via stable bridged ions. Although thiiranium ions are more stable than the corresponding thiirenium ions, smaller differences in the k_o/k_a ratios than in halogen additions are expected and were indeed observed.

The case of halogen addition to aryl derivatives that seemingly occur via open ions, yet with large k_o/k_a ratios (ca. 10^3), seemingly defies the above rationale. Here, other factors are probably involved: the differential electronic effect of the β-halogen linked to the intermediates,[23b,24] the different stability of the π complex precursors,[26c] the partial bridging of the transition states,[24] and differences in bonding energies could substantially favor the reactivity of alkenes over that of alkynes.

Finally, we wish to emphasize that the mechanism of electrophilic addition must be fully demonstrated before one undertakes to interpret the relative reactivities of alkenes and alkynes, since different modes of reaction may prevail. As an example, the syn additions of hydrogen halides[8,21,27] and chlorine[53] in nonpolar or weakly polar solvents have been explained in terms of syn-oriented tight ion pairs which collapse to products before equilibration is attained. However, there is not, as yet, enough evidence to rule out an alternative mechanism, a formally forbidden $2\sigma + 2\pi$ suprafacial cycloaddition, which may become allowed[54] when the two molecules have sufficiently different polarity.

We are indebted to our colleagues G. Capozzi, V. Lucchini, and G. Scorrano for helpful discussion, to our co-workers cited in the references, and to C.N.R., Rome, for continuous financial support. G.M. thanks also the Chemistry Department of Texas Tech University, Lubbock, TX, for its hospitality during the preparation of the manuscript.

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^{13}C NMR Chemical Shifts and the Microstructure of Polymers

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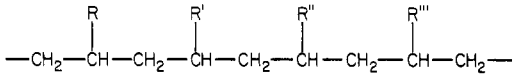
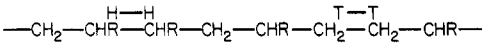
Just as the primary structures of proteins determine their biological functions, so too the microstructures of synthetic polymers fundamentally influence their unique physical properties. Whether a polymer is an amorphous glassy or rubbery solid with the ability to deform under stress without rupture or a crystalline solid possessing dimensional stability and high tensile strength depends on its microstructure, i.e., the detailed architecture of its long chains.

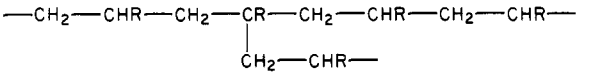
To determine the microstructure of the schematic vinyl polymer



the types and distribution of side chain substituents R, R′, R″, R‴, etc. must be specified along with their configurational arrangement, or stereosequence, as illustrated in Figure 1 for polypropylene, where all R, R′, R″, R‴, etc., are methyl groups. Furthermore, in terms of physical properties it is also important to know if head-to-head (H–H) or tail-to-tail (T–T) monomer addition



or any branching occurs during polymerization.



Aside from X-ray diffraction studies of stereoregular, crystallizable polymers, there was no method for the direct experimental measurement of vinyl polymer stereosequence until the technique of high-resolution NMR was applied to polymers.[1] Of the two nuclei ^1H and ^{13}C, which possess spin and are common to synthetic polymers, ^1H initially served as the spin probe in NMR polymer studies. However, though ^1H is more abundant than ^{13}C, ^1H NMR spectra of polymers suffer from a narrow dispersion of chemical shifts and extensive ^1H–^1H spin–spin coupling. ^{13}C NMR as currently practiced does not suffer from these difficulties.

The advent of proton-decoupled spectra recorded in the Fourier transform mode has catapulted ^{13}C NMR spectroscopy into the position as the method of choice for determining polymer microstructure.[2-4] The distribution of monomer units in binary and ternary copolymers,[3,4] the stereoregularity of asymmetric vinyl polymers,[4] the amounts and types of vinyl polymer defect structures[5] produced by other than head-to-tail

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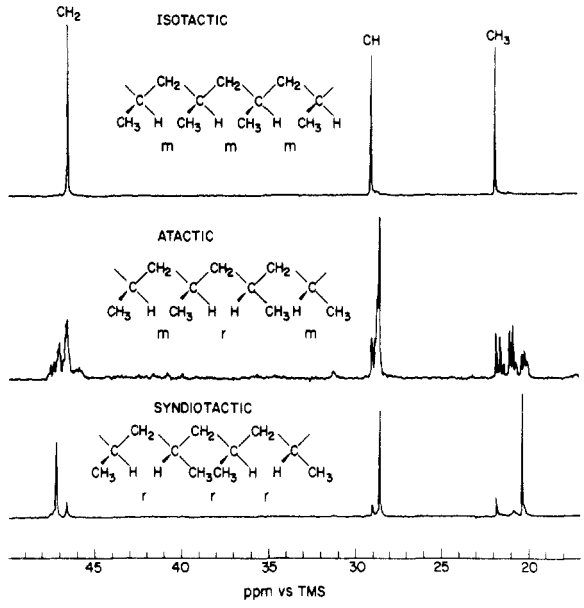

