Electronic Supplementary Material (ESI) for Polymer Chemistry.

# Supporting information for:
# A novel method for the measurement of degenerative chain transfer coefficients: proof of concept and experimental validation

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## Contents

## 1 Stepwise integration to obtain the evolution of Đ with monomer conversion with Equation (6) in the main text

For a monomer conversion step ($x_0$ → $x$)[1], Equation (9) and (10) in the main text can be analytically solved *via e.g.* the mathematics software package Maple 18 with initial conditions $\tau_1$ = $Q_1$ (mol L$^{-1}$) and $\tau_2$ = $Q_2$ (mol L$^{-1}$) at $x = x_0$. A closed expression for $\tau_1$ (Equation (S1)) is obtained and an integral expression for $\tau_2$ (Equation (S2)):

$$\tau_1(x) = \frac{\langle C_{tr}\rangle[M]_0\tau_0(1-x)}{\langle C_{tr}\rangle B - \tau_0 A} + \frac{(1-x)^D\left(Q_1 + \frac{\langle C_{tr}\rangle[M]_0\tau_0(x_0-1)}{\langle C_{tr}\rangle B - \tau_0 A}\right.}{(1-x_0)^D} \qquad \textbf{(S1)}$$

$$\tau_2(x) = (x-1)^D\left\{\frac{Q_2}{(x_0-1)^D} + \int_{x_0}^{x}\frac{\langle C_{tr}\rangle[M}{\tau_0(\langle C_{tr}\rangle + A)^2(A}\right. \qquad \textbf{(S2)}$$

in which $A = \frac{<k_t>\lambda_0}{k_p\tau_0}$, $B = \frac{<k_t>\lambda_0}{k_p} - \tau_0$, and $D = \frac{C_{tr}A}{C_{tr}+A}$. Solving the integral in Equation (S2) yields a complicated but still analytical expression for $\tau_2(x)$ which holds in the considered conversion interval (Equation (S3)):

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[1] In the Supporting Information the short notation $x$ is used instead of $x_m$.

$$
\begin{aligned}
&\tau_2(x) \\
&\quad = (1-x)^{D}(1-x_0)^{-D}\Bigg[Q_2 + \frac{\langle C_{tr}\rangle[M]_0(x-x}{\tau_0(\langle C_{tr}} \\
&\Bigg\{-(1-x_0)^{-D+1}\Bigg[(x-x_0)2\langle C_{tr}^2\rangle[M]_0\tau_0 + \frac{A}{} \\
&\quad + \frac{\langle C_{tr}\rangle[M]_0(x-1)\big(A^2\tau_0^2 - AB\langle C_{tr}\rangle\tau_0 + A\langle C}{\tau_0\big(\langle C_{tr}\rangle + A\big)^2\big(A\tau_0 - B\langle C_{tr}\rangle\big)(-} \\
&\quad + \frac{\langle C_{tr}\rangle[M]_0(x-1)^2(2\langle C_{tr}^2\rangle[M]_0\tau_0 - 2A[M]_0}{\tau_0\big(\langle C_{tr}\rangle + A\big)^2\big(A\tau_0 - B\langle C_{tr}\rangle\big)(-}
\end{aligned}
\qquad \textbf{(S3)}
$$

The analytical expression for Đ at each $x$ can be obtained by application of Equation (6) in the main text, using the expressions for $\tau_1(x)$ and $\tau_2(x)$ in respectively Equation (S1) and Equation (S3), taking into account that $\tau_0$ is constant. In Figure S1 the procedure for the stepwise integration is illustrated via both a flow chart (left) and schematic representation (right).

