

Supporting Information for:

Kinetics of radical ring opening polymerization of the cyclic ketene acetal 2-methylene-1,3-dioxepane (MDO) with vinyl monomers

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Introduction

Table S1 summarizes reactivity ratios of the copolymerization of MDO with different acrylates reported in literature.

Table S1: Reactivity ratios for the copolymerization of MDO with different acrylates. AIBN was used as initiator in all of the cases.

System	Method	Solvent	T [° C]	r_{MDO}	r_{acrylate}	Reference
MA/MDO		Benzene	50/115	0.024	26.54	¹
MA/MDO	NLLS	Cyclohexane	70	0.168 (-0.141, +0.250)	3.354 (-0.954, +2.382)	²
BA/MDO	NLLS	Cyclohexane	70	0.044 (-0.083, +0.391)	1.761 (-0.445, +0.761)	²
2EHA/MDO	NLLS	Cyclohexane	70	0.002 (-0.116, +0.171)	1.507 (-0.434, +0.854)	²
DA/MDO	NLLS	Cyclohexane	70	0.339	2.257	²

				(-0.319, +3.108)	(-0.943, +10.707)	
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Table S2 summarizes reactivity ratios for the copolymerization of MDO with VAc reported in literature.

Table S2: Reactivity ratios for the copolymerization of MDO and VAc reported in the literature.

Method	Solvent	Initiator	T [°C]	r_{MDO}	r_{VAc}	Reference
Kelen-Tüdös	Bulk	AIBN	70	0.47	1.56	3
Finemann-Ross	Bulk	AIBN	60	0.93	1.71	4
NLLS	Bulk	AIBN	60	1.03	1.22	5
NLLS	Bulk	AIBN	60	0.95	1.71	6
Kelen-Tüdös & Finemann-Ross	Bulk	TPO/Co(acac) ₂ *	30	0.14	1.89	7

*(2,4,6-trimethylbenzoyl)diphenylphosphine (TPO) as photo-induced initiator and cobalt acetylacetonate (Co(acac)₂) as mediator.

Experimental section

Determination of reactivity ratios

The material balances for each monomer for the case of a copolymerization (assuming terminal model kinetics) in batch are shown in Equation S1 and S2 in which [i] is the concentration of monomer i [mol/L], R_{pi} is the polymerization rate of monomer i [mol/L · s], k_{pij} the propagation rate constant of a radical with the terminal unit i with monomer j [mol/L · s], P_i the probability to find a radical with the ultimate unit i and $[R^*]$ the total concentration of radicals.

$$\frac{d[A]}{dt} = -R_{pA} = -(k_{pAA}P_A + k_{pBA}P_B)[A][R^*] \quad (\text{S1})$$

$$\frac{d[B]}{dt} = -R_{pB} = -(k_{pAB}P_A + k_{pBB}P_B)[B][R^*] \quad (S2)$$

The definition of probabilities shown in Equation S3 and S4 follows from Equation S1 and S2 if the Quasi-Steady-State assumption (QSSA) is fulfilled.

$$P_A = \frac{k_{pBA}[A]}{k_{pBA}[A] + k_{pAB}[B]} \quad (S3)$$

$$P_B = 1 - P_A \quad (S4)$$

Equation S5 defines the conversion of monomer A (X_A) and Equation S6 defines the overall conversion (X_T). $[i]_0$ is the initial concentration of monomer i in these two equations.

$$X_A = \frac{[A]_0 - [A]}{[A]_0} \quad (S5)$$

$$X_T = \frac{([A]_0 - [A]) + ([B]_0 - [B])}{[A]_0 + [B]_0} \quad (S6)$$

Differentiation of Equation S5 and S6 leads to Equation S7, S8 and S9.

