Head-to-Head Polymers. XVI. Polymerization of 2,3-Dimethyibutadiene-l,3 to cis- and trans-1,4-Poly(2,3,-dimethyIbutadiene)

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Head-to-Head Polymers. XVI.*
Polymerization of 2,3-Dimethylbutadiene-1,3 to
cis- and trans-1,4-Poly(2,3,-dimethylbutadiene)

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ABSTRACT

2,3-Dimethylbutadiene-1,3 was polymerized to cis- and trans-1,4-poly(2,3-dimethylbutadiene) of high stereochemical purity with triisobutylaluminum/titanium tetrachloride initiator systems in n-hexane. With a mole ratio of Al/Ti of 2:1, pure cis isomer was obtained while an Al/Ti ratio of 1:2 in the initiator system produced the trans polymer of 1,4-poly(2,3-dimethylbutadiene) free from 1,2-isomers. For the cis-isomer a 0.5 mol% initiator to monomer ratio gives maximum molecular weight while a 1 mol% ratio gives maximum yield. For the trans-polymer the ratios are 1 and 2 mol%, respectively. The cis- and trans-polymers are high melting crystalline materials of melting points of 190°C and near 280°C, respectively. The glass transition temperatures were 2 and 12°C, respectively (onset of transition). The temperature of maximum rate of degradation was 380°C for both polymers.

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INTRODUCTION

Most current research on diene polymerization [1] centers around isoprene, butadiene, and chloroprene. However, some very early efforts also dealt with the polymerization of 2,3-dimethyl-1,3-buta-diene (DMB) and, as early as 1900, work on the polymerization of DMB to a leathery material was reported [2] by heating it in the presence of alcoholic potash; later Whitby and Katz [3] summarized the work on the thermal polymerization of DMB.

A synthetic rubber based on a polymer of DMB [4, 5] was developed and used for a short period. Good polymerization methods for the emulsion polymerization of DMB were developed [6-14]; the analysis of the structure of the emulsion-polymerized DMB indicated [5, 15] that about 13% 1,2-addition product was present in the polymers. The remainder of the structure consisted of various amounts of cis and trans units.

Evaluation of the structure of poly(2,3-dimethylbutadiene) (PDMB) prepared by anionic initiators has shown [16, 17] that polymerization of DMB with butyllithium in nonpolar solvents formed a polymer with high 1,4-content. A polymer with high 1,2-linkages could be prepared with the same initiator in a polar medium. A temperature effect has also been recognized [16-18] with the arrangement of 1,2-units in the polymer predominating at lower polymerization temperatures. The influence of several parameters (temperature, solvent type, initiator concentration, pressure) upon the microstructure of anionically prepared PDMB has been reported [19]. Recently [20], the cis and trans sequence distributions were worked out for PDMB prepared by butyllithium in n-hexane and it was found to contain 74% trans-1,4, 23% cis-1,4, and 3% 1,2-linkages.

The first report of an attempt for stereospecific polymerization with transition metal coordination initiators of DMB was reported by Yen [21]. Treatment of this monomer with an Al(iBu)₃/TiCl₄ at an Al to Ti mole ratio of 1:1 (3 d) produced the cis-1,4-polymer. Polymerization conversion was listed as 25-30% and inherent viscosities of the polymer ranged from 0.6 to 0.9 dL/g (measured as 0.2% solutions in Tetralin at 100°C). The structure assignment was based solely on IR evidence and comparative x-ray powder patterns.

Yen [22] reported also the stereospecific polymerization of DMB to the all-trans-polymer. For this polymerization the Al(iBu)₃/TiCl₄ was combined at an Al to Ti ratio of 1:4, all other factors of the polymerization were essentially the same. Conversions were not reported and inherent viscosities were listed as 0.5 to 1.3 dL/g. Features of IR spectra and comparative x-ray powder patterns were again used as verification of the trans-structure. It was also suggested that the melting point of the trans-polymer, 253-259°C, compared to the cis-polymer, 189-198°C, was a strong indication of a different microstructure.

A more detailed study of the effect of initiator composition on the

polymer microstructure of DMB polymerized with Al(iBu)₃/TiCl₄ was carried out by Gaylord [23, 24], who suggested that cis-1,4-PDMB was formed when the Al component was in excess; he also detected some trans-1,4-units when the Al/Ti ratio was 1:1.

The polymerization of conjugated dienes with similar initiating systems was also investigated by Horne [25, 26]. It was recognized that the cis- and trans-ratio of 1,4-PDMB could be varied by adjusting the Al to Ti ratio. A correlation of the structure of 1,4-PDMB analyzed by IR spectroscopy [27] was made and it was found that agreement of the structural assignments with the results of NMR analysis was possible. High resolution ¹H NMR was used [20] to evaluate in detail the structure of cis- and trans-1,4-PDMB polymers prepared according to Yen's method [21, 22], which confirmed the earlier claim.

Several other methods [28-38] have been used for polymerizing DMB and identifying PDMB. Among the more novel methods have been radiation- [33] and pressure-induced [38] polymerizations. For the preparation of stereoregular cis- or trans-1,4-PDMB, polymerization with Ziegler/Natta-type initiators appeared to be the best method.

It was the objective of this work to study the conditions for the preparation of high molecular weight pure cis- and trans-1,4-PDMB, to characterize these two polymers, and to compare the data with the results of earlier investigations.

EXPERIMENTAL

Materials

The following materials were obtained from the Aldrich Chemical Co.: azobisisobutyronitrile (AIBN), 2,3-dimethyl-1,3-butadiene, and 2,3,3-trimethyl-1-butene.

AIBN was recrystallized three times from dry methanol and dried for 24 h at room temperature at 0.01 mm.

2,3-Dimethyl-1,3-butadiene (DMB) was distilled twice from CaH₂ (bp 68-60°C) immediately before use.

n-Heptane (Fisher-Scientific Co.) was heated under reflux overnight over sodium/potassium benzophenone and distilled immediately before use (bp 98-99°C).

Tri-isobutyl aluminum [Al(iBu)₃] (Ethyl Corp.) was distilled under reduced pressure (bp 86°C/10 mm) and stored under nitrogen prior to use.

Titanium tetrachloride (Ventron Corp.) was distilled (bp 136-137°C) and stored under nitrogen.

Polymerization

cis-1,4-Poly(2,3-dimethylbutadiene) by Heterogeneous Tri-isobutyl-aluminum/Titanium Tetrachloride Initiator System at an Al/Ti Ratio of 2:1

