

Investigation of Thermoreversible Polymer Networks by Temperature Dependent Size Exclusion Chromatography

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1. Details on TD SEC instrument setup

The in past studies employed ResiPore (Agilent Technologies, US) column in TCB did not yield good size-based separation of the DA network systems, mainly due to the tetralinker that experiences enthalpic interactions and is hardly eluted from the column. As shown in Figure S1, the tailor-made ABOA DMAc-Phil column (AppliChrom, Germany) in DMAc (+ 3 g L⁻¹ LiCl) leads to very good separation according to size, as the polystyrene standards (Agilent EasiCal PS 2B, Agilent Technologies, US), linear P^tBuA samples (2 in Figure 3 of the main text, and chapter 6 of the ESI) and the peaks from the HDA-Dilinker, representing its monomer, dimer and trimer state, fall onto one line. The structure HDA-Dilinker is shown in Figure S2, its synthesis is described in our previous publications.^[1,2] Our observations showed that the Dilinker undergoes multimerization at elevated temperatures, so that three peaks are obtained that correspond to monomer, dimer and trimer. The Dilinker carries the same CDTE-moieties as the Tetralinker (refer to Figure 3 in the main text) that potentially lead to enthalpic interactions with the column material. However, our experiments did not evidence any interactions, as the positions of all three peaks of the linker are in good agreement with the standard calibration.

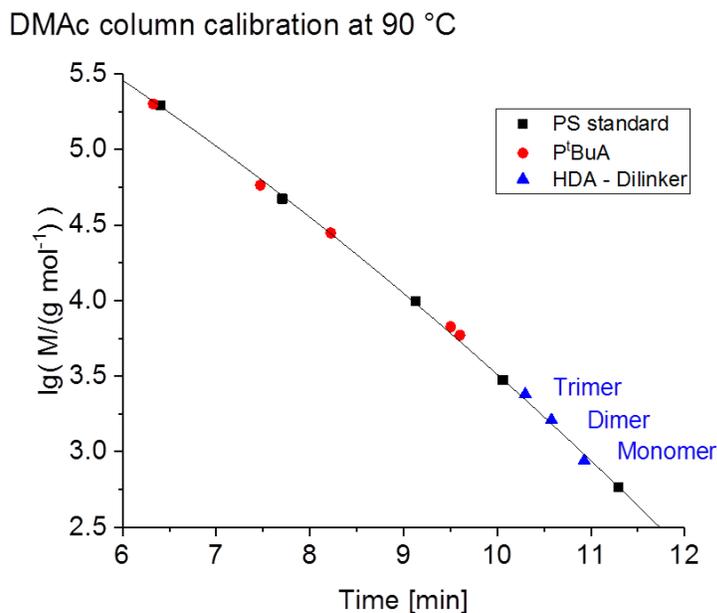


Figure S1: Molar mass calibration acquired on the ABOA DMAC-Phil-P300 column at 90 °C in DMAC (+ 3 g L⁻¹ LiCl). Flow rate was 1 mL min⁻¹.

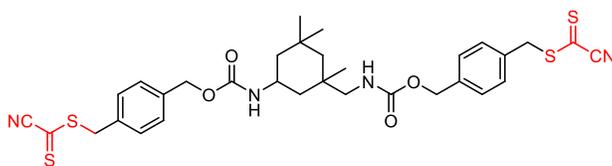


Figure S2: Structure of the CDTE-Dilinker that was used for testing interactions with the column material.

2. UV/Vis-spectra of Cp₂P^tBuA

In Figure S3 a chromatogram of the Cp₂P^tBuA is shown, as obtained at 120 °C in DMAC. After different elution times spectra were acquired with the online UV/Vis detector. As depicted in the corresponding insets, the polymer absorbs at wavelengths lower than 450 nm, although no absorption peak is apparent. The shoulder of the peak at low elution volumes of the SEC chromatogram is due to dimerization of the building blocks (the Cp moieties readily undergo dimerization).

The Cp₂-polymer was prepared from a precursor polymer carrying Br endgroups from ATRP synthesis as shown in Figure S4. The Br precursor polymer did not show any UV/Vis absorption at wavelengths exceeding 300 nm. Hence, the absorption of the Cp₂P^tBuA is due to the Cp endgroups.

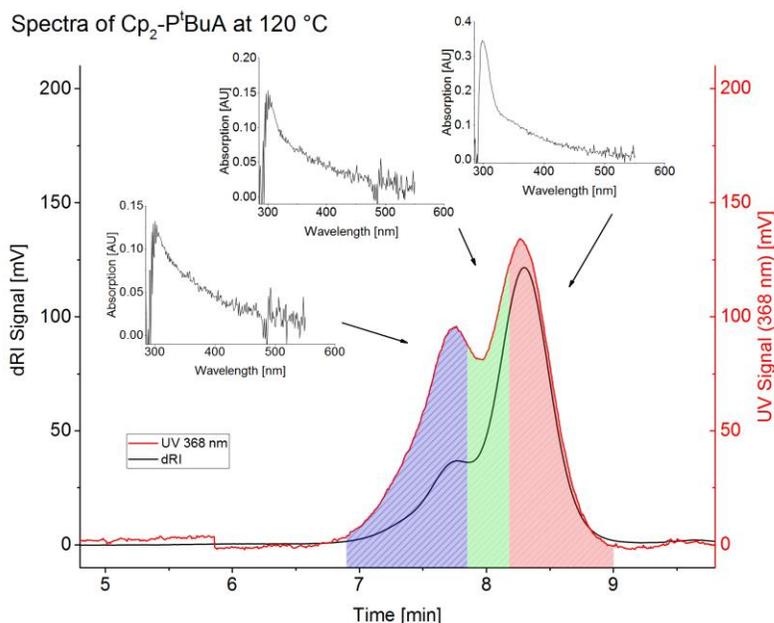


Figure S3: SEC chromatogram of the $\text{Cp}_2\text{P}^f\text{BuA}$ building block at 120 °C in DMAc (3 g L^{-1} LiCl). Due to its Cp endgroups there is a signal in the UV trace. Compared to the absorption of the C=S double bond it is relatively weak.

