Mechanism for the Formation of Chloromethyl Branches in Poly(vinyl chloride)

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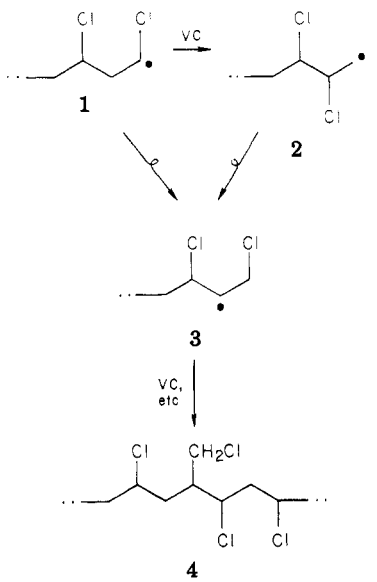
ABSTRACT: The ^{13}C NMR spectrum of $LiAlH_4$-reduced poly(vinyl-α-*d* chloride) shows that all of the pendent chloromethyl groups in the original polymer are formed by a mechanism involving head-to-head addition of monomer, followed by a 1,2-chlorine-atom shift and subsequent propagation. The migrating chlorine atom cannot be scavenged by cyclohexane and thus does not become kinetically free. However, the spectral data reveal the occurrence of a competitive β-scission process that produces chlorine atoms which can be trapped. Addition of the chlorine atoms to vinyl chloride accounts for chain transfer to monomer during vinyl chloride polymerization.

Recent studies in these laboratories have shown that the ^{13}C NMR spectrum of reductively dehalogenated poly(vinyl chloride) (PVC) can provide much useful information about the microstructure of PVC itself.[2] On the basis of this work, structure **4** is now known to be the

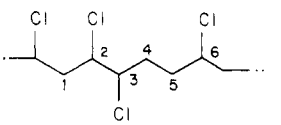


VC = vinyl chloride

principal short-branch grouping in the polymer,[2c,f,3] and its frequency of occurrence has been demonstrated to be ca. 2–3 per 1000 carbons.[2b-h]

Two mechanisms for the formation of **4** can be envisaged. One of these, originated by Rigo et al.,[3a] postulates an occasional head-to-head addition of monomer to the ordinary growing-chain radical (**1**), followed by rearrangement of the resulting primary radical (**2**) into a more stable secondary one (**3**) via a 1,2-chlorine-atom shift. Subsequent addition of monomer to **3** in the anticipated head-to-tail fashion then generates a chloromethyl branch (**4**). The other mechanism, suggested by Overberger,[4] also invokes **3** as an intermediate but postulates its direct formation from **1** by a 1,2 shift of hydrogen. Park has recently proposed that this hydrogen shift may occur via an unprecedented nonterminating interaction of two growing-chain radicals: i.e., 21 → 23.[3d] However, such a process requires a dependence of the chloromethyl branch content upon the kinetic chain length for polymerization[5] and thus seems inconsistent with the finding that the branch contents of polymers prepared in bulk are invariant with monomer conversion.[3a]

A plausible alternative fate of **2** would be its addition to monomer.[3a] Continued polymerization should then lead to the formation of head-to-head structures (**5**), and the



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detection of such groups by iodometry has, in fact, been claimed.[6] However, this interpretation has not been supported by the ^{13}C NMR spectra of numerous PVC samples,[2a,b,f,9] which have failed to exhibit the resonances expected[10] for carbons 1–6 of **5** at ca. 44, 69, 72, 32, 35, and 60 ppm (vs. Me_4Si), respectively.[11] While it might be argued that **5** is too unstable[6a,12] to survive the conditions required for pulse Fourier transform ^{13}C NMR experiments, the absence of **5** could also result from a rapid competing reaction of **2**. Rearrangement of a similar radical, $ClCH_2-CHCl-CH_2\cdot$, into $ClCH_2-\dot{C}H-CH_2Cl$ appears to be very fast at moderate temperatures[13] and is closely analogous to the rearrangement of radical **2** into radical **3**.[14] Moreover, the isomerization of radical $CH_3-CH^{38}Cl-CH_2\cdot$ into $CH_3-\dot{C}H-CH_2{}^{38}Cl$ has been reported to have the very large rate constant of $\sim 10^7\ s^{-1}$ in the vapor phase at 20 °C.[14d] It can easily be shown that a similar rate constant for the **2** → **3** interconversion would be likely to preclude the occurrence of other reactions of **2**.[15] Thus the absence of **5** does not rule out the Rigo route to **4**, which remains as a reasonable possibility on the basis of all previous experience.

