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CHEMICAL MODIFICATION OF POLY(VINYL CHLORIDE): IMPROVED THERMAL STABILITY BY PARTIAL REDUCTION WITH ORGANOBORON REAGENTS

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ABSTRACT

The thermal degradation of poly(vinyl chloride) (PVC) by a zipper-like dehydrochlorination is believed to initiate at abnormal structures present in the resin backbone. The allylic chlorines are major contributors to instability of the polymer. A selective replacement of the allylic chlorines with hydrogen on the PVC chain is accomplished by the use of organoboron reagents. Treatment of PVC with lithium triethylborohydride resulted in the reduction of chloroethyl chain ends, as well as the allylic chlorines. A considerable improvement in the static and dynamic thermal stabilities of PVC, treated with organoboron reagents, is observed. It is also demonstrated that the removal of chain end chlorines further enhances the stabilization effect. The reaction of certain model compounds, representing the defect structures present in PVC, with organoboron reagents was studied. The evidence for an addition–elimination mechanism in the reactions with substrates, containing allylic chlorines, is presented.

INTRODUCTION

The poor thermal stability of commercial poly(vinyl chloride) (PVC) resins is believed to be due not only to the facile dehydrochlorination at the normal polymer

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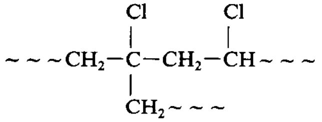
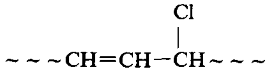
backbone but also to the presence of defects in the microstructure of the polymer. These defect structures facilitate initiation of dehydrochlorination chain reactions, which lead to the formation of conjugated unsaturation, resulting in discoloration and degradation of the resin.

The number of labile structures in PVC and the mechanism of their formation during the polymerization have been studied extensively [1]. The level of each defect structure in PVC has also been determined by NMR techniques described in the literature [2]. Among the most important defect structures present in commercial grade PVC, allylic and tertiary chlorines are known to be the major contributors to the catastrophic degradation of the resin at melt-processing temperatures.



$\sim\sim\sim CH_2-\overset{\overset{\textstyle Cl}{|}}{\underset{\underset{\textstyle CH_2\sim\sim\sim}{|}}{C}}-CH_2-\overset{\overset{\textstyle Cl}{|}}{C}H\sim\sim\sim$

Tertiary chloride



$\sim\sim\sim CH{=}CH-\overset{\overset{\textstyle Cl}{|}}{C}H\sim\sim\sim$

Internal allylic

$\sim\sim\sim CH{=}CH-CH_2-Cl$

Terminal allylic

A study of model compounds such as 2,4,6-trichloroheptane has revealed that the dehydrochlorination temperature of a defect-free PVC polymer should be ~50-60 degrees higher than that of the degradation temperature of commercial grade products [3]. The kinetics of the reaction between PVC stabilizers and the model compounds 2-chloro-2-methylbutane and 4-chloro-2-pentene were studied by Klemchuk [4]. His study showed that the allylic chloride reacted 20 times faster than the tertiary chloride with dibutyltin bis-mercaptides. He therefore concluded that allylic chlorines were the most important labile structures in PVC degradation. Although there has been much debate among the workers in this area, there seems to be general agreement that the allylic chlorines play a significant role in the initiation of dehydrochlorination and the degradation of the polymer.

Several reports in the PVC literature describe attempts to improve the thermal stability of PVC by the substitution of more stable groups for the labile chlorines in the structure of the resin. Among these efforts are stabilization by allyl xanthate substitution [5], diethylaluminum chloride-alkanol reaction [6], and treatment with di(*n*-butyl)tin bis(*n*-dodecyl mercaptide) [7]. All these posttreatment reactions introduce a new allylic substituent which is less labile than chlorine. Nevertheless, these can undergo similar elimination at slightly higher temperatures and still create a defect site on the structure of PVC.

Addition reactions to the residual double bonds have also been utilized in the chemical stabilization of PVC. For example, a slight chlorination [8] or the hydrogen addition reaction by azides [9], such as *p*-toluenesulfonazide, has improved the thermal stability of the resin.

Recently, Rogestedt and Hjertberg reported on the treatment of PVC with ethanol, trimethylaluminum, and dibutyltin maleate [10]. They found improved thermal stability in all treated samples, with trimethylaluminum being the most effective. They attributed the stabilization effect to the removal by this reagent of labile chlorines.

During the course of evaluating different hydride reducing agents for a reductive dechlorination of PVC [11], we discovered exceptional stability in the resins treated with certain organoboron reagents. The unusual reactivity of these reagents in the displacement of allylic labile chlorines in PVC, and the study of the reaction mechanisms, using model compounds, are described.

EXPERIMENTAL

Lithium triethylborohydride (Super-Hydride), lithium tri-*sec*-butylborohydride (L-Selectride), borane/triphenyl phosphite complex, borane/THF complex, and anhydrous THF were purchased from Aldrich and used without further purifications. Model compounds 1,2-dichloro-2-methylpropane, 1-chloro-3-methyl-2-butene, 3-chloro-3-methylpentane, and 3,4-dichloro-1-butene were also purchased from Aldrich and used as obtained. A commercial emulsion resin, E-PVC (IV = 1.0), and a commercial suspension resin, S-PVC (IV = 0.5), were used in this study.

