Chemical Stabilization of Poly(vinyl chloride) by Prior Reaction with Di(*n*-butyl)tin Bis(*n*-dodecyl mercaptide)[1]

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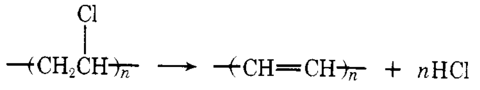
ABSTRACT: Chemical pretreatment of poly(vinyl chloride) (PVC) with the title mercaptide, or with mixtures of the mercaptide and di(*n*-butyl)tin dichloride, has afforded polymers containing only traces of residual tin (<1–68 ppm) but having thermal stabilities greater than that of the starting PVC by factors ranging up to ca. 6–9 (as measured by rates of dehydrochlorination under argon at 160.5 °C). The pretreatments were carried out in deoxygenated *o*-dichlorobenzene at temperatures ranging up to 185 °C, and the resulting polymers were purified by methanol precipitation and exhaustive extraction with hot methanol prior to the stability determinations. No correlation of polymer stability with residual tin content was observed. However, the stabilities were inversely related to the amounts of sulfur chemically bound to the polymers, with maximum stabilization being obtained at a sulfur content of approximately 0.9%. These observations are shown to provide evidence in favor of the Frye–Horst stabilization theory, which postulates that stabilization of PVC by organic metal salts results from replacement of labile halogen by anionic stabilizer moieties.

The degradation and stabilization of poly(vinyl chloride) (PVC) have been of great interest to polymer chemists and technologists for many years,[2] but the chemical reactions involved in these processes are still poorly understood at the molecular level. However, it is now generally agreed that the thermal, nonoxidative decomposition of PVC (1) (eq 1) involves sequential loss of HCl from adjacent monomer units and affords conjugated polyene structures (2) which impart undesirable color to the resin when values of *n* are sufficiently high.[2] This type of degradation has been observed with PVC at temperatures as low as 60–80 °C,[3] even though studies with model compounds in the liquid phase suggest that the polymer would be entirely stable in the absence of oxygen at temperatures well above 200 °C, if it possessed the simple structure, 1.[2b,g,4] These results seem to require the presence in PVC of defect sites that are abnormally susceptible to thermal destruction, and the existence of such sites now seems to be a generally accepted fact,[2] although some workers believe that dehydrochlorination can also be initiated, even below 200 °C, by the normal monomer units themselves.[5]



$$\underset{\mathbf{1}}{-\!\!\left(\mathrm{CH_2}\overset{\mathrm{Cl}}{\overset{|}{\mathrm{CH}}}\right)_{\!n}\!\!-} \longrightarrow \underset{\mathbf{2}}{-\!\!\left(\mathrm{CH{=}CH}\right)_{\!n}\!\!-} + n\mathrm{HCl} \qquad (1)$$

Considerable effort has been expended by previous researchers in attempts to identify the defect structures in PVC and to determine their relative contributions to the overall degradation process. These studies have been adequately summarized elsewhere,[2] and we will not attempt to review them at this time, although they do have a bearing on the present work for reasons soon to be noted. What we are primarily concerned with here is the mechanism(s) of action of the most common and effective thermal stabilizers for PVC; namely, the organic metal salts, many of which can be represented by the formula MY_2, where M is a metallic cation such as R_2Sn^{2+} (R is an alkyl group), Ba^{2+}, Ca^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, etc., and Y is an organic anion such as $R'S^-$, $R'CO_2^-$, or $R'O^-$ (R′ is a hydrocarbon residue or an organic moiety containing one or more heteroatom functionalities).[2f] These substances are bases of sufficient strength to react with HCl according to eq 2,[2a,c,f–h,6] and such reactions are expected to contribute to stabilization, since catalysis of PVC degradation by the evolving HCl is now a well-established phenomenon[2a–e,h] despite occasional failures to observe it.[8] However, other factors may well be involved in the overall stabilization process, and in recent years the stabilization theory that has attracted the greatest amount of attention has been one in which the defect structures of PVC are assigned a crucial role. First enunciated by Frye and Horst in 1959,[9] this theory[9,10] proposes that organic metal salts can undergo selective metathetical reactions (eq 3) with PVC structural defects (RCl) containing "particularly labile chlorine atoms" [9] (e.g., allylic or tertiary chlorine), thereby converting these defects into new structures (RY) that are less susceptible to thermal decomposition than the structures from which they were derived. In this way polyene production starting from defect sites should be effectively prevented or retarded; moreover, the pendant Y groups should tend to block the growth of any polyene sequences whose formation actually does begin.[9] Therefore, in addition to retarding color development by interfering with polyene generation, organic metal salts might also be expected to cause *true chemical stabilization* of PVC by reducing the rate of loss of total chloride (free HCl plus chloride bound to metal) from the thermally degrading polymer.

$$\mathrm{MY_2} \xrightarrow{\mathrm{HCl}} \mathrm{MYCl} + \mathrm{HY} \xrightarrow{\mathrm{HCl}} \mathrm{MCl_2} + \mathrm{HY} \qquad (2)$$

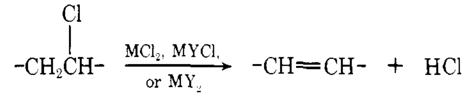
$$\mathrm{RCl} + \mathrm{MY_2} \longrightarrow \mathrm{RY} + \mathrm{MYCl} \xrightarrow{\mathrm{RCl}} \mathrm{RY} + \mathrm{MCl_2} \qquad (3)$$

R = allyl, *tert*-alkyl, etc.

