Supplementary Information for

'Differences and similarities between mono-, bi- or tetrafunctional initiated cationic ring-opening polymerization of 2-oxazolines'

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1. Cationic-ring opening polymerization toward poly(2-oxazoline): general reactions

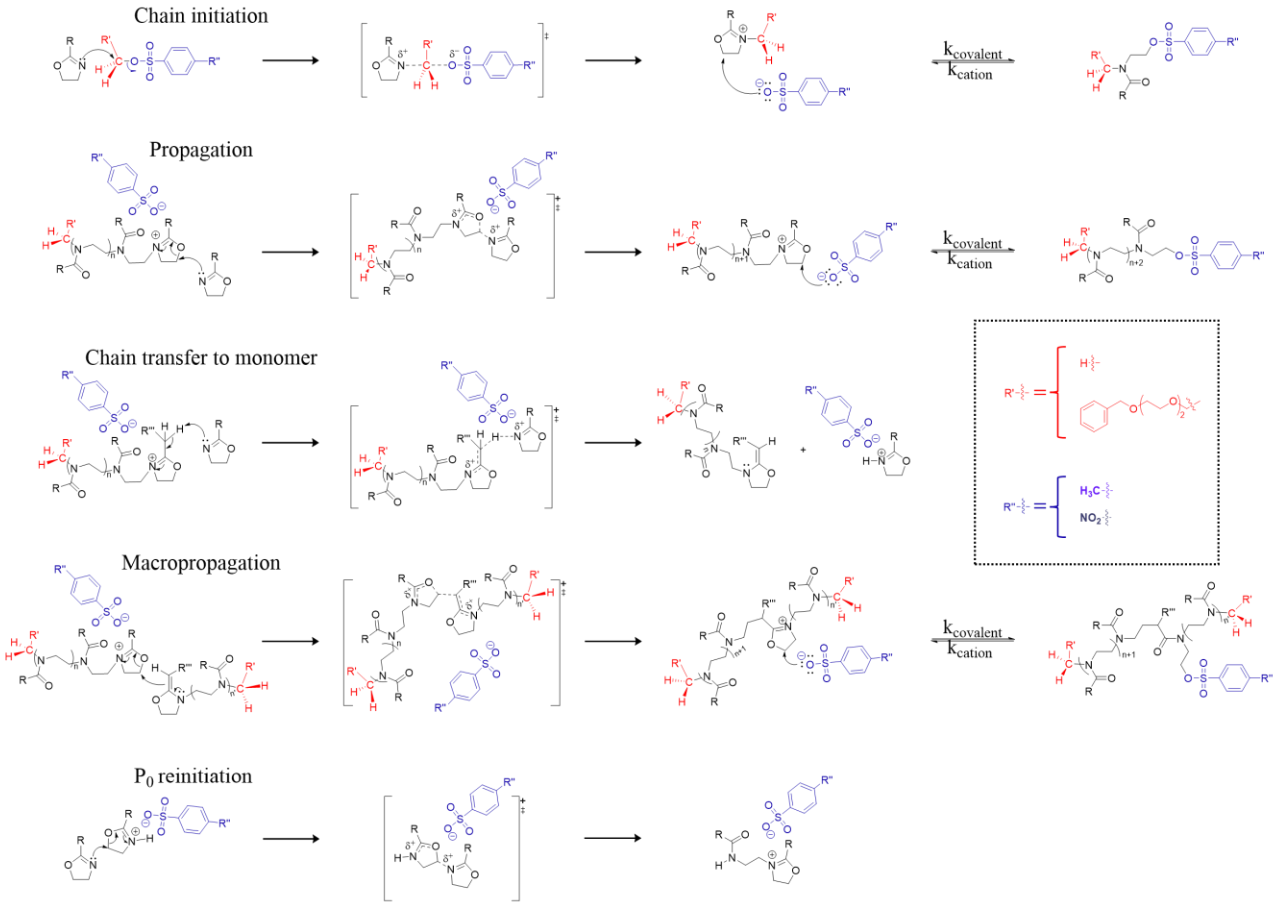


Figure S1. Representation of the reaction mechanisms for chain initiation, propagation, chain transfer to monomer, and macropropagation reactions of the cationic ring-opening polymerization (CROP) process of 2-oxazolines. Electrophilic fragments of the initiator molecules are represented in red whereas the (leaving) counter ion parts of the initiator molecules are depicted in blue. Strictly speaking, the reactions represented here correspond to a system in which mainly linear polymer chains (1-arm system) are produced. However, these reactions can occur individually in each of the arms in a multi-arm polymer system. The equilibrium between the cationic and covalent species is shown for the products of chain initiation, propagation, and macropropagation reactions.

Table S1. Rate coefficients for CROP of 2-oxazolines (PAOx) at 353 K according to the reaction scheme shown in Figure 1 in the main text.k_i, k_p, k_{trM}, k_{pm}, k_{pMid}, are the rate coefficients for chain initiation, propagation, chains transfer to monomer, macropropagation, and mid-chain cation propagation, respectively; Table S2 contains the tuned parameters for the CROP of *i*PropOx described in subsection 4.3 in the main text.

Reaction	**Equation**	**Rate coefficients (*k*) at353K ($L\cdot mol^{-1}\cdot s^{-1}$)**			
		EtOx/MeOTs/ACN[a]	EtOx/R'ONs/ACN	EtOx/R'ONs/PhCl	*n*PropOx/MeOTs/ACN
Chain Initiation	$I + M \xrightarrow{k_i} P_1 + X^-$	3.64×10^{-3}	3.64×10^{-4}	1.17×10^{-4}	5.15×10^{-4}
Propagation[e]	$P_i + M \xrightarrow{k_p} P_{i+1}$	2.74×10^{-3}	2.74×10^{-3}	5.06×10^{-3}	3.86×10^{-3}[d]
Chain transfer to monomer (β-elimination)	$P_i + M \xrightarrow{k_{trM}} D_i + P_0$	3.64×10^{-6}	3.05×10^{-6}	4.08×10^{-6}	3.86×10^{-6}
Reinitiation	$P_0 + M \xrightarrow{k_p} P_1$	2.74×10^{-3}	2.74×10^{-3}	5.06×10^{-3}	3.86×10^{-3}
Macropropagation	$P_i + D_j \xrightarrow{k_{pm}} P_{i+j}^{mid}$	5.47×10^{-3}	2.74×10^{-3}	5.06×10^{-3}	7.72×10^{-3}[b]
Mid-chain cation propagation[c]	$P_i^{mid} + M \xrightarrow{k_{pMid}} P_{i+1}$	2.74×10^{-3}	2.74×10^{-3}	5.06×10^{-3}	3.86×10^{-3}

a. Rate coefficients have been calculated from the Arrhenius parameters reported by Arraez et al[1].

