SUPPORTING INFORMATION

Copolymer chain formation of 2-oxazolines by in-situ ^{1}H-NMR spectroscopy: dependence of sequential composition on substituent structure and monomer ratios

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Contents

1 Literature overview

Table S1. Literature overview of previously studied systems listing used comonomers, solvents, initiators, polymerization temperatures and techniques

Selected studies of polymerization and copolymerization of 2-oxazolines

Used (co)monomers	Solvent	Temperature [°C]	Initiator	Literature reference
2-phenyl-2-oxazoline with 2-methyl, 2-isopropenyl, and 2-benzyl-2-oxazolines	-	120	oxazolinium perchlorate	T. KAGIYA, T. MATSUDA, *J. Macromolec. Sci. Chem.* A6, 1631-1652 (**1972**). DOI 10.1080/00222337208061125
block / 2-methyl-2-oxazoline with 2-n-butyl, 2-n-octyl-, 2-n-dodecyl-, 2-phenyl-2-oxazoline	acetonitrile	80	methyl tosylate	KOBAYASHI, Shiro, IGARASHI, Toshio, *Macromolecules*. **1986**. Vol. 19, no. 3, p. 535–541. DOI 10.1021/ma00157a006.
2-methyl-2-oxazoline, 2-phenyl-2-oxazoline	acetonitrile or nitrobenzene	80	acetyl chloride or methacryloyl chloride	DWORAK, Andrzej. *Polymer Bulletin*. **1997**. Vol. 38, no. 1, p. 7–13. DOI 10.1007/s002890050012.
2-methyl-2-oxazoline, 2-phenyl-2-oxazoline	benzene, methylene chloride, nitromethane, nitrobenzene,	80	methyl iodide, benzyl bromide	DWORAK, Andrzej. *Macromol. Chem. Phys.* **1998**. Vol. 199, p. 1843–1849 DOI 10.1002/(SICI)1521-3935(19980901)199:9<1843::AID-MACP1843>3.0.CO;2-I

	acetonitrile			
2-(pent-4-ynyl)-2-oxazoline with 2-methyl- or 2-ethyl-2-oxazoline	acetonitrile	85	methyl triflate	LUXENHOFER, Robert and JORDAN, Rainer. *Macromolecules,* **2006**. Vol. 39, no. 10, p. 3509–3516. DOI 10.1021/ma052515m.
random copolymers from 2-methyl-2-oxazoline, 2-ethyl-2-oxazoline, and 2-nonyl-2-oxazoline	N,N-dimethyl-acetamide	100	benzyl bromide	HOOGENBOOM, Richard, FIJTEN, Martin W. M., WIJNANS, Sanne, et al. **2006**. Vol. 8, no. 2, p. 145–148. DOI 10.1021/cc050087q
2-methyl-, 2-ethyl, 2-nonyl-, and 2-phenyl-2-oxazoline	acetonitrile	140, microwave	methyl tosylate	Wiesbrock, F., et al. (**2005**). *Macromolecules*, *38*(19), 7957–7966. DOI 10.1021/ma050437x
2-methyl-2- oxazoline, 2-ethyl-2-oxazoline, 2-phenyl- 2-oxazoline, 2-nonyl-2-oxazoline	acetonitrile	120 or 140	methyl tosylate	HOOGENBOOM, Richard, et al., *Polymer*. 2006. Vol. 47, no. 1, p. 75–84. DOI 10.1016/j.polymer.**2005**.11.025.
statistical copolymers of 2-nonyl-2-oxazoline with 2-methyl-2- oxazoline or 2-ethyl-2-oxazoline	--	80-190, microwave, high pressure	--	HOOGENBOOM, Richard. *Macromolecular Chemistry and Physics*. **2007**. Vol. 208, no. 1, p. 18–25. DOI 10.1002/macp.200600558
2-nonyl-2-oxazoline	Acetonitrile/dichlormethane	140, microwave	methyl tosylate	HOOGENBOOM, Richard, WIESBROCK, Frank, *Australian Journal of Chemistry* **2007**. Vol. 60, no. 9, p. 656. DOI 10.1071/CH07150.
2-phenyl-2-oxazoline	Under pressure in acetonitrile and under reflux or at the boiling point of butyronitrile	microwave, reflux 120, 125	methyl tosylate	HOOGENBOOM, Richard, et al., *Macromolecular Rapid Communications*. **2005.** Vol. 26, no. 22, p. 1773–1778. DOI 10.1002/marc.200500370.
2-methyl-, 2-ethyl-, 2-nonyl- and 2-phenyl-2-oxazoline, a 16-membered set of 12 diblock copoly(2-oxazoline)s and 4 chain-extended homopoly(2-oxazoline)s	acetonitrile	140, microwave	methyl tosylate	HOEPPENER, Stephanie, et al. *Macromolecular Rapid Communications*. **2006**. Vol. 27, no. 6, p. 405–411. DOI 10.1002/marc.200500863.
2-ethyl-2-oxazoline and 2-phenyl-2-oxazoline	acetonitrile	160, microwave	benzylinitiating group and different leaving groups, Cl^-, Br^-, I^-, and tosylates	Fijten, M. W. M., Hoogenboom, R., & Schubert, U. S. (**2008**). *Journal of Polymer Science Part A: Polymer Chemistry*, *46*(14), 4804–4816. DOI 10.1002/pola.22814
poly[(2-isopropyl-2-oxazoline)50-block-(2-methyl-2-oxazoline)50	acetonitrile	85	methyl tosylate	LEGROS, Camille, et al., *Soft Matter* **2015**. Vol. 11, no. 17, p. 3354–3359. DOI 10.1039/c5sm00313j
well-defined gradient or random copolymers 2-n-propyl-2-oxazoline and either 2-isopropyl-2-oxazoline or 2-ethyl-2-oxazoline	acetonitrile	42	methyl tosylate	PARK, Joon-Sik Sik and KATAOKA, Kazunori. *Macromolecules* **2007**. Vol. 40, no. 10, p. 3599–3609. DOI 10.1021/ma0701181
poly[(2-isopropyl-2-oxazoline)-co-(2-ethyl-2-oxazoline)	acetonitrile	42	methyl tosylate	PARK, Joon Sik and KATAOKA, Kazunori. *Macromolecules*. **2006**. Vol. 39, no. 19, p. 6622–6630. DOI 10.1021/ma0605548.
2-ethyl-2-oxazoline and 2-nonyl-2-oxazoline	butyronitrile acetonitrile	reflux microwave	methyl tosylate	FIJTEN, Martin et al. *Macromolecules* **2007**. Vol. 40, no. 16, p. 5879–5886. DOI 10.1021/ma070720r.

Selected studies using copolymerization with 2-dec-9’enyl-2-oxazoline

Used (co)monomers	Solvent	Temperature [°C]	Initiator	Literature reference
2-(dec-9-enyl)-2-oxazoline with 2-hepthyl-2-oxazoline	o-dichlorobenzene	110	methyl 4-nitrobenzene sulfonate	Cai, G., & Litt, M. H. (**1996**). *Journal of Polymer Science Part A: Polymer Chemistry*, *34*(13), 2679–2688. DOI 10.1002/(SICI)1099-0518(19960930)34:13<2711::AID-POLA15>3.0.CO;2-F
2-nonyl-2-oxazoline and 2-(9-decenyl)-2-oxazoline	acetonitrile	100	benzyl bromide	DEL RIO, Enrique, LLIGADAS, Gerard, et al., *Journal of Polymer Science Part A: Polymer Chemistry* **2011**. Vol. 49, no. 14, p. 3069–3079. DOI 10.1002/pola.24744.
