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Long-Range Steric Effects on the Carbon-13 Chemical Shift of Hydrocarbon Polymers

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ABSTRACT: High-resolution ^{13}C NMR was used to determine the microstructure of polymers having monomer units with a length of four atoms by exploiting long-range steric effects. In *trans*-1,4-polypentadiene the methyl absorption is affected by the triad steric sequence and the CH by the diad sequence. In *cis*-1,4-polypentadiene the *mm* and *rr* triads can be distinguished in the methyl absorption while the *m* and *r* diads are revealed by the CH and CH$_2$ signals. Finally the poly(1-methyltetramethylene) shows fine structure both in the methyl and in the β-CH$_2$ absorption which is attributed to triads and possibly to higher sequences.

I. Introduction

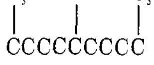
In recent years ^{13}C NMR spectroscopy has been largely applied to the study of the structure of both homo- and copolymers of hydrocarbon type, with particular reference to the determination of stereoregularity and monomer unit sequences.

This method is especially powerful in the study of the saturated carbon region because of the high sensitivity of the ^{13}C chemical shift to structural features. The correlation between chemical shift and chemical structure of the paraffinic hydrocarbons has been observed and rationalized by Grant and Paul[1] and later refined by Lindeman and Adams.[2] Both these empirical schemes are based on the substituent effect which a carbon atom has on the shift of the observed carbon. This effect has been observed for carbons placed in position α, β, γ, δ, and ϵ relative to the observed carbon. Subsequently it has been reported that the substituent effect is also related to steric structure.[3]

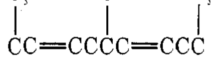
Correspondingly in the determination of microtacticity of polymers the ^{13}C method has been applied only to polymers having monomer units with length of two atoms (e.g., vinyl polymers)[4] or three atoms (e.g., polypropylene sulfide[5] and oxide[6]).

Of course the limitation of the method arises from the rapid attenuation of the substituent effect with distance, an effect which is of the δ type in the vinyl polymers and of the ϵ type in the other mentioned class of polymers.

The present work was undertaken with the aim of using the ^{13}C technique for determining triad sequences of polymers having monomer units with a length of four atoms, i.e., poly(1-methyltetramethylene) and 1,4-polypentadiene, exploiting the long-range stereospecific effect of a ζ methyl substituent on the chemical shift of the methyl group:



$$\overset{C_\zeta}{\overset{|}{C}}CCC\overset{C}{\overset{|}{C}}CCC\overset{C_\zeta}{\overset{|}{C}}$$



$$\overset{C_\zeta}{\overset{|}{C}}C{=}CCC\overset{C}{\overset{|}{C}}C{=}CC\overset{C_\zeta}{\overset{|}{C}}$$

The ζ effect shows up in the spectrum of polypropylene[7,8] in the fine structure of the methyl signal due to steric pentads. This spectrum has been assigned[9] with the aid of model compounds and rationalized[10] in conformational terms.

Considering that in the case of poly(1-methyltetramethylene) the overall chain conformation could be different because of the absence of the δ-methyl group, it seemed interesting to determine whether the ζ effect was observable even in this case.

Concerning unsaturated polymers such as the 1,4-polypentadienes there is not available in the literature any method for the quantitative evaluation of their tacticity index. For example X-ray and IR spectroscopy gave evidence[11–13] of the iso or syndiotactic structure of 1,4-polypentadiene without providing a determination of the amount of stereoregular structure.

Moreover by ^{13}C spectroscopy it was possible to characterize cis and trans stereoisomeric polypentadienes as well as 1,2 and 1,4 structures but not iso and syndiotactic stereoisomer in 1,4 structures.[14]

Thus the present investigation was undertaken also in view of the possible interest of quantitatively knowing the steric composition of substituted dienic polymers, which may be useful for studies of their polymerization mechanism.

II. Experimental Section

1. **Materials. Isotactic *trans*-1,4-polypentadiene (I)** was prepared[15] by γ irradiation of the inclusion compound between deoxycholic acid and *cis*-1,3-pentadiene. The sample studied had an optical activity corresponding to $[\alpha]^{25}{}_{\mathrm{D}}\ -21°$.

Isotactic *trans*-1,4-polypentadiene (II) was prepared[16] by γ irradiation of the inclusion compound between perhydrotriphenylene and *trans*-1,3-pentadiene.