$$dX_A = -\frac{d[A]}{[A]_0} \quad (S7)$$

$$dX_T = \frac{-d[A] - d[B]}{[A]_0 + [B]_0} \quad (S8)$$

$$\frac{dX_A}{dX_T} = \frac{[A]_0 + [B]_0}{[A]_0} \cdot \frac{R_{pA}}{R_{pA} + R_{pB}} = \frac{[A]_0 + [B]_0}{[A]_0} \cdot \left(\frac{1 + r_A \cdot \frac{[A]}{[B]}}{2 + r_A \cdot \frac{[A]}{[B]} + r_B \cdot \frac{[B]}{[A]}} \right) \quad (S9)$$

In which r_A and r_B are the reactivity ratios of monomer A and B defined as shown in Equation S10 and S11.

$$r_A = \frac{k_{pAA}}{k_{pAB}} \quad (S10)$$

$$r_B = \frac{k_{pBB}}{k_{pBA}} \quad (\text{S11})$$

Concentrations can be defined as function of X_A and X_T as depicted in Equation S12, to enable the integration of Equation S9.

$$\frac{[A]}{[B]} = \frac{[A]_0 \cdot (1 - X_A)}{[B]_0 - X_T \cdot ([A]_0 + [B]_0) + [A]_0 \cdot X_A} \quad (\text{S12})$$

The cumulative copolymer composition (Y_i , cumulative copolymer composition referred to monomer i) is defined as shown in Equation S13.

$$Y_A = \frac{[A]_0 \cdot X_A}{([A]_0 + [B]_0) \cdot X_T} \quad (\text{S13})$$

The molar monomer ratios of the experiments for each of the monomer couples are listed in **Table S3**.

Table S3: Molar monomer ratios of the experiments for each of the monomer couples.

	Experiment 1	Experiment 2	Experiment 3	Experiment 4
MDO/VAc	0.32/0.68	0.25/0.75	0.20/0.80	0.05/0.95
MDO/2OA	0.42/0.58	0.22/0.78	0.12/0.88	0.05/0.95
MDO/LMA	0.52/0.48	0.30/0.70	0.23/0.77	0.09/0.91

Results and Discussion

NMR spectra

The monomer conversions of MDO and VAc were measured following the evolution of the peaks of the protons at the carbon atoms *a* and *c* of MDO (δ [ppm] = 3.50-3.40 and 3.70-3.60) and VAc (protons at carbon atom (1) at δ [ppm] = 4.75-4.60 and (1') at δ [ppm] = 4.40-4.25) as indicated in **Figure S1**. The VAc and MDO monomer structures as well as the NMR spectra for the copolymerization of MDO/VAc and the change of intensity of the peaks over polymerization time can be seen in Figure S1.

