Microstructure of Poly(2-phenylbutadiene) Prepared by Anionic Initiators

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ABSTRACT: The 220-MHz ^{1}H 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 ^{1}H- 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*-$Bu_3Al-TiCl_4$[2] or $AlHCl_2-OEt_2-AlI_3-TiCl_4$,[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 ^{1}H- 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 $LiAlH_4$ (85 °C (37 mmHg)). The monomer was stored under argon at −15 °C.

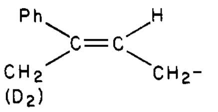
2-Phenyl-1,3-butadiene-*1,1*-d_2 (2PB-*1,1*-d_2) was prepared from acetophenone-d_3 by the same procedure as the preparation of 2PB. The acetophenone-d_3 was obtained by the repeated deuterium exchange reaction of acetophenone with D_2O in the presence of NaOD at 60 °C. The deuteration degree of 2PB-*1,1*-d_2 was 96%.

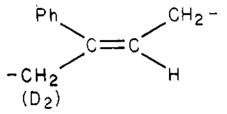
^{1}H- and ^{13}C-NMR Spectra. ^{1}H-NMR spectra were recorded using Varian HR-220 and HR-300 spectrometers. ^{13}C-NMR spectra were measured on a JEOL JNM FX 100 spectrometer (25.05 MHz). Both ^{1}H- and ^{13}C-NMR measurements were carried out at ambient probe temperature on $CDCl_3$ solutions of polymer with tetramethylsilane as an internal standard.

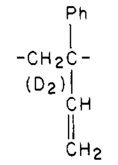
Typical conditions for the quantitative ^{13}C measurement were: spectral width 5 kHz, acquisition time 0.812 s, data points 8192, pulse width 7 μs (42°), pulse repetition 15 s, number of transients 1000–2000. Gated decoupling was employed during the sampling of the free induction decay.

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 chromtography, 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.


cis-1,4


trans-1,4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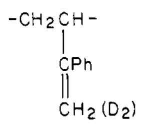
3,4

220- and 300-MHz ^{1}H-NMR Spectra of Poly2PB. Figure 1 shows ^{1}H-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

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Table I
Polymerization Conditions and Microstructure of Poly2PB[a]

no.	initiator	solvent	temp, °C	microstructure,[b] % cis-1,4	1,2	olefin H/aromatic H 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	*t*-BuLi	diglyme	50	97	3	0.20	0.21
4	Na-Naph	THF	30	95	5	0.21	0.22
5	*s*-BuLi	toluene	30	92	8	0.21	0.23
6	Na-Naph	THF	0	90	10	0.23	0.24
7	*t*-BuLi	THF	0	90	10	0.23	0.24
8	*s*-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	*s*-BuLi	THF	−78	74	26	0.31	0.30
12	*t*-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] $= 1.4 \times 10^{-2}$ mol/L. [b] Estimated from ^{13}C-NMR spectra. [c] Sodium naphthalene. [d] Estimated from ^{1}H-NMR spectra.

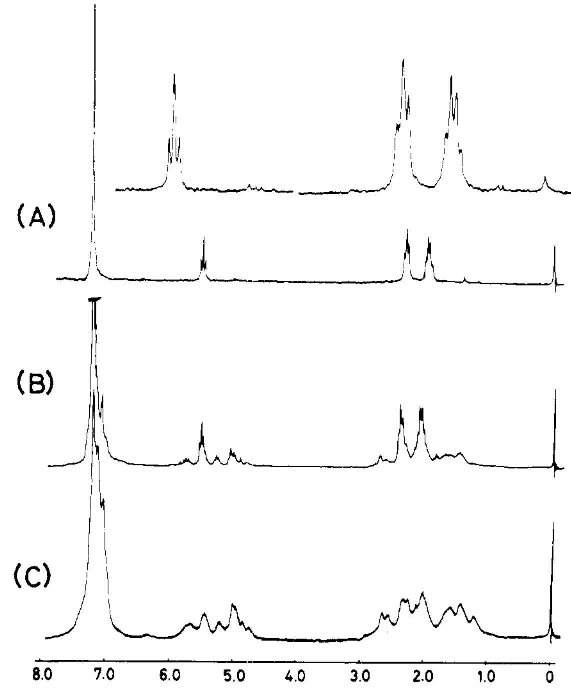


Figure 1. 220-MHz ^{1}H-NMR spectra of poly2PB: (A) no. 1; (B) no. 8; and (C) no. 11.

