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# Stabilization of Poly(vinyl chloride) by Thiols. A Mechanistic Study

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ABSTRACT: Large amounts of aliphatic or aromatic thiols will prevent the discoloration of poly(vinyl chloride) when solutions of the polymer in *o*-dichlorobenzene or benzophenone are heated in the absence of oxygen at ~160–185 °C. Polymers pretreated with thiols in this way contain very small amounts of sulfur, but their chemical stabilities (as measured by rates of nonoxidative thermal dehydrochlorination) are found to be greatly enhanced. Kinetic and structural studies show that under the pretreatment conditions, a remarkable reductive dehalogenation reaction occurs which probably has the following stoichiometry: $-CH_2CHCl- + 2RSH \rightarrow -CH_2CH_2- + RSSR + HCl$ (R = alkyl, aryl, etc.). The possible relationship of this reaction to stabilization is discussed, and it is argued that both color stability and chemical stability after thiol pretreatment must result, at least in part, from the deactivation of labile polymer defect structures, either by reductive dehalogenation or by very selective alternative routes that lead to the incorporation of only a few mercaptide groups. Possible mechanisms for the reductive dehalogenation process are considered.

The interaction of poly(vinyl chloride) (PVC) with thiols under conditions conducive to degradation of the polymer has been the object of some research and much speculation over a period of many years. Technological considerations have provided the stimuli for a major part of this attention; for example, thiols are known to be formed in situ from organotin mercaptide stabilizers for PVC, via reaction of these stabilizers with the HCl evolved from the degrading polymer.[1] Furthermore, various compounds containing the free SH group have been suggested for practical use in PVC stabilizer blends[2] and, in some cases, for use as primary stabilizers requiring no auxiliary components.[3] However, the reaction of thiols with PVC is also of interest from the standpoint of basic research, since there are reasons for believing that a detailed knowledge of this process might contribute to an understanding of the mechanism(s) of PVC degradation. Thiols are excellent radical scavengers due to the weakness of the S–H bond;[4] thus they might be expected to reduce the rate of the nonoxidative thermal degradation of PVC if radicals were involved therein.[1a,5] Alternatively, thiols could simply act as chain-transfer agents during radical–chain dehydrochlorination, thereby decreasing the average length of the chromophoric polyenes being formed and thus preventing or retarding the appearance of color without affecting the overall degradation rate.[6] Thiols have also been suggested to act as PVC stabilizers by deactivating heavy-metal dehydrochlorination catalysts,[5a] and antioxidant effects in PVC (peroxide decomposition, trapping of oxygenated radicals) due to thiols[1a,5b,c,7] and potential thiol precursors[8] have been postulated by several workers. Color stabilization of the polymer could involve the destruction of polyene chromophores rather than the prevention of their formation; such an effect might be accomplished by the homolytic or heterolytic addition of thiols to polyene double bonds.[1a,3b,5e,7b,d,9] Finally, replacement of allylic halogen by mercaptide groups derived from thiols[9g,10] could prevent color by preventing polyene elongation,[10] and it is clear that both this process and the process of C=C destruction by thiol addition might also reduce the rate of dehydrochlorination and thus cause true chemical stabilization[11] as well.

Theories of the stabilization of PVC by thiols therefore exist

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**Table I**
**Chemical Stabilization of PVC by Pretreatment[a] with Thiols: Preparative, Analytical, and Kinetic Data for Samples Decomposed in the Solid State or in *o*-Dichlorobenzene**

| Expt | Thiol (mol/(g PVC)) | Other Additive(s) (mol/(g PVC)) | React time, h | Cl, % | S, % | Sn, ppm | *k*,[b] mol HCl (g PVC)$^{-1}$ h$^{-1}$ × $10^6$ | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Solid[c] | *o*-$Cl_2C_6H_4$[d] |
| 1 | | | | 55.5 | | | 10.1 ± 0.5[e] | 2.5 ± 0.2[f] |
| 2 | | | 0.2[g] | 55.4 | | | 7.8 ± 0.8[h] | 2.2[i] |
| 3 | *n*-$C_{12}H_{25}SH$ (0.033) | | 19 | 55.2 | 0.16 | | 4.9 | |
| | *n*-$C_{12}H_{25}SH$ (0.033) | | 19 | 55.1 | <0.01 | | 5.6 | |
| 4 | *n*-$C_{12}H_{25}SH$ (0.033) | | 91 | 55.4 | 0.04 | | | 0.6 |
| 5 | *n*-$C_{12}H_{25}SH$ (0.033) | | 144 | 56.1 | 0.14 | | 3.2 | |
| 6 | *n*-$C_{12}H_{25}SH$ (0.099) | | 72 | 56.2 | 0.21 | | 2.8 | |
| 7 | *n*-$C_{12}H_{25}SH$ (0.099) | | 72 | 55.4 | 0.17 | | | 0.3 |
| 8 | *n*-$C_{12}H_{25}SH$ (0.099) | | 144 | 55.4 | 0.17 | | 1.4 | |
| 9 | *n*-$C_{12}H_{25}SH$ (0.099) | | 26[j] | *k* | *k* | | | 0.3[l] |
| 10 | PhSH (0.033) | | 19 | 55.2 | 0.14 | | 4.8 | 0.5 |
| 11 | PhSH (0.033) | | 19 | 56.4 | 0.09 | | 5.6 | |
| 12 | *p*-$MeC_6H_4SH$ (0.033) | | 20 | 56.8 | 0.03 | | 5.4 | |
| 13 | *p*-$MeC_6H_4SH$ (0.033) | | 114 | 55.9 | 0.11 | | 6.5 ± 0.4[h] | |
| 14 | *p*-$MeOC_6H_4SH$ (0.033) | | 19 | 56.3 | 0.01 | | 7.0 | |
| 15 | *p*-$ClC_6H_4SH$ (0.033) | | 19 | 55.9 | 0.02 | | 7.1 | |
| 16 | 1-Naphthalenethiol (0.033) | | 19 | 56.6 | 0.01 | | 4.4 | |
| 17 | 2-Naphthalenethiol (0.033) | | 19 | 56.7 | <0.01 | | 4.5 | |
| 18 | | Naphthalene (0.033) | 19 | 56.5 | | | 21.1 ± 2.3[h] | |
| 19 | $HS(CH_2)_8SH$ (0.033) | | 19 | 55.4 | 0.51 | | 5.6 | |
| 20 | | (*n*-$C_{12}H_{25}S)_2$ (0.033) | 19 | 56.9 | <0.01 | | 7.8 | |
| 21 | | (*n*-$C_{12}H_{25})_2S$ (0.033) | 19 | 56.6 | 0.01 | | 8.4 | |
| 22 | | S (0.033) | 19 | 55.9 | 0.27 | | 36.8 | |
| 23 | *n*-$C_{12}H_{25}SH$ (0.033) | *n*-$Bu_2Sn(S$-*n*-$C_{12}H_{25})_2$ (0.0031), *n*-$Bu_2SnCl_2$ (0.0022) | 19 | 55.5 | 0.20 | 6 | 1.9 | |
| 24 | | *n*-$Bu_2Sn(S$-*n*-$C_{12}H_{25})_2$ (0.0031), *n*-$Bu_2SnCl_2$ (0.0022) | 19 | | 0.65 | 20 | 5.7 | |
| 25 | *n*-$C_{12}H_{25}SH$ (0.033) | *n*-$Bu_2Sn(S$-*n*-$C_{12}H_{25})_2$ (0.013) | 75 | 54.1 | 0.34 | 12 | 1.8 | |
| 26 | *n*-$C_{12}H_{25}SH$ (0.033) | *n*-$Bu_2Sn(S$-*n*-$C_{12}H_{25})_2$ (0.0031), *n*-$Bu_2SnCl_2$ (0.0022) | 90 | 52.5 | 0.57 | 30 | 0.92 | |
| 27 | | *n*-$Bu_2Sn(S$-*n*-$C_{12}H_{25})_2$ (0.0031), *n*-$Bu_2SnCl_2$ (0.0022) | 75 | 51.8 | 1.05 | 17 | 4.0 | |

[a] Unless noted otherwise, pretreatments were done in *o*-$Cl_2C_6H_4$ (100 mL/g PVC) under $N_2$ or Ar at 185 ± 5 °C; MeOH extraction time ≥24 h. [b] Measured under Ar. [c] Bath temp = 160.5 ± 0.2 °C; PVC = 0.375 ± 0.002 g. [d] Solution temp = 158.4 ± 0.3 °C; PVC concn = 9.4 g/L unless noted otherwise. [e] Mean deviation for 12 runs. [f] Mean deviation for four runs. [g] React temp = 78 °C. [h] Mean deviation for two runs. [i] PVC concn = 7.2 g/L. [j] Reaction carried out in benzophenone (95 mL/g PVC). [k] See expt 32 of Table II for analytical data on a similar product. [l] PVC concn = 8.7 g/L.

