

Characterization of ageing of NC based gun propellants by molar mass degradation of nitrocellulose and its modelling by random chain scission models

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Motivations and Objectives

- Nitrocellulose (NC) is an important ingredient in gun and rocket propellants, also in **recently developed** ones, having improved IM characteristics, as the DNDA-RDX-NC based GP from Fraunhofer ICT /1, 2/ or the ECL™ series of Nitrochemie Wimmis.
This means NC has properties which are not reached by other energetic binders up today.
- Nitrocellulose decomposes slowly intrinsically and after some induction time also autocatalytically, because of low kinetic energy barriers
- The autocatalytic decomposition can be suppressed by stabilizers, but not the intrinsic one
- The intrinsic decomposition of NC leads to scissioning of the NC chains, expressed as decrease in mean molar masses with time-temperature load

- Chain scissioning of NC is accompanied by NO_x formation, which consumes stabilizers
- The chain scissioning is very sensitive to decomposition: already decomposing of one chain element leads to roughly half of the original chain length
- With decrease of chain length the mechanical strength of NC products is reduced

- **Therefore: Determination of NC chain degradation is a sensitive monitoring for NC products**

Determination of NC chain length degradation

Generally the chain length degradation of a polymer is best determined by GPC (Gel Permeation Chromatography) also called SEC (Size Exclusion Chromatography)

This is the case also with NC.

At ICT this method was introduced in the early 1980s and several publications have been published on the early results and on later work [/3, 4, 5, 6/](#).

Also at Nitrochemie Wimmis (NCW) the GPC method was introduced at the same time and some early RR on GPC have been performed between ICT and NCW. End of the 1990 AWE has started a lot of GPC work on NC and HMX bonded by NC [/7/](#).

With time the importance of this method was increasingly recognized and finally found its expression in the implementation of the GPC method in the recently updated NC-STANAG.

NC STANAG: STANAG 4178 “Assessing the Quality of Nitrocellulose Deliveries from one NATO Nation to Another”, Edition 2 [/8/](#).

For this an applicable method was worked out and especially adapted for analysing NC by collaboration between: AWE, Univ. Cranfield-Shrivenham, Fraunhofer ICT, Nitrochemie Wimmis, TNO-Rijswijk [/9, 10, 11, 12/](#).

How to use GPC results on NC degradation

First, one gets the elugramme of the size-separated NC chains, means a frequency distribution of chain length versus retention volume V_e .

This elugramme is transformed to a molar mass distribution function (MMD), by use of a calibration function between retention volume V_e and molar mass M of a calibration substance.

Then the characteristic quantities of this molar mass distribution (MMD) are calculated:

Mean molar masses M_n , M_w , M_z and polydispersity $D = M_w/M_n$

M_n : averageing done by [polymer fractional mol number](#) to weigh the fractions

M_w : averageing done by [polymer fractional mass](#) to weigh the fractions

M_z : averageing done by [polymer fractional z-weight](#) to weigh the fractions

M_p : molar mass at peak maximum of the MMD

These data can be established as function of ageing of NC or the NC in a propellant respectively.

[Here the degradation of NC in the triple base gun propellant Q5560 \(19 hole, 27mm machine gun\) is presented.](#)

Not only NC polymer chain degradation....

Random chain scissioning of polymer chains is widespread.

Hydrolysis of polymeric esters

Attack on thermoplastic elastomers by 'aggressive' substances as ADN, HNF, nitric acid plasticizers as nitroglycerine, TMETN, BTTN, NENA,..

Attack on binders as GAP and HTPB by CL-20, RDX,...

PolyvinylNitrate (PVN)

M.Ä. Bohn, J. Aniol, M. Dörich, K. Hartlieb, H. Pontius

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

Paper 73, pages 73-1 to 73-18 in Proceedings of the 37th International Annual Conference of ICT 2006, June 27 to 30, 2006, Karlsruhe, Germany. Fraunhofer-Institut für Chemische Technologie (ICT), D-76318 Pfinztal.

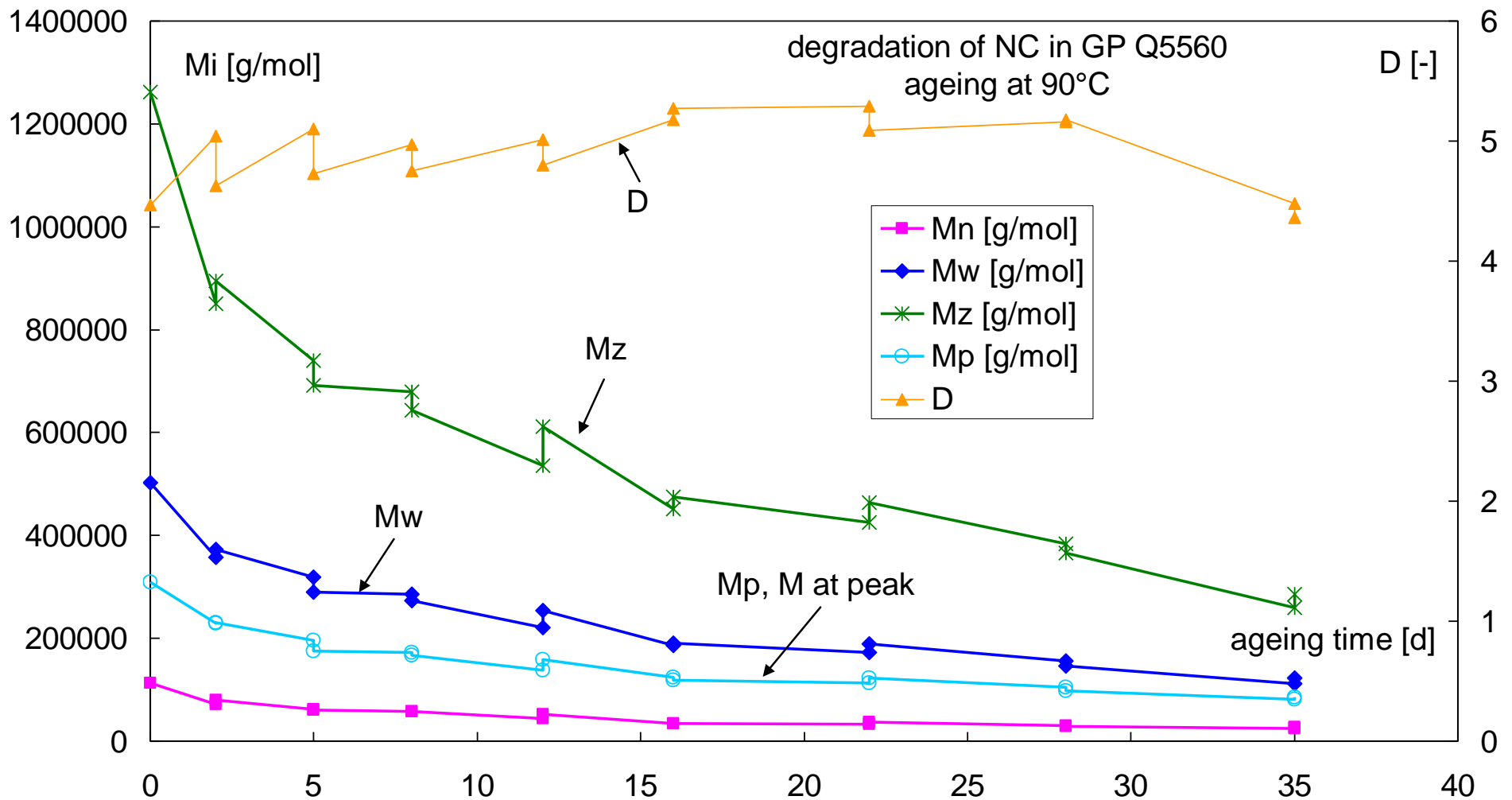
Bohn M.A., Dörich M., Aniol J., Pontius H., Kempa P.B., Thome V.

Reactivity between ϵ -CL20 and GAP in Comparison to β -HMX and GAP.

Paper 4, pages 4-1 to 4-30, in Proceedings of the 35th International Annual Conference of ICT, June 29 to July 2, 2004, Karlsruhe, Germany. Fraunhofer-Institut für Chemische Technologie (ICT), D-76318 Pfinztal-Berghausen, Germany.

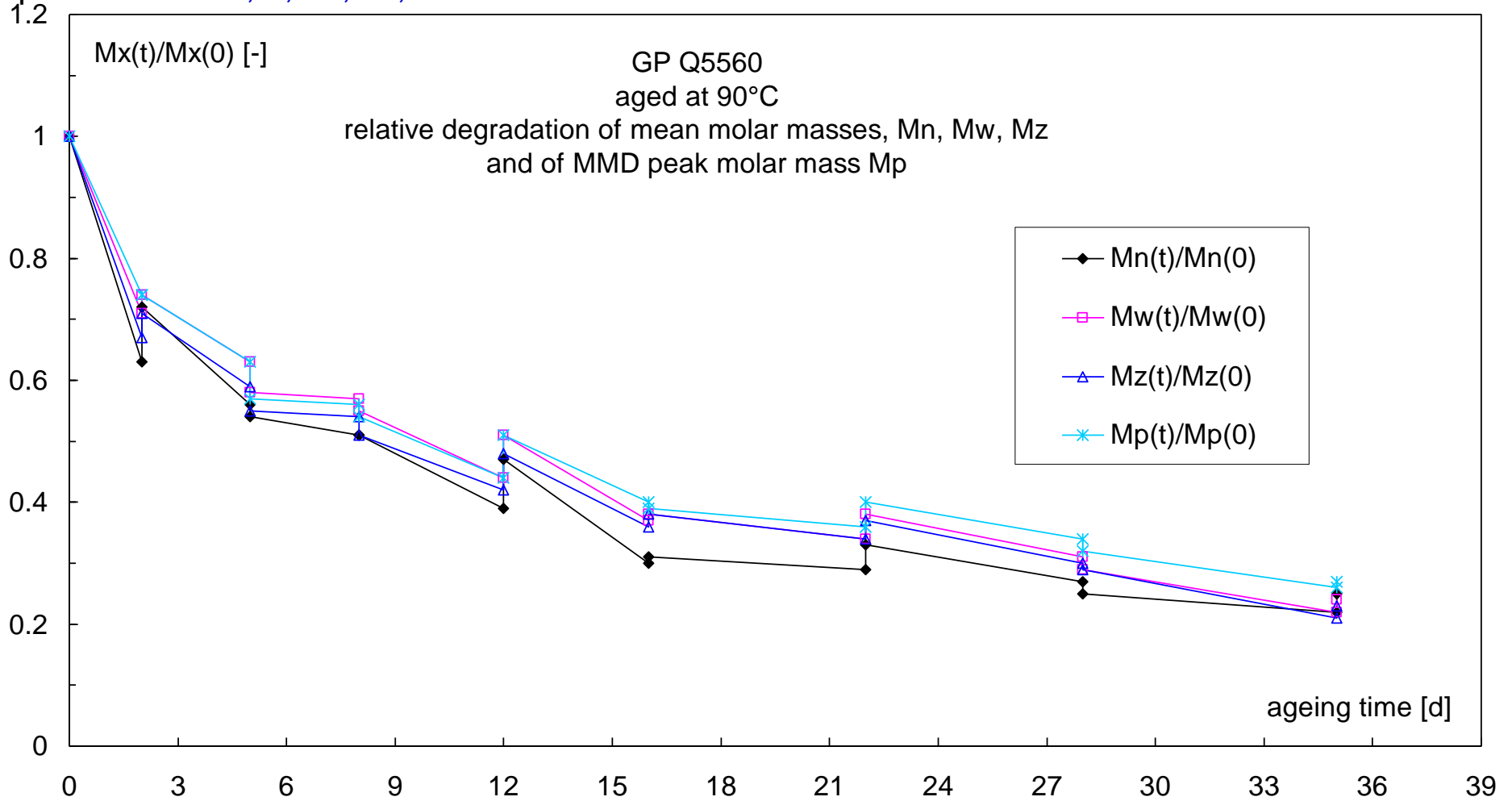
Mean molar masses Mn, Mw, Mz and MMD-peak Mp as function of ageing

Results for the NC degradation in gun propellant Q5560, 27 mm, triple base



Relative mean molar masses and MMD-peak M_p as function of ageing

If the data **are measured and evaluated well**, all the mean molar masses nearly coincide in relative representation /8, 9, 10, 11, 12/.