2-(dec-9-enyl)-2-oxazoline with either 2-methyl-2-oxazoline or 2-ethyl-2-oxazoline	nitromethane	140 microwave	methyl tosylate	KEMPE, Kristian, VOLLRATH, Antje, SCHAEFER, *Macromolecular Rapid Communications*. **2010**. Vol. 31, no. 21, p. 1869–1873. DOI 10.1002/marc.201000283
2-(dec-9-enyl)-2-oxazoline with 2-ethyl-2-oxazoline	---	100 microwave	methyl tosylate	KEMPE, Kristian, HOOGENBOOM, Richard and SCHUBERT, Ulrich S. A *Macromolecular Rapid Communications* 15, **2011** Vol. 32, no. 18, p. 1484–1489. DOI 10.1002/marc.201100271
EtOx and 2-(dec-9-enyl)-2-oxazoline	acetonitrile	120 microwave	methyl tosylate	KEMPE, Kristian et al. *Biomacromolecules* **2011**. Vol. 12, no. 7, p. 2591–2600. DOI 10.1021/bm2003847
poly(2-(dec-9-enyl)-2oxazoline) and poly(2- phenyl-2-oxazoline)	---	100 microwave	methyl tosylate	CHOJNACKA, Aleksandra, et al., *Journal of Chromatography A* **2012**. Vol. 1265, p. 123–132. DOI 10.1016/j.chroma.2012.09.080
2-(dec-9-enyl)-2-oxazoline with either 2-methyl-2-oxazoline or 2-ethyl-2-oxazoline	acetonitrile	140 microwave	methyl tosylate	DARGAVILLE, Tim R., FORSTER, Rebecca, et al., *Macromolecular Rapid Communications* **2012**. Vol. 33, no. 19, p. 1695–1700. DOI 10.1002/marc.201200249
poly(2-nonyl-2-oxazoline)80-stat-poly(2-dec-9-enyl-2-oxazoline)20	dry dichloromethane	140	methyl tosylate	Fimberger, M.; Tsekmes, I.-A.; Kochetov, R.; Smit, J.; Wiesbrock, F. , *Polymers (Basel)*. **2015**, *8* (1), 6. DOI 10.3390/polym8010006
2-(butenenyl)-2-oxazoline and 2-(dec-9-enyl)-2-oxazoline with 2-methyl-2-oxazoline	acetonitrile	140 microwave	methyl tosylate	DARGAVILLE, Tim R., LAVA, Kathleen, VERBRAEKEN, Bart and HOOGENBOOM, Richard. *Macromolecules*. **2016**. Vol. 49, no. 13, p. 4774–4783. DOI 10.1021/acs.macromol.6b00167

2 Pulse program used for kinetic measurements

```
;zg
;avance-version (06/11/09)
;1D sequence
;
;$CLASS=HighRes
;$DIM=1D
;$TYPE=
;$SUBTYPE=
;$COMMENT=

#include <Avance.incl>

"acqt0=-p1*2/3.1416"
"d2=d3-(aq+d1)*ns"

1 ze
2 30m
  d1
  p1 ph1
  go=2 ph31
  30m mc #0 to 2 F0(zd)
  d2
exit

ph1=0 2 2 0 1 3 3 1
ph31=0 2 2 0 1 3 3 1

;pl1 : f1 channel - power level for pulse (default)
;p1 : f1 channel -  high power pulse
;d1 : relaxation delay; 1-5 * T1
;NS: 1 * n, total number of scans: NS * TD0
;d2: delay between experiments
;d3: total experimental time

;$Id: zg,v 1.9 2006/11/10 10:56:44 ber Exp $
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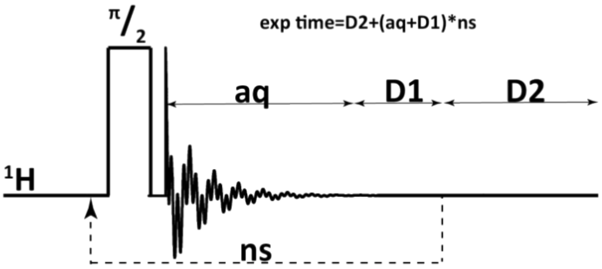


3 Peak assignments for monomers

EthylOx: (600MHz, DMF-ext), δ ppm: 4.11 (t, 9.5 Hz, 2H, OCH_2), 3.69 (t, 9.3 Hz, 2H, NCH_2), 2.18 (q, 7.4 Hz, 2H, CCH_2), 1.12 (t, 7.8 Hz, 3H, CH_3).

IsopropylOx: (600MHz, DMF-ext), δ ppm: 4.07 (t, 9.3 Hz, 2H, OCH_2), 3.65 (t, 9.6 Hz, 2H, NCH_2), 2.45 (septet, 7.0 Hz, 1H, CCH), 1.10 (d, 6.9 Hz, 6H, CH_3).

ButylOx: (600MHz, DMF-ext), δ ppm: 4.05 (t, 9.5 Hz, 2H, OCH_2), 3.64 (t, 9.5 Hz, 2H, NCH_2), 2.14 (t, 7.3 Hz, 2H, $C\mathit{CH}_2$), 1.53 (quintet, 7.4 Hz, 2H, $CCH_2C\mathit{H}_2$), 1.33 (sextet, 7.4 Hz, 2H, $CH_2C\mathit{H}_2CH_3$), 0.85 (t, 7.3 Hz, 3H, $C\mathit{H}_3$).

HeptylOx: (600MHz, DMF-ext), δ ppm: 4.04 (t, 9.3 Hz, 2H, OCH_2), 3.63 (t, 9.3 Hz, 2H, NCH_2), 2.12 (t, 7.4 Hz, 2H, CCH_2), 1.54 (quintet, 7.4 Hz, 2H, $CCH_2C\mathit{H}_2$), 1.26 (m, 7.1 Hz, 8H, CH_2CH_2), 0.83 (t, 6.0 Hz, 3H, CH_3).

NonylOx: (600MHz, DMF-ext), δ ppm: 4.00 (t, 9.2 Hz, 2H, OCH_2), 3.60 (t, 9.2 Hz, 2H, NCH_2), 2.09 (t, 7.4 Hz, 2H, CCH_2), 1.51 (quintet, 7.4 Hz, 2H, $CCH_2C\mathit{H}_2$), 1.21 (bp, 7.4 Hz, 12H, CH_2CH_2), 0.80 (t, 6.6 Hz, 3H, CH_3).

DecenylOx: (600MHz, DMF-ext), δ ppm: 5.63 (m, 6.0 Hz, 1H, $CH{=}CH_2$), 4.79 (d, 16.04 Hz, 1H, $CH{=}CH_2$), 4.73 (d, 9.62 Hz, 1H, $CH{=}CH_2$), 3.92 (t, 9.4 Hz, 2H, OCH_2), 2.00 (t, 7.0 Hz, 2H, CCH_2), 1.88 (q, 5.2 Hz, 2H, $CH_2CH{=}CH_2$), 1.46 (quintet, 7.4 Hz, 2H, $CCH_2C\mathit{H}_2$) overlapped by solvent, 1.16 (bp, 10H, CH_2CH_2).

PhenylOx: (600MHz, DMF-ext), δ ppm: 7.54 (d, 7.5 Hz, 2H, Ar), 6.99 (t, 7.2 Hz, 1H, Ar), 6.94 (t, 7.2 Hz, 2H, Ar), 3.85 (t, 9.5 Hz, 2H, OCH_2), 3.50 (t, 9.5 Hz, 2H, NCH_2).

The spectra were obtained at 100 °C, with butyronitrile used as solvent.