**Table II**
**Chemical Stabilization of PVC by Pretreatment[a] with 1-Dodecanethiol: Preparative and Analytical Data for Samples Decomposed in Benzophenone[b]**

| Expt | (Mol thiol)/(g PVC) | $Ph_2CO$, mL/(g PVC) | React temp, °C | React time, h | C, % | H, % | Cl, % | S, % |
|---|---|---|---|---|---|---|---|---|
| 28 | 0.099 | 100[c] | 178–179 | 0.3 | 38.6 | 5.0 | 55.4 | 0.04 |
| 29 | 0.099 | 94 | 178 | 0.2 | 38.5 | 4.9 | 56.5 | 0.01 |
| 30 | 0.00033 | 30 | 158 | 21 | 39.5 | 5.1 | 55.3 | 0.05 |
| 31 | 0.017 | 30 | 158 | 26 | 39.1 | 5.1 | 54.7 | 0.05 |
| 32 | 0.099 | 94 | 178–183 | 25 | 39.9 | 5.2 | 53.0 | 0.13 |
| 33 | 0.099 | 94 | 174–182 | 70 | 42.0 | 5.5 | 50.0 | 0.04 |

[a] Reactions run under $N_2$ or Ar; MeOH extraction time ≥24 h. [b] The dehydrochlorination rate curves are shown in Figure 1. [c] *o*-$Cl_2C_6H_4$.

in great abundance, but facts on which to base them have remained decidedly scarce. Some pertinent experimental observations have nonetheless been made, and there is evidence to indicate, for example, that thiols, used alone, can prevent or retard the appearance of color in degrading PVC under some conditions[3b–d,7b,10] though not under others.[2f,7a] Thiols also seem to be able to destroy the chromophores in PVC that has previously been degraded,[9c,d,g,h,j,12] and evidence has been obtained for the incorporation of sulfur-containing groups into PVC during decomposition while a thiol is present.[9a,g,h,j,10] On the other hand, thiol effects on PVC dehydrochlorination rate have received surprisingly little attention, although Popova et al.[5b] have reported rate reductions at 175 °C of up to 17 and 28%, respectively, for the dehydrochlorination under nitrogen or air of neat polymer containing "dodecyl mercaptan".

The foregoing considerations suggested to us that further studies of the effects of thiols on degrading PVC would be likely to prove worthwhile. Our initial efforts in this direction are described in the present paper, which shows that some of the chemistry involved in these systems is very unusual indeed. Thus far all of our work has been concerned with thermal degradation under nonoxidative conditions.

## Results and Discussion

**Chemical Stabilization of PVC by Prior Reaction with Thiols.** An earlier study[11a] had shown that the chemical pretreatment of PVC with di(*n*-butyl)tin bis(*n*-dodecyl mercaptide) gave polymers whose rates of nonoxidative thermal dehydrochlorination were much less than that of the virgin material. The stability enhancements could be correlated with the number of mercaptide groups chemically bound onto the resin, and they were thus attributed to the destruction of labile structural defects contained in the starting PVC. However, the stabilization effects tended to approach a constant value at higher levels of mercaptide incorporation, and several possible explanations were suggested in order to account for this result. One rationale was that the leveling phenomenon could derive from a balance between defect site destruction and creation, with the latter process being ascribed to dehydrochlorination that was catalyzed by organotins. At the outset of the present work it was therefore hoped that the creation of new defect sites might be avoided by pretreating the polymer with free thiols, since these substances (especially the aliphatic ones) were known to be only weakly acidic[13] and could thus be presumed to be rather ineffective as catalysts for the elimination of HCl. Accordingly, the pretreatment effectiveness of several thiols was investigated in the initial phase of this study, and some of the results obtained are summarized in Table I.

Columns 2–4 of Table I are concerned with pretreatment reagents and conditions; columns 5–9 contain data for the modified polymers that were formed. The *k* values are dehydrochlorination rate constants determined by our usual procedures.[11a,14] Experiments 1 and 2 are control runs for untreated virgin PVC and virgin PVC which was subjected to the usual operational sequence (dissolution, precipitation, extraction) encountered by the polymer in those experiments where additives were employed. Even when used alone, the thiols proved to be remarkably good color-stabilizing agents during the pretreatment heating step. Virgin PVC becomes badly discolored after 19 h of heating without additives under similar reaction conditions;[11a] whereas our thiol-containing solutions remained practically colorless throughout the heating periods of Table I and usually afforded snow-white polymers upon workup. The only exceptions found were in experiments 4 and 5, where some coloration was observed during the latter pretreatment stages. However, similar runs using more 1-dodecanethiol (e.g., experiment 8) gave no coloration at all.

Inspection of the *k* values of Table I reveals that all of the thiols listed, with the possible exception of *p*-methoxy- and *p*-chlorobenzenethiol (experiments 14 and 15), produced significant chemical stabilization effects when they were used alone. These effects were observed for samples decomposed in *o*-dichlorobenzene as well as in powder form, and the maximum effects were found to be comparable to the largest ones obtained in our pretreatment work with organotins.[11a,14,15] Since similar effects did not appear in control experiments 2 and 28 (data for the latter run are presented in Table II and Figure 1), it is clear that the effects obtained in the other runs must be ascribed to chemical reactions occurring during the heating periods, rather than to polymer purification or thiol occlusion within the recovered PVC.

Experiments 3–8 demonstrate increases in pretreatment effectiveness with increasing reaction time and thiol concentration, but a comparison of the *k*'s for experiments 12 and 13 shows that longer heating does not always give an improved result. No obvious correlation exists between thiol structure and the pretreatment observations, while experiment 18 shows that the activity of the naphthalenethiols is not associated with the aromatic nucleus per se. Experiments 20–22 indicate that various substances which might have been formed in situ are ineffective pretreatment reagents, and here it should be noted that the pretreated polymers of experiments 18 and 20–22 were all discolored to some extent [very badly (dark tan) in the case of experiment 22].

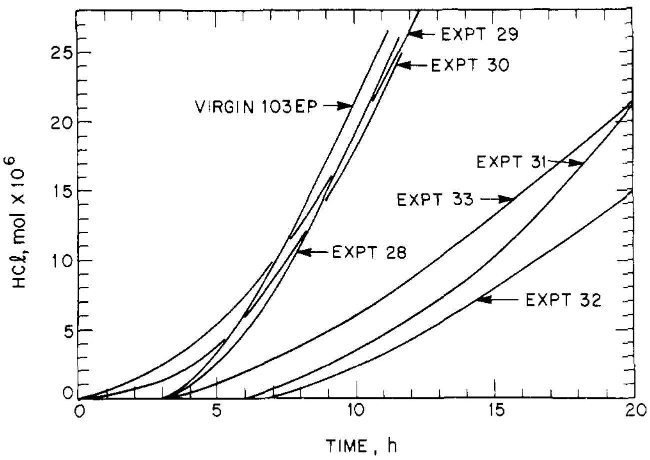

**Figure 1.** Dehydrochlorination rates under Ar at 158.4 ± 0.3 °C for solutions of PVC (0.374 ± 0.002 g) in benzophenone (44 mL). See Table II for preparative and analytical data on the samples employed.