Use of GPC results

Determine NC degradation as function of time and temperature

90°C, 80°C, 70°C, 60°C,...

Which ageing times can be chosen – orientation can be obtained from:

- time temperature loads given in AOP 48, which are adapted for NC-based materials
- generalized van't Hoff extrapolation /15/
- own ageing experience
- ageing times chosen for basic investigations
- literature data

Time-temperature data can be kinetically parameterized, with NC-based material by

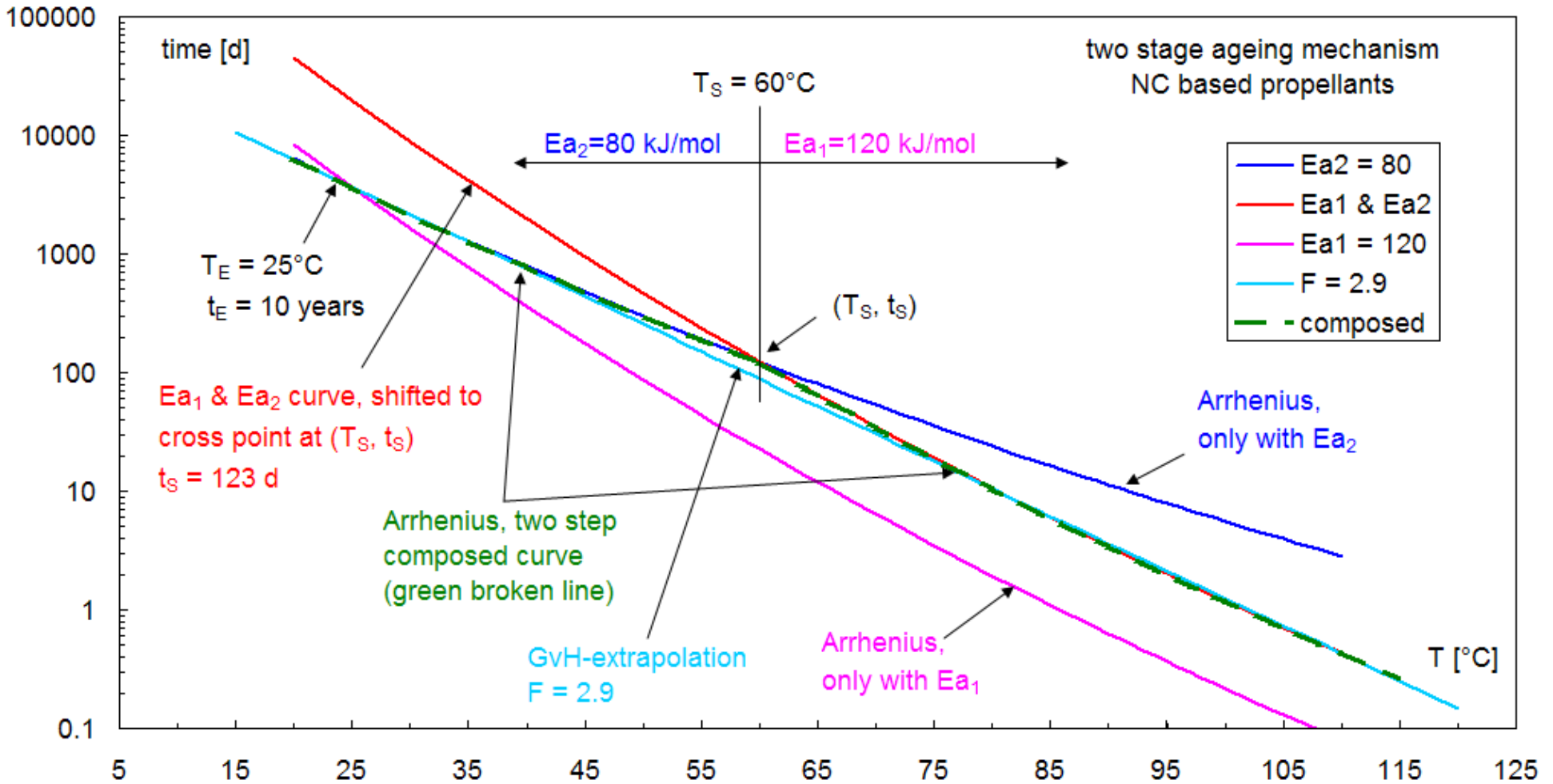
- Arrhenius $k(T)_{Arrh} = Z \cdot \exp(-Ea/RT)$
- Generalized van't Hoff (GvH) $k(T)_{GvH} = H \cdot F_{\Delta T}^{+(T/\Delta T)}$

Necessary for this is the determination of rate constants

H	GvH pre-factor
$F_{\Delta T}$	scaling factor with regard to chosen ΔT
T	temperature
ΔT	temperature scaling interval, mostly 10°C

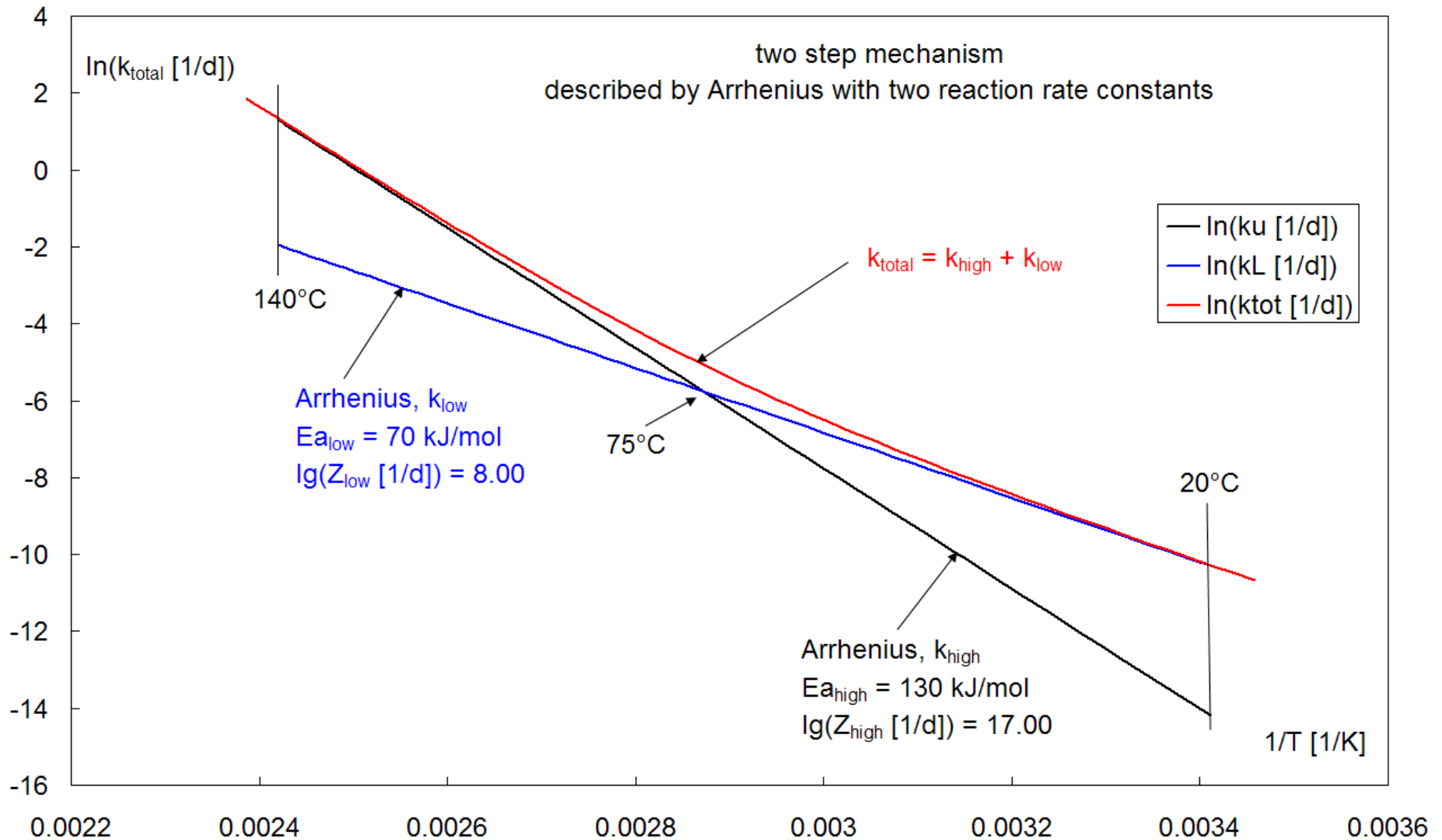
Z	expon. pre-factor
exp	Euler number e
T	temperature (absolute)
Ea	activation energy
R	general gas constant

Description of two-step ageing of NC based material with GvH

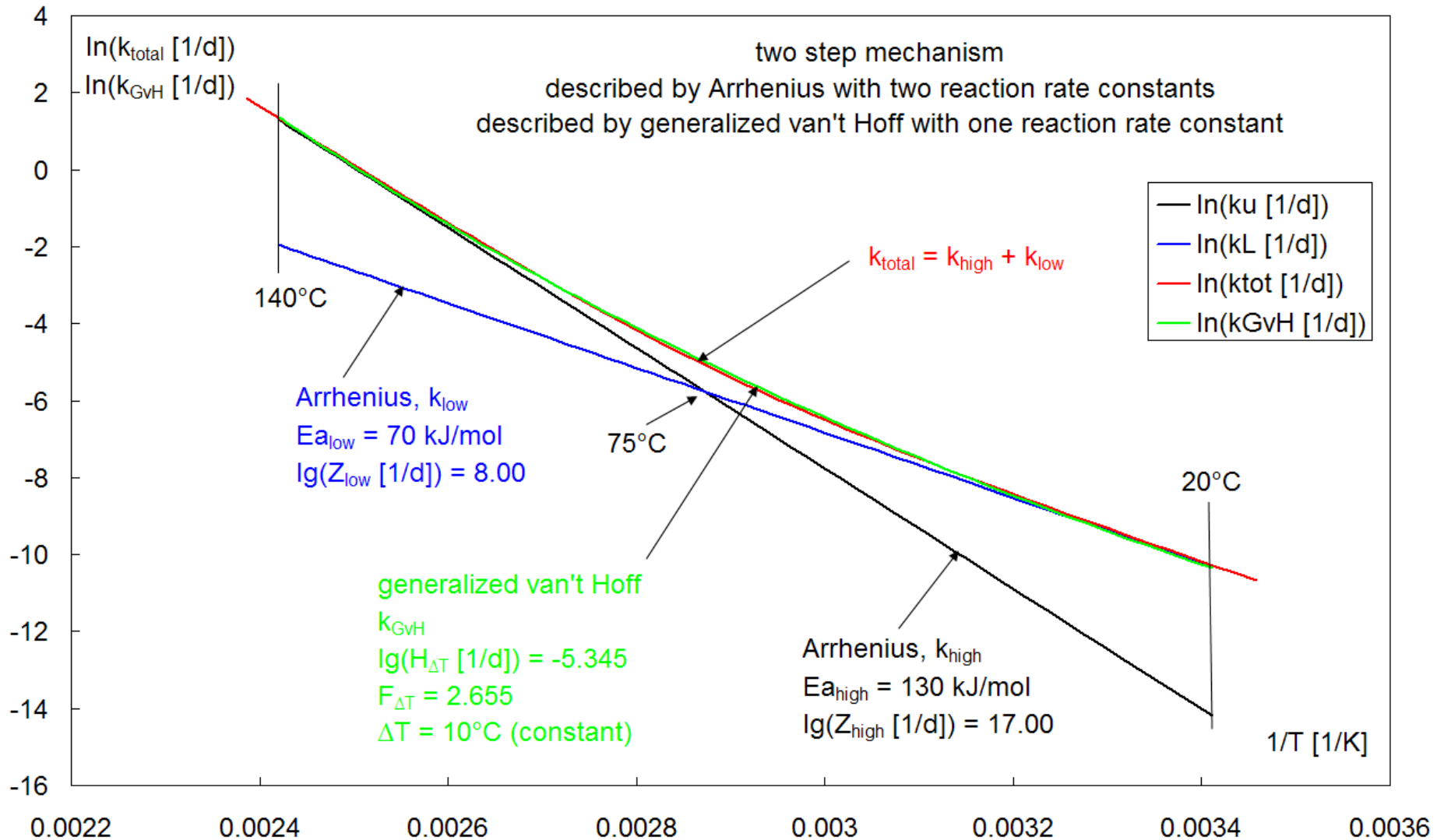


This two step mechanism for NC-based materials is included in STANAG 4582 and AOP 48, Ed. 2 /13, 14/

Description of two step mechanism by two Arrhenius rate constants



Description of two step mechanism by generalized van't Hoff (see /15/)



Choosing the type of temperature parameterization

The scission process is chemically based

Arrhenius behaviour can be expected for the rate constants.

