. The monomer cannot come close to the α -carbon due to the crowded structure at the α -position. Therefore, in the alternative way, the monomer attacks the γ -carbon to give the high 3,4 content. In THF medium such aggregation cannot occur and the resulting polymers have low 3,4 content.

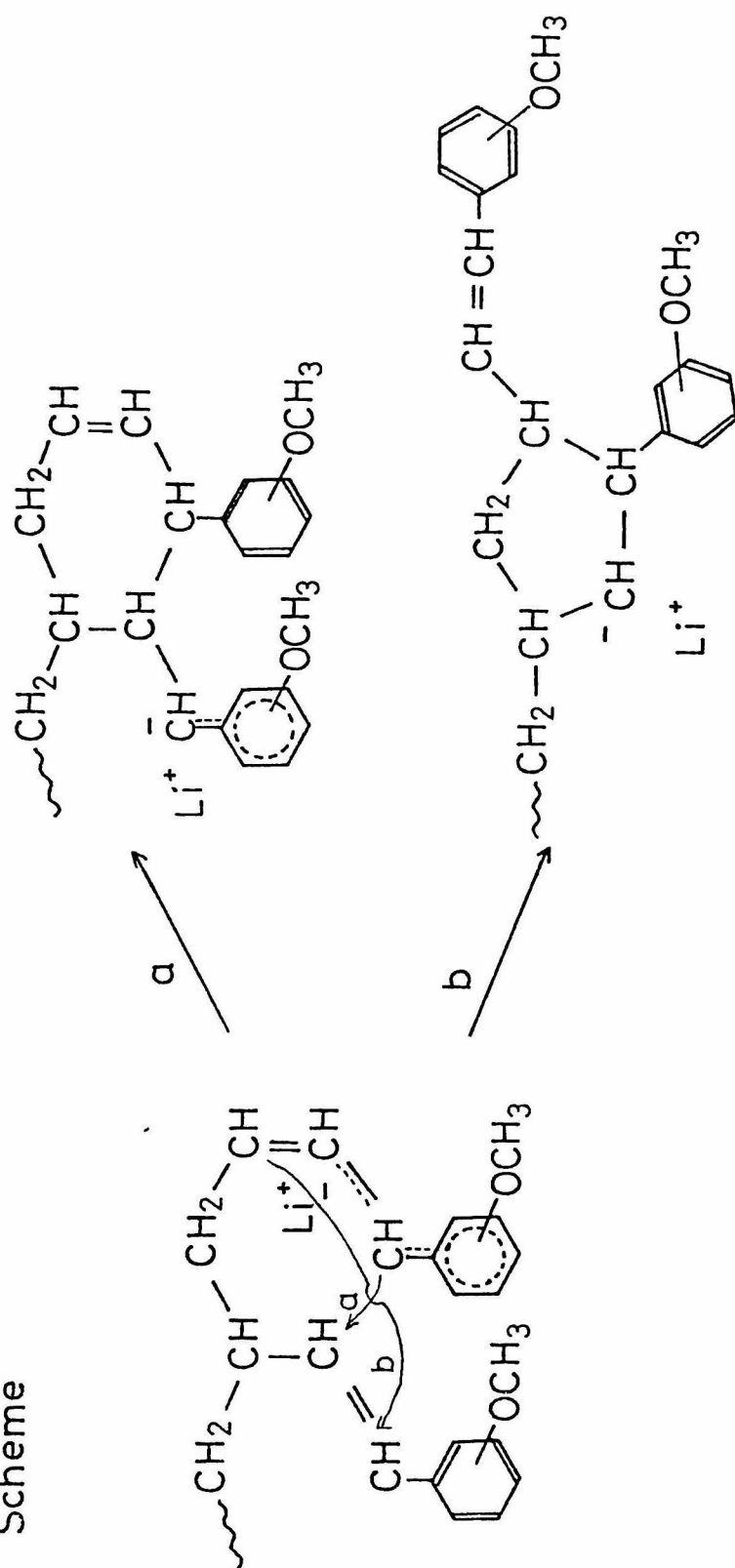
Figure 3B shows the ^{13}C NMR spectrum of the living chain end of oligomeric o-MeO-lPB in THF. In the spectrum α , β , γ , and the aromatic carbon resonances of the living anion chain end appear. The chemical shifts of the resonances are listed in Table III as well as the π -electron densities. The resonance of the γ -carbon shifted by 2 ppm to lower field and that of the α -carbon shifted by 5 ppm to higher field as compared with the corresponding carbon resonances of living oligomeric lPB chain end. This shows that the electron density of the α -carbon increased and that of the γ -carbon decreased with the introduction of the methoxy substituent into the ortho position. This means that the living chain end rather approximates to the π -benzyl type chain end which is shown in II in Figure 3. This chain end favors the in-chain 1,4 structure since the reactivity of the α -carbon is higher. However, the polymers prepared in both THF and toluene contain only 3,4 structure. The steric hindrance caused by the ortho methoxy group must affect the microstructures. The monomer cannot attack the α -carbon because of the steric hindrance of the ortho methoxy group and this leads to the in-chain 3,4 structure. Unfortunately again in hydrocarbon media the living anion chain end of

o-MeO-lPB could not be observed by the NMR spectroscopies due to the poor solubility of the anion. The living oligomer could be solubilized when \overline{DP} of the oligomer is extended to 3. However, any resonances of the anion chain end could not be observed by the NMR spectroscopies, whereas the in-chain resonances appeared. In hydrocarbon media the living anion chain end seems highly aggregated in the same manner as the case p-MeO-lPB. The aggregated chain end structure as well as the steric hindrance caused by the ortho methoxy group determine the microstructure and give 3,4 polymers.

