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Investigations of HCl influence on PVC dehydrochlorination (DHC)

Summary — The effects of several parameters such as polyethylene addition (12.6 wt. %), temperature (260—400°C) and dehydrochlorination (DHC) degree of the samples on the rate of PVC DHC process and on the time of HCl evolution, after freezing the reaction, have been investigated. Results of these investigations as well as the results of DSC and FT-IR measurements confirmed autocatalytic effect of HCl on DHC process. All experimental results are best explained by the hypothesis that DHC process is going on accordingly to the „conventional" mechanism [equation (4)]; HCl blocks also consequent reactions which stop the polyene sequence propagation [equation (5)].

Key words: poly(vinyl chloride), dehydrochlorination, mechanism, HCl role, autocatalysis.

Under the influence of light or heat, poly(vinyl chloride) (PVC) undergoes the decomposition with the elimination of HCl molecules from PVC mers. This reaction makes difficulties in material recycling of waste plastics but may be used in feedstock recycling of PVC wastes. HCl obtained in the dehydrochlorination (DHC) process may be utilized in oxychlorination syntheses whereas the solid residue after the DHC process (AD carbonizate) may be converted to hydrocarbon oil, synthesis gas or to fuel gas [1]. Gasification of PVC is not advisable, because of the low caloric value of PVC — *ca.* 18 MJ/kg; for AD carbonizate that value exceeds 30 MJ/kg. However, the process of gasification of PVC is developed by Linde KCA (Germany) and a pilot plant in Tavaux, France (capacity of 100 kg/h) has been built — editorial note.

MECHANISM OF DHC REACTION

Elimination of HCl from chlorine derivatives of hydrocarbons is already used in the industry. It may be realized on several ways: using the alkalies [2], zinc dust [3], as well as thermally. High temperature is needed, if no catalyst is used. For example, the preparation of VC from dichloroethane is carried out at the temperature of approximately 500°C [2]. The most efficient catalyst is barium chloride supported on active carbon [4], which suggests ionic ($BaCl_2$) or molecular (active carbon) mechanism of DHC reaction. No autocatalytic effect of evolved HCl was reported.

The thermal DHC reaction of PVC proceeds already at the temperature of 150°C. The reason of such high reactivity is, according to the literature data, chlorine atom in allyl group, -CHCl-CH=CH- [5, 6]. That group forms after the elimination of the first HCl molecule from PVC chain and recreates again after the elimination of every consecutive HCl molecule:

$$(CH_2-CHCl)_n \longrightarrow (CH_2-CHCl)_{n1}(CH=CH)(CH_2-CHCl)_{n2} + HCl \qquad (1)$$

This recreation accelerates the propagation of DHC reaction (1) from the chlorine atom in the allyl position to the end of PVC chain. So, a sequence of conjugated double (polyene) bonds in the PVC chain forms:

$$(CH_2-CHCl)_{n1}(CH=CH)(CH_2-CHCl)_{n2} \longrightarrow (CH_2-CHCl)_{n3}(CH=CH)_m(CH_2-CHCl)_{n2} + (m-1)\,HCl \qquad (2)$$

Such reaction is called „zip reaction" and some authors describe the formed polyene sequence as „zip", too [7].

Many forms of zip mechanism have been proposed. Despite the numerous studies, the mechanism is not fully understood yet. Radical, ionic or concerted (molecular) zip initiation is postulated [8]. Particularly, the mechanism of zip termination is unclear. The reactivity of the allyl chlorine should not depend on the number of double bonds conjugated with allyl group; it follows from the theoretical calculations of author's [9] and [10].

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Once the initiation of a zip has occurred in a chain, the propagation of the zip should follow to the end of the chain. Only a defect in the structure of the PVC chain might interrupt the recreation of allyl group.

Created polyene sequences are much shorter, than the above-presented model predicts. It follows from the analyses of UV and IR spectra [11—14]. It was found that the mean number of mers in a polyene sequence depend on temperature and did not exceed 30. This number is much lower than the number of mers in a typical PVC chain which contains usually 300—1700 mers. Such fast termination of zips cannot be caused only by defects in the structure of polymer chain. The investigations of McNeill and co-workers [15] showed that the mean number of defects in a PVC chain was lower than the number of polyene sequences. It is also evident, that the number of those defects does not depend on temperature. The mean number of mers in a polyene sequence decreases when the temperature increases [14, 16]. Also Braun [11], whose paper belongs to the most frequently cited in the literature relevant to DHC process, points out the lack of relation between the number of irregularities in the PVC chain and the rate of DHC process.

