^{1}H Nuclear Magnetic Resonance Studies of 1,2-Polybutadienes

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ABSTRACT: High-resolution nuclear magnetic resonance spectra of *o*-dichlorobenzene solutions of isotactic, syndiotactic, and atactic 1,2-polybutadiene are presented and interpreted. The methylene protons of isotactic 1,2-polybutadiene are nonequivalent, differing in chemical shift by 0.2 ppm, indicating that methylene proton resonance can provide information about the meso dyad content of 1,2-polybutadiene. The chemical shifts of methine type vinyl protons (-CH═C) in isotactic and syndiotactic 1,2-polybutadiene differ by 0.14 ppm, indicating that the resonance of such protons can provide information about the relative amounts of isotactic, heterotatic and syndiotactic triads in 1,2-polybutadiene. The resonances of other protons in 1,2-polybutadiene are not useful for microstructure studies, as they are rather insensitive to configurational differences.

Techniques are available for making reasonably uniform varieties of the various possible homopolymers of butadiene,[1] but only a limited amount of attention has been devoted to the study of their nmr spectra. The nmr spectra of *cis*- and *trans*-1,4-polybutadiene have been reported previously. The chemical shifts of methylene protons in the cis and trans polymers were shown to differ slightly, but not enough to enable the cis and trans contents of polybutadienes to be estimated.[2] The nmr spectra of syndiotactic and atactic 1,2-polybutadiene and of deuteriated analogs have been reported,[2] and chemical shifts for several of the protons present in these polymers were measured, but a detailed analysis of the spectra has not been published. The tendency of 1,2-polybutadiene to cross-link has probably discouraged most workers from working with it. As a result of this, most of the attention afforded to the resonance of the vinyl protons in polybutadienes in the past has been directed toward determining the relative amounts of 1,2 and 1,4 structure.

With the hope that an ^{1}H nmr method[3] might be developed for characterizing the tacticity of 1,2-polybutadiene, we have investigated in detail the nmr spectra of isotactic syndiotactic, and atactic 1,2-polybutadiene.

Experimental Section

Syndiotactic 1,2-Polybutadiene. A modified procedure based on the method of Parris and Rieve[4] was used to prepare a highly syndiotactic 1,2-polybutadiene. Butadiene (10 ml), $Al(C_2H_5)_3$ (0.00350 mol), and diethyl fumarate (0.00117 mol) were added in the order listed to a mixture of cobalt(III) acetylacetonate (0.00351 mol) in 100 ml of dry benzene. After maintaining the mixture at 16° for 15 hours, the polymer formed was coagulated under a nitrogen atmosphere in an excess of methanol containing phenyl-β-naphthylamine as antioxidant (approximately 4% by weight of the polymer expected). The polymer was washed with methanol and acetone and dried *in vacuo* at room temperature.

Nmr analysis indicates the polymer to contain not less than 90 mole percent of the 1,2-addition product. The infrared spectrum is practically identical to the spectrum of syndiotactic 1,2-polybutadiene (96%) reported by Natta.[5]

Attempts to prepare syndiotactic 1,2-polybutadiene according to the procedure reported oy Susa[6] were unsuccessful. Only low yields of insoluble, apparently cross-linked, polymer were obtained.

Isotactic 1,2-Polybutadiene. Isotactic 1,2-polybutadiene was obtained from the laboratories of The Firestone Tire and Rubber Co. through the courtesy of Dr. V. D. Mochel. The sample was prepared by Dr. M. E. Kimball.

Nmr analysis indicates the polymer to contain no more than 5 mol % 1,4 units. The infrared spectrum of the polymer was identical with that of the spectrum of isotactic 1,2-polybutadiene reported by Natta.[5]

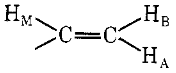
Atactic 1,2-Polybutadiene. Atactic 1,2-polybutadiene prepared by an anionic polymerization method was kindly supplied by Dr. V. D. Mochel. He had previously analyzed the ^{13}C resonance[3] of this material and found it to contain 38% isotactic, 46% heterotactic, and 16% syndiotactic units. ^{1}H nmr analysis of the polymer indicated it to contain no more than 5 mol % 1,4 units.