Figure 1. ^{13}C NMR spectra at 25 MHz for PP's dissolved (20% w/v) in 1,2,4-trichlorobenzene at 140 °C. Schematic representation illustrates *m* (meso) and *r* (racemic) dyads and polymer chain tacticity. Isotactic ∝ ....*mmmmm*....., syndiotactic ∝ ..*rrrrr*....., atactic or heterotactic ∝ ....*mmrmrrmr*.....

addition of monomer units, and the presence of branching[6] have all been fruitfully studied with high-resolution ^{13}C NMR spectroscopy. As an example, in the case of polypropylene (PP) by employing different catalysts and altering polymerization conditions, polymers with different stereoregularities can be produced. The ^{13}C NMR spectra of isotactic, atactic, and syndiotactic PP are presented in Figure 1. By comparing the spectra in Figure 1, the isotactic and syndiotactic resonances in the "atactic" PP spectrum can be identified.

This approach to the assignment of ^{13}C NMR polymer spectra requires preparation of polymers or model compounds possessing known microstructural features. Furthermore, as can be seen from the expansion of the ^{13}C NMR spectrum of "atactic" PP[7] presented in Figure 2, many resonances appear in addition to those assignable by comparison to the spectra for isotactic and syndiotactic PP (see Figure 1).

An example of the richness in detailed microstructural information provided by ^{13}C NMR is presented in Figure 2a. In the methyl carbon region of the ^{13}C NMR spectrum of "atactic" PP we observe roughly 20 resonance peaks out of a possible 36 corresponding to stereosequences at the heptad level[1] (see Figure 3a). This means that ^{13}C NMR spectroscopy can distinguish among the majority of different arrangements possible for a given methyl carbon with the three nearest neighboring methyls on either side along the PP chain. The ^{13}C NMR spectrum of PP is sensitive to stereosequences extending over six backbone bonds. It is precisely this long-range sensitivity to microstructural detail which makes ^{13}C NMR potentially so valuable in determining polymer structure.

To realize this potential the connections between microstructural features and the corresponding chemical shifts must be established. The ability to predict the ^{13}C NMR chemical shifts expected for each type of carbon atom in all possible structural environments would clearly be valuable, permitting the full potential of this spectroscopic technique to be realized and thereby eliminating the need to synthesize model compounds and polymers of known microstructure.

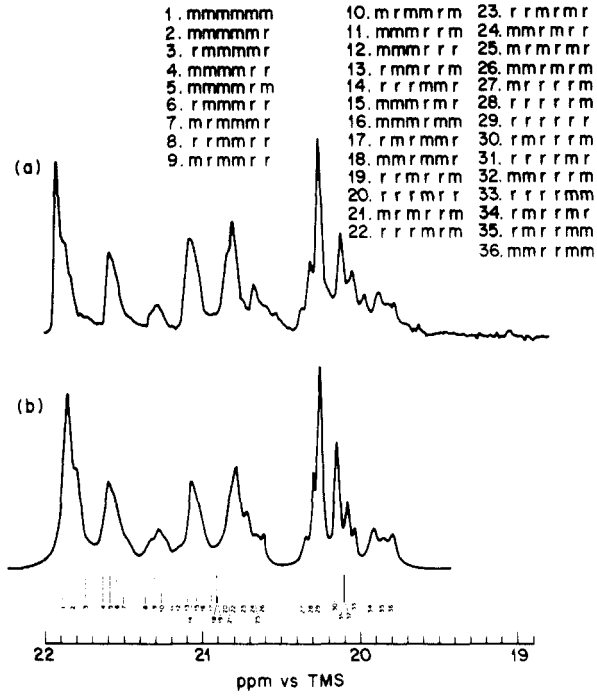

Figure 2. (a) ^{13}C NMR spectrum at 90.52 MHz of the methyl carbon region in atactic PP in 20% w/v *n*-heptane solution at 67 °C. (b) Simulated spectrum obtained from calculated chemical shifts, as represented by the line spectrum below, assuming Lorentzian peaks of <0.1 ppm width at half-height.