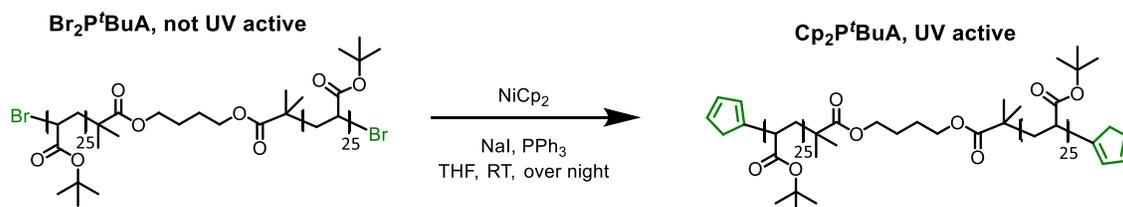


Figure S4: Synthesis of the $\text{Cp}_2\text{P}^f\text{BuA}$ from $\text{Br}_2\text{P}^f\text{BuA}$ through a Nickelocene reaction.^[2]

3. Calculating the chemical composition (CC)

In principle, the CC in terms of average ratio of building block to linker in each elution slice can be calculated by having at least two concentration detectors.^[3] Our setup offers the possibility to acquire the dRI signal and the UV/Vis absorption at two wavelengths so that in total three concentration signals can be acquired simultaneously. Mathematically each concentration signal is a convolution of the contributions of the building block and the linker, respectively, weighted by their corresponding ‘contrast factors’, as shown in Equation 1 to Equation 3. In the case of the dRI detector, the contrast factor represents the refractive index increment, (dn/dc) , in case of the UV/Vis detector the molar extinction coefficient, ϵ . We did not accurately determined these quantities but used arbitrary contrast factors in terms of the quotient given by *ObtainedSignalIntensity / WeightConcentration*, as the proper

determination of dn/dc and ϵ requires large sample amounts that we did not have accessible (note that dilution series would have to be measured at all temperatures). Our contrast factor simplification yields results of high accuracy, as long as the reference samples are measured at concentrations similar to the concentrations in the unknown samples. *I.e.*, if the expected concentration of linker in a DA polymer is approx. 0.5 mg/mL, a reference experiment with 0.5 mg/mL of the pure linker is performed for determining the contrast factors.

$$dRI = Contrast_{dRI,building\ block} \cdot c_{building\ block} + Contrast_{dRI,Linker} \cdot c_{Linker} \quad \text{Equation 1}$$

$$UV1 = Contrast_{UV1,building\ block} \cdot c_{building\ block} + Contrast_{UV1,Linker} \cdot c_{Linker} \quad \text{Equation 2}$$

$$UV2 = Contrast_{UV2,building\ block} \cdot c_{building\ block} + Contrast_{UV2,Linker} \cdot c_{Linker} \quad \text{Equation 3}$$

Having set these equations it is possible, after having determined the contrast factors, to iteratively find the values for $c_{building\ block}$ and c_{Linker} that fit best to the experimentally acquired value of dRI , $UV1$, and $UV2$.

The most significant problem is associated with the fact that both the dRI and the UV/Vis detector are sensitive to different properties of the molecules. Whereas the dRI detector basically sees the entire molecule, the UV/Vis detector is only sensitive to the C-S containing groups of the linker. Of course, the contrast factor of the linker is different when it is in a bound state (DA adduct) or non-bound (free C=S double bond). Thus, the state of the linker needs to be known, which becomes possible by inspecting the individual linker chromatograms and spectra (Figure S5):

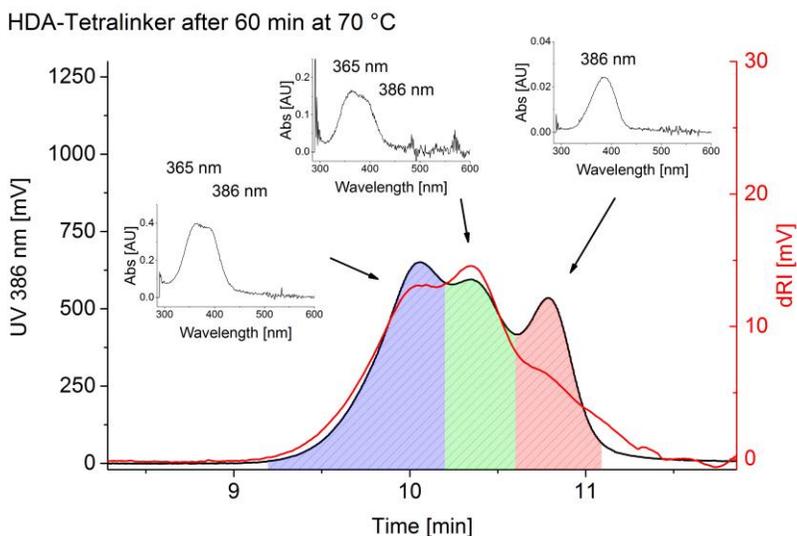


Figure S5: SEC chromatogram of the HDA-Tetralinker, acquired after heating for 60 minutes at 70 °C in DMAc (3 g/L LiCl).

Similarly to the Dilinker also the HDA-Tetralinker undergoes multimerization at elevated temperatures. Consequently a trimodal distribution is obtained in the chromatograms: The first two peaks are most

likely to represent a trimer and a dimer, as their position suits well the corresponding molar masses. However, the ratio of these three peaks to each other changes as the amount of dimers and eventually trimers increases with heating time. In addition, the recorded spectra indicate the aggregation of two or three linker molecules, respectively: Only the last peak shows the clean absorption of the C=S double bond, whereas the first two peaks show a convolution of that absorption with another with a maximum at 365 nm. The latter one has to be ascribed to the bond that links the linker molecules. Unfortunately, a precise mechanism of the multimerization could not be deduced.

It is, however, interesting to note that the UV-absorption of the linker multimers is relatively similar to the absorption that was found for the DA-adduct with a maximum at 340 nm (refer to Figure 7 in the main text). The shape of the absorption spectrum can be reconstructed by collecting chromatograms at 386 and 425 nm and calculating the ratio between both absorptions. Figure S6 illustrates the ratio for both the Tetralinker (left) and the DA P^tBuA (right).

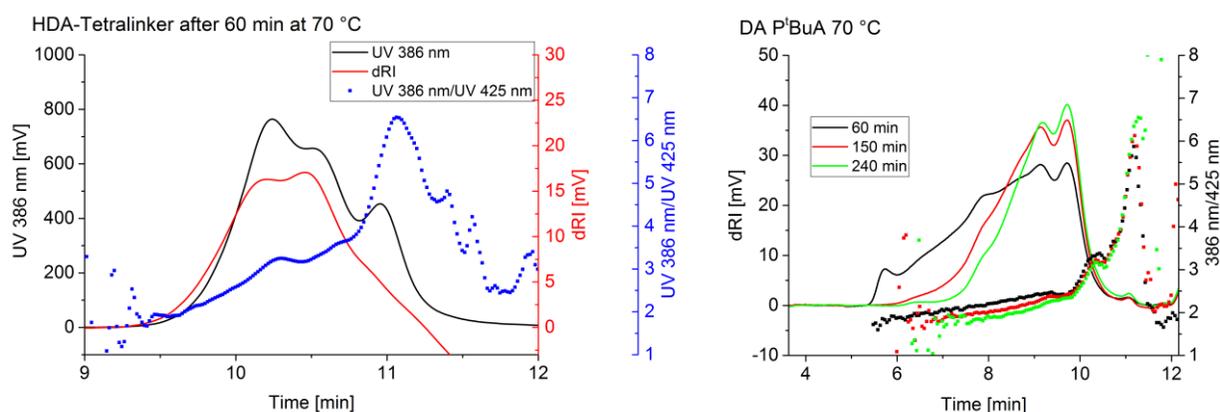


Figure S6: SEC chromatograms of the HDA-Tetralinker (left) and the DA P^tBuA (right), acquired at 70 °C in DMAc (+3 g/L LiCl). Overlaid to the chromatograms are the ratios of the absorption at 386 nm to 425 nm, indicating that the free linker is measured, when that ratio gets higher than 3.

