

# Stability, Ageing and Usetime Prediction of PolyvinylNitrate (PVN)

Manfred A. Bohn, Jasmin Aniol, Manuela Dörich, Kerstin Hartlieb, Heike Pontius

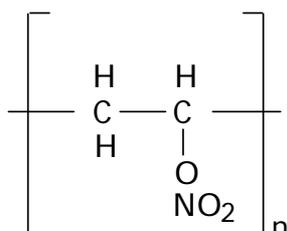
Fraunhofer-Institut für Chemische Technologie (ICT)  
Postfach 1240, D-76318 Pfinztal-Berghausen, Germany

## Abstract

PolyvinylNitrate (PVN) is an energetic speciality polymer of pale yellow-brown colour. As additive to TNT charges it improves the crystallinity structure of the TNT cast. PVN is obtained by nitration of polyvinyl alcohol. The limited stability of the nitric acid ester group is known. A stability and ageing investigation was done to quantify these important properties for unstabilized PVN. The stability methods used have been autoignition temperature at 5°C/min heat rate, mass loss at 75°C after 2 days, vacuum stability at 90°C over 40 h, adiabatic self heating and as ageing methods mass loss, heat generation rate, chain splitting as function of time and temperature in the range 65°C to 110°C. The data of the ageing methods have been described by kinetic models resulting in three sets of Arrhenius parameters for the PVN decomposition. The ones of mass loss and heat generation agree well. From the decrease of mean molar mass  $M_n$  an activation energy of 146 kJ/mol is obtained. Such values are found also for nitrocellulose (NC) in single base and double base propellants in that temperature range. Predictions of usetimes (lifetimes) obtained with all three ageing methods are given.

## 1. Introduction

PVN dissolved in mononitrotoluene (MNT) is used as additive in TNT high explosive charges to improve the crystallinity structure of the TNT cast. A certain stability of PVN must be achieved to maintain the wished effect during production of the TNT charges. The quality demands of PVN and of the solution of PVN in MNT are fixed in Technical Delivery Conditions (Technische Lieferbedingungen) of BWB, Koblenz, Germany /1,2/. Here the results on stability and ageing behaviour of one production lot of ICT are presented. PVN was obtained by classical nitration of polyvinyl alcohol with a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . The process is described in /3, 4/. The stabilization procedure in heated water was adapted to the needs of this product. The nitrogen content at degree of substitution 1 is 15.729 mass-% with the molar mass of a chain unit of 89.051 g/mol and an oxygen balance of -44.92%. The thermodynamically calculated heat of explosion  $Q_{\text{EX}}$  of PVN with theoretical N-content is 4782 J/g with reaction water condensed and 4490 J/g without condensed water. The enthalpy of formation is -102.59 kJ/mol. The ideal structure is given in the following figure.



For the real product the N-content must be  $\geq 14.7$  mass-%, the acetone insoluble part  $\leq 2.5$  mass-% and the acid content calculated as  $\text{H}_2\text{SO}_4 \leq 0.005$  mass-%. The here used product has had: 14.9 mass-% N-content, 2 mass-% acetone insoluble part and less than 0.004 mass-%  $\text{H}_2\text{SO}_4$ . The degree of substitution was 0.90, the molar mass of chain unit  $m = 84.5$  g/mol.

## 2. Methods

### 2.1 Methods used for stability testing

The stability was determined by three standardized methods: autoignition temperature with 0.2 g amount in an open glass vial inserted in a Wood's metal bath heated up with 5°C/min. The temperature at which the violent reaction occurs is taken as autoignition temperature connected with the mentioned conditions. A second test is the mass loss (ML) at 75°C, determined in open and stoppered glass vials, with amounts of 1 to 2 g. According to /1/ the criteria are  $\leq 0.5\%$  ML after two days with open vials and  $\leq 0.3\%$  ML after two days with stoppered vials. Further applied was the Vacuum Stability Test in the standard apparatus with mercury column at 90°C over 40 h with 1.5g sample amount and adiabatic self heating with 0.6 g sample amount.

### 2.2 Methods used for ageing investigation

To get some insight in the ageing of PVN the following methods have been applied:

- mass loss as function of time and temperature between 65°C and 90°C, 1g each sample
- heat generation rate (HGR,  $dQ/dt$ ) and heat generation (HG, Q) as function of time and temperature between 65°C and 90°C, 0.2 to 0.6g sample amount, air in ampoules
- gel permeation chromatography (GPC) or size exclusion chromatography (SEC) as function of time and temperature between 70°C and 80°C.

## 3. Results

### 3.1 Stability tests

The autoignition temperature with 0.2g and heat rate of 5°C/min was between 188 and 190°C. The mass loss after 2 days at 75°C was clearly below 0.3% in closed vials, see Fig. 1, and below 0.5% in open vials. The vacuum stability test gives a gas generation of 2.7 ml/g at 90°C over 40 h. Adiabatic self heating determined with an ARC™ gives a transition to deflagration at 164°C.

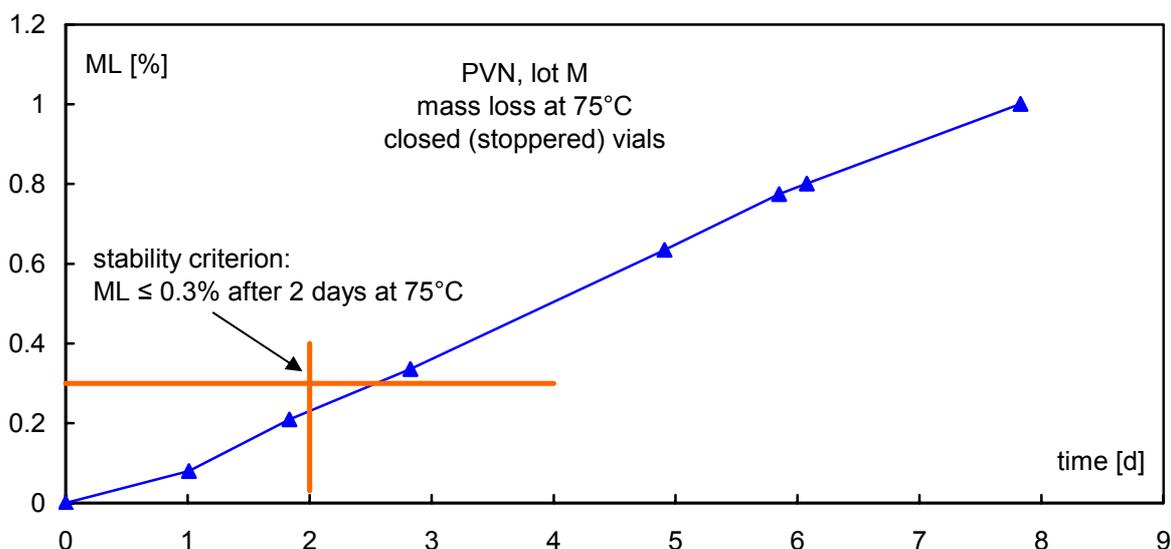


Fig. 1: Mass loss at 75°C determined in closed vials, used for stability assessment.

## 3.2 Ageing

### 3.2.1 Mass loss as function of time and temperature

In Fig. 2 the measured mass loss of PVN between 65°C and 90°C can be seen. The curves increase linearly indicating a decomposition reaction of zero order or a linearly approximated reaction of first order. Normally there is a difference between measured mass loss ML and the substance of interest A related mass loss  $ML_A$ . This is in short discussed in Eq.(1) to Eq.(5), see /5/ for details. The difference has mostly three reasons: (i) impurities, which does not react, or (ii) react in another way than the considered substance, (iii) decomposition of considered substance forms a residue. Eq.(1) shows the kinetic expression for the mass change of substance A according to a reaction of zero order. The measured mass change is given by Eq.(2). The symbols  $m_i$  are the molar masses.  $M(0)$  is given by Eq.(3), assuming the reaction  $A \rightarrow C+S$  with the split-off of gases C and forming of residual substance S with molar mass  $m_s$ . The substance S may be present already at start of investigation. The quantity  $M_N$  represents the amount of an impurity N not involved in the decomposition reaction of A. The mass loss is determined according to Eq.(4), which converts to Eq.(5) with the given definitions of  $M_r$  and  $M_{Ar}$ . OF is an offset not caused by the decomposition of A. The relation between apparent reaction rate constant  $k_{ML}$  and the substance related reaction rate constant  $k_{ML,A}$  is shown in Eq.(6), here both used for mass loss in part per 1. The scaling changes the pre-exponential factor:  $Z_{ML} = F \cdot Z_{ML,A}$ , but the activation energy is determined without difference,  $Ea_{ML} = Ea_{ML,A}$ . Fig. 3 shows the Arrhenius plot for  $k_{ML}$ . The activation energy in the temperature range 65°C to 90°C is determined to 110 kJ/mol. In /6/ 121.2 kJ/mol are reported for lower temperatures and above 120°C 154.8 kJ/mol were found, both with gas generation. The times  $ty_{ML}$  to reach the mass loss  $ML = 100\% \cdot (1 - y_M)$  with  $y_M = M(ty_{ML})/M(0)$  can be calculated with Eq.(7) and are given in Table 1.

