Residual Primary Halogen in Reductively Dehalogenated Poly(vinyl chloride)

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ABSTRACT: With the aid of ^{13}C NMR spectroscopy, several partially reduced structural defects have been detected in poly(vinyl chloride) (PVC) samples that had been subjected to very extensive dechlorination by tri-*n*-butyltin hydride or tri-*n*-butyltin deuteride. These defects are derived from the chloromethyl branches, 2,4-dichloro-*n*-butyl branches, and saturated long-chain ends of the unreduced polymer, and the only halogen in them is of the nonallylic primary type. Their presence has been confirmed by comparing their ^{13}C spectra with those of model compounds, including some previously unknown substances, whose synthesis is reported herein. Toward the reducing agents that were used, the relative reactivities of the nonallylic primary halogens, as compared to the ordinary backbone secondary halogen, have values that lie within the narrow range 0.2–0.3. Since significant amounts of the partially reduced structures remain in PVC specimens whose total extents of dechlorination are very close to 100%, their detection tends to cast doubt upon the quantitative validity of related studies by earlier workers who did not take the possible presence of these structures into account.

During the years that have intervened since its use was first described,[1] reductive dehalogenation by tri-*n*-butyltin hydride[1] or tri-*n*-butyltin deuteride,[1c-f] followed by ^{13}C NMR analysis of the polymeric reduction products,[1] has become the standard method for determining the nature and concentration of most of the structural defects in poly(vinyl chloride) (PVC).[2] In order to apply this procedure, it is necessary to infer the structure of the original (unreduced) polymer from those of the reduced materials. Thus, if the method is to be used to maximum advantage, the chemistry of the reduction must be thoroughly understood.

Abundant evidence is now available[2] to show that PVC contains allylic halogen, unactivated (nonallylic) primary halogen, and unactivated tertiary halogen, in addition to the unactivated secondary halogen that is the principal type. Toward Bu_3SnH, the reactivity order of these chloride species is primary < secondary < tertiary < allylic.[3] This sequence suggests that significant amounts of primary chloride might remain in Bu_3SnH-reduced PVC specimens from which the secondary chloride has been almost entirely removed, and the extent of this retention can be predicted with recourse to the following argument.

Reactions 1 and 2 are the respective rate-determining steps for the reduction of the unactivated primary (P) and unactivated secondary (S) C–Cl linkages by Bu_3SnH or Bu_3SnD.[3] Hence the disappearance rates of these linkages

$$\underset{\text{P}}{\text{–CH}_2\text{Cl}} + \text{Bu}_3\text{Sn}\cdot \xrightarrow{k_P} \text{–CH}_2\cdot + \text{Bu}_3\text{SnCl} \quad (1)$$

$$\underset{\text{S}}{\text{–CHCl–}} + \text{Bu}_3\text{Sn}\cdot \xrightarrow{k_S} \text{–}\dot{\text{C}}\text{H–} + \text{Bu}_3\text{SnCl} \quad (2)$$

are given by eq 3 and 4, where P and S are the chloride concentrations and k_P and k_S are rate constants. Division

$$-dP/dt = k_P P[Bu_3Sn\cdot] \quad (3)$$

$$-dS/dt = k_S S[Bu_3Sn\cdot] \quad (4)$$

of eq 3 by eq 4, followed by separation of the variables and integration within limits, produces eq 5, in which the subscripts 0 and x denote the initial and final concentrations, respectively. This equation can be used to predict

$$P_x/P_0 = (S_x/S_0)^{k_P/k_S} \quad (5)$$

the fraction of the original primary chloride (P_x/P_0) that will remain in the polymer when the fraction of the original secondary chloride (S_x/S_0) has been reduced to a given level. For example, when 99.9% of the secondary chloride has been removed (i.e., when S_x/S_0 is 1×10^{-3}), and k_P/k_S is 0.3 (as has been observed for simple straight-chain models in ether at 35 °C[3c]), it follows from eq 5 that the polymer will still contain about 13% of the original primary halogen.

These considerations strongly suggest that the concentrations of the original primary-halogen-containing polymer structures, as determined by our method, may be too low by significant extents if the presence of primary halogen after reduction is not taken into account. Consequently, in an attempt to overcome this difficulty, we have used model compounds in order to obtain the ^{13}C shifts of the partially reduced structural defects in which the only residual halogen is of the unactivated primary type, and we have used these shifts in order to search for such structures in reductively dehalogenated PVC. The results of this investigation are described in the present paper.[4]

Results and Discussion

Model Compounds. The partially reduced structural defects of interest are the ClMe, ClEt, ClBu, and ClLE arrangements that are shown in Figure 1. They would result from the incomplete dehalogenation of, respectively, the chloromethyl, 2-chloroethyl, and 2,4-dichloro-*n*-butyl branch structures and the two types of saturated long-chain end (vide infra) that the polymer is known to contain.[2] The chemical shifts of the ClLE moiety were provided by the carbon spectrum of 1-chloro-*n*-octadecane, a commercial product. However, in order to obtain the ^{13}C shifts of the ClMe, ClEt, and ClBu structures, we first had to prepare some models in which these groups were present.

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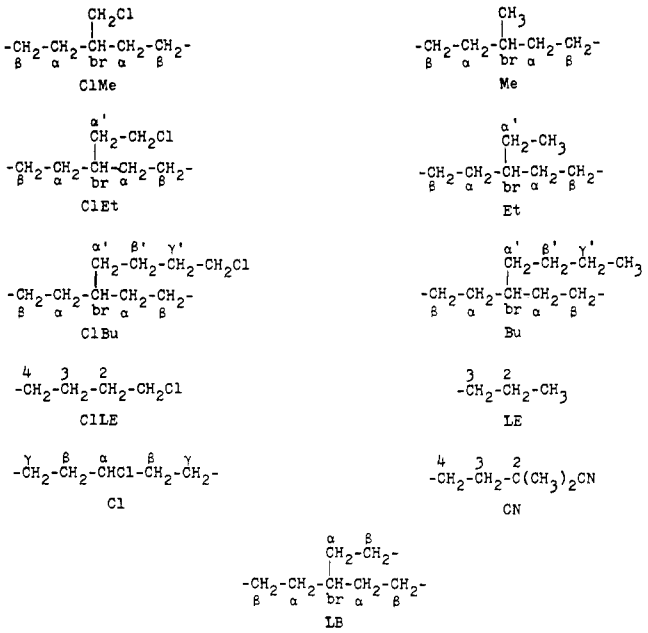

Figure 1. Some of the possible structural defects in Bu_3SnH-reduced PVC.

