Head-to-Head Polymers. XXVIII. Attempted Syntheses of Linear Head-to-Head Polyisobutylene

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Syntheses of Linear Head-to-Head Polyisobutylene

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ABSTRACT

2,2,3,3-Tetramethyl-1,4-dibromobutane, when used as monomer
for polymerization by Wurtz-type polycondensation, gave head-to-
head polyisobutylene which is branched. Under similar conditions,
2,5-dimethyl-2,5-dibromohexane gave no polymer. Copolymeriza-
tion of ethylene with tetramethylethylene under various conditions
gave polyethylene of modest molecular weight with about 5% tetra-
methylene units in the polymer. 1,1,4,4-Tetramethyl-1,3-butadiene
(2,5-dimethylhexadiene-2,4) polymerized with BF_3 initiator to high
molecular weight trans-1,4-poly-(1,1,4,4-tetramethylbutadiene-1,3).
The polymer could not be hydrogenated with soluble hydrogenation
catalysts and only partially by chemical reduction with diimide.
Under forcing conditions, incorporation of portions of the decompo-
sition products of the precursor of the diimide was observed.

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INTRODUCTION

Head-to-head (H-H) polymers have been prepared by a number of synthetic pathways; all of them were indirect routes [1]. Alternating copolymerization of ethylene (or symmetric internal olefins) with maleic anhydride gave the polymeric anhydride, which was esterified to poly(methyl acrylate) [2, 3] or substituted poly(methyl acrylates). 1,4-Polymerization of 2,3-disubstituted butadiene-1,3 followed by hydrogenation was effective for the synthesis of H-H polyolefins; 2,3-dimethylbutadiene-1,3 gave H-H polypropylene [4-6]. Recently it was found that the Grignard coupling reaction, first applied to polymer reactions by Yamamoto [7], was an effective way of synthesizing H-H polyisobutylene (PIB) of moderate molecular weight [8]. According to elemental analysis (disregarding some bromine ends), IR, and especially ^{1}H- and ^{13}C-NMR spectroscopy, this polymer is pure H-H PIB.

For the synthesis of H-H PIB, a number of other routes are, in principle, possible; in this paper we examine various alternative methods which were used for the attempted synthesis of H-H PIB.

One of the possible routes to H-H PIB was the alternating copolymerization of ethylene and tetramethylethylene (TME). It is well known that the reactivity ratios of ethylene and α-olefins are unfavorable for ethylene/α-olefin and also ethylene/2-butene copolymerization; the copolymerization must be carried out at low pressure of ethylene in the presence of a large excess of 2-butene [9] to approach alternating polymer (H-H) polypropylene. TME has not often been used as a monomer (or comonomer); tremendous pressures of 6.5 GPa were needed to achieve homopolymerization to low molecular weight polymer [10, 11].

Another conceptually possible route for the preparation of H-H PIB is the polymerization of 1,1,4,4-tetramethylbutadiene-1,3 (TMBU), more appropriately named 2,5-dimethyl-2,4-hexadiene. 1,4-Polymerization by cationic initiators to PTMBU forms the H-H bond during polymerization. Hydrogenation of the internal double bonds was then expected to give H-H PIB. Synthesis of H-H polyolefins (vinyl polymers) by initial 1,4-polymerization of the 2,3-substituted butadiene followed by hydrogenation [11, 12] is, of course, suited only for H-H vinyl polymers (which introduces hydrogen in the 2 and 3 positions) and not applicable to the synthesis of H-H polyolefins with two substituents (other than hydrogen) on one carbon atom.

Another possibility for preparing H-H PIB is the classical Wurtz condensation of 2,2,3,3-tetramethyl-1,4-dibromobutane (TMDBB). TMDBB was successfully used as monomer for Grignard polymerization to H-H PIB]1].

In this paper we discuss the various techniques which were explored in our attempts to prepare H-H PIB.

EXPERIMENTAL PART

Materials

The following chemicals were obtained from the sources* indicated.

n–Butyllithium (A), cobalt(II)-2-ethylhexanoate (PB), decahydronaphthalene (decalin) (F), cyclohexane (F), 2,5-dimethyl-2,4-hexadiene (A), 2,5-dimethyl-2,5-hexanediol (A), hydrobromic acid (48%) (MCB), lithium aluminum hydride (LAH) (ALp), mesitylene (F), phosphorus pentoxide (MCB), potassium metal (F), sodium metal (A), p-toluenesulfonyl hydrazide (A), triethylaluminum (Et), m-xylene (E), o-xylene (E), and p-xylene (E).

Decalin was distilled (bp ~190°C) under reduced pressure from LAH and stored under nitrogen.

N,N-Dimethylacetamide (DMAc) was dried over barium oxide for several days, then distilled (bp 166°C) before use.

1,1,4,4-Tetramethylbutadiene-1,3 (TMBU) was purified by a simplified zone melting procedure; it was placed in an ice bath until all but 10% was frozen, the unfrozen liquid was poured off, and the frozen core was distilled (bp 133°C).

All other solvents and reagents were used as received.

Measurements

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer with a 12-min scan rate. Solid samples were measured as KBr pellets, liquid samples as smears between NaCl plates, and gaseous samples in a 10-cm gas cell with NaCl windows. The infrared spectra of some polymers were measured as films cast from solution directly onto a NaCl plate. The peak assignments were made to the nearest 5 cm^{-1}.

The ^{1}H-NMR spectra were recorded on either a Varian T-60 60 MHz or a Perkin-Elmer Model R-24 60 MHz spectrometer. Solutions (10 to 15% concentration) were made in either $CDCl_3$, d_6-benzene, D_2O, or CD_3OD. Chemical shift values were measured as δ (ppm) relative to TMS as an internal standard.

All ^{13}C-NMR spectra were recorded on a Varian CFT-20 spectrom-

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*A = Aldrich Chemical Co.; Alp = Alfa Research Chemicals and Materials; E = Eastman Organic Chemicals; Et = Ethyl Corp.; F = Fisher Scientific Co.; MCB = Matheson, Coleman and Bell; PB = Pfaltz and Bauer Research Chemicals.

eter, fully decoupled. The measurements were carried out in a variety of solvents ($CDCl_3$, d_6-benzene, benzene, D_2O, CD_3OD, o-dichlorobenzene). When a nondeuterated solvent was used, D_2O was employed as an external lock.

Microanalyses were done by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

Preparations

Head-to-Head Polyisobutylene Preparation by Wurtz Coupling (Table 1)

Polymerization of 2,2,3,3-Tetramethyl-1,4-dibromobutane with Sodium Metal in the Bulk. A 10-mL, round-bottom flask was fitted with a condenser. Under nitrogen flow, the glassware was flamed out and allowed to cool. Clean sodium metal (0.34 g, 14.8 mmol) was transferred to the reaction flask, and TMDBB (2.0 g, 7.4 mmol) was added along with a small magnetic stirring bar. When heated gently with a small flame, at first the monomer melted and then the sodium metal began to melt. The reaction became exothermic, and the flask was placed in an oil bath at 100°C for 24 h. The polymer was extracted from the mixture with several portions of cyclohexane. The combined solutions were evaporated under reduced pressure, and the residue (H-H PIB) was dried overnight at 80°C and 0.1 mm over P_2O_5; yield 0.16 g (20%, 1.5 mmol). IR (neat): 2962, 2926, 2872 cm^{-1} ($\nu_{as}CH_3$, $\nu_{as}CH_2$, $\nu_{as}CH_3$); 1375, 1365 cm^{-1} ($\delta_s CH_3$, gem-dimethyl). ^{13}C-NMR ($CDCl_3$), δ = 40.6 ppm (branch $-\underset{|}{\overset{|}{C}}-$), 38.9 ppm ($-\underset{|}{\overset{|}{C}}-$), 31.5 ppm ($-\underline{C}H_2-$), 24.1 ppm (endgroup $-\underline{C}H_3$), 23.0 ppm (branch $-\underline{C}H_2-$), 21.38 ppm ($-\underset{|}{C}-\underline{C}H_3$) (Table 2).

