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Structural Defects in Poly(vinyl chloride) and the Mechanism of Vinyl Chloride Polymerization: Comments on Recent Studies

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Abstract

Investigations in the title areas within the past ten years are summarized and critiqued. The polymerizations studied were performed by conventional free-radical methods. A new mechanism, not yet confirmed, is suggested to explain a reported enhancement in the chloromethyl branch concentration of poly(vinyl chloride) (PVC) prepared at high conversions of monomer. This mechanism involves an intramolecular 1,5 hydrogen shift in a 1,3,5,6-tetrachlorohexyl radical. Evidence showing that most of the internal double bonds in PVC are not formed via intermolecular H abstraction from internal monomer units is tentatively rationalized, in part, by hydrogen transfer via at least one cyclic transition state containing more than eight members. The absence of free chlorine atoms from polymerizations of vinyl chloride (VC) is reaffirmed, and the copolymerization of VC with the chloroallylic chain ends of PVC is argued to be insignificant. New information in the literature does not invalidate the currently accepted mechanism of vinyl chloride polymerization.

Keywords: Poly(vinyl chloride); PVC synthesis; PVC microstructure; polymerization mechanism; chain transfer to monomer; free-radical reactions; chloromethyl branch; allylic structures; thermal stability.

1. Introduction

Poly(vinyl chloride) (PVC) still retains its status as one of the world's most important commercial polymers, a situation that seems likely to continue for the foreseeable future [1]. The principal drawback of PVC has always been its low intrinsic thermal stability, which is much less than those of the resins that are its major competitors. This deficiency has stimulated an enormous amount of research on the thermal degradation and stabilization of PVC, which has overcome the stability obstacle to a large extent.

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Nevertheless, studies in this general area continue to be of great interest to scientists and engineers who are concerned with such things as the enhancement of stability by altering the molecular microstructure of PVC, mathematical modeling of the polymerization of vinyl chloride (VC) in order to improve control of the process, and the development of thermal stabilizers for PVC that are environmentally benign. Progress in this field obviously should be expedited by the availability of information about the mechanism of polymerization, a subject reviewed by the present author in 2002 [2]. The current paper examines the basic research on this topic that has been reported since that time and endeavors to provide a definitive analysis of the new knowledge thus obtained. However, no attempt is made here to comment on all of the recent literature in this area, including that which deals with PVC that is not prepared by standard free-radical methods.

2. Background

In its early stages, the thermal degradation of PVC involves the successive loss of HCl molecules from the ordinary (head-to-tail) monomer units, a process that produces conjugated polyene sequences having various lengths [2]. This process is initiated, primarily if not exclusively, by "structural defects" in the polymer that have unusually low thermal stabilities and are now believed by most researchers to be tertiary chloride and "internal" allylic chloride groups (i.e., allylic chloride structures that are not at the ends of polymer chains) [2]. Other defects are present, but they are thought to be stable [2].

A considerable amount of information is available about the mechanisms of structural defect formation during the synthesis of PVC [2,3]. Head-to-head emplacement of monomer, which occurs infrequently, has the chemical consequences that are shown in the mechanism of Figure 1a, which was established in 1993 [4]. This mechanism produces ethyl-branch (EB) and methyl-branch (MB) segments, as well as chloroallylic end groups (A1 and A2), all of which are relatively stable to heat [2]. Conversion of radical **1** into radical **2** is so rapid that head-to-head structures resulting from the addition of **1** to monomer have never been found in PVC [4]. The abstraction of chlorine by VC from radicals **2** and **3** occurs in a single step (in both cases) and results in chain transfer to monomer during the polymerization. This transfer of chlorine does not involve unimolecular β–scission to give a chlorine atom that then is scavenged by VC [4].
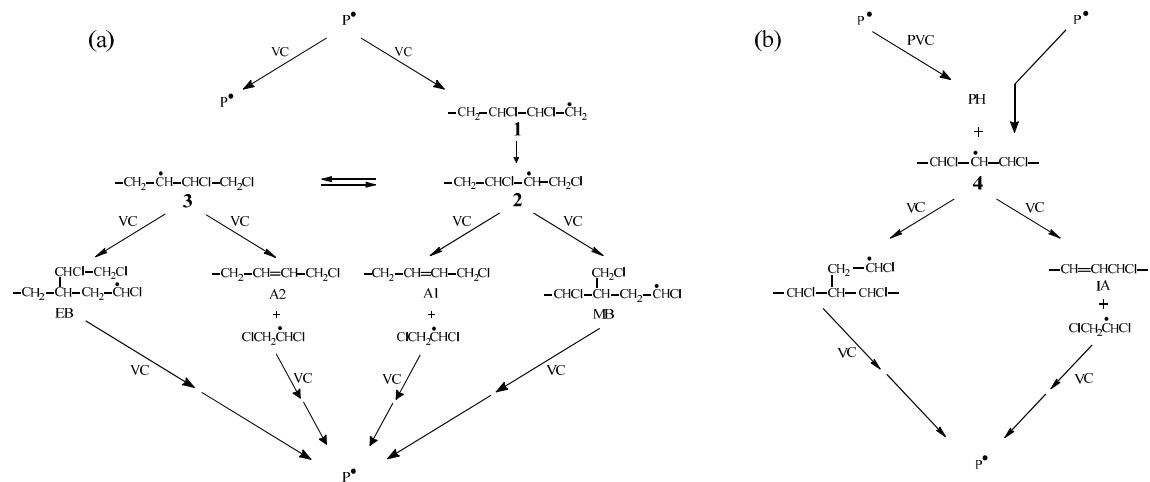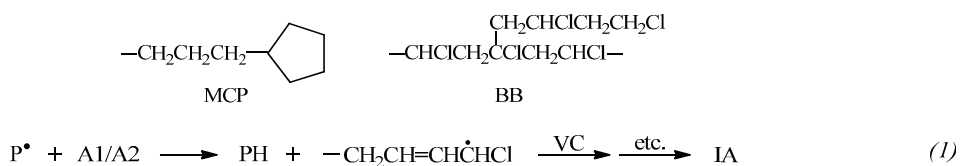

