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### Synthesis and Characterization of Polyisobutylene-Polybutadiene Diblocks

Sandor Nemes<sup>ab</sup>, Joseph P. Kennedy<sup>b</sup>

<sup>a</sup> Department of Applied Chemistry, L. Kossuth University, Debrecen 10, Hungary <sup>b</sup> Institute of Polymer Science The University of Akron, Akron, Ohio

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## SYNTHESIS AND CHARACTERIZATION OF POLYISOBUTYLENE-POLYBUTADIENE DIBLOCKS

SANDOR NEMES† and JOSEPH P. KENNEDY\*

Institute of Polymer Science  
The University of Akron  
Akron, Ohio 44325-3909

### ABSTRACT

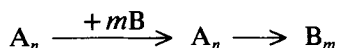
The synthesis and characterization of novel polyisobutylene-polybutadiene diblocks (PIB-*b*-PBd) are described. The total synthesis involves two steps: 1) The synthesis of *t*-chlorine terminated PIB (PIB-CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>Cl, PIB-Cl') and 2) the one-pot dehydrochlorination-metalation of PIB-Cl' by *n*-BuLi/*t*-ROK system (where *t*-R = *t*-butyl, *t*-amyl) to the PIB-CH<sub>2</sub>C(=CH<sub>2</sub>)CH<sub>2</sub><sup>-</sup>, (PIB<sup>-</sup>) anion followed by initiation of butadiene (Bd) polymerization by the macroanion. Detailed characterization studies including <sup>13</sup>H- and <sup>13</sup>C-NMR spectroscopies, GPC, fractional precipitation, and model compound studies conclusively prove the synthesis of the PIB-*b*-PBd diblocks with ~60% 1,2 and ~40% 1,4 PBd microstructure.

### INTRODUCTION

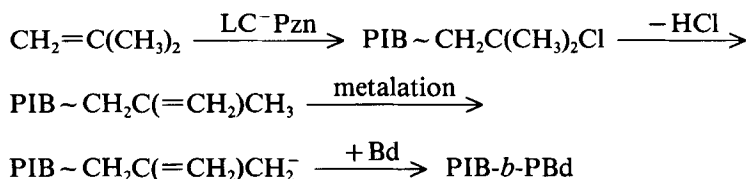
In the course of our work on the synthesis of terminally functional polymers, we became interested in exploring the possibility of synthesizing PIB<sup>-</sup> anions and using these intermediates to initiate the anionic polymerization of Bd in hydrocarbon solvent. Since isobutylene can be

†Visiting scientist. Permanent address: Department of Applied Chemistry, L. Kossuth University, H-4010, Debrecen 10, Hungary.

polymerized only by cationic mechanism, the first segment of the target diblock had to be prepared by carbocationic technique; in contrast, the synthesis of the second segment called for an anionic polymerization method. Synthesis in which two (or more) mutually exclusive polymerization mechanisms are sequentially combined are called "transformation reactions" [1-3]; schematically:



The strategy in the present instance was to prepare a PIB capped with a well-defined end-group by living carbocationic polymerization ( $LC^+Pzn$ ), transform the end group by dehydrochlorination/metalation to an anion ( $PIB^-$ ) capable of inducing the polymerization of Bd, and concluding the synthesis by the addition of Bd. Schematically:



The synthesis of the first intermediate  $PIB-Cl'$  has been worked out previously [4]. The second and third steps, the quantitative conversion of  $PIB-Cl'$  to the desired  $PIB^-$  anion by a one-pot dehydrochlorination-metalation process using *n*-BuLi/sec-BuLi mixtures in the presence of polar complexing agents, has recently been described [5]. However, preliminary experiments have shown that this metalation procedure, while quantitatively yielding the anion, is unsuitable for diblock synthesis (presence of excess reactive anions yielding high amounts of homo-PBd contaminant).

Further experiments indicated that the reactivity of the  $PIB^-$  increases significantly if the dehydrochlorination-metalation-polymerization step is carried out with *n*-BuLi/*t*-ROK combinations. The increase in reactivity observed by switching from BuLi/TMEDA (*N,N,N',N'*-tetramethylethylenediamine) to *n*-BuLi/*t*-ROK is most likely due to the presence of reactive terminal ion pairs of  $PIB^-K^+$  which aggregate with *t*-ROLi. The *t*-ROLi arises during transmetalation between *n*-BuLi and *t*-ROK [6-8]. The excess of *in-situ* formed *n*-BuK gradually decomposes [8, 9]:



However, the anion  $\text{PIB}^-\text{K}^+$  does not decompose because it is devoid of  $\beta$ -hydrogens. Thus specific conditions can be found under which the amount of residual  $n\text{-BuK}$  can be minimized in the presence of completely converted PIB.

