Polymer Nuclear Magnetic Resonance Spectroscopy. XVI. Poly(vinyl chloride) at 220 MHz

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ABSTRACT: The proton spectrum of poly(vinyl chloride) prepared by free-radical polymerization has been studied at 220 MHz and interpreted in terms of pentads for the α protons and tetrads for the β protons. The chemical shifts are in good agreement with those reported elsewhere using selectively deuterated polymers. The magnitudes of the vicinal coupling constants indicate that in the thermodynamically good solvents employed, the isotactic dyads are in approximate equilibrium between the conformations which, if repeated, result in a 3_1 helix, whereas syndiotactic dyads are probably in the conformation with the backbone in a planar zigzag structure. The tetrad and pentad relative intensities are consistent with Bernoullian chain propagation statistics, with a value P_m (the probability of isotactic placement) of 0.43.

The proton nmr spectrum of poly(vinyl chloride) (PVC) in solution has been the subject of many investigations of the stereochemical structure of this polymer.[1–17] Experiments using decoupling and selective deuteration techniques have been particularly useful. Thus, using proton–proton spin decoupling at 60 MHz, Bovey, Anderson, Douglass, and Manson[5] clearly observed dyads and triads, and Yoshino and Komiyama[8] reported tetrad fine structure in the deuterium-decoupled spectrum of poly(vinyl chloride-α,*cis*-β-d_2). Recently Cavalli, *et al.*,[17] and Johnsen and Kolbe[16] have reported well-resolved pentad resonances in the deuterium-decoupled 100-MHz spectrum of poly(vinyl chloride-β,β-d_2). Several studies[6,7,12,14,15,17] of the variation of PVC configuration with polymerization temperature have shown that in a free-radical process the chain propagation proceeds according to Bernoullian statistics with syndiotactic placements favored by amounts ranging from 300 to 600 cal/mol.

The object of the present work was to utilize previously obtained experimental data on tetrad and pentad chemical shifts from deuterated polymers in calculations of the spectrum of undeuterated polymers in order to obtain useful information on the vicinal coupling constants, which are related in a well-known fashion to the local chain conformation. For this purpose, we took advantage of the increase in chemical shifts of spectra at 220 MHz compared to those at 100 MHz, which better defines the spin-coupling fine structure by spreading the spectrum over a wider range.

Experimental Section

Poly(vinyl chloride) prepared by a free-radical process was obtained commercially from Monomer–Polymer Laboratories. Poly(vinyl chloride-α-d_1) was prepared in this laboratory by benzoyl peroxide initiation in 10% v/v cyclohexanone solution at 50°. This sample had been used in an earlier study[15] of chain configuration.

Nmr spectra were obtained at 140° using a Varian HR-220 spectrometer. For the undeuterated polymer 5% (w/v) solutions in chlorobenzene, *o*-dichlorobenzene, and pentachloroethane were employed with hexamethyldisiloxane as internal reference. The poly(vinyl chloride-α-d_1) was run in a 15% solution in chlorobenzene with TMS as reference.

Spectrum calculations were performed on a GE 645 computer using a program written by L. C. Snyder and R. L. Kornegay of Bell Telephone Laboratories. Spectra were plotted on a Stromberg-Carlson 4020 microfilm printer as the sum of Lorentzian line shapes of suitable width.

Results and Discussion

Figure 1 shows the proton spectrum of poly(vinyl chloride-α-d_1) at 220 MHz. Although the deuterium nuclei are not decoupled with a second radiofrequency irradiating field, the resolution is adequate to distinguish all tetrads. As indicated in the figure, the spectrum may be interpreted in terms of two singlets from the homosteric *mrm* and *rrr* tetrads[18] and four AB spectra with a geminal coupling of 15 Hz from the heterosteric *mmm*, *mmr*, *rmr* and *mrr* tetrads. The assignment is very similar to that given by Yoshino and Komiyama.[8] Comparing the chemical shifts in the series *mmm*, *mmr*, *rmr*, it is seen that the configuration of the second nearest asymmetric center has as large an effect on the differentiation of *syn–anti*[19] β-proton

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(19) The terms *syn* and *anti* distinguish the methylene protons in *m* dyads on the basis of their orientation with respect to the α substituent in the planar zigzag conformation.