Fig. 1. (a) Chemistry resulting from the head-to-head emplacement of VC during its polymerization and (b) auxiliary mechanism for chain transfer to the monomer during VC polymerization, where P˙ is the head-to-tail macroradical

The mechanism in Figure 1b was established in 1996 [5]. It shows that type **4** radicals are formed from polymerized VC units by inter- or intramolecular H abstraction. Removal of β-chlorine from these radicals by monomer, again in a single step (cf. Figure 1a), gives the unstable internal chloroallyl structure IA and is an alternative (or "auxiliary") mechanism for chain transfer to VC. When intramolecular abstraction ("backbiting") occurs in a 1,6 manner (i. e., from the carbon that is sixth from the end of the growing chain), abstraction of Cl· by VC from the resultant type **4** radical yields a mixture of IA moieties whose presence was confirmed by their conversion into mono(long alkyl)cyclopentane (MCP) end groups when the polymer was reductively dechlorinated with Bu₃SnH [6]. On the other hand, when backbiting by P· is a 1,5 process, subsequent addition of VC to the radical thus created yields a butyl-branch (BB) array [7], which is thermally unstable because it contains a tertiary chloride function. Another noteworthy aspect of the polymerization chemistry of VC is the conversion of chloroallylic end groups into IA structures as the monomer concentration declines (Eq. 1) [2].

$$—CH_2CH_2CH_2— \quad MCP$$

$$\overset{\overset{\textstyle CH_2CHClCH_2CH_2Cl}{|}}{—CHClCH_2CClClCH_2CHCl—} \quad BB$$

$$P^\bullet \;+\; A1/A2 \;\longrightarrow\; PH \;+\; —CH_2CH{=}CH\overset{\bullet}{C}HCl \;\xrightarrow{\;VC\;}\;\xrightarrow{\;etc.\;}\; IA \tag{1}$$

Several recent publications have addressed various aspects of the mechanism for vinyl chloride polymerization. Some of the issues raised by these studies will now be examined in detail.

3. Structural Defects

3.1. Internal allylic groups

Purmová *et al.* [8] used ^{1}H NMR to measure the IA concentrations of PVC fractions with different molecular weights that were isolated from whole polymers made by suspension polymerization at 57.5 °C. The VC conversion levels of the polymerizations were 23.7, 87.2, and 96.4%. Significantly, in all three cases, the IA contents per number-average polymer molecule increased only slightly (by ca. 0.1) over the entire M_n ranges of the fractions, all of which were quite broad (e. g., $3–95 \times 10^3$ g/mol for 87.2% conversion). Thus, most of the type **4** radicals could not have been formed by the intermolecular H abstraction shown in Figure 1b, because in that event, the IA contents of the fractions would have increased considerably with increasing values of M_n [8].