## EXPERIMENTAL

### Materials

Hexanes were refluxed with sulfuric acid washed with water until neutral, dried over anhydrous  $\text{CaCl}_2$ , and distilled over  $\text{CaH}_2$  under nitrogen. All other solvents (methanol, hexanes,  $\text{CH}_2\text{Cl}_2$ , benzene, pentane) were reagent grade (Fisher) and were used as received.  $n$ -Butyllithium ( $n\text{-BuLi}$ ) (1.6  $M$  solution in hexanes) (Aldrich), potassium- $t$ -amylate ( $t\text{-AmOK}$ ) (1.5  $M$  solution in benzene) (Morton Thiokol), and potassium- $t$ -butoxide ( $t\text{-BuOK}$ ) (Aldrich) were used as received. 2,4,4-Trimethyl-1-pentene (Tm1P) (Aldrich) was distilled over  $\text{CaH}_2$  before use. 1,3-Butadiene (Bd) (99 + %, Aldrich) was passed through a disposable inhibitor remover (Aldrich) before use. The  $(\text{CH}_3)_3\text{C} \sim \text{PIBCH}_2\text{C}(\text{CH}_3)_2\text{Cl}$  (PIB-Cl') was prepared by the polymerization of isobutylene using the  $\text{CH}_3\text{COOH}/\text{BCl}_3/\text{CH}_3\text{Cl}/-45^\circ\text{C}$  and 2-chloro-2,4,4-trimethylpentane/ $\text{TiCl}_4/\text{CH}_3\text{Cl}/n\text{-C}_6\text{H}_{14}/-45^\circ\text{C}$  system [4].

### Procedures

Metalations and polymerizations were carried out in a stainless steel dry box under a dry  $\text{N}_2$  atmosphere using large test tubes ( $\sim 75$  mL) [10] and 250 mL round-bottom flasks equipped with a rubber septum. Metalated Tm1P and PIB solutions were used for polymerization experiments. The polymer-anion solutions were quenched by addition of methanol followed by dissolving the polymer in  $\text{CH}_2\text{Cl}_2$  and precipitating into methanol. Conversions were determined after drying the polymers in vacuum at ambient temperature. The polymers were further purified by dissolving in  $\text{CH}_2\text{Cl}_2$ , filtering (to remove and quantitate the gel content), and evaporating the solvent (Rotovap). The purified polymers were analyzed by GPC and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy.

Molecular weights ( $\bar{M}_n$ ) and dispersities ( $\bar{M}_w/\bar{M}_n$ ) were determined by

a Waters high pressure GPC instrument equipped with dual RI and UV detectors and five  $\mu$ -Styragel columns. The calibration curve was constructed of narrow MWD PIB standards [11].

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were obtained with a Varian Gemini-200 spectrometer using  $\text{CDCl}_3$  solutions ( $\sim 15$  and  $\sim 30$  w/v) at room temperature. The  $^1\text{H-NMR}$  spectra were recorded at 200 MHz (the main parameters were: pulse width, 14.5  $\mu\text{s}$ ; pulse delay, 20 s; acquisition time, 5.0 s; number of transients, 64). The  $^{13}\text{C-NMR}$  spectra were recorded at 50.3 MHz under conditions of continuous proton broad-band decoupling and inverse gated decoupling [12–14] (the main parameters were: pulse width, 10.0  $\mu\text{s}$ ; pulse delay, 3 and 12 s; acquisition time, 1.0 s; number of transients, 3200). The intensities of the signals were measured by electronic integration and, since the peaks overlap somewhat, by cutting and weighing [15, 16]. For quantitative characterization of PIB-*b*-PBd's, peak intensities were obtained from proton-decoupled  $^{13}\text{C-NMR}$  spectra with suppressed nuclear Overhauser enhancement (inverse gated decoupling). We obtained the same results by using peak intensities from broad-band decoupled  $^{13}\text{C-NMR}$  spectra for measurement of relative peak ratios [17, 18].

The 1,2- and 1,4-contents of the polybutadienes were obtained by  $^1\text{H-NMR}$  spectroscopy (see the Structure Characterization Section).

#### **Procedure for Metalation of Tm1P and of Butadiene Polymerization by Metalated Tm1P with the *n*-BuLi/*t*-AmOK/Benzene System**

A charge of 0.32 mL Tm1P (2.0 mmol), 8.0 mL *t*-AmOK (1.5 *M* in benzene) (12.0 mmol), and 1.37 mL *n*-BuLi (1.6 *M* in hexanes) (2.2 mmol) was stirred in a large test tube for 5 h at room temperature. After 5 h the solution was cooled to  $-15^\circ\text{C}$  and the polymerization of Bd was started by adding the diene directly to the agitated charge. After 6 h the polymerization was quenched with prechilled methanol.

#### **Procedure for One-Pot Dehydrochlorination-Metalation of PIB-Cl' and of Butadiene Polymerization by $\text{PIB}^-$ with the *n*-BuLi/*t*-AmOK/Benzene System**

A charge of 8.57 g PIB-Cl' ( $\overline{M}_n = 2450$ ;  $\overline{M}_w/\overline{M}_n = 1.70$ ) (3.5 mmol), 28.0 mL *t*-AmOK (1.5 *M* in benzene) (42.0 mmol), and 5.50 mL *n*-BuLi (1.6 *M* in hexanes) (8.75 mmol) was stirred 5 h at room temperature. Bd

was added to the charge at  $-10^{\circ}\text{C}$  and stirred for 6 h. The polymer-anion solutions were quenched by methanol.