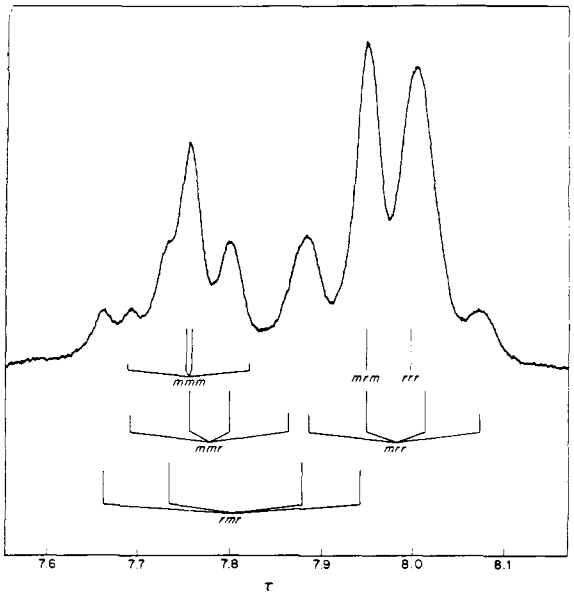

Figure 1. 220-MHz proton spectrum of PVC-α-d_1, 15% in chlorobenzene at 140°.

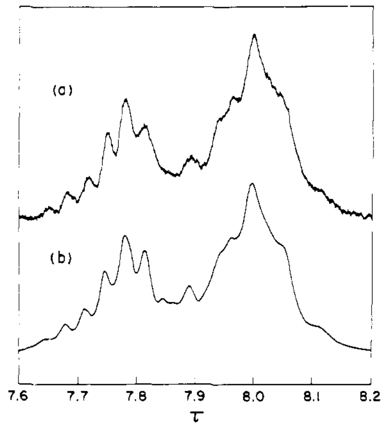

Figure 2. (a) 220-MHz β-proton spectrum of PVC, 5% in chlorobenzene at 140°. (b) Spectrum calculated with parameters in Table I.

chemical shifts as the configuration of the adjacent α carbon. The fact that the least heterosteric character is found in the *mmm* tetrad indicates that the contributions to the *syn–anti* proton chemical shift difference from the nearest and next nearest α carbons of the same configuration are similar in magnitude but opposite in sign. In contrast, the tetrad chemical shifts in poly(methyl methacrylate)[20] and polypropylene[21] show a much more rapid attenuation of the influence of the α-carbon configuration, and in other polymers such as poly(vinyl methyl ether)[22] and poly(vinyl acetate)[23] only dyads have been resolved at 100 MHz. A second consistent trend in PVC is the upfield movement of the mean tetrad chemical shift with the replacement of *m* dyads by *r*. Such a trend is also observed in poly(methyl methacrylate).[20]

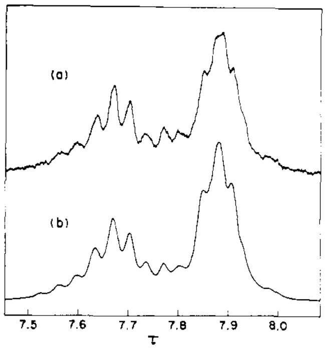

Figure 3. (a) 220-MHz β-proton spectrum of PVC, 5% in pentachloroethane at 140°. (b) Spectrum calculated with parameters in Table I.