Chloroalkane **2**, a ClMe model, was isolated in a yield of 67% from the reaction (eq 6) of the thionyl chloride–*N*,*N*-dimethylformamide complex with an alcohol[5] (**1**) whose synthesis has been described elsewhere.[6]

$$\underset{\mathbf{1}}{R_2CHCH_2OH} \xrightarrow{SOCl_2,\ DMF} \underset{\mathbf{2}}{R_2CHCH_2Cl} \quad (6)$$

$$\underset{\mathbf{3}}{R_2C{=}CH_2} \xrightarrow[2.\ Br_2]{1.\ Cp_2ZrClH} \underset{\mathbf{4}}{R_2CHCH_2Br} \quad (7)$$

$$\mathbf{4} \xrightarrow[3.\ H^+]{1.\ Mg,\ THF;\ 2.\ CH_2O} \underset{\mathbf{5}}{R_2CHCH_2CH_2OH} \quad (8)$$

$$\mathbf{5} \xrightarrow{SOCl_2,\ DMF} \underset{\mathbf{6}}{R_2CHCH_2CH_2Cl} \quad (9)$$

$$\mathbf{4} \xrightarrow[2.\ BrCH_2CH_2CH_2Cl,\ Li_2CuCl_4]{1.\ Mg,\ THF} \underset{\mathbf{7}}{R_2CH(CH_2)_3CH_2Cl} \quad (10)$$

$$\mathbf{4} \xrightarrow[2.\ BrCH_2CH_2CH_3,\ Li_2CuCl_4]{1.\ Mg,\ THF} \underset{\mathbf{8}}{R_2CH(CH_2)_3CH_3} \quad (11)$$

R = *n*-C_8H_{17}, DMF = *N*,*N*-dimethylformamide,

Cp = η^5-C_5H_5, THF = tetrahydrofuran

Preparation of the ClEt model, **6**, began with the previously reported[6] alkene, **3**, which was converted into bromoalkane **4** (yield, 62%) by the method of eq 7. This method involved the regiospecific hydrozirconation of **3** with chlorobis(η^5-2,4-cyclopentadien-1-yl)hydrozirconium, followed by treatment of the resultant alkylzirconium intermediate with bromine.[7] Compound **4** was then transformed into alcohol **5** via the sequence of eq 8, in which the Grignard reagent of **4** reacts with monomeric formaldehyde. Noteworthy features of this preparation are (a) the use of a highly activated form of magnesium[8] in order to generate the Grignard species and (b) the isolation of a byproduct that is tentatively considered to have been the formate ester of **5**.[9] This byproduct yielded additional **5** upon reduction with lithium aluminum hydride but, even so, the total isolated yield of **5** (based on **4**) was only 17%. However, the alcohol was converted easily into **6** (yield, 58%) in a reaction (eq 9) analogous to reaction 6.

Table I
^{13}C Shifts of Structures Containing Residual Primary Halogen

carbon[b]	δ,[a] ppm (±0.05) vs. Me_4Si model	polymer
ClMe-CH_2Cl	48.88[c]	48.96
ClMe-br	40.98[c]	40.97
ClMe-α	32.50[c]	32.50 (32.40)[d]
ClMe-β	27.14[c]	27.16
ClEt-CH_2Cl	43.06[e]	
ClEt-α'	37.91[e] (36.17)[d,e]	
ClEt-br	36.17[e] (37.91)[d,e]	
ClEt-α	34.09[e]	
ClEt-β	27.05[e]	
ClBu-CH_2Cl	44.74[f]	44.65
ClBu-α'	33.72[f] (33.85)[d,f]	33.64 (33.76)[d]
ClBu-β'	24.77[f]	24.70
ClBu-γ'	33.85[f] (33.72)[d,f]	33.76 (33.64)[d]
ClBu-br	38.17[f]	38.07
ClBu-α	34.49[f]	34.40
ClBu-β	27.29[f]	~27.3
ClLE-CH_2Cl	44.65[g]	44.65
ClLE-2	33.26[g]	33.16
ClLE-3	27.38[g]	~27.3
ClLE-4	29.33[g]	29.31

[a] Measured in 4:1 (v/v) 1,2,4-trichlorobenzene–*p*-dioxane-d_8 at 110 °C. [b] For nomenclature, see Figure 1. [c] Value from spectrum of compound **2**. [d] Possible alternative value. [e] Value from spectrum of compound **6**. [f] Value from spectrum of compound **7**. [g] Value from spectrum of 1-chloro-*n*-octadecane.

The ClBu model, **7**, was obtained in a yield of approximately 25% from the dilithium tetrachlorocuprate catalyzed coupling of 1-bromo-3-chloropropane (5 mol equiv) with the Grignard reagent of **4** (eq 10).[10] Lastly, a similar coupling reaction (eq 11) was used to prepare the fully reduced analogue of **7** (alkane **8**; yield, ca. 25%), which was used in the way described below in order to verify the assignments for some of the ClBu resonances.

The second column of Table I contains the chemical shifts of the diagnostic carbon resonances of the ClMe, ClEt, ClBu, and ClLE model compounds. Assignments given for these signals are unambiguous in most cases and are based on shift predictions that were made by taking for reference the ^{13}C shifts of the corresponding alkane structures[2b,11] (the Me, Et, Bu, and LE groups in Figure 1) and then introducing the incremental shift displacements (as determined in other studies[12]) that were expected to result from the substitution of chlorine for hydrogen.

Partially Reduced Structures in Dechlorinated PVC. With the aid of the model-compound shifts in Table I, we have identified partially reduced structures containing primary halogen in most of the Bu_3SnH- or Bu_3SnD-reduced PVC specimens that we have studied during the past several years. Figure 2 shows the ^{13}C spectrum of a Bu_3SnH-reduced PVC sample that is especially instructive in this regard. The original polymer used here was prepared by solution polymerization in 1,2-dichloroethane at 40 °C, using an average monomer concentration of only 0.46 M and azobis(isobutyronitrile) as a thermal free-radical source.[13] For reasons given elsewhere,[2b] the low concentration of monomer caused the number of 2,4-dichloro-*n*-butyl branches in this polymer to be unusually high. Moreover, the usual types of saturated long-chain end (**9** and **10**)[2] also were very abundant, owing to chain transfer to the solvent (eq 12 and 13), and

$$-CH_2\dot{C}HClCH_2CHCl + ClCH_2CH_2Cl \rightarrow -CH_2CHClCH_2CH_2Cl + ClCH_2\dot{C}HCl \quad (12)$$

9

$$ClCH_2\dot{C}HCl + CH_2{=}CHCl \xrightarrow{etc.} -CHClCH_2CHClCH_2Cl \quad (13)$$
10

the chloromethyl branch concentration[4a] remained near the relatively high level expected[2b] for ordinary PVC. Thus this sample was an especially attractive one in which to search for residual primary halogen following extensive reduction by Bu_3SnH.