4 Table S2 Denotations and definitions of variables

Denotation	Definition/Units	Obtained from / Equation
$\bar{M}_n$	Number average molecular weight / [g/mol]	From GPC and from NMR spectra using: $\bar{M}_n = \bar{X}_{n(f)}[(f_{1(0)} M_{w1}) + (f_{2(0)} M_{w2})]$
$\bar{M}_w$	Weight average molecular weight /[g/mol]	From GPC
$\bar{M}_{id}$	Average ideal molecular weight from starting composition / [g/mol]	From NMR, using determined ratios in initial mixture $\bar{M}_{id} = \bar{X}_{n(i)}[(f_{1(0)} M_{w1}) + (f_{2(0)} M_{w2})]$
$\bar{X}_{n(i)}$	Average degree of polymerization from starting composition	From NMR spectra - the ratio of initiator peak (unchanged in time) to monomer peak at t_0
$\bar{X}_{n(f)}$	Real average degree of polymerization	From NMR spectra - the ratio of initiator peak (unchanged in time) to polymer peak at $\alpha = 1$
$(c)_0$	Relative molar monomer concentration at time 0	From NMR spectra, relative integral of peak representing both monomer species at time *0*
c	Relative molar monomer concentration	From NMR spectra, relative integral of peak representing both monomer species at time *t*
P	Relative peak area corresponding to polymerized units	From NMR spectra, obtained from integral values of polymer peak at $\alpha = 1$
$P_{\alpha = 1}$	Relative peak area corresponding to polymerized units at $\alpha = 1$	From NMR spectra, obtained from integral value of polymer peak at $\alpha = 1$
p	Molar fraction of both polymerized monomer units	$p = \frac{P}{P_{\alpha = 1}}$
f_1, f_2	Molar fractions of each monomer with respect to monomer mixture	From deconvolution of the monomer peaks at time *t* $f_1 = \frac{c_1}{c}; f_2 = \frac{c_2}{c}, f_1 + f_2 = 1$
x	Monomer molar fraction in the reacting monomer mixture at time *t* with respect to the initial amount of both monomers	$x = \frac{c}{(c)_0}$
x_1, x_2	Molar fractions of each monomer in the whole mixture, incl. polymer	$x_1 = x f_1,\ x_2 = x f_2$ $x_1 + x_2 + p = 1$
α	Molar conversion of both monomer units (total conversion)	$\alpha = 1 - \frac{c}{(c)_0}$
α_1, α_2	Relative molar conversions of monomer 1 and 2	$\alpha_1 = \frac{c_1}{(c_1)_0},\ \alpha_2 = \frac{c_2}{(c_2)_0}$
F_1, F_2	Composition of polymer	$F_1 = \frac{(c_1)_0 - c_1}{((c_1)_0 - c_1) + ((c_2)_0 - c_2)}$ $F_1 + F_2 = 1$
$\Delta F_1, \Delta F_2$	Composition of instantaneously formed polymer	$\Delta F_1 = \frac{(c_1)_{t+\Delta t} - (c_1)_t}{((c_1)_{t+\Delta t} - (c_1)_t) + ((c_2)_{t+\Delta t} - (c_2)_t)}$ $\Delta F_1 + \Delta F_2 = 1$

5 SEC results from samples polymerized *in-situ* and in microwave

Table S3 Influence of manner of polymerization on product molecular weight and *Đ*

Polymerization conditions: Temperature 100 °C, Solvent Butyronitrile, Initiator Methyl tosylate

