New Insights into the Degradation Mechanism of Poly (vinyl chloride), Based on the Action of Novel Costabilizers. I.

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ABSTRACT: Recent legislation introduced to limit the use of heavy metal stabilizers (cadmium based) in poly(vinyl chloride) (PVC) has necessitated the use of organic costabilizers as adjuncts to alternative main stabilizer systems (barium/zinc or calcium/zinc). It has been suggested in the literature that costabilizers substitute allylic chlorine by a C-alkylation reaction; costabilizers act as reverse catalysts for the initiation of degradation by complexing the π-electron sites that would otherwise have an activating affect on labile chlorines; and costabilisers destroy carbonylallyl active sites by proton donation. To rationalize this debate, the focus of this paper is to elucidate the type of interactions that occur between a model compound for PVC and the novel costabiliser N-phenyl-3-acetylpyrrolidin-2,4-dione (P24D). The model compound chosen was 4-chloro-2-hexene (4C2H), which simulates the in-chain allylic chlorine impurities present in PVC and are considered the most labile defects present in the polymer. Results suggested that stabilisation involves concerted reactions involving metal complexes rather than a series of stepwise reactions. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2731–2743, 2004

Key words: poly(vinyl chloride); thermal degradation; stabilization; costabilizers; pyrrolidin-2,4 diones

INTRODUCTION

Although it is yet to be proven conclusively, stabilization mechanisms during the thermal processing of poly(vinyl chloride) (PVC) are widely believed to be ionic or quasiionic in nature.[1] Accordingly the course of degradation in PVC is likely to be of the same type, even if the literature reports claims to radical, ionic, and molecular (concerted) elimination mechanisms.

The main support for an ionic process arises from observations that HCl catalyzes degradation[2,3] and that the rate of DHC in solution is influenced by the dielectric constant of the solvent.[4] Starnes[5] has proposed an ion-pair mechanism to account for experimentally demonstrated polyenyl cations in degraded PVC, with the positive charge located preferentially at the center of the polyene sequences as chain length is increased. Along with Starnes, Martinsson and coworkers[6] suggest that allyl group deactivation would result from increased positive charge delocalization over the growing polyene sequence and this would limit sequence length (the limit on polyene sequence length has also been explained by Diels-Alder reactions between chains, cross-linking reactions, cyclization, and the readdition of HCl to long conjugated sequences).

The radical mechanism[7–9] seems to be supported by the accelerating effect of radical initiators[10] and presence of polyenyl radicals obtained by ESR spectroscopy.[11] Recently a polaron[12–14] mechanism has been proposed, i.e., the formation of a radical cation that is partially delocalized over several polymer segments. Furthermore the accumulation of degradation products would be important, since its formation depends on both HCl and double bond concentration. However, the presence of Lewis acids should promote polaron formation, though this would be more likely in the presence of a "cocatalyst", analogous to a Friedel-Crafts catalyst. It has been demonstrated that polarons appear only when conjugated double bonds are already formed in PVC chains, and the longer the sequence length the easier polaron formation becomes, becomes. since the polyene sequences generated have been formed in parallel reactions, the polaron mechanism cannot account for the experimental data because it requires the continuous formation of very long sequences.
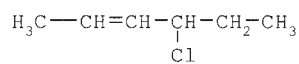
Materials

P24D

H₃C—CH=CH—CH—CH₂—CH₃
              |
              Cl

AND

H₃C—CH—CH=CH—CH₂—CH₃
      |
      Cl
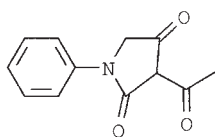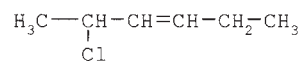
4-CHLORO-2-HEXENE AND
2-CHLORO-3-HEXENE

Results and discussion

REACTION 1

ZnSt₂

Add P24D (1: 2)

REFLUX 30 MINUTES

↓ **Add 4C2H (1:2:1)**
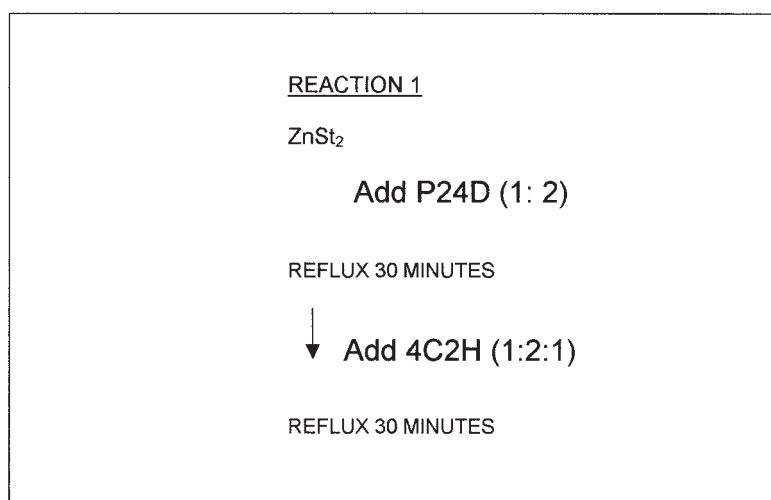
REFLUX 30 MINUTES

Figure 1 Flow chart of reaction 1.

Irrespective of the mechanism in vogue, degradation is generally believed to proceed from points of structural irregularity in PVC. Allylic chlorine has often been implicated as a labile site, though Ivan et al.[15] have demonstrated that, during the thermal degradation of PVCs containing increased concentrations of

REACTION 2

P24D

↓ **Add 4C2H (1:1)**

REFLUX 30 MINUTES

↓ **Add ZnSt₂ (1:1:2)**

REFLUX 30 MINUTES

Figure 2 Flow chart of reaction 2.

