Carbon-13 Chemical Shift Studies of the 1,4-Polybutadienes and the 1,4-Polyisoprenes

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ABSTRACT: The natural abundance carbon-13 nuclear magnetic resonance spectra of *cis*- and *trans*-1,4-polybutadiene, both natural and synthetic *cis*- and *trans*-1,4-polyisoprene, and a mixed synthetic polyisoprene have been obtained for these polymers in solution. Motional narrowing has been observed to be adequate to obtain high-resolution spectra, with proton decoupling, of bulk samples of *cis*-1,4-polybutadiene and *cis*- and *trans*-1,4-polyisoprene. Assignments have been made for all resonance peaks in the spectra of the 1,4-polymers. These spectra are consistent with the structural units arranged in the stereoregular head-to-tail sequence and are interpretable in terms of a single repeating unit. Chemical shift parameters which reflect methyl substituent and configurational features in low molecular analogs of the polymer units have been used successfully to discuss the effect of the corresponding structural features on the carbon-13 chemical shifts of the methyl and methylene groups in the various polymers.

Nuclear magnetic resonance spectroscopy has proved to be a method of considerable interest and importance for the study of physical and chemical properties of polymers.[1-3] Studies[4-6] which deal with solids, amorphous glasses or highly viscous rubbers and the spectra obtained are of the so-called "broad band" or "wide-line" type because the absorption spectra are broadened due to the influence of nuclear magnetic dipole-dipole interactions.[7] Analyses[8-14] of the width and detailed shape of absorption resonances and studies of magnetic relaxation times have yielded valuable information concerning the nature and frequency of molecular motions, such as the rotation of methyl groups and the onset of segmental motion of polymer chains. Results from such studies have contributed to the understanding of the physical properties of polymers since at any given temperature they are determined to a great extent by the internal mobility of the chains of which they are composed.[15,16] When dissolved in suitable solvents, polymer samples of low viscosity have yielded the so-called high-resolution nuclear magnetic resonance spectra in which the resonance lines are relatively narrow compared with the width of the solid state. These high-resolution spectra are of great value in providing detailed information pertaining to chain microstructure of polymer molecules.[1-3] The recent developments[17,18] in stereospecific catalysts for polymer synthesis which have led to a high degree of control over factors such as stereoregularity and branching, have given rise to increasing application of high-resolution nuclear magnetic resonance to the study of the stereochemical configuration of polymer chains. Comprehensive reviews[2,3] have recently discussed the systems for which nuclear magnetic resonance studies have thus far proved successful. In this regard, by far the largest chemical applications of nuclear magnetic resonance to polymer characterization have been concerned primarily, if not entirely, with the spectra of the proton nucleus and to a lesser extent, the fluorine nucleus. However, the suggestion of applying carbon-13 nuclear magnetic resonance techniques to polymer problems has been made on at least two occasions.[2,19] In the earlier instance,[19] a proposal was made to investigate liquid polymers and included preliminary work on the observation of the carbon-13 nuclear magnetic resonance of polyethylene glycol and polypropylene glycol, whereas the other suggestion appeared in a recent review[2] on nuclear magnetic resonance applications to polymer studies. While this present investigation was in progress, the carbon-13 nuclear magnetic resonance analysis of ethylene oxide–maleic anhydride copolymers was privately communicated[20] to the authors.

The late emergence of these studies stems in part from

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the complexity, both practical and fundamental, that occurs in research on polymers[1-3] and from the inherent difficulty[21,22] in the determinations of the nuclear magnetic resonance of carbon-13 nuclei in natural abundance. The difficulties associated with low natural abundance and inherent low sensitivity are well known.[21,22] In practice, if all the carbon-13 nuclear magnetic resonance signals corresponding to all carbons in a large molecule are to be routinely observed on a single scan, the sample is preferably run as a neat liquid or a concentrated solution. Molecular symmetry is a desirable feature in that equivalent carbons effectively increase the spectral intensity per carbon atom. The developments of a field frequency lock spectrometer[23] for the carbon-13 magnetic nucleus, time averaging methods,[24,25] and random noise decoupling[26,27] of associated protons make possible the observation of natural abundance carbon-13 nuclear magnetic resonance of certain polymers.

The purpose of this study has been to determine the feasibility of investigating the microstructural features of polymers using carbon-13 nuclear magnetic resonance techniques. Consequently, an effort has been made to investigate polymer chains which are known to have the structural unit arranged in a stereoregular sequence. It was anticipated that the spectra of polymers of high stereoregularity could be interpreted in terms of a single repeating unit, whose chemical shift data reflect the average molecular environment of the unit over all conformations of the chain. Provided that the repeating unit itself is a relatively simple structure, the problem of spectral interpretation was expected to be similar to that encountered in the analysis of low-molecular weight molecules.

The 1,4-polybutadienes and the 1,4-polyisoprenes offer an excellent opportunity for studying the microstructural features of polymers with structurally simple repeating units. The differences in fundamental properties between *cis*- and *trans*-1,4-polybutadiene and between *cis*- and *trans*-1,4-polyisoprene (natural rubber and balata or gutta percha) have long been recognized as being intimately related to the stereochemical configuration of the monomeric unit of the polymer chain.[28,29] For example, the structures of the *trans* polymers lead to brittle, powdery or hard, tough materials while the *cis* polymers make excellent elastomers at room temperature.[30,31] In addition, the natural polyisoprenes are known[29,32] to be 1,4-polymers with the monomeric isoprene structural unit arranged in a stereoregular head-to-tail sequence having essentially the all-*cis* or all-*trans* isomeric structures.

Recently, new developments[33-35] in polymer synthesis have led to a high degree of control over the stereoregularity of the geometrically isomeric 1,4-*cis* and 1,4-*trans* forms of polybutadiene and polyisoprene. It is relevant to the basic understanding of the nature of stereospecific polymerization, as well as to correlating physical properties with composition and structure, to determine the steric purity of polymers and the degree with which the synthetic polymers resemble their natural counterparts. High-resolution nuclear magnetic resonance spectroscopy has proven to be particularly valuable for this purpose.[36] The structures of *cis*- and *trans*-1,4-polybutadiene and natural and synthetic *cis*- and *trans*-1,4-polyisoprene have been investigated[37-41] by proton nuclear magnetic resonance and this method is capable of quantitatively determining *cis–trans* ratios and detecting amounts of minor microstructural units (1, 2 or 3, 4 addition). At present, carbon-13 nuclear magnetic resonance techniques[21] cannot readily achieve sensitivity comparable to that of proton magnetic resonance in the detection of minor impurities. However, the increased chemical shift range, the simplicity of proton-decoupled spectra, and the marked dependence of carbon-13 chemical shift data on substituent and conformational effects offer advantages for spectral interpretation which make nuclear magnetic resonance investigations of carbon-13 in polymers particularly attractive. Investigations of methyl derivatives of benzene,[42] cyclohexane,[43] and ethylene[44] have demonstrated the high sensitivity of carbon-13 chemical shifts of methyl and methylene carbons to changes in molecular environment peculiar to conformation and configuration. Since the differences in the fundamental properties between *cis*- and *trans*-1,4-polybutadiene and between *cis*- and *trans*-1,4-polyisoprene are intimately related to the configurations of the methyl and methylene groups relative to each other, carbon-13 magnetic resonance affords a valuable means of investigating these microstructural features of the stereoregular polymer chains.

