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Microstructure of Poly(2,3-dimethyl-1,3-butadiene) Prepared by Butyllithium in Cyclohexane. 220-MHz Nuclear Magnetic Resonance Study

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ABSTRACT: The 220-MHz nmr spectra of poly(2,3-dimethyl-1,3-butadiene) (PDMB) prepared by butyllithium in cyclohexane are compared to those of free-radical PDMB. By aid of measurements done on *cis*-1,4-and *trans*-1,4-PDMB prepared by Ziegler catalysts, it is shown that not only the overall contents of cis and trans units can be determined but also the distribution of dyads and triads of these structural units. Anionic PDMB presents long sequences of trans units giving rise to a partial crystallization observed by X-ray diffraction.

The microstructure of poly(2,3-dimethyl-1,3-butadiene) (PDMB) prepared by anionic polymerization under various conditions has been extensively studied by Schué[1] about 10 years ago. Using nmr spectroscopy this author has shown that with respect to the concentration of unsaturated side groups in the polymers formed, 2,3-dimethyl-1,3-butadiene (DMB) behaves similarly to butadiene and isoprene. DMB tends to form a polymer rich in 1,2 units in polar systems, such as with lithium in H_4furan or sodium in hydrocarbon solvents and forms a polymer having a high 1,4 content when polymerized with butyllithium or metallic lithium in nonpolar solvent.

More recently, Yuki *et al.*[2] reported essentially the same results and moreover they showed that the 1,2 content of PDMB obtained with *n*-butyllithium in pure H_4-furan depends strongly on polymerization temperature, a behavior which contrasts with those of butadiene and isoprene. With regard to PDMB prepared by *n*-butyllithium in pure hydrocarbons, contrary to Schué, these authors were not able to distinguish the cis-1,4 and trans-1,4 isomers using 100-MHz nmr spectroscopy. In a recent study of anionic polymerization of DMB by *sec*-butyllithium in cyclohexane, we were also confronted with this problem.[3] At 100 MHz the resonances of the methyl and methylene protons in trans-1,4 units are barely distinguishable from those of cis-1,4 units. In the present paper the 220-MHz spectra of anionic PDMB are compared to those of free-radical PDMB. By aid of measurements done on *cis*-1,4- and *trans*-1,4-PDMB prepared by Ziegler catalysts, it is shown that not only the overall contents of the cis and trans units can be determined but also the distribution of dyads and triads of these structural units.

Experimental Section

All preparations were carried out in sealed high-vacuum systems. 2,3-Dimethyl-1,3-butadiene of a purity of 99.9% (vapor-phase chromatography) was degassed on the vacuum line, submitted to a partial prepolymerization with *n*-BuLi and distilled in break-seal ampoules. Cyclohexane was distilled over *n*-BuLi before use. *sec*-BuLi was purified by short-path distillation, diluted to a concentration of about 10^{-2} *M* and sealed in fragile bulbs. Anionic PDMB was prepared at 60°. The reaction vessels had been previously purged with *n*-BuLi and washed by distilling solvent from its solution. *cis*- and *trans*-PDMB were prepared at 25° with triethylaluminum–titanium tetrachloride Ziegler catalysts according to the specific methods previously described by Yen.[4] The configurations of these last two samples were confirmed by means of X-ray diffraction according to Yen's data and interpretation. Finally, a free-radical sample was prepared at 60° with 0.01 mol of 2,2′-azobis(2-methylproprionitrile)/mol of monomer.

Powder X-ray diffraction patterns were recorded *in vacuo*, in a flat film Warhus camera using Ni-filtered Cu Kα radiation. Infrared spectra were measured with a Perkin-Elmer 621 spectrometer on either thin film casts or KBr dispersions. Nmr spectra were measured at 100° with a Varian HR-220 spectrometer using chlorobenzene as solvent and tetramethylsilane as internal standard. Sample concentrations were close to 5%. Peaks were resolved by hand on expanded-scale spectra.