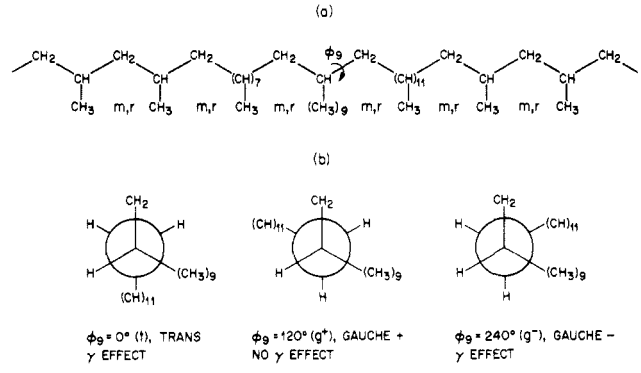

Figure 3. (a) Portion of a polypropylene chain in the all-trans, planar zig-zag conformation containing a heptad stereosequence. (b) Newman projections along bond nine in (a) illustrating the γ effect on the central methyl carbon $(CH_3)_9$.

^{13}C NMR studies[8-11] of paraffinic hydrocarbons have led to substituent rules useful in the prediction of their chemical shifts. If a carbon has substituents (carbon atoms) in the α and/or β position, then for each such substituent its resonance is shifted ca. 9 ppm downfield

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Table I
^{13}C NMR Chemical Shift Differences $\Delta\nu$ (ppm) of the 9-Methyl Carbons in 3,5,7,9,11,13,15-Heptamethylheptadecane Stereoisomers

	T = 20 °C, γ = -5.4		T = 80 °C, γ = -5.4		T = 140 °C, γ = -5.2	
stereoisomer	obsd[18-20]	calcd[23]	obsd[18-20]	calcd[23]	obsd[18-20]	calcd[23]
mmmmmr	0	0	0	0	0	0
rmmmrr	-0.39	-0.33	-0.30	-0.28	-0.22	-0.21
mrmmrr	-0.68	-0.61	-0.59	-0.52	-0.41	-0.41
mmmrrr	-0.80	-0.64	-0.77	-0.70	-0.76	-0.69
rmmrrm	-0.80	-0.74	-0.83	-0.76	-0.76	-0.72
rmmrmr	-0.91	-0.90	-0.96	-0.91	-0.91	-0.85
rrmrrr	-1.09	-1.02	-1.04	-1.00	-0.91	-0.90
rrmrmm	-1.25	-1.22	-1.18	-1.17	-1.04	-1.04
mrmrmr	-1.25	-1.25	-1.18	-1.18	-1.04	-1.05
mrrrrr	-1.53	-1.58	-1.54	-1.45	-1.45	-1.45
rmrrrr	-1.82	-1.84	-1.75	-1.77	-1.58	-1.60
mmrrmr	-2.07	-2.15	-1.90	-1.99	-1.69	-1.76

(deshielding effect) from the chemical shift of an unsubstituted carbon. On the other hand γ substituents produce an upfield chemical shift of 2–3 ppm (shielding effect). It is this shielding effect produced by γ substituents which can be employed to predict the ^{13}C NMR chemical shifts observed in polymers.

Although the source of the γ effect is not completely understood,[12] it is apparent that it is conformationally sensitive.[13,14] Not only must a carbon atom have a γ substituent[15] to experience the associated upfield chemical shift, but the γ substituent must also be in a gauche[13,14] arrangement with the observed carbon, as depicted in Figure 3, for the $(CH_3)_9$ methyl carbon in the PP heptad fragment. As an example, the γ effect provides us a means for determining the amount of gauche character possessed by the central backbone bond 9 which determines the arrangement of carbon atoms $(CH_3)_9$ and $(CH)_{11}$, information that is fundamental to the conformational characteristics[17] of a polymer chain.

To evaluate the effect of γ substituents on the ^{13}C NMR chemical shifts observed in a polymer we must be able to estimate the amount of gauche character possessed by its constituent bonds and the magnitude of the shielding effect produced by a γ substituent in a gauche arrangement with an observed carbon. Rotational isomeric state (RIS) models have been developed[17] for polymers by considering all backbone bonds each restricted to a few rotational states by thier inherent rotational barriers. For C–C single bonds usually three states, trans (t) ($\phi = 0°$) and gauche ± ($g^{\pm}$) ($\phi = \pm 120°$), are assumed (see Figure 3).