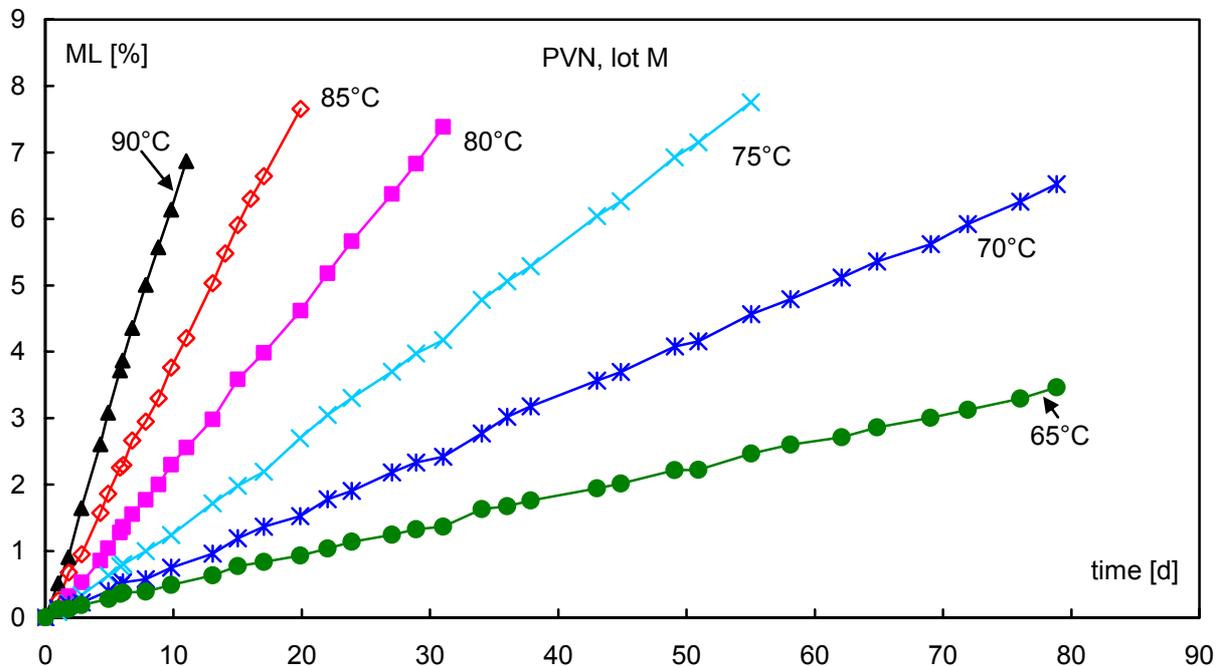


Fig. 2: Mass loss as function of time and temperature of PVN, lot M.

$$(1) \quad M_{Ar}(t, T) = \frac{M_A(t, T)}{M_A(0)} = 1 - \frac{k_A(T)}{A(0)} \cdot t = 1 - k_{ML,A}(T) \cdot t$$

$$(2) \quad M_r(t, T) = \frac{M(t, T)}{M(0)} = 1 - \frac{m_A - m_s}{m_A} \cdot \frac{M_A(0)}{M(0)} \cdot (1 - M_{Ar}(t, T)) \quad m_C = m_A - m_B$$

$$(3) \quad M(0) = M_A(0) + M_s(0) + M_N = M_A(t, T) + M_C(t, T) + M_s(t, T) + M_N$$

$$(4) \quad ML(t, T) = OF + 100\% \cdot \frac{M(0) - M(t, T)}{M(0)} = OF + 100\% \cdot (1 - M_r(t, T))$$

$$(5) \quad ML(t, T) = OF + 100\% \cdot \left( \frac{m_A - m_s}{m_A} \cdot \frac{M_A(0)}{M(0)} \cdot k_{ML,A}(T) \cdot t \right)$$

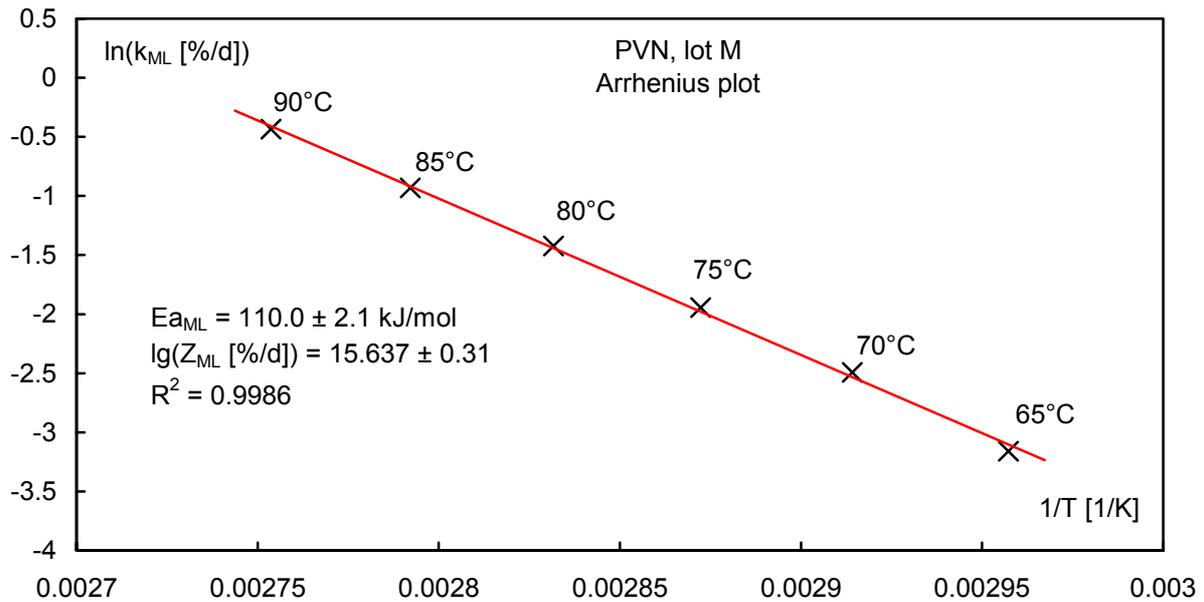


Fig. 3: Arrhenius plot of the mass loss reaction rate constants  $k_{ML}$ .

Table 1: Times  $ty_{ML}$  to reach the degree of mass decrease  $y_M = M(ty_{ML})/M(0)$  or the degree of mass loss  $y_{ML} = (1 - y_M)$  which corresponds to  $ML = 100\% \cdot (1 - y_M)$ .

temp. [°C]	times $ty_{ML}$ to reach $y_{ML} = 1 - M(ty_{ML})/M(0)$		
	$ty_{ML}$ (2% ML)	$ty_{ML}$ (3% ML)	$ty_{ML}$ (5% ML)
30	11.4 a	17.0 a	28.4 a
35	5.6 a	8.4 a	14.0 a
40	2.8 a	4.2 a	7.0 a
45	1.45 a	2.18 a	3.63 a
50	278 d	417 d	696 d
55	149 d	224 d	373 d
60	81.4 d	122 d	204 d
65	45.3 d	67.9 d	113 d
70	25.6 d	38.4 d	64.0 d
75	14.7 d	22.1 d	36.8 d
80	8.6 d	12.9 d	21.5 d
85	5.09 d	7.64 d	12.73 d
90	3.06 d	4.59 d	7.65 d

$$(6) \quad \left\{ \begin{array}{l} k_{ML}(T) = \frac{m_A - m_S}{m_A} \cdot \frac{M_A(0)}{M(0)} \cdot k_{ML,A}(T) \\ Z_{ML} \cdot \exp(-E_{a_{ML}}/RT) = \frac{m_A - m_S}{m_A} \cdot \frac{M_A(0)}{M(0)} \cdot Z_{ML,A} \cdot \exp(-E_{a_{ML,A}}/RT) \end{array} \right.$$

$$(7) \quad ty_{ML}(T) = (1 - y_M) / k_{ML}(T) \quad \text{or} \quad = 100\% \cdot (1 - y_M) / k_{ML}(T) \quad \text{with } k_{ML} \text{ in } \%/ \text{time}$$

### 3.2.2 Heat generation rate and heat generation as function of time and temperature

The heat generation rate (HGR) of PVN lot M was measured with microcalorimeters of type TAM<sup>TM</sup>, Thermometric AB, Sweden. Stainless steel ampoules with glass inserts were used. The measured data can be seen in Fig. 4 and Fig. 5. The evaluation was done as function of conversion respectively of heat generation  $Q$ . Conversion is achieved by dividing  $Q$  by a suitable reference quantity  $Q_{ref}/5$ . The  $Q$ -curves resemble the mass loss curves. The experimentally determined times  $ty_Q$  to reach a given  $Q$ , see Fig. 6, are the evaluation base. For each set of data at given  $Q$  the Arrhenius parameters are determined according to the procedure described with Eq.(8) to Eq.(14). Eq.(8) shows the Arrhenius expression in the form used here and the transformed Eq.(8) gives the time  $ty_Q$  as function of temperature and  $Q$ . The pre-exponential factor  $Z_{ty_Q}$  and activation energy  $E_{a_{ty_Q}}$  are calculated by Eq.(10) and Eq.(11).

$$(8) \quad \ln(k_Q(T_i; Q)) = \ln(Z_Q(Q)) - \frac{E_{a_Q}(Q)}{R} \cdot \frac{1}{T_i}$$

$$(9) \quad \ln(ty_Q(T_i; Q)) = -\ln\left(\frac{Z_Q(Q)}{C}\right) + \frac{E_{a_Q}(Q)}{R} \cdot \frac{1}{T_i} = -\ln(Z_{ty_Q}(Q)) + \frac{E_{a_{ty_Q}}(Q)}{R} \cdot \frac{1}{T_i}$$