[$TiCl_4$] = 10.5 mmol/mol monomer. The polymerization vessel (150 mL Schlenk tube) fitted with a magnetic stirrer was dried over-night at 120°C. It was then alternatively evacuated (to 0.1 mm), flamed out while under vacuum, and filled with prepurified dry nitro-gen. After this cycle of evacuation and filling with nitrogen, 50 mL of dry n-heptane was distilled into the Schlenk tube, which was closed with a serum stopper and maintained under a slow purge of nitrogen. Al(iBu)₃ (0.25 g, 1.3 mmol) and $TiCl_4$ (0.12 g, 0.64 mmol) were added with dry nitrogen purged syringes and the brown heterogeneous sus-pension stirred for 25 min. Freshly distilled DMB (5.0 g, 61 mmol) was added with a syringe, and the polymerization was allowed to proceed for 24 h. Addition of 10 mL of methanol containing 10% con-centrated HCl terminated the polymerization, and the contents of the tube were poured into 50 mL of methanol. The polymer was removed by filtration, washed with methanol (5 × 20 mL), and dried in the Abderhalden apparatus at 0.1 mm, 100°C; yield 3.3 g (65%, inherent viscosity 0.52 dL/g (0.1% in Tetralin, 100°C). Additional polymeri-zations of DMB were conducted varying the concentration of $TiCl_4$. The results are summarized in Fig. 1. The IR spectra showed strong
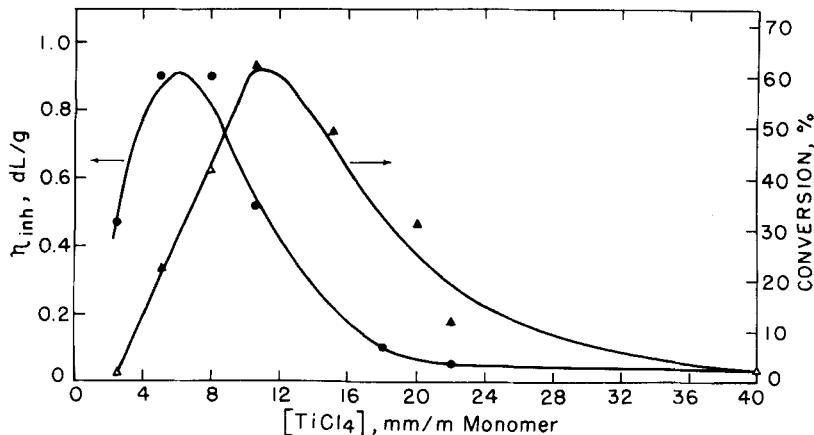

FIG. 1. Effect of $TiCl_4$ concentration on conversion and inherent viscosity in the preparation of cis-1,4-poly(2,3-dimethylbutadiene).

absorptions in the region 3000 to 2800 cm^{-1} (2963, 2918, and 2850 cm^{-1}; ν_{as} $-CH_3$, ν_{as} $-CH_2$ and ν_s $-CH_3$). Additional strong absorptions were observed at 1463 and 1377 cm^{-1} (δ_{as} $-CH_3$ and δ_3 $-CH_3$). Weak and moderate absorptions were observed at 1250, 1200, 1150, and 1120 cm^{-1} (C–C skeletal vibrations). The ^{13}C NMR spectrum (o-dichlorobenzene, 90°C, 24,600 transients) showed single absorptions at δ = 128.81 ($-\underline{C}=C$), δ = 34.04 ($-CH_3$). Differential scanning calorimetry on virgin polymer indicated the onset of melting at 162°C; the maximum in the melting endotherm was observed at 191°C. Successive scans showed two maximums in the melting peaks at 184 and 191°C. The T_g was observed at 2°C. Thermogravimetric analysis indicated the beginning of weight loss at around 287°C. Differential thermogravimetric studies showed a maximum rate of weight loss at 379°C.

trans-1,4-Poly(2,3-dimethylbutadiene) at an Al/Ti Ratio of 1:2

[$TiCl_4$] = 5 mmol/mol monomer. Into a clean dry 150 mL Schlenk tube with a magnetic stirrer was distilled 50 mL of n-heptane and the tube was closed with a serum stopper. Al(iBu)₃ (0.03 g, 0.15 mmol) and $TiCl_4$ (0.05 g, 0.30 mmol) were added with a syringe. The dark heterogeneous slurry was aged for 25 min. Freshly distilled DMB (5.0 g, 61 mmol) was injected and the polymerization allowed to proceed for 24 h. At the end of this period, 10 mL of methanol containing 10% concentrated HCl was injected and the polymer suspension poured into 50 mL of methanol. The product was isolated by filtration, washed with methanol (5 × 20 mL), and gave a white material; yield 4.0 g (80%), inherent viscosity 0.7 dL/g (0.1% in Tetralin, 100°C). Additional polymerizations were carried out by varying the concentration of $TiCl_4$. The results are summarized in Fig. 7. The IR spectrum (KBr pellet) showed strong absorption at 2960 and 2940 cm^{-1} (ν_{as}, $-CH_3$ and ν_{as}, $-CH_2$). Additional strong absorption bands were observed at 1459 and 1370 cm^{-1} (δ_{as}, $-CH_3$ and δ_s, $-CH_3$). Weak to moderate absorption bands were detected at 1220, 1150, and 1120 cm^{-1} (C–C skeletal vibrations). ^{13}C NMR (o-dichlorobenzene, 90°C, 35000 transients) showed single-chemical shifts at δ = 128.85 ($-\underline{C}=C$), δ = 33.90 ($-CH_2-$), and δ = 18.44 ($-CH_3$).

Overnight annealing at 130°C in the differential scanning calorimeter, followed by quenching, gave rise to a well-defined T_g of 22°C.

Thermogravimetric analysis indicated the onset of weight loss at around 280°C; differential thermogravimetric analysis showed a maximum rate of weight loss at 377°C.

Poly(2,3-dimethylbutadiene) from Azobisisobutyronitrile (AIBN)

Procedure. A clean and dry polymerization tube was charged with freshly distilled DMB (2.9 g, 35 mmol) and AIBN (110 mg, 6.7 × 10^{-1} mmol), and flushed with nitrogen. The tube was then degassed

by five freeze-thaw cycles at 0.01 mm, sealed at 0.01 mm, and placed in a constant temperature bath at 65°C. Polymerization was allowed to proceed for 72 h. The tube was then opened and the contents poured into 25 mL of methanol. Evaporation of the methanol by a steady stream of nitrogen, followed by overnight drying in the Abderhalden apparatus (0.1 mm, 100°C), gave a very small amount of tacky polymer. The IR spectrum (film on NaCl plate) indicated strong absorption at 2960, 2920, and 2860 cm^{-1} (ν_{as}, $-CH_3$, ν_s, $-CH_2$, ν_s, $-CH_3$). Additional strong absorption peaks were observed at 1455 and 1370 cm^{-1} (δ_{as}, $-CH_3$ and δ_s, $-CH_3$). Moderate absorption was also seen at 890 cm^{-1} ($\delta = CH_2$). The ^{13}C NMR spectrum (o-dichlorobenzene, 90°C, 27,000 transients) showed chemical shifts at $\delta = 128.87$ ($-C=C-$), $\delta = 34.60$, 33.96, 33.47 ($-\underline{C}H_2-$, ct, tt, tc) and $\delta = 18.86$, 18.52 ($-\underline{C}H_3$, cis and trans).

Measurements

Infrared spectra were recorded on a Perkin-Elmer Model 727 or Model 283 spectrophotometer. Solid samples were measured as KBr pellets and liquid samples were measured as smears or films between NaCl plates. The IR spectra of some of the polymer samples were measured as films cast directly onto a single NaCl plate from an o-dichlorobenzene solution. The peak assignments were made to the nearest 5 cm^{-1}.

^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer under complete proton decoupling. The measurements were carried out in CDCl$_3$ at room temperature with TMS as the internal standard or in o-dichlorobenzene at 90°C with an external D$_2$O, dioxane standard.

Gas chromatographic analyses were conducted on a Varian Aerograph 920 gas chromatograph with a 5 ft × 1/4 in. column packed with 100/120 mesh Varaport 30.

Thermogravimetric analyses were performed with a Perkin-Elmer Model TGS-1 thermobalance with UU-1 temperature programmer. The temperature scale of the programmer was calibrated with the magnetic standards provided with the instrument in order to optimize the agreement between the direct dial readout of the temperature programmer and the instrument furnace temperature, as indicated by transitions of the standards. Heating rates of 20°C/min were normally employed and all thermogravimetric measurements were performed under a 10-20 cc/min flow of dry N$_2$. Samples (10-20 mg) were weighed to the nearest 0.02 mg into platinum sample pans on a Perkin-Elmer AD-2 Autobalance.

