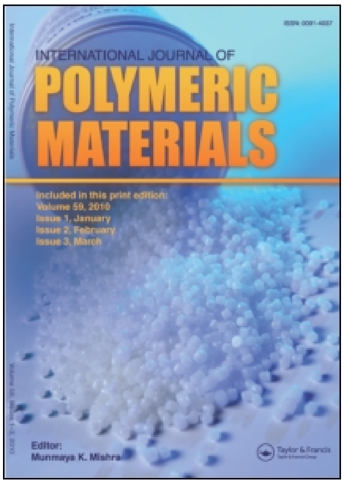

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Characteristic Effects in Degradation and Stabilization of Halogen-Containing Polymers

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Fundamental characteristics of halogen containing polymers are reviewed to identify new approaches for their stabilization.

KEY WORDS Halogen containing polymers, stabilization

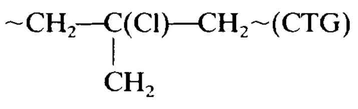
Knowledge and understanding of the fundamental characteristics intrinsic to vinyl chloride polymers identify possibilities for new non-traditional and highly effective approaches to their stabilization and to the creation of high-quality materials and products with lower content of often toxic, chemical additives. The mechanism and kinetics of vinyl chloride polymer destruction and the strategy for stabilization of rigid and plasticized homo- and copolymers of vinyl chloride, are different.

1. DESTRUCTION OF HALOGEN-CONTAINING POLYMERS

The most fundamental effect that determines the rate of destruction is the HCl-elimination rate of vinyl chloride polymers. It governs the means of stabilization and the selection of effective chemical additives. In the case of rigid materials this proves to be short and long range neighbouring group effects.[1–12]

The HCl-elimination process during the thermal decomposition of vinyl chloride (VC) polymers is an aggregate of consecutive-parallel reactions with the participation of homo- and heterotriads based on vinyl chloride chains formed within macromolecules of isolated (at random, V_s) and conjugated (polyene growth) C═C bonds.

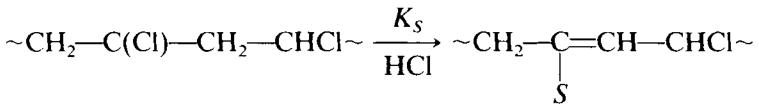
The effect of short-range neighbouring groups is determined by the heterotriads ABXBX, BXBXA, BXABX, where A denotes the second monomer chain (in the case of VC copolymers) and also abnormal groups: chlorallyl ($\sim CH_2—CH═CH—CHCl\sim$) (CAG), vicinal ($\sim CH_2—CHCl—CHCl—CH_2\sim$) (1, 1-dcl), and chlorine at tertiary carbons (at the macromolecular branch points)



$$\sim CH_2-\underset{\displaystyle CH_2}{\underset{|}{C}}(Cl)-CH_2\sim (CTG)$$

It is important to take into account that as a general rule, and for homopolymers practically always, the heterotriad decomposition (CAG, naturally being excluded) results in the formation of chlorallyl groups (CAG), for instance:

$$\sim CH_2-CHCl-CHCl-CH_2\sim \xrightarrow[-HCl]{K_s^{1,2\text{-dcl}}} \sim CH=CH-CHCl-CH_2\sim$$



$$\sim CH_2-C(Cl)-CH_2-CHCl\sim \xrightarrow[HCl]{K_S} \sim CH_2-\underset{\displaystyle S}{\underset{|}{C}}=CH-CHCl\sim$$

$$\sim CH_2-CH(COOCH_3)-CHCl-CH_2CHCl\sim \xrightarrow[-HCl]{K_S}$$

$$\sim CH_2-CH(COOCH_3)-CH=CH-CHCl\sim$$

HCl-elimination from CAG (N_x) with a reaction rate constant K_s^x results in the formation of dienes together with VC clusters within polymer molecules:

$$\sim CH_2-CH=CH-CHCl-CH_2-CHCl-CH_2\sim \xrightarrow[-HCl]{K_s^x}$$

$$\sim CH_2-CH=CH-CH=CH-CHCl-CH_2\sim$$

As a general case the dehydrochlorination rate of VC polymers is described by the equation ($V_{HCl} = \Sigma V_s + \Sigma V_p$):

$$V_{HCl} = K_s N_0 + K_s' N_1 + K_s'' N_2 + K_s^x N_x + K_s^{1,1\text{-dcl}} N_{1,1\text{-dcl}}$$

$$+ K_s^t N_t + K_p \bar{\gamma}_0 + K_p^1 \bar{\gamma}_1 \quad (1)$$

where K_s, K_s', K_s'', $K_s^{1,1\text{-dcl}}$, K_s^t are reaction rate constants during the formation of isolated C—C bonds (CAG, in fact) at random in homo(~BXBXBX~) and heterotriads (~ABXBX~ + ~BXBXA~); (~BXABX~) for VC copolymers; (~CH$_2$—CHCl—CHCl—CH$_2$~) for 1,1-dichlor-groups (vicinal chlorine atoms) and (~C(Cl)≈) for chlorine atoms at tertiary carbon atoms. The concentration of these within the macromolecules is N_0, N_1, N_2, $N_{1,1\text{-dcl}}$ and N_t, respectively, N_0, N_1 and N_2 being determined by the numerical values of the copolymerization constants r_1 and r_2, K_p and K'_p are the rate constants of $(C{=}C)_n$ bonds polyene sequence growths for the HCl-elimination reaction activated by the long range neighbouring group effect: carbonylallyl (oxovinylene) groups – ~C(O)—CH=CH—CHCl~ (CAG) and polyenes of the $\sim(CH{=}CH)_{n>1}$—CHCl—CH_2~-structure (PPS), the contents of which are denoted by $\bar{\gamma}_0$ and $\bar{\gamma}_1$ respectively.

