

Supporting Information for

Acrylate-Methacrylate Radical Copolymerization Kinetics of Sparingly Water-Soluble Monomers in Polar and Nonpolar Solvents

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Table S1 - In-situ MA/MAA copolymerization experiments at 60 °C with 0.2 wt.% AIBN for DMSO-d6 and 0.2 wt.% V-50 for D₂O/EtOD

$wt. \%_{mon,0}$	$f_{MA,0}$	Solvent	α_x^a	$X_{Overall,final}$	
50	0.20	DMSO-d6	1	72.7	
	0.50			87.5	
	0.80			88.8	
10	0.20			73.1	
	0.50			73.5	
	0.79			78.5	
50	0.20	EtOD/D ₂ O	0.50	81.4	
	0.49			88.6	
	0.80			88.0	
20	0.20			50.8, 66.9, 82.0 ^b	
	0.50			54.5, 72.6, 90.4 ^b	
	0.79			72.6	
10	0.19			84.1	
	0.49			93.6	
	0.80			82.6	
5	0.19			91.9	
	0.49			85.3	
	0.79			80.3	
10	0.20			0.75	88.5
	0.49				89.2
5	0.21				90.1
	0.48	87.9			
10	0.20	0.90	83.8		
	0.48		79.9		
	0.79		96.2		

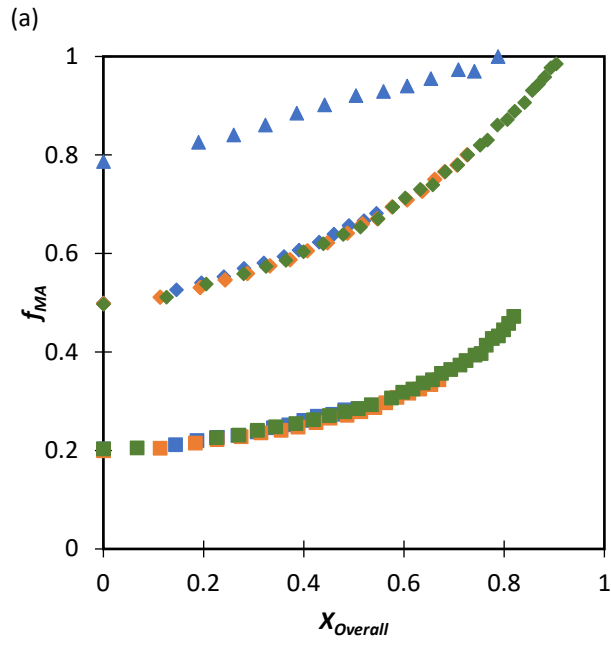
^a Refers to the mass fraction of D₂O or DMSO-d6 in the solvent mixture

^b $X_{Overall}$ values for batch experiments conducted for 40, 60 and 100 min, respectively, to check the reproducibility of data as shown in Figure S1(a) and (b).

Table S2- Summary of performed In-situ MA/DEGMEMA copolymerization at 60 °C with 2 wt.% AIBN for Toluene-d8, 0.2 wt.% AIBN for DMSO-d6 and 0.2 wt.% V50 for D₂O:EtOD.

wt. % _{mon,0}	$f_{MA,0}$	Solvent	α_x^a	$X_{Overall,final}$
10	0.21	Toluene-d8	1	82.5
	0.50			85.1
	0.79			84.5
50	0.20	DMSO-d6	1	94.4
	0.49			90.8
	0.79			93.0
10	0.19	DMSO-d6	1	86.8
	0.49			91.0
	0.79			89.5
50	0.20	EtOD/D ₂ O	0.5	96.7
	0.50			88.5
	0.80			83.1
10	0.20	EtOD/D ₂ O	0.5	93.2
	0.49			93.1
	0.79			75.3
10	0.19	EtOD/D ₂ O	0.75	95.6
	0.50			85.9
	0.79			76.7
5	0.20	EtOD/D ₂ O	0.75	93.5
	0.48			83.2
	0.78			74.7
10	0.22	EtOD/D ₂ O	0.9	93.0
	0.50			88.5
	0.79			76.4
5	0.20	EtOD/D ₂ O	0.9	94.2
	0.47			89.4
	0.78			82.9

^a Refers to the mass fraction of D₂O, toluene-d8 or DMSO-d6 in the solvent mixture



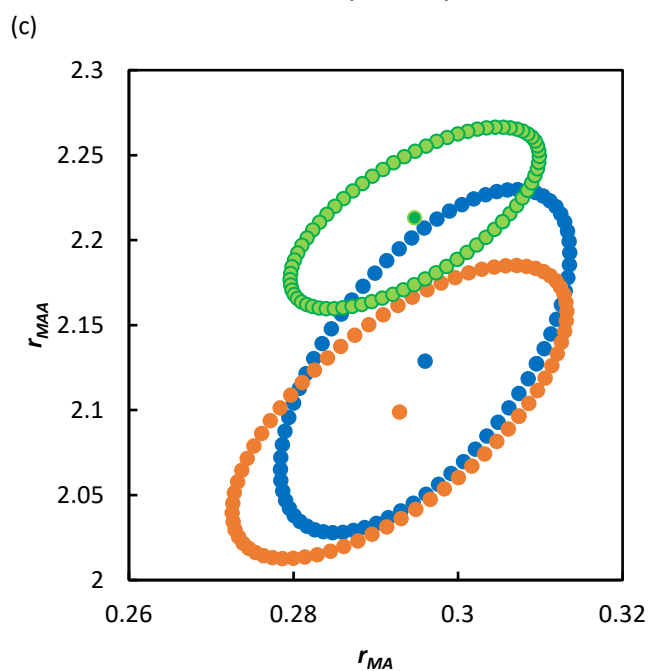
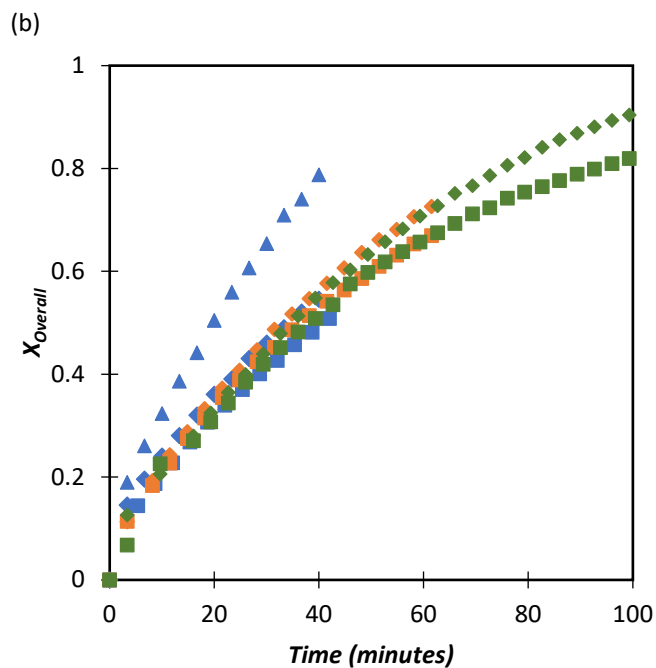