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In addition, the approach[2,3,36,45] of using simple model compounds for assistance in studying the structure of polymers has been pursued by comparing carbon-13 chemical shift data of the 1,4-polybutadienes with that of low molecular analogs of the polymer units. Furthermore, the success of finding additive substituent parameters[42–44,46,47] which correlate the carbon-13 chemical shift data for various hydrocarbon systems has prompted using the parameters which reflect substituent and configurational features in methyl-substituted ethylenes[44] to interpret the polyisoprene data. 2-Methyl-2-butene contains many of the same structural features as the isoprene unit and information of substituent and configurational effects observed[44] in this molecule forms the basis for interpreting the various polyisoprene spectra.

Experimental Section

A. Instrumentation. The carbon-13 nuclear magnetic resonance spectra were obtained using a Varian AFS-60 high-resolution spectrometer operating at 15.08 MHz. This instrument features an analog frequency sweep for carbon-13 nuclei provided by a Hewlett-Packard 5103A frequency synthesizer and a modified Varian 4311 radiofrequency unit controlled by a Varian 4313 analog programmer. The AFS-60 uses a standard Varian 12-in. magnet system equipped with a flux stabilizer and homogeneity coils. A V-4331 high-resolution probe, which had been modified by Varian for dual frequency irradiation, was double tuned to 15 and 60 MHz. The 60-MHz output derived from the stable driver frequency of the synthesizer system and suitably modulated provided field-frequency stabilization through external and internal lock signal coincidence of reference proton resonances. While operating in the external frequency lock mode, carbon-proton spin–spin couplings were selectively decoupled using a Hewlett-Packard 5105A-5110B frequency synthesizer system operating at 60 MHz; the output was amplified by a tunable Boonton Radio Co. 230A power amplifier before being fed into the probe. Broad band decoupling was achieved by modulating the average proton decoupling frequency with an audio random noise generator (constructed by Collins[48] of this laboratory based on the design of Ernst[26]). The frequency-swept spectra were obtained by driving the Varian 4313 analog programmer with MARS recorder system and accumulating on a Varian C-1024 time-averaging device operating on external trigger mode. The frequencies of the carbon-13 nuclear magnetic resonance signals were monitored with a Hewlett-Packard 5512A electronic counter and measured to ±0.1 Hz. The probe could accommodate 10 mm o.d. sample tubes and was equipped with an air-turbine arrangement for sample spinning.

B. Sample Preparation. The polybutadiene and polyisoprene polymer samples examined in this study were obtained from the Firestone Tire and Rubber Co. All of the polymers contained less than 1% stabilizers and since this low concentration was not expected to interfere with measurements, the samples were used as received.

The polybutadiene polymers examined were (1) a *cis*-1,4-polybutadiene prepared with a cobalt catalyst which was considered to contain 97.8% *cis*-1,4 units and (2) a *trans*-1,4-polybutadiene prepared with a Ziegler catalyst which was considered to be comprised of approximately 100% *trans*-1,4 units. The *cis*-1,4 sample for carbon-13 nuclear magnetic resonance analysis was prepared as an approximately 20% (wt/vol) solution of the polymer in reagent grade dichloromethane. A spectrum of the bulk *cis*-1,4 polymer was obtained from a sample prepared by gently packing small pieces of (rubbery) polymer into a sample tube. Solution difficulties were incurred with the *trans*-1,4 polymer in trying to meet carbon-13 nuclear magnetic resonance sample concentration requirements. Measurements reported were obtained from a sample prepared by stirring the coarse powdery polymer in benzene for a 24-hr period, removing excess solvent, and finally packing the resulting gelatinous material into a sample tube.

The other diene polymers were natural and synthetic *cis*- and *trans*-1,4-polyisoprene, along with a mixed synthetic polymer (content: 33.0% *cis*-1,4 units; 53.5% *trans*-1,4 units; 5.8% 1,2 units; and 7.7% 3,4 units). Samples for analysis were prepared as approximately 10% (wt/vol) solutions of polymers in reagent grade dichloromethane. The spectrum of the bulk natural rubber was obtained from a sample prepared by gently packing a mass of polymer into a sample tube. The spectrum of bulk balata was obtained from a carved cylindrically shaped sample which was forcibly inserted into a sample tube.

The solution samples were sealed in thin walled 10 mm o.d. tubes with rubber stoppers. Bulk samples were put in thick-walled 10 mm o.d. tubes.

C. Experimental Technique. The carbon-13 nuclear magnetic resonance spectra of the polymers were obtained using the external field-frequency lock system of the AFS-60 spectrometer. For the solution spectra, from which the carbon-13 chemical shift data were obtained, the internal proton resonance signal of the solvent of the sample and that of the external water reference in the probe were adjusted to give internal and external lock signal coincidence. By so doing, one facilitates the procedure for selective proton decoupling. In general, the decoupling frequency for collapsing the multiplet carbon-13 resonance signal from carbons with directly bonded hydrogens to a sharp singlet resonance signal may be obtained directly when the corresponding proton resonance frequencies at the same field strength are already known. The difference in hertz between the solvent (internal reference) proton resonance signal and a particular polymer proton resonance signal represents the number of hertz that the proton decoupling synthesizer should be offset from the lock frequency in order to decouple the corresponding polymer carbon-13 resonance signal. The carbon-13 chemical shift values, relative to benzene taken as an arbitrary reference, were calculated using eq[49] 1. In this equation, δ represents the chemical shift

$$\delta_{\mathrm{iC}^{13}} = \delta_{\mathrm{oC}^{13}} - \frac{\nu_{\mathrm{i}} - \nu_0}{\nu_0} \times 10^6 \qquad (1)$$

parameter in parts per million, ν is the carbon-13 nuclear magnetic resonance frequency, and the subscript i refers to the polymer peak and the subscript o to the solvent peak. The chemical shift values are reported with an accuracy of ±0.2 ppm.