The available experimental and calculated data testify to the fact that the dehydrochlorination rate of VC copolymers with a content of second comonomer exceeding 10–15 mol% is determined only by the effect of short range neighbouring groups[5,7]:

$$V_{HCl} = V_s = K_s N_0 + K'_s N_1 + K''_s N_2 \qquad (2)$$

In this case the long range neighbouring group effect can be neglected and macromolecule self stability as well as the rate of HCl-elimination from VC copolymers are determined by the content of heterotriads N_1 and N_2.

For copolymers with a second monomer content of up to 10–15 mol%, oxovinylene groups $\bar{\gamma}_0$(CAG) may play a marked part together with heterotriad-containing groups (ABXBX + BXBXA) (N_1) and ABXA (N_2)[5,7,12]:

$$V_{HCl} = V_s + V_p = K_s N_0 + K'_s N_1 + K''_s N_2 + K_n \bar{\gamma}_0 \qquad (3)$$

It is of importance that the numerical values of K_s and K_p are always the same as in PVC decomposition, however K'_s and K''_s are notably higher than K_s (for PVC), being characteristic only of VC copolymers. The dehydrochlorination rate of a majority (if not all) of VC copolymers, especially those with alkyl acrylates, vinyl acetates, vinyliden chloride, acrylic acid nitriles, propylene turns out to be consistently higher than the PVC dehydrochlorination rate which depends not only, (and for the case of a second monomer content of 10–15 mass% definitely not), on the CAG content ($\bar{\gamma}_0$) within the macromolecules (the long range neighbouring group effect), but on the ABXBX, BXBXA, ABXA-heterotriad content, i.e., on short range neighbouring group effect.[5,12]

The difference of K'_s and K''_s from K_s (for PVC) is a manifestation of the short range neighbouring group effect and depends on the chemical structure of the second monomer (see Table I).

The correlation constant established is approximated by the valid correlation $K''_s/K_s \simeq (K'_s/K_s)^2$,[13] obtained from the Teft correlation equation

$$1g(K_i/K_s) \neq \rho^* \Delta\sigma^* \qquad (4)$$

which determines the pure effect of short range neighbouring groups, where K_s and K_i are the rate constants of the reactions of standard and substituted aliphatic

TABLE I

Short range neighbouring group effect dependence on comonomer chemical structure in VC copolymers destruction (448 K, 10^{-2} Pa)

Vinyl chloride copolymers	Constants correlation K_s:K'_s:K''_s
Butyl acrylate	1:16:130
Vinyl acetate	1:10:100
Vinyliden chloride	1:15:?
Vinyl alcohol	1:47:1200
Methyl acrylate	1:18:190
Propylene	1:6,5:45

compounds; ρ^* being the constant characterizing sensitivity to the inductive effect of substituents and $\Delta\sigma^*$ being the algebraic sum of substituent inductive constants in the reaction center.

In the case of the transformation of frame groups occurring in VC copolymers during the polymer product decomposition, not only in vinyl chloride chains but in the second comonomer chains as well, the kinetic equations must take into consideration the transformations of the frame groups of all the heterotriad forming comonomer chains.

For instance, for copolymers of vinyl chloride and vinyl acetate[8,12]

$$\begin{aligned} V_{(\mathrm{HCl}+\mathrm{CH_3COOH})} &= (V_s + V_p)_{\mathrm{HCl}} + (V'_s + V'_p)_{\mathrm{CH_3COOH}} \\ &= K_s N_0 + K'_s N_1 + K''_s N_2 + K_p \bar{\gamma}_0 + K_{sA} N_4 \qquad (5) \\ &\quad + K'_{sA} N_5 + K''_{sA} N_6 + K'_{pA} \bar{\gamma}'_0 \end{aligned}$$

where K_{sA}, K'_{sA}, K''_{sA} are the rate constants for CH_3COOH-elimination from the BABABA-, BXBABA + BABABX- and BXBABX-triads; N_4, N_5, N_6 are the content of these triads in the BXBA-copolymer, respectively; K_{pA} is the rate constant of polyene growth in clusters from vinyl acetate (VA) chains in the vicinity with the C═C bonds; and $\bar{\gamma}'_0$ is the content of labile groups initiating polyene sequence growth in ~(=)BABA~triads.

It should be born in mind that the HCl elimination rate equation, given in Table I, (K_s:K'_s:K''_s = 1:10:100) is valid only for BXBA-copolymers, containing 25–30 mol% of vinyl acetate chains.

For the case of higher content of VA-chains within copolymer products the given correlation K_s:K'_s:K''_s changes and in the case of a second monomer chains content higher than 25–30 mol% (and up to 70 mol%) the rate of static dehydrochlorination of BXBA copolymers is decreased i.e., the short range neighbouring group effect is reduced.[8]

In particular, for the case of a vinyl acetate content of 66 mol% the correlation constant is as follows: K_s:K'_s:K''_s = 1:0.5:0.5 and the consequence of the change in intermolecular interaction of macromolecules and basicity of polymer molecules with the variation of the second monomer (VA) content is evident.