The spectrum of Figure 2 reveals the presence of a small amount of residual secondary chloride that is contained in the Cl structure which appears in Figure 1. Resonances occurring near 63.7 (not shown) and 39.0 ppm have the correct intensity ratio of 1:2 and can be assigned to the Cl-α and Cl-β carbons, respectively, on the basis of reference shift data.[1a,b,14] A separate Cl-γ signal is not observed, but since it should appear near 26.7 ppm,[14] it evidently comprises a minor part of the composite peak in this region. According to the spectrum, the Cl concentration is 0.3/(1000 C), relative to the number of ordinary backbone CH_2 carbons, which produce the very strong resonance near 30.0 ppm.[2b] Hence, in eq 5, $S_x/S_0 = 0.3/500 = 6 \times 10^{-4}$, and it follows from the analysis given above that the reduced sample should also retain significant amounts of nonallylic primary chloride.

In Figure 2 we have assigned all of the resonances associated with primary-halogen-containing segments, as well as those produced by the alkane[2b] and CN[13] structures in Figure 1 (the latter group is derived from initiator radicals[13]). Assignments also can be made for most of the unidentified signals in Figure 2, but since these resonances do not relate to the present study, we make no attempt to consider them here.

The ClMe-CH_2Cl, ClMe-br, and ClMe-β resonances occur as separate peaks in the spectrum of Figure 2, and the spectrum contains two signals in the region where the ClMe-α carbons should absorb. One of the latter signals probably is that of the quaternary CN-2 carbon, which occurs at 32.4–32.5 ppm and is expected to be much weaker than the other CN resonances.[13] However, since the ClMe-α and CN-2 shifts are virtually identical, these two resonances cannot be assigned unambiguously at this time.[15]

Unique signals arising from the ClBu-β', ClBu-α', and ClBu-γ' carbons also appear in Figure 2, but the shift similarity of the latter resonances makes their assignments somewhat uncertain as well. In Figure 3, these two resonances are shown in expanded form (partial spectrum III) and compared with an enlarged version of their counterparts in the ^{13}C spectrum of compound **7** (partial spectrum IV). The shift agreement of the partial spectra is quite satisfactory, since the data in Table I reveal a systematic downfield difference of ca. 0.1 ppm for the ClBu shifts of the model as compared to those of the polymer.

In order to verify the separation of the ClBu-br and ClBu-α signals from their nearest neighboring peaks, a reference spectrum was obtained from a mixture of the ClBu and Bu model compounds (**7** and **8**, respectively). This spectrum showed that the ClBu-α resonance occurs upfield from the Bu-α signal by 0.13 ppm, a value that is identical with the shift difference in Figure 2. In expanded spectra, satisfactory resolution of the ClBu-br and Bu-br signals also was achieved, and a comparison of the relevant traces (Figure 3) for the reduced polymer (I) and the mixture of models (II) leaves no doubt as to the accuracy of our ClBu-br assignment. In addition, the spectrum of the mixture of **7** and **8** revealed an upfield shift of 0.05 ppm for the ClBu-β resonance as compared to the Bu-β shift position. However, in Figure 2, these two resonances are not resolved from the other contributors to the relatively strong composite peak at 27.3 ppm.

The only other diagnostic resonance for the ClBu structure is that of the ClBu-CH_2Cl carbon. It occurs in Figure 2 at the correct position but is considerably stronger than the unique ClBu signals already discussed, owing to the presence of an overlapping ClLE-CH_2Cl resonance. The occurrence of the ClLE structure is further confirmed by the appearance of unique absorptions for the ClLE-2 and ClLE-4 carbons. However, in keeping with expectations, the ClLE-3 resonance is coincident with several other signals.

The third column of Table I contains the exact chemical shifts for all of the ClMe, ClBu, and ClLE resonances that appear in Figure 2. These shifts are in excellent agreement with the values, also tabulated, that were obtained from the carbon spectra of the analogous model compounds. Moreover, in all instances where appropriate comparisons can be made, the relative intensities of the polymer resonances are consistent with the ClMe, ClBu, and ClLE assignments that have been made for the polymer spectrum.

In contrast to these findings, we have not obtained conclusive evidence for the presence of the ClEt structure in reductively dehalogenated PVC. The reason for this failure seems to be simply that the ClEt concentrations of our samples have been below our detection limits, an explanation that undoubtedly applies to the sample of Figure 2. The completely reduced Et structure of this specimen should produce three unique resonances, which are those of the Et-CH_3, Et-α, and Et-br carbons.[2b] Weak signals that may be the Et-CH_3 and Et-α peaks do appear in Figure 2, but the Et-br resonance[11] is absent. Thus the spectral evidence for the occurrence of the Et moiety is not as convincing as one would like, and even if this structure were present, the spectrum shows that its concentration (derived from the Et-α peak intensity) could be no greater than about 0.3/(1000 C). However, since the chemical shifts of the ClEt-α resonance (Table I) and the Et-α signal (34.06 ppm[2b]) are essentially identical under our conditions, the Et-α intensity can actually be considered to measure the sum of the Et and ClEt concentrations. Hence the 2-chloroethyl branch concentration of the unreduced polymer (P_0) was no higher than ~0.3/(1000 C) ([Et] + [ClEt]), and if we use this value in eq 5, together with our experimental value of 6×10^{-4} for S_x/S_0 and some reasonable estimated values of k_P/k_S (see below), we find that the ClEt concentration should be well below the detection limit of ca. 0.2/(1000 C).

Similar considerations apply to the other reduced samples that we have studied, including a specimen polymerized at 100 °C, which contains the highest 2-chloroethyl branch concentration that we have found in PVC thus far [(0.7–0.8)/(1000 C)].[2b]

From the spectrum of Figure 2, it is possible to calculate the following structural-defect concentrations in units of $(1000\ C)^{-1}$: [Me], 1.5; [ClMe], 0.3; [Bu], 2.0; [ClBu], 0.6; [LE], ≥6.0; [ClLE], ≥2.2. These values can be used with eq 14 (a reorganized form of eq 5) in order to obtain the

$$k_P/k_S = \ln (P_x/P_0)/\ln (S_x/S_0) \quad (14)$$

actual values of k_P/k_S for the primary halogen that was present originally in the various structural environments. Recalling that, in each case, P_0 represents the sum of the concentrations of corresponding structures that are partially or completely reduced [e.g., for the 2,4-dichloro-*n*-butyl branch structure, P_0 = [Bu] + [ClBu] = 2.6/(1000 C)], we find in this way that k_P/k_S is 0.2 in every instance. This value is, of course, a global one in the case of the