The need to accumulate spectra on a time-averaging device was necessitated by the low concentration of the polymers in solution of low viscosity samples. Although the initially low concentration samples provided satisfactory spectra, such determinations led to almost prohibitive scanning times. Consequently, highly viscous samples were tried which proved successful and which eventually lead to running the bulk polymers. Unsatisfactory spectra of bulk *cis*-1,4-polybutadiene and bulk *cis*-1,4-polyisoprene could be observed

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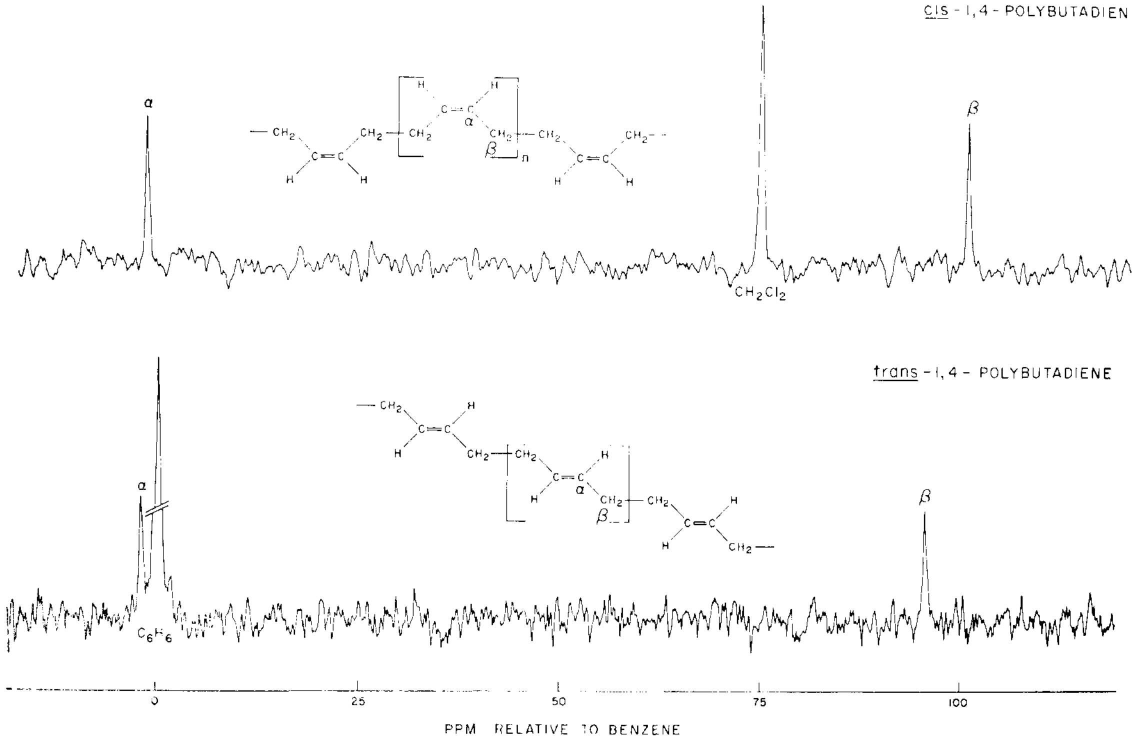

Figure 1. Random-noise, proton-decoupled 15.08-MHz carbon-13 nuclear magnetic resonance spectra of *cis*-1,4-polybutadiene and *trans*-1,4-polybutadiene. The spectrum of approximately 20% (wt/vol) solution of *cis*-1,4-polybutadiene in dichloromethane represents the time-averaged accumulation of 90 scans while the spectrum of the gelatinous sample of *trans*-1,4-polybutadiene in benzene consists of 224 scans. Each scan was swept 2156 Hz in 100 sec. Both sweep scales are equal and represent the chemical shift scale in parts per million with respect to benzene.

from a single scan. In the absence of a solvent peak a chemical shift scale was attached to the solid spectrum by lining up the resonance peaks in the solid with those in the solution. As both spectra exhibit identical patterns, it is unlikely that a constant chemical shift bias would appear in each resonance peak. In this way the usual problem of referencing solid spectra has been avoided. Bulk susceptibility corrections between solid and liquid are implicitly included in the process of lining up the two spectra.

All spectra were obtained with the samples spinning. Under the experimental conditions described above, the probe temperature was about 45° due to heating by the H_2 radio frequency field.

TABLE I
CARBON-13 CHEMICAL SHIFT DATA[a] FOR THE 1,4-POLYBUTADIENES

Polymer	Carbon position[b] α	Carbon position[b] β
cis-1,4-Polybutadiene	−1.0	101.0
trans-1,4-Polybutadiene	−1.7	95.6

[a] Chemical shift values in parts per million ±0.2 are with respect to benzene. [b] Carbon positions as designated in Figure 1.

Results

A. 1,4-Polybutadienes. The carbon-13 chemical shift data for *cis*-1,4- and *trans*-1,4-polybutadiene are presented in Table I and their time-averaged, proton-decoupled carbon-13 nuclear magnetic resonance spectra are shown in Figure 1. The spectrum of the *cis* isomer represents the time-averaged accumulation of 90 scans whereas the spectrum of the less soluble *trans* isomer represents the time-averaged accumulation of 224 scans. Inspection of Figure 1 reveals the very simple spectra obtained from the stereoregular 1,4-polybutadienes. The symmetrical units of the 1,4-polymers exhibit one resonance peak from equivalent ethylenic carbons and one resonance peak from equivalent methylene group carbons. In each spectrum, both peaks are of equal intensity and are separated by approximately 100 ppm; the resonance peak in between is that of the solvent. Resonance peaks arising from end groups were not observed. Thus, the spectra of these polymers can be interpreted in terms of a single repeating monomer unit, as indicated with the structures drawn with the spectra in Figure 1.

Although time-averaging devices with random noise modulation techniques provide spectra of sharp singlet resonance peaks for determination of chemical shift data, assignment of the resonance peaks to specific carbons was accomplished utilizing the technique of selective decoupling. The proton spectra of both polymers have been analyzed[37,38,40] and the separation between proton resonance peaks has been determined to be approximately 200 Hz for both isomers. The 1,4-polybutadienes, therefore, present a situation in which the assignment of the carbon-13 nuclear magnetic resonance peaks to specific carbon atoms can be made unequivocally by observing a spectrum first selectively decoupling the ethylenic protons and then selectively decoupling the methylene protons. It is noted that the well-established characteristic spectral region of the carbon-13 nuclear magnetic resonance absorption peaks of ethylenic and methylene carbons in hydrocarbon

TABLE II
CARBON-13 CHEMICAL SHIFT DATA[a] FOR THE 1,4-POLYISOPRENES

	Carbon position[b]									
	α		β		γ		δ		ε	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
Polyisoprene										
cis-1,4-Natural	−6.8		3.4		96.2		101.7		105.1	
Synthetic	−6.9		3.2		96.2		101.9		105.3	
trans-1,4-Natural		−6.5		4.1		88.7		101.6		112.7
Synthetic		−6.5		4.2		88.7		101.5		112.8
Mixed synthetic	−6.5 (Band)		3.1	3.9	96.5	88.5	101.7 (Band)		105.1	112.5

[a] Chemical shift values in parts per million ±0.2, are relative to benzene. [b] Carbon positions as designated in Figure 2.

systems[44,47,50–53] might have been regarded as sufficient evidence to make the peak assignments. Thus, the downfield peak of each polymer, which corresponds to the low chemical shift value, is readily assigned to the ethylenic carbons and is arbitrarily designated as the α-peak. In a similar manner, the upfield peak is assigned to the methylene carbons and is designated as the β-peak.