In both cases the ratio is in between 2 and 3 at elution times lower than 10.5, *i.e.*, where the linker is in its bound state. When the linker is in the non-bonded state (at approx. 11 minutes elution time), the ratio increases to approx. 6.5. Hence, that ratio can be used to distinguish the linker's state in the chromatogram from mainly bound or free.

The concept that was eventually used for calculating the CC according to Equation 1 to Equation 3 is displayed in Figure S7 (calculations were carried out in Scilab 5.5.2^[4]):

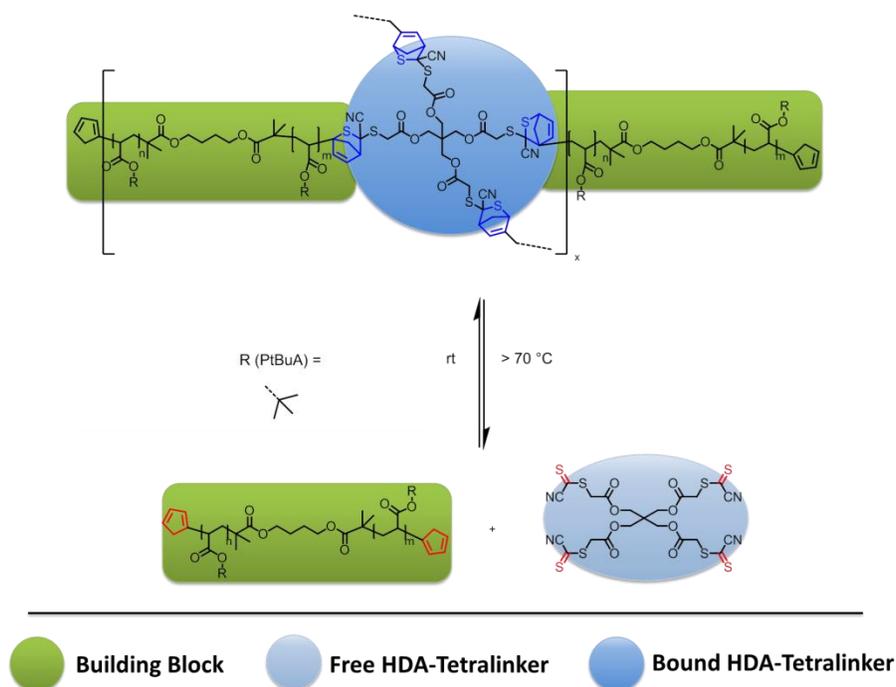


Figure S7: The DA P^tBuA network system as seen by the UV/Vis detector in a simplified way. The CDTE-Tetralinker is being treated differently (application of different contrast factors) when integrated into the DA polymer or when free.

Calculating the entire CC requires knowledge of the contrast factors for dRI and UV/Vis detector for the building block and the bound, as well as the free linker. The latter two factors were determined from chromatograms of the linker, as shown in Figure S8. According to the found ratio of UV(386 nm)/UV(425 nm), either the values of the free or the bound linker were used at the corresponding elution slice. The script subsequently takes each point of the chromatogram of the DA P^tBuA network and iteratively optimizes c_{Linker} and $c_{\text{building block}}$ until the results from Equation 1 to Equation 3 match the experimental values with the least error. These concentrations are subsequently used for calculating intrinsic viscosities and applying universal calibration. An example chromatogram with the calculated concentrations is depicted in Figure S9. Note that over a broad range the calculated weight concentration of the tetralinker agrees well with the bulk linker concentration of approx. 5 %.

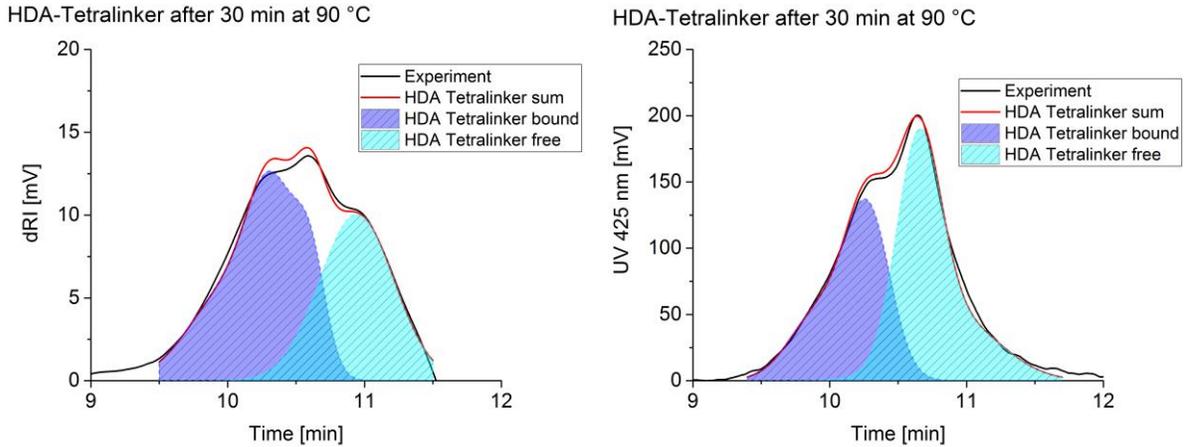


Figure S8: dRI- (left) and UV(425 nm)-trace (right) of the HDA-Tetralinker after 30 min at 90 °C in DMAc (3g L^{-1} LiCl), showing the peak areas for determining the contrast factors for free and bound linker.