With the aid of ab initio molecular orbital calculations, Purmová and co-workers [8] obtained additional evidence against two mechanisms producing IA that were already known to be highly unlikely. These schemes involved either a 1,4 backbiting step or a 1,5 intramolecular transfer of chlorine followed by the abstraction of a β–hydrogen by VC. On the other hand, three routes to IA were considered to be plausible [8]. One of them (mechanism A) involved the formation of a type **4** radical (specifically, **4a**) via the 1,5 backbite shown in Eq. 2. However, this route, followed alone, cannot be significant at VC conversions below ca. 90%, because its consumption of **2** radicals would reduce the sum of the instantaneous MB and EB concentrations, which is actually perfectly constant up to conversions of about 90%, at least [4,7].

$$\textbf{2} \;\longrightarrow\; —CHCl\overset{\bullet}{C}HCHClCH_2CHClCH_2CH_2Cl \tag{2}$$
$$\textbf{4a}$$

Another mechanism yielding IA [8] (mechanism B) was the one identified previously [6] in which **4a** results from a 1,6 backbite of P$^{\bullet}$. Purmová *et al.* affirmed its operation by detecting the MCP structure in a Bu$_3$SnH-reduced fraction of PVC [8]. The third route to IA that was considered to be reasonable [8] (mechanism C) had already been shown to be followed, as well [2,5]. This is the scheme in Eq. 1. Because it simply converts the terminal allyl structure into one that is internal, the number of IA groups that it forms per polymer chain does not depend on the value of M_n. Thus this mechanism also is consistent with the finding, mentioned above, of very similar IA contents in fractions of a given polymer specimen having different M_n values [8].

The relative importance of mechanisms B and C can be deduced from structural data published previously for PVC samples made at 55 and 80 °C under constant VC pressures that were 59% of the pressures at saturation [5,6]. At 55 °C, mechanism B yielded a maximum IA content of 0.4 per 1000 monomer units (the true value for the pressure used is probably somewhat lower, because the VC concentration in the polymer particles was less than its value at equilibrium) [6], while mechanism C gave a maximum IA content of 0.4_5 (assuming quantitative conversion into IA for the A1/A2 ends destroyed) [5]. Since the total IA concentration under the stated conditions was 1.6 [5], at least 0.7_5 of the IA groups must have been formed primarily by another intramolecular route (or routes). Similarly, the results for polymerization at 80 °C revealed maximum IA contents of 0.5 from mechanism B [6] and 0.7_5 from mechanism C [5], as well as a total IA concentration of 2.3 [5], thereby implying the predominantly intramolecular formation of 1.0_5 IA moieties in some other way (or ways).

Conceptually, at least, the alternative route(s) to IA could involve the formation of precursory type **4** radicals by sequential backbiting. This situation is illustrated in Figure 2, where only 1,5 and 1,6 backbites are considered, as they are expected to be much faster than other potential backbiting steps [8–10]. Reaction *a*(1,5) forms the radical that leads to the BB structure [7]. If this radical undergoes backbite *a*(1,6), a type **4** radical is produced. However, the increasing importance of process *a*(1,6) with decreasing VC concentration ([VC]) would tend to reduce the BB content of the polymer ([BB]) and thus cause downward curvature in the linear plot of [BB] vs. [VC]$^{-1}$ as the latter values increased [7]. Such curvature was not observed in plots made with data for polymers obtained at several temperatures and at VC conversions of up to 91% [7]. Hence, one can conclude that the *a*(1,5)/*a*(1,6) route to IA is unimportant under those conditions.
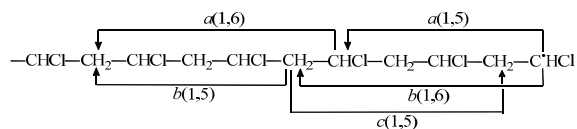

Fig. 2. Potential double-backbiting routes to a type **4** radical during the polymerization of VC

Another potential pathway to a radical of type **4** is reaction *b*(1,6) (the backbite in mechanism B, above) followed by reaction *b*(1,5). For steric reasons, the latter backbite seems likely to be slower (or at least no faster) than the competing *c*(1,5) reaction, which would be an alternative source of radical **2.** As such, the relative importance of the *c*(1,5) process would increase with decreasing [VC] because of its unimolecularity, and thus it would tend to increase the sum of the instantaneous MB and EB concentrations at increasing VC conversions. That result was not observed, even at high conversion levels [4,7], as noted above. Process *c*(1,5) also is at odds with the deuterium labeling pattern found by ^{13}C NMR for the reductively dechlorinated MB structure in poly(vinyl-α-*d* chloride) [11]. Therefore, competing process *b*(1,5) is now ruled out, as well. Moreover, the labeling pattern excludes the highly fortuitous possibility that **2** radicals formed by the *b*(1,6)/*c*(1,5) sequence compensate exactly for those lost in Eq. 2.

Thus, in view of the observations just described, the only remaining potential routes to IA via **4** would seem to be those requiring single backbites and having cyclic transition states containing more than eight members. Literature evidence for such longer backbites apparently is unavailable for any radicals that closely resemble the P$^{\bullet}$ species in the polymerization of VC. Nevertheless, it seems relevant to note that in dilute heptane solutions at 115 °C, small amounts of products resulting, apparently, from 1,10 and 1,11 backbites have been shown to be formed from *n*-dodecyl and *n*-tridecyl radicals [12].

