Influence of metal stearates on thermal stability of poly(vinyl chloride) IV. Lead stearate

P. ŠIMON, J. OREMUSOVÁ, and L. VALKO

Department of Physical Chemistry, Faculty of Chemical Technology, Slovak Technical University, CS-812 37 Bratislava

Received 7 November 1989

Kinetics of dehydrochlorination of poly(vinyl chloride) stabilized with lead stearate is examined and the kinetic data are completed with viscosimetric determination of relative molecular mass of the samples thermally stressed. The results show that lead stearate is a very efficient scavenger of HCl split off from PVC. The values of effective rate constants of dehydrochlorination decrease hyperbolically with increasing relative mole fraction of lead stearate in the blend. This led to the conclusion that lead stearate exerts a blocking effect on the propagation stage of the zip reaction. A reaction mechanism of the dehydrochlorination is suggested and the rate constants of individual reaction steps are obtained by comparing the calculated and experimental kinetic runs. Some general aspects of the dehydrochlorination of PVC stabilized with metal stearates are discussed.

Lead compounds belong to the most efficient thermal stabilizers of PVC [1—4]. Both Pb^{2+} and Pb^{4+} compounds exert the stabilizing effect [5]. Despite the fact that lead compounds have been employed in practice for years, the mechanism of their action is not fully clear yet.

In our previous papers [6—8] the mechanism of stabilizing effect of Ca, Mg, and Zn stearates has been studied and the rate constants of individual reaction steps have been obtained by comparing experimental and calculated kinetic curves. This study concerned with the stabilizing effect of lead stearate finishes the series of papers devoted to the influence of metal stearates on thermal stability of PVC.

Experimental

Suspension poly(vinyl chloride) Slovinyl S-621, montan wax, and cyclohexanone have been characterized in Refs. [6, 7]. Lead stearate $Pb(C_{17}H_{35}COO)_2$, m.p. = 110—112 °C, purity determined by elemental analysis 99 %, and lead chloride $PbCl_2$, anal. grade, were used.

Preparation of PVC foils, determination of HCl evolved from PVC samples and viscosimetric determination of relative molecular mass of PVC samples have been described in detail in Refs. [6, 7].

Results and discussion

The kinetic curves for a set of PVC foils with relative mole fraction of lead stearate 0—4.27 × 10^{-3} dehydrochlorinated in the atmospheres of nitrogen and air at 180 °C are given in Figs. 1 and 2. Fig. 3 shows the dependence of the time of thermal stability τ of PVC on the relative mole fraction of lead stearate. The values of τ are greater for the PVC dehydrochlorination in nitrogen atmosphere.

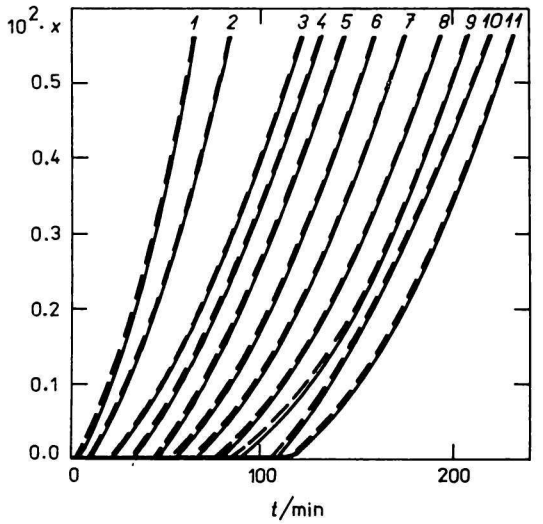

Fig. 1. Kinetic curves of thermal dehydrochlorination (conversion x) of the PVC stabilized with lead stearate in nitrogen at 180 °C. Relative mole fraction of lead stearate in mixture: *1.* 0; *2.* 0.41 × 10^{-3}; *3.* 0.81 × 10^{-3}; *4.* 1.23 × × 10^{-3}; *5.* 1.66 × 10^{-3}; *6.* 2.09 × × 10^{-3}; *7.* 2.51 × 10^{-3}; *8.* 2.94 × 10^{-3}; *9.* 3.38 × 10^{-3}; *10.* 3.82 × 10^{-3}; *11.* 4.27 × 10^{-3} —— Experimental kinetic curve, --- calculated kinetic curve.

