**Electronic Supplementary Information (ESI)** 

## Solvent-control over monomer distribution in copolymerization of 2oxazolines and the effect of gradient structure on self-assembly

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# 1.1. Detailed methods for the calculation of reactivity ratios and prediction of monomer composition in gradient copolymers

The reactivity ratios of the MeOx and PhOx were determined using the Mayo-Lewis and Extended Kelen-Tudos (EKT) methods.<sup>1,2</sup> Polymerization solutions with eight different monomer compositions were prepared, with initial molar fraction of MeOx (f1) ranging from 0.1 to 0.8, were used to determine the reactivity ratio (Table 1) of MeOx and PhOx at 100 °C, with initial total monomer concentration of 3M, either in sulfolane or in ACN. The polymerizations were stopped by cooling the reaction vials below 45 % MeOx conversion. The monomer conversions determined by GC were used to analyze the instantaneous molar fractions of the monomer in the feed (f) and the copolymer (F) (Table 54 and S5).

$$F_1 = 1 - F_2 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

 $f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]}$ where

$$\eta = \left(r_1 + \left(\frac{r_2}{\alpha}\right)\right)\xi - \left(\frac{r_2}{\alpha}\right)$$

$$\eta = \frac{f(F-1)}{F\left(\alpha + \frac{f^2}{F}\right)}, \quad \xi = \frac{\left(\frac{f^2}{F}\right)}{\left(\alpha + \frac{f^2}{F}\right)}, \quad \alpha = \left(\left(\frac{f^2}{F}\right)_{max} \times \left(\frac{f^2}{F}\right)_{min}\right)^{0.5}$$
where

V

and 
$$f = \frac{f_1}{f_2}, F = \frac{F_1}{F_2}$$

Skeist's model were used to predict the instantaneous copolymer composition (F) of the monomers during the polymerization (monomer conversion) from the reactivity ratios of the monomers.<sup>2</sup> This will help to visualize the drift of the monomer composition, along the copolymer chains.

$$Conversion = 1 - \frac{M}{M_0} = 1 - \left(\frac{f_1}{f_1^0}\right)^{\alpha} \times \left(\frac{f_2}{f_2^0}\right)^{\beta} \times \left[\frac{f_1^0 - \delta}{f_1 - \delta}\right]^{\gamma}$$

where,  $M_0$  and M are the initial and the instantaneous concentrations of the monomer,  $f^0$  corresponds to the initial mole fractions in the feed, whereas  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  are defined below

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

**Table S1** Copolymerization kinetic data of MeOx with PhOx in sulfolane at 100 °C, feed molar ratio of MeOx : PhOx = 70:30, target DP 50.

Sample No.	Polymerization	Conversion (%)		$M^{a}(ka mol^{-1})$	Ð
Sample No	time (s)	MeOx	PhOx		D
1	30	17.5		1.1	1.08
2	60	33.0	1.0	1.9	1.08
3	120	41.0	1.4	2.3	1.07
4	300	58.0	1.7	3.0	1.07
5	600	87.0	8.0	4.3	1.08
6	1800	99.5	15.5	4.8	1.07
7	3600		49.0	5.3	1.09
8	7200		84.0	5.8	1.10
9	14400		95.0	6.6	1.11

<sup>a</sup> Determined by SEC- DMAc

Sample No	Time (s)	Conversion (%)		$M_{n}^{a}$ (kg mol <sup>-1</sup> )	Đ
		MeOx	PhOx		
1	30	17.0	1.5	0.9	1.04
2	60	26.0	3.0	1.1	1.11
3	300	67.0	5.5	2.8	1.08
4	600	85.0	6.0	3.0	1.07
5	1800	99.5	20.0	3.9	1.07
6	3600		52.5	4.7	1.09
7	7200		82.5	5.7	1.10
8	14400		97.0	6.3	1.14

**Table S2** Copolymerization kinetic data of MeOx with PhOx in sulfolane at 100 °C, feedmolar ratio of MeOx : PhOx = 50:50, target DP 50.

<sup>a</sup> Determined by SEC- DMAc

Samula No.	Time (a)	Conversion (%)		$M_{a}(h_{Da})$	р
Sample No	Time (S)	MeOx	PhOx	$M_n^*(KDa)$	D
1	30	14.0		0.9	1.03
2	60	26.5		1.0	1.06
3	120	37.0	0.6	1.1	1.10
4	300	59.5	4.0	1.8	1.06
5	600	84.0	7.0	2.3	1.07
6	1800	98.5	25.0	3.3	1.08
7	3600	> 99%	47.0	4.3	1.08
8	7200		89.5	6.0	1.09
9	14400		97.5	6.4	1.10

**Table S3** Copolymerization kinetic data of MeOx with PhOx in sulfolane at 100 °C, feedmolar ratio of MeOx : PhOx = 30:70, target DP 50.

<sup>a</sup> Determined by SEC- DMAc

**Table S4** Reactivity ratios of MeOx and PhOx for the copolymerizations in sulfolane and acetonitrile at 100 °C calculated using Mayo-Lewis (ML) and extended Kelen-Tudos (EKT) models.