Contradictively, the theoretical calculations reported in reference [8] indicate that *intermolecular* H abstraction from backbone monomer units (see Figure 1b) should actually be the preferred route to **4** in the absence of diffusion-controlled propagation, which is the situation expected at VC conversions of up to ca. 90%, at least [7,13]. The same conclusion was reached in another theoretical investigation [14].

In a recent kinetic modeling study of vinyl chloride polymerization [15], the *a*(1,5) backbite in Figure 2 was stated to be the principal source of the double bonds near the ends of polymer chains. This possibility is disqualified, however, by the lack of any reasonable chemistry that would produce these double bonds from the radical formed by the backbite [8].

It has also been argued [13,15,16] that during the polymerization, chlorine atoms are always transferred to the monomer in two steps (Eq. 3), rather than by the direct abstractions shown in Figure 1. Other reactions of the alleged free chlorine atoms were considered to be important only when the VC concentration was reduced at high conversions [15]. However, Cl$^{\bullet}$ is a highly unselective radical species whose reactions proceed with extremely low energies of activation [11,17,18], and the following analysis demonstrates that the presence of free Cl$^{\bullet}$ during VC polymerization would lead to major complications that have actually been shown to be nonexistent by the extensive information now available on the microstructure of PVC.

$$-\overset{\bullet}{C}HCHCl- \longrightarrow -CH=CH- + Cl^{\bullet} \xrightarrow{VC} ClCH_2\overset{\bullet}{C}HCl \qquad (3)$$
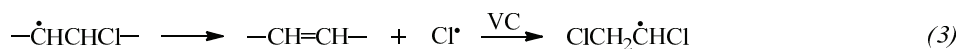
Reactivity data for chlorinated ethylenes in the liquid phase suggest that chlorine atoms add to VC about 3 times faster than they abstract hydrogen from a cyclohexane C-H bond at 25 °C [18]. (This value is in reasonable agreement with an earlier estimate of 4, which was based on gas-phase data [11].) The rate ratio of 3 can be used together with relative reactivities for H abstraction by Cl$^{\bullet}$ from several alkanes and chloroalkanes [17] in order to calculate the reactivity of VC relative to that of a PVC monomer unit (k_{VC}/k_{PVC}) with regard to chlorine-atom addition and H abstraction, respectively. Such a calculation was performed by the present author in a way designed to account quantitatively for the deactivating effects of the multiple chloro substituents in PVC, and the resulting value of k_{VC}/k_{PVC} was found to be only 5 (with H abstraction from the methylene group being 3 times faster than abstraction of the chloromethylene hydrogen). In VC polymerizations performed at 55 °C, the VC/PVC weight ratio is ca. 0.29 in the polymer phase before the liquid monomer phase disappears [5]. Thus, under these circumstances, the reaction ratio of VC:PVC is (5)(0.29), or 1.$_5$, a value which indicates that about 40% of the hypothetical free chlorine atoms would abstract hydrogen from the polymer rather than add to VC. Hence it is clear that chlorine atoms do not exist in this system under the conditions specified here. Their intervention is not ruled out, however, for situations where VC concentrations are very low and/or the polymerization is under diffusion control. Interestingly, it has been suggested [19] that the conclusive kinetic evidence reported previously [4] for chlorine-atom abstraction by VC from radicals **2** and **3** may signify the bimolecular reaction of the monomer with Cl$^{\bullet}$/alkene π−complexes.

3.2. Chloromethyl branches

Chlorinated methyl-branch (MB) structures have been shown to be formed exclusively by the mechanism of Figure 1a in aqueous suspensions at VC conversions of up to ca. 90% [4]. In this conversion range, the MB concentration per 1000 monomer units ([MB]) decreases slowly with decreases in [VC], because the rearrangement of **2** into **3** increases in importance as [VC] declines [4]. No major enhancements of [MB] have been observed in polymerizations performed, for example, under the following conditions: (a) 1,2-dichloroethane solution, 40 °C, average [VC] = 0.46 M (which corresponds to an instantaneous conversion of 97%) [20]; (b) aqueous suspension, 55 °C, 96% conversion [21]; and (c) aqueous suspension, 55 °C, 93.5% conversion [22]. Yet Purmová *et al.* have now detected remarkable increases of the isolated methyl-branch content in several samples of reductively dechlorinated PVC that were prepared in suspension at 57.5 °C with conversions ranging from about 85 to 96.4% [23]. Figure 7 of reference [23] shows that the isolated methyl-branch content per 1000 VC units ([Me]) increased from 4.45 to 5.2 upon going from ca. 86 to 95% conversion, a result requiring an average [Me] of 12.4 in that conversion range {calculated from the equation $[Me]_{average} = [(95)(5.2) − (86)(4.45)]/(95 − 86)$} and signifying an instantaneous final [Me] of 20.4 {obtained from $([Me]_{final} + 4.45)/2 = 12.4$} if the [Me] increase were linear. Purmová and associates suggested [23] that their findings differed from those of other workers because they were obtained under quasi-industrial conditions that led to diffusion control of the polymerization at relatively low conversions.

