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Molecular Structure and Polymerization Mechanism of Poly(vinyl chloride-*co*-carbon monoxide)[1]

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ABSTRACT: Vinyl chloride–carbon monoxide copolymers, prepared by free-radical initiation at 50 °C, are shown to contain the branch structure $-CH_2-CH(COCl)-CH_2-$. This structure could only have arisen from the addition of vinyl chloride to a $-CH_2-\dot{C}H-COCl$ radical that was formed from the $-CH_2-CHCl-\dot{C}O$ radical by a 1,2 halogen shift. The copolymer samples studied were made in bulk or in aqueous suspension under CO pressures ranging from 50 to 845 psi. Following esterification of their COCl groups with methanol, the copolymers were reduced sequentially with $LiAlH_4$ and Bu_3SnH, and their ^{13}C NMR spectra were then obtained. These spectra revealed the presence of the $-CH_2-CH(CH_2OH)-CH_2-$ branch grouping, together with the cis and trans isomers of 2,4-di(long alkyl)tetrahydrofuran, which evidently had been derived from the $-CH_2-CH(CH_2O^-)-CH_2-CHCl-$ anion by Cl^- displacement. In addition, small amounts of $-CH_2-CH(OH)-CH_2-$ were found, but evidence was obtained to indicate that they had been introduced via air oxidation rather than by copolymerization with carbon monoxide. Methods of synthesis are described for some low-molecular-weight model compounds that were used to obtain the ^{13}C shifts of the $-CH_2-CH(CH_2OH)-CH_2-$ structure and the 2,4-di(long alkyl)tetrahydrofurans.

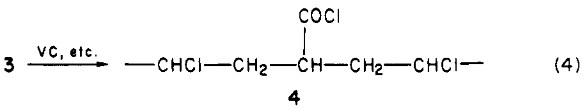
During the past several years, considerable controversy has existed with regard to the molecular structure and polymerization mechanism of the poly(vinyl chloride-*co*-carbon monoxide) (PVC-*co*-CO) that can be prepared by free-radical routes. Kawai and Ichihashi[2] have suggested a conventional mechanism that seems quite reasonable a priori and leads to the formation of structure 2 via reactions 1 and 2. Ratti et al.,[3] on the other hand, have

$$-CH_2-\dot{C}HCl + CO \rightarrow \underset{1}{-CH_2-CHCl-\dot{C}O} \qquad (1)$$

$$1 \xrightarrow{\text{VC, etc.}} \underset{2}{-CH_2-CHCl-CO-CH_2-CHCl-} \qquad (2)$$

proposed a scheme that is far more intriguing, in that it involves the apparently unprecedented rearrangement[4] (eq 3) of radical 1 into radical 3. Subsequent reaction of 3 with

$$1 \longrightarrow \underset{3}{-CH_2-\dot{C}H-COCl} \qquad (3)$$



$$3 \xrightarrow{\text{VC, etc.}} -CHCl-CH_2-\overset{\displaystyle COCl}{\overset{|}{C}H}-CH_2-CHCl- \qquad (4)$$

4

vinyl chloride (VC), as in eq 4, should then create a structure, 4, containing a chlorocarbonyl branch.[3] Kawai[2c] and Braun and Wolf[5] have reported chemical and IR evidence which has been stated[2c,5] to establish the presence of 2 in a variety of PVC-*co*-CO samples. However, on the basis of other chemical and spectral findings, Ratti et al.[3] and Braun and Sonderhof[6] have argued for the occurrence of structure 4 instead.

Apart from its intrinsic interest, the PVC-*co*-CO structural problem is important for other reasons. When the free-radical polymerization of vinyl chloride is conducted in the presence of molecular oxygen, carbon monoxide is formed in situ[6,7] and is then removed from the system by copolymerization with vinyl chloride.[6] Small amounts of residual air may remain entrapped in reactors that are used commercially for the preparation of PVC. Thus commercial PVC seems likely to contain low concentrations of adventitious moieties that are identical, structurally, with the oxygen-containing group (or groups) of deliberately synthesized PVC-*co*-CO. Identification of the oxygenated structures in PVC itself has been very desirable for some time in connection with the possible contributions of such structures to the thermal[5-8] and photochemical[5,9] instability of this polymer. Carbonyl-containing structures, in particular, are now attracting much attention in this regard, owing to the recent appearance of several papers in which certain groups of this type are claimed to cause remarkable reductions in the thermal stability of PVC.[8c-e]

Carbon-13 NMR measurements on PVC-*co*-CO are complicated by two problems, viz., the thermal lability of the copolymer under typical analytical conditions and a current lack of reference data for the chemical shifts of interest. In attempting to devise a procedure that would allow these difficulties to be overcome, we envisaged an alternative method involving the ^{13}C NMR analysis of PVC-*co*-CO specimens that had been reduced sequentially with lithium aluminum hydride and tri-*n*-butyltin hydride. The $LiAlH_4$ reduction was expected to convert the carbonyl groups of the copolymer into hydroxyl functions, and

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it was to be performed under mild conditions (room temperature) in order to avoid the side reactions encountered earlier with PVC itself.[10] Reductive dechlorination with Bu_3SnH[10,11] was then anticipated to produce a saturated polymeric alcohol whose ^{13}C signals could be assigned with recourse to the reference spectra of readily available model compounds. Our successful use of this approach is described in the present paper.[12]

Results and Discussion

The copolymers investigated during this study were prepared in bulk or in aqueous suspension, and they all were made at 50 °C in the absence of air, using azobis(isobutyronitrile) as a thermal free-radical source. The crude copolymers were purified by precipitating them with excess methanol from their solutions in tetrahydrofuran (THF), a procedure that would be expected to convert the COCl group of structure **4** into an ester function (CO_2Me). In fact, all of the purified specimens gave an IR absorption at 1735 cm^{-1}, which is the characteristic stretching frequency of an aliphatic ester carbonyl group.[14] However, this assignment is not unambiguous, for a band at this position might also have arisen from the chloroketone structure, **2**.[15]

After reduction with $LiAlH_4$ in THF solution at room temperature, the copolymers displayed no IR carbonyl absorption, but they did produce a broad new band at about 3400 cm^{-1} that could be assigned with confidence to the OH stretching vibration of an alcoholic hydroxyl function.[16] Reductive dechlorination of the $LiAlH_4$-reduced samples was carried out with Bu_3SnH, using our standard procedure.[10a,b,11] and the ^{13}C NMR spectra of the samples were then obtained at 50.31 MHz.