Retardation of PVC coloration by the use of organic metal salts is a well-documented technological observation,[2f] and the ability of these stabilizers to react selectively with allylic and tertiary chloride structures according to eq 3 has been amply demonstrated with model compounds.[2a,f,11] In some cases the products (RY) obtained from models have, in fact, been shown to be more stable thermally than their halogenated progenitors.[2g,4a,c,11e,12] Studies on model tertiary chlorides may, admittedly, be irrelevant, for there is as yet no conclusive evidence for the occurrence of tertiary halogen in conventional PVC.[4a,b,13] However, the presence of allylic chloride in this polymer now seems a virtual certainty.[2a,b,d,h] Moreover, analytical studies by Frye et al.[9,10a,d] and many other workers[14] have shown that the anionic moieties of organic metal salts are, indeed, incorporated into PVC itself during thermal treatment. Nevertheless, the Frye–Horst proposal is still not universally accepted, and many alternative theories of stabilization have been devised in recent years.[2a,c,e–h,7,8a,14g,j,l,15]

The reluctance of some workers to accept the Frye–Horst hypothesis has been based on the frequent failure of organic metal salts to product significant chemical stabilization effects (as defined above), either during dehydrochlorination induction periods[2c,g,7,14e,15e,f,16] or in later decomposition stages.[2c,g,7,8b,14e,i,16a,b,d,17] While such findings do not rule out the occurrence of Frye–Horst substitution reactions (eq 3), they do suggest that these reactions may not be responsible for the observed retardations in rates of color development.[2c,15f,18]

However, it appeared to us, during the conceptual stage of the present work, that rejection of the Frye–Horst hypothesis on the basis of a dearth of evidence for chemical stabilization was perhaps a bit premature. Since metal salt stabilizers are ordinarily used at rather low concentration levels (a few weight percent), and since their mobilities within the polymer matrix should be less than that of HCl, one might argue that the stabilizers could be largely consumed by reaction with HCl before they are able to interact with many defect structures. Furthermore, retardations in rates of chloride loss owing to defect site destruction might be counterbalanced by simultaneous increases in rates of chloride production due to the Frye–Horst reactions themselves[11a,12] (eq 3), and to the ability of metal compounds to catalyze HCl elimination from PVC by acting as Lewis acids (eq 4). Finally, prevention of visible color would seem to require only a small reduction in the average length of conjugated polyene sequences under some experimental conditions, at least,[2d,5d,7,19] so that color prevention might be accomplished in these cases with only minimal defect site removal if the stabilizers react most rapidly with those allylic chloride moieties that are adjacent to the longer polyene sequences, a possibility suggested by some of the available data on reactions of model compounds.[20] However, these rationalizations require further experimental substantiation, and the frequent absence of chemical stabilization thus remains as a problem insofar as the Frye–Horst theory is concerned.



$$\text{-CH}_2\overset{\text{Cl}}{\overset{|}{\text{CH}}}\text{-} \xrightarrow[\text{or MY}_2]{\text{MCl}_2,\ \text{MYCl},} \text{-CH=CH-} + \text{HCl} \qquad (4)$$

On the other hand, the literature does include a few positive reports of chemical stabilization effects produced by "Frye–Horst metal salts",[14m,16d,21] and the question of whether these reports can be taken as evidence for the Frye–Horst theory obviously needs to be addressed. In our view, a negative answer should be given, because the effects were obtained only with polymers containing metal compounds as well as other nonpolymeric stabilizer fragments. We consider results on such polymers to be inconclusive for reasons noted below (see Results and Discussion).

Another possible approach to the true chemical stabilization of PVC involves the use of organic metal salts as polymer pretreatment agents. Attempts to increase the intrinsic stability of the polymer by chemical modification have, in fact, been made by numerous workers, who have used a remarkable variety of reagents in order to accomplish this objective. Many of these reagents are, strictly speaking, not encompassed by the Frye–Horst stabilization scheme; they include such things as chlorine,[5a,b,22] diimide,[23] hydrogen fluoride,[24] nitrogen oxides,[25] lithium aluminum hydride,[26] dibutyl maleate,[27] organic phosphites with and without metal salts,[28] basic lead carboxylates,[14g,j] morpholine,[29] diphenylmethyllithium,[30] triphenyl- or tributylstannyllithium,[31] potassium allyl xanthate,[32] triphenylaluminum,[33] alkylaluminums,[33,34] alkylaluminums and aromatics,[34b,35] and alkylaluminums with monomeric or polymeric olefins in the presence or absence of metal cocatalysts.[34b,35,36] Polymers with enhanced stabilities were obtained in many of these experiments, but in several instances it is clear that the degrees of structural modification attained were so great as to preclude the attribution of stabilization effects to defect site destruction alone. Furthermore, in a number of these examples, the source of the stabilization effects is rendered somewhat uncertain by the absence of proof for removal of basic (HCl reactive) species that might have remained physically entrapped within the polymer matrix, and by a lack of evidence for any relationship between stability and the number of defect sites destroyed.

A few attempts have also been made to stabilize PVC by pretreatment with "Frye–Horst metal salts", but the results of all such experiments known to us have been negative or inconclusive. Frye and Horst[9] reported a stabilization effect resulting from prior reaction of the polymer with cadmium 2-ethylhexanoate, but they used color change rather than chloride evolution as the measure of stability, and they did not rigorously verify the removal of metal salts from the chemically pretreated resin. Morikawa[14f] observed "very rapid hyperchromic decomposition on reheating PVC which had been decomposed previously with addition of a [metal] benzoate", while Minsker et al.[15d,37] found that a pretreatment of PVC with dibutyltin dicaprylate did not affect the thermal stability at all. The latter result is consistent with a reported lack of correlation between the dehydrochlorination rate of PVC containing dibutyltin distearate and the number of stearate groups attached to the chain of this polymer at various dehydrochlorination levels.[14d]

The foregoing considerations suggested to us that a true chemical stabilization effect on PVC would constitute very strong evidence in favor of the Frye–Horst proposal if the effect could be demonstrated under conditions conducive to the exclusion of alternative mechanistic modes. Our initial efforts to achieve this goal are described in the present paper.

