Decomposition of *N*-chlorosuccinimide and initiation of polypropylene chlorination

I. JANIGOVÁ and J. RYCHLÝ

Polymer Institute, Slovak Academy of Sciences, CS-842 36 Bratislava

The DSC method was used for studying decomposition of *N*-chlorosuccinimide in polypropylene. The reaction of mechanically mixed powders of *N*-chlorosuccinimide and a polymer was performed in oxygen, in air or in nitrogen and parameters of the kinetic model incorporating radical chain mechanism were determined.

Chlorination of hydrocarbon polymers which is one of the ways of their modification can be carried out either in suspension or in solution [1—5]. Powdered polymer can be chlorinated by a gaseous chlorine with radiation or peroxidic initiation [6—9]. Chlorine atoms are there bound to amorphous parts of the surface polymer layers. Halogen atom bonded to tertiary carbon of the polymer lowers simultaneously the thermal stability of the polymer.

N-Chlorosuccinimide (NCS) is a selective chlorination agent, which introduces halogen to the β-position of the C=C bond. When using NCS as chlorination agent, greatest attention has been paid to such substrates as aromatic compounds, particularly toluene, and their derivatives [10—14]. Here halogenation proceeds through the radical chain mechanism initiated by thermal homolysis, photolysis, or thermal decomposition of radical sources, such as peroxides and azo compounds. The use of NCS for chlorination of powder polyolefins has so far been little studied. Remarkable exothermicity of this reaction allows its investigation by some of the methods of thermal analysis.

In this paper we studied chlorination of isotactic polypropylene (iPP) with NCS under heterogeneous conditions where NCS and polymer were mixed mechanically. DSC method was used and the courses of the rate of heat release were compared in different atmosphere (oxygen, nitrogen, air). The mechanism for chlorination and determination of the kinetic parameters of the model proposed are discussed.

Experimental

Powder isotactic polypropylene Tatren TF-411 (melt flow index 8.0—11.5 g/10 min, measured at the temperature 230 °C according to CSN 640861, sieve analysis below

0.125 mm, softening temperature 154 °C, melting temperature 163 °C) was used. The polymer did not contain stabilizers. N-Chlorosuccinimide (m.p. = 150 °C; Fluka) used as halogenation agent was applied without any further purification. Powder blends containing 20 mass % NCS were homogenized in spherical laboratory homogenizer at room temperature for 5 min. The measurements were followed by the calorimetric method on a calorimeter DSC-2 (Perkin—Elmer) connected on-line to a calculator Tektronix 31. The measurements were carried out in dynamic and isothermal modes. In isothermal mode the samples were heated to the required temperature of isotherm with the rate of 160 K min^{-1} The temperature interval for experiments was 405—425 K.

In dynamic experiments, the heating rate was 10 K min^{-1} The mass of sample was *ca.* 1 mg. The thermal and temperature calibration was done using indium and lead standards. Iodometric titration was used for determining the content of unreacted NCS in blend [15]. Elemental analysis was performed with an automatic analyzer, model 1102 in ultramicro form (C. Erba). The content of chlorine was determined by the Schöniger method [16].

Results and discussion

Nonisothermal mode

Fig. 1 shows the course of melting and decomposition of NCS and halogenation of polypropylene under nonisothermal conditions in air recorded by the DSC method. During reaction in blend, NCS melts at first (endotherm I, curve *1*) and then the second endotherm II occurs, representing melting of iPP. The decomposition of NCS alone connected with halogenation of polymer
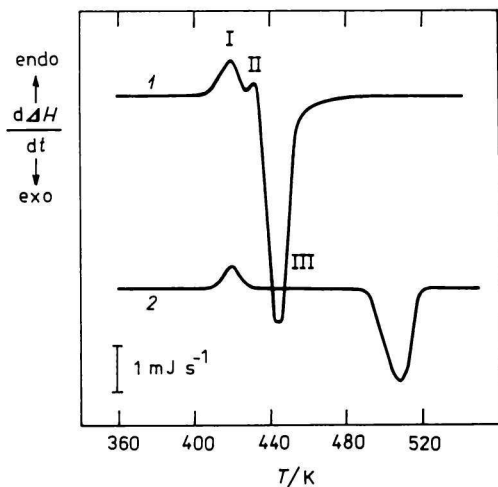

Fig. 1. DSC records of the reaction of NCS and iPP in dynamic mode (*1*) and decomposition and melting of NCS alone (*2*).