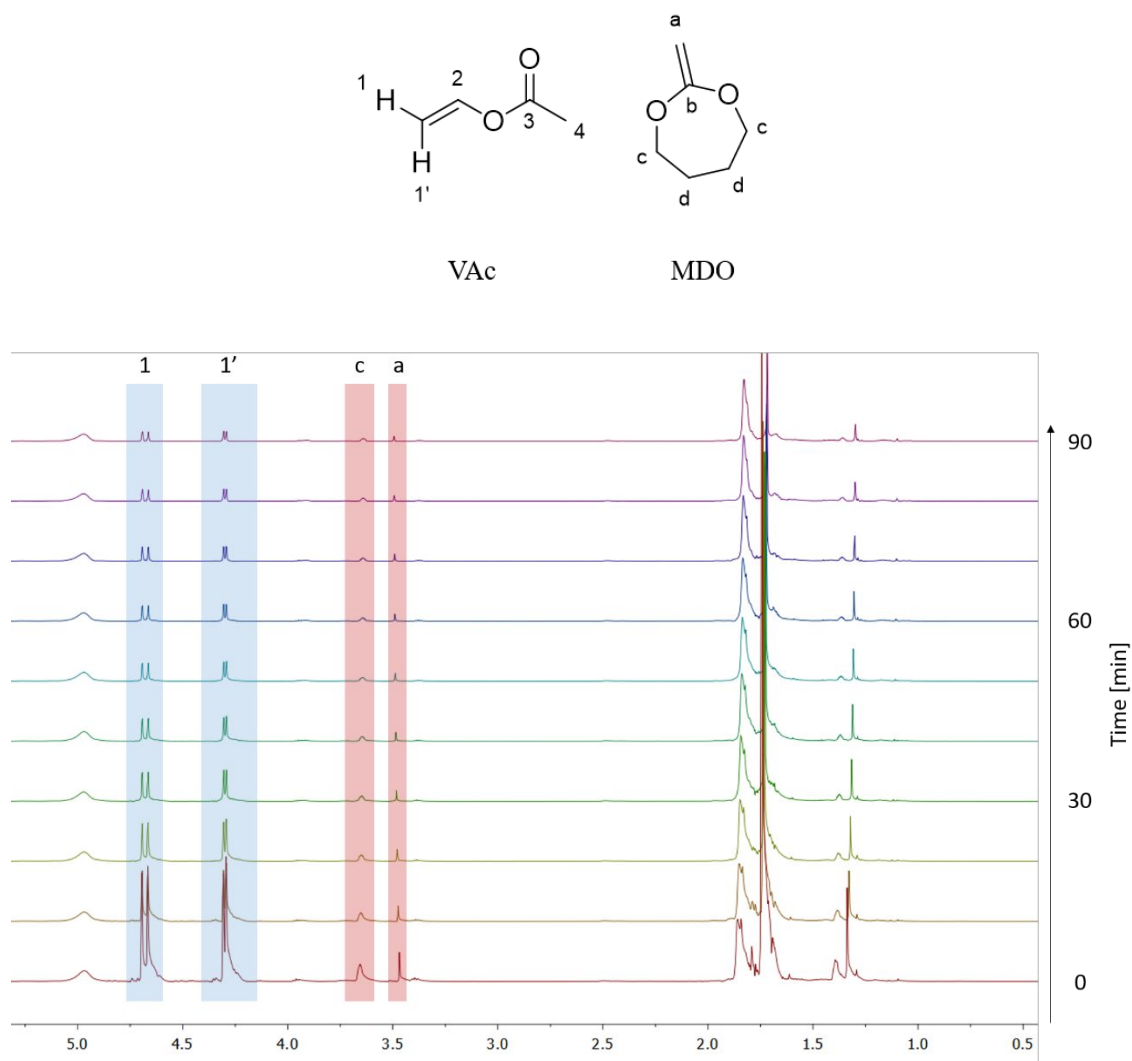


Figure S1: First 10 ^1H NMR spectra for the copolymerization of MDO/VAc with the molar ratio of 0.25/0.75. The peaks that were tracked to follow the conversion of VAc are marked in blue and the ones for MDO are marked in red.

The monomer conversions for the copolymerizations of 2OA/MDO were measured following the evolution of the peaks of the protons (1 and 1') and (2) of 2OA ((1) at δ [ppm] = 6.25-6.10, (2) at δ [ppm] = 6.00-5.80 and (1') at δ [ppm] = 5.45-5.30) and (c) of MDO (δ [ppm] = 3.70-3.60). The used peaks are assigned in **Figure S2** and an example of the evolution of the peaks for the copolymerization of MDO and 2OA is also shown. The used peaks are assigned in **Figure S2** and an example of the evolution of the peaks for the copolymerization of MDO and 2OA is also shown.