Intended Ratio	$\bar{M}_w/\bar{M}_n(10^3)$ / **Đ**	
NonOx : DecOx	NMR polymerization	Microwave polymerization
100:0	17.8/15.4/1.16	20.3/17.2/1.18
90:10	19.9/18.3 /1.09	27.6/22.0/1.11
80:20	18.8/17.4 /1.08	23.7/21.1/1.13
60:40	18.8/17.4 /1.08	23.8/21.6/1.10
0:100	14.9/13.0 /1.14	14.5/13.5/1.07

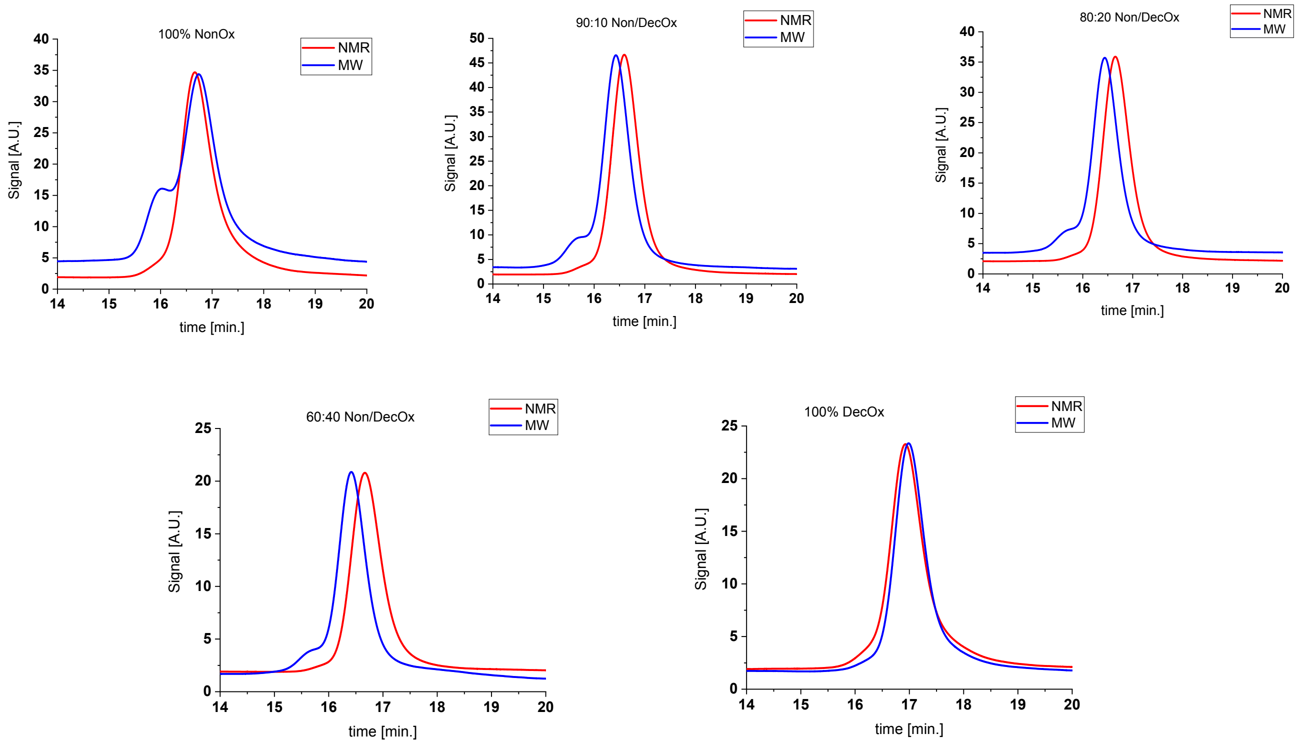


Figure S1 Comparison of chromatograms obtained from samples polymerized in NMR tubes and in microwave

6 Reproducibility of analysis from ^{1}H NMR data

Monomer molar fractions in feed evaluated from 1H NMR experiment as a function of total conversion

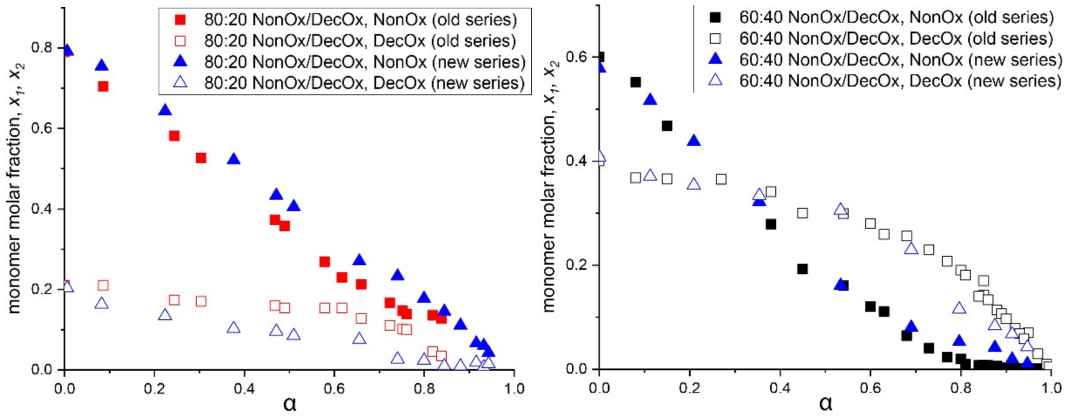


Figure S2 Two copolymerization runs (out of five) of NonOx/DecOx mixtures for ratios 80:20 and 60:40 with the largest differences (in NMR tube, temperature 100 °C, solvent Butyronitrile, initiator Methyl tosylate, reaction time 200-220 min)

Table S4 Example of experimental variation of molecular weight averages derived from NMR-based experiment with NonOx:DecOx mixture at ratio 80:20

Run	Mn	Mw	PDI
1	13000	14600	1.124
2	16300	17900	1.099
3	17400	18800	1.081
4	16100	18300	1.138
5	17200	18600	1.084

7 Course of CROP homopolymerization. Monomer conversion in time

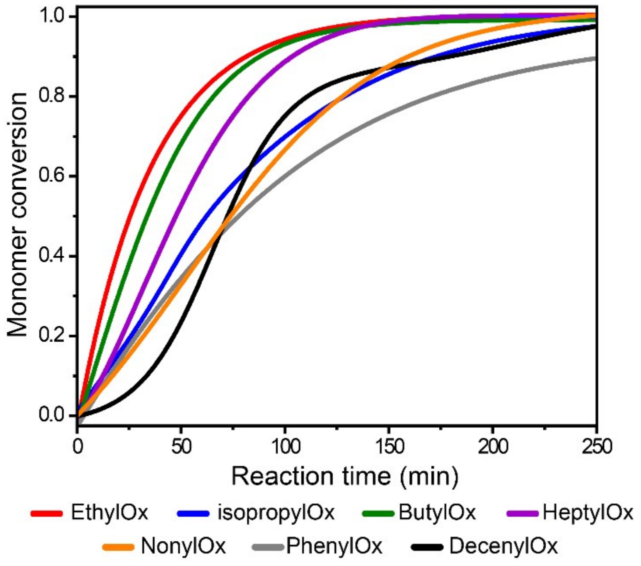


Figure S3 Monomer conversion in time in homopolymerization as obtained from integration of the increasing ^{1}H NMR spectral peak corresponding to the open-ring species (at temperature 100 °C, solvent Butyronitrile, initiator Methyl tosylate)

8 Course of CROP copolymerization. Graphs displaying data points relevant to individual peaks evaluated from ^{1}H NMR experiments

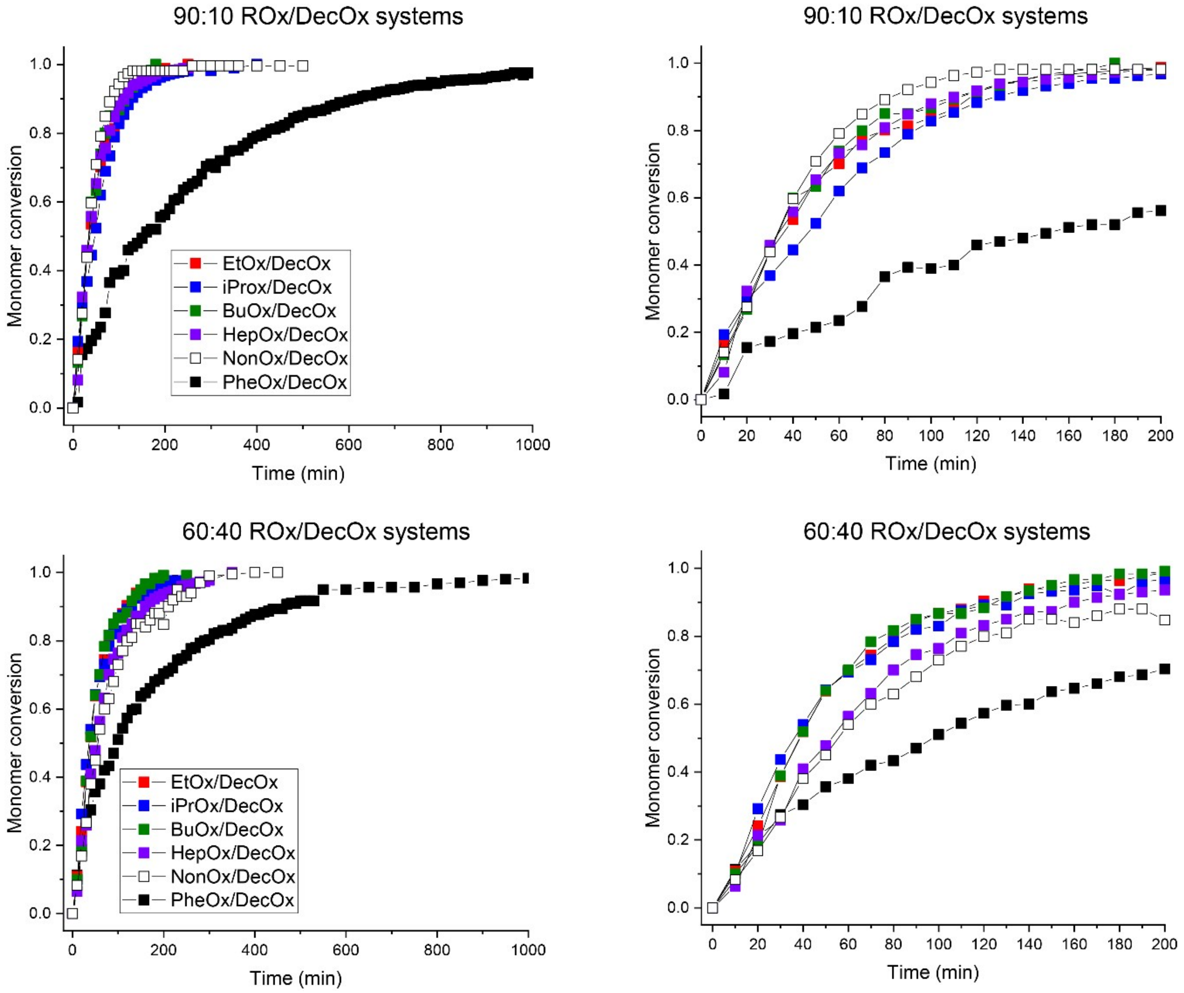


Figure S4 Monomer conversion as a function of time for 90:10 and 60:40 monomer ratios in feed, showing full conversion of the systems, with details on the right, each data point corresponds to one individual NMR measurement (at temperature 100 °C, solvent Butyronitrile, initiator Methyl tosylate)

9 Fineman-Ross copolymerization model

Copolymerization parameters $\boldsymbol{r_1}$ and $\boldsymbol{r_2}$ are according to this model calculated according to [1], calculated by

$$G = (r_1 \times F) - r_2$$

where

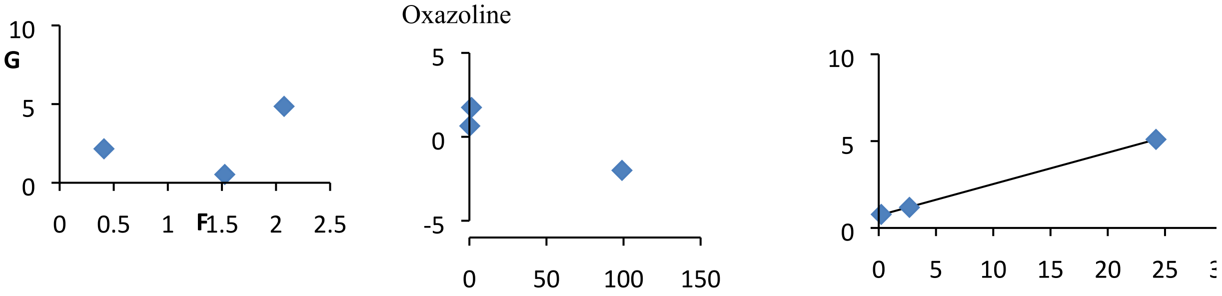
$G = X(Y-1)/Y$ and $F = X^2/Y$

It also applies that $X = \{M_1\}/\{M_2\}$ and $Y = dM_1/dM_2$

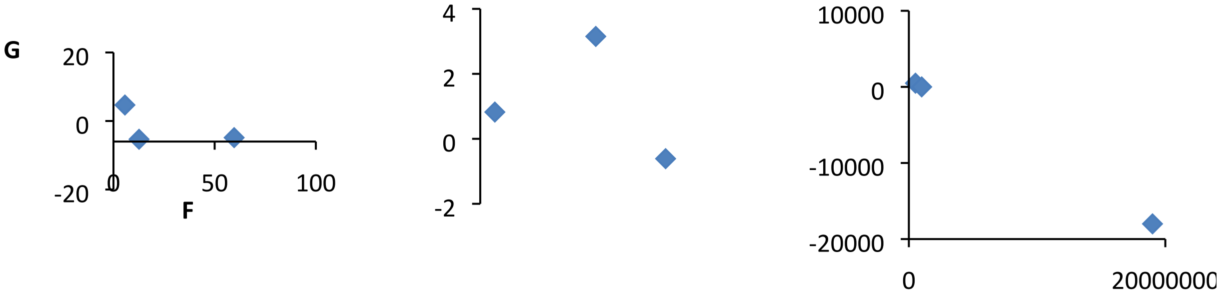
According to our definitions in the main text it applies that $M_1 = f_1$ and $M_2 = f_2$, while $dM_1 = F_1$ and $dM_2 = F_2$. From obtained plots of parameters F and f versus conversion α for both monomers values at 20 % conversion were used for calculations of G and F values for each of the comonomer mixture for each copolymer systems.