(exotherm III) takes place after the second endotherm. The figure also shows to what extent the presence of polymer influences the decomposition of NCS alone. The maximum of the decomposition exotherm of NCS (curve 2) is reached only at 506 K. In a mixture with iPP, decomposition and halogenation proceed at much lower temperature, the maximum of decomposition being at *ca.* 440 K. The temperature of the maximum melting rate of iPP crystallites is 436 K and that of NCS crystallites is 423 K.

Isothermal mode

The temperature interval suitable for studying halogenation of iPP and decomposition of NCS in iPP under isothermal conditions in air using the isothermal DSC method is between 405—425 K. The individual components do not show endotherm at these temperatures under isothermal conditions, though this temperature interval overlaps their melting region. Fig. 2 shows the characteristic DSC curves of the halogenation of polypropylene by NCS. Each curve may be characterized by the maximum rate of heat release v_{max}, time of its reaching t_{max}, and the overall area under DSC curve ΔH, which represents the total heat released during reaction (Table 1). The areas under DSC curves for different atmosphere (nitrogen, air, oxygen) were compared. It can be seen that overall reaction heat is in inert atmosphere *ca.* about 30 % lower than that in oxygen (Table 2).

The second maximum during reaction in oxygen appears after rapid decrease in the rate of heat release (Fig. 3). The second maximum does not appear either
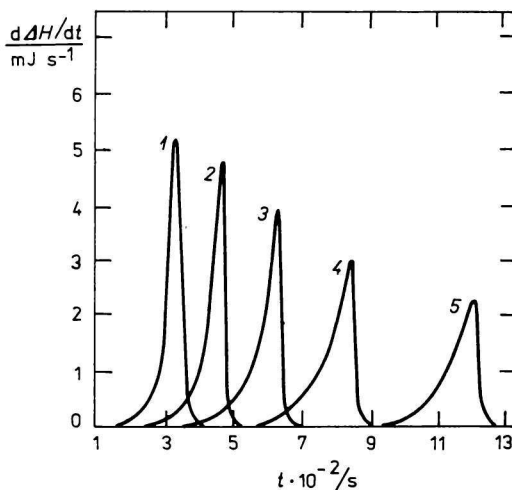

Fig. 2. Time dependence of the rate of heat release for a mixture of iPP and NCS for temperatures T/K: 425 (*1*), 420 (*2*), 415 (*3*), 410 (*4*), and 405 (*5*) measured in air.

Table 1

Data from DSC measurements of the reaction between iPP and NCS in air

T/K	$\Delta H/(\text{kJ mol}^{-1})$	t_{max}/s	$v_{max}/(\text{J g}^{-1}\text{s}^{-1})$
405	120.3	1297	2.05
410	111.3	893	2.64
415	121.2	663	3.33
420	124.7	461	4.39
425	128.5	361	5.39

Table 2

Influence of atmosphere on the values of the reaction heat ΔH, time t_{max}, and the rate of heat release v_{max} for a mixture of iPP and NCS at 420 K (values for the reaction in oxygen correspond to the first maximum)

Atmosphere	$\Delta H/(\text{kJ mol}^{-1})$	t_{max}/s	$v_{max}/(\text{J g}^{-1}\text{s}^{-1})$
Nitrogen	121.9	490	5.58
Air	124.5	461	4.39
Oxygen	171.4	399	3.75

in nitrogen or in the air. As the atmosphere changes from nitrogen to oxygen, the value of v_{max} decreases, the time t_{max} is reduced and the value of the overall heat released ΔH increases (Table 2). The lowering of the values of v_{max} obtained during reaction in oxygen with respect to those from the reaction in air indicates
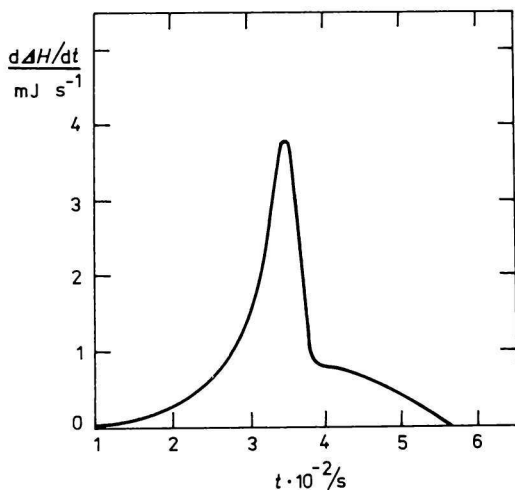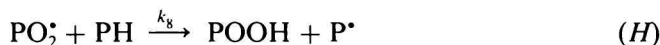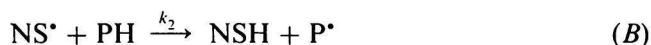