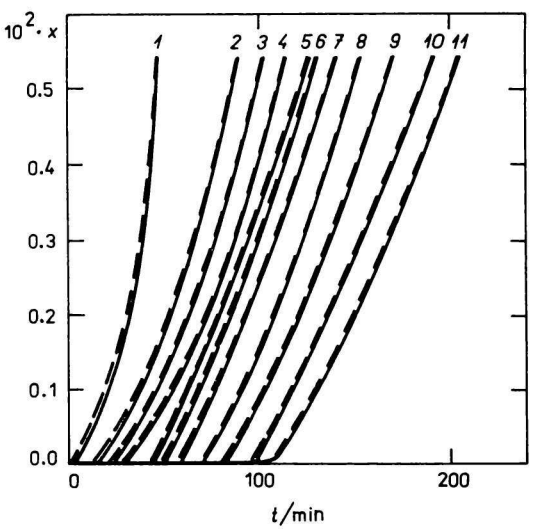

Fig. 2. Kinetic curves of thermal dehydrochlorination (conversion x) of the PVC stabilized with lead stearate in air at 180 °C. Denotation as in Fig. 1.

The effective rate constants of dehydrochlorination are obtained as the slopes of linear parts of the kinetic curves for the time $t > \tau$, their dependence on the relative mole fraction of lead stearate is demonstrated in Fig. 4. The effective rate constants decrease with increasing relative mole fraction of lead stearate, the dependence resembles a hyperbolic function.

In order to complete information on the mechanism of PVC dehydrochlorination in the presence of lead stearate, dependence of the relative mole-

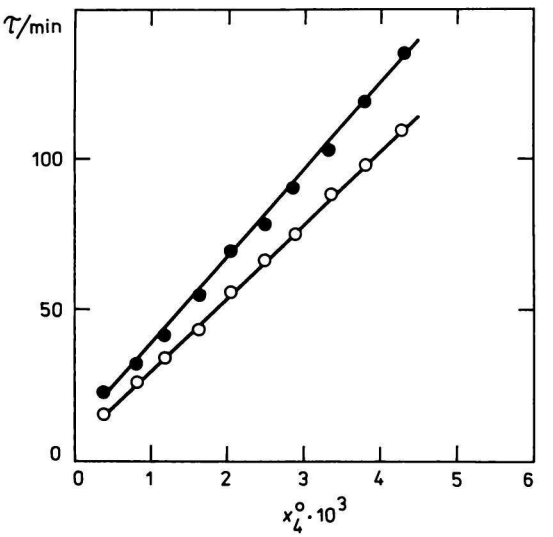

Fig. 3. Dependence of the time of thermal stability τ of PVC on the relative mole fraction of lead stearate in nitrogen (●) and air (○).

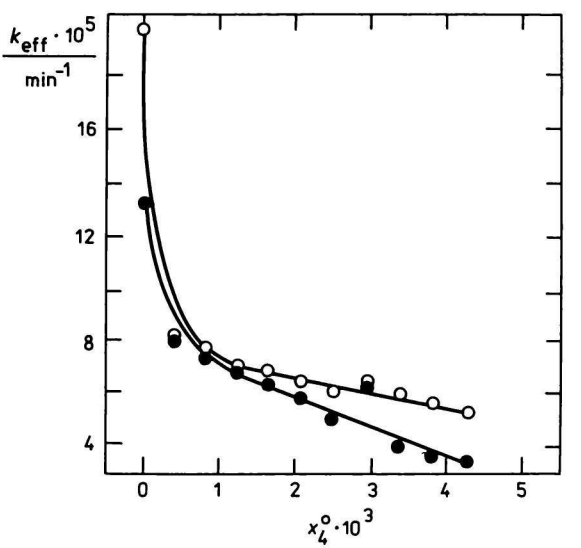

Fig. 4. Dependence of the effective rate constants of PVC dehydrochlorination on the relative mole fraction of lead stearate in nitrogen (●) and air (○).