Nuclear Magnetic Resonance Measurements. A Varian HA-100 spectrometer was used to record the spectra at 120° of approximately 5-10% solutions of polymers in *o*-dichlorobenzene. Hexamethyldisiloxane was used as an internal standard in all cases. Chemical shifts were measured downfield from the Me_6Si_2O resonance line and are reported in parts per million.

Chemical shifts and coupling constants were estimated to obtain an approximate fit of calculated lines to each spectrum. The iterative program LAOCN3 of Bothner-By and Castellano[7] was then used to obtain the best agreement between calculated and observed spectra.

Results and Discussion

It will be convenient to define structure I for the protons of the vinyl groups. Figure 1 shows the complete 100-MHz spectra of isotactic, syndiotactic, and atactic 1,2-polybutadiene. The resonance patterns centered at 1.2, 2.2, 4.8, and 5.5 ppm are due to backbone methylene, methine, A,B-type vinyl, and M-type vinyl protons, respectively. These assignments are in agreement with literature assignments.[2,8,9] A small amount of resonance due to 1,4 units may be detected at 5.35 and 2.00 ppm as highly overlapped peaks of low intensity. The observed spectrum for syndiotactic 1,2-polybutadiene is similar in appearance to one reported for this polymer prepared with a different catalyst system.[2] Analyses of each of these resonance patterns are given below.



I

Methylene Proton Resonance. Methylene resonance patterns (Figure 2) of the isotactic and syndiotactic polymers are strikingly different. The resonance of methylene protons in isotactic 1,2-polybutadiene is observed as a ten-line pattern centered at 1.30 ppm. This pattern arises because of the nonequivalence of the methylene protons in this polymer and because they are coupled with vicinal

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(1) See references listed by G. Odian, "Principles of Polymerization," McGraw-Hill Book Co., New York, N. Y., 1970, Table 8-13, p 594.

(2) Y. Tanaka, Y. Takeuchi, M. Kobayashi, and H. Tadokoro, *J. Polym. Sci., Part A-2*, **9**, 43 (1971).

(3) V. D. Mochel, *J. Polym. Sci., Part A-1*, **10**, 1009 (1972).

(4) C. L. Parris and L. S. Rieve, German Patent 2,007,052; *Chem. Abstr.*, 74, 23218*v* (1971).

(5) G. Natta, SPE *(Soc. Plast. Eng.) J.*, **15**, 373 (1959).

(6) E. Susa, *J. Polym. Sci., Part C*, **4**, 399 (1963).

(7) A. A. Bothner-By and S. Castellano in "Computer Programs for Chemistry," Vol. I, D. F. DeTar, Ed., W. A. Benjamin, Inc., New York, N. Y., 1968, Chapter 3.

(8) A. J. Durbetaki and C. M. Miles, *Anal. Chem.*, **37**, 1231 (1965).

(9) S. Hume, H. Saka, A. Takahashi, G. Nishikawa, M. Hatano, and S. Kambara, *Makromol. Chem.*, **98**, 109 (1966).