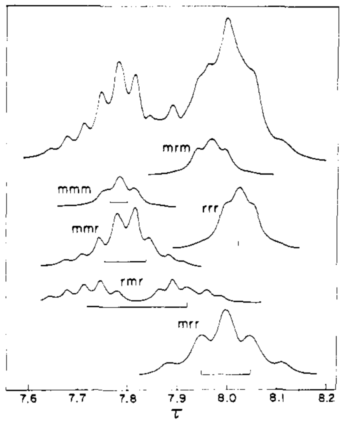

Figure 4. Tetrad spectra comprising the calculated spectrum in Figure 2.

Figures 2 and 3 show the 220-MHz experimental and calculated methylene proton spectra of PVC at 140° in chlorobenzene and pentachloroethane, respectively. Figure 4 shows the individual tetrad spectra whose sum is the calculated spectrum for the chlorobenzene case. All spectra were calculated using a six-spin cyclic dimer (AA′BB′CC′) model. Trial calculations of the *mrr* tetrad spectrum using a nine-spin cyclic model, which should better represent the actual polymer chain but which requires much more computer time, showed, however, that the small changes noticeable in a "stick" plot were completely obscured when the spectrum was plotted using a Lorentzian line shape of suitable width. The methylene spectra of the *mmm*, *mmr*, and *rmr* tetrads each form approximately the AB part of an ABX_2 system. In PVC it is not known whether the *syn* or *anti* β proton is the less shielded. The *mrm* and *rrr* methylene protons each give approximately AA′XX′ spectra while the *mrr* tetrad is an ABXX′ system. For the chlorobenzene solution, good estimates of the chemical shifts and geminal coupling constants were obtained from the spectrum of PVC-α-d_1 shown in Figure 1 and only minor changes in the chemical shifts, due presumably to different concentrations, were necessary to obtain good agreement with the experimental spectrum. For the other two solutions a little more effort was required but the process was aided by assuming that the shielding order remained substantially unchanged from the chlorobenzene solution. The determination of the vicinal

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TABLE I

	Solvent			
	Chlorobenzene	*o*-Dichlorobenzene	Pentachloroethane	Relative intensity
m centered tetrads				
mmm ν_{A}	−44.5	−40.5	−48.5	0.080
ν_{B}	−46.0	−32.5	−42.5	
mrm ν_{A}	−46.0	−42.5	−48.5	0.208
ν_{B}	−28.5	−28.5	−32.5	
rmr ν_{A}	−55.0	−49	−59.5	0.141
ν_{B}	−10.5	−10.5	−16.5	
J_{AB}	−15	−15	−15	
J_{AX}	7.5	7.5	7.5	
J_{BX}	6.5	6.5	6.5	
Line width	5.0	5.0	5.0	
r centered tetrads				
mrm	0	0	0	0.105
mrm, τ	7.96	7.90	7.87	
mrr ν_{A}	−4.0	−3.5	−4.5	0.281
ν_{B}	17.5	17.0	9.5	
rrr	12.5	12.5	1.0	0.185
$J_{\mathrm{AA'}}$	−15	−15	−15	
J_{AX}	11.0	11.0	10.0	
$J_{\mathrm{AX'}}$	2.0	2.0	3.0	
Line width	7.0	6.0	5.0	
Pentads				
mrrm	−543		−527	0.060
mrrr	−541		−525	0.160
rrrr	−537		−526	0.105
mmrm	−517		−513.5	0.091
mmrr	−517		−513.5	0.119
mrmr	−513		−507.5	0.119
rmrr	−513		−505.5	0.160
mmmm	−485		−492	0.035
rmmr	−477		−479	0.060
Line width	5.0		5.0	