Experiments 23–27 show that (organotin mercaptide)/thiol mixtures are unusually effective as pretreatment agents. The tin contents of the modified PVC's obtained in these experiments are obviously much too low to account for the observed stability improvements. In experiments 23, 25, and 26, inclusion of the thiol completely prevented the formation of a black metallic precipitate[11a] which appeared in control experiments 24 and 27.

The elemental analyses of Table I are of particular interest for several reasons. In the first place, they show that only minor structural modifications were needed in order to obtain the stabilization effects observed with the thiols alone. This finding strongly supports the idea that these effects are associated with the destruction of labile polymer defect moieties. However, the most striking aspect of the analyses is their clear-cut indication that the stabilization effects were also being achieved without appreciable incorporation of mercaptide groups into the polymer. Indeed, the lack of correlation between the sulfur contents and the vigor of the pretreatment conditions suggests that much of the sulfur was actually contained in physically occluded thiol, and, in fact, most of the sulfur percentages do seem low enough to be accounted for in this way[16] (compare the sulfur analysis for the polymer of control run 28 in Table II). These results contrast most strikingly with those obtained using di(*n*-butyl)tin bis(*n*-dodecyl mercaptide) as a pretreatment agent,[11a] and in this connection the relatively low sulfur percentages found in experiments 23, 25, and 26 (as compared to those obtained in experiments 24 and 27) are also worthy of note. However, these findings, though strongly suggestive, do not necessarily mean that the mechanism of thiol action remains unchanged when organotins are present.

Since the chlorine contents of the thiol-pretreated polymers of Table I were similar to that of the starting PVC, it appeared that the thiols may have also inhibited dehydrochlorination during the pretreatment heating step. At initial steady-state conditions[14] under argon in *o*-dichlorobenzene at 180 °C, we find the rate constant for dehydrochlorination of our virgin PVC to be about 1.0 × $10^{-5}$ mol HCl (g PVC)$^{-1}$ h$^{-1}$.[17] This

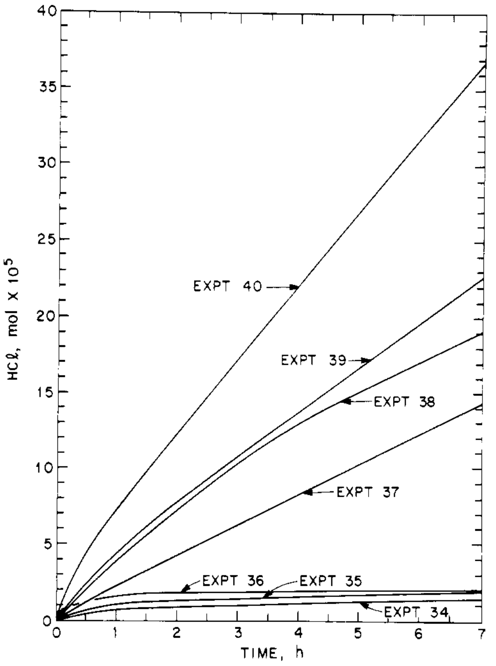

**Figure 2.** HCl evolution rates for reactions of PVC with 1-dodecanethiol in benzophenone under Ar at 159.2 ± 0.3 °C. Plots for control runs are also included; see Table III for experimental details.

**Table III**
**Effects of 1-Dodecanethiol on PVC Thermal Stability in Benzophenone at 159.2 °C[a]**

| Expt | PVC,[b] g | Thiol, g | $k$,[c] mol HCl (g PVC)$^{-1}$ h$^{-1}$ × $10^6$ 6 h | 22 h |
|---|---|---|---|---|
| 34 | 0.00 | 0.00 | *d* | |
| 35 | 0.00 | 0.10 | *d* | |
| 36 | 0.00 | 5.00 | *d* | |
| 37 | 1.50 | 0.00 | 12.8 ± 0.1 | 12.8 ± 0.3 |
| 38 | 1.50 | 0.10 | 13.2 ± 0.3 | 11.1 ± 0.1 |
| 39 | 1.50 | 0.50 | 17.2 ± 1.7 | 15.3 ± 1.7 |
| 40 | 1.50 | 5.00 | 29.2 ± 1.6[e] | 26.0 ± 1.2 |

[a] $Ph_2CO$, 44 mL; Ar atmosphere. The rate curves for HCl evolution are shown in Figure 2. [b] Virgin Geon 103EP. [c] Deviations are for duplicate runs unless noted otherwise. [d] See Figure 2. [e] Mean deviation for three runs.

value leads to a calculated chlorine content for the polymer of 54.4% after 144 h of reaction, a figure lower than those obtained in experiments 5 and 8. However, the significance of the difference is not entirely clear, since the rate constant might have decreased with time[18,20] even if the thiol had not been present. Direct kinetic measurements were attempted on the dehydrochlorination of PVC in *o*-dichlorobenzene containing 1-dodecanethiol, but successful completion of this work was prevented by the occurrence, at competitive rates, of an acid-producing side reaction between the thiol and the solvent. This unexpected process was not investigated to any major extent, although mass spectral evidence was obtained for the formation of compound 1 (presumably the ortho isomer) as one of its principal products. In any event, it was clear at this point that further progress would require a change in solvent composition, and benzophenone was eventually selected for subsequent use on the basis of screening trials.

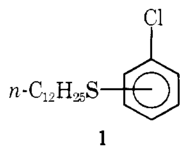

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Table II presents data for some pretreatment runs in benzophenone and for a control run in *o*-dichlorobenzene (experiment 28) that has already been referred to above. In experiments 31–33, 1-dodecanethiol was again found to be a very effective agent for color prevention during the pretreatment process. Polymers prepared in these runs were white, and the reaction solutions retained their original pale yellow hues throughout the periods of heating. Some color stabilization was observed even with the small amount of thiol used in experiment 30; this run yielded a light tan product and gave a solution which was orange but still transparent at the end of the heating time (PVC alone produced an opaque dark brown solution under comparable conditions).

Figure 1 depicts kinetic curves for the dehydrochlorination in benzophenone of virgin PVC and the polymers of Table II. Rate constants have not been calculated for these runs since the curves show obvious autoacceleration, but it is nonetheless clear from the data that significant chemical stabilization effects were achieved in the pretreatments of experiments 31–33, though not in the two control runs (experiments 28 and 29) or in experiment 30. The sulfur analyses of Table II reveal very small amounts of mercaptide incorporation, as expected from our work in *o*-dichlorobenzene (above), but the chlorine contents of the polymers prepared in experiments 31–33 are appreciably less than that of the starting resin, and it will be noted that this is a significant point of difference between these runs and the analogous runs of Table I. The absence of discoloration during pretreatment is particularly striking in the case of experiment 33, since PVC ordinarily turns black long before its chlorine content has been reduced to 50% during nonoxidative thermal dehydrochlorination.[21]

**Kinetics of PVC Dehydrochlorination in the Presence of 1-Dodecanethiol.** Table III presents the results of a brief kinetic study on the reaction of PVC and 1-dodecanethiol in benzophenone, and typical kinetic curves for the initial 7 h of reaction are shown in Figure 2. Since the benzophenone used for these experiments evolved small amounts of adventitious acid under the reaction conditions (see Experimental Section), data for appropriate blank runs (experiments 34–36) are included for comparison purposes. Inspection of Figure 2 shows that adventitious acid was undoubtedly partly responsible for the unusually rapid rates observed during the initial 2-h period of experiments 38–40. However, these fast initial rates cannot be rationalized entirely in this way, and it is tempting to speculate that their unaccounted for portions result from rapid deactivation, by the thiol, of labile structural defects contained in the starting PVC. The rate constant of experiment 37 compares reasonably well with literature values[22] but is larger than the value found for PVC in *o*-dichlorobenzene under similar reaction conditions (experiment 1, Table I). This difference is consistent with expectations based on the results of some previous solution decomposition studies, which have suggested that the rate of the nonoxidative dehydrochlorination of PVC increases with increasing polarity of the reaction medium[1,20b,24] (at 50 °C the dielectric constants of *o*-dichlorobenzene and benzophenone are 9.9 and 12 ± 1, respectively[25]).

