Cross-Linking Additives as Smoke Suppressants for Poly(Vinyl Chloride)

Steven Alfred Terranova

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CROSS-LINKING ADDITIVES AS SMOKE SUPPRESSANTS FOR
POLY(VINYL CHLORIDE)

A Thesis
Presented to
The Faculty of the Department of Chemistry
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirements for the Degree of
Master of Arts

by
Steven Alfred Terranova
1993
APPROVAL SHEET

This thesis is submitted in partial fulfillment of the requirements for the degree of

Master of Arts

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ABSTRACT

It had been suggested previously that zerovalent copper could catalyze the reductive coupling of model compounds which represent portions of poly(vinyl chloride) (PVC) chains. The high-surface-area copper had been generated by reducing the complex, CuI·PBu₃, with lithium naphthalenide. Work has now been done which proves that it was, indeed, the copper, rather than unchanged lithium naphthalenide, which was causing the coupling of 3-chloro-1-butene. These results have been supported by the development of copper(II) formate, a solid copper complex which, upon pyrolysis, produces a copper mirror that promotes coupling of 3-chloro-1-butene as well as the cross-linking of PVC. Other systems have been tested in search of a metal complex which will form a metal mirror above 250 °C and will thus be suitable for use as a cross-linking agent for PVC itself in typical end-use applications. Cross-linking of PVC during its combustion would lead to char formation and to smoke reduction.
CROSS-LINKING ADDITIVES AS SMOKE SUPPRESSANTS FOR
POLY(VINYL CHLORIDE)
INTRODUCTION

Fire and Smoke

It has been estimated that 2.5 million fires occur each year and that a majority of fire-related deaths result from inhalation of smoke.\(^1\) Obviously, fire prevention is a major concern, especially in high-risk areas where electricity may create a hazardous environment. Because of its intrinsic resistance to fire,\(^1\) the polymer, poly(vinyl chloride), PVC, \((-\text{CH}_2\text{CHCl-})_n\), has been implemented as a popular component in such commercial products as wire insulation.\(^2\) Although PVC is inherently fire resistant,\(^1^-^4\) when forced to burn, it displays two undesirable effects. The first is the evolution of HCl which, although harmful, can be diluted significantly with water and does not pose too great a threat.\(^1\) For cases where water cannot be used to extinguish existing flames, large amounts of CaCO\(_3\) or other acid scavengers may be incorporated into the polymer. The second and more important effect is the formation of smoke.\(^1^-^3\) Although PVC is fire-resistant, when supplemented with the proper materials to achieve its maximum commercial practicality, its potential to produce smoke under combustion conditions is enhanced.\(^2\) This problem can be solved by adding nonflammable fillers or by introducing a smoke-retarding additive, usually a metal or metal
compound.\textsuperscript{3} Finding the proper smoke retarder for PVC, however, is a difficult process. Many effective smoke retarders are not commercially useful for one or more of the following reasons:\textsuperscript{3}

1. They are not commercially available.
2. They are expensive.
3. They are colored and impart color to PVC.
4. They discolor PVC during processing.
5. They create other processing problems.
6. They create thermal instability.
7. They create ultraviolet instability.
8. They impart poor physical properties.

Thermal Breakdown of PVC

Boettner\textsuperscript{5} has shown, using thermogravimetric analysis (fig. 1), that by heating PVC to 600°C at the rate of 3°C per minute (in air) there is a very rapid weight loss in the polymer beginning at about 300°C.
Upon analysis of the combustion products, she concluded that roughly 60% of the weight loss was due to the removal of chlorine in the form of HCl gas which accounted for nearly all of the chlorine atoms in the polymer.\textsuperscript{5}

The second stage of thermal breakdown is the production of unsubstituted aromatics such as benzene, naphthalene, and anthracene.\textsuperscript{6} Finally, at high temperatures, alkyl-substituted aromatics such as toluene are produced.\textsuperscript{6}

After the first step, dehydrochlorination, the polymer is stripped and is left as a linear polyene (fig. 2).
This linear polyene can either undergo intramolecular cyclization to give rings from which the unsubstituted aromatics are formed, or intermolecular cross-linking. We will see later that these unsubstituted aromatics, particularly benzene, are the major source of smoke in burning PVC. Alkyl-substituted aromatics and aliphatics result from cracking or fragmentation of the polyene at high temperatures. These volatile aliphatics burn much more efficiently than the aromatics and, hence, do not promote the formation of smoke but do increase flame spread. The cross-linked polyene may also be converted into a thermally stable char, which is the most desirable result.