Results and Discussion

General Experimental Approach. From the outset it seemed that the desired objective was most likely to be attained by means of pretreatment experiments involving two steps: (a) reaction of PVC in solution with a very large excess of stabilizer [much more than the amount anticipated to be required for complete destruction of active sites], followed by (b) complete removal, if possible, of all metallic residues and stabilizer fragments that were not chemically bonded to the polymer. Carrying out the reaction in a liquid phase of low viscosity would obviously solve the stabilizer mobility problem noted above, and it was thought that the use of excess stabilizer would increase the rate of defect site removal by a mass-action effect[11a,12] if the stabilizer were chosen with care. Excess stabilizer was also expected to retard the creation of new active sites by interfering with MCl_2-catalyzed dehydrochlorination (eq 4), a result which might simply be ascribed to the presence of a large number of substituting ligands (Y groups) in the reacting system. More specifically, such an effect could derive from reaction 5, which converts MCl_2 into a species (MYCl) potentially capable of causing substitution as well as elimination of HCl.[11a]

$$MCl_2 + MY_2 \rightleftarrows 2MYCl \qquad (5)$$

Step b, on the other hand, would prevent undesirable complications arising from the occurrence of stabilizing or destabilizing reactions (e.g., eq 3 and 4) during the actual stability determinations. And in this regard it is particularly important to note that true chemical stabilization effects can also be accommodated by other previously postulated mechanisms which differ from the Frye–Horst scheme by requiring the continued presence, in the polymer, of unchanged stabilizer or stabilizer products that are not chemically attached to the polymer chain. These alternative mechanisms are, conceptually, quite diverse; they invoke phenomena such as HCl scavenging,[2a,c,e–h,14d,e,15e] radical scavenging,[2a,c,f,h,15b,g] metal catalysis of HCl addition[8a] (the reverse of eq 4), or metal complexation with defect structures.[15d,h] We supposed that step b, if implemented, would tend to allow such processes to be removed from consideration and thus greatly increase the likelihood that the Frye–Horst mechanism was, indeed, responsible for any chemical stabilization effects that might be revealed by our experiments.

The stabilizer used in this work, di(*n*-butyl)tin bis(*n*-dodecyl mercaptide), was selected on the basis of the following considerations: (1) Dialkyltin mercaptides are commonly regarded as the most effective thermal stabilizers of PVC.[2f,38] (2) This particular stabilizer had been shown to react with a model allylic chloride at a rate much faster than the probable rate of the competing spontaneous dehydrohalogenation.[11a] (3) Reaction of this stabilizer with defect sites was expected to afford substitution:elimination ratios [eq 3:eq 4] that were quite high, owing to the generally high reactivity of sulfur nucleophiles toward carbon centers.[39] Indeed, *no* elimination had been detected during substitution reactions of the stabilizer with a number of allylic[11a–c] and tertiary chloride[11b,c] models, though it is true that elimination products might have been missed because material balances were incomplete. (4) Once formed, the polymer thioether structures obtained with di(*n*-butyl)tin bis(*n*-dodecyl mercaptide) were expected to be stable under the chemical pretreatment conditions.[11c] (5) Use of this stabilizer would allow the extent of incorporation of Y moieties into the polymer to be easily determined from sulfur analyses. (6) With this stabilizer, creation of new defect sites by catalyzed dehydrohalogenation of normal monomer units (eq 4) was not expected to be a facile process. Model compound studies had shown that the stabilizer itself was not likely to react with the normal units at all under our experimental conditions,[2g,11c] while other work suggested that the product halide,[40] di(*n*-butyl)tin dichloride, was not a particularly effective catalyst for dehydrochlorination of PVC.[2f,10b,d,15d,21c,40] However, total inertness of PVC toward the dichloride seemed unlikely,[11b,14d,41] and the dichloride had been shown to be a potent catalyst for the Frye–Horst substitution reaction of our organotin mercaptide with a chloroallylic model.[2a,11a] We therefore decided to include di(*n*-butyl)tin dichloride in some of our pretreatment mixtures, hoping that its ability to catalyze substitution would outweigh its potential accelerating effect on PVC dehydrochlorination.

o-Dichlorobenzene was the solvent selected for the chemical pretreatment experiments; it dissolved PVC rapidly under the conditions employed, and its high boiling point permitted the investigation of a broad range of reaction temperatures without the necessity of altering solvent composition. Previous research with model compounds had shown that reactions of the desired type (eq 3) occurred readily in a similar solvent, chlorobenzene.[11a]

Experimental Findings and Their Interpretation in Terms of the Frye–Horst Stabilization Theory. Data acquired in the present work are summarized in Table I. Columns 2–4 contain information relating to chemical pretreatments; columns 5–7 list properties of the polymers recovered therefrom. Dehydrochlorination rate constants (*k*) were obtained with solid samples by means of acid–base titrimetry; the Experimental Section should be consulted for a procedural description with details.

Experiment 1 provides stability data for the virgin PVC used as starting material and shows that values of *k* are independent of sample weight. Exhaustive extraction of virgin PVC with methanol causes a decrease in stability,[42] though the effect is rather small (experiment 2). However, if the virgin material is dissolved in *o*-dichlorobenzene at the minimum temperature necessary to cause rapid dissolution, and is then precipitated immediately with methanol and subjected to methanol extraction, a slight (but probably significant) improvement is noted (experiment 3), presumably owing to removal of extraneous catalytic impurities and/or polymer of low molecular weight which contains a disproportionately large number of degradation sites (double bonds at the end of chains?).[2h,43] Experiments 4 and 5 show that the polymer becomes highly unstable (and also colored; see Experimental Section) when it is heated in *o*-dichlorobenzene at increasingly higher temperatures, and without additives, for extended periods of time. Thus it appears that the destruction of active sites by a direct reaction with solvent is unimportant under these conditions.

Further inspection of Table I reveals that the desired chemical stabilization effect was, in fact, achieved. The maximum stabilization factor found was ca. 6–9, with the actual value depending on the specific control run selected for purposes of comparison. In general, at constant additive concentration, the stability clearly improves as pretreatment time and temperature are enhanced. The time effect can be noted from experiments 9–12, a comparison of experiments 14 and 20, and (less convincingly) a comparison of experiment 19 with experiment 21; while the effect of temperature is shown by relationships of data within the following experimental sets: experiments 6, 10, and 14 (*k*'s for experiments 6 and 10 are probably identical within experimental error); experiments 7, 11, and 20; experiments 8 and 13.

If the dehydrochlorination *k*'s are, indeed, related inversely to numbers of defect sites, then the effect on *k* of pretreatment temperature can be rationalized in two ways. One possibility is simply that the overall activation energy for the net chemical process leading to destruction of defect sites is greater than the activation energy of the net process leading to active site creation. But, on the other hand, if the rate of the former process is considerably faster than that of the latter one throughout the temperature range employed, then the number of defect sites may decrease with increasing temperature no matter what the activation energies are. Which of these explanations applies to our situation is unknown at the present time, but the vigorous minimum conditions required to achieve a significant stabilization effect (experiment 11) are surprising in any event.