Isotactic *cis*-1,4-polypentadiene (III) was obtained by using the catalytic system:[17] 0.08 mL of titanium tetraisopropylate and 0.3 mL of (C$_2$H$_5$)$_3$Al in 13.3 mL of dry benzene. The monomer was 2.5 mL of *trans*-1,3-pentadiene.

Syndiotactic *cis*-1,4-polypentadiene (IV) was prepared[18] by adding to 10 mL of dry benzene, 0.002 mL of H$_2$O, 0.09 g of (C$_2$H$_5$)$_2$-

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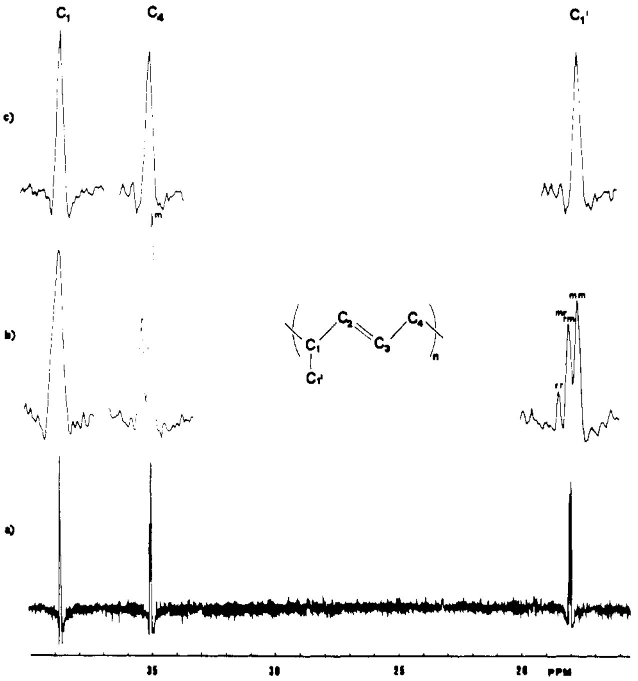


Figure 1. (a) Aliphatic region of the ^{13}C NMR spectrum of prevailingly isotactic 1,4-*trans*-polypentadiene (I). (b) Resonances of spectrum (a) on expanded scale. (c) Same as (b) for highly isotactic 1,4-*trans*-polypentadiene (II).

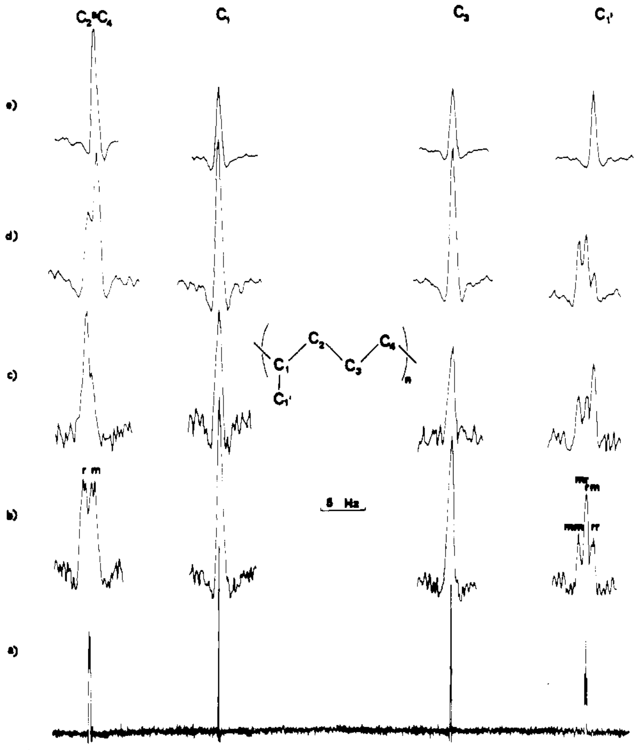


Figure 2. (a) ^{13}C NMR spectrum of atactic poly(1-methyltetramethylene). Expanded resonances of ^{13}C NMR spectra of: (b) atactic poly(1-methyltetramethylene) (V); (c) mechanical mixture of isotactic (30%) and syndiotactic (70%) poly(1-methyltetramethylene) (IX); (d) prevailingly isotactic poly(1-methyltetramethylene) (VI); (e) highly isotactic poly(1-methyltetramethylene) (VIII).