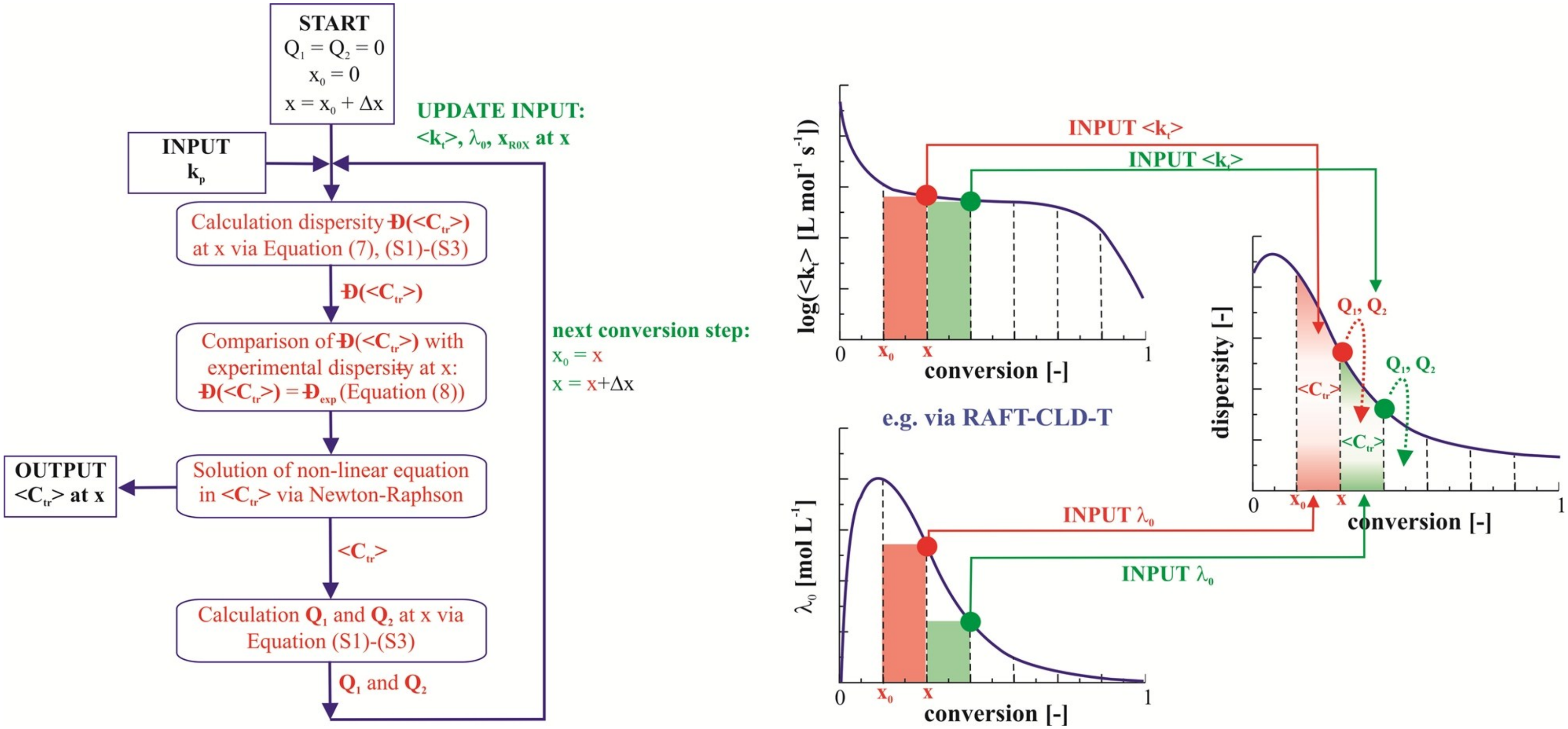

***Figure S1:*** *Summary of the methodology developed in the present work to determine $<C_{tr}>$ as function of conversion via a flow chart, including input parameters (left figure) and schematic representation of the stepwise integration procedure (right figure). In red and green two consecutive integration intervals for the conversion are indicated. $Q_1$ and $Q_2$ calculated at the conversion separating both intervals are used as initial conditions in the next integration interval (Equation (S1)-(S3)).*