If the energy differences between the rotational states can be determined, then matrix multiplication techniques[17] can be utilized to calculate properties of the chain, such as dimensions and dipole moments, which are averages over all of its many different conformations. In a like manner it is possible to evaluate the rotational state probabilities $P_t, P_{g\pm}$ for any given backbone bond in the polymer chain.

Calculation of ^{13}C NMR Chemical Shifts in Polymers

Zambelli and co-workers[18-20] have synthesized several stereoisomers of the PP model compound 3,5,7,9,11,13,15-heptamethylheptadecane (HMHD) each with ^{13}C-enriched methyl groups in the 9 position and have recorded their ^{13}C NMR spectra (see Figure 3, where addition of terminal methyl groups to the PP heptad fragment depicted yields HMHD). This series of compounds affords an excellent test of the γ-effect method of calculating stereosequence-sensitive ^{13}C NMR chemical shifts.

Suter and Flory[21] developed a RIS model describing the conformational characteristics of PP. This conformational model correctly predicts the dimensions and their temperature dependence, the epimerization equilibria, and the vicinal ^1H NMR proton–proton coupling constants[22] observed for PP and its oligomers in solution as a function of stereoregularity. Using thier RIS model we calculated[23] conformational probabilities for the 8th and 9th bonds in each HMHD stereoisomer (see Figure 3). These are the bonds about which rotation can produce gauche arrangements between $(CH_3)_9$ and $(CH)_7$ or $(CH)_{11}$.

The number of such γ interactions experienced by $(CH_3)_9$ in each stereoisomer was recorded and multiplied by a γ effect least squares fitted to achieve agreement with the observed ^{13}C chemical shifts reported by Zambelli.[20] As can be seen in Table I, γ = -5.3 ppm successfully reproduces the ^{13}C chemical shifts observed for $(CH_3)_9$ in the 12 synthesized stereoisomers of HMHD over the temperature range 20–140 °C. The long-range sensitivity of the $(CH_3)_9$ chemical shifts can be explained by the much shorter range γ interactions whose probabilities of occurrence are indeed predictably influenced by longer range stereosequence effects.

Polypropylene

The ^{13}C NMR chemical shifts of the much shorter PP model compounds 3,5-dimethylheptane (*m* and *r*), 3,5,7-trimethylnonane (*mm*, *mr* or *rm*, *rr*), and 3,5,7,9-tetramethylundecane (*mmm*, *mmr* or *rmm*, *mrm*, *rrm*

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(15) For an alternate explanation of the γ effect, see ref 16. Beierbeck and Saunders[16] believe that removal of a hydrogen on the β substituent and not the γ substituent itself is responsible for the upfield shifts caused by a gauche γ substituent. We have not been able to explain vinyl polymer ^{13}C NMR spectra based on this interpretation.
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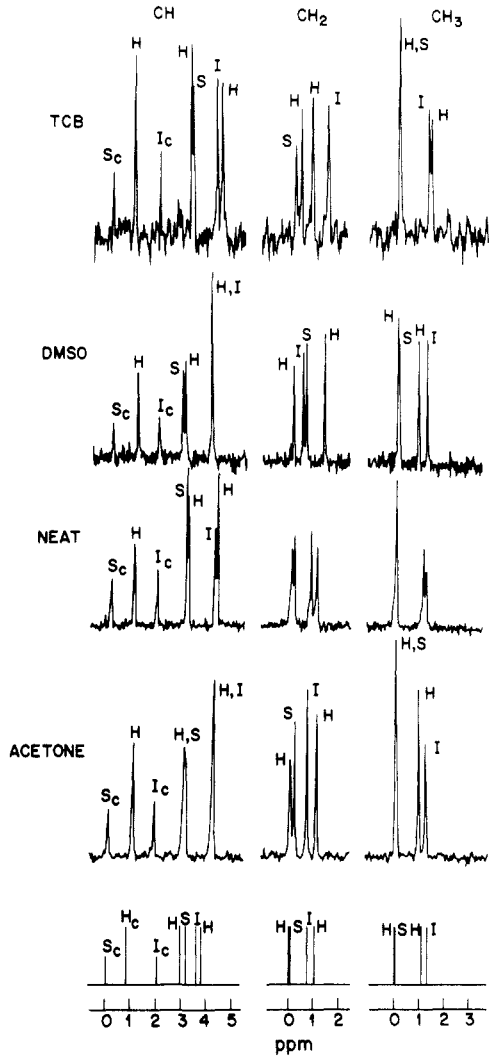