It follows from above discussion, that propagation of zips does not end spontaneously. Fast termination of zips is not caused by the degradation of the chain. DHC process runs at the temperature between 200—300°C. Light molecules formed from polyene sequences, broken from PVC-chain, should vaporized at these temperatures. Our mass balances of DHC products have shown, that volatile pyrolysis products of heating PVC to temperature of 250—300°C do not exceed 10 wt.%. It gives the evidence of a fast chemical deactivation of the allyl group rather. Zip propagation may be terminated by even faster reactions of the conjugated double bonds. There are two possible directions of such reactions: intramolecular cyclization of the chain and cross-linking reactions between the chains, according to the Diels—Alder reaction, for example [17, 18].

The other mechanism of deactivation of allyl group may be creation of the positive charge after each removal of a Cl^- ion in the course of zip propagation [13]. The longer the polyene chain is, the more delocalized is the charge and the more difficult can be H^+ ion elimination, necessary for DHC process continuation. However mentioned above temperature dependence of length of polyene sequences is an argument against that hypothesis.

The next question is a possible interaction between evolved HCl and mers of PVC or of zip. The discussion of that problem has not been finished [13, 19]. There are no cogent evidences. The interpretation of the results of experiments, in which the change of HCl concentration in the gas phase over the sample is taken into account, is especially difficult because of multitude of parameters [13, 20, 21]. The errors in analyses of small differences of HCl amount in a gas (rich on HCl) is very big. HCl evolved from the polymer is only a small part of the total stream of HCl leaving the reactor. The most common opinion at present is one that HCl catalyzes DHC process of PVC [12, 13, 22].

Aims of our present work resulted from the conclusions concerning the mechanism of DHC reaction. To explain this phenomenon we have determined among other, the effect of diluting addition of PE on the course of the process of PVC dehydrochlorination.

EXPERIMENTAL

Materials

PVC S67 (*K* number = 67) was produced by Nitrogen Works Tarnów-Mościce, while PVC plastic containing 77% of this polymer and polyethylene (PE-LD) was supplied by Orlen SA, Płock. PVC was purified by dissolution in cyclohexane and precipitation with methanol. The mixture of both polymers was prepared by rubbing powdered polymers.

HCl volumetric standard are delivered POCh Gliwice.

Methods

The experiments were performed isothermally in a glass reactor immersed in the oil bath with temperature control. This bath enables to keep the temperature constant within 1—2°C. Temperature of the experiments are given on the pictures or at discussion of the results. Samples weights of pure or (mechanically) mixed polymers were in the range 0.6—0.65 g, samples of plastics were in the range 0.6—1 g. Samples weights were measured with accuracy 0.0001 g. The evolved HCl was transferred from the reactor to the absorber with a stabilized stream of an inert gas. The amount of absorbed HCl was measured continuously by conductometric method. Concentration of HCl was counted using a curve determined during calibration with HCl solutions.

The DSG 200 Netsch calorimeter was used to record the DSC spectra. The samples were heated in helium from 40°C to 300°C with heating rate 2°C/min.

IR spectra were recorded using KBr pellet technique. The pellets were prepared by mixing and pressing either powdered PVC or powdered AD carbonizate of the known degree of DHC with the powdered KBr.

FT-IR spectra were taken on using FTS 175C IR spectrometer (production Bio-Rad).

