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MICROSTRUCTURE AND THERMAL PROPERTIES OF ETHYLENE/VINYL CHLORIDE COPOLYMERS

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ABSTRACT

The microstructure of ethylene/vinyl chloride (E/VC) copolymers, prepared by partial reduction of PVC with a variety of reagents, was analyzed using carbon-13 NMR spectroscopy. The effect of the reduction mechanism on the microstructure and stereochemistry of the copolymers was studied. The reduction with tri-*n*-butyltin hydride (TBTH) produced copolymers with higher degrees of alternating monomer units than copolymers obtained by reduction with lithium aluminum hydride (LAH). Reduction with lithium triethylborohydride (SH) produced blockier copolymers. The correlation of monomer sequence and distribution with thermal stability and dehydrochlorination rate in these copolymers was investigated. Partial reduction of PVC by all reagents was shown to produce E/VC copolymers with improved thermal stability compared to PVC. In the series of copolymers produced by TBTH reduction, improvement in thermal stability increased with an increase in E content and reached a maximum at 40% E content but dropped steadily thereafter. All copolymers from SH reduction showed a considerable drop in their dehydrochlorination rate compared to PVC. The stabilization effect reached a maximum at ~7 mol% E content and stayed constant throughout.

INTRODUCTION

Copolymers of ethylene (E) and vinyl chloride (VC) have been of interest to both manufacturers of polyethylene and poly(vinyl chloride). The combination provides reduced flammability for polyethylene and improved processability for polyvinyl chloride. However, attempts to prepare E/VC copolymers by common polymerization methods have often failed to produce copolymers with the desired composition and monomer sequence [1-3]. Alternate routes to obtain such copolymers are by partial chlorination of polyethylene [4, 5] and partial reduction (reductive dechlorination) of PVC [6-9]. The structure and properties of copolymers obtained by both methods have been the subject of many investigations [10-18].

Reductive dechlorination of PVC by lithium aluminum hydride was first investigated by Braun and his coworkers [7] and later by Millan and his group [8]. An alternative route for the reduction of vinyl chloride to polyethylene by the use of tributyltin hydride (Bu_3SnH) was introduced by Starnes et al. [9]. The microstructure and some properties of the E/VC copolymers, prepared by partial reduction of PVC, using the latter method, have been extensively studied by Tonelli and his coworkers [13-17].

Recently, Braun et al. [10] reported an unusual trend in the thermal properties of E/VC copolymers obtained by partial reduction of PVC with Bu_3SnH. They found that the copolymers with lower than ~35 mol% E content were more stable than PVC, whereas the copolymers with higher E content were less stable than PVC. They concluded that the HCl loss of the copolymers depended on their glass transition and the degradation temperature.

Braun attributed this unusual behavior to two factors which influence the dehydrochlorination rate in E/VC copolymers—the composition and the amount of HCl remaining in the samples during degradation, i.e., “inner gas.”

Naqvi presented a mechanism for PVC degradation [19] and attempted to rationalize the unusual trend in thermal stability of E/VC copolymers based on that mechanism. He attributed the low thermal stability of PVC to the presence of concentrations of like dipoles in the resin matrix that serve as high energy spots. Introduction of nonpolar groups (or the removal of polar Cl groups in this case), which might dilute or reduce such polar interactions, would be expected to impart stability. Initially, the introduction of nonpolar ethylene units results in the reduction of undesirable polar interactions within the PVC matrix, and the stability of copolymers increases. But at some critical composition, due to the appearance of phase separation between the nonpolar ethylene segments and polar vinyl chloride segments within the copolymer, the stabilization mechanism becomes inoperative and destabilization occurs.

We carried out the partial reduction of PVC, using various reagents, in order to prepare E/VC copolymers with differing degrees of blocky or alternating units of E and VC. The microstructure of these copolymers and the relationship between their structure and thermal properties are described in this paper.

EXPERIMENTAL

Tri-*n*-butyltin hydride, lithium aluminum hydride, lithium triethylborohydride (Super-Hydride), anhydrous THF, and xylene were purchased from Aldrich and used without further purification. A suspension PVC resin was used in all reductions. The resin samples were washed with methanol in Soxhlet extractors for 48 h prior to reduction.

Tri-*n*-butyltin hydride reductions were carried out as described in the literature [20]. The reaction time and the amount of reagents were modified to prepare copolymers with various compositions.

Reductions of PVC Using $LiAlH_4$ and $Li(Et)_3BH$. A methanol-washed PVC sample (15 g) was dissolved in anhydrous THF (380 mL) in a three-neck flask. The solution was cooled to an ice bath temperature, and $LiAlH_4$ (14 g) was added under a steady flow of nitrogen. The mixture was refluxed for 30 min (various reflux times in similar experiments were used to prepare copolymers with varying compositions). The mixture was cooled to an ice bath temperature, and excess reagent was decomposed by dropwise addition of ethyl acetate. The resulting polymer was then precipitated from methanol, filtered, dissolved in THF (or *p*-xylene for copolymers with high E content), and reprecipitated in methanol.

A similar procedure was used for the reductions employing $Li(Et)_3BH$ reagent (1 *M* solution in THF), except the decomposition of the unreacted reagent was carried out using methanol.

The Microstructure and Thermal Property Analysis. The structures of the copolymers were analyzed by ^{13}C-NMR spectroscopy using a Bruker AM-200. A mixture of deuterated benzene and trichlorobenzene was used as a solvent. The TGA analyses were carried out on a Dupont 951 thermogravimetric analyzer at a 10°C/min heating rate under air. The DSC data were obtained on a Mettler DSC-30 at a 10°C/min heating and cooling rate under nitrogen. The dehydrochlorination rates were determined at 190°C according to the method described by Abbas and Sorvik [21].