The *k* values of Table III reveal a direct dependence of acid evolution rate on thiol concentration and also show that the rate law for the overall process is complex. The latter finding is, in retrospect, not surprising, since our work has shown that the overall rate must represent a balance between two opposing thiol effects. One of these enhances the rate, and its chemistry is discussed below. The other effect is a reduction in the rate of the "ordinary" dehydrochlorination, due to the deactivation of defect sites, as already established above. Pretreatment experiment 31 (Table II) was performed under conditions essentially identical to those of kinetics experiment 40, and it has already been noted that the modified polymer

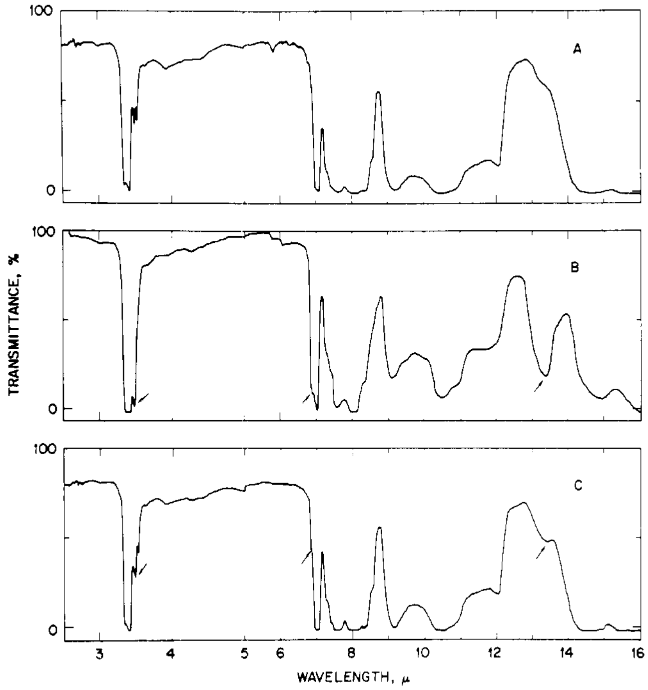


**Figure 3.** IR spectra of polymer films (the slight discontinuities at 5 μm (μm = μ) are instrumental artifacts): (A) virgin PVC; (B) polymer X; (C) polymer from experiment 8 (Table I). See text for details.

of experiment 31 was white and initially quite stable in benzophenone (Figure 1). These observations suggest that "ordinary" dehydrochlorination was relatively unimportant under the conditions of experiment 31, a conclusion which is also consistent with the elemental analysis and infrared spectrum (cf. subsequent discussion) of the polymer recovered from this run. The pseudo-first-order *k*'s for experiment 40 can thus be taken as a rough measure of the rate of the direct PVC–thiol interaction. Therefore, if the kinetics are actually first (or higher) order in thiol concentration, then the *k*'s for experiments 38 and 39 are primarily the result of the "ordinary" reaction mode. The colors observed during experiments 38–40 (no color in the case of 40) provide qualitative support for this analysis, and it is amusing to note that the rates of color development were inversely proportional to the rates of HCl evolution during the earlier (0–7 h) parts of these runs.

In experiments 38–40, the rate decreases observed between 6 and 22 h seem large enough to be considered significant, and it appears that they could result from a number of factors such as reactant depletion, deactivation of defect sites, or reduction in the intrinsic reactivity of the polymer toward the thiol with increasing conversion (see below). Calculations using the 6-h *k*'s suggest that the first factor largely accounts for the decrease found in experiment 40, whereas a combination of the first and third factors appears insufficient to account for the chemical stabilization effect observed after 22 h in experiment 38. It therefore seems reasonable to ascribe the latter effect to defect destruction, and it is, indeed, possible to devise kinetic schemes that will account for the finding of either chemical stabilization or accelerated rates in these experiments as a function of thiol concentration and reaction time. However, discussion of such schemes seems inappropriate here in the absence of detailed mechanistic information.

**Product Studies.** In order to obtain a thiol-modified polymer that would be suitable for structural characterization, virgin PVC was allowed to react with 1-dodecanethiol in benzophenone for 139 h at 181–186 °C under the conditions of experiments 32 and 33 (Table II). This preparation afforded a cream-colored product (referred to hereafter as polymer X) whose elemental analysis (Experimental Section) indicated only a minor amount of sulfur incorporation and a halogen loss of about 29%. Of much greater interest, however, was the finding that the analysis was not consistent with loss of chlorine by dehydrochlorination; instead, it was in reasonable agreement with expectations based on the *reduction* of CHCl groups to $CH_2$'s.

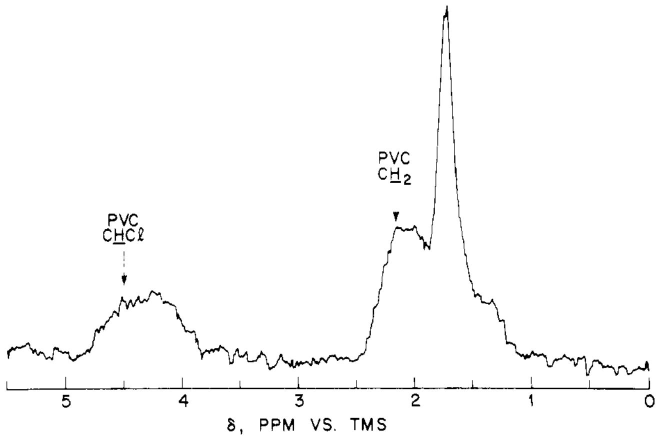


**Figure 4.** $^1$NMR spectrum (60 MHz) of polymer X in 1,2,4-trichlorobenzene solution. See text for details (TMS = $Me_4Si$).

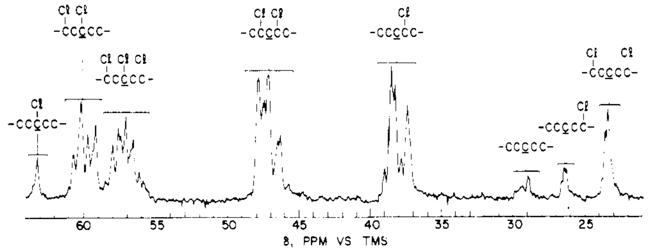


**Figure 5.** $^{13}$C NMR spectrum (25 MHz) of polymer X in 1,2,4-trichlorobenzene solution. See text for details (TMS = $Me_4Si$).

In Figure 3 the IR spectrum of polymer X (spectrum B) is compared with that of its virgin precursor (spectrum A). Spectrum B offers no conclusive evidence for the presence of olefinic linkages, but it does contain strong absorptions (arrows) at about 3.5, 6.9, and 13.3 μm which are either weak or not present in spectrum A and can be assigned to methylene CH stretching, methylene CH bending, and contiguous-methylene rocking vibrations, respectively.[26] Further evidence for CHCl reduction appears in the $^1$H NMR spectrum of a solution of polymer X in 1,2,4-trichlorobenzene (Figure 4). The upfield shifts of the complex $CH$Cl and $CH_2$ multiplets of X, as compared to their positions in virgin PVC (Figure 4, arrows), are consistent with a general decrease in molecular electronegativity owing to substitution of H for Cl, and the strong resonance at δ 1.7 ppm can be taken as further evidence for the presence of adjacent methylene groupings. The $^1$H NMR spectrum of polymer X in $CS_2$–$(CD_3)_2CO$ solution shows no absorption in the olefinic–aromatic region. Furthermore, if the integrated intensities of the $CH_2$ and $CH$Cl bands of polymer X are used to calculate the polymer's elemental composition, the results are found to be in satisfactory agreement with those obtained by microanalysis.

