Kinetics of Free-Radical Crosslinking Polymerization: a Comparative Experimental and Numerical Study

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Supplementary Information

We describe now the exact procedure that has been used to re-estimate the propagation and termination rate constants directly from MC data, and in particular their natural dependence on conversion, due to diffusion limitations. We first determined the termination rate constant as a function of the monomer conversion. The termination rate constant has been estimated from the total radical balance, assuming that pseudo-steady state approximation can be applied, leading to:

$$k_t = \frac{2k_d I_2}{R^{\cdot 2}} \tag{1}$$

where $R^{\cdot 2}$ is the total radical concentration in the system. In order to estimate k_t, the concentration of radicals has to be known. For this purpose we used the concentration of radicals given by MC simulations for the most critical condition, i.e., the case of equal amounts of monomer and crosslinker. The termination rate constant estimated in this manner has than be used to determine the propagation rate constants from the conversion profiles, by using the following equation:

$$k_{p,m} = \frac{\frac{d\Psi}{dt}}{(1-\Psi)R^{\cdot}} \tag{2}$$

This last equation just represents the overall material balance for the monomer. It is also possible to write an additional equation for the rate of consumption of pendant double bonds:

$$k_{p,d} = \frac{\frac{dPDB}{dt}}{R^{\cdot}} - \frac{0.5k_p(1-\Psi)}{(\Psi - \Psi_{PDB})} \tag{3}$$

where Ψ_{PDB} is the pendant double bond conversion. From these two equations, by knowing the time evolution of monomer and of pendant double bonds, the propagation constants can be estimated. This procedure allows us to estimate the profiles of such propagations constants with the conversion.

The results of these calculation are shown in Figure S1 and S2 for the propagation and termination rate constants as a function of conversion, respectively. It is clear that, while propagation rate

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constants appear to be mostly independent of conversion (except for uncertainties at very low and very high conversions), termination rate constants show strong dependence on the conversion, as a result of diffusion limitations. In Figure S2, the lines represent the trends obtained using Buback's equation (Equation 7 in the main body of the paper), used to obtain the kinetic simulation results shown in the paper. One can observe that MC simulations are naturally predicting the same trend as Buback's equation, depsite some quantitative difference.