In order to measure the amounts of char formed by various PVC samples, Kroenke implemented a "smoke-char" test which evaluates the ability of polymer samples to form smoke or char. The PVC is burned, and the resulting char residue is weighed. This char weight is then used to calculate %BC or percent of backbone char, which is the amount of the PVC hydrocarbon backbone which remains as a thermally stable char (fig. 3).

\[
\frac{\text{char wt.}}{\text{sample wt.}} - \frac{\text{nonburnable residue wt.}}{\text{sample wt.}} - \frac{\text{non PVC wt.}}{\text{sample wt.}} - \frac{\text{HCl wt.}}{\text{sample wt.}} = \% \text{ BC}
\]

percent backbone char

**fig. 3**
As indicated, the smoke-char test is also implemented to measure the amount of smoke evolved by a burning PVC sample. The smoke rises through a chimney and through the beam of the photometer which is coupled to an integrator. The integrator measures the total amount of smoke and calculates $S_{\text{PVC}}$, the smoke number, which represents integrated area per gram of PVC in the sample. Figure 4 provides an overview of the main components of the smoke-char tester.

the BFGoodrich smoke-char tester

fig. 4
Kroenke has shown that without any kind of smoke suppressant additive present PVC shows %BC values of roughly 10-11, but that for systems which contain metal-additive smoke suppressants, %BC values increase to 30-50.³

Smoke Origin

In order to find an efficient smoke suppressant in a nonempirical manner, the origin of smoke must be known. Lattimer and Kroenke⁴ have shown that there exists a relationship between smoke reduction and benzene reduction. As is shown in figure 2, when HCl is lost from PVC, a conjugated polyene structure remains which can undergo pyrolysis to give many hydrocarbon products. The most abundant pyrolyzate, other than HCl, is benzene.²

Mechanism of Benzene Formation

In general, benzene results from intramolecular cyclization of the conjugated polyene residue segments (remaining after HCl removal) into 1,3-cyclohexadiene structures, followed by removal of polymeric ring substituents through sequential C-C homolyses. Starnes and Edelson² consider four possible mechanisms. The first (mechanism I) contends that ring substituents (Rₙ-Rₜ) are thermally cleaved from cyclic structures (fig. 5) that are
produced by intermolecular Diels-Alder reactions of
dehydrochlorinated segments of PVC. However, O’Mara had
shown that the mechanism for formation of benzene most
probably does not include intermolecular pathways. The
second and third mechanisms proposed both involve
intramolecular pathways. The first pathway involves thermal
excitation of a conjugated triene segment into its triplet
state and then cyclization with concurrent homolytic ejection of one of the ring substituents. Benzene is formed from homolysis of a second C-C bond. This mechanism is backed by very little experimental evidence. The second proposed intramolecular mechanism for benzene formation (fig. 6)

\[
\begin{align*}
\Delta & \\
\text{R}_1\text{C}_2\text{R}_2 & \rightarrow \Delta \quad \Delta \quad \text{R}_1\cdot + \text{R}_2\text{C}_2
\\
\text{R}_2 & \quad \rightarrow \Delta \quad + \text{R}_2\cdot
\\
\text{R}_1, \text{R}_2 & = -\text{CH}_2\sim, -\text{CHCl}\sim, -\text{CH}==\text{CH}\sim
\end{align*}
\]

cyclohexadiene mechanism\textsuperscript{2}

fig. 6

8
involves a Diels-Alder cyclization of a triene into a
cyclohexadiene structure which is converted into benzene by
two successive C-C homolyses.\(^2\)

A similar cyclooctatetraene mechanism (fig. 7) has also
been proposed and must be considered.

\[
\begin{align*}
\text{cyclooctatetraene mechanism}^2 \\
\text{fig. 7}
\end{align*}
\]
Formation of benzene from polyene intermediates has considerable support. First, the rate of benzene production is enhanced by the presence of HCl,$^2$ which catalyzes the formation of polyenes from the PVC polymer.$^2$ At constant temperature, the rate of benzene formation is autoaccelerating under conditions that should lead to a constant concentration of HCl.$^2$ This would be explained if benzene were to come from a precursor such as a polyene or cyclohexadiene. In addition, preliminary thermal dehydrochlorination also increases the amount of benzene evolved at higher temperatures.$^2$ This suggests that mild thermolysis must yield intermediates which form benzene upon further heating.$^2$ The most likely mechanism for polyene growth is described in figure 8.