RESULTS AND DISCUSSION

Figure 1 presents the dependence of DHC degree versus time. The PVC sample (curve 1) was free of stabilizers. At a constant temperature, the rate of non-catalyzed PVC decomposition reaction (r_{dec}) depends on the concentration of decomposing -CH_2-CHCl- mers only:

$$r_{dec} = k\, f[\text{-CH}_2\text{-CHCl-}] \qquad (3)$$

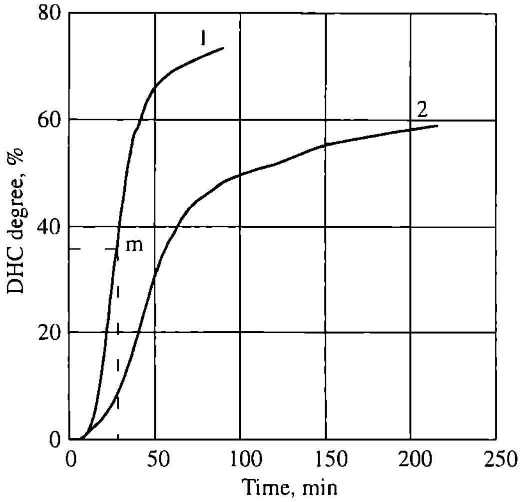


Fig. 1. Comparison of DHC curves of PVC (1) and its mixture with 12.6 wt.% of PE (2) dehydrochlorination at temp. 240°C; m — maximal DHC rate

It is evident, that the rate should decrease with time, because the number of not dehydrochlorinated -CH_2-CHCl- mers decreases with the extension of the reaction. The shape of the curve 1 presented on the Fig. 1 proves that DHC reaction of PVC runs by consecutive steps. In the first step no evolved HCl leaves the sample practically — HCl undergoes absorption in the sample. The initiation stage does not result from inertia of apparatus. Temperatures of sample and of oil bath are the same practically instantly. With the time the sample saturates with HCl and HCl diffuses to the gas phase. The rate of HCl diffusion from the sample to the gas phase raises rapidly, reaches a maximum and decreases abnormally. The decrease of the DHC rate is faster than it should be expected us a result of extension of reaction. It was found (Fig. 2) that the final step begins at lower DHC degree when the temperature of DHC reaction is lower.

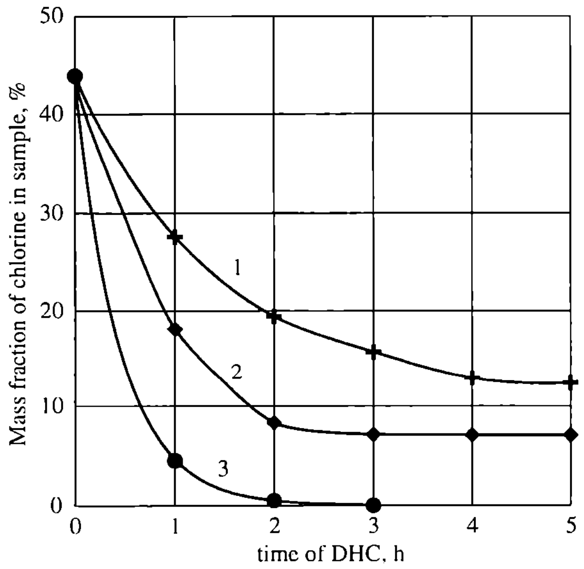


Fig. 2. Effect of temperature on PVC window profiles dehydrochlorination; temperature: 1 — 260°C, 2 — 300°C, 3 — 400°C

The experiments, based on measuring of the time of HCl evacuation from the sample after freezing of the reaction, were performed with the aim to elucidate that property. The reaction was frozen when the sample reached the assumed degree of decomposition. Figure 3 presents the dependence of the time of HCl evacuation on DHC degree for several selected temperatures. It can be seen that the plots show maximums of HCl evacuation time. Additional experiments showed that this effect is not an apparatus artifact.

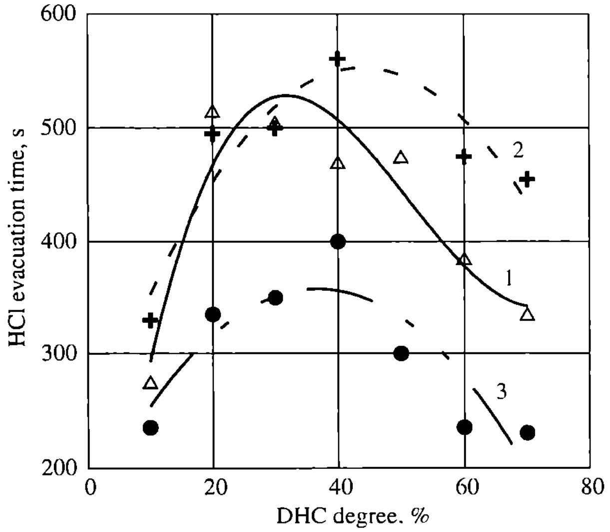


Fig. 3. Effects of DHC degree and temperature on time of HCl evacuation from PVC sample at various temperatures; temperature: 1 — 240°C, 2 — 250°C, 3 — 260°C (with higher inert gas velocity)