Analysis: Calculated for C_8H_{16}: C, 85.71; H, 14.29%. Found: C, 85.24; H, 14.80%.

Attempted Preparation of Head-to-Head Polyisobutylene by Alternating Copolymerization of Ethylene with Tetramethylethylene

Copolymerization of Ethylene with Tetramethylethylene with Benzoyl Peroxide as the Initiation. In a 600-mL Parr autoclave with a packed stirring unit and a variable temperature heating furnace was placed 100 mL of dry benzene, recrystallized benzoyl peroxide (0.15 g, 0.62 mmol), and 2,3-dimethyl-2-butene (tetramethylethylene) (1.0 g, 12.0 mmol). Polymerization-grade ethylene (99.9%) was used for 3 flusnes (pressure to 200 psi) of ethylene; finally the pressure was brought to 220 psi with ethylene and the mixture heated to 70°C. After 22 h at 300 psi, the autoclave was permitted to cool to room temperature before releasing the excess ethylene pressure. The benzene solution was poured into 300 mL of

TABLE 1. Attempted Wurtz Polymerization of 2,2,3,3-Tetramethyl-1,4-dibromobutane (TMDBB) or 2,5-Dimethyl-2,5-dibromohexane (DMDBH)

Monomer	Metal	Solvent	Temperature, °C	Time	Polymer yield
TMDBB	Na	Cyclohexane	81	1 d	Trace
TMDBB	Na	Bulk	100	1 d	20%
TMDBB	Na	Bulk	100	1 d	10%
TMDBB	Na/K	Benzene/vacuum	60	4 d	0
TMDBB	Na	Bulk/vacuum	60	4 d	0
DMDBH	Na	Cyclohexane	81	10 h	0
DMDBH	Na/K	Bulk	100	1 d	0
DMDBH	Na	Benzene	100	1 d	0

TABLE 2. ^{13}C-NMR Chemical Shift Values for Wurtz Polymerized Head-to-Head Polyisobutylene

$$
\left[
\begin{array}{c}
\overset{(1)}{CH_3}\ CH_3 \\
\underset{(2)}{CH_2}{-}\overset{(3)}{C}{-}\underset{}{C}{-}CH_2 \\
CH_3\ CH_3
\end{array}
\right]_n
$$
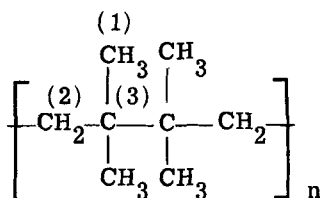
Carbon atom	Chemical shifts, ppm	
	Found	Calculated
$-CH_3$ (1)	21.8	21.3
$-CH_2-$ (2)	31.5	31.4
$-\overset{\vert}{\underset{\vert}{C}}-$ (3)	38.9	38.7
Branch $-CH_2-$	23.0	22.9
Endgroup $-CH_3$	24.1	23.8
Branch $-\overset{\vert}{\underset{\vert}{C}}-$	40.6	39.5
Minor unassigned peaks	22.5, 34.7	

methanol. The white fluffy precipitate was collected on a fritted glass funnel and washed with several portions of methanol. The polymer was dried overnight at 60°C and 0.1 mm pressure over P_2O_5 and yielded 0.31 g (23% based on 1:1 copolymer). ^{1}H-NMR (d-benzene), 1.3 ppm ($-CH_2-CH_2$) (6.8 ^{1}H), 1.0 ppm ($-CH_3$) (1.0 ^{1}H) shows 5% tetramethylethylene and 95% ethylene units. ^{13}C-NMR (d-benzene), 36.3 ppm ($-\overset{\vert}{\underset{\vert}{C}}-$), 30.1 ppm ($-CH_2-CH_2-$), 23.8 ppm ($-CH_3$).

Analysis: Calculated for $(-C_2H_4)-(-C_6H_{12})-$: C, 85.71; H, 14.29%. Found: C, 83.03; H, 13.61%.

Preparation of Head-to-Head Polyisobutylene by Hydrogenation of 1,4-Poly-(1,1,4,4-Tetramethylbutadiene-1,3)

Preparation of 1,4-Poly-(1,1,4,4-Tetramethyl-butadiene-1,3) (PTMBU). In a 2-L resin kettle was placed petroleum ether (525 mL). The container was cooled to -78°C, and

the solution was saturated with boron trifluoride (BF_3) gas. A solution of TMBU (30 g, 0.27 mol) in petroleum ether (45 mL) was added with vigorous stirring over a period of about 5 min while the temperature of the reaction was kept below -60°C. To the yellow slush was added ethanol (50 mL), followed by acetone (400 mL); the off-white precipitate became pure white. The polymer was collected by filtration, washed several times with acetone, suspended in 500 mL of dilute ammonium hydroxide solution, stirred for 30 min, filtered again, washed with distilled water and acetone, and dried at 60°C and 0.1 mm over P_2O_5. PTMBU was obtained in 70% yield (21 g), mp 263°C. IR (KBr): 1377, 1367 cm^{-1} ($\delta_s CH_3$, gem-dimethyl); 1000, 987 cm^{-1} (trans-diene). ^{13}C-NMR (o-dichlorobenzene) (120°C); 135.5 ppm (–CH=), 41.4 ppm (–C–), 23.9 ppm (–CH$_3$). The inherent viscosity (0.5 g/100 mL, decalin, 130°C) was 1.5 dL/g. The polymer was soluble only at elevated temperatures in saturated hydrocarbons or chlorinated aromatic solvents.

Preparation of Cobalt(II)/Triisobutylaluminum Hydrogenation Catalyst. To dry, distilled decalin (40 mL) was added with a syringe triisobutylaluminum (3.9 mL, 15.6 mmol) and a cobalt(II)-2-ethylhexanoate solution (6% Co) (3.8 g, 3.9 mmol) in decalin (10 mL) (Al:Co ratio of 4:1). The catalyst solution could be stored for weeks under nitrogen and remained active. A large-bore syringe needle was used to transfer the catalyst solution to the hydrogenation equipment for each experiment.

Preparation of Cobalt(II)/n-Butyllithium Hydrogenation Catalyst. Co/Li catalyst was prepared by a procedure similar to that used for the preparation of the Co/Al catalysts. n-Butyllithium (1.0 g, 15.6 mmol) was combined with cobalt(II)-2-ethylhexanoate (3.8 g, 3.9 mmol based on Co) (Li:Co ratio of 4:1) in 50 mL of dry decalin. The catalytic hydrogenation experiments are summarized in Table 3.