The enhanced [Me] values of reference [23] have been considered to result from the rearrangement of larger fractions of radical **1** into radical **2** with increasing VC conversion [15,23]. This situation was said to accrue from decreases in the rate of reaction of **1** with monomer that were caused by diffusion-controlled propagation and reductions in the concentration of VC [15,23]. That explanation is inconsistent, though, with the very rapid and essentially quantitative transformation of **1** into **2** that occurs even when monomer concentrations are very high [4]. This proposal also is incompatible with the total number of head-to-head additions, which is much too small to account for the higher values of [Me] [4,5]. (Figure 1a shows that the number of head-to-head emplacements is equal to [MB] + [EB] + [A1/A2], when the latter concentration has not been reduced by Eq. 1.) An alternative rationale for the higher [Me] values, also considered in reference [23], was that at high VC conversions, additional chloromethyl branches were produced via intermolecular H abstractions from long-chain ends, as depicted in Eqs. 4 and 5. However, the authors pointed out that the relatively high concentration of backbone monomer units should have caused such chemistry to be accompanied by analogous intermolecular abstractions leading to enormous numbers of long branches, a result that was not obtained [23].

$$P^{\bullet} + -CH_2CHClCH_2CH_2Cl \longrightarrow PH + -CH_2CHCl\dot{C}HCH_2Cl \xrightarrow{VC} \xrightarrow{etc.} -CH_2CHCl\overset{\overset{\displaystyle CH_2Cl}{|}}{C}HCH_2CHCl- \quad (4)$$

$$P^{\bullet} + -CHClCH_2CHClCH_2Cl \longrightarrow PH + -CHClCH_2\dot{C}ClCH_2Cl \xrightarrow{VC} \xrightarrow{etc.} -CHClCH_2\overset{\overset{\displaystyle CH_2Cl}{|}}{C}ClCH_2CHCl- \quad (5)$$

Eq. 6 proposes a new backbiting mechanism that would be facilitated by diffusion control of chain propagation and low values of [VC], and thus would enhance the chloromethyl branch concentration at high VC conversions. Reductive dechlorination of the resultant MB´ arrangement would produce structure Me´, whose ^{13}C NMR chemical shifts are compared in Table 1 to those of the Me moiety and the dechlorinated LE long-chain end. Because all of the tabulated shifts were not measured under the same conditions (see footnotes *a* and *b* in the table), exact agreement of the Me´ shifts with the others listed was unlikely. Nevertheless, the first five entries in Table 1 reveal a rather close conformity of the

Me´ and Me values, while the nondiagnostic Me´-γ´ and -δ´ shifts are very near those of the corresponding LE carbons. In reduced PVC, the Me´-β´ shift would be coincident with that of the principal methylene resonance [9], a circumstance that would tend to reduce the intensity of a potential composite peak at the Me-β/β´ position. Even so, the data in Table 1 still suggest that the ^{13}C NMR spectrum of Bu$_3$SnH-reduced PVC might fail to reveal the presence of minor amounts of the Me´ structure in cases where larger quantities of the Me grouping were present. On the other hand, since the chlorine substitution patterns of the parent MB´ and MB structures are different, the ^{13}C spectra of polymer samples reduced with Bu$_3$SnD might provide a conclusive answer to the question of whether or not the MB´ array is formed at high conversions.
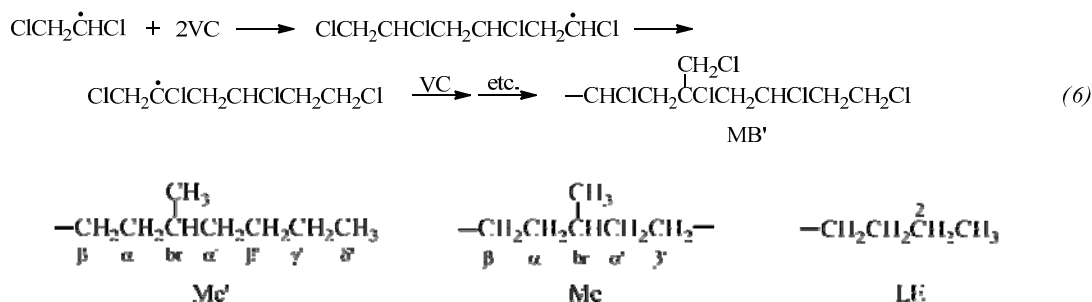
$$\text{ClCH}_2\dot{\text{C}}\text{HCl} + 2\text{VC} \longrightarrow \text{ClCH}_2\text{CHClCH}_2\text{CHClCH}_2\dot{\text{C}}\text{HCl} \longrightarrow$$

