Kinetic study on the non-catalysed and catalysed degradation of polyamide 6 with isothermal and dynamic methods

H. Bockhorn, A. Hornung, U. Hornung[*], J. Weichmann

Institut für Chemische Technik, Universität Karlsruhe (TH), Kaiserstr. 12, 76128 Karlsruhe, Germany

Abstract

The catalysed or non-catalysed thermal decomposition of polyamide 6 could be an alternative to current recycling processes, where the depolymerization of polyamide 6 to the monomer ε-caprolactam is performed with steam and phosphoric acid (Zimmer AG). Therefore, in this work the formal kinetic parameters of the thermal degradation of polyamide 6 are determined by means of isothermal and dynamic measurements. The functional amide group of polyamide 6 enables catalysis of the decomposition. Therefore, also the formal kinetic parameters of thermal degradation in presence of phosphoric acid and sodium/potassium hydroxide are determined. A mechanistic interpretation is given for the thermal degradation of polyamide 6 and the catalysed decomposition reactions. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The chemical reutilization of polyamide 6 is economically interesting because of the high value of polyamide 6. The synthesis of the monomer ε-caprolactam proceeds via a complex multi-stage process. The first step is the hydration of benzene to cyclohexane, the second step is the catalytic oxidation to cyclohexanone, the third step is formation of the oxime and finally the Beckmann-rearrangement reaction to ε-caprolactam is performed. The recovery of ε-caprolactam from waste polyamide 6 has, therefore, the potential to be economically competitive with the traditional synthesis process and has a significant positive environmental impact. A presently applied

recycling process is the Zimmer AG process [1,2], which performs the depolymerization of polyamide 6 with the help of steam and liquid catalysts such as phosphoric acid. This process can be applied only for non-mixed polyamide 6 materials. A disadvantage of this process is the high yield of salts and traces of phosphoric acid in the recovered ε-caprolactam, which is a drawback for the production of fibres. Therefore, a thermal process based on the pyrolysis of polyamide 6 — possibly catalysed by recoverable catalysts — might be more competitive.

The functional amide group of polyamide 6 enables catalysis in the thermal decomposition. Czernik et al. [3] investigated the catalysis of the thermal degradation of polyamide 6 with α-alumina supported KOH in a fluidized bed reactor. In this work the catalysed degradation of polyamide 6 is carried out between 330°C and 360°C with a yield of 85% ε-caprolactam

[*]Corresponding author. Fax:+49-721-608-4820
E-mail address: uhornung@ict.uni-karlsruhe.de (U. Hornung)

and higher. Mukherjee et al. [4] investigated the catalysis under vacuum with 1% NaOH at 250°C and determined a yield of 90.5% ε-caprolactam. In both cases the reaction takes place under heterogeneous conditions (melting point of NaOH 318.4°C). Another approach is the catalysis of liquefied polyamide 6 with liquid catalysts. Therefore, in this work the catalysis is investigated with an eutectic mixture of sodium hydroxide and potassium hydroxide (melting point of the mixture of 60 mol% NaOH and 40 mol% KOH is 185°C). Formal kinetic parameters of the non-catalysed thermal degradation of polyamide 6 are measured in comparison with that of the catalysed reaction. Two types of catalysts — NaOH/KOH and H_3PO_4 — have been employed. The formal kinetic parameters of the thermal degradation of polyamide 6 are determined by isothermal and dynamic measurements. The isothermal measurements are performed with a gradient free reactor with on-line gas analysis by means of a mass spectrometer. The dynamic measurements are carried out with a thermobalance coupled to a mass spectrometer. Based on the kinetic data a mechanistic interpretation of the depolymerization of polyamide 6 with and without catalysis is given. With the help of these data the design of recycling procedures is possible.

2. Experimental

2.1. Dynamic measurements with coupled thermogravimetry/mass spectrometry

The thermogravimetric experiments were carried with a thermobalance (DuPont 951 thermogravimetric analyser) coupled with a quadrupole mass spectrometer (Balzers QMG 420). The thermobalance was operated with heating rates from 1 to 20 K/min between ambient temperature and 800°C. Pure helium was used as purge gas. The flow rate of the purge gas was approximately 100 cm³/min. The quadrupole mass spectrometer was connected to the thermobalance via an open coupling with a differential pressure reduction via a platinum orifice (10 μm diameter). The coupling could be heated up to 500°C to prevent condensation of the evolved products. The high pressure end of the coupling was located directly above the heated polymer sample. Part of the probed gases was

pumped behind the orifice before entering the low pressure section of the coupling. The low pressure end of the coupling was inserted directly into the ion source of the mass spectrometer. The ionizing voltage of the cross-beam electron impact ionization source amounted to 30 eV.

In terms of formal rate expressions the overall decomposition rate of a heated polymer sample often can be described by degressive kinetic rate expressions

$$\frac{d\alpha}{dt} = k(T) \cdot (1-\alpha)^n, \tag{1}$$

where α is the degree of conversion which is defined as $\alpha = (m_0 - m)/(m_0 - m_\infty)$ with m_0 being the initial mass, m the actual mass and m_∞ the final mass, k is the rate coefficient and n the apparent order of the overall decomposition reaction. The rate coefficient k often has an Arrhenius type of temperature dependence $k = k_0 \cdot e^{-E_a/RT}$, where k_0 is the preexponential factor and E_a the apparent activation energy. Introducing the heating rate $\beta = dT/dt$ Eq. (1) is transformed into

$$\frac{d\alpha}{dT} = \left(\frac{k_0}{\beta}\right) \cdot e^{-E_a/RT} \cdot (1-\alpha)^n, \tag{2}$$

which can be integrated using a fourth order Runge-Kutta method to give the theoretical conversion in dependence on temperature. The overall kinetic parameters then are obtained from least square calculations [5] for the experimental determined conversions and the calculated ones.