Figure 4. Comparison of measured (33 °C) and calculated ^{13}C chemical shifts of the TCH isomers in several solvents. The most downfield resonance in each of the three spectral regions is assigned a 0.0-ppm chemical shift.

or *mrr*, *rmr*, *rrr*) have also been calculated with the Suter–Flory[21] RIS model using $\gamma = -5$ ppm. Agreement between predicted and observed chemical shifts is excellent for all three carbon types (CH, CH_2, CH_3).[24,25] With the confidence gained in our ability to predict the ^{13}C NMR chemical shifts in PP model compounds using the Suter–Flory[21] RIS model and $\gamma = -5$ ppm, we proceed to treat PP itself.

In Figure 2 we compare the observed spectrum of "atactic" PP with the chemical shifts calculated (simulated and line spectra) for each of the heptad stereosequences of the methyl carbon atoms.[7] The agreement, and consequently the assignment of observed resonances to specific stereosequences, is excellent. In addition, Suter and Nuenschwander[21b] have used our calculated chemical shifts to simulate the observed methylene carbon region of the ^{13}C NMR spectrum of atactic PP also with excellent results.

It now becomes clear how the chirality of an α-CH

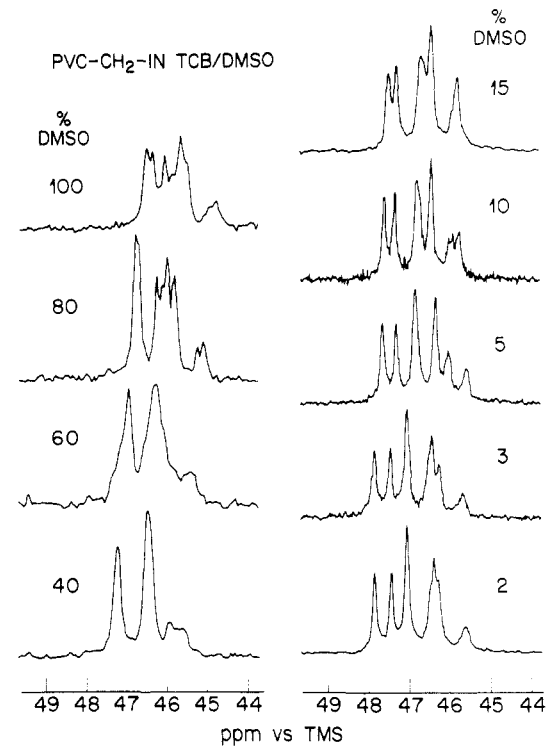


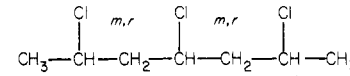
Figure 5. Methylene region of the ^{13}C NMR spectra (90.52 MHz) of atactic PVC solutions (20% w/v in 1,2,4-trichlorobenzene/Me_2SO) at 120 °C with 2, 3, 5, 10, 15, 40, 60, 80, and 100% Me_2SO.

carbon seven bonds removed can influence the methyl resonance position. As an example, compare chemical shifts of the methyl heptad stereosequences 27,28, and 29. Each of these heptads contains the *rrrr* pentad and differs only in the terminal dyads (*m* or *r*). Yet the central methyl carbon in each heptad resonates at a different frequency resulting from small differences in the trans and gauche content of the backbone bonds adjacent to the observed methyl carbon (bonds 8 and 9 in Figure 3). Clearly the long-range stereosequence dependence of the ^{13}C chemical shifts results from a predictable dependence of the much shorter range γ interactions due to changes in local bond conformations.

In addition, the same γ effect ($\gamma = -5$ ppm) has been employed to predict[26,27] the ^{13}C NMR chemical shifts observed[28–32] in ethylene–propylene copolymers as a function of monomer sequence and stereoregularity. Agreement between the observed and calculated chemical shifts is excellent.

Chloro-Substituted Polymers and Copolymers

The 2,4,6-trichloroheptanes (TCH)



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have been studied[33] as model compounds for the stereosequences in poly(vinyl chloride) (PVC). Figure 4 presents a comparison of the observed and calculated ^{13}C NMR chemical shifts for the carbon atoms in the three stereoisomers of 2,4,6-trichloroheptane (TCH),[34] i.e., I ∝ isotactic (*mm*), S ∝ syndiotactic (*rr*), and H ∝ heterotactic or atactic (*mr* or *rm*). The following γ effects were employed in the chemical shift calculations based on the RIS model derived from epimerization studies of TCH and PVC by Flory and Pickles:[33] $\gamma_{CH_2 \text{ or } CH_3CH} = -2.5$ ppm, $\gamma_{CH,CH_2 \text{ or } CH_3} = -5.0$ ppm, and $\gamma_{CH,Cl} = -3.0$ ppm, where $\gamma_{a,b}$ is the upfield shift observed at carbon a due to atom b, which is γ to a and in a gauche arrangement.