The character of the course of experimental curves, presented in Fig. 3, may be explained as follow: decomposition of PVC occurs randomly in the whole volume of PVC. At the beginning the rate of DHC reaction is greater than the rate of HCl diffusion to the gas phase, because the sample absorbs HCl evolved. The state of PVC aggregation complies with intermediate state between an amorphous solid and a liquid. The sorption capacity of such sample may be high. In the course of the decomposition process, the ratio H/C atoms in the sample gradually decreases, which causes the change of sample consistence. The dehydrochlorinated sample has the form of a sintered matter and may be easily powdered. The porous solid loses capacity of HCl absorption because of the viscosity change, what results in rapid decrease of DHC rate. The transformation from a liquid to a sintered matter proceeds at lower DHC degree, when the temperature of the sample is lower. It agrees with an observation that the last step of DHC is longer at lower temperature. That causes the decrease in HCl absorption capacity, which in turn causes the abrupt decrease of the DHC rate, in accordance with the observation that complete dehydrochlorination of PVC is impossible at low temperature. The comparison of the coordinates of the maximums presented in Fig. 3 with inflexion points at DHC kinetic curves, that are presented in Fig. 1, suggests a relation between these both characteristic points. This relation confirms that HCl shows autocatalytic effect on DHC rate.

Interesting results follow from DHC experiments performed with mixtures of PVC with PE. The polymers were mechanically mixed, but they formed an uniform *quasi*-homogeneous material after heating up to DHC temperature. It seems that mixing of those polymers should not influence the rate of DHC reaction, if the influence of PE on the rate of DHC reaction is limited to the increasing a distance between PVC chains and if zip termination is not caused by cross-linking reactions. So, it was expected that dilution of PVC by PE would not influence the rate of DHC process or it would make it easier, in proportion to the participation of cross-linking reactions between the chains at zips termination.

The dilution of PVC with PE caused the decrease in DHC rate (Fig. 1, curve 2), contrary to the expectations. The observed decrease in DHC reaction rate may be explained either by the capture of Cl radicals by -CH_2- groups of PE or by the lower activity of HCl in the sample due to its dilution. The second possibility is more probable because the -CH_2- groups are also present in poly(vinyl chloride) mers -CH_2-CHCl- and they are less distant than the -CH_2- groups in PE. The influence of the HCl concentration on DHC rate confirms the evidence of the catalytic properties of HCl in this reaction. The second, besides HCl, „product" of decomposition are the double bonds in the PVC chain, that are not influenced by PE (lack of specific effect). As it was mentioned above, HCl does not autocatalyze the known low-molecular DHC processes. It points out that during DHC of PVC, HCl catalyzes the zip propagation or it influences the zip length. It is second argument that delocalization of electric charge may not be the reason of the inhibition of DHC rate.

The described experiments demonstrate catalytic influence of HCl on the rate of DHC reaction of PVC. Figure 4 records DSC curves obtained for two PVC samples, which were heated up to 360°C. One of the samples was a powder; the other was a tablet pressed from the same PVC S70 polymer. Endothermic peak of the sample with higher density is higher and a maximum is moved to lower temperature. A difference between the curves can be explained in agreement with our hypothesis. It can be assumed that DHC reaction runs faster in the sample with higher density, because HCl diffusion rate from such a sample is lower than from a sample with lower density.