In keeping with our expectations, inclusion of di(*n*-butyl)tin dichloride along with the tin mercaptide did improve stability significantly, and it will be noted that this beneficial effect generally increased with increasing amounts of n-$\mathrm{Bu_2SnCl_2}$ (cf. experiments 13 and 14; also, experiments 17–19). These results are, of course, consistent with the Frye–Horst theory in light of the discussion above. In general, increasing the amount of tin mercaptide also enhanced the stabilization (compare experiment 13 vs. 17 and experiment 15 vs. 19; note also the insignificant effect revealed by a comparison of experiments 14 and 18). However, the stability increases just noted are obviously not linear functions of mercaptide or dichloride concentration, and in an experiment where the molar amount of dichloride *exceeded* that of mercaptide (experiment 15), the chemically modified polymer was found to be quite yellow (in contrast to usual results; see Experimental Section), and its stability was not significantly greater than that of the polymers produced in parallel runs where much less dichloride was employed (experiment 14). Furthermore, under the conditions used for experiments 20 and 21, simultaneous increases in the concentrations of both mercaptide and dichloride actually caused a stability decrease which was probably outside the range of experimental error. Possible explanations for the results of experiments 15 and 21 are considered briefly below.

Table I also shows that the sulfur contents of the chemically modified polymers were usually quite appreciable, whereas the tin contents were invariably very low. Figure 1 demonstrates the absence of any correlation between tin content and

Table I
Effects of Chemical Modification[a] on PVC Thermal Stability

Expt	Additives[b] (g/g PVC)	Reac temp,[c] °C	Reac time, h	Sulfur, %	Tin, ppm	k,[d] (mol HCl) × 10^6/(g PVC h)
1						8.2 ± 0.5[e]
2						9.9[f]
3		77	0.25			6.1
4		132	19.8[g]			10.9
5		184	19.0			48.3[h]
6	n-$Bu_2Sn(SR)_2$ (2.0) n-Bu_2SnCl_2 (0.67)	130	19.2[g]	0.008	40	6.7
7	n-$Bu_2Sn(SR)_2$ (2.0) n-Bu_2SnCl_2 (0.67)	132	75.2	0.03	49	7.4
8	n-$Bu_2Sn(SR)_2$ (2.0)	162	19.4[g]	0.06	36	7.8
9	n-$Bu_2Sn(SR)_2$ (2.0) n-Bu_2SnCl_2 (0.67)	165	5.0	0.005	7	7.4
10	n-$Bu_2Sn(SR)_2$ (2.0) n-Bu_2SnCl_2 (0.67)	165	19.0	0.11	26	7.6
11[i]	n-$Bu_2Sn(SR)_2$ (2.0) n-Bu_2SnCl_2 (0.67)	163	75.2	0.39 0.42	7 50	2.2 2.0
12	n-$Bu_2Sn(SR)_2$ (2.0) n-Bu_2SnCl_2 (0.67)	163	240.0	0.93	42	1.1
13	n-$Bu_2Sn(SR)_2$ (2.0)	184	19.0	0.02	16	6.0
14	n-$Bu_2Sn(SR)_2$ (2.0) n-Bu_2SnCl_2 (0.67)	183	19.0	0.33 0.36[k]	<2[j] 22[k]	3.5 3.7[k]
15	n-$Bu_2Sn(SR)_2$ (2.0) n-Bu_2SnCl_2 (2.7)	183	19.1	1.52	61	3.3
16	n-$Bu_2Sn(SR)_2$ (0.20) n-Bu_2SnCl_2 (0.067)	182	19.0	0.12	13	7.3
17	n-$Bu_2Sn(SR)_2$ (8.0)	183	19.0	0.23	<1[j]	4.1
18	n-$Bu_2Sn(SR)_2$ (8.0) n-Bu_2SnCl_2 (0.67)	183	19.0	0.20	50	3.3
19	n-$Bu_2Sn(SR)_2$ (8.0) n-Bu_2SnCl_2 (2.7)	184	19.0	0.63 0.59[k]	7 20[k]	2.5 2.0[k]
20	n-$Bu_2Sn(SR)_2$ (2.0) n-Bu_2SnCl_2 (0.67)	185	75.0	0.93	68	0.95
21	n-$Bu_2Sn(SR)_2$ (8.0) n-Bu_2SnCl_2 (2.7)	185	75.0	1.65	49	1.9
22[l]	n-$Bu_2Sn(SR)_2$ (8.0) n-Bu_2SnCl_2 (0.67)	185	19.5[m]			6.4
23	n-$Bu_2Sn(SR)_2$ (2.0) n-Bu_2SnCl_2 (0.67)	182	0.05[n]	0.083	46	7.0
24	RSH (1.3) R_2S (1.3) $(RS)_2$ (1.3)	85	0.05	0.054		15.4
25	S (0.23)	87	0.05	0.066		8.8
26				1.8[o]		9.9 ± 0.1[p]

[a] Except where noted otherwise, *o*-dichlorobenzene solvent = 100 ml/g PVC; N_2 atmosphere; methanol extraction time = 24 h. [b] R = n-$C_{12}H_{25}$. [c] Oil bath temperature, ±3 °C. [d] Rate constant for PVC dehydrochlorination under Ar at 160.5 ± 0.2 °C; PVC = 0.375 ± 0.002 g unless noted otherwise. [e] Average of five runs using different amounts (0.150 to 0.600 g) of virgin PVC. [f] Value for virgin PVC extracted 47 h with methanol; 0.392 g of PVC used for kinetic run. [g] Methanol extraction time = 26 h. [h] Minimum value; rate increasing rapidly when run was terminated. [i] Duplicate experiments. [j] Not detected. [k] Value for product from a parallel chemical modification experiment performed under Ar. [l] PVC from preparative part of experiment 5 used as starting material. [m] Methanol extraction time = 25 h. [n] Reaction mixture preheated under N_2 for 19.5 h at 180–182 °C before addition of PVC. [o] Percent present in a mixture of PVC (0.375 g) and n-dodecyl sulfide (0.10 g). [p] Average of two runs.

polymer stability; thus it is clear that the chemical stabilization effects observed in this work cannot be due to residual tin mercaptide or, indeed, to any other tin-containing species, whether chemically bound to the polymer or not.[44] On the other hand, the Frye–Horst theory does imply the existence of an inverse correlation between polymer stability and number of mercaptide moieties introduced. At the concentration levels studied here, the mercaptide number should be linearly related to the percentage of sulfur in the polymer, and Figure 2 shows that the anticipated correlation does obtain up to a sulfur content of about 0.9–1.2%.