Figure S1 – a) r_{MA} vs. $X_{Overall}$, b) $X_{Overall}$ vs. time and c) joint confidence region (JCR) for the copolymerization of MA/MAA ($w_{mon,0} = 0.2$) in $D_2O:EtOD$ ($\alpha_{EtOD} = 0.5$) using 0.2 wt.% V50 at 60 °C. Blue, orange and green symbols represent data for reactions followed by in-situ NMR for 40, 60 and 100 min, respectively.

S1. ¹H NMR analysis of MA/MAA copolymerization in DMSO-d6

Table S3- Details of formulation used to prepare sample with MA/MAA (20:80 mol%) with $w_{mon} = 0.5$ in DMSO-d6

Substance	MA	MAA	DMSO-d6	AIBN
Amount [g]	0.304	1.215	1.4971	0.0063
MW [g/mol]	86.09	86.06	84.17	164.21
$\frac{\text{Characteristic } H_{\text{Substance}}}{\text{Characteristic } H_{MA}} \times \frac{\text{mol}_{\text{substance}}}{\text{mol}_{MA}}$	1.00	4.00	-	-

In this set of experiments, the peak integration in the range of 3.25-4 ppm, arising from three MA hydrogen atoms (d in Figure S2), was used as the reference peak for the quantitative integration of the monomer vinyl peaks in the range of 5.25-6.5 ppm. It is shown in Figure S2(a) that the peak ratio from the vinyl bound of MAA (A, B) to MA (a, b and c) are identical to the given value (4) in Table S3 which confirms the accuracy of the quantitative calculation from NMR spectra.

Comonomer composition was calculated from Figure S1 using equation S1:

$$f_{MA} = \frac{(\int MA)_t}{(\int MAA)_t + (\int MA)_t} = \frac{(a)_t}{(a)_t + (A)_t} ; f_{MAA} + f_{MA} = 1 \quad (S1)$$

Individual monomer conversions are calculated from equation S2 and S3:

$$X_{MA,absolute} = \frac{(\int MA)_o - (\int MA)_t}{(\int MA)_o} = \frac{(a)_o - (a)_t}{(a)_o} \quad (S2)$$

$$X_{MAA,absolute} = \frac{(\int MAA)_o - (\int DMAEMA)_t}{(\int DMAEMA)_o} = \frac{(A)_o - (A)_t}{(A)_o} \quad (S3)$$

And overall conversion was calculated from Equation S4

$$X_{Overall} = \frac{[(f MA)_o - (f MA)_t] + [(f MAA)_o - (f MAA)_t]}{(f MA)_o + (f MAA)_o}$$

$$= \frac{(a)_o - (a)_t + (A)_o - (A)_t}{(a)_o + (A)_o} \quad (S4)$$

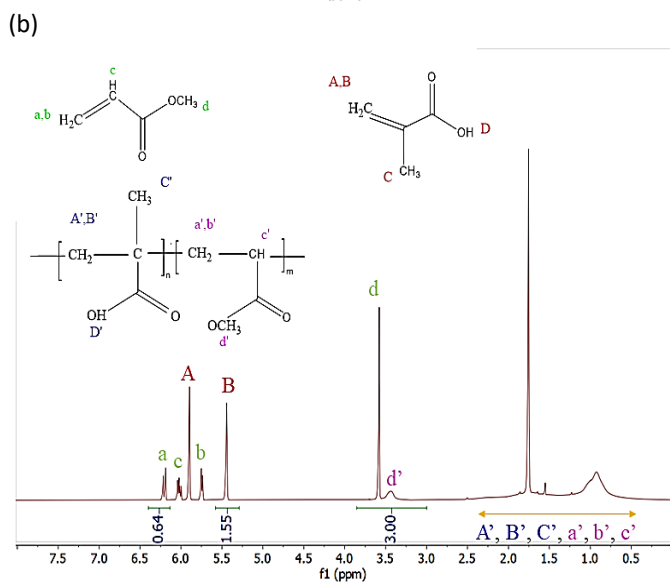
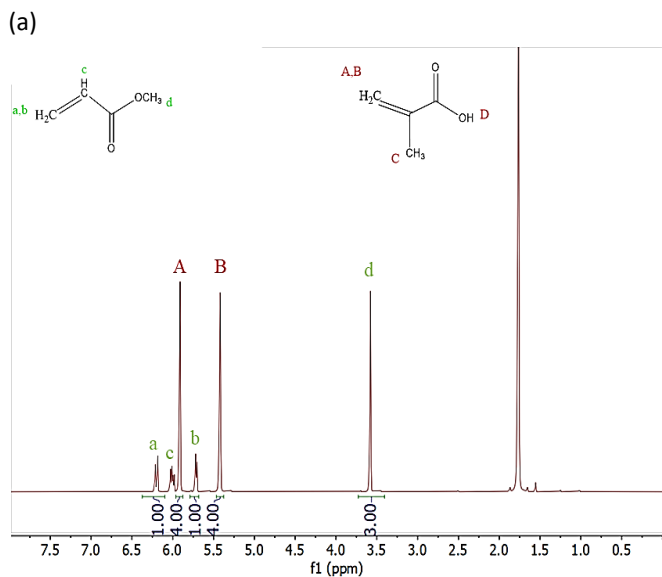