### Procedure for One-Pot Dehydrochlorination-Metalation of PIB-Cl' and of Butadiene Polymerization by PIB<sup>-</sup> with the *n*-BuLi/*t*-BuOK/Hexanes System

A charge of 29.8 g PIB-Cl' ( $\overline{M}_n = 8500$ ;  $\overline{M}_w/\overline{M}_n = 1.32$ ) (3.5 mmol) in 30 g hexanes, 2.40 g *t*-BuOK (21.0 mmol), and *n*-BuLi (1.6 *M* in hexanes) (see Table 3, column 1) was stirred 5 h at room temperature. Bd was added to the charge at  $-35^{\circ}\text{C}$  and stirred for 2 h. The charges were quenched by methanol.

### Fractional Precipitation by Addition of Nonsolvent

Fractional precipitation [19, 20] was carried out by the dropwise addition of methanol as the nonsolvent to a solution of 5.77 g PIB-*b*-PBd in 850 mL benzene ( $d = 0.874$ ) plus 500 mL pentane ( $d = 0.626$ ) in a separatory funnel at  $25 \pm 1^{\circ}\text{C}$ . Pentane was used to reduce the density of the system and thus to avoid the ascending of the precipitate. (The densities of PIB and PBd are 0.84 and 0.89, respectively [21].) Rapid stirring and slow precipitant addition prevents local precipitation. At the onset of precipitation, after permanent turbidity appeared, stirring was discontinued and the system was stored (24 h or longer) until precipitation occurred. The precipitate was separated, dried to constant weight in vacuum, and its composition was determined by  $^1\text{H-NMR}$  spectroscopy. The final fraction was obtained by evaporating the liquid.

## RESULTS AND DISCUSSION

### Syntheses of PIB-*b*-PBds

Table 1 shows conditions and results of metalation of Tm1P and initiation of Bd polymerization by metalated Tm1P. The homogeneous solutions of metalated Tm1P gave  $\sim 100\%$  conversions of Bd. The  $\text{CH}_2\text{Cl}_2$ -insoluble fraction (highly branched and/or crosslinked gel) increased with increasing Bd concentration. The  $\overline{M}_w/\overline{M}_n$ 's show a broadening tendency, but the GPC traces show no bimodality.

Table 2 shows conditions and results of the one-pot dehydrochlorina-

TABLE 1. Metalation of Tm1P and Butadiene Polymerization by Metalated Tm1P with the *n*-BuLi/*t*-AmOK/Benzene System<sup>a</sup>

Butadiene, g (mmol)	Yield, % <sup>b</sup>	$\bar{M}_n$ (by <sup>1</sup> H NMR), g/mol	$\bar{M}_n$ (by GPC), g/mol <sup>c</sup>	$\bar{M}_w/\bar{M}_n$
1.32 (24.4)	98	760	790	1.15
1.98 (36.6)	97	975	1050	1.15
2.64 (48.8)	97	1320	1410	1.26
3.30 (61.0)	95	1610	1800	1.29
3.96 (73.2)	94	2270	2540	1.38
4.62 (85.4)	90	3050	3360	1.45
5.28 (97.6)	88	3830	4280	1.45

<sup>a</sup>Metalation conditions: 0.32 mL Tm1P (2.0 mmol), 8.0 mL *t*-AmOK (1.5 M in benzene) (12.0 mmol), 1.37 mL *n*-BuLi (1.6 M in hexanes) (2.2 mmol), room temperature, 5 h. Polymerizations conditions: -15°C, 6 h.

<sup>b</sup>Exclusive CH<sub>2</sub>Cl<sub>2</sub>-insoluble fraction.

<sup>c</sup>PIB equivalent (based on PIB calibration curves).

tion-metalation-polymerization carried out with the PIB-Cl'/*n*-BuLi/*t*-AmOK/benzene/Bd system. The PIB-*b*-PBd products contain no detectable homo-PBd at low PBd/PIB ratios (entries 1–3, Table 2) and less than ~10% homo-PBd at higher PBd/PIB ratios (entries 4–7, Table 2). These analyses were performed by <sup>13</sup>C-NMR spectroscopy (see the Structure Characterization Section). According to <sup>13</sup>C analyses, 78–64% of the PIB was converted to diblocks. The conversion of PIB-Cl' decreases with increasing PBd/PIB ratio. It should be noted that the purified (CH<sub>2</sub>Cl<sub>2</sub>-insoluble fraction exclude) polymers were analyzed. Thus the CH<sub>2</sub>Cl<sub>2</sub>-insoluble fraction may contain crosslinked diblock together with PIB and PBd moieties.