The most convincing evidence for the structure of polymer X is provided, however, by its $^{13}$C NMR spectrum, which is displayed in Figure 5. In general appearance this spectrum is remarkably similar to that of an ethylene–(vinyl chloride) copolymer which was studied by Keller,[27] and the chemical shifts of the multiplets in our spectrum are in excellent agreement with values reported by Keller and Mügge.[28] If saturated sequences containing more than seven adjacent methylenes are assumed to be present in negligible concen-

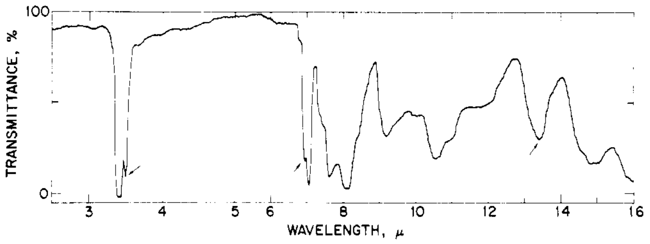


**Figure 6.** IR spectrum of the polymer obtained from a reaction of PVC with *p*-thiocresol in benzophenone solution. See text for details (μm = μ).

tration, then the relative amounts of $(CH_2)_3$, $(CH_2)_5$, and $(CH_2)_7$ sequences in polymer X can be calculated to be 16.1:1.4:1.0, respectively, from the integration data for Figure 5.

As noted above, the elemental analyses of Table I reveal little structural modification of PVC after its reaction with thiols in *o*-dichlorobenzene, and it is therefore reasonable to ask whether any CHCl reduction occurs in this solvent at all. An answer to this question is supplied by spectrum C of Figure 3, which was taken on the modified polymer prepared in experiment 8 of Table I. The three bands marked in this spectrum with arrows constitute good evidence for reduction (see above), but their low intensities confirm that the process occurs much more slowly in *o*-dichlorobenzene than in benzophenone (cf. spectrum B, Figure 3).

PVC can also be reduced by aromatic thiols, a conclusion which follows from the elemental analysis and IR spectrum (Figure 6, arrows) of a polymer treated with *p*-thiocresol under conditions comparable to those of experiment 33 (Table II). The elemental composition of this polymer (Experimental Section) was in excellent agreement with values calculated for reduction rather than dehydrochlorination, and it indicated that the former process had progressed to the extent of about 29.5%. This value is comparable to the percent of reduction observed after 139 h using 1-dodecanethiol (29.0%, polymer X) but larger than the value of 22.7% found in experiment 33. *p*-Thiocresol thus appears to be even more effective than 1-dodecanethiol as a reducing agent under these conditions, although calculations based on the reduction percentages indicate that the reactivities of these thiols differ by a factor of only about 1.2.

1-Dodecyl disulfide was isolated in 21% yield (based on the amount of reduction) from the reaction mixture obtained in the preparation of polymer X. The actual yield of the disulfide was undoubtedly much higher, since the large volume of solution from which the compound had precipitated was not concentrated to secure more material. GC–mass spectrometric analysis of aliquots taken at intervals from similar reaction mixtures also indicated that the disulfide was present (as evidenced by the parent ion at *m/e* 402) and showed that its yield increased, as expected, with increasing reaction time. Quantitative determination of the disulfide was not possible, due to partial decomposition of the substance under the conditions required for its analysis. Nevertheless, these results strongly suggest that the overall stoichiometry of the PVC–thiol redox process can be described by eq 1.

$$\text{-}CH_2CHCl\text{-} + 2RSH \rightarrow \text{-}CH_2CH_2\text{-} + RSSR + HCl \quad (1)$$

$$(R = \text{alkyl, aryl, etc.})$$

**Mechanism of Stabilization.** Our work offers no evidence to indicate that thiols can reduce the overall rate of the nonoxidative loss of HCl from PVC (in benzophenone) by acting as radical traps. Nor do they prevent color by enhancing chain transfer and thus causing polyene sequence lengths to be short. Instead, they inhibit both color and dehydrochlorination by destroying labile defect structures in the polymer, a process whose occurrence is firmly established by the finding of chemical stabilization effects resulting from thiol pretreatments. However, the overall chemical stability of PVC may actually be decreased by the presence of large amounts of a thiol, due to an unusual reduction reaction (eq 1) which seems to be favored by polar media. In passing, we note here that this reduction provides a convenient rationale for an interesting observation of Popova and co-workers,[5b] who found that ~0.5 wt % of a thiol was more effective than twice that amount for retarding the loss of HCl from neat PVC under nitrogen.

The nature of the defect sites destroyed by thiols is not clear at the present time. Peroxidic structures[29] are one possibility, but their removal seems likely to be unimportant, as they are almost certain to be present in such low concentrations that their destabilizing effects[29] will be small. Furthermore, we find that color prevention at very long heating times cannot be achieved by thiol pretreatment but requires that a thiol be present, instead, throughout the period of heating. This observation suggests that thiols are able to destroy labile allylic chloride groups that are being continually formed by dehydrochlorination during the heating process. Deactivation of such structures by reductive dehalogenation would not be inconsistent with the available facts, for the total number of defects destroyed does not necessarily have to be large, and the presence of a few olefinic groups in our pretreated PVC's is certainly not ruled out—even for cases (e.g., polymer X) in which very large amounts of a thiol were employed.[30] On the other hand, defect destruction by mechanisms that introduce sulfur has not yet been excluded completely, despite the failure of our elemental analyses to provide support for this hypothesis. The amounts of sulfur bound to our pretreated polymers might have been comparable to (or less than) the amounts incorporated by random physical occlusion, a circumstance which could have been responsible for the lack of correlation found between sulfur content and chemical stability. Elucidation of the detailed mechanism of chemical stabilization by thiols thus requires more information as to the number of defect sites actually destroyed by these reagents and the fate of various candidate structures under appropriate reaction conditions. We plan to approach the latter problem by studying model compounds.

In any event, the mechanistic situation that obtains when large amounts of thiol are present must be distinguished from that at low thiol concentrations where "ordinary" dehydrochlorination occurs. The radiochemical analytical work of Poller et al.[9h,j] shows that chemical incorporation of sulfur into PVC can occur under the latter conditions and also suggests that this incorporation is associated with color prevention. In order to test these ideas, we have performed experiments involving the reaction of 1-dodecanethiol with the degraded polymer in solution.

Decomposition of virgin PVC for 1 h under the conditions of experiment 37 (Table III) gave a dark orange solution to which 5.0 g of the thiol was added. Continued heating under these conditions caused the color to lighten slowly, and after 24 h of heating no color could be observed. Attempts to demonstrate sulfur incorporation were then made by heating solutions of virgin polymer for ~25 h before the thiol was introduced (in other respects these experiments were identical to the experiment just described). The very dark colors appearing after these longer preheating times did not undergo perceptible change after an additional 25 h of reaction, and the sulfur contents of the polymers recovered from two runs of this type were found to be 0.14 and 0.15%. These percentages are so low that their significance is uncertain. Nevertheless, if they are accepted at face value, then calculations based on the rate constants of experiments 37 and 40 show that they would correspond to the destruction, by thiol addition, of only about 12–14% of the double bonds formed during the preheating periods. Thus it is clear that under our experimental conditions, thiol addition is rather slow and does not comprise a particularly effective means for decolorizing the degraded polymer.

Another estimate of the extent of thiol addition can be made from the data of Alavi-Moghadam et al.[9h] if the rate constant for dehydrochlorination of PVC under their conditions (180 °C, chlorobenzene solution, sealed tube, in vacuo) is equated to our value for dehydrochlorination in *o*-dichlorobenzene (see above). On this basis, the amount of sulfur incorporation they found after 20 min of reaction with $n$-Bu$^{35}$SH corresponds to the addition of the thiol to ~11% of the double bonds formed during 50 min of preliminary heating. This amount of addition might be large enough to account for the bleaching effect they observed if the sequence lengths of their colored polyenes were sufficiently short (maximum values of about 25–30 C=C units have been suggested by other workers[31]), if the double bonds in the longer sequences were more reactive than those in the shorter ones, and particularly if the attachment of mercaptide groups occurred preferentially at the centers of polyenes rather than at their termini (a possibility raised by recent theoretical work[32]).[33] However, some of the color removal effected by thiols could result from secondary reactions (e.g., Diels-Alder cyclizations) of long polyenes whose growth has been terminated by reductive dehalogenation or mercaptide substitution routes. In view of the existence of these possibilities and the observations described above, we believe that the overall mechanism of thiol bleaching must be regarded as an open question at this time.

