

Characterization of ageing of NC based gun propellants by molar mass degradation of nitrocellulose and its modelling by random chain scission models including the description of the complete molar mass distribution functions

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Abstract

An example is presented of the ageing of a gun propellants (GP) followed by molar mass decrease of the nitrocellulose determined with GPC.

Two models are applied to describe the data, both using random chain scission of the NC chains. The first one is based on scission by decomposition of chain elements and is derived on the base of the statistical quantities of the MMD (molar mass distribution) of the polymer. The second model assumes chain scission by bond cleavage. This model is applied to the whole MMD of the nitrocellulose (NC) and not on the derived statistical quantities as mean molar masses or mean degree of polymerisation.

Keywords

Modelling based on random chain scission, modelling the whole molar mass distribution, modelling the change of MMD, ageing of propellant, chain length of NC.

1. Introduction

The ageing of NC-based gun propellants is an important issue and is mainly twofold: a primary safety issue because of self-ignition of overaged NC propellants. Astonishingly, this is not an academic aspect but a very practical one which is documented in several severe events of self-ignition. The prominent recent ones have happened in Finland (Ähtäri Ammunition Depot, July 1999) and Japan (August 2000 in Nagoya) and some less known in USA (Milan AAP, Tennessee, October 2004). But not only is this basic safety aspect of concern, caused by so-named chemical stability or better instability, if stabilizer consumption has reached the level of no longer stabilizing the propellant. The operational and the ballistic stability are of equal importance. Ballistic stability means that the energy loss in the propellant leads to a degraded target picture. Operational stability means the safety of gun operation, especially with medium to large calibre ammunition for tank and howitzer guns. For such high performance guns high mechanical strength of the propellant grains is an important demand. If the strength is not sufficient the grains break during the ignition cycle and by the increased burning surface a rapid pressure rise results which can be spatially inhomogeneous and the resulting pressure waves can reach or exceed the level of construction strength of the burning chamber and the breach, and finally the destruction of the gun results. Therefore the monitoring of the mechanical strength of propellant grains during ageing is a necessary demand for large calibre ammunition. This can be done by regularly dismantling and testing. A second way is the

determination of the degradation of molar mass of nitrocellulose in such propellant formulations at function of temperature and time and correlating this property with grain strength. With decreasing chain length of NC the mechanical strength of the grains decreases. By monitoring the time-temperature load of the ammunition in field use the prediction of the molar mass degradation is achieved and a prediction of grain strength can be made.

The degradation of polymeric molecules forms often smaller fragments under a variety of influences, including thermal and photo-chemical energy, mechanical stress, and oxidizing agents. Mathematical modelling assumes the polymeric molecule to exist as a chain consisting of N segments and, hence, $N-1$ bonds between the segments. In the case of thermal decomposition, a rate constant $k(T)$ depending on temperature describes the scission of one bond by some kinetic mechanism. In this paper it is assumed to be a first order reaction. Different approaches exist to formulate the probability that an individual bond is split, the simplest one being a random chain scission.

2. Theory and description of the model

2.1 Theory

2.1.1 Description with mean molar quantities and random chain scission

The simplified mathematical treatments of polymer degradation consider only average properties of the polymer chain-length distribution or molecular mass distribution (MMD). Such an approach was already applied to the degradation of nitrocellulose and single base gun propellants /1-4/ deriving formulas for the mol number averaged mean molecular mass $Mn(t)$ starting from an initial mean molar mass $Mn(0)$. The model given in Eq.(1) is based on the random chain scission by decomposition of chain elements, not of mere bond breaking.

$$\frac{Mn(t, T)}{Mn(0)} = \frac{\exp(-k_M(T) \cdot t)}{1 + \frac{Mn(0)}{m} \cdot (1 - \exp(-k_M(T) \cdot t))} \quad (1)$$

The reaction rate constant k_M describes the decomposition of chain elements according to a reaction of first order. The quantity $Mn(0)/m$ is the mol number averaged mean degree of polymerisation $Pn(0)$ and m is the molar mass of one chain element of the polymer. From Eq.(1) it is obvious that $Mn(t)/Mn(0)$ degrades rapidly already with small conversions rates, which means that $k_M(T) t \ll 1$. Therewith Eq.(1) can be approximated by Eq.(2).

$$\frac{Mn(t, T)}{Mn(0)} = \frac{1}{1 + \frac{Mn(0)}{m} \cdot k_M(T) \cdot t} \quad (2)$$

The derived kinetic parameter of $k_M(T) = Z_M \cdot \exp(-E_{a_M}/RT)$ were consistent with detailed analysis of NC decomposition /1, 4, 5/. In the Appendix the complete derivation is given for two types of random chain scission: by bond scission between chain elements and by decomposition of chain elements, see also /24, 25/.

2.1.2 Description of MMD with random chain scission by bond cleavage

To describe the MMD change by chain splitting directly the following approach is used. The complete MMD can be considered by writing down a system of differential equations including each individual polymer length M_i with $i = 1$ to N /6-8/. M_i is the number of polymer chains with length i , means one of these chains has i chain elements. In the following the random chain splitting according to bond scission is assumed. According to the number of bonds the rate of first order degradation is $(i-1) \cdot k$ (the temperature dependence of k is not explicitly shown in the following), starting with the chains M_N with length N and a probability of $P(i:j)$ to get a chain with length i (=number of chain elements) from one of length j :

$$\frac{dM_N}{dt} = -k \cdot (N-1) \cdot M_N \quad (3)$$

$$\frac{dM_{N-1}}{dt} = -k \cdot (N-2) \cdot M_{N-1} + k \cdot (N-1) \cdot P(N-1:N) \cdot M_N \quad (4)$$

$$\frac{dM_i}{dt} = -k \cdot (i-1) \cdot M_i + \sum_{j=i+1}^N k \cdot (j-1) \cdot P(i:j) \cdot M_j \quad (5)$$

The probability for random scission of a chain with length j is given by $2/(j-1)$. Then Eq.(4) and (5) reduce to:

$$\frac{dM_{N-1}}{dt} = -k \cdot (N-2) \cdot M_{N-1} + 2 \cdot k \cdot M_N \quad (6)$$

$$\frac{dM_i}{dt} = -k \cdot (i-1) \cdot M_i + 2 \cdot \sum_{j=i+1}^N k \cdot M_j \quad (7)$$

Ballauff and Wolf /10/ have shown that the equation (3), (6) and (7) can be exactly solved by a recursive approach with $m(j)$ being the initial MMD. Using a more convenient way, the MMDs can be described explicitly:

$$M_N(t) = m(N) \cdot \exp(-(N-1) \cdot k \cdot t) \quad (8)$$

$$M_{N-1}(t) = m(N-1) \cdot \exp(-(N-2)kt) + 2 \cdot m(N) \cdot (\exp(-(N-2)kt) - \exp(-(N-1)kt)) \quad (9)$$

$$M_i(t) = \left(\sum_{j=1}^N (j-i-1)m(j) + \left(-2 \sum_{j=1}^N (j-i)m(j) + \left(\sum_{j=i+1}^N (j-i-1)m(j) \right) \cdot e^{-kt} \right) e^{-kt} \right) e^{-(i-1)kt} \quad (10)$$

The handling of series is time consuming and cumbersome, therefore the discrete terms and sums in Eq.(10) were expressed by continuous functions and integrals with the following substitutions and changing the final N to infinity, Eq.(11) and Eq.(12).

$j \Rightarrow y, \quad i \Rightarrow x, \quad N \Rightarrow \infty.$

$$\sum_{j=i}^N (j-i-1) \cdot m(j) \Rightarrow \int_x^{\infty} (y-x) \cdot m(y) dy - \int_x^{\infty} m(y) dy \quad (11)$$

$$\sum_{j=i+1}^N (j-i-1) \cdot m(j) \Rightarrow \int_x^{\infty} (y-x) \cdot m(y) dy - \int_x^{\infty} m(y) dy + m(x) \quad (12)$$

Eq (10) then reads:

$$M(x, t) = \left(\int_x^{\infty} (y-x) \cdot m(y) dy - \int_x^{\infty} m(y) dy + \left(-2 \int_x^{\infty} (y-x) \cdot m(y) dy + \left(\int_x^{\infty} (y-x) \cdot m(y) dy - \int_x^{\infty} m(y) dy + m(x) \right) \cdot e^{-kt} \right) \cdot e^{-kt} \right) \cdot e^{-(x-1)kt} \quad (13)$$

The discrete system of differential Eq.(3) to (7) corresponds to an integro-differential equation describing the degradation of MMDs $M_C(x,t)$ by continuous functions:

$$\frac{dM_C(x, t)}{dt} = -f(x) \cdot M_C(x, t) + \int_x^{\infty} f(y) \cdot P(x : y) \cdot M_C(y, t) dy \quad (14)$$

For random chain scission by a first order reaction, we have: $f(x)=x$, $P(x:y)= 2/y$

$$\frac{dM_C(x, t)}{dt} = -f(x) \cdot M_C(x, t) + 2 \int_x^{\infty} M_C(y, t) dy \quad (15)$$

Eq.(14) and Eq.(15) can be solved by differentiation with respect to x and Laplace Transformation /11-15/. It was not yet proved, if Eq.(13) is solution to Eq.(15).

2.2 Application with simulating distribution functions

For some important, often used distributions, as Gauss, log-normal and gamma distribution, the integrals in Eq.(11) to (13) can be analytically solved.

The Normal Distribution (Gauss distribution)

For a Gaussian distribution, Eq.(16), as an initial MMD (as polymer fraction mol number related MMD), an example is plotted in the following Fig. 1 with $k=0.0005$ 1/s and time steps of one second. Formally any time unit can be taken. Inserting the normalized Gauss distribution Eq.(16) into Eq.(13), integrating and after some rearrangement gives Eq.(17).

$$m_{\text{Gauss}}(y) = \frac{1}{b\sqrt{\pi}} \cdot \exp\left(-\frac{(y-a)^2}{b^2}\right) \quad (16)$$

$$\begin{aligned}
 M(x,t) = & \left(b \cdot \frac{\exp\left(-\frac{(a-x)^2}{b^2}\right)}{2\sqrt{\pi}} + \frac{(a-x)}{2} \left(1 + \operatorname{erf}\left(\frac{a-x}{b}\right) \right) \right) \cdot \{ \exp(-(x-1)kt) - 2\exp(-xkt) \\
 & + (\exp(-(x+1) \cdot kt)) \} + 0.5 \cdot \left(1 + \operatorname{erf}\left(\frac{a-x}{b}\right) \right) \cdot \{ \exp(-(x-1) \cdot kt) - \exp(-(x+1) \cdot kt) \} \\
 & + \frac{\exp\left(-\frac{(x-a)^2}{b^2}\right)}{b\sqrt{\pi}} \cdot \exp(-(x+1) \cdot kt)
 \end{aligned} \quad (17)$$

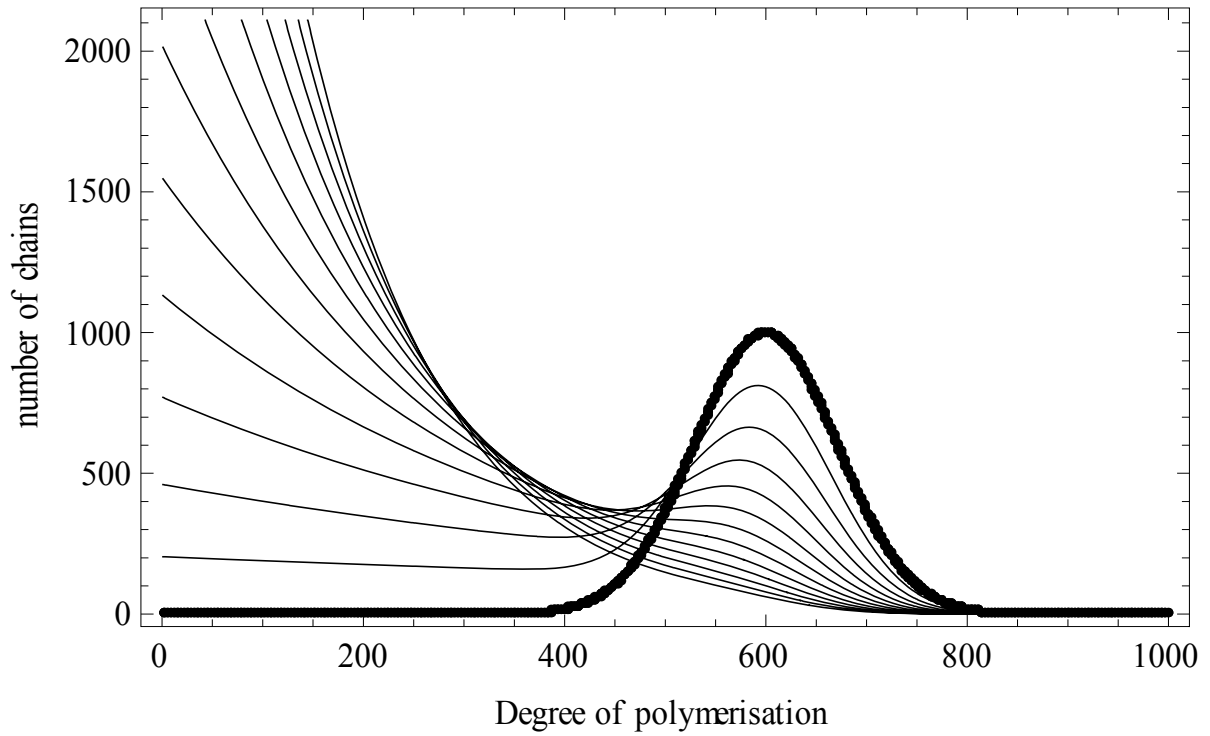


Fig. 1: Calculated time development of a MMD using Eq.(10), starting with an initial normal distribution, which is centered at a polymerization degree of 600.