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 ^{1}H-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 ^{1}H-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 ^{13}C-NMR Spectra of Poly2PB. Further studies of the microstructure of the polymer are discussed as revealed by ^{13}C-NMR spectra. Figure 3 shows the

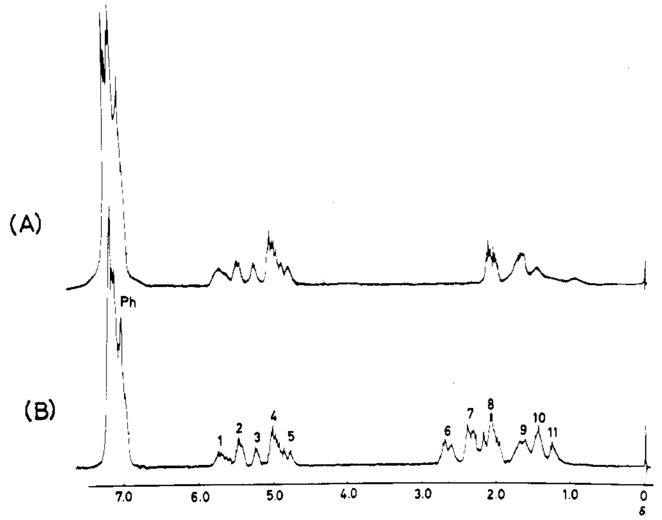


Figure 2. 300-MHz ^{1}H-NMR spectra of (A) poly2PB-*1,1*-d_2 and (B) poly2PB no. 11.

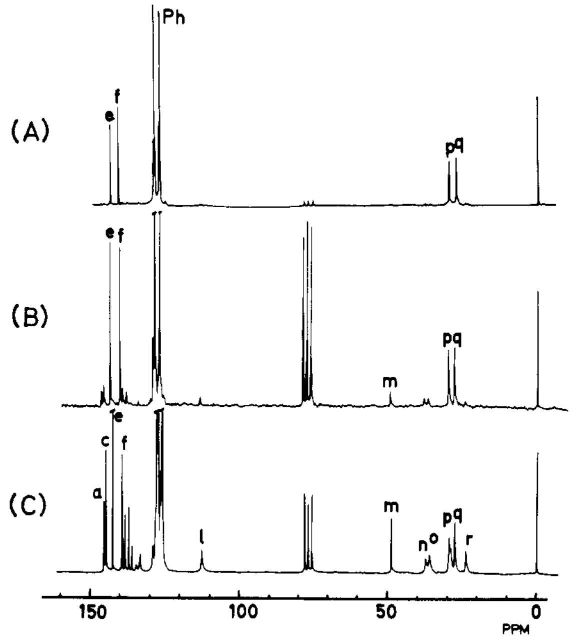


Figure 3. 25.05-MHz ^{13}C-NMR spectra of poly2PB: (A) no. 1; (B) no. 8; and (C) no. 11.

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

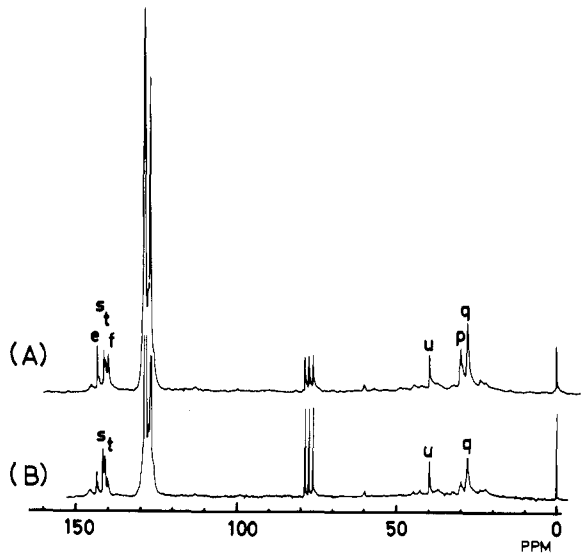


Figure 4. 25.05-MHz ^{13}C-NMR spectra of cis-trans isomerized poly2PB; UV irradiation for (A) 30 min and (B) 60 min.

