

Carbon-13 NMR studies of the structures and polymerization mechanisms of poly (vinyl chloride) and related copolymers

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Abstract — Carbon-13 NMR analysis after chemical reduction has established the following facts with regard to the structures and formation mechanisms of some chlorine-containing polymers that are prepared by free-radical routes. Poly(vinyl chloride) (PVC) contains chloromethyl, 2-chloroethyl, and 2,4-dichloro-*n*-butyl branches, as well as long branch structures. Tertiary halogen is present at all of the branch points except those bonded to chloromethyl. Abstraction of hydrogen from the polymer, followed by conventional chain propagation, leads to the 2-chloroethyl, 2,4-dichloro-*n*-butyl, and long branches; and in the case of the 2-chloroethyl and 2,4-dichloro-*n*-butyl branches, the abstraction is intramolecular. The chloromethyl branch arises *via* a head-to-head emplacement of monomer, followed by a very rapid 1,2 shift of a chloro substituent. This shift creates a radical that either propagates in the normal way (and thus produces the branch) or transfers a chlorine atom to vinyl chloride. As a result of this transfer process, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$ and $-\text{CHCl}-\text{CH}_2-\text{CHCl}-\text{CH}_2\text{Cl}$ are the principal long-chain ends in PVC. When PVC is prepared by polymerization at a low concentration of monomer, it also has a detectable number of internal double bonds. In poly(vinyl chloride-*co*-carbon monoxide), the carbon monoxide is contained in chlorocarbonyl branches. These branches are formed by the addition of monomer to $-\text{CHCOCl}$ intermediates that result from the facile rearrangement of $-\text{CHClCO}$ radicals. In poly(vinyl chloride-*co*-1,3-butadiene), the diene comonomer is introduced as a backbone 2-butene unit or as a part of a structural segment in which a 2,4-dichlorocyclohexyl branch occurs. This branch arises from the addition of vinyl chloride to the radical that ensues when a $-\text{CHCl}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{CHCl}$ chain end experiences 1,6 cyclization. If the polymerization of vinyl chloride is initiated thermally by azobis(isobutyronitrile) (AIBN), the resultant polymer contains copolymerized methacrylonitrile units as well as $\text{CN}(\text{CH}_3)_2\text{C}-$ end groups derived from initiator radicals. The methacrylonitrile is formed from the initiator *in situ*, and it also can be introduced as an impurity in the starting AIBN.

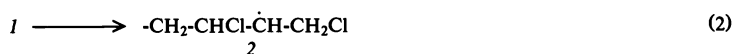
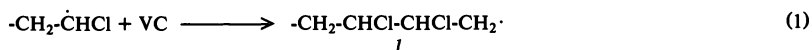
INTRODUCTION

Owing to stereochemical complications and to a lack of chemical-shift reference data, the detailed microstructures of poly(vinyl chloride) (PVC) and vinyl chloride copolymers have been difficult to determine directly by NMR techniques. Nevertheless, studies performed in this laboratory have shown that the desired information can be obtained, in certain cases, from the ^{13}C NMR spectra of polymer specimens that have been subjected to chemical reduction by lithium aluminum hydride, lithium aluminum deuteride, tri-*n*-butyltin hydride, or tri-*n*-butyltin deuteride (ref. 1). The organotin reagents are the reductants of choice when dehalogenation is needed, owing to their inability to promote side reactions and to other factors, as well (ref. 2,3). However, in general, all of these reagents can replace the halogen of the polymers by hydrogen or deuterium, a process that converts the polymers into substances that are largely paraffinic. The ^{13}C spectra of such specimens reveal the nature of the original carbon skeleton. Moreover, if a deuterated reductant has been used, the original points of chlorine attachment also can be identified, since the monodeuteration of a ^{13}C atom effects the splitting of its proton-decoupled NMR signal into a 1:1:1 triplet and causes that signal and those of adjacent carbons to undergo upfield shifts. Hence, the spectra of the reduced samples provide considerable amounts of information about the structures of the unreduced polymers and, in particular, about the "anomalous" groupings (branches, chain ends, *etc.*) that these polymers contain. Such information can be used, in turn, to elucidate important features of the mechanisms of polymerization. Summarized here are some of the major conclusions that have emerged from our studies along these lines on PVC itself and on three vinyl chloride copolymers that have been prepared by free-radical routes.

