

Supporting information:

Ethyl acetate as solvent for the synthesis of poly(2-ethyl-2-oxazoline)

Maarten Vergaelen,^a Bart Verbraeken,^a Joachim F. R. Van Guyse,^a Annelore Podevyn,^a Ali Tigrine,^a Victor R. de la Rosa^a, Bryn D. Monnery^{a, b} and Richard Hoogenboom^{a, *}

^a. *Supramolecular Chemistry Group, Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281-S4, 9000 Ghent, Belgium; *Richard.Hoogenboom@ugent.be.*

^b. *Polymer Reaction Design Group, Department of Organic and Bio- Polymer Chemistry, Hasselt University, Agoralaan Gebouw D, 3590, Belgium*

This supporting information document includes the tables from the experimental part depicted in the article entitled, Ethyl acetate as green solvent for the synthesis of poly(2-ethyl-2-oxazoline).

SI Table 1: Reprint of table 5 from ref 1 including highlighted solvents ranked according to recommendation in medical products and the possibility to retract the solvent from renewable sources. Reprinted with permission from ref 1.

Table 5 A modified version of the conclusion to the survey of solvent selection guides [57]

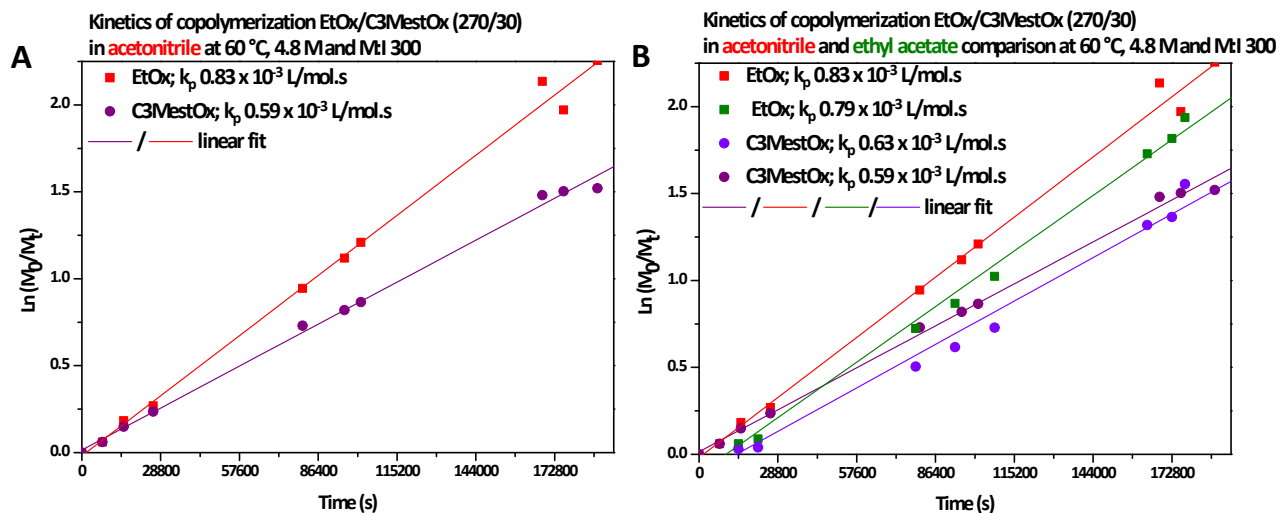
Category	Bio-based	Can be sourced renewably	Potential biomass feedstock	Not bio-based
Recommended	Ethanol (4) ^a Water	1-Butanol Ethyl acetate (2) ^a	1-Butyl acetate Isopropanol (1) ^a Isopropyl acetate	Anisole Sulpholane
Inbetween recommended and problematic		Acetic acid (9) ^a Acetone Ethylene glycol Methanol (3) ^a	Acetic anhydride t-Butanol Methyl acetate MIBK	Benzyl alcohol Cyclohexanone MEK
Problematic	DMSO {12 %} ^b 2-MeTHF			Acetonitrile (10) ^a PhCl {2 %} ^b DMPU Heptane (5) ^a Methylcyclohexane Toluene (7) ^a Xylene(s)
Inbetween problematic and hazardous		THF (6) ^a	Formic acid TBME	Cyclohexane DCM (8) ^a {48 %} ^b Pyridine
Hazardous		Triethylamine	1,4-Dioxane {0 %} ^b 1,2-DME {6 %} ^b DMAc {12 %} ^b DMF {31 %} ^b Methoxyethanol NMP {9 %} ^b	Diisopropyl ether {7 %} ^b n-Hexane {14 %} ^b Pentane
Highly hazardous			Diethyl ether {3 %} ^b	Benzene Chloroform {2 %} ^b Carbon tetrachloride 1,2-DCE {4 %} ^b Nitromethane

^a The ranking of the top ten solvents used by GSK in pilot plant operations in 2005 have been provided in parentheses, excluding water [7]