AlCl, 10 mL of *trans*-1,3-pentadiene, and finally 0.42 mg of Co(AcAc)$_2$.

Hydrogenation Procedure. Polypentadienes I, II, III, and IV and polyisoprene natural rubber were hydrogenated according to ref 19 in toluene as solvent and with a molar ratio 3:1 of *p*-toluene–sulfonylhydrazide to the monomeric units.

2. Spectra. Solutions 5% in 1,2,4-thichlorobenzene were observed at 410 K. ^{13}C NMR spectra were recorded with a Bruker HFX-90 spectrometer at 22.62 MHz in the PFT mode with broad-band proton decoupling. The deuterium signal for the lock was given by deuterated Me$_2$SO contained in a capillary tube. To store the FID 16K points were used with subsequent zero filling of 16K so that the final digital resolution in the transformed spectra was 0.005 ppm/address. The pulse width was 8 μs (90° pulse = 10 μs).

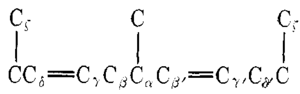
The line width of the signals was artificially reduced by multiplication of the FID with a suitable triangular function. The chemical shift differences measured in the spectra without line narrowing were the same as in the spectra with resolution enhancement.

III. Results and Discussion

1. *trans*-1,4-Polypentadiene. Two samples of this polymer have been examined, I and II. Sample I showed fine structure both in the methyl and in the CH signals (Figure 1). The methyl signal of the *mm* triad was assigned at δ 18.19 by comparison with the corresponding signal in the spectrum of the pure isotactic sample (II). The central peak of the methyl triplet in I was assigned to the two *mr* and *rm* triads and the high-frequency signal (δ 18.28) to the *rr* triad considering the relative intensity. The higher amount of *mm* triad relative to the *rr* triad is in agreement with the observed optical activity of the polymer I (see Experimental Section).

The CH signal of I shows two peaks: one signal (δ 35.01) coincident with the absorption of the isotactic sample II (δ 35.03); the other signal was attributed to the *r* diad. This assignment was checked by comparing the relative intensity of the signals due to the two diads with that observed (see section III.3) in the methylene absorption $C_{2,4}$ of the corresponding hydrogenated *trans*-1,4-polypentadiene, i.e., poly(1-methyltetramethylene) sample VI. As one can see in Figures 1 and 2 the observed intensity ratio is in both cases $m:r \simeq 2:1$.

The fact that the α-CH signal in *trans*-1,4-polypentadiene is sensitive only to the diad sequence could be rationalized in the following way. The chemical shift of C_α is affected by the relative configuration of the methyl carbon C_ζ from which it is separated by a γ–δ double bond



$$\overset{\displaystyle C_{\zeta}}{\overset{|}{C}}C_{\delta}{=}C_{\gamma}C_{\beta}\overset{\displaystyle C}{\overset{|}{C_{\alpha}}}C_{\beta'}{=}C_{\gamma'}C_{\delta'}\overset{\displaystyle C_{\zeta'}}{\overset{|}{C}}$$

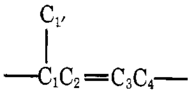
but it is insensitive to the relative configuration of the methyl carbon $C_{\zeta'}$ from which it is separated by the β'–γ' double bond. The β'–γ' double bond by imposing a rigid trans relation between C_α and $C_{\delta'}$ prevents any conformational change introduced by the methyl group $C_{\zeta'}$ from being observed on C_α. On the other side the presence of the γ–δ double bond does not result in a stiffening of the C_α–C_δ steric relation and consequently the conformational change induced by methyl C_ζ is still observable on C_α.

Recently the ^{13}C methyl spectrum of stereoirregular polypropylene has been interpreted[10] by the conformational changes induced on the central triad by the configuration of the rest of the chain. In that work was also reached the conclusion that the main mechanism in determining the stereochemical shift is the γ effect.

The present result is in agreement with the above theory extended to the methine carbon of *trans*-1,4 polypentadiene. In fact the γ effect of $C_{\delta'}$ on C_α is inhibited by the rigid trans double bond $C_{\beta'}{=}C_{\gamma'}$ while the γ effect of C_δ on C_α is still effective because of the flexibility of the $\sim C_\delta{=}C_\gamma C_\beta C_\alpha \sim$ fragment.