A final point of interest relating to the mechanism of stabilization by thiols has to do with possible effects produced by the product disulfides. Disulfides have, in fact, been reported to improve both the color and the chemical stability of PVC,[2a,b,e,8a,c,34] and in at least one case such improvements were detected under nonoxidative conditions.[34] Nevertheless, we find that 1-dodecyl disulfide reduces neither the rate of color development nor the rate of HCl evolution when it is used at the 0.1–0.4-g level under the conditions of experiment 37 (Table III).[35]

**Mechanism of Reductive Dehalogenation.** Since the nonoxidative dehydrochlorination of PVC has frequently been suggested to be a free-radical process,[1] the question arises as to whether reduction of the polymer by thiols ought to be taken as evidence for radical trapping. A reduction mechanism involving C–Cl homolysis is shown in eq 2;

$$\mathrm{RCl} \underset{b}{\overset{a}{\rightleftarrows}} \mathrm{R}\cdot + \mathrm{Cl}\cdot \xrightarrow[c]{2\mathrm{R'SH}} \mathrm{RH} + \mathrm{R'SSR'} + \mathrm{HCl} \qquad (2)$$

$$(\mathrm{RCl} = \mathrm{PVC};\ \mathrm{R'} = \text{alkyl, aryl, etc.})$$

this simple scheme is consistent with a kinetic dependence on thiol concentration if step b is faster than step c (i.e., if cage recombination is an important process). However, a mechanism of this type can be discounted on several grounds. Cage recombination reactions of radicals are favored by increasing solvent viscosity,[36] but benzophenone is more viscous than *o*-dichlorobenzene (at 180 °C the viscosities are 0.72[37] and 0.34 cP,[38] respectively). Thus eq 2 fails to account for faster reduction in the former solvent than in the latter one. Furthermore, if eq 2 applies, then the rate constant for step a is required to be at least about as large as the 6-h $k$ of experiment 40 (Table III), assuming on the basis of previous arguments that the latter value relates primarily to reduction. The Arrhenius activation energy for step a can be equated to the C–Cl bond dissociation energy, which is probably no higher than 77 kcal/mol for the ordinary C–Cl's in PVC.[39] Thus, in this scenario, step a must have an Arrhenius $A$ factor of ca. $10^{32}$ s$^{-1}$. Alternatively, an $A$ factor of ~$10^{28}$ s$^{-1}$ would be required for step a if the bond dissociation energy for C–Cl were as low as 70 kcal/mol and if reduction were responsible for only 10% of the rate measured in experiment 40. These $A$ factors are obviously far too large to be associated with a conventional C–Cl homolysis, since the $A$ factors of similar reactions are no greater than ~$10^{15}$ s$^{-1}$.[40]

A third argument against the mechanism of eq 2 is provided by our finding that a simple model compound, 7-chlorotridecane, gives ca. 30% of 6-tridecene but only a trace, at most, of reduction product after exposure to 1-dodecanethiol for 190 h under the conditions used to prepare polymer X. It seems most unlikely that the C–Cl bond energies in 7-chlorotridecane and PVC could be so different as to allow reduction by the homolytic mechanism in one case but not in the other. Furthermore, the finding of alkene, unaccompanied by alkane, in the 7-chlorotridecane product mixture appears to exclude the possibility (already quite improbable) that the reduction observed with PVC is preceded by dehydrochlorination.

Other mechanisms for the reduction must therefore be considered, and in this connection it is interesting to note that the stoichiometry of eq 1 is identical to that observed in reactions of thiols with "positive halogen" compounds.[41] Such reactions are usually considered to proceed via the sequence shown in eq 3 and 4,[41c,e,i,l] although a mechanism involving an intermediate thioether (eq 5 and 6) has been invoked in certain cases[41d,f] (eq 3–6 may involve thiolate anions rather than thiols).

$$\mathrm{R'X} + \mathrm{RSH} \rightarrow \mathrm{R'H} + \mathrm{RSX} \qquad (3)$$

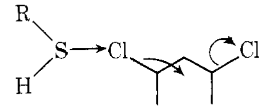
$$\mathrm{RSX} + \mathrm{RSH} \rightarrow \mathrm{RSSR} + \mathrm{HX} \qquad (4)$$

$$\mathrm{R'X} + \mathrm{RSH} \rightarrow \mathrm{R'SR} + \mathrm{HX} \qquad (5)$$

$$\mathrm{R'SR} + \mathrm{RSH} \rightarrow \mathrm{RSSR} + \mathrm{R'H} \qquad (6)$$

$$(\mathrm{R'} = \text{an electronegative residue};\ \mathrm{X} = \mathrm{Cl, Br, or\ I};\ \mathrm{R} = \text{alkyl, aryl, etc.})$$

Both of these mechanisms seem to require an effective means of stabilizing negative charge on the carbon atom undergoing reduction,[41a–f,h–o] and the usual order of halogen reactivity is I > Br > Cl.[41d,e,i,j,l,42] PVC would thus seem to be a very unlikely candidate for reactions of this type, although it might be argued that, with this particular substrate, nucleophilic displacement on halogen or sulfur could be favored by neighboring C–Cl participation (**2** and **3**, arrows), which would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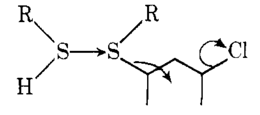
**3**

tend to localize the negative charge onto an incipient chloride anion. However, the cyclopropane moieties that would have resulted from **2** and **3** could not be detected by NMR measurements, and their absence cannot be ascribed to their reductive hydrogenolysis, since this pathway fails to account for the formation of $(CH_2)_3$ as the major reduced functionality. The structural data for the reduced polymer can, of course, be rationalized in terms of a quantitative addition of HCl to the 1,2 bonds of cyclopropane intermediates, but this possibility also seems highly unreasonable in view of the very low HCl concentration and the strong probability that acid-catalyzed ring opening in the presence of excess thiol would have led to the incorporation of mercaptide groups rather than chloro substituents.

Nevertheless, the mechanism for the reduction of PVC seems to have appreciable polar character. Experiments 32 and 33 (Table II) and the experiment in which polymer X was prepared can be regarded as one-point kinetic runs that are pseudo-first-order in thiol concentration within the intervals of 0–25, 25–70, and 70–139 h. The pseudo-first-order k's can be calculated from reduction percentages derived from the analytical data, and after making the small corrections needed to convert all of the $k$'s to the same thiol-concentration basis, the values found for $k_{0-25h}$, $k_{25-70h}$, and $k_{70-139h}$ are 81 × $10^{-6}$, 48 × $10^{-6}$, and 21 × $10^{-6}$ mol HCl (g PVC)$^{-1}$ h$^{-1}$, respectively. These numbers, though approximate, are of sufficient accuracy to show that the reactivity of the polymer decreases with increasing extent of reduction. On the other hand, if the lack of reduction observed with 7-chlorotridecane also applies to isolated halogens in the reduced polymer, then the formation of saturated sequences longer than $(CH_2)_3$ must mean that the central C–Cl bond of the $-CH_2CH_2CH(Cl)CH_2CH(Cl)-$ group can be reduced to some extent. Thus, with respect to the number of neighboring halogens, the order of reactivity of a C–Cl bond toward 1-dodecanethiol reduction is 2 $\gamma$-Cl > 1 $\gamma$-Cl > 0 $\gamma$-Cl. This is a sequence which can be rationalized in terms of inductive effects. The kinetic effects of solvents are also indicative of a mechanism with polar character, although the relatively high reactivity of *p*-thiocresol seems anomalous if nucleophilic attack by the thiol is involved. However, this finding would not be inconsistent with the intervention of thiolate anion, a very strong nucleophile whose concentration should be relatively high in the case of the aromatic thiol [in water the p$K_a$'s of *p*-thiocresol and ethanethiol are 6.5 (at 23 °C) and 10.6 (at 25 °C), respectively[43]].

