Microstructure of Poly(1-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(1-phenyl-1,3-butadiene) (poly1PB) samples prepared by anionic and coordinated catalysts were investigated. Assignments of ^{1}H 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 ^{1}H 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 ^{1}H 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 79–81 °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 Smith[10] and 1,1-diphenylhexllithium (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.

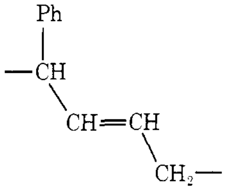
Trans–Cis Isomerization: A benzene solution of polymer (0.1–0.2 w/v %) was irradiated with a high-pressure mercury lamp. The irradiation was carried out in the presence of thiobenzoic acid (2–4 w/w % of the polymer) as a sensitizer at 20 °C. The isomerized polymer was purified by repeated reprecipitations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

^{1}H and ^{13}C NMR Spectra. ^{1}H 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 ^{1}H 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 μs (42 °), pulse interval 1.5 s, and number of transients 1000–2000.

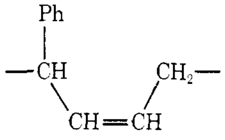
Gel-Permeation Chromatogram. Gel-permeation chromatograms were recorded on a Waters ALC/GPC 244 equipped with four columns ($10^5 + 10^4 + 10^3 + 500$ Å). The solvent was tetrahydrofuran and the flow rate was 1.5 mL/min. The molecular weight of poly1PB was determined according to calibration curves obtained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

Results and Discussion

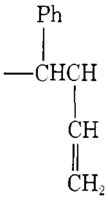
The following four structural units are contained in poly1PB. Infrared spectra of poly1PB prepared in this study were essentially the same regardless of the reaction conditions. No 1,2 units were found in the polymers, as evidenced by the absence of the absorptions at 990 and 910 cm^{-1}. The strong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



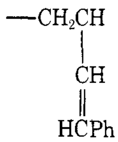
trans-1,4



cis-1,4



1,2



3,4

220-MHz ^{1}H Spectra of Poly1PB. ^{1}H 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

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Table I
^{1}H 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

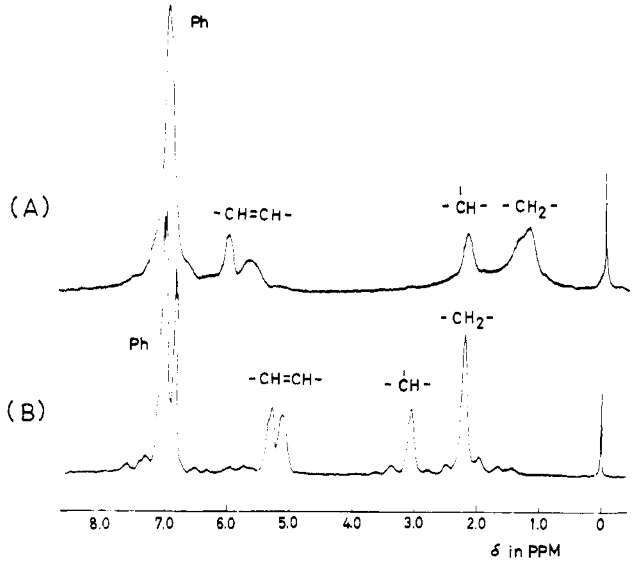


Figure 1. 220-MHz ^{1}H NMR spectra of (A) polymer no. 17 (3,4 unit, more than 98%) and (B) polymer no. 16 (1,4 unit, 92%).

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 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)[h]

			Polymerization			1,4, %			Cis-1,4/trans-1,4	
No.	Catalyst	Solvent	Temp, °C	Time, h	Conv, %	Trans	Cis	3,4, %	^{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	*n*-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	*s*-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	*t*-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	−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)$_2$–AlEt$_2$Cl, Al/Co = 3.0, Co = 0.5 × 10^{-2} mol/L. [e] VCl$_4$–Anisole–AlEt$_2$Cl, Al/Anisole/V = 3/5/1, [VCl$_4$] = 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.

