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# PROOF OF THE KINETIC REACTION MECHANISM OF PVC DEGRADATION USING TA

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The possibility of describing the kinetics of thermal degradation of PVC samples under both isothermal and nonisothermal conditions with a unique model and using the same set of parameters was investigated. Analysis of the experimental data revealed good agreement at higher temperatures (above 175 °C) when the catalytic action of generated HCl and its distribution in the sample were considered. At lower reaction temperatures, further experimental conditions and/or sample characteristics must be considered, and a modification of the model is necessary.

If a kinetic model is assumed to be a suitable description of an investigated process, it must correctly predict the time-dependence of the measured process parameters over a wide range of experimental conditions. If there are differences, the kinetic model and/or the experimental conditions have to be checked. This thesis will be discussed on the example of the thermal degradation of PVC under isothermal (140–180°) and nonisothermal (heating rate $\beta = 0.2$–$2$ deg/min) conditions.

## Experimental

The dehydrochlorination of PVC by thermal degradation was measured by using a conductometer connected to a Mettler TA 1 Thermoanalyzer. The investigations were carried out with a sample weight of 50 mg, a flow rate of nitrogen of 15 1/h, a Pt sample holder and a Pt-Pt/Rh thermocouple. Two commercial PVC types (from KCW BUNA) were investigated: the suspension PVC SCOVINYL S 6369 and the emulsion PVC SCOVINYL E 6921, both extracted with methanol.

## Results and discussion

The thermal degradation of PVC at low conversions, $\alpha \leqslant 2\%$($\alpha =$ degree of dehydrochlorination), can be described by the overlapping of at least two independent processes: the initiation at normal PVC structures (first term

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on the right side of Eq. (1)) and the initiation at a dominating kind of defect structures of concentration $F_0$ (second term), both followed by a quick dehydrochlorination 'zip' of length $r$.

However, analysis of the experimental data (Fig. 1) showed that the model based only on the first two terms leads to a defect structure ration $F_{0E}/F_{0s} \geqslant 3$, which is in disagreement with the values of the amount of tertiary chlorine at branching points (assumed to be the most effective labile structure [1]) detected by NMR [2]: $0.8 \cdot 10^{-3}$ $MU^{-1}$(SCOVINYL S) and $1.4 \cdot 10^{-3}$ $MU^{-1}$ (SCOVINYIL E).

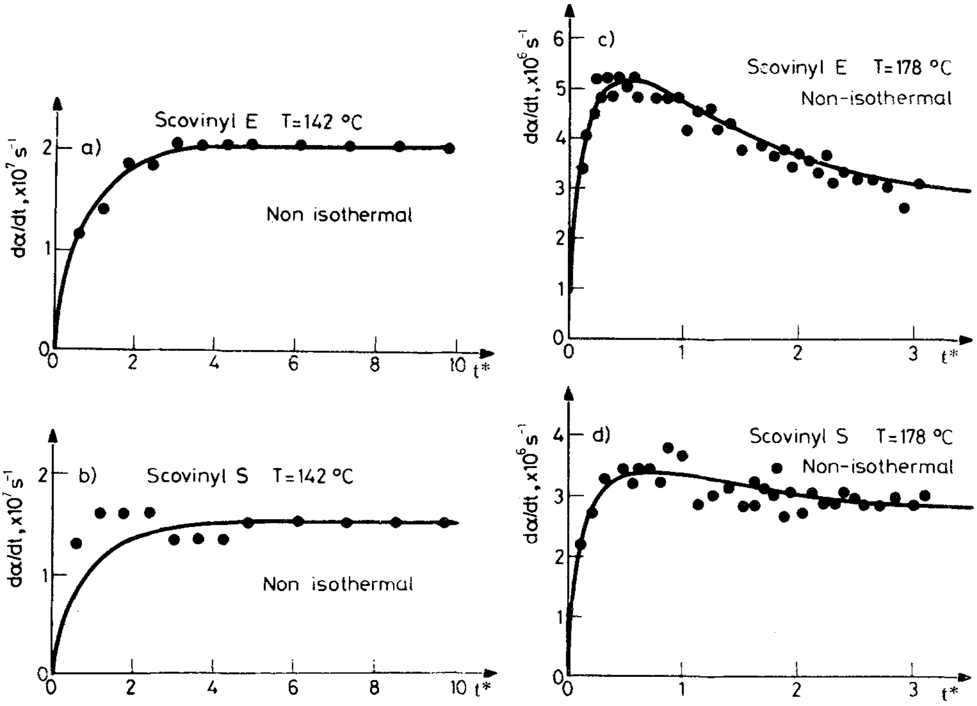

**Fig. 1** Time dependence $t^*$ (relative units) of the dehydrochlorination rate of two PVC samples obtained from isothermal investigations (single points) and calculated slope using equation 1 with a unique set of parameters (Tab. 1) and the defect structure ratio $F_{0E}/F_{0S} = 1.9$