coupling constants was simplified by assuming that the tetrads with an *m* central dyad were all described by the same set of coupling constants, and similarly for the tetrads centered on an *r* dyad. This is reasonable since the vicinal coupling constants are determined by the conformation of the central dyad, which is not expected to depend significantly on the configuration of the neighboring α carbons. In the (approximately) ABX$_2$ spectra of the *m* centered tetrads, the coupling constants were readily determined directly from the observed line positions and only minor adjustments were needed in the spectrum calculations to account for line overlapping. However, the AA'XX' and ABXX' spectra of the *r*-centered tetrads are more difficult to analyze directly. It is well known that under certain conditions,[24] which unfortunately occur in this system, the form of an AA'XX' spectrum is insensitive to $(J_{\mathrm{AX}} - J_{\mathrm{AX'}})$ provided $(J_{\mathrm{AX}} + J_{\mathrm{AX'}})$ remains constant. Although the triplet structure of the *mrm* and *rrr* spectra may be distinguished in the experimental spectra, the information derived is limited to $(J_{\mathrm{AX}} + J_{\mathrm{AX'}})$. The ABXX' spectrum of the *mrr* tetrad is much more sensitive to $(J_{\mathrm{AX}} - J_{\mathrm{AX'}})$ but the transition frequencies of this system cannot be evaluated explicitly. Hence the coupling constants for the *r* dyads were obtained by performing several trial calculations to determine the set of parameters giving the closest correspondence to the experimental spectrum. As expected, the shape of the spectrum was dictated principally by the *mrr* contribution, the *mrm* and *rrr* spectra remaining practically invariable over a wide range of values of $(J_{\mathrm{AX}} - J_{\mathrm{AX'}})$.

Table I lists the chemical shifts, coupling constants, line widths, and relative intensities used to generate the calculated spectra shown in the figures. Results are also included for *o*-dichlorobenzene solution, in which the spectrum is very similar to that in chlorobenzene. For greater clarity in the presentation, the chemical shifts are listed in hertz at 220 MHz with the *mrm* tetrad set arbitarily to zero. The τ value of the latter tetrad only is given. Negative chemical shifts are to low field. The accuracy of the parameters varies depending on the contribution of the tetrad to a prominent feature of the spectrum. Thus errors in the chemical shift of the *mmm* tetrad are large, about ±5 Hz, since this tetrad makes only a small contribution to the strong lines in the *m* region. Uncertainties in most of the other chemical shifts and in the coupling constants are ±1 Hz. Although the line widths are large, there can be no doubt that the set of parameters reported is correct, since the chemical shifts were obtained unequivocally from the spectra of deuterated polymers and no other set of reasonable coupling constants was statisfactory. All spectra were calculated assuming Bernoullian statistics[18] with P_m, the probability of isotactic placement, equal to 0.43.

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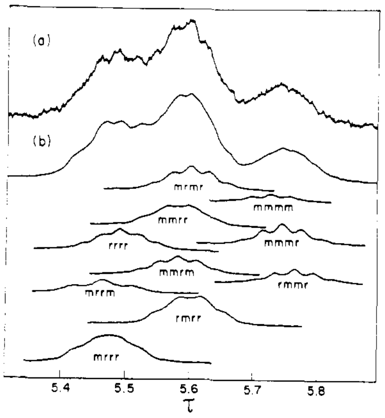

Figure 5. (a) 220-MHz α-proton spectrum of PVC, 5% in chlorobenzene at 140°. (b) Spectrum calculated with parameters in Table I, with the component pentad spectra.

Figure 5 shows the α-proton spectrum of PVC in chlorobenzene. The pentad chemical shifts were taken from the work of Johnsen and Kolbe[16] at 100 MHz with minor changes to accommodate solvent and concentration effects. It was also necessary to differentiate the chemical shifts of some pentads which were not resolved at the lower frequency. Coupling constants were taken unchanged from the simulation of the β-proton spectra described above. Figure 5 includes the ten individual pentad spectra comprising the complete calculated spectrum.

The vicinal coupling constants, which are weighted averages over the molecular internal rotation, allow access to the local chain conformation. The values determined for the isotactic dyads are very similar to those reported previously for the isotactic portions of polystyrene,[25] poly(isopropyl acrylate),[26] and polypropylene.[27] As we have discussed earlier,[25] we may conclude that *m* dyads interconvert rapidly between the two equivalent *tg* and *gt* structures shown in Figure 6a. When repeated, each conformation generates the 3_1 helix often found in crystalline isotactic polymers.