In this way the negative charge distributions of the chain ends could not interpret the changes in the microstructure of poly(p-MeO-lPB) and poly(o-MeO-lPB). The microstructures of the resulting polymers are determined by the aggregated structures of the chain ends or the steric hindrance caused by the ortho methoxy group, except for the polymerization of p-MeO-lPB in THF. These factors could not be evaluated by the NMR spectroscopic methods.

In the polymerizations in hydrocarbon media, the cyclizations of the 3,4 double bonds occur considerably. These cyclizations seem connected with the aggregated chain ends. Such sterically crowded chain ends rather attack the in-chain 3,4 double bond than the monomers (back biting). The cyclizations are considered to occur intramolecularly since the molecular weights of the cyclized polymers do not increase as compared with non-cyclized samples (about 10,000) although the molecular weight distributions become a little broader. The sample of the cyclization mechanism is proposed in the Scheme.

Scheme



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PART III Syntheses of Copolymers Having Specific
Sequence Distribution

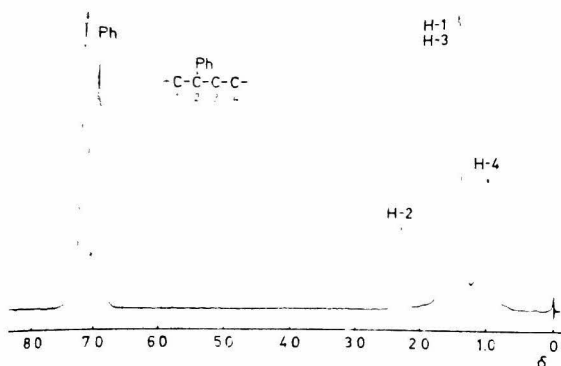


Figure 1. 220-MHz ^1H NMR spectrum of an S-E alternating copolymer prepared from 1,4-poly2PB.

Table I
Chemical Shifts^a of S-E Alternating Copolymer and Poly4P1B

	C-1	C-3	C-2	C-4	phenyl	arom C-1'
S-E alternating copolymer	36.6	45.4			125.6	146.0
	36.7		25.2		127.5	146.1
		36.9	45.5		128.0	146.2
		37.0	45.6	25.4	125.6	142.7
poly4P1B (isotactic)	33.2	36.9	32.4	40.0	125.6	142.7
					128.3	

^a Ppm from Me₄Si.

peak in the aliphatic region is assigned to the C-2 carbon because of a doublet resonance in the off-resonance spectrum. The structure of the polymer is symmetrical after hydrogenation. Therefore, the C-1 and C-3 carbons are equivalent and have the same chemical shift if the stereostructure is not taken into account. Considering the additivity law of chemical shifts in ^{13}C NMR spectra, the highest field resonance is assigned to the C-4 carbon and the multiplet peaks are assigned to C-1 and C-3 carbons. The aromatic C-1' and C-2 carbon resonances are both split into three peaks (approximate intensity ratio 1:2:1), indicating a long-range stereochemical effect of triad sequences. The C-4 carbon resonance is split into two peaks (approximate intensity ratio 1:1) by dyad sequences. These intensity ratios indicate that the alternating copolymer is completely atactic, as predicted above. The C-1 and C-3 carbon resonances appear as four peaks. This splitting can be interpreted as follows. Let us consider the C-3 carbon in Scheme II. The resonance of this carbon is separated into two peaks, owing to the relative configuration between Ph₂ and Ph₃, that is, meso (m) or racemic (r). These two peaks are further split into two peaks with strong overlapping due to the relative configuration between Ph₂ and Ph₁. The C-1 carbon is also split in a similar manner, owing to the relative configuration between Ph₂ and Ph₃ and, further, between Ph₃ and Ph₄. The intensity ratio of the four peaks is 1:1:1:1, also showing that this alternating copolymer is atactic.

The E-P alternating copolymer previously reported has a methyl substituent in place of a phenyl group. In this case,¹⁻³ the C-2 and C-4 (following our notation) carbon resonances appear as singlet peaks, respectively, giving no information concerning tacticity. The stereostructure was shown only by two carbon resonances; namely, the methyl carbon resonance was split into three peaks by triad sequences, and the C-1 and C-3 carbon resonances appear as four peaks in the same manner as observed in this study.

We now discuss S-E alternating copolymers prepared

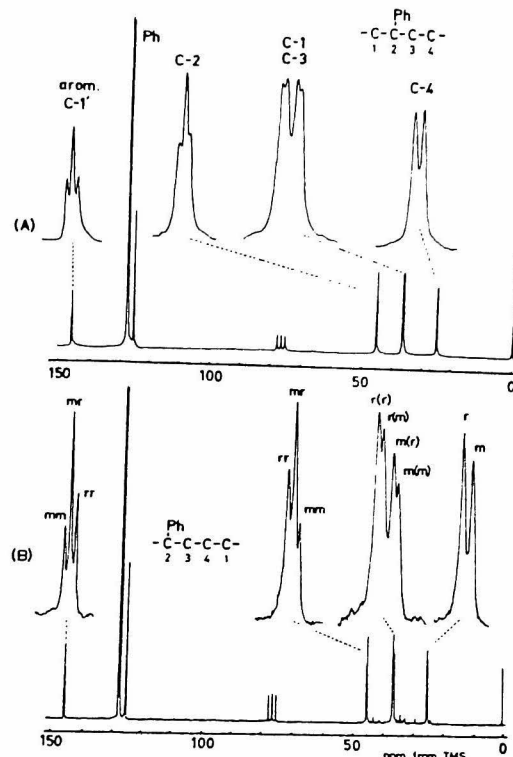


Figure 2. 25.0-MHz ^{13}C NMR spectra of S-E alternating copolymers prepared from (A) 1,4-poly2PB and (B) 1,4-poly1PB-B. In the upper traces the abscissas are expanded 16 times.