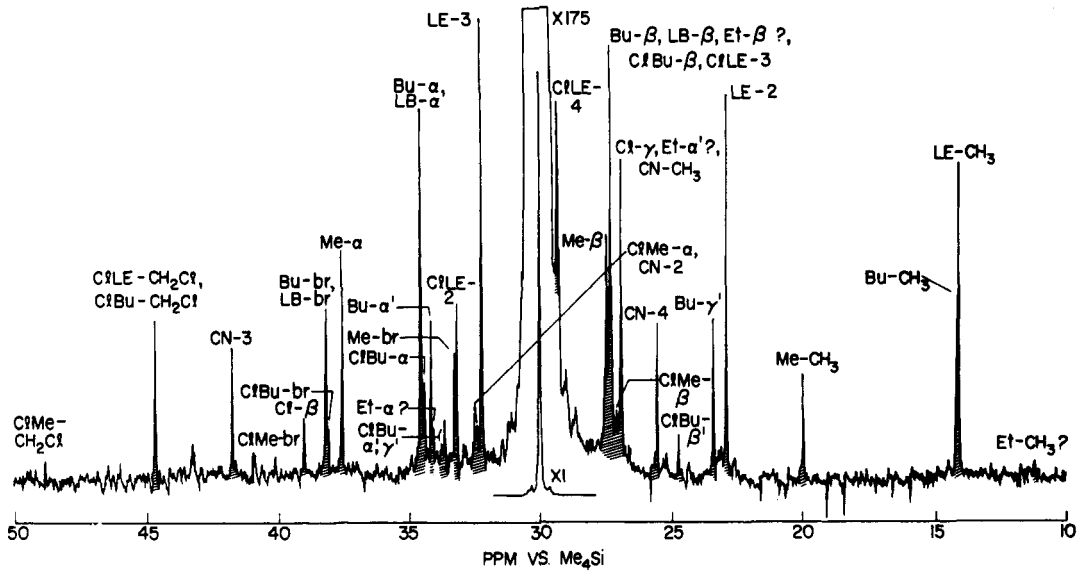

Figure 2. Proton-decoupled ^{13}C NMR spectrum (50.31 MHz) of a Bu_3SnH-reduced PVC specimen that had been polymerized at 40 °C in 1,2-dichloroethane with an average monomer concentration of 0.46 M and azobis(isobutyronitrile) (0.027 M) as a thermal free-radical source. For experimental details and nomenclature, see text and Figure 1.

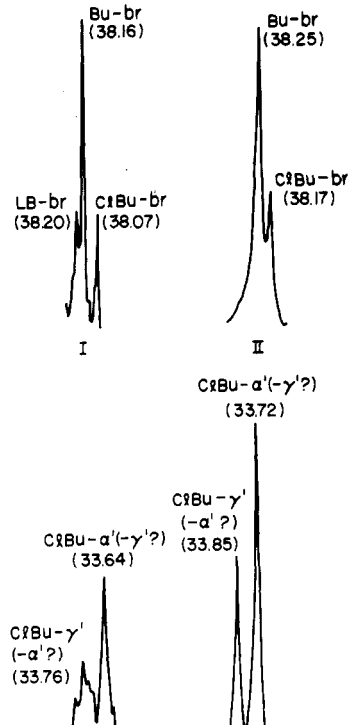

Figure 3. Expanded versions of some resonances appearing in the proton-decoupled ^{13}C NMR spectra (50.31 MHz) of: I and III, the Bu_3SnH-reduced PVC sample of Figure 2; II and IV, a mixture of compounds **7** and **8**. The values in parentheses are the exact chemical shifts in ppm (±0.05) vs. Me_4Si; see Figure 1 and the text for nomenclature and experimental details.

saturated long-chain ends, since two structures of this type (**9** and **10**) occurred in the unreduced polymer.

It might be argued here that the k_P/k_S value found for the long-chain ends is questionable, because the ClLE and LE concentrations used to compute it are too low, owing to partial saturation of the resonances of these structures.[2b] Nevertheless, under these circumstances, k_P/k_S will still be reliable when the relevant value of P_x/P_0 is correct, i.e., when the resonances used to determine the ClLE and LE concentrations are produced by carbons having comparable T_1's and comparable nuclear Overhauser enhancements. It is not entirely unreasonable to believe that this requirement was fulfilled, and it seems important to note in this regard that when the ClLE concentration was obtained from the ClLE-2 resonance intensity, the k_P/k_S value did not change significantly when the LE concentration was derived from either the intensity of the LE-2 resonance or that of the LE-3 signal.

Values of k_P/k_S also have been calculated from structural data obtained for other PVC samples that had been reduced extensively with Bu_3SnH or Bu_3SnD.[2b,13] The values derived from different samples are in very good agreement, and they are as follows: chloromethyl branch, 0.2–0.3; 2,4-dichloro-*n*-butyl branch, 0.2; saturated long-chain ends, 0.2. In the case of a Bu_3SnD-reduced specimen that had been polymerized at 100 °C, a ^{13}C spectrum was recorded with a long pulse interval (30.0 s at a 90° flip angle) in order to maximize the accuracy of the analysis for end-group carbons having long T_1's.[2b] Thus, in this particular instance, the k_P/k_S value of 0.2 found for the saturated long-chain ends (originally a 4:1 **10**:**9** mixture[2b]) should be especially reliable.

The magnitudes of k_P and k_S can be expected to depend to some degree upon experimental variables such as temperature and the nature of the solvent. Moreover, they should vary with the extent of reduction as well, owing to changes in the local environments of the different types of chloride as the reaction proceeds. Thus, strictly speaking, for our system, eq 5 and 14 are oversimplifications, and our calculated k_P/k_S ratios should apply only to samples that have been reduced by our procedure, which involves two steps: (1) removal of most of the halogen by reduction in tetrahydrofuran(THF) or 2-methyltetrahydrofuran at the solvent reflux temperature and (2) further reduction in xylene (a mixture of isomers) at ca. 90 °C.[1a,b,2b] Nevertheless, our results and those of other workers[3c] suggest that, in the case of PVC, k_P/k_S is actually rather insensitive to changes in conversion and reaction conditions. Values of k_P/k_S resembling ours might be expected to apply, therefore, to very similar systems such as that of Hjertberg and Wendel, which involves the reduction of PVC with Bu_3SnH: first at 80 °C in a mixture of THF and *p*-xylene, and subsequently at 80–90 °C in

p-xylene alone.[16] Equation 5 predicts that the maximum amount of dechlorination obtained by the Hjertberg–Wendel method (99.95% loss of unactivated secondary chloride[16]) will lead to the retention of 22% of the original unactivated primary chloride when k_P/k_S is 0.2.