b. k_{pm} value for the system *n*PropOx/MeOTs/ACN has been assessed to be twice as large as k_p, based on the ration k_{pm}/k_p from the system EtOx/MeOTs/CAN.

c. Mid-chain cation propagation (k_{pMid}) is assumed to take the same values as the rate coefficient for propagation (k_p) based on our previous work[1-3]

d. Value taken from the work of Bouten et al.[4]

e. Subscript $i > 0$

2. Extra information on the kinetic study with a monofunctional initiator

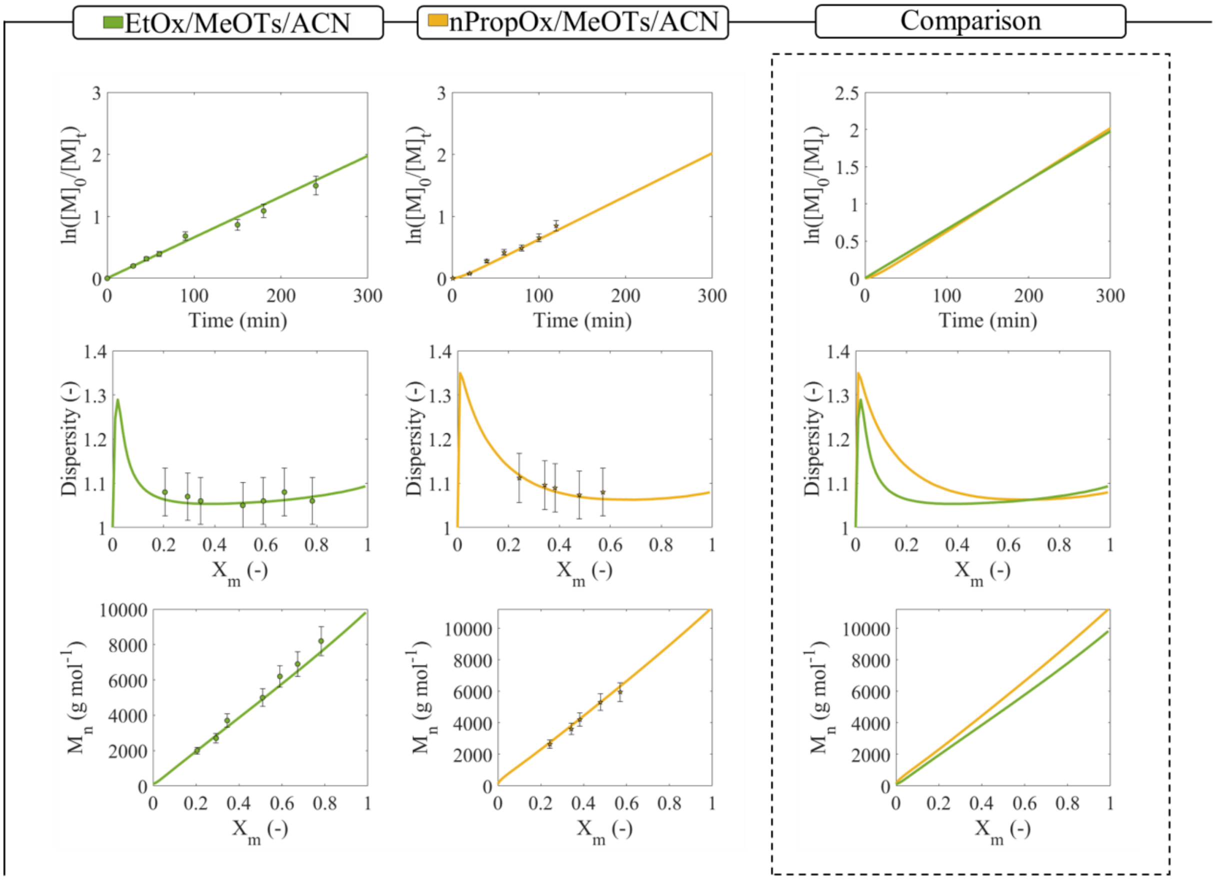


Figure S2. Comparison between experimental (scatter data) and *k*MC-simulated (solid lines) results for CROP, aiming at 1-arm (linear) poly(2-oxazolines) and the study of the effect of the side-chain substituent (EtOx in green; nPropOx in yellow). Experimental results have been obtained at 353 K and the other reaction conditions listed in Table 1in the main text. Simulation results have been obtained using the rate coefficients shown in Table S1. The error bars in the dispersity plots represent a relative error of 5%. Similarly, the error bars for both ln([M]t/[M]0) and Mn values represent a relative error of 10%; The experimental data for the system nPropOx/MeOTs/ACN have been taken from the work of Bouten et al.[4]

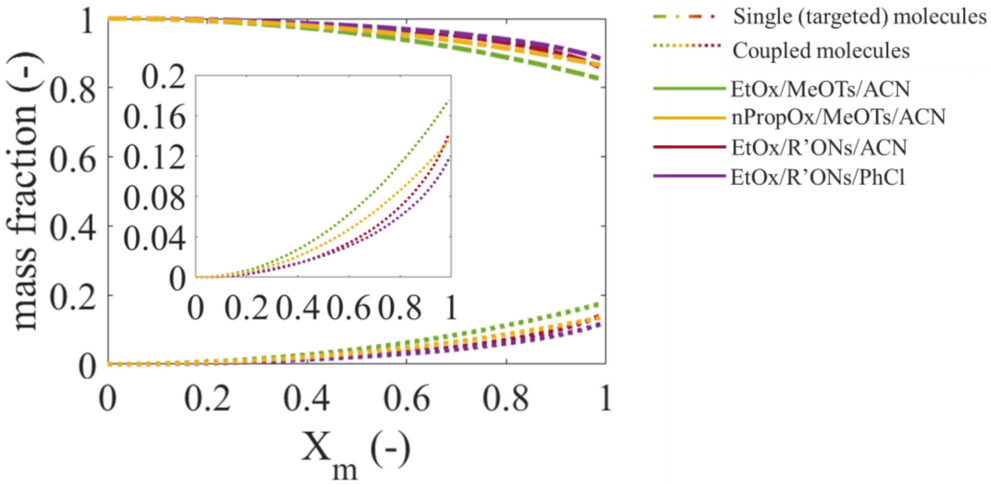


Figure S3. Evolution of the mass fraction of single (dash-dotted line) and combined (dotted line) polymer molecules as a function of monomer conversion X_m for the CROP of the four different linear (1-arm) systems studied in section 4.1 in the main text. Results have been obtained from the polymerization conditions in Table 1 in the main text as well as the rate coefficients in Table S1.

