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KINETIC MODEL OF THERMAL DEHYDROCHLORINATION OF POLY(VINYL CHLORIDE)

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ABSTRACT

A new kinetic model for thermal poly(vinyl chloride) (PVC) dehydrochlorination on the basis of Lottka's scheme has been developed. Its use allows us to reveal three kinetic transmission regimes to a stationary state. The model is expanded to account for the influence of the hydrogen chloride diffusion on the PVC dehydrochlorination kinetics. A calculation method for a quantitative estimation of this influence when the PVC macromolecular defect concentration is changed with time has also been developed. The model is general enough to analyze the tremendous variety of experimental information about PVC dehydrochlorination kinetics and to regulate PVC aging and stabilization.

INTRODUCTION

Dehydrochlorination is the fundamental process of poly(vinyl chloride) thermal decomposition [1–7]. The low thermal stability of this widely used polymer is connected with the formation of unstable groups (defects) in its macromolecules [8–14], which initiate the dehydrochlorination. The question about the type and effectiveness of these defects has been discussed [15–22]. However, the autocatalytic character of this complex process and the formation of long conjugated double bond systems in PVC macromolecules [23–26] have been experimentally confirmed. The released hydrogen chloride has a catalytic action on the rate-determining step, i.e., the initiation of the formation of these conjugated systems. The propagation of the system length precedes the zip-reaction mechanism and does not depend on the hydrogen chloride concentration [27]. The diversity of the proposed mechanisms for PVC thermal dehydrochlorination [8–22, 28, 29] is due to different assumptions about the nature of the initiating defects and the contradictory experimental kinetic results. That is why it is of interest to find a kinetic model that accounts for the common characteristics of the dehydrochlorination mentioned above and allows us to analyze the different kinetic results as well as to define the quantitative procedures for increasing PVC stability. Toward this goal, a modified Lottka's model [30, 31] is applied in this work. The calculations are made in conditional units of time (T), length (L), and concentration (C).

RESULTS AND DISCUSSION

Two regimes of thermal dehydrochlorination (kinetic and diffusion) can be divided depending on the conditions for diffusion of the released hydrogen chloride.

A. Thermal Dehydrochlorination without Diffusion Control

In accordance with Lottka's model, thermal dehydrochlorination of PVC can be represented by the following scheme:

$$\mathrm{PVC} \xrightarrow{k_0} \mathrm{A} + \mathrm{HCl} \tag{1}$$

$$\mathrm{A} + \mathrm{HCl} \xrightarrow{k_1} \mathrm{B} + n\mathrm{HCl} \tag{2}$$

$$\mathrm{S} + \mathrm{HCl} \xrightarrow{k_2'} \mathrm{C} \tag{3}$$

where A are defects in PVC macromolecules, which are formed with a constant rate $v = k_0$ [PVC] in the absence of oxygen and light and at a constant temperature. B and C are nonactive products which are formed as a result of the zip-reaction termination and the interaction of the released hydrogen chloride with the acceptor (stabilizer) S, respectively. k_0, k_1, and k_2' are kinetic constants.

A specific peculiarity of the scheme to the classical Lottka model is the parameter n which represents the average number of conjugated double bonds formed as a result of the zip reaction. From the first scheme it follows that

$$\frac{d[\mathrm{HCl}]}{dt} = v + (n - 1)k_1[\mathrm{HCl}][\mathrm{A}] - k_2'[\mathrm{S}][\mathrm{HCl}] \tag{4}$$

$$\frac{d[\mathrm{A}]}{dt} = v - k_1[\mathrm{HCl}][\mathrm{A}] \tag{5}$$

The solution of this system depends on four parameters (v, n, k_1, and k_2') and the original conditions ($[\mathrm{HCl}]_0 = [\mathrm{HCl}]|_{t=0}$ and $[\mathrm{A}]_0 = [\mathrm{A}]|_{t=0}$). It is not difficult to show, however, that the solution is asymptotically stable under stationary conditions:

$$[\mathrm{HCl}]_{\mathrm{st}} = nv/k_2 \tag{6}$$

$$[\mathrm{A}]_{\mathrm{st}} = k_2/k_1n \tag{7}$$

where $k_2 = k_2'[\mathrm{S}]$. k_2 is a constant for large values of [S]. Three different ways to reach this stationary state are possible.