Fig. 3. Time dependence of the rate of heat release for a mixture of iPP and NCS at 420 K measured in oxygen.

a decrease in the rate of polymer halogenation. The existence of the second extreme may be ascribed to an induced oxidation. The presence of some hydroperoxides in the polymer facilitates initiation of halogenation on the one hand (decrease of t_{max}) but, on the other hand, oxygen consumes in propagation reaction polymer alkyl radicals with the formation of peroxy radicals and thus retards the process (decrease of v_{max}) [17].

We tried to describe halogenation of iPP in the presence of oxygen and NCS by the following reaction scheme which takes these facts into account

$$\text{NCS} \xrightarrow{k_1} \text{NS}^{\bullet} + \text{Cl}^{\bullet} \tag{A}$$

$$\text{NS}^{\bullet} + \text{PH} \xrightarrow{k_2} \text{NSH} + \text{P}^{\bullet} \tag{B}$$

$$\text{P}^{\bullet} + \text{NCS} \xrightarrow{k_3} \text{PCl} + \text{NS}^{\bullet} \tag{C}$$

$$\text{Cl}^{\bullet} + \text{PH} \xrightarrow{k_4} \text{HCl} + \text{P}^{\bullet} \tag{D}$$

$$\text{HCl} + \text{NCS} \xrightarrow{k_5} \text{Cl}_2 + \text{NSH} \tag{E}$$

$$\text{P}^{\bullet} + \text{Cl}_2 \xrightarrow{k_6} \text{PCl} + \text{Cl}^{\bullet} \tag{F}$$

$$\text{P}^{\bullet} + \text{O}_2 \xrightarrow{k_7} \text{PO}_2^{\bullet} \tag{G}$$

$$\text{PO}_2^{\bullet} + \text{PH} \xrightarrow{k_8} \text{POOH} + \text{P}^{\bullet} \tag{H}$$

$$\text{NCS} + \text{POOH} \xrightarrow{k_9} \text{Cl}^{\bullet} + \text{PO}_2^{\bullet} + \text{NSH} \tag{I}$$

$$\text{P}^{\bullet} + \text{Cl}^{\bullet} \xrightarrow{k_{10}} \text{PCl} \tag{J}$$

The scheme includes slow monomolecular decomposition of NCS into $\text{Cl}^{\bullet}$ and succinimidyl $\text{NS}^{\bullet}$ radicals (reaction A) as well as bimolecular interaction between NCS and hydroperoxides (reaction I). This reaction is much more rapid and probably has the character of redox reaction [18] with a complex mechanism. For instance, NCS does not evidently react with *tert*-butyl hydroperoxide at 0 °C whereas HCl does [19]. Formation of hydrogen chloride is, however conditioned by slow monomolecular decomposition of NCS. The particular sequence of reactions can then be formally seen as bimolecular reaction between NCS and hydroperoxide.

Chlorine and succinimidyl radicals formed from NCS are easily transferred to polymer (PH) and HCl, succinimide (NSH) and polymer radicals P$^{\bullet}$ are formed (reactions B, D). The reaction E between HCl and NCS maintains a certain level of molecular chlorine in a system. NCS and molecular chlorine enter rapid reaction with alkyl polymer radicals with the formation of chlorinated polymer and regeneration of succinimidyl and chlorine radicals (reactions C, F) takes place. In the presence of oxygen, alkyl radicals may be transformed to peroxide radicals which give hydroperoxides through transfer reaction with polymer (reactions G, H). The only termination reaction which we have considered to be substantial for the kinetics of the process is the recombination of alkyl and chlorine radicals (reaction J).