cular mass of the polymer on the time of thermal stress has been examined. Fig. 5 shows this dependence for the degradation under nitrogen of the sample with relative mole fraction of lead stearate $x_4^\circ = 2.51 \times 10^{-3}$ The relative molecular mass remains unchanged for approximately 80 min, then it increases and after 180 min of thermal stress, a fraction insoluble in cyclohexanone is formed. The time of unchanged relative molecular mass is in correlation with the time of thermal stability which for this sample is $\tau = 77$ min. As hydrogen chloride causes crosslinking and thus the increase of the relative molecular mass [9], it can be concluded that an important task of lead stearate is to scavenge hydrogen chloride split off from PVC.

In the course of thermal stress, stearic acid and $PbCl_2$ are formed as the products of the reaction of lead stearate with hydrogen chloride. It has been shown that stearic acid slightly accelerates PVC dehydrochlorination [6]. In order to examine the influence of $PbCl_2$ on the dehydrochlorination, we prepared blends of PVC with $PbCl_2$. Fig. 6 shows that $PbCl_2$ decelerates the dehydrochlorination; again, a hyperbolic dependence of the effective rate constants on the relative mole fraction is observed. The decelerating effect of lead stearate prevails over the accelerating effect of stearic acid.

The knowledge gained from our results and papers published led to the suggestion of the following reaction mechanism for the thermal dehydrochlorination of PVC stabilized with lead stearate:

1. Thermal dehydrochlorination of PVC

$$\text{PVC} \xrightarrow{k_1} \text{dePVC} + \text{HCl}$$

where dePVC means dehydrochlorinated PVC.

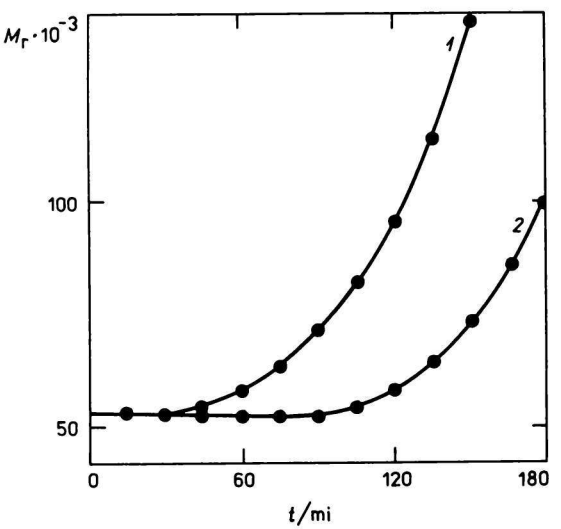

Fig. 5. Dependence of relative molecular mass of PVC on the time of thermal stress in nitrogen atmosphere. *1.* PVC; *2.* PVC stabilized with lead stearate, relative mole fraction 2.51×10^{-3}.