RESULTS AND DISCUSSION

Poly(vinyl chloride)

Structure 3 (eq. 3; VC = vinyl chloride) is the most abundant branch grouping in ordinary PVC (ref. 1). Its frequency of

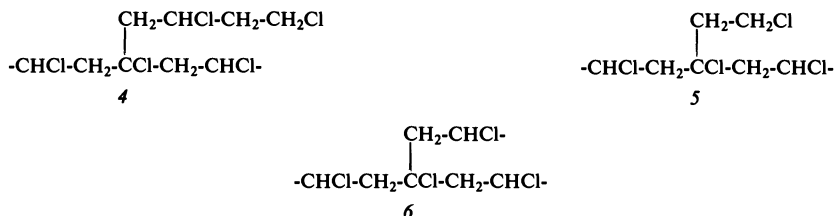


occurrence is *ca.* 2–3 per 1000 main-chain carbons (ref. 1), and its mechanism of formation has been deduced from the ^{13}C

NMR spectrum of a poly(CH₂CHDCI) sample that had been reduced with lithium aluminum hydride (ref. 4). This mechanism involves the following steps: (a) generation of radical 1 by the head-to-head addition of monomer to the ordinary growing-chain radical (eq. 1), (b) rearrangement of 1 into radical 2 by a 1,2 chlorine-atom shift (eq. 2), and (c) tail addition of 2 to monomer, followed by conventional chain propagation (eq. 3).

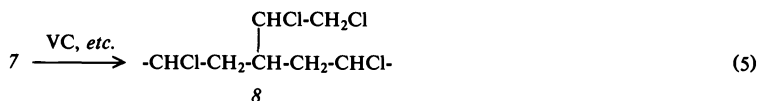
Addition of radical 1 to monomer would produce a backbone head-to-head structure, but such an arrangement has not been detected in PVC thus far. Its concentration can be no greater than *ca.* 0.2/(1000 C) when the polymer is prepared in bulk at 50°C, a conclusion that is based on the ¹³C NMR spectrum of an unreduced PVC sample containing 10% of ¹³C (ref. 5). The absence of the backbone head-to-head grouping undoubtedly is due to the great rapidity of reaction 2 (ref. 4).

Other branch structures in ordinary PVC, in order of decreasing concentration, are 4 > 5 > 6 (ref. 1). All of these structures



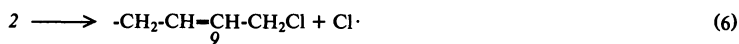
are formed by mechanisms involving the abstraction of hydrogen from a backbone CHCl moiety and subsequent head-to-tail propagation (ref. 1). The abstracting species is the ordinary growing-chain radical (ref. 1), and in the case of 4 and 5, the abstraction is intramolecular (ref. 1). In the case of the long-branch structure, 6, the abstraction produces a -CH₂-CHCl-CH₂-CH₂Cl long-chain end (ref. 1) (we define "long" branches as those containing more than five carbons, and for which the carbons comprising the branch-point grouping have chemical shifts that are identical with those of linear branches that are infinite in length). However, it should be noted that other workers have argued for the occurrence of an additional intermolecular abstraction process that involves free chlorine atoms (see below) and occurs preferentially with the CH₂ groups of the polymer (ref. 6).

In addition to 5, another type of chlorinated ethyl-branch moiety (8) might ensue from the anticipated tail addition of monomer (eq. 5) to a radical (7) resulting from the rearrangement of radical 2 (eq. 4). Structure 8 has not been detected in PVC thus far,



presumably because the formation of 7 is disfavored strongly by the juxtaposition, in that radical, of two mutually repulsive C — Cl bond dipoles (ref. 7).

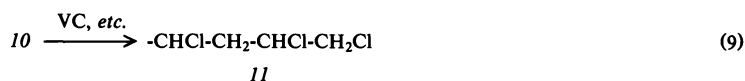
A further reaction of radical 2 is chlorine-atom β scission, which gives the unsaturated chain end, 9 (ref. 1). The β scission can be unimolecular (eq. 6), or it can involve the bimolecular reaction of 2 with vinyl chloride (eq. 7). The latter reaction might



occur in a single step or *via* a two-step pathway involving the reversible occurrence of reaction 6 within a solvent cage, followed by a rate-determining addition of Cl· to monomer.

How does the rate of reaction 7 compare with that of reaction 6? Evidence pertaining to this question has been obtained from measurements of the amounts of structure 3 in a series of PVC samples that had been made at 40°C in 1,2-dichloroethane (ref. 8, 9). These measurements showed that the concentration of 3 decreased only slightly with decreasing concentration of the monomer during polymerization (ref. 8, 9). Thus, under the conditions of this study, the β scission of 2, like the competing addition of 2 to monomer (eq. 3), seems to have occurred primarily (but not exclusively) *via* a process (eq. 7) that obeyed first-order kinetics with respect to the concentration of vinyl chloride (ref. 8, 9).

Radical 10 results from reaction 7 and from the addition, to vinyl chloride (eq. 8), of the kinetically free chlorine atom that is



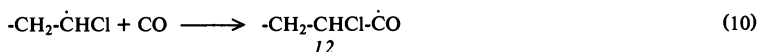
formed in reaction 6. Addition of 10 to monomer (eq. 9) continues the polymerization and produces the saturated chain end, 11 (ref. 1). Thus the mechanism of chain transfer to the monomer involves the translocation of a chloro substituent.