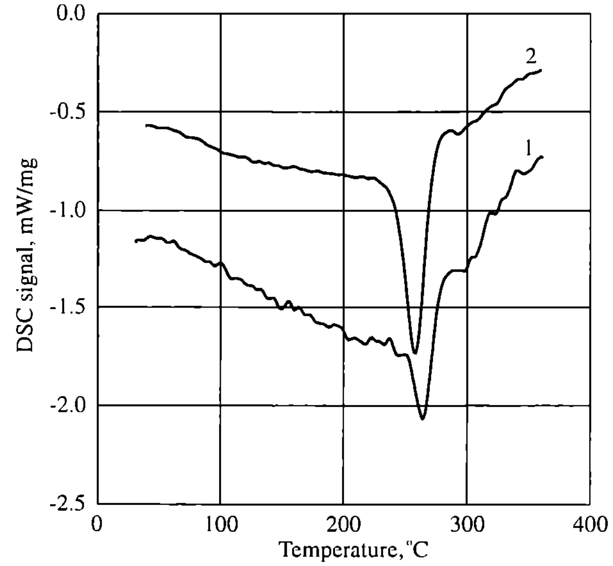


Fig. 4. DSC curves of PVC samples with different densities: 1 — powdered PVC, 2 — PVC pellet formed under pressure 1.4 MPa; heating rate 2°C/min

As we have presented, HCl concentration in a sample changes during DHC process. If HCl catalyzes propagation of zips (or it inhibits their termination), they should be shorter after inflexion point on the DHC curve (see Fig. 1). This conclusion agrees with FT-IR spectra presented in Fig. 5. They were recorded for the pure PVC and AD carbonizates with DHC degree 21% and 58%. Carbonizates were the products of the kinetic experiments conducted at the temperature of 250°C. Absorption bands, between 1600 and 1650 cm^{-1} in this Figure, belong to the stretching vibrations of the conjugated double bonds in polyenes. A clear split can be seen on that absorption band found for carbonized polymer with DHC degree 21%. This split of absorption band declines on the curve of carbonized polymer with DHC degree 58%. From this analysis it follows that polyenes with the highest number of conjugated double bonds are present in carbonized polymer with DHC degree below 50%. That difference confirms a postulate that zip length changes during DHC reaction. The diffuse absorption band observed in the range of wave numbers 1550—1850 cm^{-1}, growing with higher degree of DHC, suggests the presence of individual double bonds of different configuration. Short zips, ending with the defect of the chain, belong to that group.

Theoretically, as it was already stated, the catalytic influence of HCl on the DHC reaction may be due either to the facilitation of the initiation of the reaction or to the propagation of zips. Results of both steps are the same: HCl molecules are evolved. The measured rate of evolution is the measure of the number of mers only, which have undergone the decomposition, but not of the

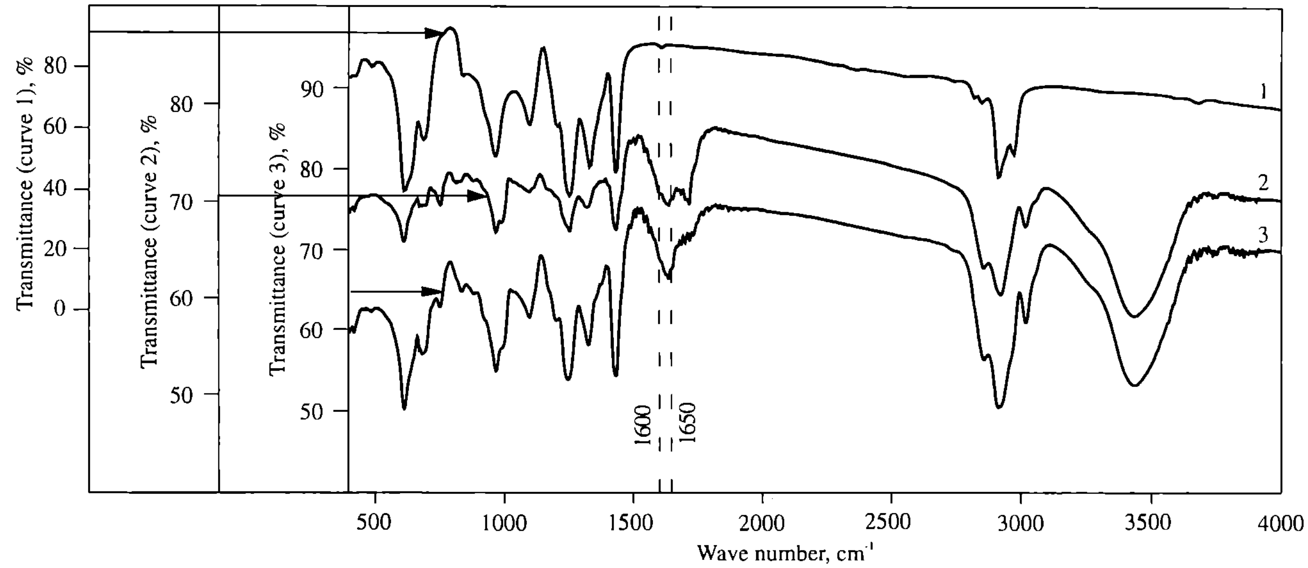
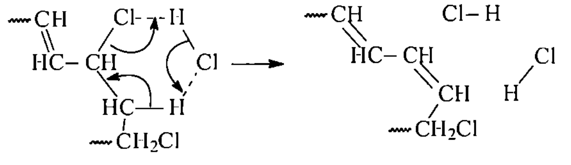