Treatment of PVC with $Li(Et)_3BH$ and $Li(sec\text{-}Bu)_3BH$

To a 500-mL three-neck flask, equipped with mechanical stirrer, addition funnel, and condenser were added 100 mL anhydrous THF and 5 g of a PVC resin. The contents were stirred under nitrogen atmosphere until a complete solution was obtained. The resulting solution was cooled to 7 °C, and 100 mL of a 1 M solution of $Li(Et)_3BH$ or $Li(\textit{sec}\text{-}Bu)_3BH$ in THF was added dropwise under an inert atmosphere. The solution was stirred overnight at room temperature, then poured into 500 mL methanol with rapid stirring. The precipitate was filtered, washed with methanol, and dried. In the case of the dispersion resin, a Waring blender was used to break up the large resin lumps formed by precipitation in methanol. Redissolving the resin in THF and reprecipitating in methanol were also necessary in some cases in order to remove residual reagent and the boron salts.

This reaction was scaled up in a 12-L flask to treat 300 g PVC resin. The ratio of the reagent to the resin was reduced 4–6-fold (1 L reagent for 300 g resin) in scale-up treatments.

Borane/THF and Borane/Triphenyl Phosphite Treatments of PVC Resins

A 5 g sample of PVC resin was dissolved in a 100 mL anhydrous THF under nitrogen atmosphere. The solution was cooled in an ice bath and a 1-M solution of borane/THF complex (8 mL) was injected slowly through a septum. The mixture was refluxed under nitrogen for 16 hours, cooled to room temperature, and poured into 400 mL methanol. The resulting resin had to be blended in methanol, using a Waring blender, to obtain a fine powder. Reprecipitation from THF into methanol was repeated whenever it was necessary to remove the residual reagents as detected by atomic absorption and NMR spectroscopy.

The reaction with borane/triphenylphosphite complex was also carried out by a similar method, using 2.62 g borane complex for 5.0 g of the resin in 100 mL anhydrous THF. The resin was treated for 20 hours at the reflux temperature, then precipitated in methanol and isolated as described above.

The Microstructure and Thermal Property Analyses

The structures of the copolymers were analyzed by ^1H-NMR spectroscopy, using a Bruker AMX-500 operating at 500.14 MHz, by dissolving the resins in THF-d_8. The structures of the reaction products from reduced model compounds were confirmed by ^1H- and ^{13}C-NMR spectroscopy using a Bruker AM-200.

Elemental analyses of polymers and model compounds were carried out on a Leemans 240-XA analyzer. The atomic absorption spectroscopy was carried out using a Perkin-Elmer 6500 ICPAAS. The TGA analyses was carried out on a Dupont 951 thermogravimetric analyzer at a heating rate of 10°C/min under air. The DSC data were obtained on a Mettler DSC-30 at a 10°C/min heating and cooling rate with samples run under nitrogen.

Dynamic thermal stability (DTS) testing of PVC powder samples was carried out using a Brabender PL-2000 Plasticorder. The dehydrochlorination rates were determined at 190°C according to the method described by Abbas and Sorvik [12].

RESULTS AND DISCUSSION

Several methods for the reduction of organic halides have been described in the literature [13]. Reagents which can react under mild conditions in solvents which can dissolve PVC, and which have the least chance of promoting side reactions, have been of the most interest to us. In the search for such a reagent, we came across a powerful organoboron complex, lithium triethylborohydride, discovered by H. C. Brown and his coworkers [14, 15]. Super-Hydride (S-H), a 1-M solution of this reagent in THF, has become commercially available from Aldrich. The reagent is prepared by combining triethylborane and lithium hydride in THF at 25°C [15]:

$$\mathrm{LiH} + (\mathrm{C_2H_5})_3\mathrm{B} \xrightarrow[25^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Li(C_2H_5)_3BH}$$

We expected similar reaction mechanisms and reactivities for the borane/THF complex and other borane hydride reagents. Therefore, in addition to S-H, we examined the reaction of several borane reagents with PVC. The results are discussed later in this paper.

A sample of methanol-washed E-PVC was treated with an excess of S-H at room temperature. After 18 hours of treatment, it was found that only 6.7% of the chlorine atoms were replaced by hydrogen as determined by an elemental analysis of the treated resin. However, a thermal analysis by a melting point apparatus of the resin in a capillary tube showed a considerable improvement in thermal stability compared to the starting material. The S-H-treated resin had a melting point of ~180°C and did not show any discoloration by dehydrochlorination below ~235°C, whereas the untreated resin turned yellow at 180°C and black at 210°C, without melting. These observations prompted further investigation of the microstructure, the thermal properties of the treated resin, and the mechanism of PVC stabilization by this treatment.

Thermal Properties of Organoboron Treated Resins

The thermal stabilities of PVC resins treated with S-H and borane/THF complex were further investigated by comparison of the dehydrochlorination rates for the samples before and after treatment. Figure 1 shows the results of HCl evolution tests for a sample of E-PVC before and after treatment with an excess of S-H reagent for 12 hours at 5–10°C and then 0.5 hour at 30–40°C.

