Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Synthesis and Characterization of Segmented Poly(ester-urethane)s (PEUs) Containing Carotenoids

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^{1}H NMR spectra of Macrodiols (HOPCLOH) prepared from 1,8-octanediol and CL

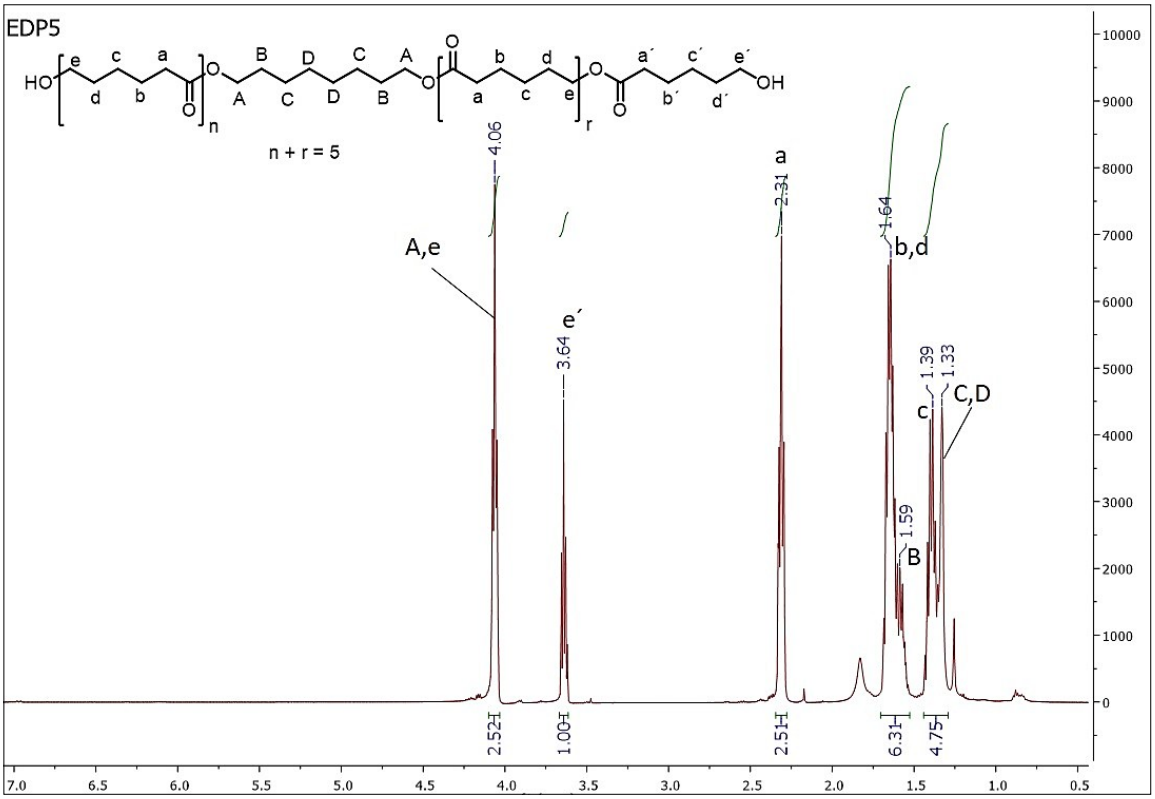

Fig. S1. ^{1}H NMR spectrum of HOPCLOH with DP = 5 (500 MHz, $CDCl_3$).