The Log-Normal Distribution

$$m_{\log-n}(y) = \frac{1}{xb\sqrt{2\pi}} \cdot \exp\left(-\frac{(\log(y)-a)^2}{2b^2}\right) \quad (18)$$

$$\begin{aligned}
M(x,t) = & 0.5 \left(\exp\left(a + \frac{b^2}{2}\right) - x \left(1 + \operatorname{erf}\left(\frac{a - \ln(x)}{b \cdot \sqrt{2}}\right) \right) + \exp\left(a + \frac{b^2}{2}\right) \operatorname{erf}\left(\frac{a + b^2 - \ln(x)}{b \cdot \sqrt{2}}\right) \right) \\
& \cdot \{ \exp(-(x-1) \cdot kt) - 2 \exp(-x \cdot kt) + \exp(-(x+1) \cdot kt) \} + 0.5 \cdot \left(1 + \operatorname{erf}\left(\frac{a - \ln(x)}{b \cdot \sqrt{2}}\right) \right) \\
& \cdot \{ \exp(-(x-1) \cdot kt) - \exp(-(x+1) \cdot kt) \} + \frac{\exp\left(-\frac{(\ln(x) - a)^2}{2b^2}\right)}{x \cdot b \cdot \sqrt{2\pi}} \cdot \exp(-(x+1) \cdot kt)
\end{aligned} \quad (19)$$

The Γ -Distribution

$$m_{\text{gamma}}(y) = \frac{b^p}{\Gamma(p)} x^{p-1} \cdot \exp(-bx) \quad (20)$$

$$\begin{aligned}
M(x,t) = & \frac{-bx \cdot \Gamma(a,b,x) + \Gamma(1+a,b,x)}{b \cdot \Gamma(a)} \{ \exp(-(x-1) \cdot kt) - 2 \exp(-xkt) + \exp(-(x+1) \cdot kt) \} \\
& + \frac{\Gamma(a,b,x)}{\Gamma(a)} \{ \exp(-(x-1) \cdot kt) - \exp(-(x+1) \cdot kt) \} + \frac{b^a}{\Gamma(a)} \cdot x^{a-1} \cdot \exp(-bx) \cdot \exp(-(x+1) \cdot kt)
\end{aligned} \quad (21)$$

Fig. 2 and 3 show the results for a Log-Normal Distribution and a Gamma Distribution, with $k=0.0005$ 1/s (or 1/time unit) and progress in time by steps of one second (or one time unit).

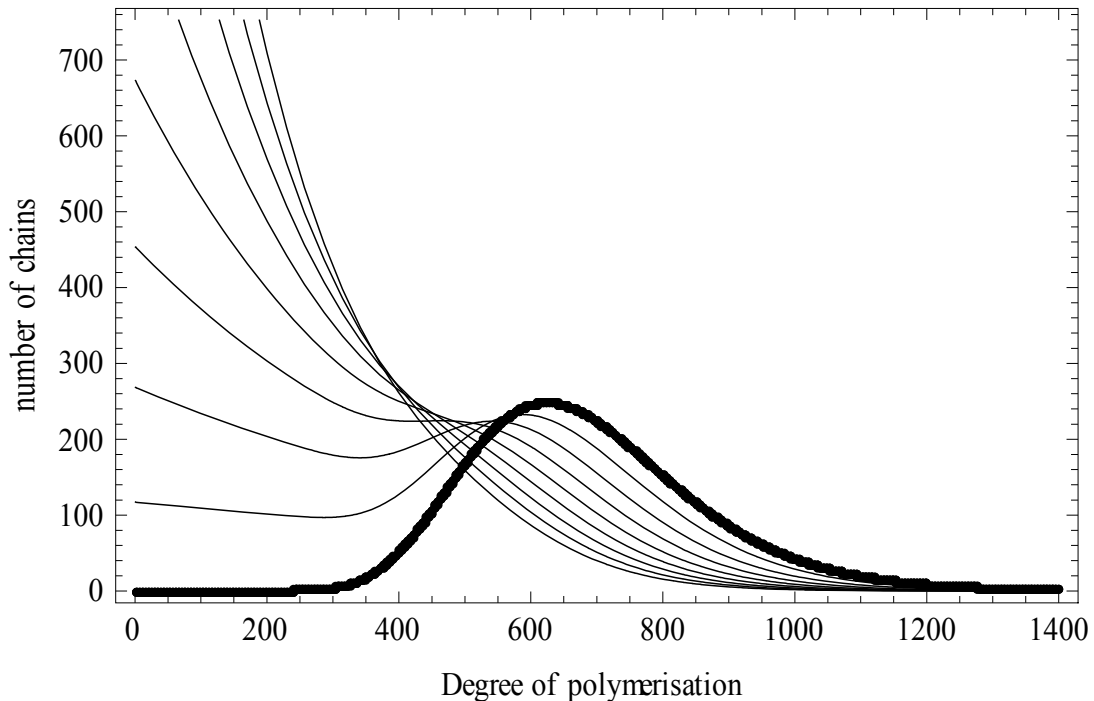


Fig. 2: Calculated time development of a MMD using Eq.(19), starting with an initial Log-Normal Distribution, Eq.(18).

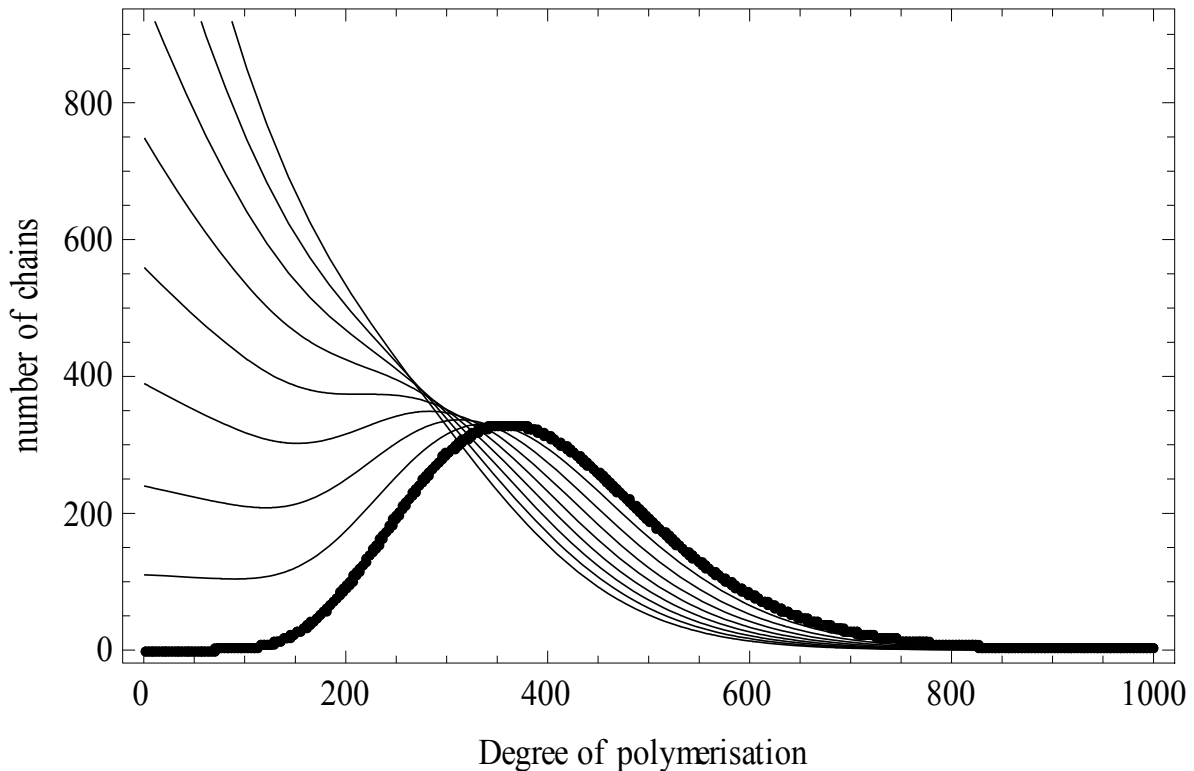


Fig 3: Calculated time development of a MWD using Eq.(21), starting with an initial Gamma Distribution, Eq.(20).

3. Application with measured molar mass distribution of NC

3.1 Experimental data

The NC used for applying the modelling was that of the gun propellant Q5560. The main components in typical concentration are given in Table 1. This propellant is stabilized by akardite II. The nitrocellulose (NC) has a nitrogen content of about 13.1 mass-%. The molar mass distributions of the NC of unaged and aged propellant have been determined by gel permeation chromatography, whereby the apparatus was calibrated with narrowly distributed polystyrene standards. The used instrumentation and the analysis conditions are compiled in the following.

Table 1: Typical composition of gun propellant Q5560

substance	content in mass-%
NC	75
N-content	13.1
DEGN	18
nitroguanidine	5.5
akardite II	1
water	0.5

Used GPC instrumentation

Isocratic high pressure pump, autosampler and RI-detector from company Agilent, type 1100 Series

Column oven type T-1000 from company WEG Dr. Bures, Berlin, Germany
 Solvent degasser from company Uniflows Co., Tokyo, Japan, type Degasys Populaire DP 4003

GPC software from company PSS; Software-Version: PSS WinGPC Unity Build 6807
 PSS Polymer Standards Service GmbH
 PO-BOX 3368, D-55023 Mainz, Germany

Sample preparation:

Solvent and mobile phase: THF stabilized with < 250 ppm BHT
 Nitrocellulose concentration: about 1.5 mg/ cm³
 Dissolution time: 1 day
 Standards for calibration: 10 narrowly distributed polystyrene, EasiCal™ PS-1, spatula A and B *)

Gel permeation chromatographic analysis

Columns: 2 (in series) PLGel™ 10µm Mixed B, 300mm x 7.5mm *)
 Column temperature: 35 °C
 RI detector cell temp. 35 °C
 Mobile phase flow rate: 1.0 cm³/min
 Sample injection volume: 100 µl
 Replicate injections: 2 per sample vial

*) from Polymer Laboratories respectively Varian Polymer Laboratories

Fig. 4 shows the elugrams of the two sets of calibration standards. The separation range is well covered, as can be seen also in Fig. 5, which shows the nominal separation range of the used column set.