As pointed out in [6] a detailed heat balance of the sample has to be considered to determine the true sample temperature T_s and heating rate β. As a first approximation homogeneous sample temperature can be assumed, which can be realized with low heating rates (2 K/min) and small sample mass (2 mg). The heat balance in Eq. (3) takes into account the contribution from reaction enthalpy of the thermal decomposition, which depends on the initial sample mass m_0 and on the actual conversion rate, and the heat transfer to the sample introducing κ as a constant overall heat transfer coefficient:

$$C_p \frac{dT_s}{dt} = \kappa (T_t - T_s) - m_0 \Delta_r H \frac{d\alpha}{dt}, \tag{3}$$

with C_p the heat capacity of the sample and T_t the thermocouple temperature.
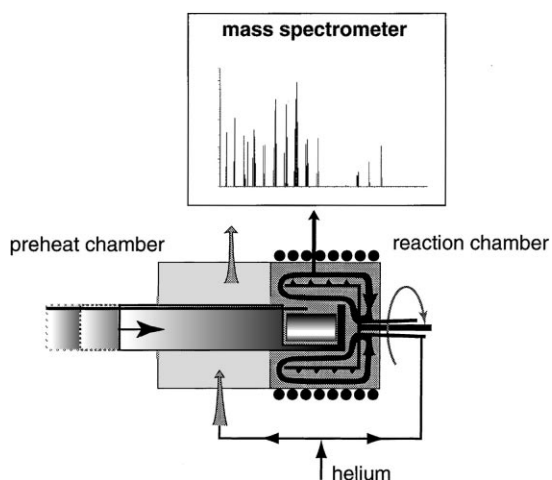
Fig. 1. Schematic of the closed loop-type reactor.

2.2. Isothermal measurements with a closed loop-type reactor

To validate the kinetic data derived from dynamic thermogravimetric measurements an isothermal closed loop-type reactor with on-line gas analysis is used [7]. Measurements can be performed up to 1 MPa and sample masses of 1 g, usually 20–40 mg, and with various gas atmospheres. In this work helium was used as purge gas. The reactor consists of a heated sliding device carrying the sample within a platinum crucible, compare Fig. 1. After preheating the sliding device the sample is moved quickly into the reaction chamber. Heat transfer to the sample is accomplished through mixing of the reactor contents by means of a small gas turbine. Heating times of the sample are about 40–50 s, which is negligible compared to reaction times of 1200–18 000 s. Perfect mixing provides as well gradient free conditions within the reaction chamber. The reaction products are analysed on-line with a quadrupole mass spectrometer (Balzers, QMG 421, analysator 400). More details are given in [7].

Kinetic data for the decomposition are obtained from on-line gas analysis with the mass spectrometer. From the detected ion currents versus time $I(t)$ the

This equation is integrated with a fourth order Runge-Kutta method to obtain the sample temperature T_s and to calculate the true heating rate ($\beta = dT/dt$).

experimental conversion $\alpha_{\exp} = (m_{tot} - m(t))/m_{tot}$ for the decomposing polymer can be derived as

$$1 - \alpha_{\exp}(t) = \frac{m(t)}{m_{tot}} = 1 - \frac{\int_0^t I(t)\bar{M}(t)\dot{V}dt + I(t)\bar{M}(t)V_R}{\int_0^\infty I(t)\overline{M}(t)\dot{V}dt},$$

$$(4)$$

with $m(t)$ being the actual mass, m_{tot} the total evolved mass, $\bar{M}(t)$ the mean molar mass at time t (also calculated from the ion currents), $\dot{V}$ the flowrate and V_R reactor volume. The normalized residue $m(t)/m_{tot}$ is equivalent to 1 minus the experimental degree of conversion $\alpha_{\exp}$. The degree of conversion is equivalent to the mass that has already left the reactor $\int_0^t I(t)\overline{M}(t)\dot{V}dt$ plus the actual mass of products in the gas phase $I(t)\overline{M}(t)V_R$ normalized by the total evolved mass of products.

Analogously to dynamic measurements the kinetic model in Eq. (1) is used to evaluate the rate coefficient k and apparent order of reaction n. The degree of conversion for isothermal degradation obtained by integration of Eq. (1) valid for $n \neq 1$ is

$$\alpha(t) = 1 - (k(T)t(n-1) + 1)^{1/(1-n)}. \qquad (5)$$

For evaluation of the kinetic data a direct search method is applied. The degree of conversion given by Eq. (5) is fitted by means of least square fit to the experimental degree of conversion given by Eq. (4) by variation of k and n.

Using an Arrhenius-like temperature dependency $k(T) = k_0 e^{-E_a/(RT)}$, the apparent energy of activation E_a and the preexponential factor k_0 are obtained by linear regression of $-\ln k$ versus $1/T$.

2.3. Quantification of pyrolysis products with GC/MS

In order to quantify the evolved pyrolysis products of polyamide 6, samples of 200 mg were pyrolysed under identical conditions as in the thermogravimetric measurements. The pyrolysis products were purged with Helium 4.6 (100 ml/min) and condensed in cold traps with liquid nitrogen. During pyrolysis heating rates of 2 K/min were used. Two kinds of measurements were performed:

- Determination and quantification of the total evolved pyrolysis products.

- Determination and quantification of fractions from certain temperature ranges in order to characterize the temperature dependence of the formation of reaction products.

The trapped pyrolysis products were analysed with GC/MS (gas chromatograph: Varian 3400, mass spectrometer: Finnigan MAT ITD 800). The gas chromatographic column was a capillary column CP-Sil (CB of Chrompack 50 m × 0.32 mm with a film thickness of 0.12 μm).

3. Results and discussion

The used polyamide 6 is a product of the BASF AG, Ludwigshafen, with the proprietary name Ultramid B3.

Qualities of polyamide 6 (Ultramid B3):

Melting point:	170–260°C
Density:	≥ 1 g/cm^3
Mean molar mass $\overline{M}$:	180 000 g/mol
Water content:	4–8 wt.%

3.1. Thermal degradation polyamide 6

The main decomposition product of polyamide 6 is ε-caprolactam ($\geq$92%). Identified by-products analysed by GC/MS are the cyclic dimer, i.e. 1,8-diaza-cyclotetradecane-2,9-dion (4%), 5-hexene acid amide (2%), 5-hexen nitrile (1%), hexane nitrile (0.5%) and 2-cyclohexen-1-one (0.5%).

The representative mass spectrum obtained during isothermal degradation at 450°C in Fig. 2 shows a fragmentation pattern similar to that of pure ε-caprolactam.

From the TG/MS measurements, compare Fig. 3, an apparent energy of activation E_a of 211.3 kJ/mol, a decimal logarithm of the preexponential factor log(k_0/min^{-1}) of 15.03 and an apparent order of reaction of 0.81 is determined.

