Supporting information for

**Poly(2-cycloalkyl-2-oxazoline)s: High melting temperature polymers solely based on Debye and Keesom Van der Waals interactions**

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**Monomer synthesis**

![Figure S1.](image)

**Figure S1.** $^1$H-NMR spectra of the intermediate products involved in the synthesis of 2-cyclobutyl-2-oxazoline. The spectra were recorded in CDCl$_3$. 

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Figure S2. $^1$H-NMR spectra of the intermediate products involved in the synthesis of 2-cyclohexyl-2-oxazoline. The spectra were recorded in CDCl$_3$.

**Kinetics of the homopolymerisations**

Figure S3. First-order kinetics plots for the cationic ring-opening polymerization of 2-cyclobutyl-2-oxazoline (cBuOx) including error bars.
Figure S4. First-order kinetics plots for the cationic ring-opening polymerization of 2-cyclopentyl-2-oxazoline (cPentOx) including error bars.

Figure S5. First-order kinetics plots for the cationic ring-opening polymerization of 2-cyclohexyl-2-oxazoline (cHexOx) including error bars.
Figure S6. SEC traces of the 2-cycloalkyl-2-oxazoline homopolymers

Thermal transitions of homopolymers

Figure S7. DSC heating-cooling cycles of (a) poly(cPentOx) and (b) poly(cHexOx).
Kinetics of the copolymerizations

Figure S8. Polymerization kinetics of the microwave-assisted statistical copolymerization of a 50:50 mixture. Monomer conversion in time: (a) EtOx:cPentOx; (c) cBuOx:cPentOx. Number average molecular weight ($M_{n,\text{exp}}$) and dispersity ($D$) as function of theoretical molecular weight ($M_{n,\text{theo}}$) for (b) EtOx:cPentOx and (d) cBuOx:cPentOx copolymers.
Figure S9. SEC traces of the poly(EtOx-cPentOx) (a) and poly(cBuOx-cPentOx) (b) copolymers; SEC traces were recorded on an Agilent HPLC system using HFIP (PEtOx-cPentOx 10-90, PEtOx-cPentOx 60-40, PEtOx-cPentOx 80-20 and PcBuOx-cPentOx 20-80) or DMAc (all other copolymers) as an eluent.

Determination of the reactivity ratio’s

Figure S10. Evolution of the actual fraction of cPentOx as function of the monomer feed composition for EtOx-cPentOx copolymerization (red) and cBuOx-cPentOx copolymerization (blue) at 30% of EtOx conversion and 30% cBuOx conversion, respectively.
Solubility overview

**Figure S11.** Solubility overview for: (a) EtOx-cPentOx and (b) cBuOx-cPentOx copolymer libraries in different solvents: Dioxane (D), chlorobenzene (CB), anisole (AN), 1, 2-dichlorobenzene (DCB), trichloromethane (TCB), dichloromethane (DCM), N,N'-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), acetonitrile (ACN), acetic acid (AA), ethanol (EtOH), formic acid (FA), and HFIP.
Thermal stability of copolymers

Figure S12. Thermal analysis of: (a) EtOx-cPentOx copolymers and (b) cBuOx-cPentOx copolymers.