If **intrinsic dual mechanistic behaviour** occurs, as it is assumed with NC-based materials (see AOP 48 and STANAG 4582), then the **generalized van't Hoff parameterization** is of advantage /15/.

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Prediction of equivalent time-temperature loads for accelerated ageing to simulate preset in-storage ageing and time-temperature profile loads.

Paper 78, pages 78-1 to 78-28 in Proceedings of the 40th International Annual Conference of ICT on 'Energetic Materials – Characterization, Modelling, Validation', June 23 to 26, 2009, Karlsruhe, Germany. ISSN 0722-4087.

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

Kinetic models to describe NC chain scission and molar mass degradation

The model must be able to describe the whole course of $M_x = f(t)$ as precise as possible

The model should have a true kinetic base, developed from the type of scission process of NC chains

Only this ensures a correct extrapolation

- Model based on random chain scission (CS) by bond scission between chain elements (BS)
no material is lost, no mass loss; model CS-BS
- Model based on random chain scission (CS) by chain element decomposition (ED)
material is lost, mass loss occurs; model CS-ED
- Model based on random chain scission (CS) by bond scission between chain elements (BS)
and recombination of chains (CR)
no material is lost, no mass loss; model CS-BS with CR
- Model based on random chain scission (CS) by chain element decomposition (ED)
and recombination of chains (CR)
material is lost, mass loss occurs; model CS-ED with CR

Which molar mass is the right one for the kinetic description of chain degradation in polymers

Kinetic processes in chemistry describe reaction of atoms or molecules and between them. The adequate quantity followed is a concentration, means 'particle' **number** per any unit (volume, mass,...)

Conclusion

The right mean molar mass is the one which 'counts' particles, means which is based on mol numbers – this is **M_n**

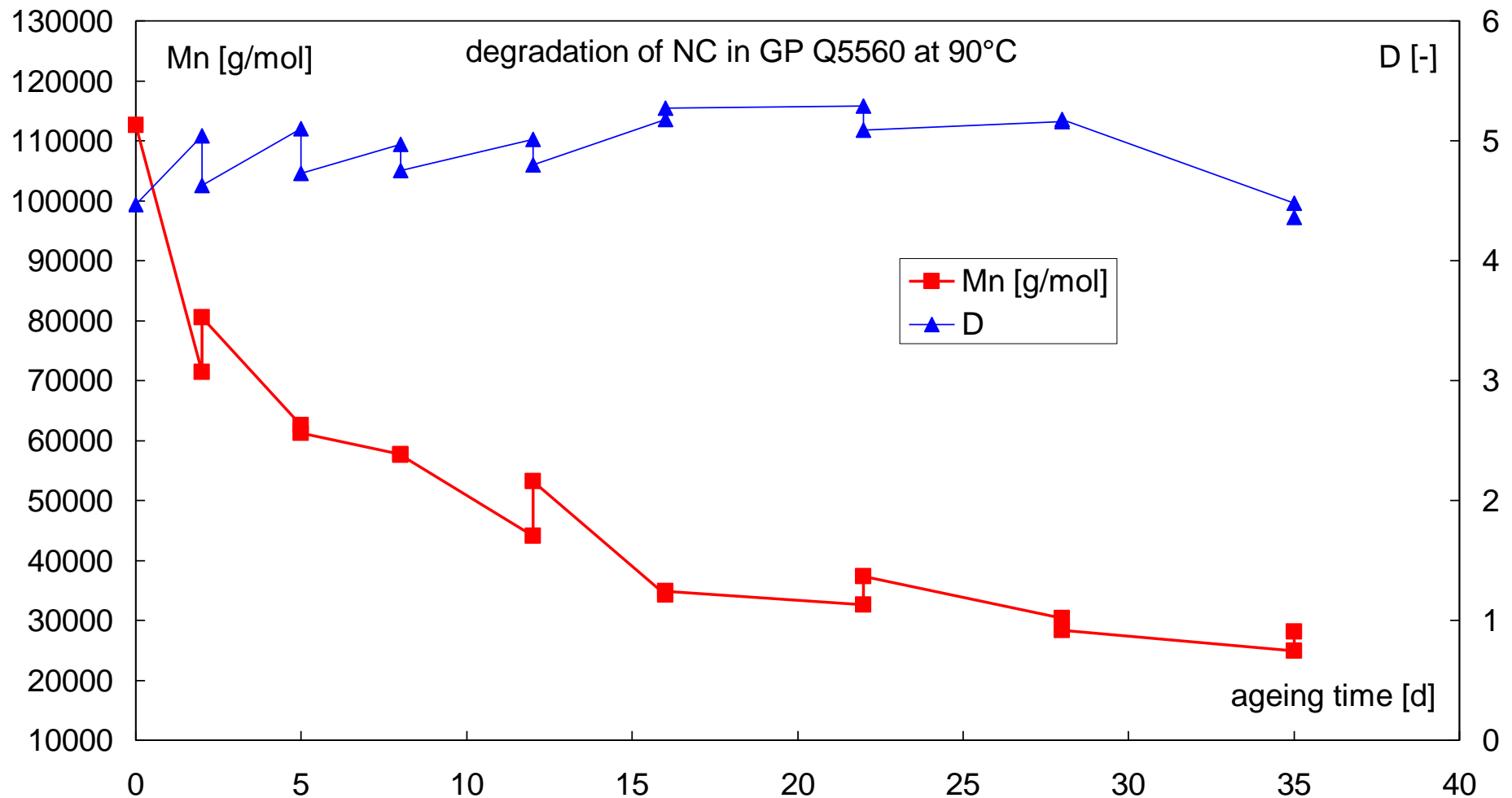
So the models are formulated with **M_n**, which is the center of gravity molar mass of the distribution function **h_n**, the fractional mol number related MMD

Remark:

With RI and UV detectors the distribution function **h_m** is determined, the fractional mass related MMD;

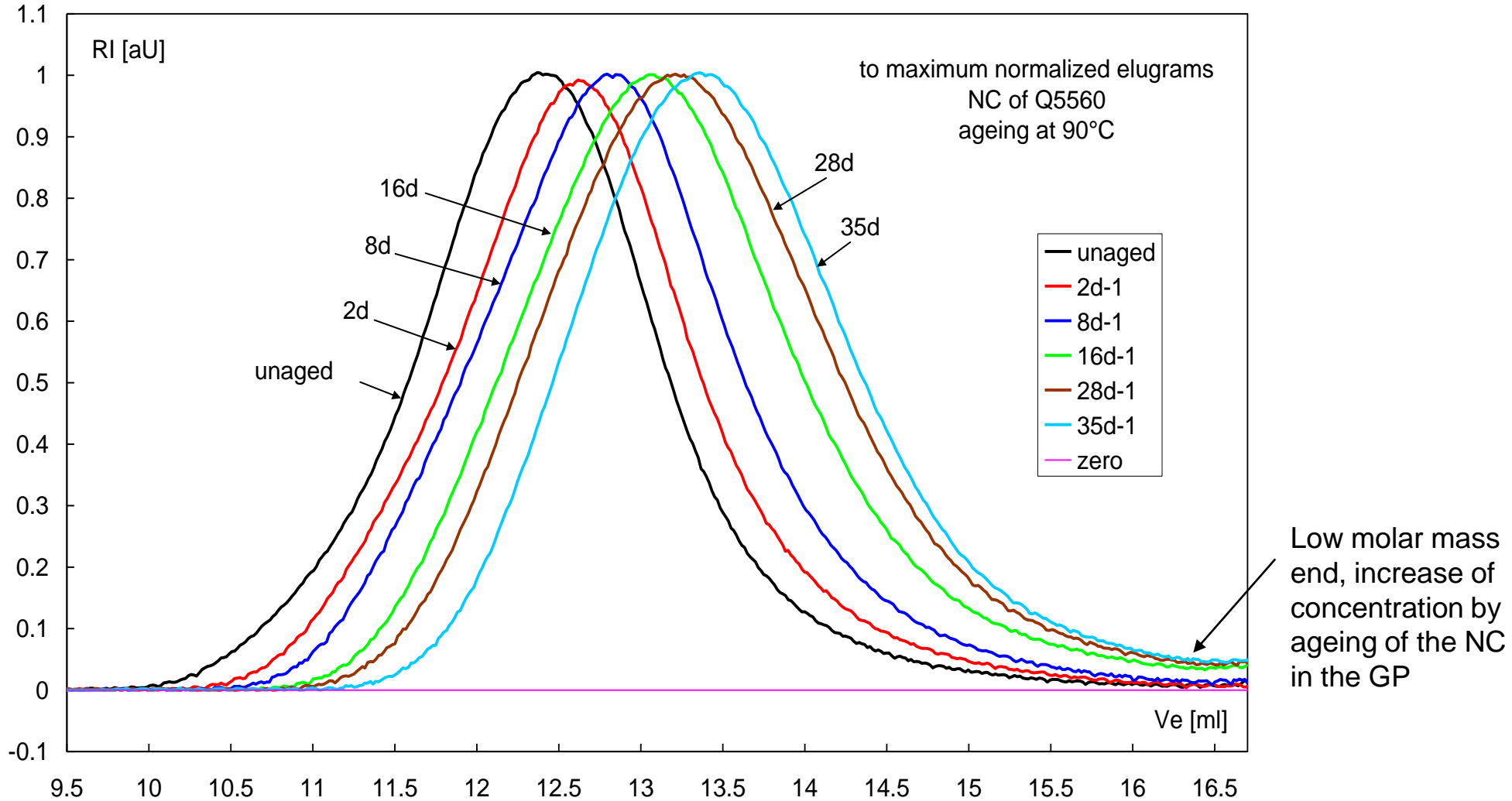
Use of kinetic modelling to get rate constants