Additional experiments focusing on the synthesis of higher molecular weight PIB-*b*-PBd diblocks indicated that the experimental conditions had to be modified on account of persistent gelation with the PIB-Cl'/*n*-BuLi/*t*-AmOK/benzene/Bd combination. We have found that by increasing the PBd sequence length, the extent of gelation increased and metalating agent efficiencies decreased. Although branching and crosslinking are likely events under the above experimental conditions, it was felt that in the presence of benzene gelation may occur and by substituting it by hexanes this problem may be alleviated. At the same time, in view of its lower cost and commercial availability, we substituted *t*-

TABLE 2. One-Pot Dehydrochlorination-Metalation of PIB-Cl' and Butadiene Polymerization by PIB<sup>-</sup> with the *n*-BuLi/*t*=AmOK/Benzene System<sup>a</sup>

Butadiene, g (mmol)	Yield, % <sup>b</sup>	PIB-Cl' conversion, % <sup>b,c</sup>	Homo-PBD, % <sup>c</sup>	$\overline{M}_n$ (by GPC), g/mol <sup>d</sup>	$\overline{M}_w/\overline{M}_n$
1.32 (24.4)	98	78	—	2770	1.72
1.98 (36.6)	98	77	—	2910	1.76
2.64 (48.8)	97	75	—	3230	1.75
3.96 (73.2)	94	73	3	3510	1.67
5.28 (97.6)	92	67	5	3820	1.85
7.92 (146.4)	86	65	6	4260	2.07
9.24 (170.8)	81	64	9	4560	2.52

<sup>a</sup>Dehydrochlorination-metalation conditions: 8.57 g PIB-Cl' ( $\overline{M}_n = 2450$ ;  $\overline{M}_w/\overline{M}_n = 1.70$ ) (3.5 mmol), 28.0 mL *t*-AmOK (1.5 M in benzene) (42.0 mmol), 5.50 mL *n*-BuLi (1.6 M in hexanes) (8.75 mmol), room temperature, 5 h. Polymerization conditions:  $-10^\circ\text{C}$ , 6 h.

<sup>b</sup>Exclusive CH<sub>2</sub>Cl<sub>2</sub>-insoluble fraction.

<sup>c</sup>By <sup>13</sup>C-NMR spectroscopy.

<sup>d</sup>PIB equivalent (based on PIB calibration curves).

AmOK with *t*-BuOK. Thus, by changing the metalating agent and the solvent, i.e., by the use of the PIB-Cl'/*n*-BuLi/*t*-BuOK/hexanes/Bd system, we were able to prepare PIB-*b*-PBd diblocks of higher PBd sequence lengths.

Table 3 summarizes the conditions found to be satisfactory for one-pot dehydrochlorination-metalation followed by BD polymerization by PIB<sup>-</sup>. Thus the PIB-Cl'/*n*-BuLi/*t*-BuOK = 1/6/6 system led to 100% Bd conversion and 4–7% easily filterable gel. Evidently the use of olefin-free hexanes at a relatively low temperature (e.g.,  $-35^\circ\text{C}$ ) for a short time ( $\sim 2$  h) is conducive for the synthesis of essentially gel-free product.

### Diblock Fractionation

The quantitative characterization of PIB-*b*-PBd is possible by <sup>13</sup>C-NMR spectroscopy provided the product  $\overline{M}_n$  is less than  $\approx 5000$ . Thus we were compelled to use classical fractional precipitation [19, 20] to



TABLE 3. One-pot Dehydrochlorination-Metalation of PIB-Cl' and Butadiene Polymerization by PIB<sup>-</sup> with the *n*-BuLi/*t*-BuOK/Hexanes System<sup>a</sup>

<i>n</i> -BuLi (1.6 M in hexanes), mL (mmol)	Bd, g (mmol)	Bd conversion, %	$\bar{M}_n$ (by GPC), <sup>b</sup> g/mol	$\bar{M}_w/\bar{M}_n$
11.0 (17.60)	34 (628)	~100 <sup>c</sup>	22,000 <sup>d</sup>	1.20
13.2 (21.00)	34 (628)	~100 <sup>c</sup>	13,800	1.42
13.2 (21.00)	41 (754)	~100 <sup>c</sup>	15,200	1.45

<sup>a</sup>Dehydrochlorination-metalation conditions: 29.8 g PIB-Cl' ( $\bar{M}_n = 8500$ ;  $\bar{M}_w/\bar{M}_n = 1.32$ ) (3.5 mmol) in 30 g hexanes; 2.4 g *t*-BuOK (21 mmol); *n*-BuLi (1.6 M in hexanes) see column 1; 5 h; room temperature. Polymerization conditions: -35°C; 2 h.

<sup>b</sup>PIB equivalent.

<sup>c</sup>Contains 4-7% gel.

<sup>d</sup>Bimodal MWD containing some starting PIB of  $\bar{M}_n = 8500$  g/mol and  $\bar{M}_w/\bar{M}_n = 1.32$ .

quantitate homopolymer contamination in relatively high molecular weight PIB-*b*-PBd ( $\bar{M}_n = 15,200$ ;  $\bar{M}_w/\bar{M}_n = 1.45$ , last entry, Table 3).