These spectra showed that the dehalogenation reaction was always essentially complete, although traces of isolated backbone secondary chloride[10] were found to remain in every specimen. In most instances these were accompanied, as expected, by minor amounts of residual primary halogen in various structural environments.[11,17] With the aid of appropriate chemical-shift reference data,[11,17,18] all of the resonances of the nonoxygenated structures were easily assigned, and from relative intensity measurements the concentrations of chloromethyl[10,11,17] and 2,4-dichloro-*n*-butyl[11,17] branches were calculated to be ca. 2.2 ± 0.2 and 0.5 ± 0.1 $(1000\ C)^{-1}$, respectively, for the original (unreduced) copolymers. The presence of long-chain branches was not established conclusively or investigated thoroughly, and the signal-to-noise ratios of the spectra usually were insufficient to allow the detection of the ethyl-branch-containing segment that would have resulted from the reduction of a 2-chloroethyl branch structure.[11] Nevertheless, all of the diagnostic resonances of this segment[11,19] were observed, at a concentration level of 0.2 $(1000\ C)^{-1}$, in the spectrum of a reduced copolymer that had been made in bulk at a CO pressure of 100 psi. Excellent evidence was also obtained for the presence of saturated long-chain ends[11,17] and for *cis*- and *trans*-1-ethyl-2-(long alkyl)cyclopentanes arising from the Bu_3SnH reduction of allylic chloride terminal groups.[18a] However, no attempts were made to record the spectra under conditions[11,18a] that would permit the accurate measurement of end-group concentrations. A few samples were found to contain *cis*- and *trans*-1,2-di(long alkyl)cyclopentanes derived from internal double bonds,[18b] but the total concentration of these structures was never greater than ca. 0.3 $(1000\ C)^{-1}$. Thus, in general, the "PVC parts" of the spectra were entirely in line with expectations based upon the results of our earlier structural studies with PVC itself.

Our sequential reduction process was expected to convert the original structures **2** and **4** into the "OH" and "HOMe" arrangements.

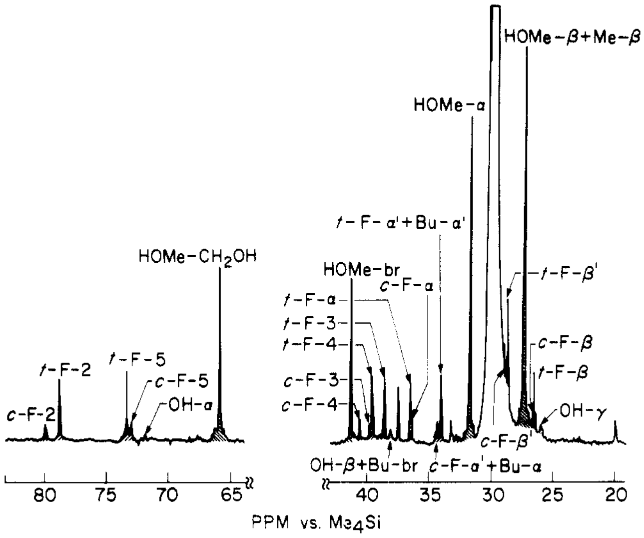
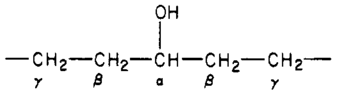
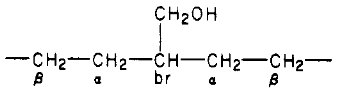


Figure 1. Proton-decoupled ^{13}C NMR partial spectrum (50.31 MHz) of a PVC-*co*-CO specimen (CO = 845 psi) that had been reduced sequentially with $LiAlH_4$ and Bu_3SnH. All of the diagnostic resonances of the "OH", "HOMe", "*c*-F", and "*t*-F" structures have been assigned; unassigned signals results from nonoxygenated groups that are mentioned in the text. See text for nomenclature and further details.



$$-\underset{\gamma}{CH_2}-\underset{\beta}{CH_2}-\underset{\alpha}{\overset{\overset{OH}{|}}{CH}}-\underset{\beta}{CH_2}-\underset{\gamma}{CH_2}-$$

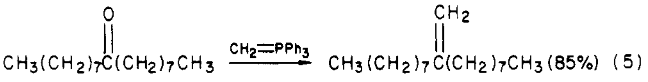
OH



$$-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-\underset{br}{\overset{\overset{CH_2OH}{|}}{CH}}-\underset{\alpha}{CH_2}-\underset{\beta}{CH_2}-$$

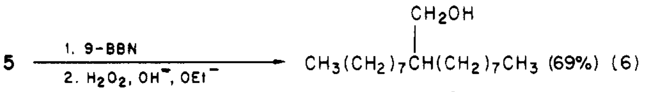
HOMe

The reference ^{13}C shifts of the "OH" moiety were easily obtained from the spectrum of 7-tridecanol, a commerical product, while those of the "HOMe" structure were determined with the aid of another model, **6**, that was synthesized very conveniently via reactions 5 and 6.



$$CH_3(CH_2)_7\overset{\overset{O}{\|}}{C}(CH_2)_7CH_3 \xrightarrow{CH_2{=}PPh_3} CH_3(CH_2)_7\overset{\overset{CH_2}{\|}}{C}(CH_2)_7CH_3\ (85\%) \quad (5)$$