3. Extra information on the kinetic study with bifunctional initiators

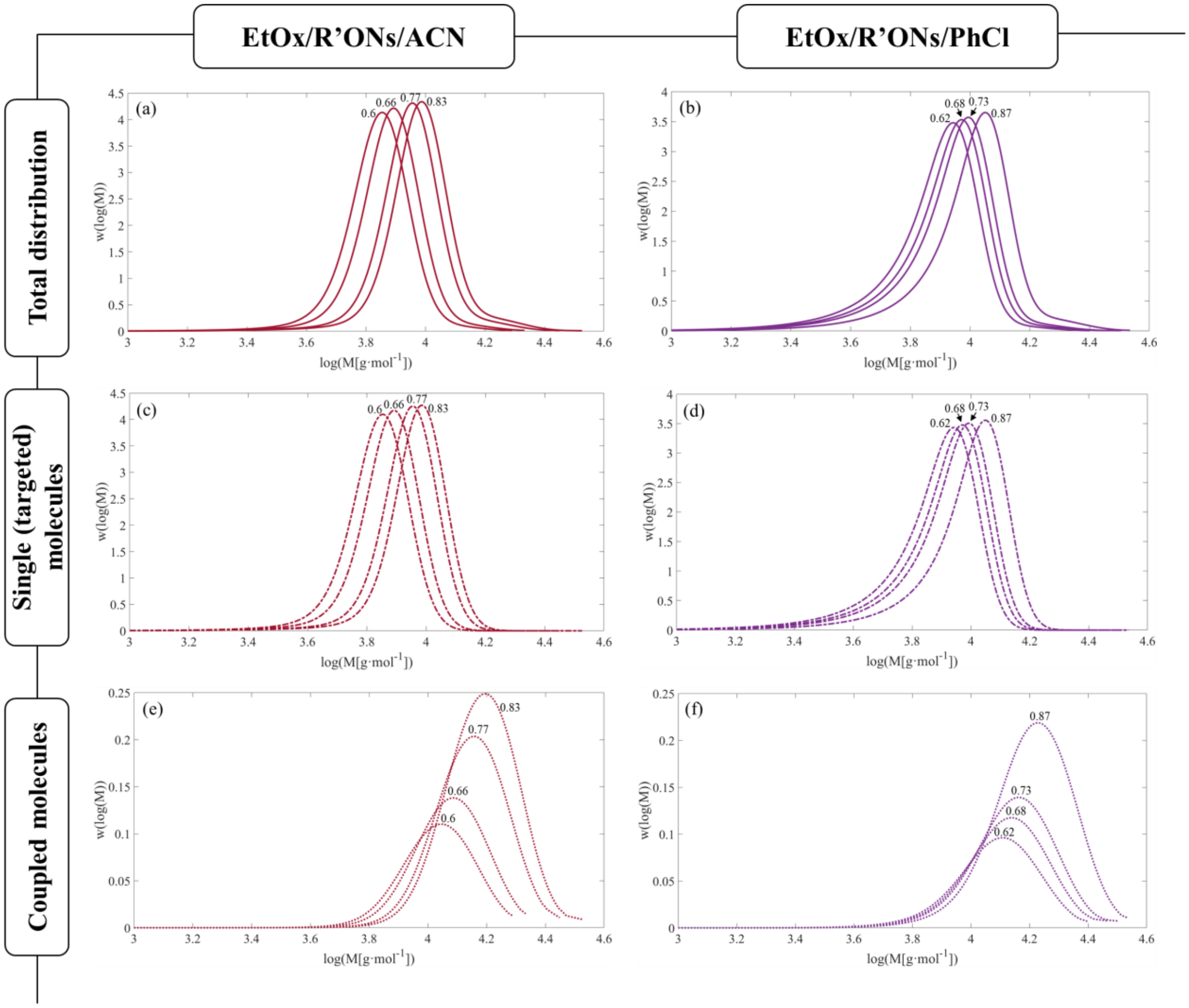


Figure S4. Simulated log-MMD (SEC traces) at different monomer conversion values (see labels on traces): The results here presented correspond to EtOx/R'ONs/CAN (red; 1-arm) and EtOx/R'ONs/PhCl (violet; 1-arm). The total distributions for both systems (a-b) are obtained from the contribution of the populations of single polymer molecules (c-d; linear polymer chains in the 1-arm case) and combined polymer molecules (e-f; branched polymer chains in the 1-arm case) formed after macropropagation reactions. The distributions shown for both populations have been multiplied by their corresponding mass fractions to the total. All the results have been obtained at 353K and other conditions listed in Table 1 in the main text as well as using the rate coefficients shown in Table S1.