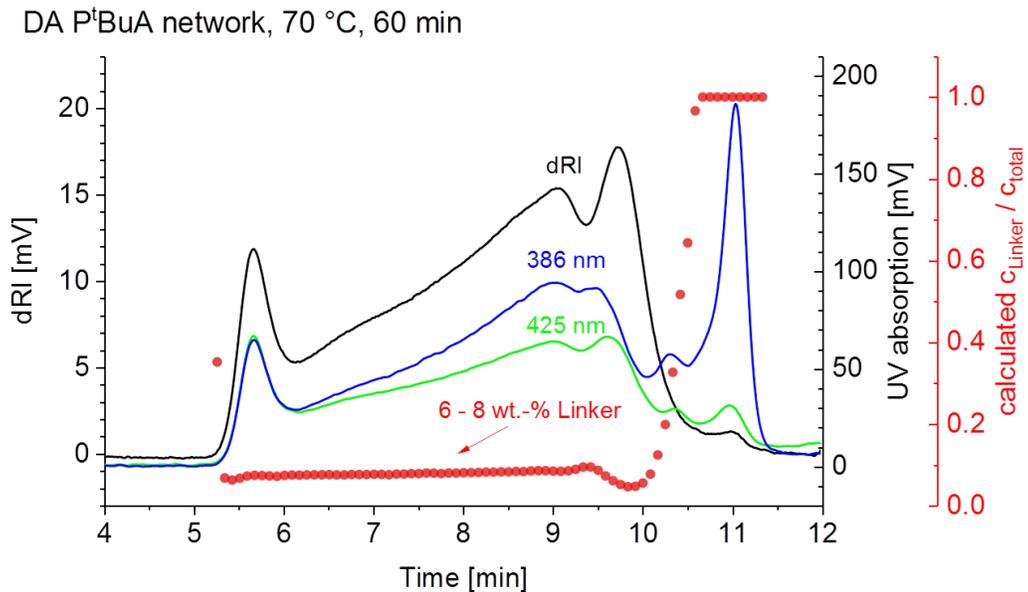


Figure S9: Chromatogram of DA P^tBuA network after 60 minutes at 70 °C, as acquired by dRI and UV-detection at 386 and 425 nm, respectively. Overlaid in red the calculated weight fraction of the linker is shown. In a broad range the obtained concentration agrees well with the bulk linker concentration (approx. 5 %).

The Scilab-script for calculating the respective linker and polymer concentrations is reads as follows:

```
Data = fscanfMat('ptbua-0151.txt', "%lg"); //read in data (columns: Time, dRI, UV1, UV2, DP visco)

Frequency = 5; //Data points/s

//Detector calibrations
kDP = 9.032535522;
IP = 31400; //Inlet Pressure in Pa

clear MM;
clear Results;
```

```
Data(:,5) = abs(Data(:,5));
```

```
//Concentration Calibrations:
```

```
dRIPolymerSlope = 12.23180339;  
dRIPolymerInterc = 0;
```

```
UV1PolymerSlope = 2.476166102;  
UV1PolymerInterc = 0;
```

```
UV2PolymerSlope = 1.835820339;  
UV2PolymerInterc = 0;
```

```
dRILinkerSlope = 50.02507407;  
dRILinkerInterc = 0.0;
```

```
UV1LinkerInterc = 0;  
UV2LinkerInterc = 0;
```

```
UV1LinkerSlope1 = 2859.05; //bound linker  
UV1LinkerInterc1 = 0;
```

```
UV2LinkerSlope1 = 4797.12;  
UV2LinkerInterc1 = 0;
```

```
UV1LinkerSlope2 = 1132.91; //free linker  
UV1LinkerInterc2 = 0;
```

```
UV2LinkerSlope2 = 851.13;  
UV2LinkerInterc2 = 0;
```

```
//Determine Peak Borders
```

```
FontSize = 4;  
clf();  
plot(Data(:,1), Data(:,3),"b");  
plot(Data(:,1), Data(:,2),"b");  
xlabel("Time (min)");  
ylabel("UV1 (mV)");  
title("Chromatogramm");  
a = gca(); //Get Current Axes (gca)  
a.font_size = FontSize; //Schriftgröße Achsenbeschriftung  
a.title.font_size = FontSize+1;  
a.x_label.font_size = FontSize;  
a.y_label.font_size = FontSize;  
a.data_bounds(1,1) = 4;  
a.data_bounds(1,2) = -10;  
a.data_bounds(2,1) = 14;
```

```
Borders = locate(2,1); //Get Peak Borders Points
```

```
Index0 = round(Borders(1,1)*60*Frequence);  
Index1 = round(Borders(2,1)*60*Frequence);
```

```
//Determine Concentrations
```

```
slice = Index0;  
counter = 1;
```

```
Results = zeros((Index1 - Index0), 7);
```

```
function f=Error(x)
```

```
    cPolymer = x(1);
```

```
    cLinker = x(2);
```

```
    dRISlope = dRIPolymerSlope * cPolymer + dRIPolymerInterc + dRILinkerSlope * cLinker + dRILinkerInterc;
```

```
    UV1Calc = UV1PolymerSlope * cPolymer + UV1PolymerInterc + UV1LinkerSlope * cLinker +  
    UV1LinkerInterc;
```

```
    UV2Calc = UV2PolymerSlope * cPolymer + UV2PolymerInterc + UV2LinkerSlope * cLinker +  
    UV2LinkerInterc;
```

```
    f = abs(dRISlope-dRI)^4 + abs(UV1Calc-UV1)^4 + abs(UV2Calc-UV2)^4;
```

```
endfunction
```

```
for counter = 1:(Index1-Index0)
```

```
    dRI = Data(slice, 2);
```

```
    UV1 = Data(slice, 3);
```

```
    UV2 = Data(slice, 4);
```

```
    if UV1/UV2 > 2.8 then
```

```
        UV1LinkerSlope = UV1LinkerSlope2;
```

```
        UV2LinkerSlope = UV2LinkerSlope2;
```

```
    else
```

```
        UV1LinkerSlope = UV1LinkerSlope1;
```

```
        UV2LinkerSlope = UV2LinkerSlope1;
```

```
    end
```

```
    c0Polymer = dRI/dRISlope;
```

```
    c0Linker = UV2/UV2LinkerSlope;
```

```
    x = [c0Polymer, c0Linker]
```

```
    [f, xopt, gopt] = leastsq(Error, x);
```

```
    //Optimization
```

```
    g = Error(x);
```

```
    cPolymer = xopt(1);
```

```
    cLinker = xopt(2);
```

```
    if cPolymer <=0 then
```

```
        cPolymer = 1E-6;
```

```
    end
```

```
    if cLinker <=0 then
```

```
        cLinker = 1E-6;
```

```
    end
```

```
    Results(slice, 1) = cPolymer;
```

```
    Results(slice, 2) = cLinker;
```

```
    Results(slice, 3) = cLinker + cPolymer;
```

```
    Results(slice, 4) = log10(4*Data(slice,5)/(IP - 2*Data(slice,5)) * kDP*10 / Results(slice,3)); // =  $\lg(4*DP/(IP - 2*DP) * kVisco / ctotal) = \lg[\eta]$ 
```

```

Results(slice, 5) = -0.78642*Data(slice,1) + 10.09731 - Results(slice,4); //Universal calibration
Results(slice, 6) = slice/300; //Time (min)
Results(slice, 7) = Results(slice, 3) + Results((slice - 1), 7); // summed mass
Results(slice, 8) = f^0.5; //Error of fit
Results(slice, 9) = (f^0.5)/(dRI + UV1 + UV2)*100; //Percent Error of fit
Results(slice, 10) = cLinker/(cLinker + cPolymer)*100;
MM(slice, 1) = Results(slice, 2)/10^Results(slice, 5); // Concentration
MM(slice, 2) = Results(slice, 2); // Concentration * Molar Mass
MM(slice, 3) = Results(slice, 2)*10^Results(slice, 5); // Concentration * Molar Mass^2

slice = slice + 1;
end

Results(:,7) = Results(:,7)/max(Results(:,7))*100; // Normalize summed mass to 100 %

MPolymer = intrtrap(Results(:,6), Results(:,1));
MLinker = intrtrap(Results(:,6), Results(:,2));
MTotal = intrtrap(Results(:,6), Results(:,3));

LinkerContent = MLinker/MTotal;

Mn = sum(MM(:,2))/sum(MM(:,1));
Mw = sum(MM(:,3))/sum(MM(:,2));
Dm = Mw/Mn;

disp(Mn, "Mn (g/mol) =");
disp(Mw, "Mw (g/mol) =");
disp(Dm, "Dm =");
disp(MPolymer, "Masse Polymer (mg) =");
disp(MLinker, "Masse Linker (mg) =");
disp(MTotal, "Gesamtmasse (mg) =");
disp(LinkerContent, "Linker content=");