Then we verified how the scheme proposed above corresponds to the experiment. We denoted instantaneous concentrations by symbols $[NCS] = x$, $[HCl] = y$, $[Cl_2] = z$, and $[POOH] = u$ and used conditions of the stationary state for the rate of the formation and decay of radicals NS$^{\bullet}$, Cl$^{\bullet}$, P$^{\bullet}$, and PO$_2^{\bullet}$ and thus formulated a set of differential equations for the time changes of the concentrations of NCS, HCl, Cl$_2$, and POOH, as follows (diffusion phenomena control is not assumed)

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -k_1 x - M x^{3/2} z^{-1/2} (k_1 + k_9 u)^{1/2} - k_5 xy - k_9 xu \qquad (1)$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = -\frac{\mathrm{d}z}{\mathrm{d}t} = -k_5 xy + N x^{1/2} z^{1/2} (k_1 + k_9 u)^{1/2} \qquad (2)$$

$$\frac{\mathrm{d}u}{\mathrm{d}t} = [O_2] P x^{1/2} z^{-1/2} (k_1 + k_9 u)^{1/2} \qquad (3)$$

where M, N, and P represent complex constants

$$M = k_3 \frac{k_4 [PH]}{k_6 k_{10}}, \qquad N = \frac{k_4 k_6 [PH]}{k_{10}}, \qquad P = k_7 \frac{k_4 [PH]}{k_6 k_{10}} \qquad (4)$$

For our conditions $w(O_2) = 0.2$ and $[PH]$ is the concentration of C—H bonds in the system. The changes of the latter were regarded as negligible during experiment. Constants k_1—k_{10} are the rate constants for particular elementary reactions A—J from the scheme.

During optimization of parameters, we assumed the rate of heat release to be proportional to the rate of the reaction C, i.e.

$$\frac{\mathrm{d}(\Delta H)}{\mathrm{d}t} = L x^{3/2} z^{-1/2} (k_1 + k_9 u)^{1/2} \qquad (5)$$

where L is the constant of proportionality. We looked for optimum values of individual parameters in eqn (5) with the use of the Marquardt's method of nonlinear regression analysis. The systems of differential equations were integrated in each iteration according to the procedure of Runge—Kutta for initial conditions: $x_o = 0.2$, $y_o = 0.2$, $z_o = 0$, $u_o = 0$. Table 3 contains the parameters k_1, k_5, k_9, M, N, P, and L for particular curves (Fig. 2).

Table 3

Parameters obtained from the scheme of the reaction mechanism (reactions *A—J*) for interpretation of the experimental courses of the time dependence of the rate of heat release ($w(NCS)_o = 0.2$)

T	$k_1 \cdot 10^5$	$M \cdot 10^2$	$P \cdot 10^2$	$k_5 \cdot 10^3$	$k_9 \cdot 10^3$	$N \cdot 10$	L
K	s^{-1}	$s^{-1/2}$	$s^{-1/2}$	s^{-1}	s^{-1}	$s^{-1/2}$	$mJ\,s^{1/2}$
405	0.14	1.62	3.47	0.63	4.48	7.79	3.6
410	1.12	1.37	4.96	1.13	5.87	8.22	3.3
415	1.67	1.78	5.34	1.58	6.77	9.55	4.6
420	0.52	1.85	6.71	2.68	8.67	12.40	4.8
425	1.67	2.00	9.36	3.57	12.50	13.20	5.1

A comparison of the experimental curve and theoretical points corresponding to the particular values of parameters (Fig. 4) shows that the agreement is fairly good; deviations observed may be caused by some imprecisions in the choice of the zero line in the data collection from the calorimeter. It may be seen that the parameters determined increase with temperature (Table 3). A consider-
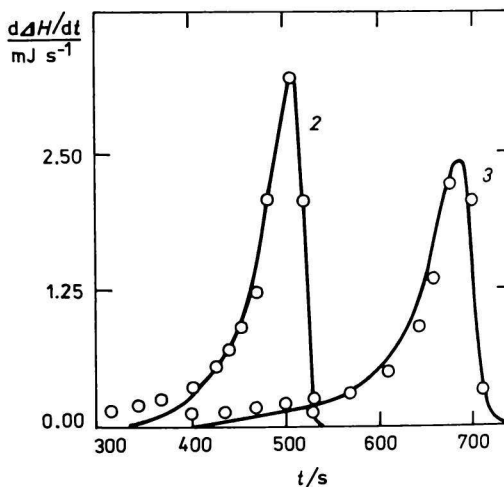