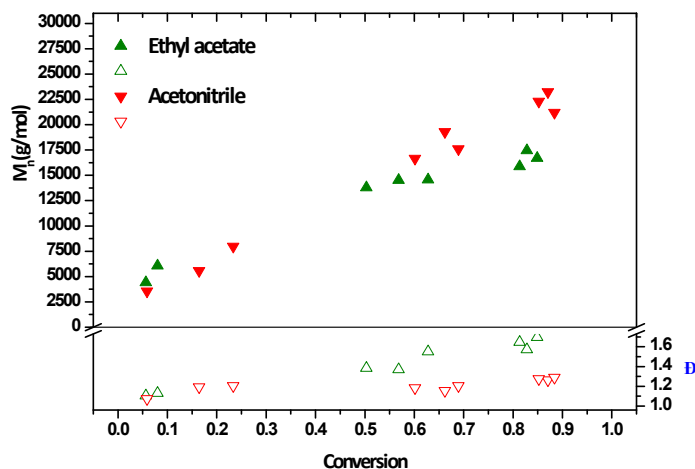
^b Usage of solvents of concern and dipolar aprotic solvents as reported in *Organic Process Research and Development* between 1997 and 2012, presented as the percentage of papers containing reactions performed in each solvent [8]. Data is not available for greener solvents

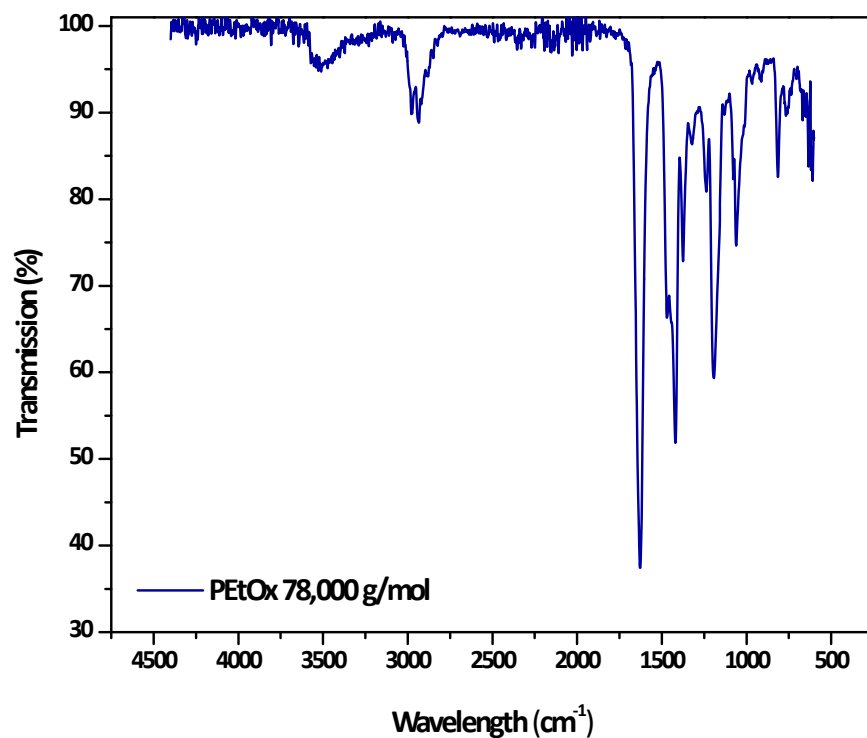
SI Table 2: Calculations for the kinetic study for the homopolymerization of EtOx in different solvents.

M	[M]/[I]	[M]	V _{stock,tot}	[I]	Vol (I)	Vol (M)	V(s)
name	ratio	mol/L	mL	mol/L	mL	mL	mL
EtOx	100	3	45	0.03	0.210	13.7	31.1



SI Figure 1. Copolymerization kinetic data plots for the CROP of EtOx and C3MestOx in acetonitrile (**A**) and the combined first order kinetic plot for the copolymerization CROP of EtOx and C3MestOx in acetonitrile and C3MestOx giving similar k_p 's (**B**).





SI Figure 3. IR spectrum of the purified 78,000 g/mol PEOx polymer synthesized according the method described in the experimental part of the manuscript.

SI Table 3: Calculations for the kinetic study for the copolymerization of EtOx and C3MestOx in ethyl acetate and acetonitrile at 60 °C. M = monomer, I = initiator, s = solvent.

M	[M]/[I]	Total [M]	V _{stock,tot}	[I]	Vol (I)	Vol (M1:M2)	V(s)
name	ratio	mol/L	mL	mol/L	mL	mL	mL
EtOx (M1): C3MestOx(M2)	270:30	4.8	12	0.016	0.112	5.23 : 0.86	5.91

SI references

- 1 F. P. Byrne, S. Jin, G. Paggiola, T. H. M. Petchey, J. H. Clark, T. J. Farmer, A. J. Hunt, C. Robert McElroy and J. Sherwood, *Sustain. Chem. Process.*, 2016, **4**, 7.