Supporting Information

Molecular Weight Distribution Modeling of Radical Polymerization in a CSTR with Long Chain Branching through Transfer to Polymer and Terminal Double Bond (TDB) Propagation

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Maximum one TDB per chain

Effect on CLD and TDB distribution of TDB propagation rate and conversion.

The effect of TDB propagation rate constant and conversion on the distributions of chain length and fraction chains with a TDB has been assessed for intermediate values of the disproportionation and transfer to polymer rate coefficients: \( k_{id} = 10^8 \text{ m}^3/(\text{kmole.s}) \), \( k_{tp} = 5 \text{ m}^3/(\text{kmole.s}) \). In view of the ranges reported earlier, these values may be considered as being fairly realistic for PVAc. The results are shown in Figs. 1 through 4. We conclude that the trends observed earlier under the limiting values of the mentioned kinetic constants persist here. Stronger TDB propagation leads to broadening of the CLD and lower values of the fraction chains with TDB. The latter phenomenon is easily explained by the fact that a higher \( k_{db} \) implies a higher reactivity of TDBs and consequently they are more likely to be inserted. CLD turns out to become broader with increasing conversion, while the fraction of dead chains with a TDB decreases. The latter phenomenon is due to the higher macroradical concentration and the less frequent insertion of TDBs caused by this.

More than one TDB per chain

Incorporation of monomer in dead and living chains. According to the model the concentration of the living chains in the CSTR is very high. To illustrate this we have constructed Fig. 5 depicting the fraction of monomer leaving the CSTR as a part of the living chains. In many cases this fraction is negligible, but here it obviously is not. According to the
moment model with increasing TDB propagation rate this fraction can amount to 18%. Such an increase is predicted by the classes model as well, but to a lesser extent.

**Comparing polydispersity $D_n$ from moment and classes model.** Since in the TDB moment model the second TDB moment distribution $\Psi_{n}^{2,0}$ is explicitly used as a variable, it is possible to compute the polydispersity $D_n$ and compare it to the one calculated from the classes model. This is shown in Fig. 6, which indicates fair agreement for the lower $k_{db}$. Both models feature slight higher polydispersity at low n, a maximum around $10^4$ and a change to practical monodispersity at long chain lengths. However, for the highest $k_{db}$ the maximum is unrealistically high. We attribute this to the $D_n = 1$ assumption, which most strongly deviates from the true $D_n$ (Fig. 14, main text) at precisely the same chain length. If one would aim at a more exact prediction of the second TDB moment $\Psi_{n}^{2,0}$, then it is recommendable to refine the TDB moment model in this respect, i.e. by accounting for an n-dependent $D_n$, like the one shown in Fig. 14, main text. In the present study we will not do this, for the more important TDB moment is $\Psi_{n}^{1,0}$, since it determines the reactivity for TDB propagation of the dead chains. We do not expect that a more precise prediction of the second moment will considerably change the outcomes as regards the first one. Consequently, we conclude that the assumption $D'_n = 1$ is acceptable for our purposes here.