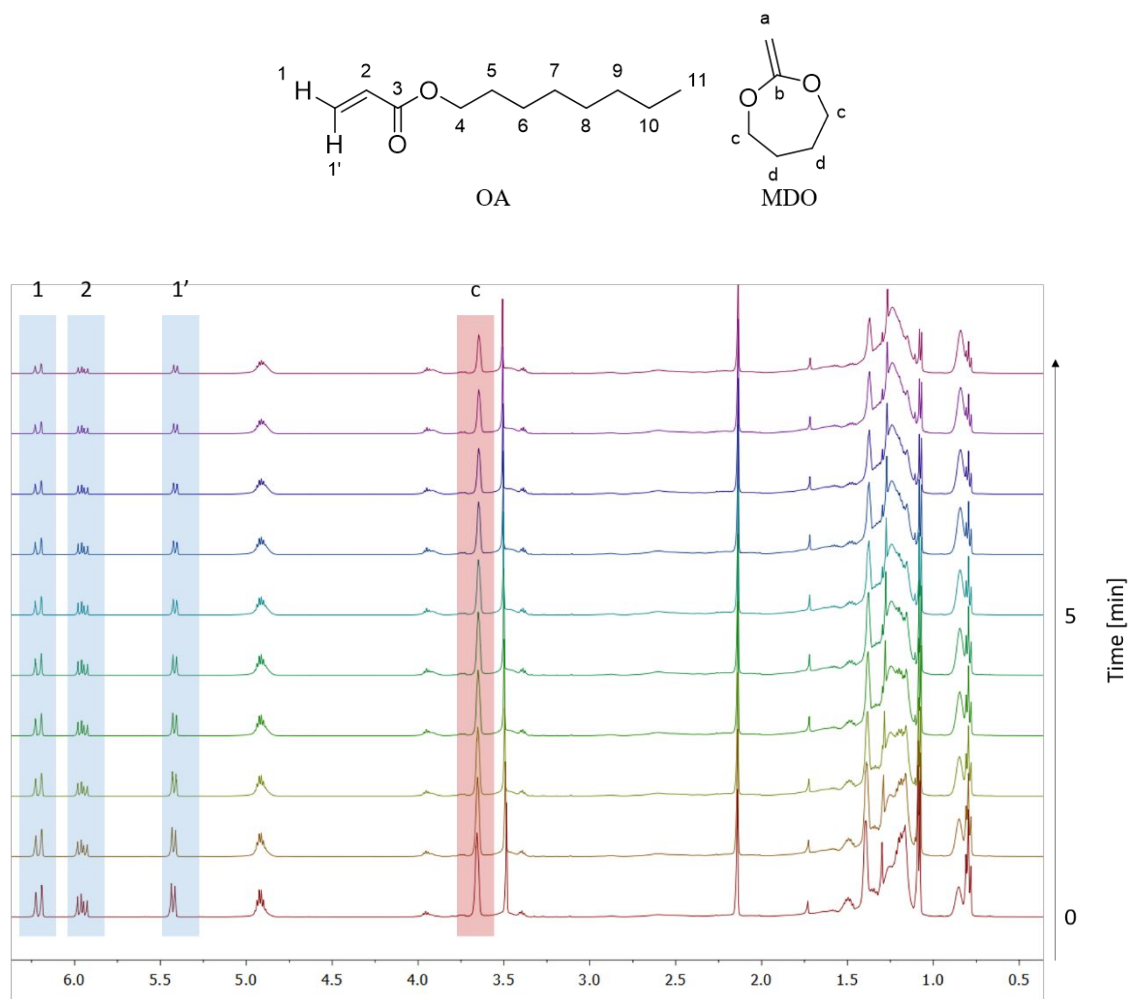
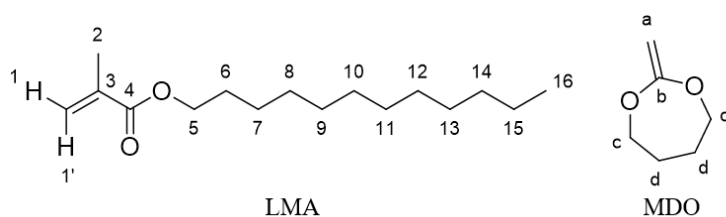


Figure S2: First 10 ^1H NMR spectra for the copolymerization of MDO/2OA in the molar ratio 0.42/0.58. The peaks used to calculate the conversion of 2OA are marked in blue and the one for MDO in red.