The Overberger mechanism, on the other hand, requires a type of hydrogen migration which, to our knowledge, has never been observed for alkyl radicals in solution[14a,b] and which seems especially unlikely in the case of radical **1**, owing to stabilization of the radical site by a proximal chlorine atom.[14b,c] Indeed, it is possible to argue that **1** is more stable than **3**. In the free-radical addition of HBr to 3,3-dichloropropene, most of the product is formed from the rearranged radical, $ClCH-CHCl-CH_2Br$, rather than from the initial adduct radical, $Cl_2CH-\dot{C}H-CH_2Br$.[14b,c] Under the conditions of this experiment, rearrangement would have to be very fast (and, therefore, presumably exothermic) in order to compete with the rapid transfer of hydrogen from HBr to the initial adduct.[16] These considerations suggest that the thermodynamic stability of primary α-chloroalkyl radicals may be greater than that of secondary alkyl radicals such as **3**[14b,c] (although, in our

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Table I
^{13}C NMR Data for $LiAlH_4$-Reduced PVC-α-*d*

carbon	δ, ppm vs. Me_4Si DCH[a]	reduced PVC[b]	reduced PVC-α-*d*	isotope shift,[c] ppm vs. Me_4Si	isotope subst pattern
M-CH_3	-	19.91	19.85	−0.06	1 neighbor
M-α	-	37.45	36.98[d]	−0.47	1 attached, 1 neighbor
M-α′	-	37.45	37.32	−0.13	2 neighbors
M-β	-	27.32	27.13	−0.19	2 neighbors
M-β′	-	27.32	26.92[d,e]	−0.40	1 attached
CH-1	38.32	-	38.10	-	-
CH-2	34.00	-	33.83	-	-
CH-3	26.87	-	26.70	-	-
CH-4	27.30	-	27.38[e]	-	-
CH-α	37.88	-	37.66	-	1 neighbor
L-C_2	-	22.81[f]	22.71	−0.10	2 neighbors
DB-α	-	32.71[f]	32.57	−0.14	2 neighbors
DB-α′	-	32.71[f]	32.35[d,e]	−0.36	1 attached
principal CH_2	-	29.95	29.80	−0.15	2 neighbors
principal CHD	-	-	29.51[d]	−0.44	1 attached

[a] *n*-Dodecylcyclohexane. [b] Unlabeled $LiAlH_4$-reduced polymer; data from ref 2c unless noted otherwise. [c] A dash (-) denotes upfield shift. [d] Triplet center. [e] Tentative assignment. [f] Reference 9.

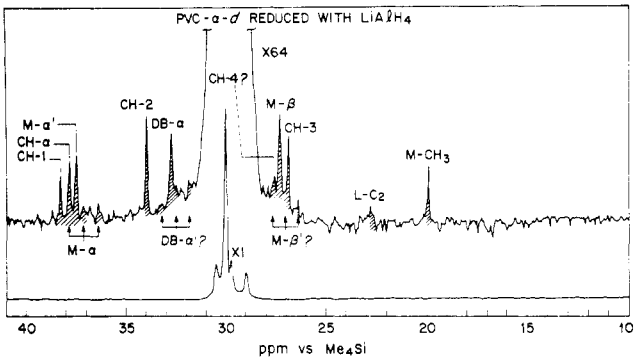


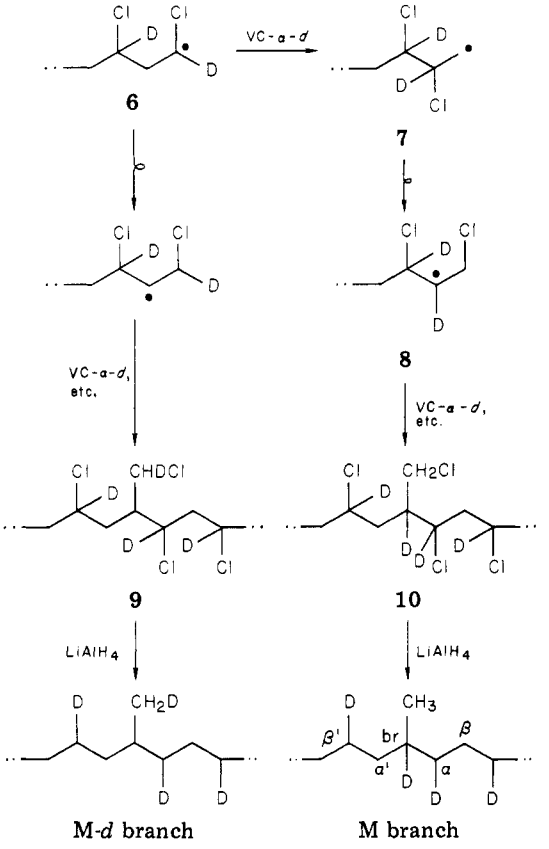
Figure 1. ^{13}C NMR spectrum (25.16 MHz) of $LiAlH_4$-reduced PVC-α-*d*. Scale refers to upper spectrum; lower spectrum can be converted to this scale by subtracting ca. 0.2 ppm. For experimental details and exact chemical shifts, see text and Table I.

opinion, the available data do not entirely rule out the possibility that the product yields obtained by Freidlina et al.[14b,c] are actually a measure of the rates of hydrogen transfer instead of the radical stabilities).

Thus, on balance, the Rigo mechanism seems to comprise the more plausible route to **4**. Nevertheless, this mechanism has been in need of experimental verification, and we now wish to describe a study in which this objective has been achieved. This work has also provided insight into other aspects of the mechanism for vinyl chloride polymerization.