\[ \text{Cl}^- \rightarrow -(\text{CH}=\text{CH})_n\text{CHClCH}_1^- \rightarrow -(\text{CH}=\text{CH})_n\cdot\text{CHCH}_1^- \rightarrow -(\text{CH}=\text{CH})_n\cdot\text{CHCH}_1^- \rightarrow \ldots \]

etc.

polyene growth$^2$

fig. 8
Of further interest is the observation that the syndiotacticity of the polymer is inversely related to the yield of benzene under combustion conditions.\textsuperscript{2} Syndiotactic portions of PVC chains contain racemic dyads; these dyads exist mainly in the trans-trans (tt) state (1) (fig. 9).\textsuperscript{2}
These segments will undergo cis elimination to form trans alkenes (2). Isotactic dyads exist mostly in the trans-gauche (tg) conformation (3). Because the Cl in (2) with the arrows pointing to and from it is equidistant from the two H's of the central methylene group, it can form either a trans (3) or a cis (4) product via pathways a and b, respectively.² Thus, the average polyene length increases with an increasing degree of syndiotacticity in the polymer because cis portions of the polyene can cyclize intramolecularly and thus interrupt the polyene conjugation. Trans polyenes cannot cyclize in this way and, as stated, yield less benzene.²

MoO₃ as a Smoke Suppressant for PVC

A great deal of background work pertaining to smoke-suppression by metals and metal complexes has been done on molybdenum(VI) oxide (MoO₃).¹ Two major contributors have done much of this work. The first is the team of Lattimer and Kroenke.⁴ Their work has also shown that volatile aromatic pyrolyzate formation is reduced, as well, and that production of unsubstituted aromatics is reduced to a greater extent than is production of mixed aliphatic aromatics. They conducted experiments that searched for hydrogen/deuterium scrambling in the aromatic products.
formed from PVC mixed with PVC-d₃ (97.3% D) and found extensive scrambling from which they concluded, incorrectly,⁸ that the formation of aromatics occurs via predominantly intermolecular pathways.

Lattimer and Kroenke proposed a "reductive coupling"³⁴ mechanism (fig. 10) for this early cross-linking in which
smoke retarders act as coupling agents during PVC thermal degradation.

The second large contribution to the experimental evidence concerning the smoke retarding action of MoO₃ has been provided by Starnes and co-workers at Bell Laboratories. They contend that MoO₃ (and/or a derivative species, MoO₂Cl₂) acts as a Lewis acid to catalyze one or several competing reactions which inhibit the formation of benzene (fig. 11). These reactions are:

1. cross-linking of polyene segments containing cis-substituted double bonds
2. formation of all-trans polyene segments from the original polymer
3. isomerization of cis-alkene units to more thermodynamically stable trans-alkene units

Benzene → Smoke
PVC → cis,trans Polyene → Cross-linked Polymer
All-trans Polyene → Char

mechanism of PVC pyrolysis
fig. 11
In general, MoO₃ can catalyze the dehydrochlorination of the polymer. The resulting HCl converts MoO₃ into the much stronger Lewis acid, MoO₂Cl₂, which accelerates the aforementioned reactions. In addition, however, as the temperature of the system increases, MoO₂Cl₂ can catalyze a "cracking" process which converts the cross-linked polymer into hydrocarbon fragments (mostly alkanes) which can burn very efficiently. Therefore, although they do not emit a relatively large amount of smoke, these aliphatic fragments can increase the flame spread at elevated temperatures.

In response to the H/D scrambling work done by Lattimer and Kroenke, Starnes et al. proceeded with ¹²C/¹³C scrambling studies. They found that, contrary to previous data, toluene, a substituted aromatic which was believed to be produced primarily by intermolecular pathways, could be produced via pathways that are intramolecular with respect to carbon, as are benzene and naphthalene. Furthermore, they found that most or all of the H/D scrambling reported by Lattimer and Kroenke resulted from intermolecular hydrogen exchange rather than intermolecular carbon exchange. Therefore, H/D scrambling is not viable evidence that pyrolysis products result from cross-linked polymer segments.
Copper Additives as Smoke Suppressants for PVC

Many transition metal compounds have shown potential as smoke suppressants for PVC. Copper compounds may fulfill this role by catalyzing the reductive coupling of PVC chains. Copper compounds are also attractive as smoke suppressants for PVC because they are not strong Lewis acids and thus will not cause high-temperature cracking of the char into the highly combustible aliphatic fragments. As noted earlier, these aliphatic fragments burn very efficiently and are responsible for the increased flame spread of MoO₃-containing systems at high temperatures.