Figure S2- a) ^1H NMR spectra of MA/MAA (20:80 mol%) with $w_{mon} = 0.5$ in DMSO- d_6 without initiator and no conversion at 60 °C and b) with 0.2 wt.% AIBN after 60 minutes of In-situ polymerization at 60 °C. The formulation for this sample is given in Table S3.

S2. ¹H NMR analysis of MA/MAA copolymerization in D₂O: EtOD

In this set of experiments, the sum of peak integrations in the range of 3.25-4.25 ppm, arising from two Ethanol-OD hydrogen atoms (E in Figure S3) and three MA hydrogen atoms (d in Figure S3), was used as the reference peak for the quantitative integration of the monomer vinyl peaks in the range of 5.5-6.5 ppm. The expected value of this integral is 76.77 for the formulation given in Table S4, as calculated by Equation S5:

$$\begin{aligned} Area_{3.25-4.25 \text{ ppm}} &= \frac{mol_{EtOD}}{mol_{MA}} \times \text{number of } H_{EtOD} + \frac{mol_{MA}}{mol_{MA}} \times \text{number of } H_{MA} \\ &= \frac{\frac{2.212}{47.08}}{\frac{0.1096}{86.09}} \times 2 + \frac{\frac{0.1096}{86.09}}{\frac{0.1096}{86.09}} \times 3 = 73.76 + 3 = 76.77 \end{aligned} \quad (S5)$$

The agreement with the measured value of 76.76 (Figure S3) is excellent. The accuracy of this methodology for calculating conversion was also checked by adding 2 wt.% 1,3,5-trioxane as an internal reference¹ to the Table S4 formulation. As shown in Figure S3, the integral of this reference peak X at 5.1 ppm to the MA peak at 6.55 ppm perfectly matches the molar ratio of the two components measured in the lab (5.73). Therefore, using the combined integration of peaks in the range of 3.25-4.25 ppm as a reference to calculate monomer conversions is reliable.

The overall conversion from the spectra given in Figure S3 was calculated from Equation S4 using the measured integrals in the range of 5.5-6.5 ppm relative to the reference peaks in the range of 3.25-4.25 ppm.

Table S4 - Details of formulation used to prepare sample with MA/MAA (20:80 mol%) with $w_{mon} = 0.1$ in D_2O : EtOD ($\alpha_{EtOD} = 0.5$) with 2 wt.% 1,3,5-trioxane.

Substance	MA	MAA	EtOD	D ₂ O	1,3,5-trioxane
Amount [g]	0.1096	0.4128	2.2112	2.1937	0.1096
MW [g/mol]	86.09	86.09	47.08	20.02	90.08
$\frac{\text{Characteristic } H_{\text{Substance}}}{\text{Characteristic } H_{MA}} \times \frac{\text{mol}_{\text{substance}}}{\text{mol}_{MA}}$	1	3.77	73.76	-	5.73

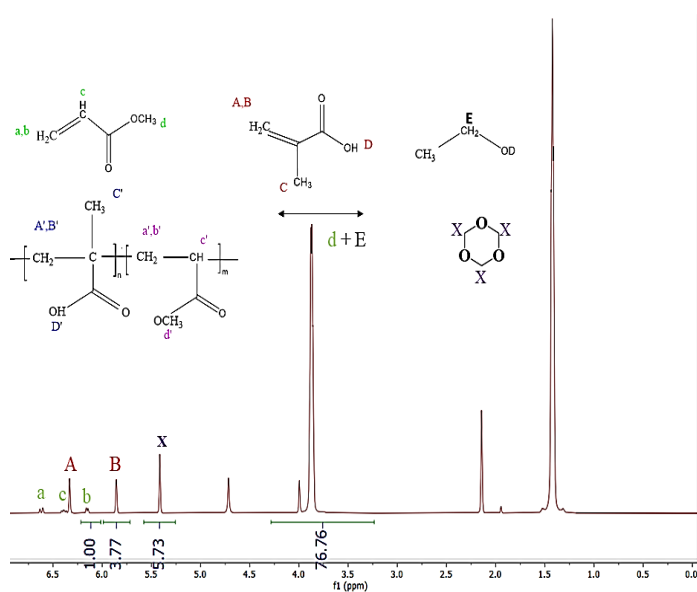


Figure S3- 1H NMR spectra of MA/MAA (20:80 mol%) with $w_{mon} = 0.1$ in % D_2O : EtOD ($\alpha_{EtOD} = 0.5$) with 2 wt.% 1,3,5-trioxane using the formulation given in Table S4.