Results and Discussion

Experimental Approach. Monodeuteration of a ^{13}C atom converts its proton-decoupled NMR signal into a 1:1:1 triplet (spacing, ~20 Hz) and causes this signal and those of neighboring ^{13}C nuclei to undergo upfield shifts.[2c,f] Thus a ^{13}C NMR spectrum can be used to identify points of deuterium attachment, particularly if the spectrum of nondeuterated material is available for comparison purposes. We therefore considered it likely that the mechanism for the formation of **4** could be deduced from the ^{13}C NMR spectrum of reduced PVC[2] that had been prepared from a deuterated monomer. Vinyl-α-*d* chloride (VC-α-*d*) was obviously the monomer of choice, since the presence of β deuterium would be expected to retard the Overberger rearrangement step by a primary kinetic isotope effect. If the Overberger mechanism (or the Park variation[3d]) were operative, the chloromethyl branch structure of PVC-α-*d* should have the deuterium labeling pattern shown in **9**. However, the branch structure would be labeled as in **10** if it were formed by the Rigo path. Reductive dehalogenation would convert **9** and **10** into "M-*d*" and "M" branches, respectively, and the ^{13}C NMR spectrum should then allow a decision as to which of these structures was present (a reference spectrum of the "M-*d*" branch was, in fact, already available[2c,f]).



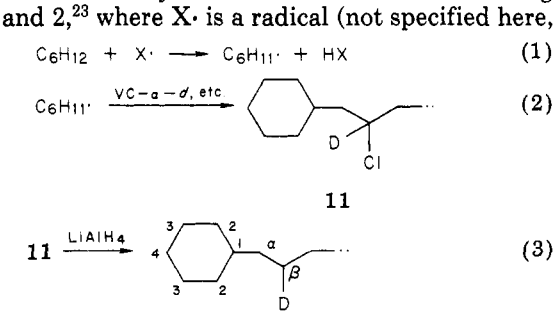
Preparation and Reduction of PVC-α-*d*. VC-α-*d* was polymerized in cyclohexane at 60 °C using azobis(isobutyronitrile) as the initiator, and the resulting polymers were reduced with lithium aluminum hydride according to our standard method (Experimental Section). The ^{13}C NMR spectrum of one of the reduced materials is shown in Figure 1, and the chemical shifts of the assigned resonances in this spectrum are listed in the fourth column

of Table I. These data pertain to a polymer isolated after 79% conversion of monomer; nearly identical results were obtained for a polymer recovered at a conversion level of 100%. Despite earlier indications for the occurrence of deuterium scrambling during $LiAlH_4$ reductions,[2d,e] no evidence for such scrambling appeared in the NMR spectra of the present work. The lower trace of Figure 1 is entirely consistent with expectations; it consists of a singlet produced by the principal CH_2 carbons and an overlapping triplet arising from the carbons of the principal CHD's. The deuterium isotope shifts of these resonances (Table I) and the ^{13}C–^{2}H coupling constant for the triplet (~18 Hz) are in satisfactory agreement with our earlier values for $LiAlD_4$-reduced PVC.[2c,f]

The presence of residual halogen in extensively reduced PVC-α-*d* should be revealed by the appearance of the structure $-CHD-CH_2-CDCl-CH_2-CHD-$, whose concentration is best determined from the intensity of its CH_2 carbon resonance, owing to the lower intensities of the triplet signals of the deuterated carbons. This CH_2 resonance can be predicted to occur at ca. 38.7–38.8 ppm on the basis of a normal shift (for nondeuterated material) of 38.9 ppm[9] and an anticipated isotope shift of −(0.1–0.2) ppm for two deuterium neighbors (Table I). No peaks appear at 38.7–38.8 ppm in the spectrum of Figure 1, and calculations based on the intensities of the two resonances that are closest to this region (39.23 and 38.51 ppm) indicate an extent of reduction greater than 99.9%.

Saturated Chain Ends. The spectrum of Figure 1 contains several strong resonances that were not observed in our earlier ^{13}C NMR studies on reductively dehalogenated PVC.[2] However, none of the polymers used previously were prepared in the presence of cyclohexane. Literature information suggests that cyclohexane should be an effective chain transfer agent for vinyl chloride polymerization under our conditions,[17,18] and this hypothesis is supported by the molecular weight of our PVC-α-*d*. The $\bar{M}_n$ of the 100% conversion sample was found to be about 14 400, a value which is lower by a factor of ca. 2.8 than the $\bar{M}_n$ expected for nondeuterated PVC that has been prepared in bulk under our conditions in the absence of cyclohexane.[21] The presence of α deuterium should have had essentially no effect on the degree of polymerization.[22] Thus, in our experiments, cyclohexane must have been acting either as an inhibitor or as an effective chain-transfer species. However, the former possibility is not supported by the results of previous work.[17a]

Chain transfer to cyclohexane should occur according to eq 1 and 2,[23] where X· is a radical (not specified here,



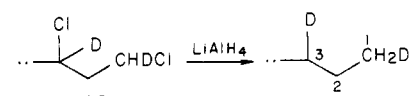
CH end

but see below) that would ordinarily be involved in normal propagation. Hydride reduction of the resulting chain ends (11) should produce "CH" ends, as shown (eq 3); their presence could account for the unusual resonances whose occurrence was noted above.