RESULTS AND DISCUSSION

A. Microstructure of E/VC Copolymers

The random or Bernoullian distribution of comonomer units in E/VC copolymers can be calculated as described in the literature [13, 22]. Figure 1 illustrates the changes in triad fractions versus the composition for random copolymers of ethylene and vinyl chloride. Any upward shift of the EEE and VVV curves would be considered a shift toward blockier copolymers. This would, of course, be associated with a downward shift in EVE and VEV curves. On the other hand, any shifts in the opposite directions would indicate a tendency toward alternating copolymers.

A random displacement of chlorine atoms from the PVC microstructure generates the various diad and triad comonomer sequences shown below. The concentration of these structures, which varies with the composition, can be easily determined by the use of ^{13}C-NMR spectroscopy [13] based on the signals corresponding to the carbons in bold type.

Diad structures:

$-CH_2CHCl\mathbf{C}H_2CHCl-$	VV
$-CH_2CHCl\mathbf{C}H_2CH_2-$	VE or EV
$-CH_2CH_2\mathbf{C}H_2CH_2-$	EE

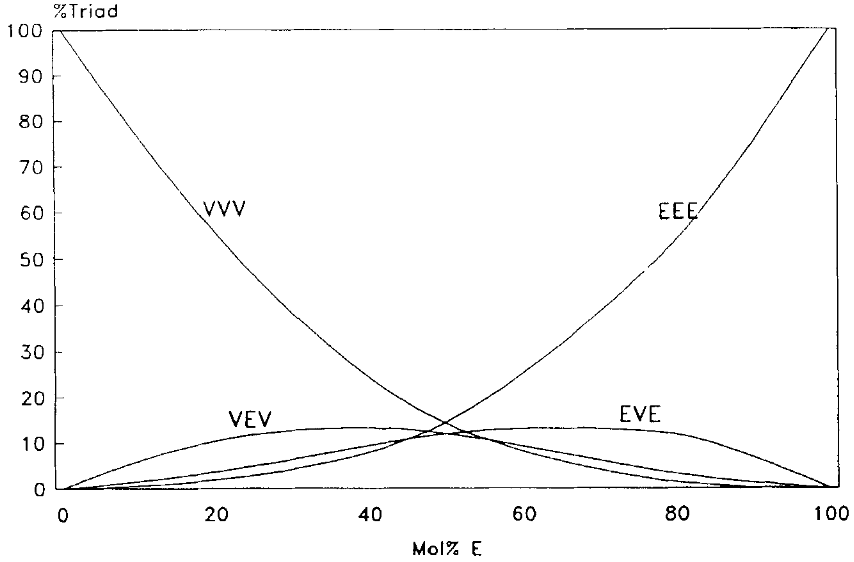


FIG. 1. Triad fractions in Bernoullian or random E/VC copolymers.

Triad structures:

$-CH_2CHClCH_2CHClCH_2CHCl-$	VVV
$-CH_2CHClCH_2CHClCH_2CH_2-$	VVE or EVV
$-CH_2CH_2CH_2CH_2CH_2CHCl-$	EEV or VEE
$-CH_2CHClCH_2CH_2CH_2CHCl-$	VEV
$-CH_2CH_2CH_2CHClCH_2CH_2-$	EVE
$-CH_2CH_2CH_2CH_2CH_2CH_2-$	EEE

For each chlorine atom removed by reduction of PVC, a methine carbon is converted into a methylene carbon. The mole percent vinyl chloride, therefore, can be calculated from

$$X_v = 100[2I_{CH}/(I_{CH} + I_{CH2})]$$

where I_{CH} and I_{CH2} are the integrals of methine and methylene signals, respectively, in the ^{13}C-NMR spectra.

The ^{13}C-NMR spectrum of an E/VC copolymer from partial reduction of PVC is shown in Fig. 2. All signals upfield of 50 ppm, labeled as VEV, EEV, EEE, VE + EV, and VV, are methylene (CH_2) signals, whereas those downfield of 50 ppm, labeled as VVV, VVE, and EVE, represent the methine (CH) carbons. Variation in the ratios of diads and triads from the reduction of PVC was easily monitored by the changes in the ratios of the integrals corresponding to each signal.

The composition of each copolymer was also determined by elemental analysis. These data, along with the molecular compositions and the ratios of diads and triads for each copolymer as calculated from the NMR data, are given in Table 1. The acronyms used for identification of each copolymer sample represent the

