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Polaron Mechanism in the Thermal Degradation and Stabilization of Poly(Vinyl Chloride)

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Polaron Mechanism in the Thermal Degradation and Stabilization of Poly(vinyl Chloride)

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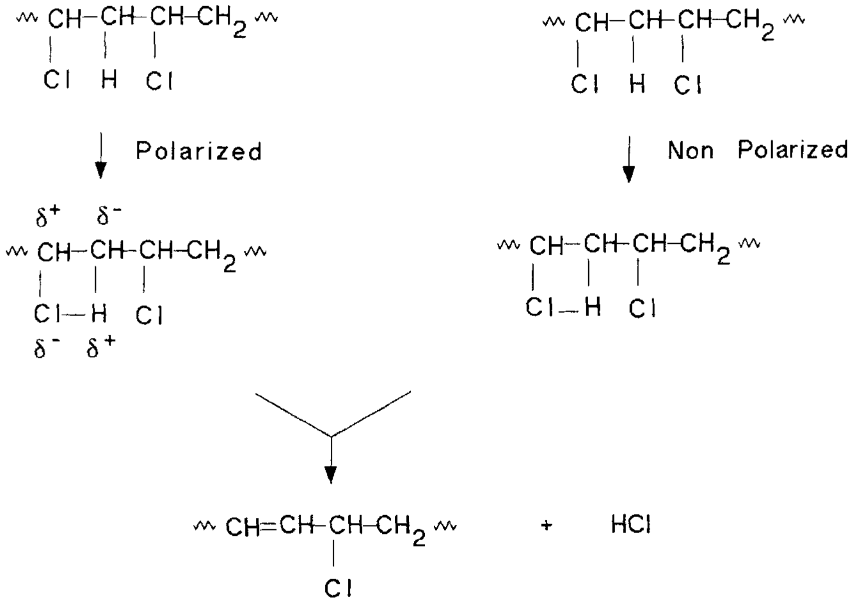
1. DEGRADATION

1.1. Introduction

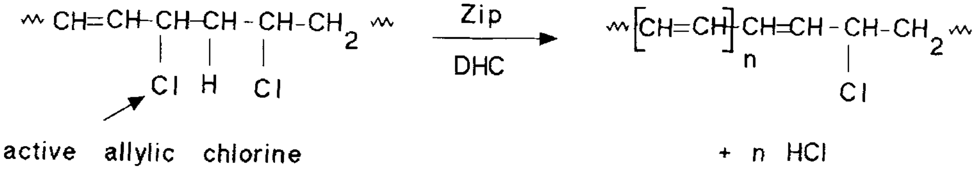
The mechanism of degradation of poly(vinyl chloride) (PVC) has long been a matter of discussion. Some excellent reviews have been published [1–4]. Over the years, different investigators have contributed to the discussion of the three main mechanisms concerning polyene propagation in the thermal dehydrochlorination (DHC) of PVC.

The partners of the unimolecular (or concerted) mechanism have suggested that DHC proceeds via a cyclic transition state formed by a PVC unity in the chain. This state is polarized [5] or not [6–13] (Scheme 1):



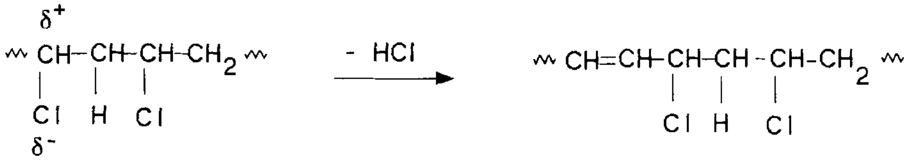
SCHEME 1.

As seen, by this process the departure of HCl is a random path and therefore is incompatible with a chain or zip DHC observed in DHC of PVC. Nevertheless, it was also proposed that, after the loss of the first molecule of HCl, the subsequent unsaturated structure formed in a PVC chain is an allylic structure that is effectively a reactive allylic chlorine. This allylic chlorine stimulates the next loss of an HCl molecule and the repeated process leads to the chain or zip DHC (Scheme 2):



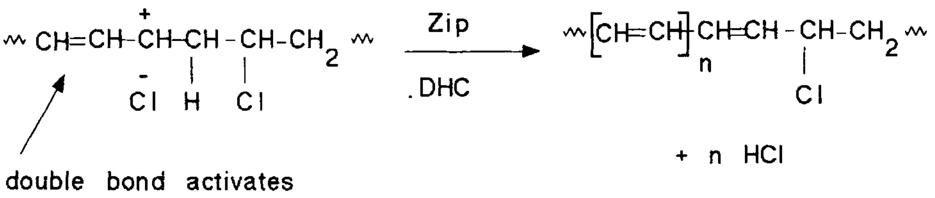
SCHEME 2.

The partners of the ionic mechanism [15–24] postulated that it is the electronic charge separations connected with the carbon–chlorine bonds that cause the loss of HCl molecules, creating new double bonds in the polymer chains (Scheme 3):



SCHEME 3.

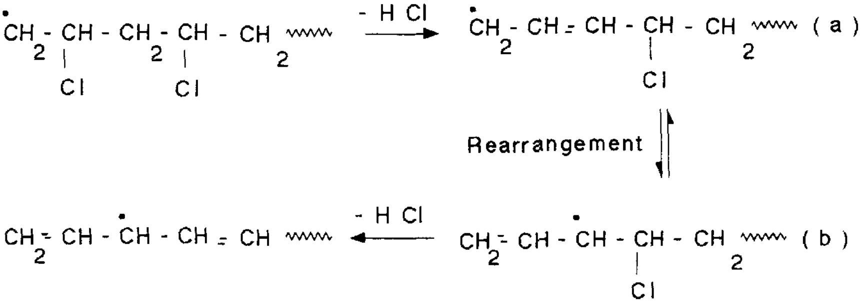
The newly formed double bond accentuates the charge separation (concealed ionization) and therefore activates allylic chlorine, propagating the zip DHC. But, according to some workers, the ionic elimination is highly allyl activated; therefore, the electronic charge is not a partial charge but an ion (ion-pair process) [3, 25, 26] (Scheme 4):



SCHEME 4.

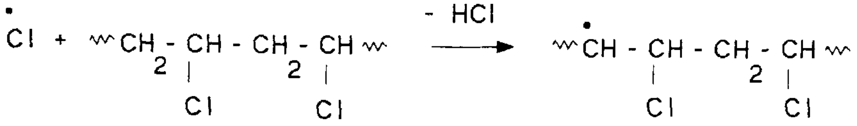
By this process, the ionic mechanism differs from the unimolecular mechanism by the first step of DHC; they are almost the same in the propagation phase due to the allylic structure.

The first radical mechanism proposed by Arlman [27] is based on the fact that the free radical of initiators (residue of initiator used in polymerization of PVC) increases the rate of DHC. On the other hand, Arlman's mechanism is similar to the allylic-activated DHC in the unimolecular or ionic mechanisms. It was suggested that a molecule of HCl is liberated from the monomer unit adjacent to a radical leading to an unsaturated macroradical (Scheme 5a). This structure, by a rearrangement, results in an activated elimination of HCl; the process repeats, leading to chain DHC (Scheme 5b):



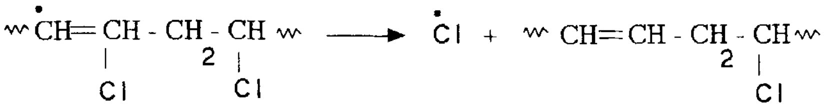
SCHEME 5.

In the mechanism of Arlman, it is the radical—considered stable due to the resonance of conjugation in polyene—on the carbon atom in the PVC molecule that propagates DHC. In those mechanisms proposed about the same time by Stromberg, Straus, and Achhammer [28] and Winkler [29], it is the free-radical chlorines that are the chain carriers. Stromberg suggested that the radical chlorine is formed by scission of the carbon-chlorine bonds in PVC, while Winkler suggested that radical chlorine originates from the macroradicals formed, for example, by the decomposition of polymerization catalyst residue [14]. On the other hand, the mechanisms of the propagation phase proposed by Stromberg and Winkler are similar. In fact, the radical chlorine propagates DHC by attacking a PVC chain, abstracting a methylene hydrogen atom to form HCl and creating a macroradical (Scheme 6a):



SCHEME 6a.

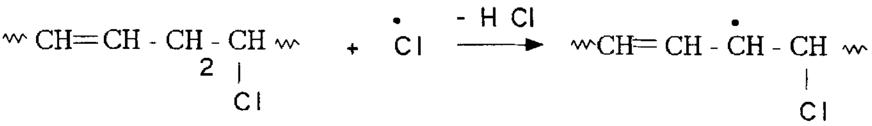
The chlorine atom adjacent to the radical dissociates from the PVC chain to regenerate free-radical chlorine and to form a carbon–carbon double bond in the polymer chain (Scheme 6b):



$$\sim\dot{\mathrm{C}}\mathrm{H}{=}\underset{\displaystyle \mathrm{Cl}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\displaystyle \mathrm{Cl}}{\underset{|}{\mathrm{CH}}}\sim \longrightarrow \dot{\mathrm{C}}\mathrm{l} + \sim\mathrm{CH}{=}\mathrm{CH}-\mathrm{CH_2}-\underset{\displaystyle \mathrm{Cl}}{\underset{|}{\mathrm{CH}}}\sim$$

SCHEME 6b.

If the Ċl formed in Eq. (b) then attacks the same PVC chain, a chain DHC occurs, leading to a conjugated polyene formation (Scheme 6c):



$$\sim\mathrm{CH}{=}\mathrm{CH}-\mathrm{CH_2}-\underset{\displaystyle \mathrm{Cl}}{\underset{|}{\mathrm{CH}}}\sim + \dot{\mathrm{C}}\mathrm{l} \xrightarrow{-\mathrm{HCl}} \sim\mathrm{CH}{=}\mathrm{CH}-\dot{\mathrm{C}}\mathrm{H}-\underset{\displaystyle \mathrm{Cl}}{\underset{|}{\mathrm{CH}}}\sim$$

SCHEME 6c.

This attack is most likely because, as reported by Geddes (1), the probability of abstracting the neighboring methylenic hydrogen is increased thanks to the relative proximity and activation by the carbon-to-carbon double bond. However, if the radical chlorine attacks another PVC molecule, DHC is terminated in the first chain and initiated in the other.

For all these proposed mechanisms, it is difficult to confirm conclusively the one by which DHC of PVC really proceeds because each mechanism has been supported or rejected equally by different experiments.

The unimolecular mechanism found support from the elimination behavior of low molecular weight compounds [16, 30] or from the first-order kinetics of the DHC rate [31, 32]. As for the process of allylic activation elimination, though it was rejected by some authors [33], it was unanimously accepted by other workers [11, 12, 32–35].

The ionic process, on the other hand, was supported by much experimental data: (1) the rate of DHC in solution was controlled by the nature and the dielectric constant of the solvent [15, 31, 35, 36, 38]; (2) the DHC was catalyzed by HCl [35, 39–41] (though this catalysis was rejected by some workers) or by some acids [42, 43] or bases [32, 44, 45] and by some metal salts [15, 18, 34, 36, 37, 46, 47]; (3) the DHC followed first-order kinetics [35, 43, 48]; (4) the substitution reaction of the chlorine atom during stabilization of low molecular weight compounds was carried out by stabilizers having ionic behavior or a nucleophilic group [9, 18, 49, 50].

Experimental support for radical mechanisms is not less important: (1) detection of radicals by electron spin resonance (ESR) in degraded PVC [51-56]; (2) increase of PVC DHC rate in the presence of radical initiators [27, 57] or by γ irradiation [58-62] and ultraviolet (UV) irradiation [63-65]; (3) increase of degradation rate of polymethylmethacrylate [66-68] and polypropylene [69] in the presence of PVC; (4) grafting of methylmethacrylate into PVC during degradation [70]; (5) fall of DHC rate of PVC by radical traps [69, 71] or decrease of DHC rate of polystyrene and PVC in PVC-PS blends [72]; (6) exchange reaction of PVC with toluene labeled [70].

However, this radical mechanism has been objected to by many arguments: (1) normal radical inhibitors [31, 33] or radical initiators [10, 73] have no effect on the rate of DHC as expected [10]; (2) the observed ESR signals do not correspond to free radicals, but more to thermoactivated electrons in the polyene system [74] or to radicals arising from aromatic structures formed in secondary reactions [75], or they are not observed during the DHC of PVC in solution [76]; (3) according to Starnes and Eldeson [25, 26, 77] and Amer and Shapiro (78), such radicals should be very mobile and also very reactive but not selective, so that it was difficult to explain how a zipper reaction in the same chain can develop, and for that reason the effect of radicals was essentially believed to be limited to the initiation process; (4) if the free chlorine atoms are formed, they can recombine, but during DHC no detection of chlorine molecule has been reported to now; (5) finally, only a few workers consider HCl catalysis consistent with a radical mechanism [61].

As discussed, the ionic and unimolecular mechanisms seem to be defended more frequently than the radical mechanism. Hjertberg and Sôrvik [4] are in favor of an ion-pair mechanism for the polyene propagation because it does not only account for the influence of solvent, HCl, and polar additives, as well as for the influence of tacticity on the rate of DHC of PVC, it also gives a reasonable explanation for the limited length of the polyene sequences in the degraded polymer. However, both cannot account for the ESR signals detected in degraded PVC.

