molecules occurs.[16] On the hexagonal net, the long rodlike molecule is only allowed to execute a very small rotation about an axis through its center and perpendicular to its length before contracting a nearest neighbor. The rotary diffusion coefficient, D_r, of a rodlike particle in a medium of vicosity η can be obtained by suitable modification of the Stokes or Einstein relation.[17] The mean-square angular displacement of the rod, θ^2, in a time t is given by the random walk formulation, $\theta^2 = 4D_rt$. Since θ can be estimated from the lattice constant d at a given concentration and the length of the helix, we can calculate t, the average time between polymer collisions for a single polymer molecule. Using published values of d, we find that the helical polypeptide molecule in the liquid crystal executes oscillatory motion about its mean direction of orientation on a time scale comparable to the Larmor frequency. For example, using the high molecular weight polypeptide with $N_p/N_s = 0.035$ and $N_p/N_s = 0.060$ we find that $1/t = 11.9$ and 45.2 MHz, respectively. Hence, in addition to being a potential source of frequency-dependent solvent relaxation, the origin of the oscillatory fluctuations, *i.e.*, macromolecular motion, suggests that it would be very useful to look for frequency-dependent spin-lattice relaxation of the polymer protons in the lyotropic polypeptide liquid crystal.

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(16) C. Robinson, J. C. Ward, and R. B. Beevers, *Discuss. Faraday Soc.*, **25**, 29 (1958).

(17) S. Broersma, *J. Chem. Phys.*, **32**, 1626, 1632 (1960).

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^{13}C, ^{19}F, and ^{1}H Nuclear Magnetic Resonance Studies of Hydroxy-Terminated Polybutadienes

Although hydroxy-terminated poly(butadienes)[1] have been studied in detail by a variety of analytical techniques, including infrared[2,3] and nmr spectroscopy,[4] as well as chemical,[5] the exact nature of the terminal groups has remained in doubt.

In this communication we report new data on the terminal groups which strongly suggest that they are predominantly primary alcohols, >95%, and that these are further divided into three types: adjacent to cis and trans double bonds, and adjacent to a saturated carbon which has a vinyl group attached.

In general, it appears that most hydroxy-terminated polybutadienes[1] possess two or more functional groups per molecule; the average is about 2.3. This number arises from the product of the number-average molecular weight as determined by vapor pressure osmometry (VPO) and the hydroxyl content from either acetic anhydride or toluene-sulfonyl isocyanate titrations. This average value of 2.3 indicates that tri- or higher functional materials are present and the extra hydroxyl groups could take the form of either primary or secondary alcohols depending upon the termination steps of the polymerization. Considerable data have been accumulated on attempts to separate the various species. The results are, however, open to question.

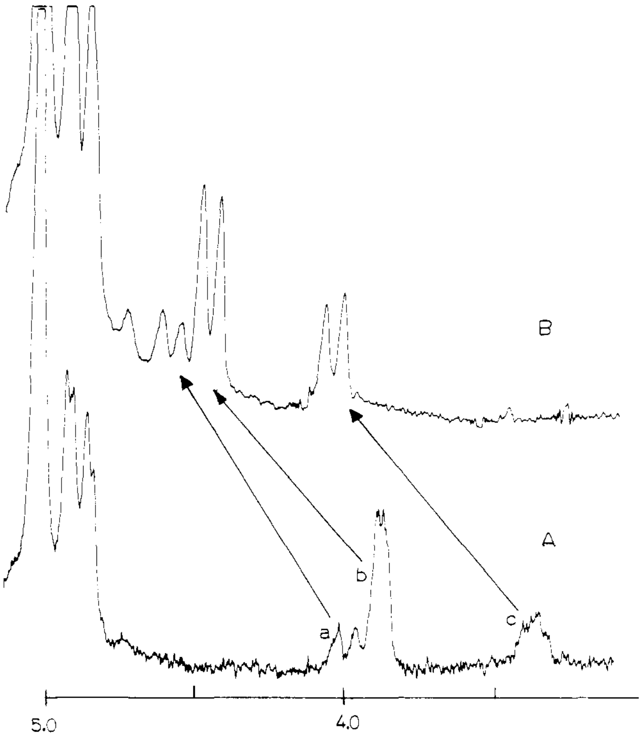
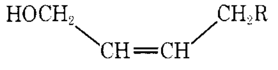
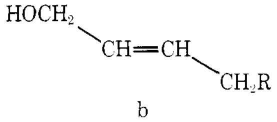