REACTION 3

4C2H

↓ **Add ZnSt₂ (2:1)**

REFLUX 30 MINUTES

↓ **Add P24D (2:1:2)**

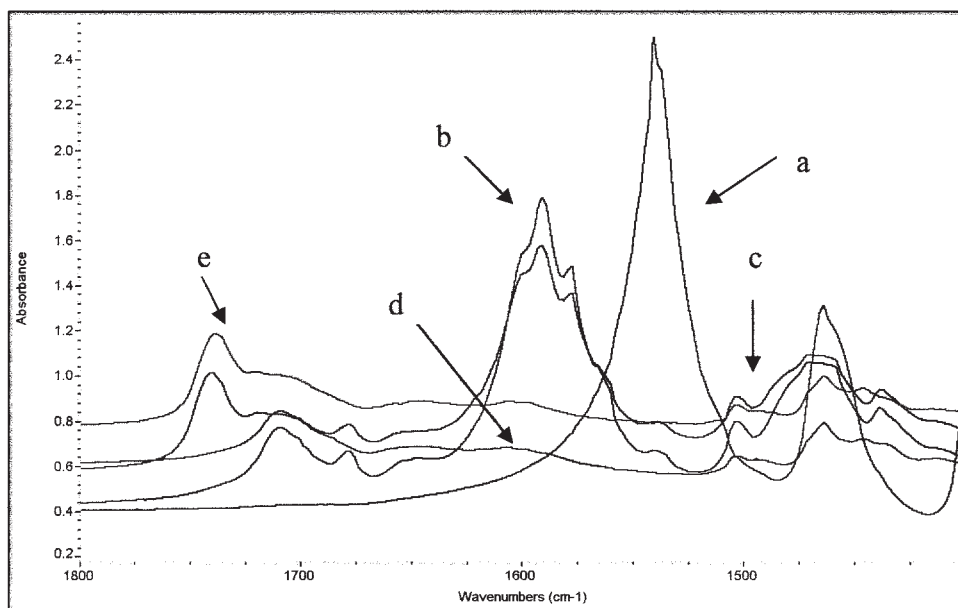REFLUX 30 MINUTES

Figure 3 Flow chart of reaction 3.

Figure 4 FTIR analysis for reaction 1: (a) $ZnSt_2$, (b) $ZnSt_2$ + P24D before, and (c) after heating, (d) $ZnSt_2$ + P24D + 4C2H before, and (e) after heating.

allylic chlorine adjacent to short polyenes, the activity of the chlorines is significantly lower that that of propagating polyenes and it is likely that allylic chlorines don't exist in the zip elimination processes at all.

Stabilization of PVC is achieved by the use of metal stabilisers (MS), along with organic costabilisers as adjuncts to this main stabiliser where required. All stabilisers increase the induction time to rapid DHC. It is important to recognize that, during the induction period, stabilisers do no inhibit the rate of initiation of DHC and that detectable amounts of short polyenes are formed, though propagation of polyenes is inhibited. At the end of the induction period there is a rapid increase in DHC and a sharp increase in the formation of long polyenes and cross-linked structures. This had led Ivan et al.[16] and Spiliopoulos et al.[17] to suggest a reversible blocking mechanism, which can explain the rapid increase in the rates of DHC, in the corresponding double bonds, and also the unchanged rate of formation of new initiating sites observed experimentally. In the presence of metal carboxylates, the carboxylate group would substitute allylic chlorines through an O-alkylation reaction. However, this substitution reaction is not permanent due to a reexchange caused by free HCl in which the ester is able to react even at room temperature to regenerate allylic chlorine atoms and carboxylic acid. However, other studies have shown that the number of ester groups grafted onto the polymer is insignificant[18,19] and that the shortening of the polyene sequences can be attributed to other causes (cyclization, etc.).

When used in conjunction with MS, auxiliary stabilisers further increase the induction time to rapid DHC, avoiding the autoaccelerating effect of HCl, providing good long-term stability, obstructing the sudden development of color and the cross-linking of PVC during processing. They can avoid the autocatalytic degradation, providing good long-term stability. Costabilisers form relatively stable complexes with the chloro derivatives of primary stabilisers (Lewis acids) and suppress their degradative effect. Nowadays, the
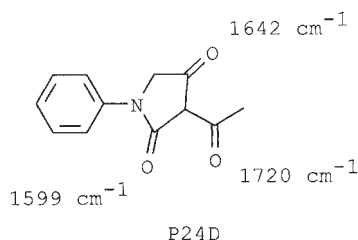
Scheme 1 FTIR wavelengths of P24D.
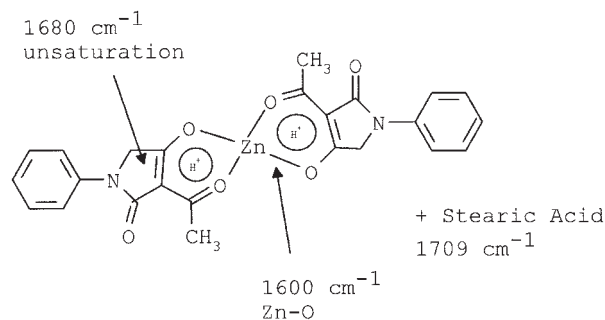
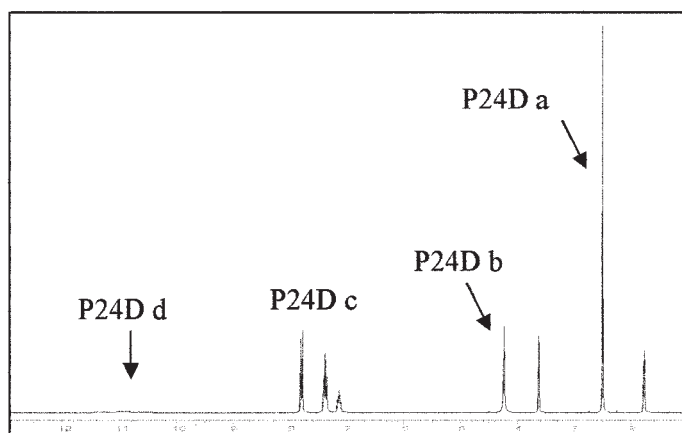**Scheme 2** Structural representation of P24D–Zn²⁺ complex.

Figure 5 ^{1}H-FTnmr spectrum of P24D.

term costabiliser has become more associated with materials that at relatively low levels enhance significantly the early color and midterm control of the PVC formulation.

In the absence of MS the costabilisers interact with HCl, substitute allylic chlorines, and complex prodegradant metal chlorides. According to Michel et al.,[20] the ability of a secondary stabiliser to permit or prevent metal chloride evolution defines a long- or short-term costabiliser. In the first case, the yellowing appears quickly from the onset of heating and develops slowly into an orange–brown color. In the second case the discoloration does not develop immediately, but the darkening does. Guyot et al.[21-24] suggest that costabilisers substitute allylic chlorines by a C-alkylation reaction and that $ZnCl_2$ facilitates grafting of the costabiliser to the PVC chain. In contrast, Grossman[25] has suggested that the costabilisers act as reverse catalysts for the initiation of degradation by complexing the π-electron sites that would otherwise have an activating effect on labile chlorines. Minsker et al. [26,27] have further proposed that costabilisers destroy carbonylallyl active sites by proton donation.