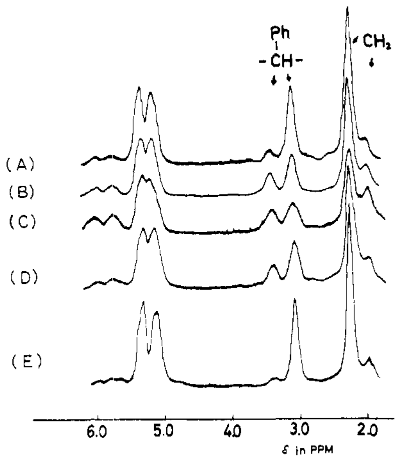


Figure 2. Partial 220-MHz ^{1}H NMR spectra of poly1PB: (A) no. 2 (B) no. 3, (C) no. 14, (D) no. 15, and (E) no. 16.

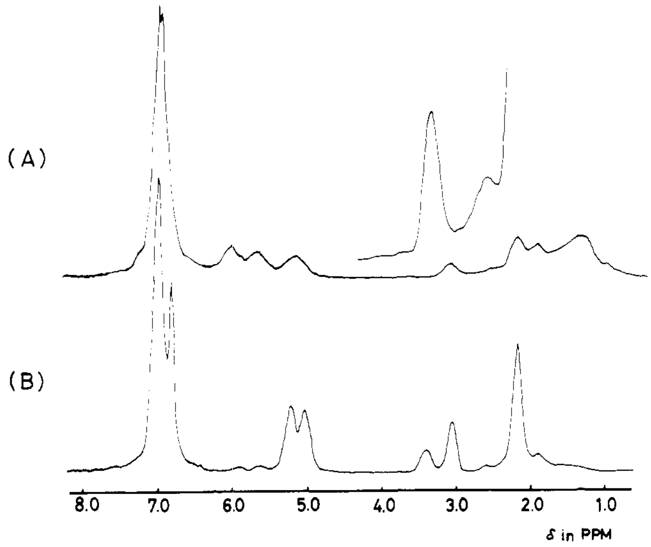
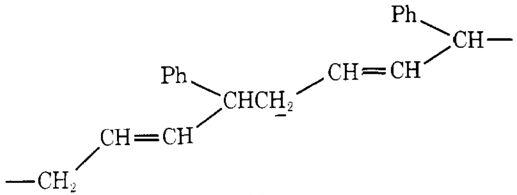


Figure 3. 220-MHz ^{1}H NMR spectra of (A) no. 18 (1,4 33%, 3,4 67%) and (B) no. 12 (1,4 92%, 3,4 8%).

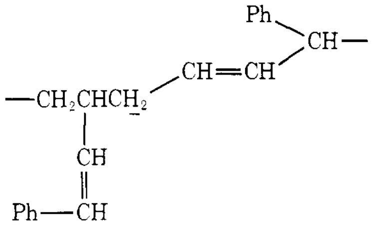
reported that poly1PB prepared in benzene by alkyl lithium contained 75% 3,4 units.[17] We cannot reproduce this, and the 3,4 content in this polymer should be less than 20% as mentioned above.

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 ^{1}H 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 ^{1}H 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.



