Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information for

Dual pH and temperature responsive helical copolymer libraries with pendant chiral leucine moieties

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Table S1 Solubility of P(Boc-L/D-Leu-HEMA), $PMEO_2MA$, and their copolymers in different solvents at 25 ^oC

Polymer	Water	DCM	$CHCl_3$	THF	DMSO	Methanol	1,4-Dioxane	Ethyl acetate
PHPL	-	+	+	+	+	+	+	+
PCPL20	-	+	+	+	+	+	+	+
PCPL40	-	+	+	+	+	+	+	+
PCPL50	-	+	+	+	+	+	+	+
PCPL60	-	+	+	+	+	+	+	+
PCPL80	-	+	+	+	+	+	+	+
$PMEO_2MA$	+	+	+	+	+	+	+	+
PCPD80	-	+	+	+	+	+	+	+
PCPD60	-	+	+	+	+	+	+	+
PCPD50	-	+	+	+	+	+	+	+
PCPD40	-	+	+	+	+	+	+	+
PCPD20	-	+	+	+	+	+	+	+
PHPD	-	+	+	+	+	+	+	+

Soluble: +, Insoluble: -.

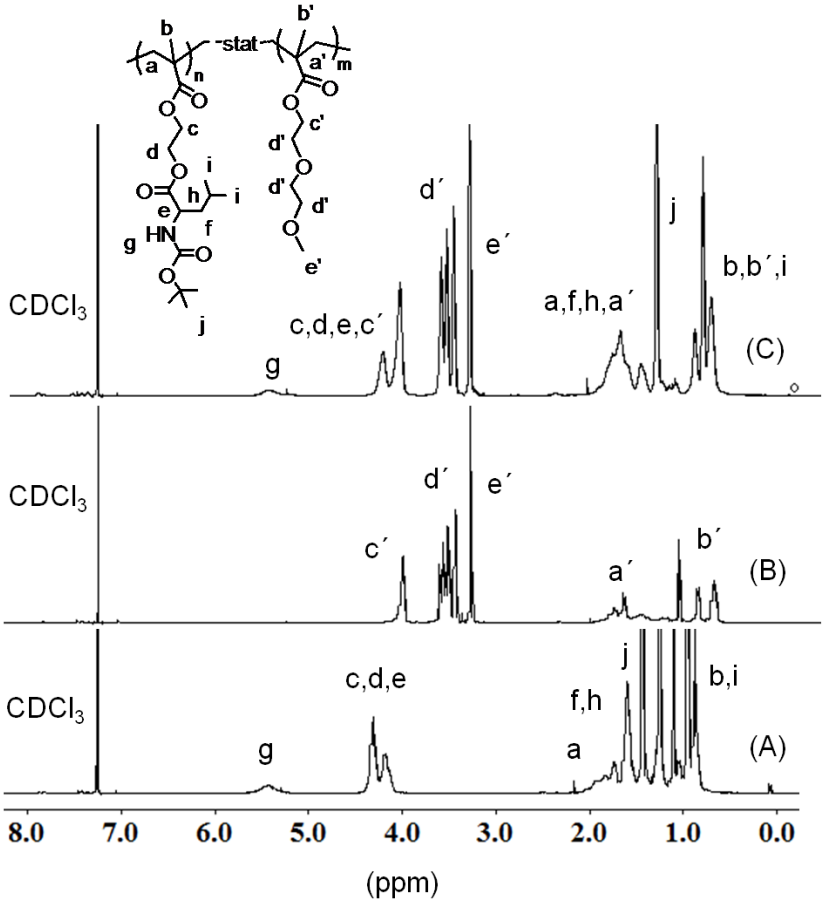

Fig. S1 ^1H NMR spectra of (A) P(Boc-D-Leu-HEMA), (B) $PMEO_2MA$, and P(Boc-D-Leu-HEMA-*stat*-MEO_2MA) (PCPD50) in $CDCl_3$.