Braun et al.[17] have published the ^{13}C NMR spectrum of a Bu_3SnH-reduced PVC specimen that had been prepared by polymerization under conditions conducive to monomer starvation. The reduction was performed according to the Hjertberg–Wendel[16] procedure,[18] and the residual chlorine content (presumably inferred from the Cl resonance intensities[17]) was stated to be about 0.5%.[17] From eq 5 it follows that for this level of secondary chloride retention, and for k_P/k_S values ranging from 0.3 to 0.2, the remanent amounts of unactivated primary halogen should range from 20% to 35% of the amounts that were present originally. Thus it is not surprising to find that the published spectrum[17] contains several resonances which, though previously unassigned,[17] can now be ascribed convincingly to the ClMe and ClBu structures. These resonances are those produced by the ClMe-α, ClMe-β, ClBu-br, ClBu-α, ClBu-α', ClBu-β', and ClBu-γ' carbons, and from their relative intensities one can estimate very roughly that about one-quarter to one-third of the corresponding original branch structures were, in fact, incompletely reduced.

The literature contains many other reports of investigations in which the concentrations of structural defects having nonallylic primary halogen were determined from PVC samples that had been reduced extensively with Bu_3SnH or Bu_3SnD.[19] These concentrations must now be regarded as suspect (i.e., perhaps too low by as much as 35%, or even more) in all cases where the possible presence of residual primary chloride was not taken into account. Its presence has been recognized in all of our own studies in this area that have been performed in recent years.[2b,4,6,13]

Experimental Section

Materials. The 1-chloro-*n*-octadecane was obtained from Aldrich Chemical Co. Synthetic details are given elsewhere[13] for the Bu_3SnH-reduced PVC sample whose ^{13}C NMR spectrum is displayed in Figure 2. The anhydrous THF required for model-compound preparations was distilled from disodium benzophenone dianion under dry nitrogen and then stored under argon. All other chemicals were of the highest purity available commercially, and they were subjected to additional purification, if necessary, according to standard procedures.

Instrumental Analysis. The pulse Fourier transform ^{13}C NMR spectrum of Figure 2 was recorded at 50.31 MHz with a Varian XL-200 instrument, using a sweep width of 8000 Hz, 32K data points, a 90° pulse with a width of 13 μs and a repetition time of 10.0 s, floating-point arithmetic, 1.000-Hz line broadening, 4:1 (v/v) 1,2,4-trichlorobenzene (TCB)–*p*-dioxane-d_8 as solvent, hexamethyldisiloxane (HMDS) as an internal reference (2.00 ppm vs. Me_4Si), and a sample solution temperature of 110 °C. The spectrum represents a total accumulation of 5400 transients from a solution in which the sample concentration was 19.1% (w/v). Proton-decoupled pulse Fourier transform ^{13}C spectra of the reference compounds and synthetic intermediates were obtained either on the XL-200 instrument or at 22.49 MHz on a JEOL FX90Q spectrometer, while the ^1H NMR spectra were recorded at ambient temperature with a Varian T-60A instrument. In experimental descriptions, ^1H peak multiplicities are designated as d (doublet), t (triplet), or m (multiplet). A Perkin-Elmer spectrometer, Model 597, was used to obtain the IR spectra. Programmed-temperature gas chromatography (GC) was carried out on a Varian instrument, Model 3700, using flame-ionization detection and a 3.0 ft × 0.125 in. (o.d.) stainless steel column packed with 10% of OV-101 on Gas Chrom Z. Analytical high-performance liquid chromatography (HPLC) was performed with a Waters Associates (WA) instrument equipped with an M6000 pump, a refractive index detector, and a Hewlett-Packard integrator (Model 3390A), using a WA μBONDAPAK/C_{18} cartridge in conjunction with a WA RCM-100 radial compression module. Preparative HPLC separations were done with a WA Prep 500 instrument that was equipped with a PrepPAK-500/C_{18} cartridge.

General Synthetic Procedures. All of the synthetic operations described below were carried out under dry nitrogen or argon. Solutions of air-sensitive reagents were introduced by syringe, and flame-dried apparatus was used for all experiments with such materials. Organic solutions were dried over anhydrous magnesium sulfate and were concentrated under low vacuum on a rotary evaporator. Boiling points are uncorrected.

1-Chloro-2-*n*-octyl-*n*-decane (2). Thionyl chloride (1.69 g, 14.2 mmol) was added cautiously with vigorous stirring to 7.0 mL of anhydrous *N,N*-dimethylformamide (DMF) at 0 °C, and then a solution of 2-*n*-octyl-1-decanol[6] (1, 3.48 g, 12.9 mmol) in dry DMF (5 mL) was introduced dropwise at 0–10 °C while stirring was continued. The mixture was stirred at 100 °C for 0.5 h, cooled to ambient temperature, mixed thoroughly with 20 mL of water, and extracted with three 30-mL portions of ether. The ether extracts were combined, washed once with water and twice with saturated aqueous sodium chloride, and then dried and concentrated. Fractionation of the residue through a short Vigreux column gave 2.5 g (67%) of **2** in a purity of 96% (by GC analysis): bp 119–120 °C (0.07 torr); IR (neat) 690 cm^{-1} (weak, C–Cl stretch), no OH; ^1H NMR ($CDCl_3$) δ 0.87 (distorted t, $J \simeq 5$ Hz, 6, 2 CH_3), 1.1–1.8 [m, 29, 2 $(CH_2)_7$ and $CHCH_2Cl$], and 3.52 vs. Me_4Si (d, $J \simeq 4$ Hz, 2, CH_2Cl); ^{13}C NMR [4:1 (v/v) TCB–*p*-dioxane-d_8, HMDS, 110 °C] δ 30.27 (C-5), 29.90 (C-6), 29.62 (C-7), 32.27 (C-8), 22.94 (C-9), and 14.04 vs. Me_4Si (C-10), in addition to the shifts in Table I.

