Mechanism of Polyvinyl Chloride) Stabilization by Studies with Model Compounds

Alain Michel[a]

[a] Laboratoire des Materieux Organiques, CNRS, Villeurbanne Cedex, France

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Mechanism of Poly(vinyl Chloride) Stabilization by Studies with Model Compounds

ALAIN MICHEL

CNRS, Laboratoire des Materieux Organiques
69626 Villeurbanne Cedex, France

ABSTRACT

4-Chloro-2-hexene can be considered a model compound for the chlorinated allylic structure appearing in PVC chains after dehydrochlorination. This model compound was used to elucidate the mechanism of reaction of primary or secondary stabilizers.

From the chemical point of view, the main problem of poly(vinyl chloride) stabilization is to prevent the zip dehydrochlorination which causes the discoloration and crosslinking of the polymer. At processing temperatures (170-200°C) and during the gelation and fusion phases it is practically impossible to prevent the elimination of the first hydrogen chloride molecule, whatever may be the radical or ionic nature of the initiation.

As shown in Eq. (1), after elimination of HCl, a chlorinated allylic structure appears in the PVC chains. 4-Chloro-2-hexene can be considered as a model structure and can be used to elucidate the mechanism of the reactions of primary or secondary stabilizers with the allylic chlorine atoms for the zinc-calcium stabilizing system [Eq. (2)].

By thermal degradation, the 4-chloro-2-hexene liberates HCl and hexadiene; the amount of these products can be easily followed by

361

Poly(vinyl chloride)

$$\sim\!\!-CHCl\!-\!\!\left[\!-CH_2\!-\!CH\!=\!CH\!-\!\!\underset{\displaystyle \mid}{\overset{\displaystyle \mid -HCl}{CH}}\!-\!CH_2\!-\!\right]\!\!-\!CHCl\!-\!\!\sim$$

$$Cl$$

(1)
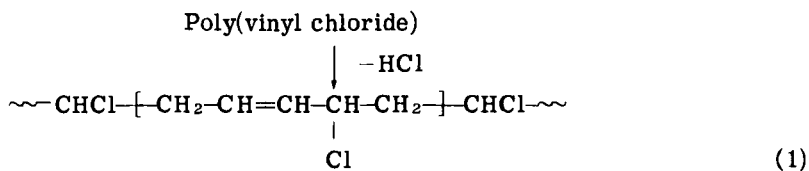
4-Chloro-2-hexene : model

compound of allylic chlorine atom

$$CH_3\!-\!CH\!=\!CH\!-\!\underset{\displaystyle \mid}{CH}\!-\!CH_2\!-\!CH_3$$

$$Cl$$

Thermal degradation

$$1/2^+ - - - - - - 1/2^+$$

$$CH_3\!-\!\!\left[\!-CH\!-\!CH\!-\!CH\!-\!\right]\!\!-\!CH_2\!-\!CH_3$$

$$Cl^{\,\delta\ominus}$$
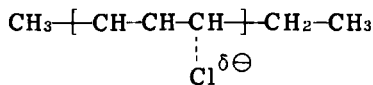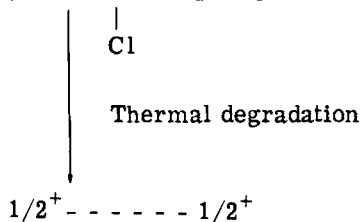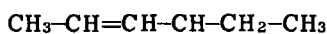
Elimination   Substitution in
                               presence of
                               stabilizers

