



A Study of Poly(Vinyl Chloride) Microstructure

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Abstract

High-field ^{13}C and ^1H NMR spectroscopies have been used to investigate some unusual features of the molecular microstructure of poly(vinyl chloride) (PVC). The results obtained have illuminated several significant aspects of the mechanism for vinyl chloride (VC) polymerization, and they also relate to the very important question of the reasons for the thermal instability of the polymer.

Several model monochloroalkanes were synthesized in order to determine ^{13}C shift increments for the replacement of H by Cl at positions that are α , β , or γ to an isolated internal double bond in a linear carbon chain. These increments then were used to predict the ^{13}C shifts of the internal allylic chloride structure in PVC. The predictions were not satisfactory, a result which showed that, as expected, the increments were not additive.

It was shown that during conventional VC polymerization, the chloroallylic chain end ($-\text{CH}_2\text{CH}=\text{CHCH}_2\text{Cl}$) does not copolymerize with the monomer and is not destroyed by a mechanism involving allylic rearrangement, macroradical addition, and chlorine-atom β -scission to produce a $-\text{CHClCH}_2\text{CH}=\text{CHCH}_2\text{CHCl}-$ structure. Nevertheless, that mechanism was found to operate during the preparation of a special type of PVC [made at 0°C with $(t\text{-Bu})_2\text{Mg}$ initiation] which contained the rearranged chain end, $-\text{CH}_2-\text{CHClCH}=\text{CH}_2$, at an abnormally high concentration.

During the preparation of PVC under subsaturation VC pressures, small amounts of a 1,3-di(2-chloroethyl) branch structure were found to be formed by a "double backbiting" mechanism involving two intramolecular H abstractions in succession. The presence of this structural defect, which is believed to be very unstable to heat, was established by the 125.77-MHz ^{13}C NMR spectra of reductively dechlorinated PVC specimens. At $55\text{-}80^\circ\text{C}$, the two backbites leading to the defect differ substantially in relative rate in that the backbiting: addition rate ratio is larger for the second backbite by a factor of 15-16 (mean value), irrespective of temperature. Remarkably, no evidence was obtained for the presence of the 2-ethyl-*n*-hexyl branch structure that would have resulted from double backbiting by an alternative route. The absence of this structure and the presence of the 1,3-di(2-chloroethyl) branch array were confirmed by spectral comparisons with the ^{13}C shifts of two reference models, 9,11-diethylnonadecane and 9-(2-ethyl-*n*-hexyl)heptadecane, that were prepared by unambiguous tactical methods.

Polymerizations of VC were performed in the presence of two potential transfer agents, *trans*-1-chloro-2-hexane and *trans*-1,5-dichloro-2-pentene. Preliminary examination of the resulting polymers by high-field NMR provided evidence for the destruction of the $-\text{CH}_2\text{CH}=\text{CHCH}_2\text{Cl}$ chain end, during polymerization, by a mechanism involving H abstraction to form the $-\text{CH}_2\text{CH}=\text{CHC}^*\text{HCl}$ radical, followed by the addition of that species to VC in order to give the thermally unstable structure, $-\text{CH}_2\text{CH}=\text{CHCHClCH}_2-$.