5



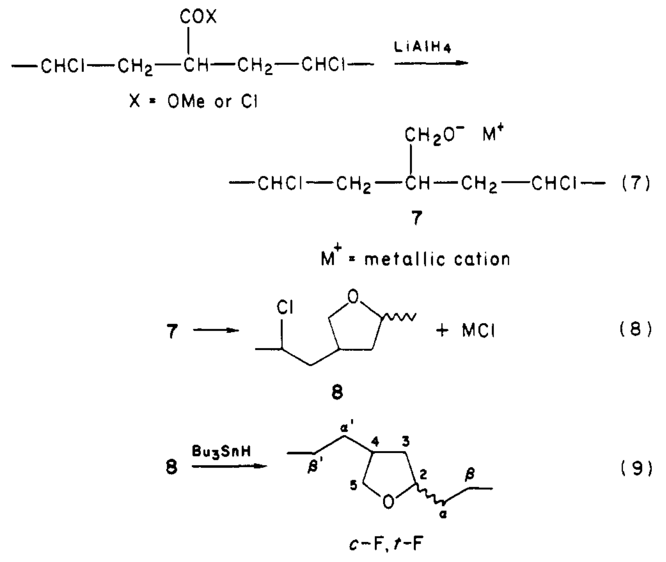
$$\mathbf{5} \xrightarrow[2.\ H_2O_2,\ OH^-,\ OEt^-]{1.\ 9\text{-}BBN} CH_3(CH_2)_7\overset{\overset{CH_2OH}{|}}{C}H(CH_2)_7CH_3\ (69\%) \quad (6)$$

6

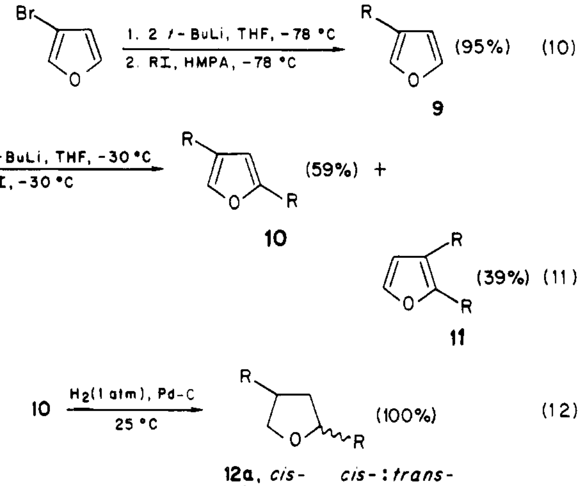
9-BBN = 9-borabicyclo[3.3.1]nonane

Figure 1 displays a partial ^{13}C spectrum of one of our reduced copolymers in which all of the "OH" and "HOMe" resonances can be found, and in Table I the chemical shifts of these signals are compared with those of the analogous model compounds. The excellent agreement of the two sets of values provides very strong confirmation for the polymer resonance assignments. Moreover, these assignments also are entirely consistent with the relative intensities of the "OH" and "HOMe" resonances in Figure 1 when the "OH-β" and "HOMe-β" intensities are corrected for the presence of coincident signals arising from *n*-butyl-[11] and methyl-branch-containing segments,[10,11] respectively, that have been completely reduced.

Figure 1 contains several other assigned resonances whose origins were puzzling at first. However, mechanistic considerations soon suggested that these signals might have arisen from "c-F" and "t-F" structures formed via reactions 7–9. This hypothesis was, in fact, supported by some predicted values for the "c-F" and "t-F" chemical shifts that were derived with the aid of the Grant–Paul rules[20] and the experimental ^{13}C chemical shifts of *cis*- and *trans*-2-ethyl-4-methyltetrahydrofuran.[21] Nevertheless, the shifts of better models were still required for direct comparison; hence some improved prototypes were synthesized according to eq 10–12.



c-F, t-F



R = n-C_8H_{17}
HMPA = hexamethylphosphoric triamide

The model compounds, **12a** and **12b**, produced all of the "c-F" and "t-F" resonances that also appear in Figure 1. The relative intensities of these resonances in the figure are consistent with the assignments given there, and Table I reveals the near-perfect agreement that was found between the "c-F" and "t-F" shifts of the models and those of the polymer system. From Figure 1 and our other polymer spectra, the "c-F":"t-F" ratio was calculated to be ca. 1:(3 ± 1). This value is qualitatively in accord with expectations, since the (presumably) more stable trans isomer of **8** should form preferentially in reaction 8. These findings leave no doubt as to the presence of the "c-F" and "t-F" structures in our reduced copolymer samples.

In theory, other cyclic ethers might have resulted from an intermediate similar to **7** that was formed during the $LiAlH_4$ reduction of **2**. However, the ^{13}C spectra of the reduced copolymers provided no evidence for the presence of any other ethereal groups.

Table I
^{13}C Shifts of Oxygenated Structures in Reduced PVC-*co*-CO

carbon	δ, ppm (±0.05) vs. Me_4Si[a] model[b]	δ, ppm (±0.05) vs. Me_4Si[a] polymer
OH-α	71.91	71.84
OH-β	38.13	38.23
OH-γ	25.98	26.07
HOMe-CH_2OH	65.81	65.81
HOMe-br	41.30	41.37
HOMe-α	31.75	31.83
HOMe-β	27.41	27.45
t-F-2	78.86	78.87
t-F-3	38.66	38.70
t-F-4	39.68	39.71
t-F-5	73.47	73.48
t-F-α	36.61	36.59
t-F-β	26.60	26.60
t-F-α'	34.16	34.17
t-F-β'	28.83	28.81
c-F-2	80.01	80.06
c-F-3	39.81	39.85
c-F-4	40.68	40.69
c-F-5	73.06	73.10
c-F-α	36.50	36.46
c-F-β	26.70	26.73
c-F-α'	34.48	34.51
c-F-β'	28.91	28.92

[a] Measured at 110 °C for samples dissolved in 4:1 (v/v) 1,2,4-trichlorobenzene/*p*-dioxane-d_8. [b] Data for 7-tridecanol, **6**, **12a**, and **12b**.