**Comparison of lower and higher TDB moment models.** The TDB moment distribution modeling approach can be employed in a lower and a higher TDB moment mode. The lower moment mode means solving the population balances of Tables 4 and 5 of the main text and applying a closure relationship for the second TDB moment distribution $\Psi_{n}^{2,0}$, while in the higher moment mode balance equations of Tables 4, 5 and 6 are solved, requiring a closure for the third TDB moment $\Psi_{n}^{3,0}$. Here, we compare the results of the two approaches for the case of moderate TDB propagation, $k_{db} = 3000$ m$^3$/kmole.s, high disproportionation, $k_{ad} = 1.5 \times 10^9$ m$^3$/kmole.s, and moderate transfer to polymer $k_{tp} = 4$ m$^3$/kmole.s. In the previous section we already found that the higher TDB moment model
yields acceptable results for a closure according to $D'_n = 1$ for all chain lengths $n$. Doing so, we found the polydispersity $D_n$ to be a function varying with chain length as depicted in Fig. 7. The corresponding distributions of chain length and numbers of TDBs per chain are shown in Figs. 8 and 9, respectively. When implementing this $D_n$ function in the lower TDB moment distribution model, we can argue that this should yield exactly the same results as the higher TDB moment model. This must be so since the second moment only depends on chain length and appears to possess a unique solution. This is indeed what we have found, the lower TDB moment model with $D_n$ according to the higher moment model (Fig. 7) yields results identical to that of the higher TDB moment model. It is now interesting to examine the contrast with the case, where no information on the second would be available. In this situation one could assume monodispersity, so $D_n = 1$ for all $n$. The results of such an assumption for MWWD and TDBD are equally shown in Figs. 8 and 9. A small but significant difference is observed. We conclude that correct results for the lower TDB moment model can be obtained, provided that a good closure relation for the second moment is available. In that case the same results can be achieved with a model containing 4 instead of 6 distribution variables. However, the closure relationship being represented by the function $D_n$ has still to be evaluated from the higher TDB moment model, or in an alternative way, e.g. from the TDB classes model. Since a closure relation for $\Psi^{2.0}_n$ generally valid for all kinetic and reactor conditions does not exist, we prefer using the higher TDB moment distribution model. Moreover, the iterative procedure to achieve convergence regarding the approximation function $A_n$ is more easily performed for the higher TDB moment model than for the lower TDB moment model.

**Fraction monomer units in living/dead chain beyond cut-off limit.** It is important to note that at this extremely long chain length the model predicts the living chain concentration to be much higher than the dead chain concentration, as is clearly visible in the double-logarithmic plot of Fig. 10. This has strong implications for the discussion that we have raised in our aforementioned article about the question, which fraction of the monomer units are present in living chains longer than the cut-off limit $L$, and which fraction exists in
similar dead chains. Figure 11 immediately makes clear that this fraction largely belongs to
the living chains beyond $L$.

**Comparison to cases with TDB production by transfer to monomer only.**
Terminal double bonds are mostly considered to be created by transfer to monomer, but the
disproportionation reaction is a possible TDB source as well. In the case of TDBs created by
the first mechanism only and in absence of termination by recombination, chains may carry
one TDB at maximum. Here, we compare the results for the situation of TDBs produced by
disproportionation to the case of maximum one TDB per chain. The chain length distributions
for the two cases and high TDB propagation rate are depicted in Fig. 16 of the main text. Figs.
12 and 13, in addition, show the results for lower values. Only for the lowest rate $k_{db} = 500$
m$^3$/kmole.s the programme is able to compute living CLDs completely, without using a cut-
off limit. We see that the CLDs are quite similar for dead chains, while a clear difference
exists for the living chains. For the higher TDB propagation rates the dead CLDs become
quite different as well.

Note finally, from Fig. 13, that the level of TDBs per chain is slightly higher when TDBs are
produced by both mechanisms, while it is obviously lower with increasing TDB propagation
rate.

**More than one TDB per chain by recombination termination.** The situation of
more than one TDB per chain can also be created by termination by recombination. We have
analyzed this situation, where the only TDB producing mechanism is transfer to monomer. It
is assumed that termination now completely is taken over by the recombination mechanism.
The results are shown in Figs. 14 and 15 for the lowest TDB propagation rate, $k_{db} = 500$
m$^3$/kmole.s. Quite remarkably, the effect of the recombination reaction on the CLDs is very
strong. Recombination has the same effect as an increased TDB propagation rate.
Appendix Derivation of moment model for the case of maximum one TDB per chain

A moment model is derived from the population balances of the TDB branching moment approach as presented in Tables 4 and 5 of the main text and the modifications due to the maximum one TDB per chain assumption in Table 7. For convenience we define the following additional moments:

\[ \mu_i = \sum_{n=1}^{\infty} n^i P_n \]
\[ \lambda_i = \sum_{n=1}^{\infty} n^i R_n \]
\[ \psi_i = \sum_{n=1}^{\infty} n^i \Psi_{i,0} \]
\[ \phi_i = \sum_{n=1}^{\infty} n^i \Phi_{i,0} \]

Next we present general equations for the \( i \)th moment of both the 0th and 1st TDB branching moment equations as presented in Tables 4 and 5 (plus modifications in Table 7), resp. We do this for both living and dead chains.