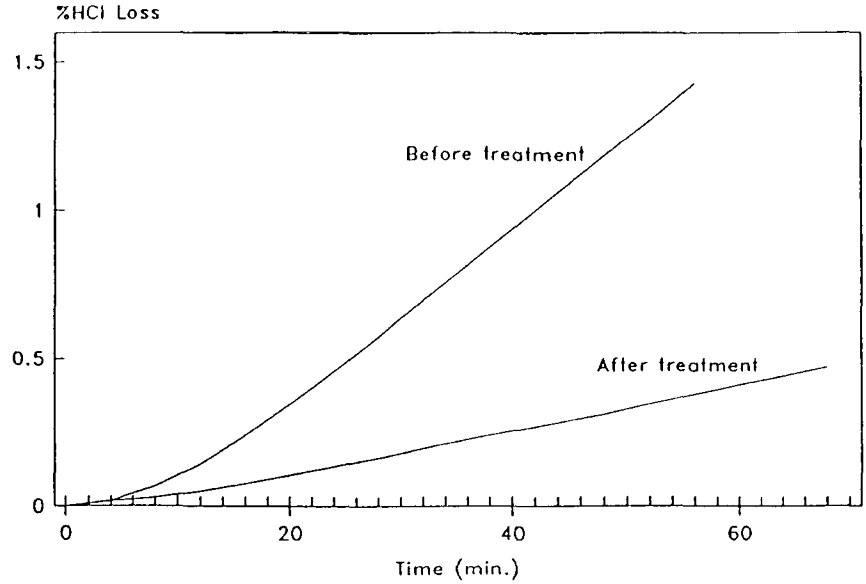


FIG. 1. HCl evolution from a sample of E-PVC before and after S-H treatment.

A sample of suspension resin, S-PVC, also showed a considerable decrease in the rate of dehydrochlorination after treatment with S-H, as shown in Fig. 2. An improvement in heat stability was also evident in the sample treated by a borane/THF complex (B-H), but the improvement was not as pronounced as in the sample from S-H treatment. Figure 2 also shows the effect of the resin morphology on the

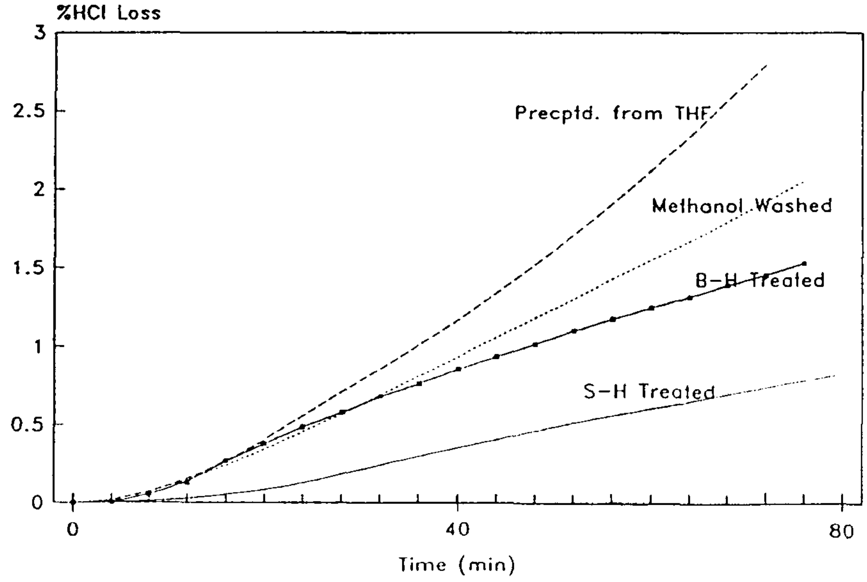


FIG. 2. HCl evolution from a sample of S-PVC before and after treatment.

rate of dehydrochlorination. There is a considerable change in the HCl evolution rate of the resin, precipitated from THF, due to the change in the morphology of the resin. The process of precipitation from THF should remove some impurities (such as residual initiators, surfactants, etc.) and some low molecular weight portions of the resin, which in turn should enhance the thermal stability. However, an increase in the dehydrochlorination rate was observed for the precipitated samples. Since the treatment with the hydride reducing agents also involved dissolution in THF and precipitation in methanol, all comparisons of the treated resins should be made with the corresponding precipitated control sample with similar morphology.

The S-H treatment was scaled up using a sample of S-PVC (300 g). The resulting resin, after precipitation and drying, showed a glass transition temperature of 76°C. To demonstrate the significance of the stabilization effect in treated resin under actual processing conditions, the thermal stability of this resin was evaluated in rigid and flexible formulations and compared with the same formulations using untreated resin. The results of some Brabender DTS tests are summarized in Table 1.

As shown in this table, both the times required to discolor and degrade are considerably prolonged in the resins treated with S-H. The improvement in dynamic thermal stability of the treated resins is more pronounced in rigid formulation R2 compared to R1. In the presence of an external stabilizer (formulations R4 vs R3 and F4 vs F3), the stabilization effect is less pronounced.

In a previous study [11] we showed that the remarkable improvement in the stability of S-H treated resin is not simply a result of the introduction of some ethylene groups into the resin structure, which in turn leads to a reduction in glass transition temperature. Undoubtedly, ethylene/vinyl chloride copolymers (E/VC) would be expected to show an improved processibility and thermal stability over PVC. However, if the defect structures in PVC remained intact, the improvement imparted to the resin's heat stability by the introduction of ethylene units would be

TABLE 1. Brabender DTS of Rigid and Flexible Compounds of PVC[a]

Ingredient	R1	R2	R3	R4	F1	F2	F3	F4
PVC	100.0	–	100.0	–	100.0	–	100.0	–
S-H-PVC[b]	–	100.0	–	100.0	–	100.0	–	100.0
Processing aid	1.0	1.0	1.0	1.0	–	–	–	–
Lubricant	0.8	0.8	0.8	0.8	–	–	–	–
DOP[c]	–	–	–	–	50.0	50.0	50.0	50.0
Tin stabilizer	–	–	2.0	2.0	–	–	2.0	2.0
Brabender DTS (200°C, 50 rpm):								
Minutes to discolor	2	21	23	>30	22	60	>60	>60
Minutes to degrade[d]	14	48	25	>30	46	>70	>60	>60

[a] S-PVC.

[b] S-H treated S-PVC.

[c] Dioctyl phthalate.