PVC destruction represents a special case, when in the general equation for the rate of HCl elimination (1) the proportions of N_1, N_2 and $\bar{\gamma}_1$ (excluding $\bar{\gamma}_1$ for some PVC emulsion grades are zero, and K_s^x, $K_s^{1,1\text{-dcl}}$, K_s are 2–4 orders less than K_p and K_p^1.[4,5,12]

According to the experimental data (Figure 1), theoretical and kinetic calculations[1-5]:

$$V_{\mathrm{HCl}} = K_s N_0 + K_p \bar{\gamma}_0 = K_s \alpha_0 + K_p \bar{\gamma}_0 \tag{6}$$

where α_0 is the HCl content in the initial polymer (mol/PVC base-mol).

Thus, PVC stability and HCl-elimination rate are practically determined by the effect of long range neighbouring groups, i.e., by the content of inner oxovinylene (carbonylallyl) groups, CAG, are essentially the only significant labile groups within PVC macromolecules[4] (Figure 1).

It should also be noted that the CAG content in PVC (the effect of long range neighbouring groups) determines the macromolecular crosslinking rate[14]:

$$V_{cr1} = K_{cr1} \bar{\gamma}_0^2 \tag{7}$$

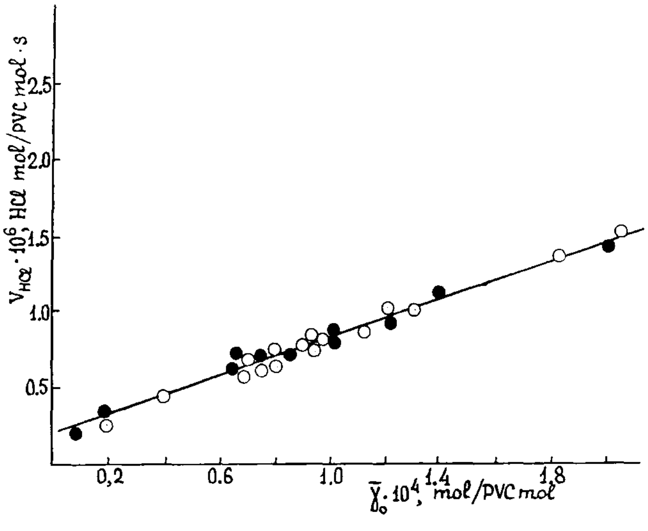


FIGURE 1 The dependence of PVC dehydrochlorination rate on the content of carbonylallyl groups within macromolecules (448 K, 10^{-2} Pa); Commercial specimens ($\bar{M}_\eta^0 \cdot 10^3$; $\bar{\gamma}_0$ mol/PVC mol × 10^4) (x): Thervyl (Czeckoslovakia) (160; 0.2); PVC-50 USA (167; 0.41); B/N 1-8000 Japan (139; 0.70); C-70, CIS (137; 0.70); Sicron 548 FM Italy (143.5; 0.75); Ravenyl RR-100 170 F, Italy (136, 0.80); M-64 CIS (108.5; 0.80); TK-1300, Japan (163; 0.88); Nicavinyl SG-1300, Japan (137.5; 0.92); C-63 CIS (104; 0.93); Solvic 223, Belgium (65.5; 0.96); Vestolyt S 6057 Germany (90; 1.10); Hostalyt, Germany (108.5; 1.19); Lucovil GB-1150, France (133; 1.31); PVC-S-64, Poland (109; 1.80); PVC-K-60-65, Korea (109; 2.02); Laboratory specimens (0): Thervyl, Czeckoslovakia (160, 0.10); (150, 0.13); CIS (83; 0.2); (215.5; 0.67); (146; 0.68); (137.5; 0.77); (119; 0.87); (89; 1.02); (89; 1.02); (124.5; 1.18); (94.5; 1.41); (61.5; 1.97).

2. DESTRUCTION OF VINYL CHLORIDE POLYMERS IN SOLUTIONS

The control of the destruction of dissolved vinyl chloride polymers is the opposite of that for individual polymer products. It is determined by different fundamental laws and may proceed either faster or slower, depending on the solvation effects of the "polymer-solvent" interaction.[15-27]

There is a linear dependence of the PVC brutto-dehydrochlorination rate (V_{HCl}) on the parameter B, solvent basicity (or its donor number D_N), with a correlation coefficient of 0.99 during thermal liquid-phase PVC destruction (Figure 2)[15]:

$$V_{HCl} = KB$$

The definite correlation $V_{HCl} = f(B)$ or $V_{HCl} = f(D_N)$ permits one to conclude that the specific interaction between PVC macromolecules (evidently, ~C(O)—CH=CH—CHCl~ and (or) ~$(CH{=}CH)_{n>1}$—CHCl~ determines the PVC decomposition rate) and the solvent molecules with the formation of the corresponding solvation complexes is of great importance.