Thermal transitions in the polymer samples were investigated on a Perkin-Elmer Model DSC-2 differential scanning calorimeter equipped with a Scanning Autozero unit. The temperature scale of the instrument was calibrated at the desired heating rate by adjusting the

direct dial temperature readout of the programmer to correspond with the transition temperature of cyclohexane (crystallization point 86.9°C, melting point 6.7°C) and indium (melting point 156.8°C). Samples were contained in sealed aluminum pans. Sample weights of 5-15 mg were used, all weighings made on a Perkin-Elmer AD-2 Autobalance.

Glass transition temperatues (T_g's) were determined from the resultant thermograms as the temperature at which the first deviation from the baseline of heat capacity (C_p) was observed. This is an arbitrary definition; for example, T_g could be defined as the temperature at which the heat capacity achieved one-half of the entire step change observed. Melting transitions (T_m's) are reported for the onset of melting as well as for the maximum in the melting endotherm.

Investigations of the x-ray wide angle scattering on our samples were carried out with an x-ray beam of a wavelength of 1.5418 Å (Cu/K_α, filtered with Ni), the beam passed through a pinhole collimator, then the samples, and finally onto a flat film camera.
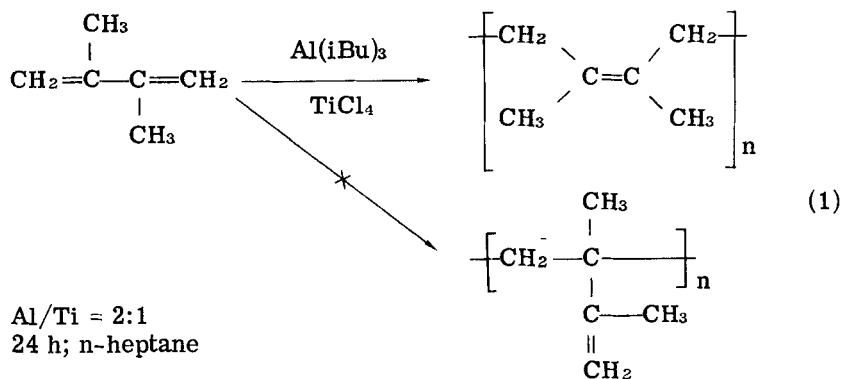
RESULTS AND DISCUSSION

DMB was polymerized to PDMB with appropriate mixtures of Al(iBu)$_3$/TiCl$_4$ as initiator. Careful adjustment of the Al/Ti ratio was necessary for the preparation of pure cis- or trans-1,4-polymer.

Preparation of cis-1,4-Poly(2,3-dimethylbutadiene):

Initiator System for Polymerization. cis-PDMB with greater than 97% pure cis stereoregularity has been produced from heterogeneous Al(iBu)$_3$/TiCl$_4$ initiators. The ratio of metal alkyl to transition metal salt was maintained at 2:1 and the initiator components being allowed to age for 25 min at room temperature before monomer addition. All reactions were carried out under an inert atmosphere in dry n-heptane and the reaction time was 24 h at room temperature. This reaction is illustrated in Eq. (1); details of the preparations were described earlier. The preparation of cis-PDMB using Al(iBu)$_3$/TiCl$_4$ at an Al/Ti ratio of greater than 1:1 is in accord with earlier descriptions of the preparation of diene polymers [23, 24].

All catalyst preparations were conducted in the solvent medium for polymerization. The desired amount of Al(iBu)$_3$ was added to the solvent, followed by addition of TiCl$_4$. At this point the solution turned dark brown and the aging period began. After 25 min, monomer was injected and polymerization was allowed to proceed for 24 h. Addition of methanol containing 10% concentrated HCl destroyed the

$$
\underset{\substack{CH_3 \\ | \\ CH_2=C-C=CH_2 \\ | \\ CH_3}}{} \xrightarrow[\text{TiCl}_4]{\text{Al(iBu)}_3}
\left[\begin{array}{c} CH_2 \qquad\qquad CH_2 \\ \diagdown \qquad\quad \diagup \\ C=C \\ \diagup \qquad\quad \diagdown \\ CH_3 \qquad\qquad CH_3 \end{array} \right]_n
$$

$$
\left[\begin{array}{c} CH_3 \\ | \\ CH_2-C- \\ | \\ C-CH_3 \\ \| \\ CH_2 \end{array} \right]_n \tag{1}
$$

Al/Ti = 2:1
24 h; n-heptane

initiator and gave an off-white polymer suspension. The product was subsequently isolated by filtration. All polymer samples were stored under an inert atmosphere in the refrigerator. Well established by other workers [39] is the oxidation in air of polydienes, even after only a few hours.

An evaluation of the mechanism of the Ziegler-Natta catalyst is complicated by several considerations. Kinetic and stereochemical behavior of the initiator has been shown [40] to depend to a very large degree on (1) metal alkyl structure, choice of metal and nature of ligands; (2) transition metal structure, choice of metal, nature of ligands, crystal structure, valence; and (3) the way the components are brought together and used in polymerizations, absolute and relative concentrations, aging, temperature, and time. An additional complication arises from the fact that certain ligand-monomer interactions are exclusive in the sense that different monomers behave differently with the same initiator [41].

Effect of (TiCl₄) on Conversion and Molecular Weight. By maintaining all other factors constant in the polymerization of DMB (initiator component ratio, aging time, temperature, time, and solvent), the influence of the $TiCl_4$ concentration on conversion and inherent viscosity could be assessed (Fig. 1). As can be seen from Fig. 1, at both very high and very low concentration of $TiCl_4$ conversion and inherent viscosity (and consequently molecular weight) are low. A maximum value of an inherent viscosity of 0.9 dL/g was found at (TiCl₄) = 5-8 mmol/mol monomer. (A number-average molecular weight, $\overline{M}_n$ = 68,500, had been established earlier for PDMB with an intrinsic viscosity of 0.66 dL/g [14].)

Accounting for a lower molecular weight and conversion at high concentration of TiCl₄, one might suspect chain transfer reactions involving the initiator to be responsible. Termination of chain growth in a Ziegler-Natta polymerization, however, has been shown to be caused by only specific reactants and complexing agents [42], not the heterogeneous initiator. For example, Natta and Pasquon [42],

TABLE 1. Infrared Absorption Bands of Poly(2,3-dimethylbutadiene) (cm^{-1})

cis-PDMB		trans-PDMB		PDMB initiated with AIBN		Assignment
				3080	w	$=CH_2 \nu$
2963	s	2958	s	2960	s	$-CH_3 \nu_{as}$
2918	s	2920	s	2920	s	$-CH_2 \nu_{a}$
2850	s	2861	s	2860	s	$-CH_3 \nu_{s}$
2720	w	2721	w	2721	w	
				1630	w	$C=C \nu$
1463	s	1463	s	1455	s	$CH_3 \nu$ da
1377	s	1370	s	1370	s	$CH_3 \nu$ ds
1250	s					
		1221	w	1220	w	
1200	s					
						$C-C \nu CH \delta$
1150	w					
		1150	s	1150	m	
1120	m					
				890	m	$-CH_2$ oop

in their study of the polymerization of propylene to isotactic polymer, found a dependence of the intrinsic viscosity of the polymer on the aluminumalkyl concentration. It was established that metal alkyls can act as terminators of chain growth and, under suitable conditions, they function as true transfer agents. Of more direct interest here, however, is earlier findings of a transfer reaction between the growing chain and transition metal compound [43]. A half-order or first-order [44] dependence on TiCl$_4$ concentration for the molecular weight dependence was established.

It is interesting to note that earlier workers [21-23] in their investigations of preparing PDMB with heterogeneous initiators reported a range of inherent viscosities and conversions along with a range of initiator concentrations. The nature of the effect, and the particular concentrations of initiator providing highest viscosities and conversion, were not reported.