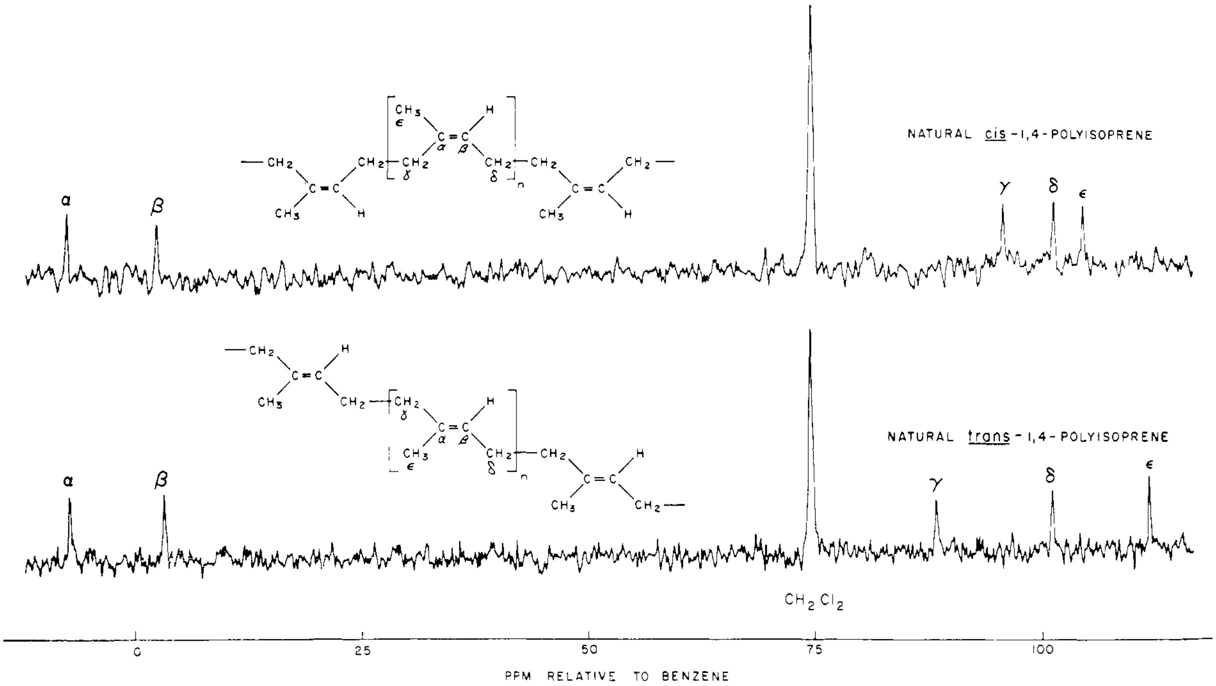

Figure 2. Random-noise, proton-decoupled 15.08-MHz carbon-13 nuclear magnetic resonance spectra of approximately 10% (wt/vol) solutions of natural *cis*-1,4-polyisoprene and natural *trans*-1,4-polyisoprene in dichloromethane. The spectrum of *cis*-1,4-polyisoprene consists of the time-averaged accumulation of 348 scans, and the spectrum of *trans*-1,4-polyisoprene is the accumulation of 183 scans. Each scan was swept 2156 Hz in 250 sec. Both sweep scales are equal and reported in parts per million with respect to benzene.

The accumulated spectrum of bulk *cis*-1,4-polybutadiene, after 239 scans, was found to be essentially the same as the corresponding solution spectrum shown in Figure 1, with the exception of very slight broadening of the resonance peaks. Although approximately 10 scans would suffice to give a satisfactory spectrum, additional scanning was continued in search of minor impurity of, for example, the 1,2-polybutadiene structure. However, minor impurities, at the concentration level present, could not be observed from the carbon-13 nuclear magnetic resonance spectra. Chemical shift values calculated using dichloromethane as an external standard were found to be within experimental error of those obtained from the corresponding solution spectrum. An attempt to obtain a spectrum of the bulk *trans*-1,4-polybutadiene sample proved unsuccessful.

B. 1,4-Polyisoprenes. The carbon-13 chemical shift data for *cis*-1,4- and *trans*-1,4-polyisoprene are given in Table II and their time-averaged, proton-decoupled carbon-13 nuclear magnetic resonance solution spectra are shown in Figure 2. The spectrum of the *cis* polymer represents the time-averaged accumulation of 348 scans whereas the spectrum of the *trans* polymer represents the time-averaged accumulation of 183 scans. The spectra of the 1,4-polyisoprenes show five clearly

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distinguishable singlet resonance peaks which can be attributed to the methyl, two methylene, and two ethylenic carbon atoms of the polymers, all of equal intensity, and a larger peak associated with the solvent. Resonance peaks arising from end groups were not observed. Thus, the spectra of these polymers can be interpreted in terms of a single repeating isoprene unit, as indicated with the structures drawn with the spectra in Figure 2. For convenience in discussing the procedure for the assignment of resonance peaks, the structural units are labeled arbitrarily as illustrated.

The resonance peaks of the two ethylenic carbon atoms occur at low field strength, whereas those of the methyl and methylene carbon atoms occur in the higher field region. Assignment of the resonance peaks to specific carbons was, in part, accomplished utilizing the technique of selective decoupling.

In this regard, the results of proton nulcear magnetic resonance investigations[32,37–41] of the structures of natural and synthetic *cis*- and *trans*-1,4-polyisoprenes have been useful. The resonance peak of the α-carbon, in which large proton couplings are absent, can easily be assigned to the lowest field peak, because it enhances to a sharp singlet over a wide range of decoupling frequencies indicating the absence of a directly bonded proton. The resonance of the β-carbon, however, collapses to a sharp singlet only when the single directly bonded ethylenic hydrogen is selectively decoupled. Of the group of three high field resonance peaks, the furthest upfield can be assigned to that of the methyl carbon by a similar procedure of selectively decoupling the methyl protons.