When PVC is synthesized at a low concentration of monomer, it incorporates a detectable number of internal double bonds (ref. 10). Upon reduction of the polymer with tri-*n*-butyltin hydride or tri-*n*-butyltin deuteride, these double bonds (ref. 10) and chain end 9 (ref. 11) yield 1,2-dialkylcyclopentane segments, whose ^{13}C shifts can be used to determine the structures of their chlorine-containing progenitors (ref. 10,11). Our NMR evidence for the presence of internal alkene linkages in PVC is discussed below in the section that deals with poly(vinyl chloride-*co*-1,3-butadiene).

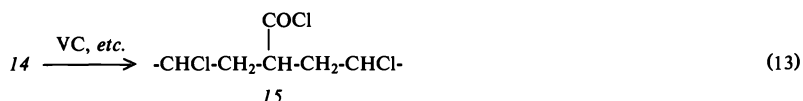
During the course of our PVC structural studies, other workers have reported spectral data that comprise supporting evidence for some of the conclusions stated above (ref. 6).

Poly(vinyl chloride-*co*-carbon monoxide)

Considerable controversy has existed for several years with regard to the molecular structure and polymerization mechanism of poly(vinyl chloride-*co*-carbon monoxide) (PVC-*co*-CO). Kawai and Ichihashi (ref. 14–16) have suggested the simple mechanism represented by eq. 10 and 11, while Ratti *et al.* (ref. 17) have proposed a scheme (eq. 10, 12, and 13) involving the



rearrangement of radical 12 via a 1,2 shift of the chloro substituent (eq. 12). Some workers (ref. 16, 18) have reported chemical



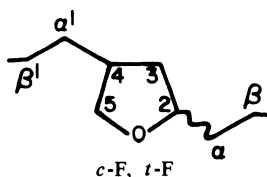
and IR evidence for the presence of structure 13, but others (ref. 17,19) have argued for the occurrence of the branched arrangement, 15, on the basis of additional chemical and spectroscopic observations.

In theory, structures 13 and 15 should be easy to distinguish with the aid of ^{13}C NMR. However, in practice, this approach is complicated severely by two problems, *i. e.*, thermal lability of the copolymer under the conditions of the analysis and a lack of chemical-shift reference data pertaining to the structures of interest. In order to circumvent these difficulties, we have subjected a number of PVC-*co*-CO specimens to a two-stage reduction process (ref. 20). The first stage is carried out with lithium aluminum hydride under mild conditions that are known to allow the efficient conversion of carbonyl groups into hydroxyl functions [in our work, the COCl group of 15 would have been changed mostly into CO_2CH_3 before reduction, owing to the use of a methanol treatment during copolymer purification (ref. 20)]. Reduction with tri-*n*-butyltin hydride then replaces the halogen by hydrogen. Thus, the overall process should convert 13 and 15 into the "OH" and "HOMe" arrangements, respectively. Since the diagnostic



^{13}C shifts of these arrangements are obtainable from model substances [7-*n*-tridecanol and 2-*n*-octyl-1-*n*-decanol are the models selected for use (ref. 20)], it has been possible to use the carbon spectra of the reduced copolymer samples in order to search for the presence of the two alcohol groups (ref. 20).

Figure 1 shows the partial ^{13}C NMR spectrum of a PVC-*co*-CO specimen that had been reduced in two stages by the method described above. This spectrum, like the others discussed in this paper, was obtained at 110°C from a solution of the sample in 1,2,4-trichlorobenzene. The spectrum contains all of the diagnostic "OH" and "HOMe" resonances, which have their anticipated relative intensities when appropriate corrections are made for the presence of overlapping peaks. The latter resonances arise from chloromethyl and 2,4-dichloro-*n*-butyl branch structures that have been completely reduced (ref. 1). In addition, the spectrum displays all of the signals expected for the stereoisomeric "c-F" and "t-F" groups. The "c-F" and "t-F" assignments are



consistent with the resonance intensities, and they have been confirmed by chemical-shift comparisons vs. the carbon resonances of *cis*- and *trans*-2,4-di-*n*-octyltetrahydrofuran (ref. 20).