1-Bromo-2-*n*-octyl-*n*-decane (4). A solution of 2-*n*-octyl-1-*n*-decene[6] (3, 19.15 g, 75.8 mmol) in dry THF (100 mL) was added dropwise to a stirred suspension of chlorobis(η^5-2,4-cyclopentadien-1-yl)hydrozirconium (21.56 g, 83.6 mmol) in dry THF (400 mL), and the resultant yellow mixture was stirred in the dark until it turned copper-brown (i.e., for ca. 2 days). It was then cooled to 0 °C and kept at this temperature while bromine (5.0 mL, 16 g, 100 mmol) was introduced dropwise with stirring (this addition yielded a clear solution having a pale bromine color). After an additional 10 min of stirring at 0 °C, the solution was diluted with chilled pentane (200 mL) and filtered with suction through a fritted-glass funnel of coarse porosity. The filter cake was washed with additional pentane (100 mL), and the filtrate and washings were combined. Concentration gave a cloudy liquid residue that was centrifuged in order to remove the suspended solid and then subjected to vacuum distillation through a short Vigreux column. The major fraction thus obtained (15.79 g) was essentially pure **4** (yield, 62%): bp 134–138 °C (0.05 torr); IR (neat) no $=CH_2$; ^1H NMR ($CDCl_3$) δ 0.88 (distorted t, $J \simeq 5$ Hz, 6, 2 CH_3), 1.1–1.8 [m, 29, 2 $(CH_2)_7$ and $CHCH_2Br$], and 3.44 vs. Me_4Si (d, $J \simeq 3$ Hz, 2, CH_2Br).

3-*n*-Octyl-1-undecanol (5). A mixture of anhydrous magnesium chloride (1.2585 g, 13.22 mmol), finely divided lithium (0.1926 g, 27.75 mmol), naphthalene (0.3589 g, 2.80 mmol), and anhydrous THF (15 mL) was stirred vigorously for ca. 24 h in a glovebox[8] and centrifuged subsequently for 20 min at 2400 rpm. The black supernatant phase was removed and replaced by a fresh portion of dry THF (20 mL), and the resultant mixture was stirred while 4.000 g (12.00 mmol) of bromoalkane 4 was introduced at a rate that sufficed to maintain room temperature in the reaction vessel. When the addition was complete, the black mixture was stirred for 10 min at room temperature and for 15 min at 50 °C. It was then diluted with 60 mL of dry THF, cooled in an ice bath, and stirred for 20 min while formaldehyde monomer was swept in below the liquid surface by an argon stream [the formaldehyde was obtained from the thermal depolymerization of paraformaldehyde (0.7400 g, 24.64 mmol of monomer units) at 190 °C].[20] Following an additional 2 h of stirring at room temperature, the mixture was treated with saturated aqueous ammonium chloride (50 mL) and filtered with suction, and the aqueous phase was extracted with two 50-mL portions of 1:1 (v/v) ether–pentane. The organic layers were combined; washed in succession with dilute hydrochloric acid, saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride, and then dried and concentrated. A preparative HPLC separation of a solution of the residue (~3.5 g) in acetone (3 mL), using pure methanol for

elution, gave four major fractions, two of which were not examined in detail. The fraction having the shortest retention time (cut 1) displayed a strong IR O–H stretching absorption at 3340 cm^{-1}, while the second fraction (cut 2) appeared to be an ester (the formate ester of **5**?), since its IR spectrum contained strong bands at 1735 (ester C=O stretch) and 1175 cm^{-1} (broad, formate C–O–C asymmetric stretch). Cut 2 (ca. 1 g) was stirred at 50 °C for 2 h with 6.4 mL of a 1 M solution of lithium aluminum hydride in THF. The excess reductant was destroyed by treatment with ethyl acetate (2.5 mL), and the mixture was subjected to a conventional aqueous workup, which afforded a product (cut 2′) whose HPLC retention time was identical with that of cut 1. As expected, the IR spectrum of cut 2′ did not show the ester bands described above, although it did reveal a strong O–H stretch at 3340 cm^{-1}. Cuts 1 and 2′ were thus presumed to be alcohol **5** (0.585 g in toto, or 17%), a conclusion that was verified by the following experiment.

1-Chloro-3-*n*-octyl-*n*-undecane (6). Anhydrous DMF (3.0 mL) was added slowly at 5 °C with stirring to 0.28 g (2.4 mmol) of thionyl chloride. Stirring at 5 °C was continued while a solution of alcohol **5** (0.585 g, 2.06 mmol) in dry DMF (5 mL) was gradually introduced, and the mixture was stirred at 95 °C for 15 min after the addition had been completed. Following treatment with water (10 mL), the mixture was extracted with three 30-mL portions of 1:1 (v/v) ether–pentane. The extracts were combined, washed twice with saturated aqueous sodium bicarbonate and once with saturated aqueous sodium chloride, and then dried and concentrated. Preparative HPLC purification of the residue with pure methanol as the eluant afforded a single major component, which was conclusively shown to be compound **6** (0.36 g, 58%) by spectroscopic observations: IR (neat) 660 cm^{-1} (medium, C–Cl stretch), no OH; ^1H NMR ($CDCl_3$) δ 0.89 (distorted t, $J \simeq 5$ Hz, 6, 2 CH_3), 1.1–2.0 [m, 31, 2 $(CH_2)_7$ and $CHCH_2CH_2Cl$], and 3.55 vs. Me_4Si (t, $J \simeq 7$ Hz, 2, CH_2Cl); ^{13}C NMR [4:1 (v/v) TCB–*p*-dioxane-d_8, HMDS, 110 °C] δ 30.34 (C-6), 29.91 (C-7), 29.61 (C-8), 32.23 (C-9), 22.91 (C-10), and 14.07 vs. Me_4Si (C-11), in addition to the shifts in Table I.

In a preliminary experiment, an attempt was made to synthesize **6** by a method analogous to that used for **7** (see below), i.e., a Li_2CuCl_4-catalyzed coupling reaction between bromochloromethane and the Grignard reagent of **4**. This experiment yielded a complex mixture of products that successfully resisted separation. However, the ^{13}C NMR spectrum of the mixture contained several minor peaks that were later found to comprise all of the diagnostic resonances of **6**.