The conformations of syndiotactic polymer sequences have not been studied as extensively as those of isotactic sequences. However, 2,4-dichloropentane and 2,4,6-trichloroheptane model compounds have been investigated[11,28] by both ir and nmr spectroscopy. These results, as well as semiempirical potential energy calculations,[29] indicate that only two conformations are important, the *tt* and *gg* structures shown in Figure 6b. The *tt* form is by far the more stable. The values of J_{AX} and $J_{AX'}$ averaged over these two conformations are given by

$$J_{AX} = J_{A'X'} = X_{tt}J_t + X_{gg}J_g$$

$$J_{AX'} = J_{A'X} = X_{tt}J_g + X_{gg}J_t$$

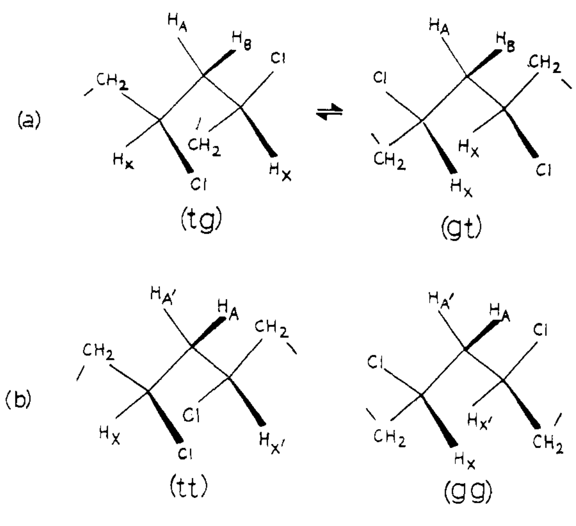

Figure 6. Low-energy conformations of (a) an *m* dyad and (b) an *r* dyad.

where $X_{tt(gg)}$ is the mole fraction of the *tt* or *gg* conformation. It has been assumed that all coupling constants between *trans* protons take a value J_t and all coupling constants between *gauche* protons take a value J_g. Such an approximation is sufficient for the purposes of this discussion. Since it is known[30] that $J_t \sim$ 11–13 Hz and $J_g \sim$ 1–3 Hz, a large value of $|J_{AX} - J_{AX'}|$ indicates a large excess of one form. (Since interchanging the values of J_{AX} and $J_{AX'}$ does not change the spectrum, nmr spectra cannot say which of *tt* or *gg* predominates. This must be decided by ir spectroscopy or potential energy calculations as mentioned above.) Doskocilova, *et al.*,[28] estimated that in the syndiotactic-like isomer of 2,4,6-trichloroheptane, for values of J_{AX} and $J_{AX'}$ of 11 and 2.5 Hz, respectively, the relative populations of the *tt* and *gg* conformations of each $CH_3CHClCH_2CHClCH_2$– dyad unit were 0.92 and 0.08 at 20°. Not unexpectedly, a comparable situation exists in *r* dyads in the polymer, but the *tt* form probably is even more highly favored in the polymer since our values of 11 and 2 Hz for J_{AX} and $J_{AX'}$ were measured at 140°. As the temperature increases ($J_{AX} - J_{AX'}$) should decrease, as Doskocilova, *et al.*, found. At 130°, they reported J_{AX} = 10.2 and $J_{AX'}$ = 3.1 Hz.

The solvents used in this work are good solvents for PVC and a probable explanation for the increase in preference for the *tt* conformation lies in the tendency for these solvents to extend the polymer chain more than if intramolecular steric interactions as judged from model compounds were the sole determining factor. It would be interesting to see if in poorer solvents a decrease in the end-to-end distance of the chain was reflected in the vicinal coupling constants.