Figure 1. Portion of ^{1}H nmr spectrum, 100 MHz, of: (A) sample of poly BD in C_6D_6 and (B) CF_3COOH derivative.

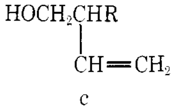
The ^{1}H nmr spectrum of sample A[6] yields, in addition to the expected olefinic and CH_2 resonances, three small bands at 3.4, 3.9, and 4.0 ppm and these are depicted in Figure 1. The three fractions from solvent precipitation A-C yield essentially the same spectra, except for intensities, and they are consistent with typical commercial samples of R-45M.[1] The first resonance corresponds to a primary alcohol (-CH_2OH) adjacent to a saturated carbon while the 3.9 and 4.0 bands were assigned to primary alcohols adjacent to olefins. Their relative intensities are in rough agreement with the overall composition of the backbone chain, 55% trans, 20% cis, and 25% vinylic. This, in turn, led to the assignment of the above ^{1}H resonances to structures a-c, with increasing field strength, respectively.



a



b



c

Further evidence supporting the above assignments was obtained from the reaction of the OH groups with CF_3COOH. At room temperature the reaction is quite slow, but requires less than 1 hr for completion at 70°, as defined by nmr. The resulting -CH_2OOCCF_3 resonances (Figure 1B) are shifted about 0.5 ppm downfield from the corresponding alcohol.

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(1) Poly BD, produced by ARCO Chemical Co., A Division of the Atlantic Richfield Co., Glenolden, Pa. 19036.

(2) R. R. Hampton, *Anal. Chem.*, **21**, 923 (1949).

(3) R. S. Silas, J. Yates, and V. Thornton, *Anal. Chem.*, **31**, 529 (1959).

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

(5) R. L. Addleman and V. J. I. Zichy, *Polymer*, **13**, 341 (1972).

(6) Sample A corresponds to the low molecular weight fraction, $M_n = 1800$, obtained by solvent precipitation from lot no. 110225 (ARCO Chemical Co., Glenolden, Pa.).

Secondly, the ^{19}F spectrum of the CF_3COOH derivative yields only a single resonance. Previous reports[7,8] have shown that the CF_3 resonances for derivatives from the reaction of CF_3COOH and primary and secondary alcohols differ by about 0.5 ppm. Therefore, collectively the ^{1}H and ^{19}F spectra suggest a predominance of primary alcohols, >95%.

The ^{13}C spectrum of sample A not only supports the above conclusions, but also yields additional data on the overall structure of the polymer chain. It is noteworthy that the spectrum is quite similar to that reported by Mochel[4] for polybutadiene polymerized with *n*-butyllithium. Nevertheless, extra peaks were observed in the alcohol, olefinic, and saturated CH_2 and CH regions. Three primary alcohols, 64.83, 62.89, and 58.10 ppm from Me_4Si are clearly indicated and they were assigned to structures c, b, and a, respectively.

The assignments of the ^{13}C resonances are substantiated by the chemical shifts of *cis*- and *trans*-3-methylallyl alcohols[9] and saturated primary alcohols.[10] The cis structure of this alcohol has a chemical shift of 57.9 ppm for the CH_2OH group while the trans structure gives rise to a value of 62.9 ppm for the corresponding group. In general, primary saturated alcohols produce resonances in the vicinity of 62 ppm. Any effect of the double bond in the vinyl structure should shift the peak downfield. Consequently, the 64.83-ppm resonance was assigned to the alcoholic group of the vinyl structure.