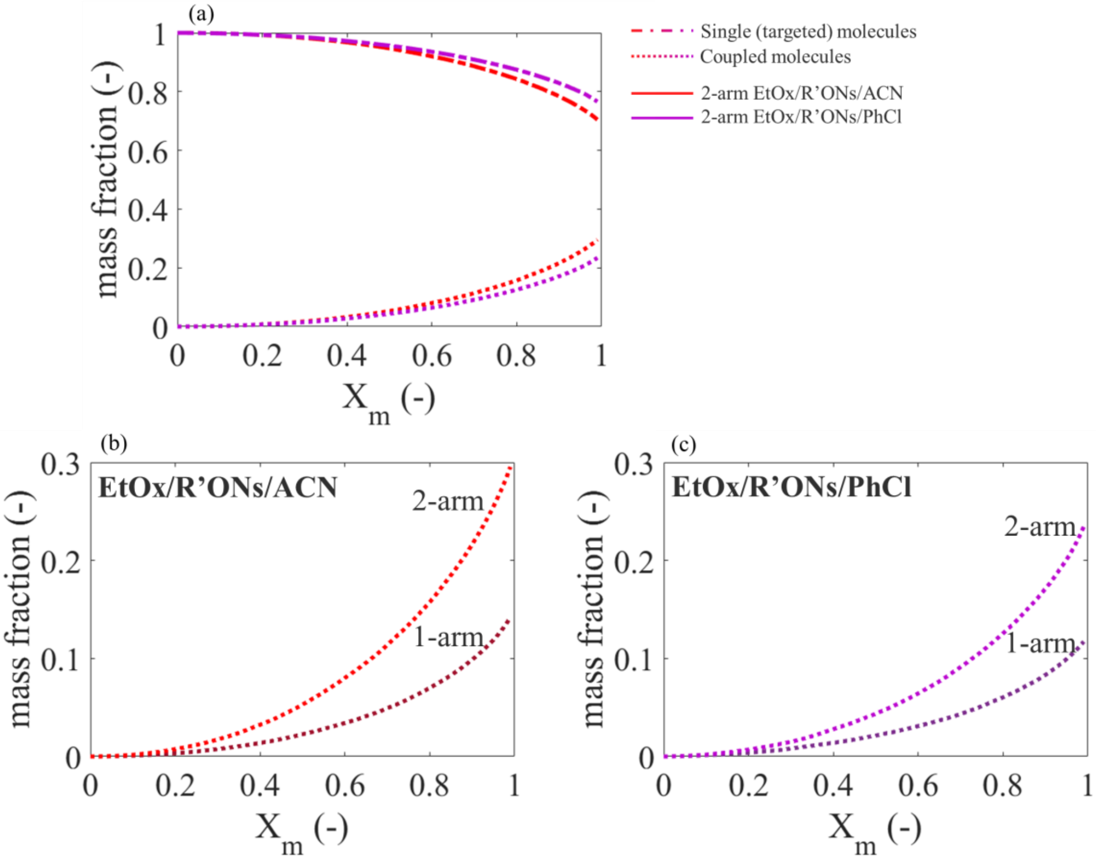
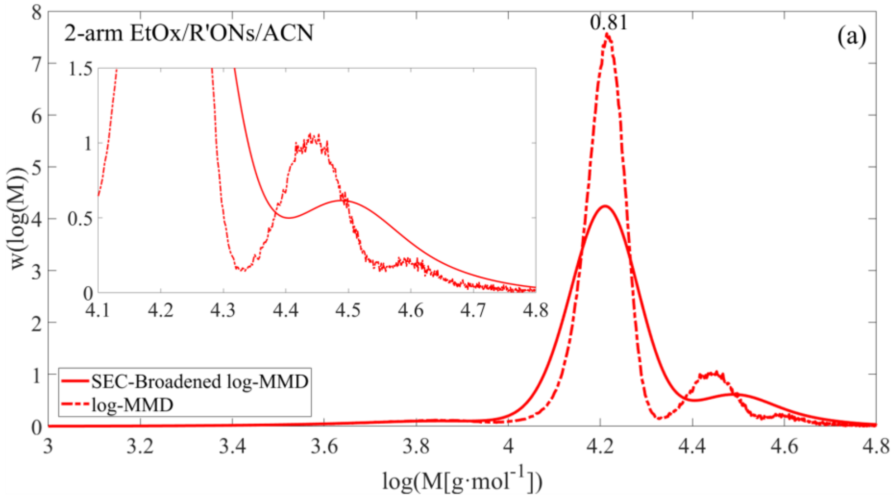


Figure S5. (a) Evolution of the mass fraction of single (dash-dotted line) and combined (dotted line) polymer molecules as a function of monomer conversion X_m for the CROP of the two different 2-arm systems studied in Subsection 4.2 in the main text. Additionally, we have included a comparison of the evolution of the mass fraction or by macropropagation coupled molecules for the 1-arm and 2-arm cases: subfigures (b) (EtOx/R'ONs/ACN) and (c) EtOx/R'ONs/PhCl. Results have been obtained from the polymerization conditions in Table 1 in the main text as well as the rate coefficients in Table S1.



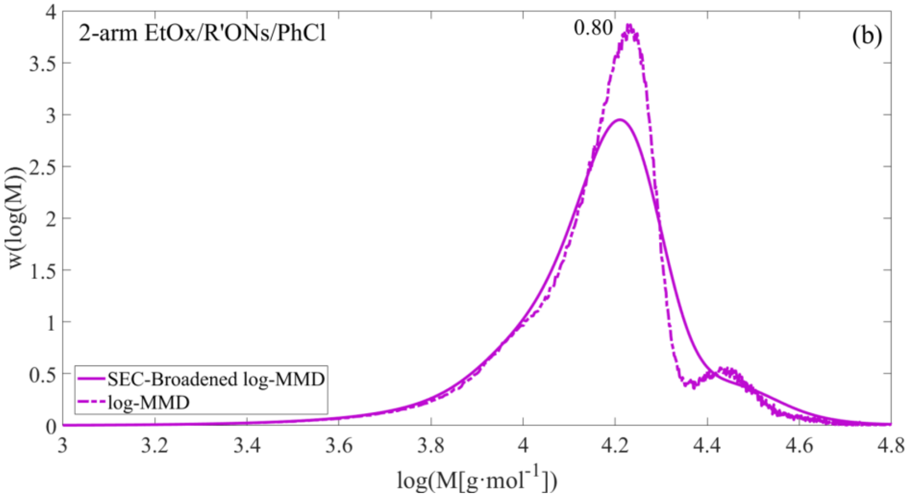


Figure S6. Simulated log-MMD distribution before SEC broadening (dash-dotted line) and after SEC broadening correction (solid lines) for the CROP of (a) 2-arm EtOx/R'ONs/ACN (bright red) and (b) 2-arm EtOx/R'ONs/PhCl (purple amethyst). These traces have been simulated under the same conditions as Figure 5 and Figure 6 in the main text as well as Figure S4.