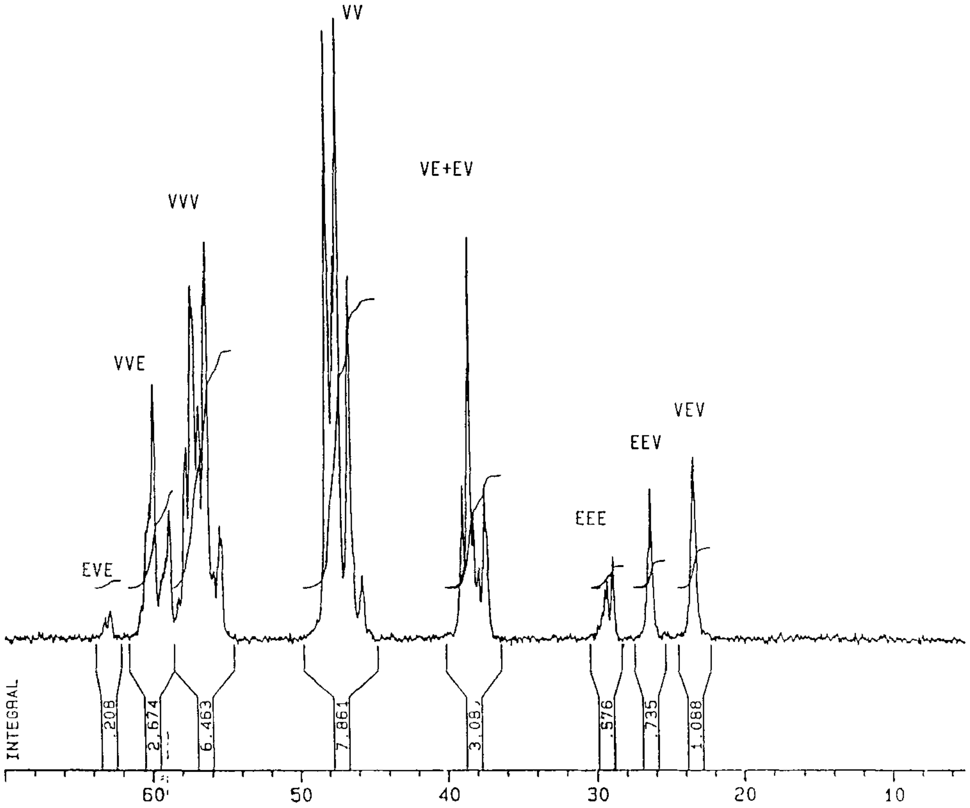


FIG. 2. Carbon-13 NMR of an E/VC copolymer.

method of reduction (T for tri-*n*-butyltin hydride, S for Super-Hydride, L for lithium aluminum hydride), and the mol% of ethylene (E) units. For example, S-E38 represent a copolymer sample obtained by Super-Hydride reduction with $X_E = 38\%$.

Table 1 shows reasonable agreement between the NMR data and the elemental analysis for the composition of the copolymers.

A comparison of these data with a random distribution of monomer units in copolymers, as shown in Fig. 1, indicates that the partial reduction of PVC by tri-*n*-butyltin hydride (TBTH) has produced copolymers with a more alternating nature than random copolymers, while the polymers from lithium triethylborohydride (SH) reduction contain a blockier monomer distribution. The copolymers from lithium aluminum hydride (LAH) reduction have a nearly random distribution.

Although there is a deviation from random distribution in the TBTH, SH, and LAH series of copolymers, none of these reactions produces a perfectly alternating or block copolymer. The deviation from a Bernoullian distribution can be easily seen in Figs. 3, 4, and 5, where the variation in each different type of triad ratio is plotted against the polymer composition for the three reactions. It is interesting to notice that the reduction with TBTH eliminates VVV triads at 72 mol% E

TABLE 1. Composition and Monomer Sequences in E/VC Copolymers

	Composition,	Diad ratios			Triad ratios					
Sample	mol% VC[a]	VV	VE+EV	EE	VVV	VVE	EVE	VEV	EEV	EEE
T-E7	93.1 (88.2)	79	20	1	62	17	10	9	1	0
T-E24	76.4 (77.1)	55	41	3	38	32	6	16	7	1
T-E41	59.4 (60.1)	34	56	10	18	32	11	19	17	3
T-E45	54.9 (52.7)	25	58	17	10	29	15	18	23	4
T-E72	27.8 (26.4)	5	49	46	0	8	20	8	35	29
T-E80	20.4 (19.3)	2	39	59	0	3	17	5	32	43
L-E10	90.4 (93.3)	82	17	1	74	16	1	7	2	0
L-E18	82.3 (84.5)	69	27	4	57	24	2	10	7	1
L-E28	72.3 (73.3)	57	35	8	44	28	2	11	12	3
L-E32	67.6 (65.5)	48	39	13	33	30	4	9	17	6
L-E66	34.0 (35.1)	18	35	47	8	20	5	7	30	30
L-E70	29.4 (28.7)	14	32	54	5	19	6	3	27	40
L-E75	25.0 (23.7)	11	29	60	3	16	6	1	25	49
S-E12	88.5 (88.0)	80	18	2	72	7	10	6	4	1
S-E26	74.1 (71.9)	59	30	11	46	26	2	8	15	4
S-E38	62.5 (58.8)	44	35	21	30	29	3	6	22	10
S-E48	52.4 (49.9)	34	35	31	20	28	4	5	26	17
S-E58	42.6 (40.9)	25	33	41	15	23	4	4	28	26
S-E71	29.0 (25.8)	13	28	59	3	8	3	0	29	57

[a] The first values were calculated from the NMR data; the values in parentheses were obtained by elemental analysis.

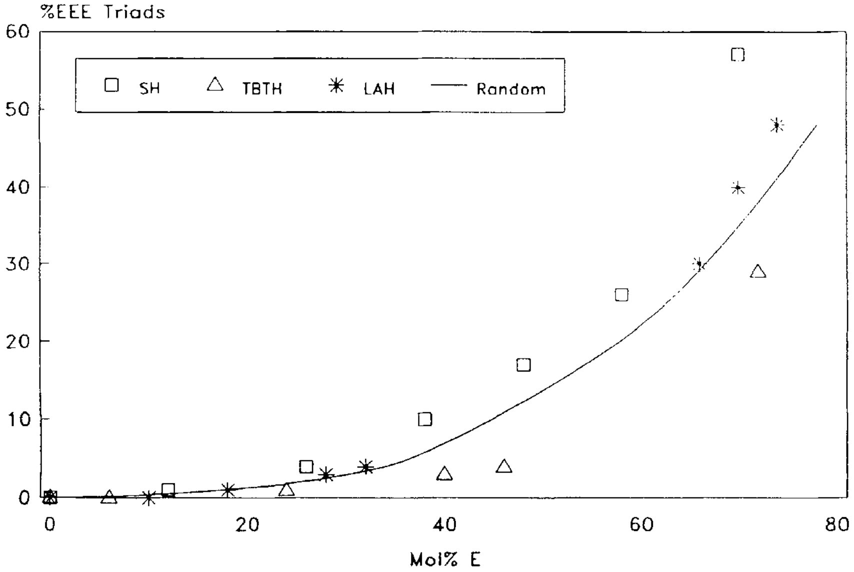


FIG. 3. EEE triad fractions in E/VC copolymers.