(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 ^{1}H-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 the irradiation and in the ^{1}H-NMR spectra of the isomerized polymers relative intensities of phenyl to olefin proton resonances are 5. These results indicate that side reactions such as cylization 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%).

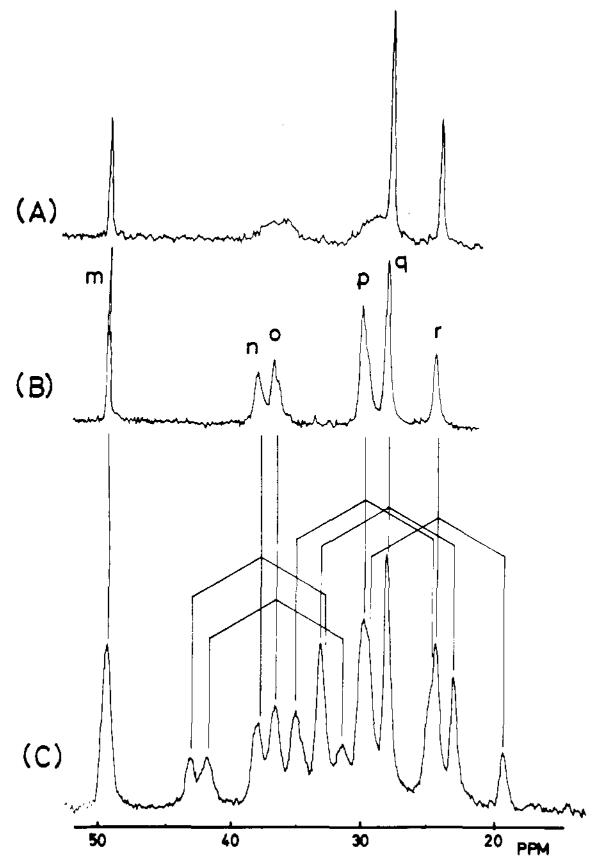


Figure 5. 25.05-MHz ^{13}C-NMR spectra of (A) poly2PB-*1,1*-d_2, (B) no. 11, and (C) proton coupled spectra of no. 11.

The 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 quarternary 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.

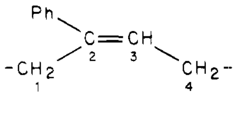
^{1}H- and ^{13}C-NMR Spectra of Poly2PB-*1,1*-d_2. In order to discuss the microstructure of the polymer more precisely, 2PB-*1,1*-d_2 was synthesized and polymerized. The microstructure of poly2PB-*1,1*-d_2 is shown above (positions of deuteriums are shown in parentheses). Figure 2A shows a ^{1}H-NMR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

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

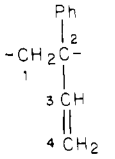
peak	chemical shift	assignment[a]	peak	chemical shift	assignment
a	145.8	V(Ph-1)	j	134.7	$\mathrm{V\underline{C}V}$(3)
b	145.6	$\mathrm{V\underline{C}V}$(Ph-1)	k	133.3	$\mathrm{V\underline{C}C}$(3)
c	145.2	V(3)	l	112.5	V(4)
d	145.0	$\mathrm{V\underline{C}C}$(Ph-1)	m	49.2	V(2)
e	142.9	$\mathrm{C\underline{C}C}$(Ph-1)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