The Mn data obtained from the MMD of NC in GP Q5560 are used for modelling



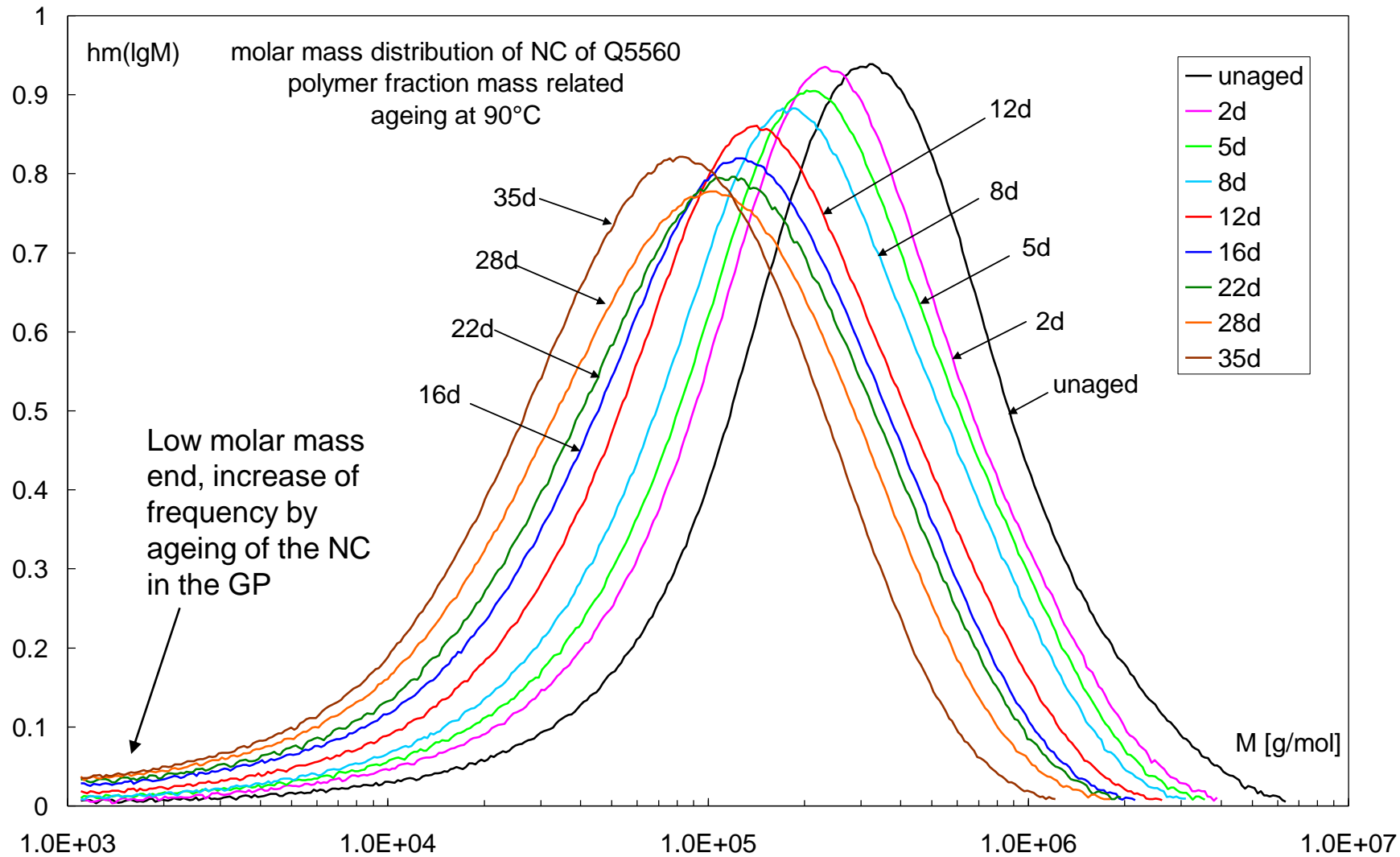
Elugrammes of the NC degradation of GP Q5560, obtained by RI detection

Concentration related elugrammes of the NC of GP Q5560, obtained by refractive index (RI) detection



Area normalized molar mass distributions hm of NC degradation

Frequency distribution of the fractional polymer parts as function of molar mass



Model with chain scission by **bond splitting** between chain elements

- B(t): number of bonds between chain elements in polymer sample
Nm(t): number of chain elements in the polymer sample
nc(t) number of polymer chains in the sample, $nc(t) = Nm(t) / (Mn(t)/m)$
Mn(t) mol number averaged mean molar mass
m molar mass of one chain element of the polymer

Model set-up

Formation rate of new chains is proportional to the present number bonds B(t) between chain elements Nm(t).

Splitting of one bond splits a chain. This process is of first order.

The number of bonds B(t) decreases to reaction of first order. **The number of chain elements stays constant. No mass loss.**

$$\frac{dnc(t)}{dt} = k_{B1} \cdot B(t)$$

$$B(t, T) = B(0) \cdot \exp(-k_{B1}(T) \cdot t)$$

Model CS-BS

$$\frac{Mn(t)}{m} = \frac{\exp(+k_{B1} \cdot t)}{\frac{m}{Mn(0)} + (\exp(+k_{B1} \cdot t) - 1)}$$

See also /18/

Model with chain splitting by chain element decomposition

- B(t): number of bonds between chain elements in polymer sample
Nm(t): number of chain elements in the polymer sample
nc(t) number of polymer chains in the sample, $nc(t) = Nm(t) / (Mn(t)/m)$
Mn(t) mol number averaged mean molar mass
m molar mass of one chain element of the polymer

Model set-up

Formation rate of new chains is proportional to the present number of chain elements Nm(t).
Destruction of one chain element splits a chain. This process is of first order. **Number of chain elements decrease steadily. Mass loss occurs.** See also /7, 8/

$$\frac{dnc(t)}{dt} = k_{M1} \cdot Nm(t)$$

$$N(t, T) = N(0) \cdot \exp(-k_{M1}(T) \cdot t)$$

Model CS-ED

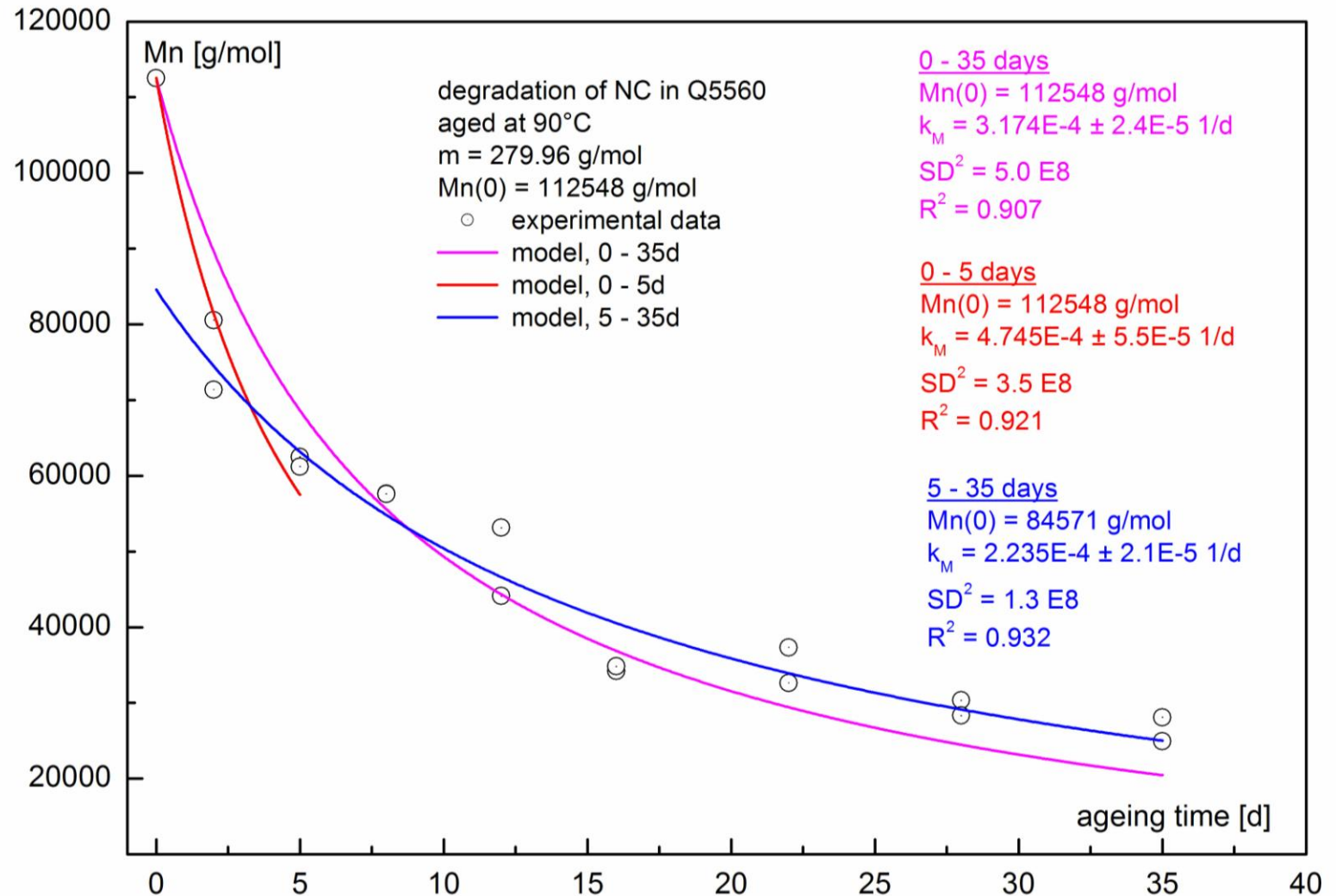
$$\frac{Mn(t)}{m} = \frac{\exp(-k_{M1} \cdot t)}{\frac{m}{Mn(0)} + (1 - \exp(-k_{M1} \cdot t))}$$

First derived by Norbert Eisenreich at Fraunhofer ICT in the 1980s
See also /16, 17, 18/

Results: model with chain element decomposition: Q5560 at 90°C

The description with model CS-ED (or CS-BS) is not satisfying.

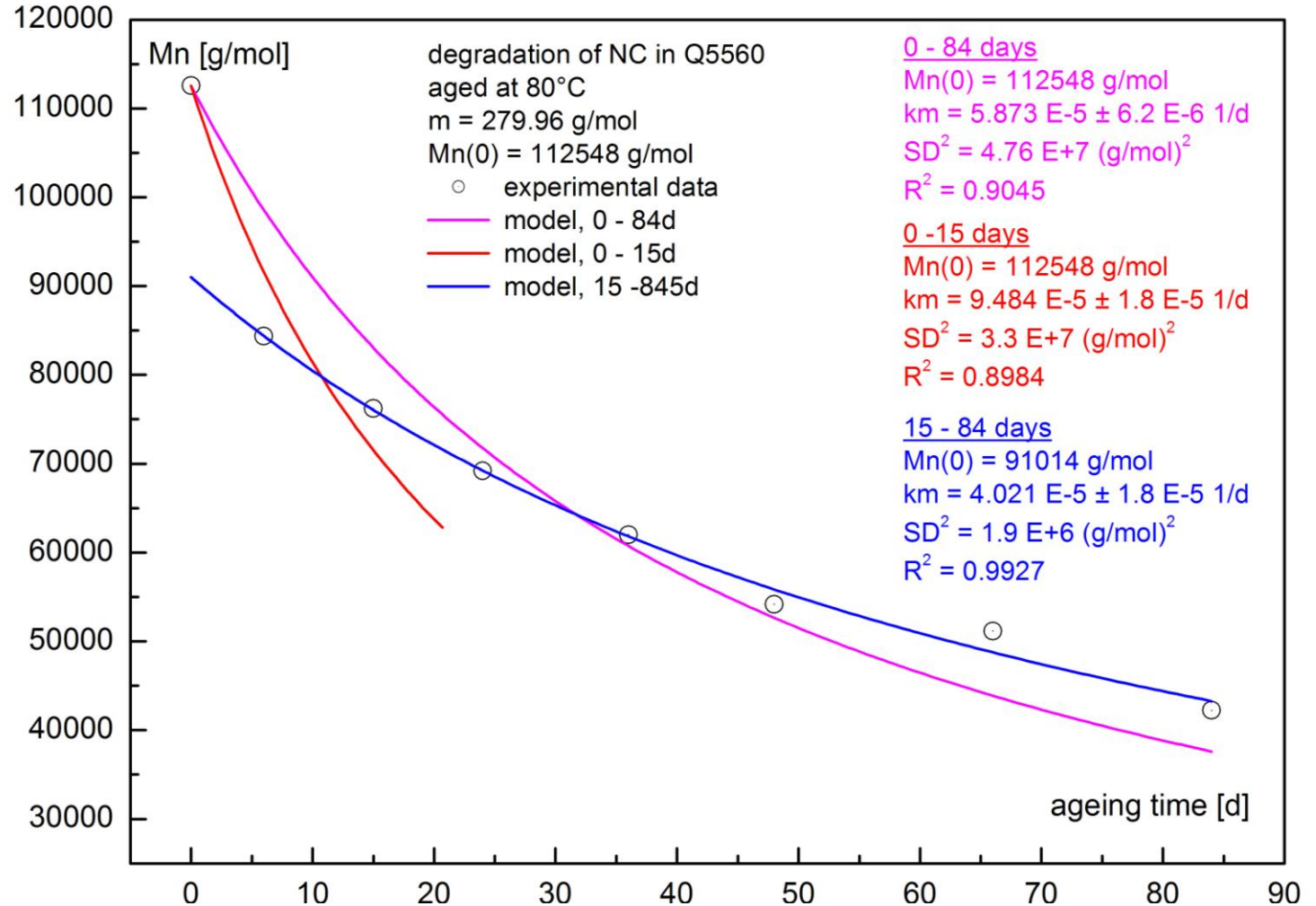
The description must be done in two steps, to get adequate modelling.