1. If the conditions

$$1 - \sqrt{1 - 1/n} < \sqrt{nvk_1}/k_2 < 1 + \sqrt{1 - 1/n} \tag{8}$$

are fulfilled, concentration oscillations of [HCl] and [A] take place. Oscillations are damping with a period

$$T = \frac{4\pi}{\sqrt{4nvk_1 - (k_2/n + nvk_1/k_2)^2}} \tag{9}$$

and a damping coefficient

$$\sigma = -\frac{k_2}{2n} - \frac{n\nu k_1}{2k_2} \tag{10}$$

Theoretical curves obtained after a numerical solution of the system [4, 5] by Eulerian's method with zero original conditions and parameter values which satisfy requirements (8) are represented in Fig. 1. Recently, the kinetic oscillations of released hydrogen chloride at thermal PVC dehydrochlorination have been experimentally proved by Denforth et al. [27].

2. If

$$1 - \sqrt{1 - 1/n} > \sqrt{n\nu k_1}/k_2 \tag{11}$$

[HCl] and [A] approach the stationary values of concentrations $[\mathrm{HCl}]_{st}$ and $[\mathrm{A}]_{st}$ monotonically. This case is represented in Fig. 2.

3. If

$$\sqrt{n\nu k_1}/k_2 > 1 + \sqrt{1 - 1/n} \tag{12}$$

no oscillations are observed, but the kinetics of hydrogen chloride release and defect formation are not monotonous. The defect concentration passes through a maximum (Fig. 3).

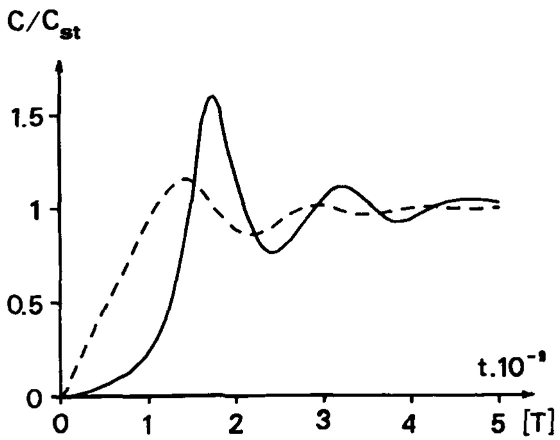

FIG. 1. Kinetics of [HCl] (——) and [A] (- -) in the kinetic regime. $\nu = 1 \times 10^{-13}$ [CT^{-1}], $k_1 = 1 \times 10^{-5}$ [C^{-1}T^{-1}], $k_2 = 2 \times 10^{-8}$ [T^{-1}], $n = 20$.

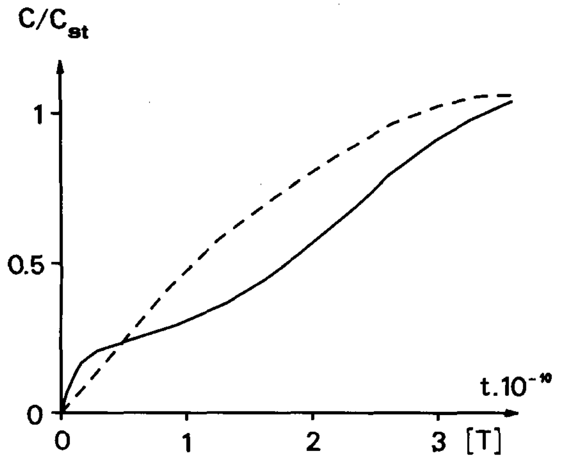

FIG. 2. Kinetics of [HCl] (——) and [A] (- -) in the kinetic regime. $\nu = 1 \times 10^{-12}$ [CT^{-1}], $k_1 = 1 \times 10^{-7}$ [C^{-1}T^{-1}], $k_2 = 1 \times 10^{-8}$ [T^{-1}], $n = 5$.