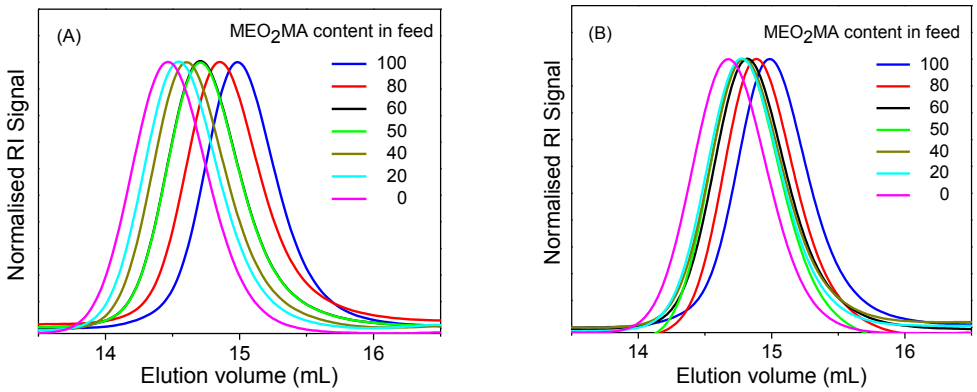

Fig. S2 The GPC RI traces of the P(Boc-L/D-Leu-HEMA-*stat*-MEO_2MA) copolymers at different Boc-L-Leu-HEMA/MEO_2MA (A) and Boc-D-Leu-HEMA/MEO_2MA (B) feed compositions.

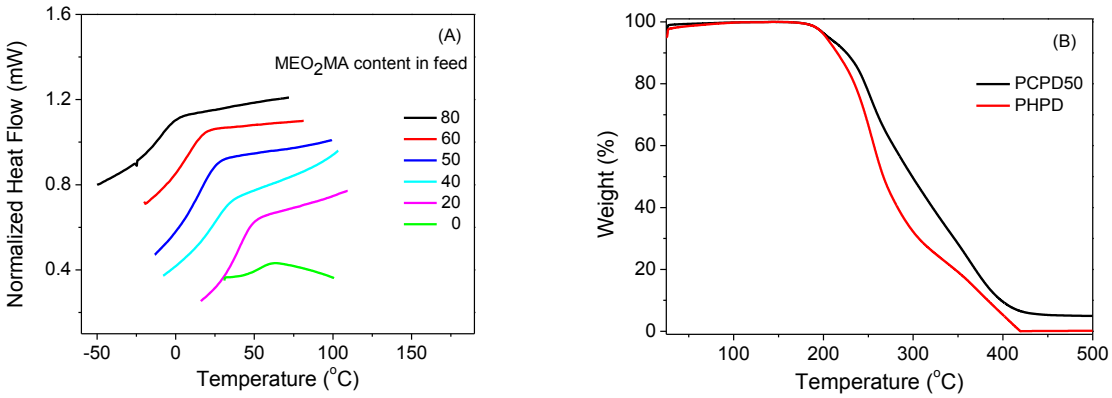

Fig. S3 The DSC curves for the P(Boc-D-Leu-HEMA-*stat*-MEO_2MA) copolymers (A) and TGA thermograms of PCPD50 and P(Boc-D-Leu-HEMA) (B).