Table II
Concentrations of Carbonyl Structures in PVC-*co*-CO Samples

CO, psi	no. per 1000 C COCl	no. per 1000 C backbone CO
845[a]	17.3 ± 0.5	0.4 ± 0.1
285[b,c]	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[b,d]	0.7 ± 0.2	2.0 ± 0.1

[a] Bulk polymerization, 50 °C. [b] Suspension polymerization, 50 °C. [c] Designated as sample 18 in Table 2 of ref 6. [d] Designated as sample 12 in Table 2 of ref 6.

Table II contains the concentrations (as determined by ^{13}C NMR) of the two types of carbonyl structure that were shown to be present in five copolymer specimens made under different CO pressures. In line with our previous discussion, the tabulated "backbone CO" values are just the "OH" concentrations found after reduction, whereas each "COCl" value represents the sum of the "HOMe", "c-F", and "t-F" concentrations in the corresponding reduced copolymer. For example, in the case of the specimen for which the CO pressure was 845 psi, the "HOMe", "c-F", and "t-F" values (as deduced from the spectrum of Figure 1) are 11.4 ± 0.3, 1.3 ± 0.1, and 4.6 ± 0.1 $(1000\ C)^{-1}$, respectively.

As expected for the operation of the mechanism of Ratti et al.[3] (reactions 1, 3, and 4), the "COCl" values decrease smoothly with decreasing CO pressure. However, if this mechanism and that of Kawai and Ichihashi[2] (reactions 1 and 2) were operating simultaneously, the "COCl": "backbone CO" ratio should be independent of CO pressure, and the sum of the "COCl" and "backbone CO" values should show a steady decrease as the CO pressure is lowered. Neither of these predictions is fulfilled by the data in Table II. It might be argued that one could explain the observed increase in the "COCl":"backbone CO" ratio at higher CO pressures by assuming that reaction 3 is essentially irreversible and that the higher CO pressures tend to decrease the solubility (i.e., the concentration) of vinyl chloride in the monomer–swollen polymer phase where most of the polymerization occurs. The higher CO pressures would then also tend to reduce the rate of reaction 2 as compared to the rate of formation of 4. On the other hand, if vinyl chloride solubility variations were indeed responsible for the "COCl":"backbone CO" ratio changes, then the dichlorobutyl branch concentration should have changed in parallel to about the same degree, since this concentration is well-known to depend inversely upon the concentration of vinyl chloride.[11] In fact, as was noted above, the dichlorobutyl branch concentration is essentially the same for all of our PVC-*co*-CO specimens. The only other apparent way to account for the "COCl":"backbone CO" trend (in terms of reactions 2–4) is to postulate some sort of catalysis, by carbon monoxide, of the process that leads to **4**. To our knowledge, such catalysis has no precedent or analogy. Hence, in view of these various considerations, we are forced to conclude that the "OH" group of our reduced copolymers is very unlikely to have been derived from **2** to any significant extent.

An alternative source of the "OH" group would be air oxidation during reduction or thereafter, even though all of our reductions were performed with apparent exclusion of air. In order to check this possibility, the reduction of one copolymer (CO = 95 psi) was repeated by using especially stringent precautions designed to ensure anaerobic conditions. The ^{13}C spectrum of the product indicated a "COCl" concentration of 2.1 ± 0.3 (1000 C)$^{-1}$ and a "backbone CO" (i.e., "OH") concentration of 1.3 ± 0.1 (1000 C)$^{-1}$, in excellent agreement with the values obtained previously (Table II).[22] Moreover, in earlier studies,[10,11,17,18] the "OH" structure had not been detected in numerous samples of dechlorinated PVC whose Bu_3SnH reduction had been performed in much the same way as that of our PVC-*co*-CO specimens. Accordingly, oxidation accompanying or following our PVC-*co*-CO reductions seems improbable at this time.

The copolymers could have undergone some air oxidation before reduction, of course, but the extent of such oxidation is difficult to foresee. However, in a related experiment, we have detected an "OH" concentration of 2.8 (1000 C)$^{-1}$ in an ($LiAlH_4$/Bu_3SnH)-reduced PVC specimen (a commercial product) that had been stored for several years under ambient conditions before being reduced. The ^{13}C spectrum of this reduced sample yielded no conclusive evidence for the presence of other groups containing oxygen, whereas the IR spectrum of the unreduced polymer displayed a rather broad (but surprisingly weak) carbonyl absorption that was centered at ca. 1735 cm^{-1} and can perhaps be ascribed to a backbone –CHCl–CO–CHCl– structure.[15]

It obviously would be desirable to obtain more information about the oxygenated backbone structures in PVC-*co*-CO and PVC itself, and we plan to approach this problem subsequently by examining the ^{13}C NMR spectra of some polymers that have been subjected to sequential reductions involving the use of one or more reagents containing deuterium ($LiAlD_4$, Bu_3SnD). Nevertheless, despite the remaining questions, we can now state with confidence that the "Ratti reaction" (eq 3) does, in fact, occur and that the mechanism of Ratti et al.[3] is very likely to be the only important mechanism for the free-radical copolymerization of vinyl chloride and carbon monoxide. Indeed, our data have already shown conclusively that this mechanism is the predominant one, at least, when the copolymerization is conducted at 50 °C under CO pressures ranging upward from 95 psi.

Why does the copolymerization prefer to follow the Ratti path? The reason must be (a) a low reactivity of radical **1** toward vinyl chloride, (b) a low concentration of this radical caused by its conversion into **3**, or (c) a combination of both of these factors. At present, we have no information that pertains directly to factor a. However, thermochemical data in the literature attest to the importance of factor b.