**Living chains, 0th TDB moment:**

\[
\frac{d\lambda_i}{dt} = k_p M \left( -\lambda_i + \sum_{n=2}^{\infty} n^i R_{n-1} \right) + k_q \left( -\mu_i + \lambda_i + \lambda_{i+1} \right) - k_d \lambda_i - k_s \lambda_i \left( -\psi_{0,0}^0 + \sum_{n=2}^{\infty} n^i \sum_{m=1}^{n-1} \Psi_{i,0}^{1,0} R_{n-m} \right) - \frac{1}{\tau} \lambda_i
\]  
(A1)

**Dead chains, 0th TDB moment:**

\[
\frac{d\mu_i}{dt} = k_q (\mu_i - \lambda_{i+1}) + k_d \lambda_i - k_s \mu_i + k_m M \mu_i - k_d \lambda_i - \frac{1}{\tau} \mu_i
\]  
(A2)

**Living chains, 1st TDB moment:**

\[
\frac{d\phi_i}{dt} = k_p M \left( -\phi_i + \sum_{n=2}^{\infty} n^i \Phi_{n-1} \right) + k_q \left( -\mu_i + \lambda_i + \lambda_{i+1} \right) - k_d \phi_i - k_s \phi_i \left( -\psi_{0,0}^0 + \sum_{n=2}^{\infty} n^i \sum_{m=1}^{n-1} \Phi_{i,0}^{1,0} \right) - \frac{1}{\tau} \phi_i
\]  
(A3)
Dead chains, 1st TDB moment:

\[
\frac{d\psi_i}{dt} = k_p (\mu_i \phi_i - \lambda_0 \psi_i) + k_d \lambda_0 \phi_i + k_s S \phi_i + k_m M \phi_i - k_{db} \lambda_0 \psi_i - \frac{1}{\tau} \psi_i
\]  
(A4)

Thus, the moment balances for the first three moments become:

Living chains (0th TDB moment):

\[
i = 0 \quad \frac{d\lambda_0}{dt} = k_p M \lambda_0 - k_d \lambda_0^2 - k_s S \lambda_0 - k_m M \lambda_0 - \frac{1}{\tau} \lambda_0;
\]  
(A5)

\[
i = 1 \quad \frac{d\lambda_i}{dt} = k_p M \lambda_0 + k_p (-\mu_1 \lambda_1 + \mu_2 \lambda_0) + \]
\[-k_d \lambda_0 \lambda_1 - k_s S \lambda_1 - k_m M \lambda_1 + k_{db} \psi_1 \lambda_0 - \frac{1}{\tau} \lambda_1;
\]  
(A6)

\[
i = 2; \quad \frac{d\lambda_2}{dt} = 2k_p M \lambda_1 + k_p (-\mu_1 \lambda_2 + \mu_3 \lambda_0) + \]
\[+ k_d \lambda_0 \lambda_2 - k_s S \lambda_2 - k_m M \lambda_2 + k_{db} (2 \lambda_1 \psi_1 + \lambda_0 \psi_2) - \frac{1}{\tau} \lambda_2;
\]  
(A7)

Dead chains (0th TDB moment):

\[
i = 0 \quad \frac{d\mu_0}{dt} = k_d \lambda_0^2 + k_s S \lambda_0 + k_m M \lambda_0 - k_{db} \lambda_0 \psi_i - \frac{1}{\tau} \mu_0;
\]  
(A8)

\[
i = 1 \quad \frac{d\mu_1}{dt} = k_p (\lambda_1 \mu_1 - \lambda_0 \mu_2) + k_d \lambda_0 \lambda_1 + k_s S \lambda_1 + k_m M \lambda_1 - k_{db} \lambda_0 \psi_1 - \frac{1}{\tau} \mu_1;
\]  
(A9)

\[
i = 2 \quad \frac{d\mu_2}{dt} = k_p (\lambda_2 \mu_1 - \lambda_0 \mu_3) + k_d \lambda_0 \lambda_2 + k_s S \lambda_2 + k_m M \lambda_2 - k_{db} \lambda_0 \psi_2 - \frac{1}{\tau} \mu_2;
\]  
(A10)