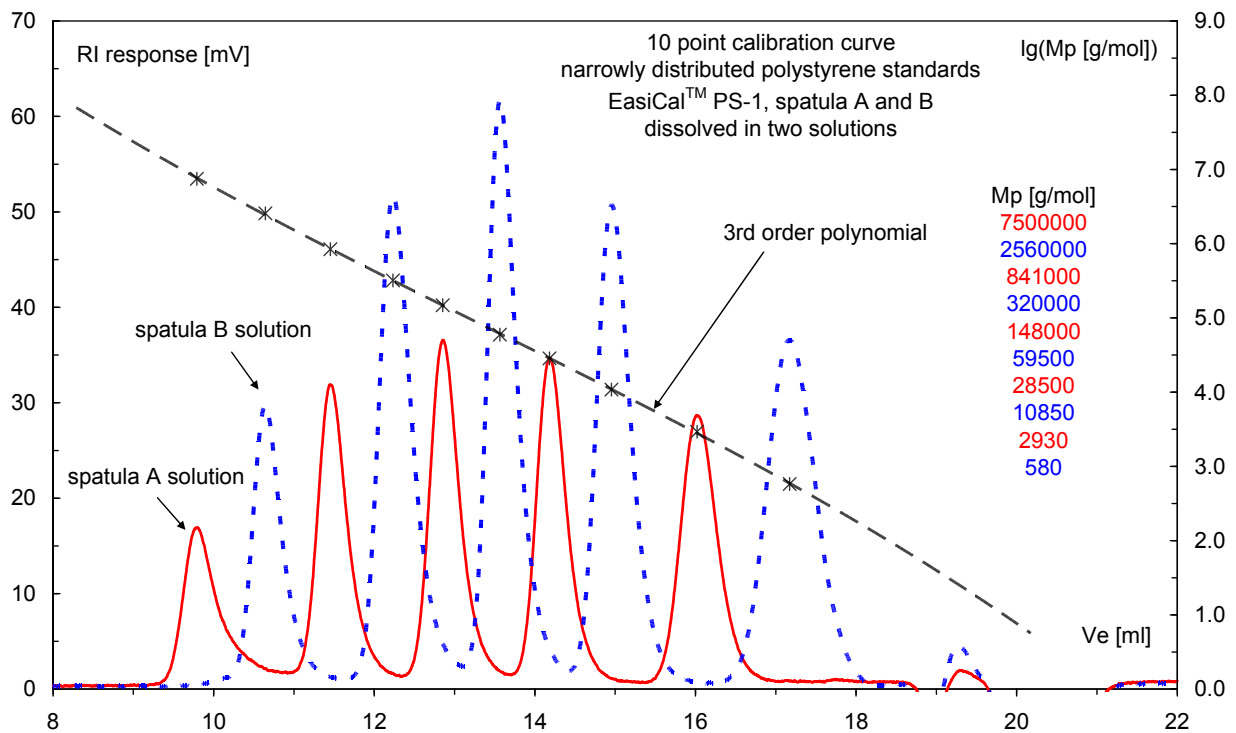


Fig. 4: Elugrams of two sets of calibration standards together with the calibration curve to convert elution volume to molar mass.

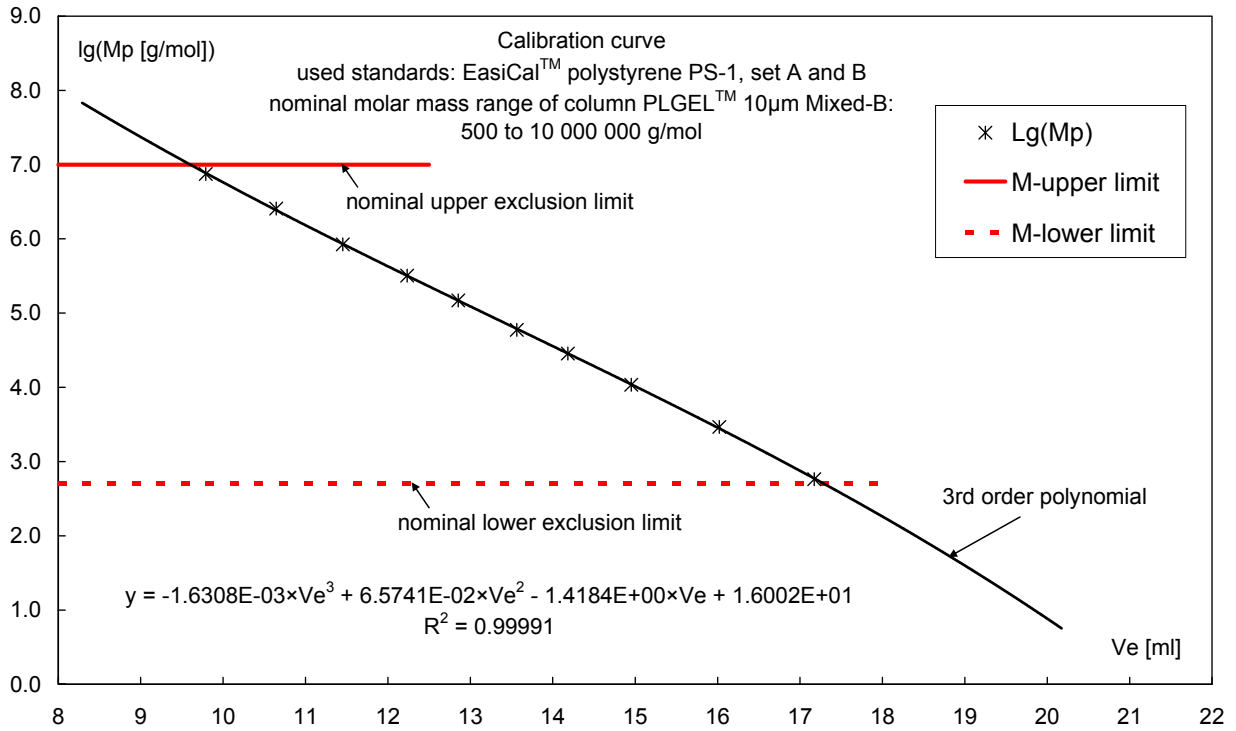


Fig. 5: Example of a calibration curve of the used GPC column set. Given are also the nominal exclusion limits of the columns.

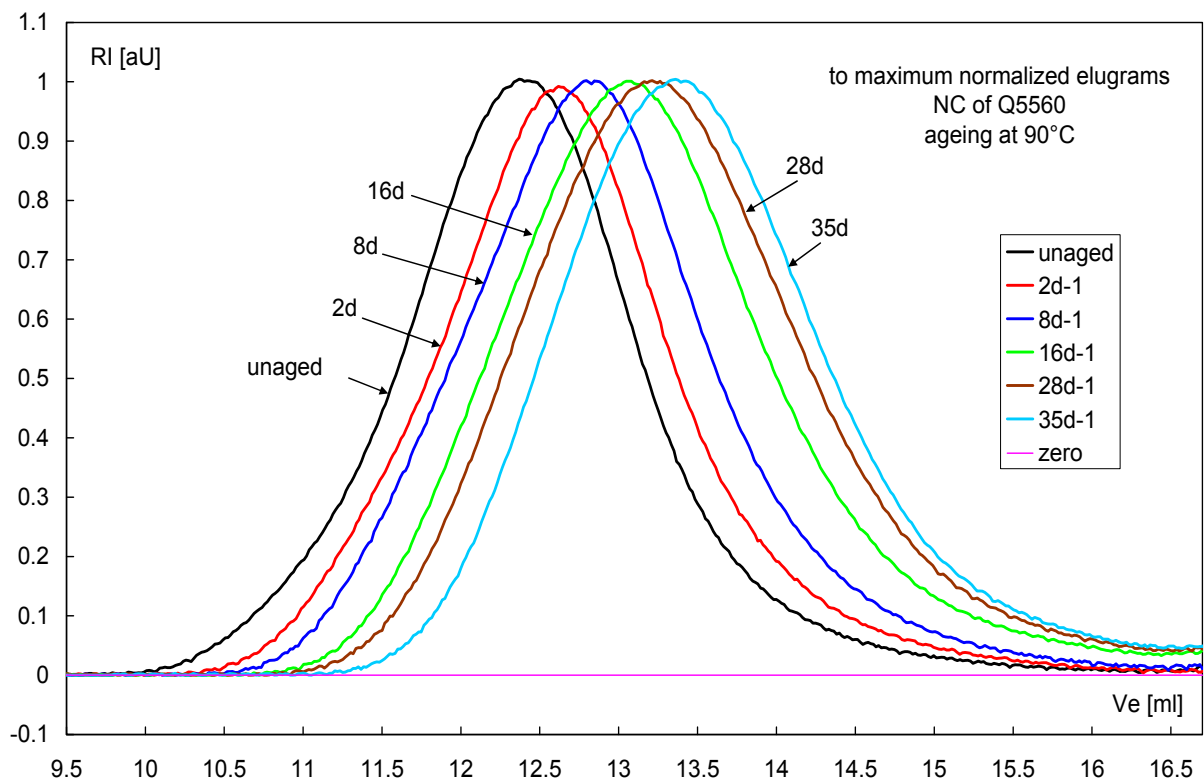


Fig. 6: Some elugrams of the NC of the aged propellant sample, normalized to equal maximum height.

The NC elugrams obtained from the ageing series of propellant Q5560 are shown in Fig. 6. The high molar masses appear on the left side. The elugrams are converted to the mo-

lar mass distribution by the calibration relation. Because the used refractive index detector is sensitive to the mass concentration of the polymer fraction in the detector cell, one gets the so-named polymer fraction mass related molar mass distribution $hm(M)$ or $hm(\lg M)$, depending on the calculation. These MMDs are shown in Fig. 7 for all the ageing times applied. Important to note is that at low molar masses the distribution values increase with ageing. This means that with ageing increasingly short NC chains are produced which therefore must express in an increase in MMD values at low molar masses. All elugrams have been evaluated to the same end value of M_e , here to 1100 g/mol. Further to see in Fig. 7 is the fact that the MMDs shift to lower molar masses. This is the case already for quite short ageing times. Even after only 2 days at 90°C one finds already a significant shift of the MMD and consequently also for the mean molar masses.

Fig. 7 shows the distribution type $hm(\lg(M_i))$; it is the mass m_i of polymer fraction i related normalized discrete molar mass probability function. The $hm(\lg(M_i))$ gives the mass fraction of molecules with a molar mass M_i in polymer fraction i . For the modelling of the distribution functions one must use the distribution type $hn(\lg M_i)$. This is the molar number n_i of polymer fraction i weighed normalized discrete molar mass probability function. The $hn(\lg(M_i))$ gives the mol number fraction of molecules with a molar mass M_i in polymer fraction i . $hn(\lg M_i)$ can be calculated from $hm(\lg(M_i))$ by Eq.(22).

$$hn(\lg M_i) = hm(\lg(M_i)) / M_i \quad (22)$$

The MMDs of type $hn(\lg(M_i))$ are shown in Fig. 8.