The enthalpy change for reaction 3 can be described by eq 13, where the first term on the right-hand side denotes

$$\Delta H^\circ_3 = DH^\circ(s\text{-C–Cl}) - \text{SE} - DH^\circ(\text{CO–Cl}) \quad (13)$$

the strength of the C–Cl bond in a simple secondary alkyl chloride, the second term is the resonance stabilization energy of an α-carbonyl alkyl radical, and the third term is the strength of the C–Cl bond in an aliphatic acyl chloride. With recourse to the bond strengths compiled by Benson,[23] the first and third terms can be inferred to have values of 81 and 82.5 kcal/mol, respectively. However, the magnitude of SE is rather uncertain, since some experimental studies have indicated it to be as low as 0–3 kcal/mol,[24] while others have pointed to much higher values of up to 10 kcal/mol.[25] In any event, it is apparent from these data that reaction 3 should be exothermic and thus presumably very fast (much faster than typical additions of carbon radicals to monoalkenes), by analogy with the rates of other exothermic 1,2 shifts of a chloro substituent.[4,26] Reaction 3 might be a mobile equilibrium, of course, but if that were the case, small exothermicities in the forward direction would cause the steady-state concentration of radical **3** to be much greater than that of **1**. For example, if SE were only, say, 2 kcal/mol, the forward exothermicity (from eq 13) would be 3.5 kcal/mol, and the concentration ratio of **3** to **1** would then be ca. 230 (at 50 °C) if the radical entropies were comparable. These considerations lend strong support to the proposition that the Ratti mechanism is preferred because the concentration of radical **1** is very low, either because reaction 3 is extremely rapid and irreversible, or because it is an equilibrium that strongly favors radical **3**.

Experimental Section

Materials. Vinyl chloride was dried by passage through a Drierite column and freed of dissolved oxygen by freeze–pump–thaw degassing (several cycles) immediately prior to use. Tetrahydrofuran (THF) was distilled from disodium benzophenone dianion under dry nitrogen and then stored under argon. All other starting materials, reagents, and solvents were of the highest purity available commercially, and they were subjected to further purification, if necessary, by means of standard methods. The commercial PVC specimen, "Geon 103EP", was manufactured by B.F. Goodrich.

Instrumental Analysis. Pulse Fourier transform ^{13}C NMR spectra of polymer samples were recorded at 50.31 MHz with a Varian XL-200 instrument, using a procedure that has been published.[11] A typical spectrum is that shown in Figure 1; it was obtained at 110 °C for a 28% (w/v) solution of the reduced copolymer in 1,2,4-trichlorobenzene (TCB) containing benzene-d_6 as the internal deuterium lock and hexamethyldisiloxane (HMDS) as an internal standard (2.00 ppm vs. Me_4Si). This spectrum represents an accumulation of 3000 transients at a pulse angle of 90° and a pulse repetition time of 5.0 s. In other reduced-polymer spectra, use of *p*-dioxane-d_8 as the deuterium lock was found to cause no significant changes in the chemical shifts. The model-compound ^{13}C spectra and most of the ^{1}H NMR spectra were obtained with a JEOL FX90Q FT instrument. Other ^{1}H spectra were recorded with a Varian T-60A spectrometer, and the

IR spectra were taken with a Perkin-Elmer instrument, Model 597. Polymer specimens were observed by IR in KBr pellets or as thin films that were made by pressing 0.1 g of material for 3 min at 120 °C and 24 000 psig. Gas chromatography (GC) was carried out with a Varian Model 3700 instrument equipped with a flame-ionization detector, a Varian CDS 111 data processor, and one of the following stainless steel columns: (a) 3.0 ft × 0.125 in. (o.d.), packed with 10% of OV-101 on Gas Chrom Z; (b) 6.0 ft × 0.125 in. (o.d.), packed with 10% of Carbowax 20M on Gas Chrom WHP. Preparative reverse-phase liquid chromatography (LC) was performed on a Waters Prep 500A liquid chromatograph, using a Waters PrepPAK/C_{18} cartridge and pure methanol as the solvent.

Preparation of PVC-*co*-CO. Bulk copolymerizations of vinyl chloride and carbon monoxide were carried out at 50 ± 1 °C in a stirred pressure reactor from which air had been removed by pumping under high vacuum. Transfer of vinyl chloride into the reactor was effected on a vacuum line. Reactions were initiated with azobis(isobutyronitrile) (2–5 mg per gram of vinyl chloride), and the vinyl chloride conversions (calculated from the yields of copolymer) were ordinarily rather low (ca. 10%). The crude copolymers were purified by dissolution in THF, precipitation into excess methanol, washing (or Soxhlet extraction) with methanol, and subsequent drying in vacuo at 50 °C.

Preparative details for the suspension copolymers are given in ref 6.

Reduction of PVC-*co*-CO and PVC. In general, the $LiAlH_4$ reductions were carried out overnight with stirring under an inert atmosphere at room temperature, using amounts of reductant that were well in excess of those anticipated to be sufficient for the removal of carbonyl groups. In a representative experiment, 5 mL of a 1 M solution of $LiAlH_4$ in THF was added cautiously to a stirred solution of PVC-*co*-CO (CO = 100 psi, 2.5 g) in THF (50 mL). On the following day, excess reductant was destroyed by adding methanol slowly **(Caution!)** until gas evolution had ceased. The mixture was then poured with stirring into a large excess of methanol, treated with 10 mL of 6 N hydrochloric acid, and filtered with suction in order to recover the polymer, which was washed thoroughly on the filter with fresh methanol and dried subsequently under vacuum at 50 °C. In cases where the copolymer carbonyl content was relatively high, the $LiAlH_4$ addition produced a gel that made stirring difficult (CO = 285 psi) or impossible (CO = 845 psi). Workup of the latter reduction was commenced by heating the mixture very briefly under reflux with shaking, in order to achieve partial liquefaction before the methanol treatment, which caused the gel to disappear. In the second reduction experiment with the copolymer prepared at CO = 95 psi (see Results and Discussion), the solvents (including those used for the Bu_3SnH reduction) were degassed very thoroughly by bubbling with argon before the reducing agents were introduced.