Hexadiene + HCl $CH_3\!-\!CH\!=\!CH\!-\!CH\!-\!CH_2\!-\!CH_3$

$$R$$

(2)

$$2\ CH_3\!-\!CH\!=\!CH\!-\!\underset{\displaystyle \mid}{CH}\!-\!CH_2\!-\!CH_3\!-\ +\ Zn\!\!\underset{\displaystyle O\!-\!C\!-\!R}{\overset{\displaystyle O\!-\!C\!-\!R}{}}$$

$$Cl$$

$$2CH_3\!-\!CH\!=\!CH\!-\!\underset{\displaystyle \mid}{C}\!-\!CH_2\!-\!CH_3\!-\ +\ ZnCl_2$$

$$O$$

$$O\!=\!C\!-\!R$$
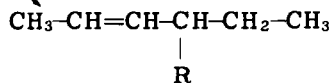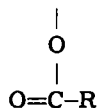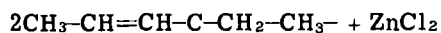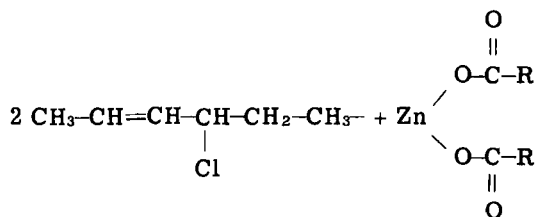
(3)
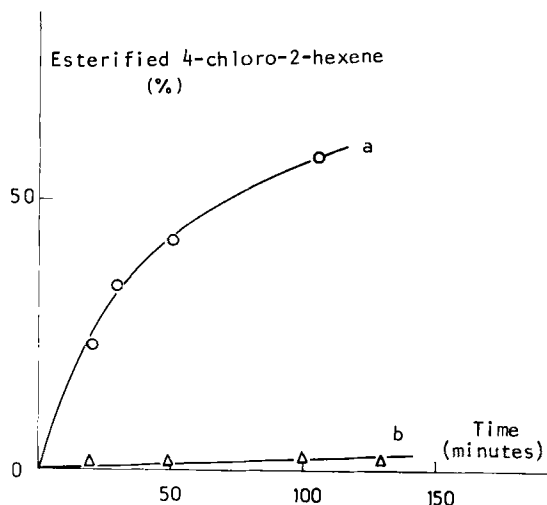
FIG. 1. Esterification of 4-chloro-2-hexene in the presence of zinc stearate in THF at 60°C: (a) without tributylphosphine; (b) in the presence of tributylphosphine. [4-Chloro-2-hexene]$_0$ = 215 mmole/liter; [Zn(OCOR)$_2$]$_0$ = 110 mmole/liter.

gaseous chromatography. In the presence of stabilizers there is a competitive substitution reaction; a quantitative estimate of it comes from the difference between 4-chloro-2-hexene consumption and hexadiene formation.

For example in the presence of zinc stearate, reaction (3) occurs.

This substitution reaction is catalyzed by zinc chloride; however, if this compound is complexed by tributylphosphine it does not occur (Fig. 1). Otherwise hydrogen chloride can react with the grafted ester group to regenerate the allylic chlorine atom according to Eq. (4).

This reaction is clearly supported by the data of Fig. 2, giving the amount of esterified 4-chloro-2-hexene versus time in nonstoichiometric conditions (curve B). By use of the model compound it has

$$CH_3-CH{=}CH-CH-CH_2-CH_3- \ + \ HCl \ \longrightarrow$$
$$\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad O$$
$$\qquad\qquad\qquad |$$
$$\qquad\qquad O{=}C-R$$