Before the development of the SSH theory [79], many ESR studies were carried out on the paramagnetic species in conjugated systems, especially for thermally degraded PVC (dhc-PVC) [52, 74, 80, 81]. Almost all these studies reported ESR signals after quenching dhc-PVC or in a solution of dhc-PVC. However, the nature of the species corresponding to these signals still remains controversial.

Ouchi [52] observed that ESR signals began to appear at an early stage of DHC of PVC and increased until DHC was virtually complete. The spin concentration is higher if the DHC is carried out in air rather than in vacuum and if it is carried out at a higher temperature. Based on the shape of the ESR signals, on the instability of free radicals, and on the infrared spectra, Ouchi ascribed the ESR signals to aromatic rings rather than to unpaired electrons associated with long conjugated double bonds.

In Hay's study [74] on the degradation of different polymers at 180°C, poly(vinylidene chlorine) first displayed an asymmetric ESR signal assigned to radicals, then the signal was progressively altered as the reaction proceeded, and finally the signal became a symmetrical line after about 30–40% conversion. Hay assigned the first asymmetric ESR signal to free radicals because this signal changed completely to a broad single line when the polymer was exposed to air at room temperature. The same result was observed in the case of degradation in air, with the final symmetrical signal obtained within minutes and at a lower extent of reaction; this signal remained unaltered over several days. Accordingly, the final singlet was ascribed to the polyene system. When the ESR signals of PVC, thermally treated or γ irradiated, were compared to those of poly(vinylidene chloride), they were different because they were developed only at relatively higher conversions and showed only one single line, which was also very stable in air, exactly the same as the final line of poly(vinylidene chloride). The conclusion of Hay was that, under the same conditions of moderate degradation, PVC did not show any evidence for the presence of radicals, and at higher conversions the spectrum was consistent only with the polyene residue [74, 82–85] or with the carbonaceous materials containing aromatic and polyene structures [52, 80, 86]. Recently, Hu et al. [76] confirmed that there were no active free radicals in the PVC degradation process.

By applying the SSH theory [79] developed for polyacetylene (PA) to the analogue polymer matrix, namely, dhc-PVC, Vancsó et al. [87] observed an ESR singlet signal at $g = 2.0026$ at an early stage of PVC degradation and have assigned it to paramagnetic polyenes:

$$\sim \text{CH2}-\dot{\text{C}}\text{H}-(\text{CH})n-\text{CHCl} \sim$$

that is, to paramagnetic solitons according to the SSH model. But, the soliton in dhc-PVC was considered to be fixed, not delocalized as in *trans*-PA. This difference, according to the authors, is due to the fact that the mean polyene length in dhc-PVC is considerably less than that in *trans*-PA. However, it must be noted that the width of paramagnetic solitons (average conjugation length of paramagnetic polyenes) is not determined by the polyene length distribution, but depends rather on radical stability. On the other hand, from molecular orbital studies taking into account the geometries, energetics, and charge densities of linear polyenes involved in the DHC of PVC, Starnes [3] concluded that polyenyl cations, experimentally detected in degraded PVC [12, 28, 88], were the species accounting for the polyene growth limit. According to Starnes, the positive charge is localized preferentially at the center of the polyene sequence, and the tendency for the cations to assume such structures was found to increase with increasing cation length (89).

With these experimental proofs, it is undeniable that the DHC of PVC must involve a mechanism different from both ionic and radical processes.

Most of the recent works on PVC have focused on the clarification of the relationships between the degradation rate and the irregular structures (allylic chlorine atoms [ACAs], tertiary chlorines at branch point [90]) or to the influence on the DHC of labile atoms of special conformation of the monomer unit of PVC (91, 92).

In recent years, polymers with conjugated sequences have been of considerable interest due to their ability to give, on either chemical or electrochemical or physical doping, electronic conducting polymers. A theory based on the concepts from physics, including solitons, polarons, and bipolarons, was introduced in the early 1980s to explain the mechanism of electronic conduction in a system of conjugated double bonds. Since PVC contains double bonds or short polyene sequences that initially existed in the chains and are developed during DHC, Tran et al. [93] have shown that the solitons, polarons, and bipolarons are formed during DHC. The presence of polarons in the degraded PVC chains has been confirmed by Owen and Al-Awar [94]. On the basis of the solitons, polarons, and bipolarons, Tran et al. [95, 96] have developed a theory, the *polaron mechanism*, capable of giving satisfactory explanations of phenomena observed in the PVC DHC.

Before presenting the polaron mechanism, some theories or concepts on which the polaron mechanism is based are briefly reviewed.

1.2. Charge Carriers in Conjugated Polyenes

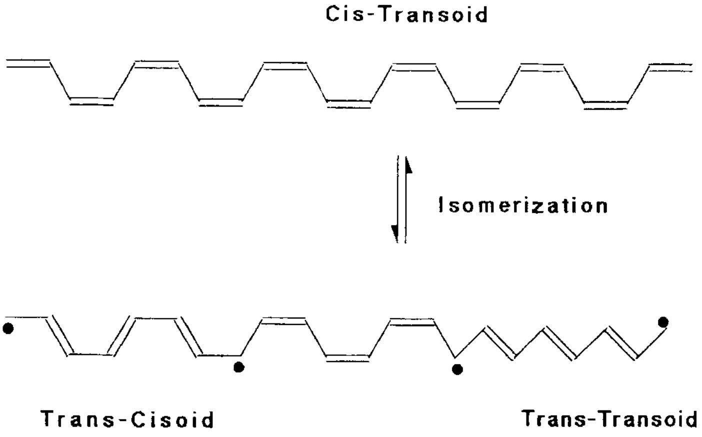
In order to explain the electronic conductivity observed in polymers containing conjugated polyene sequences, it has been proposed that the charge carriers, responsible for the electronic properties, are formed by and in the conjugated systems [97–99]. Using polyacetylene as a model polymer, the model of soliton was then developed by a number of authors [100–104]. The basic chemistry and physics of charge carrier generation and propagation (like soliton, polaron, and bipolaron) have been studied extensively [105, 106].

The author reports here various fundamental processes that give rise to different charge carriers from a conjugated unsaturated system.

1.2.1. Isomerization of Isomeric Structures

The ESR studies carried out on long conjugated polyene sequences of polyacetylene (PA) have shown that low-temperature (195 K) polymerized PA has a nearly perfect cis-transoid structure devoid of unpaired spins (soliton or neutral radical) [107, 108]. On warming this PA to 235 K or exposing it to air, a marked increase in the unpaired spin concentration [109] is observed.

The energy calculations by Karpfen and Holler [110] have shown that trans-transoid is the most thermodynamically stable structure. The isomerization from cis-transoid into trans-cisoid or trans-transoid proceeds by interchange of adjacent simple and double bonds with small energy [111]. This π-orbital phase changes, giving rise to particular energy states called *excitons*. These states correspond to two separated neutral radicals formed at the point of this structural alteration (Scheme 7):



(• neutral soliton)

SCHEME 7.

This structural defect or this free radical is considered to be able to move almost freely along the chain in the same manner as a solitary wave, hence the name *soliton*. From the electronic point of view, the nonbonding electron of the soliton is not localized at a unique carbon atom but delocalized over many CH units; it has no charge but a spin of 1/2, so solitons or neutral radicals are paramagnetic.

Chien and al. [99] have shown that the formation of soliton follows first-order kinetics, and its rate is not dependent on the inital cis content of the polymer. It increases with time and temperature, and at a given temperature it reaches an asymptotic value. The activation energy of this process is about 10 kcal/mole. An energy of about 0.4 eV estimated by Su [98, 99] for the creation of a neutral radical or soliton is in good agreement with experience [102].

1.2.2. Peierls Distortion

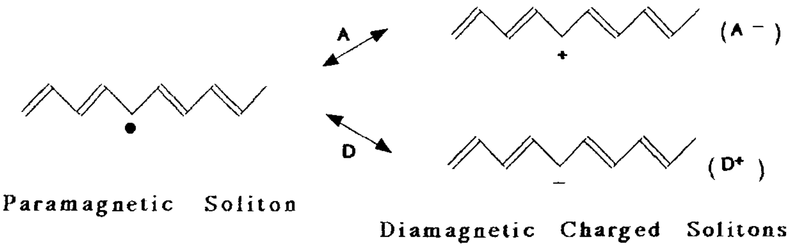
In the trans-transoid structure, adjacent CH groups move toward each other, alternately forming double bonds and single bonds (Peierls distortion). Since a trans-transoid structure presents a screw-axis symmetry, this interchange of the adjacent single and double bonds can be obtained without energy consumption, and the two resulting structures (a) and (b) are energetically equivalent [112] (Scheme 8):

SCHEME 8.

In trans-transoid PA, though solitons are confined in the conjugated double-bond chain, they can freely move on the system. It is noteworthy that the concentration of this radical formed from the isomerization or bond interchange is very low, about 1 soliton per 1000–3000 CH units. If there are barriers restricting soliton motion or recombination, the soliton concentration may be higher [105].

1.2.3. Polarization of Soliton

By interaction with an electron acceptor A or donor D, the neutral soliton becomes a positive or negative soliton (Scheme 9):



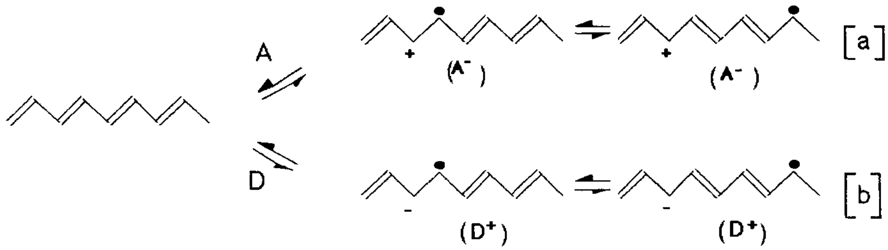
SCHEME 9.

Consequently, the charged solitons have no spin and are then diamagnetic, and A and D become counterions A^- and D^+ that stabilize the whole system.

These charged solitons are, in fact, carbocation or carbanion in more usual chemical terms. In thermally degraded PVC, the ESR signals similar to solitons have already been observed [97, 113–115] in long sequences of polyene [87], and the charged soliton or polyenylcations were also experimentally evidenced [16, 36, 116].

1.2.4. Oxidoreduction Reaction of π Electron in the Double Bonds

The electron acceptor or donor can directly oxidize or reduce the π electrons in conjugated double bonds to give a radical associated with an ion, an ion radical, or polaron. For example, with an electron acceptor A, the oxidation reaction gives a carbocation radical or a positive polaron (+ •) is formed ([a] in Scheme 10):



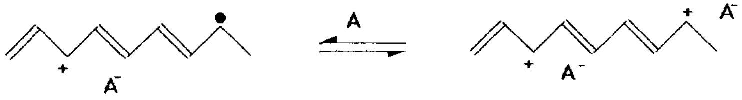
SCHEME 10.

However, a carbanion radical or negative polaron (− •) is formed by the reduction of the chain by an electron donor D ([b] in Scheme 10).

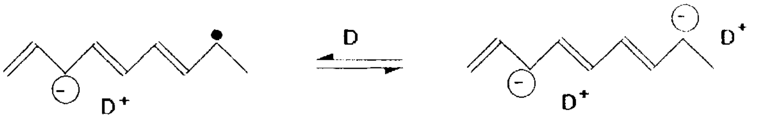
As seen, a polaron can be considered by association of a neutral and a charged soliton.

It is noted that, in solid-state physics, a radical ion that is partially delocalized over some polymer segments is called a *polaron*. It stabilizes itself by polarizing the medium around it. The mobility of the soliton or polaron is easier in conformation trans than in conformation cis of these sequences [105, p. 202].

The polaron is paramagnetic, and its density depends on the concentration of the oxidoreduction agent or dopant. However, with high dopant concentration, the polaron becomes di-ion or bipolaron (diamagnetic) after further interaction of another dopant with its neutral soliton. Scheme 11 shows, respectively, the positive and negative bipolaron formed:



Positive Bipolaron (Dication)



Negative Bipolaron (Dianion)

SCHEME 11.

Another process of bipolaron formation occurs [117] when two polarons are close together and their solitons combine to form a double bond and two charged solitons. Scheme 12 illustrates the formation of a positive bipolaron. By this process, a bipolaron is an association of two solitons of the same charge.

SCHEME 12.

As for the dopants or redox agents, they involve a wide range of compounds having properties of electron acceptors such as Lewis acids (AsF_4, $FeCl_3$, $ZnCl_2$, etc.), halogens (iodide, bromide), protonic acids (HCl, H_2SO_4, $HClO_4$, etc.), and organometallic compounds and even oxygen. The dopants having electron donors are Li, Na, K, and organoalcalins.

The possibility of interaction of each reagent depends on the ionization potential or electron affinity of the type of polyene-containing polymer [118].

The concentration of polaron can be controlled and reaches a very high value because it increases with the concentration of the reagents used for doping the polymer. However, as the unpaired electrons (solitons) in a conjugated unsaturated system are intrinsically unstable and have a tendency to combine, two polarons are converted to a bipolaron (or two charged solitons). Because of this electron recombination, a polaron can only be observed when there is an odd number of dopants in a conjugated sequence.

The interaction of a dopant with a system of conjugated double bonds is a dual effect. In fact, besides the redox reaction with π electrons, the dopant favors the isomerization of the cis-to-trans configuration of the conjugated polyene sequences [105, p. 346]. Although the redox reaction is reversible, that is, the system can go back to its inital state by reacting with a dopant of opposing character (dedoping or compensation reaction), the isomerization is not reversible, even though the system is dedoped. The same is true for a *cis*-PA that undergoes a trans isomerization induced by thermal effect (105 [p. 153 and references therein], 109, 112).

