DYNAMIC COVALENT COPOLYESTER NETWORKS BASED ON POLYCAPROLACTONE

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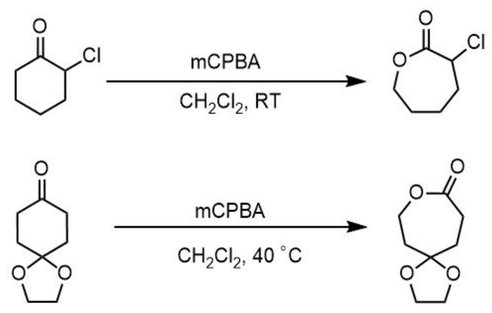
MOTIVATION

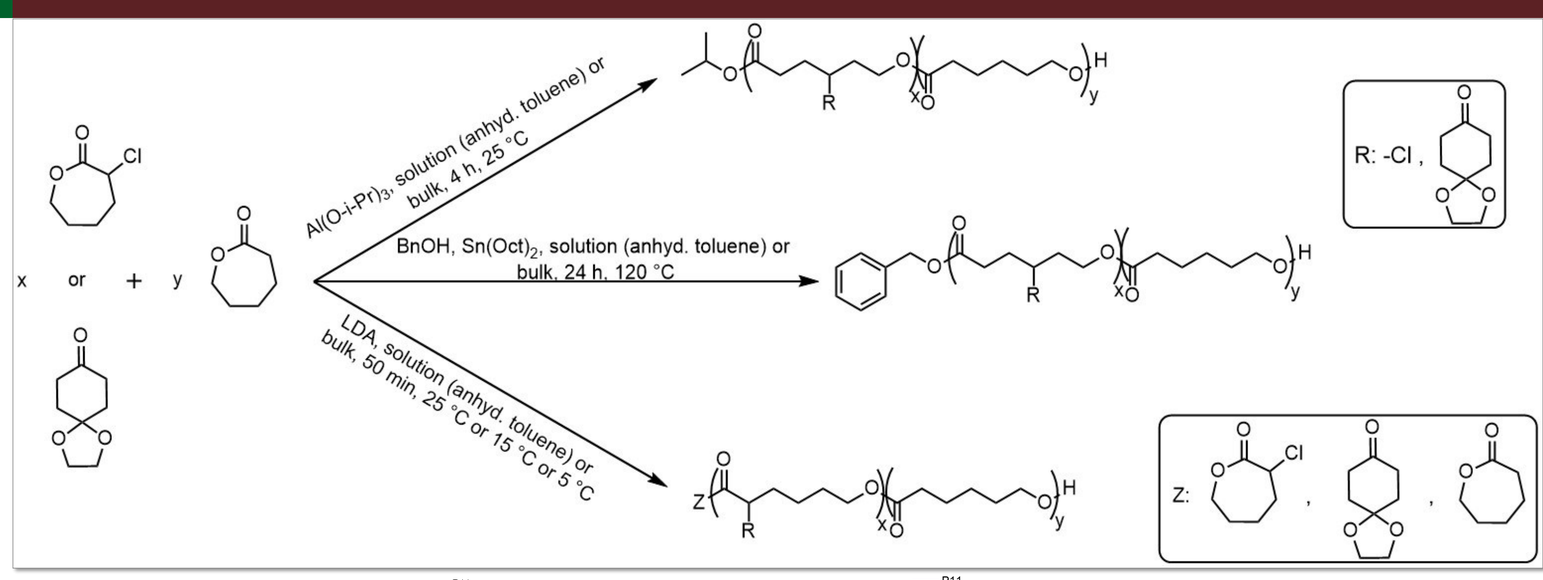
Physically or covalently crosslinked polymer chains forms networks with unique properties. Networks containing dynamic covalent crosslinks feature chain mobility and adaptivity to external triggers. This is fused in the design of shape-memory and self-healing materials as well as stimuli-responsive polymer gels.[1] It is often desired to transfer bond reversibility under ambient conditions also to the class of polyesters, rendering materials with tunable mechanical properties and frequently inherent degradability.

This project investigates the physical, thermal and morphological properties of the dynamic covalent networks derived from polycaprolactone-based copolyesters with functional comonomers such as α-chloro-ε-caprolactone (αClεCL) and/or 1,4,8-trioxaspiro-[4.6]-9-undecanone (TOSUO). The type of dynamic covalent crosslinks between the chains vary from a disulfide bridge to an imine bond concerning the –Cl and the –OH functionality on the copolymer side-chain. The bond reversibility occurs via stimuli such as light, pH or temperature.