Attempted Hydrogenation of 1,4-Poly-(1,1,4,4-Tetradimethylbutadiene-1,3) Using Cobalt(II)/Triisobutylaluminum Catalyst

Into a 600-mL Parr Autoclave was placed under nitrogen PTMBU (1.0 g, 9.1 mmol based on monomer units) and distilled decalin (100 mL). A cobalt(II)/triisobutylaluminum solution (4:1, Al:Co, 1.17 mL, 0.091 mmol of Co) (1.0 mol%) was used in the attempt to hydrogenate the polymer at 210 psi hydrogen pressure at 180°C and 6 h. The polymer was isolated in 78% yield (0.78 g) after reprecipitation from hot decalin into isopropanol and was identified as the starting material, mp 261°C. IR (KBr): 1377, 1367 cm^{-1} ($\delta_s CH_3$, gem-dimethyl); 1000, 987 cm^{-1} (trans-diene).

In experiments carried out above 190°C, no polymer and only starting monomer, TMBU, was isolated from the reaction, bp 133°C.

TABLE 3. Catalytic Hydrogenation of 1,4-Poly-(1,1,4,4-Tetramethyl-1,3-butadiene)

Polymer,[a] g	Temperature, °C	Catalyst	H_2, psi	Catalyst concentration, mol-%	Yield, g	Recovered
1.0	180	Co/Al(i-Bu)$_3$[b]	200	1	0.78	Unreacted
2.0	190	Co/Al(i-Bu)$_3$[b]	200	30	1.56	Unreacted
1.0	180	Co/Li-n-Bu	200	1	0.89	Unreacted
1.0	180	Co/Li-n-Bu	200	10 mol	0.79	Unreacted
2.0	200	Co/Al(i-Bu)$_3$	1 400	2	0	Monomer
1.0	200	Pd/charcoal	1 400	10	0	Monomer
1.0	200	Rh/charcoal	1 200	10	0	Monomer

[a]1-2% solution in decalin.
[b]The same reaction was carried out with Al/Co ratios of 4:1 and 3.3:1 with similar results.

^{13}C-NMR (CDCl$_3$); δ = 18.0 ppm ($-\underline{C}H_3$, trans), 26.3 ppm ($-\underline{C}H_3$, cis), 121.8 ppm ($-\underline{C}H=$), 131.7 ppm ($-\underline{C}=$).

Chemical Hydrogenations of 1,4-Poly-(1,1,4,4-Tetramethylbutadiene-1,3)

In m-Xylene. A 250-mL three-neck round-bottom flask was equipped with a reflux condenser, a thermometer, a nitrogen inlet and exit, and a magnetic stirring bar; under nitrogen, TMBU (2.5 g, 22.7 mmol based on repeat unit) was introduced along with 75 mL of decalin and 25 mL of m-xylene. While stirring the mixture, p-toluenesulfonylhydrazide (p-TSH) (8.4 g, 45.4 mmol) was added and the oil bath temperature was increased slowly to 160°C; the solution was stirred at this temperature for 12 h and poured into 400 mL of isopropanol to precipitate the polymer. A white solid was collected on a fritted glass filter funnel, reprecipitated, and dried at 60°C and 0.1 mm pressure; yield: 2.2 g (88%). The polymer was found to be only partially hydrogenated (estimated to be 4% by infrared analysis).

In 1,3,5-trimethylbenzene (mesitylene) in place of decalin/m-xylene and a reaction temperature of 130°C, the yield of partially hydrogenated polymer was 2.4 g (94%) (8% based on IR analysis).

In 1,2-dimethylbenzene (o-xylene) using four equivalents of p-TSH (16.8 g, 90.8 mmol) and a reaction temperature of 145°C (20 h), the polymer was recovered in 93% yield (2.3 g). Partial hydrogenation was estimated by IR to be 18%.

In 1,4-dimethylbenzene (p-xylene) using four equivalents of p-TSH (16.8 g, 90.8 mmol) and a reaction temperature of 139°C (22 h), the polymer was recovered in 95% yield (2.4 g). Partial hydrogenation was estimated by IR to be 28%. All hydrogenation experiments are summarized in Table 4.

Hydrogenation of 1,4-Poly-(1,1,4,4-Tetramethylbutadiene-1,3) by Repeated Additions of Diimide. To a 250-mL three-neck round-bottom flask equipped with a reflux condenser, thermometer, nitrogen inlet and outlet, and a magnetic stirring bar was added PTMBU (2.5 g, 22.7 mmol based on repeat unit), 75 mL decalin, and 25 mL m-xylene. While stirring the mixture, p-TSH (8.4 g, 45.4 mmol) was added and the temperature of the solution brought to 160°C using an oil bath; the mixture was stirred for 12 h. A 10-mL aliquot was removed with a pipette, worked up by pouring the solution into isopropanol to precipitate the polymer which was filtered and washed with methanol. The sample was dried at 60°C at 0.1 mm pressure over P$_2$O$_5$. IR spectroscopic analysis (KBr pellet) showed 11% hydrogenation after 12 h. The reaction was continued with the addition of 2 equivalents of p-TSH (8.4 g, 45.4 mol) every 24 h. Aliquots of 10 mL were removed and worked up after 1, 2, 4, 5, and 7 days. IR analysis showed the degree of hydrogenation, which is presented in Table 5.

Analysis of the polymer after one week of hydrogenation: Calculated for C$_8$H$_{16}$: C, 85.71; H, 14.29%. Found: C, 80.40; H, 13.79; N, 0.38; S, 0.70%.

TABLE 4. Hydrogenation of 1,4-Poly-(1,1,4,4-Tetramethyl-1,3-butadiene) Using Diimide

Solvent[a]	Temperature, °C	Time, h	Equivalents of diimide	Percent hydrogenation
Decalin/m-xylene 75:25	160	12	2.0	4
Mesitylene	130	16	2.0	8
o-Xylene	145	20	4.0	18
p-Xylene	139	22	4.0	28
Decalin/m-xylene 75:25	160	24	2.0	21
Decalin/m-xylene 75:25	160	24	4.0	37

[a]2.5 g of polymer in 100 mL of solvent.

TABLE 5. Hydrogenation of 1,4-Poly-(1,1,4,4-Tetramethyl-1,3-butadiene) by Repeated Additions of Diimide

Hours	12	24	48	96	126	174
Percent hydrogenation	11	21	39	44	48	49

TABLE 6. Hydrogenation of 1,4-Poly-(1,1,4,4-Tetramethyl-1,3-butadiene) by Repeated Reactions with Diimide

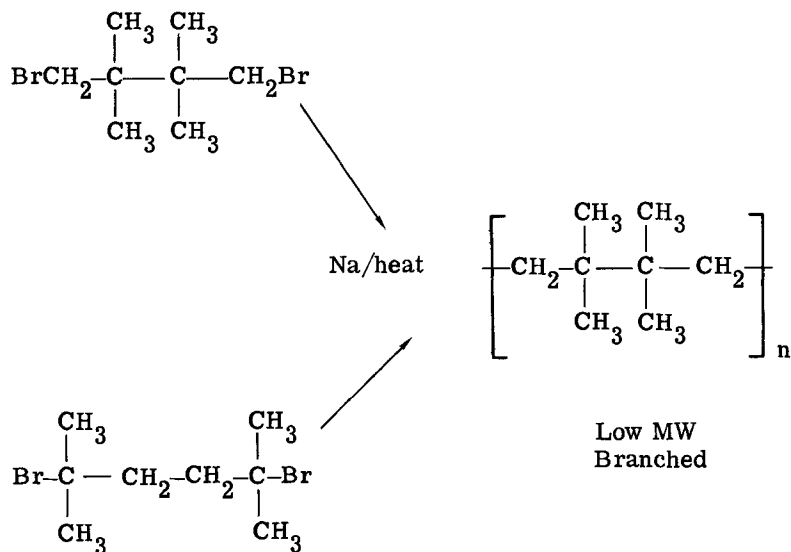| Number of reactions	1	2	3	4	5	6
Percent hydrogenation	37	60	64	68	69	70
Yield, g	2.31	2.15	2.05	1.9	1.89	1.88

Hydrogenation of 1,4-Poly-(1,1,4,4-Tetramethyl-butadiene-1,3) by Repeated Reactions with Diimide.
Using the general procedure described in the previous experiment, 4 equivalents of p-TSH (16.8 g, 90.8 mmol) were added to the polymer solution. After 24 h the reaction mixture was worked up, the polymer dried and placed into fresh reagents (same reaction conditions) for an additional 24 h. The reaction sequence was repeated six times. The degree of hydrogenation was determined by IR analysis after each experiment (Table 6). The polymer became insoluble after six reactions.