The γ- and δ-methylene resonance peaks are not separated from one another in the proton nuclear magnetic resonance spectra, and consequently, their corresponding carbon-13 nuclear magnetic resonances cannot be assigned by the selective decoupling technique. Therefore, the assignment of these peaks is made on the basis of the following structural argument. Inspection of simple models of the *cis*- and *trans*-1,4-polyisoprenes shows that the δ-methylene moiety is in a very similar environment in both polymers, and consequently, this methylene carbon might be predicted to have similar carbon-13 chemical shifts in both cases. This assumes that the effect upon the δ-methylene carbon by the γ-methylene group in the *cis* isomer and the methyl group in the *trans* isomer are essentially identical. It also assumes that long-range effects arising from neighboring isoprene units will make the same contribution to the chemical shift of the δ-carbon, whether these units are *cis* or *trans*. The best evidence for the validity of these two assumptions is the existence of peaks assigned to the δ-carbon at 101.7 ± 0.2 ppm and 101.6 ± 0.2 ppm in the carbon-13 spectra of the natural *cis*-1,4- and *trans*-1,4-polyisoprenes, respectively. The remaining peak in each spectrum is assigned by default to the γ-carbon.

The above spectral assignments of the two methylene carbons can be further corroborated with additive substituent parameters derived from an investigation[44] of a series of methyl-substituted ethylenes. The substituent and configurational features observed from the carbon-13 chemical shifts of the two interacting methyl groups which are geminal, *cis* or *trans* from one another in the methyl ethylenes faithfully reflect similar features found for the δ-methylene, γ-methylene, and methyl carbons in the repeating 1,4-polyisoprene units. A factor analysis[44] carried out on the carbon-13 chemical shift data of the methyl-substituted ethylenes indicates that the substituent parameter for a geminal methyl is -6.23 ppm, for a *cis* methyl is $+5.75$ ppm, and a *trans* methyl is -1.23 ppm. In order to use these parameters in the case of the polyisoprenes, it is necessary first to make the assumption, similar to the one above, that the effect of a methylene group on other methylenes and methyls in the repeating isoprene unit is the same as exists between the methyls in 2-methyl-2-butene. Furthermore, long-range effects between neighboring isoprene units are again assumed to be constant for both *cis* and *trans* isomeric structures. It is noted that this assumption is a very reasonable one when it is realized that the adjacent polyisoprene unit does not reveal its isomeric structure until the detailed structural features have been considered down four carbon–carbon bonds in the polymeric chain. As before, these assumptions lead to the conclusion that the δ-methylene in both isomeric structures should appear at the same position in the respective spectra.

Unlike the situation observed for the δ-carbon in both isomers, difference can be expected between the chemical shift values of the γ-methylene carbon in the *cis*- and *trans*-1,4-polyisoprenes. The different spatial relationship existing between the two methylenes introduces a *cis* substituent parameter shift of $+5.75$ ppm in the carbon of the *cis* structure and a -1.34 ppm substituent parameter shift in the *trans* structure. The difference, $+7.09$ ppm, between these two values, therefore becomes the expected separation in shifts for the γ-carbon for the *cis*- and the *trans*-1,4 polymers as the geminal substituent parameter contributes equally to the shift of the γ-methylenes in both instances. This predicted shift difference is in good agreement with the experimentally observed shift difference of 7.5 ± 0.2 ppm. The difference between the chemical shift values of the methyl carbons in the two polymers may be predicted by the analogous but reverse argument. The methyl groups are merely interchanged with the γ-methylene groups, and one now expects the *cis*-methyl carbon to be 7.09 ppm downfield from the corresponding *trans*-methyl shift. Again, for the natural polymers, the experimental difference is -7.6 ± 0.2 ppm.

The accumulated spectrum of bulk natural *cis*-1,4-polyisoprene, after 24 scans, is shown in Figure 3 along with the corresponding solution spectrum. With the exception of slight broadening of the resonance lines and nonuniform proton-decoupled peaks, the spectra are essentially the same. In addition, approximate chemical shift data estimated using dichloromethane as an external reference were found to be consistent with the chemical shift data obtained by placing the solid peaks in correspondence with the transitions in the solution spectrum.

Figure 4 shows the accumulated spectrum of bulk natural *trans*-1,4-polyisoprene, after 426 scans along with the corresponding solution spectrum. Unlike bulk *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene from which satisfactory spectra were obtained after relatively few accumulated scans, a considerably larger