$$CH_3-CH{=}CH-CH-CH_2-CH_3- \ + \ RCOOH$$
$$\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad Cl \qquad\qquad\qquad\qquad\qquad (4)$$
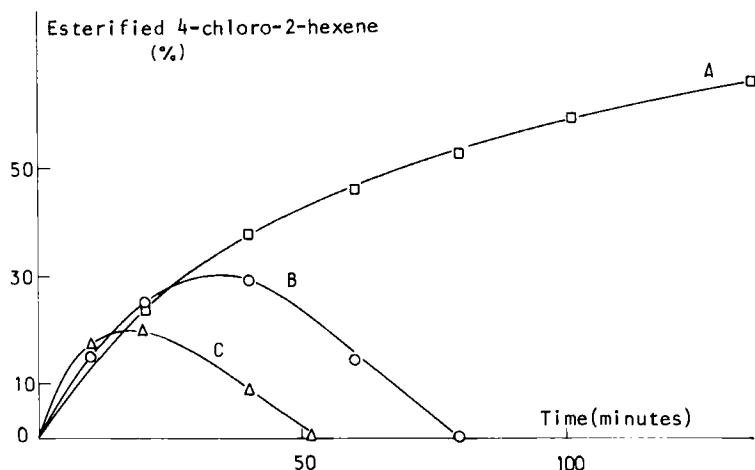
Esterified 4-chloro-2-hexene (%)
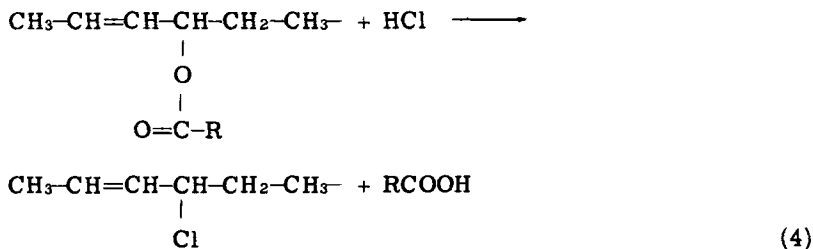
FIG. 2. Esterification of 4-chloro-2-hexene in the presence of zinc stearate (110 mmole/l.) in THF at 60°C: (A) [4-chloro-2-hexene] = 210 mmole/liter; (B) [4-chloro-2-hexene]$_0$ = 360 mmole/liter; (C) [4-chloro-2-hexene]$_0$ = 560 mmole/liter.

been possible to elucidate the reactions with different secondary stabilizers such as epoxy compounds, α-phenylindole and butanediol β-aminocrotonate.

Epoxy compounds such as epoxidized soya bean oil play two roles: first, they act as HCl acceptors according to the reaction (5):

$$\underset{/}{\overset{\backslash}{C}}\!-\!\underset{\backslash}{\overset{/}{C}} \ + \text{HCl} \longrightarrow \underset{/}{\overset{\backslash}{C}}\!-\!\underset{\backslash}{\overset{/}{C}} \tag{5}$$
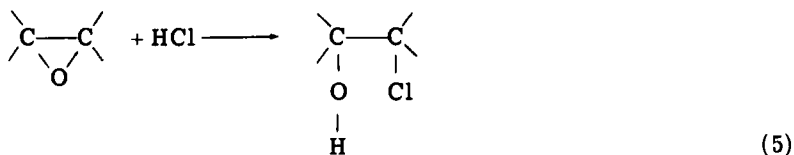
but this reaction does not prevent HCl elimination and consequently the polyene sequences formation; secondly, owing to their strong nucleophilic properties, the epoxy compounds can replace the allylic chlorine atom according to the reaction (6).

This reaction is again catalyzed by ZnCl$_2$ and prevents formation of polyene sequences and discoloration, but the α-chloro ether linkage is sensitive to HCl at temperatures as low as 60°C.

Epoxy compounds react with ZnCl$_2$ and prevent its catalytic effects in the presence of carboxylate soaps.

$$
\begin{array}{c}
\text{C}\!-\!\text{C} \\
\diagdown\text{O}\diagup
\end{array}
+ \text{CH}_3\!-\!\text{CH}\!=\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}_2\!-\!\text{CH}_3 \longrightarrow \\
\qquad\qquad\qquad\qquad\quad |\\
\qquad\qquad\qquad\qquad\text{Cl}
$$

$$
\text{CH}_3\!-\!\text{CH}\!=\!\text{CH}\!-\!\text{C}\!-\!\text{CH}_2\!-\!\text{CH}_3 \\
\qquad\qquad\qquad |\\
\qquad\qquad\quad \text{O}\\
\qquad\qquad\quad |\\
\qquad\qquad\; \text{C}\!-\!\text{C}\\
\qquad\qquad\quad |\\
\qquad\qquad\quad \text{Cl} \qquad\qquad\qquad\qquad (6)
$$
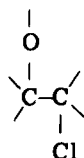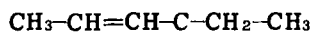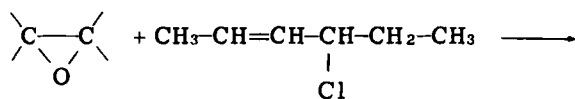
α-Phenylindole also reacts with allylic chlorine atoms and undergoes several successive substitutions on H_1, H_2, and H_3 [Eq. (7)].