TABLE 2. Chemical Shift Data (^{13}C NMR Spectra)[a] of cis- and trans-
1,4-Poly(2,3-dimethylbutadiene)

Carbon	Sequence	Chemical shift[b]
$-CH_2-$	cis	34.04
$\underset{|}{\overset{CH_3}{C}}=$	cis	128.81
$\underset{|}{\overset{\underline{CH_3}}{C}}=C$	cis	18.84
$-CH_2-$	trans	33.88
$\underset{|}{\overset{CH_3}{C}}=$	trans	128.84
$\underset{|}{\overset{\underline{CH_3}}{C}}=$	trans	18.43

[a]Measured at 90°C in o-dichlorobenzene.
[b]Dioxane reference at 67.39 ppm.

Characterization of cis-1,4-Poly(2,3-dimethylbutadiene)

1. Spectral properties. cis-PDMB obtained by polymerization
with Al(iBu)₃ and TiCl₄ was characterized by IR and ^{13}C NMR spec-
troscopy.

Strong IR absorptions were observed at 2963 cm^{-1} (ν_{as}, $-CH_3$),
2918 cm^{-1} (ν_{as}, $-CH_2$), and at 2850 cm^{-1} (ν_s, $-CH_3$) (Table 1).

The ^{13}C NMR spectrum of cis-1,4-PDMB showed chemical shift
values at 128.81, 34.04, and 18.84 ppm. The olefinic carbon atom,
assigned to the lowest field peak at 128.81 ppm, was sometimes diffi-
cult to detect because of an overlap with the meta carbons of the solvent,
o-dichlorobenzene (δ = 127.7). The methylene carbon atoms attached
cis to an olefinic linkage show a chemical shift of 34.04 ppm and the
cis methyl groups at 18.84 ppm (see also Ref. 45) (Table 2).

We have very carefully evaluated the ^{13}C NMR spectrum for small
amounts of resonance peaks which could be assigned to terminal
methylene carbon atoms and would consequently indicate the presence
of 1,2-linkages in the polymer. The ^{13}C NMR spectrum of 2,3,3-
trimethyl-1-butene was consequently studied which provides a model
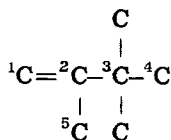for the 1,2 linkage one might observe in cis-1,4-PDMB (Table 3).

TABLE 3. Chemical Shift Data[a] (^{13}C NMR spectra) of 2,3,3-Tri-methyl-1-butene[b]

Carbon[c]	Chemical shift
1	108.42
2	153.70
3	29.46
4	35.96
5	19.92

[a]Relative to dioxane reference at 67.39 ppm.
[b]5% in o-dichlorobenzene.
[c]Carbon numbers as follows:

$$^1C{=}^2C{-}^3C{-}^4C$$

with

$$\begin{array}{c} C \\ | \\ {}^1C{=}{}^2C{-}{}^3C{-}{}^4C \\ |\quad | \\ {}^5C\quad C \end{array}$$

Two important results were concluded from that study: (1) the chemical shifts observed for the 1,2 model linkage were not found in the spectra of our polymers; and (2) less than 5% of 2,3,3-trimethyl-1-butene could not be detected reliably. Therefore, within the accuracy of our ^{13}C NMR measurements, using 20-25,000 transients, the presence of 1,2 linkages does not exceed 5% but may be 0%.

2. Melting behavior and T_g. cis-PDMB samples of the highest molecular weights were analyzed by DSC, and their glass transition temperatures and melting behavior were studied. Results of representative runs are given in Table 4. All annealing and quenching studies of the samples were performed in the calorimeter.

The glass transition temperature of all cis-PDMB appeared in the region of 2-4°C, usually difficult to see on virgin polymer but becoming more pronounced upon melting, annealing, and quenching. The amount of crystalline order in these semicrystalline polymers is apparently reduced by a thermal history of annealing above T_m and quenching which results in an increase in the amount of amorphous portions of the polymer and allows the T_g to be more readily located.

As mentioned earlier, the value of the T_g was taken as the temperature of the first deviation of the heat capacity (C_p) from the baseline. If we were to define T_g as the temperature at which C_p achieved

TABLE 4. DSC Scans of cis-Poly(2,3-dimethylbutadiene)

Polymer	Scan Sequence	Temperature range (°C)	Description	T_g (°C)	T_m (°C) onset peak maximum	Comments
η_{inh} = 0.90 dL/g, Tetralin	A	-48 to 37	Virgin polymer	-	-	No transition observed
	B	-48 to 37	After Scan A	-	-	" "
	C	117 to 227	After Scan B	-	162/183	Clear melt
	D	-48 to 68	After Scan C quenched/ rescanned	2	-	Small transition
	E	107 to 227	After Scan D	-	162/183	Clear melt
	F	-48 to 52	After Scan E quenched/ rescanned	4	-	Small transition
	G	-48 to 42	Heated to 197°C annealed 5 min/ rescanned	2	-	Clear transition

|					
η_{inh} = 0.90 dL/g, Tetralin	H	-48 to 52	After Scan G	2	–	Clear transition
	A	-48 to 27	Virgin polymer	–	–	No transition observed
	B	117 to 227	After Scan A	–	162/191	Clear melt
	C	117 to 227	After Scan B	–	162/184, 191	Two melting peaks. Higher temperature larger
	D	-48 to 17	Quenched after Scan C	2	–	Small transition
	E	117 to 227	Overnight annealing at 127° C, quenched	–	162/184, 191	Two melting peaks, Lower temperature larger
η_{inh} = 0.60 dL/g, Tetralin	A	-48 to 102	Virgin polymer	4	–	Difficult to see
	B	117 to 227	After Scan A	–	161/189	Clear melt
	C	117 to 227	After Scan B	–	158/182, 190	Two melting peaks. Higher temperature larger
	D	-48 to 112	Quenched after Scan C	2	–	Clear transition
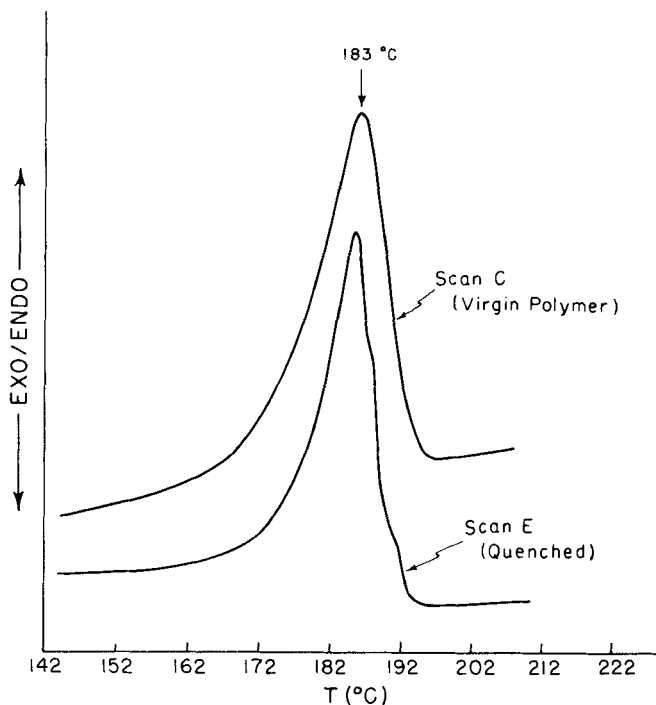
FIG. 2. DSC study of a sample of cis-1,4-poly(2,3-dimethylbuta-diene); η_{inh} = 0.9. Scans C and E.

one-half of the entire step change observed, a value of T_g = 12-14°C would be observed for cis-PDMB.

The entire glass transition phenomena was observed over a relatively broad temperature (15-20°C) region. Polymers prepared with heterogeneous initiators generally have broad molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 5-20) [46] and such distributions have enlarged regions over which T_g is observed [47].