S3. 1H NMR analysis of MA/DEGMEMA copolymerization in Toluene-d₈

In this set of experiments, the sum of peaks in the range of 3-3.75 ppm from nine hydrogen of DEGMEMA (E and F in Figure S4) and three hydrogens from MA (d in Figure S4) was used as the reference peak for the quantitative integration of the vinyl bounds peaks from monomers at the

range of 5.5-6.5 ppm. Following this idea, the corresponding integral for the given example formulation in Table S5 should be equal to 12.13 as shown in Equation S6:

$$\begin{aligned}
 Area_{3-3.75\text{ ppm}} &= \frac{mol_{DEGMEMA}}{mol_{MA}} \times \text{number of } H_{DEGMEMA} + \frac{mol_{MA}}{mol_{MA}} \times \text{number of } H_{MA} \\
 &= \frac{0.1393}{\frac{188.22}{0.0628}} \times 9 + \frac{0.0628}{\frac{86.09}{0.0628}} \times 3 = 9.13 + 3 = 12.13 \quad (S6)
 \end{aligned}$$

The overall conversion from the spectra given in Figure S4 was calculated from Equation S4 using the measured integrals in the range of 5.5-6.5 ppm relative to the reference peaks in the range of 3-3.75 ppm.

Table S5 - Details of formulation used to prepare sample with MA/DEGMEMA (50:50 mol%) with $w_{mon} = 0.1$ in Toluene- d_8 with 0.2 wt.% AIBN.

	MA	DEGMEMA	Toluene- d_8	AIBN
Amount [g]	0.0628	0.1393	0.9609	0.04
MW [g/mol]	86.09	188.22	100.18	164.41
$\frac{\text{Characteristic } H_{\text{Substance}}}{\text{Characteristic } H_{MA}} \times \frac{mol_{\text{substance}}}{mol_{MA}}$	3	9.13	-	-

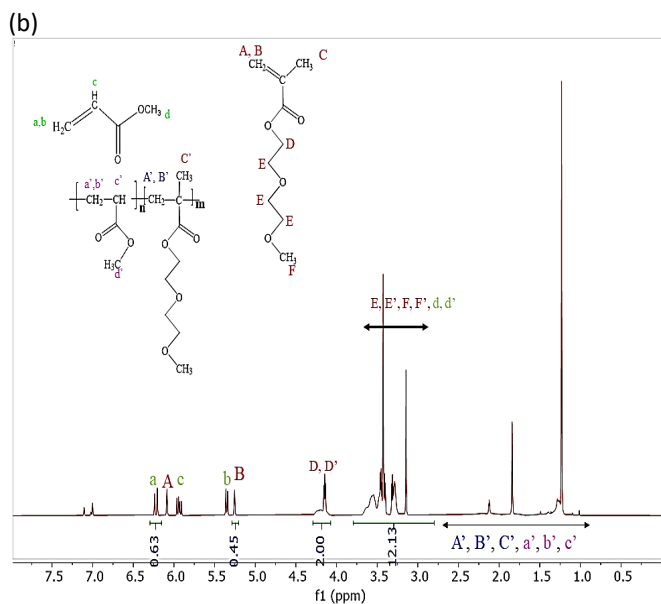
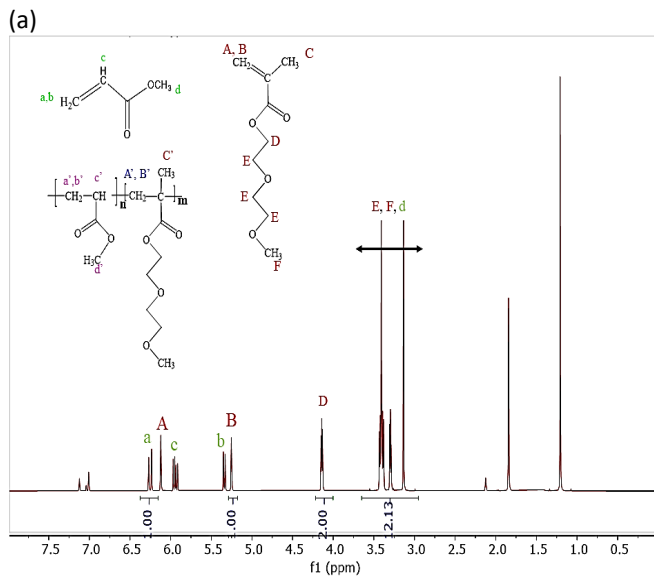


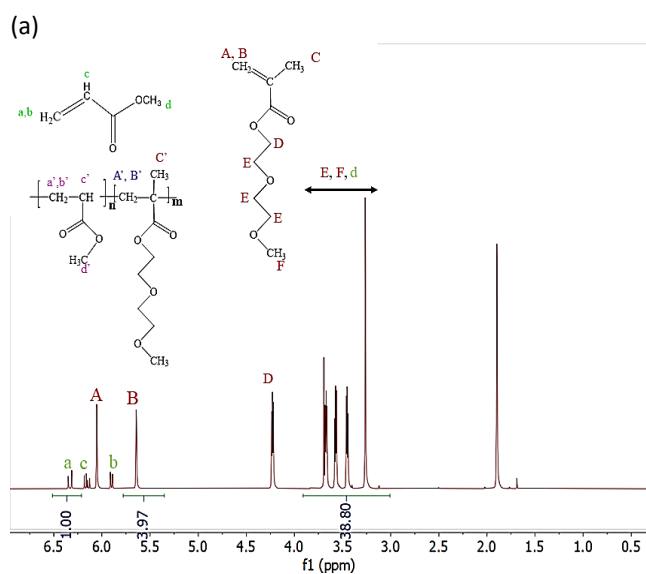
Figure S4 - a) ^1H NMR spectra of MA/DEGMEMA (50:50 mol%) with $w_{\text{mon}} = 0.1$ in Toluene- d_8 without initiator at 60 °C and no conversion and b) with 0.2 wt.% AIBN after 60 minutes of In-situ polymerization at 60 °C. The formulation for this sample is given in Table S5.

S4. ^1H NMR analysis of MA/DEGMEMA copolymerization in DMSO- d_6

The idea to calculate the conversion was like what was explained in section S3.