```

4. Challenges associated with CC calculations

Although the obtained results after calculating the CC appear reasonable, they nevertheless require careful consideration, specifically:

- The contrast factors for the linker in the DA product are determined from the linker multimers that are chemically not identical to the DA adduct. Hence, the contrast factors will be beset with a certain error.
- The linker is always considered as entirely bound or entirely free. In reality, however, each of four C=S double bonds per linker can be free or bound individually.
- The linker is very reactive; especially at higher temperatures and longer rDA times it is likely that unknown side products are formed that give different signals. Currently side products of any kind cannot be included in the calculations.

5. Determining and averaging response factors

For the approach that assumes constant CC at high molar masses only the dRI trace was taken into account. As the UV/Vis absorption is very sensitive to chemical changes of especially the tetralinker (refer to previous chapter) it was neglected. The dRI contrast of the tetralinker does not seem to reflect any changes in chemical composition, as shown in Figure S10. Here, the linker is shown after different times at 70 °C where a clear change in peak shape due to multimerization is evident. The overall peak area, however, remains essentially constant so that the resulting contrast factor can be considered reliable for bound and free linker at the same time.

HDA-Tetralinker after various times at 70 °C

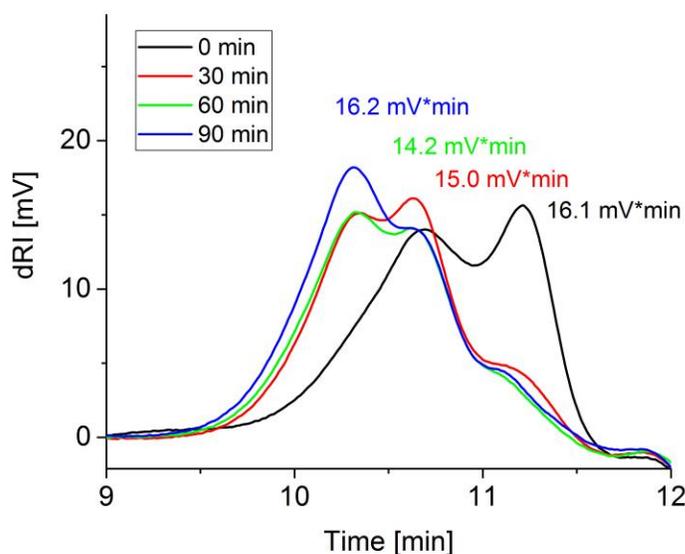


Figure S10: The dRI chromatogram of the HDA-Tetralinker after different times at 70 °C in DMAc (3 g L⁻¹ LiCl). The peak at the highest elution time (*i.e.* the monomer) is consumed and dimers and trimers are formed. The overall peak area only changes slightly, indicating that the dRI response does not sense the change in chemical structure.

Having determined the contrast factor of both, the building block and the tetralinker, the averaged contrast factors were calculated according to Equation 4. In there, A_L and A_{Block} are the reference peak areas of linker and block, respectively, and c_{Linker} and c_{Block} the corresponding concentrations. X_L is the fraction of the linker in the network that can be calculated from the molar masses or Linker and Block, M_L and M_{Block} , respectively, according to Equation 5, which is derived from the stoichiometry of the DA reaction. The molar mass of the linker was calculated from its chemical structure and the molar mass of the building block was determined by SEC with static light scattering in THF at room temperature ($M_n = 7600$ g/mol).

$$\text{Contrast}_{DA\ network} = X_L \cdot \frac{A_L}{c_L} + (1 - X_L) \cdot \frac{A_{Block}}{c_{Block}} \quad \text{Equation 4}$$

$$X_L = \frac{M_L}{M_L + 2 \cdot M_{Block}} \quad \text{Equation 5}$$

All contrast factors were acquired at the same day at which the corresponding network samples were measured for minimizing errors due to slowly changing composition of the solvent.

Having calculated the averaged contrast factors, intrinsic viscosities and molar masses are calculated with the following Scilab-script:

```
Data = fscanfMat('ptbua-0205.txt', "%1g");    //read file (columns: Time, dRI, UV1, UV2, DP)

Frequency = 5;    //Data points/s

//Detector calibrations
kDP = 9.405;
IP = 31600;    //Inlet Pressure in Pa

slope = -0.80357;
intercept = 10.15677;

clear MM;
clear Results;

Data(:,5) = abs(Data(:,5));

PeakThreshold = 0.1;

//Concentration Calibrations: Averaged response factors of linker block (i.e. = DA polymer) for dRI detector
dRIDAPolymer = 12.565;

//Determine Peak Borders

FontSize = 4;
clf();
plot(Data(:,1), Data(:,5), "b");
plot(Data(:,1), Data(:,2), "b");
xlabel("Time (min)");
ylabel("dRI (mV)");
title("Chromatogramm");
a = gca();    //Get Current Axes (gca)
a.font_size = FontSize;    //Font size axis label
a.title.font_size = FontSize+1;
a.x_label.font_size = FontSize;
a.y_label.font_size = FontSize;
a.data_bounds(1,1) = 4;
a.data_bounds(1,2) = -10;
a.data_bounds(2,1) = 14;

Borders = locate(2,1);    //Get Peak Borders Points

Index0 = round(Borders(1,1)*60*Frequency);
Index1 = round(Borders(2,1)*60*Frequency);

//Determine Concentrations
```

```

slice = Index0;
counter = 1;

Results = zeros((Index1 - Index0), 4);

for counter = 1:(Index1-Index0)

    dRI = Data(slice, 2);

    Results(slice, 1) = slice/300;      // Time
    Results(slice, 2) = dRI/dRIDAPolymer; // cPDAolymer dRI
    Results(slice, 3) = log10(4*10*Data(slice,5)/(IP - 2*Data(slice,5)) * kDP / Results(slice,2)); // = lg(4*DP/(IP - 2*DP) *
kVisco / ctot) = lg[n]
    Results(slice, 4) = slope*Data(slice,1) + intercept - Results(slice,3); //Universal calibration

    universal calibration
    slice = slice + 1;
end

dRIMax = max(Data(:, 2));

slice = Index0;
counter = 1;
for counter = 1:(Index1-Index0)
    if Data(slice, 2) > dRIMax*PeakThreshold then
        else
            Results(slice, :) = 0;
            MM(slice, :) = 0;
        end
    slice = slice + 1;
end