Analysis of the polymer after six hydrogenation experiments: Calculated for C_8H_{16}: C, 85.71; H, 14.29%. Found: C, 80.51; H, 13.94; N, 0.51; S, 0.83%.

RESULTS AND DISCUSSION

Wurtz polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane (TMDBB) gave H-H PIB of low molecular weight with a branched structure (Eq. 1). TMDBB was prepared by nucleophilic substitution reaction of the two tosylate groups of 2,2,3,3-tetramethylbutanediol-1,4-ditosylate by the bromide of tetra-n-butyl ammonium bromide. 2,5-Dimethyl-2,5-dibromohexane (DMDBH), also treated under Wurtz reaction conditions, was obtained from the corresponding glycol with HBr.

TMDBB was heated with sodium metal and underwent an exothermic reaction; 10 to 20% of the starting dibromide had been converted into polymer after 1 day; some volatiles were also obtained. Table 1 shows the results of the polymerization attempts. Only a small amount of Wurtz reaction products was obtained in cyclohexane; temperatures

$$
\begin{array}{c}
\quad\ \ CH_3\ \ CH_3 \\
\quad\quad |\quad\ \ | \\
BrCH_2\text{-}C\text{---}C\text{----}CH_2Br \\
\quad\quad |\quad\ \ | \\
\quad\ \ CH_3\ \ CH_3
\end{array}
$$

$$\text{Na/heat}$$

$$
\begin{bmatrix}
\quad\quad CH_3\ CH_3 \\
\quad\quad\ |\quad\ | \\
\text{-}CH_2\text{-}C\text{---}C\text{---}CH_2\text{-} \\
\quad\quad\ |\quad\ | \\
\quad\quad CH_3\ CH_3
\end{bmatrix}_n
$$

Low MW
Branched

$$
\begin{array}{c}
\ \ CH_3 \qquad\qquad CH_3 \\
\ \ |\qquad\qquad\qquad | \\
Br\text{-}C\text{ --- }CH_2\text{-}CH_2\text{-}C\text{-}Br \\
\ \ |\qquad\qquad\qquad | \\
\ \ CH_3 \qquad\qquad CH_3
\end{array}
$$

in excess of 80°C and preferably 100°C were necessary to cause the polymer-forming Wurtz reaction. When DMDBH was subjected to Wurtz reaction conditions in bulk or in solution, no polymer was obtained.

H-H PIB obtained by the reaction of sodium with TMDBB was found to have an inherent viscosity of 0.13 dL/g in benzene; gel permeation chromatography of some samples in THF gave molecular weights of 1000 to 2000. This would indicate a degree of polymerization of about 10 to 20. We had found in our previous study that H-H PIB of reasonable molecular weight was soluble only at elevated temperatures in high boiling hydrocarbon solvents such as decalin.

The elemental analysis and the IR data of the polymer indicated that no bromine endgroups remained in our Wurtz H-H PIB. The infrared spectrum of the polymer and the monomer in the region of the CH_2-Br stretching is shown in Fig. 1; the C–Br absorption at 650 cm^{-1} had completely disappeared. The ^{13}C-NMR spectrum of our H-H PIB (Fig. 2) shows three major maxima in this type of H-H PIB: the methylene group of the backbone, the methyl carbon atoms, and the quaternary carbon atoms. However, there are several extraneous peaks which we assign to methyl endgroups and branch point carbon atoms (Fig. 2).

Table 2 shows the ^{13}C-NMR chemical shift values for H-H PIB obtained by Wurtz polymerization. The chemical shift values were calculated by the method of Lindeman and Adams [13]. The branch point atoms were also assigned, based on model compounds from the Sadtler Index. Hexamethylethane values were used as the model compound for the identification of the methyl endgroups.
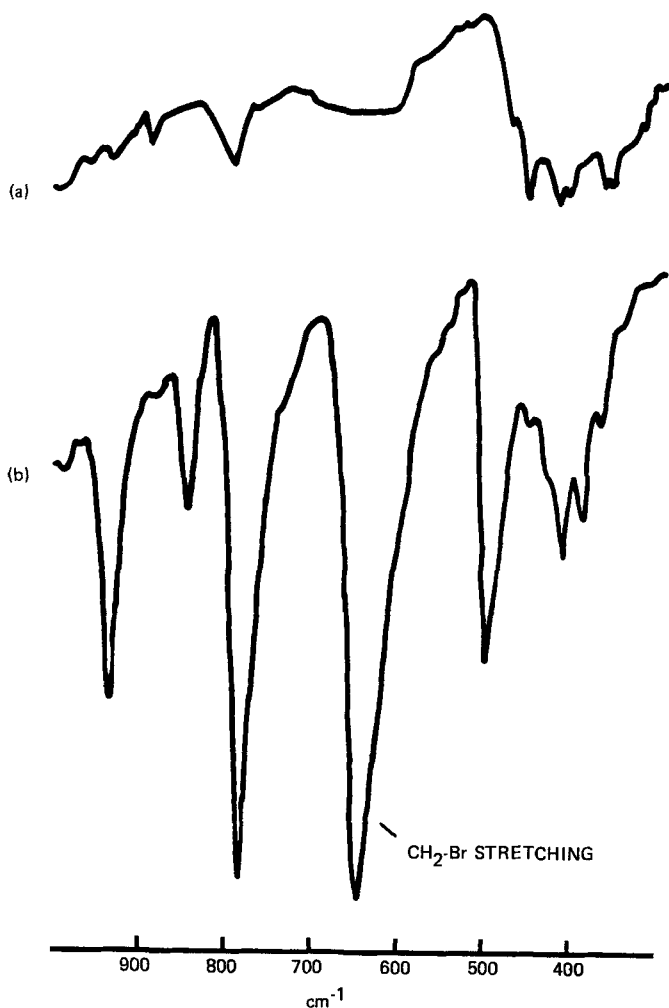
(a)

(b)

CH$_2$-Br STRETCHING

900   800   700   600   500   400

cm^{-1}

FIG. 1. Infrared spectra of –CH$_2$–Br stretching region for: (a) Wurtz polymer of H-H polyisobutylene; (b) starting 2,2,3,3-tetra-methyl-1,4-dibromobutane.