$$\text{ClCH}_2\dot{\text{C}}\text{ClCH}_2\text{CHClCH}_2\text{CH}_2\text{Cl} \xrightarrow[\text{etc.}]{\text{VC}} \overset{\overset{\text{CH}_2\text{Cl}}{|}}{-\text{CHClCH}_2\dot{\text{C}}\text{ClCH}_2\text{CHClCH}_2\text{CH}_2\text{Cl}} \quad (6)$$

$$\text{MB'}$$

$$\overset{\overset{\text{CH}_3}{|}}{\underset{\beta \quad \alpha \quad \text{br} \quad \alpha' \quad \text{F} \quad \gamma' \quad \delta'}{-\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3}} \qquad \overset{\overset{\text{CH}_3}{|}}{\underset{\beta \quad \alpha \quad \text{br} \quad \alpha' \quad \gamma'}{-\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2-}} \qquad \underset{}{-\text{CH}_2\text{CH}_2\overset{2}{\text{CH}_2}\text{CH}_3}$$

$$\text{Me'} \qquad\qquad\qquad \text{Me} \qquad\qquad\qquad \text{LE}$$

Table 1. ^{13}C chemical shifts of dechlorinated structures (ppm vs. Me$_4$Si)

Carbon	Me´[a]	Me[b]	LE[b]
CH$_3$	19.7	19.95	
br	32.7	33.25	
α	37.1 (36.8)[c]	37.52	
β	27.1	27.38	
α´	36.8 (37.1)[c]	37.52	
β´	30.0	27.38	
γ´	23.1		22.84[d]
δ´	14.2		14.07[e]

[a] Shifts of 14-methyl-2-octadecanone measured in chloroform-*d* at ambient temperature [24]
[b] Shifts of Bu$_3$SnH-reduced PVC measured in 1,2,4-trichlorobenzene/*p*-dioxane-*d*$_8$ at 110 °C [9]
[c] Possible alternative assignment
[d] LE-2 shift
[e] LE-CH$_3$ shift

3.3. Allylic end groups

Loss of terminal unsaturation from PVC during VC polymerization has been proposed to result exclusively from radical additions to double bonds [15]. In reference [23], weak signals at 32.7, 40.2, and 35.2 ppm in the ^{13}C NMR spectrum of dechlorinated PVC were taken as evidence for the presence of structure Me-LB, which would have ensued from a segment formed by the copolymerization of allylic end groups (A1/A2) with monomer. However, the resonance at 32.7 ppm can be assigned to carbons α to internal trans double bonds [9], and the 40.2-ppm peak is unlikely to have arisen, as suggested [23], from an Me-LB branch-point carbon, because those carbons should resonate at ca. 35.4 (Me-LB-br) and 42.4 ppm (Me-LB-br´). (The latter values differ from previous predictions [23] and were calculated by us from the published Me-br and LB-br chemical shifts [9], the additivity parameters of Grant and Paul [25], and a

corrective term of +4.2 pm, which is the increase in branch-point-carbon shift observed upon going from 2-methylbutane to 2,3-dimethylbutane [25].) Furthermore, reference [23] reports no resonance near 17.9 ppm, which is our predicted shift for the Me-LB-CH_3 carbon (obtained by applying the Grant-Paul parameters to the reported [9] Me-CH_3 shift value). This signal should have been easy to detect, as it would have been in a spectral region where other peaks do not interfere (see, for example, Figure 2 of reference [20]).