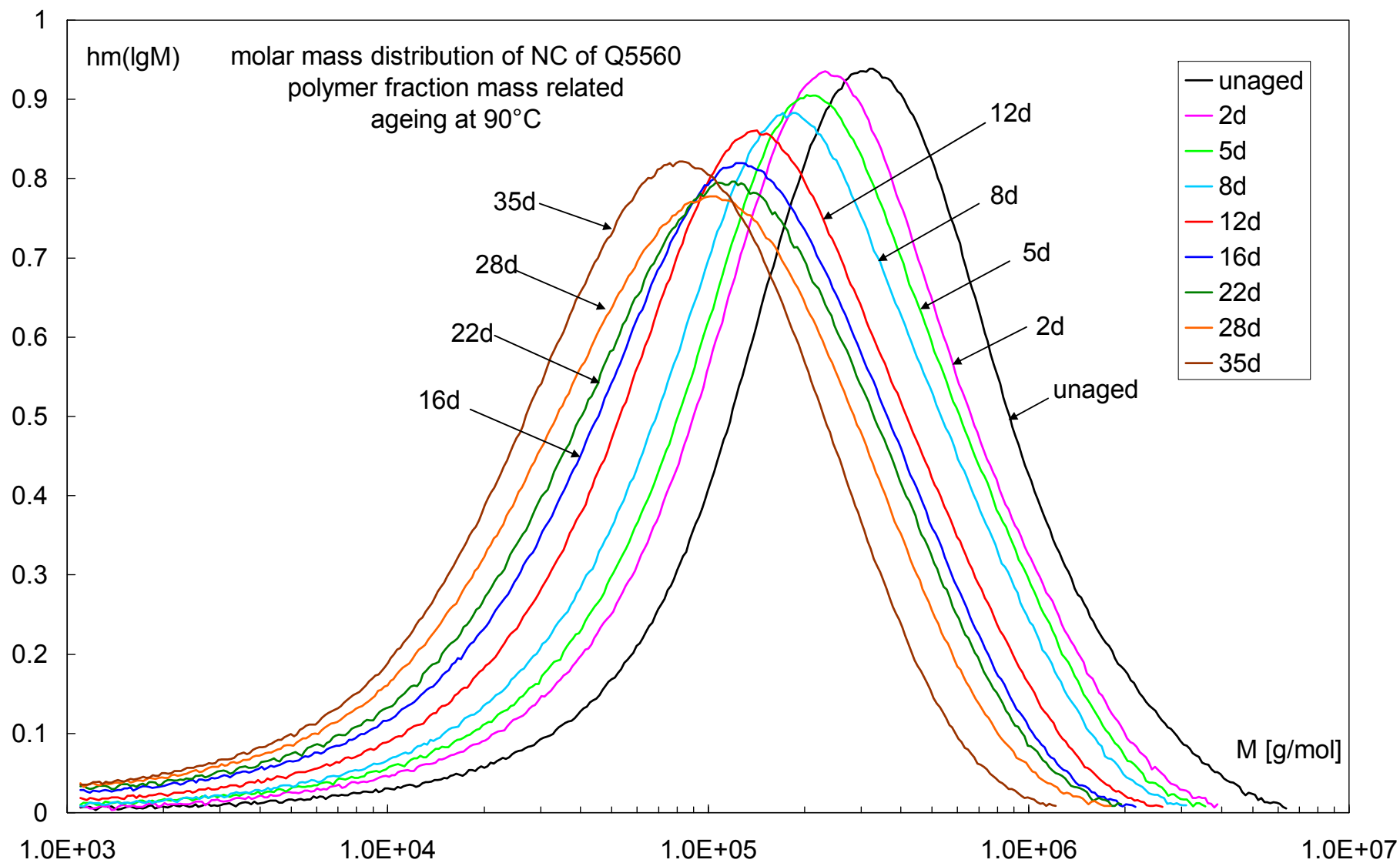


Fig. 7: Experimentally determined polymer fraction mass related MMDs $hm(\lg M)$ of the NC of Q5560, aged at 90°C.

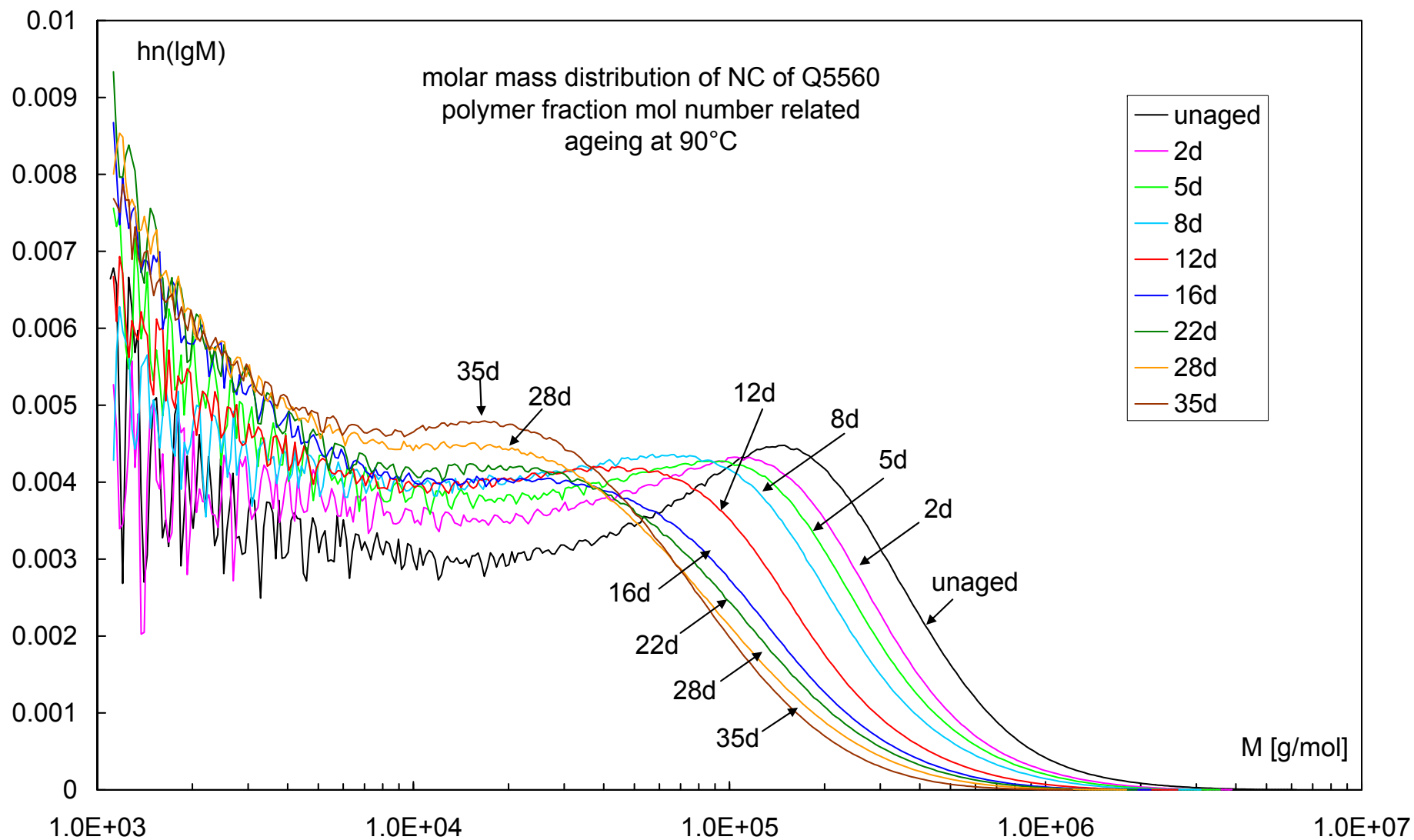


Fig. 8: Experimental MMDs of the NC of Q5560, aged at 90°C. Here polymer fraction number related MMDs $hn(\lg M)$ are shown, calculated from the polymer fraction mass MMDs $hm(\lg M)$ by $hn(\lg M)_i = hm(\lg M)_i / M_i$.

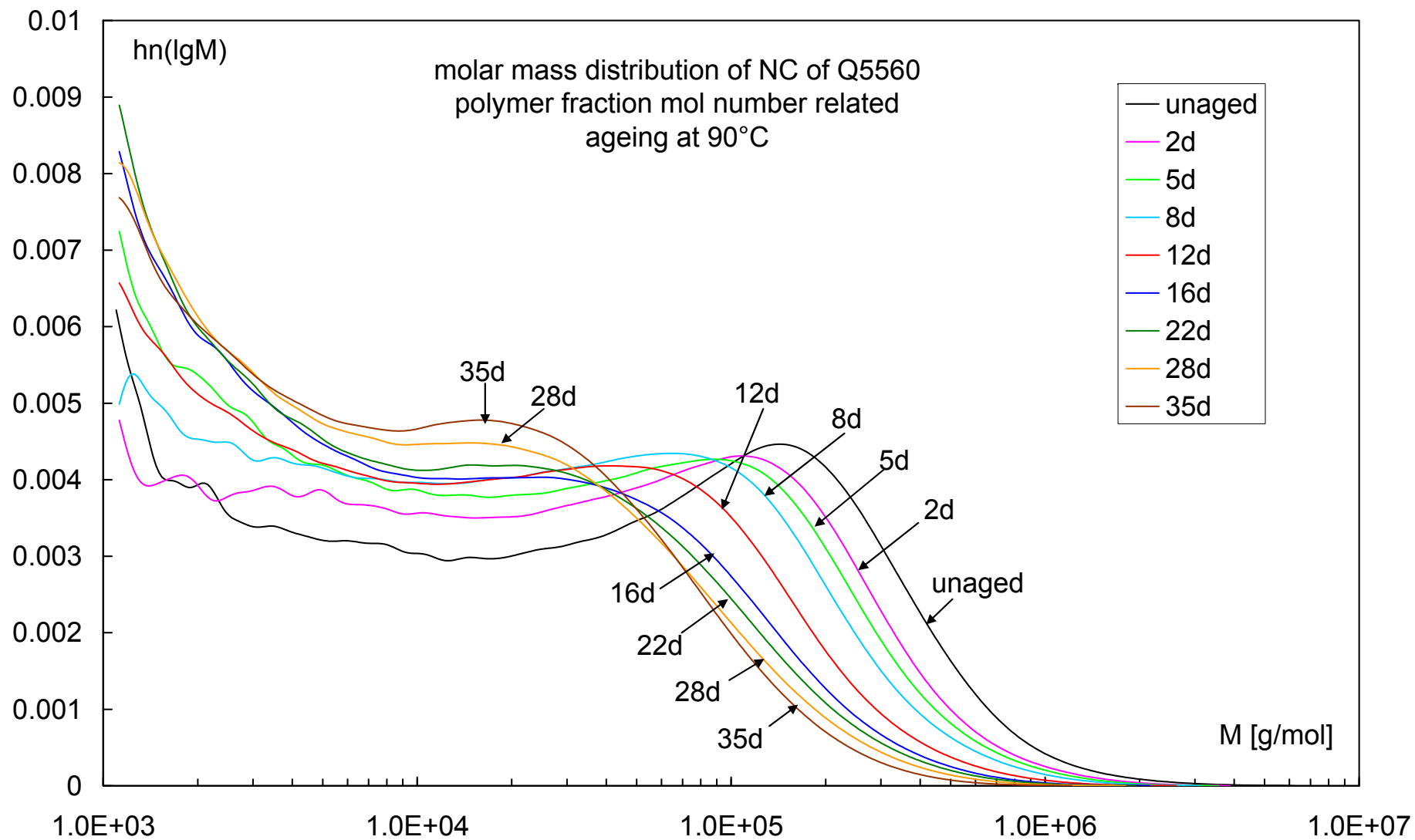


Fig. 8b: Same as Fig. 8, but with smoothed data.

In Table 2 to Table 4 the obtained data of the evaluation of the GPC elugrams of Q5560 aged at 90°C, 80°C and 70°C are compiled. The Fig. 9 to Fig. 11 show the course of Mn and of the polydispersity $D=M_w/M_n$ with ageing time. Fig. 12 presents the results of the modelling by the model based on mean quantities and random chain scission by decomposition of chain elements, see Eq.(A24). It seems that the NC in Q5560 degrades with different rates. In the beginning the degradation is faster. This was observed also at 80°C. At 70°C this effect was less pronounced. Fig. 13 shows the Arrhenius evaluations of the three parts (beginning degradation at short ageing times, degradation at longer ageing times without the first part, evaluation without distinction, see Fig. 12). In Table 5 the results of these evaluations are listed together with the Arrhenius parameters. From Fig. 13 one can conclude that the slopes of the three Arrhenius lines are not very different, the main difference arises because of the pre-exponential factor.

Table 2: Results of the GPC analysis of the NC degradation in GP Q5560 aged at 90°C.

Time [d]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]	D	Mp [g/mol]
0	112548	501971	1261386	4.47	309421
2	71382	358067	849917	5.04	228812
2	80550	372148	894162	4.63	230479
5	62502	318698	740368	5.10	196075
5	61219	289330	691429	4.73	175413
8	57641	286374	678779	4.97	172818
8	57617	273666	643746	4.75	166538
12	44116	221122	535685	5.01	137402
12	53142	254712	611190	4.80	158185
16	34225	186295	451825	5.45	123802
16	34821	190990	474984	5.49	119248
22	32637	172679	424677	5.29	112736
22	37339	189713	463758	5.09	123165
28	30332	156589	383301	5.16	104413
28	28329	146810	366451	5.18	98416
35	24964	111871	259954	4.48	81832
35	28094	122530	286009	4.36	84954

Table 3: Results of the GPC analysis of the NC degradation in GP Q5560 aged at 80°C.