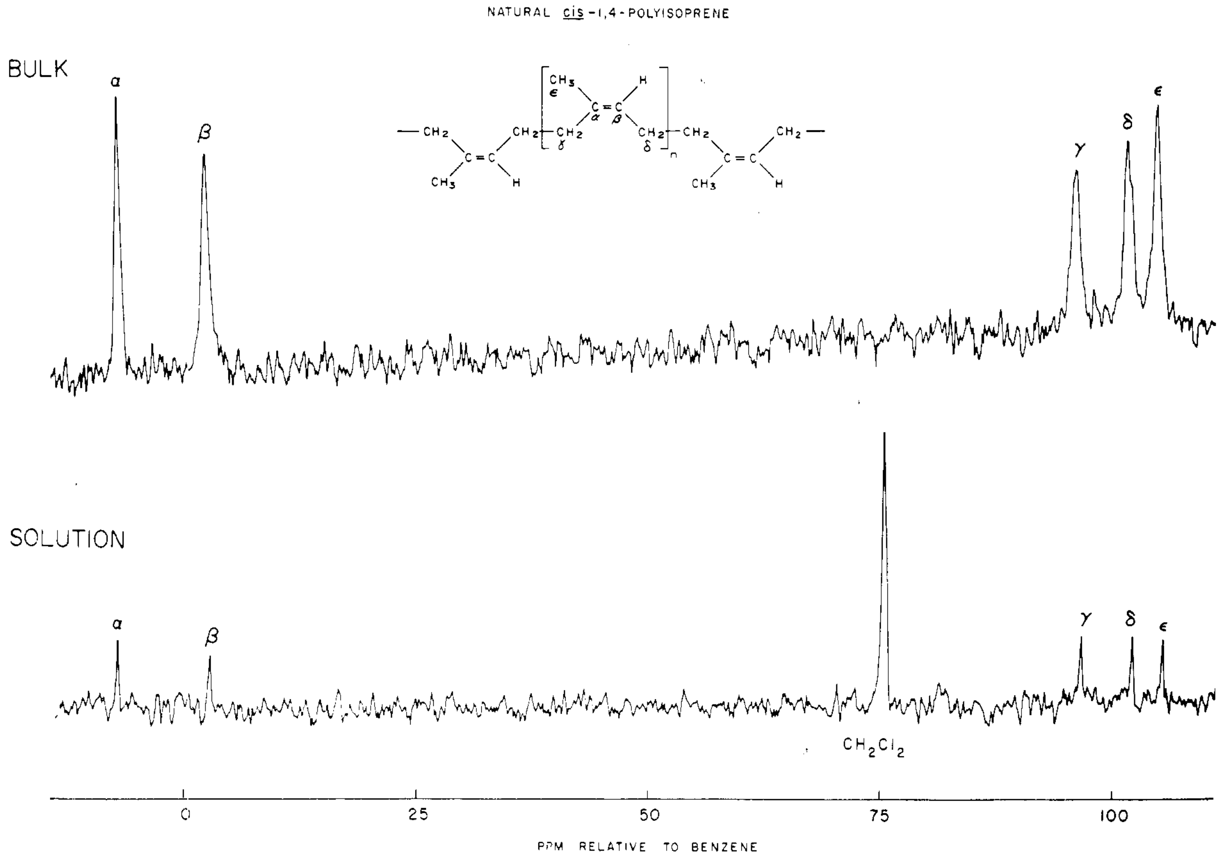

Figure 3. The random-noise, proton-decoupled 15.08-MHz carbon-13 nuclear magnetic spectra of bulk and solution samples of *cis*-1,4-polyisoprene. The solution spectrum is that shown in Figure 2. The bulk spectrum represents the time-averaged accumulation of 24 scans taken over a sweep width of 2156 Hz in a sweep time of 250 sec.

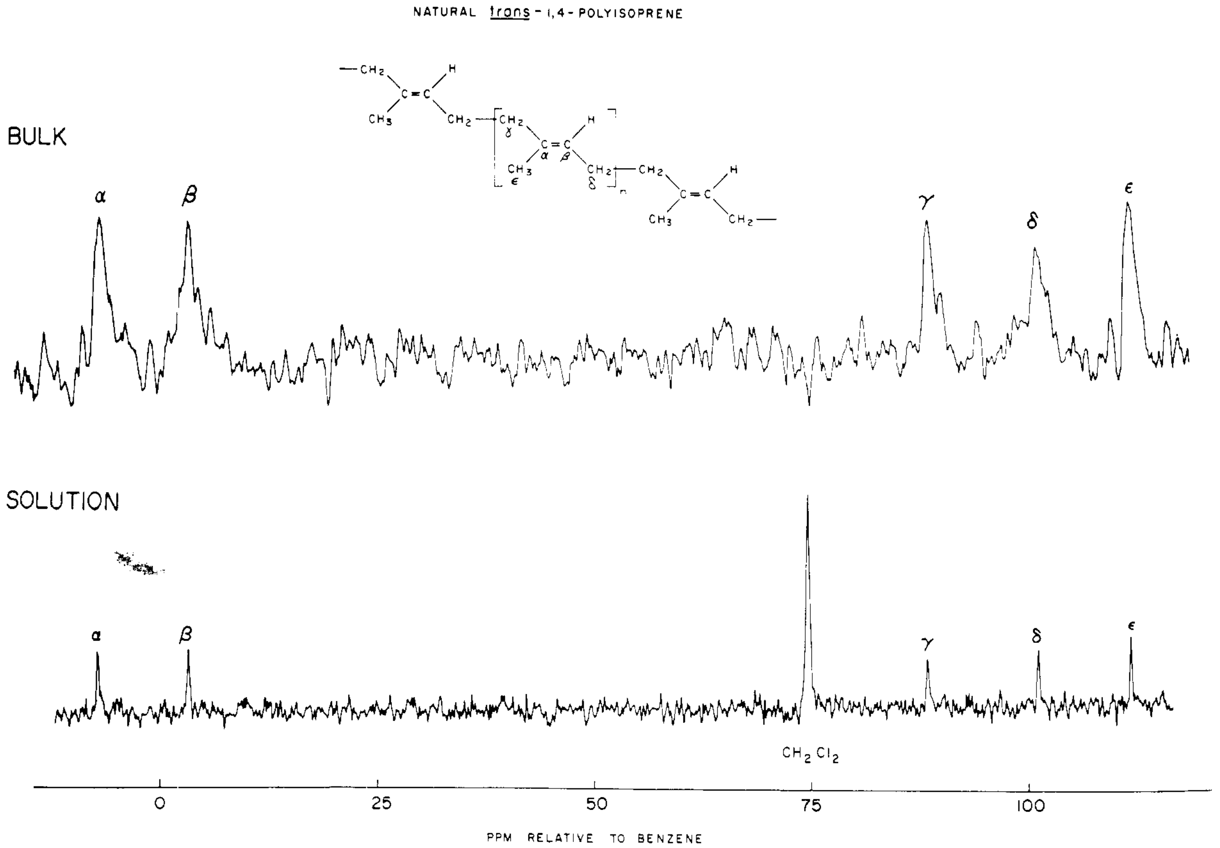

Figure 4. The random-noise, proton-decoupled 15.08-MHz carbon-13 nuclear magnetic resonance spectra of bulk and solution samples of *trans*-1,4-polyisoprene. The solution spectrum is that shown in Figure 2. The bulk spectrum represents the time-averaged accumulation of 426 scans taken over a sweep width of 2156 Hz in a sweep time of 100 sec.