```

6. The linear DA P^tBuA

As an additional reference, a linear DA P^tBuA was measured as well. Its structure is shown in Figure S11:

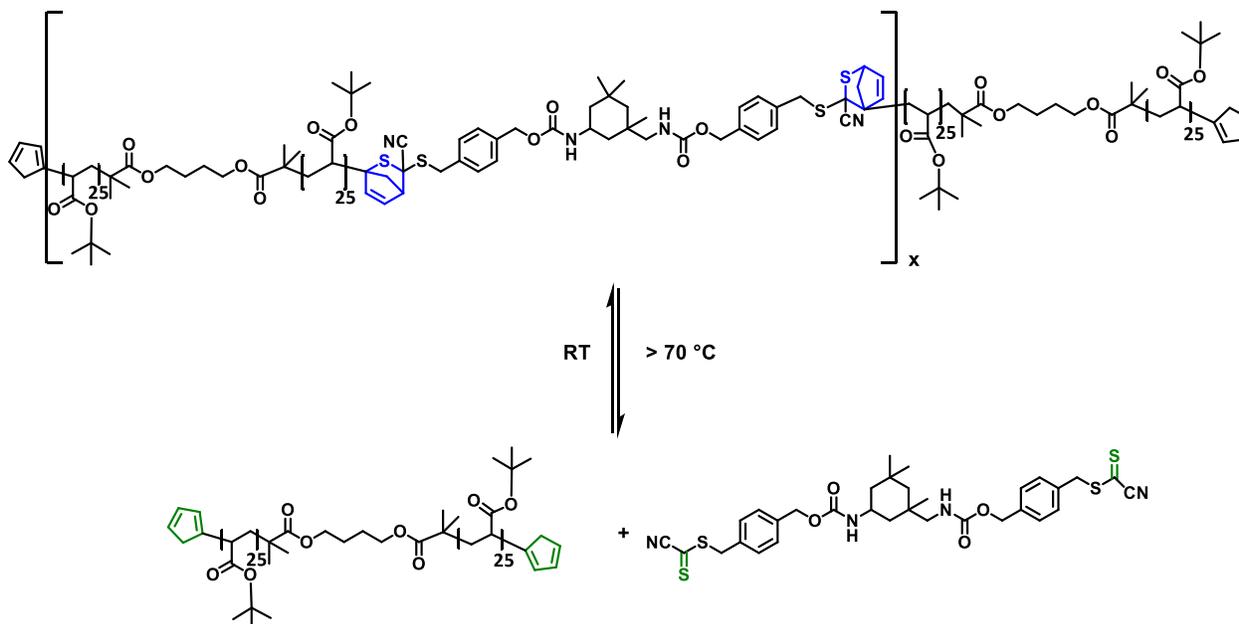


Figure S11: Structure of the linear DA P^tBuA, consisting of a P^tBuA building block and a HDA-Dilinker.

It consists of the Cp_2 end-functionalized P^tBuA building block and the HDA-Dilinker. The syntheses of the compounds is described in reference^[2].

In order to understand more profoundly the conformation of the DA polymers, a quantum chemical geometry optimization (MM2) of the CDTE-Dilinker was performed with Chem3D Pro.^[5] As a result the Dilinker appears not rod-like but adopts a V-shaped geometry. Consequently, the connected building blocks are brought together closely and have to orient in an almost parallel manner at their connection points, thus probably leading to a more compact packing of the linear polymer building blocks.

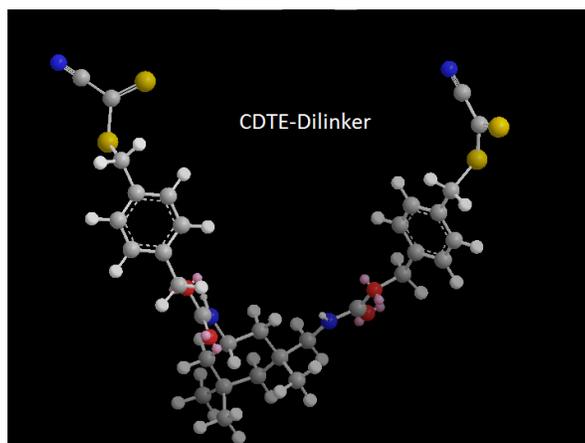


Figure S12: Optimized geometry of the CDTE-Dilinker. Color coding: gray = carbon, white = hydrogen, blue = nitrogen, red = oxygen, yellow = sulfur. The DA reaction takes place at the C=S double bond.

The hypothesis of a more compact packing of the building blocks was tested by the means of a simple self-avoiding-walk (SAW) model, in which two polymers with identical DP_n were generated at the ends of a linear and an angled linker molecule. In Figure S13, two exemplary model polymers are shown that are obtained by SAW from a linear and an angled linker molecule, respectively. The calculations were performed in Scilab 5.5.2.^[4]

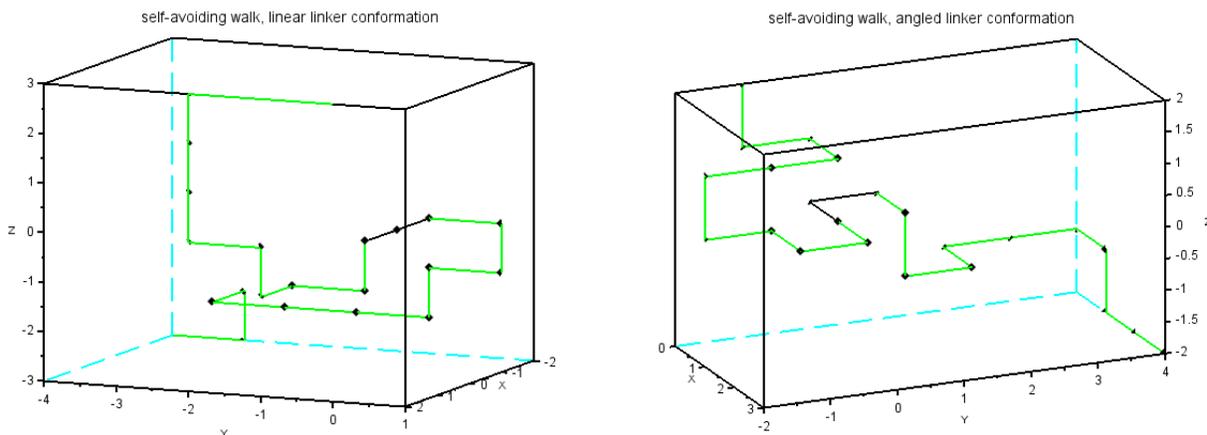


Figure S13: Examples of self-avoiding-walks generating polymers with a DP_n of 10 from a linear (left) and an angled (right) linker. The linker is represented in black.