The results of fractional precipitation are summarized in Table 4 and Fig. 1. Significantly, precipitate does not form until the volume ratio of precipitant to total solution ( $\lambda$ ) reaches ~0.23. In the range from  $\lambda = 0.23$  to 0.34, homo-PIB precipitates, accompanied by the unavoidable coprecipitation of appreciable amounts of relatively low molecular weight PIB-*b*-PBd (tail effect) [19]. According to the data, the overall homo-PIB content in our product is ~20%. At  $\lambda \approx 0.34$  the overall composition of the fractions abruptly changes, indicating massive precipitation of PIB-*b*-PBd. In the range from  $\lambda = 0.34$  to 1.17, the diblock precipitates and ~94% of the product is recovered.

The final fraction, ~6%, obtained by evaporating the liquids, was analyzed by GPC and <sup>1</sup>H-NMR spectroscopy. According to GPC this fraction contained two components (bimodal distribution), 65% diblock of  $\bar{M}_n = 6970$  and 35% PBd of  $\bar{M}_n = 1350$ . Thus the overall PBd contamination of the product is ~2%.

TABLE 4. Fractional Precipitation of PIB-*b*-PBd ( $\overline{M}_n = 15,200$ ;  $\overline{M}_w/\overline{M}_n = 1.45$ ) 5.77 g; Solvent: 850 mL Benzene + 500 mL Pentane; Precipitant: Methanol

Volume ratio of precipitant to solution, $\lambda$	Polymer precipitated <sup>a</sup>		PBd, <sup>b</sup> wt%	$\overline{M}_n$ , <sup>c</sup> g/mol
	g	%		
0.228	0.0	0.0	0.0	—
0.254	0.387	6.7	0.0	21,200
0.260	0.618	10.7	5	19,700
0.270	0.810	14.0	6	18,300
0.278	0.910	15.8	8	17,300
0.287	1.047	18.1	11	16,600
0.297	1.133	19.6	15	16,300
0.309	1.196	20.7	19	15,700
0.327	1.207	20.9	—	15,500
0.335	1.210	21.0	—	—
0.343	1.250	21.7	48	14,700
0.374	1.670	28.9	64	14,300
0.388	2.005	34.7	67	14,100
0.427	2.250	40.0	69	13,800
0.510	2.970	51.5	72	13,200
0.512	3.310	57.4	74	13,000
0.620	3.610	62.6	74	12,100
0.675	3.880	67.2	75	11,770
0.738	4.175	72.4	75	9,930
0.834	4.540	78.7	76	9,170
0.910	4.770	82.7	77	8,970
1.030	5.121	88.8	78	8,490
1.171	5.405	93.7	82	7,050

<sup>a</sup>Cumulative.

<sup>b</sup>By <sup>1</sup>H NMR.

<sup>c</sup>By GPC.

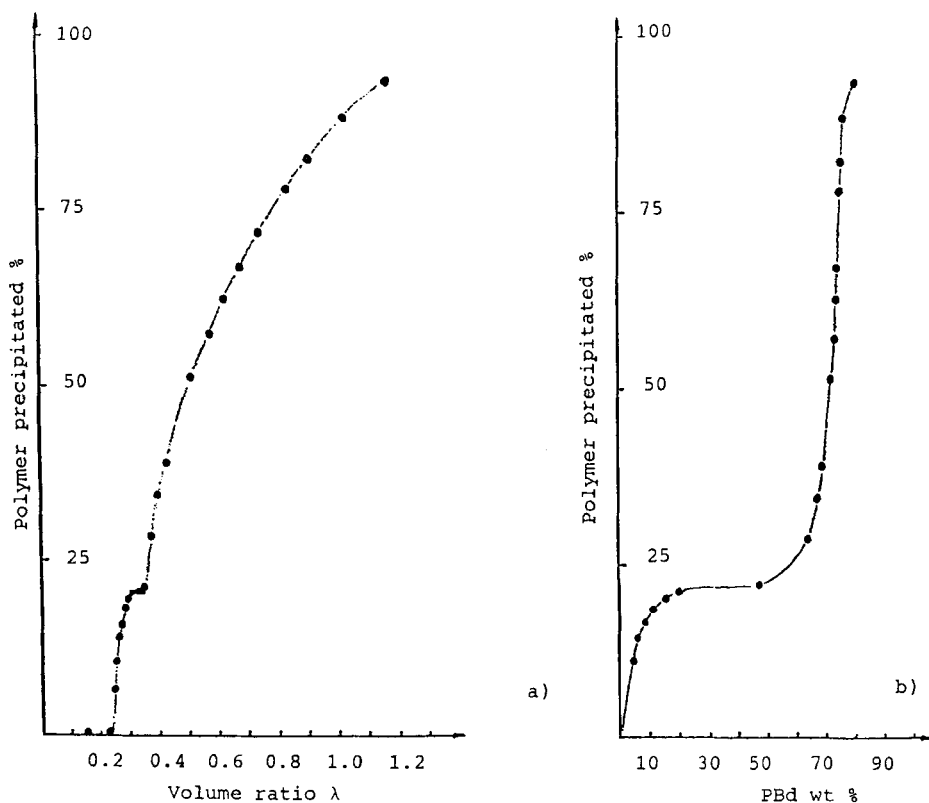


FIG. 1. Fractional precipitation of PIB-*b*-PBd. a) Percent polymer precipitated against volume ratio ( $\lambda$ ). b) Percent polymer precipitated against composition.