from 1,4-poly1PB. Before hydrogenation the tacticity of the polymer could not be revealed even if the ^{13}C NMR spectra were employed as described before. However, in the spectrum of the hydrogenated 1,4-poly1PB, all the resonances had fine structure. By the hydrogenation of the polymer, slight chemical shift differences in the flanking cis-1,4 and trans-1,4 units disappeared, and the chemical shift differences caused by the tacticity can be observed clearly. The ^{13}C NMR spectrum of the alternating copolymer prepared from 1,4-poly1PB-T (polymerized in THF) is essentially the same as Figure 2A, indicating that it is also an atactic sample. Assuming that the tacticity of the polymer is not changed by hydrogenation, it is concluded that the 1,4-poly1PB-T is atactic. The tacticity is not controlled by the anionic polymerization because the propagating chain ends are considered to be a solvent-separated ion pair in THF. When a stereospecific 1,4-poly1PB can be obtained, assignments of the split ^{13}C resonance of the alternating copolymer is possible after hydrogenation. However, such a stereospecific polymerization could not be carried out by anionic initiators or Ziegler-type catalysts. Further, an asymmetric initiator (*n*-BuLi-sparteine complex) did not give optically active polymer. Thus, the assignments of the split peaks still cannot be carried out.

Figure 2B shows the ^{13}C NMR spectrum of the alternating copolymer prepared from 1,4-poly1PB-B (polymerized in benzene). In the spectrum some deviations from the intensity ratios expected for the completely atactic polymer can be observed. The tacticity will be slightly controlled by the interaction between the anion chain end and the counteranion in considering the association of the polymer living chain ends. If the phenyl substituent has the same effect as the methyl group of the E-P alternating copolymer on the chemical shift of the C-1 and C-3 carbon resonances, the split peaks are tentatively assigned as shown in Figure 2B. In the assignment of the C-1 and C-3

carbon resonances, $m(r)$, for example, means that the resonance is split by an m dyad and then further split by an adjacent r dyad (in Scheme II, for the C-3 carbon, the $\text{Ph}_2\text{-Ph}_3$ dyad is m and the $\text{Ph}_1\text{-Ph}_2$ dyad is r). Following this assignment, the assignment of the aromatic C-1' carbon resonance of the alternating copolymer is consistent with that of an aromatic C-1 carbon resonance of polystyrene.⁹ In the spectrum of the polystyrene, the lower field resonance of the aromatic C-1 carbon is attributed to isotactic sequences and the higher field signal to syndiotactic sequences.⁹ These results support the conclusion that the S-E alternating copolymer prepared from 1,4-poly1PB-B is slightly predominant in syndiotactic sequences. However, the same shielding influence of the phenyl substituent on m and r dyads as caused by the methyl substituent in the E-P alternating copolymer is

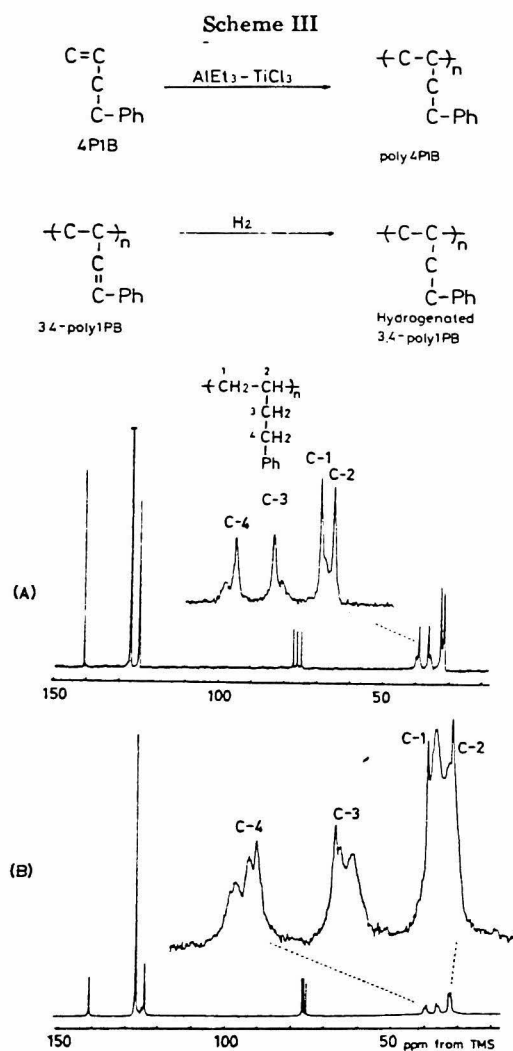


Figure 3. ^{13}C NMR spectra of (A) isotactic poly4P1BT (25.0 MHz) and (B) hydrogenated 3,4-poly1PB (50.2 MHz). In the upper traces the abscissas are expanded (A) 4 and (B) 8 times.

questionable. Therefore, the assignment of the m and r dyads mentioned above is not certain and may be interchanged.

Preparation of Poly(4-phenyl-1-butene). Pure 3,4-poly1PB was obtained by Ziegler-type catalysts in the course of the synthesis of the 1,4-polymer. The hydrogenation of the 3,4-poly1PB gives the polymer corresponding to poly4P1BT, as shown in Scheme III. On the

other hand, 4P1BT is considered to be polymerized to an isotactic-rich polymer by a Ziegler-type catalyst. It is interesting to compare the stereostructures of these two polymers.