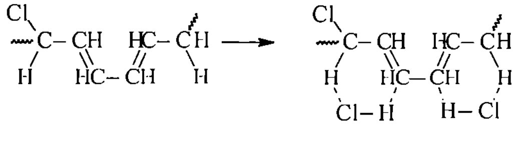
Fig. 5. FT-IR diagram of PVC and its carbonization products showing different DHC degrees: 1 — PVC, 2 — carbonization product, 21% DHC degree, 3 — carbonization product, 58% DHC degree

number of zips. It is impossible to state on this basis, which of the two steps of DHC reaction is catalysed by HCl. That may be concluded only in an indirect manner. The noticed above influence of temperature, the influence of DHC degree on the number of mers in a polyene sequences and lack of autocatalysis in low-molecular DHC reactions suggest that HCl increases average number of mers in zips.

The rate of HCl evolution due to zip propagation depends on the rate constant of this reaction step, and on the number (the concentration) of allyl groups (substrate). HCl should decrease activation energy of propagation reaction and/or it should protect allyl group against secondary reactions causing their destruction. Theoretically, we can explain the both cases: accordingly to the equation (4) — so-called concerted mechanism of


(4)

zip propagation with HCl catalysis, and equation (5) — hindrance of secondary reactions by HCl adsorption.


(5)

HCl can create a complex with an allylic chlorine atom [equation (4)], then activation energy of propagation reaction is influenced, or it creates a complex with a double bond [equation (5)], then termination reaction is inhibited. Because HCl do not catalyze the initiation step of a zip growth so more probably is the second possibility. Reaction of double bonds presented in [17] follows preferably concerted mechanism. The rates of these reactions depend on the distribution of electron density in reacting molecules. Absorbed HCl changes probably the distribution and inhibits secondary reactions, which eliminate allyl position in a zip. HCl can inhibits secondary reactions by steric hindrance too. It suggests that HCl increases average number of mers in zips by inhibition of secondary reactions of allyl group. It is only a possibility — we have not enough arguments to eliminate the other possibility, that HCl decreases the activation energy of propagation step.

PROPOSED MECHANISM IN THE LIGHT OF LITERATURE DATE

The following conclusions may be drawn basing on the presented results of experiments and on the literature:

DHC process of poly(vinyl chloride) is catalyzed by HCl, which forms complexes with polyenes. Those complexes enable the reaction to proceed accordingly to the „conventional" (molecular) mechanism. Accordingly to that mechanism, HCl may participate in all steps of DHC but the complexes of HCl with polyenes show the most important influence on the overall process rate. Those complexes make the consecutive reactions of double bonds, leading to zip termination, more difficult. Total dehydrochlorination of PVC is possible only at high temperature, because in the course of dehydrochlorination the polymer changes its consistence and looses the ability of HCl absorption. The zip propagation occurs, most probably, according to the concerted mechanism [equation (4)]. That mechanism explains well the influence of both the temperature as well as the degree of decomposition on the zip structure and the rate of the overall process. An influence of HCl concentration on the polyene sequence length follows from our investigations as well as from other authors' works [23]. The zip length should depend on DHC degree of the sample. Such dependence follows from FT-IR spectra of PVC and of carbonized polymer. The increase in the content of shorter polyene sequences with the progress of decomposition was reported in the literature [21, 22, 24]. Thallmeier and Braun [14] observed, that DHC reaction runs first slower, and then faster in a film, obtained under the pressure 500 kg/cm^2. Polyene sequences in that sample were longer.