Resulting graphs are given below. Same procedure was conducted with 10% conversion, with same results. The graphs clearly show that the model cannot be applied for these systems.

a)Ethyl/Decenyl-2-Oxazoline b) Isopropyl/Decenyl-2-Oxazoline c) Butyl/Decenyl-2-Oxazoline



d) Heptyl/Decenyl-2-Oxazoline e) Nonyl/Decenyl-2-Oxazoline f)Phenyl/Decenyl-2-Oxazoline



Graphs showing data obtained from of Fineman-Ross copolymerization model applied for the six systems for values F and G defined above at 20 % monomer conversion.

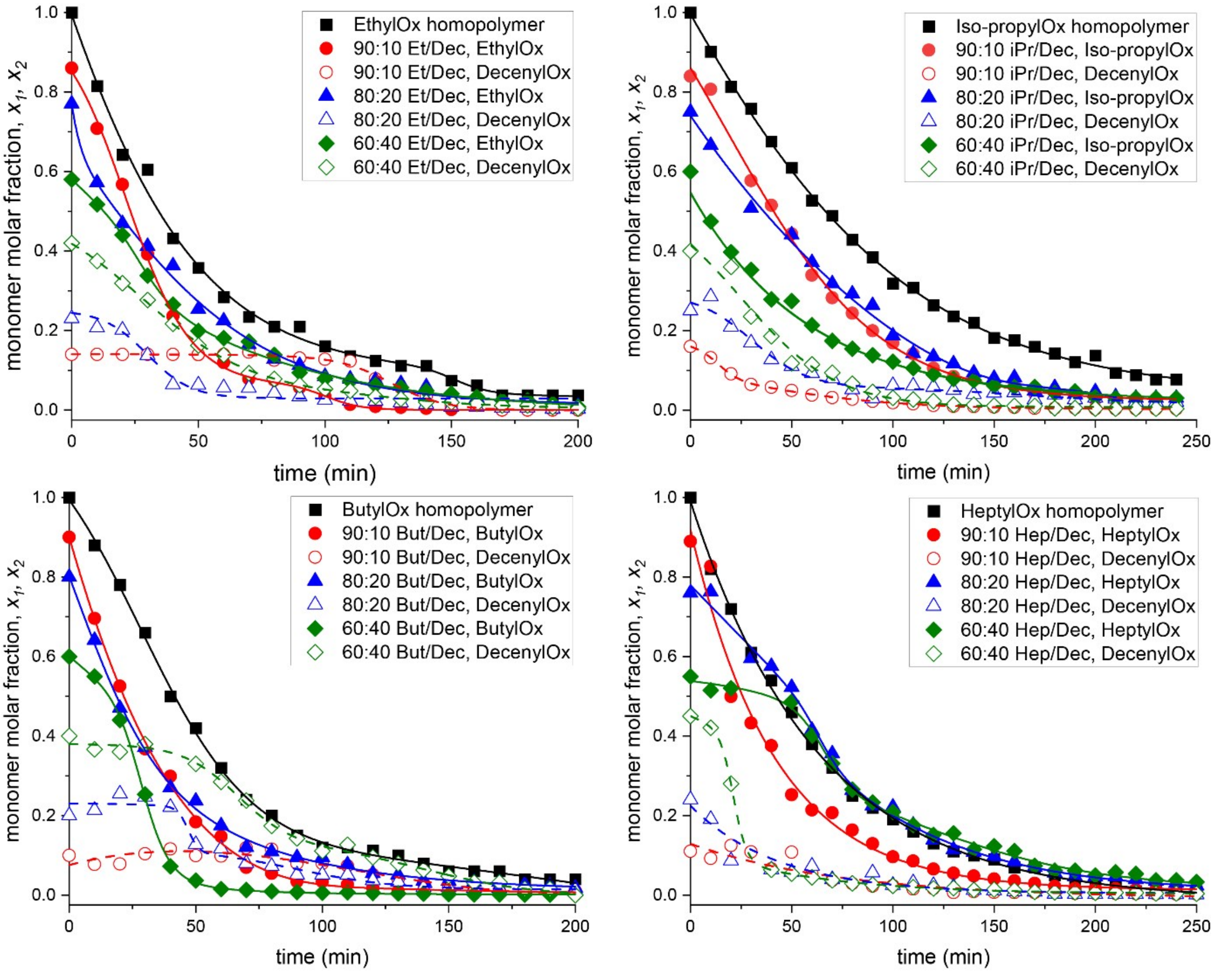
[1] G. Odian, Principles of Polymerization, 4th edition, Wiley-Interscience, 2004.