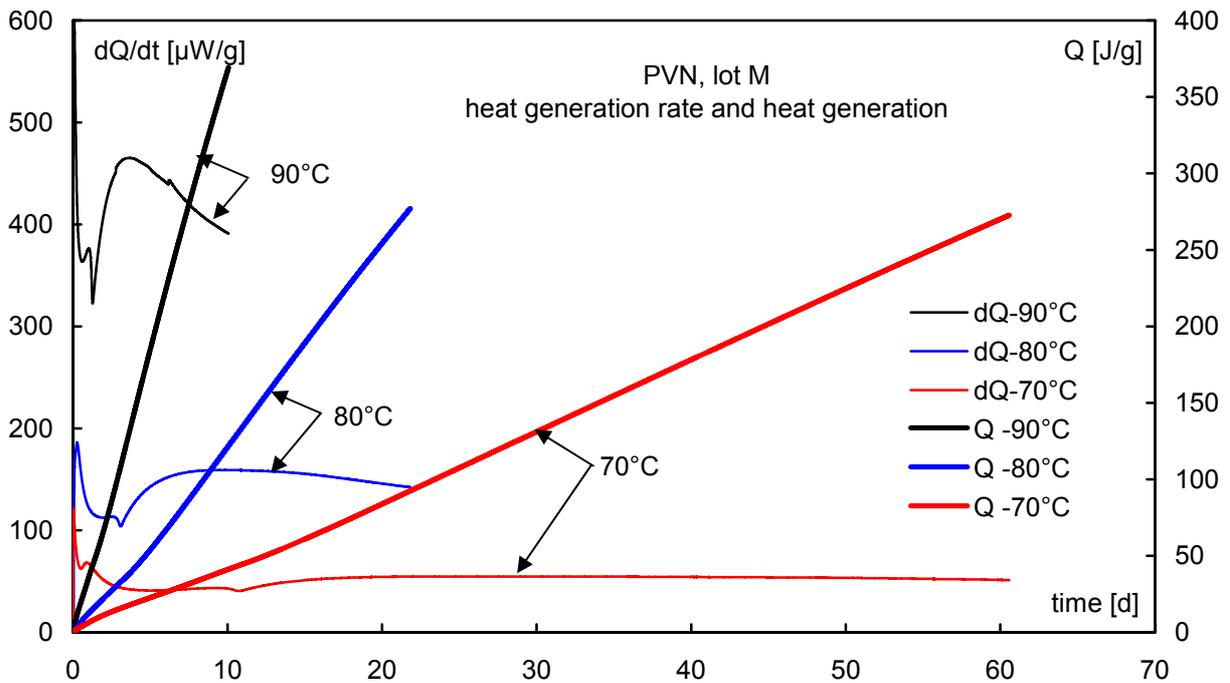


Fig. 4: Heat generation rate ( $dQ/dt$ ) and heat generation ( $Q$ ) of PVN, lot M at 70°C, 80°C and 90°C. The  $Q$ -curves are directed to the right upwards.

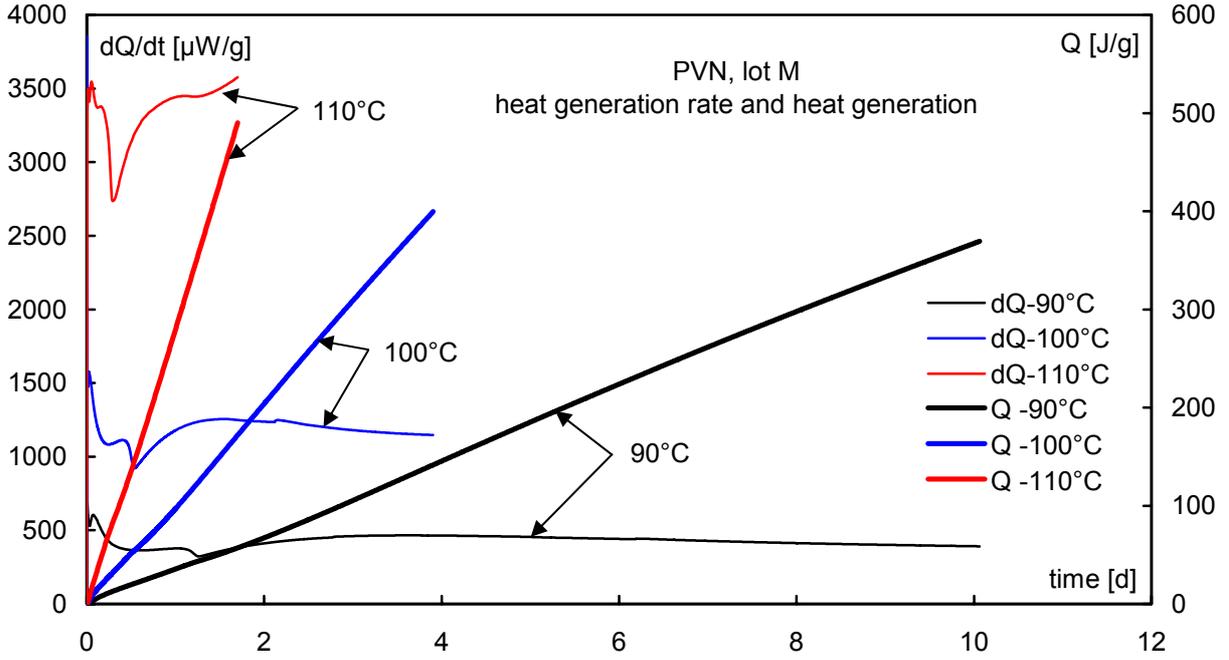


Fig. 5: Heat generation rate (dQ/dt) and heat generation (Q) of PVN, lot M at 90°C, 100°C and 110°C. The Q-curves are directed to the right upwards.

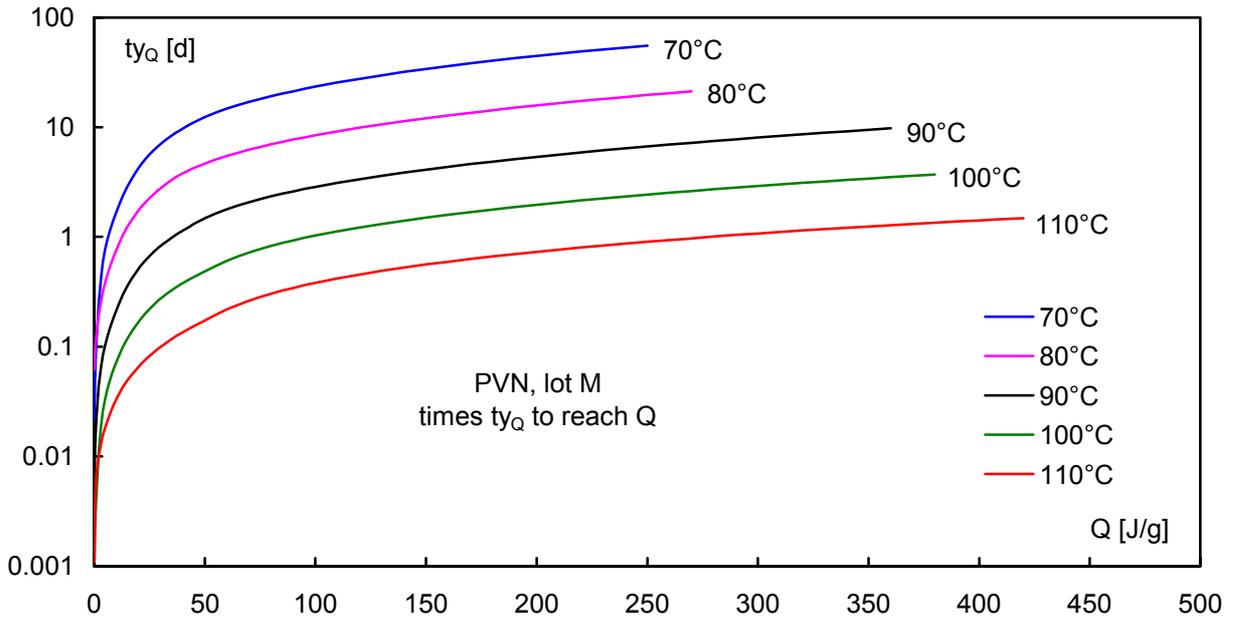


Fig. 6: Times  $ty_Q$  to reach a given Q determined from the experimental data.

In the following equations the dependence of  $ty_Q$ ,  $Ea_{ty_Q}$  and  $Z_{ty_Q}$  on Q is omitted.

$$(10) \quad \ln(Z_{ty_Q}) = - \frac{\sum_i^n \ln(ty_Q(T_i)) - \frac{Ea_{ty_Q}}{R} \cdot \sum_i^n \frac{1}{T_i}}{n}$$

$$(11) \quad E_{a_{ty_Q}} = R \cdot \frac{n \cdot \left( \sum_i^n \ln(ty_Q(T_i)) \cdot \frac{1}{T_i} \right) - \left( \sum_i^n \frac{1}{T_i} \right) \cdot \left( \sum_i^n \ln(ty_Q(T_i)) \right)}{n \cdot \sum_i^n \left( \frac{1}{T_i} \right)^2 - \left( \sum_i^n \frac{1}{T_i} \right)^2}$$

The general correlation coefficient  $R^2$  is taken to assess the evaluation quality. To calculate  $R^2$  the quantities mean of  $\ln(ty_Q(T_i))$ , Eq.(13), and sum of squared deviations FQS, Eq.(14) are needed.

$$(12) \quad R^2 = 1 - \frac{FQS}{\sum_i^n \{ \ln(ty_Q(T_i)) - M(\ln(ty_Q(T_i))) \}^2}$$

$$(13) \quad M(\ln(ty_Q(T_i))) = \frac{\sum_i^n \ln(ty_Q(T_i))}{n}$$

$$(14) \quad FQS = \sum_i^n (\ln(ty_Q(T_i)))^2 - \{ -\ln(Z_{ty_Q}) \} \cdot \sum_i^n \ln(ty_Q(T_i)) - \frac{E_{a_{ty_Q}}}{R} \cdot \sum_i^n \frac{1}{T_i} \cdot \ln(ty_Q(T_i))$$

In Fig. 7 the Arrhenius plot at one selected Q value is given. The activation energy determined over the whole measured temperature range is 112.5 kJ/mol with a small standard deviation of 1.4 kJ/mol. For the temperature range 70°C to 90°C and 90°C to 110°C the data are given also. Slight temperature dependence could be stated. The variations are somewhat outside the standard deviations.