For higher levels of sulfur incorporation, the nature of the relationship between sulfur and k is obscured by a lack of data. However, Figure 2 indicates that the correlation curve for the high-sulfur region either parallels the x axis (as drawn) or gradually rises, and further consideration suggests that the former interpretation is not necessarily ruled out by the apparent eccentricity of the points for experiments 15 and 21. Experiment 15, for example, is the only experiment we performed in which the dichloride:mercaptide ratio was greater than one. If the dichloride can, indeed, catalyze the formation of new structural defects in the polymer, then in the presence of excess dichloride the number of newly created active sites might well be higher than usual for a given sulfur content. This situation will result, of course, in an abnormally high value of k. In the case of experiment 21, the apparent deviation of the plotted point is somewhat harder to explain, but here it seems possible that a concurrent stabilizer decomposition process evoked by the unusually vigorous reaction conditions might have led to the production of a metal species whose deleterious effect on the polymer was greater than that of n-Bu_2SnCl_2.[45]

Two additional experiments may also have a bearing on the high-sulfur correlation of Figure 2, although the results of

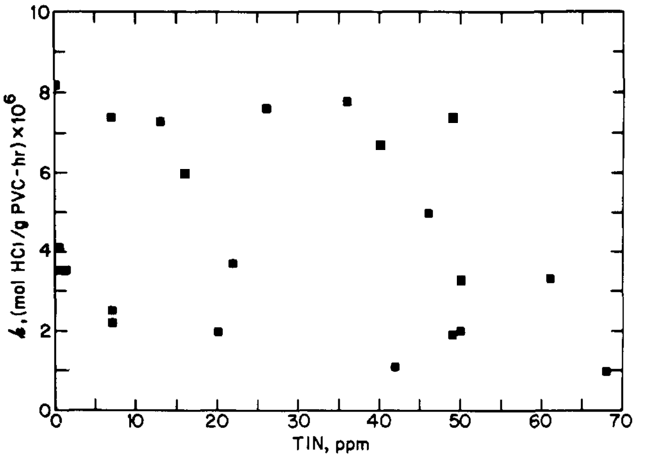


Figure 1. Dehydrochlorination rate constant vs. tin content for chemically modified PVC.

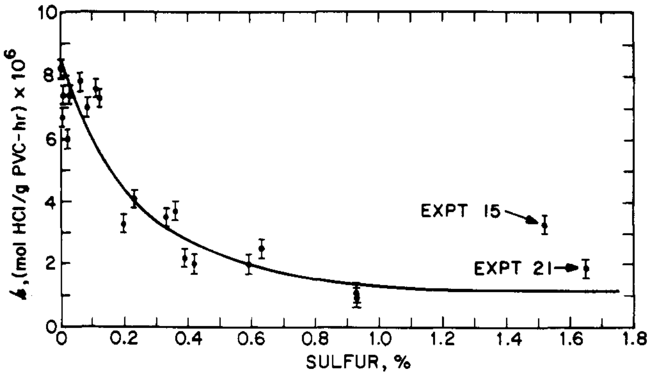


Figure 2. Dehydrochlorination rate constant vs. sulfur content for chemically modified PVC.

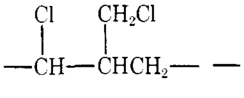
these experiments cannot be compared directly to the plotted data because of procedural differences.[46] One of the experiments (experiment A) afforded chemically modified PVC containing 48 ppm of tin and 0.82% of sulfur; this polymer had a k value of 2.8×10^{-6} (mol HCl)/(g PVC h). In the other experiment (experiment B), PVC was first exposed to the chemical pretreatment used for experiment A. The polymer was then recovered, purified as usual, and subjected again to an identical pretreatment cycle. After purification the polymer now contained <40 ppm of tin (exact tin analysis was prevented by a shortage of sample), and its sulfur content was 1.98%. However, the dehydrochlorination rate, as measured by k, was 3.7×10^{-6} (mol HCl)/(g PVC h). The results of experiments A and B suggest that the true correlation curve of Figure 2 does, indeed, rise slightly at the higher levels of sulfur, but the experimental k difference is so small that we prefer not to regard this conclusion as firm.

In any event, it must be emphasized that the Frye–Horst theory is not necessarily inconsistent with either of the possible relationships that may exist between sulfur and k when sulfur contents are high. A constant k value, for example, can be accounted for on the basis of simple kinetic considerations, which suggest that the rates of active site creation and destruction may become equal when these sites have been sufficiently reduced in number. This situation will afford an invariant, steady-state concentration of the sites, and when it is attained, introduction of more mercaptide groups will have no effect on the rate of dehydrochlorination. Alternatively, a constant k might simply result from dehydrochlorination initiated exclusively by the normal monomer units, whose number remains essentially unchanged throughout the region covered by Figure 2.

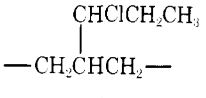
A third, more speculative rationale can explain either a constant value of k or a value that increases slightly with increasing content of sulfur. This hypothesis suggests that the decrease in k caused by destruction of active sites is opposed by an increase resulting from catalysis of HCl loss by the incorporated thioether groups. The feasibility of the latter process can be inferred from the high nucleophilicities of aliphatic sulfides, in general,[39] and experiment 26 perhaps provides a modicum of evidence for this reaction's actual occurrence.

Other chemical changes tending to decrease stability may have occurred during the more vigorous pretreatments, but experiment 22 shows that the pretreatment method also works quite well with badly degraded PVC. Nevertheless, it is interesting to note that the stability obtained in experiment 22 was less than that achieved in a parallel run (experiment 18) where virgin resin was employed.