Finally, we show now the same comparisons among MC simulations and kinetic calculations previously shown in the main body of the paper, but this time using the kinetics constants and their dependence on the conversion obtained from MC simulations. The results show that the agreement between MC simulations and kinetics calculations is excellent in this case, as a consequence of the use of the correct dependence on conversion of the rate constants.
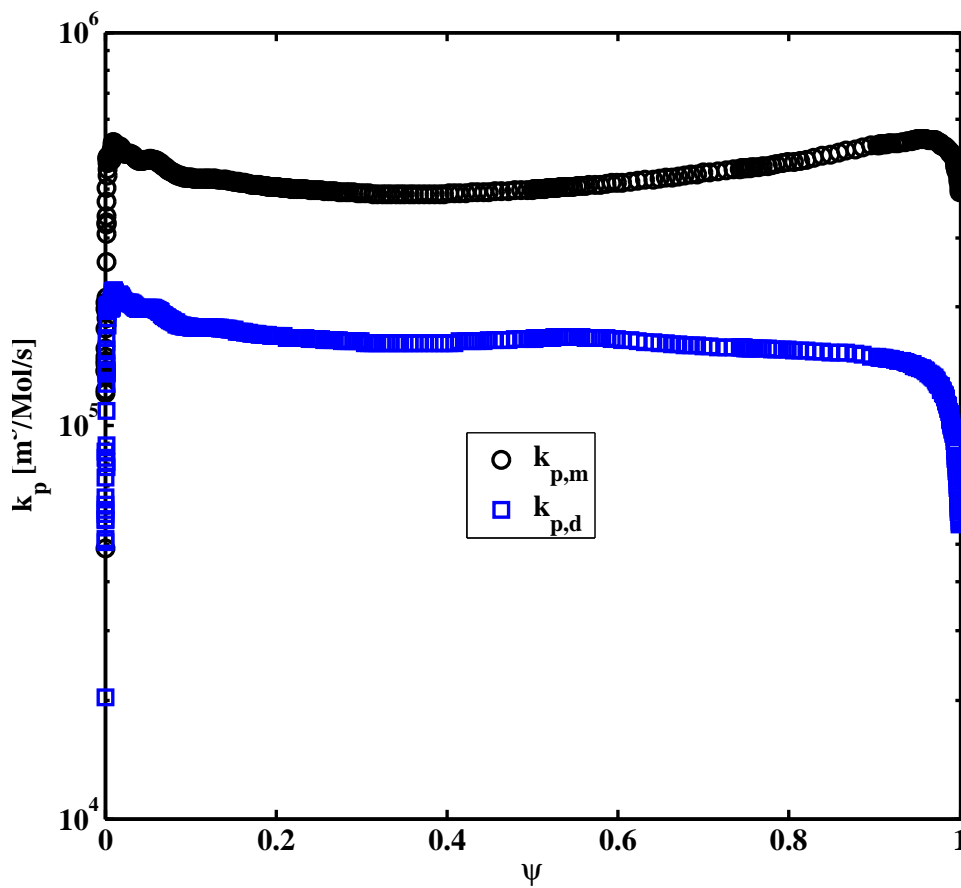
Figure S1: Propagation rate constants to monomer $k_{p,m}$ and to pendant double bonds $k_{p,d}$ as a function of monomer conversion Ψ, for $C_x = 0.1$ and $C_m = 0.1$.
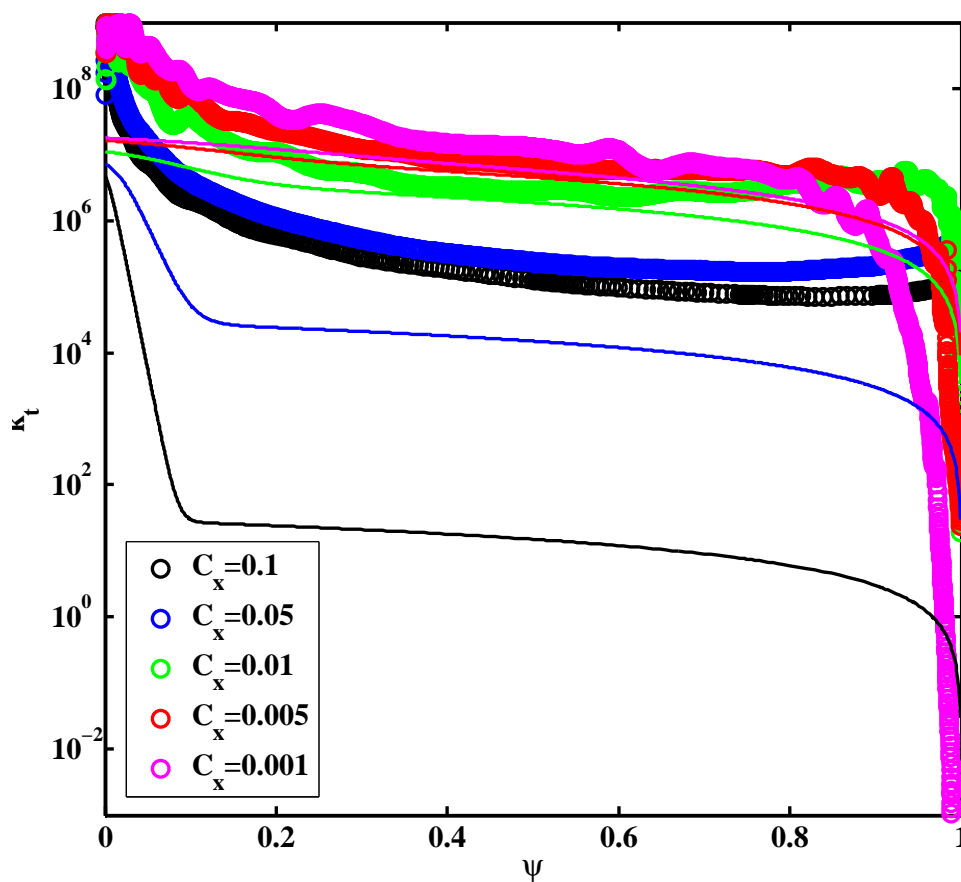