In our studies of the melting behavior of cis-PDMB by DSC (Figs. 2-4), we have observed two rather interesting phenomena. First, in all of the cis-polymers studied melting occurred over a broad temperature region. The onset of melting was observed at 162°C with maximums in the melting endotherms falling between 183-191°C which might be an indication of a broad molecular weight distribution like the broad glass transition range. Yen [21] reported a melting point of 189-198°C for his sample of cis-PDMB prepared with heterogeneous initiator. Gaylord [23] observed a melting range of 162-198°C
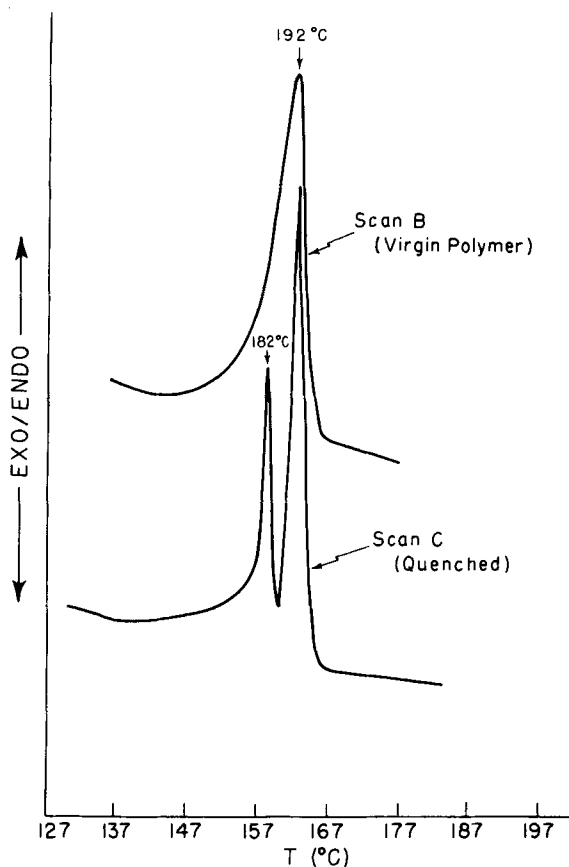
FIG. 3. DSC study of a sample of cis-1,4-poly(2,3-dimethylbuta-diene); η_{inh} = 0.6. Scans B and C.

for cis-PDMB also prepared with heterogeneous initiators. Gaylord also demonstrated a shift toward higher melting points after the removal of low molecular weight fractions.

After our virgin polymer was melted in the calorimeter, the sample was rescanned in order to confirm the temperature of the transition. Subsequent scans, however, displayed two melting endotherms (Fig. 3); the relative intensities could be altered depending on the development of (1) another crystal form in cis-PDMB or (2) a difference in crystallite size. Both factors could give rise to an additional or different endothermic transition.

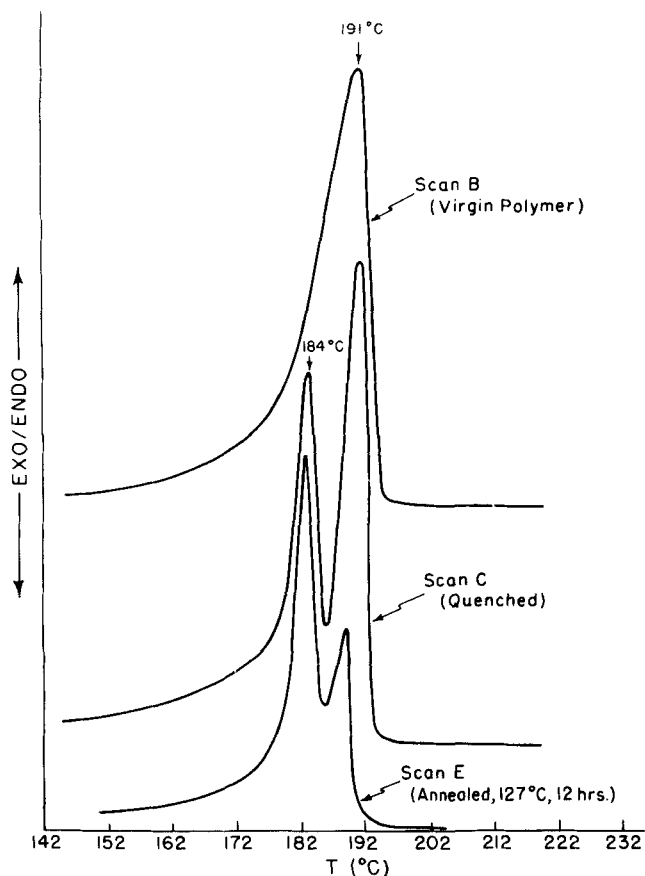First-order multitransition phenomena (noticeable by DSC) has not

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FIG. 4. DSC study of a sample of cis-1,4-poly(2,3-dimethylbuta-diene); η_{inh} = 0.9. Scans B, C, and E.

been observed in DMB polymers before, but has been found and attributed to crystal-crystal transitions in other very similar polymer systems. Natta [48], in early x-ray studies on 1,4-polybutadiene, proposed a transition between two crystal modifications at 60°C. Also of direct interest has been the observation of two crystalline forms in trans-1,4-polyisoprene [49]. One form had a melting temperature of 82.4°C, the other form a melting temperature of 79.5°C. It might be mentioned that Bunn [50], from studies of the stereochemistry of trans-1,4-polyisoprene, predicted the possibility of four different crystalline modifications. Polymorphism is known to be extremely sensitive to temperature, pressure, and applied stresses.
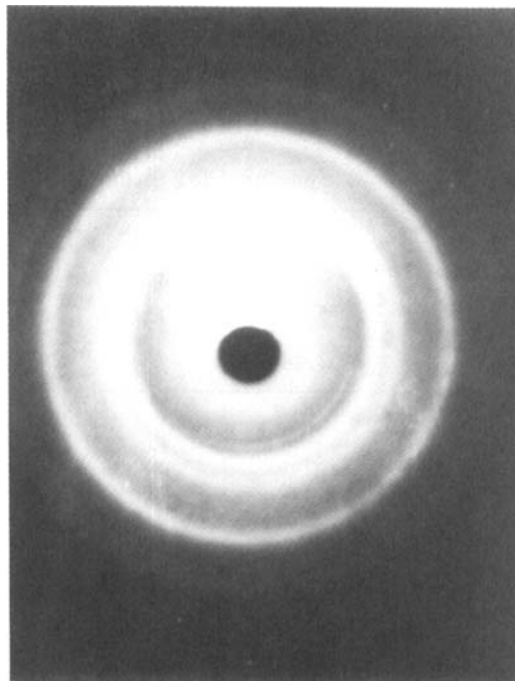
FIG. 5. Wide-angle x-ray diagram of cis-1,4-poly(2,3-dimethyl-butadiene).

3. Wide angle x-ray studies.   We also studied the polymer samples by wide angle x-ray diffractions; results of the Debye-Scherrer type diagrams are shown in Fig. 5 and Table 5. It is seen that cis-PDMB has a significant amount of crystallinity, and diffraction maxima were observed at 5.49 (m), 3.08 (s), 2.68 (m), and 2.00 Å. Also presented in Table 5 are the diffraction maxima for trans-PDMB, which will be discussed later.

4. Thermal stability of the polymers. The thermal degradation behavior of the samples of cis-PDMB was investigated and is shown in Fig. 6 for the two samples of highest molecular weight. The MDT was found to be at 380°C, a behavior similar to all of the cis-PDMB polymers studied. A clear indication of the initial degradation temperature was gained from TGA, the beginning of weight loss was observed at around 285°C. The maximum degradation temperature of cis-PDMB, 380°C, falls between the reported [51] MDT of polyisoprene, 325°C, and polybutadiene, 410°C. Poly(2,3-diphenylbutadiene) showed a MDT of 357°C [52].