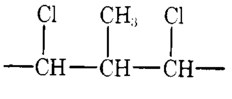
The minimum sulfur content required to achieve maximum stabilization corresponds to the attachment onto the polymer of about 20 n-dodecyl mercaptide groups per 1000 units of monomer, and it is tempting to conclude that this value represents the total number of labile halogens in our virgin PVC (or, alternatively, 85–90% of the total number, in keeping with a stabilization factor of 6–9). However, NMR measurements showed that the virgin polymer could have contained no more than 1 olefinic linkage per 1000 monomer units (no double bonds were actually detected),[47] and as noted above, there are reasons for believing that ordinary PVC contains no tertiary halide groups at all. Branching occurs, but the principal branched structure is actually **3**,[48] a grouping whose stability under our conditions should resemble that of the normal monomer units. The latter conclusion is supported by theoretical calculations on similar structures,[49] experimental stability comparisons of model compounds in the liquid phase,[4a,b] the "normal" dehydrochlorination rate (compared to PVC) of a vinyl chloride/3-chloro-1-pentene copolymer containing appreciable amounts of structure **4**[13c] (admittedly, a rather unsatisfactory model for **3**), and the lack of evidence for a relationship between branch content and thermal stability in the case of PVC itself.[2d,4a,b,26] On the other hand, a copolymer of vinyl chloride and 1-chloropropene has been shown to be less stable than PVC,[50] and since this copolymer may incorporate structure **5**,[50] its behavior might be regarded as evidence that **3** is also relatively unstable. However, the copolymer was not characterized completely, and the possibility thus remains that its instability could have been caused by other structural features. Furthermore, even if **3** were, indeed, a particularly labile structure, there currently exists no evidence to indicate that **3** would react selectively with di(n-butyl)tin bis(n-dodecyl mercaptide) under the conditions of the present work.


$—\overset{Cl}{\overset{|}{CH}}—\overset{CH_2Cl}{\overset{|}{CH}}CH_2—$

3


$—CH_2\overset{CHClCH_2CH_3}{\overset{|}{CH}}CH_2—$

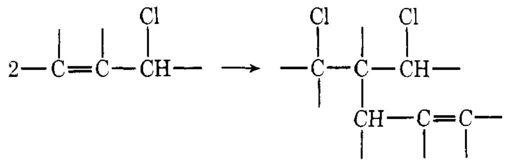
4


$—\overset{Cl}{\overset{|}{CH}}—\overset{CH_3}{\overset{|}{CH}}—\overset{Cl}{\overset{|}{CH}}—$

5

Structure **3** is present in typical PVC's to a rather large extent (ca. 2–16 chloromethyl groups per 1000 monomer units),[13c,48,51] and direct investigations of its thermal stability and reactivity toward organotins would therefore seem to be worthwhile. However, on the basis of all information now available, it appears that neither this defect structure nor any other can account for a mercaptide incorporation number of 20 per 1000 $-CH_2CHCl-$'s. Thus we conclude that, during chemical pretreatment, the organotin mercaptide (and/or species derived therefrom) must have reacted, not only with labile sites, but also with structures that were originally present in virgin PVC as ordinary monomer units. It would be interesting to know whether these units were attacked directly or after their activation due to losses of HCl.

Alternative Interpretations. Although the Frye–Horst theory seems to be strongly supported by the results presented thus far, other possible sources of chemical stabilization effects now need to be considered. For example, it might be supposed that the observed correlation of sulfur content with stability (Figure 2) is merely coincidental, and that chemical stabilization actually results from other structural changes. Cross-linking reactions have been suggested to inhibit color development in PVC stabilized with organotins,[7] and such reactions could also lead to chemical stabilization effects by destroying defect sites. For example, two allylic chloride moieties would be disposed of in the reaction of eq 6. However, cross-linking apparently does not occur until after the starting stabilizer has been consumed,[7,15d] a circumstance that was avoided in the present work by the use of high mercaptide concentrations. Furthermore, our chemically modified polymers dissolved readily in tetrahydrofuran with no appearance of gel, even after they had been subjected to thermal treatment during the kinetic experiments of Table I. Cross-linking under our conditions is thus regarded as unlikely.



$$2\!-\!\overset{|}{C}\!=\!\overset{|}{C}\!-\!\overset{\mathrm{Cl}}{\overset{|}{C}H}\!- \longrightarrow -\overset{\mathrm{Cl}}{\overset{|}{\underset{|}{C}}}\!-\!\overset{\mathrm{Cl}}{\overset{|}{\underset{|}{C}}}\!-\!\overset{\mathrm{Cl}}{\overset{|}{C}H}\!- \qquad (6)$$
$$\qquad\qquad\qquad\qquad CH\!-\!\underset{|}{C}\!=\!\underset{|}{C}\!-$$

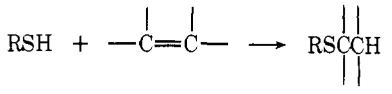
Peroxides present as impurities or as structural defects may contribute to the overall instability of PVC;[2a–d,g,h,15f,52] thus true chemical stabilization effects might also result from reactions in which peroxides are removed. Many organic sulfur compounds (e.g., certain thioethers) can destroy peroxides quite efficiently,[53] and such reactions could have occurred in our chemical pretreatment runs. However, these reactions, like cross-linking, would not lead to the chemical attachment of sulfur onto polymer; thus they are also incapable of accounting for the correlation curve of Figure 2. Furthermore, experiment 26 suggests that thioether groups resulting from sulfur attachment will not undergo peroxide decomposition (or any other) reactions that cause polymer stability to improve. Peroxide removal is thus considered to play only a minor role, at most, in the chemical stabilization process.

Another possible explanation for the observed effects of pretreatment on stability is that they result from the in situ formation of some sort of chemical species which retards PVC degradation quite effectively, contains sulfur (but not tin), and is not removed in the work-up procedure, even though the species is not chemically bound to the polymer chain at all. A reasonable structure that meets these requirements is, however, not apparent, and several other arguments can be cited against an hypothesis of this type. In the first place, the good agreement of the sulfur analyses on the products from pairs of parallel runs (experiments 11, 14, and 19) suggests that sulfur is chemically attached to these polymers, for if it were not, the analyses might have been expected to exhibit significant differences owing to a lack of experimental reproducibility in the heterogeneous extraction procedure (cf. the poor agreement of the tin analyses on these same materials). Sulfur removal was attempted by redissolving purified PVC containing 0.36% sulfur (from experiment 14) in fresh *o*-dichlorobenzene (100 ml/g of polymer) under argon at 75–80 °C, reprecipitating the polymer with methanol in the usual way (see Experimental Section), and then extracting it with hot methanol for 70 h prior to drying for reanalysis. However, the sulfur content of the PVC thus obtained was 0.34%, a value identical with that of the original material within the range of experimental error. Carbon-13 NMR measurements provided further evidence for the binding of mercaptide groups to chemically pretreated resin;[47] thus the presence of these groups in our modified PVC's now seems to be established beyond reasonable doubt. Furthermore, if a nonremovable sulfur-containing stabilizer were created in situ by a process not requiring the presence of PVC, it should have been formed to comparable extents during the preheating period of experiment 23 and the reaction period of experiment 14. The polymers prepared in these runs should then have had comparable sulfur contents and stabilities, in contrast to the results obtained.