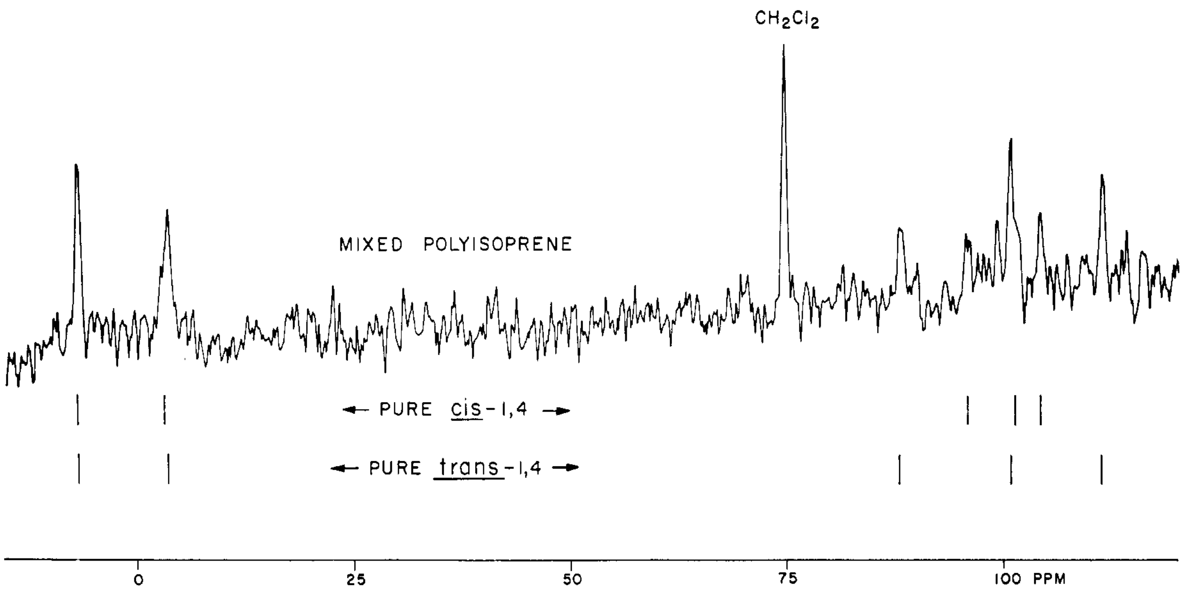

Figure 5. Random-noise proton-decoupled 15.08-MHz carbon-13 nuclear magnetic resonance spectrum of approximately 10% (wt/vol) solution of a mixed synthetic polyisoprene (33.0% *cis*-1,4 units; 53.5% *trans*-1,4-units; 5.8% 1,2 units; and 7.7% 3,4 units) in dichloromethane. The spectrum represents the time-averaged accumulation of 495 scans taken over a sweep width of 2649 Hz in a sweep time of 250 sec. The chemical shift scale, in parts per million, is given with respect to benzene.

number of accumulated scans were required for this sample. Although the resonance peaks are somewhat broadened compared to the other bulk spectra, estimated chemical shift values are, nevertheless, consistent with those determined from the corresponding solution spectrum.

The spectrum of the synthetic polymer containing largely the *cis*- and *trans*-1,4 units with minor 1,2 units and 3,4 units content is shown in Figure 5. It represents 495 accumulated scans. From an examination of the carbon-13 chemical shift data of the natural and synthetic polymers in Table II, the resonance peaks corresponding to the 1,4 units can be identified as indicated in Figure 5. Spectral peaks due to the 1,2 and 3,4 units are observed to exist, but assignment of these peaks has not yet been attempted. It is evident that questions of tacticity and head-to-tail structures must first be resolved before any final conclusions can be drawn.

Discussion

The simplicity of the proton-decoupled carbon-13 nuclear magnetic resonance spectra of the 1,4-polybutadienes and the 1,4-polyisoprenes with well-separated singlet resonance peaks provides accurate and easily interpreted chemical shift data. The simplicity is, of course, dependent on the high stereoregularity of the polymers examined. It is noted that naturally occurring *cis*-1,4-polyisoprenes range in molecular weights from 200,000 to 400,000 and that the average molecular weight of *trans*-1,4-polyisoprene (gutta percha) is approximately 42,000–100,000.[54] Nevertheless, the natural 1,4-polyisoprenes, as well as the synthetic 1,4-polyisoprenes and 1,4-polybutadienes, exhibit carbon-13 spectra which are readily interpreted in terms of a single repeating unit in which the contributions of monomer residues to observed absorption are additive. These observations immediately suggest that information about the polymer structures might be obtained by examining carbon-13 chemical shift data for low molecular analogs of the polymer units. The value of the comparison with low molecular analogs lies in the way it reveals the basis nature of the configurational and substituent effects in the polymers.

A. 1,4-Polybutadienes. It is preferable to first consider the comparatively simple *cis*- and *trans*-1,4-polybutadiene polymers and the low molecular analogs, the *cis*- and *trans*-2-butenes. Of particular interest in this case is the *cis* and *trans* configurational effects of the methylene groups in the polymer units compared with the methyl groups of the 2-butenes. In addition, it is noted that the comparison is not made for predicting the actual chemical shift values, but rather in predicting the differences in chemical shift values between different configurations. The values[44] of the chemical shifts of the equivalent methyl carbons in *cis*- and *trans*-2-butene are 117.13 ± 0.07 and 111.39 ± 0.07 ppm, respectively, and the difference between them is 5.74 ± 0.07 ppm. For the *cis* and *trans* polymers, the chemical shift values of the methylene carbons are 101.0 ± 0.2 and 95.6 ± 0.2 ppm, respectively, and the difference is 5.4 ± 0.2 ppm. A comparison of the *cis–trans* differences shows very good agreement and it therefore appears that the configurational effect observed among methyl groups of the 2-butenes is similarly reflected in the methylene groups of the polymers. The decrease in chemical shift values of the polymers compared to the 2-butenes reflects the trend expected[46] to result from a directly bonded hydrocarbon substituent which may be regarded as the nearest neighboring unit. However, it has been assumed that nearest neighboring units, whether these units are *cis* or *trans*, make approximately the same contribution to the carbon-13 chemical shifts of the structural unit. It is noted that this assumption is a reasonable one since the adjacent unit does not reveal its isomeric structure until the detailed

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(54) A. Ravve, "Organic Chemistry of Macromolecules," Marcel Dekker, Inc., New York, N. Y., 1967, p 192.

structural features have been considered down four carbon–carbon bonds in the polymeric chain.

B. 1,4-Polyisoprenes. The approach of using chemical shift structure correlations of low molecular analogs has already been indicated for the 1,4-polyisoprenes in the corroborative arguments presented in making the spectral assignments for these polymers. The earlier discussion pointed out that the substituent and configurational features observed in the carbon-13 chemical shifts of the two interacting methyl groups which are geminal, *cis* or *trans* from one another in the methyl ethylenes are faithfully reflected by similar features found in the γ-methylene, δ-methylene, and ϵ-methyl carbons in the repeating 1,4-polyisoprene units. Unlike the situation with the simple *cis* and *trans* isomeric units of the 1,4-polybutadienes, the more complicated and unsymmetrical units of the 1,4-polyisoprenes are not comparable to isomeric low molecular analogs. Rather, it has been profitable to discuss the influence of the geminal, *cis* or *trans* effects and to account for their interrelationships by applying the additive substituent parameters obtained from a linear regressional analysis[44] performed on observations of these structural features as they occur in the various methyl ethylenes.

Several features of the carbon-13 chemical shift data of the polyisoprenes warrant further comment, particularly in reference to their supporting evidence for the validity of the assumptions employed in making the peak assignments. The data show at least two distinct features. The first is that the difference of 7.5 ± 0.2 ppm between the chemical shifts of the *cis*- and *trans*-γ-methylene carbons is essentially the same chemical shift difference, 7.6 ± 0.2 ppm between the *trans* and *cis* ϵ-methyl carbons (for the natural polymers). The second conspicuous feature is the constancy of the chemical shift value of the δ-methylene carbon in both polymers. The reciprocal correlation strongly suggests a dependence of the carbon-13 chemical shift data on the relative position in the *cis* and *trans* unit configuration. When the relative positions of the γ-methylene group and the ϵ-methyl groups are *cis* to the δ-methylene group, the former are observed to experience very similar upfield shifts compared to being *cis* to a hydrogen atom. Conversely, the chemical shift value of the δ-methylene carbon remains essentially constant whether its position is *cis* to either a methyl group or methylene group. These correlations are considered as strong evidence for supporting the assumption that the difference between the effect of a methyl group and a methylene group on the chemical shifts of the *cis*- and *trans*-δ-methylene carbon can be considered negligible.