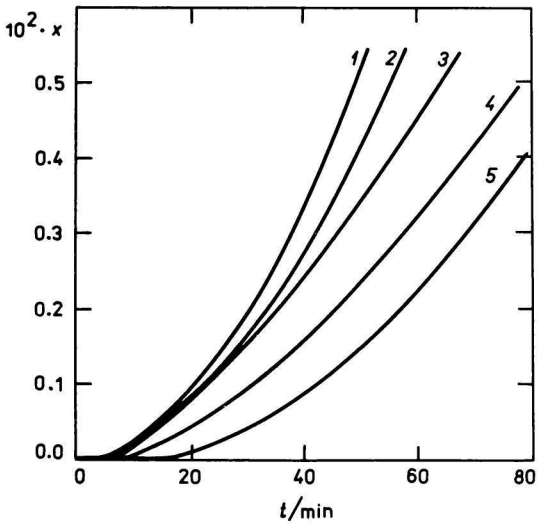

Fig. 6. Effect of $PbCl_2$ and stearic acid on the dehydrochlorination of PVC under nitrogen at 180 °C. *1.* PVC with stearic acid, relative mole fraction 4.51×10^{-3}; *2.* PVC without additives; PVC with $PbCl_2$ (relative mole fraction *3.* 2.28×10^{-3}; *4.* 4.61×10^{-3}; *5.* 6.99×10^{-3}).

2. Reaction of lead stearate with HCl split off from PVC which assumingly occurs in two reaction steps

$$PbSt_2 + HCl \xrightarrow{k_2} PbClSt + HSt$$

$$PbClSt + HCl \xrightarrow{k_3} PbCl_2 + HSt$$

where St is the stearate anion and HSt is stearic acid. As the decelerating effect of $PbCl_2$ prevails over the accelerating effect of stearic acid, the latter is neglected. Also, the accelerating effect of HCl on PVC dehydrochlorination is neglected since the thickness of PVC films is less than the critical value [10]. From infrared spectra we have not obtained any evidence for the reaction of lead stearate with HCl in two steps, but, similarly as in Ref. [8], we assume that trimolecular reaction

$$PbSt_2 + 2\,HCl \rightarrow PbCl_2 + 2\,HSt$$

is less probable.

The reaction scheme can be described by four independent kinetic equations where the relative mole fractions of individual components are denoted as follows: x_1 — HCl registered by the apparatus, x_2 — HCl in the polymer, x_3 — double bonds in PVC, x_4 — $PbSt_2$, x_5 — HSt, x_6 — PbClSt. As mentioned in Refs. [6—8], we again assume that HCl is evolved from the polymer sample after the relative mole fraction has reached its critical value x_c. The kinetic equations have then the form

For $x_2 < x_c$

$$dx_1/dt = 0$$

$$dx_2/dt = k_1(1 - x_3) - k_2x_2x_4 - k_3x_2x_6$$

For $x_2 = x_c$

$$dx_1/dt = k_1(1 - x_3) - k_2x_2x_4 - k_3x_2x_6$$

$$dx_2/dt = 0$$

The other kinetic equations are

$$dx_3/dt = k_1(1 - x_3)$$

$$dx_4/dt = -k_2x_2x_4$$

The relative mole fractions x_5 and x_6 can be expressed by the material balances

$$x_5 = x_3 - x_2 - x_1 - a$$

$$x_6 = 2(x_4^\circ - x_4) - x_5$$

where a means the HCl escaped from the sample after calendering.

Fig. 4 demonstrates that k_{eff} hyperbolically decreases with increasing relative mole fraction of lead stearate. Till now, this fact is not involved in the kinetic equations. To do this, it is necessary to take into account that k_1 is the rate constant of PVC dehydrochlorination which occurs through the zip reaction. The zip reaction includes initiation, propagation and termination of polyene sequences and k_1 is thus expressed as a combination of the rate constants of all these stages [11]

$$k_1 = k_i\left(1 + \frac{k_p}{k_t}\right) \tag{1}$$

where k_i, k_p, and k_t are the rate constants of initiation, propagation, and termination, respectively. Since in the time $t = \tau$ the stabilizer is close to be consumed up, the value of k_{eff} is determined mainly by k_1. Accordingly, the hyperbolical decrease of k_{eff} should be interpreted through the decrease of k_1. We explain it by the blocking of the propagation stage of the zip reaction by lead compounds. For the description of this effect it is necessary to follow the procedure from Ref. [11] where the dehydrochlorination of pure PVC is treated. For this case, formation of the polyene sequences under propagation is expressed as

$$\frac{dg}{dt} = k_i(1 - x) - k_t g \tag{2}$$

where g is the concentration of growing zips. Here, x means the conversion of dehydrochlorination. Since in eqn (*2*) it is assumed that polymer is not stabilized, no HCl reacts with the stabilizer and, therefore, $x = x_1 = x_3$.