[d] Minutes to the onset of torque increase.

marginal at best, especially when only a few percent of the chlorines were replaced by hydrogen as in these treatments. We have clearly demonstrated this fact by a comparison of the thermal stability of E/VC copolymers prepared by partial reduction of PVC using various hydride reagents. Figure 3 is a comparison of the HCl evolution rates for copolymers prepared by the partial reduction of PVC using lithium aluminum hydride (LAH), tri-*n*-butyltin hydride (TBTH), and S-H.

Study of the Resin Microstructure

An examination of the proton NMR spectra of S-PVC, before and after treatment with Super-Hydride (Figs. 4 and 5), and the resin treated with borane/THF Complex (Fig. 6), revealed that the allylic chlorines were preferentially displaced by hydrogens in both treatments. These spectra also revealed the differences in the microstructural changes by borane/THF and S-H treatments.

A complete assignment of proton NMR signals from various chain ends in PVC has been reported by several workers [16]. The signals corresponding to chloroethyl and 1,2-dichloroethyl chain ends along with chloromethyl branches appear at 3.65–3.95 ppm. The disappearance of these signals in the spectrum of the S-H treated sample (Fig. 5) indicates the displacement of these primary chlorines by S-H treatment. A new signal appearing at 4.0 ppm is most likely from the methine proton of $-CH_2CH_2-CHClCH_2-$ resulting from the reduction of secondary backbone chlorines, or the methine signal of the $-CHClCH_3$ group resulting from the reduction of $-CHClCH_2Cl$ chain ends. However, the assignment cannot be made with a high degree of certainty. The above-mentioned chain end and chloromethyl branch chlorines remain virtually intact after treatment with borane/THF, as shown in Fig. 6. In Figs. 4 and 6 the integration of the area under the signals,

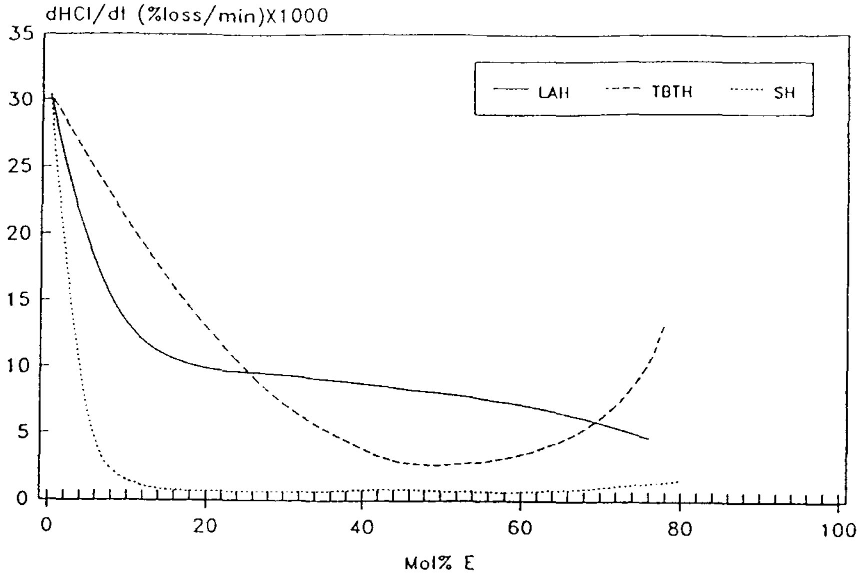


FIG. 3. HCl evolution rates for E/VC copolymers from partial reduction of PVC.

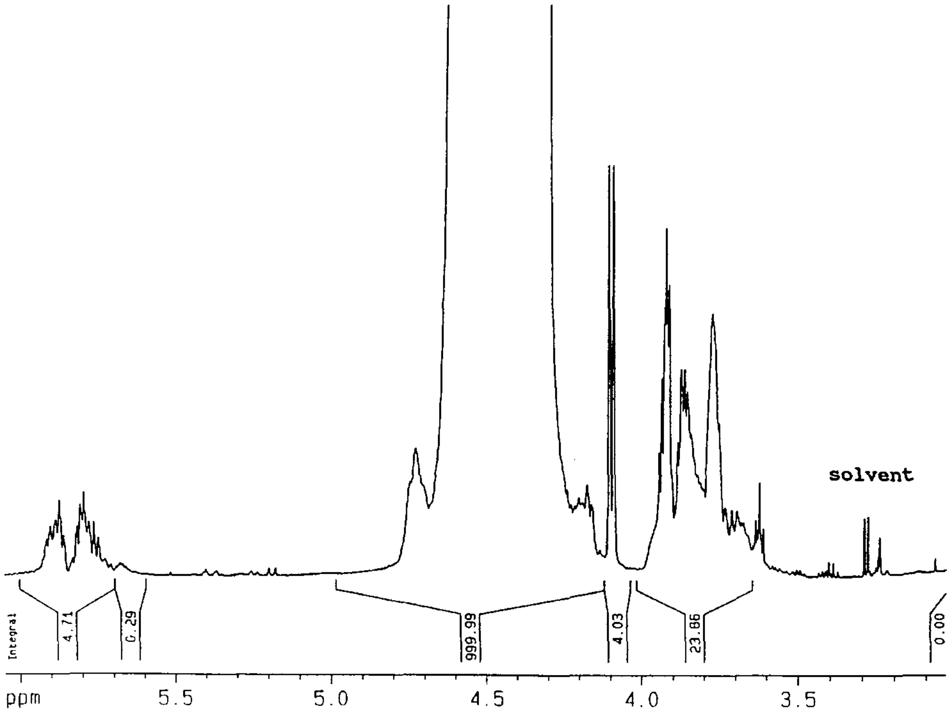


FIG. 4. ^{1}H-NMR spectrum of S-PVC (methanol washed).

corresponding to these chain ends, indicates that the ratio of these protons before and after treatment with borane/THF is the same within experimental error.