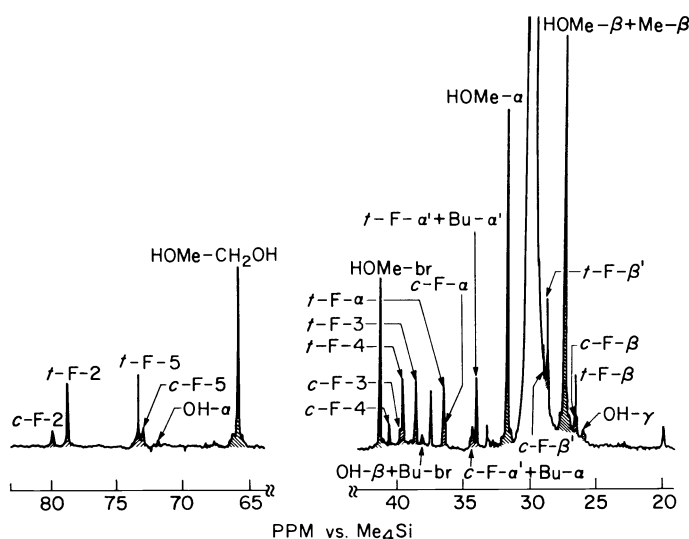


Fig. 1. Proton-decoupled ^{13}C NMR partial spectrum (50.31 MHz, 90° pulse, repetition time = 5.0 s) of a reduced specimen of PVC-co-CO (CO = 845 psi). [Adapted with permission from ref. 20, copyright 1984, American Chemical Society.]

Formation of the "c-F" and "t-F" arrangements is thought to involve the following reaction sequence: (1) conversion of structure 15 (and the corresponding methyl ester) into a $-\text{CHCl}-\text{CH}_2-\text{CH}(\text{CH}_2\text{O}^- \text{M}^+)-\text{CH}_2-\text{CHCl}-$ moiety (M^+ = a metallic cation) during the reduction with lithium aluminum hydride, (2) transformation of this intermediate into *cis*- and *trans*-2,4-di(polychloroalkyl)tetrahydrofurans, *via* the intermolecular displacement of Cl^- by the alkoxide anion, and (3) subsequent reductive dechlorination by tri-*n*-butyltin hydride.

Table 1 lists the concentrations of the two types of carbonyl structure occurring in several PVC-co-CO specimens that had been made under various pressures of carbon monoxide (ref. 20). The tabulated "backbone CO" values are the "OH" concentrations

TABLE 1. Concentrations of carbonyl structures in PVC-co-CO.

CO (psi)	no. per 1000 C	
	COCl	backbone CO
845 ^a	17.3 ± 0.5^b	0.4 ± 0.1^b
285 ^{c,d}	4.8 ± 0.3	0.5 ± 0.1
100 ^a	2.4 ± 0.3	0.4 ± 0.1
95 ^a	2.1 ± 0.2	1.1 ± 0.1
50 ^{c,e}	0.7 ± 0.2	2.0 ± 0.1

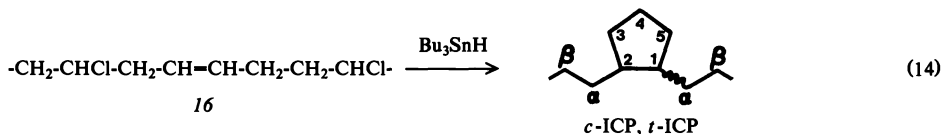
^aBulk polymerization, 50°C . ^bValue calculated from the spectrum of Fig. 1. ^cSuspension polymerization, 50°C . ^dDesignated as sample 18 in Table 2 of ref. 19. ^eDesignated as sample 12 in Table 2 of ref. 19. [Adapted with permission from ref. 20, copyright 1984, American Chemical Society.]

found after reduction, while the "COCl" values represent the sums of the "HOME", "c-F", and "t-F" concentrations of the reduced materials. In keeping with expectations based on the mechanism of Ratti *et al.* (ref. 17) (eq. 10, 12, and 13), the "COCl" values decrease smoothly as the carbon monoxide pressure is lowered. If this mechanism and that of Kawai and Ichihashi (ref. 14–16) (eq. 10 and 11) had been operating simultaneously, the "COCl": "backbone CO" ratio should have been unaffected by the pressure of carbon monoxide, and the sum of the "COCl" and "backbone CO" concentrations should have experienced a steady decrease as the carbon monoxide pressure was reduced. Both of these scenarios are inconsistent with the data of Table 1. We are therefore forced to conclude that the "backbone CO" (*i.e.*, "OH") concentrations in the table *cannot refer to a structure that was derived from carbon monoxide*. They must refer, instead, to one or more groups that were introduced by adventitious air oxidation, and the detailed microstructures of these moieties still remain to be determined. Nevertheless, we still can infer from the facts on hand that the mechanism of Ratti *et al.* is very likely to be the only one that is important under the polymerization conditions of Table 1. Owing to the operation of this mechanism, PVC-co-CO actually is a copolymer of vinyl chloride and acrylyl chloride!

Thermochemical calculations suggest that the Ratti pathway is followed because reaction 12 is irreversible and very fast, or because it is an equilibrium process that strongly favors radical 14 (ref. 20).

Poly(vinyl chloride-co-1,3-butadiene)

The copolymer of vinyl chloride and 1,3-butadiene (PVC-co-BD) was of interest in connection with the question, studied repeatedly in recent years (ref. 6, 21, 22), of the number of internal chloroallylic defects ($-\text{CH}_2-\text{CH}=\text{CH}-\text{CHCl}-\text{CH}_2-$ moieties) in PVC itself. Incorporation of butadiene into the copolymer in the usual 1,4 manner would generate a structural segment (16) that should undergo extensive conversion into a mixture of *cis* and *trans* internal cyclopentanes (“*c*-ICP” and “*t*-ICP” structures) upon reduction with tri-*n*-butyltin hydride (eq. 14) [this prediction follows from the analogous behavior of chain end 9 (ref. 11)].