As mentioned, experiments show that both the acceleration (basicity higher than

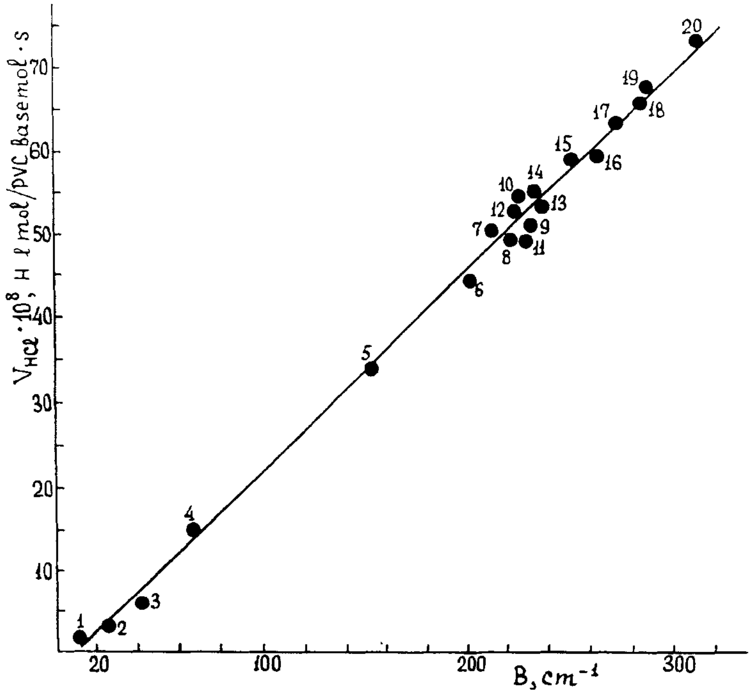
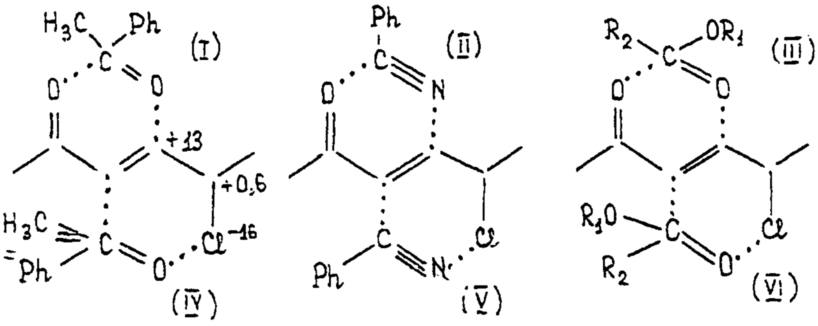


FIGURE 2 The effect of the solvent basicity on the PVC thermal dehydrochlorination (423 K, N_2) in the solution: 1-n-dichlorbenzene; 2-o-dichlorbenzene; 3-naphthalene; 4-nitrobenzene; 5-acetophenone; 6-acetophenone; 7-di-n-(chlorphenyl-chlorpropyl)phosphate; 8-triphenylphosphate; 9-phenyl-bis-(β-chlorethyl)phosphate; 10-tri-(n-chlorphenylphosphate); 11-2-ethylhexylphenyl-phosphate; 12-tricresylphosphate; 13-cyclohexanone; 14-phenyl-bix-(β-chlorpropyl)phosphate; 15-tri-β-chlorethylphosphate; 16-tri-β-chlorpropylphosphate; 17-di(2-ethylhexyl)phosphate; 18-2-ethylhexyldinonylphosphate; 19-tri-(2-ethylhexyl)phosphate; 20-tributylphosphate.

60 cm^{-1}) and the deceleration (basicity lower than 60 cm^{-1}) of the decomposition of dissolved polymer products, are caused mainly by a change in the polyene growth rate V_p. The static dehydrochlorination rate of VC polymers also changes depending on changes in the solvent basicity parameter, B [$V_s = f(B)$], but $V_p > V_s$.

Under condition in which polar solvent molecules affect the highly deformable electronic system of the labile (conjugated ~C(O)—CH=CH~ and(or) ~CH=CH—CH=CH~)-groups within the PVC macromolecules the PVC dehydrochlorination rate change should obviously be related to electromerism effects. The latter suggests the importance of the specific "polymer-solvent" interaction[15,17]:



The formation of structures (I) and (III) results in a decrease in the mobility of the Cl allyl atom which contributes to a deceleration of the PVC dehydrochlorination process.

The interaction of a solvent molecule with the free *d*-orbitals of the chlorine atom of abnormal groups within the macromolecules at the expense of the undivided electron pair of the oxygen (nitrogen, etc.) atom with the formation of structures (IV)-(VI) reduces the labile C—Cl bond and increases the HCl-elimination rate during PVC destruction.

For solutions in which the basicity (B) is more than 60 cm^{-1} the second type of interaction is predominant, and for solutions with a basicity less than 60 cm^{-1} the first type prevails.

Unexpectedly it turns out that ester plasticizers R_1-C(O)OR_2 that are widely used in the production of soft and semiductile PVC materials and products and have another high basicity ($B = 15 + 2$ cm^{-1}) and are effectively analogous to solutions with $B < 60$ cm^{-1}) decelerate 2-3 fold, the HCl-elimination rate during PVC thermal destruction (a triumph in the empiric selection of PVC chemical additives).[16-19,22] This abnormality, one of a number of the pleasant ones, is evidently the consequence of solvation of the polymer molecule by the solvent.

Thus, we can speak about another new fundamental phenomenon for the VC polymers (solvation stabilization) which takes place when the polymer products undergo destruction not only in solutions with a basicity less than 60 cm^{-1}, but in several classes of organic compounds with high basicity ($B = 150 \pm 2$ cm^{-1}) as well. True, for the latter the only example known so far, is that of esters.