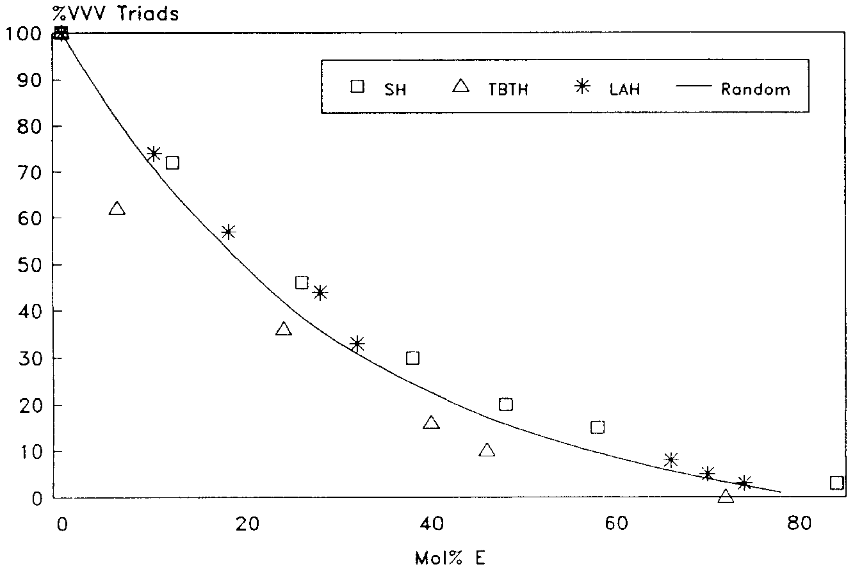


FIG. 4. VVV triad fractions in E/VC copolymers.

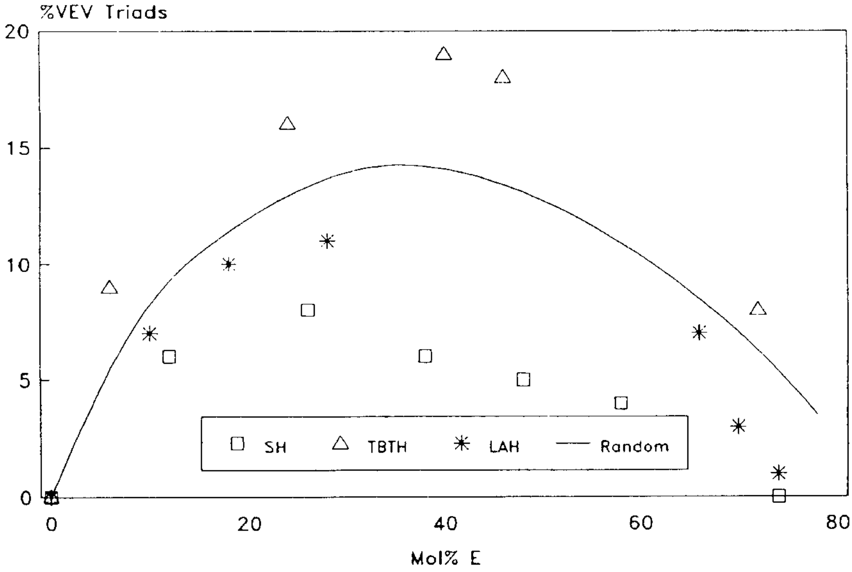


FIG. 5. VEV triad fractions in E/VC copolymers.

and beyond (see Fig. 4 and Table 1). The absence of PVC blocks is expected to eliminate the discoloration problems associated with zipperlike dehydrochlorination and the formation of long sequences of unsaturated bonds.

A closer examination of the 54–58 ppm range in the ^{13}C-NMR spectra of these copolymers (Fig. 6) shows the differences in the ease of reduction for the segments of the polymer with different tacticities. The faster disappearance of the signal at 56 ppm (the most upfield portion of the CHCl carbon) as the reduction progresses indicates the ease of reduction at isotactic segments for all three cases. The syndiotactic segment (signal at 58 ppm), on the other hand, seems to be the most resistant toward reduction. This difference in the reactivity appears to be more pronounced in the case of LAH and SH reductions than the TBTH reduction. A quantitative evaluation of the reaction rate from the NMR spectra was not possible due to the proximity of the signals and the interference of the VVE triad signals in copolymers with high E content.

B. Discussion of the Reduction Mechanisms and Selectivity

The selectivity observed during the reduction of PVC with different reagents can be explained in light of the mechanism involved in each case and the steric and electronic effects pertaining to the molecular structure of PVC.

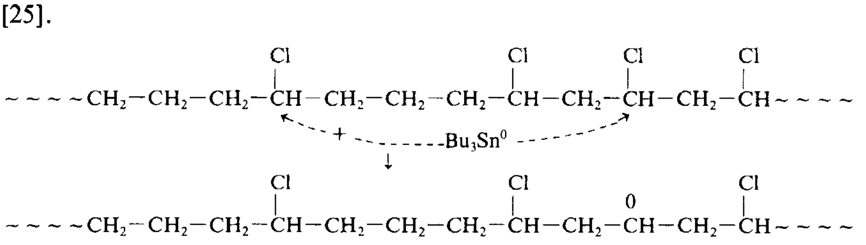
The reaction of tri-*n*-butyltin hydride with alkyl halides in the presence of a radical initiator takes place via the free radical process represented below [23].

$$I^0 + Bu_3SnH \rightarrow IH + Bu_3Sn^0$$

$$Bu_3Sn^0 + RCl \rightarrow Bu_3SnCl + R^0$$

$$R^0 + Bu_3SnH \rightarrow RH + Bu_3Sn^0$$

The same free radical process is believed to be operating during the tri-*n*-butyltin hydride reduction of PVC [24]. The rate-determining step in this process is the attack by the tributyltin radical on the alkyl halide. The Bu_3Sn^0 is known to have some nucleophilic character [25] and will preferentially attack diads and triads of vinyl chloride units during the reduction instead of the monads. The preference of a nucleophilic attack on the CHCl of diads and triads relative to monads is explained by the electron withdrawing effects of the chlorines on the neighboring units [25].