$$
\text{R : CH}_3-\text{CH}=\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_3 \qquad\qquad (7)
$$

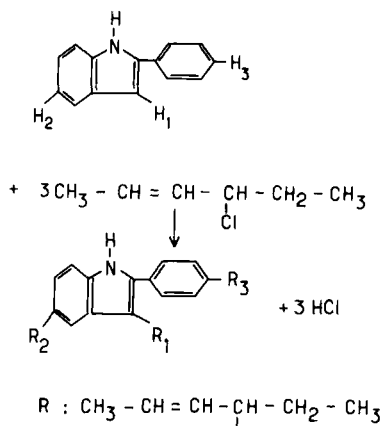These different reactions liberate HCl; the molar ratio must be well defined with carboxylate soaps to obtain the best synergistic effect. Substitution results in a carbon-carbon linkage which is less sensitive to HCl.

As shown by Tran Van Hoang [1], butanediol β-aminocrotonate can replace labile chlorine atoms according to reaction (8).

After the first substitution on the amino group there is a new structure which shows some similarity to the chemical structure of the α-phenylindole, and another substitution can take place [Eq. (9)].

It was also possible to use 4-chloro-2-hexene to explain the synergistic effects between carboxylate soaps such as zinc and calcium

$$\left[\begin{array}{c} CH_3\text{-}C\!\!=\!\!=\!\!C\text{-}C\text{-}O(CH_2)_2 \\ \quad | \quad\ | \ \| \\ \quad NH_2 \ \ H \ \ O \end{array}\right]_2 + 2\ CH_3\text{-}CH\!\!=\!\!CH\text{-}CH\text{-}CH_2\text{-}CH_3 \longrightarrow$$
$$Cl$$

$$\left[\begin{array}{c} O \\ \| \\ CH_3\text{-}C\!\!=\!\!CH\text{-}C\text{-}O(CH_2)_2 \\ | \\ HN \\ | \\ CH_3\text{-}CH\!\!=\!\!CH\text{-}CH\text{-}CH_2\text{-}CH_3 \end{array}\right]_2 + 2\ HCl \qquad (8)$$

$$CH_3\text{-}CH\!\!=\!\!CH\text{-}CH\text{-}CH_2\text{-}CH_3 \qquad + \ 2\ CH_3\text{-}CH\!\!=\!\!CH\text{-}CH\text{-}CH_2\text{-}CH_3 \longrightarrow$$
$$\begin{array}{c} | \\ N\text{-}H \quad O \\ Cl \end{array}$$
$$\left[\begin{array}{c} N\text{-}H \ \ O \\ | \ \ \ \| \\ CH_3\text{-}C\!\!=\!\!C\text{-}C\text{-}O(CH_2)_2 \\ | \\ H \end{array}\right]_2$$