As a general case the kinetics of copolymer destruction in solutions having basicity less than 60 cm^{-1} is characterized (analogously to PVC) by a reduction of the HCl-elimination rate, the short range neighbouring group effect being displayed to a

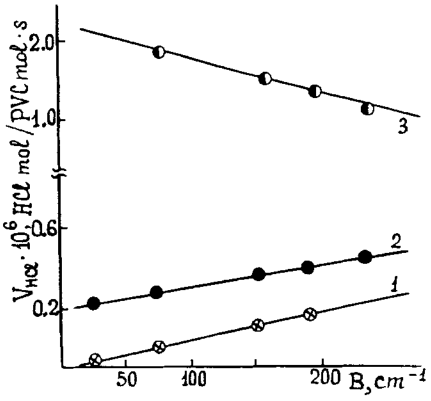


FIGURE 3 The dependence of dehydrochlorination rate of vinyl chloride and vinyl acetate (VC and VA) copolymers in the solution on the solvent basicity (423 K, Argon): VA-units content within the copolymer (mol%): 1) 5.0; 2) 15.0; 3) 32.

considerably less extent as a consequence of "polymer-solvent" solvation interactions and an essential decrease in the intermolecular interaction of macromolecules.[21,23] Unlike PVC destruction in solutions, where the variation of V_{HCl} depending on the solvent basicity (B) is connected with the rate of variation in the polyene sequence growth of C=C bonds, the destruction of VC copolymers causes a variation in the static dehydrochlorination rate of polymer products. It should be stressed that in full agreement with the rule of the dependence of V_{HCl} on the parameter B, the character of this dependence of VC copolymer dehydrochlorination rate on the solvent basicity changes with structural changes in the copolymer products. This is evident in particular for the thermal destruction of BXBA copolymers (Figure 3).[23]

If the rate V_{HCl} increases as the basicity of the medium rises (analogously to PVC) when the content of VA-chains within BXBA-copolymers is up to 20 ± 5 mol%, then with the content of VA-chains exceeding 25 ± 5 mol% the rate of elimination (V_{HCl}) of BXBA-copolymers, on the contrary, decreases as the solvent basicity increases. This is a basic feature distinguishing VC copolymer destruction from the thermal decomposition of PVC in solution.

The experimental evidence testifies to the fact that during copolymer destruction (BXBA especially) in solutions the HCl-elimination rate constant from BXBXBX-homotriads (K_s) depends on the solvent basicity the same as in the case of PVC, i.e., the solvent increase in the basicity (B) results in an increase in the numerical values of K_s.[23] The numerical values of the constants K'_s and K''_s (the constants for HCl-elimination from BABXBX + BXBXBA- and BABXBX-heterotriads) with the increase of the solvent basicity (B) can be markedly reduced. This is seen in the decomposition of copolymers of vinyl chloride and vinyl acetate, and is evidently determined by an inadequate solvation effect of the solvent on the second monomer chains within the heterotriads (VA has higher basicity than VC). As a consequence, the short range neighbouring group effect (VA, for instance) on VC-chains reactivity in the heterotriads of the respective macromolecules of VC copolymers changes with the variation in the basicity of the solvent in which the polymer destruction proceeds. Hence, with the variation of the content of second monomer chains in VC copolymers, the basicity of the macromolecules (*B* is higher or lower than 60 cm^{-1}) is changed as well, and that fact should be born in mind when considering VC copolymers.

Thus, the destruction of VC polymers in solutions is essentially different from the decomposition of individual polymer products and is characterized by a number of special features. Changes in the mechanism and kinetic laws for HCl-elimination being the first.

In the presence of atmospheric oxygen the dissolved decomposition of VC polymers is always sharply accelerated.[28-32] The HCl-elimination rate may rise two orders of magnitude or more (for instance, PVC in ester plasticizers) (Figure 4).[28-31] Moreover, such fundamental phenomena as the long range neighbouring group effects and solvation stabilization of VC copolymers are not of much significance. The thermal oxidation rate of VC polymers is determined by the oxidative stability of the solvent (plasticizer) by atmospheric oxygen, i.e., a certain parameter of the organic compound's oxidative stability (Figure 4)[31-34]:

$$K_{ef} = K_2 \cdot K_6^{-0.5} K_3^{0.5} \tag{8}$$

in the chain oxidation scheme of an organic compound:

$$RO_2^{\bullet} + RH \xrightarrow{K_2} ROOH + R\cdot$$

$$ROOH \xrightarrow{K_3}$$

$$\cdot RO^{\bullet} + HO^{\bullet}RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{K_6} R\text{—}O\text{—}O\text{—}R + O_2$$

The process proceeds according to a free radical mechanism. The free radicals

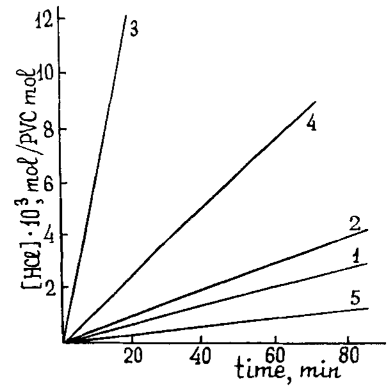


FIGURE 4 The PVC "echo"-stabilization. HCl-elimination in the process of thermal (1;2) and thermoxidative (3;4) degradation (448 K, Argon) of the PVC: in the solution of dioctylsebacate: 1,3-unstabilized PVC; 5, the PVC stabilized with 2,2-bis(4-hydroxyphenyl)propanol; (0.2 mass%) without the solvent (2,4).

formed during the solvent oxidation promote dehydrochlorination of VC polymers. This fact requires a new approach to stabilizing dissolved polymers while processing the respective compositions and using soft and semiductile materials.

