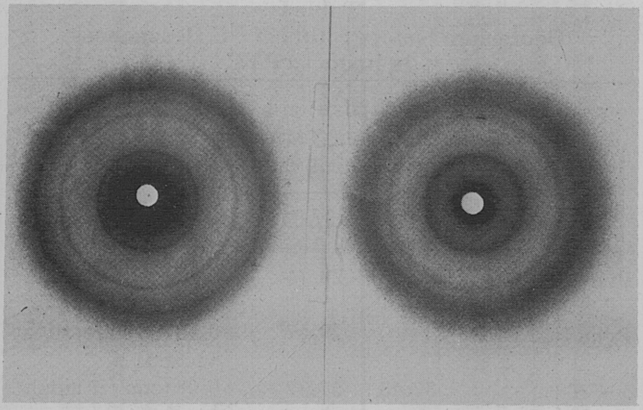

Figure 3. Powder X-ray patterns of precipitated polyelectrolyte complexes between ionene bromide and sodium poly(vinylsulfonate): (a) PVS-1; (b) PVS-2.

isotactic sequences in the poly(vinylsulfonate) to be very short (2–3 monomer units). Otherwise the polymer would acquire a helicoidal conformation forcing the SO_3^- side groups away from the linear matrix, which they must neutralize. Thus, a high number of "crossovers" into syndiotactic additions must occur and this would result, as observed, in a net increase in the number of heterotactic and isotactic triads in the poly(vinylsulfonate) prepared on the ionene matrix.

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Identification of Branches in Poly(vinyl chloride) by Reduction with $LiAlD_4$

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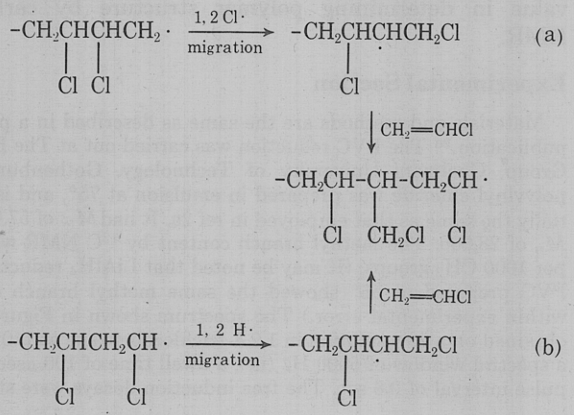
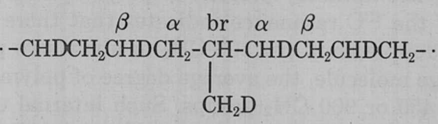
ABSTRACT: Reduction of poly(vinyl chloride) with lithium aluminum deuteride replaces each chlorine atom with a deuterium. The characteristic splittings and isotope shifts observable in the carbon-13 spectrum of the reduced product permit us to demonstrate conclusively that the branch structure in poly(vinyl chloride) is . . . $-CH_2C(Cl)H-C(CH_2Cl)H-CH_2-C(Cl)H-$. . . . This structure was previously proposed by us from the observation of the lithium aluminum hydride reduction product, but this did not provide a complete proof of structure.

In a previous paper we have shown that the polyethylene obtained from poly(vinyl chloride) by reduction with lithium aluminum hydride has approximately 3 methyl branches per 1000 CH_2 groups. Two alternative mechanisms were suggested by which such branches could arise: (a) a 1,2 Cl migration in the growing chain radical resulting from an occasional head-to-head monomer addition, as suggested by Rigo et al.; (b) rearrangement of the normal growing chain radical by a 1,2 hydrogen shift. Both mechanisms give the same branch structure:



LiAlD$_4$ Reduction. Reduction with lithium aluminum hydride confirms that one or the other of these mechanisms (or both) are operating, but does not rigorously demonstrate the structure of the branch unit, since all chlorines are replaced by hydrogen and information as to their position in PVC is lost. This information can be retained by reduction with lithium aluminum deuteride, $LiAlD_4$, which replaces each chlorine atom with a deuterium. If the branch structure proposed above is correct, the reduced product should have the structure



$$\overset{\beta}{\cdots-CHD}\overset{\alpha}{CH_2}CHDCH_2-\underset{\displaystyle CH_2D}{\overset{br}{CH}}-\overset{\alpha}{CHD}\overset{\beta}{CH_2}CHDCH_2-\cdots$$