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

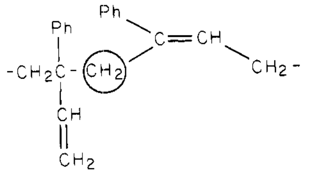
C = cis-1,4 unit



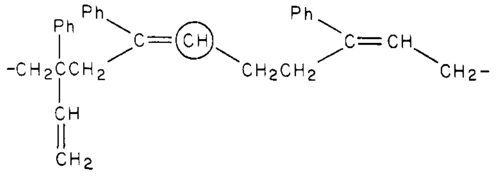
V = 1,2 unit



for example, $\mathrm{V\underline{C}}$(1) means



$\mathrm{V\underline{C}C}$(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*-d_2. 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.

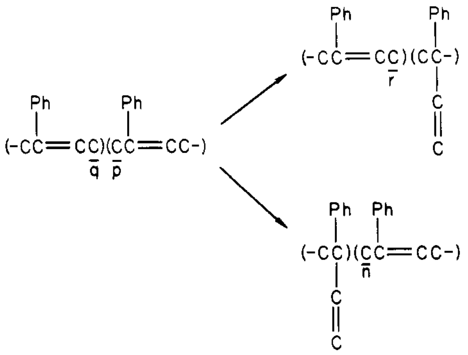
Figure 5A shows the ^{13}C-NMR spectrum of poly2PB-*1,1*-d_2. The resonances of the carbons attached to deuteriums are broadened due to ^{13}C–D couplings and quadrupole broadening. The peaks at n, o, and p are broadened in Figure 5A, indicating that the peaks at n, o, and p are attributed to the carbons 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:

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

$$I(\mathrm{n}) \propto f(\mathrm{vc})$$

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)

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

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

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 ^{1}H-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

	polymer 6			polymer 12			polymer 13			
sequence	obsd	calcd[c]	calcd[d]	obsd	calcd[c]	calcd[e]	obsd	calcd[c]	calcd[f]	peak[a]
				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 substracting 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 ^{1}H-NMR Spectra of Poly2PB

			intensities[b]			
peak	δ from Me_4Si	assignment[a]	obsd		calcd	
1	5.75	V(3)	0.27	total 1.51	0.27	total 1.51
2	5.49	$C\underline{C}C$(3)	0.35		0.36	
3	5.24	$C\underline{C}V$(3)	0.16		0.16	
4	5.02	V(4)	0.51		0.54	
5	4.76	$V\underline{C}C$(3) + $V\underline{C}V$(3)	0.22		0.23	
6	2.70	$V\underline{C}C$(1) + $V\underline{C}V$(1)	0.47	total 3.46	0.46	total 3.50
7	2.38	$C\underline{C}C$(1)	0.69		0.72	
8	2.09	$C\underline{C}C$(4) + $C\underline{C}V$(1)	0.98		1.02	
9	1.67	$C\underline{C}V$(4) + $V\underline{C}C$(4)	0.56		0.62	
10, 11	1.42, 1.19	V(1) + $V\underline{C}V$(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 atrributed 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 $C\underline{C}C$(3) and $C\underline{C}V$(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 ^{13}C-NMR spectra.

Sequence Distribution in Poly2PB. The fractions of dyad and triad sequence distributions are obtained from ^{13}C-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.

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

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

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.