Purmová *et al.* also polymerized VC in the presence of 1-chloro-2-butene, a model for A1/A2 ends, and found resonances at ca. 37.3 and 42.8 ppm in the spectra of the resultant polymers after reduction with Bu_3SnH [23]. These signals were assigned to the α and branch-point carbons of structure Me-Me, whose presence would indicate copolymerization of the model with VC [23]. However, the assignments are inconsistent with our predicted shifts for these peaks, which are 35.0 and 37.5 ppm, respectively (calculated from the Me-α and Me-br shifts [9] in the way already described). Moreover, the authors [23] reported no Me-Me-CH_3 resonance, which we predict to occur at 17.5 ppm in the spectral window referred to above (obtained from the Me-CH_3 shift [9] and the Grant-Paul γ parameter [25]). On the other hand, they did obtain evidence for H abstraction from the chloromethylene group of the model compound and concluded that such a reaction also occurred with the allylic ends of PVC. Subsequently, the same research group argued that this abstraction process is an important source of internal double bonds in the polymer [8], as discussed above in Section *3.1*. This conclusion reinforces our previous assertion that Eq.1 is the only significant mechanism for the loss of the A1/A2 ends [2]. Full details of our work on this problem, a part of which involved the polymerization of VC in the presence of 1,5-dichloro-2-pentene, still remain to be published.
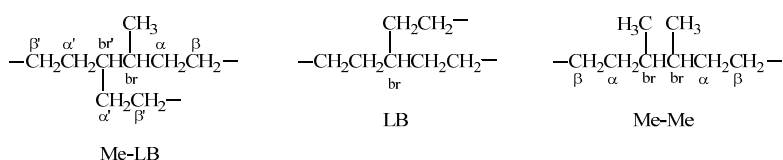
Recent ^{13}C NMR observations also have indicated the presence of very low concentrations of two additional unsaturated ends in PVC [23]. One of these is the –CHClCH=CHCl structure, whose formation can be accounted for most reasonably by a disproportionation reaction (or reactions) of the $P^{\bullet}$ macroradical. The other exiguous end, –CH_2CCl=CH_2, was suggested to result from the addition to VC of an α–chlorovinyl radical formed by H abstraction from the monomer [23]. However, this abstraction has been shown to be highly unlikely by a theoretical (ab initio) study, which also demonstrated that abstractions of β–H or Cl from VC, as well as the transfer to VC of a β–H atom from $P^{\bullet}$, are even more improbable [14].

3.4. Other relevant studies

Krallis and associates [26,27] developed comprehensive kinetic models for VC polymerization that were based on highly abbreviated versions of the mechanism established previously [4,5]. In spite of their chemical simplicity, these models satisfactorily predicted several types of experimental results [26,27]. Similarly, a model constructed by Wieme *et al.* [15,28] afforded acceptable predictions for the contents of a number of defect structures, notwithstanding the numerous problems with the chemistry on which this model was based (see above). Theoretical calculations [14] have supported several mechanisms for structural defect formation that the present paper has favored, and they have affirmed that the

rearrangement of radical **1** into radical **2** is essentially irreversible [8,14,29], whereas the rearrangement of **2** into **3** is not [8,14,29].

Quantum chemistry has also been used to probe the frequency of head-to-head additions during VC polymerization [30] and to predict the ^{1}H and ^{13}C NMR chemical shifts of various actual or potential structural defects in unreduced PVC [31,32]. Other theoretical work has attested to the importance of reaction $a(1,5)$ in Figure 2 and has rationalized the well-known failure of the α–chloro radicals formed by backbites to undergo C-C β–scission during the preparation of PVC [33].

4. Conclusion

In recent years, the anomalous structures in PVC and the mechanisms of their formation have continued to be of great interest to many researchers, who have investigated topics in this area that range from the ab initio computation of fundamental molecular properties to the kinetic modeling of industrial polymerization techniques. Notwithstanding the occasional promulgation of divergent views, the mechanisms established previously seem to have stood the test of time. Nevertheless, some new aspects of the relevant chemistry have now emerged, the most interesting of which are a second mechanism (or mechanisms) for the formation of one-carbon branches and the discovery that intermolecular H abstraction from internal VC units plays only a minor role in the creation of internal double bonds. A full understanding of these particulars will require further work but, even so, it is clear already that all of the thermally labile structural defects result from reactions that are favored by low monomer concentration and by propagation that is under diffusion control. Decreasing the VC conversion can help to alleviate these difficulties in the synthesis of PVC.

Acknowledgement

References

[1] Plastics News. Economic recovery to stimulate PVC market. http://plasticsnews.com/headlines2.html?id=21039 (accessed Oct 2011).

[2] Starnes, Jr. W.H., *Prog. Polym. Sci.* 2002; **27**: 2133–2170.

[3] Starnes, Jr. W.H., *J. Polym. Sci., Part A: Polym. Chem.* 2005; **43**: 2451–2467.

[4] Starnes, Jr. W.H., Wojciechowski B.J., *Makromol. Chem., Macromol. Symp.* 1993; **70/71**: 1–11.

[5] Starnes, Jr. W.H., Chung H., Wojciechowski B.J., Skillicorn D.E., Benedikt G.M., *Adv. Chem. Ser.* 1996; **249**: 3–18.

[6] Starnes, Jr. W.H., Zaikov V.G., Chung H.T., Wojciechowski B.J., Tran H.V., Saylor K., Benedikt G.M., *Macromolecules* 1998; **31**: 1508–1517.