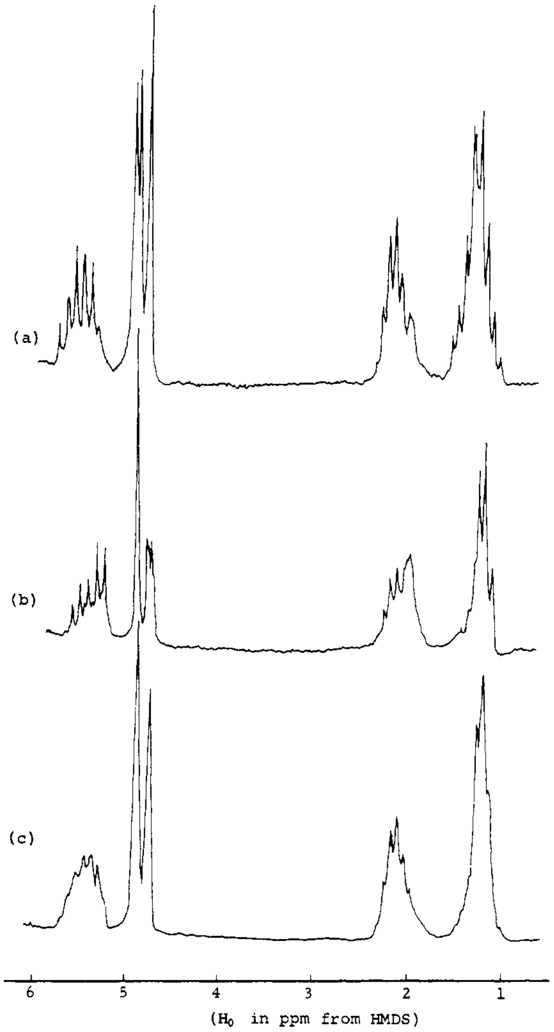
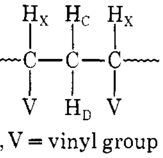


Figure 1. Complete 100-MHz nmr spectra of (a) isotactic 1,2-polybutadiene; (b) syndiotactic 1,2-polybutadiene; (c) atactic 1,2-polybutadiene (in *o*-dichlorobenzene at 120°).

methine protons. This resonance pattern can be analyzed in terms of the following spin model (structure II), where $J_{CD} \sim |14|$ cps, $J_{CX} \sim |6|$ cps, and $J_{DX} \sim |7|$ cps, as is commonly done for similar polymers, such as isotactic polypropylene[10] and polystyrene.[11]



$$\begin{array}{ccccc} & H_X & H_C & H_X & \\ \sim & C & -\,C\,- & C & \sim \\ & V & H_D & V & \end{array}$$

II, V = vinyl group

In evaluating chemical shifts and coupling constants consistent with the observed spectrum, it was assumed that the resonance of the D methylene proton occurred at higher field than that of the C proton, since the former was considered to experience greater shielding than the latter. The methylene resonance of isotactic 1,2-polybutadiene was therefore analyzed as an ABX_2 (CDX_2) system. The iterative method of Bothner-By and Castellano was used to obtain the parameters that provide the best fit of calculated and experimental spectra. The values obtained (Table I) are very similar to those observed for isotactic polypropylene[10] and isotactic polystyrene.[11] The fit of a "stick" spectrum, calculated using the parameters listed above, to the experimental one is indicated in Figure 2b.

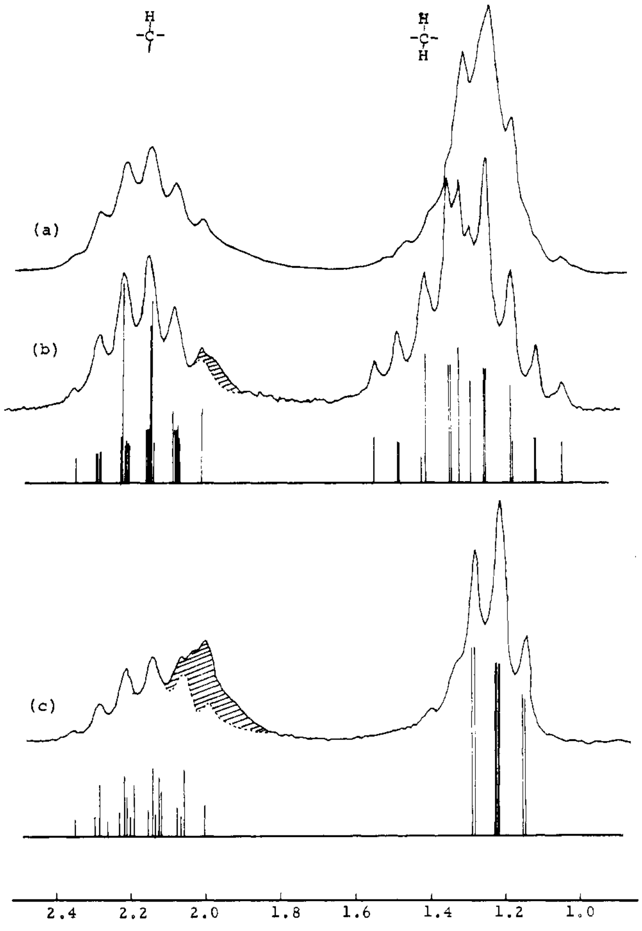
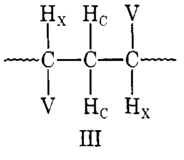