The presence of "CH" ends was confirmed by comparing the ^{13}C NMR spectrum of a model compound, *n*-dodecylcyclohexane (DCH), with the spectrum of Figure 1. Results of this comparison are summarized in Table I; they show that the latter spectrum contains resonances that can be assigned to the four types of carbon in the cyclohexyl ring. The "CH-4" assignment is to be regarded as tentative, however, since other possible sources of this resonance can be proposed. In fact, there is a strong possibility that the "CH-4" resonance is actually superimposed on the "M-β" signal (see below). Table I also shows that the polymer spectrum contains a resonance that can be ascribed to the methylene carbon α to the cyclohexyl group. This resonance is presumably shifted slightly upfield by the deuterium atom on the β carbon, but the magnitude of the shift cannot readily be assessed, since the normal position of the resonance probably cannot be equated with the "CH-α" shift of DCH. Indeed, the shifts of all of the other assigned "CH" resonances of the polymer differ from their counterparts in DCH by ca. 0.1–0.2 ppm, apparently owing to slight differences in the spectral measurement conditions.

For DCH, the carbon β to the ring appears at 27.38 ppm. In the reduced polymer, this carbon bears deuterium; thus its resonance should appear as a triplet centered at ca. 27 ppm. Conclusive evidence for the presence of this triplet is lacking, but its occurrence cannot be ruled out, since it is likely to be obscured by the other resonances at 26–28 ppm. Further comparisons with the DCH spectrum showed that the resonances of all of the other carbons near the polymer cyclohexyl group would be hidden beneath the resonances of the principal CH_2's and CHD's. Finally, we note that the relative intensities of the polymer "CH" resonances are in qualitative agreement with the assignments we propose.

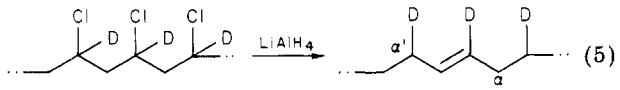
Abstraction of hydrogen by radical 6 would produce a second type of long-chain end (12), whose hydride reduction should afford the "L" end shown in eq 4. A



12 L end

resonance that can be assigned to the "L-C_2" carbon of this structure appears in the spectrum of Figure 1; its chemical shift is consistent with the presence of two neighboring deuterium atoms (Table I). On the basis of previous work[2a,b,d-f,9] and an assumed isotope shift of −(0.4–0.5) ppm (Table I), the C_1 and C_3 carbons of the "L" end can be predicted to appear as triplets centered near 13.5–13.6 and 31.7–31.8 ppm, respectively. These resonances cannot be detected in Figure 1, but their absence is easily explained by line broadening[2c] and the normal threefold reduction in intensity expected upon going from a singlet to a triplet signal. In fact, the nonappearance of the C_1 and C_3 triplets can actually be taken as strong evidence for the bonding of deuterium to these carbons. No C_1 singlet[2a,b,d-f] appears near 14 ppm, and none of the small resonances near 32 ppm can be assigned with confidence to a nondeuterated C_3 carbon,[2b,d-f] even if the possible isotope shifts of neighboring deuterium are considered. Thus all of the ordinary saturated long-chain ends seem to be labeled as in structure **12**.

Double Bonds. Our previous work showed that $LiAlH_4$- or $LiAlD_4$-reduced PVC contains isolated trans double bonds[2c,f-h] which are formed primarily during the reduction process.[2d,e,g,h] If the double-bond moieties in reduced PVC-α-*d* are formed from the "normal" (head-to-tail) monomer units, they will have the "DB" structure depicted in eq 5. The spectrum of Figure 1 contains a resonance that can be assigned to the "DB-α" carbon of



(5)

DB

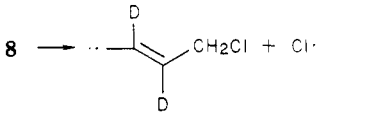
this grouping; its chemical shift (Table I) is in accordance with the labeling pattern shown. Resonances also appear which can be ascribed to the "DB-α'" triplet (spacing, ~18 Hz), but the low intensity of the peak at ca. 33 ppm tends to place this assignment in doubt. The double-bond structures would not have the "DB" labeling pattern if they were formed at head-to-head linkages (cf. **5**); this possibility is consistent with Carrega's[24] finding that the reaction of $LiAlH_4$ with poly(1,2-dichloroethylene) leads to the immediate appearance of color that may result from polyene formation.

If the "DB" structure is considered to be correct, a double-bond content of 3.0/(1000 C) can be calculated from the spectrum of Figure 1.

