Macromol. Symp. **2005**, *228*, 299-313

Achievements and Research Tasks for Poly(vinyl chloride) Ageing and Stabilization

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Summary: Perspectives of PVC manufacture, not containing of labile groups in a backbone are considered. It will provide drastic increase of an intrinsic stability of polymeric products, possibility of PVC processing with the minimal contents or in total absence of stabilizers and other chemicals - additives and opportunity of creation of materials and products on a PVC basis with the essentially increased service life-time. Presented data allow to create rigid, semi-rigid and flexible (plasticized) materials and products with the minimal contents of chemicals - additives and increased life-time of their service at exploitation in natural and special conditions.

Keywords: ceolites, modified clays; chemical-, structural-physical, solvatational, and "echo" stabilization; labile groups; non-toxic chemical-additives

Introduction

Poly(vinyl chloride) (PVC) is one of the most known multi-tonnage and practically important polymeric products. Thousand of rigid, semi-flexible, and flexible (plasticized) materials and products based on PVC widely used practically in all spheres of a national economy and everyday life. PVC was synthesized first by E. Baumann in 1872, but it's industrial manufacture had begun much later – since 1935 in Germany according to the literature data and in 1930 in the USA according to the data of the DuPont company.

The global PVC production is impressed: 220 thousand ton in 1950, about 1.5 million ton in 1960, more than 3 million ton in 1965, more than 5 million ton in 1970; now its production is estimated for more than 15 million ton.

The basic PVC problem is its low stability. Under action of heat, UV-light, oxygen, radiations etc. it easily disintegrates under the law of transformation of framing groups with elimination of hydrogen chloride and formation of sequential double carbon-carbon bonds in macromolecules with appearance of undesirable coloration (from yellow up to

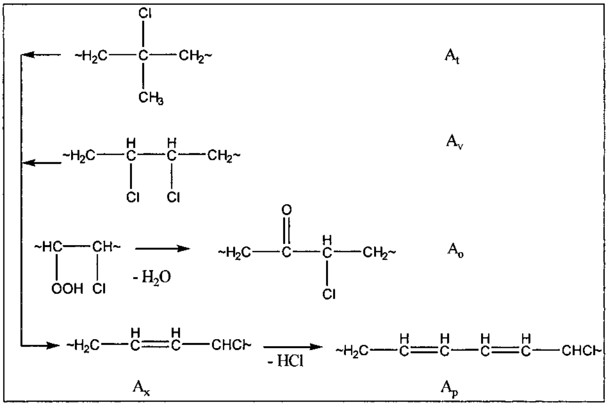
DOI: 10.1002/masy.200551027

black). Therefore, it is necessary to apply set of methods leading to its increased stability to action of the various factors at a storage, processing and exploitation of PVC as well as at the synthesis, storage and the use of materials and products on its basis.

It is logical to assume that among many aspects causing low stability of PVC and rather short life-time of materials and products on its basis, the primary importance has a knowledge of the reasons of abnormally high rates of disintegration of its macromolecules compare to low-molecular weight models. This problem has appeared to be rather complex for understanding of the experts involved to synthesis and processing of PVC and, on – essence, is still being discussed now. The researchers of industrial centers of the different countries to the present time can't find the general point of view concerning identification of a weak site in structure of the PVC macromolecule, which determines its abnormal low stability. However, sometimes it is believed that it is done on purposely, though it is not so clear - what for?.

Who is responsible for low stability of PVC?

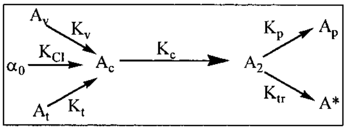
The low PVC stability used to be connected to possible presence of labile groups at the macromolecules' structure, which activate polymer's disintegration. These labile groups are distinct from sequences of regular vinyl chloride repeating units $\sim CH_2CHCl\text{-}CH_2\text{-}CHCl\text{-}CH_2\text{-}CHCl\sim$. The overwhelming majority of the researchers believe that such groupings are: a) chlorine atoms bonded to tertiary atoms of the carbon C-Cl (A_t); b) vicinal chlorine atoms in the macromolecule's structure $\sim CH_2\text{-}CHCl\text{-}CHCl\text{-}CH_2\sim$ (A_v); c) unsaturated end-groups such as $\sim CH{=}CH_2$ and/or $\sim CCl{=}CH_2$; d) β-chloroallyl groups $\sim CH_2\text{-}CH{=}CH\text{-}CHCl\sim$ (A_c); e) oxygen-containing hydroxy- and peroxy groups (A_0) [1-8]. Meanwhile, even after brief consideration of the process of PVC disintegration it becomes obvious that, on - essence, there are much less amount of labile groups (which can be considered as the cause of low PVC stability) in the macromolecules, because at PVC dehydrochlorination tertiary chlorine (A_t) and vicinal (A_v) groups turn into the β-chloroallyl ones and the hydroperoxide groups transform in to carbonyl groups:



Besides, the world practice of PVC research has shown that initial (freshly synthesized) PVC macromolecules (which are processed in materials and products) do not contain di - (A_2), tri - (A_3) and/or polyene (A_p) groups [2, 3, 9 - 14]. Internal peroxide groups ~CH_2-CHCl-O-O-CH_2-CHCl~ are not found as well, since if they are formed at PVC synthesis they would quickly collapse in result of hydrolysis and/or homolytic break of O-O bond. There are reliable experimental results, including ones received at study of thermal destruction of fractioned PVC, showing that although unsaturated end-groups are present at structure of polymeric molecules, they do not affect on PVC's disintegration rate [10, 13-15].

Thus, the process of gross – dehydrochlorination of PVC (V_{HCl}) with sufficient proximity can be described by the Scheme 1, where α_0 - the contents of regular vinyl chloride ~CH_2-CHCl~ groups, and K_{Cl}, K_t, K_v, K_c, K_p – rate constant of the appropriate dehydrochlorination reactions of PVC; K_{tr} – rate constant of destruction of polyenes' growth reaction.

Following from the scheme, V_{HCl} - $K_{Cl}\alpha_0 + K_cA_c + K_pA_p$ with real values of: $K_{Cl} = 10^{-8}$ - 10^{-7} s^{-1} and α_0 = 1 mol/mol PVC; $K_t = 10^{-4}$ s^{-1} and $[A_t] = 10^{-3}$ mol/mol PVC; $K_c = 10^{-4}$ - 10^{-5} s^{-1} and $[A_c] = 10^{-4}$ mol/mol PVC; $K_v = 10^{-3}$-10^{-4} s^{-1} and $[A_v] = 10^{-5}$ mol/mol PVC; $K_p = 10^{-2}$ s^{-1} (448 K).



Scheme 1.

It's obvious that the Scheme 1 assumes the concept of β-chloroallyl activated disintegration of PVC accepted by the majority of the researchers, but without the serious proofs [1 - 5]. However, this postulate is in the contradiction with many experimental facts [16, 17]. In particular:

1). Calculated values of V_{HCl} drastically differ from the experimental ones;

2). The β-chloroallyl activation of PVC disintegration assumes an auto-acceleration of PVC gross - dehydrochlorination process in time [16 - 18]. The linear dependence is observed experimentally (Fig. 1). A gross-rate constant of PVC disintegration, according to experimental data and Fig. 1 at $K_c = 10^{-4}$ -10^{-5} s^{-1} should contain the expression with $K_p \cong 10^{-2}$ s^{-1} (at 448 K) from the very beginning of PVC thermo-destruction.

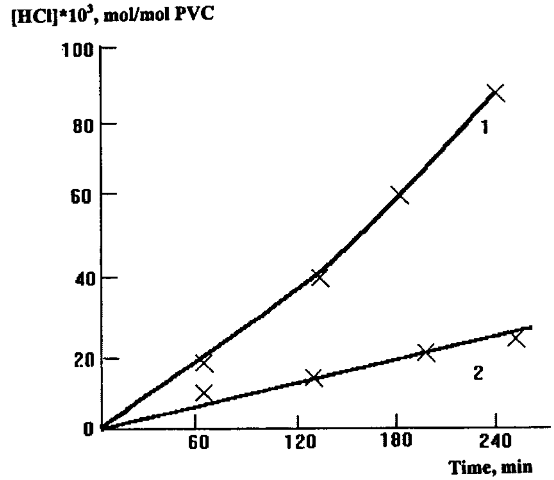


Figure 1. Kinetic curves of PVC dehydrochlorination. β-chloroallyl activation:
1 – calculated data, 2 – experimental data, (448 K, 10^{-2} Pa).