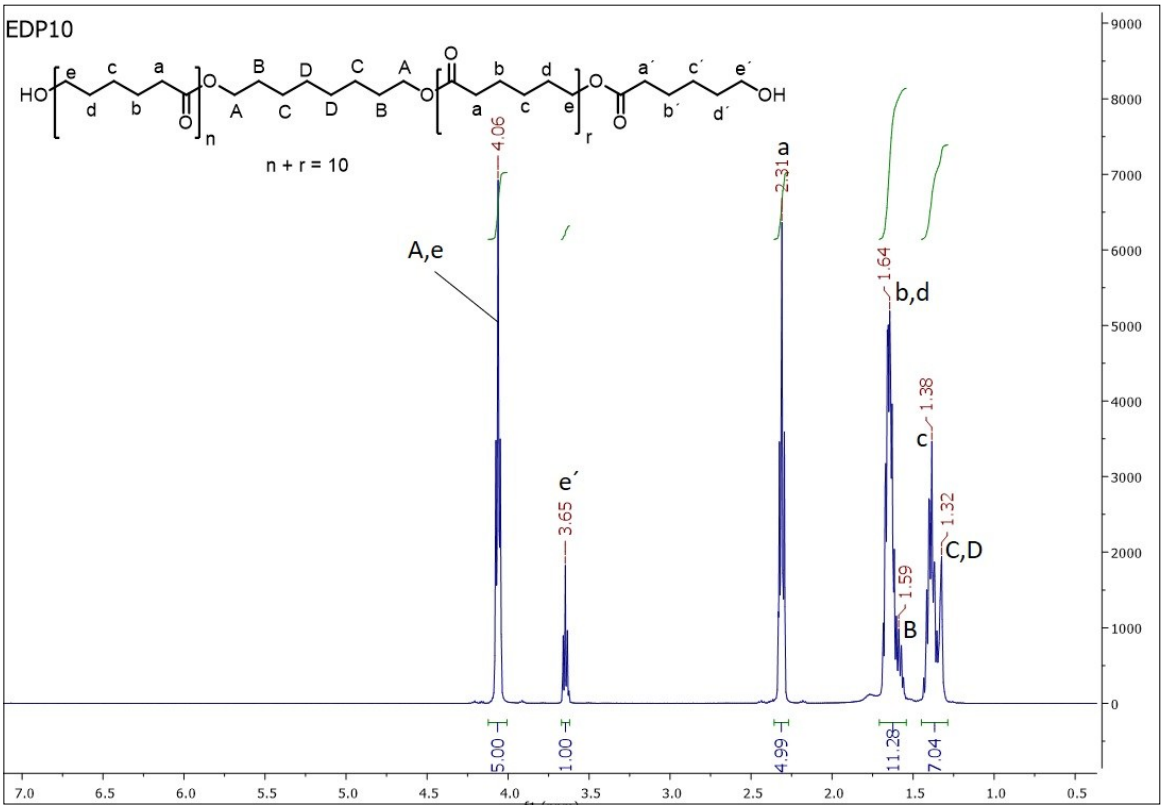

Fig. S2. ^{1}H NMR spectrum of HOPCLOH with DP = 10 (500 MHz, $CDCl_3$).