Time [d]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]	D	Mp [g/mol]
0	112548	501971	1261386	4.47	309421
6	84361	378622	906605	4.27	233038
15	76223	342059	801636	4.50	216294
24	69179	310580	740723	4.49	196944
36	61995	283068	676353	4.57	177743
48	54183	236097	560842	4.39	150575
66	51157	224501	522369	4.40	146157
84	42234	193337	462837	4.58	127783

Table 4: Results of the GPC analysis of the NC degradation in GP Q5560 aged at 70°C.

Time [d]	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]	D	Mp [g/mol]
0	112548	501971	1261386	4.47	309421
18	96942	453068	10690289	4.69	279409
45	94849	425309	1378573	4.50	232546
108	75000	332000	1619548	4.43	196394
144	60542	266749	629459	4.41	159968
198	52250	215626	508135	4.13	128392
252	47324	200000	502131	4.23	129417

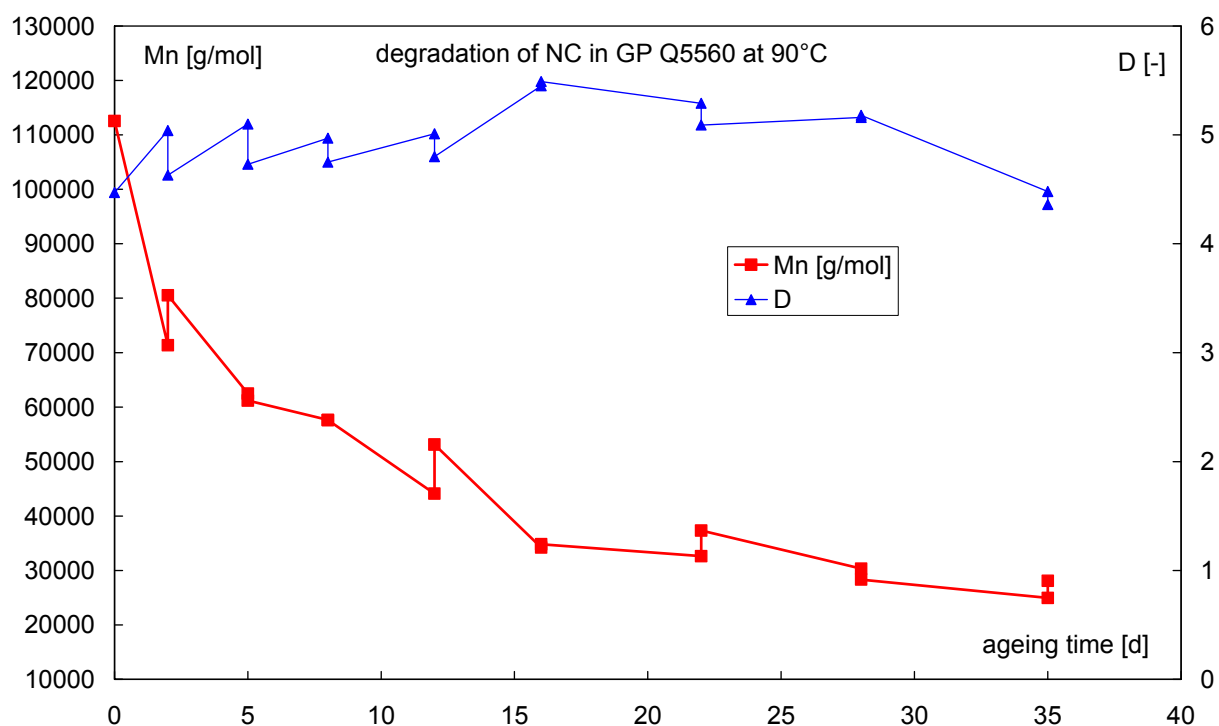


Fig. 9: Decrease of Mn of NC in Q5560 during ageing at 90°C. Shown is also the degree of polydispersity $D=M_w/M_n$.

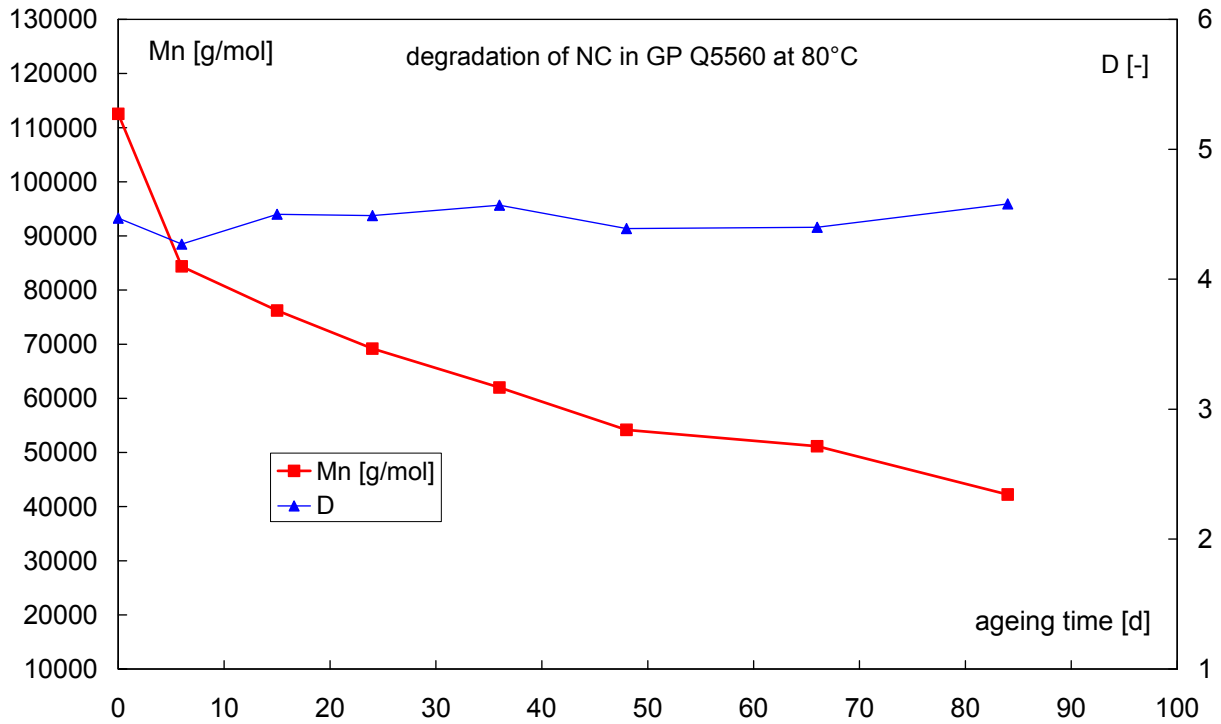


Fig. 10: Decrease of Mn of NC in Q5560 during ageing at 80°C. Shown is also the degree of polydispersity $D=M_w/M_n$.

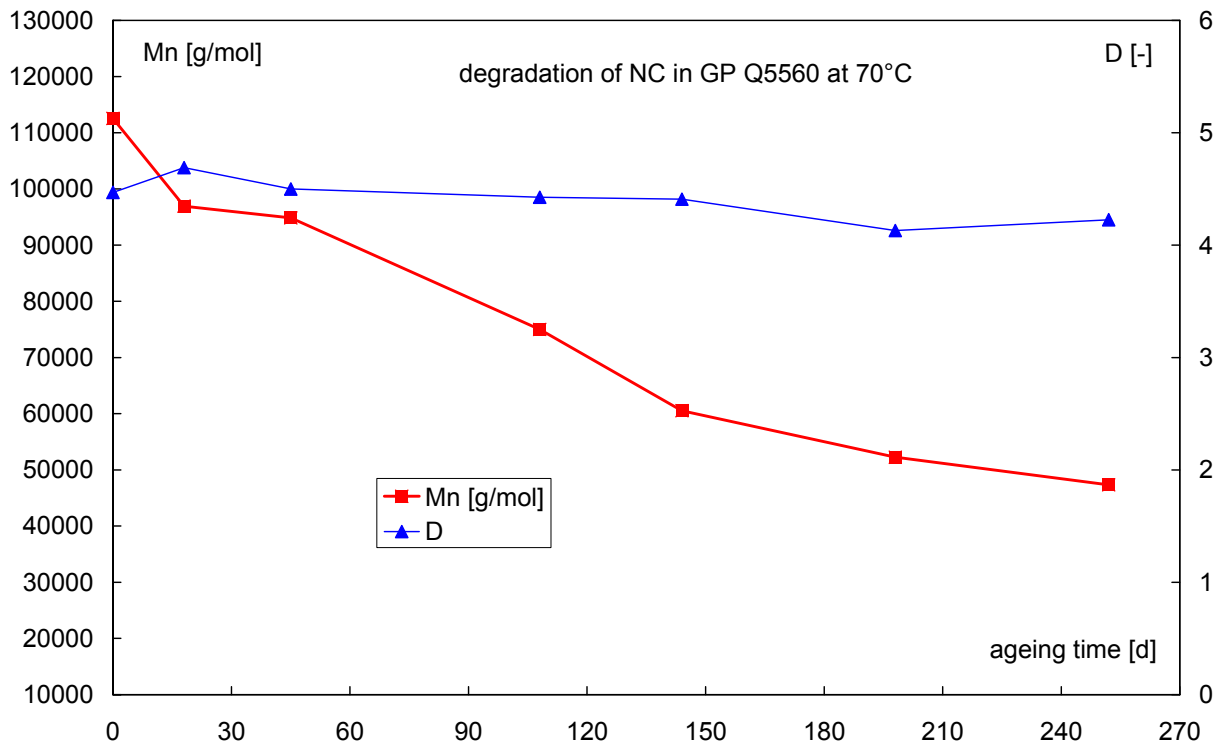


Fig. 11: Decrease of Mn of NC in Q5560 during ageing at 70°C. Shown is also the degree of polydispersity $D=M_w/M_n$.

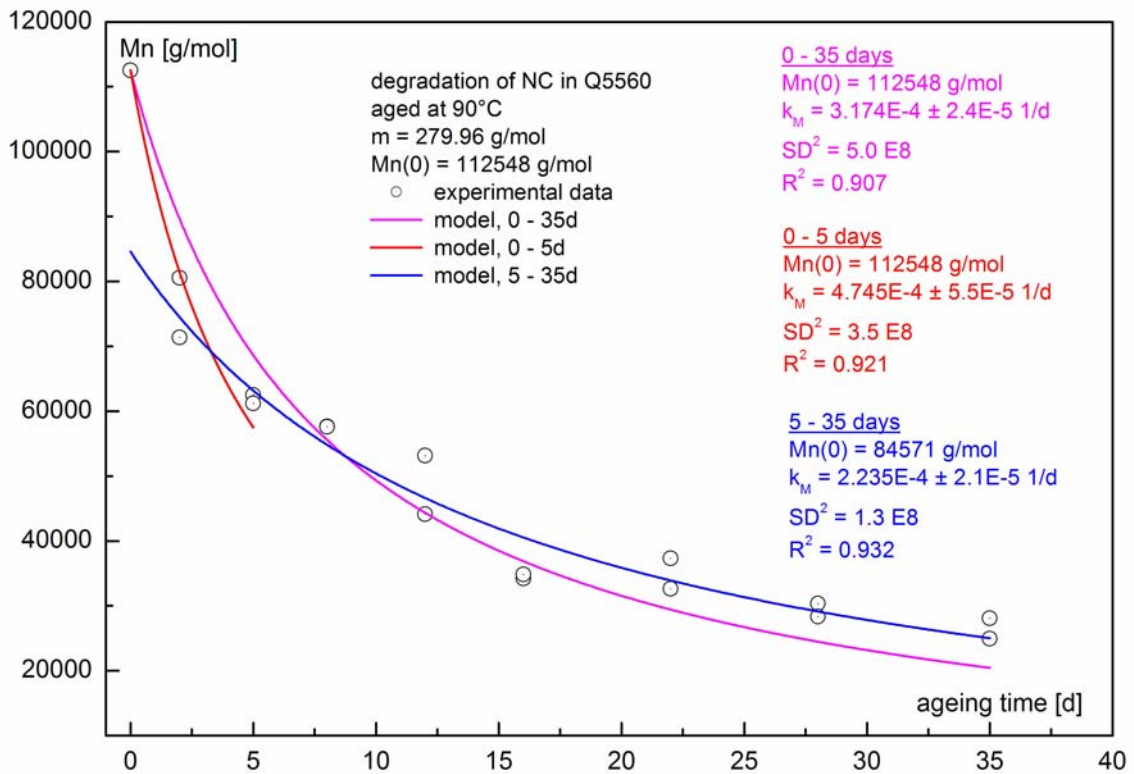


Fig. 12: Modelling of the Mn decrease of NC in GP Q5560 with the model of random chain scission by decomposition of chain elements, see Appendix, Eq.(A24). It seems that the NC degradation is faster at the beginning of the ageing. The reaction rate constant values are between $5.5 \text{ E-}9$ and $2.6 \text{ E-}9$ $1/\text{s}$.