Chloromethyl Branches. With the preceding spectral assignments in hand, the resonances associated with the reduced chloromethyl branch can be assigned with considerable confidence (Table I). They are in excellent agreement with expectations for the branch structure denoted as "M". The "M-CH_3" carbon appears as a singlet, shifted slightly upfield by the presence of a neighboring deuterium atom. On the basis of previous work[2c] and a probable isotope shift of approximately −0.5 ppm (Table I), the deuterated "M-br" carbon should appear as a triplet centered at ca. 32.6 ppm. However, this resonance is likely to be even weaker than the resonances of the deuterated methylene carbons, owing to the decreased nuclear Overhauser enhancement factor and increased spin–lattice relaxation time expected for a carbon bearing no protium.[25] The branch carbon of the "M-d" structure produces a singlet at 33.01 ppm[2c] which is clearly absent from the spectrum of Figure 1. Thus the nonappearance of any "M-br" resonance is uniquely consistent with structure "M". The "M-α'" singlet appears in its predicted position, and its intensity is similar to that of the "M-CH_3" signal, as required. Two resonances that can be ascribed to the "M-α" triplet are found (spacing, ~18 Hz). The "M-β" singlet exhibits its anticipated isotope shift but is somewhat stronger than the "M-α'" and "M-CH_3" resonances. This difference can be attributed to signal overlapping, and there is a possibility that one of the underlying signals is the "CH-4" singlet discussed above. The "M-β'" triplet cannot be distinguished clearly, but the spectrum contains some evidence for its occurrence nonetheless (spacing, ~17 Hz?). Since there is no evidence whatsoever for the presence of "M-d" branches, we conclude that all of the pendent chloromethyl groups in PVC are formed by the Rigo path.

Long Branch Points. No evidence for the presence of long branch points[2a,b,d-f] appears in the spectrum of Figure 1, and the same result was provided by the spectrum (not shown) of the reduced 100% conversion polymer. Trifunctional long-chain branching was anticipated at the polymerization temperature[2g,h] and conversion levels employed; in fact, the $\bar{M}_w/\bar{M}_n$ ratio (2.85) of the 100% conversion polymer is not inconsistent with this expectation. The long branch points may have been altered structurally during the $LiAlH_4$ reduction process,[2d,e,g,h] but their absence can also be attributed to a diminished rate of chain transfer to polymer, owing to the operation of a primary kinetic isotope effect. In a subsequent paper,[26] we will show that tertiary halogen is present at all of the long branch points in PVC and that the long branches originate from radical sites that are formed by hydrogen abstraction (results obtained with polymers prepared in bulk at 100 °C[26]).

Mechanism of Chain Transfer to Monomer and Cyclohexane. From Figure 1 the concentrations of "L" ends and "CH" ends can be estimated to be about 0.8/(1000 C) and 2.0/(1000 C), respectively. Similar results were obtained for the reduced 100% conversion polymer using a pulse interval of 3.0 s. In order to minimize inaccuracies resulting from partial saturation of the end-group carbon resonances, the spectrum of the reduced 100% conversion polymer was re-recorded using a pulse interval of 30.0 s and 8000 transients; under these conditions the concentrations of the "L" ends and "CH" ends were found to be 1.5/(1000 C) and 2.4/(1000 C), respectively.[27] From this result it follows that radical **6** cannot have been the only species that abstracted hydrogen from cyclohexane (eq 1), for the number of "L" ends would have been at least as large as the number of "CH" ends in that event. However, the preponderance of "CH" ends is easily understood if the "extra" abstraction from cyclohexane is considered to have been performed by *chlorine atoms*. These could have resulted from β scission of radical **7** or radical **8** (eq 6; we favor this route at the present time[15a]);



(6)

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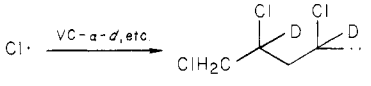

(7)

14

in the absence of a scavenger such as cyclohexane they would be expected to add to monomer and thus continue the polymerization (eq 7). The lack of evidence for unsaturated end groups can be rationalized on these grounds, since this mechanism requires these groups to be labile allylic chloride moieties (**13** or an isomeric structure) which would have been likely to initiate "zipper" dehydrochlorination[28] under the polymerization or reduction conditions. This type of dehydrochlorination leads to the formation of conjugated polyene sequences,[28] which are notoriously difficult to detect by NMR.[29]