At any rate, a mechanism involving nucleophilic displacement has not yet been established for PVC, and the available data for this system would also appear to be in accord with other interesting possibilities, including certain chain-reaction mechanisms involving radicals and radical ions. No attempt will be made here to enumerate all of the various options. Nevertheless, we do wish to note, in closing, that nucleophilic displacement on chlorine but not on carbon would be a most remarkable event indeed, since sulfur nucleophiles are known to have very strong affinities for saturated carbon centers[44] and have apparently never been found to attack the halogen atoms of PVC[45] or those of other unactivated alkyl chlorides. Our work on the reduction mechanism is continuing, and we hope to report our findings in due course.

## Experimental Section

**Materials.** The starting PVC was Geon 103EP, an unstabilized commercial polymer manufactured by B. F. Goodrich. 1-Dodecanethiol (Aldrich) had a nominal boiling point of 152–156 °C (24 Torr) and a nominal purity of 98%; GC–mass spectrometry (see below) indicated that this thiol contained no more than ca. 1.5% of the corresponding disulfide. Burdick & Jackson "distilled in glass" *o*-dichlorobenzene contained traces of *p*-dichlorobenzene and chlorobenzene (analysis by GC–mass spectrometry). The benzophenone was Fisher "certified" material; typical batches had a melting point range ≤1.0 °C. All other reagents and solvents were commercial products of the highest available purity. The composition of di(*n*-butyl)tin bis(*n*-dodecyl mercaptide) was verified by elemental analysis, as previously described;[11a] purities of other key materials were checked by IR analysis, GC–mass spectrometry, and melting point determinations.

**Analysis.** Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. GC analyses were carried out with a Varian 3700 instrument equipped with a CDS-111 data collection system, a flame ionization detector, and a 6-ft × 0.125-in. (o.d.) stainless steel column containing 5% of OV-1 on 100–120 mesh Chromosorb W. Helium (30 mL/min) was used as the carrier gas, and the injection port temperature was 250 °C. Column temperature was increased from 110 to 160 °C at the rate of 10 °C/min. GC–mass spectrometry was performed with a Varian MAT-112 instrument using an ionization potential of 72 eV, TIC detection, an injection port temperature of 275 °C, and helium (20 mL/min) as the carrier gas. A 6-ft × 0.125-in. (i.d.) stainless steel column was employed; it contained 3% of OV-17 on 100–120 mesh Chromosorb W and was programmed from 200 to 250 °C at the rate of 10 °C/min. IR spectra were taken with a Beckman IR8 instrument. The polymer films used for IR analysis were prepared by molding ~0.1-g samples for 1–3 min at 140 °C under a pressure of 20 000 lb in a Carver Laboratory Press (model B). $^1H$ NMR spectra of nonpolymeric materials were obtained with a Varian T-60A instrument using tetramethylsilane ($Me_4Si$) as internal standard. Polymer $^1H$ NMR spectra were recorded with a Jeolco JNM-C-60HL spectrometer using ~10% (w/v) solutions of polymer in [a] 1,2,4-trichlorobenzene (TCB) at ca. 100 °C (Figure 4) or [b] $CS_2-(CD_3)_2CO$ at ambient temperature. $Me_4Si$ and hexamethyldisiloxane (HMDS, $\delta$ 0.06 ppm vs. $Me_4Si$) were employed as internal standards for measurements made under conditions b and a, respectively. In order to improve the accuracy of the polymer $^1H$ NMR integrations, these were performed with a Bruker WH-90 instrument at 110 °C on ~10% (w/v) solutions of polymer in TCB containing HMDS and ca. 20% (v/v) of $C_6D_6$. The C$H_2$/C$H$Cl ratios thus obtained (see below) represent averages of 15 scans. The $^{13}C$ NMR spectrum recorded in Figure 5 was observed with a Varian XL-100 spectrometer modified for pulse Fourier transform spectroscopy and interfaced with a Nicolet model 1080 computer. Protons were decoupled from the carbon nuclei using a random noise decoupling field. Free induction decays were stored in 8K computer locations using a dwell time of 100 $\mu$s, i.e., a spectral window of 5000 Hz. The pulse width was 23 $\mu$s (for a 90° pulse), and the pulse interval was 4.0 s. HMDS was employed as internal reference ($\delta$ 2.0 ppm vs. $Me_4Si$), and the internal deuterium lock signal was provided by *p*-dioxane-$d_8$. The spectrum represents 16 000 accumulations of the free induction decay and was obtained at 110 °C on a 10% (w/v) solution of the polymer in TCB.

**Chemically Modified PVC.** The chemical modification reactions were carried out under nitrogen or argon in *o*-dichlorobenzene or benzophenone solution, and the resulting polymers were recovered by methanol precipitation and purified by methanol extraction. Details of the procedure employed for preparative runs have previously been described.[11a] In the present work, some of the chemically modified polymers were obtained by isolating them in the usual way[11a] from solutions which had been used for kinetics experiments (see below). The precipitation of polymer from reaction solutions was shown to be complete in every case, in that further separation of polymer did not occur when the filtrates were treated with additional methanol. However, a white precipitate did appear when excess methanol was added to the filtrate obtained after the recovery of polymer X (see text, above). This precipitate was separated by suction filtration and washed with fresh methanol; it weighed 0.6 g and was shown to be pure 1-dodecyl disulfide by melting point, mixture melting point, and IR spectral comparisons with authentic material.

Elemental analysis of polymer X gave the following values. Found: C, 45.81; H, 6.37; Cl, 46.91; S, 0.29. These numbers agree reasonably well with those calculated for a material containing 0.290 $CH_2CH_2$, 0.706 $CH_2CHCl$, and 0.005 $CH_2CH(SC_{12}H_{25})$ units (Calcd: C, 46.35; H, 6.45; Cl, 46.91; S, 0.29), but they differ significantly from those corresponding to a polymer containing $CH{=}CH$'s rather than $CH_2CH_2$'s (Calcd: C, 47.36; H, 5.44; Cl, 46.91; S, 0.29). (Both sets of calculated values were obtained by using the experimental numbers for Cl and S to compute values for C and H.) The weight of the starting PVC was 1.50 g; thus the isolated amount of disulfide corresponds to 21% of the theoretical yield for 29.0% reduction. Integration of the $^1H$ NMR spectra of the reduced polymer and a control sample of virgin PVC gave C$H_2$/C$H$Cl ratios of 3.72 and 1.96, respectively. The theoretical ratio for PVC is 2.00; hence the corrected ratio for the reduced material is (2.00/1.96)3.72 = 3.80. Use of this value to compute the elemental composition of the reduced polymer gives numbers (Found: C, 46.37; H, 6.44; Cl, 47.19) that are in satisfactory agreement with those obtained by direct analysis (see above) if the low sulfur content of the reduced polymer is ignored. Integration of the $^{13}C$ NMR spectrum of polymer X (Figure 5) gave the following results [listed as approximate $\delta$ (ppm), area %]: 63, 3.0; 60, 17.1; 56, 18.3; 47, 26.5; 38, 21.3; 29, 2.4; 26, 2.6; 23, 8.7. The reliability of the peak areas may be open to question due to possible differences in nuclear Overhauser effects and spin–lattice relaxation times. However, if the number of saturated sequences containing more than seven contiguous $CH_2$'s is assumed to be negligible, the total area for CHCl carbons + $CH_2$ carbons generated by reduction can be computed from the integration data to be 50.3% (in good agreement with the theoretical value of 50.0%), and the extent of reduction can be calculated as 23.7% (vs. 29.0% from elemental analysis, as noted above).

The polymer whose IR spectrum is recorded in Figure 6 was prepared by allowing virgin PVC to react with *p*-thiocresol [0.099 mol/(g PVC)] in benzophenone for 70 h under the conditions of experiment 33 (Table II). The elemental analysis of this polymer (Found: C, 46.24; H, 6.41; Cl, 47.08; S, 0.28) corresponds to the composition calculated for a product containing 0.295 $CH_2CH_2$'s, 0.700 $CH_2CHCl$'s, and 0.005 $CH_2CH(SC_{12}H_{25})$'s (Calcd: C, 46.28; H, 6.36; Cl, 47.08; S, 0.28).