If the ^{13}C NMR spectrum of the reduced copolymer did contain “ICP” resonances, and if they could be assigned, then this information could be used as reference data in order to establish the presence (or absence) of isolated internal unsaturation in the vinyl chloride homopolymer.

Figure 2 displays the carbon spectrum of a PVC-co-BD sample that had been reduced with tri-*n*-butyltin hydride (ref. 10). The

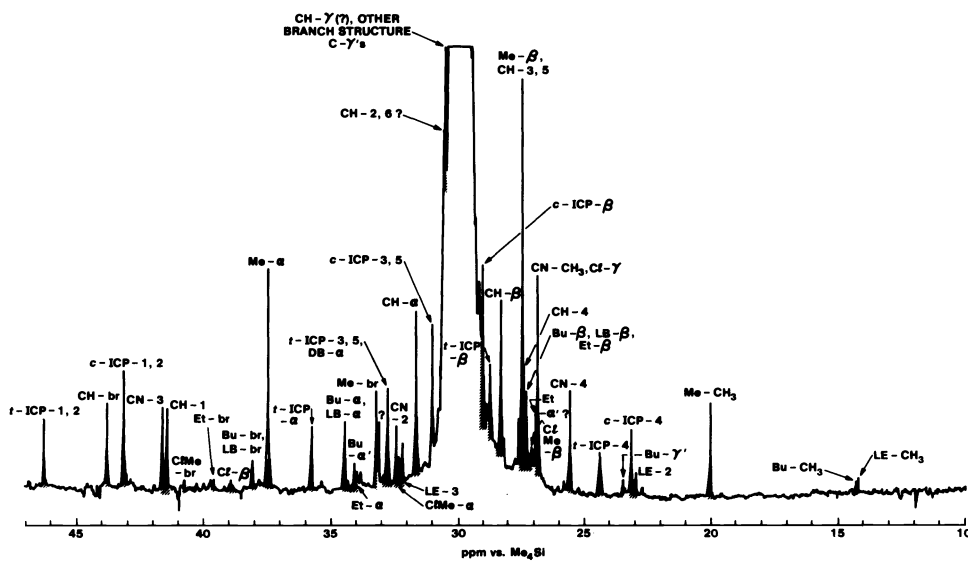
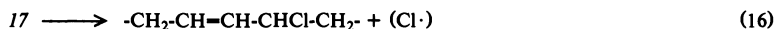
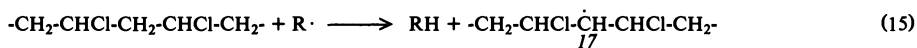


Fig. 2. Proton-decoupled ^{13}C NMR spectrum (50.31 MHz, 90° pulse, repetition time = 5.0 s) of a reduced specimen of PVC-co-BD.

original polymer was obtained by copolymerization at 40°C in 1,2-dichloroethane, using azobis(isobutyronitrile) as a thermal free-radical source (ref. 10). Inspection reveals that the spectrum does, indeed, contain several resonances that can be designated as “ICP” signals. Their assignments are consistent with their relative intensities and with their chemical shifts, which are identical with the shifts of the “ICP” model compounds, *cis*- and *trans*-1,2-di-*n*-nonylcyclopentane (ref. 10). Furthermore, in keeping with the mechanism proposed for “ICP” formation (ref. 23), the spectrum shows that the *cis:trans* “ICP” isomer ratio is about 1.7:1.

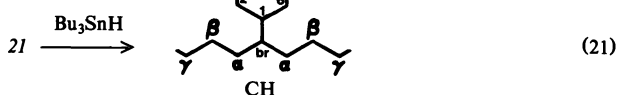
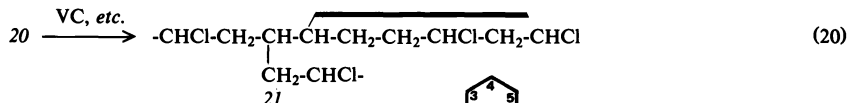
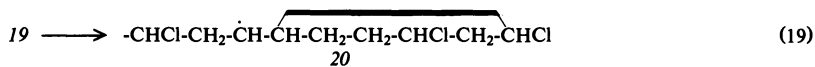
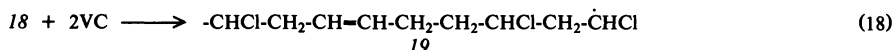
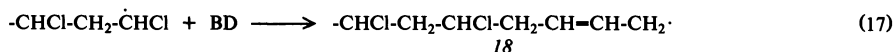
Appropriate spectral comparisons (ref. 10) have revealed that the “*c*-ICP-1,2” and “*t*-ICP-1,2” signals can be used in order to search for the presence of “ICP” structures in reductively dehalogenated PVC. Spectral examination has shown, in fact, that “ICP”s are present at the level of *ca.* 0.3/(1000 C) in a reduced PVC specimen that had been prepared at 40°C in 1,2-dichloroethane, using a rather low concentration of vinyl chloride (0.5 M) (ref. 10). However, “ICP” groups have not been found in several reduced PVC samples that had been obtained by polymerization at higher concentrations of the monomer (ref. 10). Therefore, low monomer concentration seems to favor the formation of internal alkene linkages in PVC. This finding can be rationalized by the mechanism of eq. 15 and 16, where $\text{R}\cdot$ is either a polymeric radical or $\text{Cl}\cdot$, and $(\text{Cl}\cdot)$ represents a species that