Figure 3A shows the ^{13}C NMR spectrum of the predominantly isotactic poly4P1BT prepared by $\text{AlEt}_3\text{-TiCl}_3$,¹⁰ and Figure 3B shows the spectrum (50.2 MHz) of the hydrogenated 3,4-poly1PB. The 50.2-MHz spectrum shows better resolution than the 25-MHz spectrum. The assignment of C-2 carbon was carried out by off-resonance decoupling, and the other aliphatic resonances are assigned using the additive parameters reported by Conti et al.¹¹ In Figure 3B, the aliphatic carbon resonances appear as complex multiplets. The lower field peak of the C-3 resonance and the higher field peak of the C-4 resonance (as compared with Figure 3A) are attributed to isotactic sequences. The other split peaks, however, could not be interpreted in terms of simple triad sequences. This must arise from higher order sequence distribution or unidentified structural features of the polymer. However, from the spectrum it is safe to say that the poly4P1BT prepared from 3,4-1PB is not stereoregular. Assuming that the tacticity of the 3,4-poly1PB is not changed by hydrogenation, the 3,4-poly1PB is regarded as also atactic. In the ^{13}C NMR spectrum of the 3,4-poly1PB several resonances had fine structures attributed to stereostructure. However, since we did not know the tacticity of the polymer, we could not determine them. Thus, the $\text{AlEt}_3\text{-TiCl}_3$ catalyst system polymerizes the diolefin to the atactic 3,4-polymer, whereas it polymerizes the α olefin to the isotactic polymer.

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Chapter 8

Anionic Block Copolymerization of Phenylbutadienes with Styrene or Butadiene

ABSTRACT: Anionic block copolymerization of 1-phenyl-1,3-butadiene (1PB) or 2-phenyl-1,3-butadiene (2PB) with styrene (St) or butadiene (Bd) were carried out in THF or in toluene. The behavior in the block copolymerization was investigated by gel-permeation chromatograph of the product. In THF medium, the reactivities of living poly-1PB and poly-2PB end toward St is low and considerable amount of the starting block remained unreacted, whereas that of living poly-St end toward 1PB or 2PB is high enough to produce A-B type block copolymer. On the other hand, in toluene medium, for all the cases studied the reactivities of the living ends were high.

We have recently investigated the 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 two monomers behaved in quite different way from butadiene (Bd) or isoprene in anionic polymerization. The characteri-

zations of the living anion chain end of oligomeric 1PB and 2PB have been carried out by means of ^{13}C and ^1H NMR spectroscopies, showing that the negative charge distribution on the living chain end of oligomeric 1PB is π -benzyl type³ and that of oligomeric 2PB is π -allylphenyl type⁴.

In the anionic copolymerization of Bd and styrene (St)^{5,6} in hydrocarbon media, the relative reactivity of Bd is much higher than that of St. Therefore, such copolymerization gives almost St-Bd block copolymer in the absence of some additives^{7,8}.

In this study we have studied the reactivities of living poly-1PB and poly-2PB ends through the anionic block copolymerization of 1PB or 2PB with St or Bd, and the behavior of the copolymerization is investigated using gel-permeation chromatograph.

EXPERIMENTAL

Materials

1PB, 2PB, and BuLi were synthesized by the methods described in previous papers¹⁻⁴. THF and toluene were purified by the distillations over LiAlH_4 .

Block Copolymerization

Block copolymerization was carried out in a three-necked flask under argon atmosphere with t-BuLi in THF or s-BuLi in toluene at 0°C by sequential monomer feed. The monomer A is first reacted with BuLi for 2 h: $[\text{monomer A}] = 0.23 \text{ mol dm}^{-3}$ and $[\text{monomer A}]/[\text{BuLi}] = 15.0$. Then the eqimolar monomer B was successively added to the

living poly-A end and the reaction was carried out for another 2.0 h. Bd was used as a toluene solution (2.42 mol dm^{-3}). When THF was used as the solvent, it was evaporated off and equal volume of benzene was added. The whole reaction mixture was washed with water and saturated NaCl aq, then dried with molecular sieves (3A 1/16).

Gel-permeation Chromatogram

Gel-permeation chromatogram (GPC) was recorded on a Waters ALC/GPC 244 equipped with four columns (μ styragel; $10^5+10^4+10^3+500A$). THF was used as an eluent and the flow rate was set at 1.5 ml/min. The molecular weight of the sample was determined according to the calibration curve obtained with standard poly-St's.

RESULTS AND DISCUSSION

Figure 1 shows the GPC of the product obtained in the block copolymerization of lPB with St in THF medium. In Figure 1(A) lPB is polymerized to the starting block whose average degree of polymerization (\overline{DP}) is 15^9 . The broken line in Figure 1(A) shows the GPC of the poly-lPB prepared in the same condition as formation of the starting block. The number-average molecular weight (\overline{Mn}) of the sample agreed with the theoretical value (2,000). The solid line in Figure 1(A) shows the GPC of the whole product recovered after adding St to the living poly-lPB end. The upper trace is recorded by the ultraviolet (UV, 254 nm) detector and the lower one by the differential refractometer (RI). The GPC is bimodal. The peak at the lower molecular