The monomer conversions for the copolymerization of MDO with LMA were measured by following the evolution of the peaks of the protons attached to the carbon atom 1 of LMA ((1) at δ [ppm] = 6.10-6.00 and (1') at δ [ppm] = 5.35-5.25) and the protons at the carbon atoms (a) and (c) of MDO ((a) at δ [ppm] = 3.50-3.40 and (c) at δ [ppm] = 3.70-3.60). **Figure S3** shows an example of NMR spectra for the copolymerizations of MDO/LMA, the signals used for the determination of conversions are assigned to the carbon atoms of the monomers.



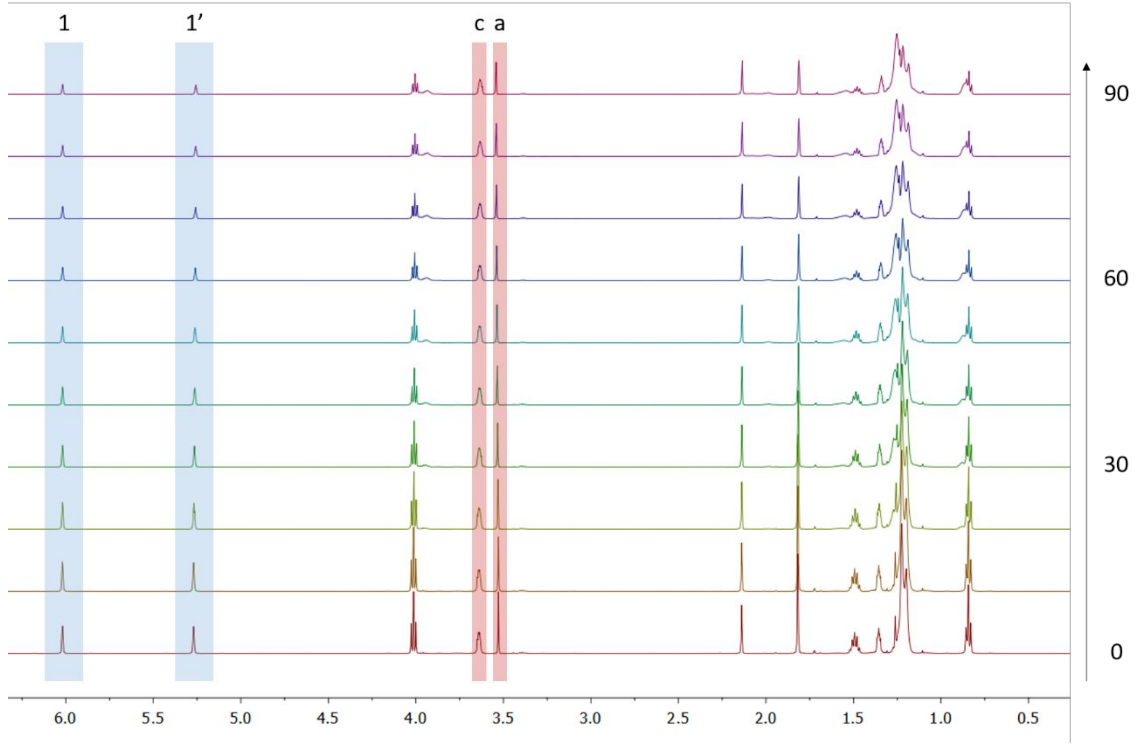


Figure S3: First 10 recorded ^1H NMR spectra for the copolymerization of MDO/LMA with the molar ratio 0.30/0.70. The peaks used to calculate the conversion of LMA are marked in blue and the ones for MDO in red.