## 2 Procedure to assess the sensitivity to a (apparent) chain length dependent RAFT transfer reactivity

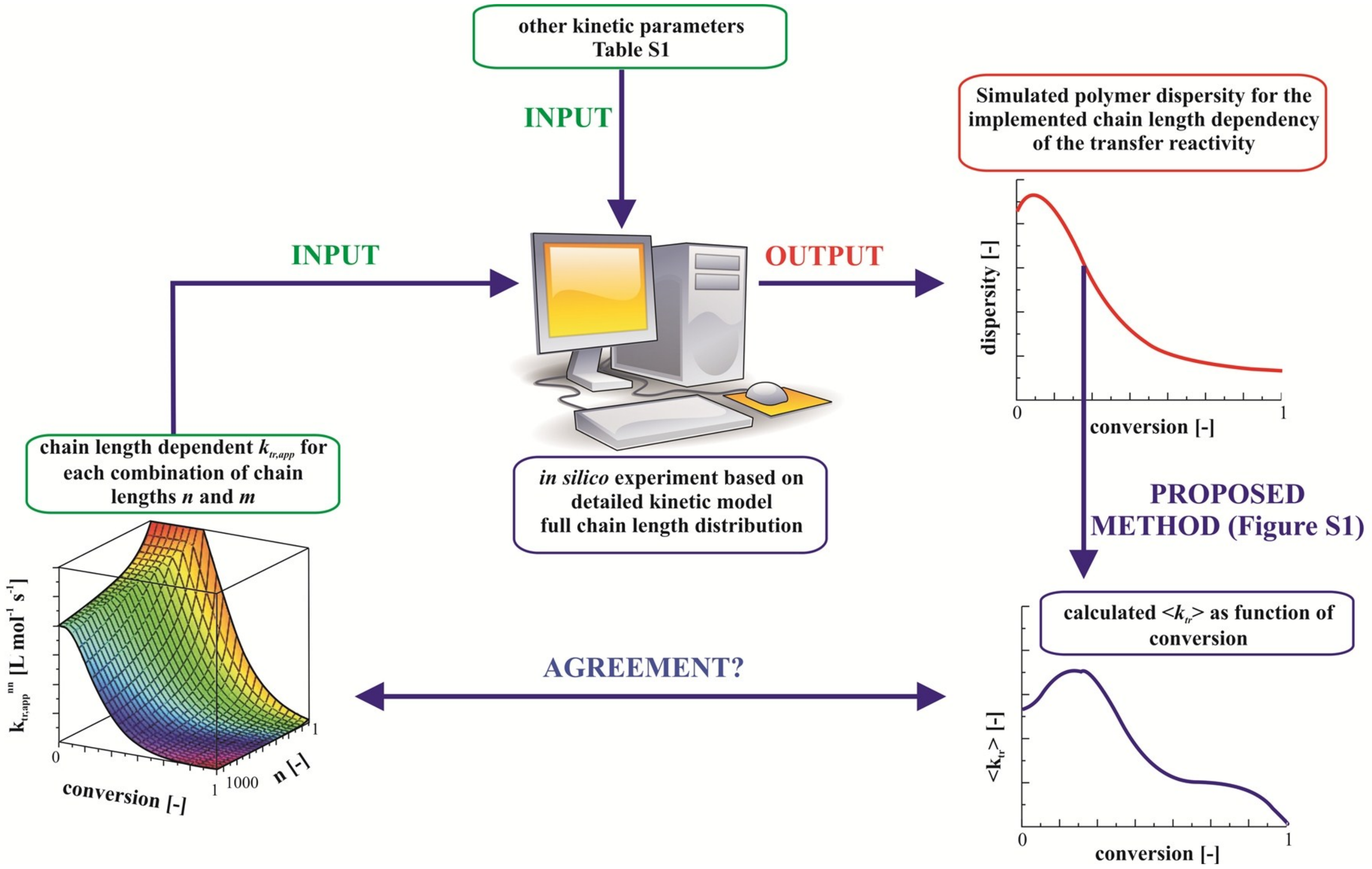

***Figure S2:*** *In silico procedure applied to assess the sensitivity of the developed methodology (Figure S1) for possible chain length dependent RAFT transfer kinetics.*

The apparent RAFT reactivities for the theoretical cases with a deliberately very strong dependency are calculated in a similar way as typically done for termination, using the RAFT-CLD-T technique (all parameters except $k_{t,11}^{app}$ from the work of Johnston-Hall *et al.*; main text):

$$for\ i < i_{gel}\ and\ i < i_{SL}: k_{t,ii}^{app} = k_{t,11}^{app} i^{-\alpha_s}$$

$$for\ i < i_{gel}\ and\ i \geq i_{SL}: k_{t,ii}^{app} = k_{t,11}^{app} i_{SL}^{\alpha_l - \alpha_s} i^{-\alpha_l}$$

$$for\ i \geq i_{gel}\ and\ i < i_{SL}: k_{t,ii}^{app} = k_{t,11}^{app} i_{gel}^{\alpha_{gel} - \alpha_s} i^{-\alpha_{gel}}$$

$$for\ i \geq i_{gel}\ and\ i < i_{SL}: k_{t,ii}^{app} = k_{t,11}^{app} i_{SL}^{\alpha_l - \alpha_s} i_{gel}^{\alpha_{gel} - \alpha_l} i^{-\alpha_{gel}}$$

The apparent dependency is implemented explicitly, thus for each $k_{trn,m}(x)$ individually in Table 1. An initial theoretical value for $C_{tr}$ of 120 at $x = 0$ and $x_n = 1$ is used (replacement of $k_{t,11}^{app}$). For simplicity, a geometric mean model has been assumed to determine $k_{trn,m(x)}$ for n ≠ m.

## 3 Numerical solution procedure to solve the main Equation (8) in the main text

In Figure S3, the use of the Newton-Rhapson method is illustrated for the determination of the RAFT transfer reactivity via the methodology presented in the main text. The non-linear function of which the root, *i.e.* the population averaged RAFT transfer reactivity $<C_{tr}>$, needs to be found is the difference between the calculated dispersity Đ($<C_{tr}>$) based on Equation (6) in the main text and the experimental dispersity at the considered conversion (Figure S5). If convergence is reached at a particular conversion step (convergence criterion denoted with '*e*'; a deviation of 1% is used), the obtained value for $<C_{tr}>$ will serve as an initial guess for the solution of the non-linear equation $f(<C_{tr}>) = 0$ in the next conversion step.