These values excellently agree with those from the isothermal method. In Fig. 4 the experimental degree of conversion for several temperatures as a function of time calculated with Eq. (4) from the mass spectrometric data are shown. With the help of this data the
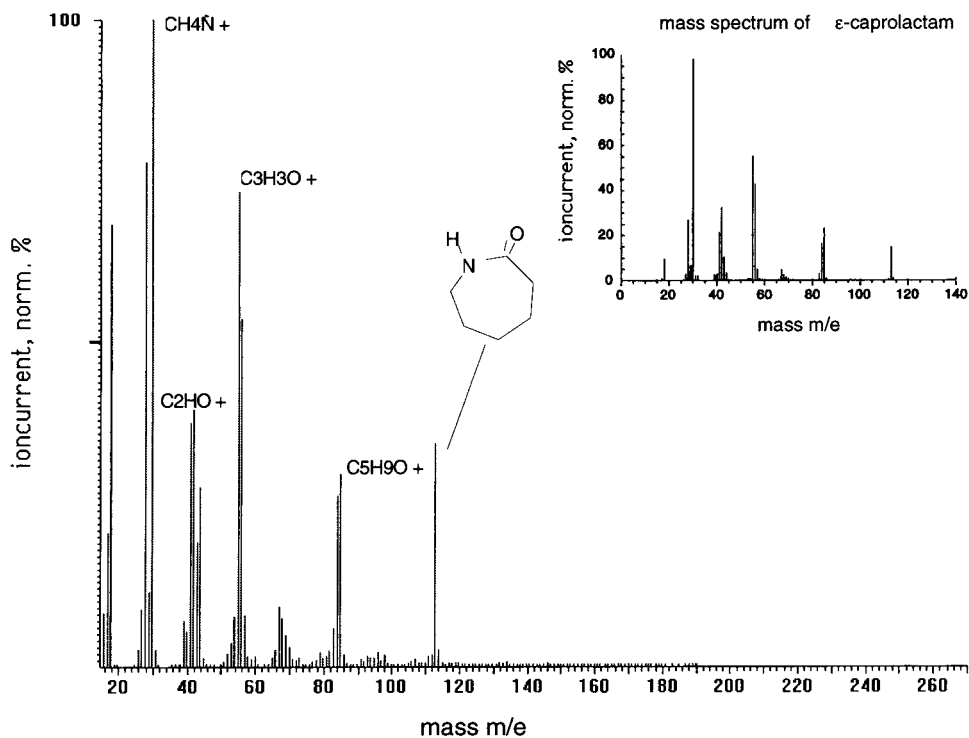

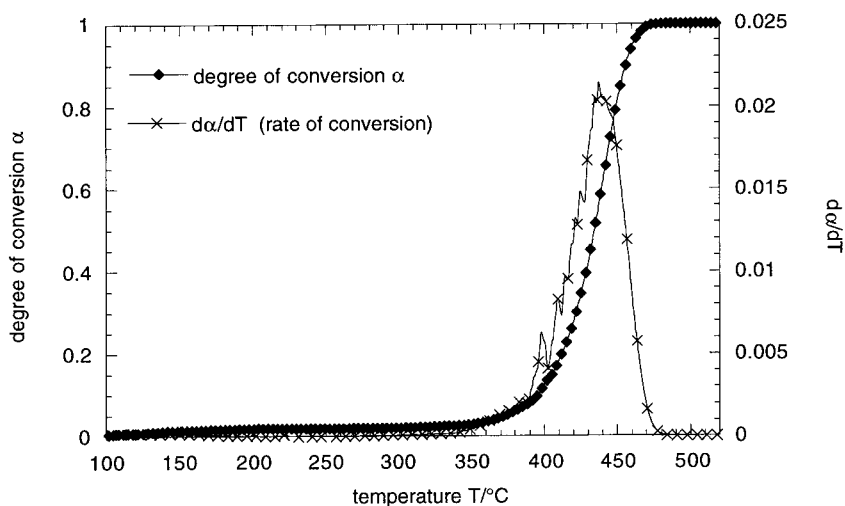Fig. 2. Mass spectrum obtained by isothermal degradation of polyamide 6 at 450°C.

Fig. 3. Thermogravimetric curve (TG) and first negative derivative of the thermogravimetric curve (DTG) of a 20 mg sample of polyamide 6; heating rate $\beta = 10$ K/min.

rate coefficients and the apparent order of reaction are obtained by least square fit. All determined rate coefficients are summarized in an Arrhenius plot, compare Fig. 5. From that an apparent energy of activation of 211 ± 3 kJ/mol and a preexponential factor of $\log(k_0/\text{min}^{-1}) = 14.9 \pm 0.05$ is determined for the overall process of polyamide 6 degradation, compare Fig. 5.

In case of isothermal decomposition of polyamide 6 a shift of the apparent reaction order from first order to

1.29 is observed above 420°C. This behaviour is correlated with the formation of by-products above 415°C. In Fig. 6 the yield of the determined by-products in dependence on temperature is shown.

In order to trace back the shift in reaction order to the formation of by-products, representative ion currents of ε-caprolactam are analysed separately. From that a constant apparent order of reaction of 0.98 is found for the formation of ε-caprolactam within the
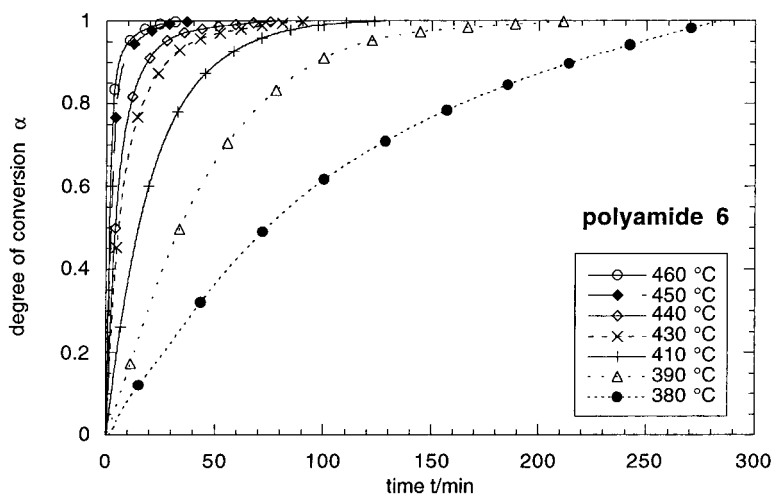