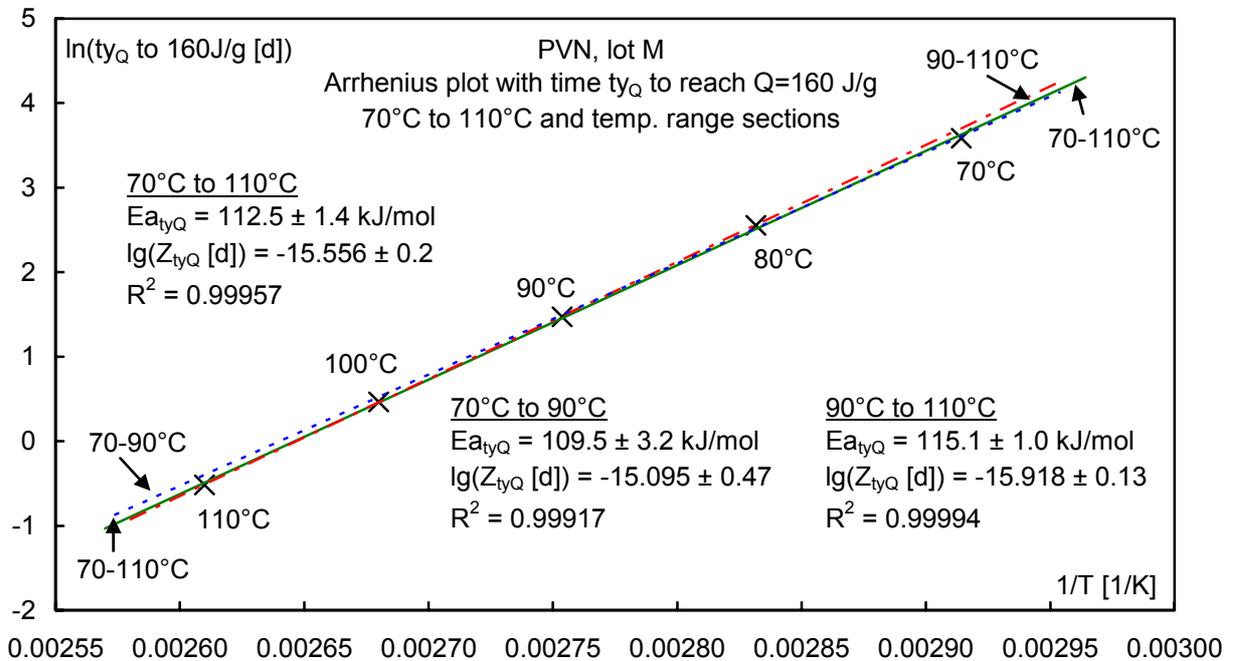
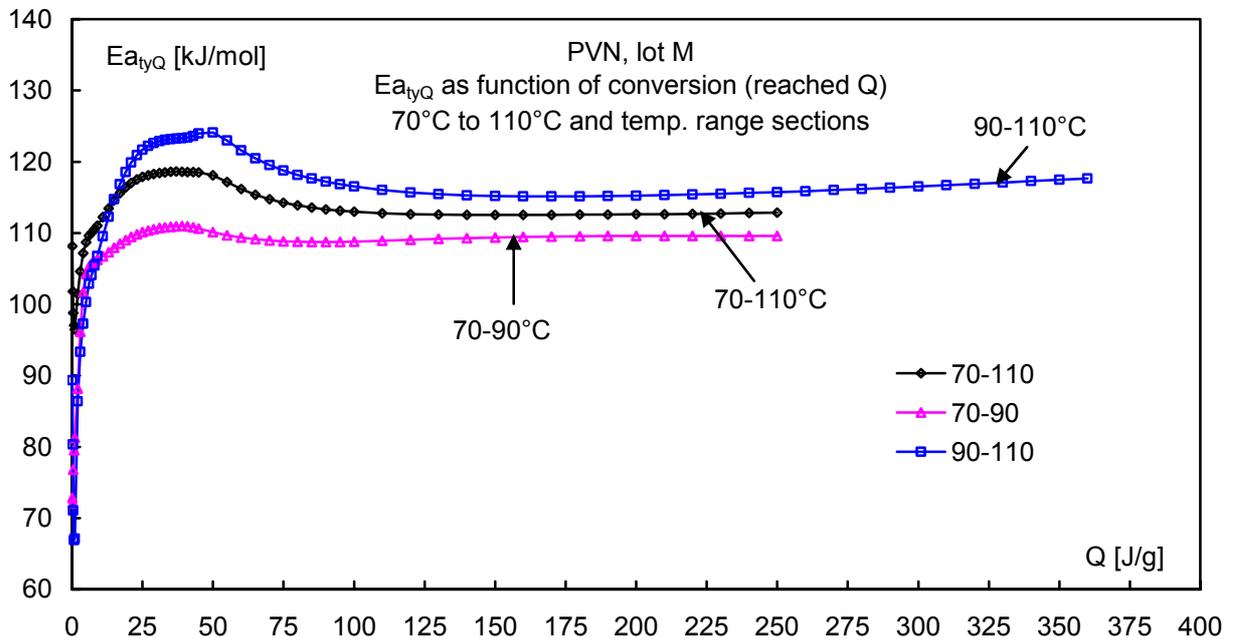


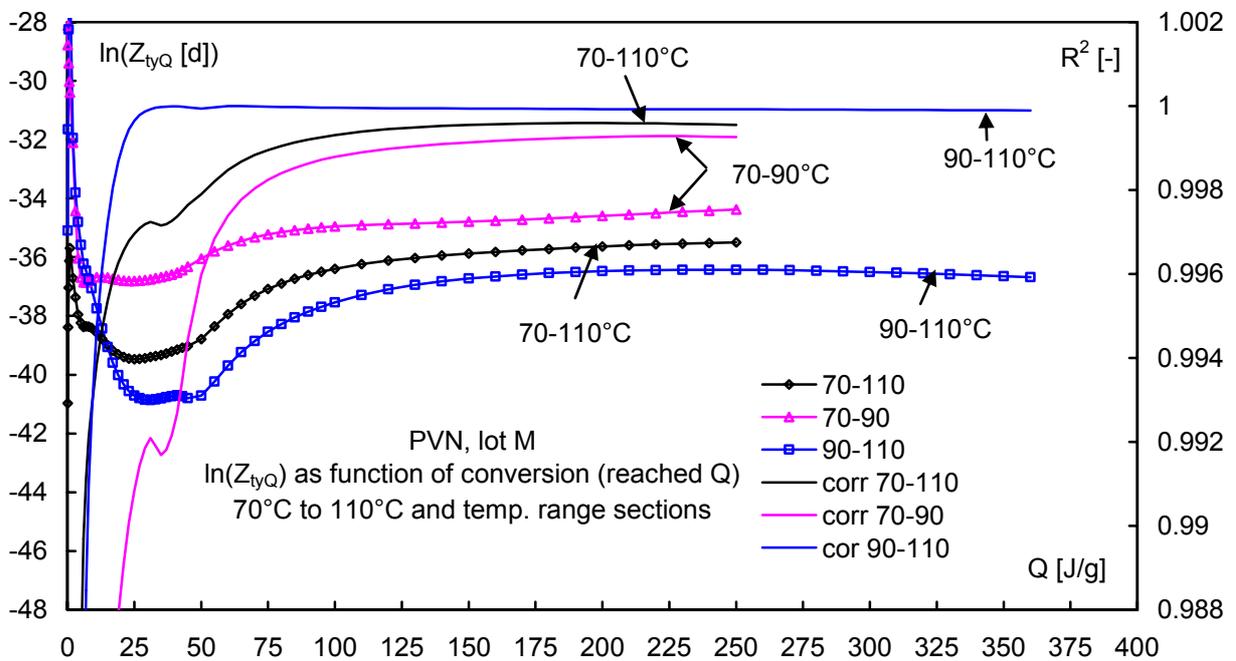
Fig. 7: Arrhenius plot of  $ty_Q(T)$  to  $Q = 160$  J/g. A slight variation of Arrhenius parameters with selected temperature range can be found.

The complete evaluation of the Arrhenius parameters as function of Q can be seen in Fig. 8 for the activation energy and in Fig. 9 for the pre-exponential factor. In Fig. 9 the general correlation coefficient  $R^2$  is shown also. The weak temperature dependence is recog-

nizable. The correlation coefficient reaches good values after 25 to 50 J/g of heat generation. Fig. 10 shows the extrapolated times  $t_{yQ}$  using the Arrhenius parameters and in Table 2 these data are listed.



**Fig. 8:** Activation energy of heat generation and of  $t_{yQ}$  to reach  $Q$  of PVN, lot M as function of  $Q$ . A small variation of  $E_{a_{t_{yQ}}}$  can be found with selected temperature ranges.



**Fig. 9:** Pre-exponential factor of  $t_{yQ}$  to reach  $Q$  as function of  $Q$ . As with  $E_{a_{t_{yQ}}}$  a small variation with selected temperature ranges is found. Further the corresponding correlation coefficient  $R^2$  can be seen. Only from 25 to 50 J/g on the value of  $R^2$  is high enough to regard the values of  $Z_{t_{yQ}}$  and  $E_{a_{t_{yQ}}}$  as reliable.

**Table 2:** Times  $t_{yQ}$  to reach  $Q$  (= given off energy), calculated with  $E_{a_{tyQ}}$  and  $Z_{tyQ}$  obtained between 70°C and 90°C. General correlation coefficient  $R^2$  given for the calculation of both Arrhenius parameters as function of  $Q$ .  $Q_{ref} = 4000$  J/g Times are all in days.