The preferential displacement of allylic chlorines by both treatments is evident by the disappearance of the allylic CHCl proton signals at 4.0–4.2 ppm in the NMR spectra and an upfield shift or the complete disappearance of the signals at 5.65–5.95 ppm, corresponding to the vinylic protons. The shift of the vinylic signals from 5.65–5.95 in Fig. 4 to 5.35–5.60 ppm in Fig. 5 indicates the absence of allylic chlorine in the S-H treated sample. However, the integration of the area under the signals, appearing at 5.35–5.60 ppm, shows a reduction in the residual unsaturation (from 4.9/1000 VC units to 2.5/1000 VC units). Therefore, partial reduction of the unsaturation by S-H treatment has occurred in addition to substitution of the chlorines. This provides further evidence in support of the addition-elimination/substitution mechanism, proposed later in this paper, for the S-H reaction. Treatment with borane/THF, followed by precipitation in methanol, results in complete removal of residual unsaturation.

Elemental analysis of the S-H treated sample showed the loss of chlorines from 6.7 mol of VC units due to reduction. The integration of the areas under the NMR signals for the untreated sample (Fig. 4) indicates the presence of ~28/1000 VC units (2.8 mol%) of $-CH_2Cl$ chain end protons or 1.4 mol% primary chlorines. Since all primary chlorines are removed by the treatment, the ratio of secondary/primary chlorines reduced by the S-H treatment is estimated to be 4/1.

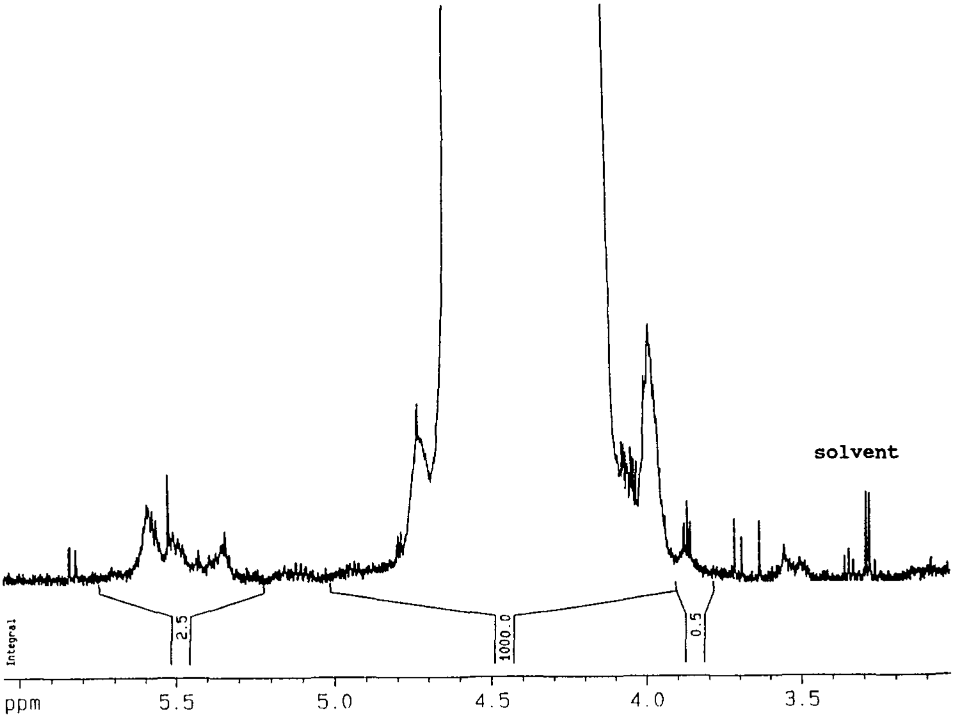


FIG. 5. ^{1}H-NMR spectrum of S-PVC treated with $Li(Et)_3BH$.

The weak signals observed at 3.3–3.5 ppm in the NMR spectra are due to residual solvents, i.e., THF and methanol, in the samples. No other significant modifications in the structure of PVC were manifest in the NMR spectra of the treated resins. Neither was there any evidence for incorporation of groups from the organoboron reagent pendant on the resin backbone. The precipitation of the treated polymers in methanol results in the decomposition of the borane–resin complex and the replacement of the borane moiety with hydrogen. Analysis by atomic absorption spectroscopy also confirmed the absence of boron in the treated samples. Further, no residual boron or any moieties from organoboron reagents were found in the treated model compounds discussed in the following section.

In summary, borane/THF reductive dechlorination seems to take place exclusively at the allylic sites while the treatment with S-H results in the removal of primary and allylic chlorines as well as some secondary chlorines. Since the results shown in Fig. 2 demonstrate that S-H-treated samples are more stable than borane/THF-treated samples, our data indicate that the removal of primary chlorines, in addition to allylic chlorines, has induced further stabilization in PVC.