However, at higher monomer conversions for which the variation of the dispersity becomes less pronounced, a significant overshoot of $<C_{tr}>$ occurs, as indicated in the main text. This is due to the shape of the non-linear curve of which the root needs to be found: $f(<C_{tr}>) = 0$. In particular, for such monomer conversions, in the close proximity of the root, the derivative of $f(<C_{tr}>)$ becomes very small (*cf.* Figure S4) so that small deviations in $f(<C_{tr}>)$ cause very large variations in $<C_{tr}>$. Hence, small inaccuracies in the analytical expression for Đ($<C_{tr}>$) will shift the corresponding root $<C_{tr}>$ of the function $f(<C_{tr}>)$ towards substantially higher values. For this the use of sensitivity testing is recommendable (see main text and Figure S5).

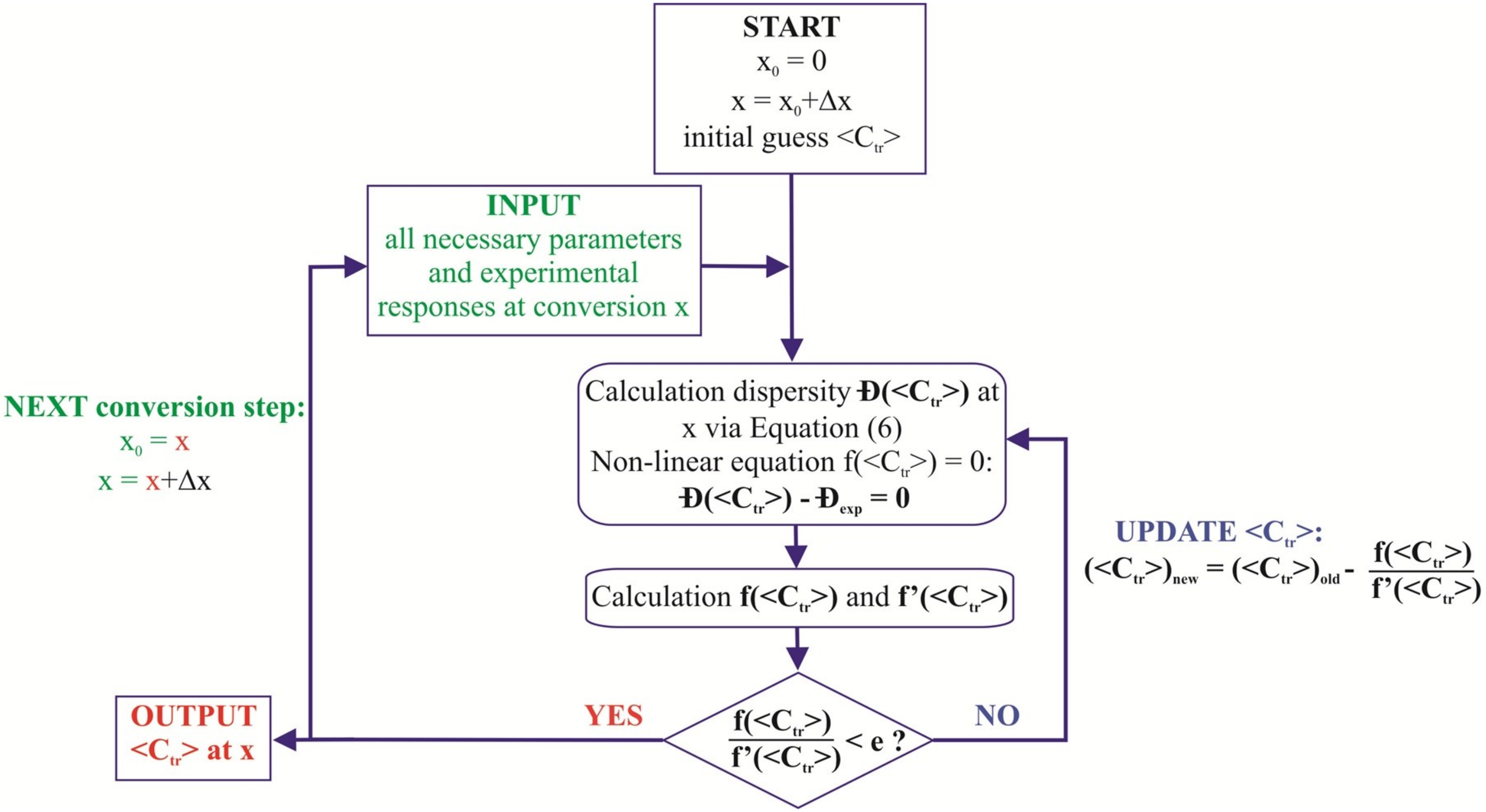

***Figure S3:*** *Newton-Raphson procedure applied in the methodology developed in the present work to determine the RAFT chain transfer reactivity* $<C_{tr}>$ *based on a comparison between experimental dispersity data* ($Đ_{exp}$) *and calculated dispersity data via analytical expressions* ($Đ(<C_{tr}>)$, *Equation (6)).*