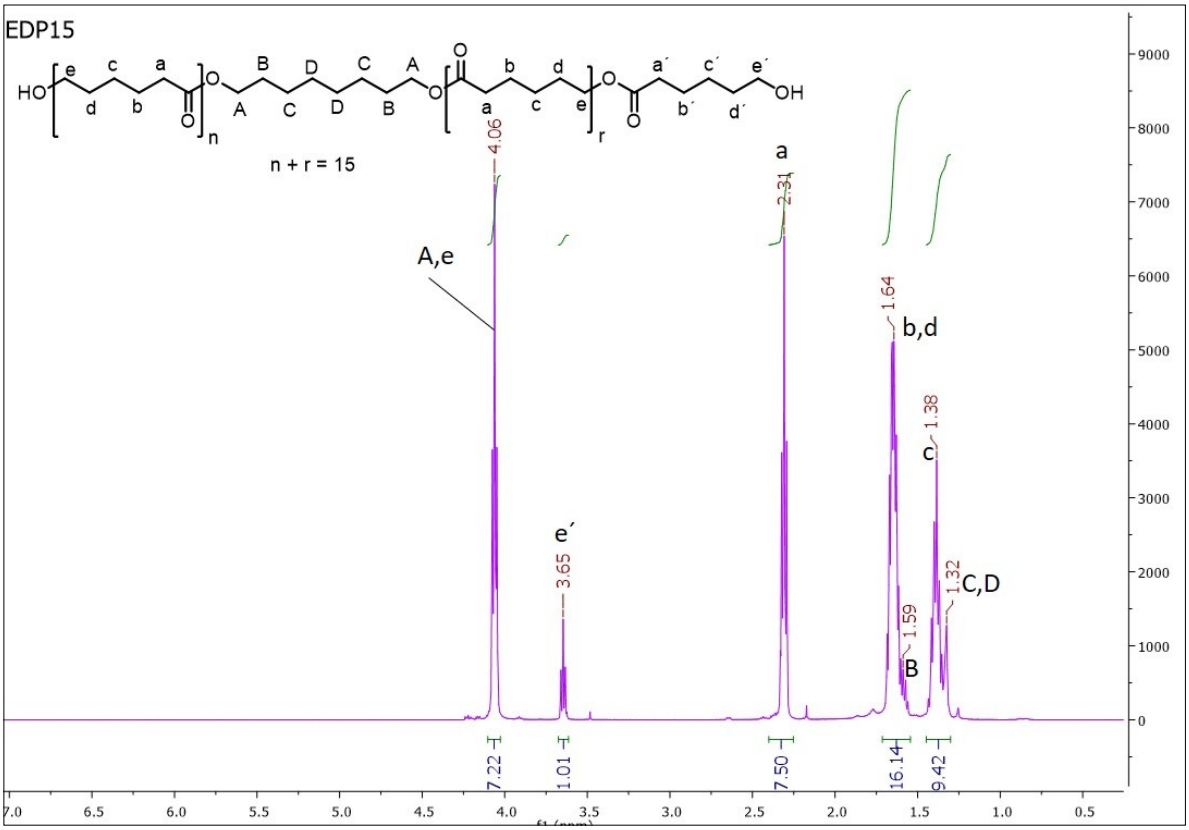

Fig. S3. ^{1}H NMR spectrum of HOPCLOH with DP = 15 (500 MHz, $CDCl_3$).