In experiments 24 and 25, PVC was precipitated from solutions containing large amounts of potential decomposition products derived from the organotin mercaptide. The recovered polymers did not show enhanced stabilities and, more significantly, their sulfur contents were relatively low. These observations show that neither of the sulfur-containing materials used in experiments 24 and 25 could have caused the stabilization effects observed in other runs. And in this connection it may be instructive to note again the results of experiment 26, which provide further support for the idea that stabilization is associated with the chemical attachment of mercaptide moieties to polymer, rather than with the mere presence of mercaptide groups, per se.

All of our dehydrochlorination rates were measured on pulverized samples of PVC containing particles of comparable dimensions. Even so, small particle-size variations from run to run might have influenced the stabilities to some extent.[2g,h,43,54] However, if particle size had been a variable of major importance, the stabilities would have been likely to scatter randomly instead of exhibiting the correlation of Figure 2.

Lastly, there is the possibility that unsaturated sites in the polymer were destroyed by the addition of *n*-dodecanethiol which was generated in reaction 2. Mechanistically, the addition process (eq 7) can be either homolytic or ionic,[55] and there are indications for its occurrence with degraded PVC in which lengthy polyene sequences are contained.[14l,15d,37] On the other hand, studies with simple chloroallylic monoenes[11a–c] have provided no evidence for thiol addition under conditions similar to ours. We therefore prefer not to invoke this reaction here in order to explain our results. And regardless of whether or not it occurred under the conditions of our experiments, thiol addition still seems to fall within the province of the central idea upon which the Frye–Horst theory is based, namely, that defect sites can be selectively removed by means of chemical transformations.



$$\mathrm{RSH} + -\overset{|}{C}\!=\!\overset{|}{C}- \longrightarrow \mathrm{RS}\underset{|}{\overset{|}{C}}\underset{|}{\overset{|}{C}}\mathrm{H} \qquad (7)$$

$$R = n\text{-}C_{12}H_{25}$$

Concluding Remarks. It now appears that di(*n*-butyl)tin bis(*n*-dodecyl mercaptide) does, indeed, function as a stabilizer for PVC by deactivating labile structures in the manner suggested by Frye and Horst. This conclusion is based primarily upon the following observations: (1) When it is used as a pretreatment reagent, the stabilizer produces a true chemical stabilization effect. (2) This effect can be correlated with the number of mercaptide moieties introduced into the polymer. (3) There is no correlation of polymer stability with amount of residual tin. (4) The stabilizer reacts in the predicted way with appropriate model compounds.[11a–c]

Reactions such as peroxide decomposition and thiol addition (eq 7) may have been responsible, in part, for the stabilization phenomena we observed, but the intervention of such processes is not required by the extant data. However, our results do not rule out the possibility that these reactions and others (see above) are involved in the overall mechanism of color prevention which operates in "technological" situations, i.e., in situations where the stabilizer and its nonpolymeric reaction products are allowed to remain in the polymer matrix.

In closing, we wish to call attention to a point which is perhaps not entirely unobvious, viz., that all mechanistic studies performed to date on the stabilization of PVC have been done without the benefit of full knowledge as to this polymer's constitution, particularly with respect to the nature and number of the structural defects it contains. More information of this type would undoubtedly be of considerable value, and it is hoped that further progress will soon be reported along these lines.

Experimental Section

Materials. The PVC starting material was Opalon 660, an unstabilized commercial product (Monsanto) having a number-average molecular weight of approximately 50 000. Solvents, additives, and inert gases were of the highest purity available commercially and were used as received. Purities of sulfur compounds and organotins were verified by infrared measurements, melting point determinations, and, in the case of the organotin mercaptide, by an elemental analysis[56] for tin.

Anal. Calcd for $C_{32}H_{68}S_2Sn$: Sn, 18.67. Found: Sn, 18.71.

Chemical Modification of PVC. These reactions were carried out in a three-necked round-bottom flask heated by a thermostatically controlled oil bath and equipped with a Teflon-coated magnetic stirring bar, a reflux condenser connected to a pressure release valve, a ground glass stopper, and an inert-gas inlet tube (fritted disk bubbler) extending well below the surface of reaction mixtures. In a typical procedure (applicable to all experiments in Table I except experiments 1, 2, and 24–26), an *o*-dichlorobenzene solution of all reactants except PVC (*o*-dichlorobenzene alone in experiments 3–5) was stirred rapidly and bubbled with inert gas while the temperature of the solution (or pure solvent) was adjusted to the desired value using the oil bath. This procedure ordinarily required ca. 1–2 h, and the use of different times had no apparent effect on results. The flask was then unstoppered to allow introduction of PVC and quickly resealed while heating, stirring, and degassing were continued. Complete dissolution of the polymer usually occurred within a few minutes under all of the conditions employed. At the end of the desired reaction period, the mixture was cooled to ca. 50–60 °C with continued introduction of inert gas and then poured slowly into methanol (2.33 ml/ml of *o*-dichlorobenzene) to afford a heterogeneous mixture which was agitated very vigorously (magnetic stirrer) throughout the course of the addition. In experiment 22 the cooled reaction mixture was filtered through fritted glass to remove a small amount of dark precipitate (vide infra) prior to treatment with methanol. After several minutes of stirring, the precipitated polymer was recovered by suction filtration (fritted glass) and washed several times on the filter with fresh methanol. (Incremental addition of more methanol to the filtrate did not cause precipitation of additional material in any of these experiments.) The polymer was then subjected to Soxhlet extraction with hot methanol for at least 24 h (see Table I) and dried overnight at 42–50 °C (1 mm) before analysis[56] or use in kinetic runs. PVC samples thus obtained were odorless and usually snow white or pale cream colored. The exceptional cases were those in which the polymer had simply been heated in solution without additives for long periods of time (experiments 4 and 5; products from these runs were quite yellow), the case involving use of yellow, decomposed PVC as starting material (experiment 22; the product was also yellow), the single case where moles of di(*n*-butyl)tin dichloride exceeded moles of organotin mercaptide (experiment 15; the product was yellow), and two cases where the polymer was pale gray owing to contamination with a finely divided black precipitate formed during the reaction period (experiment 21) or during preheating (experiment 23). The amounts of the black precipitate were always quite small (a few milligrams, at most), and it was also detected in a few other runs; however, in these cases it was separated by filtration (experiment 22, vide supra) or decantation (experiments 12 and 20) prior to the methanol treatment. The black precipitate was not identified conclusively, although its color and solubility properties (insoluble in water or common organic solvents, soluble in dilute aqueous KOH, soluble in concentrated HCl with production of a faint H_2S odor) suggested that it was a tin salt containing ionic sulfur (SnS?).