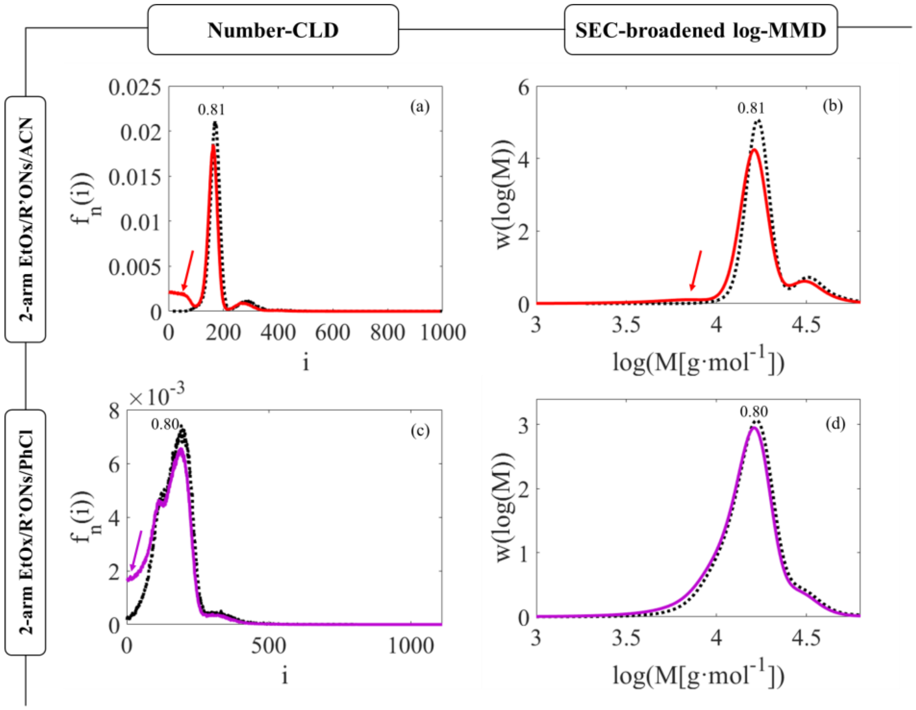


Figure S7. Simulated number chain length distributions (number-CLD) and log-MMD distributions for the CROP of (a, c) 2-arm EtOx/R'ONs/ACN (bright red) and (b, d) 2-arm EtOx/R'ONs/PhCl (purple amethyst). These traces have been simulated under the same conditions as Figure 5 and Figure 6 in the main text as well as Figure S4. The log-MMDs distributions here presented are the same as in Figure S5 after SEC broadening correction. Additionally, black dotted lines in the four plots shown above correspond to the distributions obtained for the case in which the reinitialization reaction of the oxazolinium cation (P_0), formed from the chain transfer to the monomer reaction (see Figure 1 in the main text), is excluded.

4. Simplified kinetic Monte Carlo models for the study of the CROP of 2-arm PAOx

In Subsection 3.3 in the main text, we have described a *k*MC modeling approach to model the CROP of 2-am PAOx on one arm basis. This approach has been called the “Implicit 2-arm *k*MC model”, and the results obtained from its implementation are shown in Figures S8 and S9, labeled as Option 1 (black dotted lines). However, this is not the only approach that could be tried to obtain a simplified model for the representation of 2-arm polymer chains. Here we briefly describe two other alternatives to accomplish the desired task. However, as already indicated in the main text, neither one of these approximate methods offers a reliable representation and prediction of the molecular properties of 2-arm PAOx systems. Since Option 1 is already described in Subsection 3.3 of the main text, attention will be given to the details for the implementation of Option 2 and Option 3. Nonetheless, the initial conditions for the three simplified kMC models are the same (see Figure 7e in the main text).

Focusing on Option 2, 2-arm polymer chains are modeled as if there were 1-arm linear polymer chains with a target chain length twice as long as that of the individual arms of the 2-arm systems. In the reactions in which monomer consumption takes place, only *one* monomer molecule is consumed. This is one of the main differences with the implementation of Option 1 (with always two monomer molecules). In addition, the calculation of the probabilities of the reactions is conducted by taking twice the rate coefficients of the 1-arm systems (Table S1). This is done to produce the same reaction rates of the 2-arm PAOx. However, this is only true at the very beginning of the polymerization process and, as soon as the polymerization has started, the reaction rates between models (in comparison to the explicit 2-arm model) diverge. As shown in Figures S8 and S9, the evolution of the properties predicted by the Option 2 approach (black dashed lines) diverges considerably from the results predicted by the explicit 2-arm kMC model (solid red lines), and only a good match with M_n is displayed.

Concerning option 3, this approach consists of a mixed implementation of Option 1 and Option 2. Similarly to option 1, each time a reaction channel is sampled in which monomer consumption occurs, two monomer molecules are consumed. Also, as in Option 2, the reaction probabilities are calculated by considering twice the value of the rate coefficients of the 1-arm systems. As can be seen in Figures S8 and S9 (black dotted lines), this approach predicts that polymerization will progress considerably faster compared to the explicit model (red solid line; a factor two difference is observed between the slopes of the predicted ln-plots). This unequivocally shows how the combination of the modeling fundamentals of Options 1 and 2 leads to an overestimation of the system under study.