10 Half-times of copolymer reactions for individual monomers

Table S5. Half-times of reactions $t_{1/2}$ (min) for homopolymers (first column) and copolymers showing monomer pairs separately

R-	$t_{1/2}$, [min] 100%	90:10		80:20		60:40	
		$t_{1/2}$ (R-)	$t_{1/2}$ (DecOx)	$t_{1/2}$ (R-)	$t_{1/2}$ (DecOx)	$t_{1/2}$ (R-)	$t_{1/2}$ (DecOx)
EthylOx	34	27	132	31	34	37	41
IsoPropylOx	65	50	26	58	45	36	38
ButylOx	35	26	103	29	56	27	67
HeptylOx	43	31	55	64	28	81	20
NonylOx	38	47	68	43	83	40	89
PhenylOx	79	214	23	223	21	274	22
DecenylOx	78	-	-	-	-	-	-

11 Course of CROP copolymerization. Monomer relative molar concentrations x_1 and x_2 plotted as a function of reaction time and total monomer conversion α



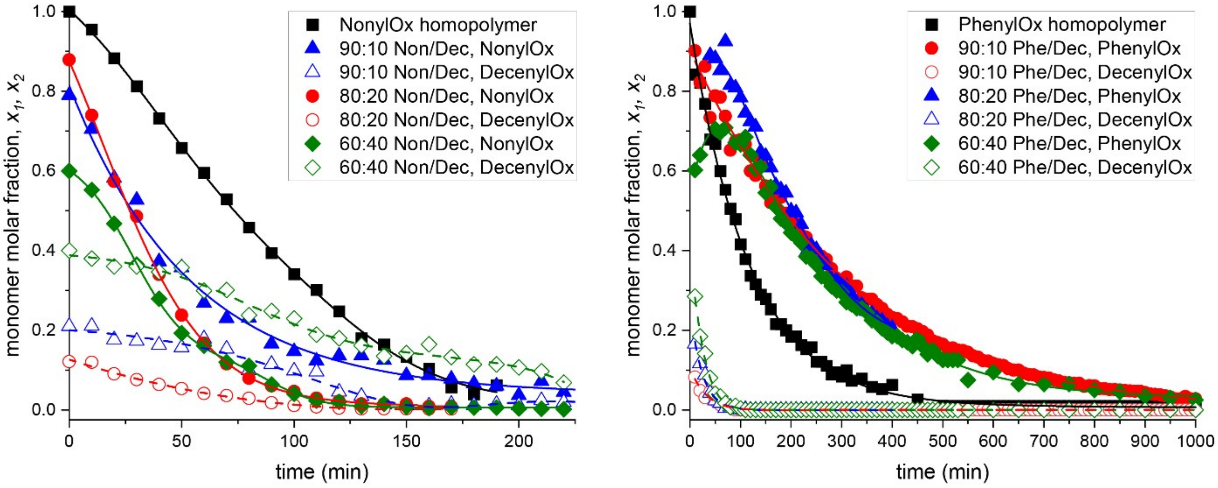
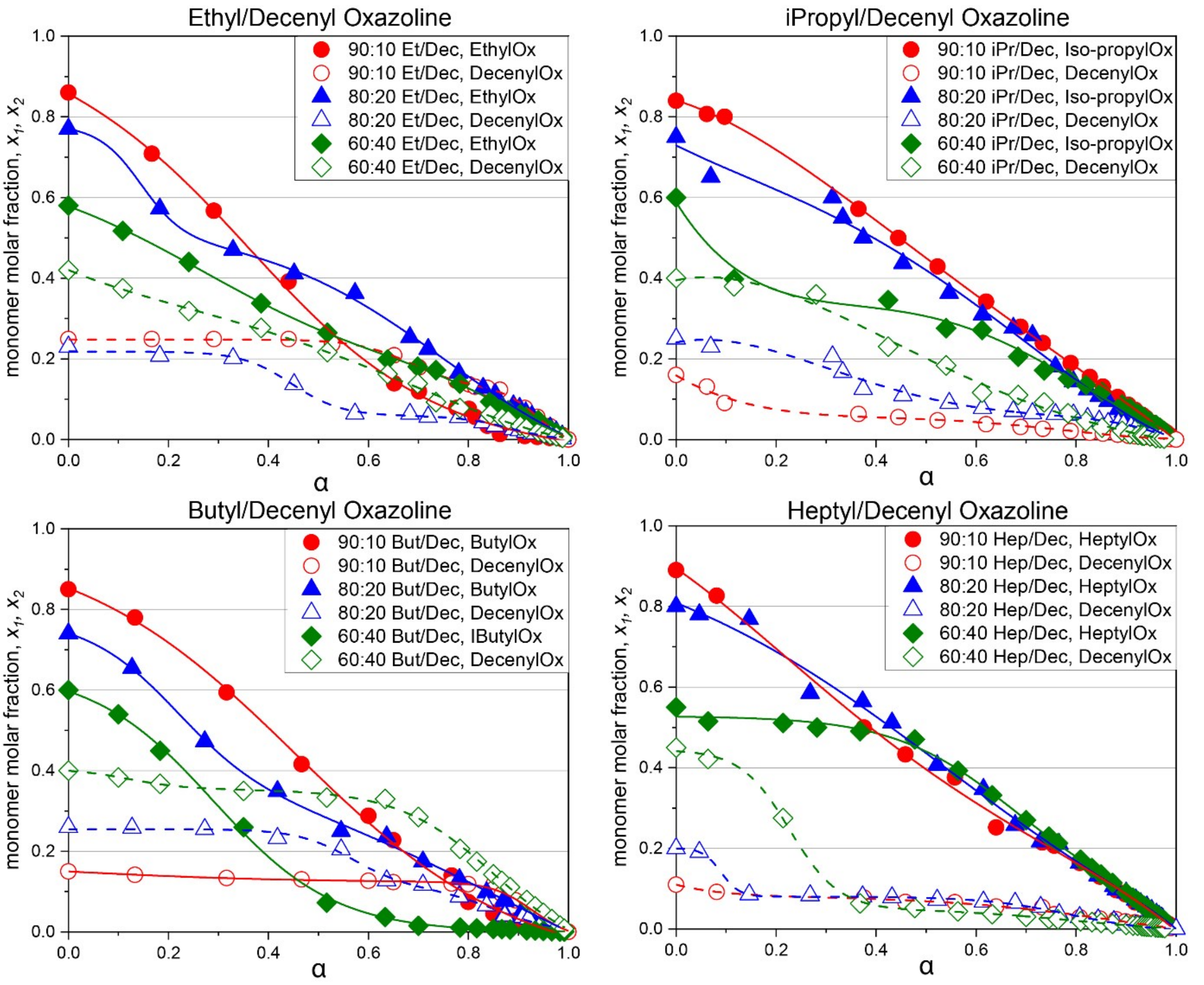


Figure S5 Decreasing monomer molar fractions in feed for individual 2-oxazoline monomer x_1 and DecOx, x_2, as a function of reaction time for each ROx/DecOx system.



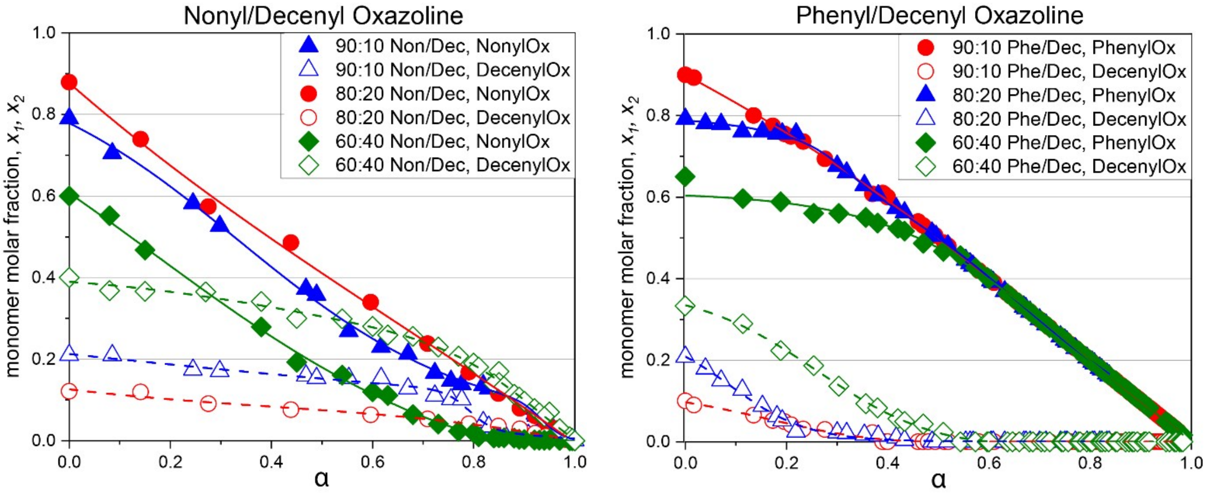


Figure S6 Molar fractions of ROx and DecOx monomers as a function of total monomer conversion α

12 Course of CROP copolymerization. Graphs of parameters f_1, F_1, ΔF_1 showing individual points

The graphs in Figures S7-10 characterize the copolymer structure as it develops in time by considering the changes in composition of monomer mixture (f_1), integral (F_1) and differential (ΔF_1) compositions of the copolymer and the conversions of the comonomers (α_1, α_2).