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

$$\downarrow \; Bu_3Sn^0$$

$$\sim\sim\sim\sim CH_2-CH_2-CH_2-\overset{Cl}{\overset{|}{C}H}-CH_2-CH_2-CH_2-\overset{Cl}{\overset{|}{C}H}-CH_2-\overset{0}{C}H-CH_2-\overset{Cl}{\overset{|}{C}H}\sim\sim\sim\sim$$

The reaction of simple alkyl halides with $LiAlH_4$ [26] and $Li(Et)_3BH$ [27] is known to proceed by a S_N2 mechanism. However, the reduction of PVC with either one of these reagents does not seem to be a pure S_N2 reaction. Starnes et al. [25] suggested an alternate mechanism for $LiAlH_4$ reduction of PVC involving a rate-determining attack on halogen by an electrophile, E^+, which could be a lithium cation or some other metallic species formed during the reduction process. In any

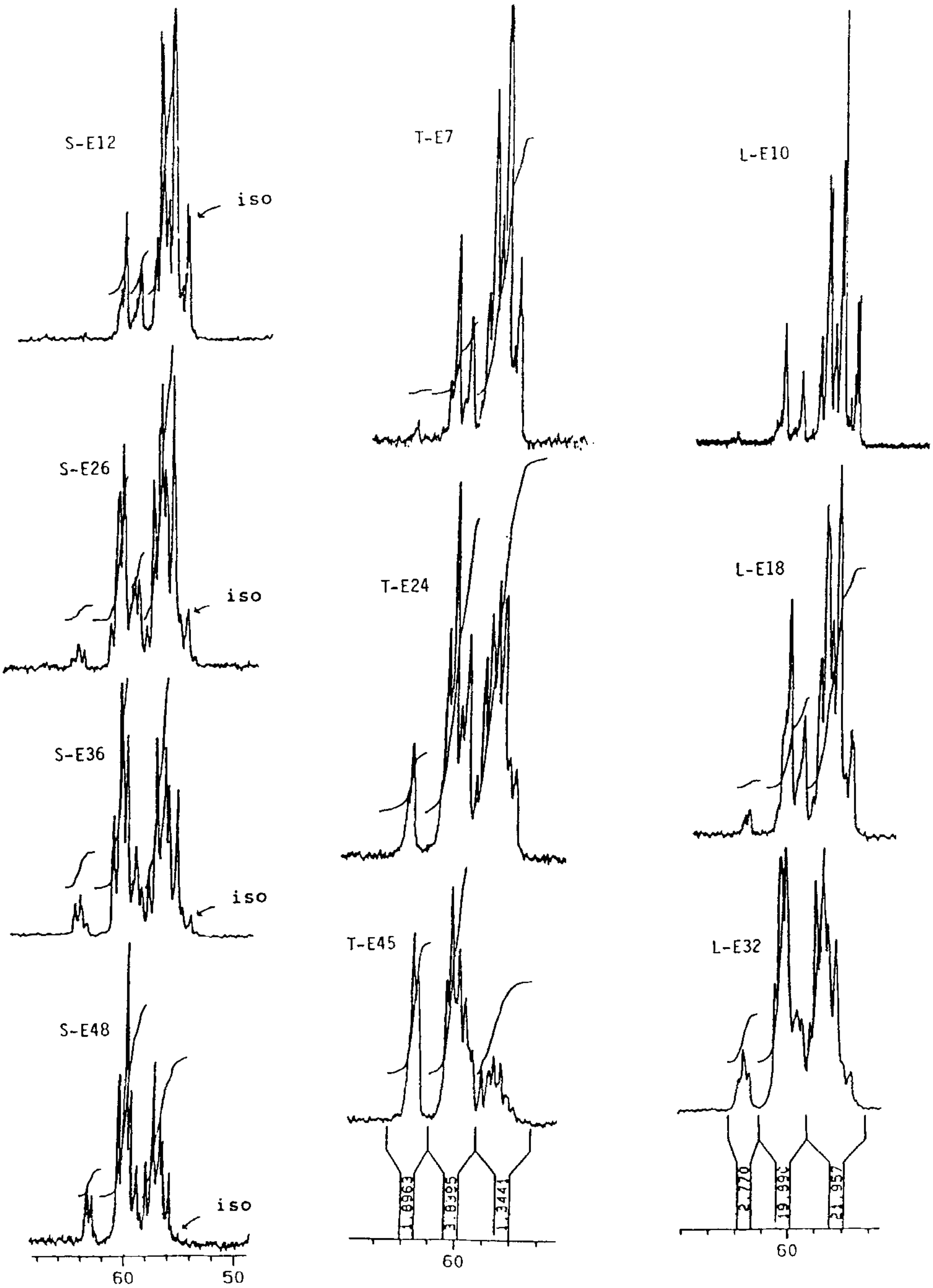


FIG. 6. The variation in the CHCl signal of VC units in E/VC copolymers.

case, the preference in the reduction of monads over diads and triads is observed with this reagent [8, 25].

In addition, the resistance of the syndiotactic segments of the polymer toward reduction with $LiAlH_4$ is reported by several groups [7, 8, 25]. These observations are explained based on the conformational effects and steric crowding of the chlorine atoms which result in preferred nucleophilic substitution at monads relative to diads and triads as well as on the preference for the reduction of heterotactic and isotactic segments compared to the syndiotactic triads.

Starnes attributed the higher reactivity of monads over diads and triads to the inductive effect of the neighboring chlorines in diads and triads, since the electrophilic attack on chlorine is expected to generate some positive charge on the C—Cl carbon of the polymer, rendering this carbon less prone to attack by E^+ [25].

In any event, overall, the reduction with $LiAlH_4$ results in a nearly random distribution of comonomer units in the structure of the copolymers. The reduction with $Li(Et)_3BH$, however, shows a more pronounced selectivity, which leads to the formation of block polymers. Therefore, the aforementioned conformational and steric effects controlling the nucleophilic substitution may be more significant here due to the larger size of the counterion ($LiEt_3B^+$) associated with the attacking nucleophile. However, the mechanism in this case is also more complicated than a pure S_N2 type. A detailed study of the mechanism and the reactivity of Super-Hydride and similar reagents with PVC will be discussed elsewhere [28].