However, according to the data on thermo-disintegration of low molecular weight model compounds [19 - 21] this is observed only at destruction of the model compounds containing a chlorine atom in a β-position to conjugated $(C=C)_n$ bonds (at n≥2) [19-21], *i.e.* at occurrence of the effect of the adjacent group of the long-range order (Table 1). Thus, even the primary analysis of experimental results concerning the concept of β-chloroallyl activation of the PVC dehydrochlorination, does not sustain criticism and has no right on existence. It is the erroneous point of view.

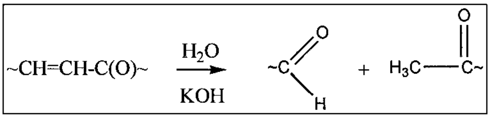
Table 1. Dehydrochlorination rate constant at thermo-destruction of low molecular weight model compounds.

#	Compound	Temperature area where the compounds start to degrade with a noticeable rate, K	Groups' index	Decomposition's rate constant, K, s^{-1}
1	2,4-dichloro-pentane	563 – 593	α_0	$2.6*10^{-9}$
2	*meso*-2,4-di-chloropentane	563 – 593	α_0	$1.9*10^{-9}$
3	3-ethyl-3-chloropentane	488 – 553	A_t	$7.9*10^{-6}$
4	4-chlorohexene-2	433 – 463	A_c	$5.1*10^{-4}$
5	4-chlorodecene-2	438 – 468	A_c	$5.0*10^{-5}$
6	7-chloronona-diene-3,5	343 – 369	A_p	$3.4*10^{-2}$
7	6-chloroocta-diene-2,4	360 – 386	A_p	$2.6*10^{-2}$

It has to be noted that on the basis of theoretical consideration of PVC thermal degradation in view of all available experimental data following can be concluded: even if internal β-chloroallyl groups (as well as tertiary chlorides and vicinal ones) are present in the macromolecules' structure, they do not contribute much to the process of PVC gross-dehydrochlorination due to of their sufficient relative stability. It was assumed and then proved that such a group is an oxovinylen (carbonylallyl) conjugated dienophile group, at which the unsaturated bond is activated by the adjacent electrophilic group C=O ($-C(O)-CH=CHCl-CH_2-$) which, apparently, comprises in PVC macromolecules in rather small amounts $\gamma \cong 10^{-4}$ mol/mol PVC, but disintegrates with the rather high rate ($K_p \cong 10^{-2}$ s^{-1}) with HCl elimination [14, 17, 22 - 24].

It is extremely important to emphasize that the concept of oxovinylene activation of PVC disintegration does not contradict to any of known (up to date) experimental facts. Meantime, new (including the original ones) proofs of existence of the basic groups in the structure of PVC macromolecules have received recently. In particular, oxovinylene groups which are included into a PVC macromolecules, are easily (in mild conditions) splited at alkaline hydrolysis (5 % aqueous solution KOH, 5 % solution of PVC in cyclohexanone) [13, 14] – a characteristic reaction for α, β-unsaturated ketones [25].

Reaction 1:



Using this reaction it's easy to estimate contents of labile oxovinylene groups in the macromolecules' structure (γ_0) by a decrease of PVC's viscosity-average molecular weight [13 - 17].

How can we identify carbonylallyl groups?

It's important to specify that both β-chloroallyl and polyene groups are inert to an alkaline hydrolysis but easily decomposed at oxidizing (at presence of hydrogen peroxide) ozonolysis [13]. The ozonolysis method allows to estimate a complete amount of internal unsaturated (β-chloroallyl, chloropolyenyl, and oxovinylene) groups in the PVC macromolecules' structure by a decrease of PVC molecular weight. Thus, it's experimentally shown that practically all internal unsaturated groups included in PVC's initial macromolecules are oxovinylene ones and PVC dehydrochlorination rate linearly connected to the contents of the internal labile oxovinylene groups in polymeric molecules [14, 26], determined by a method of alkaline hydrolysis (Fig. 2).