is either incipient or exists as such (in reaction 16, as in reaction 7, the chlorine atom could be transferred directly to the monomer without becoming kinetically free). A low concentration of vinyl chloride would tend to increase the relative importance of reaction 15 and the unimolecular scission of 17 by decreasing the rates of the competing additions of $\text{R}\cdot$ and 17 to the monomer.

The spectrum of Fig. 2 contains many other resonances that are found in the ^{13}C NMR spectra of reductively dehalogenated samples of PVC itself. These resonances have been discussed elsewhere (ref. 1, 12, 13, 24). However, the spectra of the reduced homopolymer do *not* display the “CH” signals assigned in Fig. 2. Relative intensity measurements and chemical-shift comparisons *vs.* the shifts of a model compound, 9-cyclohexyl-*n*-heptadecane (ref. 10), have shown that the “CH” resonances are produced, in fact, by a structural segment that contains a cyclohexyl branch!

A reasonable route to the "CH" structure is presented in eq. 17–21. This mechanism is supported very strongly by the



following observations (ref. 10): (a) A relative reactivity calculation, based on kinetic data from the literature, suggests that reaction 19 should have been able to compete effectively with the addition of radical 19 to vinyl chloride or butadiene under the polymerization conditions that were used; (b) another relative reactivity calculation, also based on literature information, shows that any conceivable 1,6 free-radical cyclization, occurring during the reduction process, would have been much too slow to compete perceptibly, under our reduction conditions, with the donation of tin-bound hydrogen to polymeric carbon radicals; (c) there seems to be a complete lack of plausible pathways leading to any of the possible precursory groups whose 1,6 cyclization during reduction could have led to the "CH" arrangement.

Remarkably, the spectrum of Fig. 2 shows that, in the unreduced copolymer, about 40% of the incorporated butadiene was contained in 21. This structure signifies the occurrence of a type of cyclopolymerization that seems to have escaped detection until now, but which eventually may be found to occur, as well, during the free-radical copolymerization of other monoene-diene pairs.

Poly(vinyl chloride-co-methacrylonitrile) Formed Adventitiously

Methacrylonitrile (MAN) is a minor product resulting from the thermolysis of the well-known free-radical initiator, azobis(isobutyronitrile) (AIBN) (ref. 25–27). In fact, MAN is formed when AIBN is purified by a standard method: recrystallization from hot methanol (ref. 28). Therefore, when vinyl polymerization is initiated thermally by AIBN, the resultant polymer could contain copolymerized MAN units that were derived from MAN which was formed *in situ* or was introduced as an impurity in the starting AIBN. Obviously, the polymer must contain end groups arising from the addition of initiator $(\text{CH}_3)_2\text{CCN}$ radicals to the monomer. It is of interest to know the relative amounts of the two types of polymer-bound initiator fragment, and we have sought to answer this question in the case of PVC (ref. 24).

For PVC, structures 22 and 23 are expected to result, respectively, from the addition of $(\text{CH}_3)_2\dot{\text{C}}\text{CN}$ radicals to vinyl chloride and from the copolymerization of vinyl chloride with MAN. Reductive dechlorination with tri-*n*-butyltin hydride should convert these two arrangements into the "CN" and "CN'" structures of eq. 22 and 23.