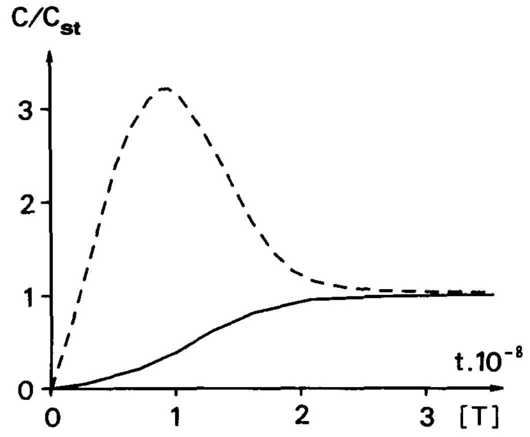

FIG. 3. Kinetics of [HCl] (——) and [A] (- -) in the kinetic regime. $\nu = 1 \times 10^{-12}$ [CT^{-1}], $k_1 = 1 \times 10^{-4}$ [C^{-1}T^{-1}], $k_2 = 1 \times 10^{-8}$ [T^{-1}], $n = 5$.

In this way the proposed model is general enough to allow for an explanation of the different types of experimentally obtained kinetic dependences. In addition, critical relationships between the parameters contained in Eqs. (10)–(12) are obtained, which permit discrimination of the different kinetic regimes. The practical use of the model includes control of the thermal dehydrochlorination of PVC by the regulation of v, k_1, k_2, and n. Their values depend on temperature, dehydrochlorination degree, nature, and concentration of stabilizer. The easiest control is realized by variation of these parameters.

B. Diffusion-Controlled Thermal Dehydrochlorination

In most cases, PVC products are thick enough, and the influence of the hydrogen chloride diffusion on its local concentration, its interaction with defects A, and its rate of release from the product surface are significant [7, 29]. For a PVC film with thickness 2L, for example, consideration of hydrogen chloride diffusion in Lottka's model leads to a change in the kinetic scheme (1–3) and Eq. (4) is transformed to

$$\frac{\partial[\mathrm{HCl}]}{\partial t} = v + (n - 1)k_1[\mathrm{HCl}][\mathrm{A}] - k_2[\mathrm{HCl}] + D\frac{\partial^2[\mathrm{HCl}]}{\partial l^2} \qquad (13)$$

where D is a diffusion coefficient of the hydrogen chloride in the film. In this case [HCl] and [A] are functions of t and l ($-\mathrm{L} \leq l \leq \mathrm{L}$). An analytical solution of Eq. (13) is obtained only for [A] = constant [7, 29]. Therefore, it is interesting to obtain a numerical solution of the System (5, 13) at the determined original ([A]0,l) and [HCl](0,l)) and boundary conditions, characterizing hydrogen chloride release from the film surface:

$$\left.\frac{\partial[\mathrm{HCl}]}{\partial t}\right|_{l=\pm\mathrm{L}} = v + (n - 1)k_1[\mathrm{HCl}](t, \pm\mathrm{L})[\mathrm{A}](t, \pm\mathrm{L})$$
$$- k_2[\mathrm{HCl}](t, \pm\mathrm{L}) - K[\mathrm{HCl}](t, \pm\mathrm{L})$$
$$- (\pm D)\left.\frac{\partial[\mathrm{HCl}]}{\partial l}\right|_{l=\pm\mathrm{L}} \qquad (14)$$