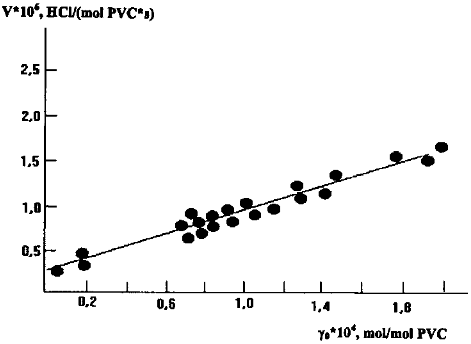


Figure 2. Dependence of PVC dehydrochlorination rate of the contents of carbonylallyl groups in the polymer molecules (448 K, 10^{-2} Pa).

It is characteristic that the polymeric products synthesized in an absence of oxygen, always were noticeable more stable than PVC received in the industry due to the presence in the first case of stable enough internal β-chloroallyl (not oxovinylene) groups (oxidative ozonolysis) in PVC macromolecules' structure. As a whole, the real process of HCl elimination at PVC disintegration on reaction of transformation of framing groups is complex, since generally this or that contribution is brought in by all abnormal groups contained in the macromolecules' structure. However, apparently, the contribution of different reactions to this process varies and in a number of cases some of them can be neglected.

The kinetic analysis taking in account the real contents of characteristic (including abnormal) groups in PVC and rate constants of their disintegration (Table 2) has precisely shown [14, 17, 24, 27] that the ratio of the appropriate reaction rate constants $K_{Cl}:K_c:K_t:K_p \cong 1:100:100:100000$ and for this reason PVC's own thermal stability, on - essence, is determined by an effect of the adjacent group of the long-range order (conjugation effect) and for this reason the total elimination rate of HCl from PVC is described by the simple equation with sufficient accuracy:

$$V_{HCl} = \frac{dHCl}{dt} = K_{Cl}\alpha_0 + K_p\gamma_0 = V_{Cl} + V_p \qquad (1)$$

Even at the account of PVC disintegration with participation of tertiary chloride (A_t) and β-chloroallyl (A_c) groups the contribution of the expression $V_p = K_p\gamma_0$ comprises of about 90 % and more of total gross - rate of PVC dehydrochlorination, that precisely concludes about oxovinylene (not β-chloroallyl) activation of the gross – process of PVC thermal disintegration.

The development of the concept of oxovinylene activation of PVC thermodestruction appeared to be an important mark in the theory and practice of PVC chemistry and objectively defines necessity of the new specific approach to study of various aspects of destruction and stabilization of PVC.

In particular, new characteristic reactions with unsaturated ketones, confirming the presence of oxyvinylene groups in PVC structure, are the interaction of ~C(O)-CH=CH-CHCl~ groups with organic phosphites $P(OR)_3$ [29 - 33] and dienes [34, 35].

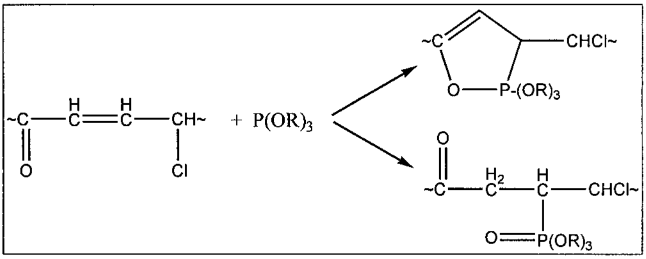
Table 2. Rate constants of dehydrochlorination of characteristic groupings and their contents in the initial PVC structure.