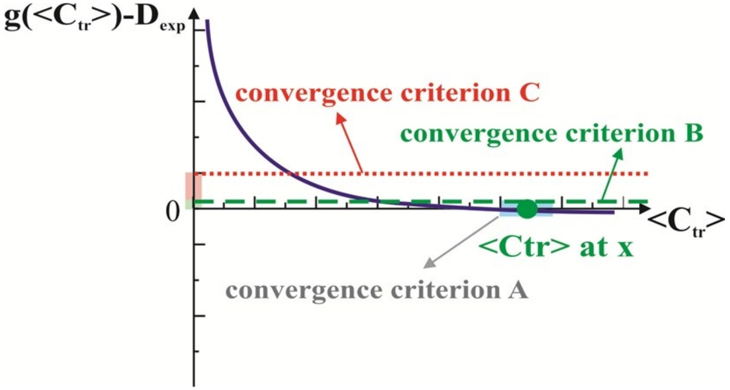

***Figure S4:*** *Shape of the non-linear Equation (8) as function of <*$C_{tr}$*> obtained for each conversion x in the methodology developed in the present work. The Newton-Raphson method is indicated in blue, the additional solutions for sensitivity testing are highlighted in respectively green and red and are used. Note strictly absolute values on the y-axis.*

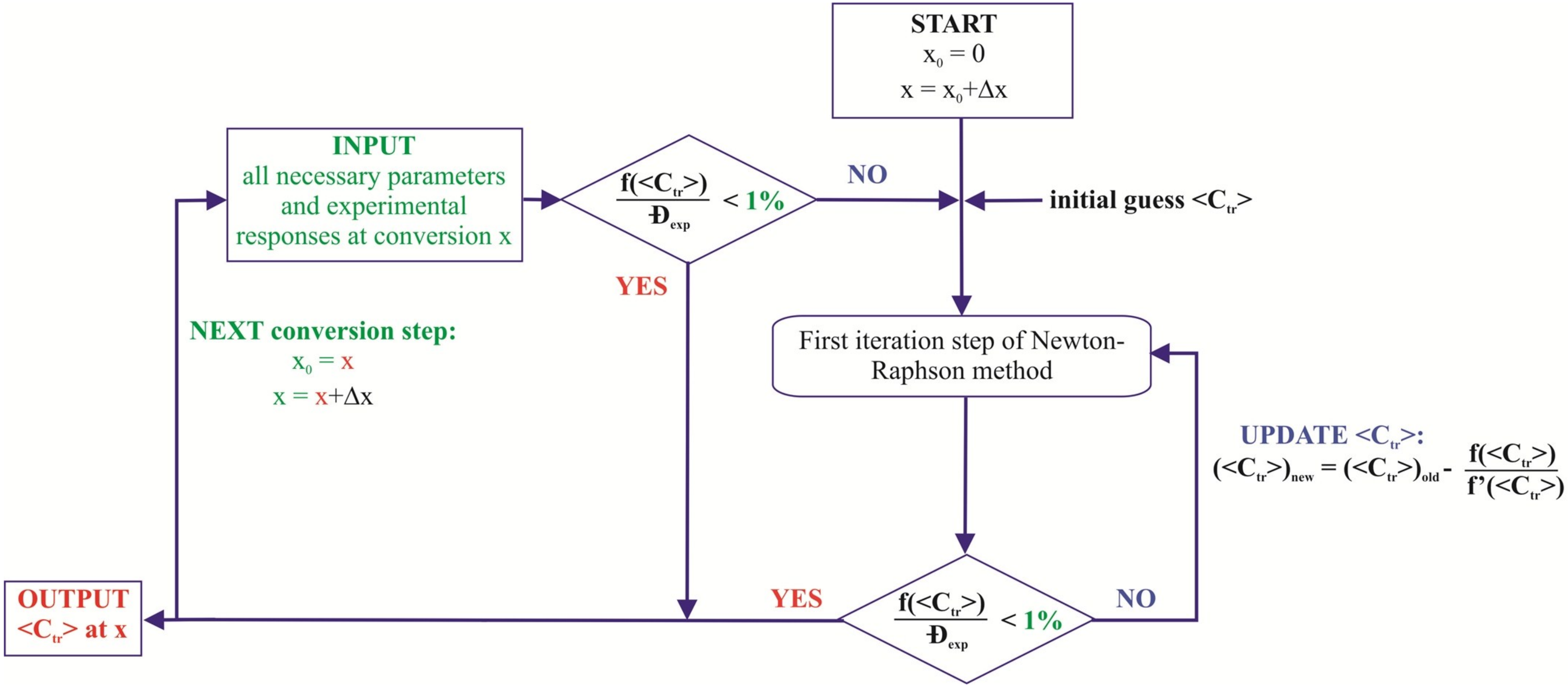

***Figure S5:*** *Addition for Figure S4: additional sensitivity testing (here 1% deviation case).*

## 4 Additional input parameters and experimental protocol for reliable measurement of the RAFT transfer reactivity

The proposed methodology in the present work to determine the RAFT transfer reactivity relies on the accurate knowledge of several quantities as input, *i.e.* the average (apparent) termination ($<k_t>$) and propagation ($k_p$) rate coefficient, the total radical concentration ($\lambda_0$) and the RAFT chain transfer agent conversion ($x_{R_0X}$). For each conversion at which a reliable value for the population averaged RAFT transfer reactivity $<C_{tr}>$ is desired via the developed method, $<k_t>$, $k_p$, $\lambda_0$ and $x_{R_0X}$ need to be precisely known. Each of them will be discussed separately after which two possible experimental protocols are suggested in which references are made to the supplementary Excel file for the calculation of $<C_{tr}>$.

### *4.1 Propagation reactivity*

Via pulsed laser polymerization (PLP) – size exclusion chromatography (SEC) accurate values for $k_p$ for a range of monomers have been already determined,[1] and, even for acrylate monomers, correction factors have been introduced to account for the lower propagation reactivity of the tertiary radicals,[2-4] allowing the application of the developed methodology. Furthermore, the reported intrinsic chain length dependency of the propagation reactivity for low chain lengths (CL < 10)[5,6] will only interfere with the obtained results if very low targeted chain lengths (TCLs) are considered. In general, the highest accuracy of the proposed method is obtained for high TCLs (*cf.* main text) with consequently a negligible influence of this intrinsic chain length dependency of $k_p$. Diffusional limitations due to the increasing viscosity throughout a radical polymerization experiment have been shown to only interfere with the propagation reactivity at very high conversions ($x > 0.8$).[7,8]