The shortening of polyene sequences might be caused by reasons other than stabilisation per se. The literature mentions the following possibilities: (1) cross-linking, such as Diels-Alder or intermolecular condensation[28,29] and (2) readdition of HCl.[30-32] Any compound that can shorten conjugated polyenes produces a noticeable effect on HCl elimination.

To rationalize this debate, the focus of this paper is to investigate the stabilisation route that the novel costabiliser N-phenyl-3-acetylpyrrolidin-2,4-dione takes in the presence of a model compound for PVC, e.g., 4-chloro-2-hexene (4C2H).

EXPERIMENTAL

Synthesis of 4-chloro-2-hexene(4C2H)

Synthesis of 2-hexen-4-ol

To a stirred solution of ethyl magnesium bromide in ether, a mixture of crotonaldehyde (84.11 g, 1.2 mol) in dry ether (100 ml) in a freezing mixture of crushed ice and anhydrous calcium chloride was added dropwise. The reaction product was poured upon crushed ice and the basic magnesium bromide was dissolved by addition of 100 ml of 15% sulphuric acid. The aqueous layer was separated from the ethereal solution with four 50-ml portions of ether, which was then left to dry overnight over anhydrous potassium carbonate. After filtering and removing the ether, the final product was distilled under reduced pressure (90–95°C at 130
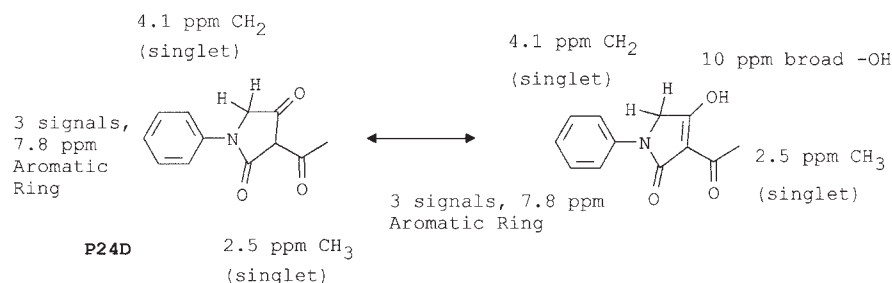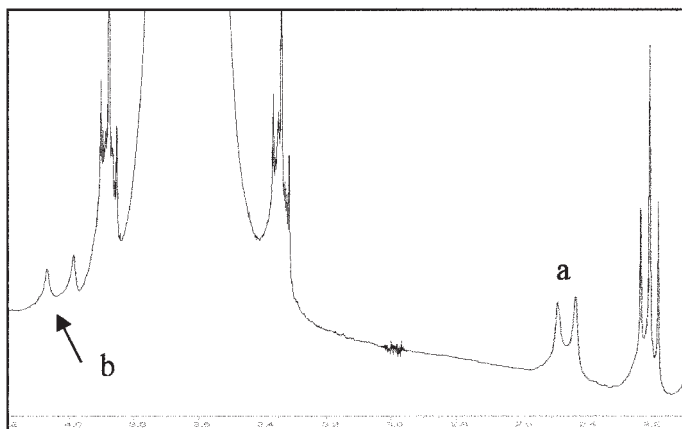

Scheme 3 NMR data of P24D

Figure 6 ^{1}H-FTnmr spectrum of sample ZnSt$_2$ + P24D before heating.

mmHg). The 2-hexen-4-ol is a colorless liquid with a strong odor.

IR : ν (cm^{-1}) (neat) : OH (3351.79), CH=CH (3030.28, 975.62) δ_H (ppm) (CDCl$_3$) 5.6 (1H, m, CH=CH), 5.49 (1H, m, CH=CH), 3.9 (1H, q, CHOH), 2.5 (1H, s, COH), 1.7 (3H, d, CH$_3$—CH=CH),1.68 (2H,q, CH$_2$—CH$_3$), 0.91 (3H, t, CH$_2$—CH$_3$)

Synthesis of 4-chloro-2-hexene

A mixture of 2-hexen-4-ol (40.1 g, 0.4 mol) with pyridine (15.8 g, 0.2 mol) was added dropwise with stirring, to phosphorous trichloride (54.8 g, 0.4 mol) at 0°C temperature. The mixture was left for 12 h at room temperature with continuous stirring until an upper organic layer separated, which was distilled under reduce pressure (45–50°C at 80 mmHg). The product obtained was also a colorless liquid with a strong odor.

IR : ν (cm^{-1}) (neat) : CCl (643.74, 589.98), CH=CH (3030.28, 964.15) δ_H (ppm) (CDCl$_3$) 4.53 (1H, m, CHCl),

4.2 (1H, m, CHCl), 1.8 (2H, m, CHClCH$_2$), 1.56 (3H, d, CH$_3$CHCl).

Samples for the model compound studies were prepared in a concentration of 0.1M in THF, where 0.1M corresponded to 1 in the 1 : 2 ratio.

Fourier-transform infrared analysis

Samples taken from the reaction mixture were left to dry in a desiccator. The FTIR spectra were carried out in KBR pellets on a Nicolet Nexus 670/870 at an average of 64 scans and at a resolution of 4 cm^{-1}.

Fourier-transform nuclear magnetic resonance analysis

For the identification of the products, ^{1}H spectra were obtained by using a Jeol 270 MHz FT-NMR spectrometer. The samples were used directly from the reaction vessel and contained THF and a few drops of deuterated THF. Therefore the broad bands observed at 1.75
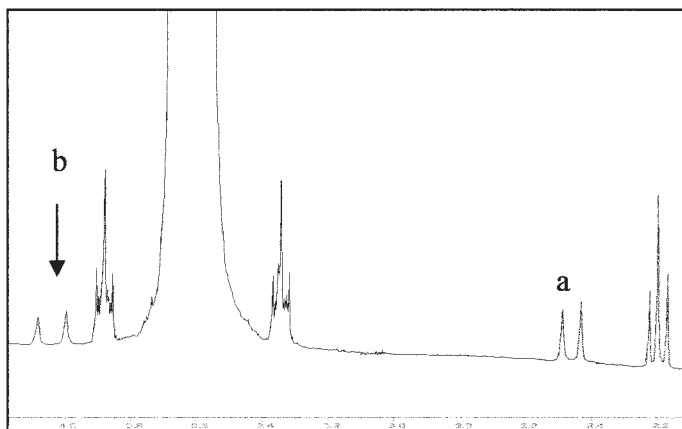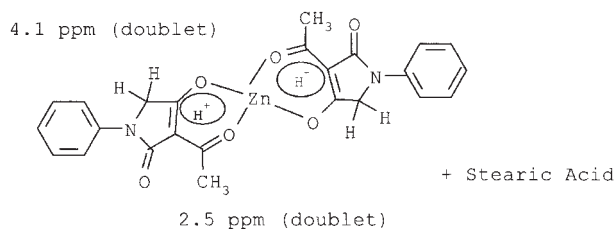

Figure 7 ^{1}H-FTnmr spectrum of sample ZnSt$_2$ + P24D after heating.