TABLE 5. Wide-Angle X-Ray Studies: Interplanar Spacings of
Crystalline cis- and trans-1,4-Poly(2,3-dimethylbutadiene) (Å)

cis-PDMB		trans-PDMB		
Spacing	Relative intensity	Spacing	Relative intensity	Yen [22]
5.49	(m)	4.27	(s)	4.3 (s)
3.08	(s)	3.78	(w)	3.9 (w)
2.68	(m)	2.99	(s)	3.1 (w)
2.00	(s)	2.44	(s)	
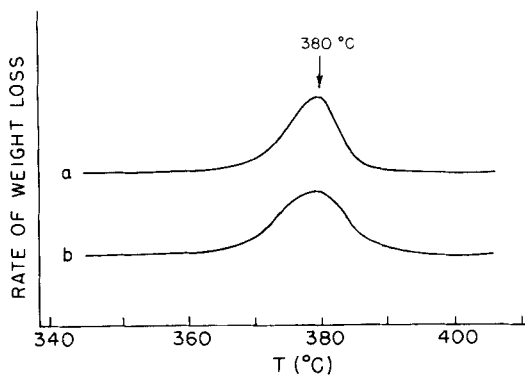
FIG. 6. DTG studies of cis-1,4-poly(2,3-dimethylbutadiene) (heat-
ing rate 20°C/min under nitrogen).

Preparation of trans-1,4-Poly(2,3-dimethylbutadiene)

Initiator System for Polymerization.   Trans-PDMB
with greater than 95% pure trans stereoregularity has been produced
from heterogeneous Al(iBu)₃/TiCl₄ initiators. The ratio of metal
alkyl to transition metal salt was maintained at 1:2, representing the
only change in conditions compared to the preparation of cis-PDMB.
The results of our study of reaction conditions are illustrated below.
Details of the preparations were discussed earlier.
    Effect of [TiCl₄] on Conversion and Molecular
Weight.   In a study similar to the preparation of cis-PDMB, the
influence of the TiCl₄ concentration (at constant Al/Ti ratio 1:2) on
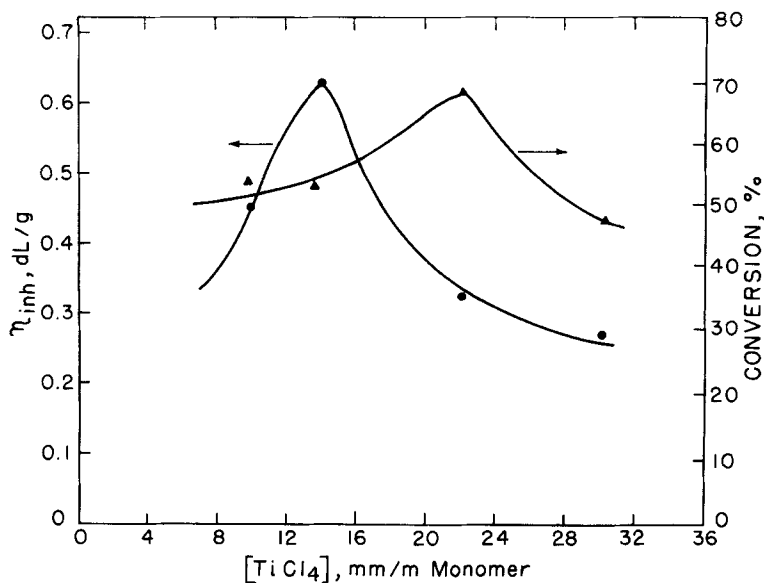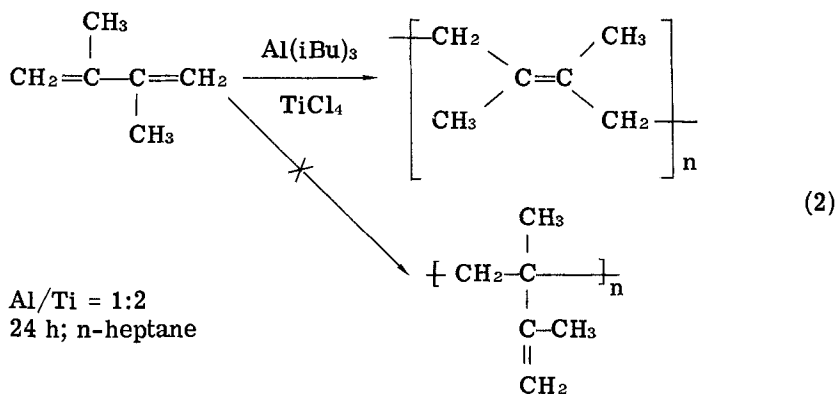conversion and molecular weight was investigated (Fig. 7). As can

FIG. 7. Effect of TiCl$_4$ concentration on conversion and inherent viscosity in the preparation of trans-1,4-poly(2,3-dimethylbutadiene).

(2)

Al/Ti = 1:2
24 h; n-heptane

be seen from Fig. 7, at very high and very low initiator concentrations, conversion and inherent viscosity (and consequently molecular weight) are low. A maximum value of an inherent viscosity of 0.65 dL/g was found at (TiCl$_4$) = 14 mmol/mol monomer. It is interesting to note that this concentration at which optimum results were found was approximately twice that observed in the preparations of cis-PDMB. Clearly, this is a result of an overall change in initiator composition,
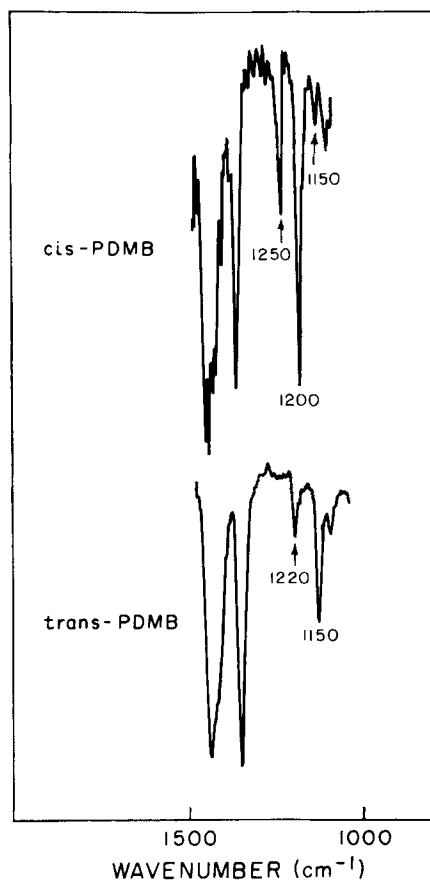
FIG. 8. Infrared spectrum of the 1500-1000 cm^{-1} region of cis- and trans-1,4-poly(2,3-dimethylbutadiene).

cis-polymer having been prepared at an Al/Ti ratio of 2:1, whereas the trans-polymer was produced when the Al/Ti ratio was 1:2. The major objective of this part of our investigation was to produce trans-PDMB at optimum conversion and molecular weight. Like in the preparation of cis-PDMB, some reactions compete with polymerization and are influenced by changing the TiCl$_4$ concentration. Previous workers [22, 23] have investigated the preparation of trans-PDMB with heterogeneous initiators. However, as in prior work on cis-PDMB, factors that influenced the conversion and inherent viscosities were not reported.

Characterization of trans-1,4-Poly(2,3-dimethylbutadiene)

1. Spectral properties. Trans-PDMB obtained by heterogeneous polymerization with $Al(iBu)_3$ and $TiCl_4$ was characterized by IR and ^{13}C NMR spectroscopy.