Figure 2. Observed and calculated methine and methylene proton resonance spectra of atactic (a), isotactic (b), and syndiotactic (c), 1,2-polybutadiene. Spectra are of polymers in *o*-dichlorobenzene solution at 120°. Shaded areas are attributed to resonance of protons in 1,4-butadiene units.

Methylene proton resonance of syndiotactic 1,2-polybutadiene is observed as a triplet centered at 1.21 ppm. A triplet is observed because the methylene protons are equivalent and are coupled with vicinal methine protons ($J_{vic} \approx 7$ Hz). A minor amount of resonance due to structural irregularities is also observed in the methylene resonance area, signals at 1.40 and 1.33 ppm being especially noteworthy. The methylene proton resonance of the syndiotactic polymer was analyzed in terms of the following A_2X_2 (C_2X_2) spin model (structure III), and the parameters most consistent with the observed spectrum are listed in Table I. Figure 2c shows the correspondence of the observed spectrum with a stick spectrum calculated using parameters listed in Table I.



$$\begin{array}{ccccc} & H_X & H_C & V & \\ \sim & C & -\,C\,- & C & \sim \\ & V & H_C & H_X & \end{array}$$

III

Dr. F. A. Bovey has kindly pointed out that the methylene proton resonance of syndiotactic 1,2-polybutadiene should be analyzed as an AA′XX′ (CC′XX′) system and that the values of J_{AX} and $J_{AX'}$ obtained from such an analysis should provide an indication of the relative popu-

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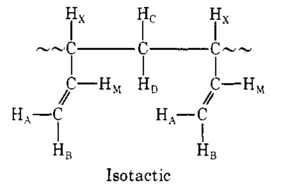
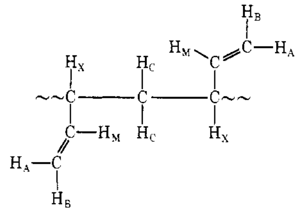
(10) F. Heatley, R. Salvey, and F. A. Bovey, *Macromolecules*, **2**, 619 (1969).

(11) F. Heatley, and F. A. Bovey, *Macromolecules*, **1**, 301 (1968).

Table I
Chemical Shifts and Coupling Constants for Isotactic and Syndiotactic 1,2-Polybutadiene



Isotactic



Syndiotactic

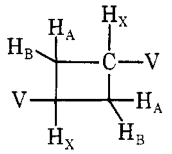
Chemical Shifts (ppm)	J (cps)	Chemical Shifts (ppm)	J (cps)
$H_A = 4.90$	$J_{AB} = 1.6$	$H_A = 4.87$	$J_{AB} = 2.2$
$H_B = 4.87$	$J_{AM} = 17.8$	$H_B = 4.88$	$J_{AM} = 17.3$
$H_C = 1.40$	$J_{AX} = -0.6$	$H_C = 1.21$	$J_{AX} = -0.5$
$H_D = 1.20$	$J_{BM} = 10.2$	$H_M = 5.45$	$J_{BM} = 10.5$
$H_M = 5.59$	$J_{BX} = -0.1$	$H_X = 2.19$	$J_{BX} = -0.3$
$H_X = 2.20$	$J_{MX} = 8.2$		$J_{MX} = 8.9$
	$J_{CX} = 6.1$		$J_{CX} = 6.8$
	$J_{CD} = -14.0$		$J_{CC} = -14.0$
	$J_{DX} = 7.0$		