C. Thermal Properties of E/VC Copolymers

The dehydrochlorination and thermal degradation properties of the copolymers were studied by the measurement of HCl evolution rates at 190°C, as measured by conductivity, and thermogravimetric analysis. The HCl loss from E/VC copolymers from PVC reductions using LAH and SH are shown in Figs. 7 and 8. In contrast to the results reported by Braun et al. [10] for the samples of PVC reduced by TBTH, the dehydrochlorination rates for all our samples from the LAH, SH, and TBTH reductions of PVC were lower than that of PVC, as shown in Fig. 9. However, as is also shown in this figure, the same trend in variation of dehydrochlorination rate with the change in composition is evident for the TBTH series, in agreement with Braun [10]. The sample with the lowest rate of HCl loss in this series appears to be the one with 45 mol% E.

The copolymers T-E72 and T-E80 were of the most interest to us, since the NMR analyses of these samples indicated no PVC blocks (triads or higher) were present. A sample of T-E72 was melt-pressed to form an opaque film. The loss of transparency was an indication of a microphase separation due to the formation of a highly crystalline PE phase. This film sample showed no discoloration upon heating under nitrogen at 180°C for 2 h, followed by an additional 2 h at 220°C. The oven-aged samples showed no UV absorption due to the formation of conjugated double bonds.

It is interesting that the trend in the rate of HCl loss observed for the TBTH-reduced samples is absent in the copolymers prepared by the other two methods. In the case of the LAH reduction, a relatively fast drop in the rate is observed at the early stages of the reduction, then the remaining compositions show a somewhat similar stability, with no significant changes, even in samples as high as 75 mol% E content.

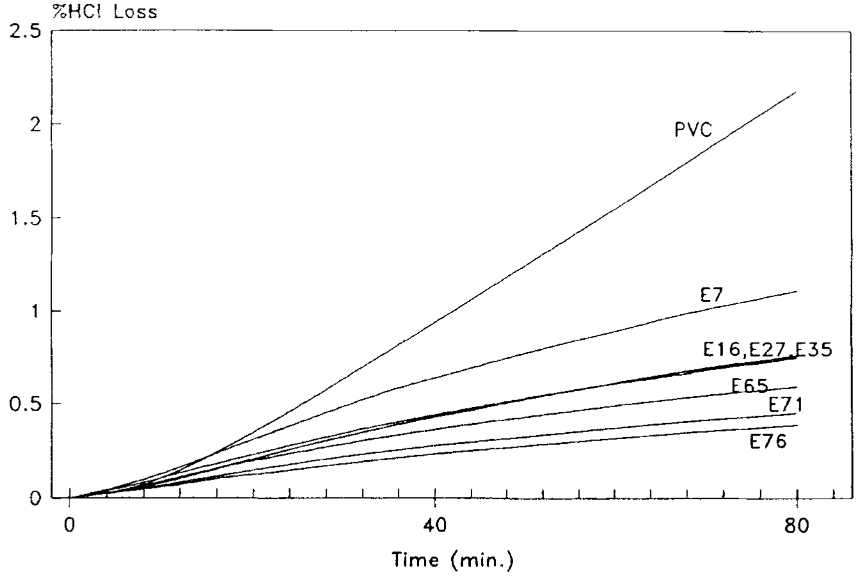


FIG. 7. HCl loss from E/VC copolymers from partial reduction of PVC by LAH.

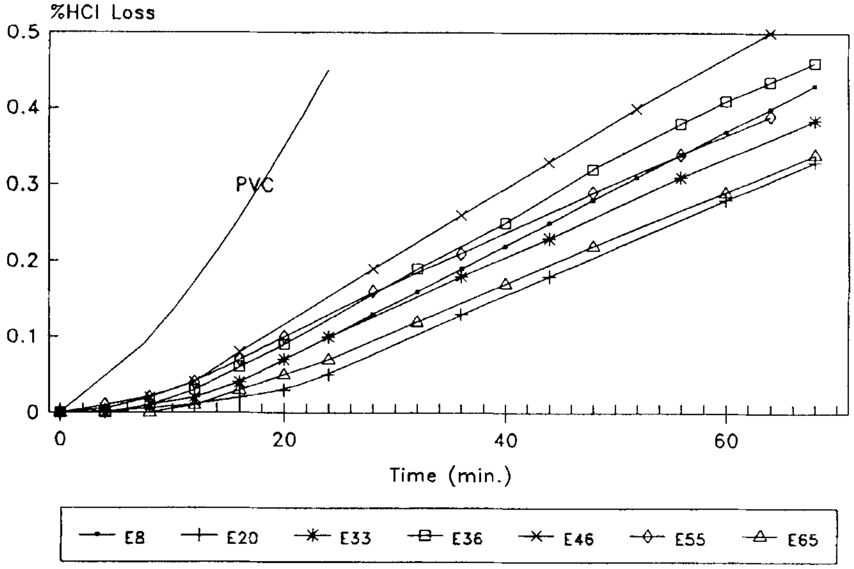


FIG. 8. HCl loss from E/VC copolymers from partial reduction of PVC by SH.