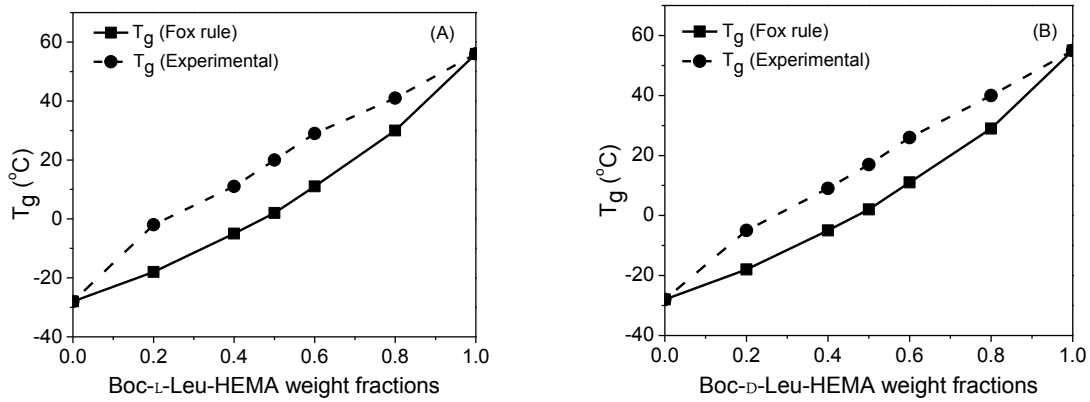

Fig. S4 Comparison of the experimental (from the DSC measurement) and theoretical T_g values (calculated from the Fox relationship) for copolymers (A) P(Boc-L-Leu-HEMA-*stat*-MEO_2MA), and (B) P(Boc-D-Leu-HEMA-*stat*-MEO_2MA).

Table S2 Extended Kelen-Tüdös parameters for the RAFT copolymerization of MEO_2MA with Boc-L-Leu-HEMA and Boc-D-Leu-HEMA in DMF at 70 °C

$f_{Boc\text{-}L\text{-}Leu\text{-}HEMA}$	$F_{Boc\text{-}L\text{-}Leu\text{-}HEMA}$	Conv. (%)	z	F	G	ξ	η
0.8	0.748	61	0.56602	9.26488	3.47737	0.80632	0.30263
0.6	0.532	63	0.59818	3.17685	0.22861	0.58805	0.04232
0.5	0.432	64	0.60603	2.07081	-0.39509	0.482	-0.09196
0.4	0.336	66	0.60237	1.39459	-0.82006	0.38524	-0.22653
0.2	0.158	70	0.59246	0.5346	-1.37116	0.19369	-0.49678
$f_{Boc\text{-}D\text{-}Leu\text{-}HEMA}$	$F_{Boc\text{-}D\text{-}Leu\text{-}HEMA}$	Conv. (%)	z	F	G	ξ	η
0.8	0.748	60	0.57322	9.03341	3.43365	0.80566	0.30624
0.6	0.538	62	0.63364	2.90038	0.25961	0.57101	0.05111
0.5	0.429	64	0.59175	2.1456	-0.42026	0.49614	-0.09718
0.4	0.341	65	0.63363	1.28882	-0.76156	0.37165	-0.21961
0.2	0.156	67	0.59279	0.52599	-1.37513	0.19445	-0.50837

f, F are the mole fraction of monomer in feed and in copolymer, respectively, and the other parameters such as z, F, G, ξ, η are depicted in reference 26 in the main text.

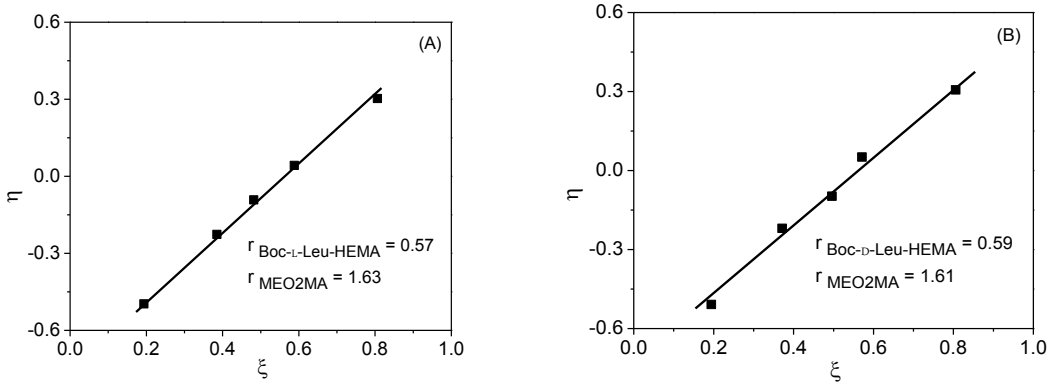

Fig. S5 Determination of reactivity ratios by the extended Kelen-Tüdös method for the copolymerizations of MEO_2MA with (A) Boc-L-Leu-HEMA and (B) Boc-D-Leu-HEMA.