Reaction of Organoboron Reagents with Model Halides; Study of the Reaction Mechanism

Brown and Krishnamurthy [14] reported the nucleophilicity of lithium triethylborohydride to be considerably higher than most simple nucleophiles available for

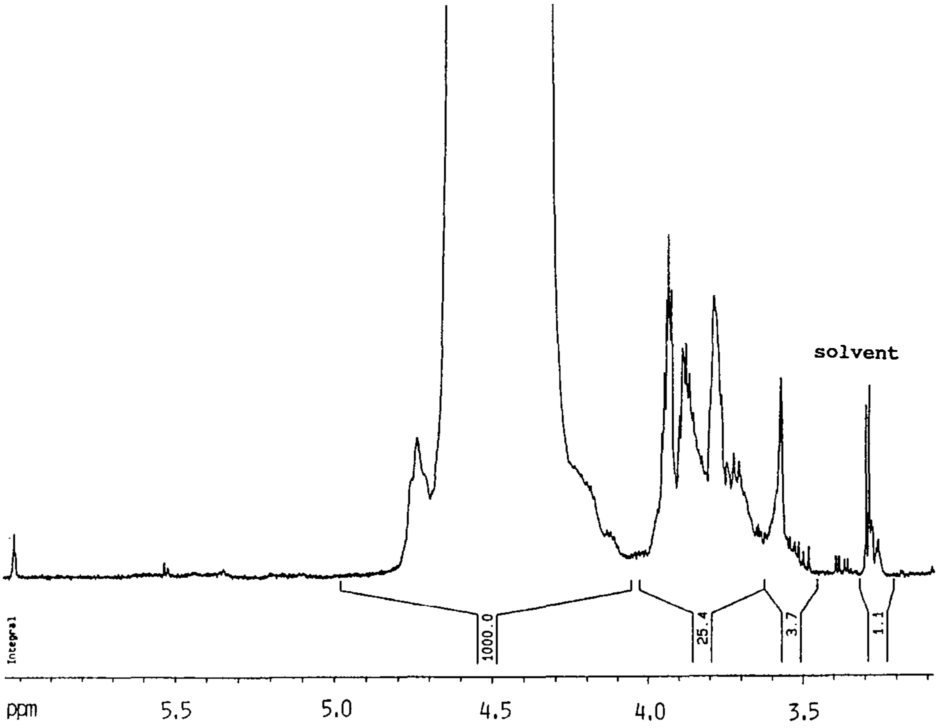


FIG. 6. ^{1}H-NMR spectrum of S-PVC treated with BH_3/THF.

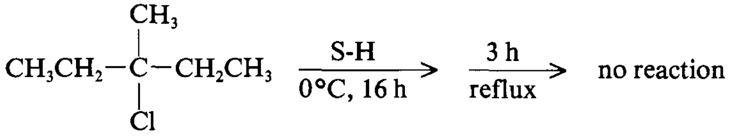
S_N2 displacements. By studying the kinetics of the reaction with simple halides, they found that allylic and benzylic bromides were reduced instantly whereas the reaction with secondary halides was somewhat slower. The reaction of tertiary bromides was slow and resulted predominantly in elimination.

We examined the reaction of S-H with several model alkyl chlorides, representing the possible defects in PVC structures, to determine which types of structures were being affected by our treatment and at what rates. In the case of simple alkyl halides, the reaction seems to follow the pattern of an S_N2 reaction as evidenced by the following examples.

The reagent reacts quite readily with 1-chlorooctane to produce *n*-octane in an almost quantitative yield in 10 minutes at room temperature [14]:

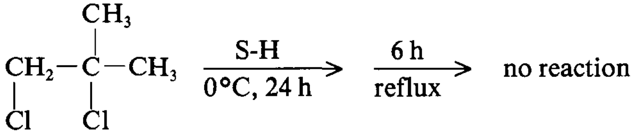
$$CH_3(CH_2)_6CH_2Cl \xrightarrow[25\,°C,\ 10\ \text{min}]{\text{S-H}} CH_3(CH_2)_6CH_3 \qquad (1)$$

The reaction with tertiary chlorines was found to be extremely slow, as Brown reported for tertiary alkyl bromides. However, contrary to Brown's findings in the reaction of tertiary bromides, we could not detect any elimination product in our reactions. The reaction of 3-chloro-3-methylpentane with $Li(Et)_3BH$ in THF for 16 hours at ice-bath temperature and 3 hours at reflux showed no change in the structure of the starting alkyl halide.



$$CH_3CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}-CH_2CH_3 \xrightarrow[0°C,\ 16\ h]{S\text{-}H} \xrightarrow[reflux]{3\ h} \text{no reaction} \quad (2)$$

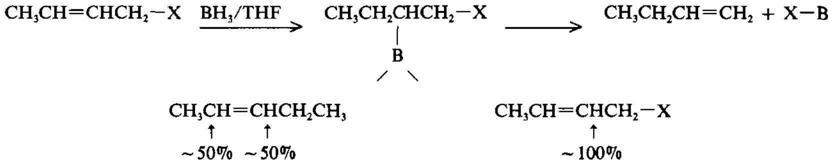
In addition, the reaction of S-H with primary halides showed a considerable sensitivity to steric factors, typical of an S_N2 reaction. When a sample of 1,2-dichloro-2-methylpropane was treated with an excess of S-H for 24 hours at ice-bath temperature and 6 hours at reflux, the starting material was recovered, with both chlorines intact.



$$\underset{\displaystyle Cl}{CH_2}-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}-CH_3 \xrightarrow[0°C,\ 24\ h]{S\text{-}H} \xrightarrow[reflux]{6\ h} \text{no reaction} \quad (3)$$

Therefore, the reactivity of S-H with simple alkyl halides seems to be controlled by steric factors. However, in the case of allylic halides, the electronic factors also play an important role in the activation/deactivation of the substitution sites and the control of the reaction kinetics. This effect, which is clearly demonstrated in the following examples, is in opposition to S_N2-type reactions and has not been reported before.

