

On the mechanism of autocatalytic effect of hydrogen chloride on poly(vinyl chloride) thermal dehydrochlorination

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Dedicated to Professor Ing. A. Hrivík, CSc., in honour of his 60th birthday

The mechanisms of PVC thermal dehydrochlorination in HCl atmosphere have been divided into two groups from the point of view of HCl interaction with double bonds of dehydrochlorinated parts of polymer chains. It has been experimentally shown that HCl catalyzes the dehydrochlorination by preventing zips termination.

Механизмы термического дегидрохлорирования поливинилхлорида в атмосфере HCl разделены на две группы с точки зрения взаимодействия HCl с двойными связями дегидрохлорированных частей полимерных цепей. Экспериментально показано, что HCl катализирует процесс дегидрохлорирования посредством предотвращения реакции обрыва цепи.

The influence of hydrogen chloride on the dehydrochlorination of poly(vinyl chloride) (PVC) was a matter of dispute for years. Recently it was shown without any doubt that the PVC dehydrochlorination in HCl atmosphere in an autocatalytic reaction even under constant pressure of HCl [1], but the mechanism of the process is not yet fully clear. There have been made several attempts to explain this catalytic action of HCl [1—7]. At first, *Braun* proposed that the HCl molecule interacts with a nondehydrochlorinated unit in the PVC chain [2] and the HCl elimination occurs *via* a six-membered cyclic transition state. From the point of view of statistical model of PVC dehydrochlorination [8], in this way an increase in the dehydrochlorination rate should be obtained but no autocatalysis should occur so far as the pressure of HCl is constant.

Under constant HCl pressure, the autocatalytic course of the dehydrochlorination needs to be explained by interaction of HCl with the double bonds of dehydrochlorinated parts of polymer chains. All the mechanisms suggested can be divided into two groups:

i) HCl prevents the termination of zips (for terminology see Ref. [8]), *i.e.* under the influence of HCl the growth of zips is unlimited. The mechanisms offered in [1, 3, 5—7] can be involved in this group.

ii) C=C bonds produced in the dehydrochlorination in cooperation with HCl

molecules form new zips in the nondehydrochlorinated parts of the polymer, *i.e.* the initiation reaction is autocatalytic. This group includes both mechanisms proposed in [4].

The aim of the present paper is to make a trial to decide to which group belongs the mechanism of PVC dehydrochlorination in HCl atmosphere.

Experimental

Materials

Commercial PVC Vestolit 7055 with viscosimetric molar mass $M = 62\,000\text{ g mol}^{-1}$ (C. W. Hüls AG., GFR) was used without further purification.

Dehydrochlorinated PVC was prepared by dehydrochlorination of Vestolit 7055 in HCl atmosphere according to the procedure described in [9]. The degree of dehydrochlorination determined from the relative mass loss was 96.1 %. After dehydrochlorination, it was milled so that the diameter of particles was less than 100 μm .

Equimolar mixture of PVC and dehydrochlorinated PVC was prepared from the components by their mixing. Mass ratio of dehydrochlorinated PVC and PVC was 1 : 2.4.

Measuring procedure

Dehydrochlorination of PVC in HCl atmosphere was performed by the method shown in [1] at 219 °C.

Results and discussion

The main features of both groups of mechanisms are the following:

i) The dehydrochlorination of monomer units situated in the neighbourhood of zips is catalyzed according to the mechanisms of the first group. Addition of C=C bonds in the form of dehydrochlorinated PVC should not have any influence on the course of the dehydrochlorination.

ii) The formation of zips is catalyzed by arbitrary C=C bond in the case of the second group of mechanisms. Addition of dehydrochlorinated PVC should accelerate the dehydrochlorination.

Let us assume that we have an equimolar mixture of PVC and dehydrochlorinated PVC, *i.e.* an equimolar mixture of units $\sim\text{CH}=\text{CH}\sim$ and $\sim\text{CH}_2=\text{CHCl}\sim$. If the mechanisms of the first group are in operation, the kinetic run of the PVC dehydrochlorination should be as that shown in Fig. 1, curve *a*. In the case of the other group, the shape of the kinetic curve should be as the magnified upper half-curve *a* (Fig. 1, curve *b*), or at least, the rate of the dehydrochlorination should accelerate.