I propose that the copper in copper-containing systems undergoing combustion is reduced to copper metal which has a high surface area and is, therefore, very reactive. High-surface-area copper (HSAC) was generated by reducing the complex, CuI·PBu₃, with lithium naphthalenide under argon gas (to provide an inert atmosphere). My work has demonstrated that model compounds resembling portions of a PVC chain can be coupled by HSAC formed this way. The complex is destroyed by the reducing agent before coupling takes place. Although we believed that the coupling was due, in fact, to the HSAC, some speculation arose that it was caused by the lithium naphthalenide that had not reacted with the CuI·PBu₃. In response to this, work was done by Paul Jeng, a colleague, in which the reduction by-products
were extracted, leaving only copper, and coupling still was observed. However, more convincingly, I began to experiment with other solid metal complexes which consist of certain ligands coordinated to a central metal atom (usually copper). Upon thermal degradation, these metal complexes lost the ligands as gases. This process allows the resulting metal atoms to precipitate into a very thin layer which forms a mirror (HSAC if a copper complex) on the inner surface of the reaction vessel. This result is very exciting, in that the high-surface metal is generally the only component left and is, therefore, the cause of subsequent model-compound coupling. The first such metal complex studied was copper(II) formate, Cu(HCOO)$_2$, which was tested with the model compound 3-chloro-1-butene and with the PVC polymer itself. Copper(II) formate degrades and forms a thin-layer copper mirror between 185 and 195 °C, a result which makes it somewhat attractive as a cross-linking additive for PVC, which begins to degrade at about 200 °C. However, other systems are being sought which form the metal mirror at about 250-300 °C. This type of system will be more practical for real fire conditions where temperatures are higher.

Objectives

The purpose of this work was twofold. The first
objective was to prove that coupling of 3-chloro-1-butene in previous work\textsuperscript{10} was not due to unchanged lithium naphthalenide. The second objective was to find a suitable solid metal complex which would couple 3-chloro-1-butene and also would cross-link PVC.
EXPERIMENTAL

Instrumentation

All sample analyses were done by gas chromatography-mass spectroscopy. Specifications of the mass selective detector used are shown in figure 12.¹

![Functional components of the mass selective detector](fig.12)
Our system consists of a Hewlett-Packard Series II 5890 gas chromatograph coupled to a Hewlett-Packard Vectra 386/25 data processor and a Hewlett-Packard Laserjet III printer.

Synthesis of CuI·PBu₃⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻�
with DI water and 95% ethanol and allowed to air-dry. The crystals were purified by two recrystallizations from a hot mixture of 115 mL of 95% ethanol and 75 mL of isopropyl alcohol. The final crystals (mp 72-75 °C; lit mp 75°C\textsuperscript{1}; yield = 50%) were then dried overnight under vacuum.

**Preparation\textsuperscript{*} of Activated (High-Surface-Area) Cu\textsuperscript{i-}

Lithium (0.153 g, 22 mg-atoms) was introduced into a round-bottom flask (all glassware was oven-dried overnight and was flame-dried just prior to use) containing 2.96 g (23 mmol) of naphthalene and a stir bar. The flask was sealed with a rubber serum cap (which allowed for injection) after this addition. Then 15-20 mL of the solvent, tetrahydrofuran (THF), was injected into the flask, and the resulting mixture was stirred for 2 h until it turned a very dark green which indicated that all of the lithium had dissolved. The crystals of CuI·PBu\textsubscript{3} (7.86 g, 20 mmol) were then placed in a round-bottom flask. After this flask was sealed with a rubber serum cap, 5 mL of THF was injected into it; its contents were then purged with argon and shaken until the copper complex dissolved. Finally, the contents of this flask were injected into the flask containing the lithium naphthalenide and the stir bar. After mixing was complete (solution turned dark brown), the mixture was divided among three small round-bottom flasks.
(about 8 mL of the mixture per flask), each containing a stir bar. Model compounds could then be injected in order to search for coupling.