Remarkable selectivity in the hydroboration of unsaturated compounds, containing an electron-withdrawing substituent (X) at the allylic position, was reported in 1963 by Brown and Gallivan [17].

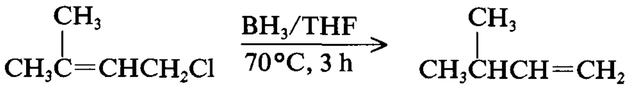


$$CH_3CH{=}CHCH_2{-}X \xrightarrow{BH_3/THF} CH_3CH_2\underset{\displaystyle B}{CH}CH_2{-}X \longrightarrow CH_3CH_2CH{=}CH_2 + X{-}B \quad (4)$$

$$\underset{\sim 50\%\ \ \sim 50\%}{CH_3CH{=}CHCH_2CH_3} \qquad \underset{\sim 100\%}{CH_3CH{=}CHCH_2{-}X}$$

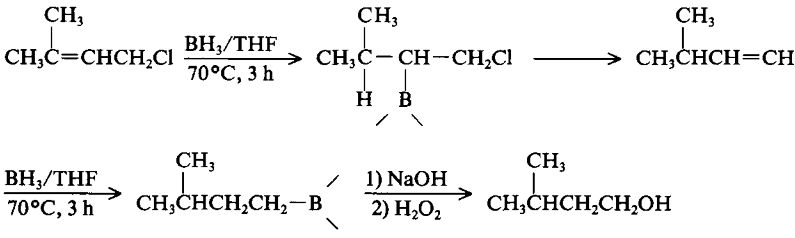
They found that in butenyl and related compounds, the major product resulted from an attachment of the boron to the position adjacent to the substituent. The product also showed a great tendency to undergo elimination. With no allylic substituent, the hydroboration of 2-pentene shows no regioselectivity.

We examined the reaction of borane/THF complex with some model alkyl chlorides. The reaction of 1-chloro-3-methyl-2-butene with borane after 3 hours at 70°C gave 3-methyl-1-butene, which was isolated by distillation as the only product. The reaction did not proceed when carried out at ice-bath temperature.



$$CH_3\overset{\displaystyle CH_3}{C}{=}CHCH_2Cl \xrightarrow[70°C,\ 3\ h]{BH_3/THF} CH_3\overset{\displaystyle CH_3}{C}HCH{=}CH_2 \quad (5)$$

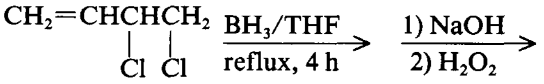
To further our understanding of the course of the addition–elimination reaction resulting in the rearrangement of the double bond, we repeated Reaction (5). However, instead of distillation of the hydroboration product, we oxidized the intermediate addition product in alkaline solution. The sole product obtained from this reaction was 3-methyl-1-butanol, which is believed to form by the following sequence of reactions:



$$\mathrm{CH_3\overset{CH_3}{C}{=}CHCH_2Cl \xrightarrow[70°C,\ 3\ h]{BH_3/THF} CH_3\overset{CH_3}{\underset{H}{C}}{-}\underset{\underset{/\ \backslash}{B}}{CH}{-}CH_2Cl \longrightarrow CH_3\overset{CH_3}{C}HCH{=}CH_2}$$

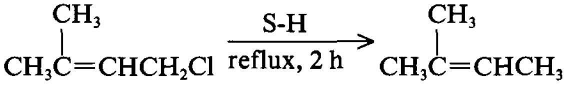
$$\mathrm{\xrightarrow[70°C,\ 3\ h]{BH_3/THF} CH_3\overset{CH_3}{C}HCH_2CH_2{-}B\!\!< \xrightarrow[2)\ H_2O_2]{1)\ NaOH} CH_3\overset{CH_3}{C}HCH_2CH_2OH} \qquad (6)$$

The hydroboration reaction on another model compound, 3,4-dichloro-1-butene, afforded 1-butanol. This represents a double addition–elimination reaction, leading to the formation of 1-butene in some stage, and a subsequent oxidation, resulting in the formation of 1-butanol:



$$\mathrm{CH_2{=}CH\underset{Cl}{C}H\underset{Cl}{C}H_2 \xrightarrow[reflux,\ 4\ h]{BH_3/THF} \xrightarrow[2)\ H_2O_2]{1)\ NaOH} CH_3CH_2CH_2CH_2OH} \qquad (7)$$

While the facile reduction of allylic chlorines with borane/THF complex can be easily explained by the addition–elimination mechanism discussed above, the reaction of lithium trialkylborohydrides with similar model compounds indicates major differences in the course of the reaction. These complex hydride reagents provide evidence for both an S_N2 mechanism and an addition–elimination type reaction, depending on the structure of the halide substrate. For example, treatment of 1 mol 1-chloro-3-methyl-2-butene with 1.2 mol S-H provided 3-methyl-2-butene with no rearrangement in the product, even at the reflux temperature for 2 hours. The product was distilled and collected in a dry-ice trap.

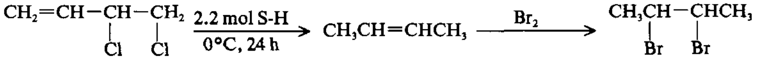


$$\mathrm{CH_3\overset{CH_3}{C}{=}CHCH_2Cl \xrightarrow[reflux,\ 2\ h]{S\text{-}H} CH_3\overset{CH_3}{C}{=}CHCH_3} \qquad (8)$$

Although Reaction (8) strongly indicates a simple nucleophilic substitution as described in the literature, the reaction of S-H with other alkyl halides suggests a more complex mechanism.