The ratios of the three alcoholic ^{13}C resonances, as determined from the undecoupled spectrum are: 24:58:18 (vinyl, trans, cis). They are in fair agreement with the ^{1}H data and agree very well with the microstructure determined by infrared 25:55:20 (vinyl, trans, cis).

Since no other resonances are detectable in ^{13}C, ^{19}F, or ^{1}H alcohol regions, a reasonable limit of 5% secondary alcohol was established.

(7) S. L. Manatt, D. D. Lawson, J. D. Ingham, N. S. Rapp, and J. P. Hardy, *Anal. Chem.*, **38**, 1063 (1965).
(8) G. Jung, W. Voelter, E. Breitmaier, and E. Bayer, *Anal. Chim. Acta*, **52**, 382 (1970).
(9) J. B. Strothers, "Carbon-13 NMR Spectroscopy," Organic Chemistry—A Series of Monographs, Vol 24, Academic Press, New York, N. Y., 1972, p 188.
(10) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 1338 (1970).

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CORRECTIONS

"Calculation of the Conformation of the Pentapeptide *cyclo*(Glycylglycylglycylprolylprolyl). III. Treatment of a Flexible Molecule," by Gregory C.-C. Niu, Nobuhiro Gō, and Harold A. Scheraga, Volume 6, Number 1, January-February 1973, page 91.

On page 93, Table ID, lines 5 through 8 in columns 2 through 6 should each be lowered by one line.

The first line at the top of the first column on page 95 should be replaced by the following: "values of K_θ were determined from those used in the".

"Stastical Mechanics of Random-Flight Chains. IV. Size and Shape Parameters of Cyclic, Star-like, and Comb-like Chains," by Karel Šolc, Volume 6, Number 3, May-June 1973, page 378.

On page 379 the material between equations 3 and 4 should read:

Here σ^2 is the mean square bond length and $\mathbf{y}_k$ is the $(N - 1)$-dimensional vector of the kth coordinates of the beads, $\mathbf{y}_k \equiv \mathbf{x}_k^{(1)}, \mathbf{x}_k^{(2)}, \ldots, \mathbf{x}_k^{(N-1)}$. The normalization constant can be determined by integration over all coordinates: *e.g.*, for chains without any rings, const = 1, for chains containing one ring of N_r bonds, const = $N_r^{3/2}$, etc. The matrix **V** can be set up easily for any definite structure without painful consideration of the individual bond probabilities p of eq 2 by observing the following rules. Designate the $N - 1$ freely moving beads of the macromolecule by integers from 1 to $N - 1$, preferably in a way which results in a convenient form of the matrix **V**. Then the matrix **V** is made up of two kinds of contributions. (1) Each bond attached to the nth bead contributes $\frac{1}{2}$ to the (n,n) element in the main diagonal of **V** (*e.g.*, an end bead is represented by $\frac{1}{2}$, beads in the linear part of the chain by 1 and n-functional branch points by $n/2$). (2) A bond connecting the nth and the mth beads contributes $-\frac{1}{2}$ to the (n,m) and (m,n) elements of **V**. The size of the symmetrical matrix **V** is $(N - 1) \times (N - 1)$ since only $N - 1$ freely moving beads have to be considered. Obviously one topological structure can be represented by many different matrices, depending upon the way of numbering the beads, and it is only the matter of convenience which way is chosen.

The symmetrical tensor of random orthogonal components X_{kl} of the square radius, referred to our coordinate system, is given by

Also on p 379 equation 10 should read:

$$\langle C^u C^v C^w \rangle = (1/6)(C_1^u C_2^v C_3^w + C_1^u C_3^v C_2^w + C_2^u C_1^v C_3^w + C_2^u C_3^v C_1^w + C_3^u C_1^v C_2^w + C_3^u C_2^v C_1^w) \quad (10)$$