Model Compound Reactions

Before applying coupling additives to the model compound, 3-chloro-1-butene, two control experiments were performed. First, the model compound was injected into the GC/MS instrument to search for the presence of contamination or the prior occurrence of spontaneous dimerization. Neither was detected. Next, the model compound was injected into the glassware apparatus shortly after it had been flame dried, swirled in the slightly warm round-bottom flask for about a minute, and injected into the GC/MS instrument. Again, no dimerization was observed, a result which showed that in future reactions between the model compound and the coupling agents, any coupling observed would not be due to residual heat from flame drying.

For reactions of 3-chloro-1-butene with the activated copper from the copper complex, CuI·PBu₃, the model compound was always added to a slight molar excess of activated copper suspension under argon. Reductive coupling of the model compound is shown in Figure 13. In previous work,¹² the coupled product was observed as well.
As mentioned, speculation arose that the lithium reagent could be causing the coupling. Therefore, several control experiments were run using only the lithium naphthalenide and 3-chloro-1-butene (no HSAC). Because coupling was observed, work was done in which any remaining (plus other products - see fig. 18)

homocoupling of 3-chloro-1-butene  
fig. 13

As mentioned, speculation arose that the lithium reagent could be causing the coupling. Therefore, several control experiments were run using only the lithium naphthalenide and 3-chloro-1-butene (no HSAC). Because coupling was observed, work was done in which any remaining
lithium naphthalenide was extracted with a syringe before the model compound was added, in order to leave only the HSAC in the bottom of the vessel. This result was verified by the absence of naphthalene traces in subsequent GC/MS runs.

The coupling behavior of the model compound, 3-chloro-1-butene, was also extensively studied using copper formate as the source of the HSAC. The apparatus used for these experiments is shown in figure 14.
First, all glassware was oven-dried and flame-dried, and the system was placed under an argon atmosphere. About 0.30 g (1.94 mmol, an excess) of cupric formate was placed in the round-bottom flask and heated with a flame until a reddish-brown smoke formed, followed by a copper mirror. After the vessel cooled, 0.30 mL (2.98 mmol) of 3-chloro-1-butene was injected onto the mirror with a long syringe. The reactants were then swirled for about a minute and a 0.1-μL sample of the product was injected into the GC/mass spectrometer. Percentage yields were calculated by dividing the abundance of the product by the abundance of the 3-chloro-1-butene plus that of the product and multiplying this quotient by 100. This procedure was followed because the copper(II) formate was in excess.

PVC Reactions with HSAC Formed from Cupper(II) Formate

Each set of reactions consisted of a control reaction which was run simultaneously with a reaction with HSAC. For the control reaction, 1 g of PVC was placed in a clean, dry 10-mL beaker. For the HSAC reaction, 1 g of PVC was ground together with 0.10 g of cupric formate by using a mortar and pestle; the resulting light blue powder was then placed in a separate 10-mL beaker. These beakers were then immersed in a Wood's metal bath which had been preheated to about 200 °C and were heated for 35 to 40 min at 200-235 °C. After
heating, the beakers were allowed to cool and the resulting char from each was placed in a separate preweighed extraction thimble. The thimbles containing the char were then weighed, and the total amount of residue was determined (cross-linked PVC plus noncross-linked PVC plus copper species). Each thimble was then subjected to Soxhlet extraction in THF under nitrogen for 24 h to remove all noncross-linked PVC. Next, the thimbles containing cross-linked PVC were dried in a vacuum oven to constant weight, and this weight was recorded. To get the char weight, the weight of the thimble was subtracted from the weight of the thimble plus the char. The percentage of cross-linking was then calculated by dividing this char weight (which represents the weight of cross-linked PVC plus that of copper species) by the total char weight and multiplying this dividend by 100.