4.1 ppm (doublet)

Scheme 4   NMR data of complex P24D–Zn^{2+}.

and 2.6 ppm correspond to the two solvents peaks of THF. Chemical shifts are expressed in ppm with reference to tetramethylsilane.

Materials

N-phenyl-3-acetylpyrrolidin-2,4-dione (P24D) and zinc stearate were supplied by Akcros Chemicals (Akzo Nobel). d$_8$-THF was obtained from Gross Scientific Instruments Ltd.

RESULTS AND DISCUSSION

To study all of the individual interactions, three different combinations were carried out, as indicated by the following flow charts (Figs. 1, 2, and 3).

In reaction 1, P24D was added to a solution of ZnSt$_2$ in THF in a 1 : 2 Zn^{2+}/P24D ratio. As can be seen by the FTIR analysis (Fig. 4), on addition of P24D there is strong evidence that suggests the formation of a complex between P24D and Zn^{2+} even on simple mixing. This complex is characterized by the evolution of two bands at 1,680 and 1,600 cm^{-1} (Scheme 1). The former is attributed to the unsaturation formed due to the coordination with the metal, whereas the latter is indicative of the interaction of the metal with the carbonyl groups of P24D. Due to this coordination, the band at 1,642 cm^{-1} of P24D seems to have shifted

toward higher wavelengths and the band at 1,720 cm^{-1} due to the 3-acetyl group is overlapped with the band attributed to the stearic acid (1,709 cm^{-1}) evolved as a result of the complexation. A structural representation of this complex is given in Scheme 2.

This structure is largely unchanged on heating. However, on addition of the model compound, the two bands assigned to the complex (1,680 and 1,600 cm^{-1}) disappear, suggesting the breaking up of the complex and subsequent C-alkylation reaction between P24D and 4C2H. A new broad band between 1,690 and 1,760 cm^{-1} can then be seen. In view of these facts, it can be inferred that the locking of P24D is immediate in the presence of the model compound, as well as stable despite the heat treatment. Moreover, the evolution of the band based at 1,740 cm^{-1} reveals that, not only the C-alkylation reaction takes place, but also the substitution of the allylic chlorine with the more stable ester groups of the zinc stearate. This fact may also imply a somewhat strong competition for the labile sites.

The ^{1}H-FTnmr spectrum of P24D in Figure 5 shows two singlet peaks at 2.5 (P24D a) and 4.1 ppm (P24D, b) attributed to the CH$_3$ and CH$_2$ groups, respectively. The three peaks between 7 and 8 ppm are assigned to the three kinds of protons in the aromatic ring (P24D c). A broad absorption band above 10 ppm corresponds to the enol form of the costabiliser (P24D d); this indicates that the P24D exists mainly as the enol form at room temperature (Scheme 3). Figures 6 and 7 show quite distinctively two doublets at 2.5 [Figs. 6(a) and 7(a)] and 4.05 ppm [Figs. 6(b) and 7(b)] attributed to the CH$_3$ and CH$_2$ groups of P24D, respectively. These doublets are assigned to the complex. As was inferred from the FTIR analysis, the complex is stable under refluxing (Scheme 4). On addition of the 4C2H (Fig. 8) the doublets become singlets [2.5 ppm, Fig. 8(a); 4.1 ppm, Fig. 8(b)], indicating the decomposition of the complex. At the same time, a triplet based at
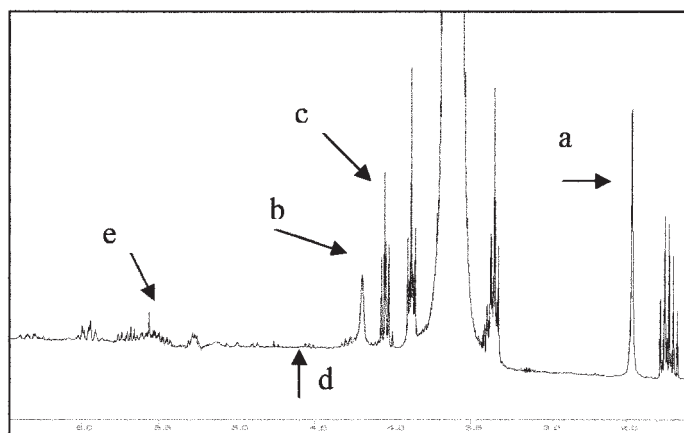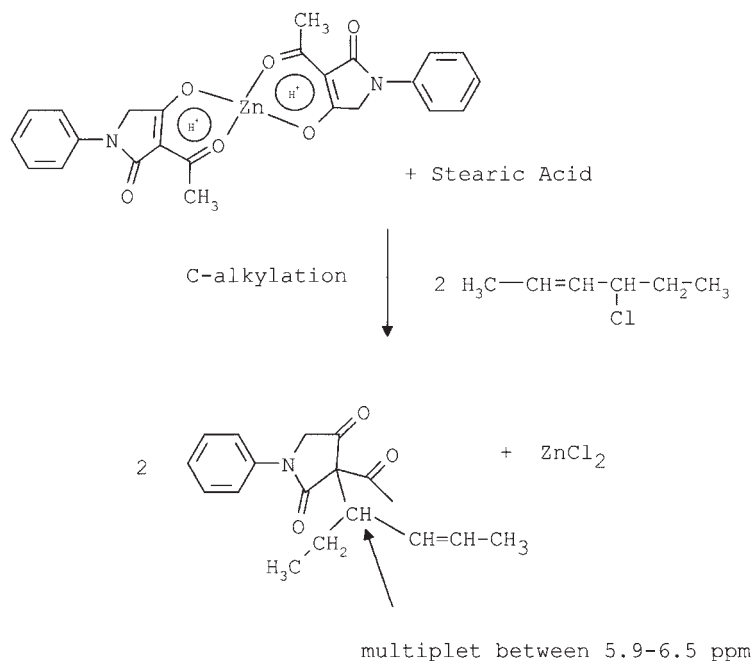

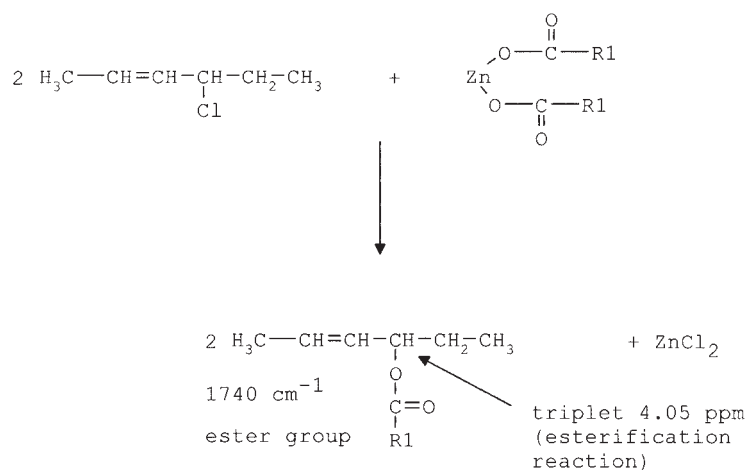**Figure 8** ^{1}H-FTnmr spectrum of sample ZnSt$_2$ + P24D + 4C2H before heating.