As solitons, polarons, and bipolarons are mobile and can move along the polymer chain by rearrangement of the conjugated system, they can also hop from one chain to another. The theories of charge transport in amorphous semiconductors have been advanced by many workers [119–126]. These intrachain and interchain motions are responsible for the remarkable electrical conduction and optical properties of conjugated polymers.

1.3. Polarons in Poly(vinyl Chloride)

Like solitons, polarons have also been found in polyene sequences other than PA. For instance, in β-carotene (a compound with nine conjugated trans double bonds and a β-ionone ring at each end), Huggins and Leblanc [127] have indicated a value of 0.01–0.02 spin per molecule of $C_{40}H_{56}I_3$ in a freshly prepared sample (β-carotene with iodine). From Raman and absorption spectra of a mixture of iodine or sulfur trioxide with β-carotene, Harrada et al. [128] have demonstrated the transfer of an electron from a local site in β-carotene to iodine or sulfur trioxide and the resulting shortening of the length of the double bond conjugated. This type of charge transfer complex was also the origin of the apparent color observed in a conjugated unsaturated system from degraded PVC in the presence of metal chlorides as suggested by Iida et al. [129, 130].

Recently, Tran et al. [93] have followed, by ERS, the spin density during the degradation of PVC powder in different conditions (Fig. 1). They have observed that the spin concentration is proportional to the DHC time and that a partially degraded PVC kept its spin concentration almost constant after one day under nitrogen or air atmosphere, as already observed by Hay [74]. Therefore, they confirmed that the spin observed is not from conventional active radicals (resulting from a σ-bond scission) that would combine due to their high reactivity [52] and no spin could be observed. Furthermore, after being degraded at 180°C under nitrogen, PVC dis-

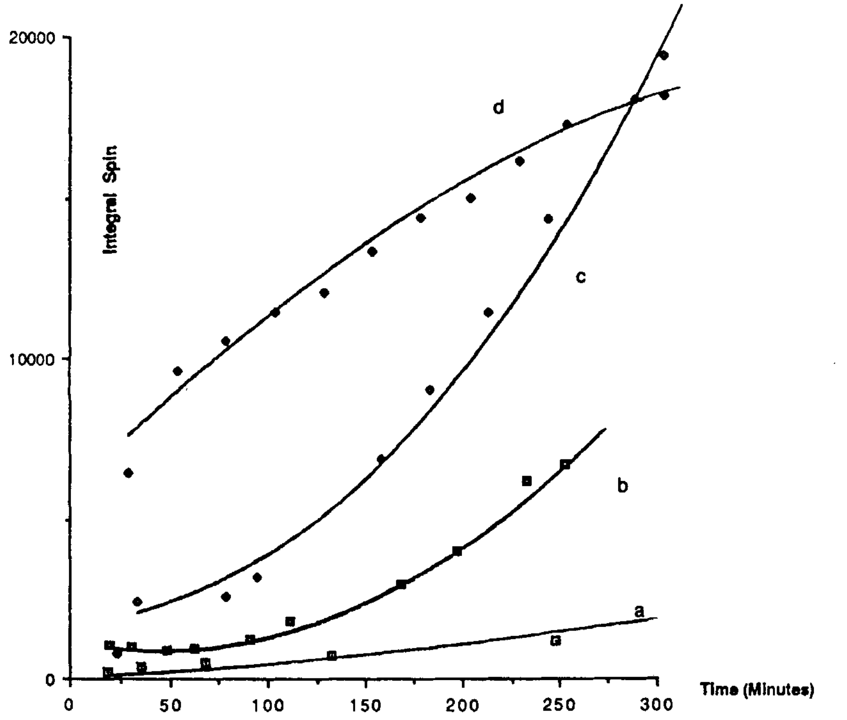


FIG. 1. Spin intensity changes during degradation of PVC at 180°C under nitrogen atmosphere: (a) 100 mg PVC; (b) 100 mg PVC + 10 mg β-carotene; (c) 100 mg PVC (in air); and (d) 100 mg PVC + 2 mg zinc stearate. (After Ref. 131.)

played a reduced spin concentration when the temperature was gradually lowered (Fig. 2). This decrease in spin concentration can be explained by the fact that the spins are effectively associated with the thermoactivated electrons in polyene. Furthermore, these solitons are less delocalized than in *trans*-PA, as suggested by Vanscó et al. [87].

Since a redox agent can polarize the soliton or the interaction with the π electron of conjugated double bonds, the spin in degraded PVC is substantially affected by the dopants. In fact, the spin density of a degraded PVC greatly increased under heating, and it reduced rapidly when flushed with a nitrogen stream. The variation of spin number can be explained by the effect of HCl on the spin formation in the conjugated double bonds: when HCl is swept away, the polyene is depoped, so the spin concentration is reduced. Nevertheless, in the presence of PVC, which liberates HCl, the spin number of the β-carotene considerably increases; it is even higher than

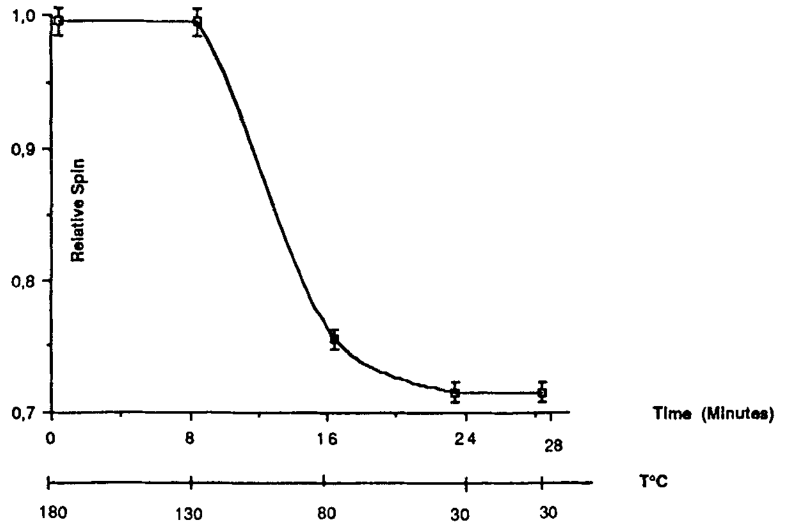


FIG. 2. Change in spin concentration of 100 mg of PVC, which had been heated under nitrogen at 180°C for 24 hours, on cooling under nitrogen. (After Ref. 131.)

that in PVC alone [93] (Curve b in Fig. 1). This can be explained as the dual effect of HCl as dopant: (1) the isomerization of cis-to-trans configuration of the conjugated polyene sequences and (2) oxidation of the π electron into paramagnetic polarons. It was also shown that the spin concentration in the DHC of PVC in the presence of zinc stearate (which, by reacting with HCl, is converted gradually into $ZnCl_2$ during the heat treatment) or in the presence of air has a very high spin concentration compared with that of PVC alone (Curves a, c, d in Fig. 1). However, with time the spin number of a partially degraded PVC decreases when $ZnCl_2$ concentration is important (Curve d in Fig. 1). The same is true when $octylSnCl_3$ or $ZnCl_2$ are added at room temperature to degraded PVC because these powerful Lewis acid or electron acceptors polarize the separated neutral solitons (or neutral solitons of the polaron) to form diamagnetic charged solitons or bipolarons having no spin (Fig. 3). On the other hand, the polaron formation can also come from a system of only two conjugated double bonds, though it is rather difficult. For example, with hexadiene, HCl can form a charge transfer complex [35] at room temperature, but ESR signals appeared only when $ZnCl_2$ was also present in the system [131]. The formation of polaron is expected to be due to the oxidation of the double bond by the cocatalyst, which is a mixed product of HCl and $ZnCl_2$ (chlorozincic acid, $HZnCl_3$, known as a very powerful Lewis acid).

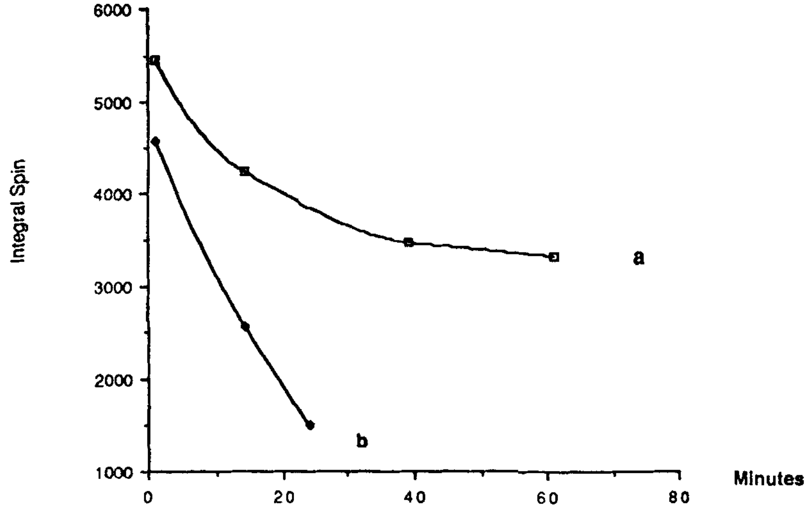


FIG. 3. Change in spin intensity on the interaction between degraded PVC and Lewis acid compounds: (a) $OctSnCl_3$; and (b) $ZnCl_2$. (After Ref. 131.)

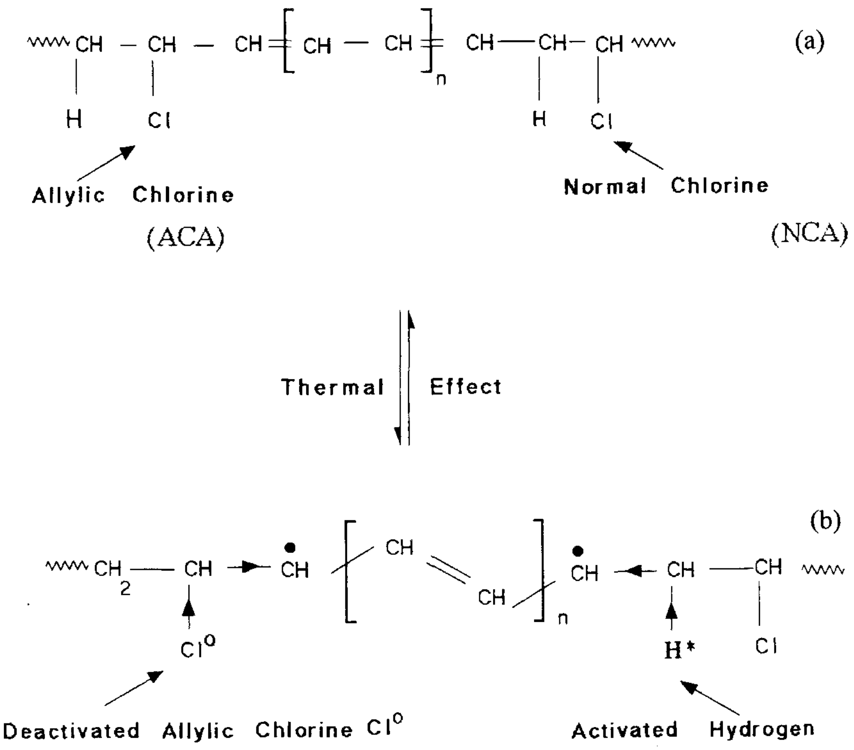
1.4. The Polaron Mechanism in Poly(vinyl Chloride) Degradation

In the literature, the mechanisms proposed for chain DHC are either unimolecular and ionic (via allylic chlorine) or radical (via radicals). Therefore, the propagation phase of DHC involves either an allylic chlorine atom or radicals in the PVC chains. However, the departure of the first HCl molecule gives rise to a double bond. Whether the configuration of the conjugated polyene sequence is one cis double bond flanked by two sequences of conjugated trans double bonds [3, 78, 132] or a trans structure [133], the polyene length is not infinite as in PA, but it is limited at the extremity of the $-CH_2Cl-$ units. By this reason, the radicals/ion radicals/di-ions formed during the DHC in PVC chains cannot totally delocalize as in PA but are much more localized; they are, in fact, polarons, as speculated in solid-state physics. However, due to the thermal effect, these polarons can be considered more or less delocalized.

As these polarons are shown to be responsible for the chain or zip DHC of PVC, the corresponding mechanism is therefore called a *polaron mechanism* [95]. It involves solitons, polarons, and bipolarons and begins to operate as soon as polyene sequences are formed. Therefore, it is concerned with the propagation of the degradation of PVC. By this polaron mechanism, it has been shown that, for thermal DHC, there is a unique mechanism in which it is the polarons that control the rate and the process of degradation.