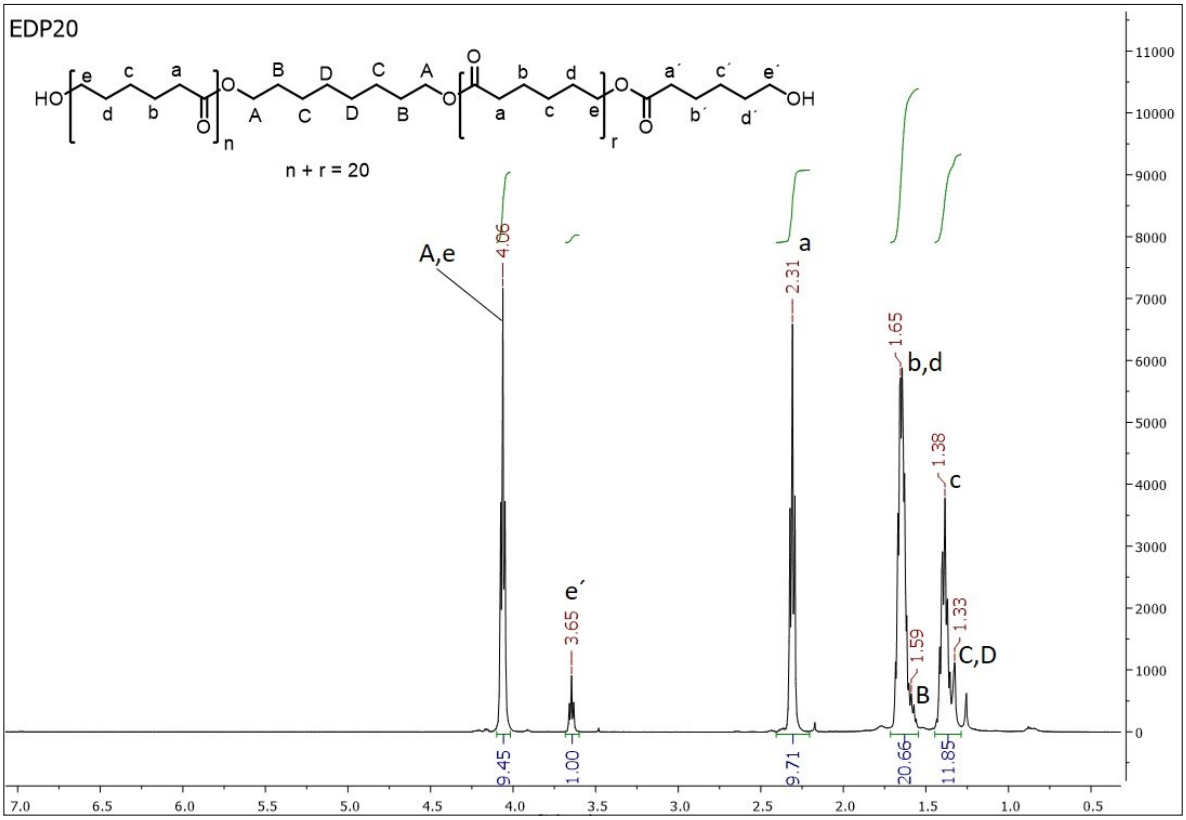

Fig. S4. ^{1}H NMR spectrum of HOPCLOH with DP = 20 (500 MHz, $CDCl_3$).

^{1}H, ^{13}C, and 2D NMR spectra of Carotenoids and ^{1}H NMR of PEU

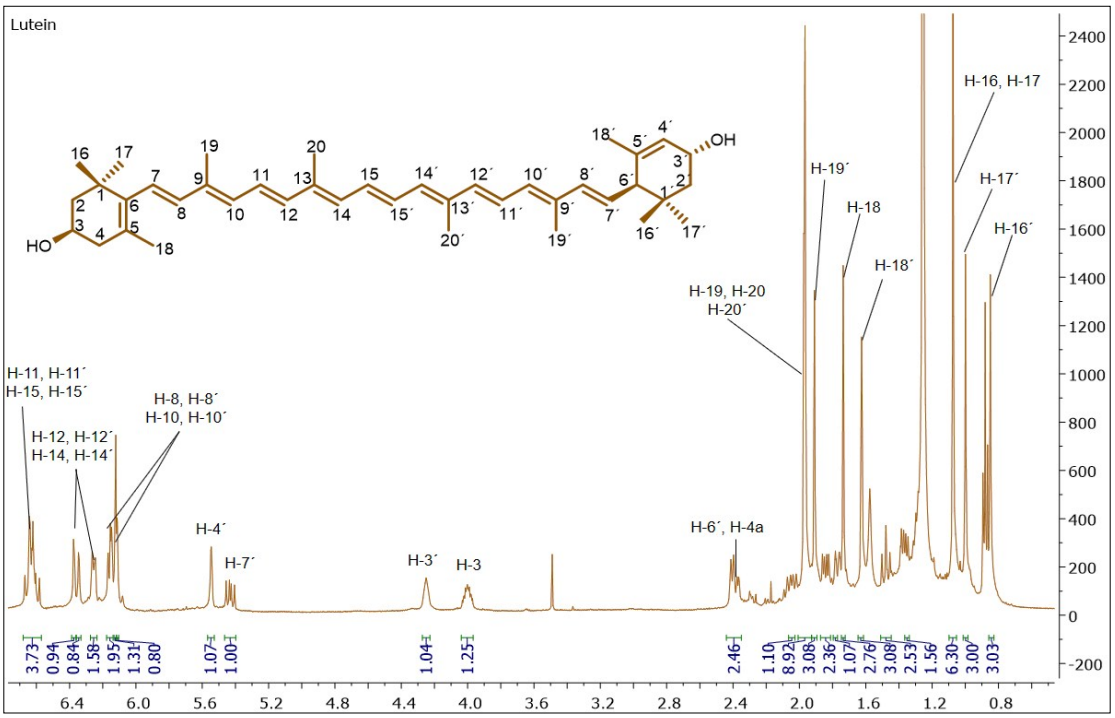

Fig. S5. ^{1}H NMR spectrum of (3*R*,3´*R*,6´*R*)-Lutein (**1**) (500 MHz, $CDCl_3$).