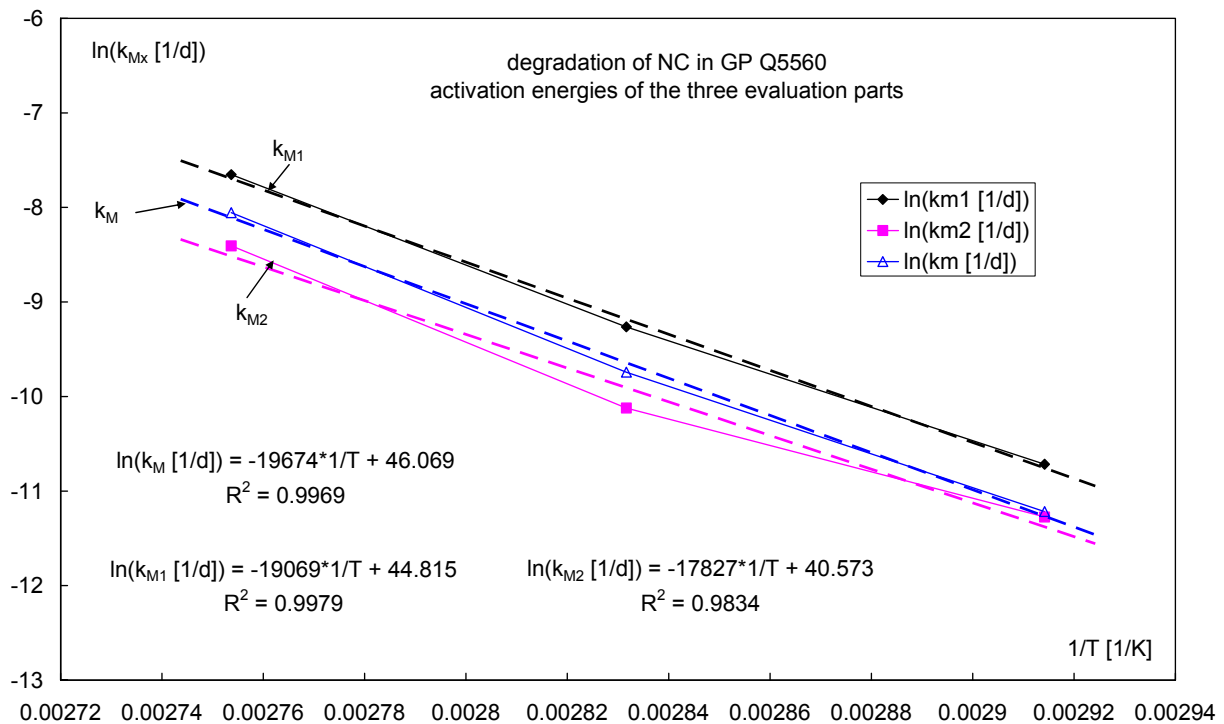


Fig. 13: Arrhenius plots of the evaluation in three parts of the NC degradation of GP Q5560

Table 5: Experimental rate constants for NC degradation in GP Q5560, determined with the model assuming random chain scission by decomposition of one chain element, see Appendix Eq.(A24). The corresponding Arrhenius parameters are given also.

T [°C]	k_{M1} [1/d]	k_{M2} [1/d]	k_M [1/d]
	first part	second part	total
90	4.7450E-04	2.2350E-04	3.1740E-04
80	9.4835E-05	4.0210E-05	5.8735E-05
70	2.2187E-05	1.2708E-05	1.3460E-05
Ea [kJ/mol]	159	148	164
lg(Z [1/d])	19.463	17.621	20.008
R ²	0.9979	0.9834	0.9969

3.2 Molar mass distribution functions related to different quantities

In the following some of the definitions of the statistical quantities to describe polymeric samples are compiled.

$hn(M)$ molar number of polymer fraction weighed normalized continuous molar mass density function.

$hn(M_i)$ molar number n_i of polymer fraction i weighed normalized discrete molar mass probability function.

$$hn(M) \cdot dM = \frac{hn_u(M) \cdot dM}{\int_{Ma}^{Me} hn_u(M) \cdot dM} \quad \int_{Ma}^{Me} hn(M) \cdot dM = 1$$

$$hn(M) = hn(\lg(M)) \cdot \frac{1}{M} \quad d\lg(M) = \frac{1}{M} \cdot dM$$

$$hn(\lg M) \cdot d\lg(M) = \frac{hn_u(\lg M) \cdot d\lg(M)}{\int_{\lg(Ma)}^{\lg(Me)} hn_u(\lg M) \cdot d\lg(M)} \quad \int_{Ma}^{Me} hn(\lg M) \cdot d\lg M = 1$$

$$hn_i(M) = \frac{hn_{u,i}(M)}{\sum_i hn_{u,i}(M)} \quad \sum_i hn_i(M) = 1$$

The probability density $hn(M)$ has the dimension of reciprocal molar mass. In using relative molar mass quantities (with unit dalton, $M(\text{relative}) = M(\text{real})$ divided by unit molar mass or molar mass of hydrogen) $hn(M)$ is formally dimensionless in ignoring dalton as an attached unit. $hn(M)$ and $hn(\lg(M))$ are polymer fraction mol number related normalized molar mass distribution density functions.

The probability quantity $hn(M)dM$ is dimensionless and gives the mol number fraction (=normalized mol number) of molecules with a molar mass M in the polymer fraction range from M to $M+dM$.

The probability quantity $hn_i(M)$ or $hn(M_i)$ is dimensionless and gives the mol number fraction of molecules with a molar mass M_i in polymer fraction i .

$hm(M)$ mass of polymer fraction weighed normalized continuous molar mass density function.

$hm(M_i)$ mass m_i of polymer fraction i weighed normalized discrete molar mass probability function.

$$hm(M) \cdot dM = \frac{hm_u(M) \cdot dM}{\int_{Ma}^{Me} hm_u(M) \cdot dM} \quad \int_{Ma}^{Me} hm(M) \cdot dM = 1$$

$$hm_i(M) = \frac{hm_{u,i}(M)}{\sum_i hm_{u,i}(M)} \quad \sum_i hm_i(M) = 1$$

The quantity $hm(M)dM$ is dimensionless and gives the mass fraction of molecules with a molar mass M in the polymer fraction range from M to $M+dM$.

The probability quantity $hm_i(M)$ or $hm(M_i)$ is dimensionless and gives the mass fraction of molecules with a molar mass M_i in polymer fraction i .

The m -weight or mass weight of the polymer fraction i is obtained by multiplication of molar number n_i of the polymer fraction i with molar mass M_i of the polymer fraction i
 $m_i = M_i \cdot n_i$

The probability functions $hm(M_i)$ is interrelated to $hn(M_i)$ in the following way:

$$hm(M_i) = hn(M_i) \cdot M_i / \sum (hn(M_i) \cdot M_i)$$

$$hm(M_i) = \frac{hm_u(M_i)}{\sum_i hm_u(M_i)} = \frac{hn_u(M_i) \cdot M_i}{\sum_i hn_u(M_i) \cdot M_i}$$

In continuous description, one has the following relations.

$$hn(M) \cdot dM = \frac{hn_u(M) \cdot dM}{\int_{Ma}^{Me} hn_u(M) \cdot dM} = \frac{\frac{hm_u(M)}{M} \cdot dM}{\int_{Ma}^{Me} \frac{hm_u(M)}{M} \cdot dM}$$

$$hn(\lg M) \cdot d\lg(M) = \frac{hn_u(\lg M) \cdot d\lg(M)}{\int_{\lg(Ma)}^{\lg(Me)} hn_u(\lg M) \cdot d\lg(M)} = \frac{\frac{hm_u(\lg M)}{\lg(M)} \cdot d\lg(M)}{\int_{\lg(Ma)}^{\lg(Me)} \frac{hm_u(\lg M)}{\lg(M)} \cdot d\lg(M)}$$

$$hm(M) \cdot dM = \frac{hm_u(M) \cdot dM}{\int_{Ma}^{Me} hm_u(M) \cdot dM} = \frac{hn_u(M) \cdot M \cdot dM}{\int_{Ma}^{Me} hn_u(M) \cdot M \cdot dM}$$

3.3 Application of the new random scission model to experimental data

The measured MMD curves show similar profiles as the curves calculated by Eq.(10) or Eq.(14). Using these equation, a least squares fit could generate rate constants in modelling the experimental MMD data. A measured MMD is used as starting distribution and a resulting MMD is calculated by fitting the reaction rate constant. This means that the experimental MMD was used on the one hand as $m(i)$, initial curve, and on the other hand as an experimental MMD at a later time step. Then it is taken as the distribution $M_i(t)$ to be fitted with two fit parameters, namely the reaction rate constant k and a factor for multiplying $m(i)$. The least square fit procedures used the minimization procedure of Powel /16/, which was already applied to problems of thermal analysis /1, 4, 17/.

The matching of the calculated best modelling curve to the experimental curve to be fitted is rather moderate, with standard deviations between 5 and 10%. The k -values scatter, too, as listed in Table 6. They are in the same order of magnitude of values for NC obtained by other methods /4/. The measured MMD seems to contain a shift, which are not fully consistent with the time steps when compared to calculated curves. For example already at the beginning the step from the very initial curve to the next after 2 days is larger than others, this is also true for other time intervals. More consistent data are expected if pure nitrocellulose is investigated which will follow in a future paper. Some evaluation examples with the present data are plotted in the following figures 14 to 17.