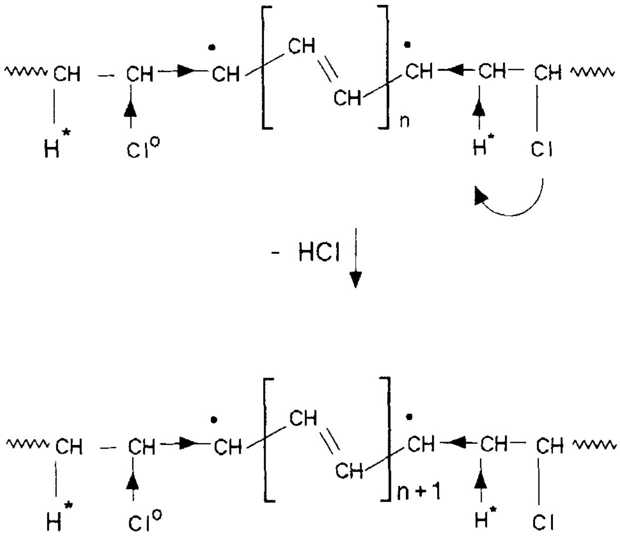
1.4.1. General Mechanisms

After the departure of HCl molecules in the same PVC chain, conjugated double bonds are formed. At the two adjacent parts of the conjugated double bonds are an allylic chlorine atom (ACA) and a normal chlorine atom (NCA) (Scheme 13).



SCHEME 13.

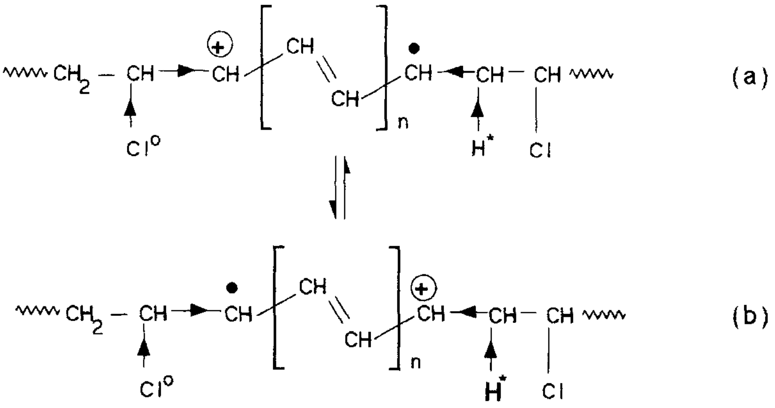
Under thermal effects combined with the dual effect of HCl, the polyene sequence must be in the trans configuration, and neutral solitons are generated. These solitons introduce a deficiency in electron density into the atoms at their α positions (Scheme 13b). Therefore, the ACA is then deactivated, whereas the methylene hydrogen atom (MHA) becomes activated. As a consequence, the DHC occurs only at the right part of the chain, where the activated MHA is split off by the vicinal NCA, giving rise to the departure of HCl (Scheme 14)



SCHEME 14.

and the same process repeats, leading to chain DHC.

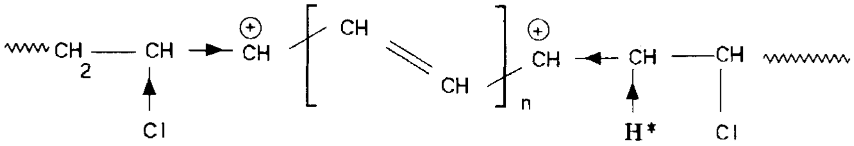
As long as DHC goes on, HCl molecules are accumulated. Being an oxidizing dopant, they oxidize solitons into positive solitons or directly oxidize double bonds into neutral soliton and positive solitons (or positive polarons) (Scheme 15):



SCHEME 15.

Due to the adjacent positive charge, the ACA becomes deactivated (Scheme 15b) or highly deactivated (Scheme 15a). On the other hand, the MHA becomes activated (Scheme 15a) or highly activated (Scheme 15b). In any case, the DHC also proceeds via a polaron mechanism as discussed above, but with a higher rate.

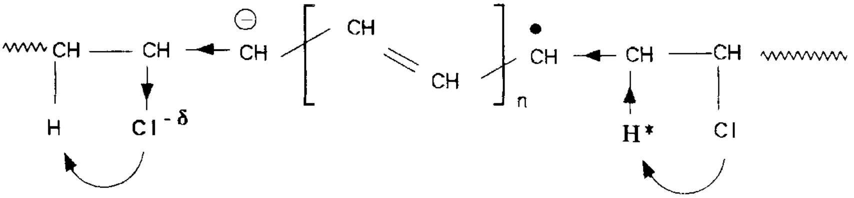
If a positive bipolaran is formed (two positive solitons), the MHA is overactivated due to the high deficiency in electrons of C–H bond (Scheme 16) and leads to DHC with a much higher rate of HCl departure.



SCHEME 16.

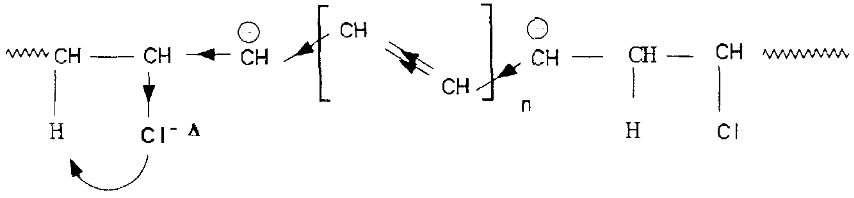
When the conjugated system contains solitons or positive polarons, the DHC proceeds via a normal chlorine atom, but not via an ACA, as shown by the polaron mechanism.

However, when electron donors (or Lewis bases) are present in the medium, the process is different. In fact, due to the reduction reaction, neutral or negative solitons first appear in the PVC chains. By the electroaffinity of chlorine atoms, the negative charge of the double-bond system must shift to the nearest ACA. By an induction effect, the ACA becomes partially negative and becomes active. On the other part of the conjugated double bonds, MHA is also active because of an electronic deficiency caused by the neutral soliton, as discussed above (Scheme 17a). Therefore, the DHC proceeds actually via the ACA and via the NCA, which abstracts the corresponding adjacent MHAs:



SCHEME 17a.

If the concentration of electron donor is high, only negative solitons are formed because all neutral solitons are reduced. The ACA is then effectively overactivated by the high density of the negative charge. The DHC occurs via this chlorine, which abstracts easily the vicinal MHA (Scheme 17b):



SCHEME 17b.

The whole process of the PVC DHC can be summarized as follows: At the beginning of the DHC, when there are no solitons or polarons in the PVC chain, DHC is initiated by labile structures in the PVC chain. The first formed double bond gives rise to an ACA that, activated through an induction effect, continues DHC. As the number of double bonds increases, solitons or polarons appear, and the DHC propagates by the polaron mechanism. This is in agreement with the results obtained from kinetic studies of PVC DHC by Troitskii et al. [134]. These authors stated that (for DHC of PVC in the absence of additive compounds, but HCl generated *in situ*) for up to 0.5–1% conversion, degradation of an unstable fragment gave the greatest contribution to the overall DHC of polymer and that from 2% converstion, the rate of DHC was determined only by the rate of decomposition of normal links (NCA) of macromolecules.

In conclusion, on the basis of the polaron theory, it is clearly shown that the DHC mechanisms of PVC depend on the nature of the polarons or solitons (1) when the solitons are neutral or positive, DHC proceeds only via the activated methylene hydrogen atom AMHA (or the normal chlorine atom NCA) and (2) when the solitons are negative or in the absence of solitons, DHC proceeds by the ACA.

1.4.2. Thermal Dehydrochlorination of Poly(vinyl Chloride) in Different Media

In the literature, many attempts have been made to explain the rate dependence of solvents. Stepek, Vymazal, and Dolezel explained it in entropy terms [135]. According to Mukherjee and Gupta [33], the effect could not be satisfactorily explained in terms of the dielectric constant of the solvent as suggested by Bengough and Varma [136], but it was the solvent–

polymer interaction that reduced the strength of the carbon–hydrogen and carbon–chlorine bonds. Finally, Zafar and Mahmood [36] and Zuoyun, Xingzhou, and Gang [13] attributed the solvent effect to the polarity of the solvent. On the contrary, Naqvi suggested that the medium or the nonpolar group (from the stabilizer, for example) reduced the interaction of like-poles (formed by clusters of partially negatively charged chlorine atoms) randomly distributed in the polymer matrix because these like-poles constitute the weak spots that are the possible sites of initiation of thermal DHC [137].

Solvents have been classified in terms of Brönsted or Lewis acids and bases [138, pp. 61–67], and they have an effect on conformational or cis/trans isomerization equilibria [138, pp. 110–117]. Moreover, in a recent study of the polaron formation by doping polyconjugated polymers with nonoxidizing protonic acids, Han and Elsenbaumer [139] have postulated that the ionization potential of a conjugated polymer would correlate with its Lewis and Brönsted basicity. Therefore, the interaction between solvents and CjPS is also a redox reaction. Furthermore, it is noteworthy that, in the doping of conjugated polymers to create polarons, there exist some types of dopant (nonoxidizing protonic acids such as HCl, for instance) whose interaction with polymers does not directly involve an oxidoreduction reaction [139–142], but the redox process follows the protonation of the polymer backbones [139].

In order to discuss the polaron mechanism proposed for DHC of PVC and to clarify the dependence of the DHC rate on the medium or any other chemical additives, Tran et al. [96] studied the interactions of medium (solvent and chemical additives) on the π electrons of double bonds in dhc-PVC and discussed the influence of medium, as well as side reactions such as the cross-linking and cyclization reaction during DHC. They demonstrated that the solvents, by their doping or redox power, create with π electrons of the double bonds in PVC polarons that control the DHC mechanisms, accelerate the DHC rate, and govern the length distribution of the polyene sequences.

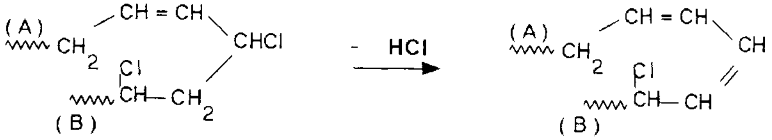
1.4.2.1. Neutral Medium.

Dehydrochlorination: Media can be considered neutral, for instance, if they have no electron donors or acceptors versus CjPS. This is the case of long-chain or saturated hydrocarbons such as dodecane or decahydronapthalene, which induce a much smaller DHC effect compared with the other redox solvents. These neutral compounds cannot create polarons with CjPS, and they also favor the isomerization trans to cis of the CjPS. Since the CjPS of the cis structure is devoid of solitons, the ACA is then the sole activated species in the chain as discussed in Section 1.4.1. Consequently, the DHC proceeds via the ACA. But, this process, operative at the earlier portion of DHC (initiation reaction), cannot continue for a long time because under thermal effects and HCl formed *in situ*, solitons or polarons appear as the polyene sequence length grows. As a result, solitons or positive solitons lead to the DHC according to Schemes 14 and 15.

In the literature, low molecular crystalline polyethylene [143], as well as polyisobutylene [144], were also shown to stabilize PVC. In fact, the lower rate of PVC DHC in long-alkyl-chain-containing solvents may have the same origin as the loss in electronic conductivity of doped conjugated polymers when the latter are grafted with long alkyl chains [145–149] or, especially, with branched alkyl chains [150].

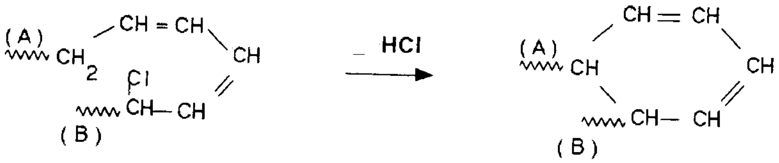
Although this is a well-known phenomenon in the field of electroactive polymers, its mechanism is not yet well clarified or explained. Tran et al. [96] have suggested that, besides their influence on the planarity of the chain-conjugated polymer [145], the alkyl chains introduce two other effects. First, the interaction between alkyl chains and conjugated polymer chains (solvation) makes the access of dopants (HCl, for example) to the conjugated polymers more or less difficult. Second, the eventual interaction between the π electrons in double bonds and hydrogen atoms in alkyl chains may reduce or alter the oxidoreduction power of the conjugated polymers. Such interactions are expected in dhc-PVC and particularly in the cis arrangement of conjugated double bonds. Furthermore, there exists a competition of effects on the trans/cis isomerization of CjPS caused by thermal effects and HCl on the one hand and on the other hand by the neutral solvent. Due to this permanent competition, the formation of polarons must be slowed, and therefore the rate of DHC must be reduced [96, 151].

CjPS Distribution: Due to the flexibility of the single C–C bond, a chain of polymer may have the configuration shown in Scheme 18. As no solitons are formed, DHC continues via the allylic chlorine atom:



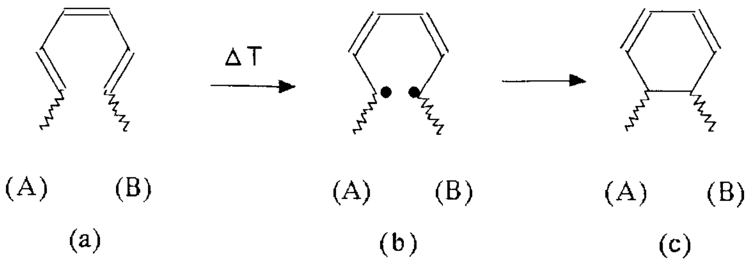
SCHEME 18.

This conformation favors the chain cyclization that takes place through HCl elimination from the combination of hydrogen and allylic chlorine atom belonging to two parts A and B of the polymer chain (Scheme 19):



SCHEME 19.

Furthermore, the cyclization can proceed by a polaron mechanism whenever the π electrons are affected by thermal effects (in neutral medium) to produce neutral solitons that permit the closing of the cycle (Scheme 20):



SCHEME 20.