### Structure Characterization

The structure of representative PBd and PIB-*b*-PBd samples has been investigated by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy. Figure 2 shows the  $^1\text{H}$ -NMR spectrum of a PBd sample (Table 1, entry 1) obtained by  $\text{Tm}1\text{P}^-$ . The chemical shift ranges are listed in Table 5 [16, 22-24].

According to  $^1\text{H}$ -NMR spectroscopy [22, 23], the samples contain  $60 \pm 2\%$  1,2 and  $40 \pm 2\%$  1,4 enchainment. The 1,2 and 1,4 contents calculated from the olefinic and aliphatic regions are essentially the

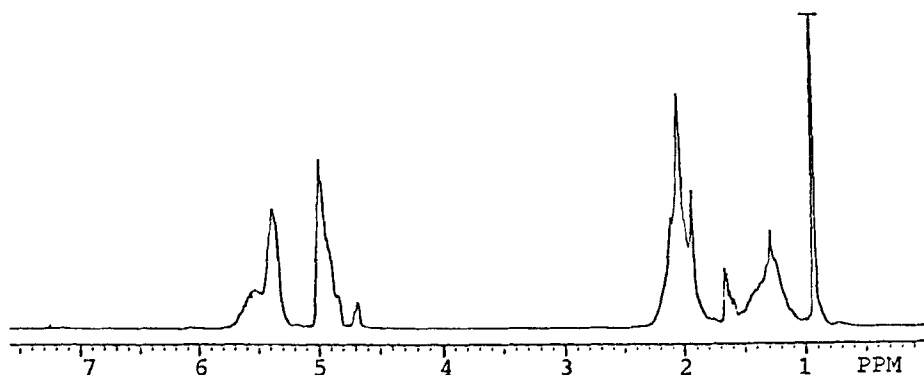


FIG. 2.  $^1\text{H-NMR}$  spectrum of a polybutadiene sample (Table 1, entry 1) initiated by  $\text{TmIP}^-$ .

TABLE 5.  $^1\text{H-NMR}$  Chemical Shifts of Main Chain and Chain End Protons of Polybutadiene

Structure	Chemical shift, ppm
1,2 $-\text{CH}_2-$	1.00-1.55 <sup>a</sup>
1,2 $-\text{CH}$	1.70-2.25 <sup>a</sup>
1,2 $=\text{CH}_2$	4.80-5.03 <sup>a</sup>
1,2 $=\text{CH}-$	5.25-5.70 <sup>a</sup>
1,4 $-\text{CH}_2-$	2.00-2.15 <sup>a</sup>
1,4 $=\text{CH}-$	5.25-5.45 <sup>a</sup>
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-$	0.72
$(\text{CH}_3)_3\text{C}-\text{CH}_2-$	0.92
$-\text{C}(=\text{CH}_2)-$	{ 4.68 4.84 <sup>b</sup>
$-\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$	1.54-1.67

<sup>a</sup>References 16 and 22-24.

<sup>b</sup>Highly overlapped.

same. The calculations have been carried out by the following equations. For the olefinic region:

$$[1,2] + [1,4] = 1$$

$$\frac{I(4.80-5.03 \text{ ppm}) - I(4.68 \text{ ppm})}{I(5.25-5.70 \text{ ppm})} = \frac{2[1,2]}{2[1,4] + [1,2]}$$

and for the aliphatic region:

$$[1,2] + [1,4] = 1$$

$$\frac{I(1.00-1.55 \text{ ppm})}{I(1.70-2.25 \text{ ppm})} = \frac{2[1,2]}{4[1,4] + [1,2]}$$

where [1,2] and [1,4] are the mole fractions of the 1,2 and 1,4 units, respectively, and  $I$  is the signal intensity in the chemical shift region given in the parentheses.

The number-average molecular weights ( $\overline{M}_n$ ) were also calculated from  $^1\text{H-NMR}$  spectra. The signal intensity due to the 1,2 structure was the internal standard:

$$\frac{I(4.80-5.03 \text{ ppm}) - I(4.68 \text{ ppm})}{I(0.92 \text{ ppm})} = \frac{2[1,2]\overline{DP}_n}{9}$$

$$\overline{M}_n = \overline{DP}_n \cdot 54 + 111$$

where  $\overline{M}_n$  and  $\overline{DP}_n$  are the number-average and molecular weight degree of polymerization, and 54 and 111 are the weights of the repeat unit and Tm1P initiator moiety, respectively.

The number-average end functionality  $\overline{F}_n = 0.97 \pm 0.03$  was obtained from the respective intensities of the sharp peak due to  $(\text{CH}_2)_3$ ,  $\text{C}-\text{CH}_2-\text{C}(\text{=CH}_2)-\text{CH}_2-$  and the very small peak due to  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ . Samples from control experiments (that is, experiments carried out in the absence of Tm1P) showed the presence of *n*-butyl and phenyl moieties in the polymers. Evidently in the absence of Tm1P the *n*-BuLi/*t*-AmOK combination metalates benzene (i.e., the solvent for *t*-AmOK) which in turn initiates butadiene polymerization. This side-reaction is negligible in the presence of Tm1P. The reactivity order of organolithium polymerization initiators was butyl  $\gg$  benzyl  $\sim$  allyl  $>$  vinyl  $\sim$  phenyl [25]. We assume the same order for the alkyl-potassiums.