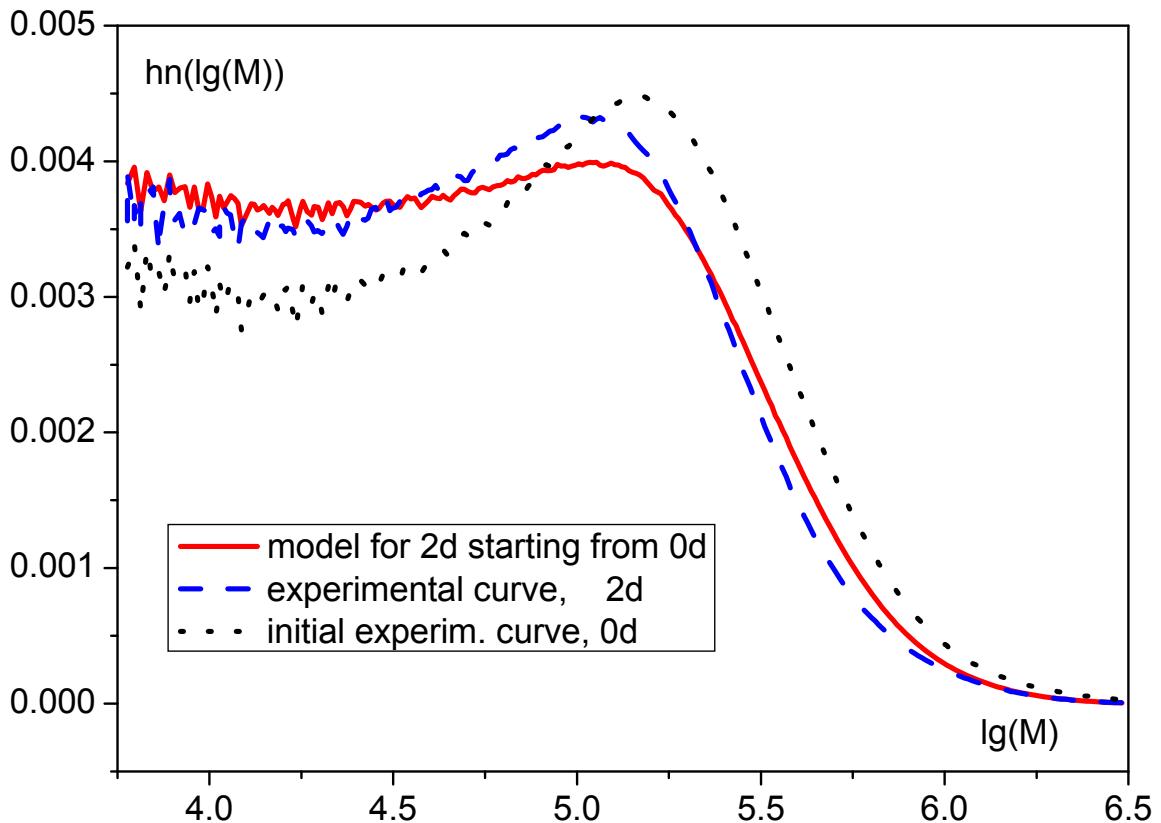


Fig 14: NC-Propellant O5560 stored at 90°C: MMD between 0 day and 2 days, $k t = 0.000145$.

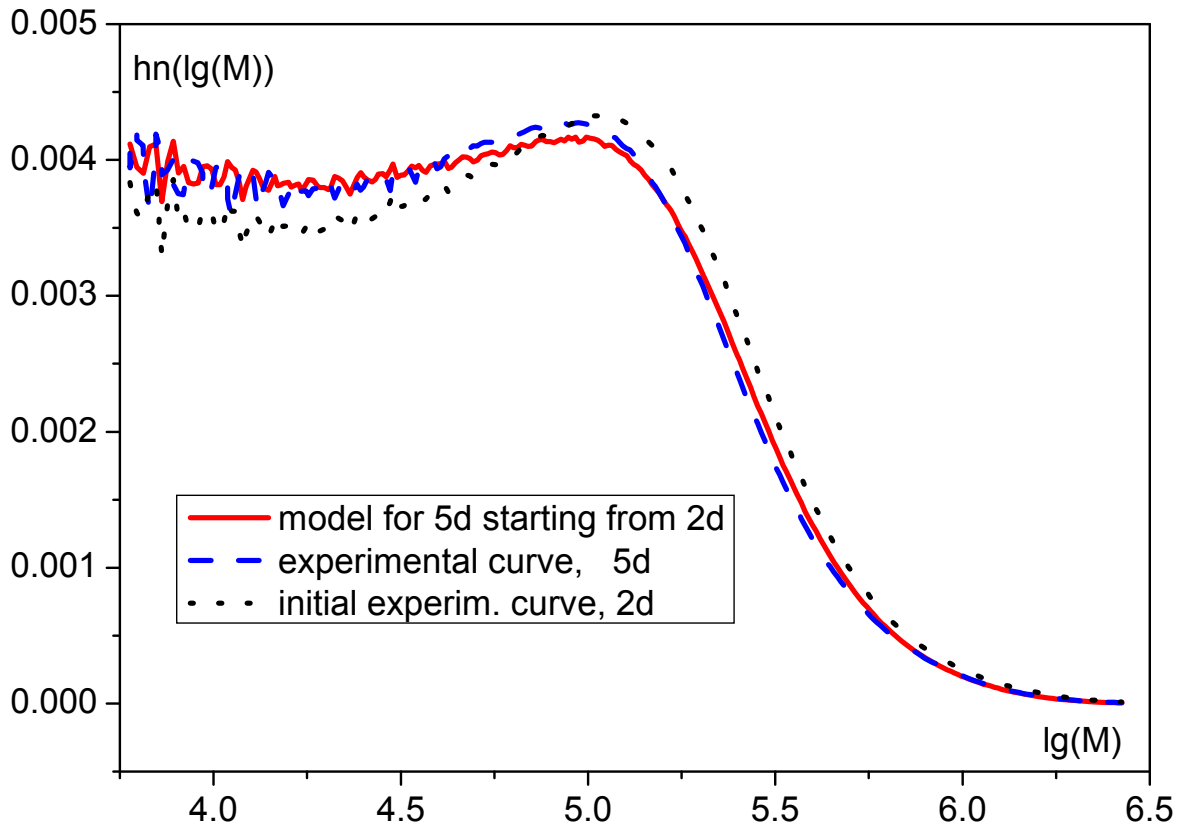


Fig. 15: NC-Propellant Q5560 stored at 90°C: MMD between day 2 and 5, $k t = 0.00013$.

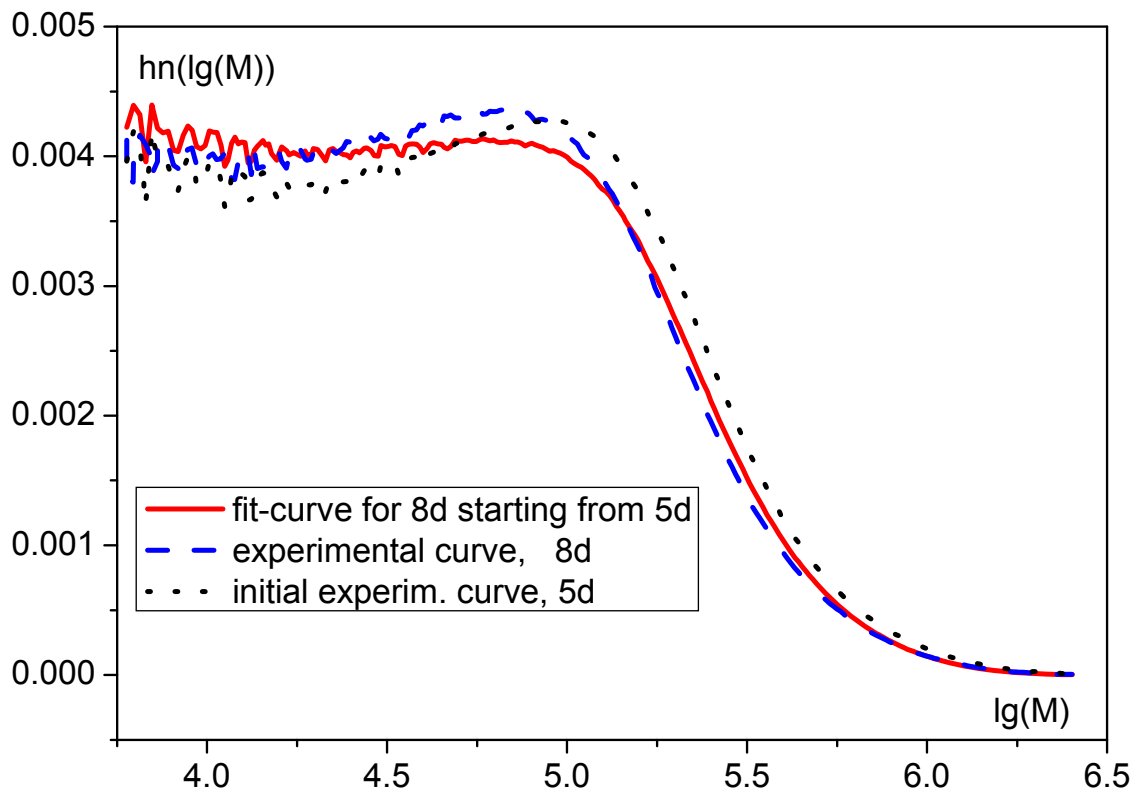


Fig. 16: NC-Propellant Q5560 stored at 90°C: MMD between 5 days and 8 days, $k t = 0.00012$.

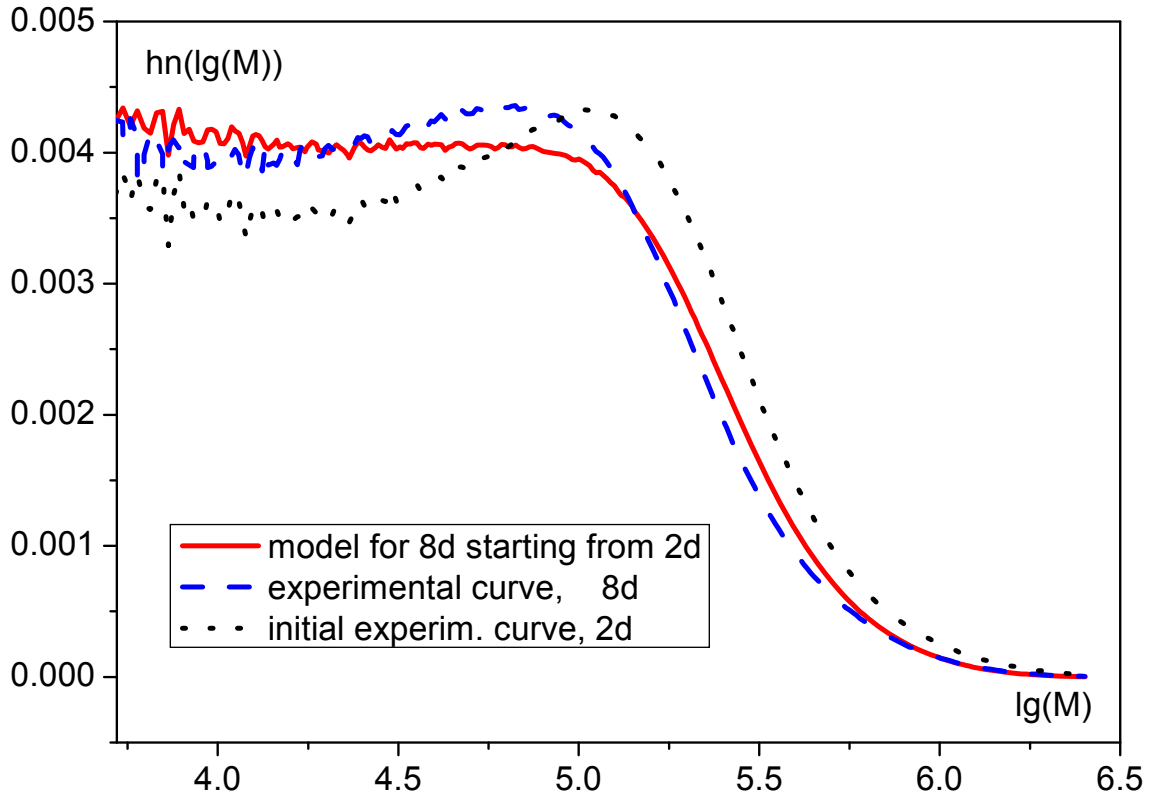


Fig. 17: NC-propellant Q5560 stored at 90°C: MMD between 2 days to 8 days, $k \cdot t = 2.13E-4$.

Table 6: Determined reaction rate constants of chain scission obtained by fit of Eq.(14) to the experimentally determined MMDs of a NC propellant.

propellant aged at 90°C [d]	time period of MMD modelling [d]	k [1/s] determined by MMD modelling	k·t [-]	lg(Z [1/s])=16.6 Ea=42.6 kcal/mol k [1/s] /4/
0 - 2	2	8.40 E-10	1.45 E-04	9.9×10^{-10}
2 - 5	3	5.10 E-10	1.32 E-04	
5 - 8	3	4.60 E-10	1.19 E-04	
0 - 5	5	2.00 E-09	8.64 E-04	
0 - 8	8	7.80 E-10	5.39 E-04	
2 - 8	6	4.10 E-10	2.13 E-04	
0 - 12	12	9.20 E-10	9.54 E-04	

4. Summary and conclusions

The degradation of the nitrocellulose (NC) in gun propellant (GP) Q5560 was investigated with GPC using two mixed bed columns in series. The ageing of the GP was at 70°C, 80°C and 90°C. The obtained data on the mol number averaged mean molar mass M_n have been described with a kinetic model based on random chain scission of the NC chains by decomposition of chain elements, not by mere bond scission. It seems th NC degrades in

two steps with a faster degradation at the beginning of the ageing. This effect was observed already earlier with a rocket propellant see /2b/. Further one can conclude that the slopes of the three Arrhenius lines of the three evaluation parts are not very different and the main difference in the rates arises because of the pre-exponential factor.