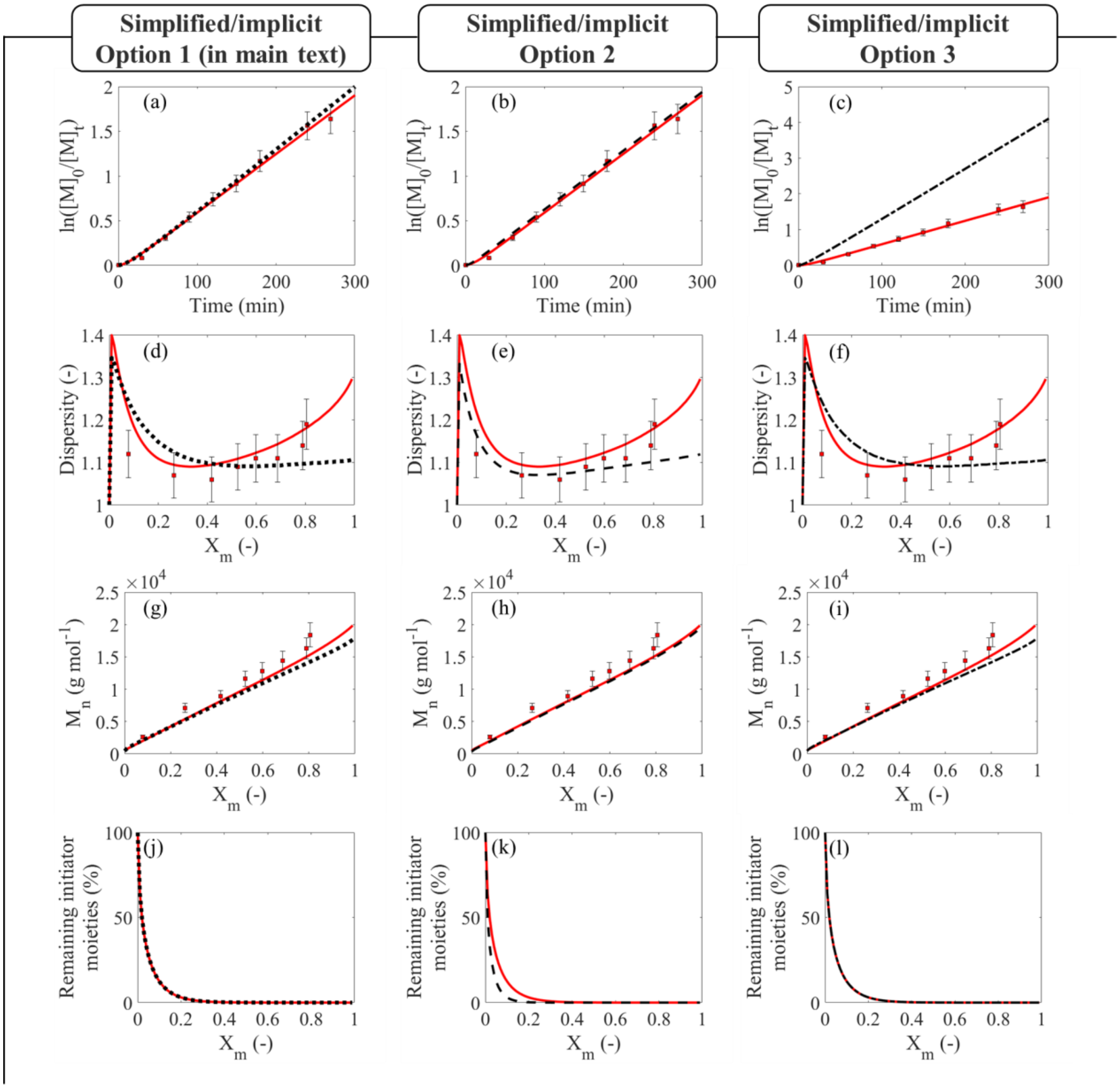


Figure S8. Comparison between modeling approaches for the simulation of CROP of 2-arm PAOx. The simulation results displayed correspond to the system 2-arm EtOx/R'ONs/ACN. 1 (results shown in the main text section 4.2). Three different approaches to account for the implicit representation of the 2-arm systems, starting from the tree-based kMC model described in the work of Arraez et al.[1] for the simulation of linear (1-arm) polymer chains are also shown. Results obtained from the implementation of Option 1 (described in section 3.3 in the main text; result shown in Figure 7 in the main text) are represented by black dotted lines (first column; a, d, g, j). Option 2, results are displayed as dashed lines (second column; b, e, h, k). Option 3, results are shown as dash-dotted lines (third column; c, f, i, l). Simulations have been conducted from conditions listed in Table 1 in the main text and rate coefficients shown in Table S1 (EtOx/R'ONs/ACN system).

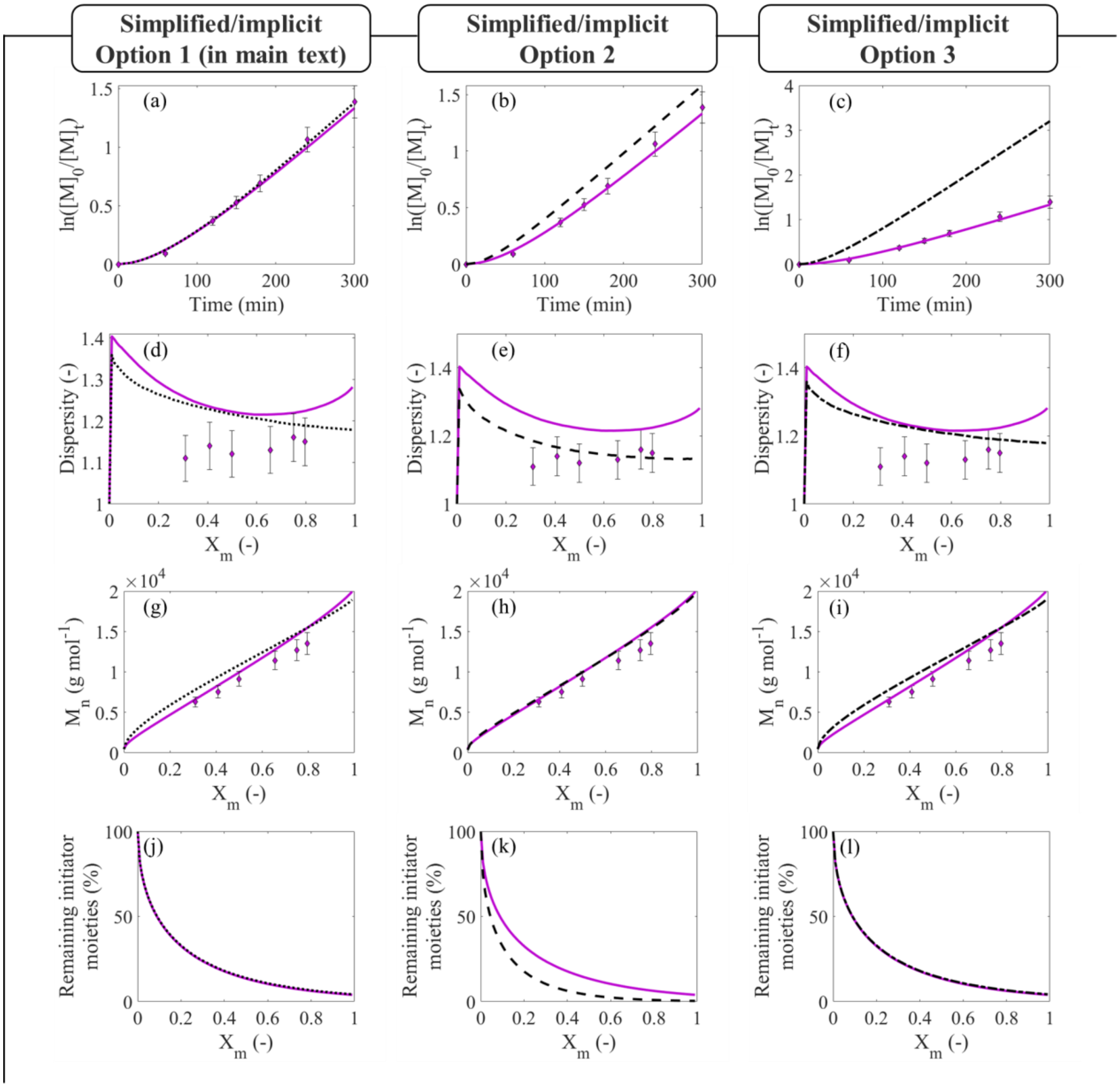


Figure S9. Comparison between modeling approaches for the simulation of CROP of 2-arm PAOx. The simulation results displayed correspond to the system 2-arm EtOx/R'ONs/PhCl. The results obtained from the implementation of the explicit multi-arm kinetic Monte Carlo model described in section 3.2 of the main text are represented in purple amethyst (results shown in the main text section 4.2). Three different approaches to account for the implicit representation of the 2-arm systems, starting from the tree-based kMC model described in the work of Arraez et al.[1] for the simulation of linear (1-arm) polymer chains are also shown. Results obtained from the implementation of Option 1 are represented by black dotted lines (first column; a, d, g, j). Option 2, results are displayed as dashed lines (second column; b, e, h, k). Option 3, results are shown as dash-dotted lines (third column; c, f, i, l). Simulations have been conducted from conditions listed in Table 1 in the main text and rate coefficients shown in Table S1 (EtOx/R'ONs/PhCl system).