A better description is achieved when the catalytic action of free HCl (third term) and its concentration gradient in the sample (last term) are additionally taken into consideration:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_o r + K_F r F_o e^{-K_{\mathrm{F}} t} + K_k r \alpha + D \nabla \alpha \tag{1}$$

(isothermal case). With the solution of Eq. (1) [3], it is possible to describe the dehydrochlorination processes of the two samples at 178° and at 142° with the same set of parameters (Table 1), considering only a defect structure ratio of 1.9, in agreement with the defect structure ratio calculated with the values of the amount of tertiary chlorine mentioned above (Fig. 1).

**Table 1** Kinetic parameters of dehydrochlorination of PVC (preexponential factor $A$, activation energy $E$) according to Eq. 1

| | | |
|---|---|---|
| $A_s \cdot r$ | $5.32 \cdot 10^{10}$ | $s^{-1}$ |
| $E_s$ | 141 | $\mathrm{kJ \cdot mol^{-1}}$ |
| $A_F$ | $1.09 \cdot 10^{22}$ | $s^{-1}$ |
| $E_F$ | 216 | $\mathrm{kJ \cdot mol^{-1}}$ |
| $A_K \cdot r$ | $3.83 \cdot 10^{8}$ | $s^{-1}$ |
| $E_K$ | 112 | $\mathrm{kJ \cdot mol^{-1}}$ |
| $C_0^*$ | $2.12 \cdot 10^{-8}$ | $s^{-1}$ |
| $E_c$ | −37 | $\mathrm{kJ \cdot mol^{-1}}$ |

* $C = \pi^2 D/l^2$, where $l = f(T)$ is an effective sample thickness

Attempts to analyse nonisothermal data too by using an equation analogous with Eq. (1):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A_s r}{\beta} e^{-\frac{E_{\mathrm{S}}}{RT}} + \frac{A_F r F_o}{\beta} e^{-\frac{E_{\mathrm{F}}}{RT}\left(1 + \frac{R^2 T^3}{\beta E_{\mathrm{F}}{}^2} e^{-\frac{E_{\mathrm{F}}}{RT}}\right)} + \tag{2}$$

$$+ \frac{A_k r}{\beta} e^{-\frac{E_{\mathrm{K}}}{RT}} \alpha + \frac{D_o}{\beta} e^{-\frac{E_{\mathrm{D}}}{RT}} \nabla \alpha$$

were not so successful, because of the difficulties in the mathematical handling. Attempts to overcome these by using Eq. (1) and changing the temperature in the calculation in a stepwise way failed, because in this case the starting conditions of the solution of Eq. (1) permanently changed. Only in special cases and in the lower temperature range was a description of nonisothermal dehydrochlorination curves possible by using only the first two terms of Eq. (2) [4]. This allows, for example, a distinction between different kinds of defect structures and an estimation of their concentration $F_0$ in the sample.

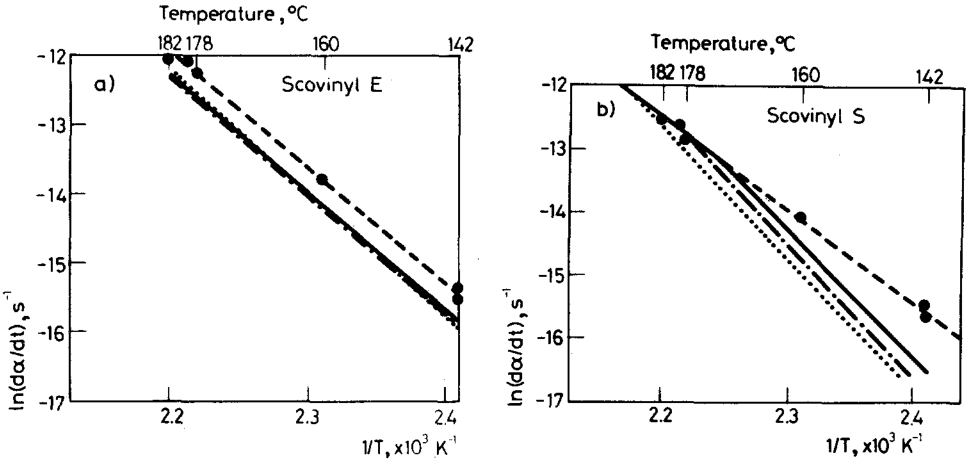

Fig. 2 Comparison of the overall dehydrochlorination rate of two PVC samples under isothermal conditions (single points) and calculated from nonisothermal data at different heating rates (—— –0.2, –·–·– –0.5, – – – – –2.0 deg min$^{-1}$)·