Q [J/g]	100%Q/ $Q_{ref}$	$\ln(Z_{tyQ} [d])$	$E_{a_{tyQ}}$ [kJ/mol]	$R^2$	90°C	80°C	70°C	60°C	50°C	40°C	30°C
1	0.025	-30.401	81.3	0.66580	0.031	0.066	0.15	0.35	0.86	2.27	6.36
2	0.050	-32.105	88.2	0.83937	0.055	0.125	0.30	0.76	2.03	5.78	17.6
3	0.075	-34.428	96.1	0.91879	0.075	0.185	0.48	1.32	3.87	12	41
4	0.100	-36.044	101.7	0.95168	0.095	0.246	0.67	1.97	6.12	21	74
5	0.13	-36.693	104.3	0.96450	0.115	0.306	0.86	2.58	8.26	29	107
15	0.38	-36.692	107.9	0.98436	0.386	1.061	3.10	9.63	32.16	116	455
25	0.63	-36.810	110.1	0.99084	0.713	2.003	5.98	19.03	65.14	241	973
35	0.88	-36.677	110.9	0.99169	1.043	2.949	8.86	28.45	98.18	367	1494
50	1.25	-36.046	110.1	0.99598	1.539	4.323	12.90	41.09	140.7	521	2102
80	2.00	-35.145	108.8	0.99840	2.405	6.669	19.63	61.63	207.8	757	3002
100	2.50	-34.953	108.8	0.99879	2.927	8.119	23.90	75.06	253.1	922	3658
120	3.00	-34.879	109.0	0.99949	3.434	9.547	28.17	88.72	300.0	1096	4364
130	3.25	-34.850	109.2	0.99952	3.685	10.26	30.31	95.59	323.6	1185	4723
150	3.75	-34.791	109.4	0.99913	4.189	11.68	34.60	109.3	371.1	1362	5443
160	4.00	-34.757	109.4	0.99917	4.443	12.40	36.74	116.2	394.7	1449	5800
170	4.25	-34.721	109.5	0.99920	4.697	13.12	38.89	123.1	418.3	1537	6156
180	4.50	-34.683	109.6	0.99923	4.953	13.84	41.05	130.0	442.0	1625	6511
190	4.75	-34.643	109.6	0.99925	5.211	14.56	43.21	136.9	465.6	1713	6864
200	5.00	-34.598	109.6	0.99927	5.472	15.29	45.38	143.8	489.1	1799	7213
210	5.25	-34.551	109.6	0.99928	5.734	16.03	47.56	150.7	512.6	1886	7559
220	5.50	-34.504	109.6	0.99928	5.999	16.77	49.75	157.6	536.1	1972	7905
230	5.75	-34.456	109.6	0.99928	6.266	17.51	51.95	164.5	559.6	2058	8250
240	6.00	-34.416	109.6	0.99927	6.533	18.23	54.17	171.6	583.6	2147	8604
250	6.25	-34.374	109.6	0.99926	6.804	19.01	56.41	178.7	607.7	2235	8959

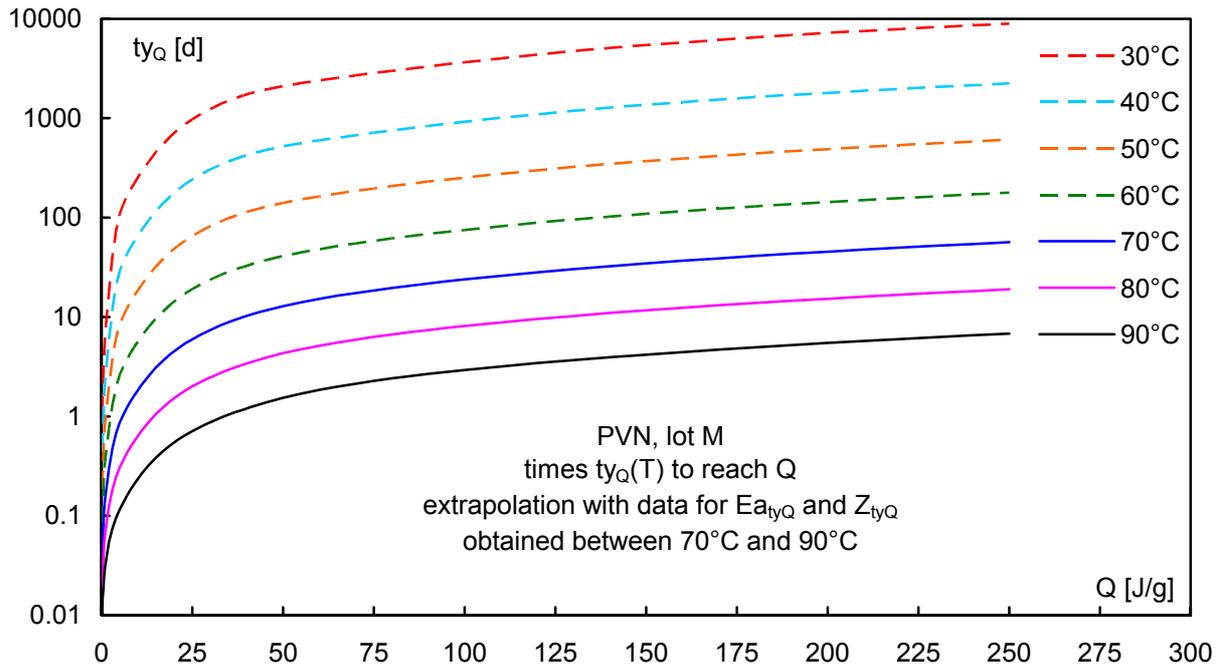


Fig. 10: Times  $ty_Q$  extrapolated to temperatures 30°C to 60°C (broken lines) with the Arrhenius parameters obtained between 70°C and 90°C.

### 3.2.3 Molar mass distribution and chain splitting as function of time and temperature

From nitrocellulose it is known that its chains are split during ageing and temperature stress. This process can be followed by gel permeation chromatography (GPC), named also size exclusion chromatography (SEC), and shows itself in shifting the molar mass distribution (MMD) from higher to lower molar masses  $M$ . There are several quantities to quantify the molar mass distribution function. Two common ones use the polymer fraction mol number related MMD  $hn(M)$  and the polymer fraction mass related MMD  $hm(M)$ . It is common to use normalized distribution functions, means the integral over it gives the value one, see Eq.(15), where  $hn_u(M)$  means the un-normalized distribution. The most used mean molar masses are  $M_n$  and  $M_w$ , the polymer fraction mol number averaged mean molar mass and polymer fraction mass averaged mean molar mass respectively, see Eq.(16) and Eq.(17).

$$(15) \quad hn_i(M) = \frac{hn_{u,i}(M)}{\sum_i hn_{u,i}(M)} = \frac{\frac{hm_{u,i}(M)}{M_i}}{\sum_i \frac{hm_{u,i}(M)}{M_i}}$$

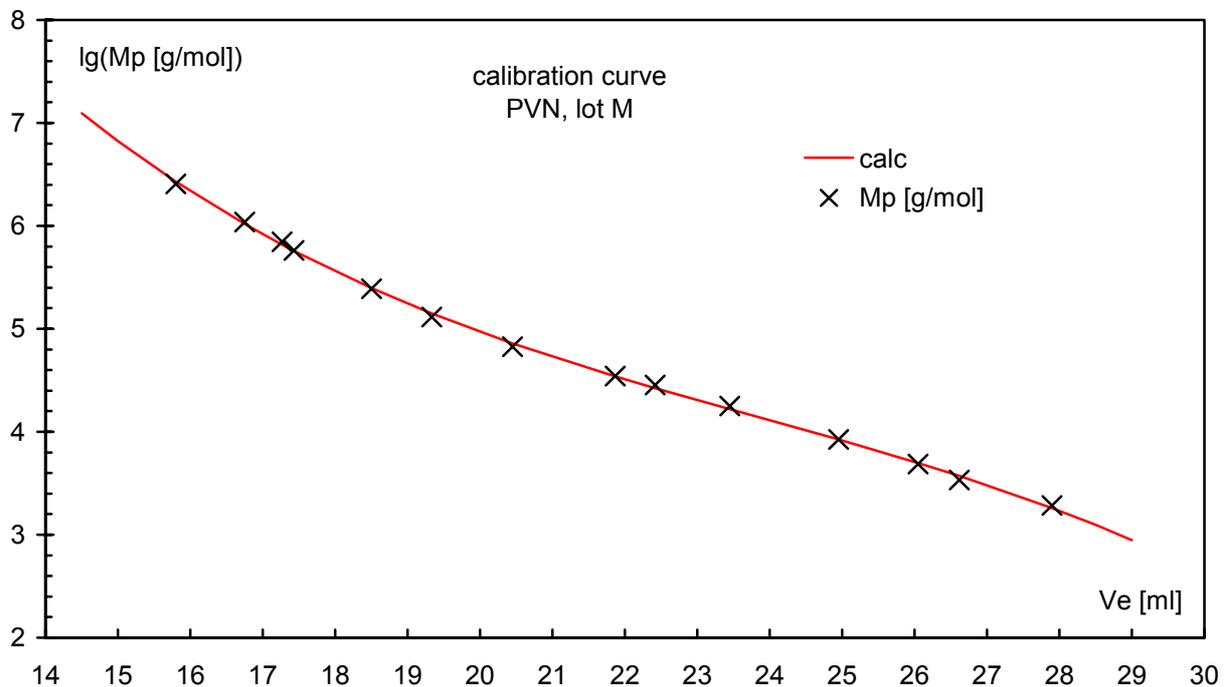
$$(16) \quad M_n = \frac{\sum_i hn_{u,i}(M) \cdot M_i}{\sum_i hn_{u,i}(M)} = \frac{\sum_i hm_{u,i}(M)}{\sum_i \frac{hm_{u,i}(M)}{M_i}}$$

$$(17) \quad M_w = \frac{\sum_i hn_{u,i}(M) \cdot M_i \cdot M_i}{\sum_i hn_{u,i}(M) \cdot M_i} = \frac{\sum_i hm_{u,i}(M) \cdot M_i}{\sum_i hm_{u,i}(M)}$$

$$(18) \quad M_z = \frac{\sum_i hn_{u,i}(M) \cdot M_i \cdot M_i \cdot M_i}{\sum_i hn_{u,i}(M) \cdot M_i \cdot M_i} = \frac{\sum_i hm_{u,i}(M) \cdot M_i \cdot M_i}{\sum_i hm_{u,i}(M) \cdot M_i} = \frac{\sum_i hz_{u,i}(M) \cdot M_i}{\sum_i hz_{u,i}(M)}$$

hn(M)	polymer fraction mol number related normalized molar mass distribution
hm(M)	polymer fraction mass related molar normalized mass distribution
hz(M)	polymer fraction z-weight related normalized molar mass distribution
Mn	polymer fraction mol number averaged mean molar mass
Mw	polymer fraction mass averaged mean molar mass
Mz	polymer fraction z-weight averaged mean molar mass