Figure S2: Termination rate constants k_t as a function of monomer conversion Ψ, for different crosslinker concentrations, as indicated in the legend and $C_m = 0.1$. The symbols are MC simulations results, while the continuous lines are the dependence of termination rate constants obtained by Buback' equation (Equation 7 in the main body of the paper) and used to reproduce MC simulations.
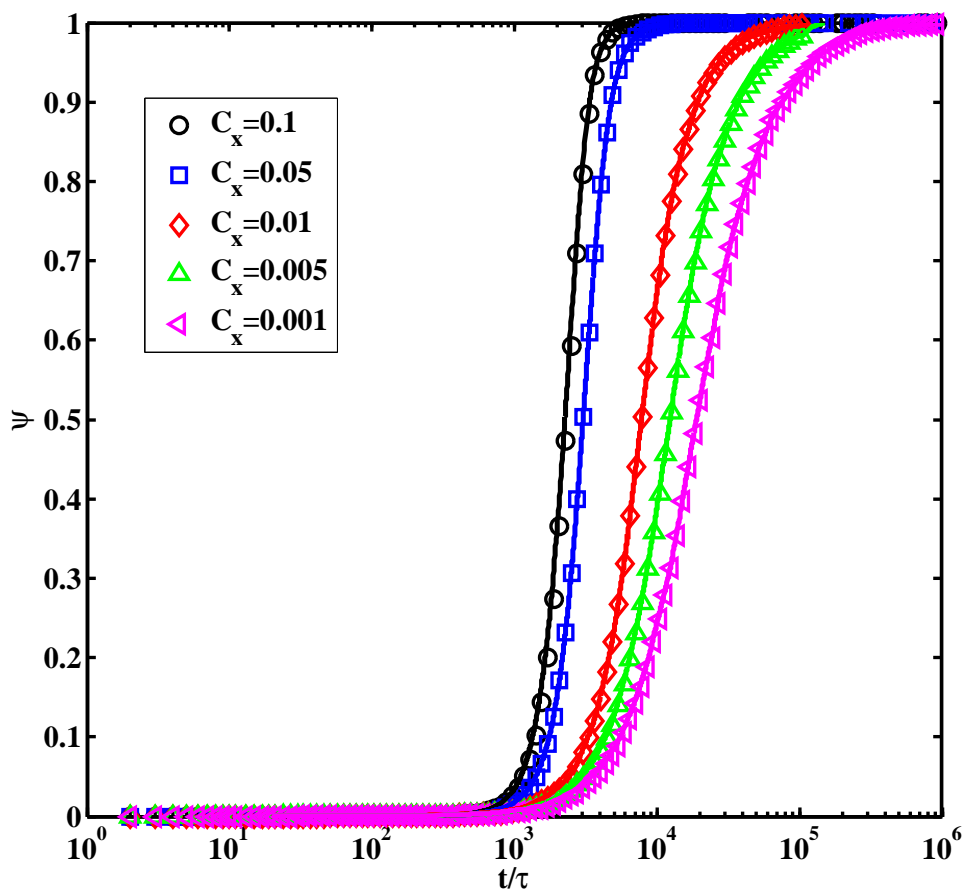
Figure S3: Sum of monomer M and cross-linker X conversion versus time, for initial cross-linker concentrations of $C_x = 0.001, 0.005, 0.01, 0.05, 0.1$ (from left to right) and monomer concentration $C_m = 0.1$. The symbols are MC simulations results, while continuous lines are predictions obtained with the kinetic model using the kinetic constants obtained from MC data.
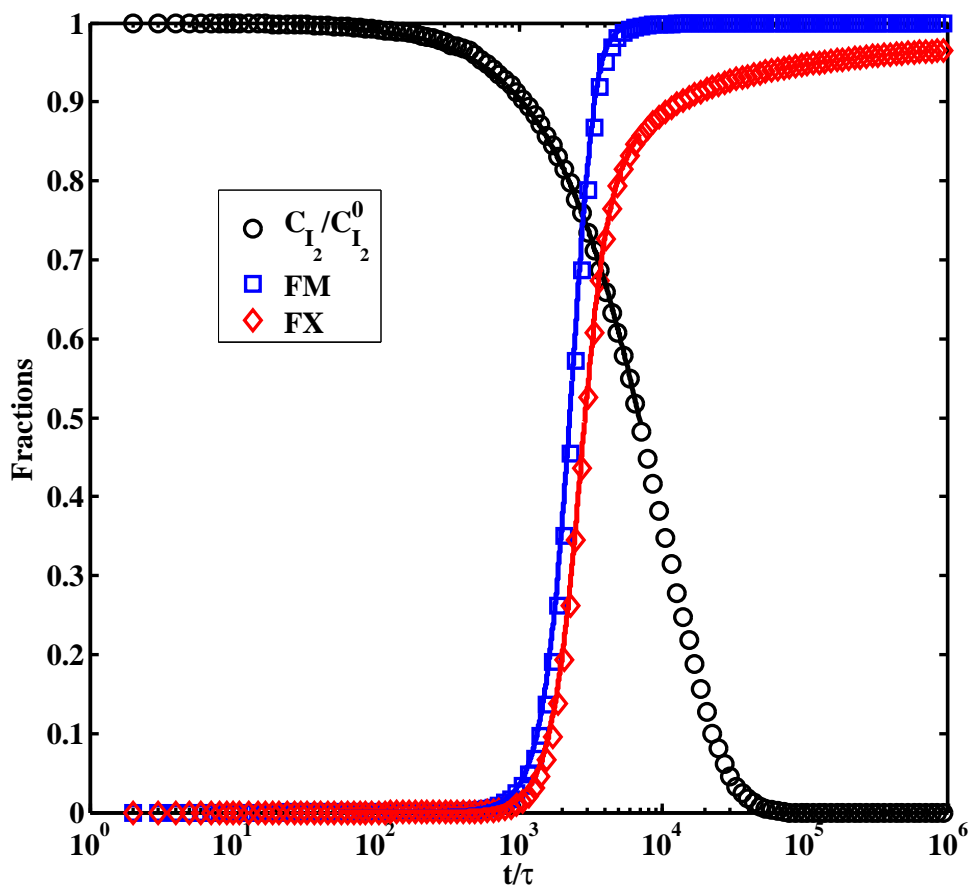