The structure of PVC in solution is now well characterized. Both the configurational and conformational probabilities are known, and it should be possible to compute other properties such as the mean-square end-

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to-end distance. It has been suggested[31] that in isotactic chains in solution the 3_1 helix extends undisturbed for a considerable number of units. The only allowed helix reversal if of the type (*gt*)(*tg*), the junction (*tg*)(*gt*) being sterically forbidden. Since we have shown that in PVC, the *r* sequences are almost as conformationally regular as *m* sequences, then the majority of "kinks" in a PVC chain would occur at *m–r* junctions of the form (*tg*)(*tt*) and (*gt*)(*tt*) or their mirror images.

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Cooperativity in Poly-L-proline I–II Transitions

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ABSTRACT: The poly-L-proline I–II transition is known to exhibit positive cooperativity. This effect has hitherto been only qualitatively explained. In this study, the contributions of intramolecular steric and electrostatic interactions to this phenomenon are computed. The calculations suggest that the total end effects are +11.5 kcal/mol for form I but only +3.3 kcal/mol for form II. Similar calculations for a polyproline molecule with a junction between form I and form II, and between form II and form I, yield intramolecular junction free energies of −0.8 and +2.3 kcal/mol for these two structures. The minimum intramolecular junction free energy J for simultaneous formation of a I–II and a II–I junction, +1.5 kcal/mol, arises from a +2.1-kcal/mol electrostatic term and a −0.6-kcal/mol van der Waals term. Since the observed value of J is +4 to +7 kcal/mol, these calculations suggest that, in contrast to the α-helix–random coil transition, the poly-L-proline I–II transition derives much of its cooperativity from polymer–solvent interactions.

Poly-L-proline is known to undergo a reversible conformational transition from a right-handed helix with *cis* peptide groups, termed form I, to a left-handed helix of *trans* peptide units, termed form II.[1,2] This conformational transition occurs over a narrow range of solvent composition,[3] suggesting that it is characterized by positive cooperativity. That is, under solvent conditions in which form I and form II are, on the average, equally probable, individual polymer chains possess long sequences of peptide groups in identical conformation rather than containing a truly random distribution of *cis* and *trans* units. This observation can be introduced into a thermodynamic description of the phaselike I–II transformation by assigning a "junction energy" to each intramolecular junction between form I units and adjacent form II units. A positive junction energy then yields positive cooperativity. Indeed, this junction energy has been measured by two different techniques and found to lie between +4 and +7 kcal/mol.[4–6] The molecular origin of this junction energy is the primary subject of the present paper.

The positive cooperativity of polyproline has been ascribed to three distinguishable phenomena. The first, suggested by Schimmel and Flory,[7] is best viewed as a van der Waals end effect in form I. These authors point out that form I, which occurs in poor solvents, must possess more favorable intramolecular van der Waals interactions than form II. Since residues at the ends of form I sections are deprived of their full share of these intramolecular interactions, these end residues will be energetically unfavorable in comparison to residues within a long form I chain. Thus, under solvent conditions in which forms I and II both have significant average probability, *cis* units will usually be found only in long, all-*cis* sequences. Long all-*trans* sequences must then also occur, lending positive cooperativity to the I–II transition.

The second proposal, suggested by Rifkind and Applequist,[5] can best be described as intramolecular steric hindrance at the junction between form II and form I. According to them, molecular model studies of junctions give evidence for extensive overlap of atoms near the junction. Thus the first and second proposals are essentially of a steric nature, but neither has been placed on a quantitative basis.

Recently, a third source for the cooperativity, the electrostatic interactions of peptide dipoles with one another, was suggested.[8] Calculations of the intramolecular peptide interaction, in dipole–dipole approximation, show that a positive junction energy of 1–2 kcal/mol arises from this source. However, since the observed junction energy is 4–7 kcal/mol, electrostatic interactions are unable to account fully for the observed effects.

In order to establish quantitatively whether intramolecular steric interactions make a significant contribution to the cooperativity, we have calculated the van der Waals energy and have examined for steric hindrance junctions between the two forms. In addition, the electrostatic energy is calculated in monopole ap-

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