If the blocking of the zip propagation by lead compounds is considered, the latter equation takes the form

$$\frac{dg}{dt} = k_i(1 - x) - k_t g - k_{Pb} x_{Pb} g \tag{3}$$

where k_{Pb} is the rate constant of premature zip termination caused by lead compounds and x_{Pb} is the relative mole fraction of lead compounds. After a very short time, dynamic equilibrium is established between the formation and termination of the growing polyene sequences, which is expressed as

$$\frac{dg}{dt} = 0 \tag{4}$$

Combination of eqns (*3*) and (*4*) gives

$$g = \frac{k_i(1 - x)}{k_t + k_{Pb} x_{Pb}} \tag{5}$$

The rate of dehydrochlorination is given as the sum of terms describing the initiation and propagation of polyene sequences

$$\frac{dx}{dt} = k_i(1 - x) + k_p g \tag{6}$$

Taking into account eqn (*5*), eqn (*6*) gets the form

$$\frac{dx}{dt} = k_i \left(1 + \frac{k_p}{k_t + k_{Pb} x_{Pb}}\right)(1 - x) \tag{7}$$

Formally, this is the first-order kinetic equation with the rate constant

$$k_1 = k_i \left(1 + \frac{k_p/k_t}{1 + (k_{Pb}/k_t)\, x_{Pb}}\right) \tag{8}$$

Eqn (*8*) considers the blocking effect of lead compounds, k_1 is a hyperbolic function of x_{Pb}. This expression of k_1 is used when solving the set of kinetic equations for the dehydrochlorination of PVC stabilized with lead stearate. Of course, the kinetic equations involve the reaction of lead stearate with HCl split off from PVC. For this reason, the rate constant k_1 refers to the double bond formation in PVC chain, *i.e.* to the relative mole fraction x_3.

The set of kinetic equations is solved by the fourth-order Runge—Kutta method. The values of rate constants are obtained by the nonlinear least-squares method, the sum of deviations between the experimental and theoretical values of conversion (x_1) is minimized by the simplex method [12]. The minimization parameters are the ratios k_p/k_t and k_{Pb}/k_t, the rate constants k_i, k_2, and k_3, and the critical relative mole fraction x_c. The parameters corresponding to the minimum sum of deviations are listed in Table 1. Similarly as in Refs. [6—8] the thermal stress during calendering is taken into account in calculation. The least sum of squares is reached when it is assumed that all lead compounds block the zip propagation, *i.e.* when $x_{Pb} = x_4^{\circ}$. Figs. 1 and 2 demonstrate the excellent agreement reached between experimental and calculated kinetic runs which documents reasonability of the suggested reaction scheme.

Table 1

Kinetic parameters for the dehydrochlorination of PVC stabilized with lead stearate

Parameter	Atmosphere	
	Nitrogen	Air
k_i/min^{-1}	1.89×10^{-5}	2.34×10^{-5}
k_p/k_t	2.95	3.49
k_{Pb}/k_t	183	373
k_1/min^{-1} [a]	7.47×10^{-5}	$1.05 \times 10^{-}$
k_2/min^{-1}	453	391
k_3/min^{-1}	27.4	7.12
x_c	$4.13 \times 10^{-}$	1.5×10^{-3}

a) Calculated from eqn (*1*).