2. *cis*-1,4-Polypentadiene. The isotactic (III) and the syndiotactic (IV) samples were prepared for studying this polymer. The difference between the two configurations shows up (Table I) in the CH$_3$, in the CH, and moreover in the CH$_2$ signals. However, due to the absence of detectable amounts

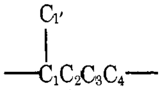
Table I
^{13}C Chemical Shifts of 1,4-Polypentadienes



$$-\overset{C_{1'}}{C_1}C_2{=}C_3C_4-$$

Sample	Double bond configuration	Tacticity	$C_{1'}$			C_1		C_4	
			mm	*rm* *mr*	*rr*	*m*	*r*	*m*	*r*
I	Trans	Prevailing isotactic	18.19	18.24	18.28	35.01	35.06	38.65	38.65
II	Trans	Highly isotactic	18.20			35.03		38.66	
III	Cis	Highly isotactic	18.64			30.45		33.60	
IV	Cis	Syndiotactic			18.76		30.57		33.64

Table II
Chemical Shifts of Poly(1-methyltetramethylene)



$$-\overset{C_{1'}}{C_1}C_2C_3C_4-$$

Sample	Tacticity	$C_{1'}$			C_1	C_2		C_3
		mm	*mr* *rm*	*rr*		*m*	*r*	
V	Atactic	18.01	17.97	17.93 17.94	31.26	35.91 35.92	35.95 35.96	22.85
VI	Prevailing isotactic	18.01	17.98	17.95	31.26			22.85
VII	Highly isotactic	18.00			31.27	35.91		22.85
VIII	Syndiotactic	18.00	17.97	17.94	31.26	35.91	35.95	22.86
IX	Isotactic + syndiotactic	18.00	17.97	17.93	31.25	35.92	35.94	22.85

of atactic segments in both III and IV the *mr* and *rm* signals could not be measured.

The spectrum of the syndiotactic sample synthesized for the present work contains other signals which were assigned[14] in the following way:

1,2 units	CH_3	δ 15.7	
	CH	δ 41.0	
	CH_2	δ 37.0	
trans 1,4 units	CH_3	δ 18.20 *mm*	
		δ 18.26 *mr rm*	
		δ 18.31 *rr*	CH_2 δ 38.67
	CH	δ 35.01 *m*	
		δ 35.05 *r*	

The chemical shift of the trans-1,4 units is in fair agreement with that observed in the authentic sample of atactic *trans*-1,4-polypentadiene (I).

The presence of trans atactic units in the syndiotactic *cis*-1,4-polypentadiene (IV) accounts for the *mr* signal observed in the corresponding hydrogenated polymer VII and in the mechanical mixture IX (see section III.3).

3. Poly(1-methyltetramethylene). As described in the Experimental Section poly(1-methyltetramethylene) was prepared by hydrogenation of either natural rubber or 1,4-polypentadiene. Hydrogenation was in any case complete, as shown by the absence of olefinic carbon signals in the ^{13}C spectrum, measured in $CDCl_3$ for analytical purposes. Moreover the ^{13}C spectrum did not show any difference in the samples obtained from the hydrogenation of the various unsaturated polymers, apart from the steric fine structure and the relative intensity of its components.

The high-resolution measurements were performed at high temperature on the samples of poly(1-methyltetramethylene) obtained in the following way: sample V, hydrogenation of polyisoprene (natural rubber); sample VI, hydrogenation of *trans*-1,4-polypentadiene (I); sample VII, hydrogenation of *trans*-1,4-polypentadiene (II); sample VIII, hydrogenation of *cis*-1,4-polypentadiene (IV); and sample IX, mechanical mixture of hydrogenated III and IV.

The chemical shifts of the polymers are reported in Table II and the spectrum of V is reproduced in Figure 2 together with the corresponding absorptions of VI, VII, and IX.

It can be seen that while the methyne C_1 and the methylene C_3 signals are singlets the methyl shift $C_{1'}$ is sensitive to the configurational triads and the methylene $C_{2,4}$ is sensitive to the diads.

Assignments of V were obtained straightforwardly by comparison with samples of known steric structure. It appears that the chemical shifts of a given triad are the same in the different samples independently of the hydrogenation substrate. In particular the isotactic signal *mm* was assigned by comparison with the spectrum of VII, the hydrogenated isotactic *trans*-1,4-polypentadiene. The *rr* signal was assigned by comparison with the spectrum of VIII, the hydrogenated syndiotactic *cis*-1,4-polypentadiene. The assignment of hetero and syndiotactic triads was checked with IX, a mechanical mixture of hydrogenated iso and syndiotactic *cis*-1,4-polypentadiene containing 70% by weight of the syndiotactic fraction.