Figure S4: Fraction of saturated monomers $FM = 1 - \frac{C_m}{C_m^0}$, fully saturated crosslinkers $FX = 1 - \frac{C_x}{C_x^0} - \frac{PDB}{2C_x^0}$ (PDB is the concentration of pendant double bonds) and unreacted I_2 initiators for initial cross-linker concentration $C_x = 0.1$ and a monomer concentration $C_m = 0.1$. The symbols are MC simulations results, while the continuous lines are predictions obtained with the kinetic model using the kinetic constants obtained from MC data.
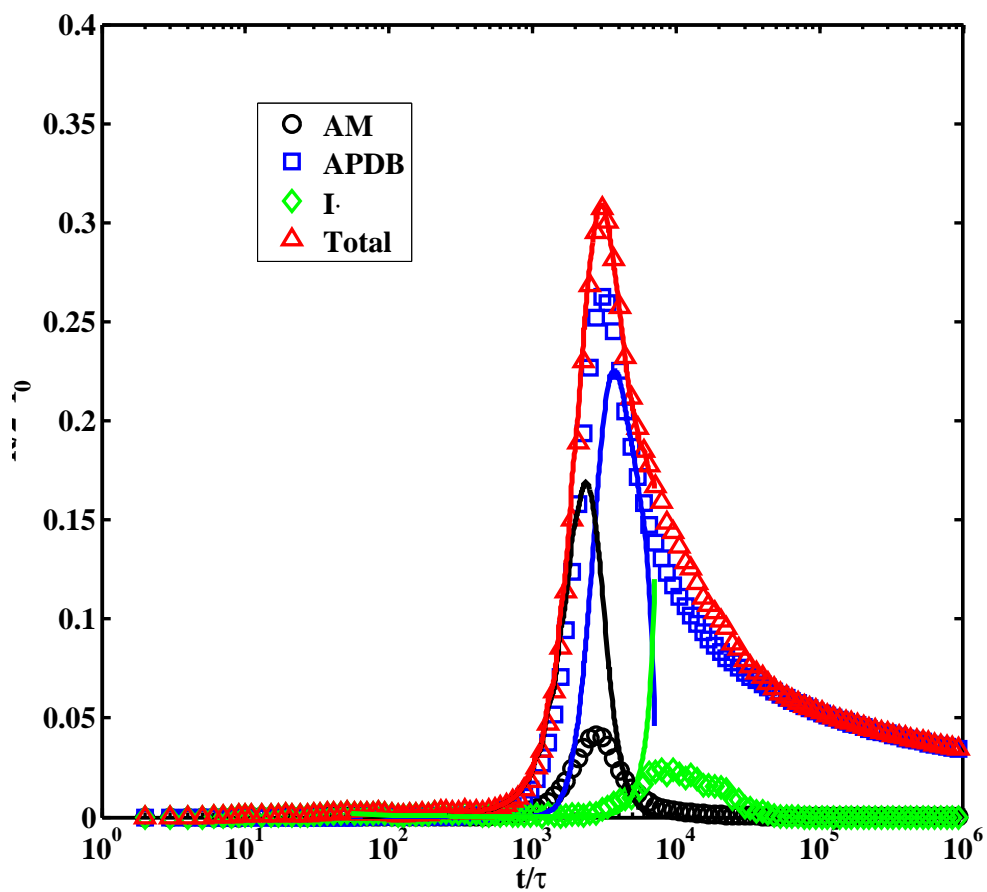
Figure S5: Fraction of initiator fragments $I\cdot$, active monomer units AM, active pendant double bonds $APDB$ and total radicals versus time for initial cross-linker concentration $C_x = 0.1$ and a monomer concentration $C_m = 0.1$. The symbols are MC simulations