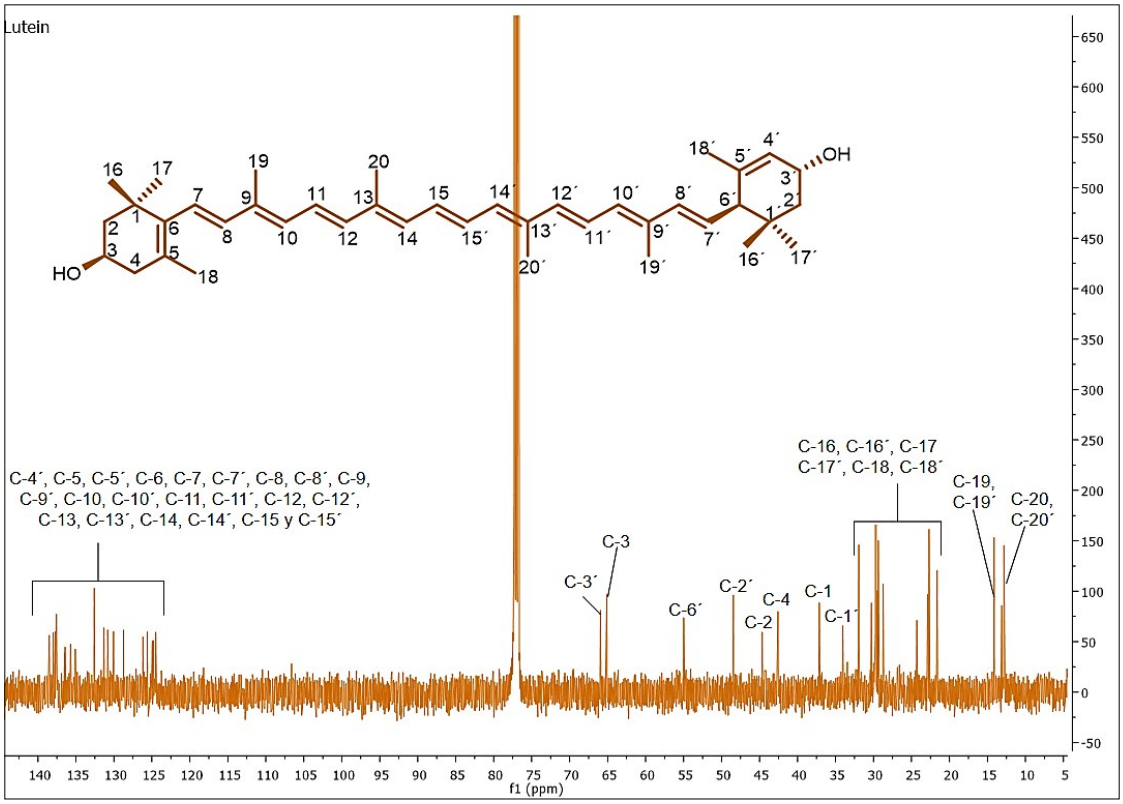

Fig. S6. ^{13}C NMR spectrum of (3*R*,3´*R*,6´*R*)-Lutein (**1**) (125 MHz, $CDCl_3$).