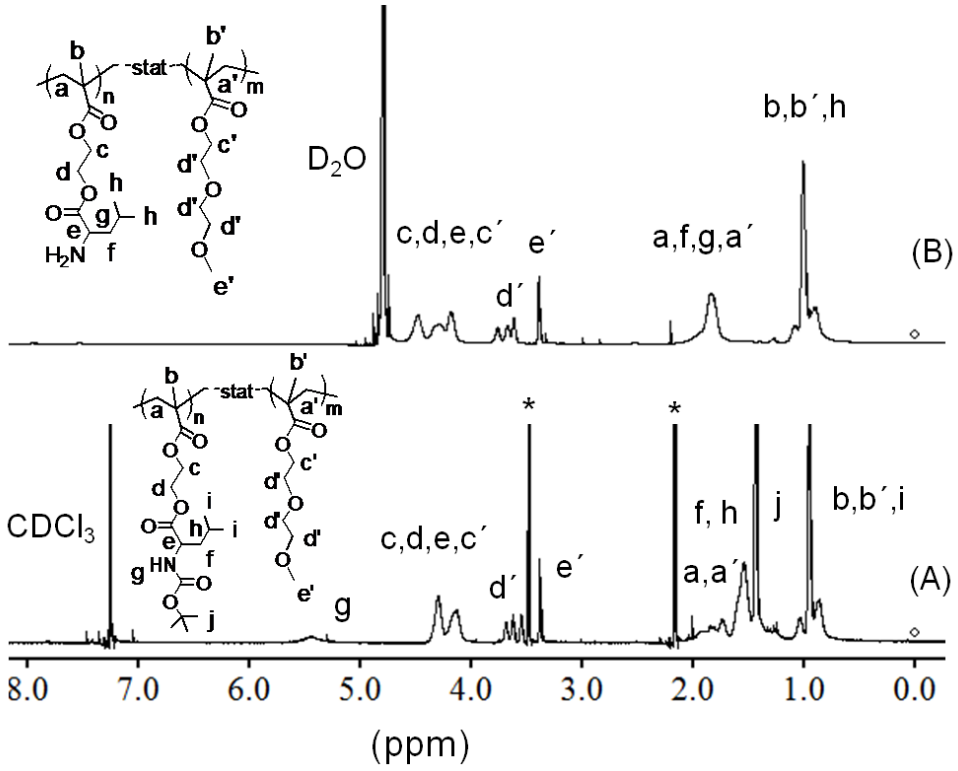

Fig. S6 The ^{1}H NMR spectra of (A) P(Boc-L-Leu-HEMA-*stat*-MEO_2MA) in $CDCl_3$ and (B) P(NH_2-L-Leu-HEMA-*stat*-MEO_2MA) in D_2O. The PCPL40 in Table 1 (main document) is used in this study.