Scheme 5 C-alkylation reaction.

4.05 ppm evolves [Fig. 8(c)], and the multiplet at around 4.5 ppm due the CH in the 4C2H seems to disappear [Fig. 8 (d)]. The disappearance of this band is concomitant to the evolution of multiplets between 5.9 and 6.5 ppm due to the locking of P24D [Fig. 8 (e)].

It emerges from these results that, on addition of the model compound, the P24D–Zn^{2+} complex breaks down and there seems to be a strong competition for the allylic chlorine since both the C-alkylation reaction (multiplet between 5.9 and 6.5 ppm) (Scheme 5) and the esterification reaction (triplet at 4.05 ppm and infrared band at 1,740 cm^{-1}) (Scheme 6) take place on simple mixing. After refluxing, no changes were observed, except for the two new multiplets above 6

ppm that appeared better outlined (Figure 9). This may indicate that the heat treatment facilitates the C-alkylation reaction to reach a higher degree of conversion.

In the second reaction, when the model compound was added to a solution of P24D in THF in 1 : 1 ratio, no changes were observed in the FTIR spectra (Fig. 10), despite the heat treatment. This indicates that P24D does not interact with the model compound on its own. On addition of the metal soap, the spectrum exhibits a broad band centerd at 1,700 cm^{-1} that can be ascribed to the stearic acid formed. The band due to the 3-acetyl group of P24D (1,720 cm^{-1}) has shifted and is now embedded in the broad band at 1,700
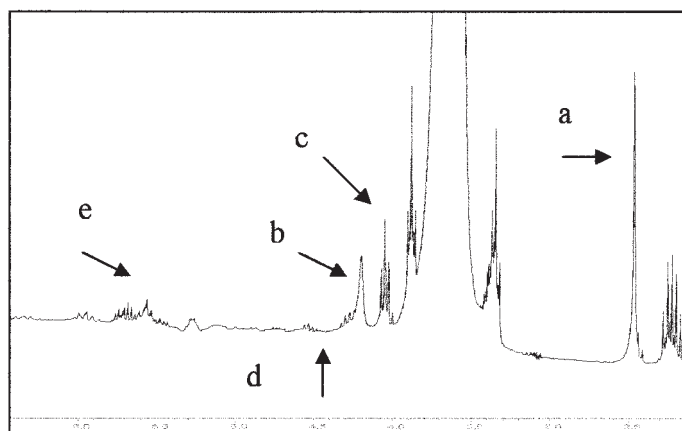

Scheme 6 Esterification reaction.

Figure 9 ^{1}H-FTnmr spectrum of sample ZnSt$_2$ + P24D + 4C2H after heating.

cm^{-1}. Furthermore, the bands at 1,640 cm^{-1} and 1,600 cm^{-1} due to P24D also seem to shift. After refluxing, the evolution of a band at 1,740 cm^{-1} can be observed, which may correspond to the stretching vibration of the COO$^-$ group due to the esterification reaction between the model compound and ZnSt$_2$. Despite the fact that all three bands of P24D seem to have shifted, there is no clear indication of the complex occurring.

The ^{1}H-FTnmr analysis shows in Figure 11 two singlets at 2.5 [Fig. 11 (a)] and 4.2 ppm [Fig. 11 (b)] due to P24D. The multiplet of 4C2H ($-$C*H*Cl) at 4.55 ppm [Fig. 12(c)] suggests that, despite refluxing, P24D is unable to substitute the chlorohexene on its own, i.e., to do so requires the planar conformation derived from the coordination with the metal. On addition of

the zinc stearate (Fig. 13), despite the poor quality of the spectrum, both singlets [Figs. 13 (a and b)] due to P24D can again be seen. The three peaks above 7 ppm [Fig. 13 (c)] are due to the three kinds of protons in the aromatic ring of P24D. After the heat treatment (Fig. 14), the spectrum reveals the presence of a triplet above 4 ppm [Fig. 14(a)] (esterification reaction) and two multiplets between 5.9 and 6.4 ppm [Fig. 14(b)]. Previous work[33] has suggested that the appearance of multiplets between 5.9 and 6.4 ppm was indicative of the C-alkylation reaction between P24D and 4C2H. However, the present results imply that the esterification reaction also gives rise to the same type of multiplets. In this instance, there is little evidence of the complex taking place, therefore the multiplets observed around 6 ppm can be attributed to the chemical
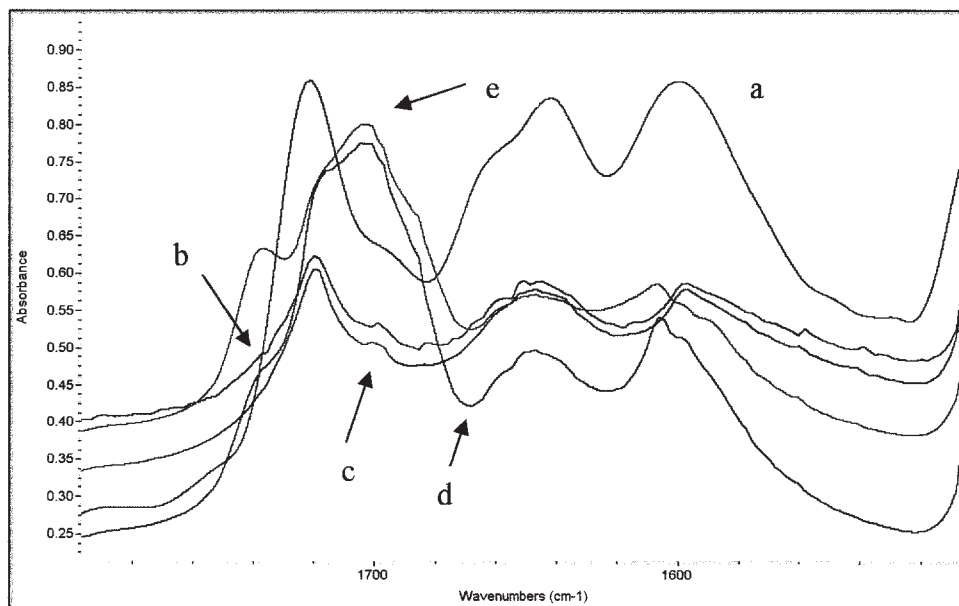