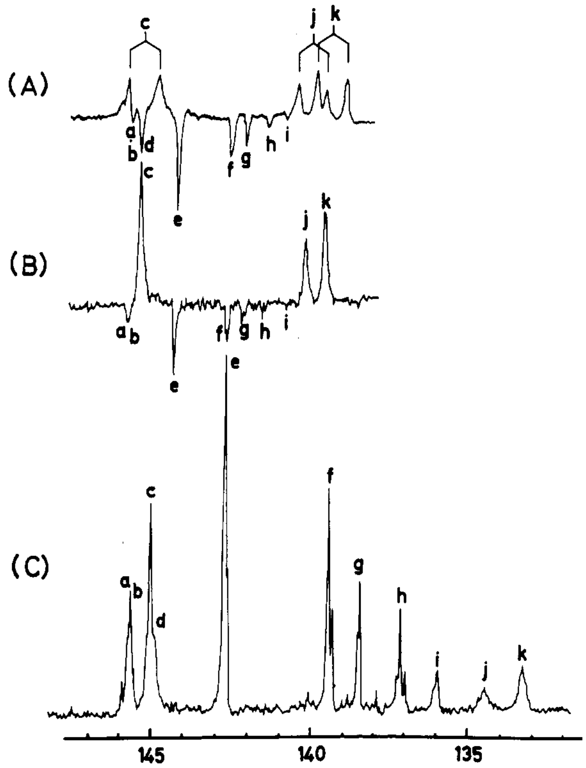


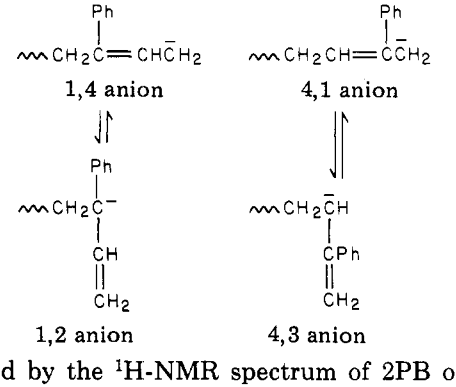
Figure 6. 25.05-MHz ^{13}C-NMR spectra of No. 13. Partially relaxed spectra by applying a 3.0 s–180°–0.6 s–90° pulse sequence: (A) off-resonance and; (B) noise decoupled spectra; (C) partial spectrum with an increase in computer resolution (0.24 Hz).

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-d*$_2$. 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.

Schuê et al. studied a living oligomer of poly2PB prepared with *t*-BuLi-d_9 in benzene-d_6 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 ^{1}H-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. Stille[2] 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. Asami[6] 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, Ambrose[7] 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.

References and Notes

(1) T. Suzuki, Y. Tsuji, and Y. Takegami, *Macromolecules*, **11**, 639 (1978).
(2) J. K. Stille and E. D. Vessel, *J. Polym. Sci.*, **49**, 419 (1961).
(3) W. Marconi, A. Mazzei, G. Lugli, and M. Bruzzone, *J. Polym. Sci., Part C*, **16**, 805 (1967).
(4) T. Masuda, T. Mori, and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2065 (1974).
(5) R. Asami and K. Hasegawa, *Polym. J.*, **8**, 67 (1976).
(6) R. Asami and A. Shoji, *Asahi Garasu Kogyo Gijutsu Shorei-Kai Kenkyu Hokoku*, **12**, 505 (1966); *Chem. Abstr.*, **68**, 50119v (1968).
(7) R. J. Ambrose and W. L. Hergenrother, *Macromolecules*, **5**, 275 (1972).
(8) C. S. Marvel and R. G. Woolford, *J. Org. Chem.*, **23**, 1658 (1958).
(9) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, p 80.
(10) Y. Tanaka and H. Sato, *Polymer*, **17**, 113 (1976), and the references therein.
(11) K. Hatada, K. Ohta, Y. Okamoto, T. Kitayama, Y. Umemura, and H. Yuki, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 531 (1976).
(12) The fractions of unsymmetrical CCV and VCC sequences are estimated to have equal intensities according to statistical calculations: By statistical methods only, therefore, the assignments of the carbons or protons in the central unit in these two sequences cannot be distinguished. In this study these assignments are carried out by considering the shielding effects of the phenyl group or olefin double bond on the carbon or proton under consideration. The possibility of the reverse assignment between these two sequences still remains.
(13) B. Kaempf, A. Maillard, F. Schuê, J. Sommer, and C. Taniêlian, *Bull. Soc. Chim. Fr.*, 1153 (1972).
(14) J. Sledz, B. Kaempf, and F. Schuê, *Macromol. Chem.*, **176**, 459 (1975).
(15) M. Morton, R. D. Sanderson, R. Sakata, and L. A. Falvo, *Macromolecules*, **6**, 186 (1973).