Table S6 - Details of formulation used to prepare sample with MA/DEGMEMA (20:80 mol%) with $w_{mon} = 0.5$ in.% DMSO-d₆ with 0.2 wt.% AIBN.

	MA	DEGMEMA	DMSO-d ₆	AIBN
Amount [g]	0.1026	0.8974	0.9964	0.004
MW [g/mol]	86.09	188.22	84.17	164.41
$\frac{\text{Characteristic } H_{\text{Substance}}}{\text{Characteristic } H_{\text{MA}}}$ $\times \frac{\text{mol}_{\text{substance}}}{\text{mol}_{\text{MA}}}$	3	35.80	-	-



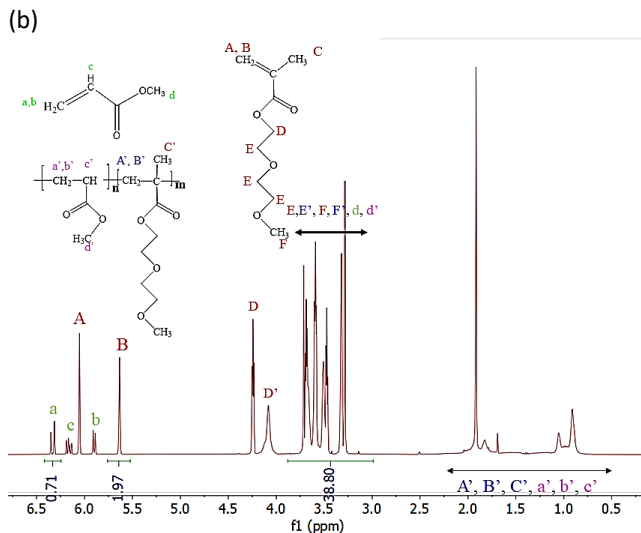


Figure S5 - a) ^1H NMR spectra of MA/DEGMEMA (20:80 mol%) with $w_{\text{mon}} = 0.5$ in DMSO- d_6 without initiator at 60 °C and no conversion and b) with 0.2 wt.% AIBN after 60 minutes of In-situ polymerization at 60 °C. The formulation for this sample is given in Table S6.

S5. ^1H NMR analysis of MA/DEGMEMA copolymerization in $\text{D}_2\text{O}/\text{EtOD}$

In this set of experiments, the sum of peaks in the range of 3.25-4.25 ppm from nine hydrogens of DEGMEMA (E and F in Figure S6), three hydrogens from MA (d in Figure S6) and two hydrogens from Ethanol $_\text{OD}$ (G in Fihure S6) was used as the reference peak for the quantitative integration of the vinyl bounds peaks for monomers at the range of 5.5-6.5 ppm. Following this idea, the corresponding integral for the given example formulation in Table S9 should be equal to 17.80 as shown in Equation S7:

$Area_{3.25-4.25\text{ ppm}}$

$$\begin{aligned}
 &= \frac{mol_{DEGMEA}}{mol_{MA}} \times \text{number of } H_{DEGMEMA} + \frac{mol_{MA}}{mol_{MA}} \times \text{number of } H_{MA} \\
 &+ \frac{mol_{EtOD}}{mol_{MA}} \times \text{number of } H_{EtOD} = \frac{0.6882}{0.3148} \times 9 + \frac{0.3148}{0.3148} \times 3 + \frac{0.4987}{0.3148} \times 2 \\
 &= 9 + 3 + 5.80 = 17.80 \quad (S7)
 \end{aligned}$$

Table S7 - Details of formulation used to prepare sample with MA/DEGMEMA (50:50 mol%) with $w_{mon} = 0.5$ in D_2O :
EtOD [50:50] with 0.2 wt.% V50.

	MA	DEGMEMA	EtOD	D ₂ O	V50
Amount [g]	0.3148	0.6882	0.4987	0.4980	0.004
MW [g/mol]	86.09	188.22	47.07	20.02	271.19
$\frac{\text{Characteristic } H_{\text{Substance}}}{\text{Characteristic } H_{MA}} \times \frac{mol_{\text{substance}}}{mol_{MA}}$	3	9	5.80	-	-

(a)

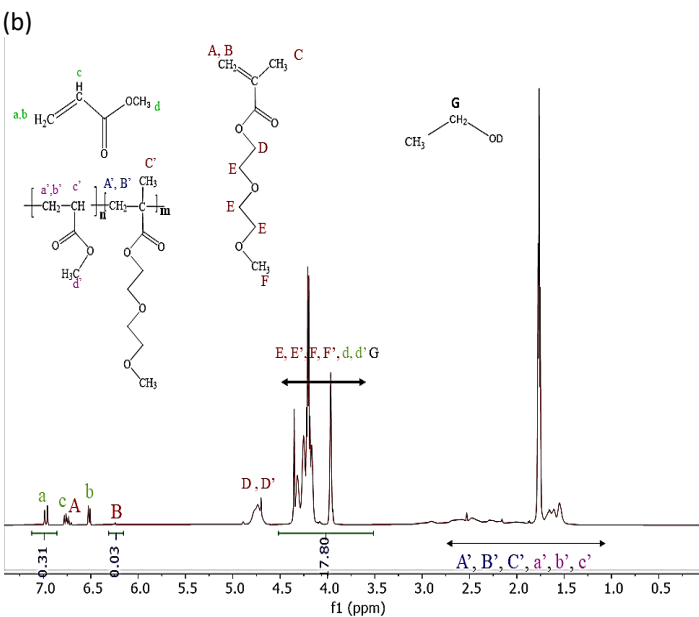
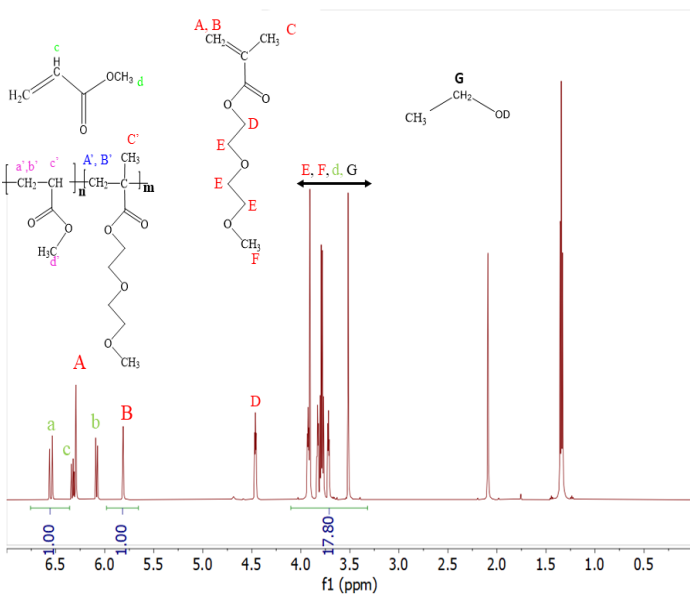