FUNCTIONAL COMONOMERS



COPOLYMER SYNTHESES

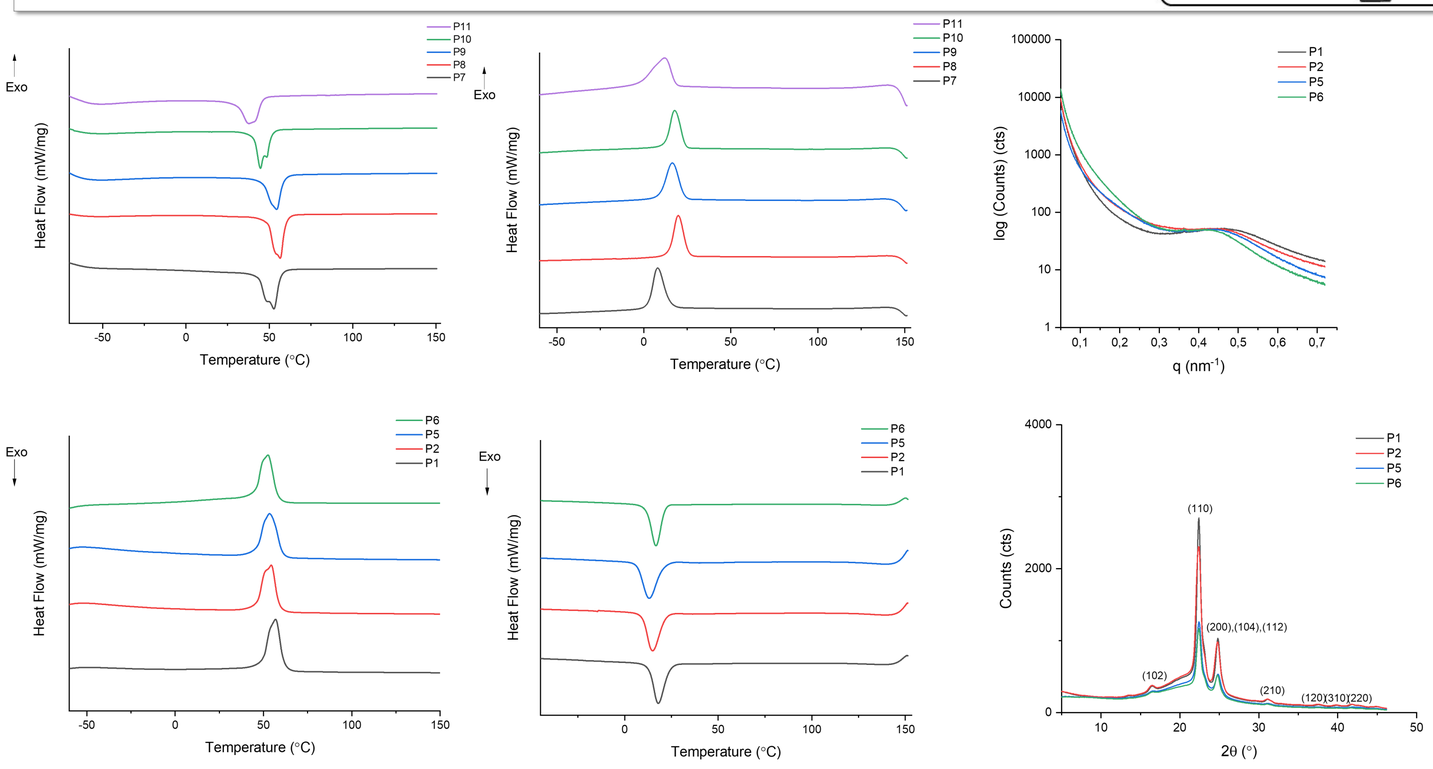


Copolymer	Composition	$\overline{M_n}$ (kg/mol) (^{1}H NMR)	$\overline{M_n}$ (kg/mol) (SEC)	Dispersity (Đ) (SEC)
P1 (2 wt% αClεCL)	P(αClεCL$_8$-co-εCL$_{214}$)	25.4	21.9	1.62
P2 (5 wt% αClεCL)	P(αClεCL$_7$-co-εCL$_{154}$)	18.7	20.6	1.65
P3 (7.5 wt% αClεCL)	P(αClεCL$_8$-co-εCL$_{95}$)	11.8	15.8	1.79
P4 (2 wt% αClεCL)	P(αClεCL$_8$-co-εCL$_{313}$)	37.0	33.4	1.67
P5 (5 wt% αClεCL)	P(αClεCL$_{29}$-co-εCL$_{839}$)	77.2	42.9	1.73
P6 (7.5 wt% αClεCL)	P(αClεCL$_{18}$-co-εCL$_{264}$)	32.9	31.6	1.69
P7 (7.5 wt% αClεCL)	P(αClεCL$_{11}$-co-εCL$_{171}$)	21.2	39.7	1.18
P8 (2 wt% αClεCL)	P(αClεCL$_4$-co-εCL$_{252}$) P(αClεCL$_2$-co-εCL$_{110}$) P(αClεCL$_1$-co-εCL$_{56}$)	29.4, 12.9, 6.6	17.8	1.13
P9 (2 wt% αClεCL)	P(αClεCL$_4$-co-εCL$_{95}$)	11.6, 11.5	56.3	1.70
P10 (10 wt% αClεCL)	P(αClεCL$_4$-co-εCL$_{47}$)	6.1	9.4	1.25
P11 (20 wt% αClεCL)	P(αClεCL$_8$-co-εCL$_{50}$)	7.0	9.2	1.23
P12 (15 wt% TOSUO)	P(TOSUO$_{13}$-co-εCL$_{193}$)	24.3	14.4	1.66