Results and Discussion

Contrary to free-radical PDMB, anionic PDMB prepared by butyllithium in pure cyclohexane is a partially crystalline polymer. As shown in Table I, a powder X-ray diffraction pattern of this polymer presents "*d*" spacings identical to those of the trans polymer. On the other hand, as shown in Figure 1, the infrared spectrum of the anionic PDMB is apparently very similar to that of the free-radical PDMB, except for the relative intensities of

Table I
"d" Spacings (Å) from Powder X-Ray Diffraction Patterns

Anionic PDMB	*trans*-PDMB	*cis*-PDMB
7.4 (w)	7.3 (w)	6.2 (s)
5.3 (s)	5.2 (s)	5.4 (s)
4.3 (s)	4.3 (s)	4.7 (w)
3.7 (w)	3.8 (w)	4.0 (s)
2.9 (w)	3.0 (w)	3.3 (m)
		3.0 (m)

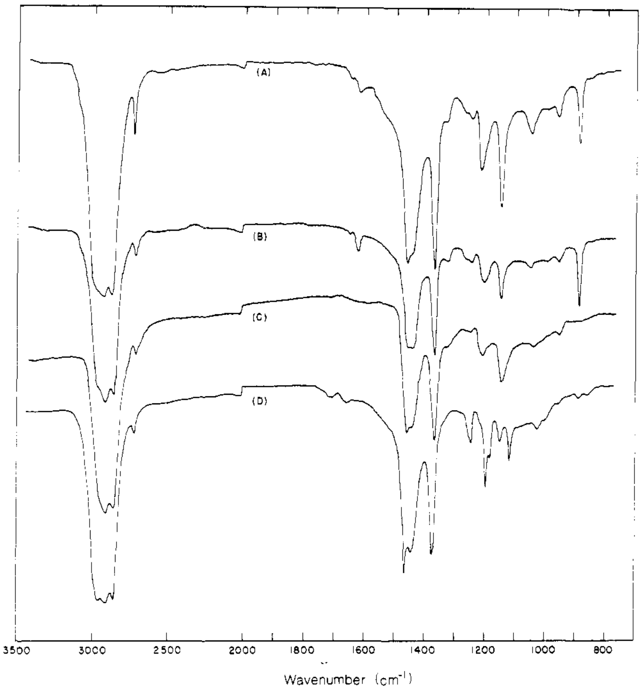

Figure 1. Infrared spectra of poly(2,3-dimethyl-1,3-butadiene): (A) polymer prepared by *sec*-BuLi in cyclohexane; (B) polymer prepared by free-radical initiator; (C) trans polymer; (D) cis polymer.

the bands at 1630 and 890 cm^{-1} which are characteristic of the 1,2 structure. With respect to the other bands, both spectra reveal great similitude with that of the *trans*-PDMB. For instance, they show a strong band at 1150 cm^{-1}, where an equally strong band is observed for the trans polymer but they do not present any significant absorption at 1120 cm^{-1} where a strong band is observed for the cis polymer.

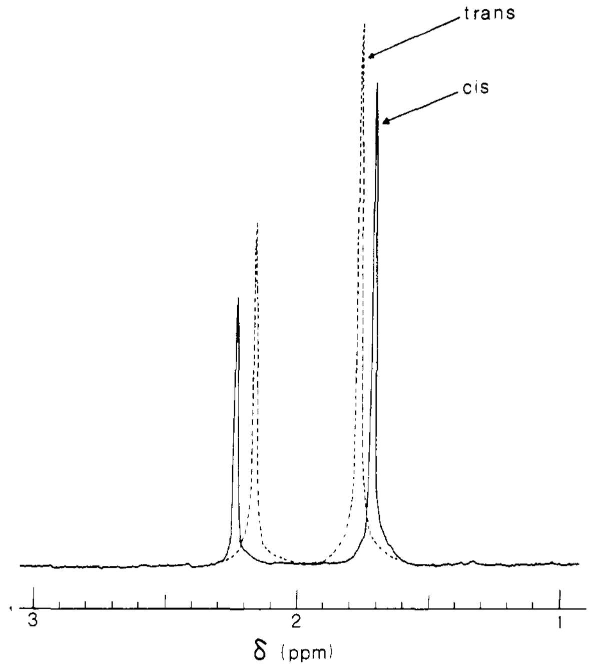

Figure 2. 220-MHz nmr spectra of *cis*- and *trans*-poly(2,3-dimethyl-1,3-butadiene).