Our two-stage Bu_3SnH reduction procedure is described elsewhere in detail;[10a,b,11] THF was used as the first-stage solvent in all of the present work.

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 requiring such materials. Organic solutions were dried over anhydrous magnesium sulfate and concentrated under low vacuum on a rotary evaporator. Boiling points are uncorrected. "Usual workup" refers to the following procedure: addition of 1:1 (v/v) pentane/ether equal in volume to that of the reaction mixture, washing the resultant organic solution in succession with about one-third its volume of saturated aqueous sodium bicarbonate, distilled water, and saturated aqueous sodium chloride, drying, suction filtration, and removal of all volatile materials by concentration.

2-*n*-Octyl-1-*n*-decene (5). A 1.55 M solution of *n*-butyllithium in hexane (Aldrich, 145.8 mL, 0.226 mol) was added incrementally during 20 min to a well-stirred slurry of methyltriphenylphosphonium bromide (80.73 g, 0.226 mol) in dry ether (275 mL). After an additional 1.3 h of stirring, the orange-red mixture (which still contained some white solid) was cooled in an ice bath, and a slurry of 9-heptadecanone (50.0 g, 0.185 mol based on a purity of 94%, as determined by GC analysis on column a) in dry THF (150 mL) was introduced cautiously while stirring was continued. Much frothing occurred during this addition, and a white precipitate was formed. The mixture was stirred at room temperature until the exothermic reaction had subsided (i.e., for ca. 15 min). It was then heated overnight under gentle reflux, cooled to ice-bath temperature, mixed cautiously with water (50 mL), and subjected to suction filtration. The filter cake was washed thoroughly with pentane, and the filtrate and washings were combined and concentrated in order to remove the organic solvents. Following redissolution of the organic layer in pentane, the aqueous layer was separated and extracted with 3 75-mL portions of fresh pentane. Drying of the combined organic layers, followed by concentration (with an intervening suction filtration to remove precipitated solid) and fractionation of the residue through a short Vigreux column, gave 40.0 g (85%) of **5**, bp 95–105 °C (0.05–0.10 torr), in a purity of 95%, according to GC analysis on column a. This material was suitable for use in subsequent synthetic operations. However, in some experiments its gas chromatogram revealed the presence of a small amount of unchanged ketone, which was removed conveniently by allowing a warm ethanol solution of the product to stir overnight with 2,4-dinitrophenylhydrazine reagent that had been prepared in ethanol–phosphoric acid according to a published procedure.[27] Careful redistillation of a sample that had been purified in this way and then recovered by a conventional aqueous workup gave **5** in a purity of >98% (by GC analysis on column a): bp 83.0–83.5 °C (0.05 torr); IR (neat) 890 (strong, $=CH_2$ out-of-plane bend), 1650 (medium, C=C stretch), and 3080 cm^{-1} (weak, vinyl CH stretch); ^1H NMR ($CDCl_3$) δ 0.88 (distorted t, $J \cong 5$ Hz, 6, 2 CH_3), 1.1–1.7 [m, 24, 2 $CH_3(CH_2)_6$], 2.01 [distorted t, $J \cong 7$ Hz, 4, 2 $CH_3(CH_2)_6CH_2$], and 4.73 ppm vs. Me_4Si (distorted s, 2, $C=CH_2$); ^{13}C NMR [4:1 (v/v) TCB/*p*-dioxane-d_8, HMDS, 110 °C] δ 108.94 (C-1), 150.20 (C-2), 36.64 (C-3), 28.42 (C-4), 29.89 (C-5 and -6), 29.64 (C-7), 32.27 (C-8), 22.96 (C-9), and 14.10 ppm vs. Me_4Si (C-10).

2-*n*-Octyl-1-*n*-decanol (6). The procedure used for this preparation was adapted from that of Scouten and Brown.[28] A solution of alkene **5** (5.39 g, 21.3 mmol) in anhydrous THF (12 mL) was added to a stirred THF solution of 9-borabicyclo[3.3.1]nonane (Aldrich, 0.5 M nominal concentration, 42.8 mL, 21.4 mmol assuming an actual concentration of 0.500 M), and the mixture was heated under gentle reflux for 2 h while stirring was continued. It was then cooled to 0 °C and stirred while absolute ethanol (12.8 mL), 6 N aqueous sodium hydroxide (4.3 mL), and (cautiously) 30% aqueous hydrogen peroxide (8.6 mL) were introduced in succession. After an additional 1.5 h of stirring at 50 °C, the mixture was cooled to room temperature, and the organic layer was separated, dried, and concentrated. Fractionation of the residue through a short Vigreux column afforded 4.0 g (69%) of **6** in a purity of >98% (according to GC analysis on column a): bp 123–124 °C (0.05 torr); IR (neat) 1035 (medium, CO stretch) and 3335 cm^{-1} (strong, OH stretch); ^1H NMR ($CDCl_3$) δ 0.88 (distorted t, $J \cong 5$ Hz, 6, 2 CH_3), 1.1–1.8 [m, 30, 2 $(CH_2)_7$ and $CHCH_2OH$], and 3.4–3.7 ppm vs. Me_4Si (m, 2, CH_2OH); ^{13}C NMR [4:1 (v/v) TCB/*p*-dioxane-d_8, HMDS, 110 °C] δ 65.81 (C-1), 41.30 (C-2), 31.75 (C-3), 27.41 (C-4), 30.42 (C-5), 29.88 (C-6), 29.58 (C-7), 32.18 (C-8), 22.84 (C-9), and 14.00 ppm vs. Me_4Si (C-10).