Fig. 4. A comparison of experimental and theoretical courses of the rate of heat release as function of time for a mixture of iPP and NCS at 415 K (*3*) and 420 K (*2*) measured in air.
○ Theoretical points, ——— experimental record.

able scatter of the values of k_1 representing monomolecular decomposition of NCS can be explained by the fact that the decomposition of NCS is also caused by inhomogeneously distributed defects in iPP such as unsaturations, peroxy groups, *etc.*

The activation energies (Table 4) determined for individual kinetic constants according to the Arrhenius equation for halogenation represented by the parameters M and N are rather low, about 20 kJ mol^{-1} and 42 kJ mol^{-1}, respectively. The activation energy of oxidation (parameters P and k_9) is 67 kJ mol^{-1}, whereas that for the decomposition of NCS represented by monomolecular reaction and interaction with HCl (reactions A and E) is about 120 kJ mol^{-1}. The values from Table 3 lead to the following ratios of the individual rate constants (Table 5). An important finding is that the rate constant k_6 of the reaction of alkyl radicals and chlorine is *ca.* twice higher than k_7 (reaction of alkyl radicals and oxygen), the rate constant k_3 (reaction of alkyl radicals with NCS) being 2.5-times lower.

Elemental analysis (w_i(found): 80.39 % C, 13.58 % H, 5.67 % Cl, 0.36 % O) showed that 5—6 mass % of chlorine was bound to polymer.

Table 4

Experimental activation energy E and preexponential factors A determined for individual kinetic constants following from the reaction scheme (reactions A—J). Dimension of A corresponds to the particular constant, r is the correlation coefficient

Parameter	$E/(\text{kJ mol}^{-1})$	$\ln A$	r
k_1	121	23.3	0.638
M	21	1.9	0.782
P	65	16.1	0.981
k_5	124	29.5	0.995
k_9	70	15.3	0.988
N	42	12.1	0.973

Table 5

Ratios of the rate constants from the reactions A—J obtained from Table 3

T/K	k_6/k_7	k_3/k_7	k_6/k_3
405	2.25	0.47	4.8
410	1.75	0.29	6.0
415	1.79	0.33	5.4
420	1.84	0.27	6.7
425	1.41	0.21	6.6

Fig. 5 shows time variations of the amount of active chlorine in NCS determined iodometrically at three temperatures. The reactions exhibit initial slow decrease of NCS. After some induction period, the concentration of chlorine radicals decreases rather rapidly. Arrows in Fig. 5 represent the values of t_{max} from DSC measurements. Considering the difference in the experimental arrangement, there is satisfactory agreement between the results of iodometric titrations and DSC measurements, where the content of active chlorine starts to decrease remarkably with times from DSC for the maximum rate of heat release.
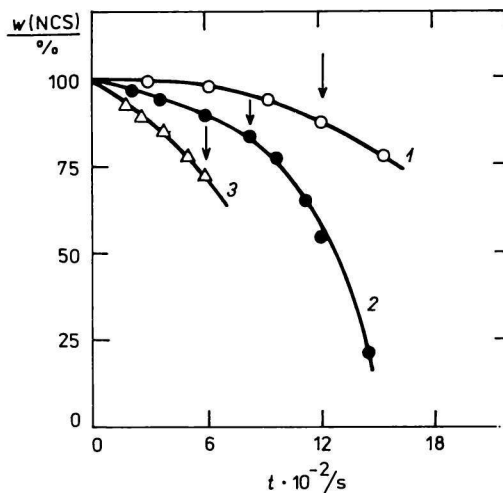

Fig. 5. Time variations of the NCS amount in a mixture with iPP at temperatures T/K: 405 (*1*), 410 (*2*), and 415 (*3*).

Conclusion

The results obtained show that decomposition of NCS and chlorination of iPP with NCS can be reliably interpreted by the scheme of substitution halogenation proceeding through the radical chain mechanism. Decomposition of NCS as well as chlorination of iPP are autocatalytic reactions where oxygen plays an important role.

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