P13 (30 wt% TOSUO)	P(TOSUO$_6$-co-εCL$_{69}$)	9.0	3.7	1.72
P14 (15 wt% TOSUO)	P(TOSUO$_{20}$-co-εCL$_{183}$)	24.4	21.0	1.26
P15 (15 wt% TOSUO+αClεCL)	P(TOSUO$_5$-co-αClεCL$_{39}$-co-εCL$_{233}$)	33.3	3.5	1.55
P16 (30 wt% TOSUO+αClεCL)	P(TOSUO$_2$-co-αClεCL$_{36}$-co-εCL$_{92}$)	16.3	3.2	1.45
P17 (15 wt% TOSUO+αClεCL)	P(TOSUO$_3$-co-αClεCL$_{16}$-co-εCL$_{146}$)	19.6	14.8	1.44

= In./Cat.: BnOH/Sn(Oct)$_2$ = In./Cat.: LDA

= In./Cat.: Al(O-i-Pr)$_3$ = In./Cat.: BnOH/Sn(Oct)$_2$, Solution

= In./Cat.: Al(O-i-Pr)$_3$, BnOH = In./Cat.: BnOH/Sn(Oct)$_2$, Bulk

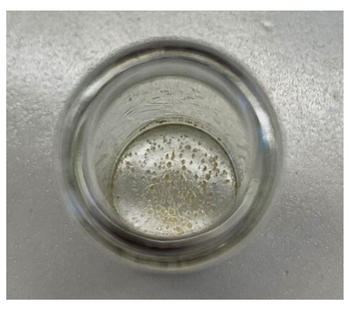


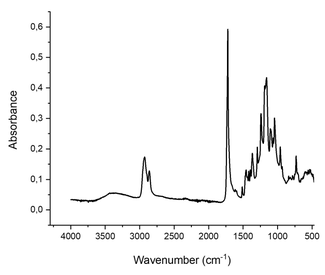
DSC scans of P7-11 (table left) with T_ms (44 °C-50 °C) (1st row left) and T_cs (8 °C-20 °C) (1st row middle) without discernible T_gs. Minute variations in T_ms and T_cs with M_n and Đ

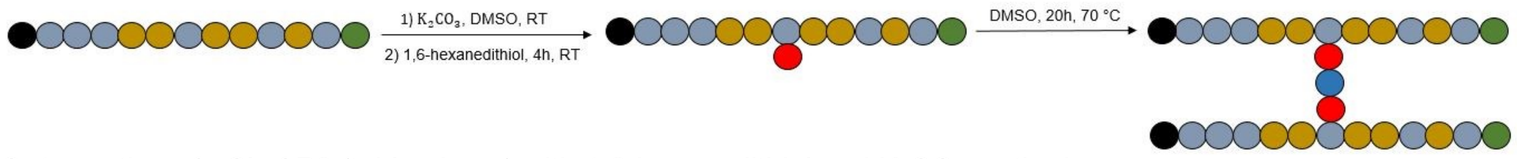
DSC scans of P1-6 (table left) with T_ms (52 °C-56 °C) (2nd row left) and T_cs (14 °C–17 C) (2nd row middle) without discernible T_gs. Shift to lower T_ms and T_cs with higher αClεCL content and M_n