3-*n*-Octylfuran (9). A solution of 3-bromofuran (1.4967 g, 10.18 mmol) in anhydrous THF (100 mL) was stirred at −78 °C while a solution of *tert*-butyllithium in pentane (Aldrich, 1.9 M nominal concentration, 10.72 mL, 20.37 mmol assuming an actual concentration of 1.900 M) was introduced during 5–10 min. After *no more than 5 min* of stirring, dry hexamethylphosphoric triamide (10.0 mL) was added to the yellow solution and followed immediately by neat 1-iodooctane (2.445 g, 10.18 mmol). The reaction mixture was then stirred for an additional 15 min at −78 °C, quenched with saturated aqueous ammonium chloride (10.0 mL), and subjected to the usual workup in order to obtain 1.84 g (100%) of material that was shown by GC analysis (column b) to consist almost entirely (>96%) of **9**, together with only ca. 3% of 2-*n*-octylfuran. A careful distillation through an efficient column afforded **9** in a purity of >98% (by GC analysis on column b): bp 92 °C (4 torr); IR (neat) 2930 and 2855 (strong, CH_2 stretches), 1470 (medium, CH_2 scissor), 1162 (medium, furan ring), 1024 (strong, furan ring), 872 (strong, furan ring), and 779 cm^{-1} (strong, furan ring); ^1H NMR ($CDCl_3$) δ 0.88 (distorted t, $J \cong 5$

Hz, 3, CH_3), 1.1–1.7 [m, 12, $CH_3(CH_2)_6$], 2.39 (t, $J \cong 7$ Hz, 2, CH_2 α to ring), 6.23 (distorted s, 1, vinyl H), 7.1–7.2 (m, 1, vinyl H), and 7.25–7.4 ppm vs. Me_4Si (m, 1, vinyl H); ^{13}C NMR ($CDCl_3$) δ 111.06, 125.38, 138.75, and 142.59 (ring C's); 14.13, 22.75, 24.86, 29.41 (two C's), 29.51, 30.12, and 31.98 ppm vs. Me_4Si (*n*-octyl C's); mass spectrum[29] (70 eV) *m/e* 180 (M^+, 5.5% of base peak), 95 ($M^+ - C_6H_{13}$, 24%), 82 ($M^+ - C_7H_{14}$, 100%, base peak), and 81 ($M^+ - C_7H_{15}$, 38%).

This synthesis was equally successful (90–95% isolated yields) when it was performed on a 50-mmol scale using a 0.13 M solution of 3-bromofuran and identical reaction times.

2,4-Di-*n*-octylfuran (10). A solution of **9** (5.47 g, 30.3 mmol) in dry THF (300 mL) was stirred at −25 °C and treated with a solution of *n*-butyllithium in hexane (Aldrich, 1.6 M nominal concentration, 18.90 mL, 30.2 mmol assuming an actual concentration of 1.60 M). After 3.5 h of stirring at −30 °C, 1-iodooctane (7.27 g, 30.3 mmol) was added, and the mixture was stirred for an additional 2 h at −30 to −40 °C. It was then allowed to warm to room temperature overnight, treated with saturated aqueous ammonium chloride (30 mL), and carried though the usual workup procedure, which afforded 9.10 g of crude product. Analysis of this material by GC (column b) revealed the presence of 5 area % of starting materials, together with 95 area % of a 60:40 mixture of **10** and **11** (yields, 59% and 39%, respectively). An attempt to separate this mixture by vacuum distillation was unsuccessful. However, a preparative reverse-phase LC separation of the pot residue gave 1.40 g of **10** in a purity of 95% (by GC analysis on column b): IR (neat) 2940 and 2865 (strong, CH_2 stretches), 1470 (medium, CH_2 scissor), 1125 (medium, furan ring), and 800 cm^{-1} (medium, 2,4-disubstituted furan ring); ^1H NMR ($CDCl_3$) δ 0.88 (distorted t, $J \cong 5$ Hz, 6, 2 CH_3), 1.1–1.8 [m, 24, 2 $CH_3(CH_2)_6$], 2.34 (t, $J \cong 7$ Hz, 2, CH_2 α to ring), 2.55 (t, $J \cong 7$ Hz, 2, CH_2 α to ring), 5.83 (s, 1, vinyl H), and 7.03 ppm vs. Me_4Si (s, 1, vinyl H); ^{13}C NMR ($CDCl_3$) δ 106.29, 126.01, 136.67, and 156.59 (ring C's); 25.12, 28.13, 28.24, and 30.10 (CH_2's α and β to ring); 14.13, 22.75, 29.34, 29.45, 29.54, and 31.98 ppm vs. Me_4Si (remaining *n*-octyl C's).

The ^1H NMR spectrum ($CDCl_3$) of a mixture of **10** and **11** was very similar to that of **10** alone, with the most noteworthy difference being the presence of the vinyl H resonances of **11** at 6.16 (d, $J \cong 1.5$ Hz, 1) and 7.19 ppm vs. Me_4Si (d, $J \cong 2$ Hz, 1). From the same mixture, the ^{13}C NMR spectrum ($CDCl_3$) of **11** was deduced: δ 111.34, 118.88, 139.68, and 151.23 (ring C's); 24.79, 26.07, 28.78, and 30.73 ppm vs. Me_4Si (CH_2's α and β to ring); remaining *n*-octyl shifts identical with those of **10** within experimental error.