There is a close correspondence between the calculated and observed chemical shifts of the methyl and methine carbons in a variety of solvents. On the other hand, the chemical shifts observed for the methylene carbons are extremely solvent sensitive and appear to agree with the calculated shifts only when observed in acetone.

Solvent sensitivity of the methylene carbon chemical shifts is also observed in PVC (see Figure 5). Gradual addition of Me_2SO to PVC dissolved in 1,2,4-trichlorobenzene causes certain of the observed methylene resonances to shift dramatically, while the methine carbon region (not shown) is virtually independent of Me_2SO addition and agrees quite well with the predicted ^{13}C chemical shifts calculated[34] to the pentad level of stereosequence.

The solvent-dependent behavior of the methylene carbon chemical shifts must be a specific nonconformational effect, because the same bonds are involved in the γ effects of both the methine and methylene carbons. Also the methylene carbons in the meso and racemic isomers of 2,4-dichloropentane exhibit[35] various degrees of nonequivalence in different solvents, and yet there are no nonhydrogen atoms γ to these methylene carbons. We are currently attempting to learn the origins of the solvent sensitivity of the methylene carbon chemical shifts observed in PVC and its model compounds, which is not observed in the spectra recorded for PP.[7]

With the knowledge of γ effects gained from our study[34] of PVC and its model compounds, we are able to calculate the ^{13}C chemical shifts expected for carbon atoms in the various microstructures present in ethylene–vinyl chloride (E–VC) copolymers (see Figure 6). The necessary bond rotation probabilities are obtained from the RIS model developed by Mark[36] for E–VC copolymers.

The ^{13}C chemical shifts predicted[37] for the methine and methylene carbons in E–VC copolymers are presented in Figure 6. Predicted methine carbon resonances occur in three well-separated regions encompassing nearly 6 ppm in overall spread due to different E and VC monomer sequence distributions. Methylene carbon chemical shifts are expected to range over 30 ppm depending on E–VC copolymer microstructure.

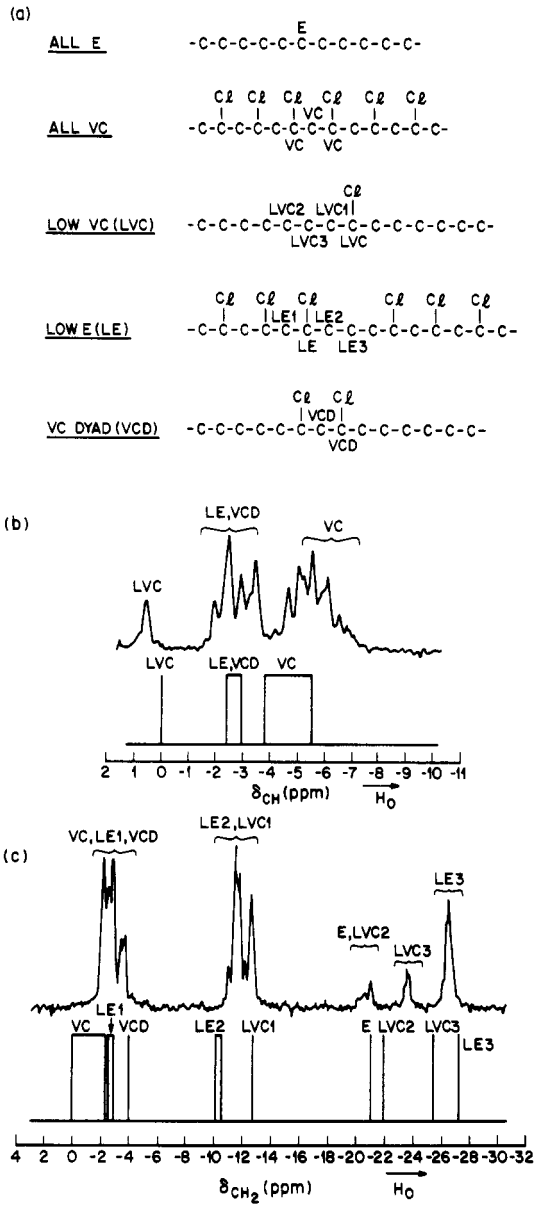

Figure 6. (a) Representative microstructures in E–VC copolymers. ^{13}C chemical shifts observed for reduced PVC[41] and calculated at 100 °C for the methine (b) and methylene (c) carbons residing in the various E–VC microstructures illustrated here. The widths of the calculated resonances result from chemical shift dispersion produced by the stereoregularity of adjacent VC units.