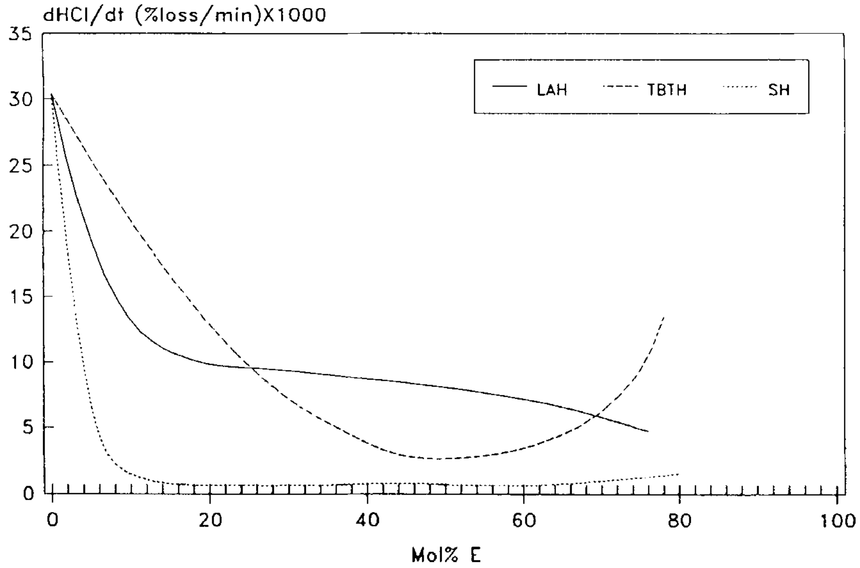


FIG. 9. HCl evolution rates for E/VC copolymers from partial reduction of PVC.

The reduction with lithium triethylborohydride produces a significant drop in the dehydrochlorination rate for the entire range of compositions. This significant stabilization, introduced into the samples, is due to an unprecedented reactivity of organoboron reagents toward certain defect structures in PVC. This occurs at the very early stages of the reduction. The mechanism of this stabilization effect and the subject of the reaction of organoboron reagents with PVC defect structures will be dealt with elsewhere [28].

The thermogravimetric analysis (TGA) of E/VC copolymers shows a two-step degradation mode for all these samples. The first step presumably corresponds to the dehydrochlorination of the vinyl chloride units in the sample, while the second step represents the ultimate degradation and chain scissions involving all segments of the copolymer.

A cross-plot of the TGA thermograms for E/VC copolymers with various compositions obtained by the partial reduction of PVC with $Li(Et)_3BH$ is shown in Fig. 10. These TGA data also show that all copolymer samples have an improved thermal stability compared to their progenitor. Although the maxima of the second transition in degradation continuously move toward higher temperatures with the increase of E segments in the copolymers, the same order is not evident in the initiation of dehydrochlorination.

The DSC analyses of the copolymers show a steady drop in glass transition temperature with an increase in E content for all three series of samples, as expected. There seems to be some deviation from the calculated T_g values for random copolymers in all three series, as shown in Fig. 11.

The deviation from the calculated values increases with a higher E content, and it is more pronounced for the LAH and SH series than for the TBTH-reduced samples. Considering the blockier structure of the former series compared to the alternating nature of TBTH samples, this is not unexpected. There may be some

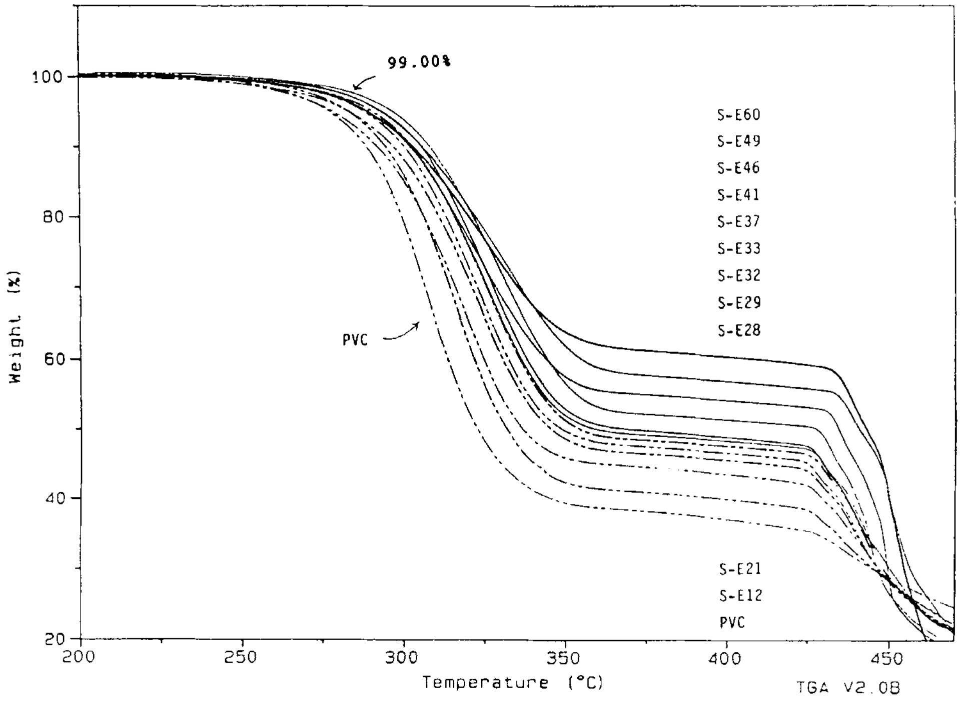


FIG. 10. TGA thermograms of E/VC copolymers from SH reduction of PVC.