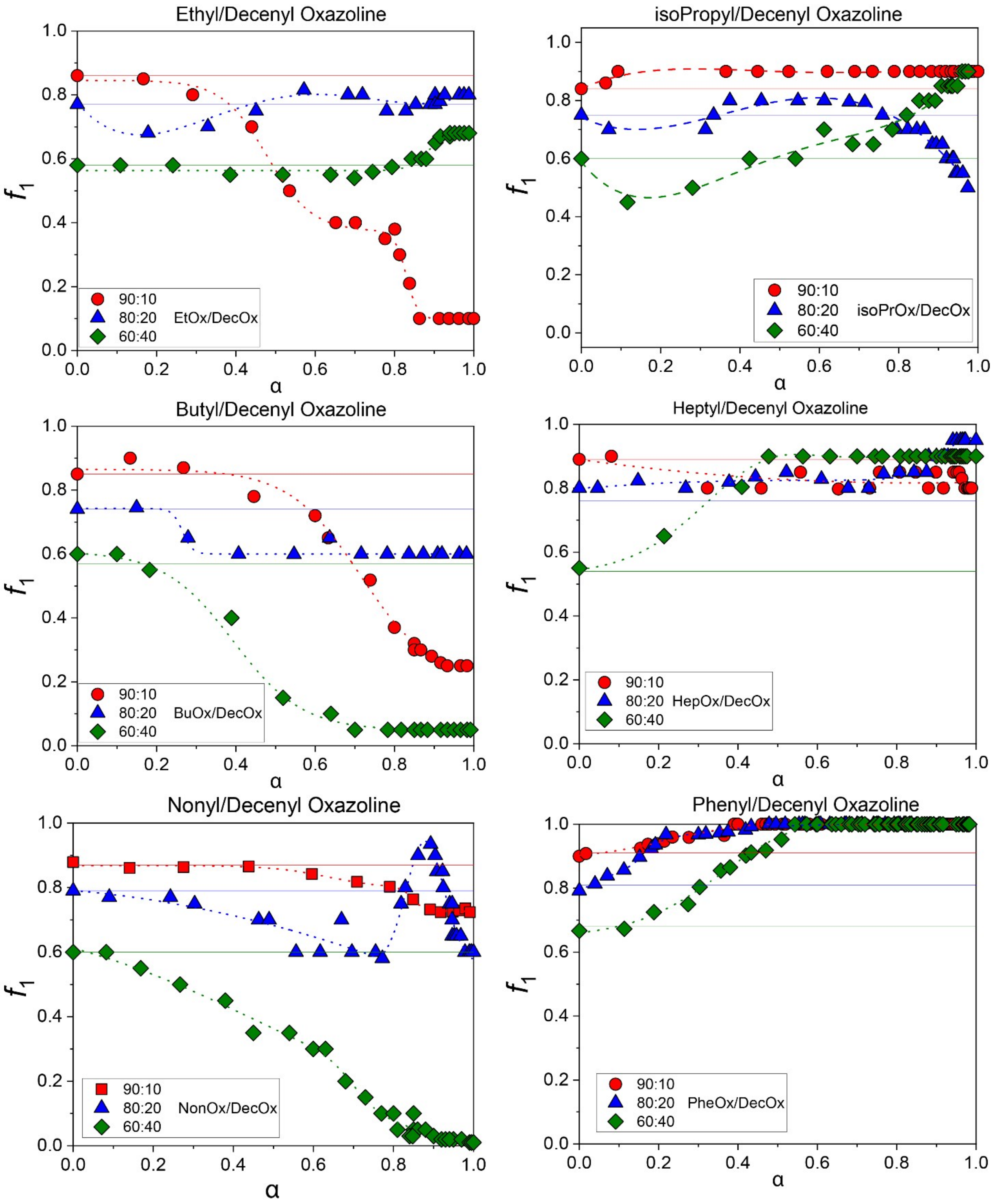


Figure S7 Detailed graphs depicting changes in composition of monomer mixture (f_1) as a function of monomer conversion α, each point represents one measured ^{1}H NMR spectrum.

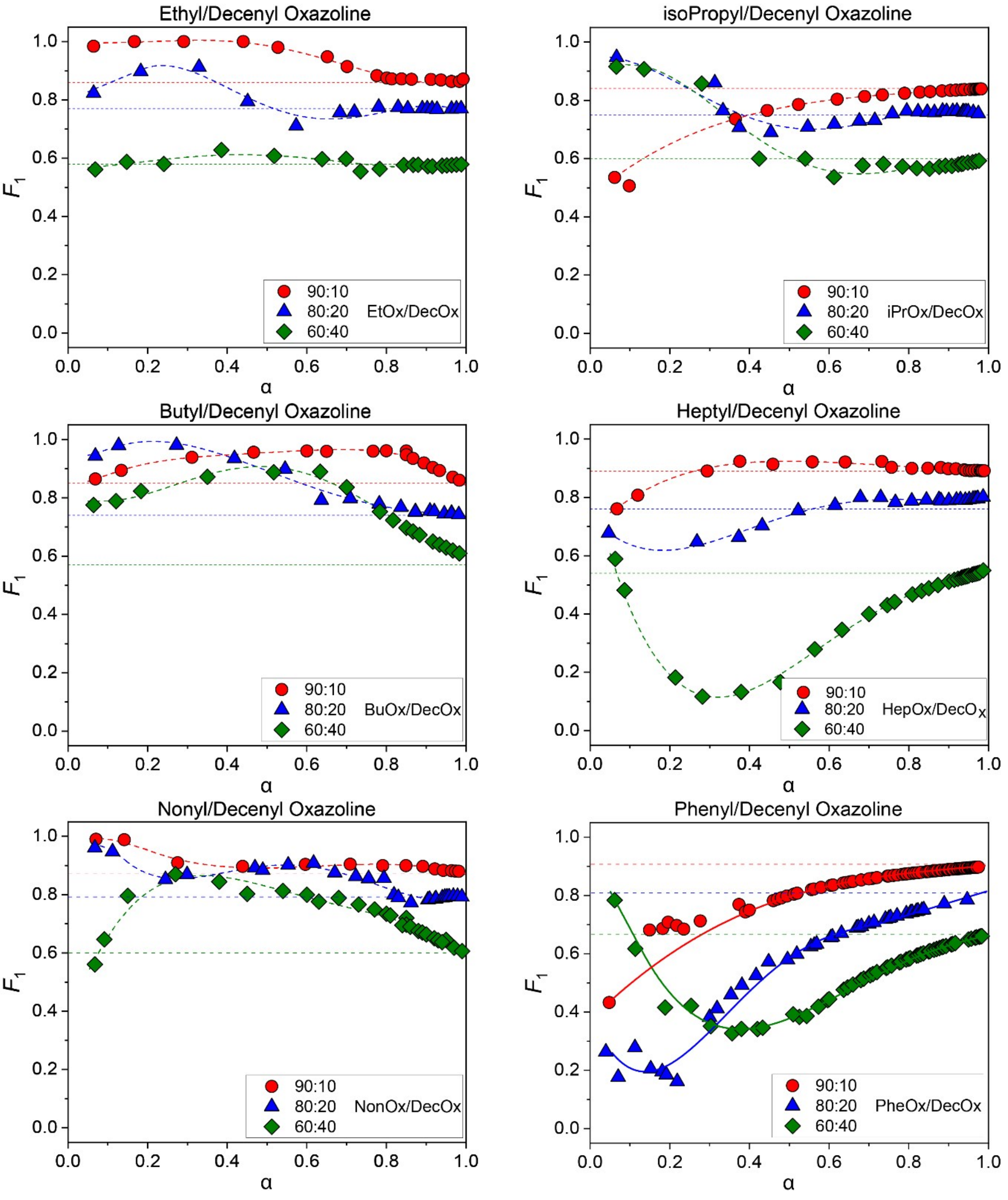


Figure S8 Detailed graphs depicting composition of polymer (F_1) as a function of monomer conversion α, each point represents one measured ^{1}H NMR spectrum.