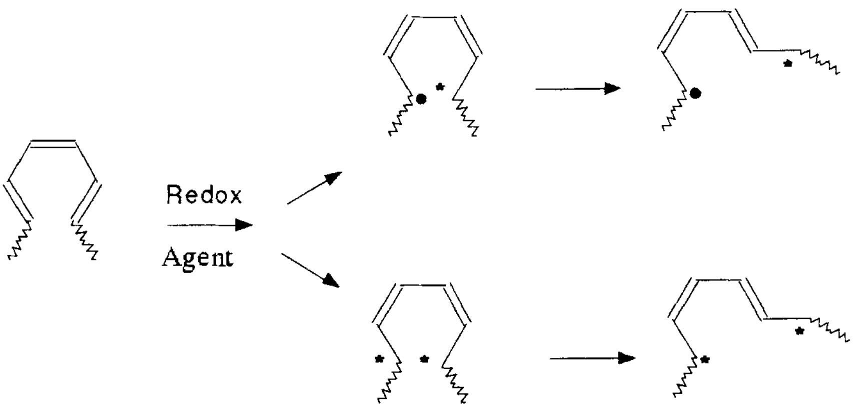
Although the mechanisms of cyclization could be different, the final cyclized structures are the same ones proposed by Kelen et al. [152]. It is noteworthy that, at 150–165 °C, benzene is formed in a trace quantity (153); therefore, these cyclized compounds are only the precursor of benzene formation and do not necessarily lead to benzene, with a formation that nevertheless requires a much higher pyrolysis temperature [3 and references therein, 154]. However, the cyclization mechanism accounts for the short length of CjPS in the dhc-PVC. It also leads to the suppression of the allylic chlorine structure. This fact can provide a further explanation of how the DHC of PVC in solution, in general, takes place at a lower rate than in the solid state. However, this does not mean that the DHC is blocked forever in parts A and B of the polymer because, under the thermal and HCl effects, solitons can be created in the double bonds of the cyclized compounds, and the DHC propagates again.

1.4.2.2. Redox Medium.

Dehydrochlorination: Compounds or solvents that can be considered as electron donor agents versus CjPS are triphenyl phosphine (TPP), pyridine (Py), and dimethyl formamide (DMF) because, with CjPS, they create polarons [96]. In fact, it has been proposed that phosphine compounds favor the radical mechanism in PVC DHC [70] or create free-radical formation from the π electrons in dhc-PVC [155]. Briggs and Wood [156] have observed that phosphines accelerate DHC. Bengough and Grant [157] have attributed to the higher DHC rate the basic character of the dimethylformamide (DMF) solvent, as well as the catalysis of the dimethylammonium chloride formed in the reaction of DMF with HCl generated from DHC. As discussed, the DHC of PVC in these media must proceed via an activated allylic chlorine atom (AACA) according to Scheme 17 because the negative solitons are formed in the degraded PVC chains. The rate of DHC depends effectively on the basicity of the medium.

As for electron acceptor compounds, aromatic derivatives can be considered as compounds of mild effect because their electron withdrawal power can be quantified by the chemical shifts in nuclear magnetic resonance (NMR) analysis. Tran et al. [96] have shown that those with their nucleus protons shifted to the lower field compared with the benzene protons can be considered as electron acceptor compounds due to the lower electron density of the aromatic ring, and that the larger the chemical shifts are, the higher is the electron affinity or oxidation power of the compound. Other Lewis acid compounds, such as organotin chlorides $R_nSnCl_{(4-n)}$, have their electron acceptor power higher when the alkyl group is replaced by the phenyl group and when the number of phenyl rings is increased [134, 158–160]. Among electron acceptors, the most powerful for degrading PVC are $ZnCl_2$ and $SnCl_4$ because of their very strong Lewis acidity [18, 161]. Finally, oxygen is also an electron acceptor [109, 162], and besides its various side reactions giving rise to peroxide radicals, hydroperoxide or carbonyl groups, and the like, it effectively oxidizes the π electron to form positive solitons. As any redox compound, oxygen is found to increase the DHC rate (see Ref. 1 and references therein). This can be well explained by the polaron theory since under the effect of these electron acceptors, positive solitons are formed in the CjPS and the DHC of PVC is via a normal chlorine atom (see Schemes 15 and 16). The higher the rate of DHC is, the more powerful is the electron acceptor.

CjPS Distribution: When DHC is carried out in the presence of a redox solvent, the CjPS is of the trans configuration with charged solitons in the chain. Because of these charges, intrachain cyclization cannot occur as shown in Scheme 21, but the propagation of DHC on the chain continues; consequently, the length of CjPS must be longer. However, the conjugated length of dhc-PVC is not unlimited because of the interchain cross-linking from the combination of the two neutral solitons of two different chains [93].



(* is positive or negative soliton)

SCHEME 21.

These mechanisms show clearly that the distribution of CjPS in dhc-PVC obviously depends on the nature of the medium. Furthermore, the results obtained are in good agreement with those reported in the literature. For instance, long polyene sequences were observed from the PVC DHC that gave rise to *trans*-alkene formation [163, 164], and a decreased yield of benzene occurred either in the polymers that, on DHC, produced *trans*-alkene [see Ref. 3 and references therein] or by introducing Lewis metal chlorides [165] or their precursor oxides [165, 166] into PVC during pyrolysis. All these observations can be explained by the redox medium, which does not favor the formation of cyclized compounds being responsible for the short CjPS length and being the precursor of benzene formation.

In Ref. 167, Tran et al. clarified the mechanism of thermal DHC of PVC in solution in the presence of different metal chlorides and organometallic chlorides (such as $ZnCl_2$, $CdCl_2$, $R_nSnCl_{(4-n)}$, etc. formed *in situ* during stabilization of PVC with metal soaps or organotin [OT] compounds as a result of the reaction between HCl and the corresponding stabilizers) and particularly their catalytic action on the readdition reaction of HCl to the double bonds in degraded PVC to delay DHC. The stabilizing effect of organotin on DHC of PVC has been well explained in terms of the polaron mechanism rather than the isomerization of allylic chlorine, as suggested by Wirth and Andreas [168], or than the eventual cleavage of the C–Sn bond, which, as proposed by Keynon [169], yields alkyl radicals that react with the radicals in PVC. Furthermore, the complex formed between metal chlorides and double bonds in the polyene chain reported by many authors [129, 170–172] should be of the same nature as the species that arise from the oxidation of metal chlorides on the π electrons of the conjugated double bonds (i.e., solitons, polarons, or bipolarons) responsible for the zipper DHC of PVC in the propagation phase and for the coloration developed during DHC.

Although there are fundamental differences among their points of view, strikingly similar results are obtained from the polaron mechanism and from the two different degradation mechanisms proposed by Martinez et al. from their investigation of CjPS length distribution in dhc-PVC [173]. For example, according to these workers the mechanisms of PVC thermal DHC depend markedly on the tacticity distribution of the polymer regardless of whether the degradation occurred either in the solid state or in solution [163]. The first mechanism involves syndiotactic sequences that give rise to *trans*-alkene structures through steric DHC and, although these syndiotactic sequences are thermally stable units (i.e., normal structures) in PVC, they enhance polyene growth, accelerate cross-linking reactions, and decrease the yield of benzene formation. The second mechanism involves the isotactic sequences (considered as the labile or initiation site of DHC), which can give both cis and trans double bonds but lead only to a lower DHC rate in the propagation phase [173, 174]. However, in the most recent article, Rogestedt and Hjerberg [175] showed that labile chlorine contributes mostly to the initial degradation rate and that tacticity was of minor importance; when degradation was performed in an atmosphere containing HCl, the DHC rate was increased, and the polyene sequence distribution was shifted toward longer polyenes.

1.4.2.3. Mixed Media. Solvents that have, at the same time, long alkyl chains and a redox-property-containing group in the structure (dioctylphthalate, for example) can have an intermediate effect, as shown by the experimental data [38]. Their mild effect can be explained by the competition of the oxidoreduction of the redox function of the aromatic ring on the one hand and the cis structure isomerization favored by the alkyl chains' link to the metal atom on the other. This is evidenced by organotin chlorides $R_nSnCl_{(4-n)}$. In fact, when the alkyl group R is longer and/or the number n is greater, the oxidation power of these compounds is decreased [47, 176], and the rate of DHC is therefore slowed.

1.5. Conclusion

By the polaron theory, it has been shown that the solvents or media, by their doping or redox power, create polarons with π electrons of the double bonds in PVC in exactly the same way that a dopant reacts with double bonds in conjugated polymers. The interaction between solvent and the π electrons of double bonds in dhc-PVC controls the different process in thermal DHC of PVC.

When the media are oxidant, DHC proceeds via the NCA, but the DHC proceeds by the ACA when the media are reductant or neutral. The more powerful the redox of a medium is, the higher is the DHC rate, the longer is the trans CjPS, and the more important is the cross-linking reaction. In contrast, in neutral media, DHC occurs via allylic chlorine, leading to a lower rate and resulting in a relatively shorter CjPS length because of the cyclizability of the conjugated double bonds of the cis configuration favored by the solvent.

The polaron theory can also provide better explanations for the zipper characteristics of the HCl elimination reaction, accelerated degradation due to catalysis by HCl or oxygen and Lewis acid compounds, and the limit of the polyene sequence length.

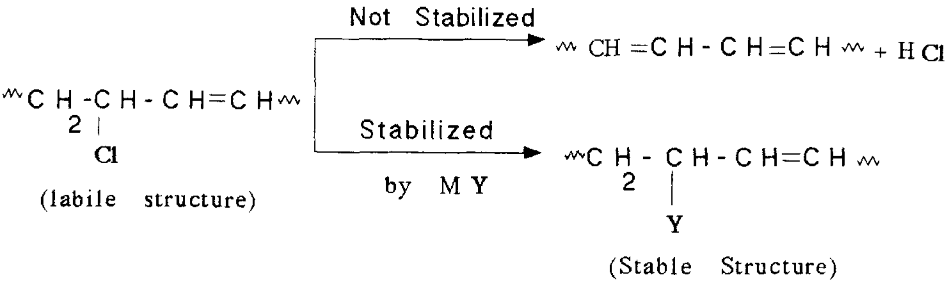
2. THERMAL STABILIZATION

2.1. Introduction

Two main classes of stabilizers have been intensively studied in the thermal stabilization of PVC: metal carboxylates (or metal soaps, MS) and organotin (OT) compounds. Although all these stabilizers had been considered HCl scavengers, there are no common features in the MS and OT compounds that ensure the stabilization of polymer in several different pathways. However, following the work of Frye and coworkers [177, 178], they were almost unanimously believed to have a similar and essential ultimate action in thermal stabilization, that is, substitution of the labile chlorine atoms in the PVC backbone by the stabilizer moieties. Since the retention of moieties, as well as the shorter average length of the polyene sequence in the backbone of stabilized PVC [177, 179–181], could not be easily explained other than by the substitution of labile sites in PVC (such as allylic chlorine or tertiary chlorine atoms) in stopping the zipperlike elimination of HCl [9, 180, 182], the theory proposed by Frye and coworkers has been widely accepted and is considered the basic theory in the thermal stabilization of PVC [18, 182–191].

The PVC containing an irregular structure (allylic structure, tertiary carbon, etc.) is sensitive to DHC, but when these labile chlorine atoms are replaced by a moiety group *Y* of stabilizer *MY*, the polymer becomes thermally stable.

The mechanism of the stabilization can be illustrated by Scheme 22:



SCHEME 22.

As reported in the literature, the OT compounds, in contrast to the MS stabilizers, give a more quantitative grafting yield and much longer induction periods. Furthermore, due to the OT structure in which four organo groups are bound to the tin metal, the reactions of OT compounds with PVC are shown to be much more complex, involving many types of interaction during the stabilization.

In practice, the metal (Cd, Zn) carboxylates are used together with secondary stabilizers (SS) in order to increase the induction time, as well as to block the sudden development of coloration and cross-linking of PVC during processing. These are the synergistic or the long-term effects of these two stabilizers. The action of these SS is also extensively studied. Most of them interact with HCl. They can also substitute the allylic chlorine atom [29, 50, 192, 193] or give a complex with the metal chloride regenerated by the principal stabilizers [18, 50, 53] or even hydrogenate the unsaturated polymer chain [193].

While the mechanisms of thermal degradation of PVC are still discussed in terms of different basic mechanisms (ionic, radical, and unimolar), those of PVC thermal stabilization are in a different situation because the partners of a radical mechanism are in the minority for MS [194, 195] and for OT stabilizers [187, 196]. As for the mechanism of the exchange reaction of allylic chlorine by the MS moiety, the ionic process has been widely accepted. However, according to Menczel et al. [195], the lower spin observed in PVC stabilized by barium stearate compared with unstabilized PVC could be explained by the fact that the barium derivative gave free-radical exchange with the macroradical of PVC in reducing the spin density. However, for pure calcium stearate, the ESR result using the spin trapping technique shows no free radical, even at 180°C, in the presence of different spin traps [221]. Therefore, the mechanism of PVC stabilization by MS stabilizers cannot be a radical process. However, the reduction of the spin density reported by Menczel et al. can be easily explained by the polaron theory.