Fig. 4. Degree of conversion for the decomposition for polyamide 6 for several temperatures.
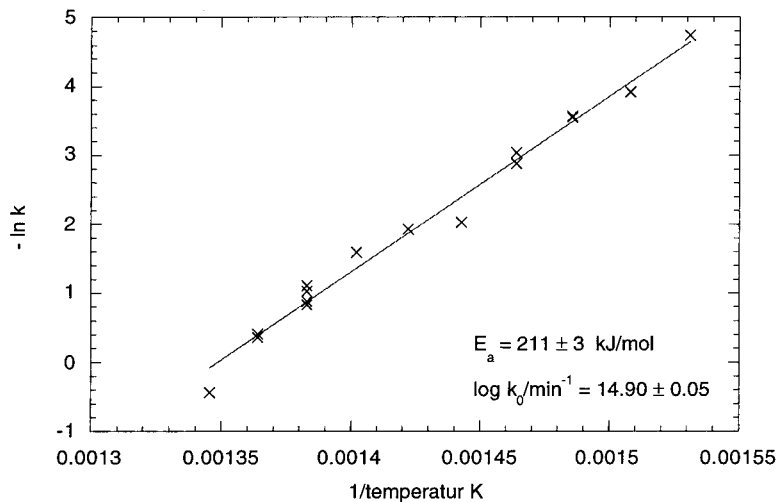
Fig. 5. Arrhenius plot of the overall rate coefficients of the decomposition of polyamide 6.

investigated temperature range, compare Fig. 7. For the formation of ε-caprolactam an apparent activation energy of 205 ± 1 kJ/mol and a preexponential factor of $\log(k_0/\mathrm{min}^{-1}) = 14.5 \pm 0.03$ are obtained, compare Fig. 8.

The increase of reaction order of the overall decomposition of polyamide 6 above 420°C is correlated with the formation of by-products. Especially, the formation of the cyclic dimer seems to be a second order reaction, which is responsible for the increase of the overall reaction order.

The observed first order reaction of ε-caprolactam formation is consistent with the mechanism of cis-elimination suggested by Lüderwald [8–11]

(Scheme 1). The cis-elimination proceeds via a six-membered intermediate.

Assuming a quasi-equilibrium for the formation of the cyclic intermediate (I)

$$\frac{d[P]}{dt} = -k_1[P] + k_{-1}[I] \quad \text{and}$$

$$\frac{d[I]}{dt} = -k_1[P] + k_{-1}[I] - k_2[I]$$

which is fast compared with the cis-elimination ($k_1 + k_{-1} \gg k_2$), then
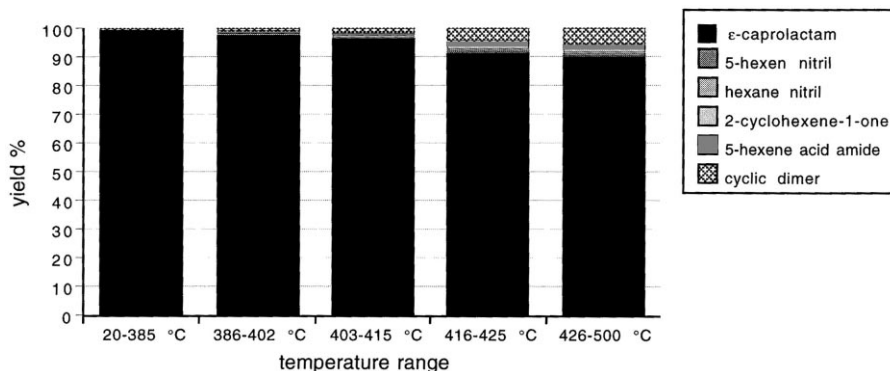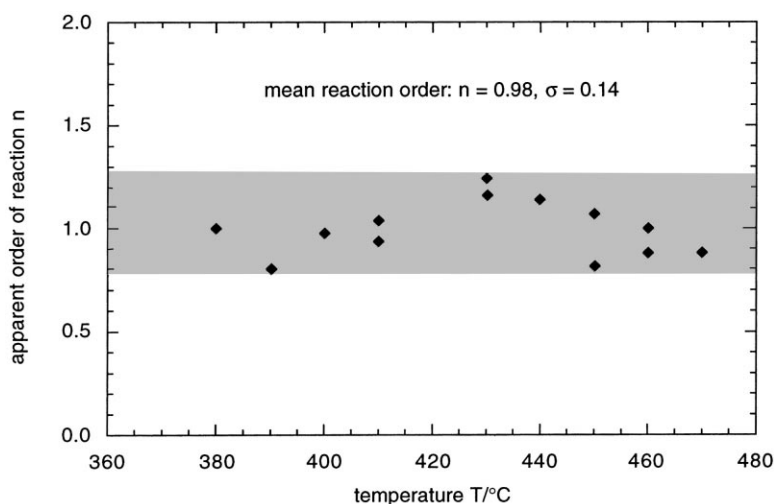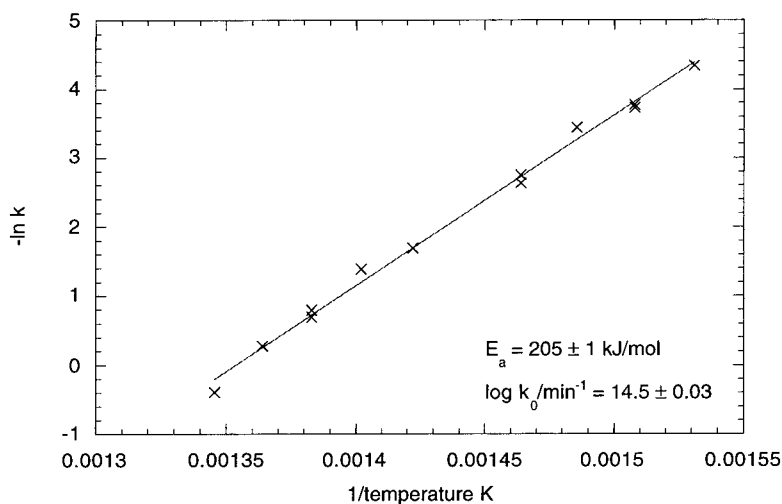
$$[I] = \frac{k_1}{k_{-1}}[P] = K_1[P]$$

Fig. 6. Yield of the determined by-products in dependence on temperature.

Fig. 7. Apparent order of reaction of the formation of ε-caprolactam.