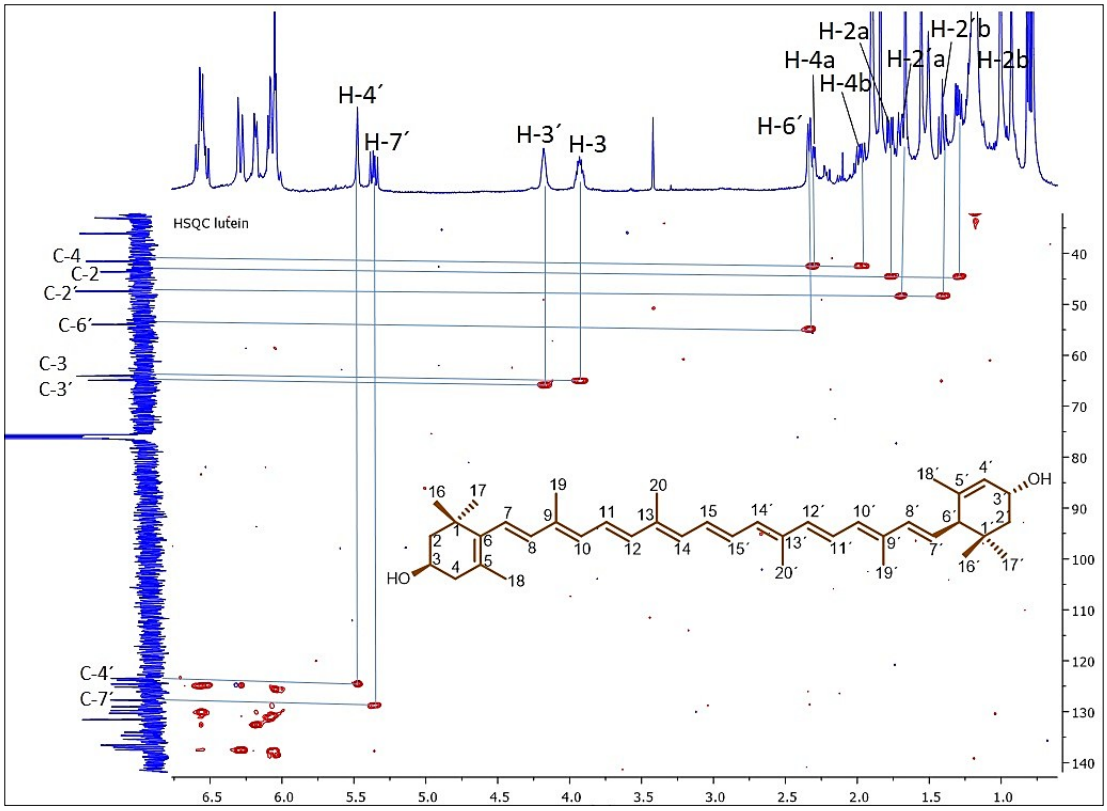

Fig. S7. HSQC of (3*R*,3´*R*,6´*R*)-Lutein (**1**).

Table S1. NMR data of compound **1**.

Lutein (1)		
Position	δ_C (125 MHz), type	δ_H (500 MHz, *J* values in Hz)
1	37.1, C	–
2	44.7, CH_2	1.36 dd *J* = 13.1, 7.0 Hz, 1.84 dd, *J* = 13.1, 7.5 Hz
3	65.1, CH	4.00 m
4	42.6, CH_2	2.05 dd, *J* = 16.5, 9.5 Hz; 2.39*
5	126.2, C	–
6	138.0, C	–
7	125.6, CH	6.12 m
8	138.5, CH	6.12 m
9	135.1, C	–
10	130.8, CH	6.15 m
11	124.9, CH	6.64*
12	137.6, CH	6.35 m
13	136.5, C	–
14 & 14´	132.6, CH	6.24 m, 6.26 m
15	130.0, CH	6.64 m
16	30.3, CH_3	1.07* s
17	28.7, CH_3	1.07* s
18	21.4, CH_3	1.74 s
19	13.1, CH_3	1.97* s
20	12.8, CH_3	1.97* s
1´	34.0, C	–
2´	48.4, CH_2	1.48 t, *J* = 12.0 Hz;1.8 m
3´	65.9, CH	4.25 s
4´	124.5, CH	5.55 s
5´	137.8, C	–
6´	54.9, CH	2.41 d, *J* = 8.1 Hz
7´	128.7, CH	5.44 dd, *J* = 15.5, 10.0 Hz
8´	138.5, CH	6.11 m
9´	135.7, C	–
10´	131.3, CH	6.15*
11´	124.8, CH	6.64*
12´	137.7, CH	6.37 m
13´	136.4, C	–
15´	130.1, CH	6.64 m
16´	29.5, CH_3	0.85 s
17´	24.3, CH_3	1.00 s
18´	22.9, CH_3	1.63 s
19´	13.1, CH_3	1.91 s
20´	12.8, CH_3	1.97*