2.20 ppm



1.97 ppm

^{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-

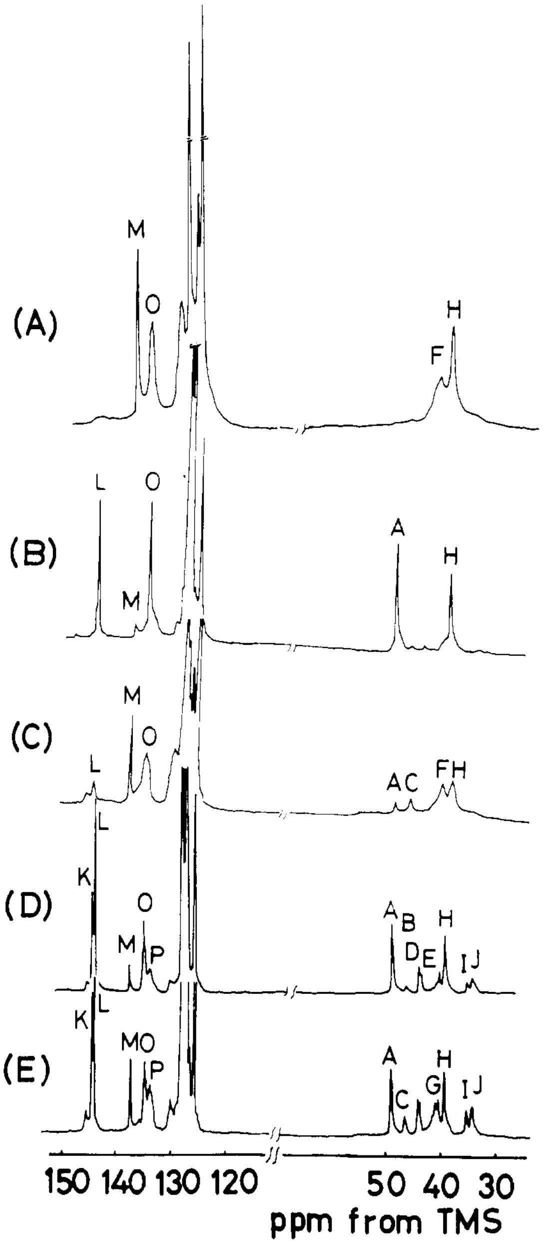


Figure 4. 25.0-MHz ^{13}C NMR spectra of (A) no. 17, (B) no. 16, (C) no. 18, (D) no. 12, and (E) no. 14

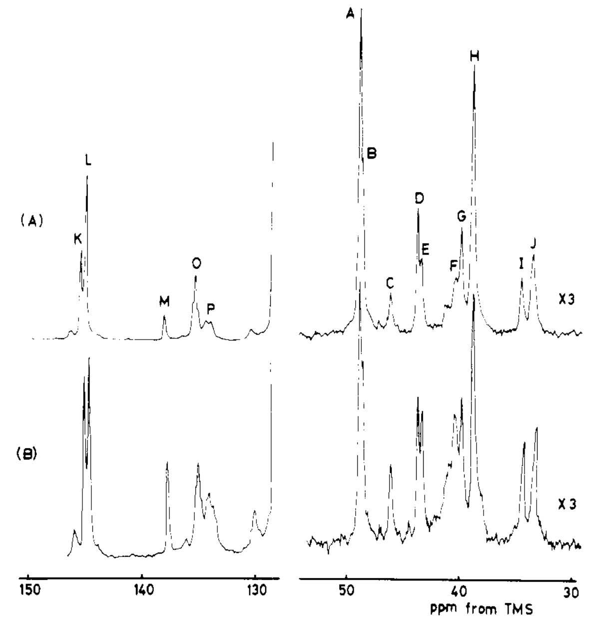


Figure 5. Expanded ^{13}C NMR spectra of (A) no. 12 and (B) no. 14.

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 irradiation 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.

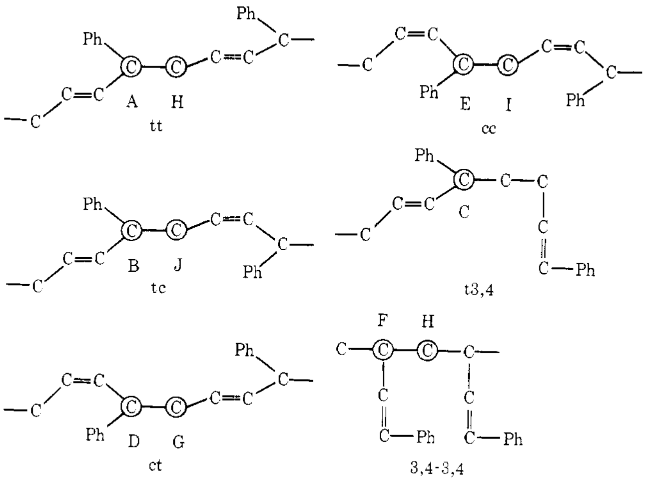
^{13}C NMR spectra and gel permeation chromatograms of sample no. 13 irradiated with UV light for 30, 120, and 240 min are shown in Figure 6. The resonances at B, D, E, G, I, and J in the aliphatic carbon region and K and P in the olefin carbon region increased in proportion to the irradiation time. On the other hand peaks at C, F, and M disappeared immediately after the irradiation. In the ^{1}H 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 Conti[22] 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 Obsd	Chemical shift, ppm Calcd	Diff
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:



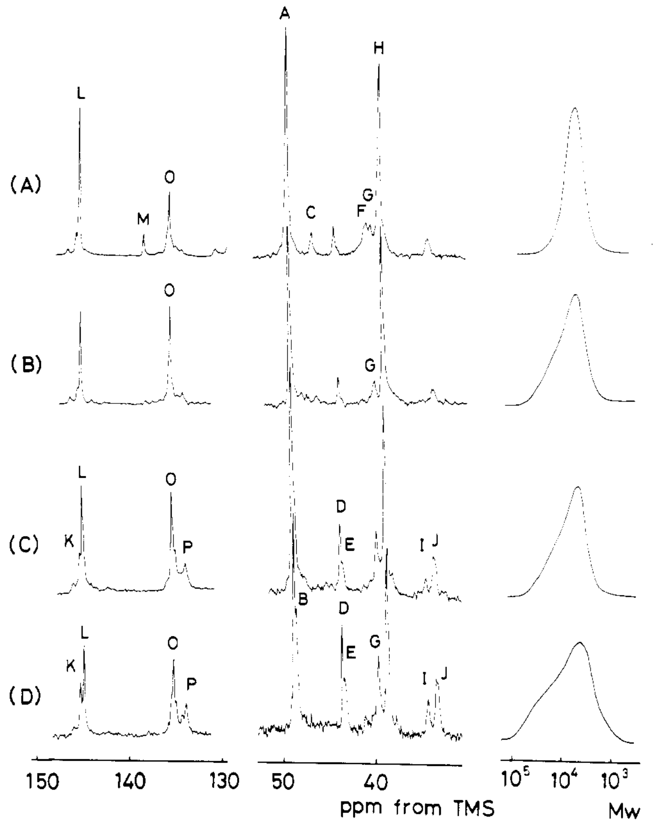


Figure 6. ^{13}C NMR spectra and gel-permeation chromatograms of trans–cis isomerized poly1PB: (A) original polymer (no. 13), (B) UV irradiation for 30 min, (C) UV irradiation for 120 min, and (D) UV irradiation for 240 min.

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 ^{1}H 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.

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

The results are listed in the last column in Table II compared with the values obtained from the ^{1}H 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 inducation 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 No. 16 Obsd	No. 16 Cald	No. 12 Obsd	No. 12 Cald	No. 14 Obsd	No. 14 Cald	UV irrad. Obsd	UV irrad. Cald	Peak[b]
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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Chain Dimension and Effective Potential Energy of Globular Proteins

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ABSTRACT: In this study, a statistical analysis on chain dimensions of irregular parts in native proteins, three-dimensional structures of which are known, has revealed that *short* segments (up to $n = 8$) of the irregular backbone conformations in a protein can be treated, in the sence of a statistical ensemble, as the "unperturbed" (devoid of explicit long-range interactions) polypeptide chain. The single-residue energy primarily responsible for this unperturbed chain dimension is, however, the Pohl's empirical potential energy rather than the atom pair potential energy usually employed. The distinct quantitative difference between the Pohl's energy map and the atom pair energy map is clearly shown in the difference of the characteristic ratios calculated from both energy maps. These evidences indicate that the potential energy for a single residue within a globular protein is modified due to long-range interresidue interactions. Theoretical calculations were carried out on the unperturbed polypeptide chain to obtain the mean squares of end-to-end distances by the method of Flory and distributions of end-to-end distances by the Monte-Carlo technique and served for comparison with the corresponding observed data taken from 19 globular proteins.

Accumulation of high-resolution x-ray data of globular proteins has enabled one to analyze three-dimensional structures of proteins and roles of the constituent amino acid residues in the folding of polypeptide chains by various statistical methods.[1–4] Recently Crippen[5] has presented the dependence of the chain dimension (the mean value of end-to-end distances) of protein segments on the separation of amino acid residues. Also, Monte-Carlo simulations of chain statistics have been carried out for several simple polypeptides.[6–9] The combination of these two methods, i.e., the comparison of the chain dimension observed in globular proteins with that of randomly coiled polypeptides, would provide information about the character of interacting forces within a protein molecule. In our knowledge, there have been few publications of the study along this line; e.g., for a rather limited case of β-turn conformations a comparison of calculated and observed distributions of end-to-end distances has been made.[10]

Although a native protein is by no means a random coil, a large amount of structural data of native proteins may be regarded as a statistical ensemble. The compact shape of a native protein, however, suggests that long-range net attractive forces are dominant in determination of the chain statistics of protein segments. The terms used here, short- and long-range interactions, are atomic interactions within a single residue and all the other interactions between residues, re-