Figure S6 - a) ^1H NMR spectra of MA/DEGMEMA (50:50 mol%) with $w_{\text{mon}} = 0.1$ in $\text{D}_2\text{O}:\text{EtOD}$ ($\alpha_{\text{EtOD}} = 0.5$) without initiator at 60°C and no conversion and b) with 0.2 wt.% V50 after 60 minutes of In-situ polymerization at 60°C . The formulation for this sample is given in Table S9.

S.6. Reactivity ratio estimation

The analytical solution to Skeist's equation presented by Meyer and Lowry² is:

$$1 - X = \left(\frac{f_1}{f_{10}}\right)^\alpha \left(\frac{f_2}{f_{20}}\right)^\beta \left(\frac{f_{10} - \delta}{f_1 - \delta}\right)^\gamma \quad (\text{S8})$$

$$\alpha = \frac{r_2}{1-r_2}, \quad \beta = \frac{r_1}{1-r_1}, \quad \gamma = \frac{1-r_1r_2}{(1-r_1)(1-r_2)}, \quad \delta = \frac{1-r_2}{2-r_1-r_2}$$

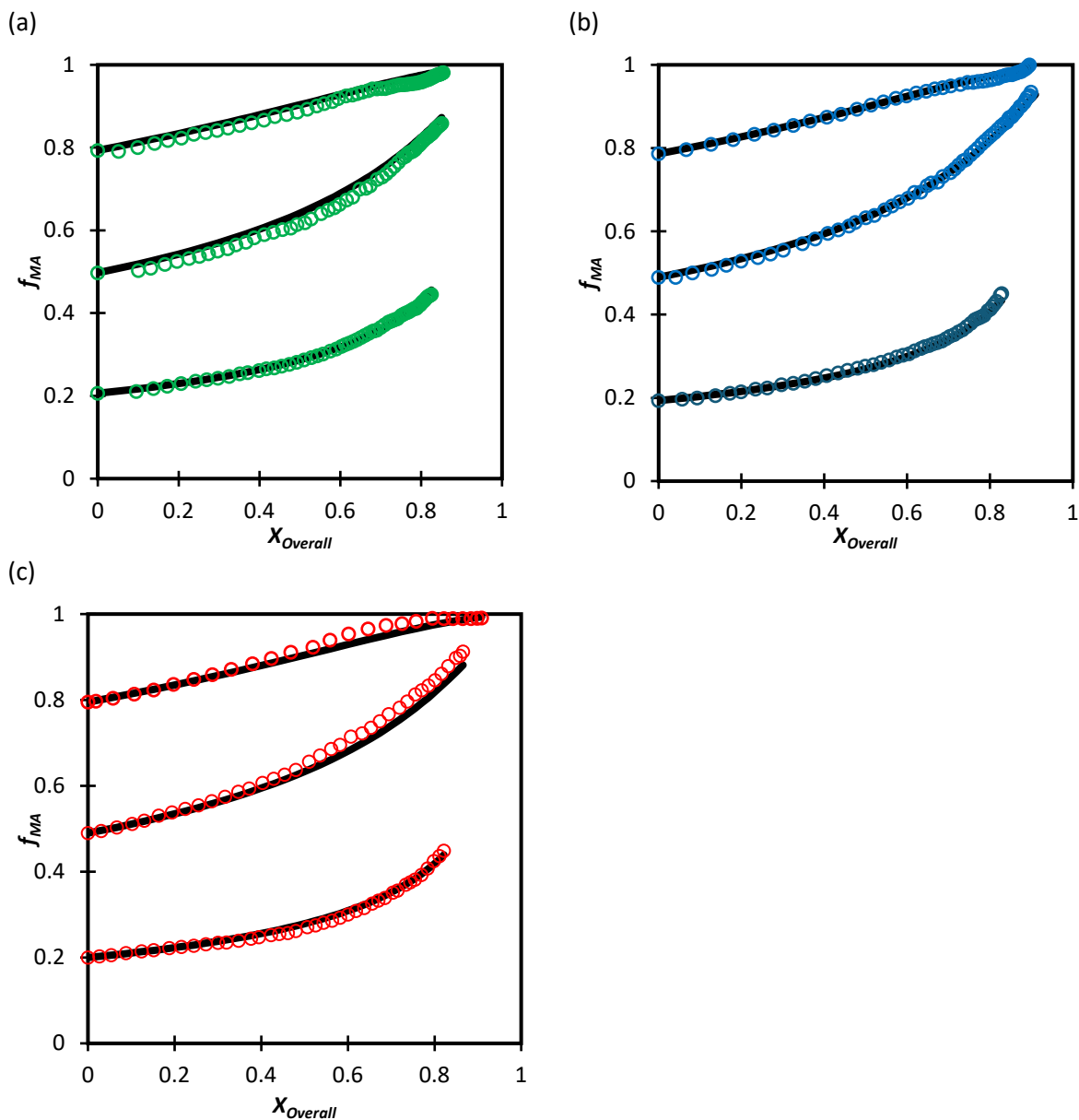