The PVN samples were aged at 70°C, 75°C and 80°C in closed ampoules used also for measurements of HGR in TAM<sup>TM</sup> microcalorimeters. The GPC was done with an instrument compiled by PSS, (Polymer Standard Service GmbH) D-55120 Mainz, Germany. From company Agilent some instruments of the 1100 series were taken: pump, autosampler, RI detector. The GPC software was from PSS, type WinGPC Unity. The column set used was from company Phenomenex and consisted of two columns: 1 x Phenogel 20µm x 10<sup>3</sup> Å and 1 x Phenogel 20µm x 10<sup>5</sup> Å. Column temperature was held constant at 35°C with an oven. Injection volume was 100µl, eluent flow 0.7 ml/min and sample concentration between 1.1 and 1.6 mg/ml. N-methyl pyrrolidone (NMP) was the mobile phase and solvent. Only NMP was found to dissolve PVN in a satisfactory manner. Calibration was done with narrowly distributed polystyrene standards (from PSS, Mainz) in the Mp range of 1920 to 2570000 g/mol. The calibration curve is shown in Fig. 11.



**Fig. 11:** Calibration curve of the GPC apparatus used to analyse the gel permeation chromatograms of PVN, lot M. Calibration with narrowly distributed polystyrene standards.

The MMD curves for the ageing series at 80°C can be seen in Fig. 12. The evaluation data are given in the Tables 3 to 5, using only the high molecular part, Fig. 13, which is separated from the lower part by the strong dip in the curves at 40700 g/mol and which was

the end value  $M_e$  in MMD evaluation also. The molar mass start value  $M_a$  is used as high molecular base line point and as start of the MMD evaluation.

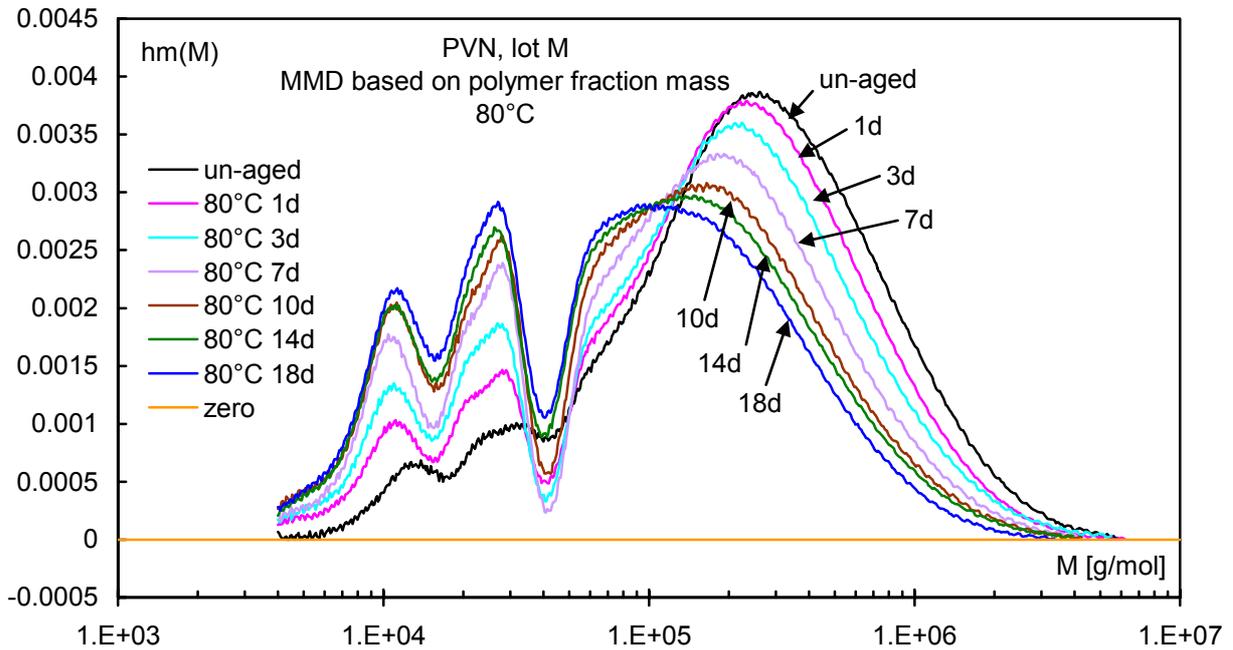


Fig. 12: Molar mass distribution functions of the ageing series at 80°C of PVN, lot M.

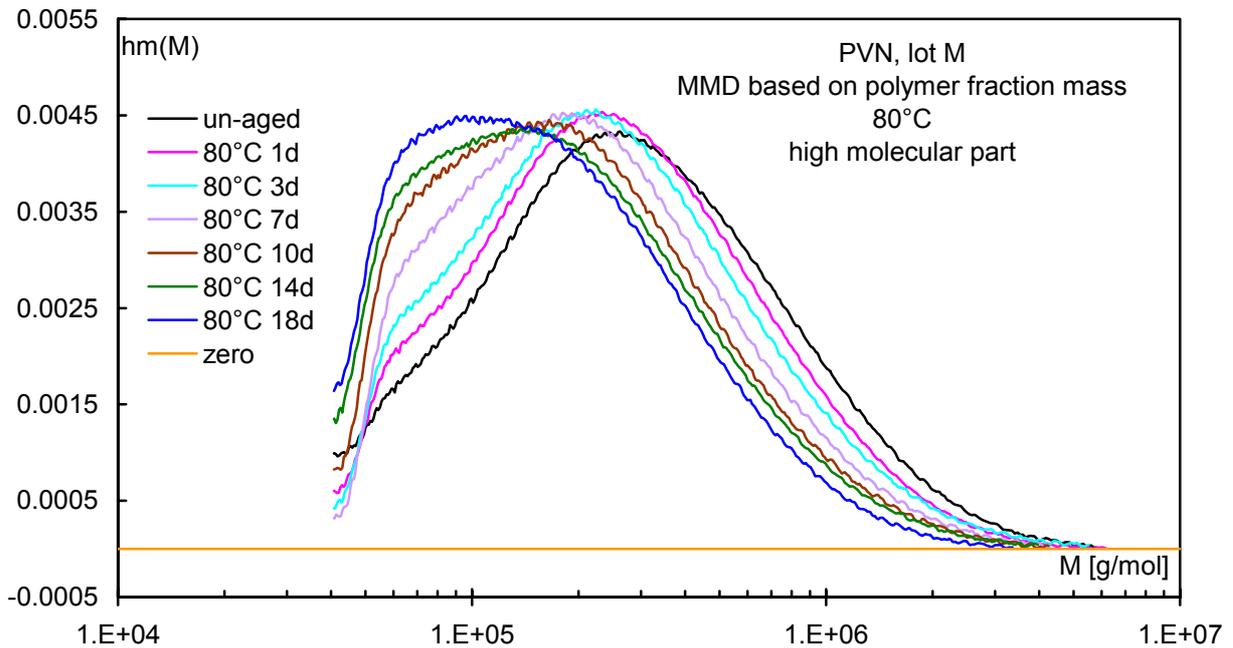


Fig. 13: High molecular part of the molar mass distribution functions of the ageing series at 80°C of PVN, lot M. The lower molecular mass end was always at  $M_e = 40700$  g/mol.

In /6/ from the C,N,O material balances between gaseous decomposition products and residue it was concluded that nearly with every split-off of N atom one C atom is brought to the gas phase. This means a considerable chain splitting of the PVN backbone during ageing.

**Table 3:** Evaluation data of 80°C ageing series. Me was always 40700 g/mol. Model data are  $k_{Mn} = 1.4307E-05$  1/d;  $m = 84.5$  g/mol;  $Mn(0) = 189600$  g/mol.

time [d]	Experimental data					Mn-calc [g/mol]
	Ma [g/mol]	Mp [g/mol]	Mn [g/mol]	Mw [g/mol]	D = Mw/Mn	
0	5857160	307900	189600	450500	2.38	189600
1	6179914	268000	178200	395800	2.22	183700
2	4297487	264700	172900	370900	2.15	178156
3	5572360	245900	169600	380300	2.24	172937
7	4328681	220500	156000	330000	2.12	154798
10	4296317	191500	140600	296700	2.11	143508
14	4002248	191500	131900	281100	2.13	130788
18	3394772	165200	123800	246500	1.99	120139
20	-	-	-	-	-	115440
25	-	-	-	-	-	105155

**Table 4:** Evaluation data of 75°C ageing series. Me was always 40700 g/mol. Model data are  $k_{Mn} = 6.2405E-06$  1/d;  $m = 84.5$  g/mol;  $Mn(0) = 189600$  g/mol.

time [d]	Experimental data					Mn-calc [g/mol]
	Ma [g/mol]	Mp [g/mol]	Mn [g/mol]	Mw [g/mol]	D = Mw/Mn	
0	5857160	307900	189600	450500	2.38	189600
1	6316265	292600	186100	431200	2.32	186981
2	6161357	274800	192200	440300	2.29	184433
4	5921440	271400	181100	414600	2.29	179539
7	6549746	248900	172100	403200	2.34	172668
12	6106517	234200	162500	373700	2.30	162313
18	6274653	225900	147500	332800	2.26	151417
25	5710140	191500	136700	304700	2.23	140419
32	5695925	207800	137000	320200	2.34	130910
35	-	-	-	-	-	127218
40	-	-	-	-	-	121506