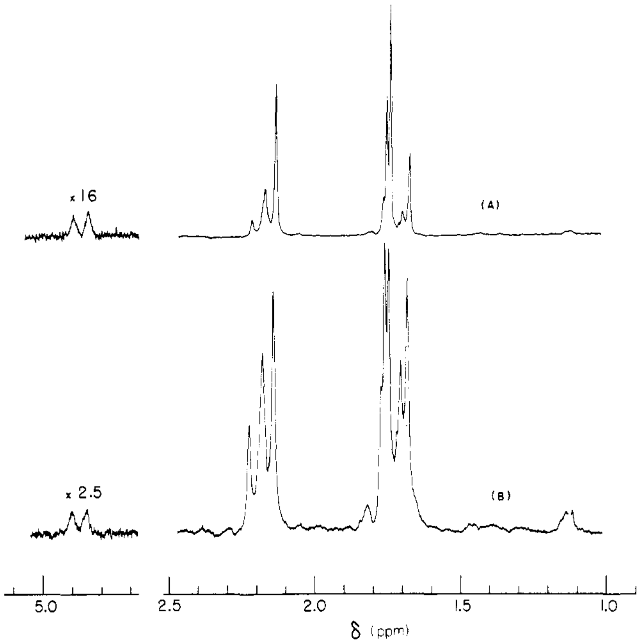

Figure 3. 220-MHz nmr spectra of poly(2,3-dimethyl-1,3-butadiene) (A) prepared by *sec*-BuLi in cyclohexane and (B) prepared by free-radical initiator.

The 220-MHz nmr spectra of the *cis* and the *trans* polymers are shown in Figure 2. In contrast with polyisoprene, the methyl groups of the cis units in the *cis*-PDMB are more shielded than those of the trans units in the *trans*-PDMB. The *cis*- and *trans*-methyl resonances appear at 1.73 and 1.77 ppm, respectively. The situation is inverted for the methylene group which shows resonances at 2.24 ppm for the cis isomer and at 2.16 ppm for the trans isomer. Figure 3 shows the spectra obtained for both the anionic and the free-radical polymers. These two spectra, which are more complex than anticipated, are very similar with regard to the number and position of peaks observed. Three methylene resonances are observed at 2.16, 2.20, and 2.24 ppm, respectively, while with respect to the 1,4 structure, six methyl resonances are observed in the region between 1.70 and 1.80 ppm. Thus, contrary to infrared spectroscopy, nmr spectroscopy indicates clearly the presence of cis isomers in these polymers. On the other hand, a smaller peak appears at 1.85 ppm and this corresponds to the methyl group adjacent to the double bond in the 1,2 structure. The 1,2 content can be evaluated either from this peak at 1.85 ppm or from the olefinic resonance appearing as a doublet at 4.85 and 4.90 ppm. The results of this analysis yield 3 and 8% of 1,2 units to the anionic and to the free-radical sample, respectively.

Since the 1,2 content is relatively small for both these polymers, we postulate that the unexpected intermediate peak appearing at 2.20 ppm in the methylene region, belongs to the methylene groups joining a cis and a trans unit in a cis-trans (ct) dyad. However, the two methylene groups involved in this junction are in chemically nonequivalent environments and should give rise to a doublet. In fact, at 2.20 ppm a very broad singlet is observed and indeed it may be a doublet since it is much broader than the two adjacent peaks at 2.16 and 2.24 ppm. On the