Figure S7 – Drift in MA comonomer composition (f_{MA}) with overall monomer conversion for MA/DEGMEMA in (a) toluene-d8 with $w_{mon} = 0.1$, (b) DMSO-d6 with $w_{mon} = 0.5$ and (c) DMSO-d6 with $w_{mon} = 0.1$. Symbols are experimental data and blacklines are simulated using the overall best-fit reactivity ratios estimated from the combined data set ($r_1=0.36$, $r_2=2.16$).

(a)

(b)

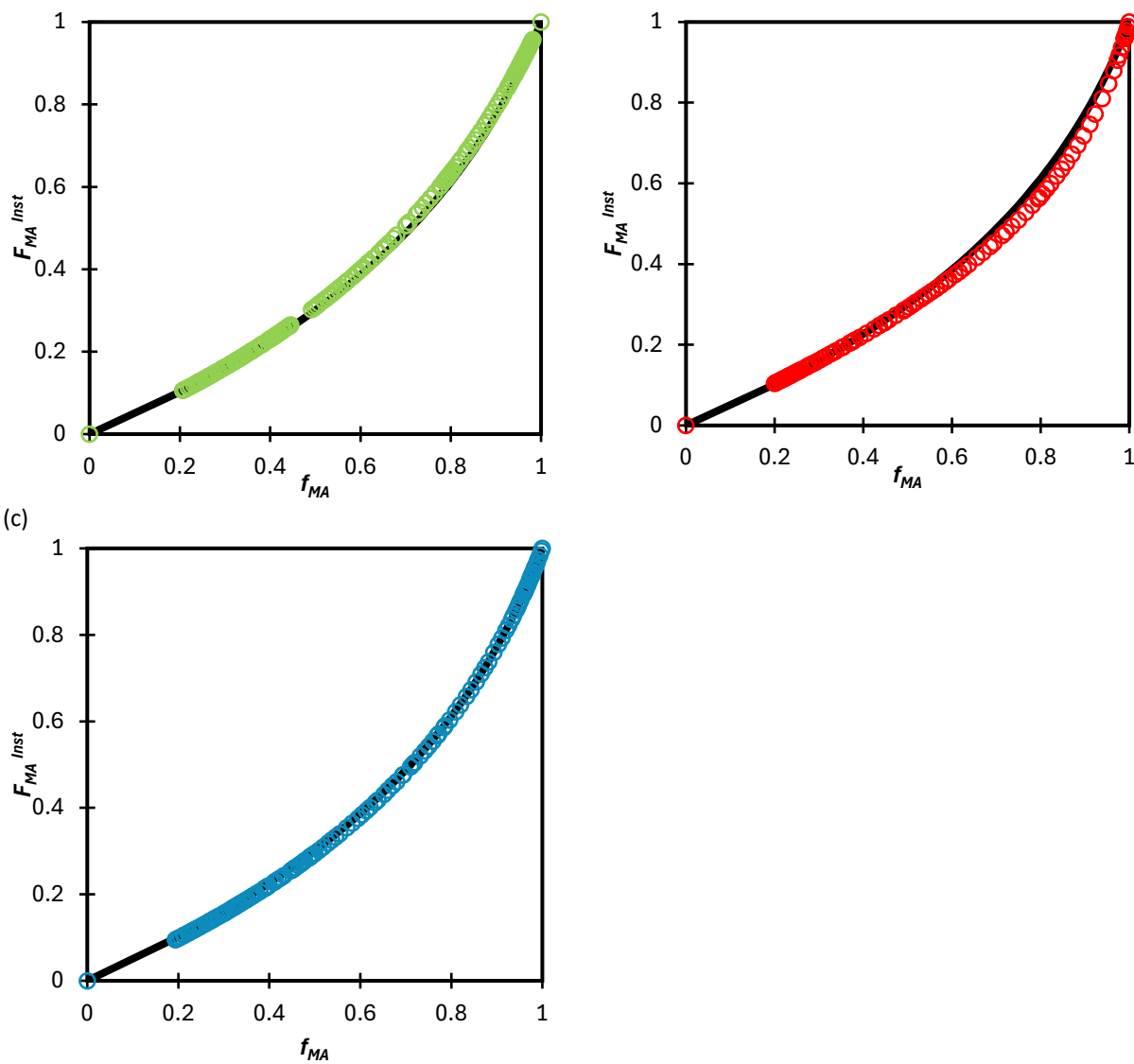


Figure S8 – Calculated F_{MA}^{Inst} for the copolymerization of MA/DEGMEMA in (a) toluene-d8 ($w_{mon}=0.1$) (green), (b) DMSO-d6 ($w_{mon}=0.5$) (red) and (c) DMSO-d6 ($w_{mon}=0.1$) (blue) using reactivity ratios (DNI technique) estimated from datasets "A", "B" and "C" in Table 1, respectively compared to F_{MA}^{Inst} (black line) from overall dataset "D" in Table 1.