In fact, in the presence of barium stearate, HCl was neutralized to $BaCl_2$ (which is not a Lewis acid like HCl). It follows that the dual effects of HCl on the CjPS in dhc-PVC to produce polarons [197], such as the isomerization of the oxidization reaction of CjPS, are eliminated. Accordingly, the stabilization mechanisms were widely believed to be ionic in nature. This conclusion has been supported by many factors: (1) all the primary stabilizers possess ionic behavior and nucleophilic groups; (2) no free radicals are detected in the PVC DHC [74, 76]; (3) nucleophilic substitution reactions were fully supported by the results of various studies carried out with model compounds bearing such defect structures [9, 16, 19, 180, 189, 198–202]; and (4) stabilizers do not give spin dioctyltin thioglycolate (DOTTG) even at 180°C for 5 hours [203].

Nevertheless, the main controversy in the stabilization of PVC by MS stabilizers does not concern the substitution reaction mechanisms, but the esterification of the labile chlorine itself. In fact, recent works dealing with solid or molten polymers or polymers in solution have all concluded that the esterification reaction or substitution reaction could not be regarded as a prominent process in stabilization since the quantity of moiety grafted onto the polymer chains either by MS [196] or by OT compounds [204] is insignificant and the grafting occurs only during the induction period [158, 193, 204–207] on the one hand, and on the other the shortening of the polyene sequence observed in the stabilization might be caused by the cyclization of polyenes [208].

With OT stabilizers, the saturation of the degraded PVC seems to be a stabilization reaction; for example, thio by-products have been added to the double bonds in the degraded polymer [158, 182, 185, 186, 204]. Moreover, many workers [73, 178, 184, 188, 209–212] have attributed the dienophilic properties of maleic compounds to the long-term stabilization. More recently, Sabaa et al. [213] developed a new class of maleimide stabilizers (totally organic stabilizers) that are more effective than MS stabilizers or organotin maleate compounds. This superiority, according to the authors, can be explained by the Diels–Alder reaction, but is ascribed to a two-step radical reaction leading to the substitution of the allylic chlorine by the ethylenic carbon of the maleate group. On the other hand, in a model study Tran and coworkers [214] showed that hexadiene did not give Diels–Alder condensation with maleates but only with maleic anhydride.

On the other hand, in the thermal treatment of PVC diluted in different long alkyl chain solvents, an induction period can never be obtained, though a lower DHC rate was observed. Thus, the induction period observed in the thermal stabilization of PVC must have its origin in the stabilizer, for instance, the substitution of allylic chlorine atoms. Furthermore, in the stabilization of PVC by MS compounds, the effectiveness of stabilization was shown to occur only during gelation [215], and the quantity of grafted stabilizer on polymer was very tiny [196, 204]. Many pertinent works have been devoted to quantitative studies of the esterification reaction. By Fourier transform infrared (FTIR) studies carried out for the detection of grafted moiety during the stabilization in solution of PVC with MS [29, 42, 192] or OT stabilizers [193, 205–207, 209], it was shown that the esterification reaction did occur because of the identified residue of carboxylate group grafted on the stabilized polymers. This reaction also occurred only during the induction period, and the quantity of moiety residue was found to be of the same order as the number of labile chlorine atoms initially existing in the PVC resin.

Accordingly, many stabilization alternatives have been put forward for the stabilization mechanism. For example, the effectiveness of MS stabilizers could be assigned to a complex formation of different types. According to Vymazal, Mastný, and Vymazalová [216], the mechanism of thermal stabilization of PVC depends on the ability of the metal carboxylates to form complexes with chlorine atoms of the polymer chain in preventing the formation of the long polyene sequences responsible for the coloration of the dehydrochlorinated polymer (dhc-polymer) [198, 216]. The complex could even arise from the interaction of carboxylic acid with the decomposition products of MS stabilizers [217]. Furthermore, the ability of the transition metal ions to coordinate bond formation could accelerate intermolecular cross-linking, which hinders both the elimination reaction of HCl and the cyclization reaction [218]. The stabilization can also be due to the radicals formed from stabilizers and incorporated into the polymeric macroradicals inhibiting DHC [24, 25, 54, 198, 219].

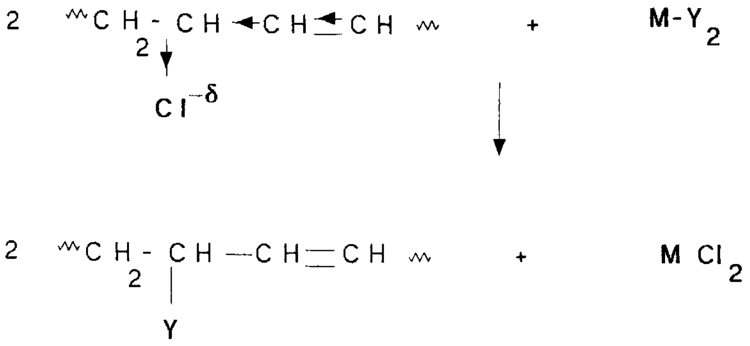
Two new concepts have also been proposed. The first, postulated by Naqvi [137], was mentioned above. The second concept, proposed by Ivan et al. [220], involves the blocking effect of stabilizers on the zip-elimination process during the induction period. After the stabilizers have been consumed, zip dehydrochlorination occurs because of the subsequent deblocking effect.

2.2. The Polaron Mechanism in Poly(vinyl Chloride) Stabilization

2.2.1. *General Mechanisms*

As shown in the first part of this review, under thermal effects and depending on the nature of the medium, either ACA or MHA are activated, leading to DHC. The stabilization reaction must involve the substitution of these activated sites by stabilizer moieties and the saturation of the double bonds by the by-products generated during the stabilization.

The process of the stabilization of PVC with stabilizers in a neutral solvent can be suggested as follows: At the beginning of the stabilization, the alkyl chain of the stabilizer favors the cis configuration of the double bonds that exist initially or are developing in the polymer. As no solitons or polarons are yet formed in the cis CjPS, the chlorine atom of allylic structure (ACA) is active because of the induction effect, which introduces a fractional negative charge to the ACA (Scheme 23):

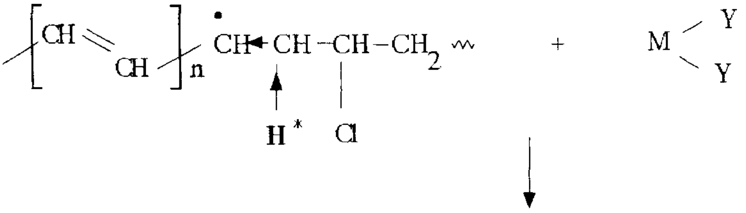


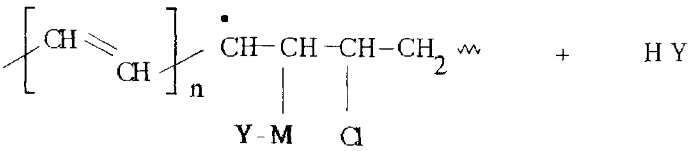
(Fractional negative charge Allylic Chlorine $Cl^{-\delta}$)

SCHEME 23.

As soon as MCl_2 (by-product of stabilizer from the substitution reaction or from reaction with HCl) is produced in the medium, being a Lewis acid, it enhances the cis-to-trans isomerization of CjPS and oxidizes the π electrons in the double-bond systems. Both of these effects result in proliferating polarons. The ACAs are then deactivated (Schemes 13b, 14–16); consequently, the substitution reaction is inhibited, but the degradation reaction begins to propagate via AMHA, even if the stabilizer is not yet all consumed.

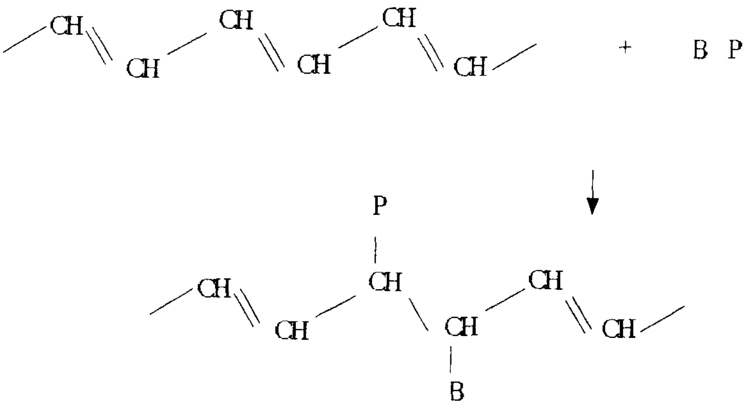
Moreover, if the stabilizer reacts with the AMHA, it effectively stops the DHC (Scheme 24):





SCHEME 24.

Finally, the by-products (HCl from PVC and compounds from stabilizers) give addition reactions with double bonds of degraded PVC (Scheme 25):

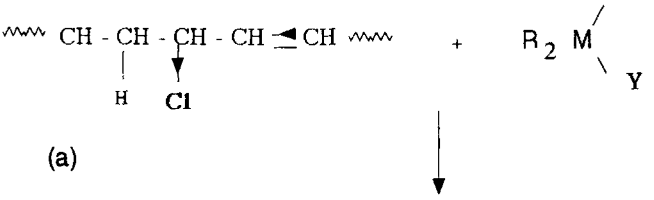


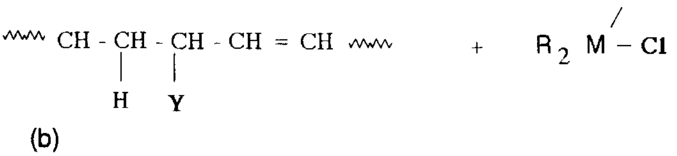
SCHEME 25.

This reaction, which reduces or suppresses the conjugation length of CPS, contributes efficient stabilization since it inhibits the formation of polarons.

2.2.2. Stabilization of Poly(vinyl Chloride) by Different Stabilizers

2.2.2.1. Substitution of Activated Allylic Chlorine Atom (AACA). As described above, stabilization involves the substitution of ACAs by the stabilizer moiety. Scheme 26 illustrates the reaction:





$$\sim CH-\underset{H}{CH}-\underset{Y}{CH}-CH=CH\sim \quad + \quad R_2M-Cl$$

SCHEME 26.

where, for OT compounds, *R* is an alkyl group, *M* is the central metal atom, *Y* is a moiety group such as $-O-C-OR'$, $-SCH_2COOR'$, $-SCH_2CH_2COO-$, $-OOC-CH=CH-COOR'$, or the like and, for MS compounds, $R = O$, $M =$ Cd, Zn . . . , and *Y* is the carboxylate group.

From the polaron mechanism point of view, the alkyl chains link to the metal atom by interacting with the CjPS of degraded PVC, controlling its cis/trans configuration, and a long alkyl chain favors the cis configuration, therefore inhibiting the formation of solitons [221]. Therefore, the nature and the length of alkyl groups affect the induction period. In fact, with the MS compounds, the stabilizing effectiveness is better when the carboxylate group is derived from a long hydrocarbon chain. This could explain why $ZnCO_3$ or $Zn(CH_3CO_2)_2$ are not used in practice for stabilization, contrary to hexanoate or stearate derivatives. The same is true with OT compounds because the stabilization is more effective with octyl than with butyl or methyl chains [184].

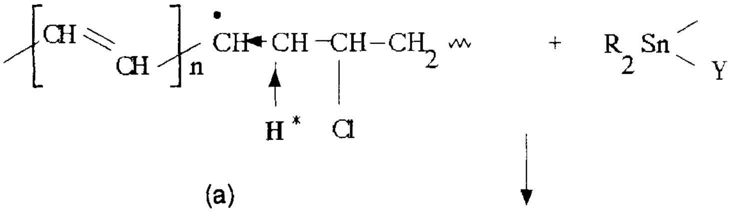
The effect of long alkyl chains has been confirmed in many studies, though the explanations are different. According the Naqvi [137], the long alkyl chain has an important bearing on thermal stabilization because it acts as a diluent to reduce any polar interaction in the polymer, whether these polar origins come from either the polymer itself (cluster of partially charged chlorine atoms) or the incorporation of the moieties of stabilizers in PVC [143]. These polar groups constitute the weak spots that are the initiation sites of DHC [137]. Recently, in a thermodynamic approach to the mechanism of thermal stabilization of PVC, the effect of the alkyl length of zinc carboxylates on stabilization was also observed [222].

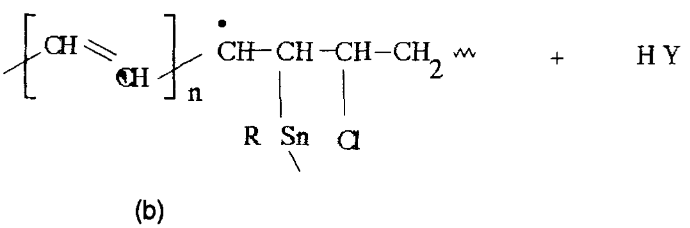
However, when the alkyl chain of the tin compounds is very long (longer than octyl), it can produce a negative effect on the stabilization for two reasons: (1) the longer and bulkier alkyl groups, being a steric hindrance, reduce the coordination ability of tin stabilizer in a nucleophilic reaction, and (2) a very long hydrocarbon chain can undergo a partial crystallization and become incompatible with the polymer.

When R_2MCl_2 (by-product of the substitution reaction) is present in the medium, the rate of polaron formation depends on the nature of these by-products. In fact, because of the low Lewis acidity [47] of organotin chlorides R_2SnCl_2, their effects on the cis-to-trans isomerization of CjPS or on the oxidation of the π electrons in the double-bond systems are not as important as those of the metal chloride MCl_2 (by-product of MS stabilizers). Since these metal chlorides regenerated during the stabilization have no alkyl group (MCl_2, with M = Zn, Cd, . . .), they are powerful Lewis acids; therefore, they enhance the cis-to-trans isomerization of CjPS and oxidize the π electrons in the double-bond systems [167]. This explains why the induction period of the stabilization with MS stabilizers is short.