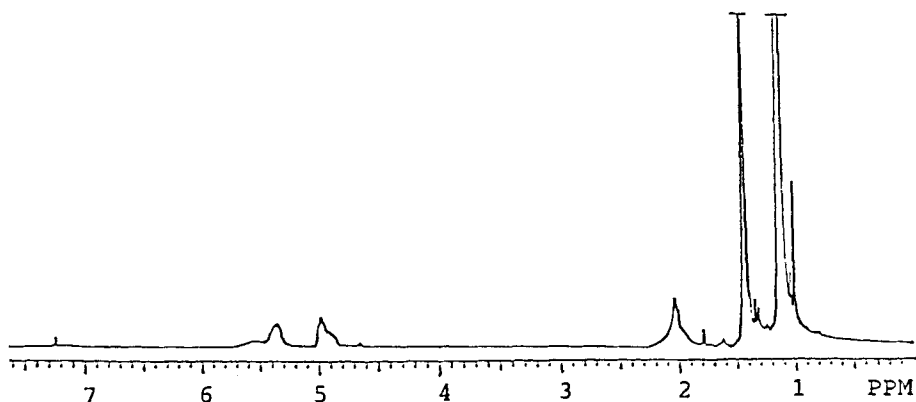
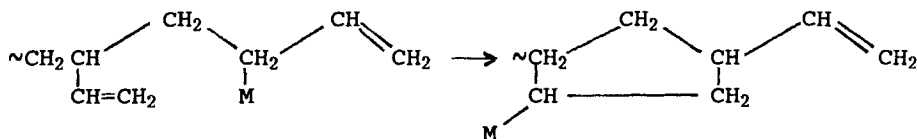


FIG. 3.  $^1\text{H-NMR}$  spectrum of a PIB-*b*-PBd sample (Table 2, entry 4).

There is no evidence for the presence of cyclopentane rings in PBd which would arise by attack of the living chain end upon a penultimate 1,2-unit [26, 27]:



This is an anticipated result since cyclic structures are absent when all the monomer is present at the onset of the reaction [27].

Figure 3 shows the  $^1\text{H-NMR}$  spectrum of a PIB-*b*-PBd sample (entry 4, Table 2). The resonances in the aliphatic region (i.e., 1–2.5 ppm) overlap severely. In contrast, resonances in the olefinic region (i.e., 4.5–6.5 ppm) are sufficiently resolved, and the microstructure of PBd in PIB-*b*-PBd can be determined. According to this analysis, the microstructure of PBd in the block is the same (i.e.,  $60 \pm 2\%$  1,2 and  $40 \pm 2\%$  1,4 enchainment) as that of PBds prepared by  $\text{Tm}1\text{P}^-$  in model experiments.

The change in the diluent, metalating reagent (*n*-BuLi/*t*-BuOK), and polymerization temperature had little effect on PBd microstructure. According to  $^1\text{H-NMR}$  analysis, the diblocks prepared by the PIB-Cl/*n*-BuLi/*t*-BuOK/hexanes/Bd system contain  $58 \pm 2\%$  1,2 and  $42 \pm 2\%$  1,4 enchainment.

The quantitative characterization of PIB-*b*-PBd is possible by  $^{13}\text{C}$ -

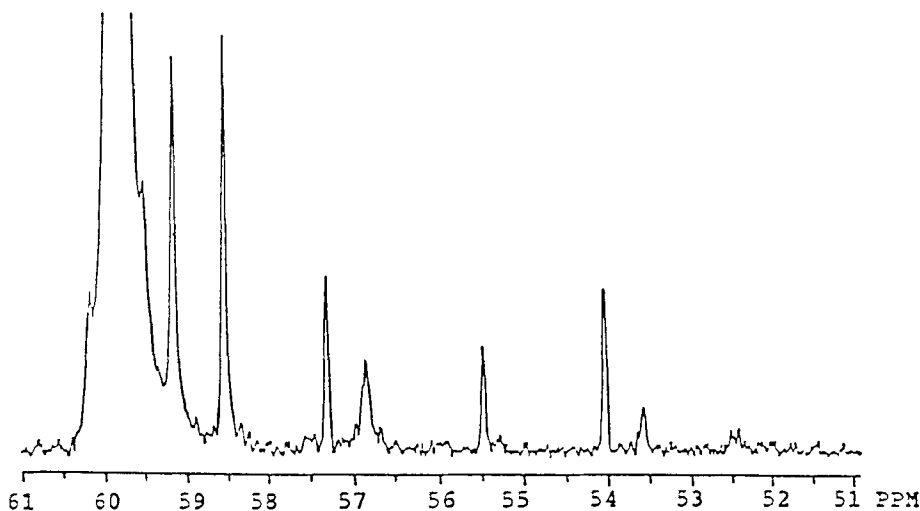
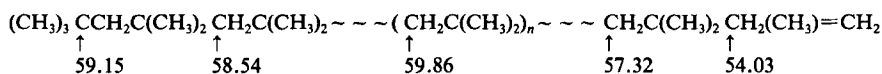


FIG. 4.  $^{13}\text{C}$ -NMR proton decoupled spectrum of a PIB-*b*-PBd sample (Table 2, entry 5) between 51 and 61 ppm.