**Reaction of *o*-Dichlorobenzene with 1-Dodecanethiol.** A well-stirred solution of 1-dodecanethiol (5.0 g) in *o*-dichlorobenzene (36 mL) was degassed by bubbling with nitrogen and then heated under reflux for several days with continued introduction of nitrogen. Qualitative analysis of the solution by GC–mass spectrometry showed, in addition to the starting materials, only one additional major GC peak, which was identified as chlorophenyl-1-dodecyl sulfide (**1**) on the basis of the mass spectral data: *m/e* 314 (weak, parent ion, $C_{18}H_{29}\,{}^{37}ClS$), 312 (weak, parent ion, $C_{18}H_{29}\,{}^{35}ClS$), 169 (weak, $C_{12}H_{25}$), 168 (weak, $C_{12}H_{24}$), 145 (strong, $C_6H_4\,{}^{37}ClS$), 143 (strong, $C_6H_4\,{}^{35}ClS$), 113 (strong, $C_6H_4\,{}^{37}Cl$), and 111 (strong, $C_6H_4\,{}^{35}Cl$). The intensities of the halogenated peaks were in the correct ratio for ions containing one atom of chlorine.

**Kinetics.** The procedures used to measure rates of HCl evolution from solid samples[11a] and solutions[14] of PVC have previously been described. In the present work, all titrations were performed with a Sargent Recording pH Stat, Model S-30240, and all samples (or solutions) were subjected to 15.0 min of equilibration at the reaction temperature prior to the start of kinetic runs. Rate constants obtained with *o*-dichlorobenzene solutions were corrected in the usual way[14] for the evolution of adventitious acid from the solvent. Under the kinetic conditions, no detectable acid was evolved from neat 1-dodecanethiol, but small amounts of unidentified acidic material were evolved from some batches of solvent benzophenone and from their mixtures with the thiol. Complications arising from this source were avoided by performing each series of kinetic runs with aliquots taken from a separate masterbatch of benzophenone which had been prepared by powdering and dry blending. In the case of the masterbatch used for the experiments of Table III and Figure 2, control runs for adventitious acid evolution showed excellent reproducibility, whereas no adventitious acid was evolved from the benzophenone used in the experiments of Table II and Figure 1. Rapid argon bubbling through reaction solutions was continued during sample removal or the addition of thiol at intermediate reaction times. Samples were analyzed by GC–mass spectrometry; 1-dodecyl disulfide was identified by comparing its retention time and mass spectrum with those of authentic material.

**Preparation of 7-Chlorotridecane.** This procedure is based on a published method[46] for converting secondary alcohols to the corresponding chlorides without rearrangement. Thionyl chloride (16.4 g, 0.138 mol) was added dropwise with stirring and continuous degassing (nitrogen ebullition) to 50 mL of *N*,*N*-dimethylformamide (DMF) while the temperature was kept at 0–10 °C by external cooling (CAUTION: The complex formed from thionyl chloride and DMF has been reported to undergo violent exothermic decomposition upon long standing at room temperature in the presence of traces of metallic impurities;[47] although these conditions were not encountered in the present preparation, this reaction should be carried out with appropriate precautions). 7-Tridecanol (25.0 g, 0.125 mol) was then introduced slowly (15 min) at 0–10 °C, and the resulting mixture was heated at 100 °C for 0.5 h with continued degassing and stirring. After cooling to room temperature and addition of water (ca. 200 mL), the mixture was extracted with several 100-mL portions of ether, and the combined extracts were washed in succession with water and saturated sodium chloride solution. Drying of the ether solution over Drierite, followed by concentration under vacuum and distillation under reduced pressure (10 Torr) through an 80-plate spinning band column, afforded the following fractions [fraction number, boiling point (°C), weight (g)]: 1, 86, 1.78; 2, 86.5–87, 2.32; 3, 109–111, 15.86; 4, 111, 3.69. Fractions 1 and 2 were shown to be pure 6-tridecene [lit. bp 98°C (8 Torr),[48] 90.8–92.0 °C (6 Torr)[49]; yield, 18%] by spectral measurements: IR (neat) 965 (strong, trans double bond, lit.[50] IR 965 $cm^{-1}$) and 725 $cm^{-1}$ (medium, adjacent methylenes, lit.[50] IR 725 $cm^{-1}$), identical with the spectrum of a commercial sample (Chemical Samples Co.); $^1H$ NMR (60 MHz, $CDCl_3$) $\delta$ 5.2–5.5 (multiplet, 2, $=CH$), 1.7–2.3 (multiplet, 4, $=CHCH_2$), 1.0–1.6 [multiplet, 14, $(CH_2)_3CH_3$ and $(CH_2)_4CH_3$], and 0.93 ppm (distorted triplet, 6, $J \sim 5$ Hz, $CH_3$). Fractions 3 and 4 were identified as 7-chlorotridecane (yield, 72%): IR (neat) no OH or C=C; $^1H$ NMR (60 MHz, $CDCl_3$) $\delta$ 3.81 (pentuplet, 1, $J \sim 6$ Hz, $CHCl$), 1.0–2.0 (multiplet with prominent absorptions at $\delta$ 1.24 and 1.59 ppm, 20, $CH_2$), and 0.90 ppm (distorted triplet, 6, $J \sim 6$ Hz, $CH_3$). Anal. Calcd for $C_{13}H_{27}Cl$: C, 71.36; H, 12.44; Cl, 16.20. Found (fraction 3): C, 72.01; H, 12.73; Cl, 15.51. The small analytical discrepancies result from contamination by ~4 wt % of 6-tridecene, as shown by GC measurements.

**Reaction of 7-Chlorotridecane with 1-Dodecanethiol.** A solution of 7-chlorotridecane (5.25 g, 0.0240 mol) and 1-dodecanethiol (30.0 g, 0.148 mol) in benzophenone (142 mL) was heated at 180–185 °C with continuous stirring and nitrogen degassing. After 190 h the solution was analyzed by GC and GC–mass spectrometry and found to contain the starting chloride and 6-tridecene in a ratio of ca. 70:30, respectively. A very small chromatographic peak (<1 area%) had a retention time close to that of authentic *n*-tridecane, but this peak was not of sufficient size to permit its conclusive identification.

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# Conformation Study on Poly($N^\epsilon$-carbobenzoxy-L-lysine) in Helicogenic Solvents by Small-Angle X-Ray Scattering

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**ABSTRACT:** Small-angle x-ray scattering of poly($N^\epsilon$-carbobenzoxy-L-lysine), (CbzLys]$_n$, in four solvents, dimethyl formamide(HCONMe$_2$), pyridine, *m*-cresol, and hexamethylphosphoric triamide [(Me$_2$N)$_3$PO], was measured to determine the mass per unit length, $M_q$, and the radius of gyration of the cross section, $\langle S_q^2 \rangle^{1/2}$. It was confirmed from the values of $M_q$ that (CbzLys)$_n$ exists in an $\alpha$-helical conformation in these solvents. The value of $\langle S_q^2 \rangle^{1/2}$ increases in the order of *m*-cresol < HCONMe$_2$ < pyridine < (Me$_2$N)$_3$PO. It was indicated that the side-chain conformation was varied in accordance with the kind of solvent. It was elucidated from the calculations on $\langle S_q^2 \rangle^{1/2}$ that the side chains are moderately extended in (Me$_2$N)$_3$PO and come in loose contact with the main chain in *m*-cresol, and the side chains in HCONMe$_2$ and pyridine exist in an intermediate conformation between those in (Me$_2$N)$_3$PO and *m*-cresol.

Studies on poly(amino acids) in dilute solution have been mainly concerned with the determination of the main-chain conformation and the elucidation of the influences of various parameters such as molecular weight, solvent, temperature, salt, pH, amino acid composition, etc., on its conformation.[1,2] However, little has been elucidated on the side-chain conformations.

It is important to clarify the side-chain conformation itself, since poly(amino acids) show various specific structures and properties according to the kind of side chain. The side-chain

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