Table 2 Comparison of kinetic parameters got from brutto dehydrochlorination curves under isothermal and nonisothermal conditions

| | Scovinyl S | | Scovinyl E | |
|---|---|---|---|---|
| | $A, s^{-1}$ | $E$, kJ·mol$^{-1}$ | $A, s^{-1}$ | $E$, kJ·mol$^{-1}$ |
| isothermal | $2.96 \cdot 10^8$ | 121 | $3.37 \cdot 10^{10}$ | 137 |
| nonisothermal | | | | |
| $\beta = 0.2$ deg·min$^{-1}$ | $7.09 \cdot 10^{13}$ | 167 | $3.20 \cdot 10^{10}$ | 138 |
| * | $4.66 \cdot 10^8$ | 124 | $4.54 \cdot 10^8$ | 122 |
| $\beta = 0.5$ deg·min$^{-1}$ | $5.13 \cdot 10^{14}$ | 175 | $3.11 \cdot 10^{10}$ | 138 |
| * | $1.65 \cdot 10^8$ | 120 | $4.28 \cdot 10^8$ | 122 |
| $\beta = 2.0$ deg·min$^{-1}$ | $2.31 \cdot 10^{14}$ | 173 | $1.63 \cdot 10^{11}$ | 144 |
| * | — | — | — | — |

* $T \geqslant 175$ °C

Nevertheless, as Fig. 2 and Table 2 show, for the sample SCOVINYL E the kinetic parameters of the dehydrochlorination process obtained under nonisothermal conditions are nearly independent of the heating rate and comparable with those obtained under isothermal conditions (see also Fig. 1). For the sample SCOVINYL S, only at higher temperatures (above 175°) was a good accordance found; at lower temperatures, the description of the experimental data was not satisfactory, for reasons not considered in Eqs (1) and (2) (e.g. morphology).

## Conclusions

1. The attempt to describe the kinetics of thermal dehydrochlorination of PVC samples under both isothermal and nonisothermal conditions with a unique model and with the same set of parameters leads to a better understanding of the complex process investigated.
2. At higher temperatures (above about 175°), the overall process is obviously influenced by the catalytic action of the reaction product HCl (as recently mentioned in a more detailed analysis of previous results in [5]). Under such conditions, the model according to Eqs (1) and (2) works well and the third term becomes dominant. 120 ± 10 kJ $\text{mol}^{-1}$ seems to be an appropriate value for the activation energy of this process.
3. At lower temperatures, the influence of the dehydrochlorination initiated at defect structures (second term in Eqs (1) and (2) is more distinguished, but other influencing factors must also be taken into account (sample *S*), and a further checking of the experimental conditions and sample characteristics followed by a model modification is necessary.

## References

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**Zusammenfassung** – Es wird die Möglichkeit untersucht, die Kinetik des thermischen Abbaus von PVC sowohl unter isothermen wie unter nichtisothermen Bedingungen durch ein einziges Modell und unter Verwendung des gleichen Parametersatzes zu beschreiben. Die Analyse der Messdaten zeigt gute Übereinstimmung bei hohen Temperaturen (über 175 °C), wenn die katalytische Aktivität des entwickelten HCL und seine Verteilung in der Probe berücksichtigt werden. Bei tieferen Temperaturen müssen weitere experimentelle Bedingungen und/oder Probeneigenschaften berücksichtigt werden, was eine Modifizierung des Modells erforderlich macht.

**РЕЗЮМЕ** — Изучена возможность описания кинетики термического разложения поливинилхлорида в изотермических и неизотермических условиях с помощью одной единственной модели с использованием того же самого нароба параметров. Анализ экспериментальных результатов показал хорошее совпадение при более высоких температурах (выше 175°), где учитывалось каталитическое действие получаемого хлористого водорода и его распределение в объеме образца. При более низких температурах реакции следует учитывать дальнейшие экспериментальные условия и характеристики исследуемого образца, а также необходимость модификации такой модели.