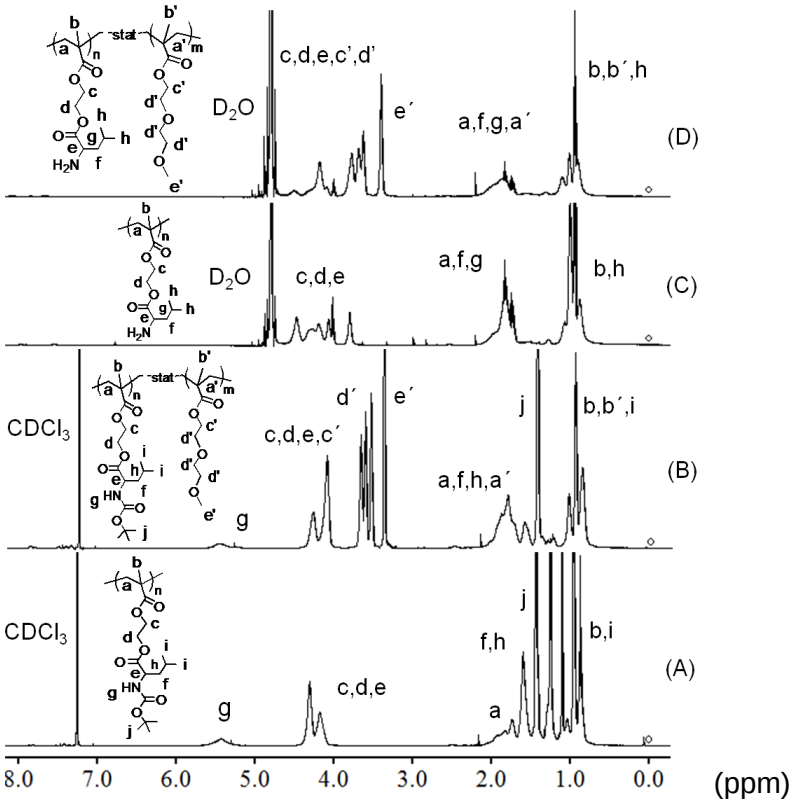

Fig. S7 The ^{1}H NMR spectra of P(Boc-D-Leu-HEMA) (A) and P(Boc-D-Leu-HEMA-*stat*-MEO_2MA) (B) in $CDCl_3$, and P(NH_2-D-Leu-HEMA) (C) and P(NH_2-D-Leu-HEMA-*stat*-MEO_2MA) (D) in D_2O. The PCPD60 copolymer in Table 1 (main document) is used in this study.

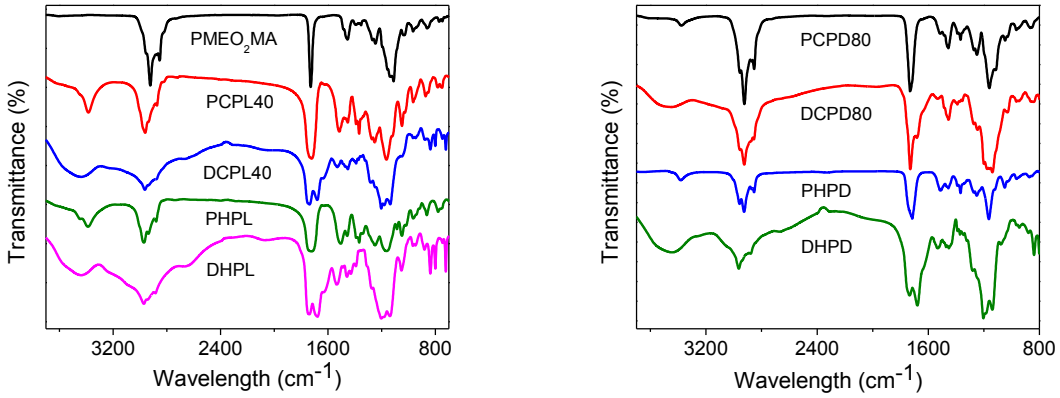

Fig. S8 FT-IR spectra of various homo- and copolymers before and after Boc-deprotection. Left side: from L-series; Right side: from D-series.

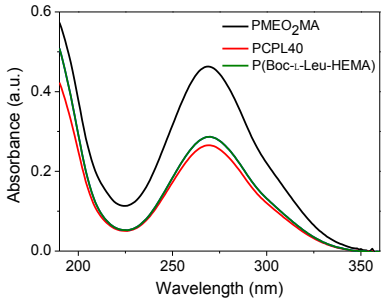

Fig. S9 UV-vis spectra of $PMEO_2MA$, PCPL40 and P(Boc-L-Leu-HEMA) in methanol.