SAXS patterns of P1-6 (table left) with reflexes (0.4 nm^{-1}-0.5 nm^{-1}), crystal domain spacings (13 nm-15 nm), crystallite sizes (56 nm-133 nm) (1st row right) and WAXS patterns with crystal plane diffractions and degrees of crystallinity (69%-73%)

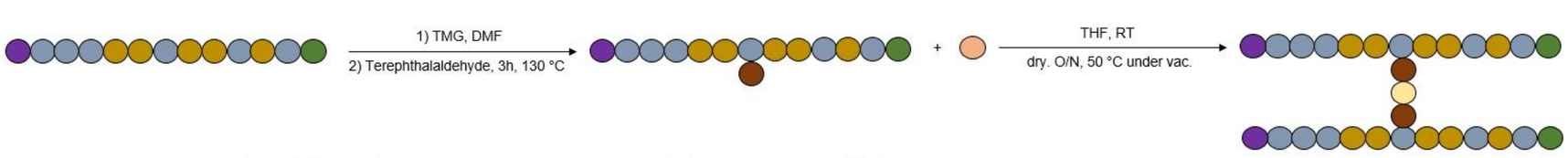
DYNAMIC COVALENT NETWORK FORMATION



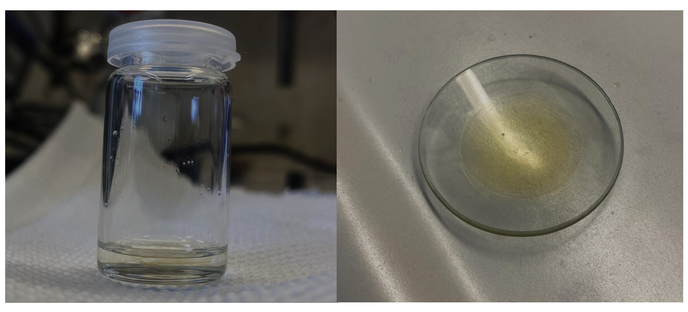


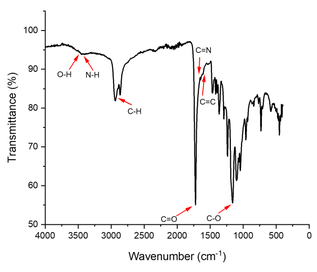


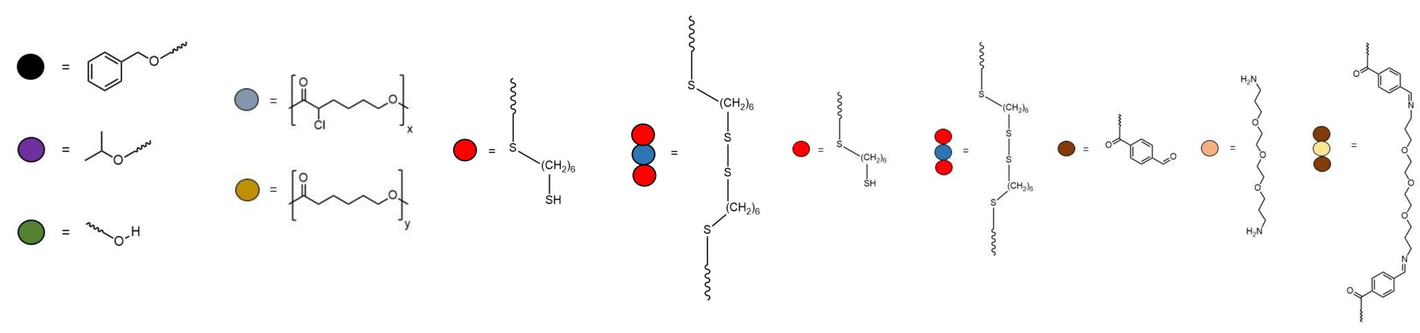
S_N1 reaction of –Cl of P6 (table above) with 1,6-hexanedithiol and K_2CO_3 as the base
Formation of disulfide bridges under air



S_N1 reaction of –Cl of P7 (table above) with terephthalaldehyde and TMG as the base
Formation of imine bonds with TOTDAA







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