Dehydrochlorination of equimolar mixture of PVC and dehydrochlorinated PVC was carried out at 219 °C. At this temperature, PVC is molten so that the contact of both substances may be perfect. The kinetic curve is drawn in Fig. 2. As can be seen, no acceleration of the dehydrochlorination of the mixture in comparison with pure PVC was observed. The difference between both curves shown in Fig. 2 is within the range of experimental error. Then, from the presented results it can be concluded that the catalytic action of HCl occurs *via* affecting zips growth.

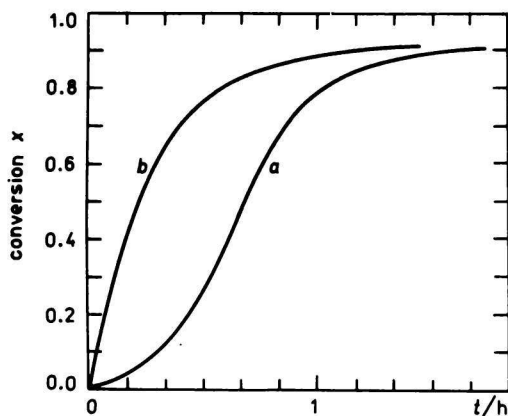


Fig. 1. Theoretical curves of dehydrochlorination of the equimolar mixture of PVC and dehydrochlorinated PVC.

a) The case of mechanisms of the first group (the curve is identical with that obtained by dehydrochlorination of pure PVC at 219 °C); b) the case of mechanisms of the second group (the curve is the magnified upper half-curve *a* in the scale of 2:1).

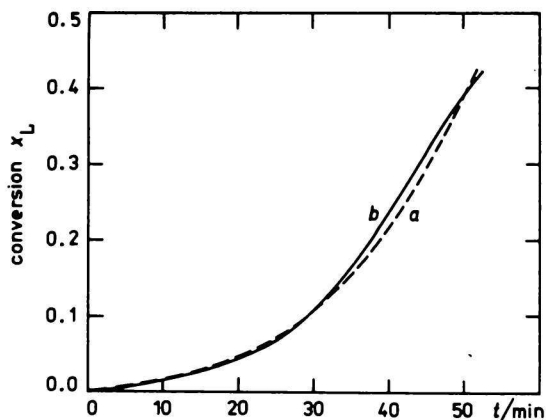


Fig. 2. Kinetic runs of the dehydrochlorination in HCl atmosphere.
a) Equimolar mixture of PVC and dehydrochlorinated PVC; b) pure PVC.

A similar result has been obtained by *Minsker et al.* [10] who followed the number of zips in degraded PVC via ozonolysis. They observed that the number of chain scissions was the same when the PVC dehydrochlorination was carried out in nitrogen or in HCl atmosphere. Furthermore, *Hjertberg* and *Sörvik* [11] found by means of UV spectroscopy that the PVC samples degraded in HCl atmosphere showed the shift of the average zip length towards a higher value in comparison with the samples degraded in nitrogen. In both quoted papers, a conclusion has been drawn that the increase of rate of propagation reaction (*i.e.* acceleration of zips growth) is responsible for the increase of dehydrochlorination rate. Our results completely confirm this conclusion and show that it is valid not only for low degrees of the PVC dehydrochlorination but for high ones, too. In addition, as the course of PVC dehydrochlorination in HCl atmosphere is autocatalytic, from the point of view of statistical model of PVC dehydrochlorination [8], the number of zips being terminated in a time unit must be less than that of those being formed. It means that the growth of zips is unlimited or, at least, zips are of great length, *i.e.* HCl prevents the termination of zips. Thus, on the basis of the above-said facts it can be concluded that a mechanism accounting for the PVC dehydrochlorination in HCl atmosphere should belong to the first group of mechanisms.

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