The chain transfer constant of vinyl chloride is essentially unaffected by α deuteration[22] and has a value of ca. 16×10^{-4} at 60 °C,[20] corresponding to the formation of 1.6/(1000 C) total chain ends, or 0.8/(1000 C) allylic ends and 0.8/(1000 C) **14** ends according to the mechanism proposed above. If this mechanism is indeed operative, the absence of **14** ends from the spectrum of Figure 1 must be ascribed to Cl· scavenging by the solvent (eq 1). Both eq 1 and the addition of Cl· to monomer should be essentially irreversible under the reaction conditions.[15a] Thus the ratio of **14** ends to "CH" ends formed by Cl· scavenging ($[14]/[CH]_{Cl}$) will be given approximately by $\int_{r_0}^{r_x}(k_7/k_1)r\,dr/(r_x - r_0)$, where k_7 is the rate constant for Cl· addition (i.e., for the first step of eq 7), k_1 is the rate constant for eq 1 with X· = Cl·, r is the VC-α-d/cyclohexane mole ratio, and the subscripts on the limits refer to percent conversion of monomer. The k_7/k_1 ratio has apparently not been measured directly in the liquid phase. However, liquid-phase reactivities toward Cl· addition, relative to k_1, have been obtained for all of the other chloroethylenes by direct competition studies.[30] Also, absolute rate constants have been determined in the vapor phase for the addition of Cl· to most of these haloalkenes and to vinyl chloride as well.[31] The relative reactivities in the two phases appear to be

roughly equivalent.[30,31] Thus the two sets of data[30,31] can be compared to obtain an estimated value for k_7/k_1 of ca. 0.3 in the liquid phase at 25 °C (the secondary deuterium isotope effect on k_7 is undoubtedly very small[32] and can be neglected for our purposes). Using this value of k_7/k_1 as a reference, k_7/k_1 can be calculated to be about 0.2 in the liquid phase at 60 °C by taking 1.5 kcal/mol as the activation energy for abstraction[33] and assuming that the activation energy for addition is negligible.[30,33,34] As used here, k_7 is actually the sum of the rate constants for addition at the two ends of the deuterated monomer. However, addition of Cl· to the chlorinated end should be only a minor process,[30,31,34] since it is strongly disfavored by the overall thermodynamics[34c] and may be retarded significantly by kinetic factors[30] as well.

For the polymerization carried out to 79% conversion (see Experimental Section), the values of r_0 and r_x are 1.7 and 0.36, respectively. Incorporation of these limits and the 60 °C value of k_7/k_1 into the integrated form of the differential equation given above affords a value of 0.2 for $[14]/[CH]_{Cl}$. This result corresponds to the scavenging, by cyclohexane, of about 83% of the chlorine atoms formed. Therefore, the number of **14** ends produced in the 79% conversion experiment is predicted to be only about 17% of the "usual" number, or ca. 0.1/(1000 C). This value would be significantly lower if an appreciable fraction of the chlorine atoms abstracted hydrogen (or deuterium) from the polymer itself, although such a possibility seems rather unlikely at the present time.[15a] In any event, a **14** concentration of 0.1/(1000 C) would be well below our limit of detection under the conditions used to obtain the spectrum of Figure 1. Thus the apparent absence of the **14** ends is entirely consistent with the reaction mechanism we propose.

For the polymerization taken to 100% conversion (Experimental Section), $r_0 = 1.4$, and $r_x = 0$. These integration limits lead to a $[14]/[CH]_{Cl}$ value of 0.1, corresponding to the entrapment of 91% of the chlorine atoms by cyclohexane, or to the formation of 0.7/(1000 C) of the "CH" ends via the Cl· scavenging process. According to our mechanism, the remaining 1.7/(1000 C) of the "CH" ends are required to be formed via hydrogen abstraction from cyclohexane by radical **6**. Thus the number of "L" ends produced should also be 1.7/(1000 C), a value that agrees with the number found by experiment [1.5/(1000 C)] within the probable range of experimental error. If the 100% conversion polymer contains no long branches, its total number of chain ends (other than pendent chloromethyl groups) should be equal to twice the number of "CH" ends plus twice the number of **14** ends, or about 5.0/(1000 C). This number is in fair agreement with the value of 4.4/(1000 C) that can be estimated from the number-average molecular weight, but the data are not of sufficient accuracy to warrant the firm conclusion that no long branches are present.

In the preceding discussion, the polymerizations have been considered to be homogeneous insofar as the reactions of Cl· are concerned. This would appear to be a very reasonable assumption in view of the small mass and size of chlorine atoms, which should allow their rapid diffusion throughout the heterogeneous system. As an analogy for this hypothesis, we note that a fast distribution of small radicals between the monomer- and polymer-rich phases has been shown to provide a reasonable explanation for the kinetic effects of chain transfer agents during the bulk polymerization of vinyl chloride.[35]

The chain-transfer constant of cyclohexane can be estimated in two ways from the data for the 100% conversion polymer. Acceptance of our proposed mechanism allows one to write the expression

$$([CH]_{Cl} + [14])/[CH]_6 \approx \int_{r_0}^{r_x} (C_M/C_{CH}) r \, dr/(r_x - r_0)$$

in which $[CH]_6$ is the concentration of "CH" ends produced by the cyclohexyl radicals that are generated from cyclohexane and radical **6**, C_M and C_{CH} are the chain transfer constants of the monomer and cyclohexane, respectively, and the other terms have the meanings defined above. Solution of this equation for C_{CH} yields a value of 24×10^{-4}. Alternatively, a C_{CH} value of 20×10^{-4} can be obtained from the Mayo equation[19] on the reasonable assumption that $\overline{DP}_{n,0}$ is determined solely by transfer to monomer.[21] Although these values are in line with other estimates,[18] they must be regarded only as apparent constants whose applicability is restricted to our specific set of heterogeneous conditions.