Results: model with chain element decomposition: Q5560 at 80°C

The description with model CS-ED (or CS-BS) is not satisfying.

The description must be done in two steps, to get adequate modelling.



Model chain splitting by **bond scission** with **chain recombination** - $k_{B2} \cdot (n(t) - n(0))$

Model CS-BS with CR

Model set-up

- Formation rate of new chains is proportional to the present number of bonds $B(t)$ between chain elements $Nm(t)$.
Splitting of one bond splits a chain. This process is of first order.
The number of bonds $B(t)$ decreases to reaction of first order. **The number of chain elements stays constant. No mass loss.**
- The loss rate of chains is proportional to the number of chains $n(t) - n(0)$ already formed.
The active ends arising by splitting are radicals and attack the reservoir of chains.
The second reactant of this bimolecular reaction is nearly constant and is included in the reaction rate constant k_{B2}

$$\frac{dnc(t)}{dt} = k_{B1} \cdot B(t) - k_{B2} \cdot (nc(t) - n(0))$$

$$Mn(te) = m \cdot \frac{k_{B1} + k_{B2}}{k_{B1} + k_{B2} \cdot \frac{m}{Mn(0)}}$$

$Mn(te)$ =plateau value in Mn at t versus ∞ ; **Note:** $Mn(te, T)$ is T-dependent via the $k_{B1}(T)$ and $k_{B2}(T)$

$$\frac{Mn(t)}{m} = \frac{1}{\frac{m}{Mn(0)} \exp(-(k_{B1} + k_{B2}) \cdot t) + \frac{k_{B1} + k_{B2} \cdot \frac{m}{Mn(0)}}{k_{B1} + k_{B2}} \cdot (1 - \exp(-(k_{B1} + k_{B2}) \cdot t))}$$

Model chain splitting by element decomposition with chain recombination- $k_{M2} \cdot (n(t) - n(0))$

Model CS-ED with CR

Model set-up

1. Formation rate of new chains is proportional to the present number of chain elements $N_m(t)$.
Destruction of one chain element splits a chain. This process is of first order.
The number of chain elements decrease steadily. Mass loss occurs.
2. The loss rate of chains is proportional to the number of chains newly formed already, $n(t) - n(0)$.
The active ends arising are radicals and attack the great reservoir of chains. The second reactant of this bimolecular reaction is nearly constant (in initial conversion range) and is included in the reaction rate constant k_{M2} .

$$\frac{dn(t)}{dt} = k_{M1} \cdot N_m(t) - k_{M2} \cdot (n(t) - n(0))$$

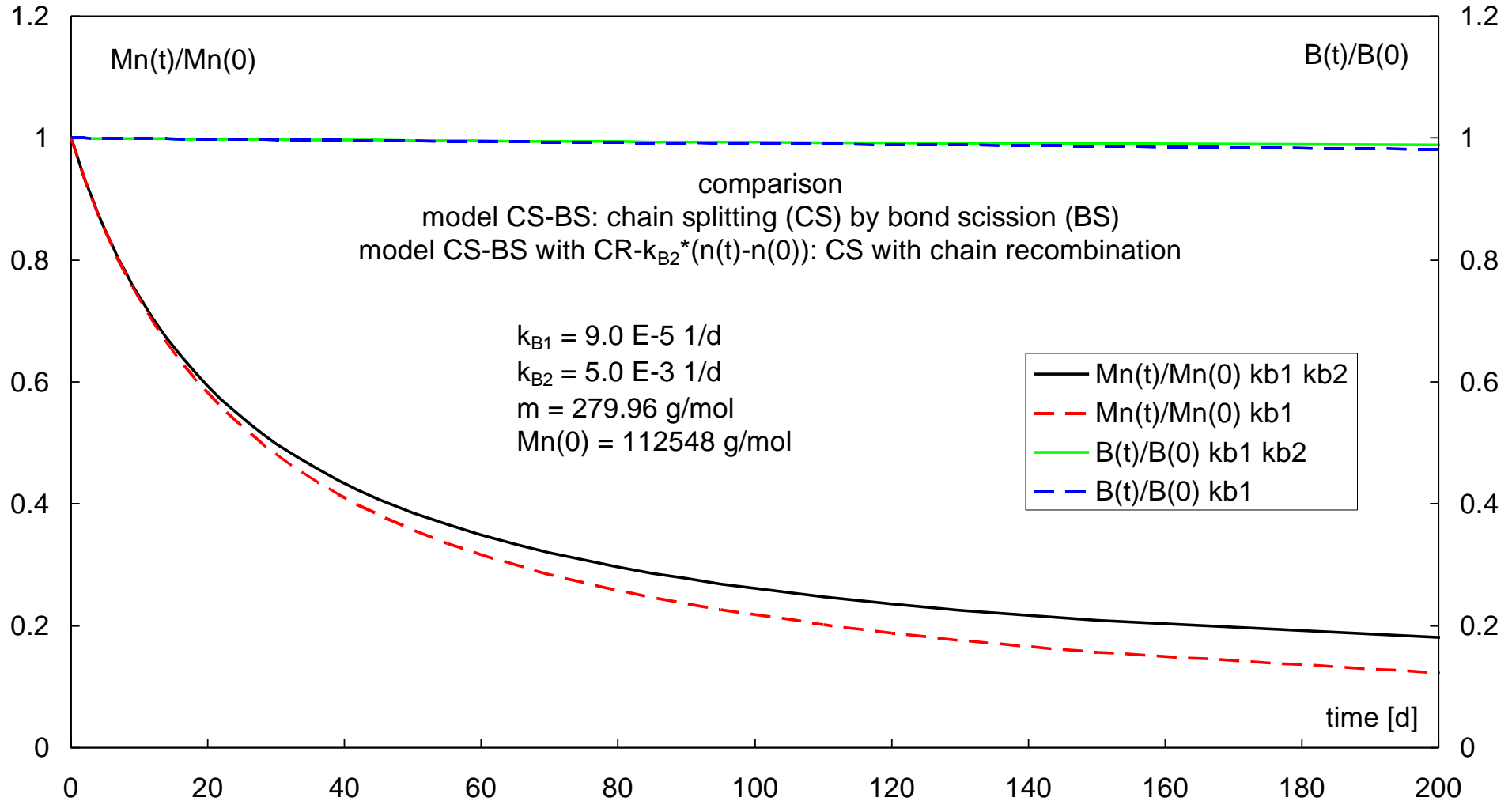
$N_m(t, T) = 0$ at t versus ∞ at every T

Means all chain elements will be decomposed

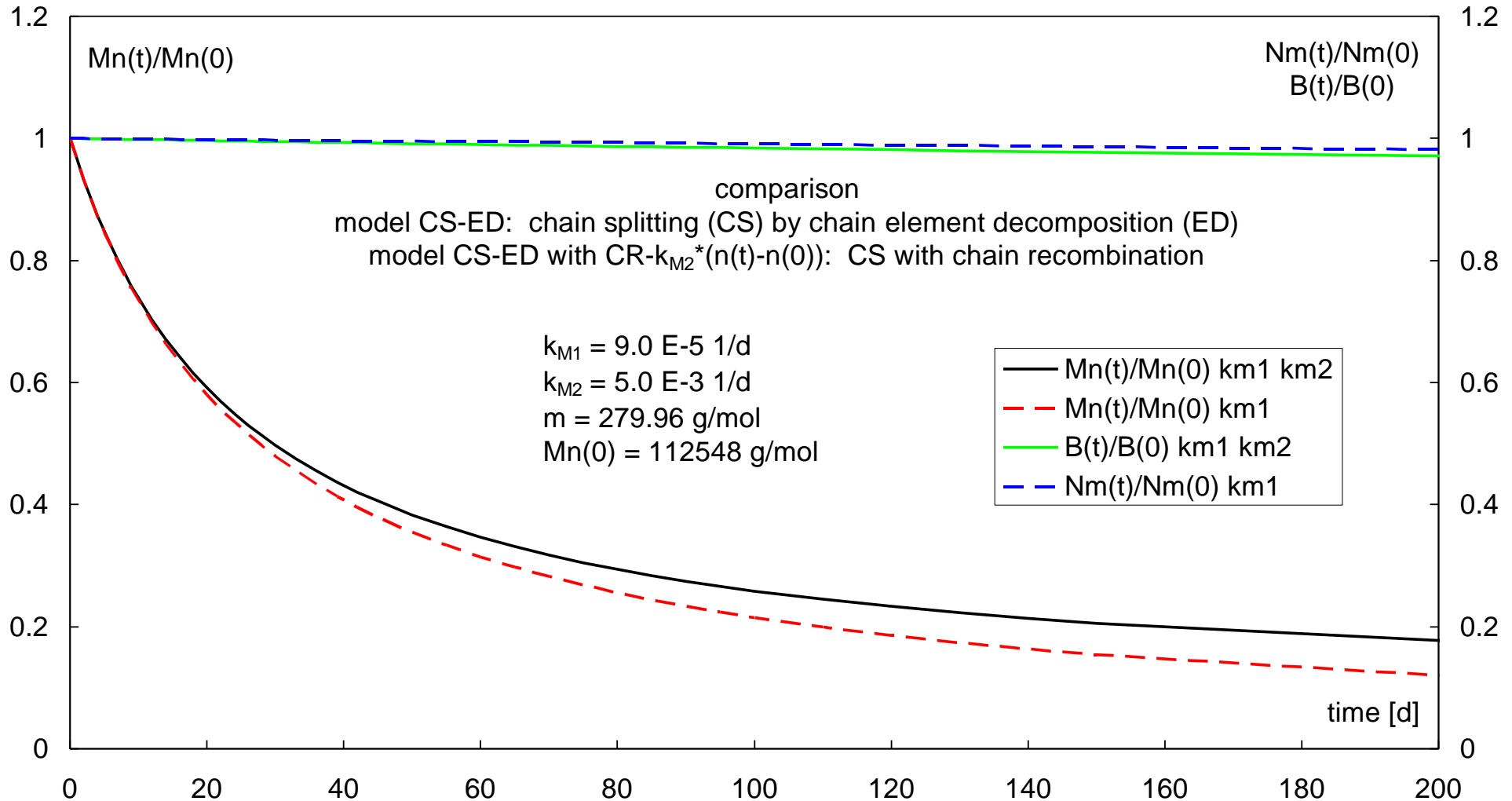
$$N(t, T) = N(0) \cdot \exp(-k_{M1}(T) \cdot t)$$

$$\frac{N(t)}{m} = \frac{\exp(-(k_{M1} - k_{M2}) \cdot t)}{\frac{m}{N(0)} + \frac{k_{M1}}{k_{M1} - k_{M2}} \cdot (1 - \exp(-(k_{M1} - k_{M2}) \cdot t)) + \frac{m}{N(0)} \cdot (\exp(+k_{M2} \cdot t) - 1)}$$