Strong absorptions were observed at 2958 cm^{-1} (ν_{as}, $-CH_3$), 2920 cm^{-1} (ν_{as}, $-CH_2$) and at 2861 cm^{-1} (ν_s, $-CH_3$). Table 1 summarizes the IR absorption bands of both cis- and trans-1,4-poly(2,3-dimethyl-butadiene). Also listed in Table 1 are the absorptions observed in PDMB initiated with AIBN.

Figure 8 shows the most distinct differences one observes in the IR spectra: the absorption bands of C–C stretching, skeletal vibrations. cis-PDMB shows medium absorption at 1250 cm^{-1}, strong absorption at 1200 cm^{-1}, and a small band at 1150 cm^{-1}. The trans-polymer, however, shows no absorption at 1250 cm^{-1}, a weak band at 1220 cm^{-1}, and medium absorption at 1150 cm^{-1}.

Infrared spectroscopy alone does not allow a quantitative evaluation of polymer structure. The development of a characteristic finger-print in the 1500-1100 cm^{-1} region does provide, however, a strong indication of the predominating structure.

The ^{13}C NMR spectra of trans-PDMB showed magnetic resonance chemical shifts at 128.84, 33.88, and 18.43 ppm. Table 2 lists the assignments for these peaks. The chemical shift of all carbon atoms of the polymer chain appears to be influenced by the polymer struc-ture, the cis-unit appearing at 34.04 ppm, while the trans-unit is at 33.88. Clearly distinguishable also are the carbon atoms of the methyl groups. cis-Configuration shows $\delta(CH_3)$ = 18.84 ppm, trans-configuration showing $\delta(CH_3)$ = 18.43 ppm.

The assignments of chemical shift data agree with earlier work [45]. It is interesting to note that the methyl group in cis-polyiso-prene was observed at 23.25 ppm. shifting to higher fields, 15.87 ppm, in the trans-polymer [53]. Recent work on 2,3-dialkyl-1,3-butadienes also indicated a shift to higher fields for trans-alkyl units [54, 55] similar to our observation for the carbon atoms in trans-PDMB.

2. Melting behavior and T_g. DSC studies on trans-1,4-PDMB are summarized in Table 6. Whereas the melting behavior of the cis-polymer could be readily investigated by DSC, the trans-polymer was found to decompose at temperatures slightly above T_m, with an indi-cation for the beginning of the melting near 275°C. Other reports on trans-PDMB indicated T_m's of 240-250°C [33], 253-259°C [22], and 270°C [23]. In no cases did the earlier authors ever mention possible polymer decomposition, and all T_m values were determined from melting point measurements in a capillary.

The melting region for the trans-polymer is nearly 100°C higher than that of the cis-polymer. It has been established that differences in melting point are caused by differences in steric and energetic

TABLE 6. DSC Scans of trans-1,4-Poly(2,3-dimethylbutadiene)

| Polymer	Scan	Sample Description	T_g (°C)	Comments
Inherent viscosity (η in dL/g, Tetralin)				
0.65	A	Virgin polymer	12	Difficult to see
	B	Quenched, rescanned	12	" " "
	C	Heating to 277°C, annealed 5 min, quenched	12	Clear transition
	ʼ	After Scan C quenched and rescanned	12	"
0.45	A	Virgin polymer	7	Clear transition
	B	Heating to 277°C, annealed 5 min, quenched	7	"
	C	After Scan B quenched and rescanned	7	"
	D	After Scan C quenched and rescanned	7	"
0.70	A	Virgin polymer	–	Small transition
	B	Heated to 277°C, annealed 5 min, quenched	22	Clear transition
	C	After Scan B quenched and rescanned		"
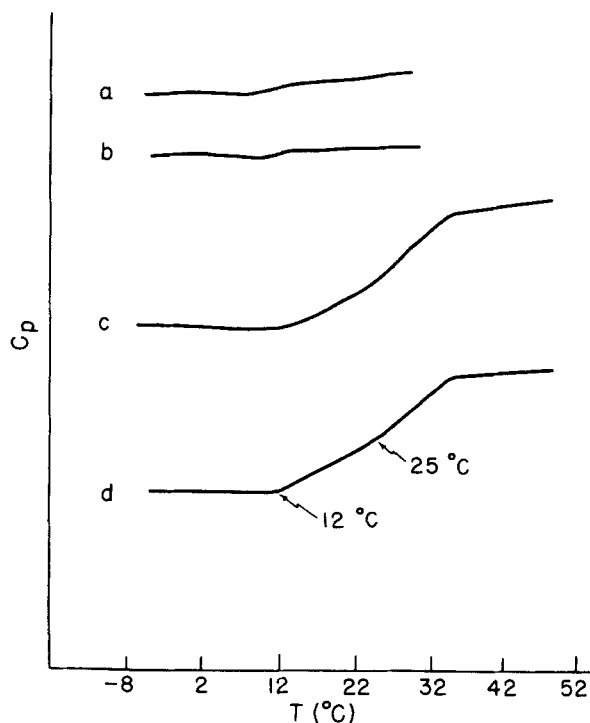
FIG. 9. DSC scans of a sample of trans-1,4-poly(2,3-dimethylbuta-diene); η_{inh} = 0.65.

barriers to rotation, which stiffen the polymer chain, and by the different angles that bonds make with one another [56]. The relatively high melting region of trans-PDMB is somewhat unusual for a linear carbon-chain polymer. A collection of thermal transition temperatures (T_g's and T_m's) of selected diene and polyolefin polymers is presented in Table 7.

The T_m of 135-145°C for trans-1,4-polybutadiene is lowered to 68°C when one hydrogen atom is substituted by a methyl group in the 2-position. Apparently, molecular symmetry is restored with the replacement of another hydrogen for a methyl in the 3-position which would result in closer packing of the crystalline portions with the observed substantial increase in T_m.

Table 6 and Figs. 9 and 10 summarize our results on the study of the glass transition behavior of trans-PDMB. Annealing at elevated temperatures followed by quenching developed a sufficient change in
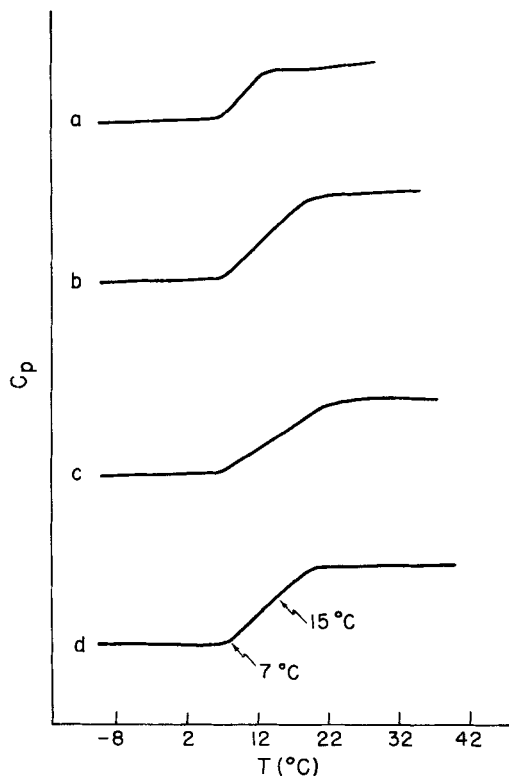
FIG. 10. DSC scans of a sample of trans-1,4-poly(2,3-dimethyl-butadiene; η_{inh} = 0.45.

C_p difference to have a T_g clearly observed. Polymer of η_{inh} = 0.65 dL/g showed a T_g = 12°C and a polymer of η_{inh} = 0.45 showed a slightly lower T_g of 7°C. This difference may be to a large part caused by the lower molecular weight of the polymer sample. The T_g of an insoluble polymer sample was found to be at 22°C but this polymer sample was suspected to be cross-linked.