Figure 10 FTIR analysis for reaction 2: (a) P24D, (b) P24D + 4C2H before and (c) after heating, (d) P24D + 4C2H + ZnSt$_2$ before and (e) after heating.
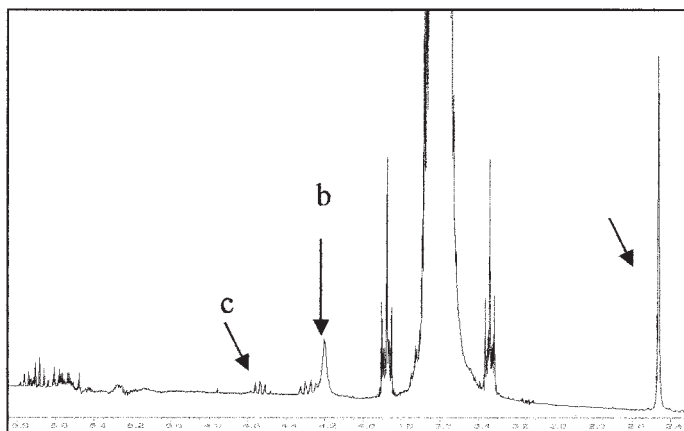
Figure 11 [1]H-FTnmr spectrum of sample P24D + 4C2H before heating.

shift of the C*H*=C*H* protons due to the presence of the ester groups. In fact, evidence for the esterification reaction can also be found in the FTIR analysis, from the band at 1,740 cm^{-1} that seems to evolve only after reflux.

In reaction 3 the FTIR analysis (Fig. 15) shows that the addition of zinc stearate to a solution of 4C2H in 2 : 1 ratio in THF led to the substitution of the allylic chlorine by the more stable ester group. As a result of this reaction, a sharp band emerging at 1,740 cm^{-1}
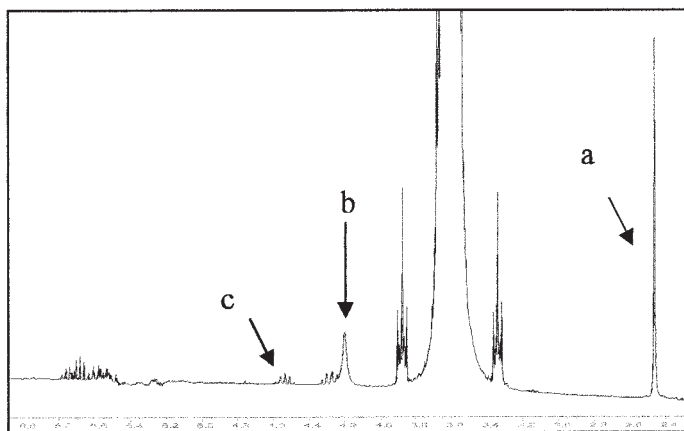

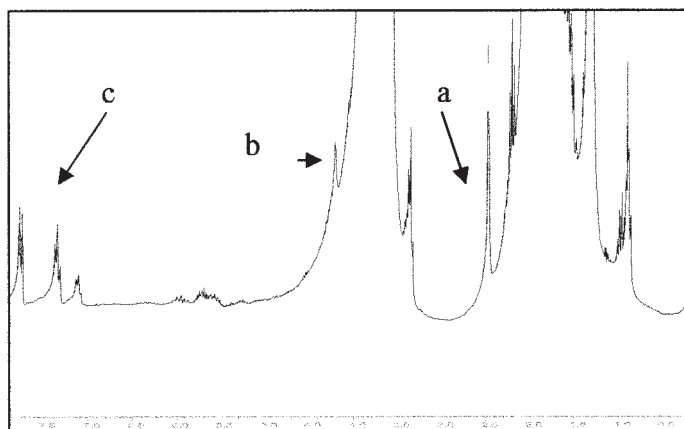**Figure 12** [1]H-FTnmr spectrum of sample P24D + 4C2H after heating.

Figure 13 [1]H-FTnmr spectrum of sample P24D + 4C2H + ZnSt$_2$ before heating.
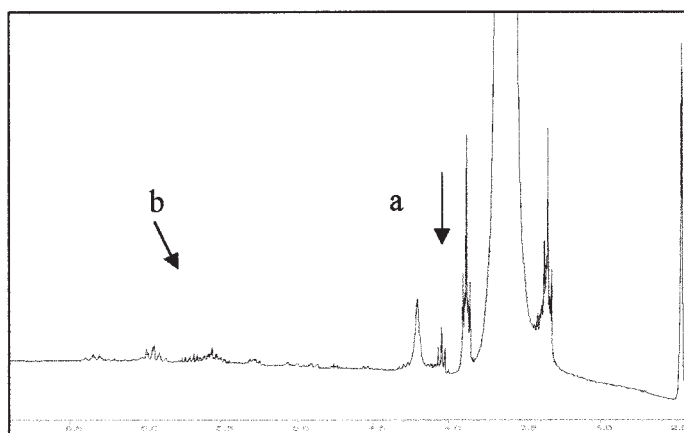
Figure 14   ¹H-FTnmr spectrum of sample P24D + 4C2H + ZnSt$_2$ after heating.

was attributed to the stretching vibration of the COO⁻ group. The infrared spectra also shows that the zinc stearate can interact with some of the HCl released from the model compound prior to heating, leading to the formation of stearic acid; hence the band at 1,705 cm^{-1}. Even the band at 1,452 cm^{-1} due to the stretching of CH in the model compound seems to have shifted toward a higher wavelength due to the esterification reaction. In addition, the double bond of the 4C2H appears now at 1,607 cm^{-1}, as a result of the substitution reaction. The new structure seems stable under the refluxing conditions and the addition of P24D does not appear to have any effect even under further heating.