The spectra shown in Figure 1 are entirely in accordance with this prediction. The lower spectrum, marked "1×", shows only the main resonances for CH_2 and CHD carbons. The latter is a triplet from $^{13}C-^{2}H$ scalar coupling of 19.0 Hz, corresponding to a $^{13}C-^{1}H$ coupling of 123.8 Hz, a normal value for a paraffinic chain. Direct bonding of deuterium to ^{13}C shifts the resonance upfield, as can be clearly seen. The main CH_2 resonance is itself also shifted upfield from the normal polyethylene position (see Table I and discussion below). The lines of the CHD triplet are somewhat

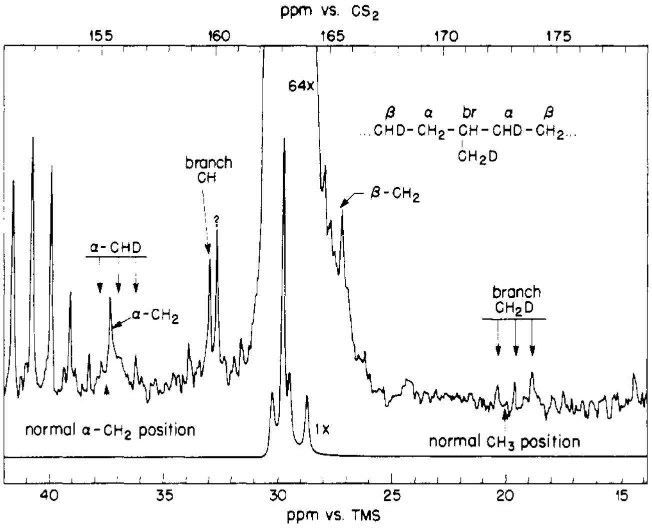


Figure 1. ^{13}C spectrum (25 MHz) of poly(vinyl chloride) reduced with $LiAlD_4$. (See text for details.)

broader than those of the CH_2 singlet. This may be in part a reflection of the stereochemical irregularity of the chain, which presumably preserves that of the original PVC, but is probably mainly due to scalar relaxation of the second kind, owing to the flipping of the deuterium electric quadrupole under the influence of chain segmental motion.

With regard to branch structure, the principal features of the upper spectrum, recorded at 64× greater gain than the lower spectrum, are as follows.

(i) The methyl singlet of the methyl branch is replaced by a triplet (19 Hz spacing), shifted 0.30 ppm upfield from the normal position.

(ii) The branch carbon remains a singlet, shifted upfield by 0.13 ppm from the normal position.

(iii) The resonances of the carbons α and β to the branch should each consist of a singlet superimposed on a triplet. This can be seen for the α carbons (near 37 ppm) but in the β-carbon region (ca. 27 ppm) only a singlet can be clearly seen (owing to severe overlap by the principal CH_2 and CHD resonances) and the deuterium neighbor isotope shift seems smaller than expected.

These observations are entirely consistent with the proposed branch structure, but of course do not distinguish between mechanisms (a) and (b). This can be done by deuterium labeling of the vinyl chloride monomer, and this work is now in progress.

Double Bond Content. The resonance at 32.7 ppm marked with a question mark probably represents carbons α to an internal trans double bond. The existence of this double bond is clearly shown in the infrared spectrum of the $LiAlH_4$-reduced polymer by a C–H bending band at 965 cm^{-1}, not normally present in polyethylenes. The intensity of the ^{13}C resonance indicates that there is about one such double bond per 500 CH_2 or about two per number-average molecule, the average degree of polymerization being ca. 450 or 900 CH_2 groups. Such internal unsaturation in the original PVC could provide a significant weak point for the initiation of dehydrochlorination, but at present it appears likely that the double bond is actually formed during the course of lithium aluminum deuteride (or hydride) reduction. The internal unsaturation in PVC, as determined by ozonolysis combined with gel permeation chromatography, is very low. The polymer reported here has an internal double bond content of the order of 1 per 100,000 carbon atoms. However, the total unsaturation would be higher, as this measurement is not sensitive to double bonds close to chain ends. Suzuki and Nakamura have reported total double bond contents in commercial PVC of 1 to 3 per 1000 monomer units.