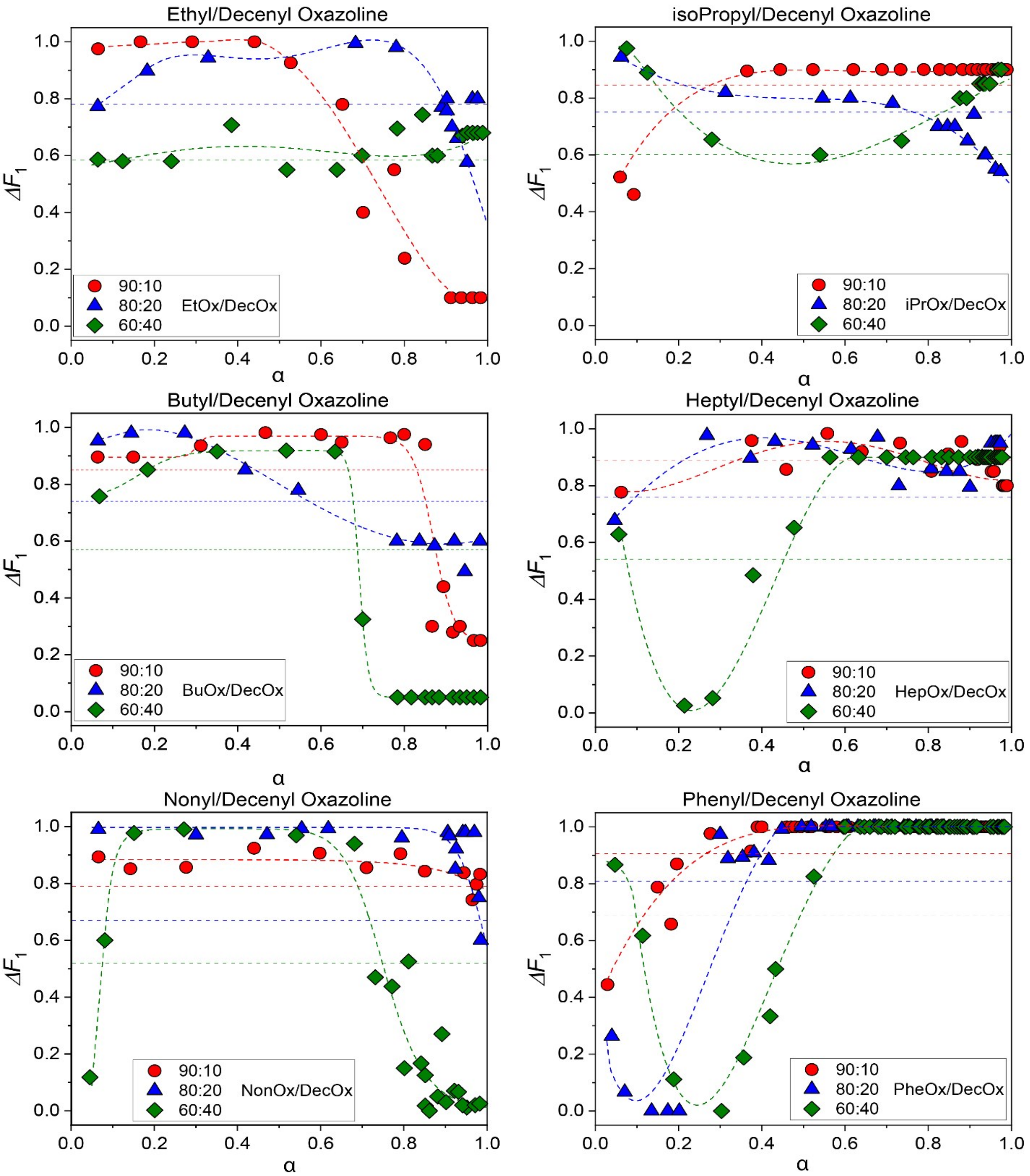


Figure S9 Detailed graphs depicting instantaneous changes in composition of polymer (ΔF_1) as a function of monomer conversion α, each point represents one measured ^{1}H NMR spectrum.

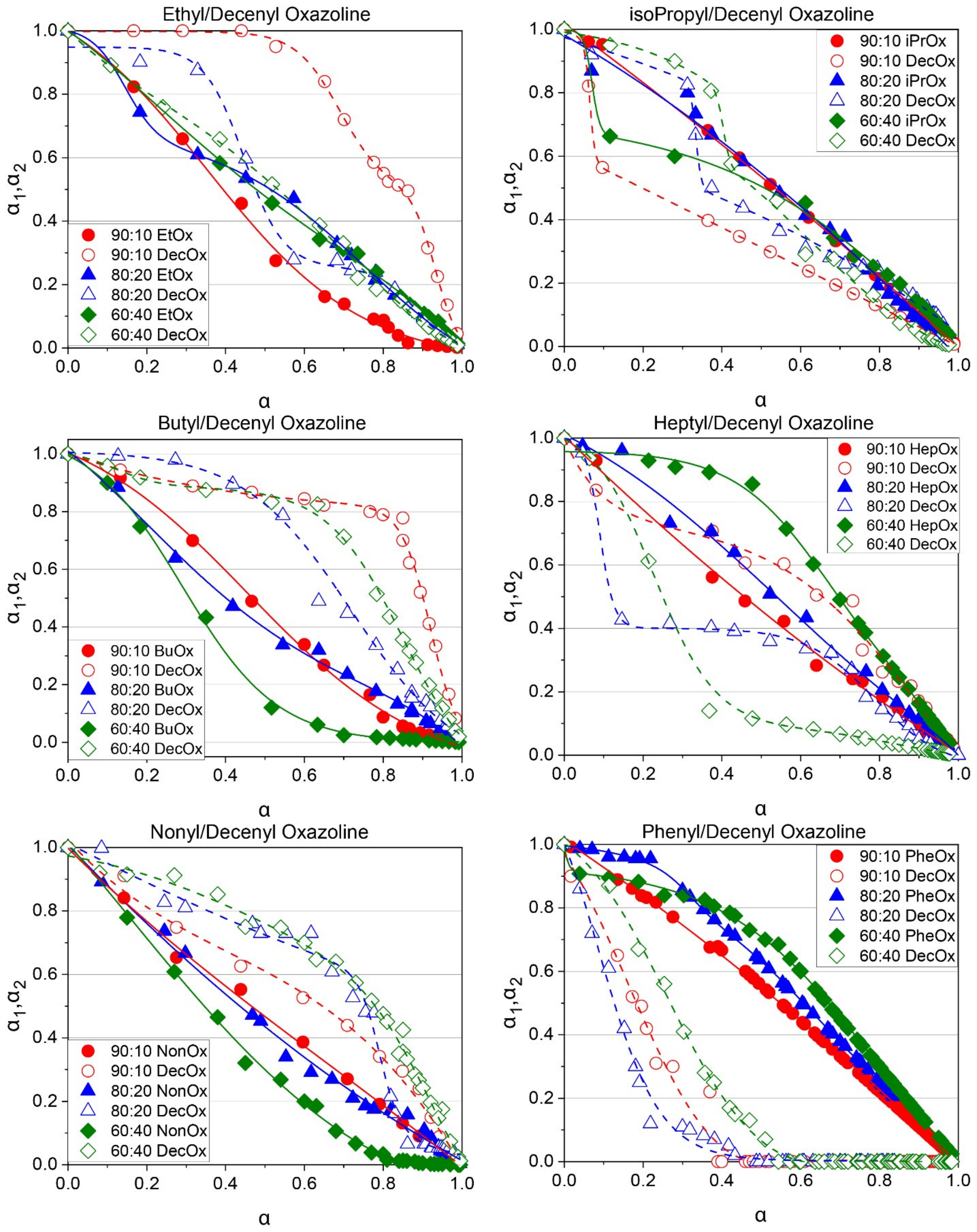


Figure S10 Detailed graphs depicting the relative molar conversions of monomer 1 and 2 (α_1, α_2) as a function of monomer conversion α, each point represents one measured ^{1}H NMR spectrum.