***cis*- and *trans*-2,4-Di-*n*-octyltetrahydrofuran (12a and 12b).** A solution of **10** (456.9 mg) in absolute ethanol (20 mL) was stirred under hydrogen (1 atm) at room temperature for 18 h in the presence of activated palladium on carbon (500 mg, 5 wt % Pd). Suction filtration and concentration of the filtrate afforded a quantitative yield of a mixture of **12a** and **12b** in a ratio of ~7:1, respectively, as determined by ^{13}C NMR: IR (neat) 2940 and 2865 (strong, CH_2 stretches), 1470 (medium, CH_2 scissor), and 1045 cm^{-1} (medium, broad, CO stretch); ^1H NMR ($CDCl_3$) δ 0.88 (distorted t, $J \cong 5$ Hz, 6, 2 CH_3), 1.05–1.7 [m, 29, 2 $CH_3(CH_2)_7$ and ring 4-CH], 1.9–2.3 (m, 2, ring 3-CH_2), 3.2–3.55 (m, 1, ring 2-CH), and 3.6–4.0 ppm vs. Me_4Si (m, 2, ring 5-CH_2); ^{13}C NMR [4:1 (v/v) TCB/*p*-dioxane-d_8, HMDS, 110 °C] δ 14.07 (CH_3's); 22.93 (CH_3CH_2's); 32.23 ($CH_3CH_2CH_2$'s); 29.61, 29.91, and 30.17 ppm vs. Me_4Si (other *n*-octyl CH_2's, exact assignments uncertain), in addition to the resonances assigned in Table I.

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Poly(vinyl chloride) Structural Segments Derived from Azobis(isobutyronitrile)

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ABSTRACT: Poly(vinyl chloride) (PVC) prepared in 1,2-dichloroethane solution at 40 °C is shown to contain two types of nitrile structure derived from the polymerization initiator, azobis(isobutyronitrile) (AIBN). These structures have been identified by comparing the ^{13}C NMR spectra of their Bu_3SnH reduction products with those of appropriate models, whose synthesis is described. One of the nitrile moieties, an end group, results from the expected addition of the initiator radical, $(CH_3)_2\dot{C}CN$, to monomer, followed by conventional chain propagation. However, the other nitrile segment is internal and could only have been introduced by the copolymerization of vinyl chloride with methacrylonitrile (MAN). Kinetic analysis shows that the requisite amount of MAN could not have been formed in situ in all of the polymerizations that were studied, and that MAN must therefore have been present in the starting initiator at levels of $\leq 0.1_5$ wt %. The conclusive identification of MAN units in PVC reopens the question of the relative amounts of PVC chain termination by disproportionation and combination, as deduced from labeling studies with AIBN containing ^{14}C.

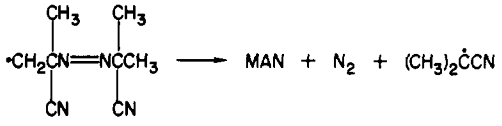
For many years azobis(isobutyronitrile) (AIBN) has been firmly entrenched in the role of a very popular initiator for free-radical polymerization. Its frequent use for this purpose has led to many detailed inspections of its thermolysis chemistry[1] and to its inclusion in numerous studies where mechanisms of polymerization have been addressed. For instance, ^{14}C-labeled AIBN and radiochemical assay have been used to determine the number of initiator fragments in poly(vinyl chloride)[2] (PVC) and, thus, to deduce the ratio of combination to disproportionation during the termination of PVC chains.[2a,c]

In the absence of contravening structural evidence, the assumption has been made frequently (e.g., for PVC)[2] that the AIBN moieties in polymers occur exclusively at chain ends. Nevertheless, it has long been recognized[3] that AIBN decomposition is a likely source of methacrylonitrile (MAN), whose free-radical polymerization and copolymerization are well-known. Hence, MAN units are conceivable "impurities" in all vinyl polymers that have been prepared using AIBN. This possibility was considered (but not confirmed) for poly(vinyl acetate) at least as early as 1955.[4]

There are several potential mechanisms for MAN formation during polymerization reactions, including (a) the disproportionation of carbon radicals derived from the AIBN (eq 1),[1a,3-5] (b) the disproportionation of one of these radicals with a polymeric radical, R· (eq 2),[5a] and (c) the decomposition (eq 3) of a radical (1) formed from AIBN by hydrogen abstraction.[6] Moreover, MAN may also be introduced into polymerizing systems as an impurity in AIBN, since it is formed when the initiator is subjected to a standard method of purification (recrystallization from hot methanol).[8] However, several quantitative product studies have shown that AIBN thermolysis gives MAN in yields that are low at best, the major organic products being a ketenimine, $(CH_3)_2C{=}C{=}NC(CH_3)_2CN$, and tetramethylsuccinonitrile.[1,3,5,6a,9]

$$2(CH_3)_2\dot{C}CN \longrightarrow \underset{\text{MAN}}{H_2C{=}C(CH_3)CN} + (CH_3)_2CHCN \qquad (1)$$

$$(CH_3)_2\dot{C}CN + R\cdot \longrightarrow \text{MAN} + RH \qquad (2)$$



$$\cdot CH_2\underset{CN}{\overset{CH_3}{C}}N{=}N\underset{CN}{\overset{CH_3}{C}}CH_3 \longrightarrow \text{MAN} + N_2 + (CH_3)_2\dot{C}CN \qquad (3)$$

1

At present, the most convincing evidence for the occurrence of anomalous structures in polymers consists of NMR spectra in which the diagnostic resonances of such structures can be conclusively assigned. From ^{13}C NMR measurements, we have previously obtained such evidence for the presence of $(CH_3)_2C(CN)CH_2CH_2-$ chain ends in reductively dehalogenated PVC that had been polymerized with AIBN having a natural abundance of ^{13}C.[10] More recently, Bevington et al.[11] have also used ^{13}C spectra in order to identify similar end groups in a number of vinyl polymers. However, in their studies[11] the AIBN was enriched with ^{13}C, and not all of the unique resonances of the end groups were detected.

The present paper reports the details of earlier experiments[10] and of others relating to PVC which have shown that this polymer contains both terminal and internal segments arising from AIBN. These segments have been

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