Fig. 8. Arrhenius plot of the rate coefficients of the formation of ε-caprolactam.

follows. The rate equation for amide formation (*A*) can be expressed as

$$\frac{d[A]}{dt} = k_2[I] - k_3[A] = k_2 K_1[P] - k_3[A]$$

$$\Rightarrow \frac{d[A]}{dt} + \frac{d[C]}{dt} = k_2 K_1[P].$$

With quasi-stationarity for [*A*], because of a very low amide concentration (compare GC/MS analysis),

the formation of ε-caprolactam[c] can be described as a first order reaction

$$\frac{d[C]}{dt} = k_2 K_1[P].$$

The measured apparent energy of activation of ε-caprolactam formation is consistent with the apparent activation energy of the pyrolysis of carbonic acids which proceeds via a cyclic transition state as well
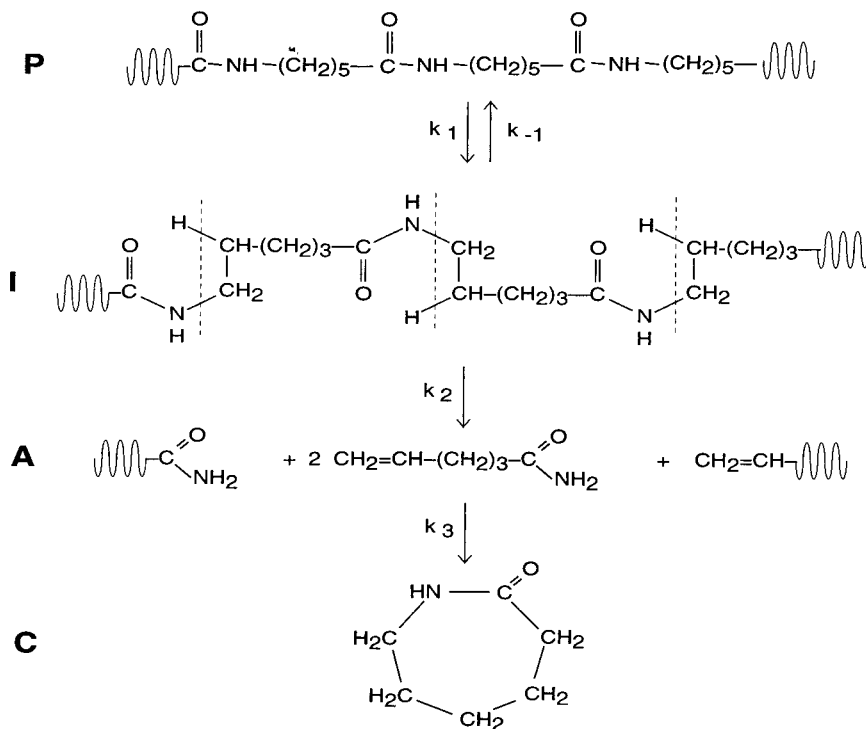
Scheme 1. Degradation of polyamide 6 via *cis*-elimination [8–11].
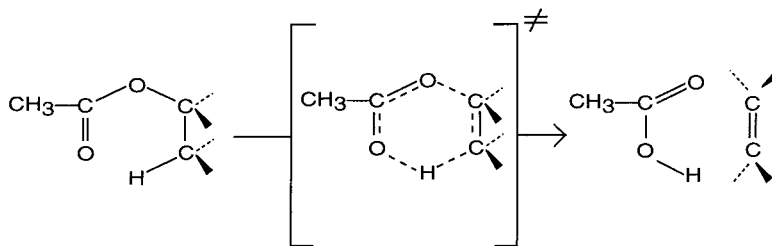
Scheme 2. Pyrolysis of carbonic acids.

(Scheme 2). In case of methyl ethyl ester an apparent energy of activation of 200 kJ/mol and a preexponential factor of 14.3 $\log(k_0/\text{min}^{-1})$ is determined [12].

The preexponential factor is in good agreement with the activation entropy of the cyclic transition state derived from the loss of degree of freedom [12].

3.2. Catalysis with phosphoric acid

From the thermogravimetric measurements it is obvious that phosphoric acid catalyses the thermal degradation of polyamide 6, compare Fig. 9. The experiments were conducted with the addition of 10 wt.% ortho-phosphoric acid (85%). Degradation temperatures are lowered by about 100°C. The yield of ε-caprolactam increases to 97.4%. Detected by-products from GC/MS are the cyclic dimer, i.e. 1,8-diazacyclotetradecane-2,9-dion (2%), 5-hexene acid amide (0.1%), 5-hexen nitrile (0.3%), hexane nitrile (0.2%). The formation of by-products occurs above 320°C. 2-cyclohexen-1-one is not detected under these conditions.
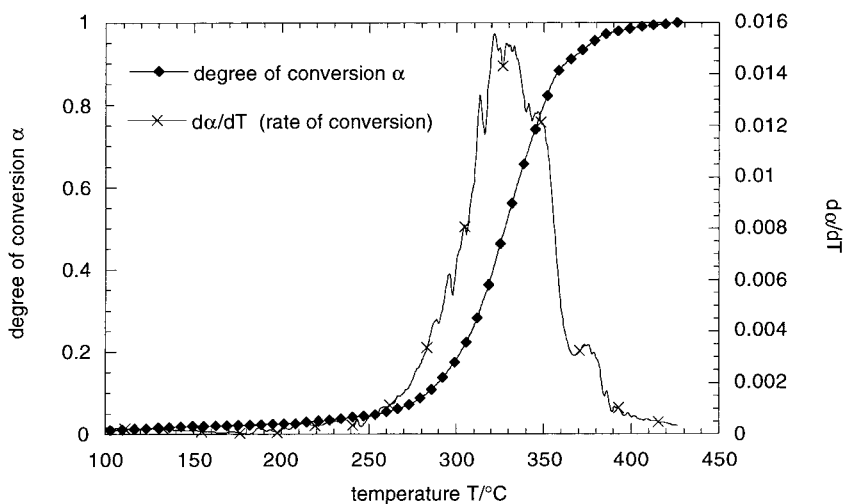
Fig. 9. Thermogravimetric curve (TG) and first negative derivative of the thermogravimetric curve (DTG) of a 20 mg sample of polyamide 6 with 10 wt.% phosphoric acid; heating rate β = 10 K/min.