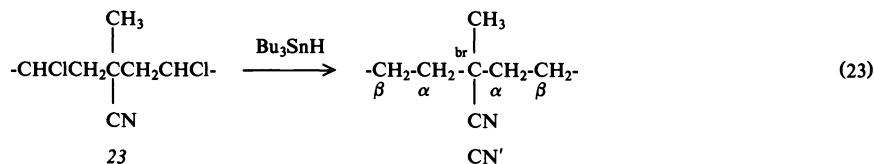
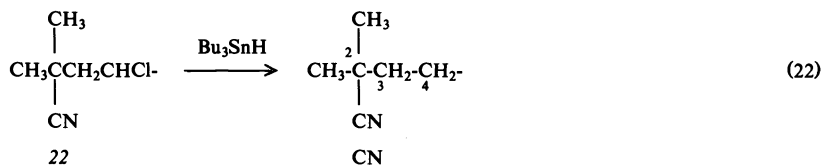


Figure 3 displays a partial ^{13}C NMR spectrum of a reduced sample of PVC that had been prepared by polymerization in solution with thermal initiation by AIBN (ref. 24). This spectrum contains evidence for the presence of eight of the resonances that should arise from the "CN" and "CN'" structures, and these are the only signals for which assignments have been made. The "CN-2", "CN'-br", "CN-CN", and "CN'-CN" resonances are expected to be relatively weak, since none of the carbons producing these resonances is bonded directly to protium. However, in spite of its low intensity, the "CN'-CN" absorption could be detected in the downfield region of the spectrum that has been omitted from Fig. 3, and the "CN-CN" signal was found in the carbon spectrum of another reduced sample of PVC, which contained a higher concentration of the "CN" structure. The chemical shifts of all of the "CN" and "CN'" resonances are in excellent agreement with those of the analogous model compounds, 2,2-dimethyl-*n*-dodecanonitrile and 2-methyl-2-*n*-nonyl-*n*-undecanonitrile (ref. 24). Moreover, the relative intensities of all of the "CN" and "CN'" resonances produced by protonated carbons are in reasonable accord with expectations when the "CN-CH₃" and "CN'-CH₃" intensities are corrected for the presence of the coincident signals that are noted in Fig. 3 [all of the overlapping peaks in the figure have been discussed in previous papers (ref. 1,10–13)]. Thus the spectral evidence for the presence of the "CN" and "CN'" structures is completely convincing.

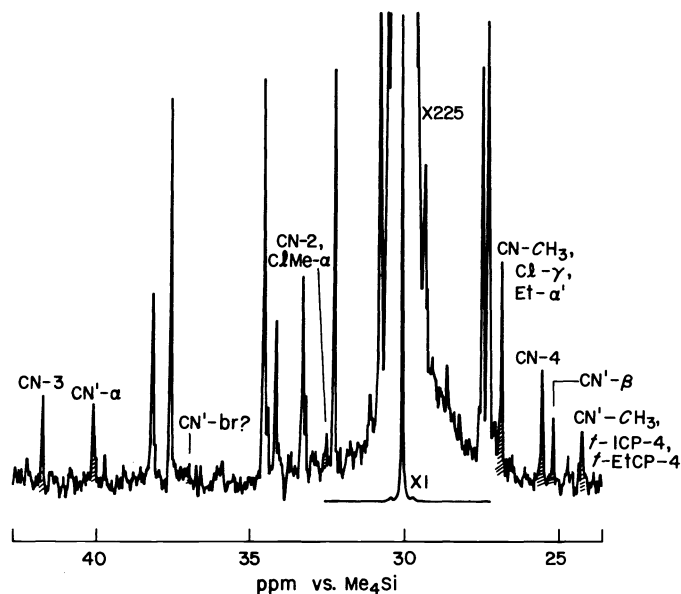


Fig. 3. Proton-decoupled ^{13}C NMR partial spectrum (50.31 MHz, 90° pulse, repetition time = 10.0 s) of a reduced PVC specimen that had been polymerized at 40°C in 1,2-dichloroethane with an average monomer concentration of 0.91 M and AIBN (0.027 M) as a thermal free-radical source. [Adapted with permission from ref. 24, copyright 1984, American Chemical Society.]

TABLE 2. Concentrations of the nitrile structures in reduced samples of AIBN-initiated PVC.

[VC] _m ^a (M)	no. ($\pm 10\%$) per 1000 C	
	CN	CN'
4.61	0.2	$\leq 0.1^b$
0.91	1.0 ^c	0.4 ^c
0.46	2.1	0.1 ₅

^aMean monomer concentration during polymerization at 40°C in 1,2-dichloroethane with initiation by 0.027 M AIBN. ^bNot detected. ^cValue calculated from the spectrum of Fig. 3. [Adapted with permission from ref. 24, copyright 1984, American Chemical Society.]

Table 2 lists the concentrations of the nitrile structures in three reduced samples of PVC that had been prepared by polymerization in solution at different concentrations of vinyl chloride (ref. 24). From simple kinetic considerations, it can be shown very easily (ref. 24) that the experimental "CN" concentration, $[\text{CN}]_{\text{ex}}$, in units of $(1000 \text{ C})^{-1}$, will be given by eq. 24 if