**Table 5:** Evaluation data of 70°C ageing series. Me was always 40700 g/mol Model data are  $k_{Mn} = 3.3522E-06$  1/d;  $m = 84.5$  g/mol;  $Mn(0) = 189600$  g/mol.

time [d]	Experimental data					Mn-calc [g/mol]
	Ma [g/mol]	Mp [g/mol]	Mn [g/mol]	Mw [g/mol]	D = Mw/Mn	
0	5857160	307900	189600	450500	2.38	189600
2	6179914	278200	195700	433800	2.22	186789
6	4297487	292600	190300	442800	2.33	181409
10	5572360	285300	183000	414900	2.27	176331
15	4328681	258200	175100	421000	2.40	170369
22	4296317	237000	159100	370100	2.33	162669
30	4002248	225900	153300	380000	2.48	154679
40	3394772	220500	146400	355700	2.43	145732
50	6179914	215400	140400	321900	2.29	137763
55	-	-	-	-	-	134096

For kinetic evaluation of the change of mean molar mass  $M_n$  the reaction kinetic model described already earlier [7, 8] was applied. It is based on statistical chain splitting by decomposition of chain elements, whereby the total number of chain units in the sample decrease according to a reaction of first order. The resulting model is Eq.(19). In former publications the form of the model shown in Eq.(20) was used, or also the approximation, Eq.(21) [9,10]. Here the form given in Eq.(22) is taken and fitted directly to the data with  $k_{Mn}$  as parameter.  $M_n(0)$  and  $m = 84.5$  g/mol are known quantities. The results are shown graphically in Fig. 14 and the evaluation data  $k_{Mn}$  and calculated  $M_n(t,T)$  are given in the Tables 3 to 5. The Arrhenius plot of the reaction rate constant  $k_{Mn}$  can be seen in Fig. 15. With Eq.(23) the times  $ty_{Mn}$  to reach given degrees of molar mass decrease  $y_{Mn} = M_n(ty_{Mn})/M_n(0)$  can be calculated. Table 6 lists such data.

$$(19) \quad \frac{1 + \frac{m}{M_n(t, T)}}{1 + \frac{m}{M_n(0)}} = \exp(+k_{Mn}(T) \cdot t)$$

$$(20) \quad \ln\left(1 + \frac{m}{M_n(t, T)}\right) = \ln\left(1 + \frac{m}{M_n(0)}\right) + k_{Mn}(T) \cdot t$$

$$(21) \quad \frac{m}{M_n(t, T)} = \frac{m}{M_n(0)} + k_{Mn}(T) \cdot t$$

$$(22) \quad M_n(t, T) = \frac{m}{\left(1 + \frac{m}{M_n(0)}\right) \cdot \exp(+k_{Mn}(T) \cdot t) - 1}$$

$$(23) \quad ty_{Mn}(T) = \frac{1}{k_{Mn}(T)} \ln\left(\frac{1 + \frac{M_n(0)}{m}}{\frac{y_{Mn}}{1 + \frac{M_n(0)}{m}}}\right)$$

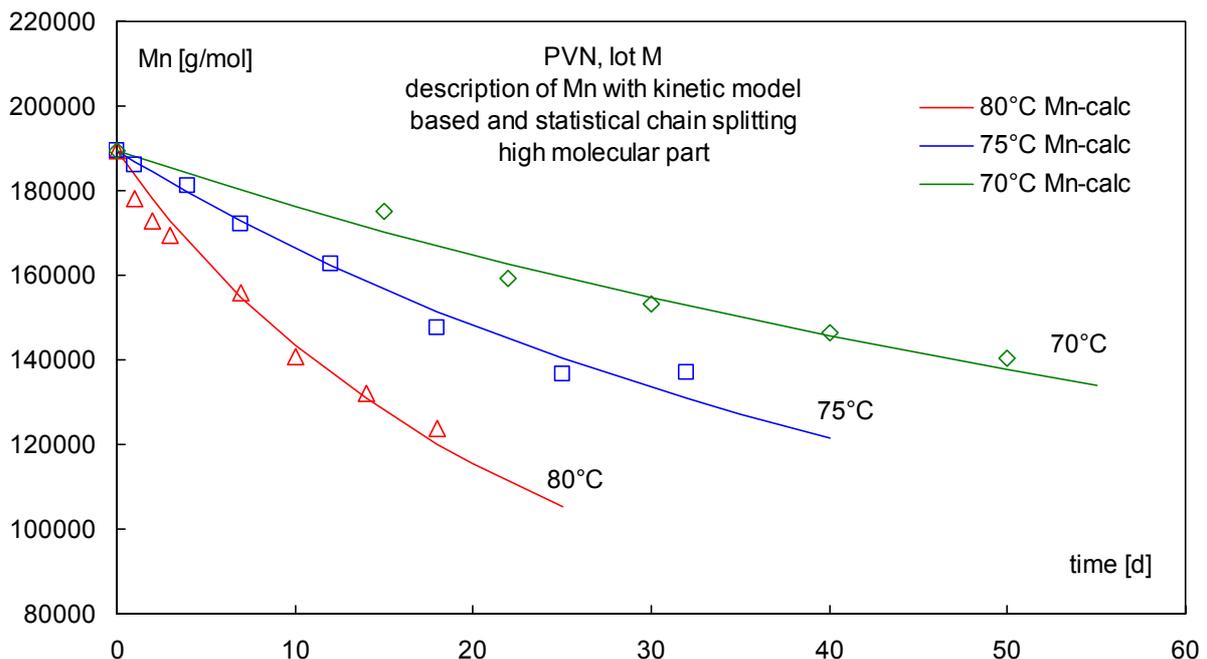
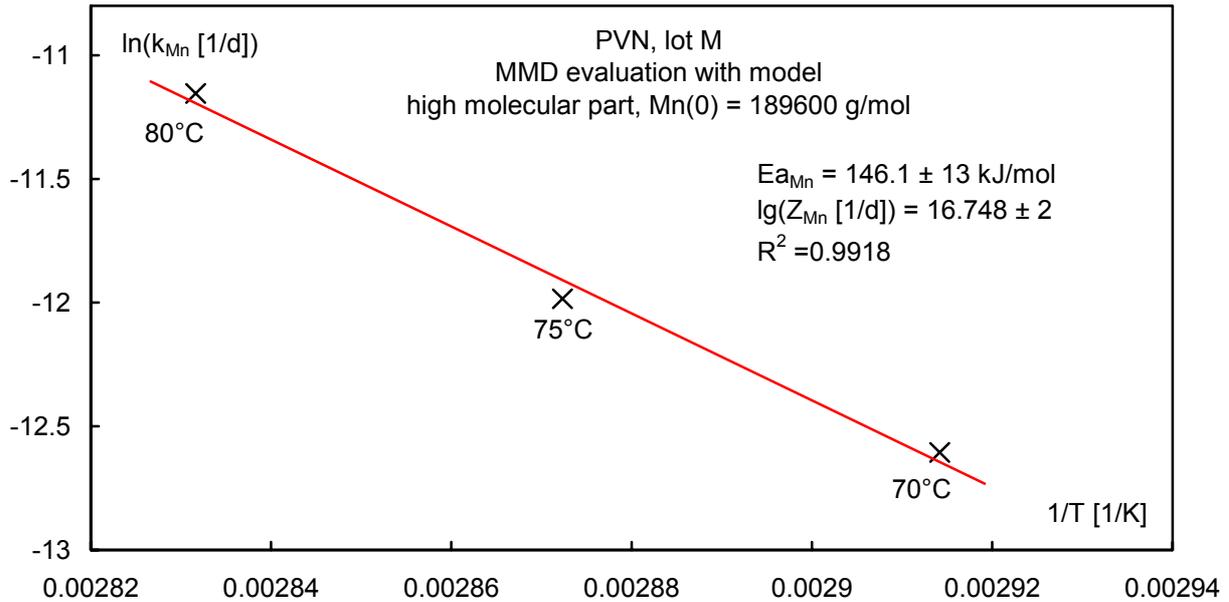


Fig. 14: Reaction kinetic description of the decrease of  $M_n$  of PVN lot M.



**Fig. 15:** Arrhenius plot of the reaction rate constant  $k_{Mn}$  of chain splitting of PVN, lot M.

**Table 6:** Times  $ty_{Mn}$  to reach the degree of molar mass decrease  $y_{Mn} = Mn(ty_{Mn})/Mn(0)$ ; parameters are  $m = 84.5$  g/mol,  $Mn(0) = 189600$  g/mol.

temp. [°C]	time $ty_{Mn}$ to reach $y_{Mn} = Mn(ty_{Mn})/Mn(0)$				
	3%	5%	10%	15%	20%
30	10.1 a	17.1 a	36.1 a	57.3 a	81.2 a
35	3.9 a	6.68 a	14.1 a	22.4 a	31.7 a
40	1.58 a	2.69 a	5.67 a	9.0 a	12.8 a
45	0.65 a	1.11 a	2.35 a	3.73 a	5.28 a
50	0.28 a	0.47 a	1.0 a	1.59 a	2.25 a
55	44.4 d	75.5 d	159 d	253 d	359 d
60	19.9 d	34 d	71 d	113 d	161 d
65	9.1 d	15.5 d	32.7 d	51.9 d	73.6 d
70	4.27 d	7.3 d	15.3 d	24.4 d	34.5 d
75	2.05 d	3.48 d	7.4 d	11.7 d	16.5 d
80	1.00 d	1.70 d	3.6 d	5.7 d	8.1 d
85	0.50 d	0.85 d	1.80 d	2.85 d	4.04 d
90	0.25 d	0.43 d	0.91 d	1.45 d	2.06 d