## 4.2 Apparent termination reactivity

Similar to the case of propagation, the termination reactivity has been widely studied for an extended range of monomers.[9,10] However, in contrast to propagation, termination is greatly affected by diffusional limitations due its high intrinsic reactivity. Hence, an apparent termination rate coefficient needs to be considered which changes throughout the course of the polymerization reaction. Via both PLP-based techniques and the RAFT – chain length dependent – termination (RAFT-CLD-T) method, the chain length and conversion dependency of the termination rate coefficients has been accurately mapped into a surface function $<k_t(n,x)>$ which depends both on the chain length $n$ and the conversion $x$, and this for several monomers.[9] Since for RAFT polymerizations, typically a good control over the chain length distribution (CLD) is established, the polymerization mixture can be assumed to be characterized by a single chain length $n$ at each conversion $x$.[11,12] Hence, the literature reported surface function $<k_t(n,x)>$ for the considered monomer can be safely used.[13] Only for low transfer reactivities ($C_{tr,0} < 5$) care should be taken as a broader CLD will be obtained, leading to less reliable results.

## 4.3 RAFT CTA conversion

Several experimental methods are available to monitor the RAFT CTA conversion $x_{R_0X}$. Spectroscopic analysis techniques based on UV absorption or $^1$H nuclear magnetic resonance ($^1$H-NMR) are commonly applied to directly measure the concentration decay of $R_0X$.[14-17] On the other hand, indirect methods based on the evolution of the chain length also yield a reliable estimate for $x_{R_0X}$,[14] albeit with a slight loss of accuracy as the corresponding SEC measurements are less precise. In the main text, $x_{R_0X}$ is determined via the indirect method for the evaluation of the transfer reactivity for the RAFT polymerization of methyl methacrylate with cyano-isopropyl dithiobenzoate at 353 K (Equation (13)-(14) in the main text).