The ¹H-FTnmr analysis shows in Figure 16 the evolution of a multiplet at 4.05 ppm [Fig. 16(a)], assigned to the C*H*—OCO—R group in the model compound, due to the esterification reaction. After the heat treatment no changes were observed (Fig. 17) and on addition of P24D (Fig. 18) both characteristics singlets [Figs. 18(a and b)] could again be observed. However, owing to the fact that most of the zinc stearate has been consumed, no complex can be formed and, therefore, no changes were observed even on further heating (Fig. 19).

From the results obtained above it can be concluded that zinc stearate is more reactive toward allylic chlorines than previously observed, and, in order for the complex P24D–Zn^{2+} to take place, no allylic chlorine must be present, since it would appear that the reactivity of the zinc stearate toward this labile site is greater than toward complexation. Therefore, the fol-
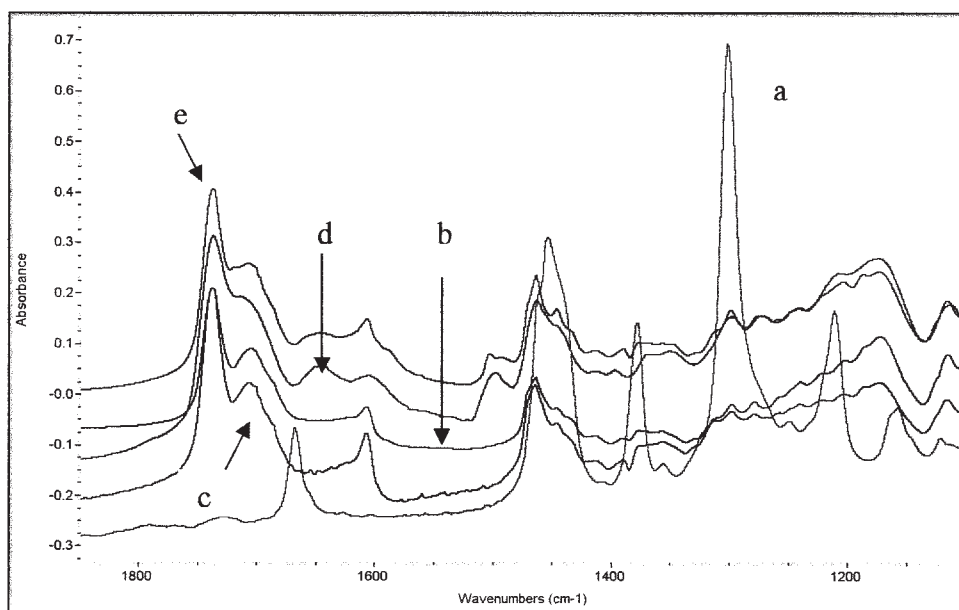

Figure 15.   FTIR analysis for reaction 3: (a) 4C2H, (b) 4C2H + ZnSt$_2$ before and (c) after heating, (d) 4C2H + ZnSt$_2$ + P24D before and (e) after heating.
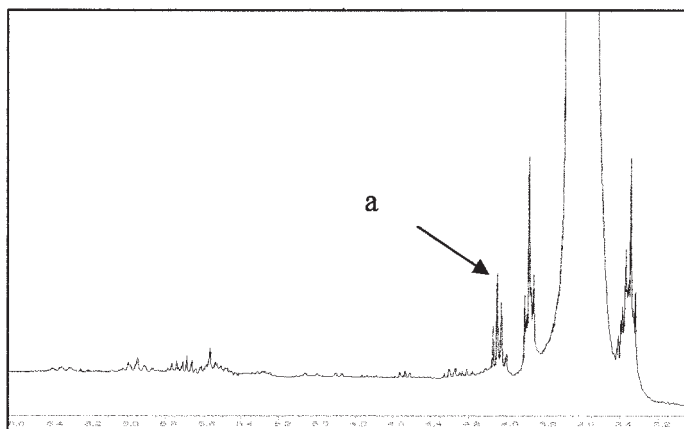
Figure 16 ^{1}H-FTnmr spectrum of sample 4C2H + ZnSt$_2$ before heating.

lowing mechanism can be proposed as to the reaction path for the locking of P24D across the PVC chain (Scheme 7).

CONCLUSION

It is likely that, in the early stages, PVC degradation is dominated by unimolecular elimination via a con-certed mechanism. As the concentration of HCl builds up in the presence of ZnSt$_2$, stearic acid and ZnCl$_2$ are generated. At higher concentrations of HCl the "acid-catalyst" H$^+$ZnCl^{3-} is formed (analogous to the AlCl$_3$–HCl Friedel-Crafts superacid catalyst). This has an acid strength capable of protonating a double bond in a short polyene sequence, resulting in the formation of a resonance-stabilised polyenyl-cation/radical-cat-
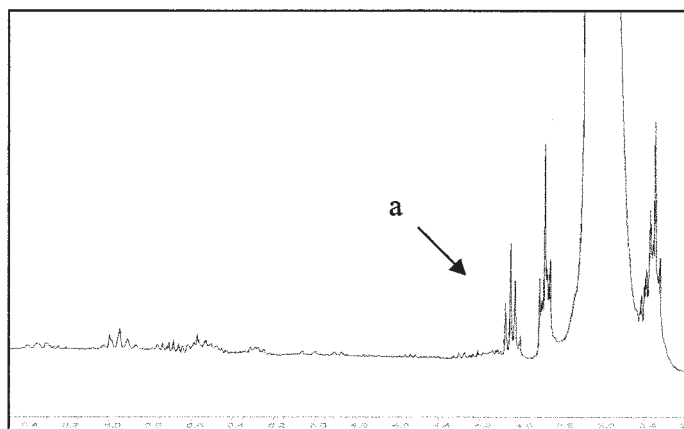

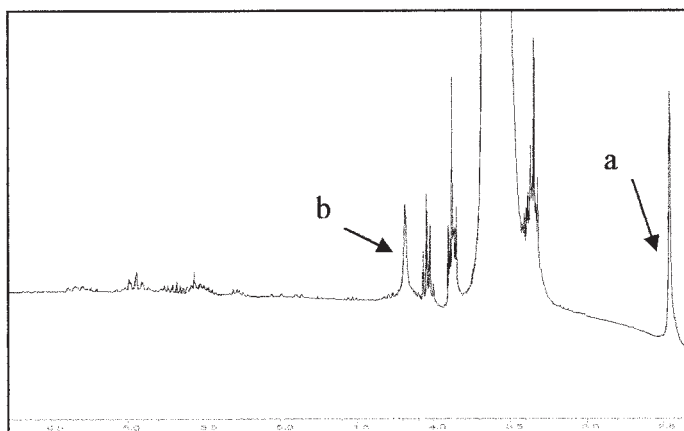**Figure 17** ^{1}H-FTnmr spectrum of sample 4C2H + ZnSt$_2$ after heating.