$$CH_3\text{-}CH\!\!=\!\!CH\text{-}CH\text{-}CH_2\text{-}CH_3$$
$$| \\ N\text{-}H \ \ O$$
$$\left[\begin{array}{c} N\text{-}H \ \ O \\ | \ \ \ \| \\ CH_3\text{-}C\!\!=\!\!C\text{-}C\text{-}O\ (CH_2)_2 \\ | \end{array}\right]_2 + 2\ HCl \qquad (9)$$
$$CH_3\text{-}CH\!\!=\!\!CH\text{-}CH\text{-}CH_2\text{-}CH_3$$
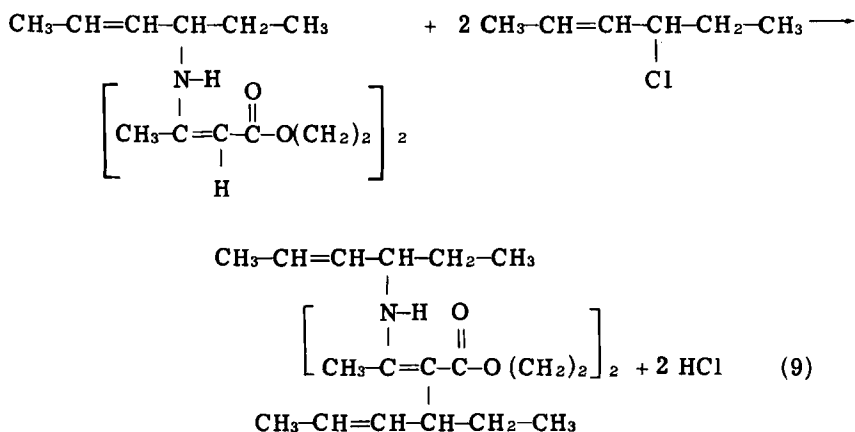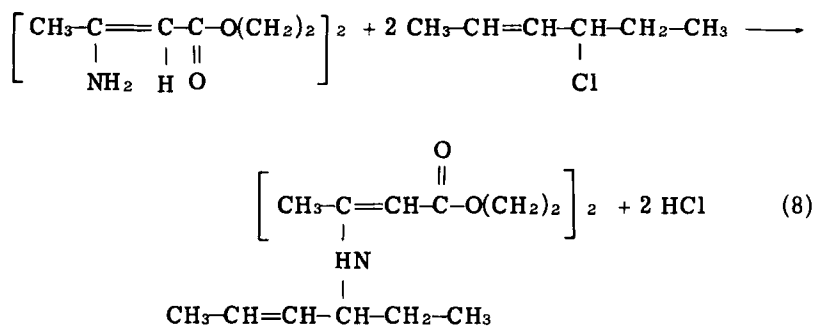
stearates. This last carboxylate does not react with model compound without the presence of $ZnCl_2$ which exchanges its ligands with calcium stearate to regenerate zinc stearate. This exchange reaction .is equilibrated, and the existence of a complex between zinc chloride and calcium stearate has been put in evidence. It may contribute to the partial inhibition of $ZnCl_2$ in the dehydrochlorination but its first role in the synergistic effect is the exchange reaction to regenerate zinc stearate which can replace allylic chlorine atom even in absence of $ZnCl_2$.

From a general point of view but in the particular case of the zinc-calcium stearate binary stabilizing system it is possible to determine the best molecular ratio between these compounds to reduce or prevent dehydrochlorination of the model compound, that is to say, to define the best conditions to prevent hexadiene evolution. From Fig. 3 we can see that for a Ca/Zn molar ratio of 5 the amount of evolved hexadiene is practically nil, but the esterification rate is the greater when this ratio is the smaller (Fig. 4).
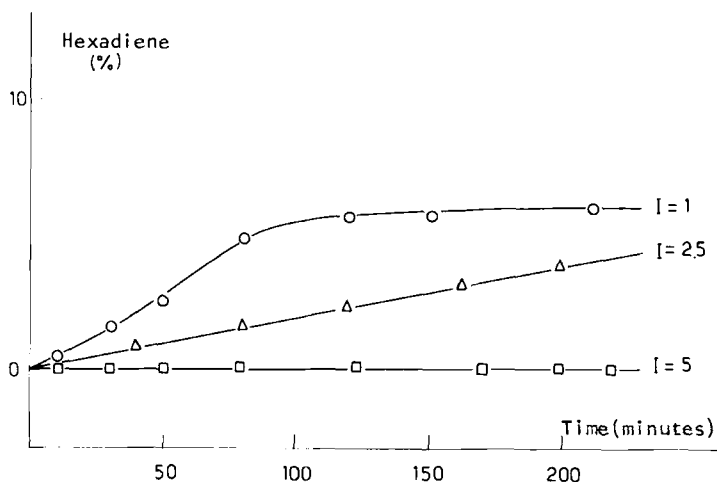
FIG. 3. Degradation of 4-chloro-2-hexene (320 mmole/l.) in the presence of zinc stearate and calcium stearate (160 mmole/liter) in THF at 60°C. I = [Ca(OCOR)$_2$] /[Zn(OCOR)$_2$].
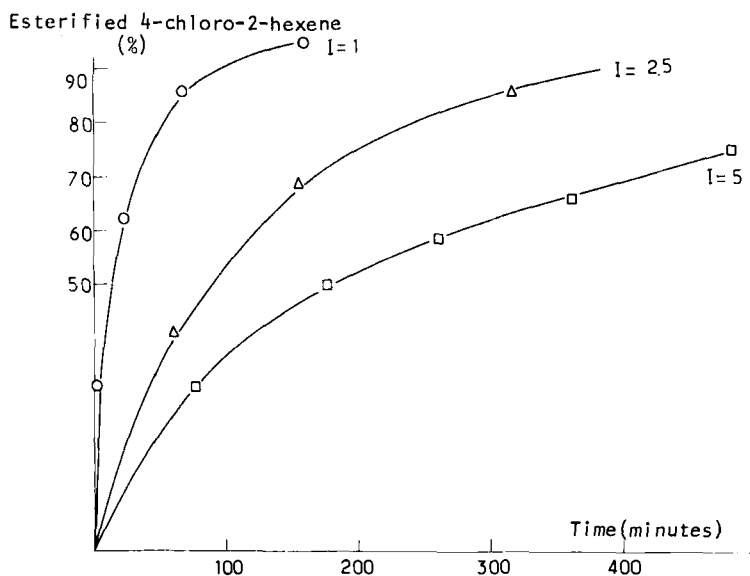