Branching which is produced during the Wurtz-type polymerization reaction is caused by the free radicals obtained by the reaction of sodium on TMDBB or on polymeric –CH$_2$Br endgroups. These radicals are primary radicals and, when they are not able to recombine imme-

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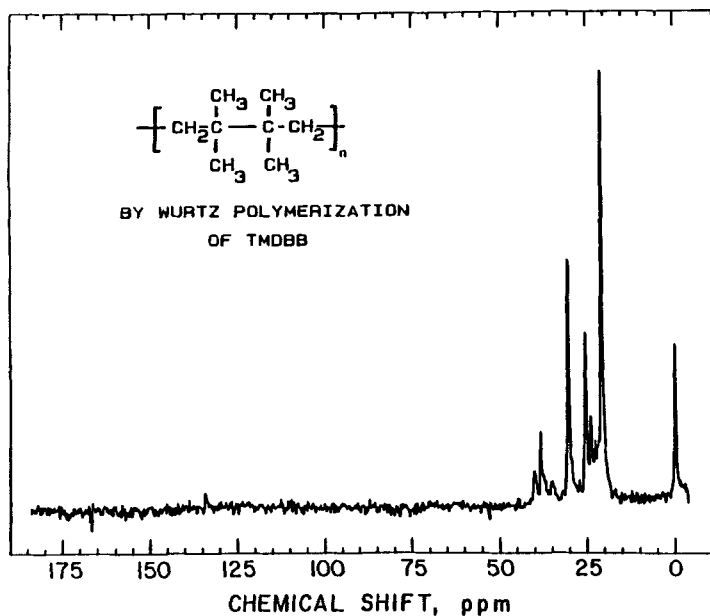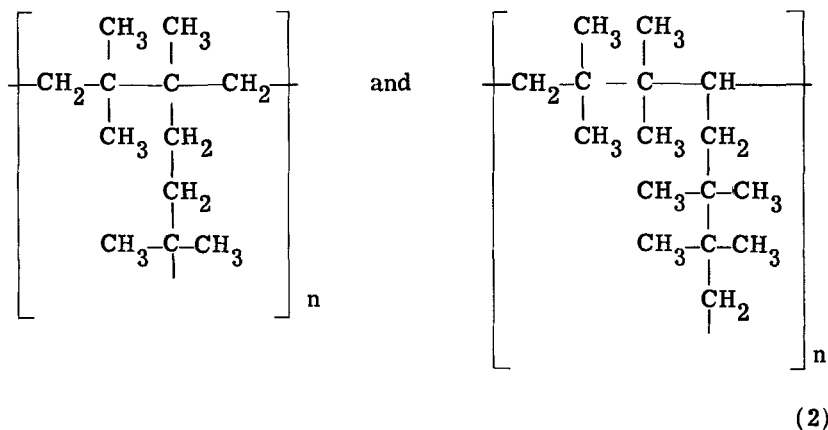

FIG. 2. ^{13}C-NMR spectrum of Wurtz polymer of 2,2,3,3-tetra-methyl-1,4-dibromobutane.

diately to form carbon-carbon bonds, they are capable of abstracting a hydrogen atom from any methyl or methylene groups of already formed polymer. This hydrogen abstraction leads to the formation of methyl endgroups and branches:
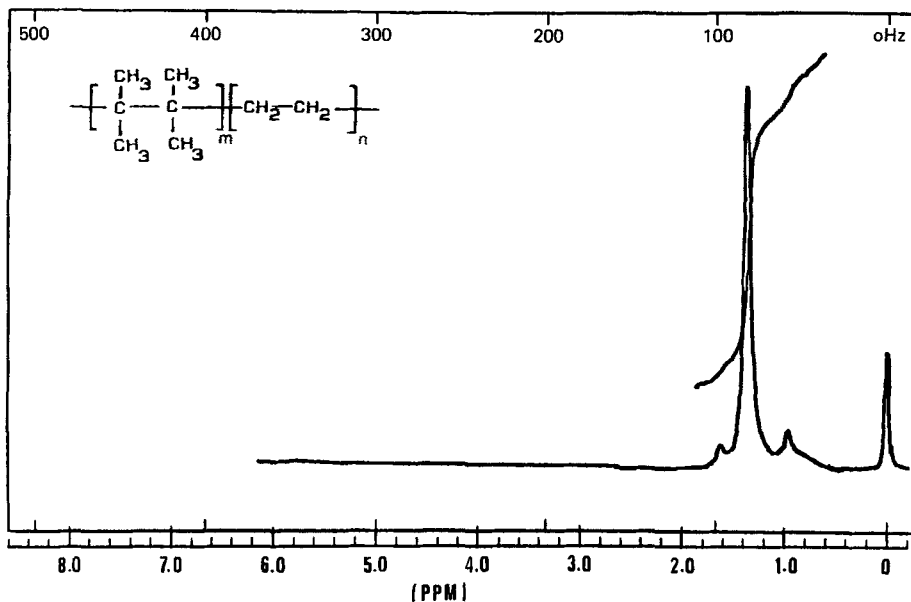
and

(2)

FIG. 3. ^{1}H-NMR spectrum of copolymers of tetramethylethylene and ethylene.

Intramolecular backbiting abstraction of polymeric radicals is also a possibility for the branching reactions.

The Wurtz reaction to prepare H-H PIB provided us with branched and low molecular weight polymer not sufficient in molecular weight for measurement of properties.

Another possibility for preparing H-H PIB was the alternating co-polymerization of ethylene and TME. Attempts at copolymerization were made with benzyl peroxide as the initiator at ethylene pressures of 100 to 1000 psi and temperatures of 70°C, and a solid, waxy copoly-mer was obtained. ^{1}H- and ^{13}C-NMR spectra of the copolymer clear-ly show that only a small amount of TME had been incorporated into the copolymer (Figs. 3 and 4). In the ^{13}C-NMR spectrum, one major peak at 30.1 ppm is predominant, which is characteristic for the methyl-ene carbon atoms of polymethylene. Two other peaks are located at 23.8 and 36.3 ppm and are assigned to the methyl carbon atoms and the quaternary carbon atoms for the TME unit of the copolymer. These two ^{13}C-NMR chemical shift values are shifted by about 2 ppm from the ^{13}C resonances found for the known H-H PIB where the carbon atoms of the methyl groups are found at 21.7 ppm and the quaternary carbon atoms at 38.8 ppm. Since the TME units are expected to be distributed randomly throughout the polyethylene chain and are separated by more than two methylene groups, this change in the ^{13}C-NMR chemical shift values is not surprising.
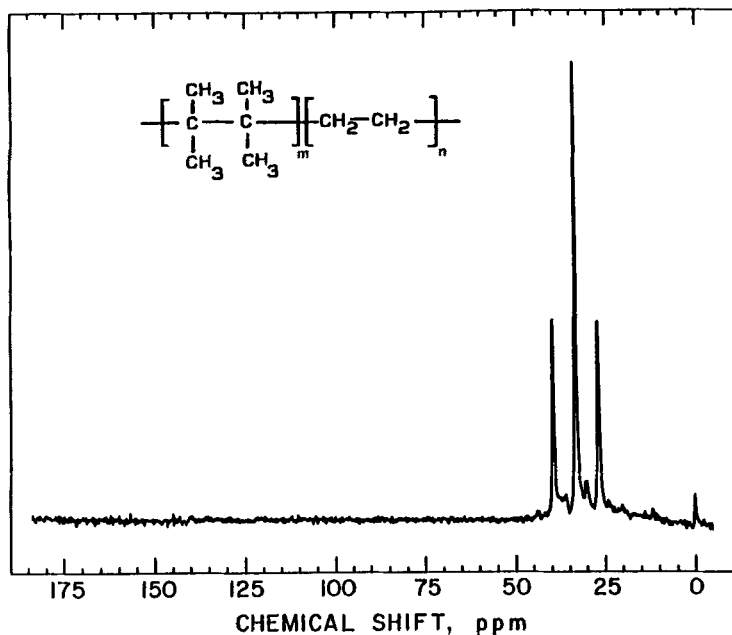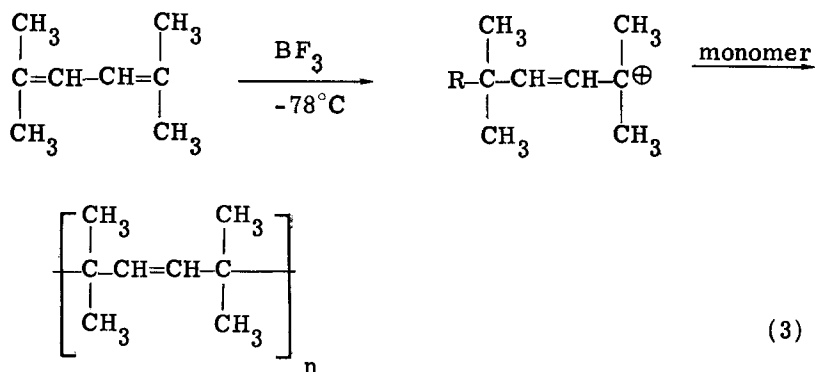
FIG. 4.   ^{13}C-NMR spectrum of copolymers of tetramethylethylene and ethylene.