Table 1 reveals that the initiation step of the zip reaction proceeds more quickly in air. The ratios k_p/k_t show that also the propagation kinetic chain is longer in air. Both these facts result in the higher value of k_1 for the air dehydrochlorination atmosphere. From the value of k_{Pb}/k_t it can be deduced that the blocking effect of lead compounds on the zip propagation can reach up to 50 %. The values of k_2 and k_3 show that lead stearate is an efficient scavenger of HCl, the first step of the reaction is much more rapid than the other one. The kinetic parameters obtained make it possible to calculate the consumption of lead stearate during calendering which is 3—13 %, the consumption in the time $t = \tau$ (95—98 %, calculated as the decrease of Pb—St bonds), time dependences of relative mole fractions of individual components in PVC blend (Fig. 7), *etc.*

This is the closing paper of our series devoted to the study of influence of

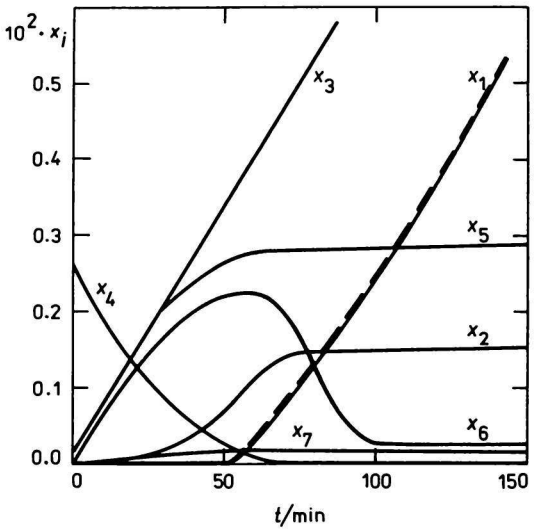

Fig. 7. Calculated dependences of the relative mole fractions of components in the blend on the time of thermal stress in nitrogen ($x_4^o = 2.51 \times 10^{-3}$). x_1 — Conversion of dehydrochlorination; x_2 — HCl in polymer; x_3 — double bonds in polymer; x_4 — $PbSt_2$; x_5 — HSt; x_6 — PbClSt; x_7 — $PbCl_2$. —— Experimental kinetic curve, --- calculated kinetic curve.

metal stearates on PVC dehydrochlorination. Thus we would like to present some general remarks. The first one is concerned with the expression of the reaction rate which has been done *via* the relative mole fractions. The reaction rate v is defined [13] as

$$v = \frac{1}{\nu_i} \frac{\mathrm{d}n_i}{\mathrm{d}t} \tag{9}$$

where ν_i is the stoichiometric coefficient and n_i means the amount of substance of the i-th component. For the conditions of constant volume, eqn (*9*) can be expressed as

$$v = \frac{V}{\nu_i} \frac{\mathrm{d}c_i}{\mathrm{d}t} \tag{10}$$

where V is volume and c_i is concentration of the i-th component. Dividing eqn (*10*) by volume one obtains the reaction rate in a volume unit v_1

$$v_1 = \frac{1}{\nu_i} \frac{\mathrm{d}c_i}{\mathrm{d}t} \tag{11}$$

This rate is usually called the reaction rate. In the course of dehydrochlorination, the volume of the polymer changes, it is not constant. Therefore, we cannot use eqn (*11*) for the expression of the reaction rate. The relative mole fraction is defined as

$$x_i = \frac{n_i}{n_0} \tag{12}$$

where n_0 stands for the amount of substance of vinyl chloride monomeric units. For the polymers degrading *via* splitting-off of small molecules, the number of links in the polymer chain does not change in the course of degradation. Combination of eqns (*9*) and (*12*) gives

$$v = \frac{n_0}{\nu_i} \frac{\mathrm{d}x_i}{\mathrm{d}t} \tag{13}$$

Dividing eqn (*13*) by n_0, we obtain

$$v_0 = \frac{1}{\nu_i} \frac{\mathrm{d}x_i}{\mathrm{d}t} \tag{14}$$

The rate v_0 is the reaction rate per mole of monomeric units of the polymer. This is the expression of reaction rate we have used. It seems to us to be the most appropriate for the polymers splitting-off of small molecules in their degradation.