FIG. 4. Esterification of 4-chloro-2-hexene (320 mmole/liter in the presence of zinc stearate and calcium stearate (160 mmole/liter) in THF at 60°C.
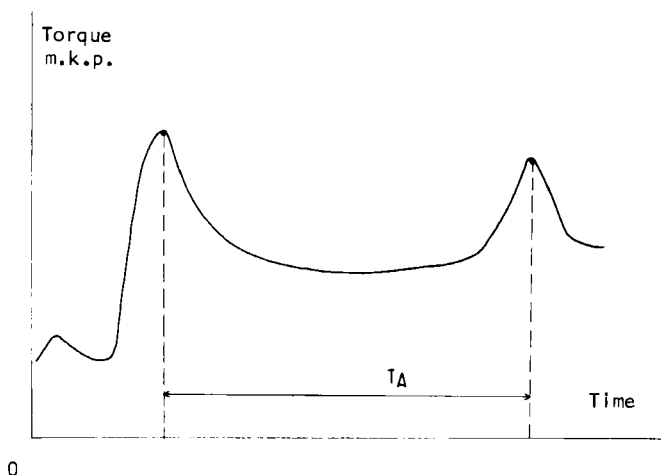
FIG. 5. Typical plastogram of PVC plasticized with dioctyl
phthalate (DOP) and stabilized with zinc stearate. PVC, 30 g; DOP,
9 g; Zn(OCOR)$_2$, 1.8 g.

Now the problem is to find a way to correlate the results obtained
with model compound to the polymer. With the Brabender Plasti-
corder it is possible to define one parameter, the so-called action
time of stabilizer, which represents the time between the maxima
of gelation and crosslinking peak (Fig. 5). This parameter includes
the influence of stabilizer but also the influence of by-products of
the stabilization reactions, and it is possible to compare its varia-
tions with the esterification yield of 4-chloro-2-hexene versus
the molecular ratio Ca/(Ca + Zn), the total amount of these two
stabilizers being kept constant. Figure 6 shows the similarity of
these two curves and suggests that the chemical reactions are the
same in both cases.

Finally, a new method for measurement of consumption of
carboxylates in the polymer has been developed on the basis of a
new analytical process involving metal chlorides titration by coulo-
metric method and carboxylic acid determination by a potentiometric
method in organic solvent.