lation of G-G and T-T conformations present in the polymer. A series of AA′XX′ (CC′XX′) spectra were calculated using the chemical shifts listed in Table I, and using various J_{AX} and $J_{AX'}$ values, such that $J_{AX} + J_{AX'} = 13.6$, but $J_{AX} - J_{AX'} = 0$, 1.6, 3.0, 4.2, 5.4, or 6.6. When half-widths of 3 cps were used to construct line envelopes, the calculated spectra were indistinguishable for $J_{AX} - J_{AX'} = 0$, 1.6, and 3.0 cps and they represented the high-field part of the methylene triplet quite well. (The low-field part was complicated by the presence of resonance due to impurities.) The line envelopes based on those cases where $J_{AX} - J_{AX'} \geqslant 4.2$ cps did not fit the experimental spectrum satisfactorily. The methylene resonance of syndiotactic 1,2-polybutadiene, when analyzed as a CC′XX′ system is thus consistent with $J_{CX} = 6.8$–8.3 and $J_{CX'} = 5.3$–6.8. In view of the uncertainty of the coupling constants, no effort was made to calculate conformational information.

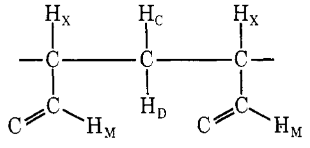
The methylene resonance of atactic 1,2-polybutadiene (Figure 2a) is very similar to that of the racemic polymer although isotactic methylene proton resonances are evident.

The most significant feature of the methylene proton resonances of these polymers is the fact that the chemical shift of the C protons in the isotactic polymer is considerably different from the chemical shifts of the other methylene protons. This suggests that studies of the resonance of methylene protons decoupled from methine protons may provide information about the relative amounts of meso and racemic diads present in 1,2-polybutadiene.

It has been pointed out[11,12] that a six-spin dimer model, of the type shown below (AA′BB′XX′) (structure IV), is more appropriate for calculating the methylene proton resonance patterns of isotactic vinyl polymers than is the ABX_2 model employed here. This is most certainly correct in a theoretical sense, but in a practical sense, the apparent line widths obtainable in polymer spectra are too broad to justify the use of the more complex model, at least in the case of spectra recorded with high-field spectrometers. This was shown by using the parameters derived from the four-spin analysis to calculate the spectrum of the six-spin model. The resulting spectrum consisted of a large number of lines that were grouped around each of the groups of lines calculated for the spectrum of the four-spin model. The maximum difference between the extreme lines in each group was 1 cps—well below the resolution apparent in the experimental spectrum. The relative intensities of the line groups in the six-spin model spectrum agreed within 0.4% (generally within 0.1%) with the relative intensities of line groups calculated for the four-spin model spectrum. The same result was obtained using the following six-spin model (structure V). Finally it should be noted that when four-spin and six-spin models were used to calculate the resonance of methylene protons in isotactic polystyrene, as observable at 220 MHz, using Bovey's parameters,[11] the collected envelopes of the line shapes were identical for both models. In constructing the envelopes, Lorentzian line shapes having half-widths of 3 cps were assumed. This half-width is narrower than that required to fit the calculated spectrum to the experimental one. Thus, we believe that it is reasonable to use four-spin models to analyze the methylene proton resonance patterns.



IV



V

Methine Proton Resonance. Unlike the methylene resonances, the methine resonance patterns of the polymers (Figure 2) are very similar. They consist of six peak patterns centered at $\sim$2.20 ppm. This indicates that methine resonance is rather insensitive to configuration. This was supported, in part, by decoupling studies. When the methine protons of atactic 1,2-polybutadiene were simultaneously decoupled from the methylene and M-type vinyl protons, the methine resonance was observed as a single

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(12) F. A. Bovey, F. P. Hood, E. W. Anderson, and L. C. Snyder, *J. Chem. Phys.*, 42, 3900 (1965).