Group	Contents in PVC			Rate constant of degradation at 448 K		
	Index	Amount, mol/mol PVC	Authors	Index	Value, s^{-1}	Authors
~CO-CH=CH-CHCl~	γ_0	~10^{-4}	K.Minsker, 1978 E.Sorvik, 1984 G.Zimmerman, 1984	K_p	10^{-1}-10^{-2}	K.Minsker, 1977 W.Starnes, 1985
$(\sim CH_2)CCl\text{-}CH_2\text{-}CH_2Cl\sim$	A_{Cl0}	0	K.Minsker, 1978 G.Zimmerman, 1984	K_{Cl}	10^{-5}-10^{-4}	Z.Meyer, 1971 B.Troitsky, 1973 W.Starnes, 1983
$-CCl\text{-}CH_2CH_2Cl$	A_t^0	~10^{-3}	E.Sorvik, 1984 A.Caraculaku, 1981 V.Zegelman, 1985	K_t	10^{-4}	W.Starnes, 1983 Z.Meyer, 1971
$\sim CH_2\text{-}(CH=CH)_{n>1}\text{-}CHCl\sim$	A_p	0	K.Minsker, 1976	K_p	~10^{-2}	Z.Meyer, 1971 K.Minsker, 1984
$\sim CH2\text{-}CHCl\text{-}CH_2\text{-}CHCl\sim$	α_0	1	-	K_{Cl}	10^{-7}-10^{-8}	Z.Meyer, 1971 K.Minsker, 1972

Principal ways for stabilization of PVC

Organic phosphites in mild conditions (290 - 330 K) easily react with oxovinylene groups at the presence of the proton donors with formation of stable ketophosphonates:

Reaction 2:



Reaction kinetics of interaction of organic phosphites with oxovinylene groups are shown on Fig. 3. The formation of ketophosphonate structures according to the reaction (2) results in disappearance of internal unsaturated C=C bonds in PVC structure. As a result, neither, oxidizing ozonolysis of a polymeric product, nor especially alkaline hydrolysis, do not result to degradation of macromolecules and decrease of PVC's molecular weight.

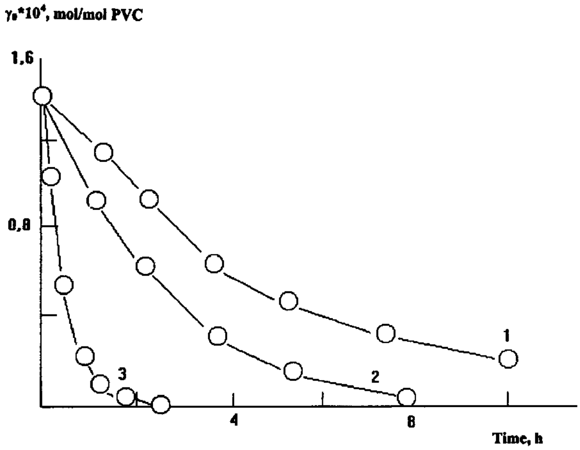
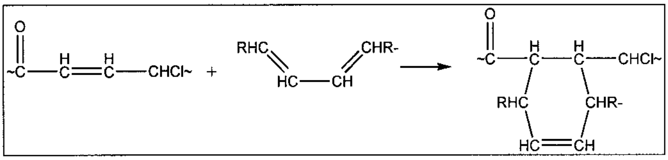


Figure 3. A change of the ~C(O)-CH=CH~ groups contents in PVC at interaction with tri-(2-ethylhexyl)phosphite (1-3) ($C_0 = 10^{-2}$ mol/mol PVC): 1 - 289; 2 - 298; 3 - 448 K.

It's important to specify that organic phosphites do not react with β-chloroallyl groups that is confirmed by a method of competing reactions of organic phosphites (trialkty-, arylalkyl- and triarylphosphites) with a mixture (1:1 mol/mol) of methylvinylketone (model of an oxovinylene group) and 4-chloropentene-2 (model of a β-chloroallyl group) at 353 K. An organic phosphite selectively, practically quantitatively (regarding to a proton donors) reacts with methylvinylketone, while 4-chloropentene-2 is practically quantitatively allocated after realization of reaction, excluding of some (less than 7 wt. %) amount of products of its dehydrochlorination. The CH_3-C(O)-CH2-CH2-P(OR)$_2$ is the main reaction product (up to 75 wt. %). In this reaction trialkyl- and alkylarylphosphites are more active than triarylphosphites.

Dienophylic oxovinylene groups react with conjugated dienes according to the Diels-Alder reaction:

Reaction 3:

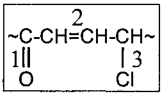


It is new not known earlier reaction for PVC proceeds in mild conditions (353 K) with cyclopentadiene, piperylene, isoprene, 5-methylheptatriene-1,3,6 *etc.* and results (see Reaction 3) in liquidation of internal unsaturated C = C groups in PVC chains similarly to organic phosphites.