### *4.4 Total radical concentration*

The determination of the total radical concentration $\lambda_0$ is less straight forward and goes hand in hand with the proposed experimental protocol in the next section. Direct measurement of the total radical concentration is difficult and requires expensive equipment, *e.g.* electron paramagnetic resonance spectroscopy,[18-20] for which calibration for absolute concentration measurements can be a tedious task. On the other hand, indirect methods enable a simple determination of $\lambda_0$, based on the measurement of the polymerization rate $r_{pol}$:

$$r_{pol} = -\frac{d[M]}{dt} = k_p[M]\lambda_0 \quad \textbf{(S5)}$$

$$\lambda_0 = \frac{r_{pol}}{k_p[M]} \quad \textbf{(S6)}$$

in which $[M]$ is the monomer concentration (mol $L^{-1}$). The polymerization rate can be easily accessed as a function of conversion via isothermal differential scanning calorimetric (DSC) measurements as performed when applying the RAFT-CLD-T technique.[16] In addition, a very easy way to calculate the polymerization rate is by determining the slope of the conversion-time profile:

$$r_{pol} = -\frac{d[M]}{dt} = [M]_0 \frac{d\left(\frac{[M]_0 - [M]}{[M]_0}\right)}{dt} = [M]_0 \frac{dx}{dt} \quad \textbf{(S7)}$$

in which $[\,]_0$ denotes the initial concentration (mol $L^{-1}$). Via Equation (S6) a value for $\lambda_0$ is again obtained. In order to apply Equation (S7) highly time-resolved conversion measurements are required to be able to accurately determine the slope of the conversion-time profile. Therefore, Equation (S7) is often only applied to the start of the polymerization reaction as typically a linear increase of the conversion with time is initially obtained and, hence, no on-line monitoring of the conversion is required. For an accurate measurement of the first conversion point $x_0$ at time $t_0$, in principle, the polymerization rate can be calculated as:

$$r_{pol} = [M]_0 \frac{x_0}{t_0} \tag{S8}$$

If at the time $t_0$ (conversion $x_0$) also an accurate measurement of the dispersity and $x_{R_0X}$, and accurate input parameters for $k_p$ and $<k_t>$ are available, the value of $C_{tr,0}$ can be accurately determined from one single experimental data point, as shown in the main text.

### *4.5 Experimental protocol*

Based on the discussion in the previous section on the determination of the total radical concentration, two experimental protocols can be identified for (*i*) the determination of $<C_{tr}>$ for the complete conversion region, and (*ii*) the determination of only $<C_{tr}>$ (= $C_{tr,0}$) at the start of the RAFT polymerization. Both options (*i*) and (*ii*) are implemented in the supplementary Excel file for the direct calculation of $<C_{tr}>$.

#### 4.5.1 Determination of $<C_{tr}>$ for the complete conversion region

In order to apply the developed methodology in the present work for the complete conversion region of the considered RAFT polymerization, two parallel analyses for the *same RAFT polymerization mixture* need to be performed. One in which the conversion or the polymerization rate is monitored on-line (**a**) with a sufficiently high time-resolution (e.g. DSC, FTIR) to be able to retrieve accurate values for the polymerization rate, and another parallel one in which samples are taken (**b**) to measure the dispersity and chain length via SEC. It is recommended to also verify the agreement between the sampling experiment and the on-line experiment by an additional off-line conversion analysis of the samples taken, as highlighted before in the work of Derboven *et al.*[13] Ideally, the same conversion for a given time should be obtained in both experiments. Note that instead of the highly time-resolved conversion measurements **(a)**, the total radical concentration can also be directly monitored via *e.g.* EPR. The different steps that need to be taken to obtain values for $<C_{tr}>$ via the method in the current work after successfully performing the parallel experiments (**a**) and (**b**) are presented below. Always reference is made to the corresponding input in the supplementary spreadsheet that can be obtained upon request (indicated in blue).

*Step 0:* Specify which monomer is used in step 1 of the input spreadsheet. Enter the initial concentration of monomer and RAFT CTA ($R_0X$) in step 2 of the input spreadsheet.

*Step1:* Calculation of the total radical concentration $\lambda_0$ from $x$ or $r_{pol}$ measured in the on-line experiment (**a**) via Equation (S5)-(S7) at the times of the samples taken in experiment (**b**). Alternatively the $\lambda_0$ is measured directly via *e.g.* EPR. Enter the obtained values for $\lambda_0$ in cell F59-... in step 7 of the input spreadsheet.

*Step 2:* Calculation of $<k_t>$ from available surface functions in literature at the specific conversion and chain length of each sampling point in experiment (**b**), and look for a reliable value of $k_p$ in the scientific literature.[1] RAFT-CLD-T or PLP based data for $<k_t>$ and $k_p$ are recommended above kinetic data from stationary experiments.[9,21] Enter the value for $k_p$ in step 3 of the input spreadsheet, or, in case the considered monomer is styrene or methyl methacrylate, specify the temperature at which $k_p$ needs to be calculated. If the termination rate coefficient $k_t$ is directly measured, enter the obtained values in cell H59-... in step 7 of the input spreadsheet. If not, follow the instructions in step 5 of the input spreadsheet, leave the $k_t$ data in step 7 of the input spreadsheet blank, and provide additionally values for the number average chain length $x_n$ in cell L59-... in step 7 of the input spreadsheet.