Table I
Deuterium Isotope Shifts of ^{13}C Resonances in Reduced PVC

Group	Peak position (ppm from TMS) in reduced polymer[a]		Diff (+ denotes upfield shift)
	$LiAlH_4$	$LiAlD_4$	
Principal CH_2	29.95	29.74	+0.21 (two ^2H neighbors)
Principal CHD		29.47[b]	+0.48 (^2H directly attached)
α-CH_2	37.45	37.37	+0.08 (one ^2H neighbor)
α-CHD		36.97[b]	+0.48 (^2H directly attached)
β-CH_2	27.32	27.21	+0.11 (two ^2H neighbors)
Branch CH	33.14	33.01	+0.13 (two ^2H neighbors)
Branch CH_3	19.91		
Branch CH_2D		19.61[b]	+0.30 (^2H directly attached)

[a] Error ca. ±0.02 ppm. [b] Triplet center.

Deuterium Isotope Chemical Shift Effects. Isotope effects, particularly that of deuterium on proton chemical shifts, have been recognized for many years, but the effects of deuterium on carbon-13 have received only very limited attention, mostly with respect to substituted benzenes, although the effects are large enough to lead to interpretive errors in complex spectra if ignored. The now universal use of predeuterated compounds as internal locks in C-13 spectroscopy could also lead to error, perhaps as large as 1 ppm, if the lock signal is also used as reference without correcting for the isotope shift.

The isotope shifts in the present system are summarized in Table I. They are comparable in magnitude to those reported in the literature for aromatic rings.

The largest effect is caused by direct attachment of the deuterium, as might be expected; this is larger for CHD than for CH_2D, and so evidently depends on the fraction of H replaced by D. Explanations could be offered in terms of the slightly shorter C–D bond length and altered vibrational levels, both of which could increase the electron density at the carbon nucleus. The unmistakable *neighbor* deuterium effect, however, is considerably more difficult to rationalize. Whatever the explanation, it appears that deuterium splittings and shifts may have considerable diagnostic value in determining polymer structure by carbon-13 NMR.

Experimental Section

Materials and methods are the same as described in a previous publication.[2a] The PVC reduction was carried out at The Polymer Group, Chalmers University of Technology, Gothenburg. The polyvinyl chloride was prepared in emulsion at 75°, and is essentially the same as that employed in ref 2a. It had $\bar{M}_w$ of 57,000 and $\bar{M}_n$ of 28,000. The methyl branch content by ^{13}C NMR was ca. 3 per 1000 CH_2 groups. (It may be noted that $LiAlH_4$ reduction of a PVC prepared at 56° showed the same methyl branch content within experimental error.) The spectrum shown in Figure 1 was obtained on a 20% solution in 1,2,4-trichlorobenzene at 110°, using a spectral window of 5000 Hz (i.e., a dwell time of 100 μsec) and a pulse interval of 2.8 sec. The free induction decays were stored in

8K computer locations. The spectrum represents an accumulation of 26,000 scans.

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Poly(alkyl α-chloroacrylates).
VI. Transitions and Relaxations

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ABSTRACT: Melting points (T_m's) and glass transition temperatures (T_g's) of stereoregular poly(methyl α-chloroacrylates), poly(ethyl α-chloroacrylates), and poly(isopropyl α-chloroacrylates) have been determined by differential scanning calorimetry (DSC). Relaxation processes accompanying these T_g's and secondary relaxation phenomena have been studied by dynamic mechanical and dielectric relaxation. It was found that the extrapolated T_g values for high molecular weight syndiotactic poly(alkyl α-chloroacrylates) and high molecular weight isotactic poly(alkyl α-chloroacrylates) differed by the following amounts: 92° for the methyl esters; 83° for the ethyl esters; and 68° for the isopropyl esters. A secondary relaxation, labeled β, and associated with motions of the ester side chains, occurs in the highly syndiotactic methyl and ethyl polymers and is absent in the isopropyl polymers regardless of their degrees of stereoregularity. Evidence was obtained for the formation of stereocomplexes of isotactic and syndiotactic chains in the case of the poly(methyl α-chloroacrylates).