## 4. Discussion

With the three methods used for investigating the ageing behaviour of PVN several problems of the decomposition reactions are applied:

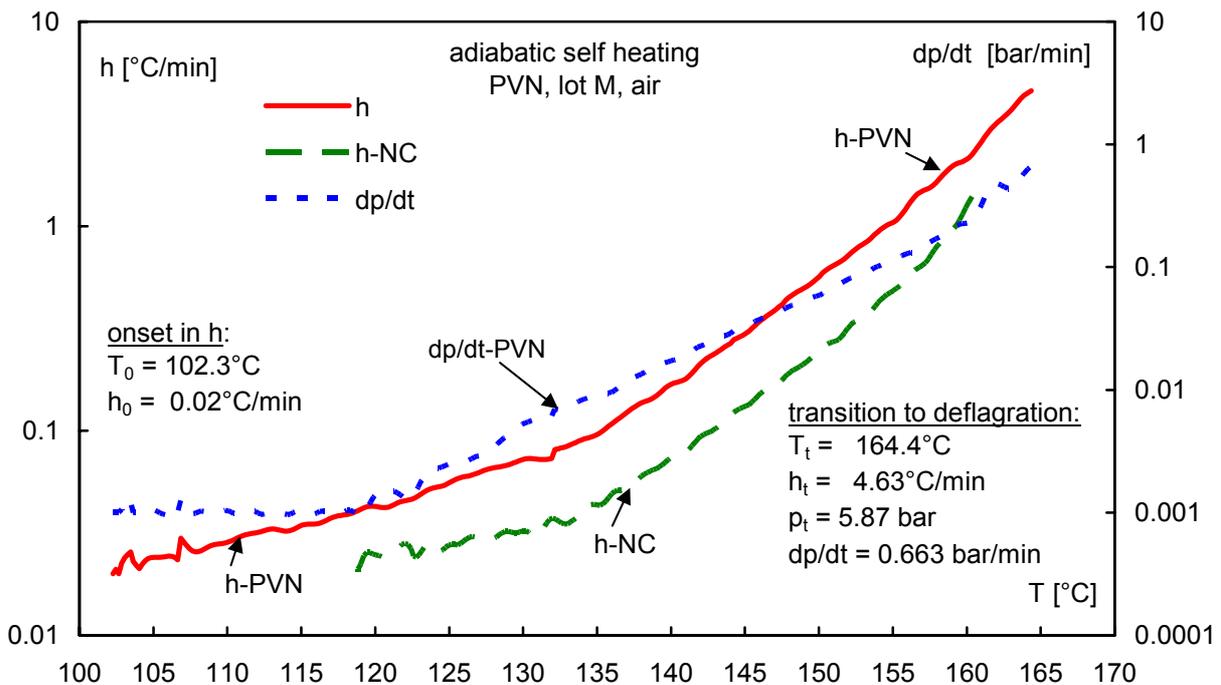
- split-off of gases by mass loss
- net heat of reaction by integrated heat generation rate
- mean chain length of the polymer as molecular property

The comparison of decomposition parameters is made with the compilation in Table 7.

**Table 7:** Comparison of Arrhenius parameters for PVN, lot M obtained from three measurement methods.

	Mass loss ML	Heat generation at $Q=160$ J/g	Heat generation at $Q=160$ J/g	Heat generation at $Q=160$ J/g	Mn decrease
temp. range	65°C to 90°C	70°C to 90°C	70°C to 110°C	90°C to 110°C	70°C to 80°C
index i	ML	$ty_Q$	$ty_Q$	$ty_Q$	Mn
$Ea_i$ [kJ/mol]	$110.0 \pm 2.1$	$109.5 \pm 3.2$	$112.5 \pm 1.4$	$115.1 \pm 1.0$	$146.1 \pm 13$
$\lg(Z_i$ [unit])	$15.637 \pm 0.31$	$-15.095 \pm 0.47$	$-15.556 \pm 0.2$	$-15.918 \pm 0.13$	$16.748 \pm 2$
unit of $Z_i$	%/d	d	d	d	1/d
$R^2$ [-]	0.9986	0.99917	0.99957	0.99994	0.9918

Because of the special data evaluation with heat generation only the activation energies can be compared directly between mass loss and heat generation. In the range of standard deviation both methods provide the same values. But the results with heat generation give the impression that there is slight temperature dependence for the activation parameters. The  $Ea_{ty_Q}$  values for 70°C to 90°C and 90°C to 110°C differ more than the scattering. With chain splitting the activation energy is significantly higher, which indicates the probing of another rate determining step in the decomposition process. The value of  $Ea_{Mn} = 146.1$  kJ/mol is in the range of the values found with NC degradation in gun propellant A 5020 /9/ and two double base rocket propellants /10/. From the decomposition mechanism of NC it was concluded that such a value is a mix of thermolytic and hydrolytic decomposition of the nitrate ester group. It seems that such a mechanism is applicable for PVN also and that the decomposition of the nitrate ester group is the rate determining step seen with the probing of molar mass decrease in the considered temperature range.



**Fig. 16:** Adiabatic self heating of PVN lot M and a high nitrated nitrocellulose.

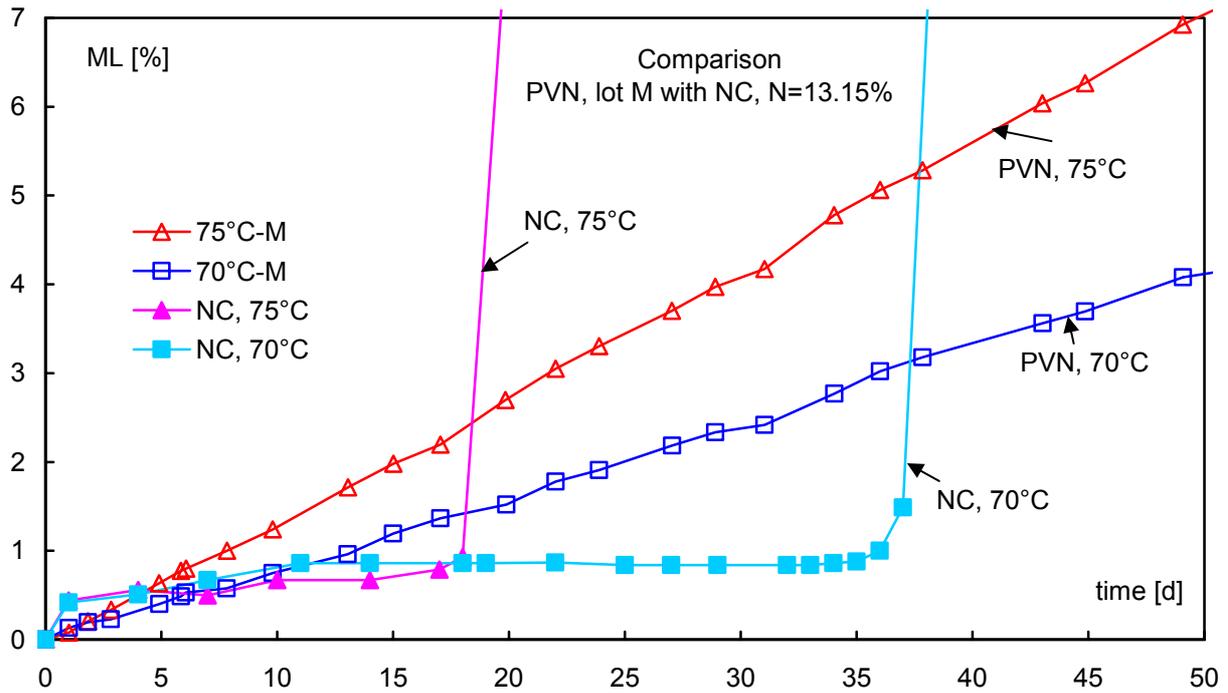


Fig. 17: Comparison of mass loss between PVN, lot M and unstabilized nitrocellulose with N = 13.15 mass-%.

In Fig. 16 the behaviour of PVN during adiabatic self heating (determined with ARC<sup>TM</sup>, Accelerating Rate Calorimeter) in the temperature range 100°C to 170°C is compared to the one of a high nitrated (N = 13.15 mass-%) unstabilized nitrocellulose. The principle course of the two self heatings is the same. The difference in the height of the curves seems not a significant distinction. This means that at higher temperatures the decomposition behaviours of both substances are controlled by the nitrate ester group decomposition in a similar way. The comparison at lower temperatures is made with Fig. 17. The mass loss behaviour is clearly different. NC is at the beginning somewhat more stable than PVN but shows strong autocatalytic effect, which is not the case with PVN.

## 5. Summary and conclusion

The stability of PVN was assessed by autoignition temperature at 5°C/min heating rate, mass loss at 75°C over 2 days, vacuum stability at 90°C over 40 h and adiabatic self heating. The ageing behaviour of unstabilized PVN was investigated with three methods: (i) mass loss as function of time and temperature in the range 65°C to 90°C, (ii) heat generation rate and heat generation as function of time and temperature in the range 70°C to 110°C, (iii) chain splitting by determining the molar mass distribution function as function of time and temperature at 70°C, 75°C and 80°C and subsequent determination of mean molar mass  $M_n$ . The methods mass loss and heat generation give nearly the same activation energies for the decomposition of PVN. With heat generation a slight temperature dependence in activation energy can be recognized. PVN has about the same stability as unstabilized nitrocellulose. The decrease of mean molar mass  $M_n$  with time and temperature could be kinetically modelled providing an activation energy of 146 kJ/mol, which is similar to values of NC degradation in single base and double base propellants. With the three sets of Arrhenius parameters obtained from the three experimental methods predictions of usetime were made. To reach 3% of mass loss, energy loss and molar mass decrease needs at 30°C: 17 years, 12 year and 10 years respectively. With mass loss the 17 years are the apparent time, the real PVN related time to 3% is about 10 years /11/.

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