Furthermore, these correlations, as well as the *cis*-*trans* configuration effect of the 1,4-polybutadienes are consistent with a conseration of nonbonded hydrogen–hydrogen repulsive interactions[55–57] and the effect of such steric perturbations on the chemical shift. Carbon-13 nuclear magnetic resonance studies[43,58] of steric interaction existing between proximate hydrogens on two sterically perturbed carbon–hydrogen bonds of methyl groups have led to the conclusion that the steric perturbation can contribute to a significant upfield carbon-13 chemical shift. The model proposed[58] suggests that such interaction sterically induces polarization of electronic charge in the direction along the H–C bonds, thereby further shielding the carbons and increasing their chemical shift values. It is concluded that the steric perturbation model is a satisfactory explanation for the observed correlations of upfield shifts of carbon in *cis* configurations.

In addition, it has been assumed that the *cis* and *trans* configurations and conformations of nearest neighboring units make approximately the same contributions to the carbon-13 chemical shifts of the isoprene unit. Again, it is noted that this assumption is a very reasonable one when it is realized that the adjacent polyisoprene unit does not reveal its isomeric structure until the detailed structural features have been considered down four carbon–carbon bonds in the polymeric chain. The following points are also emphasized to support this assumption. The consistent trends in the methyl and methylene carbon-13 chemical shifts are observed from a consideration of *cis* or *trans* configurational effects within the isoprene unit treated as an entity by itself, and also, the substituent parameters[44] of the methyl ethylenes can be successfully applied to the polymers without modification. Furthermore, the constancy of the δ-methylene carbon-13 chemical shift shows no sign of appreciable difference in unit–unit interaction in the pure *cis* or pure *trans* polymer. Finally, there appears to be no difference in unit–unit interaction based on the data of the mixed polyisoprene in which the pure *cis* and pure *trans* characteristics are preserved.

C. General Discussion. The results of this investigation show that carbon-13 nuclear magnetic resonance spectroscopy affords an extremely sensitive means of studying the stereochemical configurations of the 1,4-polybutadienes and the 1,4-polyisoprenes. Carbon-13 chemical shifts of the polymers are much larger and more sensitive to molecular environment than proton shifts of the hydrogens bonded to the corresponding carbon atoms. For example, the *cis* and *trans* forms of polybutadiene are virtually indistinguishable by proton nuclear magnetic resonance[3,37] at 60 MHz whereas the methylene carbon-13 chemical shifts differ by 5.4 ± 0.2 ppm and the ethylenic carbon-13 chemical shifts differ by 0.7 ± 0.2 ppm. In the case of the *cis*- and *trans*-1,4-polyisoprenes, the chemical shift difference between the methyl proton resonances has been reported to be 0.07 ppm[32] in carbon tetrachloride solution at 100 MHz and 0.14 ppm[37] in benzene solution at 60 MHz while the corresponding difference in the methyl carbon-13 resonances is 7.6 ± 0.2 ppm. Furthermore, the two different methylene carbon resonances are easily distinguished whereas the methylene proton resonances are not resolvable.

An interesting observation of this study is the high resolution quality of the carbon-13 nuclear magnetic resonance spectra of the bulk *cis*-1,4-polybutadiene and the bulk *cis*- and *trans*-1,4-polyisoprenes. The resonance peaks corresponding to the methyl, methylene, and ethylenic carbons in the various polymers are well resolved and the resonance line widths are narrow, par-

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(55) J. E. Mark, *J. Amer. Chem. Soc.*, **88**, 4354 (1966).
(56) J. E. Mark, *ibid.*, **89**, 6829 (1967).
(57) M. L. Huggins, *Pure Appl. Chem.*, **15**, 369 (1967).
(58) D. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, **89**, 5315 (1967).

ticularly in the *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene spectra. As concluded previously in proton nuclear magnetic resonance studies[8–13] on natural rubbers, the narrow line widths indicate that in addition to the rotation of the methyl groups about the threefold axis, the chain segments are undergoing a considerable amount of random reorientational motions to produce motional narrowing[5,7,59] of the resonance lines. It is noted that the temperature of the probe during the carbon-13 nuclear magnetic resonance experiment was 45° which is considerably above the region of the glass transition temperatures[30,60,61] at which the onset of motion of chain segments occurs in the amorphous regions of these polymers. Below the region of the glass transition temperature[61,62] the segments of an amorphous polymer undergo mainly vibratory motions about fixed positions in a disorganized quasi lattice. Increasing above the region of this temperature, the segments exhibit translational and diffusional motions and the properties change from glassy to rubbery.[61,62] Thus, at the temperature of 45°, the molecular motion of these polymers apparently is sufficiently rapid and extensive in amplitude to effectively average out the magnetic dipolar interactions from the magnetic moments of neighboring nuclei that are normally experienced by a nucleus in a rigid solid.[7] Therefore, motional narrowing, to the degree which occurs in the rubbery state, is adequate for obtaining high resolution carbon-13 nuclear magnetic resonance of polymers in the bulk state.

Another feature of the bulk spectra is interesting. It was noted that a relatively large number of accumulated scans was required to obtain a satisfactory spectrum of the *trans*-1,4-polyisoprene compared with the results of the *cis* isomer. In addition, the resonance line widths at half height of the former were found to be approximately two to three times that found for the latter. However, the melting point of the *cis* isomer[30,60] is below the temperature at which the spectrum was obtained whereas the melting of the two polymorphs of the *trans* isomer[12,63] occurs above this temperature. Below the true thermodynamic melting point, the bulk *trans* polymer may be expected to contain small regions of crystallinity.[12,62] Presence of relatively immobile segments of the *trans*-polymer chain at this temperature, therefore, would effectively result in a loss of intensity in the high-resolution component of the spectrum and would also account for increased line widths. However, the difference between resonance line widths and the incomplete understanding and characterization of the distribution of motions[11] suggests the desirability of carbon-13 magnetic relaxation studies over a range of temperatures to confirm this interpretation.

From a comparison of the carbon-13 chemical shift data of Table II, it seems reasonable to conclude that the synthetic *cis*- and *trans*-1,4-polyisoprenes closely resemble their natural counterparts in chemical composition. However, attempts of proton nuclear magnetic resonance studies[32] to determine the content of minor microstructure units in natural polyisoprenes have concluded that these polymers are essentially 100% 1,4 structures and are at least 99% of one isomeric form. Carbon-13 nuclear magnetic resonance techniques employed in this study have not been able to achieve comparable sensitivity, although the observation that high resolution studies can be obtained from the bulk state does have possibilities for quantitative determinations.

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