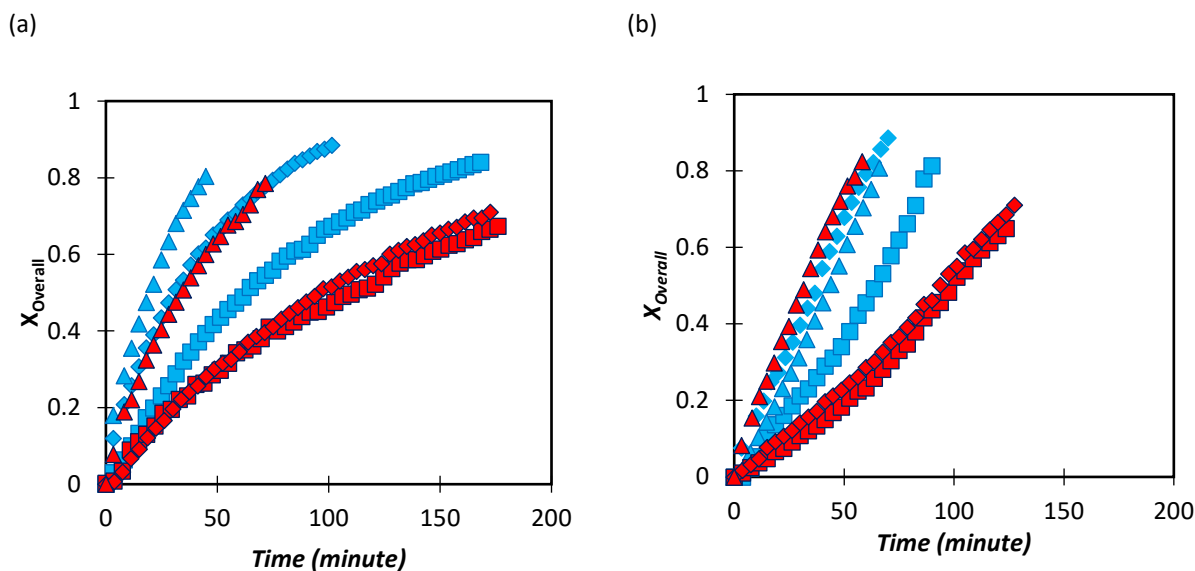


Figure S9 – Monomer conversion profiles for the copolymerization of MA/MAA with monomer ratio of 20:80 (\square), 50:50 (\diamond) and 80:20 (Δ) (mol%) in $DMSO-d_6$ (red) vs. $D_2O:EtOD$ ($\alpha_{EtOD} = 0.5$) (blue) with (a) $w_{mon,0} = 0.1$ (b) $w_{mon,0} = 0.5$.

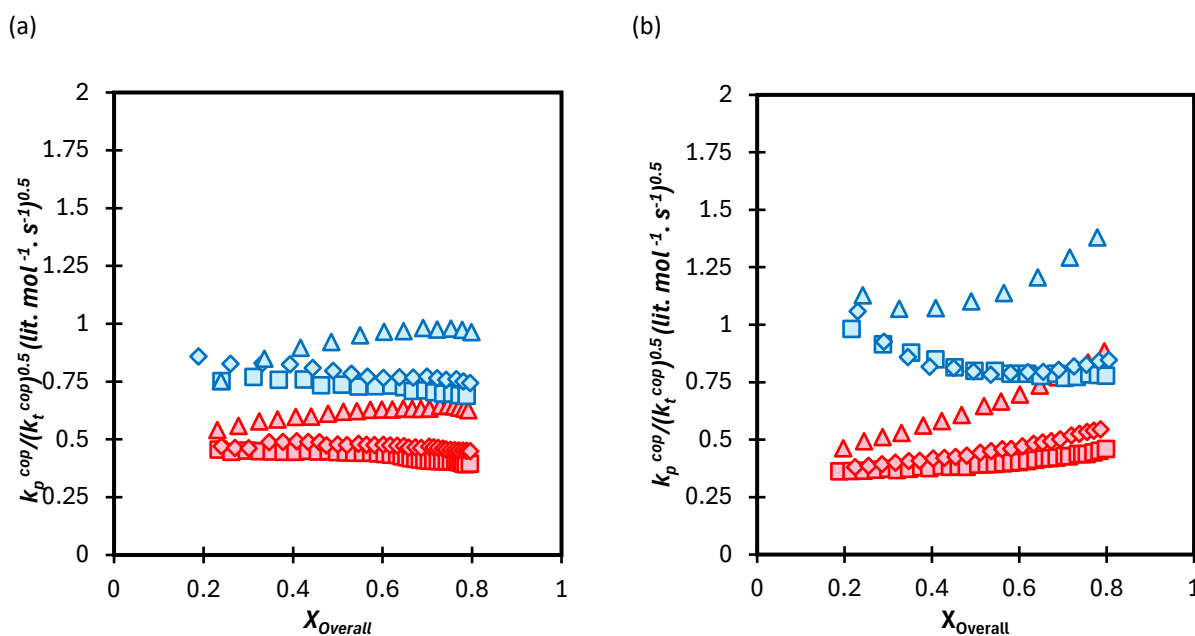


Figure S10- a) Lumped rate coefficient ($k_p^{cop}/(k_t^{cop})^{0.5}$) vs. conversion for the copolymerization of MA-DEGMEMA with a) $w_{mon,0} = 0.1$ and b) $w_{mon,0} = 0.5$ with monomer ratio of 20:80 (\square), 50:50 (\diamond) and 80:20 (Δ) (mol%) in $DMSO-d_6$ (red) vs. $D_2O:EtOD$ ($\alpha_{EtOD} = 0.5$) (blue).

References:

- 1 S. T. Eberhart, A. Hatzis and R. Rothchild, Quantitative NMR assay for aspirin, phenacetin, and caffeine mixtures with 1,3,5-trioxane as internal standard, *J. Pharm. Biomed. Anal.*, 1986, **4**, 147–154.
- 2 V. E. Meyer and G. G. Lowry, Integral and Differential Binary Copolymerization Equations, *J. Polym. Sci. PART A*, 1965, **3**, 2843–2851.