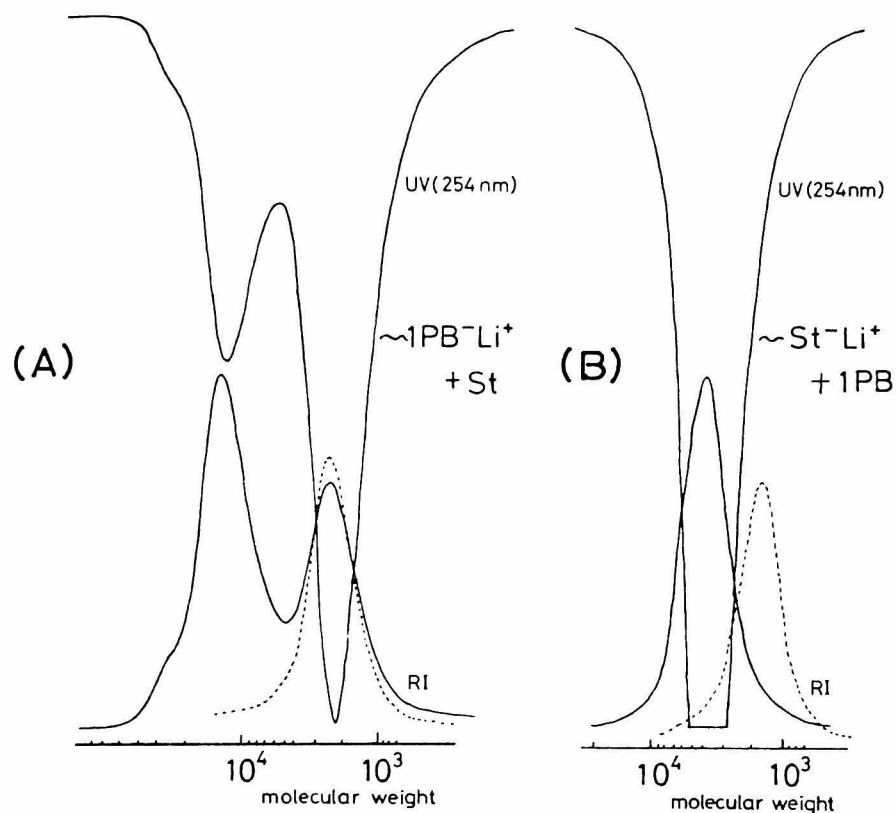


Figure 1 The gel-permeation chromatograms of the product formed by anionic block copolymerization of 1PB with St in THF; (A) sample 1 and (B) sample 5

weight region is corresponding to the poly-lPB starting block without St unit shown in the broken line above. The \overline{Mn} of the peak (13,000) at higher molecular weight region is too high for the block copolymer (\overline{Mn} 3,600) formed by uniform addition of St to the living poly-lPB end. Furthermore, the peak intensity ratio of the upper trace (UV detector) ¹⁰ to the lower one (RI detector) at the higher molecular weight region is 0.8, which is 3.5 times larger than that of poly-St homopolymer. These results indicate that only small amount of the living poly-lPB end could initiate the polymerization of St and most of the living poly-lPB end remains unreacted without adding any St unit. As for the higher molecular weight part, the short poly-lPB block (15 unit) is attached to the long poly-St block (106 unit). On the other hand, when the monomer addition sequence is reversed, GPC of the whole reaction mixture shows interesting difference as shown in Figure 1(B). St is polymerized to a starting block whose \overline{DP} is 15. The broken line in Figure 1(B) shows the GPC of the starting poly-St block. The \overline{Mn} of the sample is theoretical value (1,600) showing absence of unconverted monomer. The solid line in Figure 1(B) shows the the GPC of the whole product formed by adding the equal molar lPB to the living poly-St end. Different from Figure 1(A), the GPC is unimodal indicating all the living poly-St end initiates the polymerization of lPB uniformly to give A-B type block copolymer. The \overline{Mn} of this copolymer is consistent with the theoretical value (3,600).

Figure 2 shows the results of the block copolymerization of 2PB with St. 2PB is polymerized to the starting block whose \overline{DP} is 15. The broken line in Figure 2(A) shows the GPC of the poly-2PB starting block. The \overline{Mn} of this sample agreed with the theoretical value (2,000) and unconverted 2PB could not be detected. The solid line in Figure 2(A) shows the GPC of the whole product formed by adding equal molar St to the living poly-2PB end. The GPC is bimodal similarly to Figure 1(A) and the peak at lower molecular weight region is corresponding to the poly-2PB starting block without St unit, which was shown by the broken line above. \overline{Mn} of the peak at higher molecular weight region (29,000) is too high for the block copolymer (3,600) formed by uniform addition of St to the living poly-2PB end. The peak intensity ratio of the upper trace (UV detector) to the lower one (RI detector) at the higher molecular weight region is 1.2, which is 5.3 times larger than that of poly-St homopolymer. These results indicate that only small amount of the living poly-2PB end could initiate the polymerization of St and most of the living poly-2PB end remains unreacted similarly to the case of Figure 1(A). As for the higher molecular weight part the poly-2PB block (15 unit) is attached to the longer poly-St block (260 unit). On the other hand, when the monomer addition sequence is reversed, that is, St is polymerized first and then 2PB is added to the living poly-St end, the GPC of the whole product is unimodal in the same manner as Figure 1(B). All the living poly-St end initiate the polymerization of 2PB