In order to estimate the density of the obtained polymers the radius of gyration r_g was calculated according to **Equation 6**, where N is the number of monomers and r_k and r_{mean} represent the vectors to the k th monomer and center of mass, respectively.

$$r_g = \sqrt{\frac{1}{N} \sum_{k=1}^N (r_k - r_{mean})^2} \quad \text{Equation 6}$$

The calculations were performed for three values of DP_n , namely 5, 10 and 25. Within this simplified model, the monomers do not necessarily represent the actual chemical monomers, but rather segments that can be jointed freely in space. In the case of the P^tBuA building blocks, 50 ^tBuA units constitute one building block, and, thus, the contour length of the polymer is at around 13 nm (approx. 0.13 nm per C-C bond, approx. 100 bonds). In our previous work we determined the persistence length of P^tBuA in THF to be 2.2 nm^[2], which results in approximately 6 segments.

In order to obtain representative values, for each DP_n and linker conformation 20,000 polymers were simulated. Their r_g were calculated as described above and averaged. In Figure S14, the ratio of the r_g of the polymers with linear and angled linker conformation are shown. All values exceed 1, implying that in fact the polymers that were obtained from the linear linker configuration are characterized by a larger r_g than their counterparts from the angled linker. Moreover, the effect is becoming more pronounced for lower segment numbers DP_n . As stated above, for the P^tBuA system the segment number is expected to be between 5 and 10. Hence, our estimation underlines that it is likely that the DA P^tBuA is more compact than the pure P^tBuA, due to the angled nature of the CDTE-Dilinker.

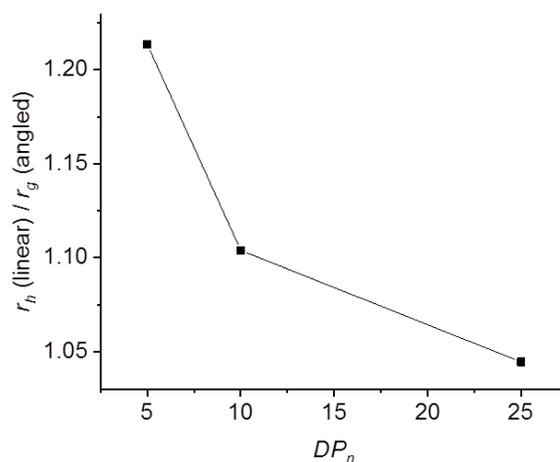


Figure S14: Ratio of r_g of two polymer blocks joined at a linear and angled linker as function of the segment number DP_n .

The Scilab-script for the SAW and r_g -calculation is reads as follows:

```

clear;
NumIterations = 20000;
DPn = 10; //The dpn of each chain attached
DisplayInterval = 1000;

//Dilinker Coordinates
Coords(DPn + 1, 1:3) = [1 0 0];
Coords(DPn + 2, 1:3) = 0;
// Coords(DPn + 3, 1:3) = [-1 0 0]; //linear
Coords(DPn + 3, 1:3) = [0 1 0]; //angled

function [IsOverlapping]=CheckOverlap(NewPoint, Coords)
    IsOverlapping = 0;
    for Index=1:length(Coords(:, 1))
        if Coords(Index, :) == NewPoint then
            IsOverlapping = 1
        end
    end
endfunction

function [NewPoint]=GetNewPoint(OldPoint)
    RandomNumber = rand()*6;
    if RandomNumber < 1 then
        NewPoint(1) = OldPoint(1) + 1;
        NewPoint(2) = OldPoint(2);
        NewPoint(3) = OldPoint(3);
    elseif RandomNumber < 2 then
        NewPoint(1) = OldPoint(1) - 1;
        NewPoint(2) = OldPoint(2);
        NewPoint(3) = OldPoint(3);
    elseif RandomNumber < 3 then
        NewPoint(1) = OldPoint(1);
        NewPoint(2) = OldPoint(2) + 1;
        NewPoint(3) = OldPoint(3);
    elseif RandomNumber < 4 then
        NewPoint(1) = OldPoint(1);
        NewPoint(2) = OldPoint(2) - 1;
        NewPoint(3) = OldPoint(3);
    elseif RandomNumber < 5 then
        NewPoint(1) = OldPoint(1);
        NewPoint(2) = OldPoint(2);
        NewPoint(3) = OldPoint(3) + 1;
    else
        NewPoint(1) = OldPoint(1);
        NewPoint(2) = OldPoint(2);
        NewPoint(3) = OldPoint(3) - 1;
    end
    NewPoint = NewPoint';
endfunction

DisplayIntervalCounter = 1;

for Iteration=1:NumIterations
    DisplayIntervalCounter = DisplayIntervalCounter + 1;
    Coords(1:DPn, :) = 0;
    Coords(DPn+4:2*DPn+3, :) = 0;
    GrowthIndices = [DPn+1 DPn+3];

```

```

//Perform self-avoiding walk
for i=1:DPn
    //Grow first chain
    WasAborted = 0;
    IsOverlapping = 1;
    Counter = 1;
//    Checked
    while IsOverlapping == 1
        NewPoint = GetNewPoint(Coords(GrowthIndices(1), :));
        IsOverlapping = CheckOverlap(NewPoint, Coords);
        Counter = Counter + 1;
        if Counter > 60 then
            disp('Self-Avoiding-Walk got stuck at iteration ' + string(Iteration));
            WasAborted = 1;
            break;
        end
    end

    end

    if WasAborted == 1 then
        break
    else

        Coords(GrowthIndices(1)-1, :) = NewPoint;
        GrowthIndices(1) = GrowthIndices(1)-1; //decrement growth index

        IsOverlapping = 1;
        Counter = 1;
        while IsOverlapping == 1
            NewPoint = GetNewPoint(Coords(GrowthIndices(2), :));
            IsOverlapping = CheckOverlap(NewPoint, Coords);
            Counter = Counter + 1;
            if Counter > 60 then
                disp('Self-Avoiding-Walk got stuck at iteration ' + string(Iteration));
                WasAborted = 1;
                break;
            end
        end
        end
        Coords(GrowthIndices(2)+1, :) = NewPoint;
        GrowthIndices(2) = GrowthIndices(2) + 1; //increment growth index

        //Calculate Rg
        //get Rmean
        rmean = [mean(Coords(:, 1)) mean(Coords(:, 2)) mean(Coords(:, 3))];
        rg2(Iteration) = 0;
        for l=1:length(Coords(:, 1))
            rg2(Iteration) = rg2(Iteration) + (Coords(l, 1) - rmean(1) + Coords(l, 2) - rmean(2) + Coords(l, 3) - rmean(3))^2;
        end
        rg2(Iteration) = rg2(Iteration)/length(Coords(:, 1));
        rgmean(Iteration) = mean(rg2^0.5);

        if DisplayIntervalCounter > DisplayInterval then
            disp('Iteration ' + string(Iteration) + ' of ' + string(NumIterations) + ', Rg2 mean = ' + string(rgmean(Iteration)));
            clf();
            plot2d(linspace(1, Iteration, Iteration), rgmean);
            DisplayIntervalCounter = 1;
        end
    end
end

end
end
end