The chlorine contents of the chemically modified polymers were calculated from the sulfur analyses of Table I on the assumption that every Cl lost was replaced by a single n-$C_{12}H_{25}S$ substituent. Since these chlorine values differed from values that were obtained by direct analysis[56] by no more than 0–1%, it was concluded that the modified polymers had not been extensively degraded during the chemical pretreatment runs. This inference was substantiated by infrared spectral comparisons of molded films prepared from the modified polymers and virgin PVC.

In experiments 24 and 25, ca. 93% of the desired quantity of *o*-dichlorobenzene was degassed and preheated to the appropriate temperature in the manner previously described. The PVC was then added, and when it had dissolved (5 min) a solution of the desired additive(s) in the remaining 7% of solvent was immediately introduced, the time of the latter addition being taken as zero time. In other respects the procedure for experiments 24 and 25 was identical with that described above.

PVC Dehydrochlorination Kinetics. The dehydrochlorinations were carried out in an all-glass apparatus similar to that described by Geddes.[43] In a typical run, a weighed sample of PVC powder was introduced into the reaction vessel in a thin, uniform layer. The apparatus was degassed by blowing with argon for at least 20 min at room temperature and then immersed in a thermostated oil bath which had previously been adjusted to the desired dehydrochlorination temperature. Gas exiting from the reactor was bubbled through a capillary tube into a magnetically stirred vessel containing distilled water; the pH of the water was monitored continuously using a Beckman Zeromatic SS-3 pH meter. Fifteen minutes was allowed for thermal equilibration, and kinetic points were then taken at appropriate intervals by titrating the dissolved HCl with 0.0100 N sodium hydroxide solution. Titration end points were represented by the pH value previously recorded at zero time; in various runs this value fell within the range 7.0 ± 0.5, and appropriate checks showed that differences in initial pH had no effect on results. Plots of amount of added caustic vs. time showed autoacceleration in the early stages of reaction and then exhibited excellent linearity;[57] all values of k were calculated from straight lines fitted to the linear portions by visual inspection. Rate constants from duplicate runs were reproducible to within ±5–10% or better, and control experiments showed that the measured values of k were not appreciably influenced by large changes in argon flow rate when the chosen rate (approximately 140 ml/min) was employed. Runs were ordinarily continued for at least 1.5–2 h after the autoacceleration stage had been passed; total extents of decomposition (based on theoretically available HCl) ranged from ca. 0.02 to 0.35% in various experiments. The final samples of decomposed polymer were yellow, yellow-orange, or pink; rates of color development qualitatively paralleled rates of dehydrochlorination.

In experiment 26 a solution of *n*-dodecyl sulfide in petroleum ether (bp 39–54 °C) was added to the dehydrochlorination reactor after introduction of PVC. The solvent was evaporated by blowing with argon at room temperature, and the experiment was then performed in the usual manner. Control runs carried out using petroleum ether alone gave k's within the usual range observed for virgin polymer (experiment 1).

Acknowledgment. Stimulating discussions of this work with Dr. L. D. Loan are hereby acknowledged with thanks.

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(44) Simple calculations based on stoichiometry provide further support for this conclusion. For example, in the kinetic runs of experiments 3 and 20, the total amounts of titratable HCl evolved from 0.375 g of polymer after 185 min of reaction were 4.71×10^{-6} and 1.00×10^{-6} mol, respectively. For the modified polymer of experiment 20, a computation based on sulfur content suggests that ca. 1.9% of the original chlorines were replaced by *n*-dodecyl mercaptide groups. The number-average molecular weight of this polymer should thus be about 5.0% higher than that of the polymer used in experiment 3. On an equimolar basis, the amount of HCl evolved in experiment 20 should then have been $(1/1.05)(4.71 \times 10^{-6}) = 4.49 \times 10^{-6}$ mol, and the corrected difference in total HCl for experiments 3 and 20 is $(4.49–1.00) \times 10^{-6} = 3.39 \times 10^{-6}$ mol. The tin analysis for the polymer of experiment 20 corresponds to 2.15×10^{-7} g-atom of tin, an amount capable of scavenging 8.60×10^{-7} mol of HCl if a stoichiometry of 4HCl/Sn is assumed.[7] However, this value represents only $(8.60 \times 10^{-7})100/(3.39 \times 10^{-6}) = 25\%$ of the scavenging capacity needed in order to account for the corrected HCl difference. And even if HCl scavenging by tin species did occur during the kinetic runs of Table I, it was probably confined to the induction periods and could thus have had no effect on the measured values of *k*, since these values were always calculated from the linear portions of the kinetic plots (see Experimental Section). Attainment of kinetic linearity would not be expected as long as residual scavenger remained, since a continuation of the process of scavenger consumption should lead to continued autoacceleration.

(45) A small portion of the stabilizer mixture apparently did decompose extensively, but the products of this decomposition were not identified conclusively (see Experimental Section). At elevated temperatures, n-BuSnCl$_3$ and SnCl$_4$ are evidently able to induce the catastrophic degradation of PVC;[7,40] thus the formation of these substances during chemical pretreatment (even in low yields) might prove to be quite harmful.

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(57) Other workers have observed similar behavior for PVC powder dehydrochlorinations; e.g., see ref 43. The autoacceleration stage may be an artifact resulting from approach of the system to steady-state conditions.[43]