where K is the mass-transfer coefficient of hydrogen chloride release from the film surface. At stationary conditions

$$[\mathrm{HCl}]_{st}(l) = a - b \cdot ch(c \cdot l) \qquad -\mathrm{L} \le l \le +\mathrm{L} \tag{15}$$

$$[\mathrm{A}]_{st}(l) = \frac{v}{k_1[\mathrm{HCl}]_{st}(l)} \tag{16}$$

where:

$$a = nv/k_2 \tag{17}$$

$$b = \frac{aK}{\sqrt{k_2 D}\, sh(\mathrm{L}\sqrt{k_2/D}) + (K + k_2)ch(\mathrm{L}\sqrt{k_2/D})} \tag{18}$$

$$c = k_2/D \tag{19}$$

From these equations it follows that the concentration of the hydrogen chloride in the middle and of the defects in the surface part of the film are the highest. Under other equal conditions, hydrogen chloride concentration is lower and defect concentration is higher than the corresponding concentration in the kinetic regime.

If the double bond concentration in the film is denoted by [DB], then from the kinetic equations (5) and (13) it follows that

$$\frac{d[\mathrm{DB}]}{dt} = (n - 1)k_1[\mathrm{HCl}][\mathrm{A}] \tag{20}$$

By Eq. (16) for steady-state conditions:

$$\frac{d[\mathrm{DB}]_{st}}{dt} = (n - 1)v \tag{21}$$

As far as [DB] is a measure for the degree of dehydrochlorination of PVC, it follows from the last equation that at steady-state conditions, PVC dehydrochlorination proceeds in the whole film volume at a constant rate and does not depend on hydrogen chloride diffusion but depends only on values of parameters v and n. As the latter depend on the degree of PVC dehydrochlorination and stabilizer concentration, the rate of formation of conjugated double bond systems depend on them as well.

The system (5, 13) may be solved numerically. For this objective, the film is divided into $2m$ layers. The dehydrochlorination reaction proceeds of each of them, and hydrogen chloride moves from the inner to the external layers. The Eulerian method leads to the following equations:

$$[A_i]_{t+\Delta t} = (1 - \hat{k}_1[HCl_i]_t)[A_i]_t + \hat{v} \qquad (i = 1, 2, \ldots, m) \tag{22}$$

$$[HCl_1]_{t+\Delta t} = \{1 + (n - 1)\hat{k}_1[A_1]_t - \hat{k}_2 - \hat{K} - \hat{D}\Delta l\}[HCl_1]_t + \hat{D}\Delta l[HCl_2]_t + \hat{v} \tag{23}$$

$$[HCl_i]_{t+\Delta t} = \{1 + (n - 1)\hat{k}_1[A_i]_t - \hat{k}_2 - 2\hat{D}\}[HCl_i]_t + \hat{D}[HCl_{i-1}]_t + \hat{D}[HCl_{i+1}]_t + \hat{v} \quad (i = 2, 3, \ldots, m - 1) \tag{24}$$

$$[HCl_m]_{t+\Delta t} = \{1 + (n - 1)\hat{k}_1[A_m]_t - \hat{k}_2 - \hat{D}\}[HCl_m]_t + \hat{D}[HCl_{m-1}]_t + \hat{v} \tag{25}$$

where layer 1 is on the film surface and layer m is in the middle, Δt is a time interval, $\Delta l = L/m$, $k_i = k_i\Delta t$ $(i = 1, 2)$, $\hat{D} = D\Delta t/\Delta l^2$, and $\hat{K} = K\Delta t$. The solutions of the System (22)–(25) under zero original conditions, where $m = 4$ for two different sets of values for k_1, k_2, v, n, and K, are shown in Figs. 4 and 5. From the latter it is clear that under hydrogen chloride diffusion control, concentration oscillations for [A] and [HCl] take place in time but there is some phase lag of the concentrations on the film surface in comparison with the middle.