Mayo-Lewis plots

The theoretical instantaneous copolymer composition, F_A of a monomer A has been calculated from the reactivity ratios r_A and r_B of the comonomers A and B and the instantaneous fraction of the feed f_A and f_B of the monomers A and B using the Mayo-Lewis equation (Equation S14).⁸

$$F_A = \frac{r_A \cdot f_A^2 + f_A \cdot f_B}{r_A \cdot f_A^2 + 2 \cdot f_A \cdot f_B + r_B \cdot f_B^2} \quad (\text{S14})$$

where f_A and f_B are readily obtained from the evolution of the fractional conversions of each monomer. The experimental instantaneous copolymer compositions have been calculated from the time evolution of the fractional conversions of each of the monomers, A and B. The derivative of fractional conversions of each monomer yields, the polymerization rate of each monomer at each sampling time; $R_{p,i}$. The instantaneous copolymer composition, F_A , is then readily calculated as follow:

$$F_A = \frac{R_{p,A}}{R_{p,A} + R_{p,B}} \quad (\text{S15})$$

The Mayo-Lewis plot for the MDO/2OA system is shown in Figure S4. The theoretical evolution of instantaneous copolymer composition for the MDO/2EHA system is plotted as well using the reactivity ratios estimated by Lena et al.²

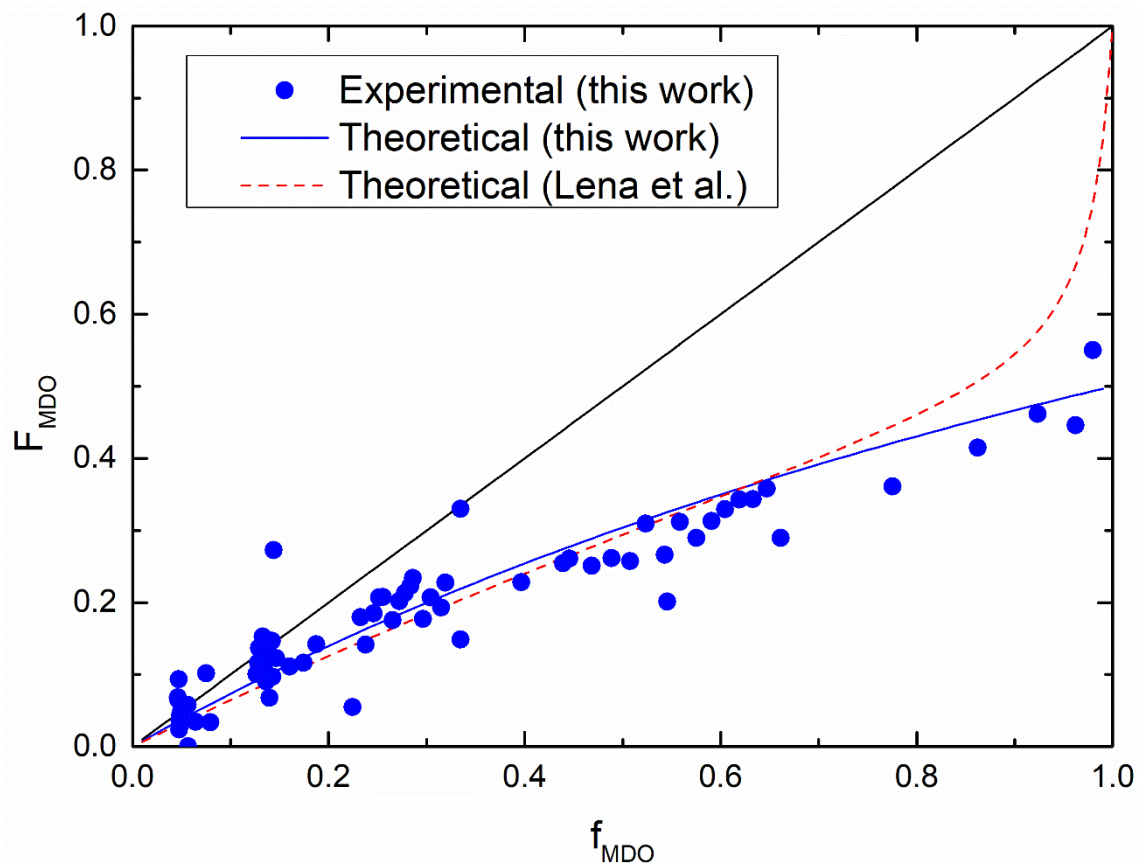


Figure S4: Mayo-Lewis plot for the MDO/2OA system. The theoretical instantaneous copolymer composition calculated from the reactivity ratios of this work (blue line), the instantaneous copolymer composition for the MDO/2EHA system using the reactivity ratios reported by Lena et al.² (red, dashed line), and the instantaneous copolymer composition determined from the evolution of the individual monomer conversions of MDO and 2OA (blue circles).