On the other hand, the Lewis acidity of OT compounds is correlated to the nature and the length of the organo R group. If the R group is a shorter alkyl chain, the Lewis acidity of the organotin compound is higher, but it is highest when R is an aryl group [223]. These dual effects of the OT compounds, the cis/trans configuration control and the oxidation power of the π electron of the CjPS, are the reasons for their distinguished effectiveness compared with their MS homologues. In fact, the stabilization effect of PVC by OT compounds derives from their by-products, the dialkyltin dichloride or the metal dichloride. The metal dichloride, having no organo group, is a more powerful electron acceptor than the organotin dichloride [167], so it preferentially creates positive polarons or bipolarons with CjPS as the induction period is shorter and the grafting yield of moiety is lower when PVC is stabilized with MS stabilizers. The same phenomenon is observed with the organotin stabilizers containing a phenyl group instead of an alkyl group because, due to the resonance effect, the C–Sn bond of phenyltin is very sensitive to HCl to give products progressively from dichlorides to stannic chloride $SnCl_4$ [134, 158]; the last Lewis acid is as powerful as $ZnCl_2$ [18] and consequently oxidizes the π electrons into bipolarons. The number of alkyl groups also increases the stabilization effect because dialkyltin dichlorides have been shown to be more effective than the monoalkyltin trichlorides [184].

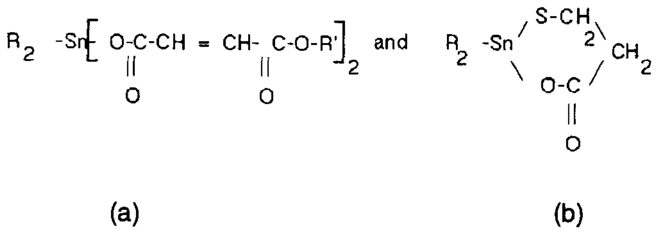
2.2.2.2. Substitution of Activated Methylene Hydrogen Atom (AMHA). Since chloride salts initiate the DHC via AMHA, however, if the stabilizer can react with the AMHA, it stops the DHC. This reaction does not take place with MS compounds because of its difficulty in forming the carbon-metal (C–M) (M = Zn, Cd, . . .) bond. Nevertheless, with OT compounds, the reaction easily takes place in competition with the DHC reaction (Scheme 27).





SCHEME 27.

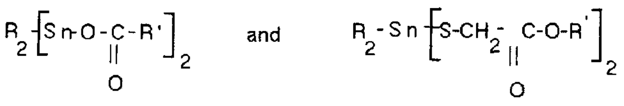
By this mechanism, stabilizers of higher basicity (or nucleophility) such as bis-monomethyl maleate (due to the vinylene structure, Scheme 28a) and β-mercaptopropanoate (due to the cyclic structure, Scheme 28b)



$R_2\text{-}Sn[O\text{-}C(=O)\text{-}CH=CH\text{-}C(=O)\text{-}O\text{-}R']_2$

SCHEME 28.

can easily react with AMHA. This, observed in the studies of Frye, Horst, and Paliobagis [178], can account for the higher efficiency of these two compounds compared with the two other OT compounds of lower nucleophilicity, dibutyltin bis(2-ethylhexanoate) and dibutyltin thioglycolate, which structures are shown in Scheme 29.



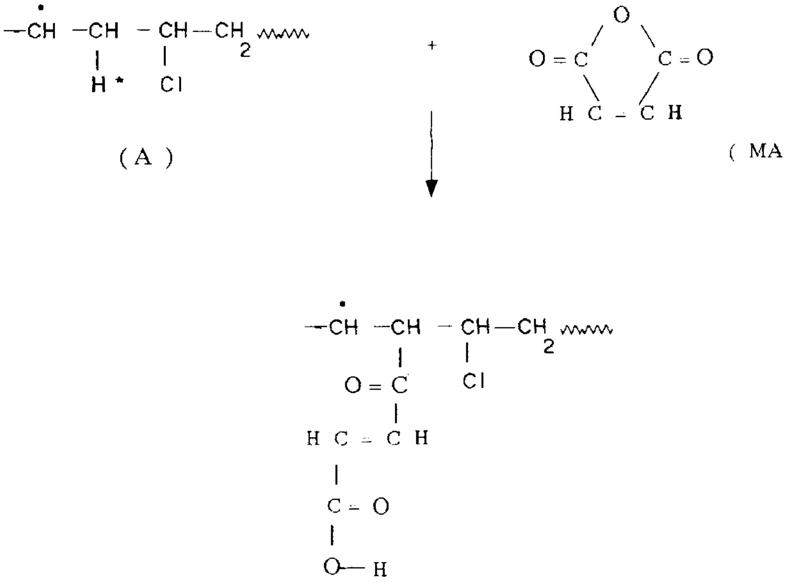
$R_2\text{-}[Sn\text{-}O\text{-}C(=O)\text{-}R']_2$ and $R_2\text{-}Sn[S\text{-}CH_2\text{-}C(=O)\text{-}O\text{-}R']_2$

SCHEME 29.

Furthermore, the esterification reaction of AMHA can explain the high efficiency of OT stabilizers compared with MS stabilizers.

2.2.2.3. Stabilization of By-Products

By-Product of Organotin Maleates: Under thermal effect, organotin maleates give maleic anhydride (MA) as a by-product [178, 211, 212, 214]. A Diels-Alder reaction between MA and degraded PVC has been suggested by many workers [73, 178, 184, 188, 209-212]. However, this reaction has not been conclusively confirmed [207]. Tran, Nguyen, and Molinié [203] have proposed that MA, due to its cyclic structure, gives a reaction with AMHA in CjPS as shown in Scheme 30:

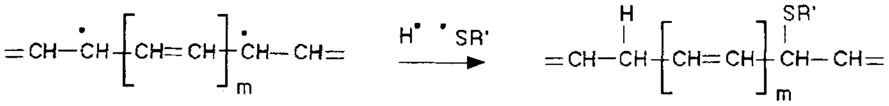


SCHEME 30.

This mechanism explains how the maleates are the long-term stabilizer because the maleate by-products have given rise to a *C*-alkylation product that is insensitive to HCl acidolysis compared with the *O*-alkylation bond [49, 176].

By-Product of Organotin-Thioglycolate: When dioctyltin thioglycolate (DOTTG) reacts with HCl, it gives octylthioglycolate acid $HSCH_2COO(octyl)$. In the work of Alavi-Moghadam, Ayrey, and Poller [204], the thiol moieties have been shown to be massively and permanently grafted onto the polymer. In fact, by using di(butyl ^{35}S thioglycolato) dibutyltin, the authors observed that there was only limited uptake of radioactivity during the induction period. This was ascribed to the exchange between allylic chlorine atoms in the polymer. At the end of the induction period, incorporation of radioactivity occurred more rapidly; this, according to the authors, was due to the addition of liberated thiol to double bonds in the degraded polymer. On the other hand, it was also shown that free thioglycolate ester gave substitution reactions with allylic chlorine of a model compound [202].

The fact that DOTTG, at a temperature as high as 180°C, can give spin only after 5 hours suggests that the radicals observed are from their decomposed product thio derivatives rather than from the stabilizer itself. Therefore, free radicals such as thioglycolic acid butylester (BuO-COCH$_2$SH) have been detected in the by-product [203]. The radical addition reaction is illustrated in Scheme 31:



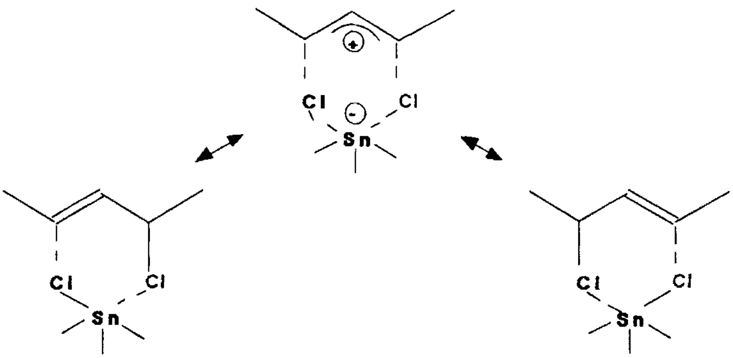
(Solitons •) (m=0,1,2....)

SCHEME 31.

Furthermore, when the medium contains a concentration of R_2SnCl_2 high enough to oxidize solitons, the addition of thiol derivatives proceeds by the same mechanism as that of HCl, as discussed next.

By HCl Catalyzed by Organotin Chloride: HCl can contribute to stabilization by its addition reaction to the double bonds of the degrading PVC, particularly in the presence of R_2SnCl_2 acting as a catalytic agent [176]. The reaction mechanism of this addition reaction has been explained by the polaron theory [167].

The unexpected retardation effect of alkyltin chlorides on the thermal DHC of PVC explained by Wirth and Andreas [168] as the result of a formation of a π-allyl complex between the double bond of the allylic chlorine and the tin chloride is outlined in Scheme 32:



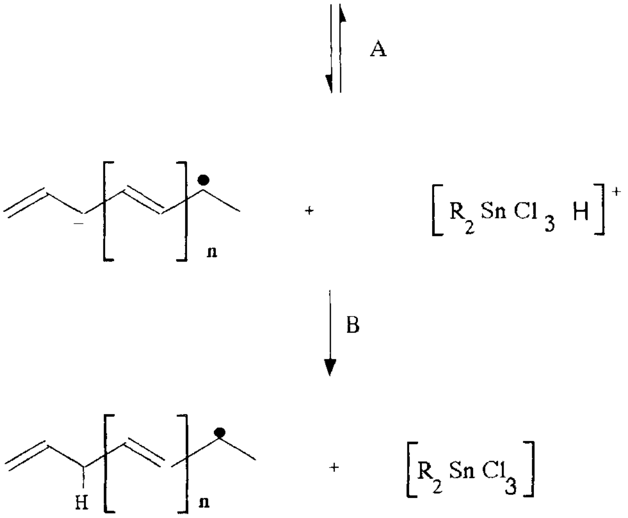
SCHEME 32.

According to the authors, such a complex is able to isomerize the double bond; this isomerization should lead to the blocking of the HCl elimination [224]. However, as the proposed isomerization gives rise unavoidably to an allylic structure, it is unlikely that isomerization is responsible for the DHC retardation.

As is seen, the complex proposed by Wirth and coworkers may be seen to involve only positive and negative charges, but not paramagnetic species (i.e., solitons or polarons). However, the spin was significantly detected even in the early period of PVC DHC in the presence of dioctyltin dichloride (DOTDC) [167]. This clearly reveals that the tin compound has affected CjPS by some other process than a simple coordination of chlorine atoms (i.e., by an electrochemical reaction). This reaction gives rise to a complex that is responsible for the coloration formation reported by Schlimper [170], as well as by Iida and Goto [130]. In terms of the polaron mechanism, the interaction is the oxidation of the π electron to create polarons [93–96].

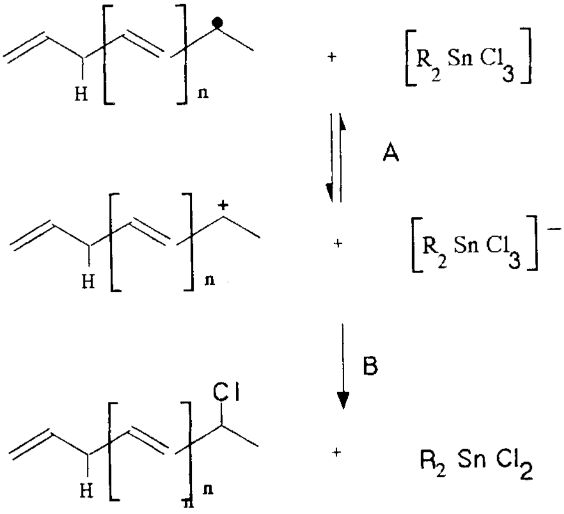
The addition reaction, catalyzed by the organotin chloride, was intensively studied for HCl and hexadiene (used as a model compound of CjPS), and it has been proposed that the reaction is ionic [49]. Also, the readdition mechanism of HCl is not a radical for the following reasons: (1) the high spin in the PVC stabilized with organotin chlorides; (2) neither hydrogen nor chlorine are detected during the DHC, which proves that there are no hydrogen or chlorine radicals to recombine into molecules; (3) no homoscission of C–Sn bond is observed when dialkyltin dichloride is thermally treated at 180°C, and no free radicals are detected when Oct_2SnCl_2 is heated at 150°C with 2-4-6-tri-ter-butylnitrobenzene as the spin trap for 3 hours; (4) furthermore, when the organo group is aryl, such as in $\phi_nSnCl_{(4-n)}$, the C–Sn bond should be more sensitive to thermal homolysis than the alkyl derivative, but the DHC is highly accelerated. For these reasons, the retardation effect cannot be ascribed to the grafting onto the PVC backbone of the radicals that arise from the C–Sn cleavage, as has been previously reported [169, 225, 226].