3. HALOGEN-CONTAINING POLYMERS STABILIZATION

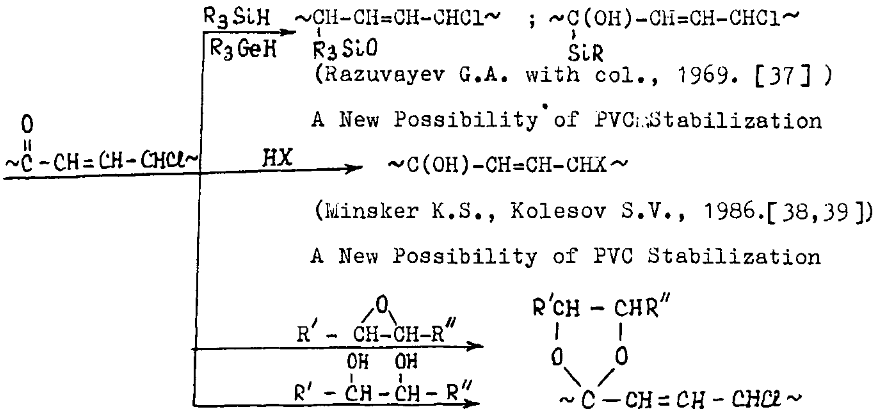
The principles of VC polymers stabilization in creating rigid and plasticized materials, and also solutions, are basically different due to the controlling effect of characteristic fundamental phenomena: effects of neighbouring groups of the long range type for PVC, and of the short range type for VC copolymers when the second monomer content exceeds 15 ± 5 mol%; solvation stabilization of polymer products in solution (plasticizers), and the solvent oxidation product initiated decomposition of VC polymers during thermal oxidation in the presence of atmospheric oxygen. The effective stabilization of PVC and VC copolymers with a second monomer content less than 15 ± 5 mol% is based on the principle of increasing the polymer molecules self-stability by the influence of some chemical, physical etc. factors at the expense of a directional change in the chemical structures of the active centers that determine the decomposition rate of polymer products (oxovinylene (carbonylallyl) groups (CAG) when they chemically interact with various chemical additives (stabilizers) resulting from the polymer-analogous reactions). This new approach has been called chemical stabilization of macromolecules.[5,35,36]

As already noted, the relatively low stability of PVC and VC copolymers with a low content of second monomer, is due to an abnormally high HCl elimination rate during the thermal destruction of the polymer products. This is controlled mainly by the content within macromolecules of oxovinylene (carbonylallyl) groups in accordance with equation (6). With this point in mind, chemical stabilization is based on using compounds (chemical stabilizers), that interact with at least one of the CAG reaction centers: $\overset{\diagdown}{\underset{\diagup}{}}\mathrm{C{=}O}$, $\sim\mathrm{CH{=}CH}\sim$, $-\overset{\diagdown}{\underset{\diagup}{\mathrm{C}}}-\mathrm{Cl}$. These prove to be fruitful for the practical stabilization of VC polymers of this type.[5,35,36]

$$\delta - \ |\delta +' \quad \delta +$$

The conjugation $\mathrm{O{=}C{-}CH{=}CH}$ must be decomposed in the oxovinylene group (CAG) and/or a labile chlorine atom must be substituted by a more stable frame group:

1) Polymer-analogous reactions on the $\mathrm{C{=}O}$ group of CAG:



(Razuvayev G.A. with col., 1969. [37])

A New Possibility of PVC Stabilization

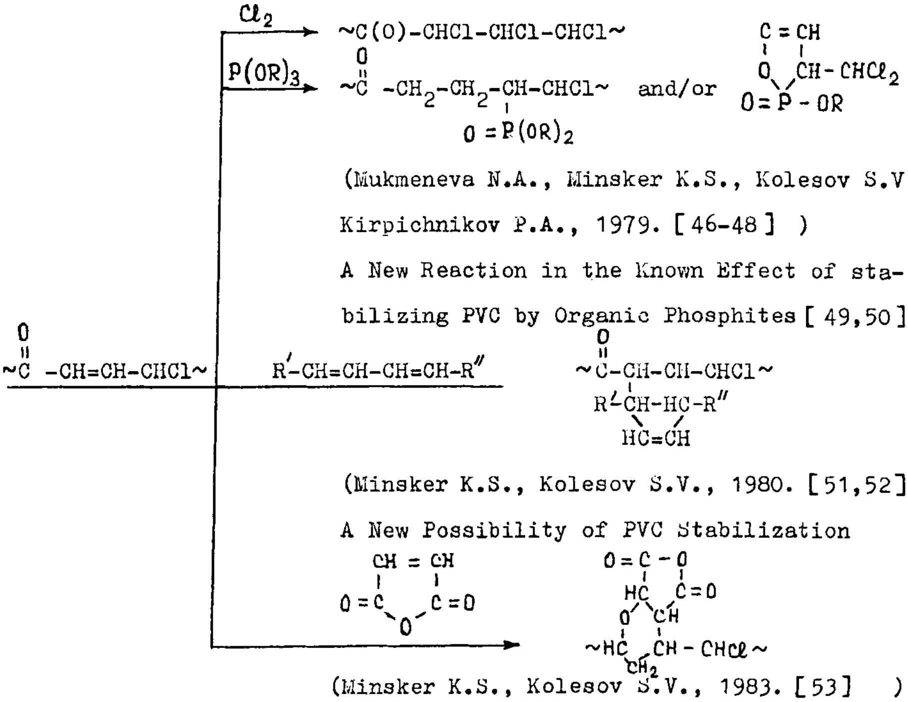
(Minsker K.S., Kolesov S.V., 1986.[38,39])