From thermogravimetry/mass spectrometry (TG/MS) an apparent energy of activation E_a of 163.9 kJ/mol, a decimal logarithm of the preexponential factor $\log(k_0/\text{min}^{-1})$ of 14.02 and an apparent order of reaction of 1.9 is determined. Hence, acid catalysis reduces the apparent activation energy by about 50 kJ/mol and the reaction changes to a second order reaction. In an investigation of Baixing et al. [13] a comparable apparent energy of activation E_a of 162.6 kJ/mol and a preexponential factor $\log(k_0/\text{min}^{-1})$ of 13.7 are determined for the thermal degradation of polyamide 6 in presence of 12% H_3PO_4. Similar results are obtained during polyamide 6 degradation in presence of polyvinylchloride [14,15]. Due to the hydrogen chloride formation polyamide 6 degradation takes place in this case at lower temperatures [14,15], the activation energy is lowered by about 70 kJ/mol [15] and the apparent reaction order is also 1.9 [15].

As obvious from dynamic measurements, acid catalysis changes the degradation mechanism to a second order reaction. Katorzhnov and Strepikheev [16] confirmed that water, which is difficult to remove completely from the polymer (in case of Ultramid B3, 4–8% by weight), plays an important role in hydrolyzing amide linkages and creating new amino and acid groups. The mixture of polyamide 6 and phosphoric acid contains 1.5% water from the acid. Additional water is formed through the condensation of phosphoric acid to polyphosphoric acid and metaphosphoric acid, respectively. Therefore, it seems reasonable that a hydrolytic scission of the amide group takes place (Scheme 3).
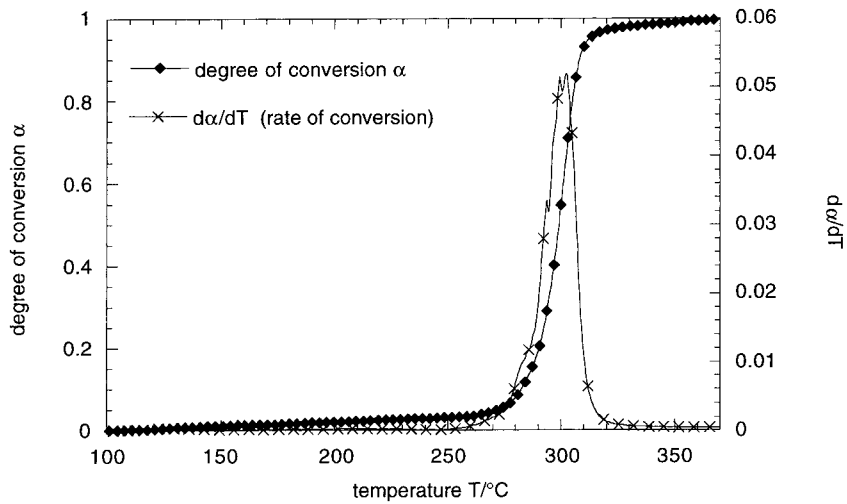
3.3. Catalysis with sodium/potassium hydroxide

To investigate the influence of basic catalysts on the thermal degradation of polyamide 6, polymer samples were mixed with an amount of 10% by weight of an eutectic mixture of sodium hydroxide and potassium hydroxide (60% by mole NaOH and 40% by mole KOH [17]). KOH and NaOH are dried before measurement.

From TG/MS measurements it is obvious that bases accelerate the thermal degradation of polyamide 6, compare Fig. 10. Degradation temperatures are even below those in acid catalysis. The yield of ε-caprolactam increases to 98.4%. All detected by-products are below 1% (1% 1,8-diazacyclotetradecane-2,9-dion, 0.1% 1,11-diaminundecane-6-one, 0.1% 5-hexene acid amide, 0.4% 5-hexen nitrile). The formation of by-products occurs above 260°C. In contrast to the degradation of polyamide 6 with acids and without additives the formation of 1,11-diaminundecane-6-one takes place. This compound is formed via the condensation of the tautomeric oxims from ε-capro-
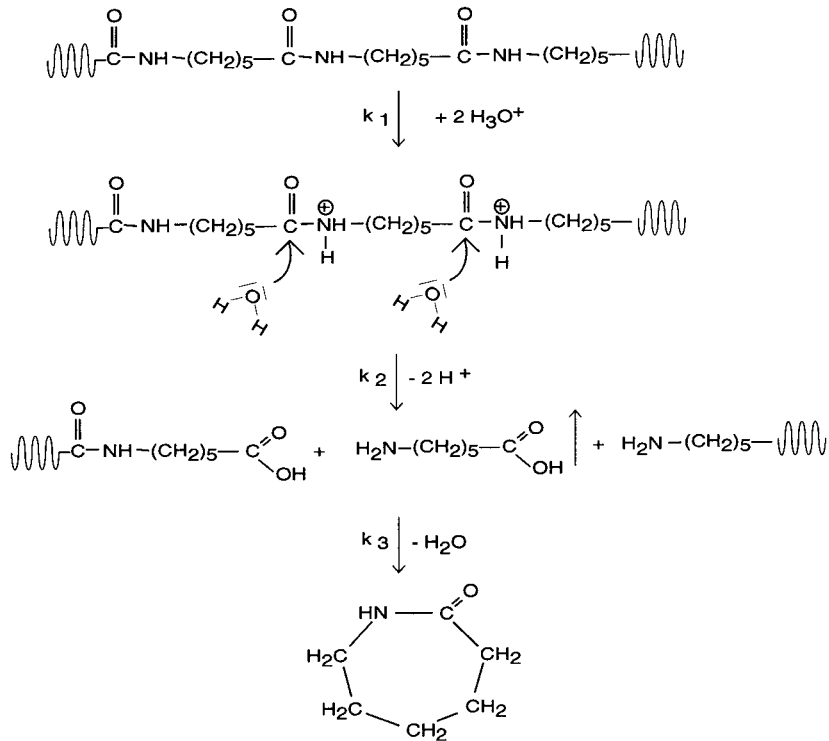
Scheme 3. Acid hydrolytic scission of the amide linkage.