PVC stabilization, *i.e.* a complex of methods used with the purpose of increase of the polymer's stability to action of the various factors (such as heat, light, oxygen *etc.*) in terms of storage, processing and exploitation is closely connected to a level of development of PVC degradation theory. Therefore, it is clear that significant change of theoretical developments about the reasons of PVC's thermal instability (a presence of oxovinylene groups in the backbone), mechanism of the process (fundamental influence of the adjacent groups of the long-range order) and kinetics of their disintegration, have shown a necessity and have enabled a new look at determination of new effective ways of PVC stabilization at thermal and other influences.

According to the equation (2) it is impossible (and is not necessary) to increase stability of PVC macromolecules due to reduction of rate V_{Cl} since this process is rather slow. According to the experimental data, the rate of PVC statistical (law of randomness) dehydrochlorination V_{Cl} does not depend on how polymer was synthesized and its molecular weight and is constant. Hence, it is the fundamental characteristic of PVC, showing that all parts in clusters ~BXBXBX~ participate similarly in process of HCl elimination under the law of a randomness, whereas the rate of formation of the conjugated systems (V_p) can noticeable differ, since it linearly depends on the contents of oxovinylene groups in initial macromolecules of PVC (γ_0) (Fig. 2).

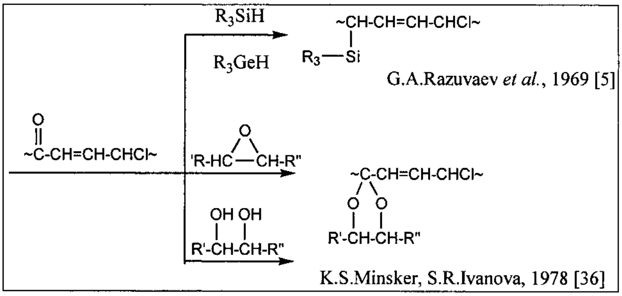
Thus, the basis of effective PVC stabilization which determines both operational properties and durability of rigid materials and products from PVC, is a principle of increased self-stability of PVC macromolecules [17, 40 - 43]. This can be reached first of all due to of a chemical stabilization of PVC - destruction of labile oxovinylene groups whose are present in initial PVC macromolecules on specific polymer-analogous reactions with either of the reaction centers (1) - (3):



$$\sim\underset{\underset{O}{1\|}}{C}-CH\overset{2}{=}CH-\underset{\underset{Cl}{|3}}{CH}\sim$$

The conjugation ~C(O)CH=CH~ has to be destroyed and/or labile chlorine atom has to be replaced with a more stable framing group at interaction with the appropriate chemicals - additives (stabilizers). This principle underlies stabilization of PVC in real formulations at manufacture of rigid materials and products.

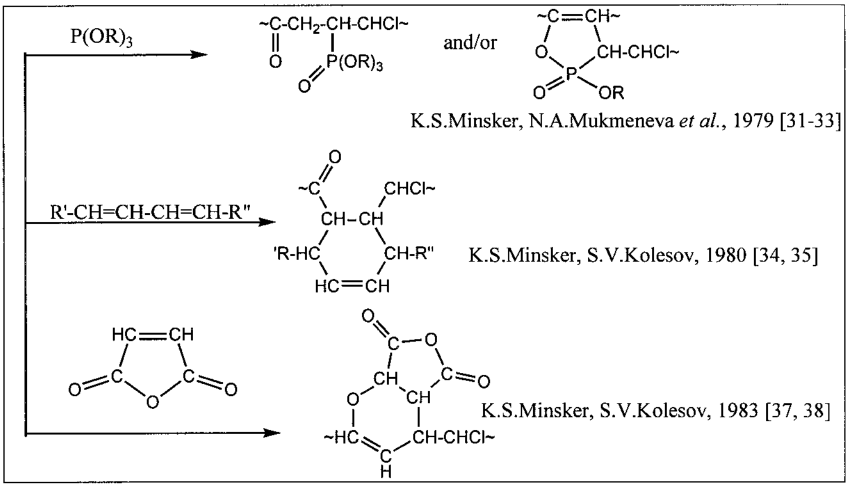
1) Polymer-analogous reactions on >C=O fragments of oxovinylenchloride groups:



G.A.Razuvaev *et al.*, 1969 [5]

K.S.Minsker, S.R.Ivanova, 1978 [36]

2) Polymer-analogous reactions on >C=C< fragments of oxovinylene groups:

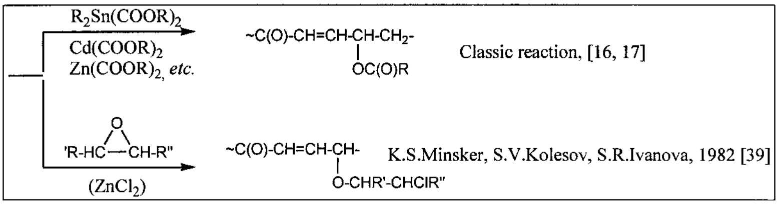


K.S.Minsker, N.A.Mukmeneva *et al.*, 1979 [31-33]

K.S.Minsker, S.V.Kolesov, 1980 [34, 35]

K.S.Minsker, S.V.Kolesov, 1983 [37, 38]

3) Polymer-analogous reactions on labile ≥C-Cl groups:



Classic reaction, [16, 17]

K.S.Minsker, S.V.Kolesov, S.R.Ivanova, 1982 [39]

This method is called “chemical stabilization“ of PVC [17, 40, 41].

It is important that the concept of oxovinylene activation of macromolecules’ disintegration at PVC destruction has allowed to reveal new unexpected possibilities of effective not only thermal, but also light-stabilization of this polymer. This also allows to use for its stabilization previously unknown classes of chemical compounds, in particular, conjugated diene hydrocarbons, adducts of Diels-Alder reaction, protonic acids, α, β - dicarbonic comcpounds, *etc.* [34 - 38, 44 - 46]. It also has enabled to reveal new real reactions proceeding at PVC chemical stabilization, including at application of known chemicals - additives to PVC, which are used for a long time for PVC stabilization (for instance, organic phosphites, epoxy compounds, proton-donating compounds, *etc.*), and on this basis to manage PVC aging process more effectively (Scheme 2). The connection between chemical structure of chemicals - additives and their efficiency as stabilizers for PVC determines an opportunity of scientific - based and economically expedient selection of the appropriate stabilizers and their synergistic combinations at creation of rigid materials based on PVC.

Tasks for a future

Thus, a creation of high-quality and economic semi-rigid and flexible materials and products on a basis of PVC, including ones where solvents are employed, require the specific approach, essentially differing from principles of manufacture of rigid materials and products from PVC. In particular, account and use of the fundamental phenomena: solvatational, structural - physical and "echo" - stabilization of a polymer in a solution.

As to paramount tasks of fundamental and applied research in the field of PVC's manufacture and processing in the beginning of XXI century, obviously they are following:

Manufacture of an industrial PVC, not containing of labile groups in a backbone. It will provide drastic increase of an intrinsic stability of polymeric products, possibility of PVC processing with the minimal contents or in total absence of stabilizers and other chemicals - additives and opportunity of creation of materials and products on a PVC basis with the essentially increased service life-time;

Wide use of the latest achievements in area of destruction and stabilization of PVC, both at presence and absence the solvents. First of all, phenomena of chemical, solvatational, structural - physical, self- and "echo" - stabilization of PVC will allow to create rigid, semi-rigid and flexible (plasticized) materials and products with the minimal contents of chemicals - additives and increased life-time of their service at exploitation in natural and special conditions;

The use of non-toxic, non-flammable products which do not emit toxic and other poison gaseous and liquid products at elevated temperature at manufacture of materials and products from PVC;

Complete slimination of all toxic and even low-toxic (particularly compounds based on Pb, Cd, Ba, *etc.*) chemicals – additives from all formulations;

Search of non-toxic and highly effective inorganic chemicals - additives, first of all, stabilizers of a zeolite - type, modified clays, *etc.*

At the same time new "surprises" may be expected, which undoubtedly will be presented us by this outstanding polymer - puzzle, a plastic's "working horse" for many decades. Certainly it will give new stimulus in development of scientific bases and practical development with opening of new pathways, conducting to essential delay of PVC's ageing in natural and special conditions at reduction of amounts of the appropriate chemicals - additives, down to their complete elimination

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