Therefore, the readdition of HCl should proceed by a polaron mechanism. First, the complex $H^+(R_2SnCl_3)^-$, formed from HCl and R_2SnCl_2 (49, 223), reduces the π electrons of CjPS to a negative polaron (or reduces a soliton to a negative soliton) in the backbone of the polymer (Scheme 33, A). Then H^+ of $[H^+(R_2SnCl_3)]$ reacts with the carbanion in the chain and (R_2SnCl_3) is liberated (Scheme 33, B):



SCHEME 33.

Then (R_2SnCl_3) oxidizes the π electrons of CjPS to a positive polaron (or oxidizes a soliton to a positive soliton) (Scheme 34, A). In the next step, Cl^- of $(R_2SnCl_3)^-$ attacks the carbocation, and R_2SnCl_2 is regenerated (Scheme 34, B):



SCHEME 34.

The readdition and elimination reactions of HCl are in competition when polarons are formed. But, contrary to the organotin chloride, the free-alkyl metal chloride with its very powerful oxidation cannot give any stabilizing effect because the rates of creation of polaron/bipolaron and of subsequent DHC are much faster than those of HCl readdition.

2.2.3. *Stabilization with Secondary Stabilizers*

2.2.3.1. Action of Secondary Stabilizers in the PVC Thermal Stabilization. Because of the short induction period that MS stabilizers give in the stabilization, they have been used together with secondary stabilizers (SS) in order to delay the discoloration of the polymer. The synergetic effects obtained by SS in the presence of metal (Cd, Zn) carboxylates have been explained by their reactivity toward HCl, allylic chlorine atoms, and metal chlorides [18, 50, 155, 192, 193, 227]. More recently, the effect has also been found to be due to the hydrogenation of the double bonds in dhc-PVC [193].

These stabilization effects can also be well explained in terms of the polaron theory. In fact, at the beginning of the stabilization, the SS induce a cis configuration of CjPS, hence the ACA substitution is favored. After the induction period, or when polarons are formed, the SS can give a substitution reaction with AMHA, a reaction similar to that of MA (Scheme 30). The outstanding long-term efficiency of SS such as epoxide or dihydropyridine derivatives can be attributed to their substitution reaction with AMHA rather than with ACA.

2.2.3.2. Effect of Secondary Stabilizers on the CjPS Configuration. During stabilization, the SS affects the configuration of CjPS of dhc-PVC. This effect, which is a common property of the class of SS but not yet revealed or clarified, arises from the long alkyl chain incorporated into the stabilizer molecules. The mechanism of interaction between alkyl chains and double bonds leading to the cis structure of CjPS has been proposed in Refs. 96 and 221. As a matter of fact, most efficient SS contain long alkyl chains. For instance, barium and calcium stearates are known to be good partners of cadmium or zinc stearates [18]. Dihydropyridine derivatives that give a better synergic effect with metal soaps during the stabilization in solution [193] have two dodecyl chains in the structure. For the phosphorus compounds, it was shown that the stabilization effect is greater when the alkyl length in trialkyl phosphites is longer [41, 156]. This is also verified for β-diketone compounds. Alone, diketone compounds give very good performance as far as initial color is concerned, which must be attributed to their isomerization power. The induction periods obtained with the mixture of metal soaps and diketone derivatives have been shown to be longer when stearyl or branched alkyl chains are incorporated in the diketone structure [192]. In contrast, the efficiency of stabilization becomes much poorer when the SS contain an aryl group, as in the case of phenylphosphites [155, 156], dibenzoylmethane [192], and benzyl ether of polyols (monobenzyl ether or ditrimethylolpropane) [226].

2.2.3.3. Inhibition of MCl_2 *Activity in Polaron Formation.* The action of SS on MCl_2 and HCl has been intensively studied. It was found that compounds such as barium or calcium stearates [18], phosphite [155], epoxide [50], and the like destroy MCl_2, while phosphine [155], dihydropyridine [193], and polyols [226 and references therein] form a complex with them. We have shown that these reactions' effects are to reduce polaron formation in the PVC backbone [221]. As a result, the DHC rate must be reduced.

2.2.4. Stabilization in Air Atmosphere

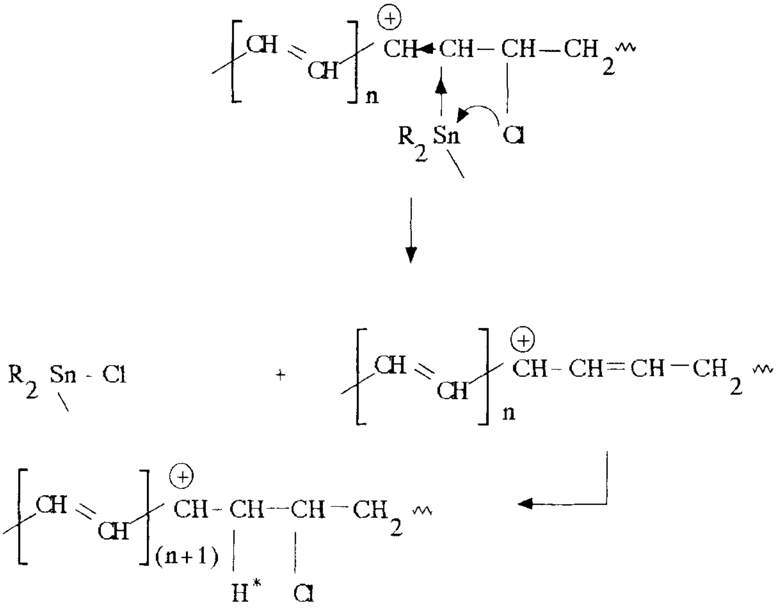
In our recent work [206, 207], the stabilization of PVC carried out in air saw the induction periods greatly reduced regardless of the nature of the OT stabilizer used. This accelerated DHC in the presence of oxygen has been reported previously by other workers [29, 228, 229]. Tudos et al. [230, 231] have shown that the total energy of HCl elimination is almost the same under an inert or air atmosphere. However, many workers have agreed that the accelerated DHC is due to a parallel mechanism: a reaction of DHC by successive activation of allylic chlorines and a radical reaction of DHC by decomposition of unstable structures such as peroxides [1, 10, 29, 73, 228, 232, 233]. The DHC mechanism of PVC in the presence of oxygen is therefore complicated because DHC proceeds by many different pathways.

Here, the polaron theory also contributes to the mechanism of DHC of PVC in the presence of oxygen [93, 95]. Being an electron acceptor, oxygen oxidizes the π electrons in the double bonds to form positive polarons/bipolarons. Considering the much higher oxygen concentration than that of double bonds in degrading polymer (as well as of R_2SnCl_2 generated *in situ*), the positive bipolarons are predominant. In this case, the overactivated hydrogen atoms are the favorite sites for the zipper DHC. On the other hand, if the substitution reaction was in competition, the resulting substitution products should be destroyed later by HCl or by the charged soliton, discussed below. Thus, the induction period of the stabilization must be much reduced.

2.2.5. Retrodegradation

Retrodegradation occurs when the substitution product is destroyed during the stabilization.

2.2.5.1. *By Charged Solitons.* The retrodegradation can occur with the substitution product itself whenever the medium becomes highly reduced (by accumulation of Lewis acid). In fact, in this case the soliton is oxidized to a charged soliton. This leads to the reduction in electronic density of the tin atom of the substitution product and favors the attack of the vicinal chlorine atom on the tin atom (Scheme 35):



SCHEME 35.

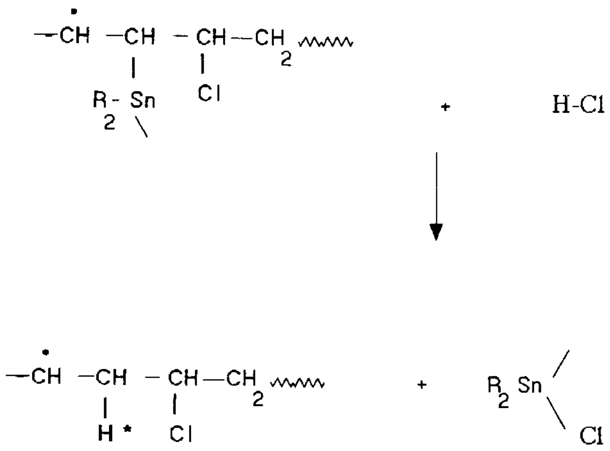
This retrodegradation reaction forms a new double bond and a new AMHA that gives rise to DHC.

With MS stabilizers, if their reaction with AMHA can take place to give a substitution product, the latter immediately undergoes a retroactive reaction since the metals zinc or cadmium have a high electroaffinity. On the other hand, the retroaction is enhanced by the MCl_2, a powerful Lewis acid. This explains well why soap stabilizers have a very short induction time.

2.2.5.2. *By HCl.* HCl can cleave some bonds in the substitution products.

C-Sn Bond: The structure of the substitution product (Scheme 27b) is similar to R_3SnR'; therefore, it is very reactive with HCl [134, 158, 159].

The reaction of HCl on the substitution product generates the initial labile structure (Scheme 36):



SCHEME 36.

O—C or S—C Bonds: As we have reported [18, 50], when the substitution reaction proceeds via an *O*-alkylation, the resulting structure (Scheme 26b) is very sensitive to HCl acidolysis to give back the allylic structure. We think that the same is true for an *S*-alkylation product.

The retrodegradation reactions caused by HCl acidolysis and by the charged solitons are responsible for the maximum and the fall observed by Frye and Horst in the radioactivity retention during the stabilization of PVC [178].

2.3. Conclusion

The whole process of thermal stabilization of PVC by stabilizers can be summarized as follows: At the beginning of the heat treatment, the alkyl chains of stabilizers control the cis configuration of CjPS to delay the DHC and assist the substitution by stabilizer moities of active labile chlorine atoms according to the mechanism proposed by Frye and coworkers [177, 178].

During stabilization, the metal chloride is accumulated because the stabilizer is consumed by the substitution reaction or by HCl regenerated from the elimination reaction. If the electron affinity of the metal chloride is strong enough, the double bond is then oxidized, and polarons are formed in the polymer chain. Induced by the charge of polaron, the allylic chlorine atom becomes deactivated and blocks the substitution reaction but accelerates the zip DHC. Furthermore, a medium of high oxidation can lead to retrodegradation, a reaction that has the effect of converting the substitution product to the initial labile structure.

The action of secondary stabilizers in the presence of metal soap essentially consists of lengthening the induction period. In fact, in the earlier period of stabilization and during the induction period, the secondary stabilizer maintains the activity of allylic chlorine atoms in the substitution reaction and inhibits the retrodegradation reaction by disfavoring the formation of polarons in the polymer chains. They also give a substitution reaction with MHA.

3. CONCLUSIONS

For a long time, the thermal degradation, as well as the thermal stabilization, of PVC have been explained on the basis of ionic, radical, and unimolar (nonionic, nonradical) mechanisms.

The paramagnetic signals observed in PVC during heat treatment has brought support to the radical mechanism; however, they do not belong to the conventional active radicals resulting from a σ-bond cleavage, but are associated with unpaired electrons of the π system. They are, in fact, the polarons, which are the result of the oxidoreduction of the electron of the double bonds.

From the mechanistic point of view, the polarons are not only the consequence of the degradation itself but, in turn, they enhance the degradation via a process that is not a unimolecular, ionic, or radical mechanism. The process is polaron, by which DHC occurs via allylic, as well as normal, chlorine atoms. They also control the stabilization mechanism, which proceeds less via the allylic chlorine atom but more via the activated methylene hydrogen atoms. Briefly, it is the media (solvent, by-products of salt chlorides) that, by their doping or redox power, give oxidoreduction reaction with the π electrons of double bonds in dhc-PVC to give rise to polarons. The more powerful the redox of a medium is, the easier the polaron formation, the higher is the DHC rate, the longer is the *trans*-CjPS, and the more important is the cross-linking reaction. In contrast, in neutral medium, DHC occurs with a low rate and results in a shorter CjPS length due to the cyclizability of the conjugated double bonds of the cis configuration favored by the medium.

Also, by the polaron theory, it has been shown that efficient stabilizers of PVC, including secondary stabilizers, are those that contain long alkyl chains in the molecules because these long alkyl chains, being a neutral medium, minimize the polaron formation. Organotin stabilizers are more efficient than metal soap stabilizers because they have not only the effect of long alkyl chains attached to the central tin metal, they also substitute the activated methylene hydrogen atom or, with their by-products, reduce the polaron formation by the readdition reaction of the double bonds to stop the DHC. As far as the synergism due to costabilization of the secondary stabilizers and metal soap is concerned, the polaron theory has also shown that the efficiency of a secondary stabilizer arises essentially from the blocking of the polaron formation to favor the substitution reaction of allylic chlorine atoms and to disfavor the retrodegradation.

To summarize, the polaron mechanism gives satisfactory explanations concerning all the phenomena observed in the PVC thermal dehydrochlorination: zipper characteristics of the HCl elimination reaction, accelerated degradation catalyzed by redox compounds, the cross-linking reactions, and the limit of the polyene sequence length. More than eight different reaction mechanisms in the thermal stabilization of PVC (substitution of allylic chlorine atom, substitution of activated methylene hydrogen atom, readdition reaction of by-products to double bonds, stabilization by long alkyl chains, etc.) have been clarified by the polaron theory. Among these stabilization mechanisms, seven are already known. Newly proposed by the polaron theory is the substitution reaction of the activated methylene hydrogen atom for both principal and SS stabilizers. This reaction is one of the most essential in the stabilization and can help in developing new, efficient stabilizers.

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