$$[\text{CN}]_{\text{ex}} = 500[2k_t(R_i)_m]^{1/2}/k_p[\text{VC}]_m \quad (24)$$

no end groups are introduced by the coupling of $(\text{CH}_3)_2\text{CCN}$ radicals with growing-chain polymer radicals (in eq. 24, k_t is the rate constant for chain termination; $(R_i)_m$ is the mean rate of initiation; k_p is the rate constant for chain propagation; and $[\text{VC}]_m$ is the mean molar concentration of vinyl chloride). Therefore, if this requirement is met, a plot of $[\text{CN}]_{\text{ex}}$ vs. $[\text{VC}]_m^{-1}$ should be linear and extend through the origin. Both of these predictions are borne out by the data of Table 2. Furthermore, from the slope of the plot and an independently measured value of the rate of initiation, it is possible to calculate a value of $4.4 \text{ M}^{-1/2} \cdot \text{h}^{-1/2}$ for $k_p/k_t^{1/2}$ (ref. 24). This value is in very good agreement with the value of $4.1 \text{ M}^{-1/2} \cdot \text{h}^{-1/2}$ that was obtained by Tkachenko *et al.* (ref. 29) from a very detailed kinetic study of the free-radical polymerization of vinyl chloride in dichloroethane [apparently the 1,2 isomer (ref. 24)] at 40°C .

The kinetic treatment that leads to eq. 24 can be applied (with minor modifications) to other initiators and vinyl polymers. Thus it should be possible to use the approach that has just been described in order to obtain the values of $k_p/k_t^{1/2}$ for the free-radical polymerization of other monomers.

Table 2 shows that the "CN'" concentration attains its maximum value when $[\text{VC}]_m$ is 0.91 M. Indeed, at this intermediate concentration of monomer, about 30% of the polymer-bound initiator fragments occur in the "CN'" structure. This very surprising finding has been explained with the aid of another kinetic analysis, which has led to the derivation of eq. 25 (ref. 24).

$$[\text{CN}']_{\text{ex}} = \frac{500}{([\text{VC}]_0 - [\text{VC}])} \left\{ \left[[\text{MAN}]_0 - \frac{\gamma k_d [\text{I}]_0}{Ck_p'} \right] (1 - e^{-Ck_p't}) + \gamma [\text{I}]_0 (1 - e^{-k_p't}) \right\} \quad (25)$$

In this equation, $[\text{CN}']_{\text{ex}}$ is equivalent to CN' in Table 2; t is the total time of polymerization; $[\text{VC}]_0$ and $[\text{VC}]$ are, respectively, the initial and final molar concentrations of vinyl chloride; $[\text{MAN}]_0$ is the molar concentration of MAN that is present in the original reaction mixture, owing to the occurrence of MAN as an adventitious impurity in the starting AIBN; γ is the fractional yield of MAN from AIBN thermolysis; k_d is the rate constant for this thermolysis; $[\text{I}]_0$ is the initial molar concentration of AIBN; C is the steady-state concentration of polymer radicals having a $-\text{CH}_2\text{CHCl}$ terminus; and k_p' is the rate constant for the addition of these radicals to MAN.

Experimental values are available for every term in eq. 25 except the quantity $[\text{MAN}]_0$. Therefore, with recourse to this equation, one can calculate the amounts of MAN in the starting samples of AIBN that were used to prepare the PVC specimens for which the conditions of polymerization are summarized in Table 2. The results show that in the case of the 0.91-M $[\text{VC}]_m$ polymer, about 0.15 wt% of MAN was present in the starting AIBN, and that the "CN" concentration would have been reduced by a factor of 6 if this impurity had been absent (ref. 24). Also, eq. 25 indicates an $[\text{MAN}]_0$ value of zero for the 0.46-M $[\text{VC}]_m$ specimen and shows that 0.15 wt% of MAN in the starting AIBN would not have led to a detectable number of "CN" structures in the reduced 4.61-M $[\text{VC}]_m$ sample (ref. 24). The latter result is consistent with the relevant datum in Table 2.

Copolymerized MAN units may exist in many other vinyl polymers whose polymerization has been initiated thermally by AIBN. In fact, there is some recently published evidence for the presence of such units in AIBN-initiated polystyrene (ref. 30). Copolymerization with MAN now would seem to be at least a potential source of significant error in any mechanistic investigation where all of the polymer-bound fragments from AIBN are required to occur at the ends of chains.

CONCLUDING REMARKS

The topics discussed in this brief review exemplify the great power and versatility of an approach to polymer structural analysis involving three basic steps: (1) chemical conversion of the polymer into a substance whose structure is relatively simple, (2) characterization of this substance by a modern analytical technique, and (3) use of the data thus collected in order to deduce the microstructure of the original polymer specimen. It cannot be emphasized too strongly that if this approach is to be successful, the chemistry occurring in step 1 must be well-understood. This has been the case, of course, for the examples presented here. With the aid of other simplifying chemical changes, which will differ, perhaps, in many major respects from the ones we have used thus far, it may be possible to unravel the structural intricacies of other classes of synthetic polymers.

ACKNOWLEDGMENTS

The author is greatly indebted to the many co-workers whose names appear in the references, and to Dr. D. Braun for providing the suspension copolymer samples that are identified in Table 1.

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