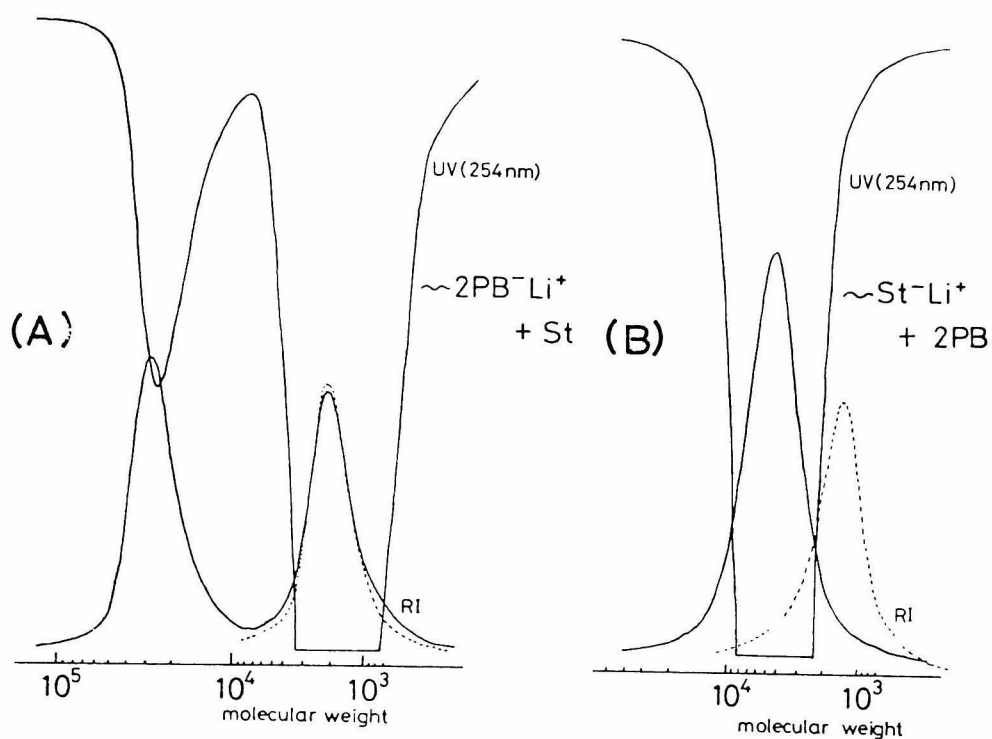


Figure 2 The gel-permeation chromatograms of the product formed by anionic block copolymerization of 2PB with St in THF; (A) sample 3 and (B) sample 6

uniformly to give A-B type block copolymer. The \overline{M}_n of this copolymer is consistent with the theoretical value (3,500).

In this way, the reactivities of the living poly-1PB and poly-2PB end toward St is low and most of the starting block remains unreacted, whereas that of the living poly-St end toward 1PB or 2PB is high enough to produce A-B type block copolymer in THF medium. Although the GPC of some samples are bimodal, the two peaks are separated enough and the molecular weight distribution of each peak is rather narrow. Therefore, the block efficiency can be defined and calculated with the molecular weight of the each peak by eq (1). M is the \overline{M}_n of the block copolymer (\overline{M}_n of the

$$\text{Block efficiency} = \frac{15M_B}{M - (15M_A + 57)} \times 100 \quad (1)$$

higher molecular weight peak when GPC is bimodal). M_A and M_B is the molecular weight of the monomer A and B. 57 means the molecular weight of Bu group. 15 indicates the molar ratio of the monomer A or B to the BuLi. Table I shows the block efficiencies in the copolymerization thus defined. The results of the block copolymerizations of Bd with 1PB or 2PB are also listed in Table I. The high block efficiency means $k_1 \geq k_2$ and low block efficiency $k_1 \ll k_2$ in Scheme.

Scheme



The absolute values of k_1 for St and other several monomer

Table I List of Block Efficiencies

Run	Medium ^{a)}	monomer ^{b)}		Block Efficiency ^{c)} /%
		A	B	
1	THF	1PB	St	14
2	THF	1PB	Bd	35
3	THF	2PB	St	6
4	THF	2PB	Bd	16
5	THF	St	1PB	~ 100
6	THF	St	2PB	~ 100
7	THF	Bd	1PB	~ 100
8	THF	Bd	2PB	~ 100

a) When the block copolymerizations are carried out in *toluene*, the block efficiencies of all the cases listed in this Table are almost 100%

b) see the experimental section

c) estimated with Eq (1)

pairs were determined by Szwarc et al.¹¹. However, in this way the relative reactivity of living chain end can be estimated by means of GPC.

Surprising results are obtained in the block copolymerization carried out in toluene. In all cases which appear in Table I the block efficiencies are ~100% regardless of the monomer pairs and the monomer addition sequence. One example of the GPC in those cases are shown in Figure 3 for the block copolymerization of 1PB with St. In other cases almost the same GPC are obtained. The molecular weight distributions are rather narrow and the \overline{M}_n of the block copolymer are theoretical values.

In THF the negative charge was delocalized to larger extent on the living chain end of 1PB³ and 2PB⁴ than on that of St and Bd. The more delocalized chain end may be attributed to the low block efficiencies observed in THF medium. Furthermore, comparing 1PB with 2PB, 2PB has more delocalized living chain end and consequently may have lower block efficiency than 1PB. On the other hand, in toluene all cases studied the block efficiencies are high and almost 100%. We cannot explain this drastic change with the changes in the negative charge delocalizations, since we have concluded by means of NMR spectroscopies that the living chain end of 1PB or 2PB has almost similar charge distribution both in THF and hydrocarbon media. In THF a solvent-separated ion pair is predominant, whereas in toluene chain end is presented as a contact ion pair. Such different ion pair may causes the drastic change of the block efficiency in this study.