If we were to define T_g as that temperature at which C_p reaches one-half its step change, we would record T_g's of 25 and 15°C for the polymer samples indicated above.

From Table 7 we can see that the T_g of trans-PDMB is the highest of all the aliphatic 1,3-diene type polymers. Gerke [72] in some early work on second-order transition temperatures of diene rubbers reported

TABLE 7. Thermal Transition Temperatures of Selected Diene and Polyolefin Polymers

| Polymer	Glass transition temperature (°C)	Melting temperature, T_m (°C)	Refs.
cis-1,4-Polybutadiene	-102	0-6	57, 47
trans-1,4-Polybutadiene	-58	135-145	58, 47
cis-1,4-Polyisoprene	-73	28	59, 60
trans-1,4-Polyisoprene	-58	68	61, 62
Poly-1,4-(2-t-butylbutadiene)	20	106	63, 64
Poly-1,4-(2-phenylbutadiene)	10	175	65, 66
cis-1,4-Poly(2,3-dimethylbutadiene)	2-4	162-191	This work
trans-1,4-Poly(2,3-dimethylbutadiene)	12	>275	This work
Poly-1,4-(2,3-diphenylbutadiene)	116	-	52
Poly(1-butene)	-23	126	67, 68
Poly(3,3-dimethyl-1-butene)	64	260	69, 70
Polyvinylcyclohexane (isotactic)	138	300	71
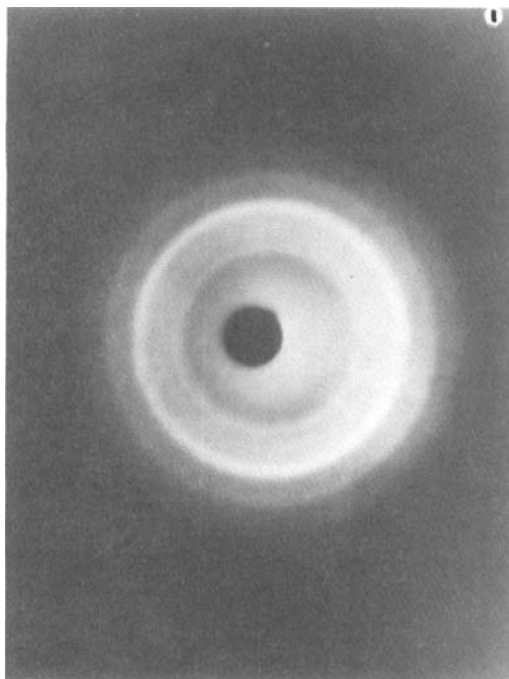
FIG. 11. Wide-angle x-ray diagram of trans-1,4-poly(2,3-dimethyl-butadiene).

a T_g of -11°C for PDMB, but no information on the polymer structure
was provided. It should be pointed out that the recently prepared
symmetrical diene, poly(2,3-diphenylbutadiene), showed a T_g of
116°C [52].
    3. Wide angle x-ray studies.   Trans-PDMB was also studied by
wide angle x-ray diffraction. Results of the Debye-Scherrer diagrams
shows (Fig. 11 and Table 5) that this polymer has a considerable
amount of crystallinity. In comparison to cis-PDMB, the rings are
more intense and occur at significantly different positions.
    4. Thermal stability of the polymers.   The thermal stability of
samples of trans-PDMS under nitrogen was investigated by both TGA
and DTG (Fig. 12). The initial weight loss was found to occur at
280°C. Maximum rate of weight loss occurred at 383°C; this very
similar MDT had been found for the cis-polymer. It is important to
note, however, that the DTG curve for the trans-polymer is skewed
toward higher temperatures, a result different from the behavior of
the cis-polymer (Fig. 6). This slight increase in thermal stability is be-
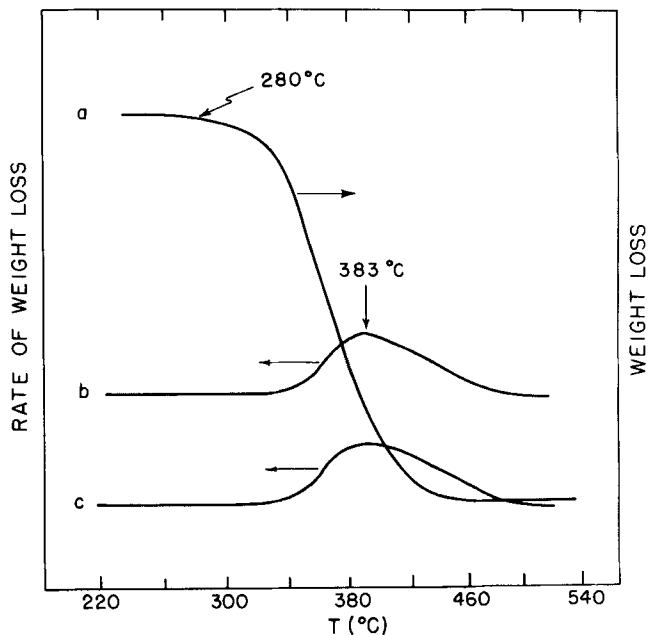lieved to be caused by higher crystallinity in the trans-polymer. Any

FIG. 12. TGA and DTG studies of trans-1,4-poly(2,3-dimethyl-butadiene).

factors which reduce the mobility of polymer chains have led to an increase in thermal stability [73].

Other Initiator Systems Investigated for the Polymerization of 2,3-Dimethyl-1,3-butadiene

The preparation of PDMB at an Al/Ti ratio of 1:1 was also investigated. Yen [21] initially reported that such an initiator composition gave pure cis-polymer. Gaylord [23] shed some doubt on this issue, suggesting that at an Al/Ti ratio of 1:1, some trans-units are also present in the chain. Prudhomme [20], the only author who employed NMR techniques to determine the stereochemistry of PDMB, supported Yen's finding. Horne [26] claimed a predominance of cis-1,4-structure at an initiator component ratio of Al/Ti = 1, but implied the possibility of trans-linkages.

The results of our work indicate that an Al/Ti ratio of 1:1 leads to the formation of cis-PDMB with a small amount of trans-linkages. The ^{13}C NMR spectrum showed two peaks for the methyl carbon atom at 18.81 and 18.43 ppm which from our work on pure cis- and pure

TABLE 8. Chemical Shift Data in ^{13}C NMR Spectra of Poly(2,3-dimethylbutadiene) Initiated with AIBN

Carbon	Sequence	Chemical shift
$-CH_2-$	ct	34.60
$-CH_2-$	tt	33.96
$-CH_2-$	tc	33.47
$-CH_3$	c	18.86
$-CH_3$	t	18.52
$-\underset{\underset{\underset{\underline{CH_2}}{\|}}{\underset{\|}{C-CH_3}}}{C}-$	1, 2	111.69

trans-polymer samples could be assigned: the 18.81 ppm peak to $-CH_3$(cis) and the peak at 18.43 ppm to $-CH_3$(trans). Expansion of the resonance signal followed by area measurements have indicated that the cis-linkage is present to a level of approximately 75%. (All quantitative estimations of ^{13}C NMR spectra are limited to the assumption of equal Nuclear Overhauser Effect and negligible spin-lattice relaxation.)

Polymerization of DMB with AIBN gave a tacky polymer in low conversion. The IR analysis of this polymer indicated the predominance of 1,4-trans-configuration along with 1,2-type linkages. ^{13}C NMR spectra (Table 8) indicated both cis- and trans-structures (trans-units evaluated to be approximately 60%) and approximately 10% of 1,2-units were present in the polymer.

ACKNOWLEDGMENTS

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