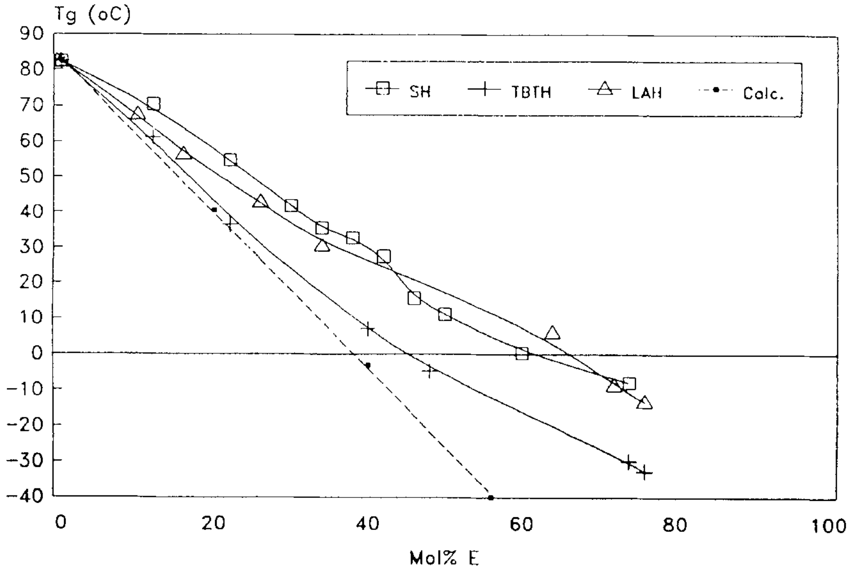


FIG. 11. Glass transition temperatures of E/VC copolymers.

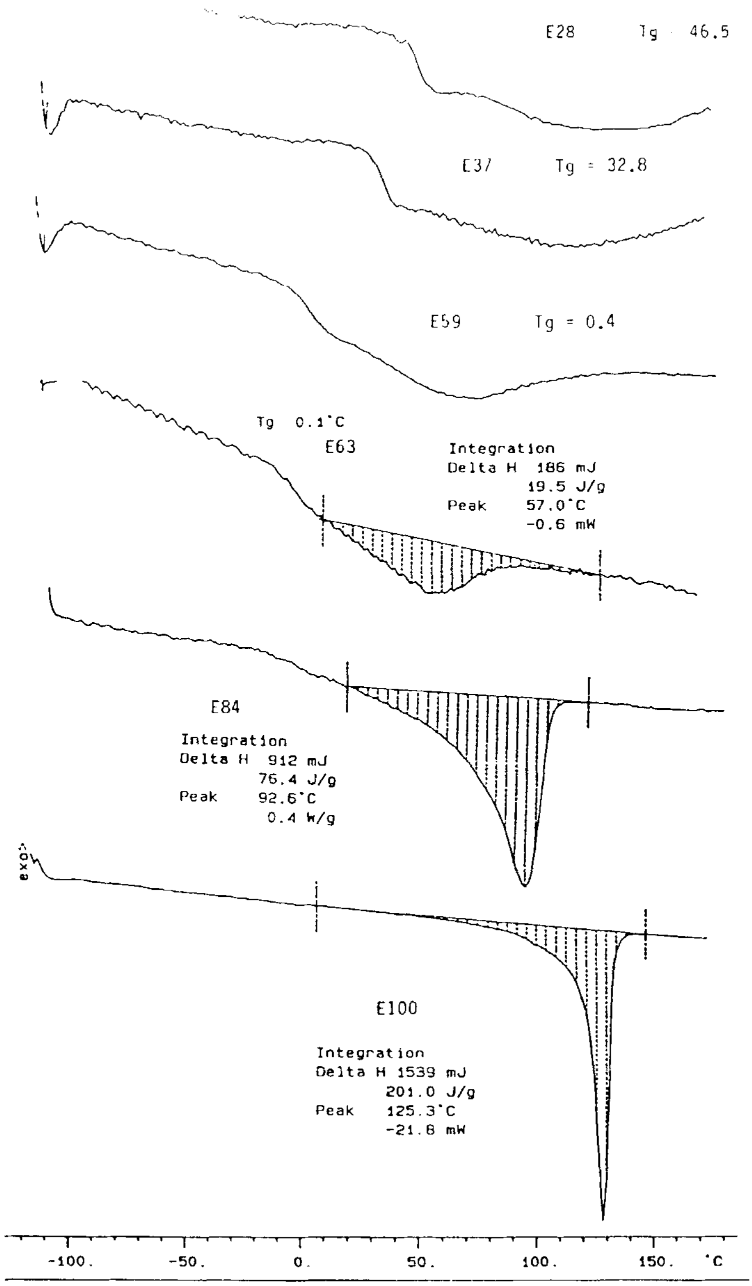


FIG. 12. DSC thermograms of E/VC copolymers.

microphase separation in the samples with high E content, leading to deviation from the theoretical composition. However, the glass transition of the polyethylene microphase is not evident in the DSC thermograms. Samples with greater than ~50 mol% E content exhibit a distinct melt behavior, as shown in Fig. 12. The melting endotherm gradually shifts toward the melting point of polyethylene with an increase in E content and reaches the melting point when the reduction is complete.

CONCLUSIONS

Partial reduction of PVC with various metal hydride reagents produces E/VC copolymers with improved thermal stability as compared to PVC homopolymer. The mechanism of each reduction reaction was found to have a profound effect on the microstructure and the thermal properties of the resulting copolymers. Copolymers with higher degrees of alternating ethylene-vinyl chloride units are formed by a free radical mechanism (TBTH), while the nucleophilic substitution (S_N2 type, LAH and SH) reaction prefers the formation of blockier copolymers.

In contrast to reports in the literature [10, 19], all E/VC copolymers appear to have a better thermal stability than PVC, regardless of the copolymer composition and the monomer sequences. An exceptional improvement in the thermal stability of the copolymers prepared by Super-Hydride reduction compared to lithium aluminum hydride and tri-*n*-butyltin hydride reductions was observed.

The thermal stability of the copolymers increased with an increase in E content. However, in the case of the copolymers from TBTH reductions, a maximum stability was observed at ~45 mol% E content, with a decrease in the stability of the copolymers thereafter. Since the same trend is absent in similar copolymers prepared by other reduction methods, the theories offered by Braun and others do not seem to be valid explanations of this behavior. The problem in the case of TBTH reduction could be the alteration of the backbone structure by a free radical reaction or substitution of trace amounts of alkyltin moieties on the structure of copolymers with greater than 45 mol% E content. This does not seem unreasonable since samples with higher E content have experienced longer treatment by the reagent. Nevertheless, further work is needed to substantiate this hypothesis.

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