[7] Starnes, Jr. W.H., Wojciechowski B.J., Chung H., Benedikt G.M., Park G.S., Saremi A.H., *Macromolecules* 1995; **28**: 945–949.

[8] Purmová J., Pauwels K.F.D., Agostini M., Bruinsma M., Vorenkamp E.J., Schouten A.J., Coote M.L., *Macromolecules* 2008; **41**: 5527–5539.

[9] Starnes, Jr. W.H., Schilling F.C., Plitz I.M., Cais R.E., Freed D.J., Hartless R.L., Bovey F.A., *Macromolecules* 1983; **16**: 790–807.

[10] Hayes C.J., Burgess, Jr. D.R., *J. Phys. Chem. A* 2009; **113**: 2473–2482.

[11] Starnes, Jr. W.H., Schilling F.C., Abbâs K.B., Cais R.E., Bovey F.A., *Macromolecules* 1979; **12**: 556–562.

[12] Nedelec J.Y., Lefort D., *Tetrahedron* 1975; **31**: 411–417.

[13] De Roo T., Heynderickx G.J., Marin G.B., *Macromol. Symp.* 2004; **206**: 215–228.

[14] Van Cauter K., Van Den Bossche B.J., Van Speybroeck V., Waroquier M., *Macromolecules* 2007; **40**: 1321–1331.

[15] Wieme J., Reyniers M.-F., Marin G.B., *Macromolecules* 2009; **42**: 7797–7810.

[16] De Roo T., Wieme J., Heynderickx G.J., Marin G.B., *Polymer* 2005; **46**: 8340–8354.

[17] Hendry D.G., Mill T., Piszkiewicz L., Howard J.A., Eigenmann H.K., *J. Phys. Chem. Ref. Data* 1974; **3**: 937–978.

[18] Poutsma M.L., Hinman R.L., *J. Am. Chem. Soc.* 1964*;* **86**: 3807–3814.

[19] Dneprovskii A.S., Kuznetsov D.V., Eliseenkov E.V., Fletcher B., Tanko J.M., *J. Org. Chem.* 1998; **63**: 8860–8864.

[20] Starnes, Jr. W.H., Villacorta G.M., Schilling F.C., Plitz I.M., Park G.S., Saremi A.H., *Macromolecules* 1985; **18**: 1780–1786.

[21] Llauro-Darricades M.-F., Bensemra N., Guyot A., Pétiaud R., *Makromol. Chem., Macromol. Symp.* 1989; **29**: 171–184.

[22] Mao S., Ohtani H., Tsuge S., Niwa H., Nagata M., *Polym. J. (Tokyo)* 1999; **31**: 79–83.

[23] Purmová J., Pauwels K.F.D., van Zoelen W., Vorenkamp E.J., Schouten A.J., Coote M.L., *Macromolecules* 2005; **38**: 6352–6366.

[24] Do N.D., Kinjo M., Taguri T., Adachi Y., Yamakawa R., Ando T., *Biosci. Biotechnol. Biochem.* 2009; **73**: 1618–1622.

[25] Breitmaier E., Voelter W., *Carbon-13 NMR spectroscopy: high resolution methods and applications in organic chemistry and biochemistry*. 3rd ed. New York: VCH; 1990, p. 183–186.

[26] Krallis A., Kotoulas C., Papadopoulos S., Kiparissides C., Bousquet J., Bonardi C., *Ind. Eng. Chem. Res.* 2004; **43**: 6382–6399.

[27] Krallis A., Kiparissides C., *Plast. Rubber Compos.* 2008; **37**: 436–441.

[28] Wieme J., Marin G.B., Reyniers M.-F., *Chem. Eng. Sci.* 2007; **62**: 5300–5303.

[29] De Vleeschouwer F., Toro-Labbé A., Gutiérrez-Oliva S., Van Speybroeck V., Waroquier M., Geerlings P., De Proft F., *J. Phys. Chem. A* 2009; **113**: 7899–7908.

[30] Van Cauter K., Van Speybroeck V., Waroquier M., *ChemPhysChem* 2007; **8**: 541–552.

[31] d'Antuono P., Botek E., Champagne B., Wieme J., Reyniers M.-F., Marin G.B., Adriaensens P.J., Gelan J.M., *Chem. Phys. Lett.* 2007; **436**: 388–393.

[32] d'Antuono P., Botek E., Champagne B., Wieme J., Reyniers M.-F., Marin G.B., Adriaensens P.J., Gelan J.M., *J. Phys. Chem. B* 2008; **112**: 14804–14818.

[33] Cuccato D., Dossi M., Moscatelli D., Storti G., *Macromol. Symp.* 2011; **302**: 100–109.