Every time 3,4-dichloro-1-butene was treated with Super-Hydride, the formation of a strongly pyrophoric compound, resistant to acid, frustrated our efforts to effectively isolate and identify the products. This was not the case for the reaction described earlier where BH_3/THF was used for the reduction.

However, we were able to distill some olefinic product from the reaction of 3,4-dichloro-1-butene with S-H. The product was found to be 2-butene by NMR analysis. In order to avoid the loss of other volatile products, the distillate was also brominated directly as it evolved from the distillation pot. The analysis of the brominated product indicated the presence of 2,3-dibromobutane alone.

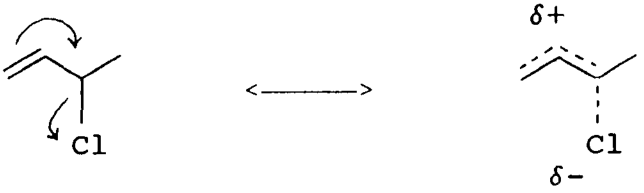


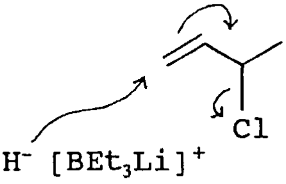
$$\mathrm{CH_2{=}CH{-}\underset{Cl}{CH}{-}\underset{Cl}{CH_2} \xrightarrow[0°C,\ 24\ h]{2.2\ mol\ S\text{-}H} CH_3CH{=}CHCH_3 \xrightarrow{Br_2} CH_3\underset{Br}{CH}{-}\underset{Br}{CH}CH_3} \qquad (9)$$

DISCUSSION OF THE REACTION MECHANISM

The double bond shift in Reaction (9) clearly indicates that the reduction with S-H is not a pure S_N2 reaction. On the other hand, the formation of 2-butene indicates that unlike hydroboration (Reaction 7), this reaction is not pure addition–

elimination either. It appears that while the chlorine at the chain-end is being substituted by an S_N2 reaction, the allylic chloride is being removed by an entirely different mechanism. The presence of an electron-withdrawing substituent adjacent to the mobile π-electrons tends to polarize the double bond and enhance the electron deficiency of C-1 just enough to promote a hydride attack on that carbon with a concurrent shift of the electrons and the cleavage of the carbon—chlorine bond:





Since the reaction is carried out in a polar solvent at low temperatures and in a basic medium, any other rearrangement pathway through a free radical or carbonium ion intermediate seems highly unlikely. However, further kinetic studies need to be carried out in order to establish the most feasible mechanism.

CONCLUSION

Reductive dechlorination of allylic chlorines in PVC resins by certain organoboron reagents imparted a remarkable heat stability to the resins. A THF solution of lithium triethylborohydride (Super-Hydride) was found to be an especially effective reagent in the selective reduction of labile and chain-end chlorines, thereby enhancing the thermal stability of the resin.

The mechanism of the reaction for the reduction of allylic chlorines with organoboron reagents was shown to be different than that of the simple alkyl halides. A new mechanism is postulated for the reaction of lithium trialkylborohydrides with the allylic chlorines in PVC, based on reactions with several model compounds. Our results indicate that these reactions proceed via a combination of addition-elimination and substitution (S_N2) mechanisms.

A comparison of the dynamic and static heat stabilities of a S-H-treated resin and untreated PVC shows that the removal of certain labile chlorines might impart stability to the resin, comparable to the addition of the most effective PVC stabilizers available today.

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REFERENCES

[1] T. Hjertberg and E. M. Sorvik, *Degradation and Stabilization of PVC* (E. D. Owen, Ed.), Elsevier Applied Science, New York, 1984, p. 21, and references therein.

[2] W. H. Starnes Jr., F. C. Schilling, I. M. Plitz, R. E. Cais, D. J. Freed, R. L. Hartless, and F. A. Bovey, *Macromolecules, 16*, 790 (1983).

[3] M. Asahina and M. Onozuka, *J. Polym. Sci., A1*(2), 3505, 3515 (1964).

[4] P. P. Klemchuk, *Adv. Chem. Ser., 85*, 1 (1968).

[5] J. D. Nichols, *J. Polym. Sci., Polym. Lett. Ed., 11*, 705 (1973).

[6] N. G. Gaylord and A. Takahashi, *J. Polym. Sci., Part B, 8*, 349 (1970).

[7] W. H. Starnes Jr. and I. M. Plitz, *Macromolecules, 9*, 633 (1976).

[8] B. Baum and L. H. Wartman, *J. Polym. Sci., 28*, 537 (1958).

[9] T. Nakagawa and M. Okawara, *J. Polym. Sci., Part A.1*(1), 1795 (1968).

[10] M. Rogestedt and T. Hjertberg, *Macromolecules, 25*(23), 6332 (1992).

[11] N. Pourahmady, P. I. Bak, and R. A. Kinsey, *J. Macromol. Sci.—Pure Appl. Chem., A29*, 959 (1992).

[12] K. B. Abbas and E. M. Sorvik, *J. Appl. Polym. Sci., 17*, 3567 (1973).

[13] For a review, see A. R. Pinder, *Synthesis*, 425 (1980).

[14] H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc., 95*(5), 1669 (1973).

[15] H. C. Brown, S. C. Kim, and S. Krishnamurthy, *J. Org. Chem., 45*(1), 1 (1980).

[16] G. M. Benedikt, *J. Macromol. Sci.—Pure Appl. Chem., A29*(2), 85 (1992) and references therein.

[17] H. C. Brown and R. M. Gallivan Jr., *J. Am. Chem. Soc., 90*(11), 2906 (1968).

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