Table II
Overall Microstructure of the Anionic and the Free-Radical Polymers

	Anionic PDMB	Free-Radical PDMB
1,2	0.03	0.08
cis-1,4	0.23 (0.25)[a]	0.38 (0.44)
trans-1,4	0.74 (0.72)	0.54 (0.49)

[a] Values in parentheses were obtained from the methyl resonance.

other hand, by comparison with the spectra of the cis and the trans polymers, the resonances at 2.24 and 2.16 ppm can be assigned to the methylene groups joining a cis-cis (cc) and a trans-trans (tt) dyad, respectively. In a first step, these assignments were used in order to establish the overall microstructure of both the anionic and the free radical samples. The results are given in Table II. They show that the anionic sample is largely trans. In fact, this sample has 74% trans units while the free-radical sample has 54%. In a second step, assuming a completely 1,4 structure, we have evaluated the distribution of cc, ct, and tt dyads as well as the number average lengths $\bar{n}_c$ and $\bar{n}_t$ of cis and trans sequences in these polymers. The results are given in Table III. They show that the anionic polymer presents a number-average length of trans sequences twice as large as that of the free-radical polymer.

Turning now to the methyl region, we see that the six peaks observed are appearing as two groups of three peaks each. This is particularly evident in the spectrum of the anionic sample. By comparison with the spectra of the cis and the trans polymers we can postulate that the more shielded group of three peaks belongs to the cis structure. In fact, as shown in Table II, the overall microstructure evaluated on this basis is in good agreement with that previously established from the methylene resonance. On the other hand, the fact that three peaks are distinguished for each of these groups means that the chemical shift of the methyl groups in a given unit is influenced by the structure of its two neighbour units. This means that the six peaks observed correspond to the six possible triads obtained with two different types of units. Analysis of these peaks have been made using the following statistical relationships relating the probabilities of occurrence of the dyads to those of the triads

$$(cc) + (ct) + (tt) = 1$$
$$(ccc) + (tcc) + (tct) + (ttt) + (ctt) + (ctc) = 1$$
$$(cc) = (ccc) + (tcc)/2$$
$$(tt) = (ttt) + (ctt)/2$$
$$(ct) = (tct) + (ctc) + (tcc)/2 + (ctt)/2$$

Assignments compatible with these necessary relationships as well as the corresponding distribution of triads are listed in Table III. The distribution of triads for the free radical sample is not shown since the methyl peaks are not well resolved in that case. These assignments show that the methyl groups in both trans and cis units are most shielded when the unit is between two trans units and less shielded when between two cis units. Note that while the assignment of the ttt triads (1.77 ppm) corresponds exactly to the peak position of the trans polymer, the assignment of the ccc triads (1.74 ppm) differs slightly from the peak position (1.73 ppm) of the cis polymer.

Table III
Distribution of Dyads, Distribution of Triads, and Number-Average Lengths of Cis and Trans Sequences

	Peak Position (ppm)	Anionic PDMB	Free-Radical PDMB
Dyads			
(cc)	2.24	0.07 (0.06)[a]	0.17
(ct)	2.20	0.35 (0.38)	0.47
(tt)	2.16	0.58 (0.56)	0.36
Triads			
(tct)	1.70	0.17	
(tcc)	1.73	0.07	
(ccc)	1.74	0.02	
(ttt)	1.77	0.42	
(ctt)	1.78	0.28	
(ctc)	1.80	0.04	
Number-average length			
$\bar{n}_t$		4.2	2.5
$\bar{n}_c$		1.3	1.7

[a] Values in parentheses give dyads distribution calculated from triads distribution.

From this global analysis it is clear that anionic PDMB prepared by butyllithium in cyclohexane present long sequences of trans units giving rise to the partial crystallization observed by X-ray diffraction. This tendency is also apparent for free radical PDMB which show an important ttt triad resonance compared to a small ccc triad resonance, but in this case the sequences of trans units are apparently not long enough to give rise to crystallization. According to the data given in Table III both polymers are Bernoullian with probabilities of cis placement of 0.24 and 0.40, respectively.

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