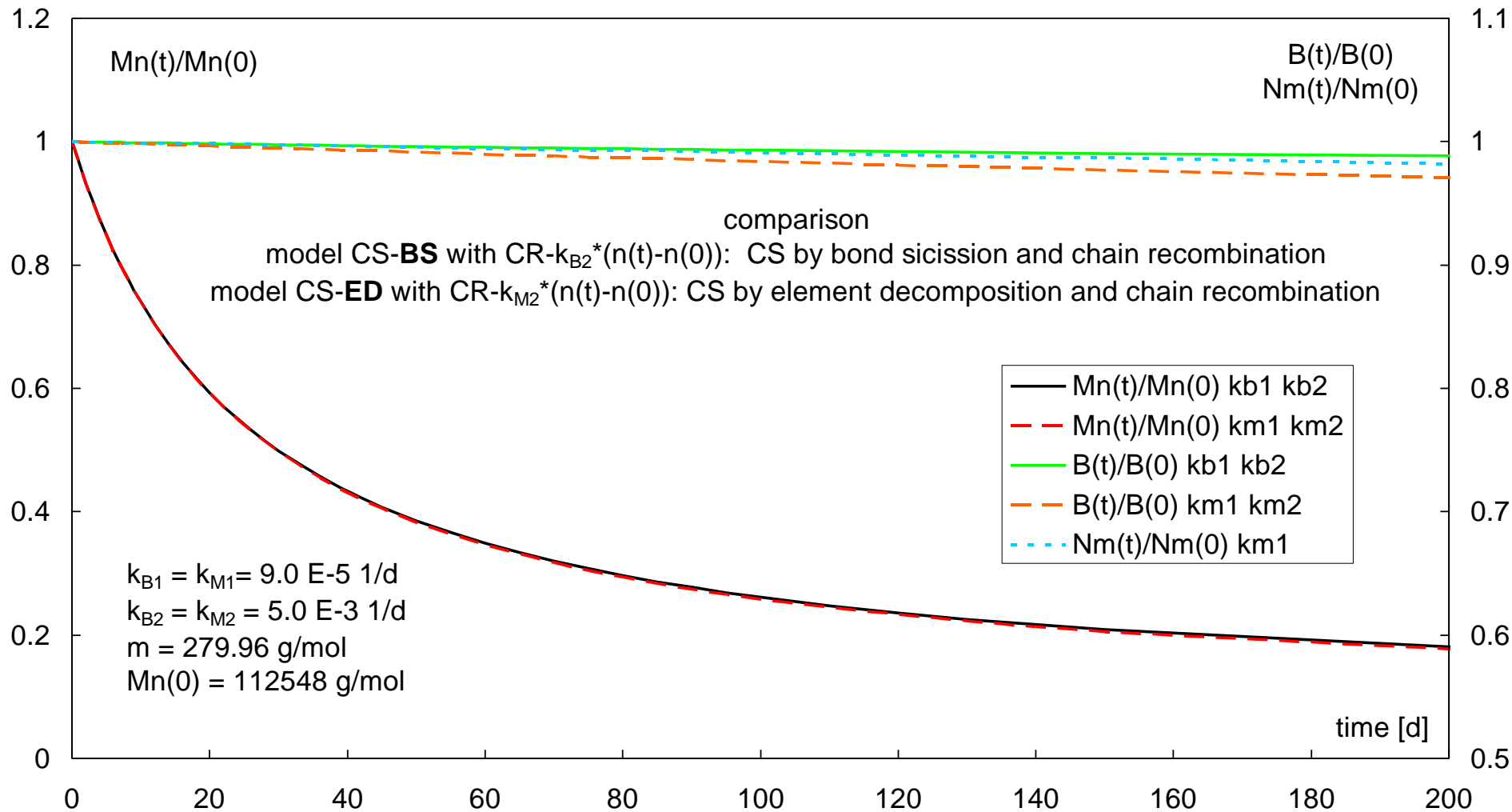
Comparison of models: CS-BS versus CS-BS with CR



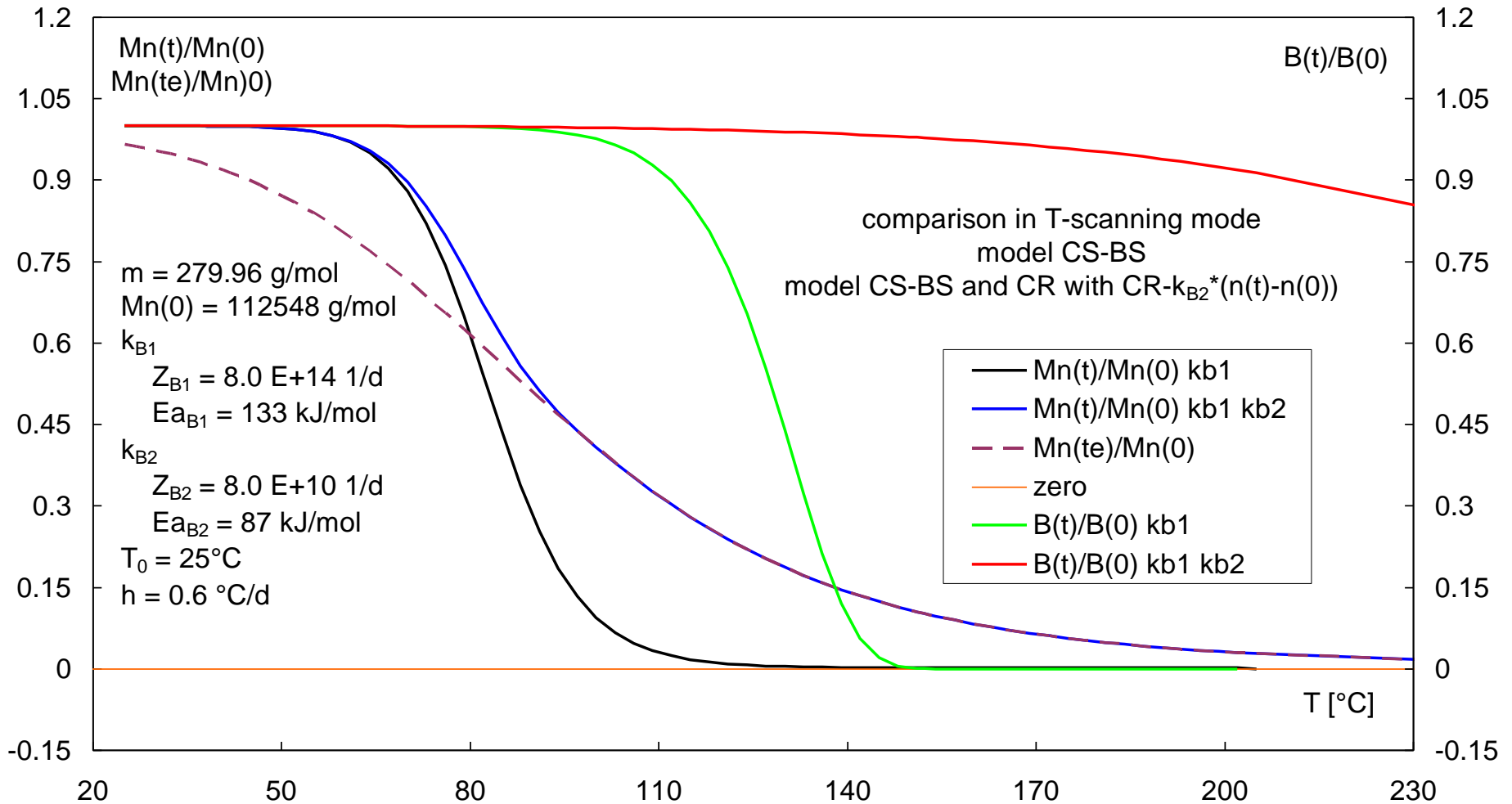
Comparison of models: CS-ED versus CS-ED with CR



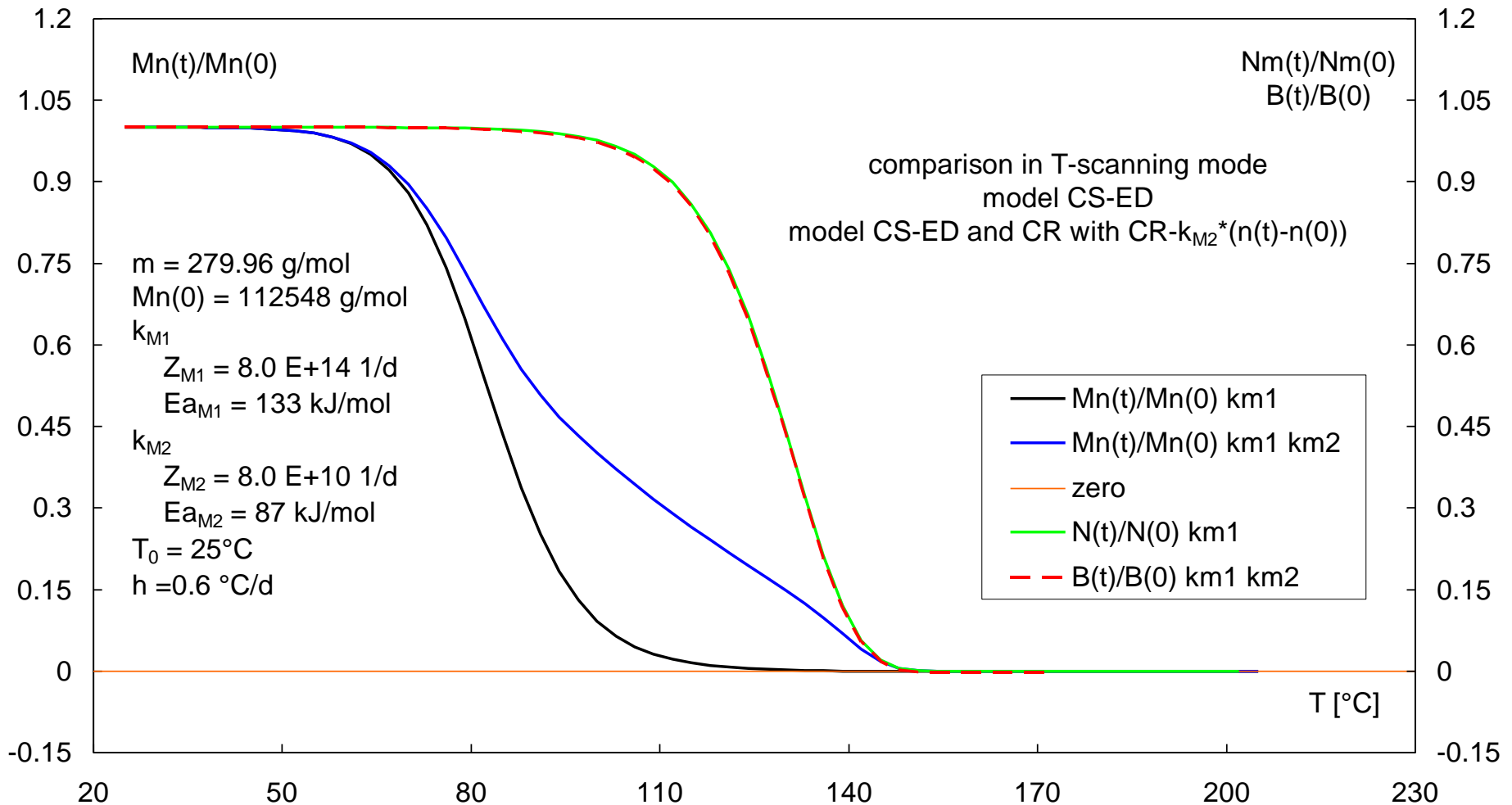
Comparison of models: CS-BS with CR versus CS-BS with CR