Study of Other Additives

A variety of other compounds was studied as possible alternative coupling agents for 3-chloro-1-butene. These included molybdenum(0) hexacarbonyl, copper(II) oxalate, copper(II) acetylacetonate, copper(II) ethylacetoacetate and copper(II) gluconate. These structures are shown in figure 15.
copper(II) formate

Mo(CO)₆

molybdenum(0) hexacarbonyl

copper(II) oxalate

copper(II) acetylacetonate

copper(II) ethylacetoacetate

copper(II) gluconate

structures of additives

fig. 15
In each case, the compound was placed in the apparatus shown in figure 14 under an argon atmosphere and was heated with a Bunsen burner.
After the compounds had degraded (signified by the formation of either a metal mirror or a blackened powder), excess 3-chloro-1-butene was injected to determine if coupling was possible. Approximate degradation temperatures also were measured. These measurements were done by placing 0.10 g of each metal compound (three at a time - see fig. 16) in separate, clean, dry glass vials and submerging them in a silicone oil bath which was placed on a heating plate. A thermometer also was suspended in the bath with the bottom of the bulb about even with the bottoms of the vials. Heat was applied, and approximate temperature ranges were determined beginning when the compounds began to degrade and ending when they either formed char or mirrors.
Model Compound Reactions

In a previous paper, it was contended that 3-chloro-1-butene could be coupled in the presence of HSAC formed from the complex, CuI·PBu3, (fig. 17).
The seven peaks beginning at about 0.75 min all represent homocoupled model compound (molecular weight = 110 g/mol). This result shows that all of the possible structural isomers are contributing to the total product. The first set of peaks (retention times about 0.75-1.25 min) seems to represent isomers which are low in stability because they display an ion peak of 95 which corresponds to the loss of a methyl group from the unfragmented homocoupled product. Further fragmentation of the lower-stability isomers corresponds well to that of isomers displaying the molecular ion peak of 110. The second and third sets of peaks result from contributors which are more stable and display the molecular ion peak of 110. Possible isomers for the 3-chloro-1-butene homocoupling product are shown in figure 18.

![Isomers for 3-chloro-1-butene homocoupling product](fig. 18)
As stated earlier, speculation arose that the coupling could have been due to lithium metal or to the lithium naphthalenide which was used to reduce the copper in the copper complex to Cu°. In response to this, several experiments were performed during which the 3-chloro-1-butene was allowed to react only with the lithium naphthalenide; coupling of the model compound still was observed (fig. 19).
homocoupling of 3-chloro-1-butene
lithium naphthalenide only
fig. 19
As can be seen in figure 19, the coupling patterns for homocoupling of 3-chloro-1-butene are extremely similar for experiments run with and without the HSAC. Because coupling of the model compound was observed, attempts were made to extract the lithium naphthalenide from the reaction vessel once the copper mirror was generated. Although coupling still was observed in at least two separate attempts by Paul Jeng, I was unable to reproduce these results in six attempts. There are two possible reasons for this. First, although the contents of the vessel were ultracentrifuged before extracting the lithium naphthalenide in order to allow the Cu° to settle at the bottom, any slight movement of the vessel caused the Cu° to be suspended and, hence, potentially removed along with the lithium naphthalenide. Second, the lithium naphthalenide was removed and was replaced with new, freshly distilled THF many times and over a span of 10-20 min (this procedure was done slowly so as not to suspend the Cu°). Although the vessel was placed under an inert argon atmosphere, because these additions and removals were done via syringe (separate syringes), air or moisture may have entered the system and oxidized any existing Cu°, thereby destroying its coupling capabilities.

That HSAC alone can cause reductive coupling has been supported by the work which has been done with copper(II) formate. Solid metal complexes that are precursors of metal
mirrors are attractive for study because once the metal mirror is formed, it is generally the only component left in the reaction vessel (ligands are generally removed as vapor). Figure 20 shows homocoupling of 3-chloro-1-butene with copper(II) formate as the source of HSAC. As can be seen, the coupling patterns and the retention times of the isomers for the coupled product are quite similar to those demonstrated in previous coupling experiments (coupled product retention times - 0.773 min, 0.869 min, 0.916 min, 1.144 min, 1.096 min - not all isomers detectable in this trace).
3-chloro-1-butene homocoupling
copper(II) formate
fig. 20
PVC Reactions

Solid metal complexes that produce metal mirrors when heated are attractive as cross-linking agents for PVC because they can be incorporated into the polymer itself to induce cross-linking. It has been demonstrated (see table 1) that copper formate indeed does perform this task when incorporated into PVC. In each experiment, percentage cross-linking of PVC with copper(II) formate was enhanced relative to percentage cross-linking of the polymer alone. In each case, when copper formate was applied, the weight of copper metal used was calculated and was not used in the percentage yield calculations.