Living chains (1st TDB moment):

\[
i = 0 \quad \frac{d\phi_0}{dt} = k_p M \Phi_0 - k_d \lambda_0 \phi_0 - k_s S \phi_0 - k_m M \phi_0 - \frac{1}{\tau} \phi_0;
\]  
(A11)

\[
i = 1 \quad \frac{d\phi_1}{dt} = k_p M \phi_0 + k_p (-\mu_1 \phi_1 + \lambda_0 \psi_2) + \]
\[-k_d \lambda_0 \phi_1 - k_s S \phi_1 - k_m M \phi_1 + k_{db} \psi_1 \phi_0 - \frac{1}{\tau} \phi;
\]  
(A12)
\[ i = 2; \quad \frac{d\phi_2}{dt} = 2k_p M\phi_i + k_p (-\mu_i\phi_2 + \lambda_0\psi_3) + \]
\[ + k_{id}\lambda_0\phi_2 - k_s S\phi_2 - k_m M\phi_2 + k_{db} (2\phi_1\psi_1 + \phi_0\psi_2) - \frac{1}{\tau} \phi_2; \]  
\[ (A13) \]

**Dead chains (1st TDB moment):**

\[ i = 0 \quad \frac{d\psi_0}{dt} = k_{id}\lambda_0^2 + k_s S\lambda_0 + k_m M\theta_0 - k_{db}\lambda_0\psi_1 - \frac{1}{\tau} \mu_0; \]  
\[ (A14) \]

\[ i = 1 \quad \frac{d\psi_1}{dt} = k_{id}(\mu_0\phi_1 - \lambda_0\psi_2) + k_{id}\theta_0\phi_1 + k_s S\phi_1 + k_m M\phi_1 - k_{db}\lambda_0\psi_1 - \frac{1}{\tau} \psi_1; \]  
\[ (A15) \]

\[ i = 2 \quad \frac{d\psi_2}{dt} = k_{id}(\mu_0\phi_2 - \lambda_0\psi_3) + k_{id}\theta_0\phi_2 + k_s S\phi_2 + k_m M\phi_2 - k_{db}\lambda_0\psi_2 - \frac{1}{\tau} \psi_2; \]  
\[ (A16) \]

A closure problem exists here, since the transfer to polymer terms contain the third moment.

We decided to use the explicit closure relationship as developed by Hulbert & Katz.\(^{25}\) Note that in earlier work we compared the results from moment models with a closure at 3rd, 4th and 5th level, which in principle can be performed here as well, but we will restrict ourselves here to the 3rd level. Another issue is that we need closure relationships for the 3rd moments of both the 0th and 1st TDB moment distribution. Deciding that we take the same equation for both distributions, we have:

\[ \mu_3 = \frac{\mu_3}{\mu_0\mu_1} \left( 2\mu_2\mu_0 - \mu_1^2 \right) \]  
\[ (A17) \]

\[ \psi_3 = \frac{\psi_3}{\psi_0\psi_1} \left( 2\psi_2\psi_0 - \psi_1^2 \right) \]  
\[ (A18) \]
Fig. 1
Sensitivity of chain length distribution to rate of TDB propagation for intermediate values of disproportionation and transfer to polymer constants: $k_{id} = 10^8 \text{ m}^3/(\text{kmole.s})$, $k_{tp} = 5 \text{ m}^3/(\text{kmole.s})$. Conversion in all cases 50 %.
Fig. 2
Sensitivity of TDB distribution to rate of TDB propagation for intermediate values of disproportionation and transfer to polymer constants: $k_{td} = 10^8 \text{ m}^3/(\text{kmole.s})$, $k_{tp} = 5 \text{ m}^3/(\text{kmole.s})$. Conversion in all cases 50%.
Fig. 3
Sensitivity of chain length distribution to conversion for intermediate values of disproportionation, transfer to polymer and TDB propagation constants: $k_{td} = 10^8 \text{ m}^3/(\text{kmole.s})$, $k_{tp} = 5 \text{ m}^3/(\text{kmole.s})$, $k_{db} = 2500 \text{ m}^3/(\text{kmole.s})$. 