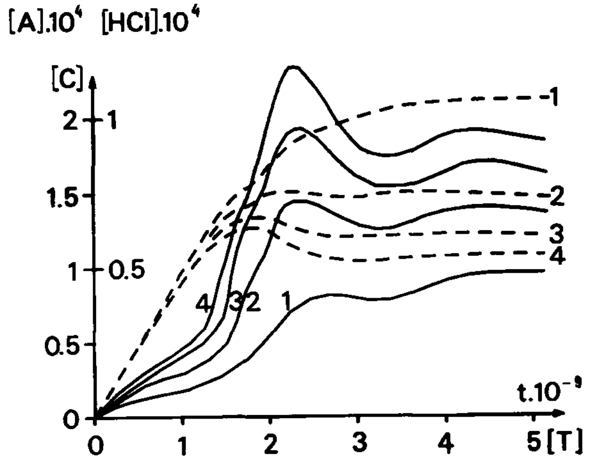

FIG. 4. Kinetics of [HCl] (——) and [A] (- -) in the diffusion regime. $v = 1 \times 10^{-13}$ [CT⁻¹], $k_1 = 1 \times 10^{-5}$ [C⁻¹T⁻¹], $k_2 = 1 \times 10^{-8}$ [T⁻¹], $n = 10$, $D = 1 \times 10^{-9}$ [L²T⁻¹], $K = 1.48 \times 10^{-8}$ [T⁻¹, $L = 1$[L], $i = 1, 2, 3, 4$ is the layer number.

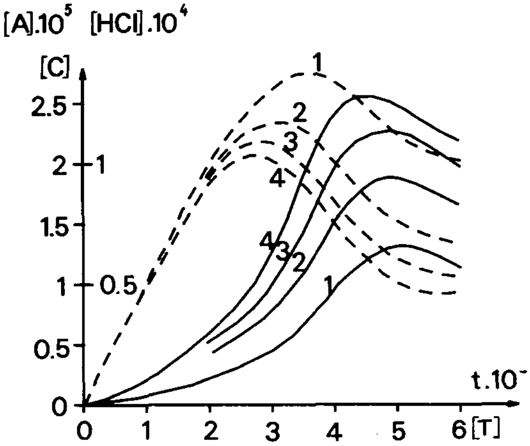

FIG. 5. Kinetics of [HCl] (——) and [A] (- -) in the diffusion regime. $\nu = 1 \times 10^{-13}$ [CT^{-1}], $k_1 = 1 \times 10^{-4}$ [C^{-1}T^{-1}], $k_2 = 1 \times 10^{-8}$ [T^{-1}], $n = 10$, $D = 1 \times 10^{-9}$ [L^{2}T^{-1}], $K = 1.48 \times 10^{-8}$ [T^{-1}]^1, $L = 1$[L], $i = 1, 2, 3, 4$ is the layer number.

CONCLUSIONS

The proposed model accounts for the most essential features of the thermal dehydrochlorination of PVC: the autocatalytic effect of the released hydrogen chloride and the formation of conjugated double bond systems by the zip-reaction mechanism. The dependence of the kinetics of this complex reaction on the values of the model parameters is shown, as well as the existence of critical values of the complexes between these parameters which separate the different transition regimes to stationary. Thus, it explains the critical appearance of PVC dehydrochlorination in the kinetic regime. So far the critical behavior of PVC dehydrochlorination is related to diffusion control of the hydrogen chloride released [7, 29]. That is why the model allows for the classification and analysis of the enormous amount of kinetic information about PVC dehydrochlorination without the introduction of a large number of parameters in the model [15, 16, 26, 27]. The following steps in model improvement will take into account the variation of the defect formation ν. It will be the subject of future work.

The universality of the proposed method and its clear physical essence allows for its use for the regulation of PVC aging and stabilization. On the other hand, experimental verification of the model will contribute to its development to a more adequate description of PVC thermal and thermooxidative dehydrochlorination.

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