We have previously reported the synthesis, characterization, and some preliminary physical properties of stereoregular poly(methyl α-chloroacrylates), poly(ethyl α-chloroacrylates), and poly(isopropyl α-chloroacrylates).[1–5] It has been determined by DSC that the T_g differences between the most isotactic and most syndiotactic polymers prepared are 72° for the methyl ester, 57° for the ethyl ester, and 59° for the isopropyl ester. However, when these values are corrected to "infinite" molecular weight and extrapolated to the 100% isotactic and syndiotactic forms the results are 92° for the methyl ester, 80–86° for the ethyl ester, and 68° for the isopropyl ester.[5] In addition to the T_g behavior, crystalline melting points, T_m's, were observed by DSC for isotactic poly(methyl α-chloroacrylate) at 186°, isotactic poly(ethyl α-chloroacrylate) at 109°, and isotactic poly(isobutyl α-chloroacrylate) at 191°. In the present work we examine the T_g results in light of a general theory for the T_g's of stereoregular vinylidene polymers.[6] In addition, the relaxation behavior accompanying these transitions observed by dynamic mechanical relaxation and dielectric relaxation is reported. In general, two relaxation regions are discernible below T_m and these are labeled α and β in order of decreasing temperature. The α relaxation, which is present in all the polymers, arises from microbrownian segmental motion accompanying the glass transition, while the β relaxation, which is present only in the syndiotactic poly(methyl α-chloroacrylates) and poly(ethyl α-chloroacrylates), arises from motions of the ester side group. Activation energies derived from the slopes of plots of the logarithms of the maximum frequencies of the loss peaks versus the reciprocal of the absolute temperature generally correlate well for the various processes for both the dielectric and mechanical techniques, indicating that the underlying motions responsible for these relaxations are the same. Comparisons are made between these polymers and results obtained for the stereoregular poly(alkyl methacrylates).

Experimental Section

The preparation and characterization of the stereoregular poly(alkyl α-chloroacrylates) used in this study have been previously described in detail.[4,5] Relevant characterization data for the samples used for property studies are collected in Table I. Films were prepared for mechanical and dielectric testing by casting 4–12% (w/v) solutions of the polymers in CHCl$_3$ onto clean plate glass and allowing the solvent to evaporate slowly. This procedure produced films of 4–8 mils thickness which were then dried in a vacuum oven at 60° for 1 to 2 days. After this treatment, it was found that the residual solvent, estimated to be less than 0.5% by weight by pyrolysis gas chromatography, caused a decrease in T_g of up to 50° in the case of the syndiotactic poly(methyl α-chloroacrylates) and about 25 to 30° in the case of the syndiotactic poly(ethyl α-chloroacrylates) and poly(isopropyl α-chloroacrylates). This residual solvent could not be removed by heating in a vacuum oven, and it was found necessary to extract the films with methanol at ambient temperature for several days followed by a similar extraction with water. It is postulated that the large effect on T_g was due to some sort of complex formation between the polymer and the CHCl$_3$. Further studies are necessary to elucidate the nature of this complex.

The mechanical measurements were carried out on a Rheovibron Dynamic Viscoelastometer, Model DDVII. The frequencies employed were 3.5, 11, and 110 Hz and the temperature range was from −100 to +170° depending on the T_g of the polymer under observation. Tan δ, E', and E'' were obtained at the quoted frequencies as functions of temperature by standard techniques.

Dielectric measurements were carried out with a General Radio capacitance bridge, Type 1620-A, in conjunction with a Balbaugh