Integration of the ^{1}H-NMR spectrum was used to determine the co-polymer composition. The ^{1}H-NMR resonance at 1.3 ppm is due to the methylene protons of polymethylene and at 1.0 ppm to the methyl groups of the TME unit. The integration ratio of the CH_2 to the CH_3 protons gave a copolymer composition of 95% ethylene and 5% TME units.

It is interesting that a small amount of TME incorporated into the copolymer under our relatively mild reaction conditions. Only one re-port of TME polymerization has been described in the literature, which had led to an oily, viscous homopolymer of TME at very high pressure [10, 11]. It was not surprising that ethylene and TME did not copoly-merize to an alternating copolymer and led to only a small amount of incorporation of TME.

The other potential method for the preparation of H-H PIB was the preparation of PTMBU and its attempted hydrogenation. The polymer-ization of TMBU was carried out as described previously by Moody and outlined in the following equation [14, 15]:

$$
\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}=CH-CH=\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \quad \xrightarrow[-78°C]{BF_3} \quad R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\oplus \quad \xrightarrow{monomer}
$$

$$
\left[-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}- \right]_n \tag{3}
$$

TMBU was found by ^{13}C-NMR spectroscopy to be polymerized to a strictly 1,4-polybutadiene. Only three types of carbon atoms were identified at $-CH_3$, $-\overset{|}{\underset{|}{C}}-$, and $-CH=$; no indication of a 1,2 or 3,4 linkage in the polymer was observed in the ^{13}C-NMR spectrum. PTMBU is highly crystalline and the double bond in the polymer chain has trans stereochemistry. PTMBU is soluble only above 160°C in solvents such as decalin and trichlorobenzene. It has a melting point of 260°C; however, it begins to decompose around 190°C and reverts back to the monomer TMBU by an unzipping mechanism. The IR spectrum of PTMBU is shown in Fig. 5 and the ^{13}C-NMR spectrum in Fig. 6.

Hydrogenation of PTMBU was attempted with both heterogeneous and homogeneous catalysts which have been proven successful for polymer hydrogenations. A number of conditions with varying catalysts, catalyst concentrations, hydrogen pressure, and temperature were used (Table 3) [4, 5]. A temperature of about 160°C was chosen for the attempted hydrogenation of PTMBU to allow for solution of the PTMBU samples. The ratio of the intensity of the doublet of the gem-dimethyl group at 1367 cm^{-1} to the intensity of the trans $-CH=CH-$ absorption at 1000 cm^{-1} was used to measure quantitatively the degree of hydrogenation, but no hydrogenation was achieved. When the hydrogenation conditions were more severe by raising the temperature and pressure, the polymer degraded and a substantial amount of monomer TMBU was found in the reaction mixture.

Hydrogenation of PTMBU was also attempted by chemical techniques using diimide [16-18] which was generated by thermal decomposition of p-TSH. Several different solvents and solvent combinations were studied for this reaction; it was essential that the solvent dissolved p-TSH and would at least swell PTMBU. The degree of hydrogenation was again measured by IR spectroscopy. For quantitative hydrogenation of polybutadiene or polyisoprene, two equivalents of p-TSH and reaction times of 4-5 h are needed; 1,4-poly(2,3-dimethylbutadiene-1,3) or polychloroprene are more difficult to reduce.
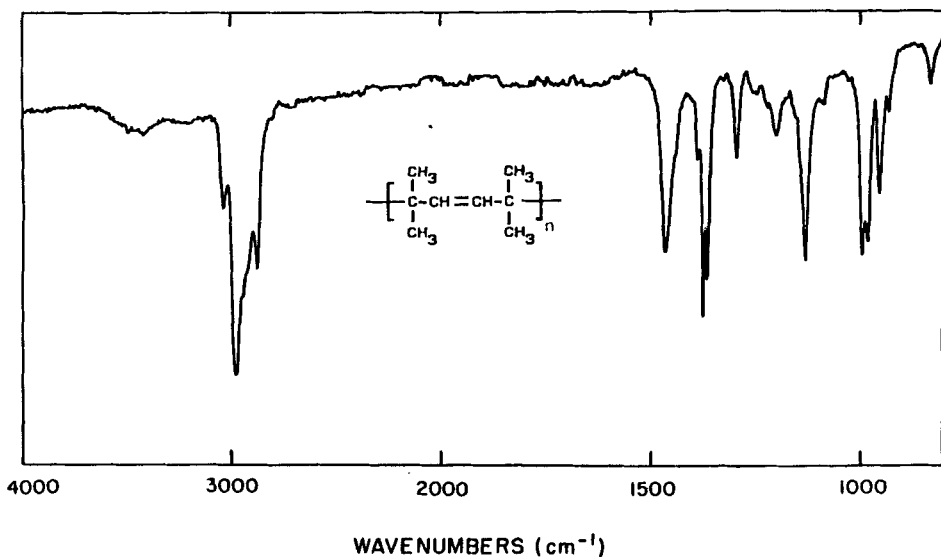
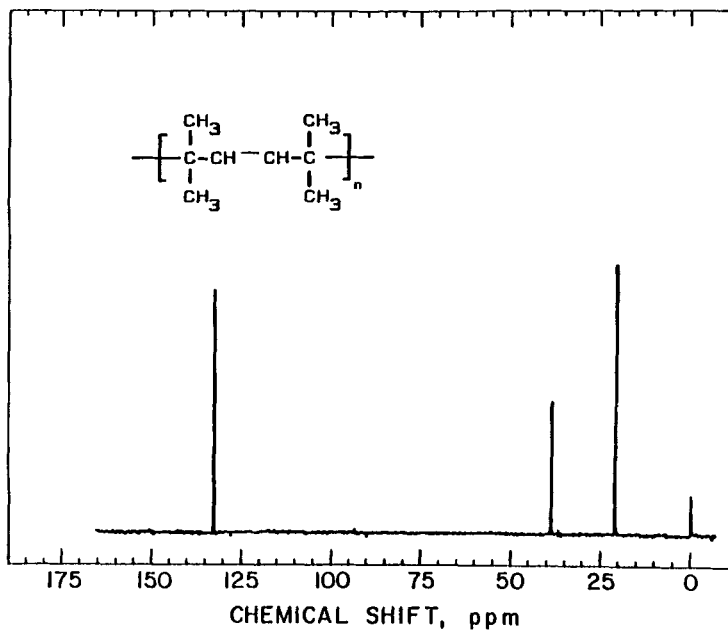FIG. 5. Infrared spectrum of 1,4-poly-(1,1,4,4-tetramethyl-1,3-butadiene).