1-Chloro-5-*n*-octyl-*n*-tridecane (7). A suspension of activated magnesium was prepared by heating a well-stirred mixture of anhydrous magnesium chloride (7.452 g, 78.3 mmol), potassium (5.562 g, 142.3 mmol), and potassium iodide (11.811 g, 71.2 mmol) in dry THF (150 mL) under gentle reflux for 3 h, followed by stirring for an additional 1.5 h at room temperature.[21] Bromoalkane **4** (15.79 g, 47.4 mmol) was added dropwise to the metal suspension with stirring and occasional external cooling, and the mixture was stirred subsequently at room temperature for 0.5 h. It was then transferred to centrifuge tubes under argon pressure via cannula and centrifuged for 0.3 h at 2000 rpm. The black supernatants were combined, and an aliquot portion of this 0.287 M Grignard-reagent solution (55.0 mL, 15.8 mmol) was added dropwise at 0 °C to a stirred solution of 1-bromo-3-chloropropane (12.44 g, 79.0 mmol) and Li_2CuCl_4 (0.099 g, 0.45 mmol) in anhydrous THF (34.5 mL) [the Li_2CuCl_4 was introduced as a 4.5-mL aliquot of a 0.100 M solution that had been prepared[22] by stirring a mixture of lithium chloride (0.8478 g, 20.0 mmol) and anhydrous cupric chloride (1.3445 g, 10.0 mmol) in dry THF (100 mL) for 18 h]. Following overnight stirring at ambient temperature, the mixture was agitated with 100 mL of 5% aqueous sodium bicarbonate. The layers were separated, and the aqueous layer was extracted with pentane (2 × 30 mL); then the organic layers were combined, washed with a saturated aqueous solution of sodium chloride, dried, and concentrated. Analysis of the residue by HPLC with 30:70 (v/v) CH_2Cl_2–CH_3CN as the eluant showed that the major product of the reaction was 9-methyl-*n*-heptadecane and that the desired product, **7**, had been formed in a yield of ca. 25%. Preparative HPLC separation of the crude material, using 30:70 (v/v) CH_2Cl_2–CH_3OH for elution, gave 1.5 g of a 1:2 **7**–9-methyl-*n*-heptadecane mixture from which the carbon chemical shifts of **7** were determined very easily: ^{13}C NMR [4:1 (v/v) TCB–*p*-dioxane-d_8, HMDS, 110 °C] δ 30.52 (C-8), 30.08 (C-9), 29.69 (C-10), 32.31 (C-11), 22.95 (C-12), and 14.03 vs. Me_4Si (C-13), in addition to the shifts in Table I. Within the expected error limits of ±0.05 ppm, the unique shifts of the 9-methyl-*n*-heptadecane coproduct were identical with those reported elsewhere[2b] for the methyl branch structure of reductively dechlorinated PVC.

An alternative route to **7** involved the following steps: (a) conversion of 9-heptadecanol into 9-bromo-*n*-heptadecane by treatment with dibromotriphenylphosphorane, (b) formation of the 9-bromo-*n*-heptadecane Grignard reagent by reaction with activated magnesium[21] (commercial magnesium turnings were ineffective under all conditions that were tried), and (c) Li_2CuCl_4-catalyzed coupling of the Grignard reagent with 1-bromo-4-chlorobutane. Although step c gave *n*-heptadecane as the major product, it did afford a minor HPLC fraction containing **7** and *n*-heptadecane in a mole ratio 1:3.4, respectively, as determined by ^{13}C NMR. The ^{13}C spectrum displayed all of the resonances of **7** but indicated that step c had produced this substance in a yield of only ca. 2%.

9-*n*-Butyl-*n*-heptadecane (8). An aliquot portion of a 0.287 M THF solution of the Grignard reagent of **4** (55.0 mL, 15.8 mmol) was added rapidly at 0 °C to a stirred solution of 1-bromopropane (9.72 g, 79.0 mmol) and Li_2CuCl_4 (0.099 g, 0.45 mmol) in anhydrous THF (34.5 mL), and the mixture was treated subsequently in exactly the way described above for the analogous mixture that had yielded **7** (the same stock solutions of Li_2CuCl_4 and the Grignard reagent were used in both preparations). Analytical HPLC measurements with 30:70 (v/v) CH_2Cl_2–CH_3CN as the eluant indicated that 9-methyl-*n*-heptadecane was again the major product and that the yield of alkane **8** was approximately 25%. Preparative HPLC separation with elution by 30:70 (v/v) CH_2Cl_2–CH_3OH gave 1.0 g (21%) of purified **8**: ^{13}C NMR [4:1 (v/v) TCB–*p*-dioxane-d_8, HMDS, 110 °C] δ 14.02 (C-1), 22.95 (C-2), 32.30 (C-3), 29.67 (C-4 and Bu C-2), 30.01 (C-5), 30.55 (C-6), 27.34 (C-7), 34.61 (C-8), 38.25 (C-9), 34.26 (Bu C-1), 23.46 (Bu C-3), and 14.06 vs. Me_4Si (Bu C-4).

References and Notes

(1) (a) Starnes, W. H., Jr.; Hartless, R. L.; Schilling, F. C.; Bovey, F. A. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1977**, *18* (*1*), 499. (b) *Adv. Chem. Ser.* **1978**, No. *169*, 324. (c) Starnes, W. H., Jr., presented at the Joint Meeting of the Southeastern Ohio Section of the Society of Plastics Engineers and the Ohio Valley Section of the American Chemical Society, Marietta, OH, Oct 1977. (d) Starnes, W. H., Jr.; Schilling, F. C.; Abbås, K. B.; Cais, R. E.; Bovey, F. A., presented at the Joint Chemical Congress of the American Chemical Society and the Chemical Society of Japan, Honolulu, HI, Apr 1979. (e) Starnes, W. H., Jr., presented at the International Conference on Advances in the Stabilization and Controlled Degradation of Polymers, Luzern, Switzerland, Aug 1979; "Proceedings", p 113. (f) Bovey, F. A.; Schilling, F. C.; Starnes, W. H., Jr. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20* (2), 160.

(2) For reviews, see: (a) Starnes, W. H., Jr. *Dev. Polym. Degrad.* **1981**, *3*, 135. (b) Starnes, W. H., Jr.; Schilling, F. C.; Plitz, I. M.; Cais, R. E.; Freed, D. J.; Hartless, R. L.; Bovey, F. A. *Macromolecules* **1983**, *16*, 790. (c) Hjertberg, T.; Sörvik, E. M. In "Degradation and Stabilisation of PVC"; Owen, E. D., Ed.; Elsevier: New York, 1984; Chapter 2.

(3) (a) Menapace, L. W.; Kuivila, H. G. *J. Am. Chem. Soc.* **1964**, *86*, 3047. (b) Carlsson, D. J.; Ingold, K. U. *Ibid.* **1968**, *90*, 7047. (c) Barber, J. J.; Whitesides, G. M. *Ibid.* **1980**, *102*, 239.

(4) Preliminary accounts of this work have been presented orally and published: (a) Starnes, W. H., Jr.; Schilling, F. C.; Plitz, I. M.; Cais, R. E.; Bovey, F. A.; Park, G. S.; Saremi, A. H., presented at the 23rd Rocky Mountain Conference, Denver, CO, Aug 1981; Abstr. 72. (b) Starnes, W. H., Jr.; Villacorta, G. M.; Schilling, F. C.; Plitz, I. M., presented at the 28th Macromolecular Symposium of the International Union of Pure and Applied Chemistry, Amherst, MA, July 1982; "Proceedings, IUPAC MACRO 82", p 226. (c) Starnes, W. H., Jr.; Haynie, S. L.; Katz, H. E.; Plitz, I. M.; Villacorta, G. M., presented at the 187th National Meeting of the American Chemical Society, St. Louis, MO, Apr 1984; American Chemical Society: Washington, DC; Abstr. POLY 142.