Fig. 10. Thermogravimetric curve (TG) and first negative derivative of the thermogravimetric curve (DTG) of a 20 mg sample of polyamide 6 with 10 wt.% sodium/potassium hydroxide; heating rate β = 10 K/min.
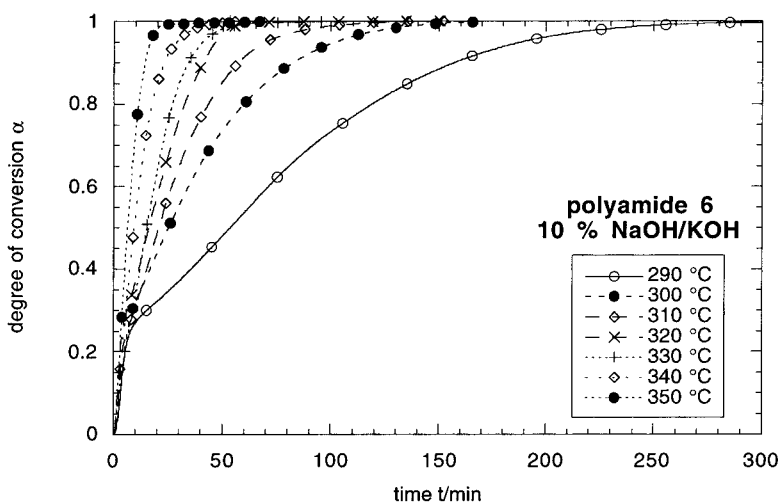
Fig. 11. Degree of conversion for the decomposition for polyamid 6 in presence of an eutectic mixture of NaOH and KOH for several temperatures.

lactam and following hydrolysis and decarboxylation to the Schiff's bases of 1,11-diaminundecane-6-one [18].

In Fig. 11 the experimental degrees of conversion from isothermal measurements for different temperatures are shown. With these data an apparent energy of activation for the overall process of 113 ± 4 kJ/mol and a preexponential factor of $\log(k_0/\text{min}^{-1}) =$ 8.67 $\pm$ 0.06 are determined, compare the Arrhenius plot in Fig. 12. The apparent order of reaction is constant within the investigated temperature range, the mean value is about 1.06 with a standard deviation of $\sigma = \pm 0.07$, compare Fig. 13.

The observed first order reaction is consistent with a unimolecular polymerization–depolymerization model of Wichterle and Sebenda [19], who studied
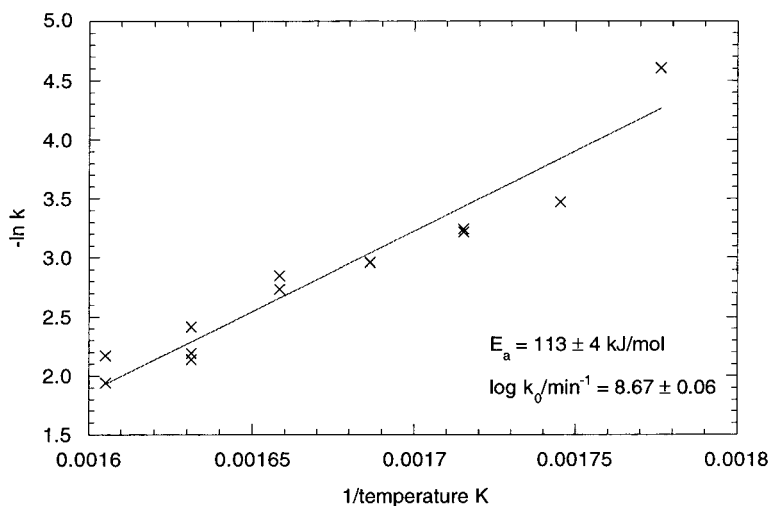

Fig. 12. Arrhenius plot of the over-all rate coefficients of the decomposition of polyamide 6 in presence of an eutectic mixture of NaOH and KOH.
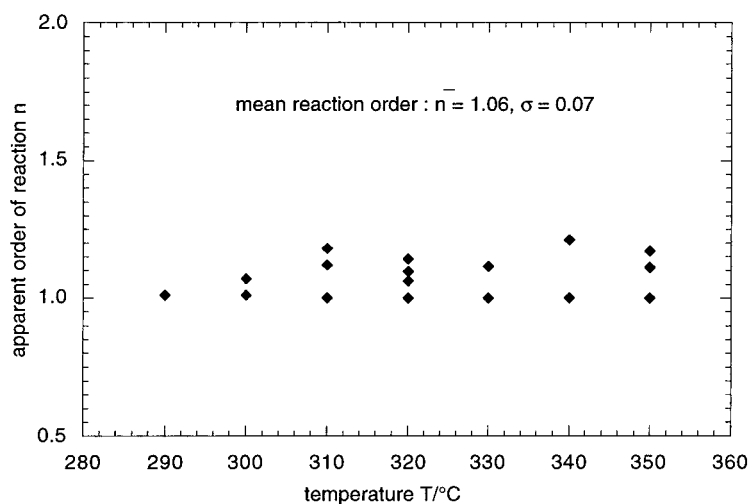
Fig. 13. Apparent order of reaction of the decomposition of polyamide 6 in presence of an eutectic mixture of NaOH and KOH.

the polymerization and depolymerization of polyamide 6 in presence of sodium hydroxide and sodium carbonate. They proposed an anionic polymerization–depolymerization model, in which base catalysed deprotonation of amide groups is followed by intramolecular cyclization that generates lactam units. Wichterle and Sebenda [19] also proved the route of the polymerization/depolymerization in presence of sodium hydroxide via the amine anion. However, the observed time dependence of reaction rates and the neutralization equilibrium of the amide anion and amine anion, which is definitely on site of the amide, favours the amide model. According to the proposed mechanism, the base catalysed degradation of polyamide 6 proceeds via an anionic chain mechanism, which explains the high reaction rates in contrast to the non-catalysed and acid catalysed reaction as well as the apparent energy of reaction, which is about 100 kJ/mol lower, in comparison to the non-catalysed reaction.

4. Conclusion

The thermal degradation of polyamide 6 has been investigated under non-catalysed and catalysed conditions with dynamic and isothermal methods. By means of TG/MS, an apparent energy of activation E_a of 211.3 kJ/mol, a decimal logarithm of the pre-

exponential factor $\log(k_0/\text{min}^{-1})$ of 15.03 and an apparent order of reaction of 0.81 is determined for the non-catalysed reaction. This values excellently agree with those from the isothermal method. From that an apparent energy of activation of 211 ± 3 kJ/mol and a preexponential factor of $\log(k_0/\text{min}^{-1}) = 14.9 \pm 0.05$ is determined for the overall process of polyamide 6 degradation. In case of isothermal decomposition of polyamide 6 a shift of the apparent reaction order from first order to 1.29 above $420°C$ due to the formation of by-products above $415°C$ is observed. For the formation of ε-caprolactam an apparent activation energy of 205 ± 1 kJ/mol, a preexponential factor of $\log(k_0/\text{min}^{-1}) = 14.5 \pm 0.03$ and a mean reaction order of 0.98 are obtained with the isothermal method which corresponds with a unimolecular mechanism (Scheme 1).