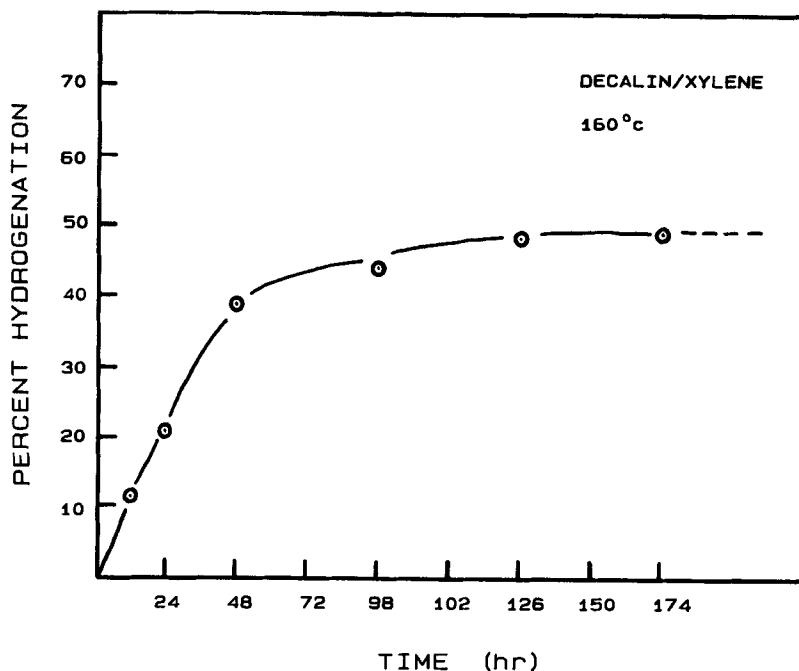FIG. 6. ^{13}C-NMR spectrum of 1,4-poly-(1,1,4,4-tetramethyl-1,3-butadiene).

FIG. 7. Degree of hydrogenation as a function of reaction time for the diimide reduction of 1,4-poly-(1,1,4,4-tetramethyl-1,4-butadiene); reaction temperature 160°C.

In this work it was found that single reactions with diimide were not sufficient to achieve much hydrogenation of PTMBU as only 5 to 20% reduction of the unsaturation (Table 4) was observed. The time of reaction and amount of diimide seems to be very important. For this reason, two sets of experiments were explored in attempts to fully hydrogenate PTMBU; the first experiment involved repeated addition of p-TSH. Fresh p-TSU (to produce the diimide) was added to the polymer solution at intervals of 1, 2, 4, 5, and 7 days. After the completion of each addition, an aliquot was withdrawn and the polymer was isolated in order to determine the degree of hydrogenation. Figure 7 and Table 5 show the degree of hydrogenation of PTMBU as a function of time. The reaction was terminated after 6 days when the degree of hydrogenation had reached about 50% and the reduction did not proceed any further.

In a second experiment the hydrogenated PTMBU was isolated after each 24 h of reaction time, redissolved, and subjected to fresh p-TSH (diimide) for further hydrogenation. This procedure was repeated six times with 4 equivalents of diimide each time; the results
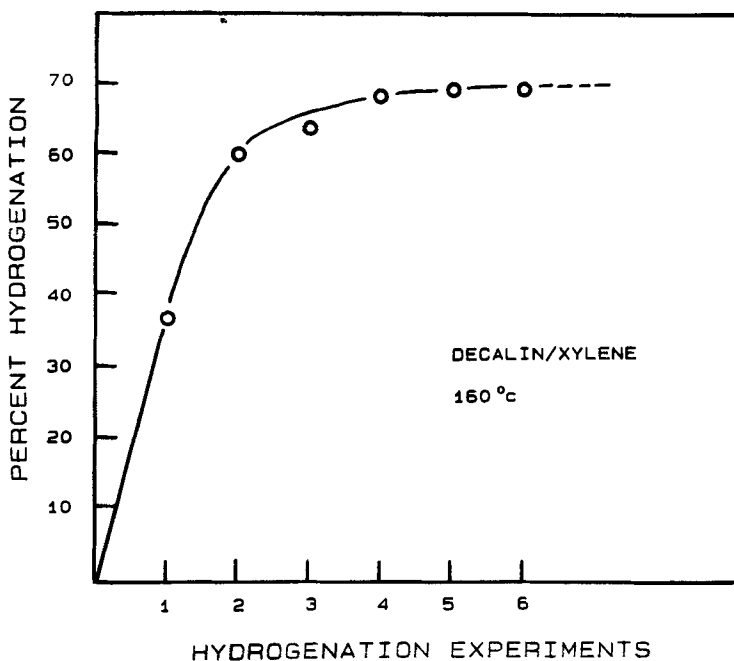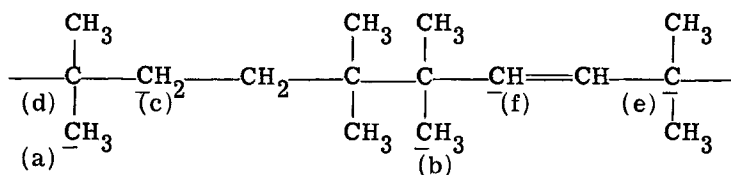
FIG. 8. Degree of hydrogenation as a function of number of additions of the diimide reagent for the diimide reduction of 1,4-poly-(1,1,4,4-tetramethyl-1,3-butadiene).

are shown in Fig. 8. The degree of hydrogenation is plotted against the number of hydrogenation experiments. After this set of experiments, the polymer became insoluble in the reaction solvent as well as in decalin up to 180°C. The degree of hydrogenation was, however, higher, namely 70%, according to IR analysis. The insolubility of the polymer is undoubtedly caused by the polymer having undergone cross-linking reactions. The elemental analysis was lower than that calculated for carbon and hydrogen, but 0.8% of sulfur and 0.5% of nitrogen were found in the polymer, indicating that incorporation of the toluene-sulfonyl group and sulfonyl hydrazide had occurred. Incorporation of sulfur and nitrogen into polymers has been observed previously when chemical hydrogenations of unsaturated polymers were carried out with diimide (using p-TSH) under forcing conditions and long reaction times.

From our experience it was demonstrated again that chemical hydrogenation of polymers with diimide is not free of side reactions. The exact nature of the crosslinking reaction which occurred during hydrogenation has not been evaluated, but is undoubtedly caused by recombination of polymer radicals.