A New Possibility of PVC Stabilization

(Minsker K.S., Ivanova S.R., 1978, [40])

A New Reaction in the Known Effect of Stabilizing PVC by Epoxycompounds [41-45]

2) Polymer-analogous reactions on ~CH=CH~ bonds:



(Mukmeneva N.A., Minsker K.S., Kolesov S.V. Kirpichnikov P.A., 1979. [46-48])

A New Reaction in the Known Effect of stabilizing PVC by Organic Phosphites [49,50]

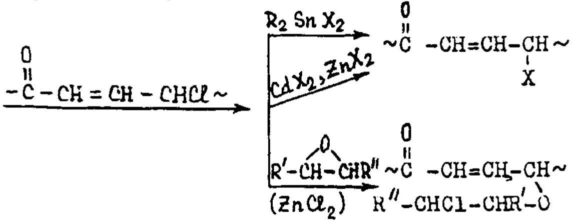
(Minsker K.S., Kolesov S.V., 1980. [51,52])

A New Possibility of PVC Stabilization

(Minsker K.S., Kolesov S.V., 1983. [53])

A New Reaction in the Known Effect of Stabilizing PVC by Maleic Anhydride [54,55] .

3) Polymer-analogous reactions on ≡C—Cl labile bonds



(Minsker K.S., Kolesov S.V., Ivanova S.R., 1982 [56]

A New Reaction In the Known Effect of Stabilizing PVC by Epoxycompounds [41-45] .

These polymer-analogous reactions of various classes of chemical additives with VC polymers, wherein the rate of HCl elimination from the polymer products is determined by the content of oxovinylene groups ($\bar{\gamma}_0$), and the kinetic equations obtained[36] allow an exact interpretation of mechanism of stabilizing effect of the many well known classes of PVC stabilizers (organic phosphites,[46-48] epoxy compounds,[40,56] dienophiles.[53] New possible ways to stabilize PVC chemically are being discovered at the same time (conjugated diene compounds,[52,53] Dils-Alder adducts, α, β-dicarbonyl compounds,[57-59] proton acids,[38,39] etc.

The dependence of an additive's effectiveness on its chemical structure allows us to substantiate from a scientific point of view the selection of proper chemical stabilizers for VC polymers.

It is of importance that chemical stabilization is not limited only to VC polymer dehydrochlorination inhibition. Polymer-analogous conversions of oxovinylene (CAG) groups and polyene groups leads to an increase in color stability for the polymer products[60,61] as well as inhibition of macromolecular crosslinking.[60-62] This improves the operating characteristics of the PVC materials when the fundamental phenomenon of chemical stabilization of polymer products is used for VC polymers, the decomposition rate of which is determined by the CAG content ($\bar{\gamma}_0$). In this case dienophiles, conjugated dienes, and Diels-Alder adducts are especially efficient.

There exists another highly important and practical consequence of VC polymers chemical stabilization, an increase in their photostability[60,61] (Figure 5).

CAG conversion into cyclohexane, dioxalane, dihydropirane etc. groups results in optical density of the polymer in the Ultraviolet. New groups, forming in the polymer-analogous reactions of chemical stabilizers (dienes, dienophiles, organic phosphites, epoxy compounds, diols) with CAG, appear to be internal color stabilizers.[60] In principle, these correspond to the formation of VC-based self-stabilizing polymer products. All the above allows us to speak about a new effect, self-photostabilization of VC polymers.[60]

Means of VC polymer stabilization with a second monomer content more than 20 ± mol% are different from the stabilization of PVC and copolymers with a second monomer content less than 15 ± 5 mol%. In the former case the chemical stabilization of the polymer product is not so effective (or not effective at all) and

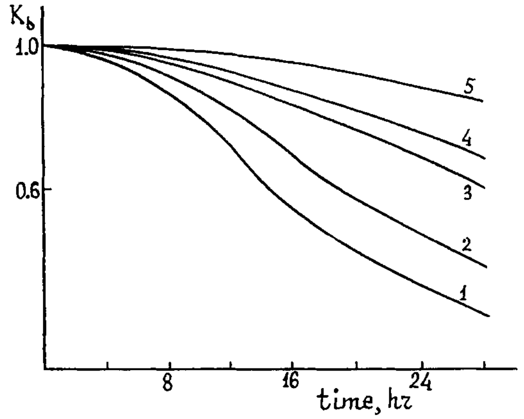


FIGURE 5 The dependence of the coefficient of white colour conservation of the PVC films on the irradiation time as consequence of the PVC chemical stabilization; 1) unstabilized PVC; the polymer treated by: 2) tri-(2-ethylhexyl)phosphite; 3) 2-ethylhexyl-9-10-epoxystearate in the presence of $ZnCl_2$; 4) by piperilene; 5) cyclopentadiene. (295 K, λ = 254 mm; I = 1.5 × 10^{15} quantum/s·cm^2).

their only effective stabilization means is elimination of the catalytic action of HCl, O_2, UV-irradiation, $MeCl_n$ etc. during thermal destruction of VC copolymers. This is a pecularity distinguishing the stabilization of VC polymers from PVC stabilization.