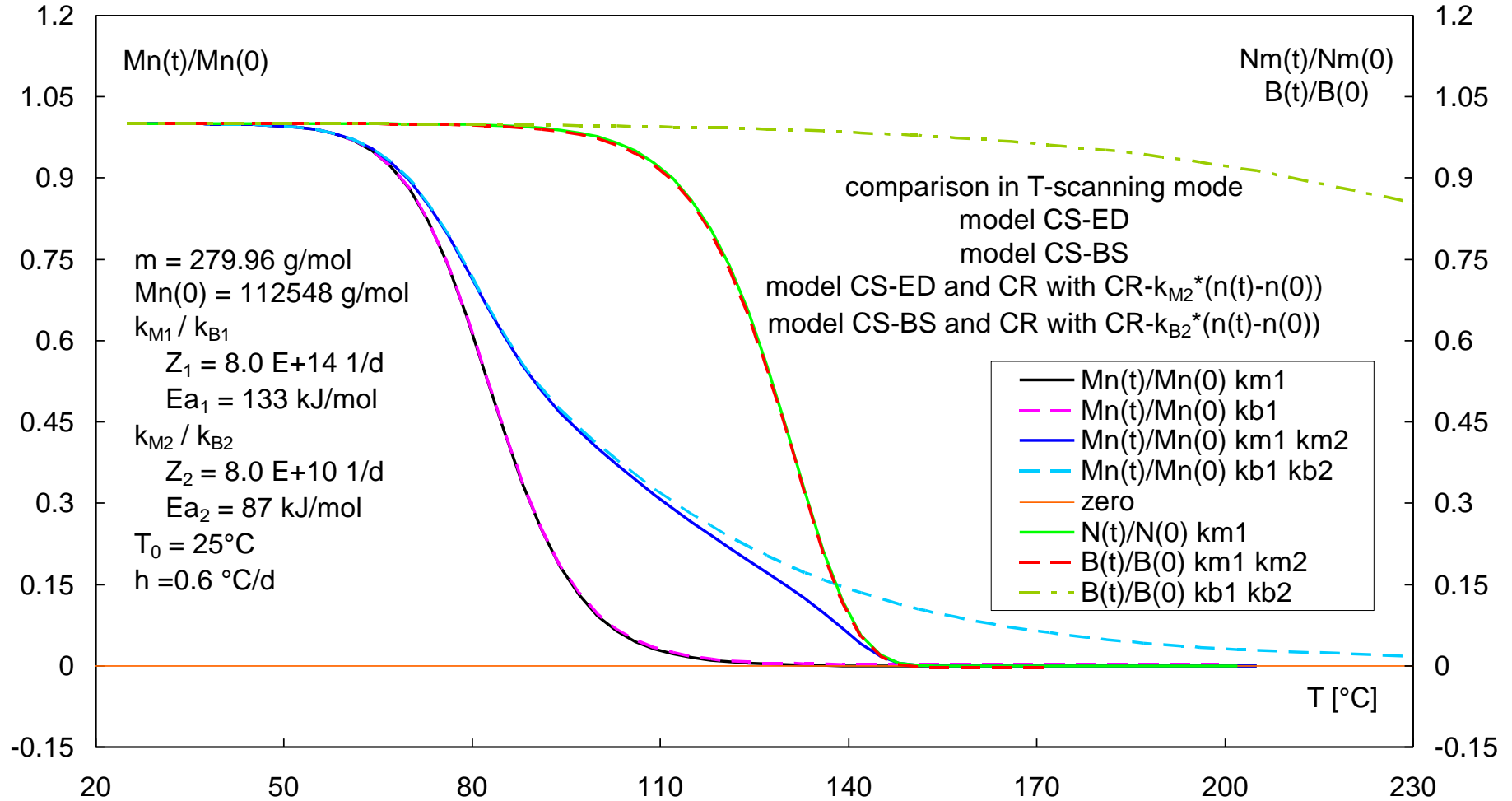
In T-scan: Comparison of models: CS-BS versus CS-BS with CR



In T-scan: Comparison of models: CS-ED versus CS-ED with CR

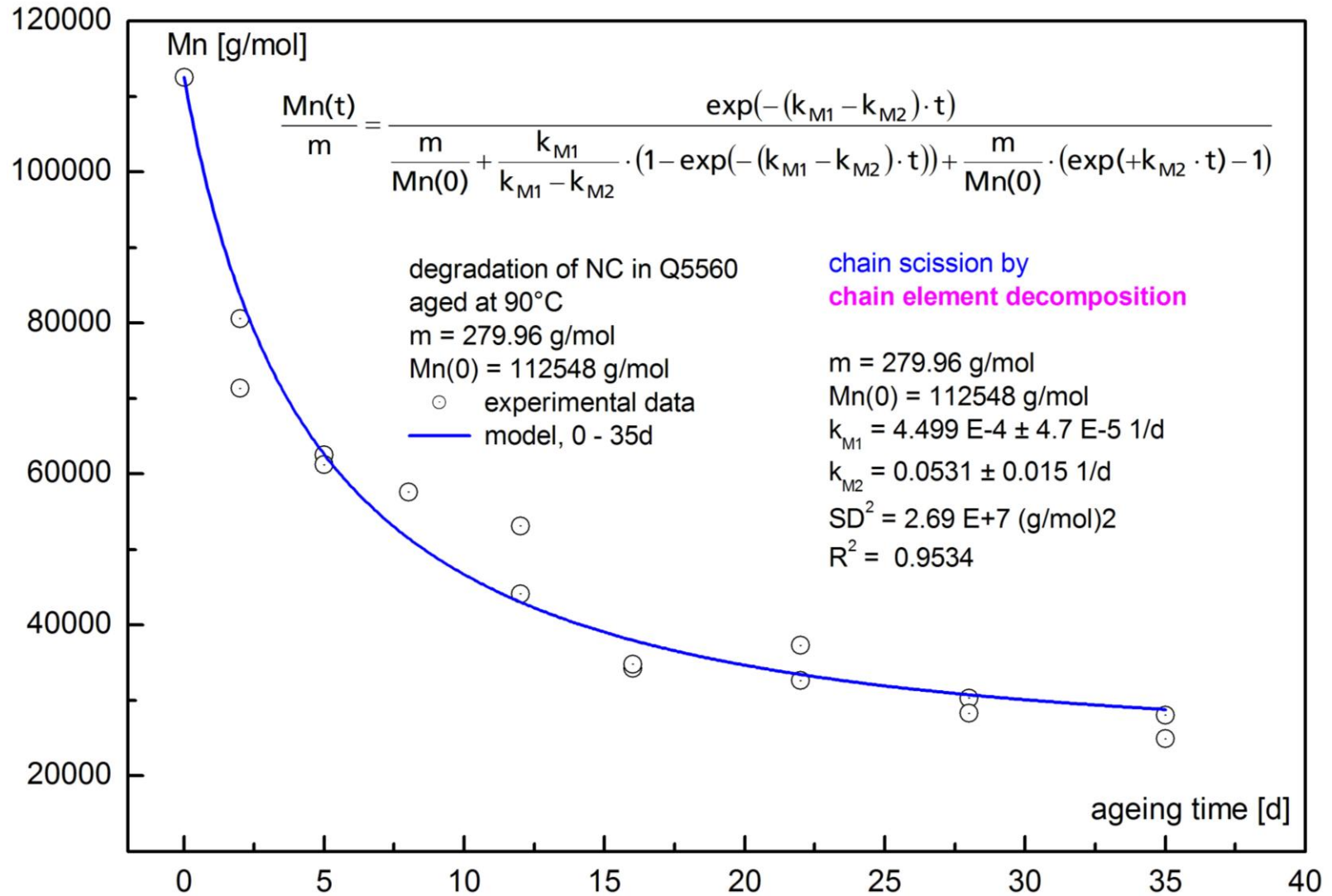


In T-scan: Comparison of models: CS-BS with CR versus CS-BS with CR



Results: Description of data by model CS-ED with CR

The description with model CS-ED with CR is now satisfying.

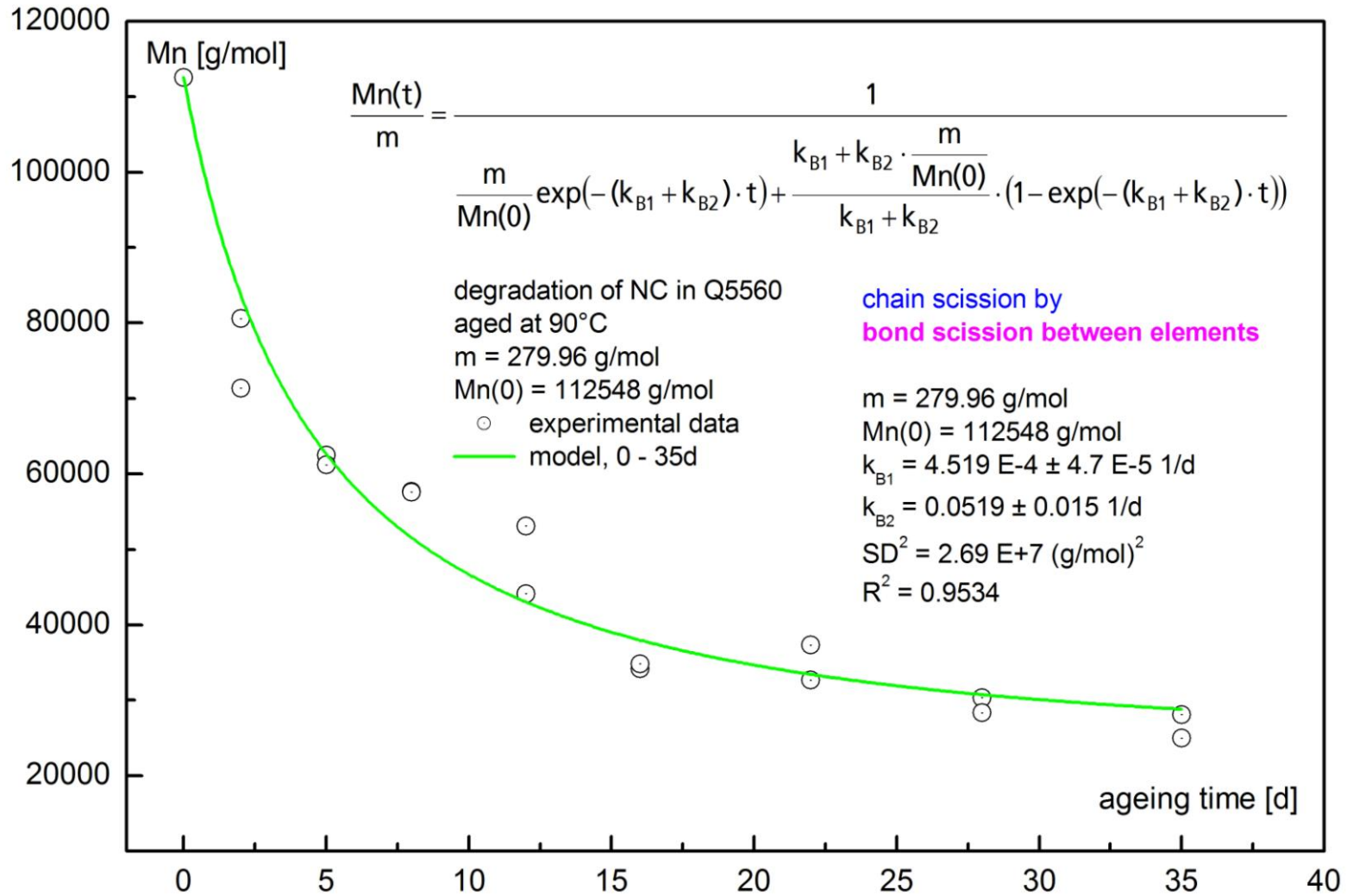


Results: Description of data by model CS-BS with CR

Also the description with model CS-BS with CR is now satisfying.