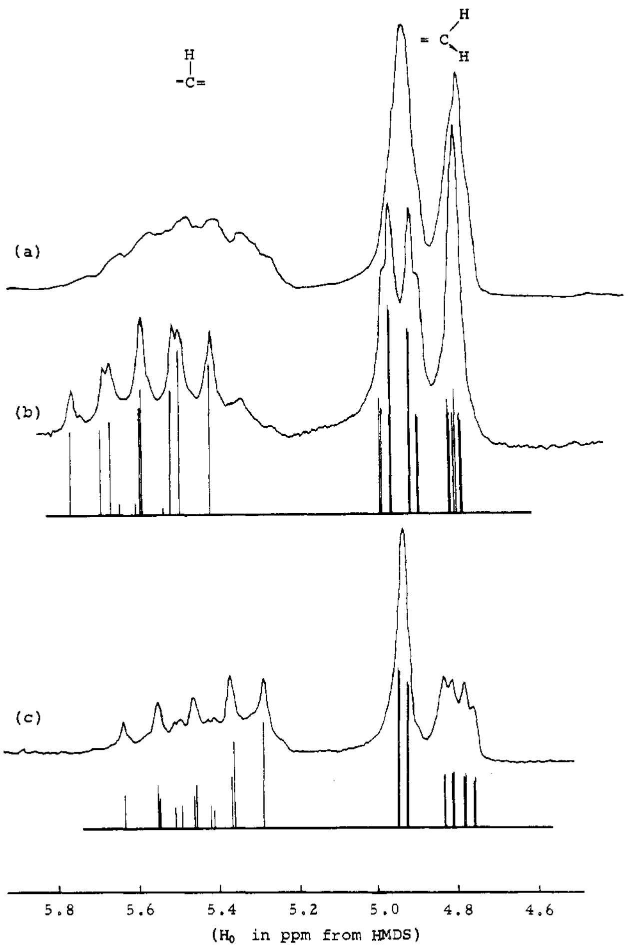


Figure 3. Observed and calculated vinyl proton resonance spectra of atactic (a), isotactic (b), and syndiotactic (c) 1,2-polybutadiene. Spectra are of polymers in *o*-dichlorobenzene solution at 120°.

peak. Figure 2 compares the methine proton resonance patterns observed for the isotactic and syndiotactic polymers with stick spectra calculated from chemical shifts and coupling constants listed in Table I.

Vinyl Proton Resonance. Casual examination of the vinyl proton resonances shown in Figure 1 would suggest that A,B-type vinyl proton resonance (4.9 ppm) should be useful for studying the microstructure of 1,2-polybutadiene; the resonance patterns are quite different for the two polymers. It turns out, however, that the different spectra observed for the isotactic and syndiotactic polymers are due to relatively small differences in the chemical shifts of the A and B protons.

The vinyl proton resonance patterns of isotactic and syndiotactic 1,2-polybutadiene were analyzed in terms of the following ABMX model (structure VI). Chemical shifts and coupling constants for vinyl compounds have been reported previously.[13,14] Parameters were selected which gave an approximate fit of calculated spectra to experimental spectra. Bothner-By and Castellano's program[7] was then used to obtain sets of refined chemical shifts and coupling constants for the vinylic and methine protons in syndiotactic and isotactic 1,2-polybutadiene. The values obtained are included in Table I. Figure 3b,c shows the correspondence of observed resonances with "stick" spectra calculated from the parameters listed in Table I.