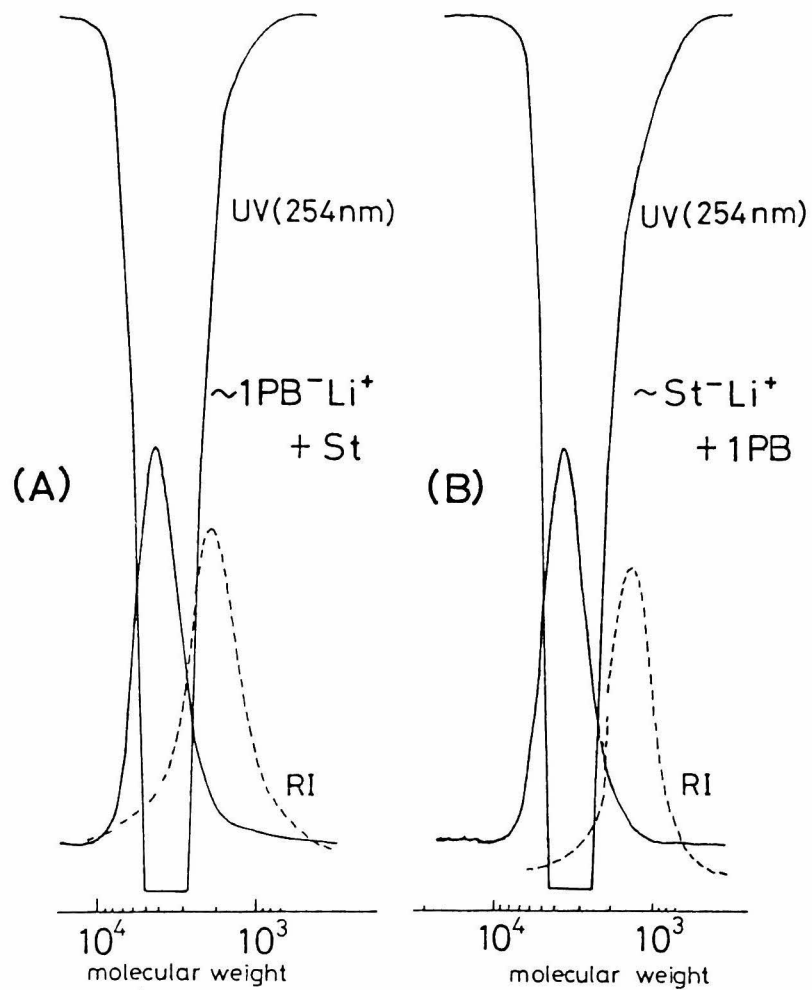


Figure 3 The gel-permeation chromatograms of the product formed by anionic block copolymerization of 1PB with St in toluene

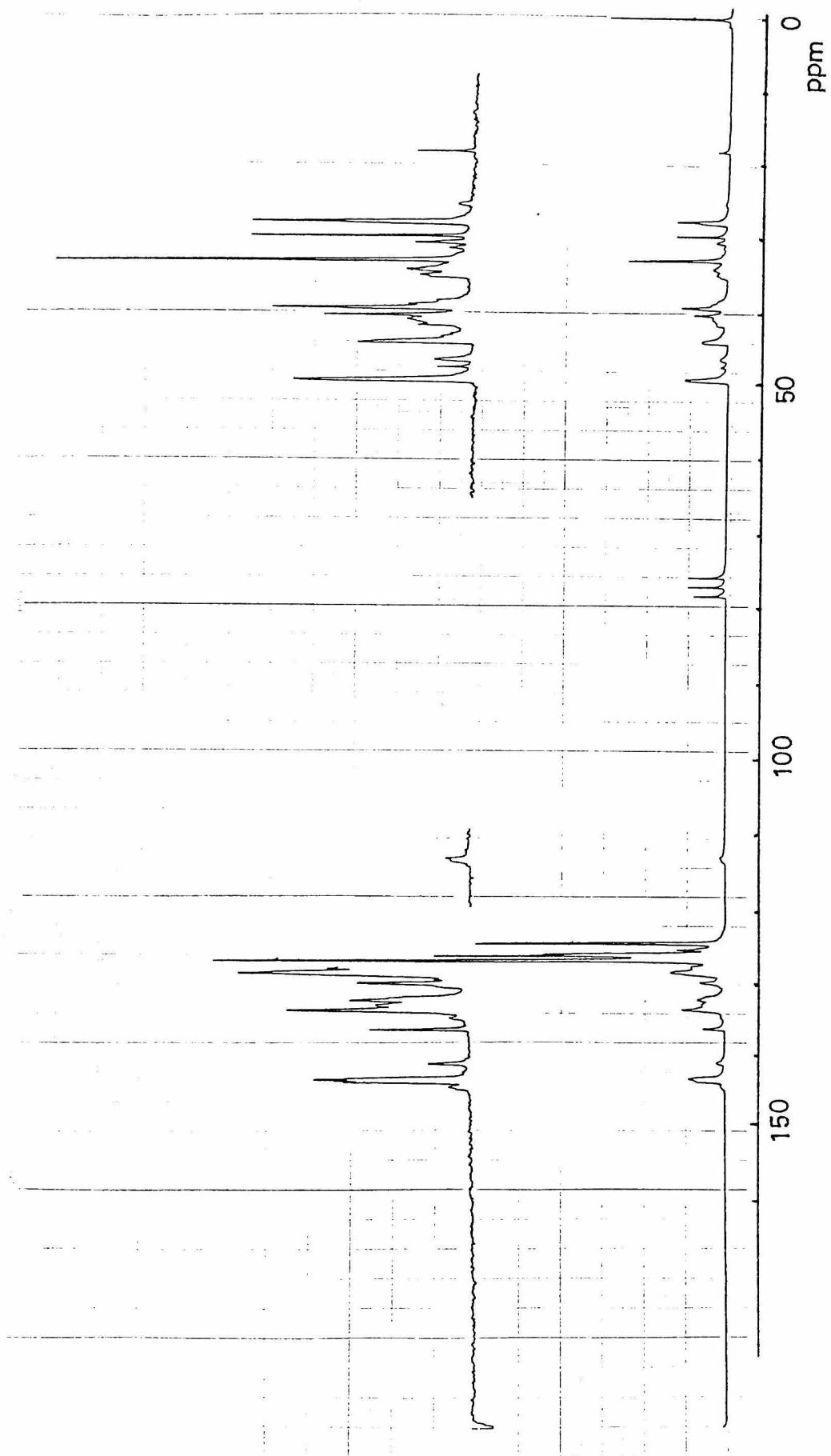


Figure 4 ^{13}C NMR spectrum of the random copolymer of IPB with Bd

The random copolymerization of LPB with Bd was carried out in toluene. It is rather difficult to obtain the random copolymer of Bd with St. LPB has a intermediate structure between Bd and St. Figure 4 shows the random copolymer of LPB with Bd. The aromatic C-1 carbon resonance indicates the copolymer is random, not block.

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- (9) The GPC equipped with four μ styragel columns does not have enough resolution for high molecular weight samples. Therefore, we carried out the block copolymerizations within low molecular weight.
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depends on the microstructure, decreases as follows;
poly-2PB > poly-1PB > poly-St.