In a forthcoming publication,[26] we will provide direct structural evidence for chain transfer to monomer via the chlorine-atom mechanism described above. The present work offers strong support for such a mechanism in light of the preceding discussion.

Mechanism of Chlorine Migration. The conversion of radical **2** (or **7**) into radical **3** (or **8**) could be a true intramolecular process, or it could proceed by a two-step mechanism involving β scission of a chlorine atom (cf. eq 6), followed by readdition of this atom to the unsubstituted end of the resulting terminal alkene. However, if the latter mechanism were operative, Cl· scavenging by cyclohexane would tend to prevent the readdition step and thus greatly reduce the number of pendent chloromethyl groups in the finished polymer. From Figure 1, the content of **10** prior to reduction is estimated to be about 2.7/(1000 C); this value may be compared with the **4** content of ca. 2.5/(1000 C) expected for nondeuterated PVC that has been prepared at our polymerization temperature in the absence of radical scavengers.[2g,h] Secondary deuterium kinetic isotope effects should increase the chloromethyl branch content by ca. 0.2/(1000 C);[15a] thus the **10** content determined from Figure 1 is in excellent agreement with expectations based on the intramolecular rearrangement path. The only conceivable alternative is β scission followed by Cl· readdition within the solvent cage. However, this possibility seems most unlikely in view of literature data which suggest that rearrangement[14d] would be faster than β scission[36] by several orders of magnitude. In any event, it is clear that the migrating chlorine atom does not become kinetically free.

Experimental Section

Materials. VC-α-*d* (Merck) was subjected to freeze–thaw degassing and vacuum distillation immediately prior to use. The ^{1}H NMR spectrum of a PVC-α-*d* sample obtained from this material showed that the α position was deuterated to the extent of 98.6%. Cyclohexane (Eastman Practical grade) was stirred with concentrated sulfuric acid, washed in succession with several portions of water and aqueous potassium hydroxide, dried over potassium hydroxide pellets, filtered through activated alumina, and then distilled. Azobis(isobutyronitrile) (Polysciences) was recrystallized twice from methanol. The tetrahydrofuran used as solvent for the $LiAlH_4$ reductions was purified in the manner previously described.[37] All other chemicals were commercial products of the highest available purity; they were used as received.

Preparation of PVC-α-*d*. A mixture of VC-α-*d* (5.0 g), azobis(isobutyronitrile) (98.3 mg), and cyclohexane (5.0 mL, 3.9 g) was placed in a thick-walled Pyrex ampule and frozen in liquid nitrogen. The ampule was then sealed under vacuum and immersed in an oil bath whose temperature was maintained at 60.0 ± 0.1 °C. After the reaction had continued for 22 h, the ampule

was opened at liquid-nitrogen temperature, and the contents were slurried in methanol and filtered in order to isolate the polymer (3.9_5 g, 79% monomer conversion), which was purified by precipitation from tetrahydrofuran–methanol, followed by drying in vacuo for several hours at 50 °C. Reduction of this polymer gave the material whose spectrum is shown in Figure 1. Another run was performed in a similar manner using 4.2 g of monomer, 80 mg of azobis(isobutyronitrile), 3.9 g of cyclohexane, and a reaction time of 24 h. This preparation afforded 4.2 g (monomer conversion, 100%) of polymer having $\bar{M}_n$ = 14 400 and $\bar{M}_w$ = 41 000 (values determined by gel permeation chromatography with calibration vs. a PVC sample of known molecular weights).

Reduction of PVC-α-d with Lithium Aluminum Hydride. The reductions were carried out in tetrahydrofuran solution at 100 °C under nitrogen, using ca. 1.25 mol of $LiAlH_4$ per mol of VC-α-d monomer units. Procedural details are given in an earlier publication.[37]

^{13}C NMR Measurements. The spectra were observed with a Varian XL-100 spectrometer modified for pulse Fourier transform spectroscopy and interfaced with a Nicolet Model 1080 computer. Protons were decoupled from the carbon nuclei using a random noise decoupling field. The pulse angle was 90°; free induction decays were stored in 8K computer locations (16K for DCH) using a dwell time of 100 μs (i.e., a spectral window of 5000 Hz). Hexamethyldisiloxane was used as an internal reference (2.0 ppm vs. Me_4Si), and the internal deuterium lock signal was provided by benzene-d_6 (polymer samples) or p-dioxane-d_8 (DCH). Polymer samples were observed as 33–34% (w/v) solutions in 1,2,4-trichlorobenzene at 110 °C; DCH was measured as a 28% (v/v) solution in 1,2,4-trichlorobenzene at 120 °C. The spectrum of Figure 1 represents an accumulation of 19 000 transients at a pulse interval of 4.0 s. Under the conditions employed, T_1 for the principal CH_2 carbons of reduced, nondeuterated PVC is about 1.3 s. The spectrum of DCH was obtained using a pulse interval of 5.0 s and an accumulation of 1000 scans. Concentrations of polymer structures were determined from the intensities of the "M-α'", "CH-2" or "CH-1", "L-C_2", and "DB-α" resonances (for nomenclature, see text); chemical shifts (Table I) are estimated to be accurate within ±0.03 ppm.