The greater sensitivity of the methylene carbon chemical shifts to E–VC microstructure results[37] from from the different number of Cl atoms which may be β[38] to a methylene carbon depending on E–VC monomer sequence. Each such β-Cl substituent serves to shift the methylene carbon resonance ca. +10 ppm downfield.[38]

Also presented in Figure 6 is the ^{13}C NMR spectrum of partially reduced PVC,[39] which serves as a model[40] E–VC copolymer. Note the close correspondence[41] between observed and calculated ^{13}C chemical shifts in both the methine and methylene regions of the spectrum.

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(40) In the reduction of PVC[41] Cl atoms are removed, yielding E–VC copolymers.

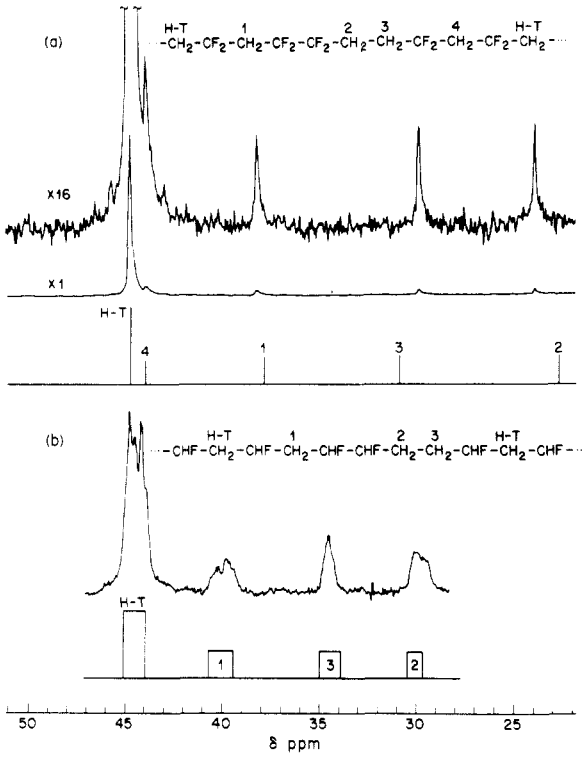

Figure 7. Methylene regions of the 25-MHz ^{13}C NMR spectra of PVF_2 (a) and PVF (b) at 25% w/v in ethylene carbonate solution (95 °C). Spectra recorded with simultaneous proton and fluorine broad-band decoupling. The labeled line spectrum (a) represents the calculated ^{13}C chemical shifts for PVF_2. The spreads in the calculated chemical shifts for PVF (b) are due to stereosequence effects.

The ^{13}C chemical shifts calculated for E–VC copolymers also compare favorably[37] with the chemical shifts reported for the methine and methylene carbons in chlorinated polyethylenes by Keller and Mugge.[42] It appears that comparison of the ^{13}C NMR spectra of E–VC copolymers with the calculated chemical shifts presented in Figure 6 will aid in the determination of thier microstructure.

Fluoro Polymers

The ^{13}C NMR spectrum of the methylene carbons in poly(vinylidene fluoride) (PVF_2) is presented in Figure 7a. Resonances of minor intensity are produced by head-to-head:tail-to-tail (H–H:T–T) defect structures which were not found to be present in PP or PVC. The line spectrum inserted in Figure 7a is calculated by using the RIS model developed for PVF_2 by one of the present authors[43] and the following γ and β effects: $\gamma_{CH_2,CH_2} = -5.3$, $\gamma_{CH_2,CF_2} = -2.2$, $\gamma_{CH_2,F} = -3.8$, and $\beta_{CH_2,2F} = +8.0$ ppm.

The observed effect of H–H:T–T defect structure on the ^{13}C chemical shifts of the PVF_2 methylene carbons are faithfully reproduced by the calculated shifts. This enables the assignment of minor resonances to specific CH_2 carbons in the vicinity of the defect.