Rogestedt and Hjertberg [24] have found a strong relation between the content of labile chlorine (*i.e.*, internal allylic and tertiary chlorine) and the rate of DHC reaction in nitrogen. When decomposition was performed in an atmosphere containing HCl, the polyene sequence distribution was shifted toward longer polyenes. The validity of conclusions (*e.g.*, the rate of DHC is limited by rate of initiation of zips) is limited to the begining of DHC only because during experiments at the most 0.2% of HCl was eliminated. Experiments were performed at 190°C (*i.e.* below the softening point of PVC). This temperature is too low for PVC decomposition. Danforth and co-workers [19] suggest that HCl facilitates the initiation of zips. However, this conclusion is only intuitive. These authors give no explanation of the mechanism of the interaction of HCl with -CH_2-CHCl- mers. If HCl catalyzes the initiation of a zip, otherwise an elimination of HCl molecule from an organic molecule, such autocatalytic activity of HCl should be observed — but was not observed — in other DHC reactions also, which are popular in organic synthesis.

REFERENCES

1. German K., Pielichowski J., Pielichowski K.: „Report from Scientific Project PB/71/S2/94/06" (in polish), 1997.
2. Weissermel K., Arpe H. J.: „Industrielle Organische Chemie", 5th edition, Wiley-VCH, Weinheim 1998.
3. Rassaerts H., Witzel D.: „Ullmanns Enzyklopädie der Technischen Chemie", 4th edition, Verlag Chemie, Weinheim 1975.
4. *US Pat.* 2 779 804 (1957).
5. Ayrey G., Head B. C., Poller R. C.: *J. Polym. Sci. Macromol. Rev.* 1974, **8**, 1.
6. Braun D.: in „Degradation and Stabilization of Polymers" (Ed. Gueskens G.), Viley, New York 1975, p. 23—41.
7. Šimon P.: *Polym. Degr. Stab.* 1990, **29**, 155.
8. Pielichowski K., Pielichowski J., German K.: *Polimery* 1995, **6**, 317.
9. Šimon P., Valko L.: *Polym. Degr. Stab.* 1990, **29**, 253.
10. Meier R. J., Kip B. J.: *Polym. Degr. Stab.* 1991, **38**, 69.
11. Braun D.: *Pure Appl. Chem.* 1971, **26**, 173.
12. Patel K., Velasquez A., Calderon H. S., Brown G. R.: *J. Appl. Polym. Sci.* 1992, **46**, 179.
13. Martinsson E., Hjertberg T., Sörvik E.: *Macromolecules* 1988, **21**, 136.
14. Thallmaier M., Braun D.: *Makromol. Chem.* 1967, **108**, 241.
15. McNeill I. C., Memetea L., Cole W. J.: *Polym. Degr. Stab.* 1995, **49**, 181.
16. Tüdös F., Kelen T., Nagy T. T., Turcsanyi B.: *Pure Appl. Chem.* 1974, **38**, 201.
17. German K., Kulesza K.: *Polimery* 1999, **44**, 548.
18. Lattimer R. P., Kroenke W. J.: *J. Appl. Polym. Sci.* 1982, **27**, 1355.
19. Danforth J. D., Spiegel J., Bloom J.: *J. Macromol. Sci. Chem.* 1982, **A17**, 1107.
20. Troitskii B. B., Troitskaya L. S.: *Eur. Polym. J.* 1995, **31**, 533.
21. Talamini G., Cinque G., Palma G.: *Mater. Plast.* 1964, **30**, 318.
22. Crosato-Arnaldi A., Palma G., Talamini G.: *Mater. Plast.* 1966, **32**, 50.
23. Šimon P., Gatial A., Valko L.: *Polym. Degr. Stab.* 1991, **35**, 249.
24. Rogestedt M., Hjertberg T.: *Macromolecules* 1993, **26**, 60.

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