Acid catalysis with H_3PO_4 reduces the apparent activation energy by about 50 kJ/mol and the reaction changes to a second order reaction ($E_a = 163.9$ kJ/mol, $\log(k_0/\text{min}^{-1}) = 14.02$ and an apparent order of reaction $n = 1.9$, derived from TG/MS). The reaction proceeds via an acid catalysed hydrolytic scission of the amide group (Scheme 3).

Bases, like the eutectic mixture of NaOH/KOH, reduce the apparent activation energy by about 100 kJ/mol in comparison to the non-catalysed reaction ($E_a = 113 \pm 4$ kJ/mol, $\log(k_0/\text{min}^{-1}) = 8.67 \pm 0.06$, mean value of the apparent order of reaction
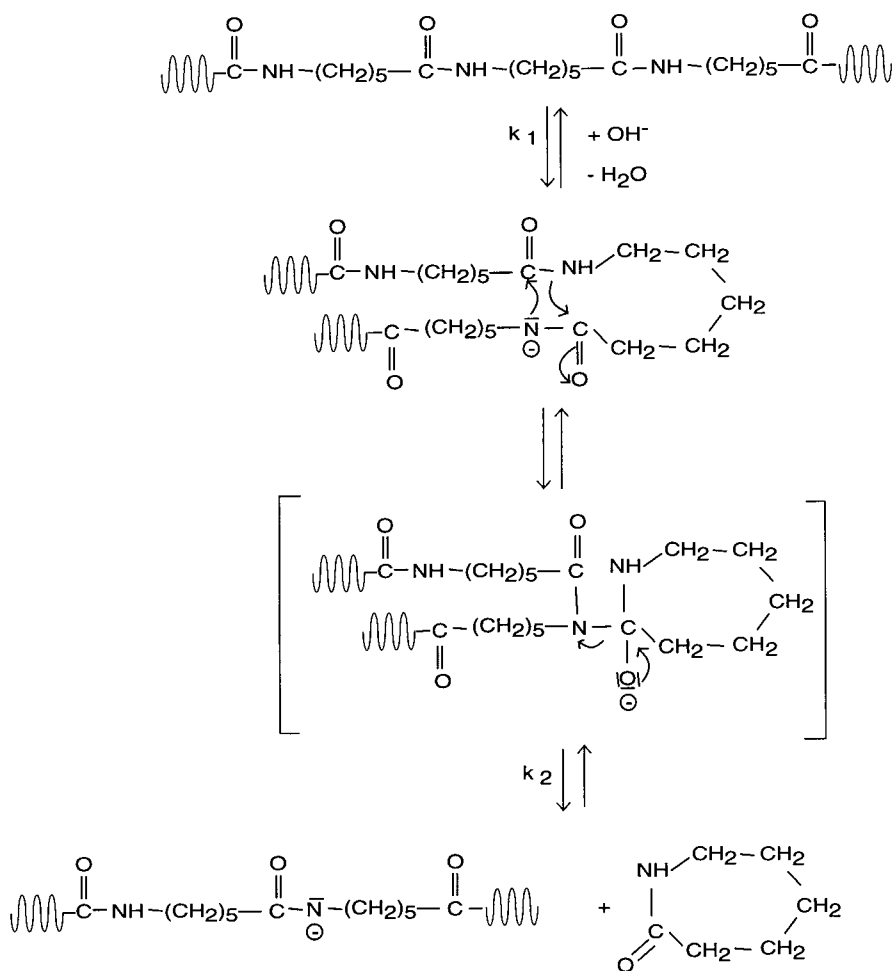
Scheme 4. Anionic chain reaction of polyamide 6 degradation in presence of bases.

$n = 1.06$, derived from the isothermal method). The base catalysed degradation of polyamide 6 proceeds via an anionic chain mechanism, which explains the high reaction rates in contrast to the non-catalysed and acid catalysed reaction (Scheme 4).

For these reasons, the base catalysed degradation of polyamide 6 seems to be the best possibility for an application in a procedure for ε-caprolactam recovery from polyamide 6 waste.

Acknowledgements

References

[1] K.R. Wolff, Chemiefasern/Textilindustrie 30/82 (1980) 500–506, E68–E69.
[2] A.G. Zimmer, Caprolactam Recovery Process.
[3] S. Czernik, C.C. Elam, R.J. Evans, R.R. Meglen, L. Moens, K. Tatsumoto, J. Anal. Appl. Pyrolysis 46 (1998) 51.
[4] A.K. Mukherjee, D.K. Goel, J. Anal. Appl. Pyrolysis 22 (1978).
[5] H. Bockhorn, A. Hornung, U. Hornung, S. Teepe, J. Weichmann, Combust. Sci. Technol. 116/117 (1996) 129.
[6] H. Bockhorn, A. Hornung, U. Hornung, J. Anal. Appl. Pyrolysis 50 (1999) 77–101.
[7] U. Hornung, A. Hornung, H. Bockhorn, Chem. Eng. Technol. 21 (1998) 332–337.
[8] I. Lüderwald, F. Merz, M. Rothe, Angew. Makromol. Chem. 67 (1978) 193.

[9] I. Lüderwald, H.R. Kricheldorf, Angew. Makromol. Chem. 56 (1976) 173.

[10] U. Bahr, I. Lüerwald, R. Müller, H.-R. Schulten, Angew. Makromol. Chem. 120 (1984) 163.

[11] I. Lüderwald, H.-R. Schulten, Teubner-Texte, Phys. Prog. Polym. Spectrosc. 9 (1984) 22.

[12] S.W. Benson, Thermochemical Kinetics, Wiley, New York, 1976.

[13] H. Baixing, Y. Zheng, Y. Shenying, H. Mei, X. Ruili, J. Sichuan Univ. Natural Sci. Edn. 29 (1992) 302.

[14] R. Knümann, H. Bockhorn, Combust. Sci. and Tech. 101 (1994) 285.

[15] R. Knümann, Dissertation, Darmstadt, 1992.

[16] N.D. Katorzhnov, A.A. Strepikheev, Zh. Prikl. Khim. 32 (1958) 655.

[17] W.O. Harry, R.P. Seward, J. Chem. Eng. Data 9 (1964) 504.

[18] G. Nawrath, Angewandte Chemie 72 (1960) 1002.

[19] O. Wichterle, J. Sebenda, Collect. Czech. Chem. Commun. 22 (1957) 1353.