results, while the continuous lines are predictions obtained with the kinetic model using the kinetic constants obtained from MC data.
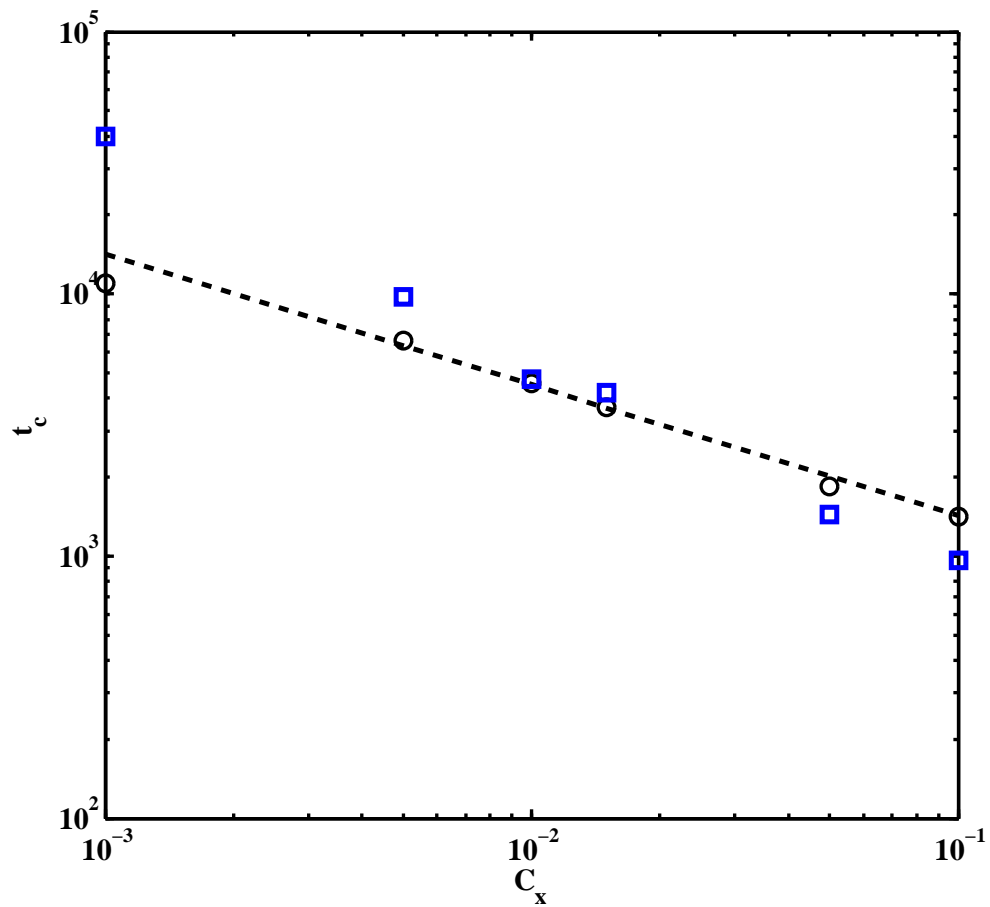
Figure S6: Percolation time as a function of cross-linker concentration for a monomer concentration $C_m = 0.1$. The dotted line is the power law $t_c \sim C_x^{-\sigma}$ with $\sigma = 0.5$. The symbols are MC simulations results, while the continuous line is the prediction of the kinetic model using the kinetic constants obtained from MC data.

Table S1: List of parameters used in Equation (7) (in the main body of the paper) for the different simulated cross-linker concentrations.

C_X	0.1	0.05	0.015	0.01	0.005	0.001
C_η	150	70	25.5	19.5	12.5	8
a	1	0.35	0.35	0.35	0.35	0.35
C_{RD}	1e-4	0.1	6.0	12.5	30	35