$n^2P_n$ vs. Chain Length $n$ for $x = 0.1, 0.3, 0.5, 0.7$. 

$kmole/m^3$
Fig. 4
Sensitivity of TDB fraction to conversion for intermediate values of disproportionation, transfer to polymer and TDB propagation constants: $k_{id} = 10^8 \text{ m}^3/\text{(kmole.s)}$, $k_{tp} = 5 \text{ m}^3/\text{(kmole.s)}$, $k_{db} = 2500 \text{ m}^3/\text{(kmole.s)}$. 
Figure 5
Comparison of fraction monomers contained in living chains as a function of TDB propagation coefficient $k_{db}$ from TDB moment and TDB classes model.
Polydispersity $D_n$ as a function of chain length for various $k_{ab}$ from the TDB classes and TDB moment model.

$$D_n = \frac{\Psi_n^{2,0}}{\Psi_n^{1,0}} \bigg/ \frac{\Psi_n^{1,0}}{P_n}$$
Figure 7
Polydispersity $D_n$ calculated from higher TDB moment distribution model (with $D'_n = 1$).
Standard reaction conditions with $k_{db} = 3000 \text{ m}^3/(\text{kmole.s})$, $k_{td} = 1.5 \times 10^9 \text{ m}^3/(\text{kmole.s})$, $k_{tp} = 4 \text{ m}^3/(\text{kmole.s})$. 
Figure 8

Chain length distribution from lower TDB moment distribution model with two different closure relationships for $\Psi_{n}^{2,0}$: $D_{n} = 1$ and $D_{n}$ from higher TDB moment distribution model. Standard reaction conditions with $k_{db} = 3000$ m$^3$/kmole.s, $k_{td} = 1.5 \times 10^9$ m$^3$/kmole.s, $k_{tp} = 4$ m$^3$/kmole.s.
Figure 9
TDB distribution from lower TDB moment distribution model with two different closure relationships for $\Psi_n^{2,0}: D_n = 1$ and $D_n$ from higher TDB moment distribution model. Standard reaction conditions with $k_{db} = 3000 \text{ m}^3/(\text{kmole.s})$, $k_{dl} = 1.5 \times 10^9 \text{ m}^3/(\text{kmole.s})$, $k_{ip} = 4 \text{ m}^3/(\text{kmole.s})$. 
Figure 10
Close-up of living and dead CLDs from higher TDB moment distribution model for various $k_{db}$. Slope decrease only visible for $k_{db} = 500 \text{ m}^3/(\text{k mole.s})$; for higher $k_{db}$ located beyond cut-off limit $L = 10^{10}$. 
Figure 11
Comparison of dead and living CLDs for the cases of terminal double bonds created by transfer to monomer only (maximum one TDB per chain) and by both transfer to monomer and termination by disproportionation (more than one TDB per chain); $k_{db} = 500 \text{ m}^3/(\text{kmole.s})$. 

$k_{db} = 500 \text{ m}^3/(\text{kmole.s})$
Comparison of dead and living CLDs for the cases of terminal double bonds created by transfer to monomer only (maximum one TDB per chain) and by both transfer to monomer and termination by disproportionation (more than one TDB per chain); $k_{db} = 2500 \text{ m}^3/(\text{kmole.s})$.
Figure 13

TDB density distribution, $\Psi^{1.0}_a/(nP_a)$ for various $k_{db}$, corresponding to TDB distribution of Fig. 12 for the case of TDB production by transfer to monomer and termination by disproportionation. Beyond $n = 10^7$ a constant density is observed. Deviation for highest $k_{db}$ attributed to numerical inaccuracy.
Figure 14
Comparison of dead and living CLDs for the cases of termination by disproportionation and recombination. Fraction monomer units in living chains: disproportionation: 1 \%; recombination: 10 \%.
Figure 15
Comparison of TDB density distributions, $\Psi_{n}^{1,0}/(nP_n)$, for the cases of termination by disproportionation and recombination.