<table>
<thead>
<tr>
<th>trial #</th>
<th>PVC alone % cross-linking</th>
<th>PVC+Cu(II) formate % cross-linking</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>42</td>
<td>69</td>
</tr>
</tbody>
</table>

cross-linking of PVC

Table 1
Search for New Coupling Additives

The discovery of copper formate as a solid cross-linking additive for PVC has prompted the search for other, more realistic additives. Because PVC frequently is processed industrially at about 200 °C, cross-linking agents should decompose (form zerovalent metal) at higher temperatures in order to be considered as realistic fire-retardant additives for actual PVC systems; it would be most beneficial to have the zerovalent metal generated at temperatures which are characteristic of actual fires. Copper(II) formate decomposes at about 195 °C and, though it serves as a good model for future work, is probably not going to be commercially practical because of its low degradation temperature. Molybdenum(0) hexacarbonyl provides an excellent molybdenum mirror upon decomposition. Figure 21 shows the coupling patterns of 3-chloro-1-butene with molybdenum(0) hexacarbonyl as the coupling agent. Again, the coupling patterns and the retention times of the isomers for the coupled product are similar to those demonstrated in previous experiments. Molybdenum(0) hexacarbonyl actually couples 3-chloro-1-butene about three times as well as does copper(II) formate (see table 2) but, unfortunately, degrades at a low temperature.
3-chloro-1-butene homocoupling
molybdenum(0) carbonyl
fig. 21
<table>
<thead>
<tr>
<th>metal complex</th>
<th>% homocoupling of 3-chloro-1-butene</th>
<th>degradation temperature range (°C)</th>
<th>m or c*</th>
</tr>
</thead>
<tbody>
<tr>
<td>copper(II) formate</td>
<td>3-4</td>
<td>185-195</td>
<td>m</td>
</tr>
<tr>
<td>molybdenum(0) hexacarbonyl</td>
<td>11-12</td>
<td>130-155</td>
<td>m</td>
</tr>
<tr>
<td>copper(II) oxalate</td>
<td>0</td>
<td>300-320</td>
<td>c</td>
</tr>
<tr>
<td>copper(II) acetylacetonate</td>
<td>0</td>
<td>215-295</td>
<td>m</td>
</tr>
<tr>
<td>copper(II) ethyl acetoacetate</td>
<td>NT</td>
<td>175-195</td>
<td>m</td>
</tr>
<tr>
<td>copper(II) gluconate</td>
<td>NT</td>
<td>175-195</td>
<td>m</td>
</tr>
</tbody>
</table>

alternative metal complex coupling additives

Table 2

*m = mirror; c = char
NT = not tested because degradation temp. too low

40
Copper(II) oxalate and copper(II) acetylacetonate were found to degrade at desirable temperatures (see table 2) and, hence, were studied more extensively than the other additives. Copper(II) oxalate, however, did not form a copper mirror upon degradation and, not surprisingly, the degradation residue did not promote coupling of 3-chloro-1-butene. Copper(II) acetylacetonate, on the other hand, formed a copper mirror upon degradation, but this mirror did not promote coupling when it was exposed to 3-chloro-1-butene. Because of this negative result, several other procedures were performed on this additive. First, attempts were made to generate the copper mirror in the presence of the model compound. However, due to the low-boiling nature of 3-chloro-1-butene (bp 62-65 °C), this outcome was impossible to achieve with the apparatus available for use. Next, believing that the lack of coupling was due to some organic coating left over the copper mirror (a black residue was always observed which covered the mirror - the mirror was visible from the bottom side of the vessel), 0.15 g of copper(II) acetylacetonate was placed in the degradation apparatus and heated for about 20-30 min at 310 °C in a Wood’s metal bath in order to volatilize the organic residue; the black residue remained and, again, no coupling was observed. Finally, this procedure was repeated using a Bunsen burner as a heat source for 15 min, but still no coupling occurred.
Conclusions and Comments

The discovery of solid metal complexes useful as cross-linking additives for PVC may prove to be valuable technologically. The focus of much of the related work being done now at William and Mary is to find a complex with physical and chemical properties which will allow it to be used in commercial PVC formulations. The discovery of an innocuous additive which will allow burning PVC to demonstrate its inherent fire-resistance while at the same time prevent it from evolving smoke will prove to be exciting environmentally and with respect to public safety. This additive should also help to yield a char which is relatively easy to remove after a fire and will not promote damage to the environment if exposed to soil or river water.
REFERENCES


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