It should be noted that since the dehydrochlorination rate of VC copolymers is determined by the content of heterotriads within the macromolecules, there appears to be an unusual opportunity to increase to some extent the self-stability of VC copolymer macromolecules with a second monomer content exceeding 15 ± 5 mol%, i.e., decreasing the compositional uniformity of the copolymer product macromolecules leading to a lower content of the respective heterotriads within the macromolecules.[64]

4. THE STABILIZATION OF VC POLYMERS IN SOLUTIONS

The fundamental phenomenon of PVC solvation stabilization should be used in the stabilization of PVC and VC copolymers with a second monomer content up to 15 ± 5 mol% and solvent basicity less than 60 cm^{-1}.[16-20] This is achieved by effectively protecting the solvent (plasticizer) from oxidation by atmospheric oxygen through the use of stabilizers (antioxidants) or their synergetic combinations. In this case (as a consequence of the inhibition of the reaction leading to formation of hydroperoxides in the solvent (plasticizer) molecules) the thermal destruction rate of VC polymers in the liquid phase V_{HCl} becomes 1.5–2 orders lower. Within limits (of solvent oxidation by atmospheric oxygen is effectively inhibited) the HCl-elimination rate from the polymer products may reach a value of V_{HCl}, characteristic of thermal destruction in solutions, i.e., for solvents with B < 60 cm^{-1} (and for ester plasticizers too), and essentially lower compared with the value of V_{HCl} under the analogous conditions of decomposition of individual polymer products (Figure 6).

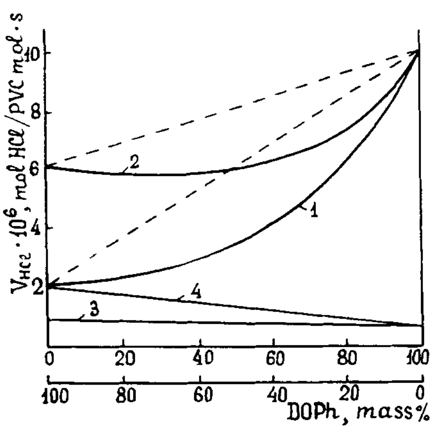


FIGURE 6 "Auto-echo"-stabilization of the PVC in thermoxidative degradation of the PVC in the solution of the mixed solvents (448 K); 1) dioctylphthalate + tricresylphosphate; 2) dioctylphthalate + tri(2-ethylhexyl)phosphate; 3,4) thermal degradation of the PVC in the solution of mixed solvents (448 K, Argon), 1,2, respectively.

This fundamental phenomenon, characteristic of the stabilization of VC polymers in solution, has been called "echo-stabilization."[65] In this case effective stabilization of VC polymers during thermal destruction in solutions where the fundamental effect of solvation stabilization of VC polymers takes place, is performed through solvent (plasticizer) stabilization under the conditions of oxidation by atmospheric oxygen. Solvation stabilization of polymer products is "echoed" due to a specific interaction of polymer and solvent causing lower mobility of allyl chlorine in CAG, i.e., solvate complexes of the I–III types are formed.

Hence, "echo"-stabilization of VC polymers requires a specific approach to creating soft and semiductile materials, basically different from the principles of rigid PVC stabilization.

One cannot so far distinguish specific approaches to VC polymer stabilization when using solvents with basicity $B > 60\ \text{cm}^{-1}$. Therefore, traditional methods of introducing stabilizers (HCl acceptors), antioxidants, etc. are used in the thermal destruction of VC polymers. During solvent oxidation inhibition with $B > 60\ \text{cm}^{-1}$ (excluding ester stabilizers) the HCl elimination rate during the destruction of VC polymers in solution increases in comparison with the rate of thermal destruction of individual polymer products due to formation of IV–VI solvation complexes.

However, in the case when mixtures of phosphate ($B = 210\text{–}315\ \text{cm}^{-1}$) and ester plasticizers (in production of materials with low flammability) are used, despite the fact that phosphates contribute to the acceleration of VC polymer decomposition not only in thermal but thermoxidative destruction of polymer products, a marked reduction of the brutto-dehydrochlorination rate is observed. This including VC polymers with an ester plasticizer content of up to 80–90%, without (and it is extremely important) specially introducing stabilizers (antioxidants) (Figure 7). Thanks to the additive character of the above solvent effect in polymer product destruction one should expect an increase in the HCl elimination rate during the thermal oxidation of polymer products in solutions containing a mixture of phosphate and ester plasticizers. This fundamental and characteristic phenomenon has been called "auto-echo" stabilization[66] and represents a new possibility for VC-based dissolved polymers stabilization. The rate of thermoxidative destruction of polymer products is not reduced at the expense of specially introduced stabilizers (antioxidants), but at the expense of the formation "*in situ*" during phosphate plasticizer oxidation of the corresponding phenols and alcohols that inhibit oxidation of ester plasticizer by atmospheric oxygen.

This new possibility, "auto-echo" stabilization of VC polymers in solutions, as the above "echo" stabilization of PVC and VC copolymers with a low content of the second monomer allows opportunities for effective and economical selection of chemical additives when creating soft and semiductile materials and products, and also in processing VC polymers in solution.

Thus, fundamental characteristic phenomena, in particular, the effect of neighbouring groups of short- and long range, chemical solvation, "echo"- and "auto-echo" stabilization form the basis for strategies in creating high-quality and economical rigid, semiductile and soft (plasticized) materials and products.

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