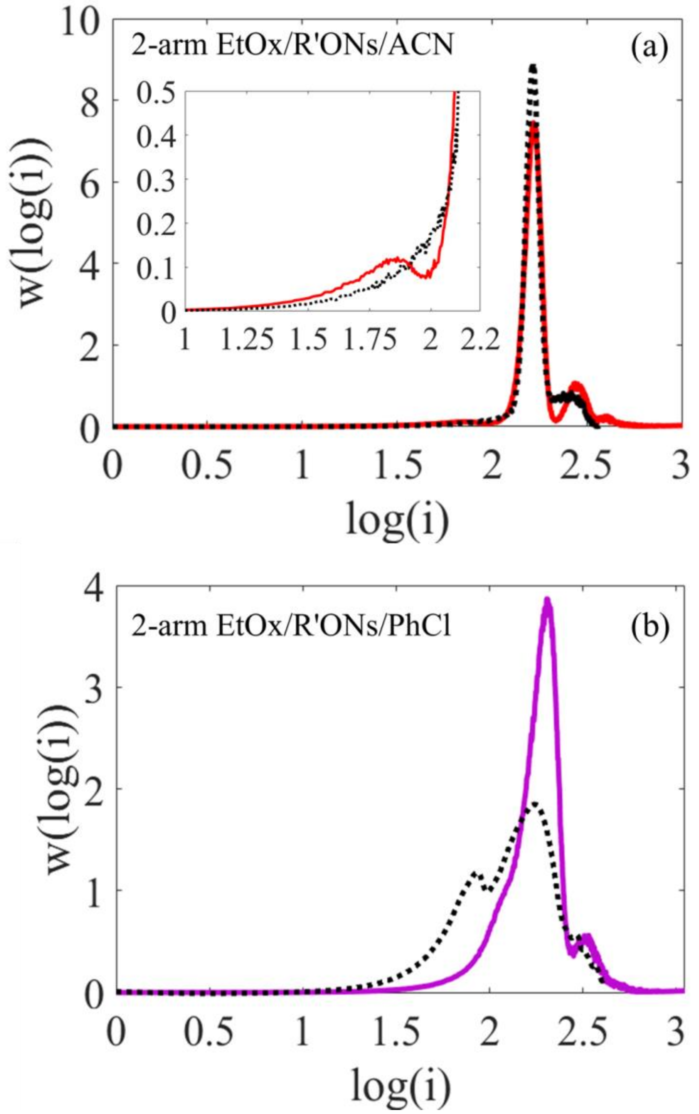


Figure S10. Comparison between the logarithmic chain length distributions (log-CLD) obtained from the different modeling approaches described in Subsection 3.2 (explicit multi-arm kMC; solid lines) and 3.3 (implicit 2-arm *k*MC model "option 1" in SI; dotted lines) of the main text for the simulation of CROP of 2-arm PAOx. Simulations have been conducted from conditions listed in Table 1 in the main text and rate coefficients shown in Table S1. The two 2-arm system under study are here represented: (a) 2-arm EtOx/R'ONs/ACN and $X_m = 0.81$; (b) 2-arm EtOx/R'ONs/PhCl and $X_m = 0.8$. In the inset in Subfigure a, it is observed how the implicit model does not represent the contribution of the 1-arm polymer chains formed after the re-initialization of the oxazolinium cation P0. Differences in the distribution tails are also evident, in which the contribution of the chains coupled after macropropagation reactions is represented.

5. Extra information on the kinetic study with tetrafunctional initiator

Table S2. Tuned rate coefficients used for the simulations of the CROP of iPropOx at 353 K in acetonitrile and MeOTs as initiator.

Reaction	Equation	Rate coefficients ($L{\cdot}mol^{-1}{\cdot}s^{-1}$)
Chain Initiation	$I + M \xrightarrow{k_i} P_1 + X^-$	1.20×10^{-4}
Propagation[a]	$P_i + M \xrightarrow{k_p} P_{i+1}$	5.98×10^{-4}
Chain transfer to monomer (β-elimination)	$P_i + M \xrightarrow{k_{trM}} D_i + P_0$	2.57×10^{-8}
Macropropagation	$P_i + D_j \xrightarrow{k_{pm}} P_{i+j}^{mid}$	1.20×10^{-3}
Mid-chain cation propagation	$P_i^{mid} + M \xrightarrow{k_{pMid}} P_{i+1}$	5.98×10^{-4}