From CaCl$_2$ or ZnCl$_2$ titration it is possible to follow the con-
sumption of calcium and zinc stearates by the plastogram obtained
with the Brabender Plasticorder at 190°C. Calcium chloride imme-
diately appears during gelation, and then its amount continuously
increases with time as does discoloration. In the same time, the
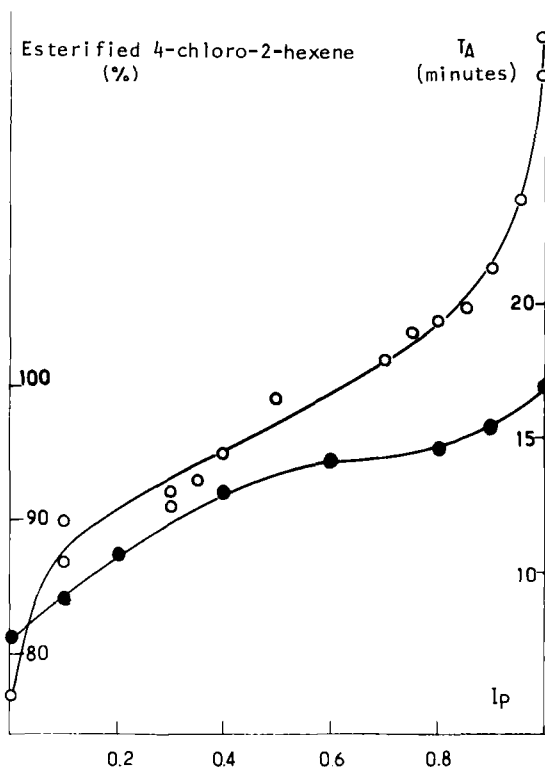amount of stearic acid increases more quickly, especially until

FIG. 6. Correlation between 4-chloro-2-hexene esterification and action time of stabilizer (T_A) for the stabilizing system zinc-calcium stearate: (o) T_A versus I_p; (●) 4-chloro-2-hexene esterification in THF at 60°C versus I_p. $I_p = [Ca(OCOR)_2] / \{[Ca(OCOR)_2] + [Zn(OCOR)_2]\}$; and $[Ca(OCOR)_2] + [Zn(OCOR)_2]$ = constant.

about 50% conversion; this suggests that calcium stearate acts only as a hydrogen chloride acceptor with the competitive formation of an intermediate organo compound, ClCaOCOR.

On the contrary, when zinc stearate is used alone, zinc chloride formation is very weak during the gelation phase; stearic acid formation is a little more important in the gelation phase and then is constant as zinc chloride during the fusion phase (Fig. 7). The cross-linking of PVC appears with ZnCl₂ liberation and all these results suggest that zinc stearate replaces allylic chlorine atoms in two
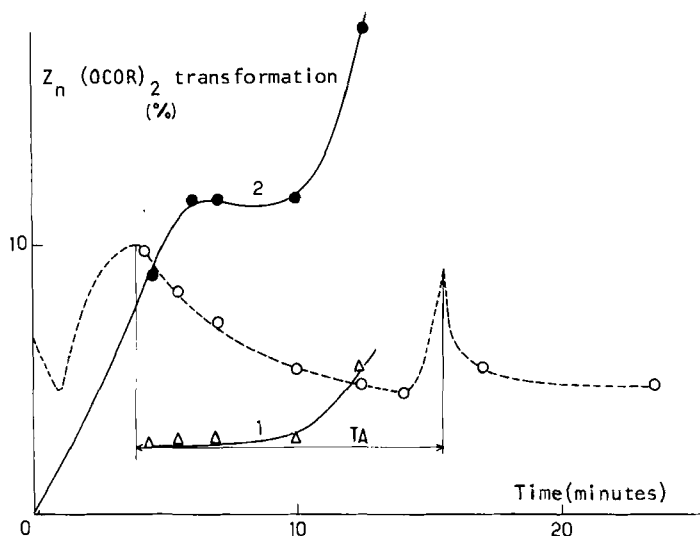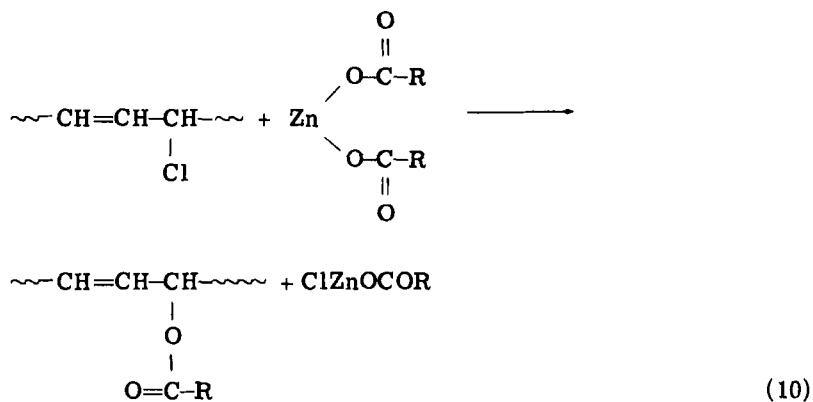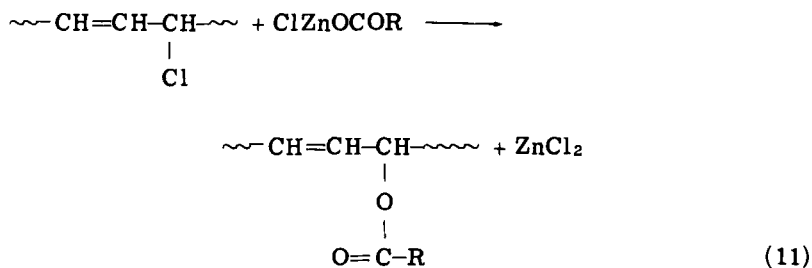
$Z_n(OCOR)_2$ transformation (%)