(5) Cf.: Hudson, H. R.; de Spinoza, G. R. *J. Chem. Soc., Perkin Trans. 1* **1976**, 104.

(6) Wescott, L. D., Jr.; Villacorta, G. M.; Schilling, F. C.; Plitz, I. M.; Starnes, W. H., Jr. *Polym. Mater. Sci. Eng.* **1984**, *50*, 290; *Macromolecules* **1984**, *17*, 2501.
(7) Cf.: Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115.
(8) Cf.: Rieke, R. D.; Li, P. T.-J.; Burns, T. P.; Uhm, S. T. *J. Org. Chem.* **1981**, *46*, 4323.
(9) Such a product conceivably could have resulted from the reaction sequence of eq i and ii, where the latter reaction can be regarded formally as a hydride-transfer process.

$$(n\text{-}C_8H_{17})_2CHCH_2CH_2OMgBr \xrightarrow[i]{CH_2O} (n\text{-}C_8H_{17})_2CHCH_2CH_2OCH_2OMgBr \xrightarrow[ii]{CH_2O} (n\text{-}C_8H_{17})_2CHCH_2CH_2OCHO + CH_3OMgBr$$

(10) Cf.: Friedman, L.; Shani, A. *J. Am. Chem. Soc.* **1974**, *96*, 7101.
(11) Owing to a typographical error, Table I of ref 2b contains an erroneous shift value for the Et-br carbon resonance. The correct value is 39.69 ppm vs. Me_4Si.
(12) For example, see: Katz, H. E.; Starnes, W. H., Jr. *J. Org. Chem.* **1984**, *49*, 2758.
(13) Starnes, W. H., Jr.; Plitz, I. M.; Schilling, F. C.; Villacorta, G. M.; Park, G. S.; Saremi, A. H. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1984**, *25* (2), 75; *Macromolecules* **1984**, *17*, 2507; **1985**, *18*, 310.
(14) Abbås, K. B.; Bovey, F. A.; Schilling, F. C. *Makromol. Chem., Suppl.* **1975**, *1*, 227.
(15) The ^{13}C spectrum of a mixture of **2** and 2,2-dimethyl-*n*-dodecanonitrile (an excellent CN model[13]) might provide information that would allow the ambiguity to be resolved.
(16) Hjertberg, T.; Wendel, A. *Polymer* **1982**, *23*, 1641.
(17) Braun, D.; Holzer, G.; Hjertberg, T. *Polym. Bull. (Berlin)* **1981**, *5*, 367.
(18) Braun, D.; Holzer, G. *Angew. Makromol. Chem.* **1983**, *116*, 51. Hjertberg, T., private communication, 1984.
(19) Since these investigations are so numerous, we make no attempt to list them here. Some of them are referred to elsewhere.[2b,c]
(20) The apparatus and procedure used here were similar to those recommended in: Benkeser, R. A.; Snyder, D. C. *J. Org. Chem.* **1982**, *47*, 1243.
(21) Cf.: Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775.
(22) Cf.: Tamura, M.; Kochi, J. *Synthesis* **1971**, 303.

Notes

Low-Frequency Raman Spectra as a Conformational Probe for Polypeptides and Proteins

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The low-frequency domain of the vibrational spectra of biologically important molecules contains a wealth of information but has remained little explored due to difficulties in obtaining accurate data and their interpretation. Peticolas[1] recently reviewed the very low-frequency vibrational modes of polypeptides and proteins. Earlier, Painter et al.[2] had reexamined the low-frequency Raman modes of proteins but were unable to find a correlation of a strong band at ~28 cm^{-1} and its satellite at ~36 cm^{-1} with the secondary structure. The origin of low-frequency vibrational modes seems to be complex in nature and therefore has remained obscure. Nevertheless, interesting observations have been reported by a number of workers[3-6] in the frequency range 200–600 cm^{-1} for poly(α-amino acids) which have served as model systems for studies of proteins. Normal coordinate analysis has shown that the torsional modes about the single bonds in the polypeptide backbone occur in the low-frequency range,[6] and therefore we have begun an investigation of these bands as potential conformational probes for polypeptides and proteins. In this note, we discuss the low-frequency Raman spectra of the polypeptide poly(γ-benzyl glutamate), which occurs in the α-helical conformation,[7-10] and the polymer (Pro-Pro-Gly)$_{10}$ and the protein collagen, both of which exist in a triple-helical conformation.[11-13] Another objective of the present study is to explore whether low-frequency Raman modes will help distinguish between these two classes of polypeptide structures, since their vibrational modes in the "fingerprint" region of the vibrational spectra often overlap, precluding a clear-cut distinction.

Materials and Methods

Poly(γ-benzyl glutamate), M_r = 28000, was purchased from Sigma Chemical Co., St. Louis, MO. (lot 92F-5046), and (Pro-Pro-Gly)$_{10}$ was obtained from the Protein Research Foundation, Osaka, Japan. Chick skin type I collagen was a gift from Dr. J. Gross, Massachusetts General Hospital, Boston, MA.

The low-frequency Raman spectra of poly(γ-benzyl glutamate) and (Pro-Pro-Gly)$_{10}$ were obtained with a Spex Ramalog 4 double monochromator as previously described[14] at M.I.T., Cambridge, MA. The 488-nm line of an argon ion laser (Coherent Radiation CR-3) was used for the excitation. The spectra were obtained with a spectral slit width of 6 and 8 cm^{-1} respectively for poly(γ-benzyl glutamate) and (Pro-Pro-Gly)$_{10}$ at a scan speed of 0.2 cm^{-1}/s, a gain of 1 × 100K, and an integration time of 2 × 1K. The frequencies were calibrated by using acetonitrile as a standard and are accurate to about ±2 cm^{-1}. The back-scattering configuration was used to obtain the spectra.

The low-frequency Raman spectra of chick skin type I collagen were obtained with the 457.9-nm line of an argon ion laser (Spectra-Physics Model 164) with output power typically about 300 mW. A Spex Ramalog Model 1401 spectrophotometer at the University of Georgia, Athens, GA, was used. The spectral slit width was generally 8 cm^{-1}. The points in the spectrum were taken every 2 or 3 cm^{-1} with counts averaged at that point for 3 s. The spectra displayed are an overlay (ensemble average) of four or five such scans. The displayed spectra have also been subjected to a standard three-point smoothening, either once or twice. The frequencies were calibrated by using acetic acid as a standard and are accurate to about ±2–3 cm^{-1}. The spectrophotometer is controlled by a Digital PDP-11/34 dedicated computer which is used to store, manipulate, and display the spectra.[15] The spectrum

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