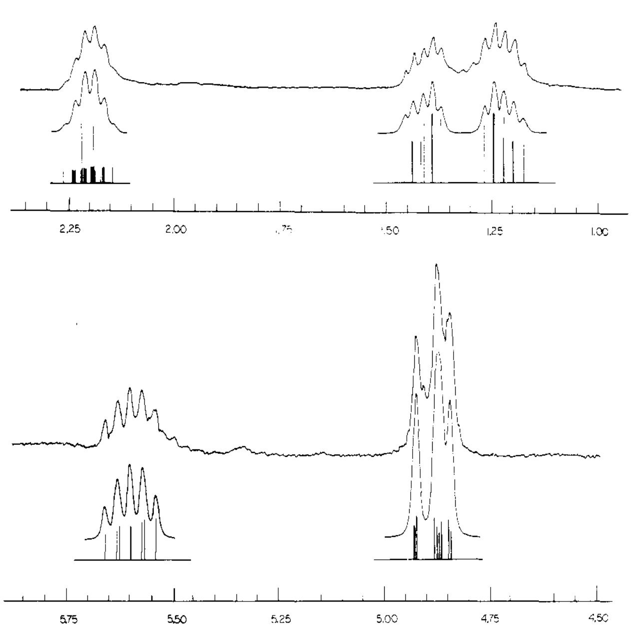
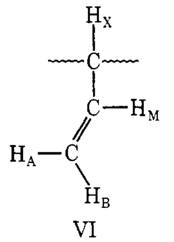


Figure 4. Observed and calculated spectrum of isotactic 1,2-polybutadiene in *o*-dichlorobenzene solution at 140°. Calculated spectra are based on the coupling constants given in Table I and on the following chemical shifts (relative to Me_6Si_2O): H_A = 4.89; H_B = 4.86; H_C = 1.41; H_D = 1.215; H_X = 2.20; H_M = 5.59. Half-widths of 4.5 cps were assumed in calculating line envelopes.



VI

It is interesting to compare values of the various parameters listed in Table I. The coupling constants associated with vinylic protons in either isotactic or syndiotactic polymers are very similar, as should be the case. The different vinylic proton resonance patterns observed for the two polymers must be attributed to differences in the chemical shifts of the various vinylic protons.

In the case of AB-type vinyl protons, small displacements in the chemical shifts of A,B protons cause dramatic changes in the resonance patterns observed at (4.7–5.0 ppm). This suggests that resonance observed in this area should be very sensitive to solvent effects. In fact, the resonance observed at 4.7–5.0 ppm in the spectra of isotactic 1,2-polybutadiene in hexachlorobutadiene was observed to be very similar to that of syndiotactic 1,2-polybutadiene in *o*-dichlorobenzene. For polymers in *o*-dichlorobenzene, the chemical shifts of the trans protons (A) in the isotactic and syndiotactic polymers are 4.90 and 4.87 ppm, respectively, whereas the chemical shifts of the cis protons (B) are 4.87 and 4.88 ppm, respectively. It is interesting that the relative ordering of these chemical shifts are in reverse directions for the cis and trans protons. Since the chemical shifts of the A and B protons are very similar in both polymers, it is not likely that study of the resonance of such protons can provide useful information about tacticity.

The chemical shifts of M-type vinylic protons in the isotactic (5.59 ppm) and syndiotactic (5.45 ppm) polymers

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(13) A. A. Bothner-By, C. Naar-Colin, and H. Günther, *J. Amer. Chem. Soc.*, 84, 2748 (1962).

(14) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, pp 358–360.

are quite different, so it seems that studies of M-type proton resonance may be of value for tacticity measurement. Because of coupling effects, rather complex patterns are obtained for the resonance of M-type protons, and it should be a formidable task to unravel the pattern observed for the atactic polymer (Figure 3a). However, studies on polymers of 1,2-poly(1,1,4,4-tetradeuteriobutadiene),[2] with methine protons decoupled should make the task relatively simple.

300-MHz Spectra. After this paper was submitted for publication, we had occasion to record the 300-MHz nmr spectrum of isotactic 1,2-polybutadiene. The spectrum is provided in Figure 4, along with computed spectra. The chemical shifts required to fit calculated spectra (see Figure 4 caption) to experimental spectra are slightly different from those given in Table I. The differences may be due to the fact that the 100- and 300-MHz spectra were recorded at different temperatures.