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Gas Chromatographic and Static Measurements of Solute Activity for a Polymeric Liquid-Crystalline Phase

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ABSTRACT: Inverse gas chromatographic methods allow measurements of solvent activity over polymeric liquid-crystalline phases. Aqueous solutions of hydroxypropyl cellulose form an ordered fluid phase at high polymer concentrations and also exhibit a lower critical solution temperature. Several gas chromatographic and static techniques were used to measure the activity of water in concentrated hydroxypropylcellulose solutions. The results are compared with osmotic pressure measurements in the literature. Within experimental precision, the activity appears to vary smoothly with concentration. It is suggested that in this system the polymer–solvent interaction parameter may have the same value at each end of the concentration range, but the entropy of mixing changes from that predicted by Flory's theory for rodlike mixing at high polymer concentrations to that for Flory–Huggins mixing in dilute solution.

Gas chromatography has proved useful for the examination of polymer physical properties and in particular for the measurement of the thermodynamics of polymer–solvent mixing at high polymer concentrations.[1,2] The fundamental relationship for GC measurements may be written as[1,3]

$$q = \frac{1}{w}\int_0^c V_R(c)\, dc \qquad (1)$$

where q (mol/g) is the concentration of solvent "probe" vapor in the polymer stationary phase, c (mol/mL) is the corresponding concentration of solvent vapor in the vapor phase, and w (g) is the mass of the polymer in the GC column. The value of $V_R(c)$, the GC retention volume (mL) of a concentration c of probe vapor, corrected for the column vapor phase volume, may be determined by several different finite concentration gas chromatographic methods.[3] At sufficiently low probe concentrations, in the so-called "infinite dilution" region, the concentration of vapor may obey a linear partition equation of the form $q = \beta c$, where β (mL/g) is a partition coefficient per unit mass of stationary phase. In this limit, $V_R(c)$ becomes independent of c, and comparison with eq 1 shows that the GC retention volume is simply related to the partition coefficient by $V_R = \beta w$. The partition coefficient is often expressed as the specific retention volume $V_g = (273.2/T)\beta$, which corresponds to the volume of carrier gas, measured at 273.2 K, which is required to elute a small pulse of the probe vapor through a column at temperature T (K) containing 1 g of stationary phase.

The specific retention volume may be related to weight- or volume-fraction activity coefficients at infinite dilution of vapor in the polymer phase.[4] Neglecting the minor effects of gas-phase imperfections and the volume changes on mixing, these activity coefficients are given by

$$\Omega_1^\infty = (a_1/w_1)^\infty = \frac{273.2R}{p_1^0 V_g M_1} \qquad (2)$$

$$\ln (a_1/\phi_1)^\infty = \ln (a_1/w_1)^\infty + \ln (v_2/v_1) \qquad (3)$$

where a_1 is the solvent activity, w_1 and ϕ_1 are the solvent weight and volume fractions, respectively, R is the gas constant, p_1^0 and M_1 are the saturated vapor pressure and molecular weight respectively of the probe, and v_1 and v_2 are the specific volumes of the probe and the polymer.

The activity of a solvent over a polymer solution according to the familiar Flory–Huggins theory is given by[4]

$$\ln (a_1/\phi_1) = (1 - 1/x)\phi_2 + \chi_{FH}\phi_2^2 \simeq 1 + \chi_{FH}(\phi_2 \to 1, x \to \infty) \qquad (4)$$

where ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, respectively, and x is the number of segments in the polymer chain. The polymer–solvent interaction parameter, χ_{FH}, quantifies the segment–solvent interaction, together with all other noncombinatorial contributions to the free energy of mixing. Combining eq 2, 3, and 4 gives[5]

$$\chi_{FH}^\infty \simeq \ln \frac{273.2Rv_2}{p_1^0 V_g V_1} - 1 \qquad (5)$$

where V_1 is the molar volume of the liquid probe, and χ_{FH}^∞ is the value of the interaction parameter at infinite dilution.

The effect of the relative orientation of the polymer segments is not considered in the Flory–Huggins theory. However, for rodlike molecules an additional factor becomes evident at higher concentrations, where parallel arrangements must be favored over random orientation of rods. Flory developed a lattice theory for semiflexible[6] and rodlike molecules which predicts the appearance of an anisotropic or ordered phase above a certain polymer concentration. The solvent activity above such a phase is given by[7,8]

$$\ln (a_1/\phi_1) = 2/y + \left(\frac{y-1}{x}\right)\phi_2 + \chi_R\phi_2^2 \qquad (6)$$

where the degree of orientation of the rods is given by y ($1 < y \leq x$) with $y = 1$ for perfect orientation. The subscript on the polymer–solvent interaction parameter, χ_R, is used to indicate its origin in the rigid rod theory. For

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