a. Subscript $i > 0$

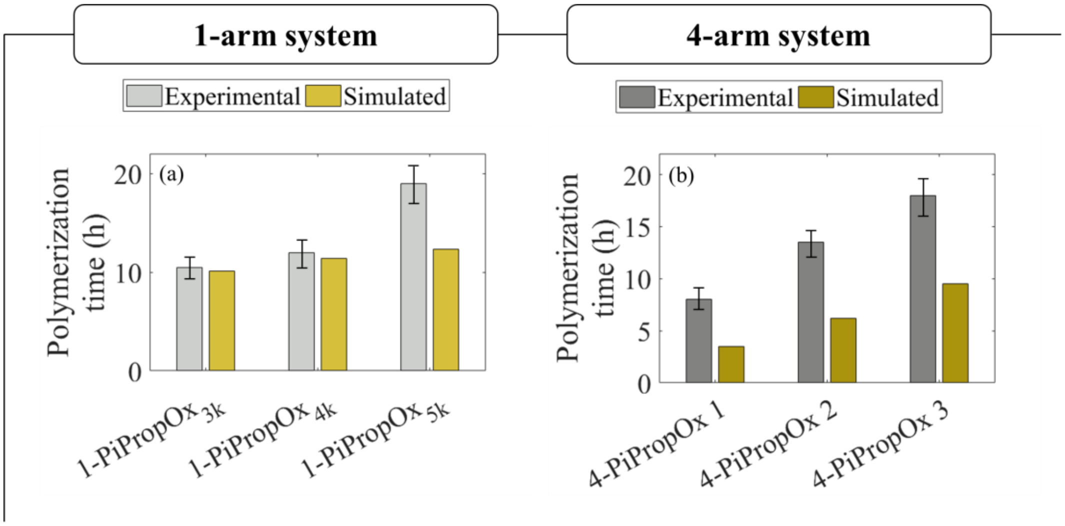


Figure S11. Comparison between experimental and predicted polymerization time in hours (h) for the synthesis of 1-arm and 4-arm PiPropOx polymer molecules. Values have been determined at the corresponding monomer conversion values listed in Table 2 in the main text. Simulations were performed using the (approximate) rate coefficient values shown in Table S2.

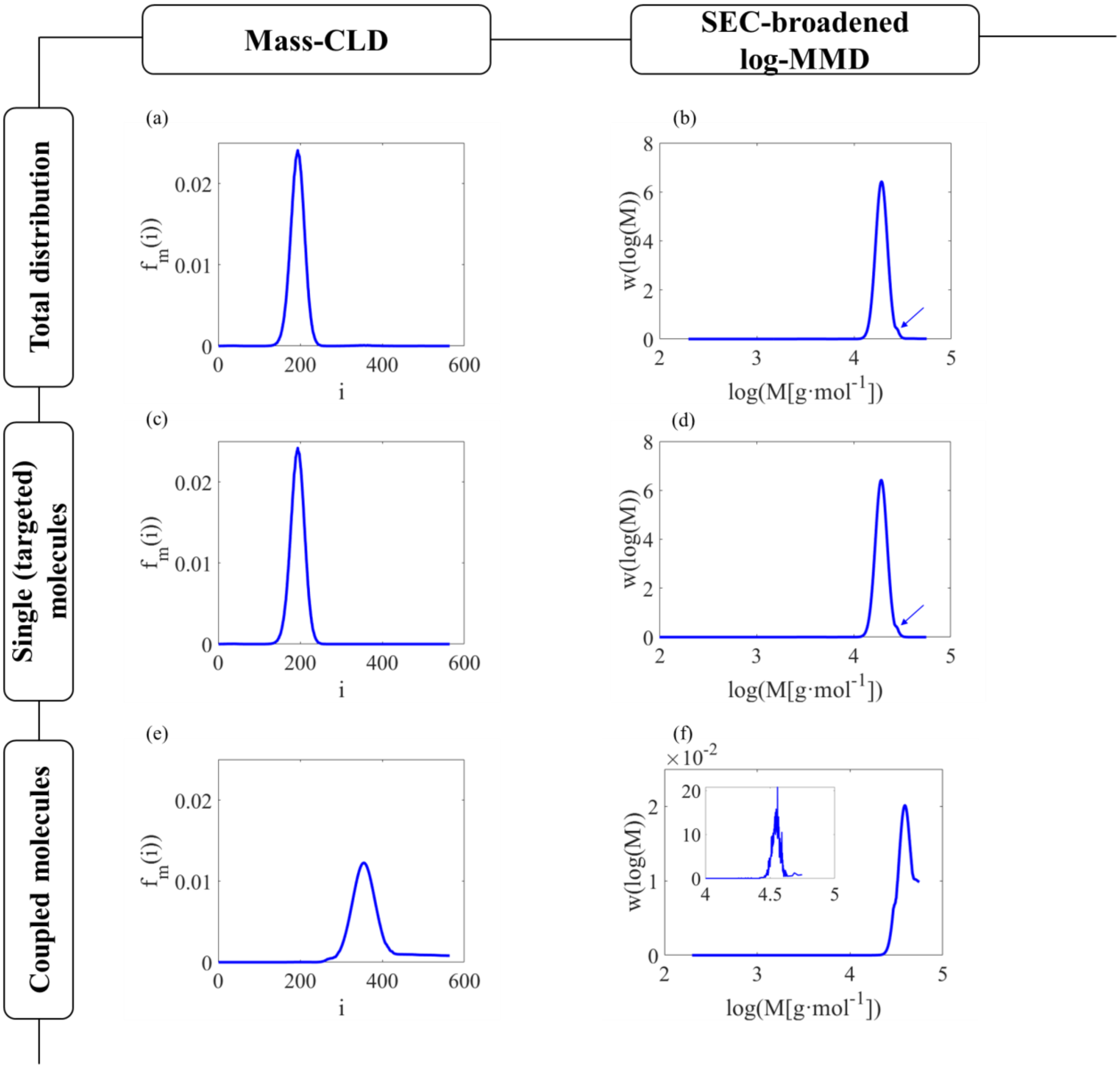


Figure S12. Simulated mass chain length distributions (mass-CLD) and (SEC-broadened) log-MMD distributions for the CROP of the 4-PiPropOx 3 samples. The total distributions (a-b) are obtained from the contribution of the populations of single polymer molecules (c-d; uncoupled polymer stars in the 4-arm case) and combined polymer molecules (e-f; coupled polymer stars in the 4-arm case) formed after macropropagation reactions. In figure f an inset has been added to show the log-MMD of combined molecules before SEC-broadening has been applied. Simulations were performed using the (approximate) rate coefficient values shown in Table S2 and conditions in Table 2 in the main text.

References

1. F. J. Arraez, X. W. Xu, P. H. M. Van Steenberge, V. V. Jerca, R. Hoogenboom and D. R. D'hooge, *Macromolecules*, 2019, **52**, 4067-4078.
2. P. H. M. Van Steenberge, B. Verbraeken, M.-F. Reyniers, R. Hoogenboom and D. R. D’hooge, *Macromolecules*, 2015, **48**, 7765-7773.
3. P. H. M. Van Steenberge, O. Sedlacek, J. C. Hernandez-Ortiz, B. Verbraeken, M. F. Reyniers, R. Hoogenboom and R. D'Hooge D, *Nat Commun*, 2019, **10**, 3641.
4. P. J. M. Bouten, D. Hertsen, M. Vergaelen, B. D. Monnery, S. Catak, J. C. M. van Hest, V. Van Speybroeck and R. Hoogenboom, *Journal of Polymer Science Part A: Polymer Chemistry*, 2015, **53**, 2649-2661.