The literature on polymer degradation and the modelling of this important phenomenon is quite large. The given references /1 to 23/ concentrate on publications dealing in some way with the kinetic modelling of polymer degradation. Several of them are dealing with the modelling of the whole molar mass distribution (MMD) function, as it was presented here also. The numerical treatment of this model is not a trivial task. This work is a first step in trying to model the degradation of nitrocellulose (NC) and other polymeric material, which can be treated by random chain scission. The results so far obtained are promising. The modelling of the NC degradation via the MMDs could describe the change in MMD by ageing. Starting with a MMD at some time, the MMD at later times was created by varying the rate constant for random chain scission. The obtained values for the reaction rate constants at 90°C are in the range obtained by other methods /4/.

5. Appendix: Kinetic models of molar mass decrease based on averaged quantities of molar mass distribution function

5.1 Random scission of chains by bond splitting between chain elements

First consider the total number of bonds $B(0)$ between chain elements in the sample, which decreases according to a reaction of first order, Eq.(A1).

$$B(t,T) = B(0) \cdot \exp(-k_B(T) \cdot t) \quad (\text{A1})$$

$B(0)$ total number of bonds in sample at time zero
 $B(t,T)$ total number of bonds in sample at time t
 $k_B(T)$ reaction rate constant of first order decrease of bonds

The total number of bonds at time zero in the sample is determined by Eq.(A2)

$$B(0) = \sum_{j=1}^{n_C} B_j(0) = \sum_{j=1}^{n_C} (N_j(0) - 1) = N(0) - n_C(0) \quad (\text{A2})$$

$N(0)$ total number of chain elements: $N(0)$
 $n_C(0)$ total number of chains
 $B_j(0)$ number of bonds in chain j
 $N_j(0)$ number of chain elements in chain j

The total number of bonds at any time t in the sample is determined by Eq.(A3). The total number of chain elements does not change, so $N(t,T)=N(0)$.

$$B(t,T) = N(0) - n_C(t,T) = N(t,T) - n_C(t,T) \quad \text{with } N(0) = N(t,T) \quad (\text{A3})$$

With Eq.(A2) and (A3) the ratio of total number of bonds according to Eq.(A4) is determined.

$$\frac{B(t,T)}{B(0)} = \frac{N(0) - n_C(t,T)}{N(0) - n_C(0)} = \frac{1 - \frac{n_C(t,T)}{N(0)}}{1 - \frac{n_C(0)}{N(0)}} \quad (\text{A4})$$

Introducing via the degree of polymerisation the mol number averaged mean molar mass Mn , Eq.(A5) and Eq.(A6), one arrives at Eq.(A7) in combining Eq.(A4) and Eq.(A1).

$$\frac{n_C(t,T)}{N(0)} = \frac{m}{Mn(t,T)} \quad (\text{A5})$$

$$\frac{n_C(0)}{N(0)} = \frac{m}{Mn(0)} \quad (\text{A6})$$

$Mn(0)$ polymer fraction mol number averaged mean molar mass at time zero
 $Mn(t,T)$ polymer fraction mol number averaged mean molar mass at time t
 $Pn(0)$ polymer fraction mol number averaged degree of polymerisation at zero
 $Pn(t,T)$ polymer fraction mol number averaged degree of polymerisation at time t

$$\frac{1 - \frac{m}{Mn(t,T)}}{1 - \frac{m}{Mn(0)}} = \frac{1 - \frac{1}{Pn(t,T)}}{1 - \frac{1}{Pn(0)}} = \exp(-k_B(T) \cdot t) \quad (\text{A7})$$

Eq.(A7) is already the final formulation of the decrease of the mean molar mass Mn by random chain splitting caused by pure bond splitting. It may be applied in the forms of Eq.(A8) or Eq.(A9), whereby Eq.(A9) is preferable. The differential kinetic expression of Eq.(A8) or Eq.(A9) is given in Eq.(A10).

$$\ln\left(1 - \frac{m}{Mn(t,T)}\right) = \ln\left(1 - \frac{m}{Mn(0)}\right) - k_B(T) \cdot t \quad (\text{A8})$$

$$\frac{Mn(t,T)}{Mn(0)} = \frac{\exp(+k_B(T) \cdot t)}{1 + \frac{Mn(0)}{m} \cdot (\exp(+k_B(T) \cdot t) - 1)} \quad (\text{A9})$$

$$\left(\frac{d\left(\frac{Mn(t,T)}{m}\right)}{dt}\right)\Bigg|_T = -k_B(T) \cdot \left(-\left(\frac{Mn(t,T)}{m}\right) + \left(\frac{Mn(t,T)}{m}\right)^2\right) \quad (\text{A10})$$

With the approximation shown in Eq.(A11) one transforms Eq.(A8) to Eq.(A12)

$$\ln(x) \approx x - 1 \text{ for } x \text{ about } 1 \quad (\text{A11})$$

$$\frac{m}{Mn(t,T)} = \frac{m}{Mn(0)} + k_B(T) \cdot t \quad (\text{A12})$$

Another allowed approximation, which may be found not so obvious than the one shown, is to assume that k_B is always very small and the product $k_B \cdot t$ is also small. Then by usual approximation of an exponential one arrives from Eq.(A9) at Eq.(A13), The differential kinetic expression is given in Eq.(A14). From the last two equations one may recognize that the decrease of mean molar mass follows formally the equation of a reaction of second order.

$$\frac{Mn(t,T)}{Mn(0)} = \frac{1}{1 + \frac{Mn(0)}{m} \cdot k_B(T) \cdot t} \quad (A13)$$

$$\left(\frac{d\left(\frac{Mn(t,T)}{m}\right)}{dt} \right) \Bigg|_T = -k_B(T) \cdot \left(\frac{Mn(t,T)}{m}\right)^2 \quad (A14)$$

5.2 Random scission of chains by decomposition of chain elements

Another modelling base for describing the decrease of mean molar mass is the random chain scission by decomposition of one chain element or monomer unit, see also /1/. This model is especially suitable for nitrocellulose, because with NC the chain scission is accompanied by real material degradation, which is recognizable by the formation of small degradation products as water CO_2 , CO , N_2 and others. It is assumed the total number of chain elements is $N(0)$ at time zero and that this number decreases according to a reaction of zero order, Eq.(A15). The number $N(0)$ can be expressed by the number of chains $n_C(0)$ in the sample multiplied by the mol number averaged degree of polymerisation $Pn(0)$, Eq.(A16). The same procedure is possible for $N(t,T)$, Eq.(A17).

$$N(t,T) = N(0) \cdot \exp(-k_M(T) \cdot t) \quad (A15)$$

$$N(0) = n_C(0) \cdot Pn(0) = n_C(0) \cdot \frac{Mn(0)}{m} \quad (A16)$$

$$N(t,T) = n_C(t,T) \cdot Pn(t,T) = n_C(t,T) \cdot \frac{Mn(t,T)}{m} \quad (A17)$$

$N(0)$	total number of chain elements at time zero
$n_C(0)$	total number of chains at time zero
$Pn=Mn/m$	degree of polymerization
m	molar mass of chain element E
Mn	polymer fraction mol number averaged mean molar mass

There is a formation of one new chain by every decomposition of one chain element, except if an end-standing element decomposes. But because the number of elements is much larger than the number of chains for a normal polymer, it is a very good approximation to assume the forming of a new chain by decomposing a chain element. The number of new chains, $K(t,T)$ is then given by Eq.(A18) and Eq.(A19) gives the total number of chains at time t. Inserting $N(0)$ and $N(t,T)$ from Eq.(A16) and Eq.(A17) into Eq.(A19) results in Eq.(A20), which gives by rearrangement Eq.(A21). Forming the ratio of chain

elements gives Eq.(A22), from where the derivation of Eq.(A23) and finally Eq.(A24) follows, the model formulation.

$$K(t, T) = N(0) - N(t, T) \quad (\text{A18})$$

$$n_c(t, T) = n_c(0) + N(0) - N(t, T) \quad (\text{A19})$$

$$n_c(t, T) + n_c(t, T) \cdot \frac{Mn(t, T)}{m} = n_c(0) + n_c(0) \cdot \frac{Mn(0)}{m} \quad (\text{A20})$$

$$n_c(t, T) = n_c(0) \cdot \frac{1 + \frac{Mn(0)}{m}}{1 + \frac{Mn(t, T)}{m}} \quad (\text{A21})$$

$$\frac{N(0)}{N(t, T)} = \frac{n_c(0) \cdot \frac{Mn(0)}{m}}{n_c(t, T) \cdot \frac{Mn(t, T)}{m}} = \frac{\frac{Mn(0)}{m}}{\frac{1 + \frac{Mn(0)}{m}}{1 + \frac{Mn(t, T)}{m}} \cdot \frac{Mn(t, T)}{m}} = \frac{1 + \frac{m}{Mn(t, T)}}{1 + \frac{m}{Mn(0)}} \quad (\text{A22})$$

$$\frac{n_c(0) \cdot \frac{Mn(0)}{m}}{n_c(t, T) \cdot \frac{Mn(t, T)}{m}} = \frac{1 + \frac{m}{Mn(t, T)}}{1 + \frac{m}{Mn(0)}} = \frac{1 + \frac{1}{Pn(t, T)}}{1 + \frac{1}{Pn(0)}} = \frac{N(0)}{N(t, T)} = \exp(+k_M(T) \cdot t) \quad (\text{A23})$$

$$\frac{1 + \frac{m}{Mn(t, T)}}{1 + \frac{m}{Mn(0)}} = \frac{N(0)}{N(t, T)} = \exp(+k_M(T) \cdot t) \quad (\text{A24})$$

$$\ln\left(1 + \frac{m}{Mn(t, T)}\right) = \ln\left(1 + \frac{m}{Mn(0)}\right) + k_M(T) \cdot t \quad (\text{A25})$$

$$\frac{Mn(t, T)}{Mn(0)} = \frac{\exp(-k_M(T) \cdot t)}{1 + \frac{Mn(0)}{m} \cdot (1 - \exp(-k_M(T) \cdot t))} \quad (\text{A26})$$

$$\left(\frac{d\left(\frac{Mn(t, T)}{m}\right)}{dt}\right)\bigg|_T = -k_M(T) \cdot \left(\left(\frac{Mn(t, T)}{m}\right) + \left(\frac{Mn(t, T)}{m}\right)^2\right) \quad (\text{A27})$$

The model according to Eq.(A24) can be used in the forms of Eq.(A25) or Eq.(A26), whereby Eq.(A26) should be preferred. The Eq.(A27) shows the differential kinetic expression.

From Eq.(A26) it is obvious that $Mn(t)/Mn(0)$ degrades rapidly already with small conversions rates, which means that $k_M(T) t \ll 1$. Therewith Eq.(A26) can be approximated by Eq.(A29). Eq.(A28) follows from Eq.(A25) by the usual approximation $\ln(x) \approx x-1$ with small x . In this approximation the differential kinetic expression is given by Eq.(A30).

$$\frac{m}{Mn(t, T)} = \frac{m}{Mn(0)} + k_M(T) \cdot t \quad (A28)$$

$$\frac{Mn(t, T)}{Mn(0)} = \frac{1}{1 + \frac{Mn(0)}{m} \cdot k_M(T) \cdot t} \quad (A29)$$

$$\left(\frac{d\left(\frac{Mn(t, T)}{m}\right)}{dt} \right) \Bigg|_T = -k_M(T) \cdot \left(\frac{Mn(t, T)}{m}\right)^2 \quad (A30)$$

In comparison with the above discussed model one can see that in the approximated forms the two models are not distinguishable.

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