When the γ and β effects derived from our ^{13}C NMR study of PVF_2 are applied to poly(vinyl fluoride) (PVF), we obtain the results shown in Figure 7b. ^{13}C chemical shifts calculated for the methylene carbons closely mimic the observed resonances. The effects of stereosequence and H–H:T–T defect structure are both accounted for successfully by the predicted chemical shifts. This agreement lends support to the γ effects derived for PVF_2 and provides confirmation for the RIS model developed for PVF by one of us.[44] We have for the first time in the case of PVF used the γ-effect method of calculating chemical shifts to obtain conformational information, as well as the usual microstructural details.

The γ and β effects used to calculate the ^{13}C NMR chemical shifts in PVF_2 and PVF also lead to calculated chemial shifts[45] which agree with the resonances observed in two additional fluoro polymers, poly(fluoromethylene) and poly(trifluoroethylene). The assignments made by comparing calculated ^{13}C chemical shifts with the observed spectra, such as in Figure 7, are confirmed by ^{19}F NMR studies[46–49] performed on the same polymers.

Concluding Remarks

As evidenced by the many examples discussed in this Account,[50] it appears possible to predict the ^{13}C NMR spectra[53] of asymmetric polymer chains. Because of the nature of the method employed in calculating the ^{13}C chemical shifts (γ effects), our ability to predict the ^{13}C NMR spectrum of a polymer means we have knowledge of both its microstructure (stereosequence, monomer sequence, defect content) and its conformational characteristics. Obviously this information is fundamental to the many varied physical properties unique to polymers.

This approach would appear generally applicable to the study of ^{13}C NMR chemical shifts in conformationally flexible organic molecules as evidenced by our successful prediction of the ^{13}C chemical shifts in several small oligomeric model compounds. The application of the γ-effect method of calculating ^{13}C NMR chemical shifts to low molecular weight organic molecules would likely yield useful information regarding thier conformations and configurations.

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(41) If the differences between the β effects produced by secondary and tertiary carbons are accounted for, then the agreement is improved. As an example, $\beta_{CHCl,CH_2} = +6.8$ ppm as deduced from data in ref 38 on 1-chloroalkanes, and $\beta_{CHCl,CHCl} = +6.2$ ppm from ref 34. Methine carbons LVC in Figure 6 should be moved downfield 0.6 ppm and VC methine's upfield 0.6 ppm from the LE and VCD methine carbons, because LVC is β to two CH_2, LE and VCD are β to one CH_2 and one CHCl, and VC is β to two CHCl carbons.

(42) F. Keller and C. Mugge, *Faserforsch. Textiltech.*, **27**, 347 (1976).

(43) A. E. Tonelli, *Macromolecules*, **9**, 547 (1977). The RIS model developed in ref 43 correctly describes the observed dimension[43] and dipole moments (G. Khanarian, unpublished observations) of PVF_2.

(44) A. E. Tonelli, *Macromolecules*, **13**, 73 (1980).

(45) A. E. Tonelli, F. C. Schilling, and R. E. Cais, *Macromolecules*, **14**, 560 (1981).

(46) V. M. Görlitz, R. Minke, W. Trautvetter, and G. Weisgerber, *Angew. Makromol. Chem.*, **29/30**, 137 (1973).

(47) R. C. Ferguson and E. G. Brame, Jr., *J. Phys. Chem.*, **83**, 1397 (1979).

(48) R. E. Cais, *Macromolecules*, **13**, 806 (1980).

(49) A. E. Tonelli, F. C. Schilling, and R. E. Cais, in preparation.

(50) The γ effect method has also been used successfully to calculate the ^{13}C NMR chemical shifts expected in polystyrene and its oligomers[51] and in polypeptides.[52]

(51) A. E. Tonelli, *Macromolecules*, **12**, 252 (1979).

(52) A. E. Tonelli, *J. Am. Chem. Soc.*, **102**, 7635 (1980).

(53) It appears[49] that the conformations, configurations, and defect structures of fluorine-containing polymers can also be studied by ^{19}F NMR spectroscopy via the γ-effect method. In fact the γ effects experienced by fluorine atoms involved in three-bond gauche arrangements with either another fluorine or a carbon atom correspond to upfield chemical shifts of 10 to 30 ppm relative to their trans arrangement. ^{19}F NMR provides a potentially more sensitive means than ^{13}C NMR to determine the microstructures of fluorine-containing polymers because of the much larger γ effects experienced by the ^{19}F nucleus ($\gamma_{F,F \text{ or } C} \simeq -10$–$30$ ppm, $\gamma_{C,C \text{ or } F} = -2$ to -5 ppm).