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GENERAL CONCLUSION

The anionic polymerization of phenylbutadienes, 1-phenyl-1,3-butadiene and 2-phenyl-1,3-butadiene, have been investigated. The thesis is divided into three parts. Part I deals with microstructures of poly(phenylbutadiene)'s prepared by anionic initiators. Part II is concerned with characterization of active species in anionic polymerizations of phenylbutadienes. In Part III copolymers having specific sequence distributions are synthesized.

The conclusion of each chapter is summarized as follows.

[PART I]

In chapter 1 the microstructure of poly(1-phenyl-1,3-butadiene) (poly1PB) prepared by anionic and coordinated catalysts were revealed mainly by the ^1H and ^{13}C NMR spectroscopies. The microstructure is affected predominantly by nature of the polymerization solvent. The polymer samples prepared by alkyl lithium in hydrocarbon media contain 50-60% trans-1,4, 24-28% cis-1,4, and 8-24% 3,4 structures, whereas samples prepared by sodium-naphthalene or alkyl lithium in THF had 78-84% trans-1,4, 8-13% cis-1,4, and 8-10% 3,4 contents respectively. The observed dyad sequence distributions estimated from ^{13}C NMR spectra were in good agreement with those calculated from Bernoulian statistics.

In chapter 2 the microstructure of poly(2-phenyl-1,3-

butadiene) (poly2PB) prepared by anionic initiators were investigated. The microstructure is mainly affected by the polymerization solvent. The polymer sample polymerized at 57°C has 98% cis-1,4 content and with a decrease in the polymerization temperature, 1,2 content increases. The sample prepared at -100°C contains 67% cis-1,4 and 33% 1,2 content. The observed dyad and triad sequence distributions estimated from the ^{13}C NMR spectra were in good agreement with those calculated from the first-order Markov chain end.

[PART II]

In chapter 3 the living anion chain end of oligomeric 1-phenyl-1,3-butadienyllithium and the model anion of it were characterized by ^1H and ^{13}C NMR spectroscopies. The propagating species of 1PB is concluded to be 4,1 anion. A negative charge on the chain end is localized at the α -carbon and the phenyl ring and delocalization to the γ -carbon was small regardless of the polymerization solvent. Therefore, in the polymerization the monomer attacks the α carbon and consequently in-chain 1,4 unit is predominant even in THF medium. The configuration of the in-chain 1,4 unit is determined by that of the anion 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 end.

In chapter 4 the living anion chain end of oligomeric 2-phenyl-1,3-butadienyllithium and the model anion of it were

characterized. The propagating species of 2PB is concluded to be 1,4 anion. A negative charge on the chain end delocalizes to π -allyl system and to the phenyl ring over the temperature range studied. The configuration of the chain end is (E). In the case of butadiene and isoprene, such ionic chain ends lead mainly to in-chain 1,2 unit. However, in the case of 2PB the monomer will not be able to attack the γ -carbon due to the steric hindrance of the bulky phenyl group. This increases in-chain 1,4 structure. A small amount of the charge of the α -carbon is transferred onto the γ -, β -carbon, and the phenyl ring with a decrease in the sample temperature. This leads to a considerable increase in 1,2 unit in the polymer obtained at lower temperature.

In chapter 5 the reactivities of several substituted phenylallyllithiums have been investigated in the reactions with electrophiles. The differences in the negative charge distributions do not affect the product distributions and reactivities of the α -positions are high in the reaction with methanol. When MeI is reacted, the products are reflected by the negative charge distribution, whereas steric effects at the α - or γ -carbons rules regioselectivities of the products in the reaction with trimethylchlorosilane or trimethylchlorotin. The steric requirement in the transition state determined the product distribution in the reactions with acetone or ethylene oxide.

In chapter 6 1-(4-methoxyphenyl)-1,3-butadiene (p-MeO-1PB) and 1-(2-methoxyphenyl)-1,3-butadiene (o-MeO-

-1PB) are synthesized, and the microstructures of the resulting polymers and the negative charge distributions on the living anion chain ends are investigated. Poly-(p-MeO-1PB) polymerized in THF has mainly trans-1,4 structure, whereas polymer sample polymerized in toluene or benzene contains more than 98% 3,4 structure with cyclization. Poly(o-MeO-1PB) polymerized in THF has more than 98% 3,4 content without any cyclization, whereas polymer sample polymerized in toluene also has 3,4 structure and the double bond of the 3,4 unit is considerably consumed by cyclization.

[PART III]

In chapter 7 styrene-ethylene alternating copolymers are prepared by hydrogenating 1,4-poly1PB and 1,4-poly2PB. The ^{13}C NMR spectra indicated that the alternating copolymers obtained from 1,4-poly1PB polymerized in THF and 1,4-poly2PB are atactic and polymer sample prepared from 1,4-poly1PB polymerized in benzene is slightly rich in syndiotactic sequence. The hydrogenation of 3,4-poly1PB gives the polymer corresponding to poly(4-phenyl-1-butene). The obtained samples is concluded to be not stereoregular.

Chapter 8 describes the anionic block copolymerization of 1PB or 2PB with butadiene or styrene. Block efficiency of the copolymerization varies drastically for the copolymerization carried out in THF medium. Whereas, in toluene medium block efficiencies of all cases are almost 100%. The random copolymer of 1PB with styrene is obtained in toluene medium.

LIST OF PUBLICATION

PART I

Chapter 1; *Macromolecules*, 1978, 11, 639

Chapter 2; *Macromolecules*, 1979, 12, 234

PART II

Chapter 3; *Polymer J.*, 1979, 11, 651

Chapter 4; *Polymer J.*, 1979, 11, 937

Chapter 5; *Polymer J.*, 1981, submitted

Chapter 6; *Polymer J.*, 1981, **in press**

PART III

Chapter 7; *Macromolecules*, 1980, 13, 849

Chapter 8; *Macromolecules*, 1981, **in press**