TABLE 7. ^{13}C-NMR Chemical Shift Data of Hydrogenated 1,4-Poly-(1,1,4,4-Tetramethyl-1,3-butadiene) (PTMBU)

$$
\begin{array}{c}
\text{CH}_3 \qquad\qquad\qquad \text{CH}_3\ \ \text{CH}_3 \qquad\qquad\qquad \text{CH}_3\\
|\qquad\qquad\qquad\qquad\ |\qquad\ |\qquad\qquad\qquad\qquad\ |\\
{-}\!\!-\!\!\underset{(d)\ |}{\text{C}}\!\!-\!\!-\underset{(c)}{\text{CH}_2}\!\!-\!\!-\text{CH}_2\!\!-\!\!-\underset{|}{\text{C}}\!\!-\!\!-\underset{|}{\text{C}}\!\!-\!\!-\underset{(f)}{\text{CH}}\!\!=\!\!\text{CH}\!\!-\!\!-\underset{(e)\ |}{\text{C}}\!\!-\!\!-\\
\underset{(a)}{\text{CH}_3} \qquad\qquad\qquad \text{CH}_3\ \ \underset{(b)}{\text{CH}_3} \qquad\qquad\qquad \text{CH}_3
\end{array}
$$

Carbon	Chemical shift, ppm	H–H polyisobutylene, ppm	PTMBU
(a)	21.9	21.7	
(b)	23.6		23.9
(c)	32.1	31.4	
(d)	38.5 (39.1)	38.8	
(e)	42.1		41.4
(f)	135.5		135.5

The infrared spectrum of partially hydrogenated PTMBU is shown in Fig. 9 and the ^{13}C-NMR spectra in Fig. 10. The values for the ^{13}C-NMR chemical shifts are shown in Table 7. From the data it can be recognized that the polymer is approximately a 50:50 copolymer of H-H PIB and PTMBU since all the carbon atoms in the spectrum can be assigned to these two units in the polymer. The spectrum could be further interpreted, and the copolymer be recognized as blocky in nature because the methyl and quaternary carbon atom chemical shifts are well defined for each comonomer unit. It is not unreasonable to believe that the hydrogenation might proceed in a blocky manner as seen in chlorination of 1,4-polybutadiene-1,3 [19].

The reason for unsuccessful hydrogenation of PTMBU by either catalytic or chemical techniques is probably steric hindrance of the four methyl groups surrounding each double bond in the TMBU units of PTMBU and consequently the inaccessibility of the polymer double bonds.

In conclusion, pure H-H PIB has not been obtained by Wurtz polymerization of TMDBB with sodium or sodium/potassium alloy; only branched structures of relatively low molecular weight have been isolated. Alternating copolymerization of ethylene and TME, as expected, gave a copolymer of modest molecular weight with ~5% incorporation of TME units. Although polymerization of TMBU proceeded smoothly and almost quantitatively to high molecular weight 1,4-PTMBU, catalytic hydrogenation failed completely. Chemical hydrogenation pro-
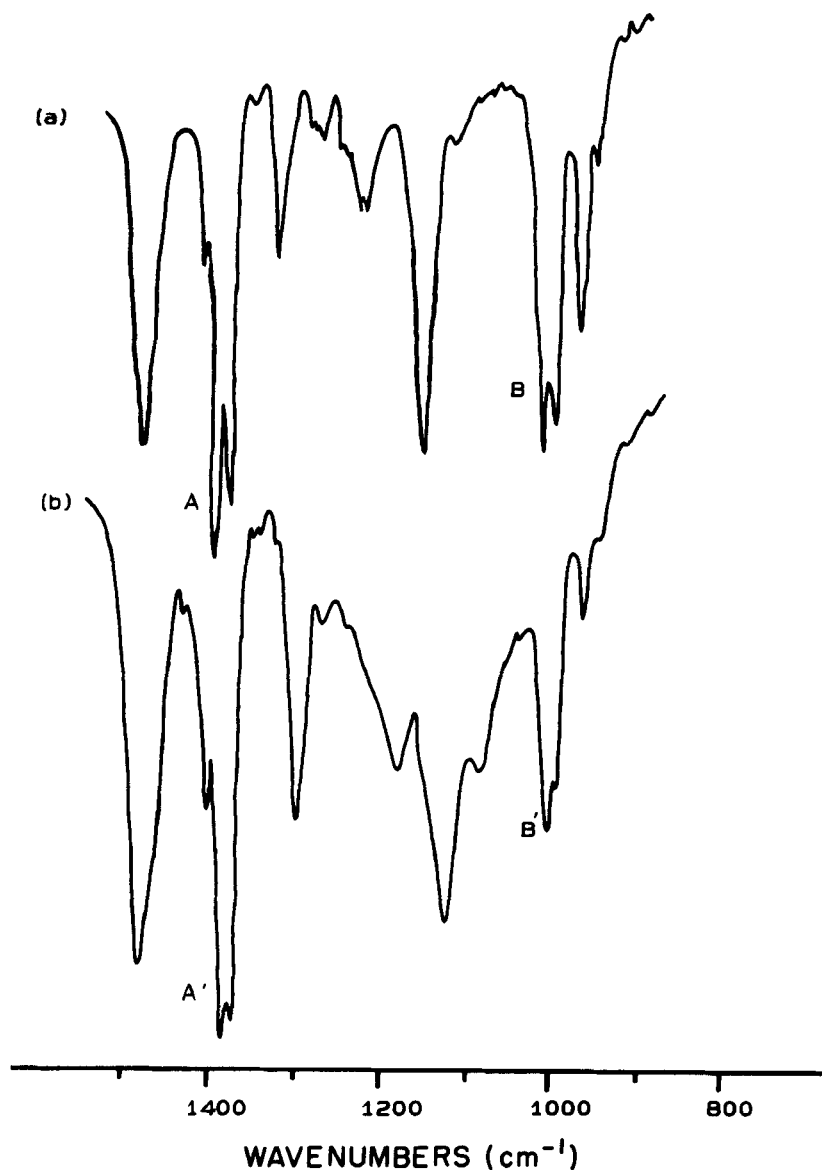
FIG. 9. Infrared spectra of the gem-dimethyl stretching (A, A') and trans —CH=CH— stretching (B, B') regions for: (a) 1,4-poly-(1,1,4,4-tetramethyl-1,3-butadiene); (b) partially hydrogenated 1,4-poly-(1,1,4,4-tetramethyl-1,3-butadiene).
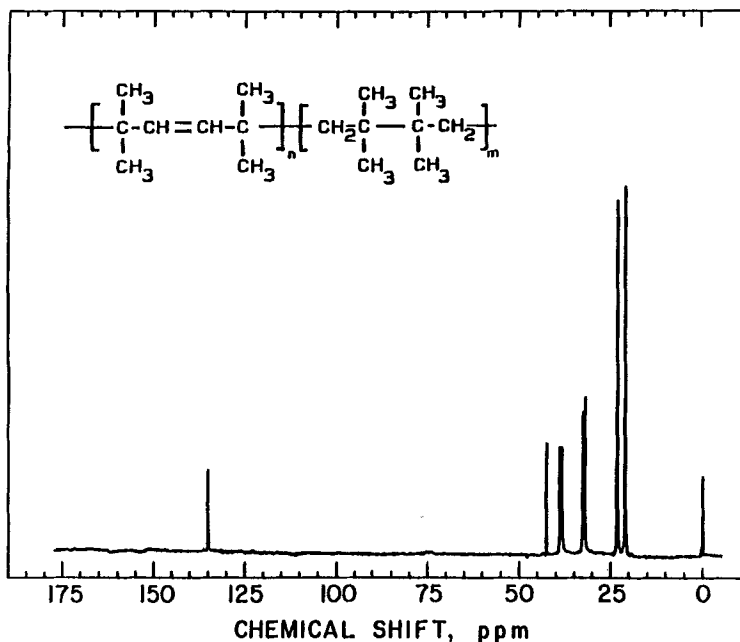
FIG. 10. ^{13}C-NMR spectrum of partially hydrogenated 1,4-poly-(1,1,4,4-tetramethyl-1,3-butadiene).

ceeded up to 70% under forcing conditions, but sulfur and nitrogen are then incorporated into the polymer and crosslinking of the polymer resulted when the reaction was extended.

ACKNOWLEDGMENTS

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