The rate constant k_1 describes the splitting-off of HCl from PVC. It is rather surprising that the values of k_1 are for all stabilizers studied in this series of papers lower than the rate constants of the dehydrochlorination of non-stabilized PVC which are $k_1 = 1.31 \times 10^{-4}\ \mathrm{min}^{-1}$ in the nitrogen atmosphere and $k_1 = 1.93 \times 10^{-4}\ \mathrm{min}^{-1}$ for the dehydrochlorination under air. This general decrease in k_1 seems to us to be convincing enough to conclude that the stabilizers affect elimination of HCl from PVC also in another way than we have considered. It could be the Frye—Horst mechanism of esterification of labile chlorines [14], or the reversible blocking mechanism [15]. However, for calcium stearate, *Vymazal et al.* have shown that the esterification takes place to a low extent only [16]. Also, chemistry of the reversible blocking mechanism is not satisfactorily understood. These are the reasons why we did not include these mechanisms to our reaction schemes. The values of k_1 unequivocally show that the stabilizers exert an additional stabilizing effect which affects the rate of HCl elimination from PVC.

The values of k_2 and k_3 show that metal stearates are efficient scavengers of HCl. From the calculations it follows that the parameters k_2, k_3, and x_c are not linearly independent in the region of the minimum sum of squares. As a consequence, fairly broad intervals of these parameters correspond to the minimum so that their values carry great errors (about 30 %).

In this series of papers we have presented the quantitative kinetic description of thermal dehydrochlorination of PVC stabilized with metal stearates. The method is far from being perfect, it should be understood only as a first attempt.

It has been demonstrated that the kinetic parameters make possible to calculate such characteristics as the consumption of stabilizer in the time of thermal stability, *etc.* We believe that, despite the imperfection, the kinetic parameters can be used for further consideration on the mechanisms of stabilization and for the estimation of the durability of PVC blends.

References

1. Deanin, R. D., Reynolds, H. H., and Oczayir, Y., *J. Appl. Polym. Sci. 13*, 1247 (1969).
2. Matsusaka, K. and Sugimoto, Y., *Polym. Commun. 26*, 371 (1985).
3. Eremina, I. M. and Fedoseeva, G. T., *Vysokomol. Soedin., B 29*, 619 (1987).
4. Ayrey, G., Head, B. C., and Poller, R. C., *J. Polym. Sci. — Macromol. Rev. 8*, 1 (1974).
5. Misker, K. S. and Fedoseeva, G. T., *Destruktsia i stabilizatsia polivinilkhlorida.* (Destruction and Stabilization of Poly(vinyl chloride).) Khimiya, Moscow, 1979.
6. Oremusová, J., Šimon, P., Valko, L., and Kovařík, P., *Chem. Papers 43*, 721 (1989).
7. Šimon, P., Oremusová, J., Valko, L., and Kovařík, P., *Chem. Papers 45*, 127 (1991).
8. Oremusová, J., Šimon, P., Valko, L., and Kovařík, P., *Chem. Papers 45*, 379 (1991).
9. Marks, G. C., Benton, L. J., and Thomas, C. M., *J. Appl. Polym. Sci. 22*, 2415 (1978).
10. Carenza, M., Moiseev, Y. V., and Palma, G., *J. Appl. Polym. Sci. 17*, 2685 (1973).
11. Šimon, P. and Valko, L., *Polym. Degrad. Stab. 29*, 253 (1990).
12. Nelder, J. A. and Mead, R., *Comput. J. 7*, 308 (1965).
13. Moore, W. J., *Physical Chemistry*. Englewood Cliffs, New Jersey, 1972.
14. Frye, A. F. and Horst, R. W., *J. Polym. Sci. 40*, 419 (1959).
15. Iván, B., Kelen, T., and Tűdős, F., *International Conference on Advances in the Stabilization and Controlled Degradation of Polymers*, p. 61—78. Luzern, Switzerland, 1989.
16. Vymazal, Z., Volka, K., Vymazalová, Z., Mastný, L., and Sabaa, M. W., *Eur. Polym. J. 23*, 331 (1987).

Translated by P. Šimon