Figure 18 ^{1}H-FTnmr spectrum of sample 4C2H + ZnSt$_2$ + P24D before heating.
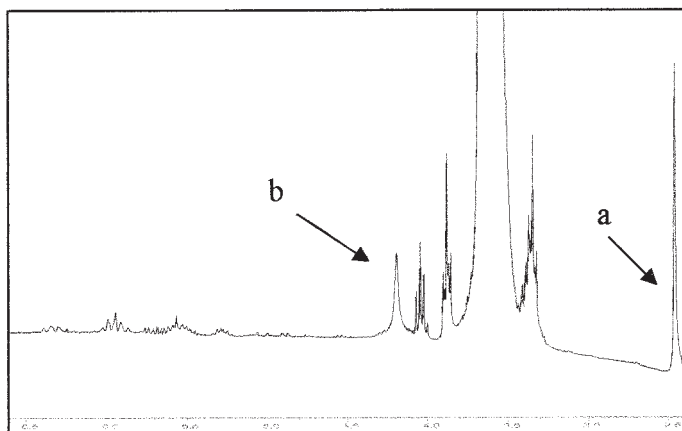
Figure 19 ^{1}H-FTnmr spectrum of sample 4C2H + ZnSt$_2$ + P24D after heating.

ion. The polyenylcation/radical-cation thus formed can then participate in the cyclization and cross-linking reactions, which lead to the rapid blackening of the PVC.

A long-term costabiliser inhibits the formation of the "acid-catalyst" by complexing any ZnCl$_2$ formed. However, ZnCl$_2$ builds up during the course of degradation as more HCl is released, if it is appreciated that stabilisers have no effect on the rate of initiation. This leads to a gradual build up of color in the PVC. The ZnSt$_2$ complexes with double bonds in the PVC

chain, preventing the formation of the polyenyl-cation/radical-cation.

A short-term costabiliser forms a complex with ZnSt$_2$ preventing its reaction with HCl and leads to the formation of ZnCl$_2$ in the early stages of degradation. The costabilizer–Zn^{2+} complex can then interact with double bonds and, therefore, a reason for the enhanced performance of the complex would be to facilitate grafting of the costabiliser to the PVC chain by a Diels-Alder reaction with conjugated dienes
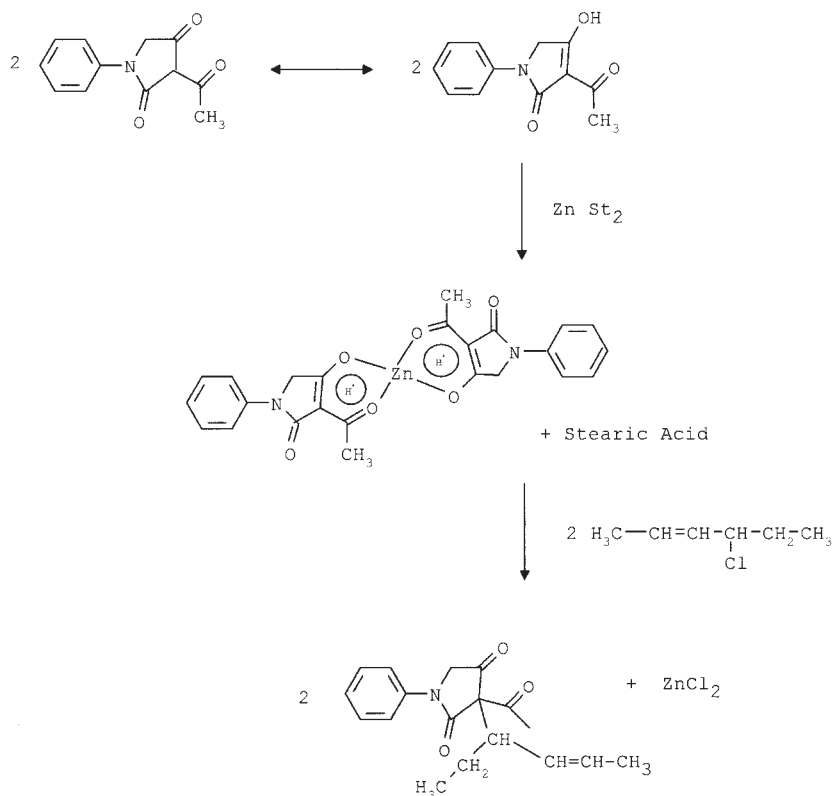
Scheme 7   C-alkylation mechanism for the interaction between P24D and 4C2H.
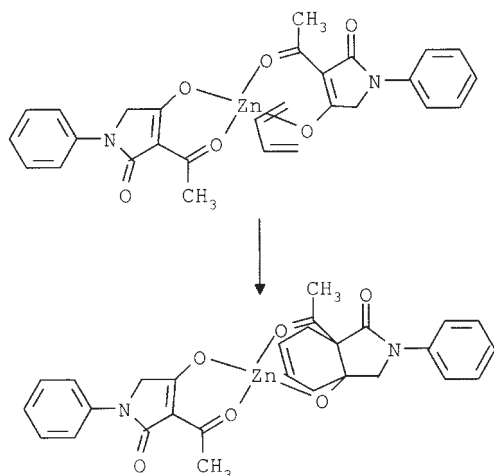
Scheme 8 Schematic interaction of the complex P24D–Zn^{2+} with a diene.

(Scheme 8). As the concentration of HCl builds up, complex stability is reduced and the zinc is suddenly released, leading to the rapid formation of ZnCl$_2$ and an abrupt blackening of the PVC. The role of Zn^{2+} is that of a Lewis acid, which forms a P-complex with conjugated dienes leading to stability in the early stages of degradation. ZnCl$_2$ also complexes with 4C2H though it acts only as prodegradant via its superacid H*ZnCl^{3-}. Such a mechanism would support observations that suggest that the grafting of the costabilisers is limited. Following this line of thought, it seems crucial to ascertain the optimal P24D/Zn^{2+} ratio; the factor that can determine the route that the stabilisation mechanism is going to take.

If the nature of the degradation is more quasiionic in nature, i.e., radical-cations are formed, then this could go further to explain why even in the absence of metal stearate stabilisers, costabilisers such as Uracil are effective. The fact that only those Uracil analogues, which are electron-deficient useful stabilisers, suggests that they operate as electron traps.

Whether carbonylallyl sites or allylic chlorines are there in PVC, they are unlikely to be as important as the presence of conjugated dienes, since it appears that the stabilisation involves concerted reactions involving metal complexes rather than a stepwise series of reactions.

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