The 300-MHz spectrum contains unexpected resonances at 1.28 and 1.31 ppm in the methylene region and at 4.86 and 4.91 ppm in the vinyl region. These are attributed to structural imperfections. The resonances at 1.28 and 1.31 are believed to be due to methylene protons in 1,4 units. It is interesting that the methylene resonance observed from 1.15 to 1.27 ppm is more intense than that observed from 1.35 to 1.50 ppm. This indicates that an appreciable concentration ($\sim$12%) of racemic placements is present in the polymer. The presence of racemic dyads in the polymer may account for the resonances observed at 4.86 and 4.91 ppm.

Acknowledgments. The authors are grateful to Dr. V. D. Mochel for providing several of the samples studied. This work was supported by grants from the National Science Foundation (GP-24759) and The Firestone Tire and Rubber Co.

Poly(vinyl macrocyclic polyethers). Synthesis and Cation Binding Properties

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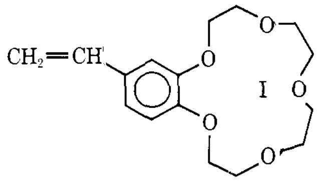
ABSTRACT: The synthesis of the 4′-vinyl derivatives of monobenzo-15-crown-5, of monobenzo-18-crown-6, and of dibenzo-18-crown-6 are described in detail. The monomers can be polymerized to high molecular weight polymers by radical or anionic initiators. The latter method produces living polymers if carried out at low temperatures. The polymers strongly chelate with cations, and their efficiency and selectivities in binding cations are compared with those of their monomeric analogs by using data obtained from salt distribution equilibria in water–methylene chloride and from conductance measurements. For all cations the polymers are found to extract the salt from the aqueous phase more efficiently than the monomers, but this is partially caused by differences in partition coefficients between the respective crown species. However, cation complexation constants for polymers are considerably enhanced in cation–crown systems which form stable 2:1 crown to cation complexes. This is usually the case when the cation diameter exceeds that of the crown ether cavity. The stoichiometries of the various crown complexes were determined from conductance measurements and from distribution equilibria in the presence of excess salt. These measurements also provide information on the maximum number of ions that can be bound per polymer molecule. Viscosity measurements indicate that the neutral poly(crown ethers) in the presence of salts undergo conformational changes resembling those of polyelectrolytes, the reduced viscosity being enhanced as the polymer–salt mixture is diluted.

In a recent communication[1] we reported on the cation binding properties of two neutral macromolecules, *viz.*, the polymers of 4′-vinylmonobenzo-15-crown-5 (I) and of 4′-vinylmonobenzo-18-crown-6 (II). The two polymers were found to be considerably more effective in binding cations than the corresponding monomeric macrocyclic polyethers or crown ethers, a class of compounds recently synthesized and studied by Pedersen[2] and subsequently by many other researchers.[3-12] The ion selectivities of the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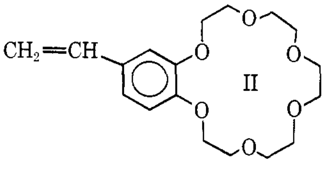
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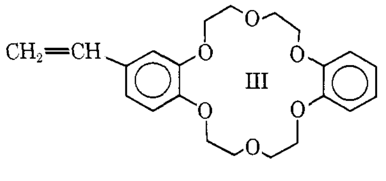
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(1) S. Kopolow, T. E. Hogen Esch, and J. Smid, *Macromolecules*, **4**, 359 (1971).

(2) (a) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); (b) C. J. Pedersen, *ibid.*, **92**, 386, 391 (1970); (c) C. J. Pedersen, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **27**, 1305 (1968).

(3) (a) H. K. Frensdorff, *J. Amer. Chem. Soc.*, **93**, 600 (1971); (b) H. K. Frensdorf, *ibid.*, **93**, 8684 (1971).

(4) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, 11, 16 (1972).

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(7) (a) G. Eisenman, S. M. Ciani, and G. Szabo, *J. Membrane Biol.*, **1**, 294 (1969); (b) G. Eisenman, S. M. Ciani, and G. Szabo, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **27**, 1289 (1968).