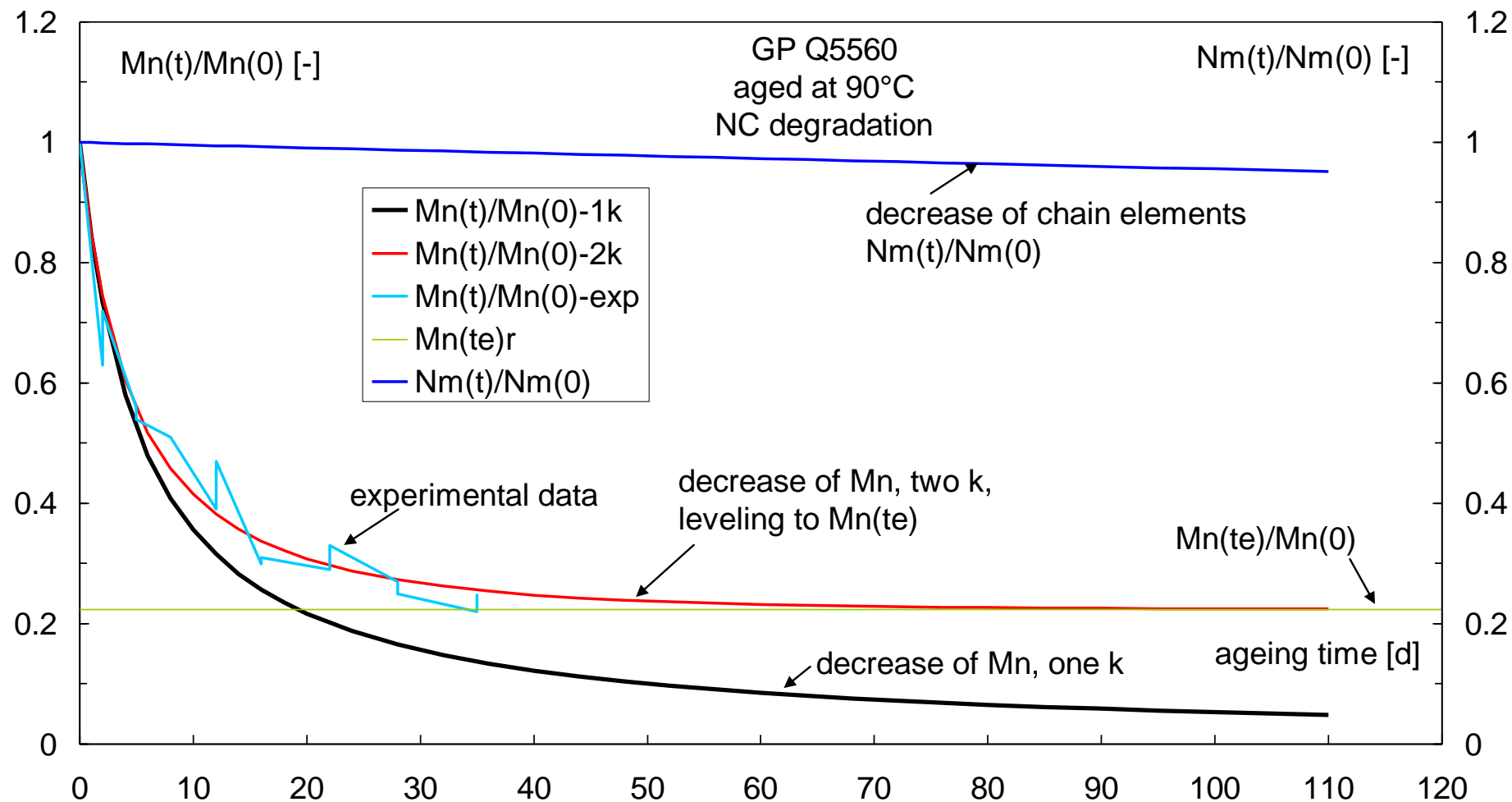
At isothermal conversions not to high both models are nearly equal in description quality.

But from mechanistic point of view model CS-ED with CR is the right one



Comparison: chain scission alone versus scission and recombination

Correct description is achieved with model CS-ED with CR;
 illustration here done with model CS-BS with CR in order to get the value for $Mn(te)$ at $t \rightarrow \infty$



Summary and Conclusions

Decrease of NC chain length is a [very sensitive probing of ageing of NC based materials](#)

Decrease of chain length of polymers can be well determined by GPC (also named SEC)

The chain degradation of NC is expressed in decrease of the mean molar masses

To use the data, suitable modelling is applied to extract the rate constants of the degradation process

Models using [chain splitting by chain element decomposition](#) are nearest to the reality of the splitting process for NC

With NC it seems that [besides chain splitting also recombination of chains](#) occur.

Best model for NC: chain splitting by chain element decomposition with recombination of chains

Acknowledgement

To my colleague Dr. Norbert Eisenreich

For the development of the model 'chain splitting by chain element decomposition' in the early 1980s.

For always helpful discussions in set-up and handling of kinetic models.

To my colleagues in the 'stability group' at ICT

providing me with measurement results of high quality:

Manuela Doerich, Heike Pontius

Kerstin Wimmer, Monika Raab, Juergen Hickmann

References – part 1 of 3

- 1/ M.A. Bohn, D. Mueller
Insensitivity aspects of NC bonded and DNDA plasticizer containing gun propellants
2006 Insensitive Munitions & Energetic Materials Technology Symposium, April 24-28, 2006, Bristol, UK.
- /2/ D. Mueller, M.A. Bohn, W. Langlotz
LTC propellants based on DNDA plasticizer.
Paper on the 33rd International Pyrotechnics Seminar July 16 to 21, 2006, Fort Collins, Colorado, USA. Organized and proceedings by International Pyrotechnics Seminar USA, Inc. and the International Pyrotechnics Society.
- /3/ M. A. Bohn, F. Volk.
Aging Behavior of Propellants investigated by heat generation, stabilizer consumption, and molar mass degradation.
Propellants, Explosives, Pyrotechnics, 17, 4 (1992) 171 – 178.
- /4/ F. Volk, M.A. Bohn, G. Wunsch.
Determination of chemical and mechanical properties of double base propellants during aging.
Propellants, Explosives, Pyrotechnics, 12 (1987) 81 – 87.
- /5/ M.A. Bohn
The Use of Kinetic Equations to Evaluate the Ageing Behaviour of Energetic Materials – Possible Problems.
Proceed. 11th Symp. on 'Chemical Problems Connected with the Stability of Explosives' (held in Båstad, May 24 to 28, 1998), pages 89-151. Editor: Jan Hansson, Ola Listh. 1999, Sundbyberg, Sweden.
- /6/ M.A. Bohn, J. Aniol, M. Dörich, K. Hartlieb, H. Pontius
Stability, Ageing and Usetime Prediction of Polyvinylnitrate (PVN).
Paper 73, pages 73-1 to 73-18, in Proceedings of the 37th International Annual Conference of ICT, June 27 to 30, 2006, Karlsruhe, Germany. Fraunhofer-Institut für Chemische Technologie (Fraunhofer ICT), D76318 Pfinztal, Germany.
- /7/ C. L. Bauer, P. R. Deacon, R. N. Garman, A. M. Emsley, J. R. Jones.
Low Temperature Non-Isothermal Aging of Nitrocellulose.
Propellants, Explosives, Pyrotechnics 30 (2005), No. 3.

References – part 2 of 3

- /8/ GPC method described in
STANAG 4178 “Assessing the Quality of Nitrocellulose Deliveries from one NATO Nation to Another”, Edition 2.
- /9/ H. Pontius, M. Dörich, M.A. Bohn.
Gel permeation chromatography of nitrocellulose (NC) and NC containing substances. - I. Parameter study for preparation of NC solutions and chromatogram evaluation.
Paper 69, Pages 69-1 to 69-15, in Proceedings of the 39th International Annual Conference of ICT, ‘Energetic Materials – Processing and Product Design’, June 24 to 27, 2008, Karlsruhe, Germany. ISSN 0722-4087. Fraunhofer-Institut für Chemische Technologie (ICT), D-76318 Pfinztal-Berghausen. Germany.
- /10/ Manfred A. Bohn.
Gel permeation chromatography of nitrocellulose (NC) and NC containing substances. - II. Remarks on calibration, molar mass distributions and mean molar masses.
Paper 70, pages 70-1 to 70-22, in Proceedings of the 39th International Annual Conference of ICT on ‘Energetic Materials – Processing and Product Design’, June 24 to 27, 2008, Karlsruhe, Germany. Fraunhofer-Institut für Chemische Technologie (ICT), D-76318 Pfinztal-Berghausen, Germany.
- /11/ Heike Pontius, Manuela Dörich, Manfred A. Bohn.
Gel permeation chromatography of nitrocellulose (NC) and NC containing substances. - III. Recent results from a continued parameter study on the GPC of NC samples.
Paper 80, pages 80-1 to 80-12 in Proceedings of the 40th International Annual Conference of ICT on ‘Energetic Materials – Characterization, Modelling, Validation’, June 23 to 26, 2009, Karlsruhe, Germany. ISSN 0722-4087. Fraunhofer-Institut für Chemische Technologie (ICT), D-76318 Pfinztal-Berghausen. Germany.
- /12/ P. Deacon, A. Macdonald, P. Gill, N. Mai, M.A. Bohn, H. Pontius, M. Van Hulst, W. de Klerk, C. Baker
An update on the Round Robin test to evaluate the nitrocellulose SEC method in STANAG 4178 (Ed.2).
Paper 81 in Proceedings of the International Annual Conference of ICT, 2009, Karlsruhe, Germany.
- /13/ NATO Standardization Agreement (NATO STANAG) 4582 ‘Explosives, Nitrocellulose Based Propellants, Stability Test Procedure and Requirements Using Heat Flow Calorimetry’
Military Agency for Standardization, NATO Headquarters, Brussels, Belgium.

References – part 3 of 3

- /14/ NATO Allied Ordnance Publication (NATO AOP) 48, edition 2
Explosives, Nitrocellulose-based Propellants, Stability Test Procedures and Requirements Using Stabilizer Depletion.
Military Agency for Standardisation, NATO Headquarters, 1110 Brussels, Belgium.
- /15/ Manfred A. Bohn
Prediction of equivalent time-temperature loads for accelerated ageing to simulate preset in-storage ageing and time-temperature profile loads.
Paper 78, pages 78-1 to 78-28 in Proceedings of the 40th International Annual Conference of ICT on 'Energetic Materials – Characterization, Modelling, Validation', June 23 to 26, 2009, Karlsruhe, Germany. ISSN 0722-4087.
Fraunhofer-Institut für Chemische Technologie (ICT), D-76318 Pfinztal-Berghausen. Germany.
- /16/ A. Pfeil, H. H. Krause, N. Eisenreich.
The Consequences of Beginning Slow Thermal Decomposition of the Molecular Weight of Nitrated Cellulose.
Thermochim. Acta, 1985, 85, 395.
- /17/ N. Eisenreich and A. Pfeil.
Non-linear least-squares fit of non-isothermal thermoanalytical curves: Reinvestigation of the kinetics of the autocatalytic decomposition of nitrated cellulose.
Thermochim. Acta 61 (1983) 1 – 13.
- /18/ Manfred A. Bohn und Norbert Eisenreich.
Kinetic modelling of the change of molar mass distribution function of nitrocellulose during ageing.
Paper 86, pages 86-1 to 86-24 in Proceed. of 41th International Annual Conference of ICT on 'Energetic Materials – High Performance, Insensitive Munitions, Zero Pollution', June 29 to July 2, 2010, Karlsruhe, Germany. ISSN 0722-4087.
Fraunhofer-Institut für Chemische Technologie (ICT), D-76318 Pfinztal-Berghausen. Germany.

Thank you for your attention

Questions ?