	In sulfolane <sup>a</sup>		In acetonitrile <sup>b</sup>	
Kinetic model				
	r <sub>MeOx</sub>	r <sub>PhOx</sub>	r <sub>MeOx</sub>	r <sub>PhOx</sub>
ML	21.62±2.22	0.088±0.019	10.05±2.19	0.30±0.08
EKT	20.69±1.19	0.081±0.015	7.49±0.52	0.17±0.02

calculated using the data from <sup>a</sup> Table S5 and <sup>b</sup> Table S6.

Feed ratio <sup>a</sup> (f)		Copolymer composition <sup>b</sup> (F)		
MeOx	PhOx	MeOx	PhOx	
0.8	0.2	0.99	0.01	
0.7	0.3	0.98	0.02	
0.6	0.4	0.97	0.03	
0.5	0.5	0.94	0.06	
0.4	0.6	0.91	0.09	
0.3	0.7	0.90	0.10	
0.2	0.8	0.84	0.16	
0.1	0.9	0.65	0.35	

**Table S5** Monomer composition in feed and in the copolymer used to determine the reactivity ratios of MeOx and PhOx in sulfolane at 100 °C, target DP 50.

<sup>a</sup> molar fraction of the monomers in the feed mixture determined using GC. <sup>b</sup> molar fraction of the monomers in the copolymers determined from the conversion of monomers using GC. All the samples were taken after 2 min of copolymerization. The conversions of MeOx were below 32 %. **Table S6** Monomer composition in feed and in the copolymer used to determine the reactivity ratios of MeOx and PhOx in ACN at 100 °C, target DP 50.

Feed ratio <sup>a</sup>		Copolymer composition <sup>b</sup>		
MeOx	PhOx	MeOx	PhOx	
0.8	0.2	0.97	0.03	
0.7	0.3	0.92	0.08	
0.6	0.4	0.91	0.09	
0.5	0.5	0.89	0.11	
0.4	0.6	0.82	0.18	
0.3	0.7	0.81	0.19	
0.2	0.8	0.62	0.38	
0.1	0.9	0.34	0.66	

<sup>a</sup> molar fraction of the monomers in the feed mixture determined using GC. <sup>b</sup> molar fraction of the monomers in the copolymers determined from the conversion of monomers using GC. All the samples were taken after 2 min of copolymerization. The overall conversions of MeOx were below 44 %.



Figure S1 Copolymerization kinetic plots for the living CROP of MeOx with PhOx in sulfolane at 100 °C and target DP = 50 with feed molar ratio of A) MeOx : PhOx = 70:30 B) MeOx : PhOx = 30:70.



**Figure S2** Copolymerization kinetic plots for the living CROP of MeOx and PhOx in ACN at 100 °C and target DP = 50 with feed molar ratio of MeOx : PhOx = 50:50.



**Figure S3** SEC traces of the PMeOx-grad-PPhOx copolymers synthesized in sulfolane at 100 °C with feed ratio of MeOx : PhOx = 50:50, target DP 50, at different polymerization time.



Figure S4 Determination of the reactivity ratios of MeOx (M1) with PhOx (M2) for the copolymerization in sulfolane from EKT Plot of  $\eta$  versus  $\xi$ .



Figure S5 Determination of the reactivity ratios of MeOx (M1) with PhOx (M2) for the copolymerization in ACN from A) Mayo-Lewis method, plot of MeOx fraction in the monomer feed (f1) vs the incorporated fraction in the copolymer (F1) determined via GC-measurements at ~40% MeOx conversion and B) EKT Plot of  $\eta$  versus  $\xi$ .



**Figure S6** Monomer conversion (%) against time plots for the copolymerization of MeOx and PhOx in sulfolane at 140 °C with feed composition of MeOx : PhOx = 50:50, DP 50.



Figure S7<sup>1</sup>H NMR spectrum of CP1 at 400 MHz, 25 °C in CD<sub>3</sub>OD (\* solvent Peak).



Figure S8<sup>1</sup>H NMR spectrum of CP3 at 400 MHz, 25 °C in CD<sub>3</sub>OD (\* solvent Peak).

#### **1.2.** Critical micelle concentration (CMC) of the copolymers in water

The critical micelle concentrations (CMC) of the copolymers were determined by fluorescence spectroscopy using pyrene as a probe (5 x  $10^{-7}$  M) in the water at 25 °C. The photophysical properties of pyrene change depending on the surrounding environment. In micelles, pyrene preferentially partitions into the hydrophobic core and changes the intensity of emission spectra observed.<sup>3</sup> The CMC is determined from the onset change in the plot of intensity ratio (I<sub>384</sub>/I<sub>373</sub>) vs. the logarithm of copolymer concentration.







**Figure S9** Intensity ratio of pyrene emission spectra ( $I_{373}/I_{384}$ ) versus concentration of (A) CP1 and (B) CP2 (C) CP3 in water at 25 °C.



**Figure S10** Intensity Weigthed Distribution of the micelle's radius (DLS) from the copolymers in 20 wt% EtOH-water mixture at 25 °C (c = 10 mg/mL).

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