*Step 3:* Calculation of the RAFT CTA conversion $x_{R_0X}$ from either on-line concentration measurements or indirect methods based on the SEC measurements of the samples in experiment (**b**) (*cf.* Equation (14)-(15) in the main text). If $x_{R_0X}$ is directly measured, enter the obtained values in cell J59-... in step 7 of the input spreadsheet. If the calculation of $x_{R_0X}$ via the indirect method is desired, follow the instructions in step 6 of the input spreadsheet and leave the $x_{R_0X}$ data in step 7 of the input spreadsheet blank. In the latter case, additional $x_n$ and time data need to be provided in respectively cells L59-... and N59-... in step 7 in the input spreadsheet.

*Step 4:* Calculation of $<C_{tr}>$ via the method proposed in the present work (*cf.* main text, Figure 1). For each conversion, the comparison of the solutions obtained (Equation (11)-(12) in the main text) will provide a notion of the reliability of the obtained results. Note that once such comparison is done at very low conversion to get to $C_{tr,0}$ and one a the depletion of the initial small RAFT CTA te get to *Ctr*. Verify whether all input is provided and press the "START" button in step 7 of the Excel input spreadsheet. The results will be displayed in the sheet "results". An example input is provided in the sheet "example".

### 4.5.2 Determination of only $<C_{tr}>$ at the start of the RAFT polymerization, i.e. $C_{tr,0}$

The procedure to determine $C_{tr,0}$ via application of the presented methodology in main text at the start of the considered RAFT polymerization, is much easier and only involves one experiment in which in principle only one sample needs to be taken at low conversion $x_0$ at time $t_0$. For this single sample, the CLD, $x$ and $x_{R_0X}$ need to be measured via the appropriate method in order to allow the determination of $C_{tr,0}$ via the methodology of the present work, as explained by the stepwise procedure below. Again, reference is made to the corresponding input in the supplementary spreadsheet available upon request.

*Step 0:* Specify which monomer is used in step 1 of the input spreadsheet. Enter the initial concentration of monomer and RAFT CTA ($R_0X$) in step 2 of the input spreadsheet.

*Step1:* Calculation of the total radical concentration $\lambda_0$ from the polymerization rate $r_{pol}$ being the initial slope of the conversion profile (Equation (S8)) via Equation (S6). Enter the polymerization time in step 4 of the input spreadsheet for the calculation of $\lambda_0$.

*Step 2:* Calculation of $<k_t>$ from available surface functions in literature at the specific conversion $x_0$ and corresponding chain length determined from the SEC measurement, and look for a reliable value of $k_p$ in the scientific literature.[1] RAFT-CLD-T or PLP based data for $<k_t>$ and $k_p$ are recommended above kinetic data from stationary experiments.[9,21] Enter the value for $k_p$ in step 3 of the input spreadsheet, or, in case the considered monomer is styrene or methyl methacrylate, specify the temperature at which $k_p$ needs to be calculated. If the termination rate coefficient $k_t$ is directly measured, enter the obtained values in cell H59 in step 7 of the input spreadsheet. If not, follow the instructions in step 5 of the input spreadsheet, leave the $k_t$ data in step 7 of the input spreadsheet blank, and provide additionally a value for the number average chain length $x_n$ in cell L59 in step 7 of the input spreadsheet.

*Step 3:* Calculation of $x_{R_0X}$ from either concentration measurements of the RAFT CTA or indirect methods based on the SEC measurement of the sample (*cf*. Equation (13)-(14) in the main text). If $x_{R_0X}$ is directly measured, enter the obtained value in cell J59 in step 7 of the input spreadsheet. If the calculation of $x_{R_0X}$ via the indirect method is desired, follow the instructions in step 6 of the input spreadsheet and leave the $x_{R_0X}$ data in step 7 of the input spreadsheet blank. In the latter case, additional $x_n$ and time data need to be provided in respectively cells L59 and N59 in step 7 in the input spreadsheet.

*Step 4:* Calculation of $<C_{tr}>$ via the method proposed in the present work (*cf.* main text, Figure 1). For each conversion, the comparison of the solutions (Equation (11)-(12) in the main text) will provide a notion of the reliability of the obtained value for $C_{tr,0}$. Verify whether all input is provided and press the “START” button in step 7 of the input spreadsheet. The results will be displayed in the sheet “results”.

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