FIG. 7. Consumption of zinc stearate during heat and mechanical treatments at 190°C in Brabender Plasticorder: (1) from zinc chloride titration; (2) from stearic acid titration. PVC, 30 g; DOP, 9 g; $Zn(OCOR)_2$, 2 g.

steps, with formation of an intermediate organo compound according to the reactions summarized in Eqs. (10) and (11).

$$\sim\!\!\text{CH}=\text{CH}-\underset{\underset{\text{Cl}}{|}}{\text{CH}}-\!\!\sim \;+\; Zn\underset{\underset{\|}{\underset{O}{}}}{\overset{\overset{O}{\|}}{\underset{O-C-R}{O-C-R}}} \longrightarrow$$

$$\sim\!\!\text{CH}=\text{CH}-\underset{\underset{O=C-R}{\underset{|}{O}}}{\text{CH}}\!\!\sim\!\!\sim \;+\; ClZnOCOR \qquad\qquad (10)$$

$$\sim\text{CH}=\text{CH–CH}\sim + \text{ClZnOCOR} \longrightarrow$$

$$\sim\text{CH}=\text{CH–CH}\sim + \text{ZnCl}_2 \tag{11}$$
$$\underset{\underset{O=C-R}{|}}{\overset{|}{O}}$$

ZnCl$_2$ liberated in reaction (11) catalyzes the dehydrochlorination of PVC, and the HCl evolved may react with the organozinc compound but also with the grafted ester groups to regenerate labile chlorine atoms [Eq. (12)].

$$\sim\text{CH}=\text{CH–CH}\sim + \text{HCl} \longrightarrow \sim\text{CH}=\text{CH–CH}\sim + \text{RCOOH} \tag{12}$$
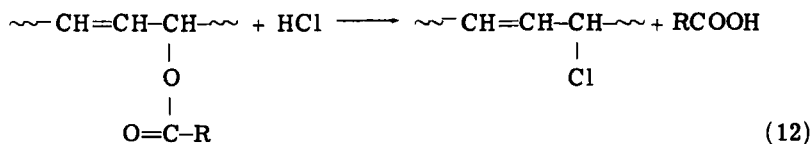
This reaction explains the simultaneous formation of ZnCl$_2$ and stearic acid as well as the autocatalytic degradation and crosslinking of the polymer.

REFERENCES

[1] T. V. Hoang, A. Michel, and A. Guyot, J. Macromol. Sci.–Chem., A12, 411 (1978).