The difference of about 0.03 ppm between the three different triad configurations indicates that the ζ effect is much lower than in the case of polypropylene where the corresponding effect is of the order of magnitude of 0.2 ppm. However, the sign of the effect is the same in the two polymers: namely a methyl with an *m* relation to the observed methyl has a shielding effect while a *r* relation is deshielding.

From the above data it appears that introducing a methyl group between the two methyls results in a considerable increase of the ζ effect.

The splitting of the high-field component in the methyl signal in sample V could be attributed to the effect of the steric pentads. However, this hypothesis shall be tested in further investigation.

Finally the methylene $C_{2,4}$ absorption was affected by the diad and triad configuration as recently reported in the literature.[20]

IV. Conclusions

The results of the present work show that the microstructure of polymers having monomer units with a length of four atoms can be determined by ^{13}C NMR spectroscopy. Long-range steric effects observed on the methyl group of both saturated and unsaturated polymers allow a measurement of the tacticity index. This nondestructive determination of tacticity avoids cumbersome chemical treatments such as hydrogenation or oxidative cleavage.

The chemical shift of the methyl signals due to the different steric sequences in poly(1-methyltetramethylene), i.e., $\delta_{mm} > \delta_{mr} > \delta_{rr}$, is inverted by introducing double bonds in the polymer chain both in cis and trans polypentadienes, i.e., $\delta_{rr} > \delta_{mr} > \delta_{mm}$.

This would suggest that, although the effect of the ζ substituent is stereospecific and additive both in hydrogenated and unsaturated polymers, the introduction of double bonds in the polymer chain changes the numerical values of the additive parameters for the meso and racemic ζ substituent.

The double bonds also slightly affect the CH absorption by removing the degeneracy observed in the saturated polymer.

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Compatibility in PVF_2/PMMA and PVF_2/PEMA Blends as Studied by Pulsed NMR

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ABSTRACT: The transient Overhauser effect in blends of PVF_2 and PMMA has been exploited to provide information on the degree of mixing of the two component polymers. Based upon the conviction that cross-relaxation effects imply near-neighbor dipolar interactions between protons and fluorine nuclei, the cross-relaxation data, supported by $T_{1\rho}$ and T_2 measurements, indicate that a substantial fraction of the two component polymers are intimately mixed in the amorphous regions. There are indications of premelting in the blends. Similar conclusions apply to PVF_2/PEMA blends.

Several recent studies[1-12] have demonstrated compatibility between certain polymer pairs over a wide range of blend composition. The extent to which compatibility exists has been decided according to criteria such as the transparency of the blend, consideration of the solubility parameters involved, and transition temperatures in the blend, in particular the glass transition temperature T_g.[6] Recently, the degree of polarization of the longitudinal Brillouin peaks has been used as a sensitive measure of compatibility.[13] Molecular weight, tacticity, and blend composition are factors which influence, in a crucial way, the ultimate compatibility achieved. For example, isotactic PMMA forms an incompatible system with PVC while syndiotactic PMMA and PVC are compatible.[6]

Even though two polymers are deemed compatible it remains to determine the topology, graininess, or homogeniety, or whatever other term appropriately characterizes the blend structure. Different experiments, such as microscopy, light scattering, NMR, and X-ray diffraction, examine this structure over decreasing characteristic lengths and combine to generate a composite picture of the blend structure. This paper presents NMR data, sensitive to short-range interactions, which emphasize results obtained from cross-relaxation experiments designed to augment line width and spin–lattice relaxation experiments and to circumvent complexities sometimes resulting from spin diffusion.[7,10,11]

The materials chosen for study are blends of poly(vinylidine fluoride)/poly(methyl methacrylate) (PVF_2/PMMA) and poly(vinylidine fluoride)/poly(ethyl methacrylate) (PVF_2/PEMA) blends of different composition which have received much attention of late by other methods.[12-14] In many respects these blends are particularly suited to study by pulsed NMR since preliminary experiments on the component polymers have been performed[11,15,16] and, additionally, cross-relaxation between the two unlike ^1H and ^{19}F spin sys-

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