```

```
end
```

```
Coords2(1, 1:3) = [1 0 0];  
Coords2(2, 1:3) = 0;  
// Coords2(3, 1:3) = [-1 0 0]; //linear  
Coords2(3, 1:3) = [0 1 0]; //angled  
  
clf();  
param3d1(Coords(:, 1), Coords(:, 2), Coords(:, 3));  
a = gca();  
a.thickness = 2;  
a.font_size = 2;  
title('self-avoiding walk, angled linker conformation', 'fontsize', 3);  
h = a.children; //get the handle of the param3d entity: an Compound composed of 2 curves  
h.foreground = 3;  
h.mark_style = 4;  
h.thickness = 2;  
  
clear h a;  
  
param3d1(Coords2(:, 1), Coords2(:, 2), Coords2(:, 3));
```

7. Linear P^tBuA samples as reference

The molar masses of the reference P^tBuA samples were determined by SEC in THF using universal calibration. In Table S1 the molar masses are summarized:

Table S1: Molar masses of reference P^tBuA samples

M _n (g/mol)	M _w (g/mol)	D _m
5900	7080	1.2
25000	29000	1.15
58000	70000	1.2

8. Simulating the effect of IDD on α

The effect of IDD on the resulting α parameter was done by a simple script in Scilab 5.5.2.^[4] Its general structure is described in the following:

- (1) Generate Gauss peak of particular width (0.5 = narrow, 0.7 = broad, 0.9 = very broad) → represents concentration signal
- (2) Assume arbitrary, yet realistic, calibration function for assigning a molar mass to each point.
- (3) For each point calculate corresponding viscosity according to $[\eta]_0 = K \cdot M^\alpha$, where K is, for simplicity, set to 1 and α is chosen to be 0.3, 0.5 or 0.7 in order to represent a highly branched, a moderately branched and a linear polymer, respectively.
- (4) The corresponding viscosity trace is then calculated by multiplying the concentration with the intrinsic viscosity.
- (5) The two peaks are now “ideal” peaks so that, when the normal procedure for calculating the KMH plot is applied, exactly the α parameter is obtained that was assumed in step (3).
- (6) The viscosity peak is artificially offset in a range of ± 0.05 min in 9 steps, thus introducing the “IDD Error”.
- (7) For each “IDD Error” the calculations for the KMH plots are performed and the slope of the plot is then taken as the corresponding α .

The thereby obtained values are compared to the experimentally acquired, as shown in Figure S15:

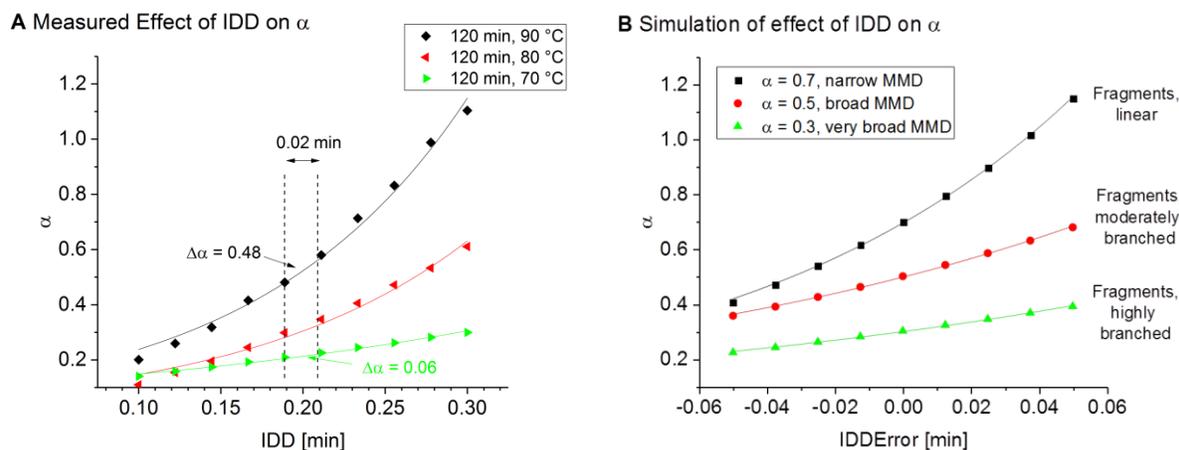


Figure S15: A: The resulting α parameters of the DA network fragments after calculating with different values of IDD. B: The theoretical effect of the IDD on α for different hypothetical peaks that represent different states of debonding.

Two phenomena can be observed: Firstly, the relative order of the α curve seems to reflect the trend of the α values depicted Figure S15 A, namely $\alpha(90\text{ °C}) > \alpha(80\text{ °C}) > \alpha(70\text{ °C})$. Secondly, the overall impact of the IDD on the α -calculation is much stronger for the higher temperatures and can easily introduce significant errors, i.e. an error in the IDD of 0.02 min translates into an error in α of 0.1. The increasing effect is to be addressed to the width of the peak: An error of *e.g.*, 0.02 min in IDD will have a smaller effect on a very broad peak (*i.e.*, $\Delta\alpha = 0.06$ at 70 °C) than on a narrower peak (*i.e.*, $\Delta\alpha = 0.48$ at 90 °C). Both effects can be corroborated by our simple simulation as shown in Figure S15 B. Here, the same calculations were performed for three hypothetical chromatograms that reflect the proposed states of the rDA de-crosslinking: (i) a compact polymer ($\alpha = 0.3$) with a very broad distribution, (ii) a less compact one ($\alpha = 0.5$) yet still comprising a broad peak and eventually (iii) a linear polymer ($\alpha = 0.7$) with a relatively narrow peak. In fact, the appearance of the experimentally obtained IDD error can be reconstructed, at least in a qualitative manner: A higher α shifts the entire curve upwards and a narrower MMD makes the curve steeper. The agreement of simulation and experiment on the one hand indicates that, again, the obtained results appear to be reasonable, but on the other hand, the determination of a precise α is becoming more difficult at higher degrees of debonding (*i.e.*, at higher temperatures).

A very effective way for monitoring changes in the IDD would be to add marker molecules that do not overlap with the actual polymers but are still visible in all detectors. With that regard the viscometer is critical as it is usually insensitive to molecules of low molar mass that elute later than the polymers. It would be interesting to assess if enthalpic contributions could be harnessed to retain a narrowly distributed polymer of a few thousands g/mol so that it elutes in HPLC mode after the solvent peak.

Ideally, that polymer would be equipped with functional groups that provoke enthalpic interactions for late elution and, at the same time, render it visible also in UV/Vis detection. Such studies will be subject of future work, rendering multi-detection SEC less vulnerable to errors due to interdetector delays.

9. Bibliography

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- [4] **2015**, Scilab 5.5.2 (www.scilab.org).
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