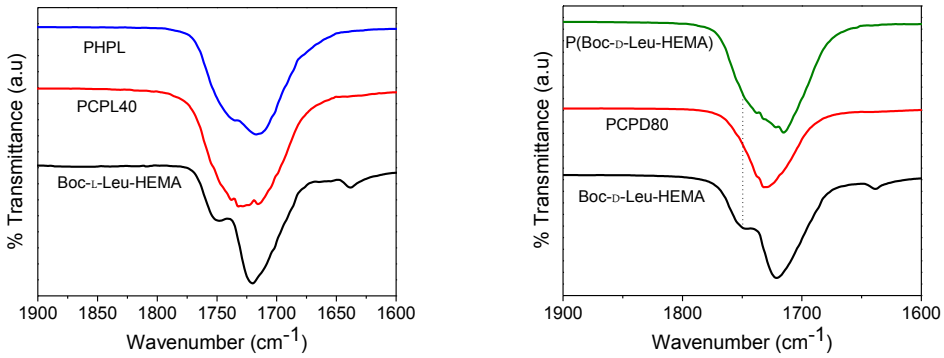

Fig. S10 Partial FT-IR spectra of monomer, various homo- and copolymers before Boc-deprotection. Left side: from L-series; Right side: from D-series.

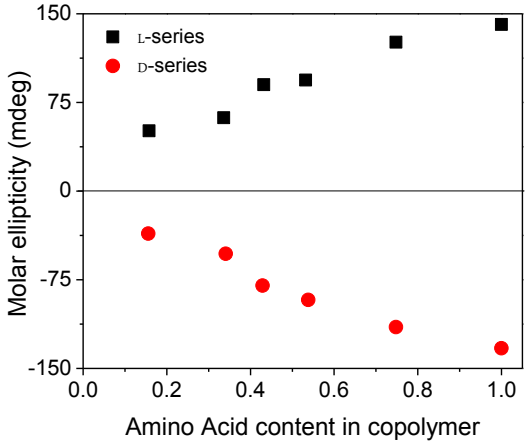

Fig. S11 Variation of molar ellipticity at λ = 210 nm versus leucine content in the copolymer.

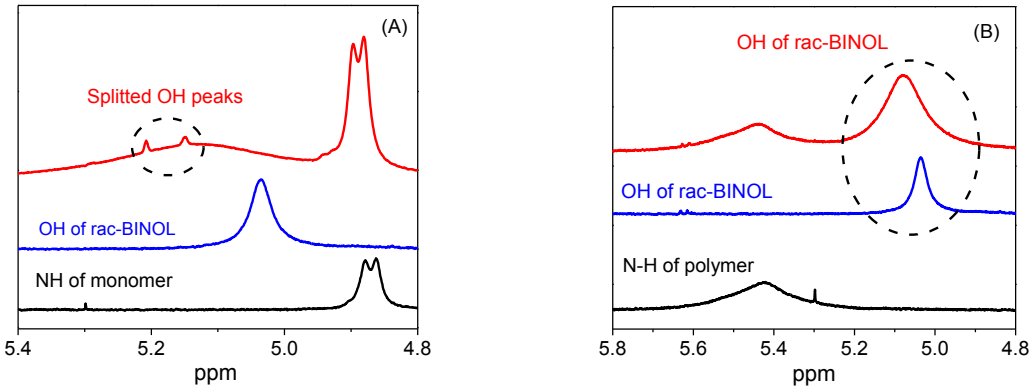

Fig. S12 ^{1}H NMR spectra (A) of Boc-D-Leu-HEMA (lower), *rac*-BINOL (middle), mixture of *rac*-BINOL and Boc-D-Leu-HEMA monomer at 1:1 molar ratio (upper), and (B) P(Boc-D-Leu-HEMA) (lower), *rac*-BINOL (middle), mixture of *rac*-BINOL and P(Boc-D-Leu-HEMA) at 1:1 molar ratio (upper).