NMR spectroscopy at  $\overline{M}_n$  below 5000. Figure 4 shows the  $^{13}\text{C}$ -NMR spectrum of a PIB-*b*-PBd sample (entry 5, Table 2) in the region from 51 to 61 ppm. The spectra of PBd's are devoid of resonances in this region [16, 28, 29] except for the characteristic  $-\text{CH}_2-$  group resonances of PIB which appear between 51 and 61 ppm [30]. Thus, well-separated new  $-\text{CH}_2-$  signal(s) were anticipated to appear due to the blocking of the PBd segment from PIB $^-$ . The assignment of  $-\text{CH}_2-$  carbons in  $(\text{CH}_3)_3\text{C} \sim \text{PIB} \sim \text{C}(\text{CH}_3)=\text{CH}_2$  [30] is as follows:

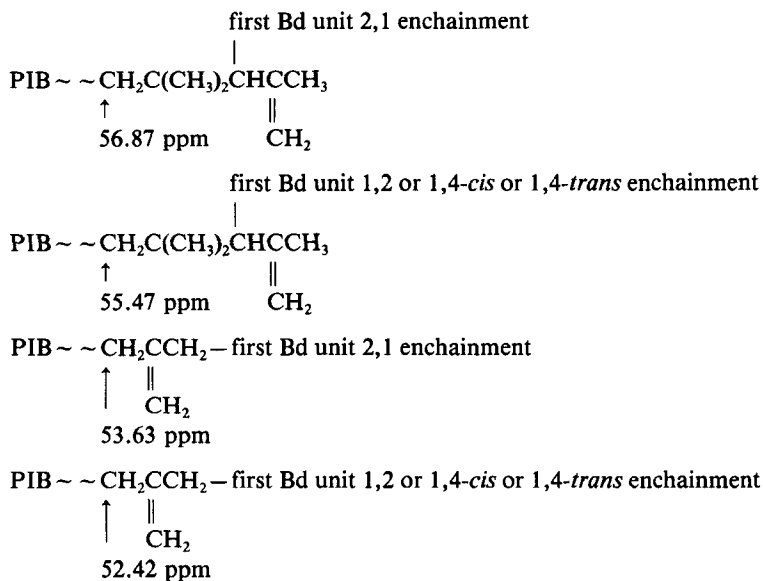


Significantly, examination of  $^{13}\text{C}$ -NMR spectra of PIB-*b*-PBd's showed four new signals between 51 and 61 ppm, i.e., at 56.87, 55.47, 53.63, and 52.42 ppm. The identification of these resonances was central to our analytical work.

We could not calculate (predict) these chemical shifts because of lack of relevant empirical chemical shift additivity parameters. However, a thorough analysis of several parameter sets relevant for the calculation of  $^{13}\text{C}$  chemical shift of alkanes [31] and shift positions convinced us

that the appearance of the new resonances characteristic of  $-\text{CH}_2-$  groups is due to the blocking of Bd from  $\text{PIB}^-$ .

The exact position of the resonance is determined by the microstructure of the first Bd unit, i.e., whether it is of 1,2, and 1,4-*cis*, 1,4-*trans*, or 2,1 enchainment. The newly arising  $\gamma$ ,  $\sigma$ , and  $\epsilon$  carbons (particularly the shielding by the  $\gamma$  carbon), due to the first Bd unit, affect the specific location of the resonances:



According to molecular models, the first two structures, while congested, are not impossible to arise. The four new signals represent 78%–64% of the resonance area relative to the resonance area of the unreacted carbon (at 57.32 and 54.03 ppm). Comparison of the resonance intensity at 22.7 ppm (due to the  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$  carbon in the initiator moiety), relative to the resonance intensities of reacted and unreacted chain end  $-\text{CH}_2-$  carbons, can be used to estimate the homo-PBd content.

### Mechanistic Speculations

According to Hsieh and Wofford [32], the polymerization of butadiene by alkyllithium compounds in the presence of other-than-lithium alkali metal alkoxides gives rise to increased vinyl enchainment. The microstructure of PBd segments prepared by our methodology, i.e., by  $\text{TmIP}^-\text{K}^+$  and/or  $\text{PIB}^-\text{K}^+$  ion pairs in the presence of alkoxides



(formed by  $\text{Li}^+/\text{K}^-$  exchange during metalation), most likely also arises by this mechanism and yields high 1,2-enchainment.

The relatively highly ionic organopotassium compounds, whose ionic character is further enhanced by the electron-donating alkali metal alkoxide, induces high electron density at the  $\gamma$ -carbon atom of the anion, and thus enhances the reactivity of this site which in turn increases 1,2-addition [33–36].

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