The Mayo-Lewis plot for the MDO/LMA system is depicted in Figure S5.

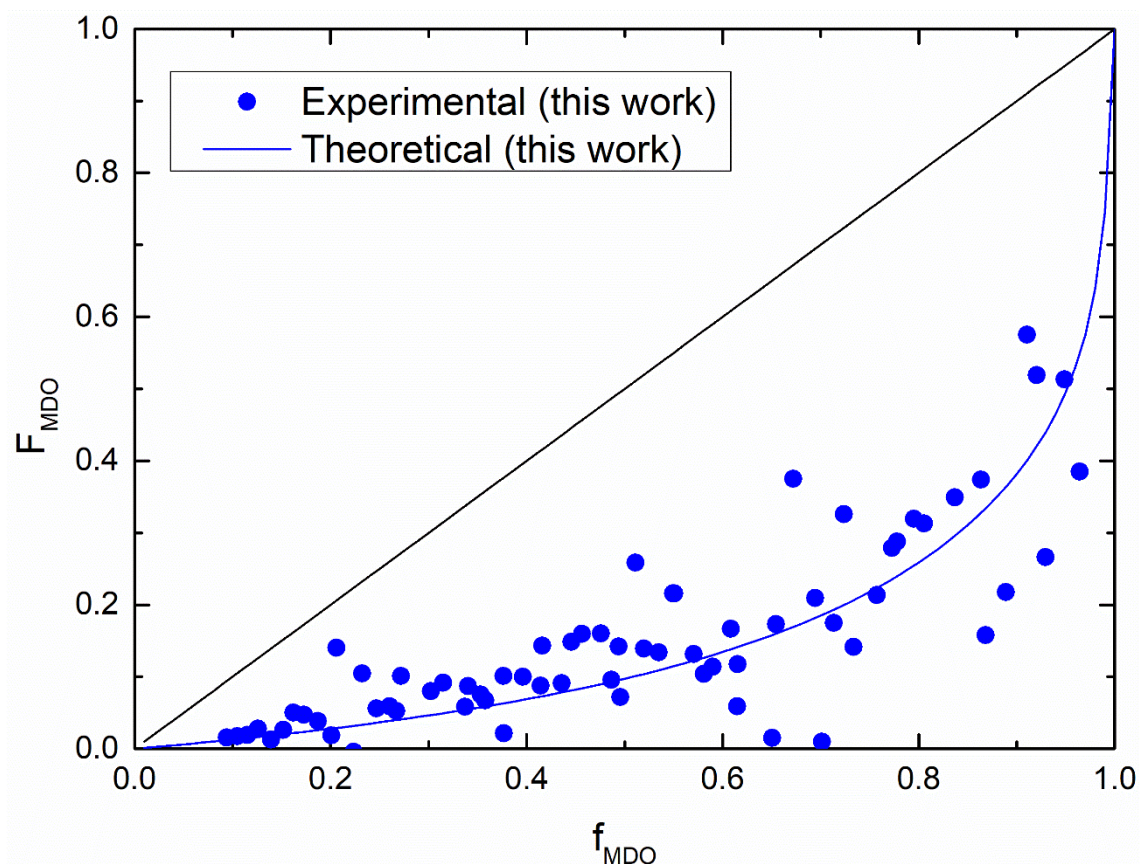


Figure S5: Mayo-Lewis plot for the MDO/LMA system. The instantaneous copolymer composition calculated with the reactivity ratios for MDO/LMA reported in this work (blue line) and instantaneous copolymer composition determined from the evolution of the fractional conversions of MDO and LMA (blue circles).

Literature

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