* Overlapped

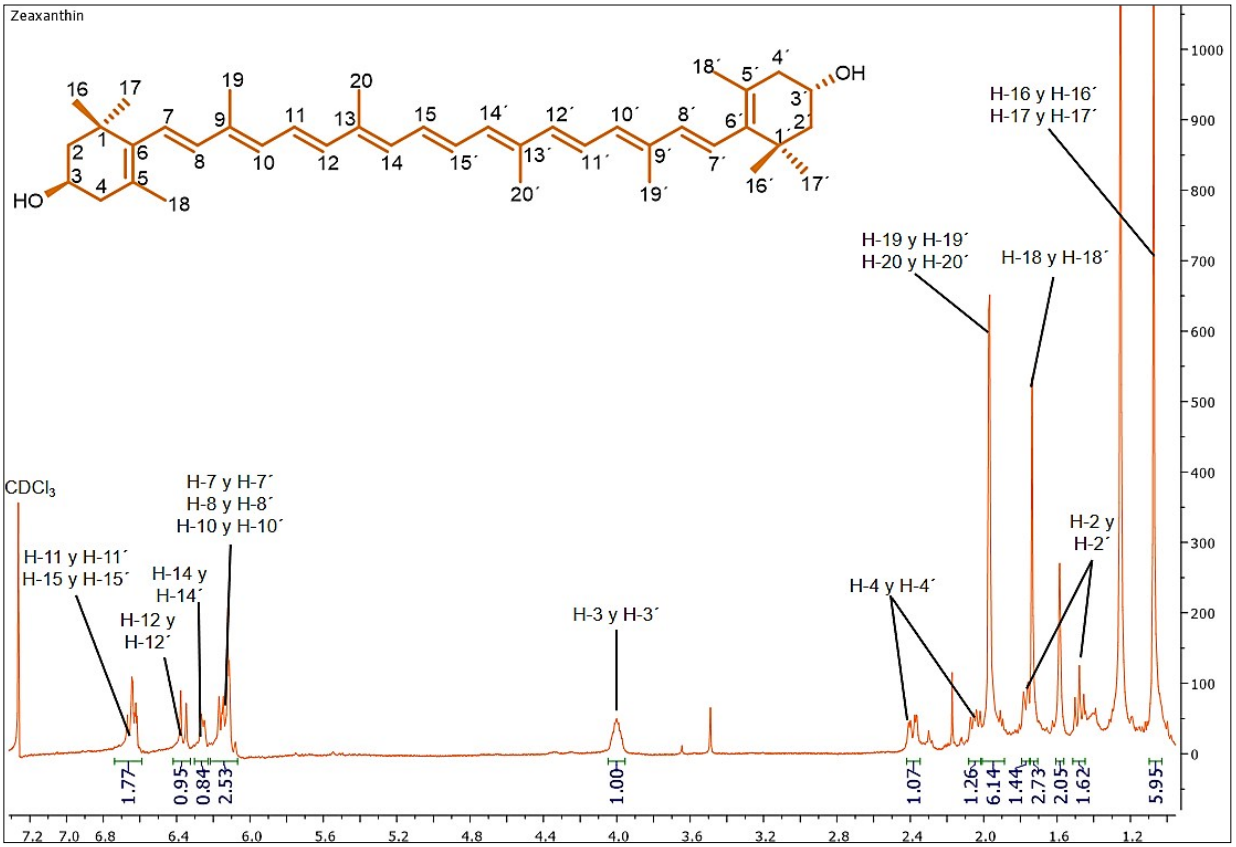

Fig. S8. ^{1}H NMR spectrum of (3*R*,3´*S*)-Zeaxanthin (**2**) (500 MHz, $CDCl_3$).

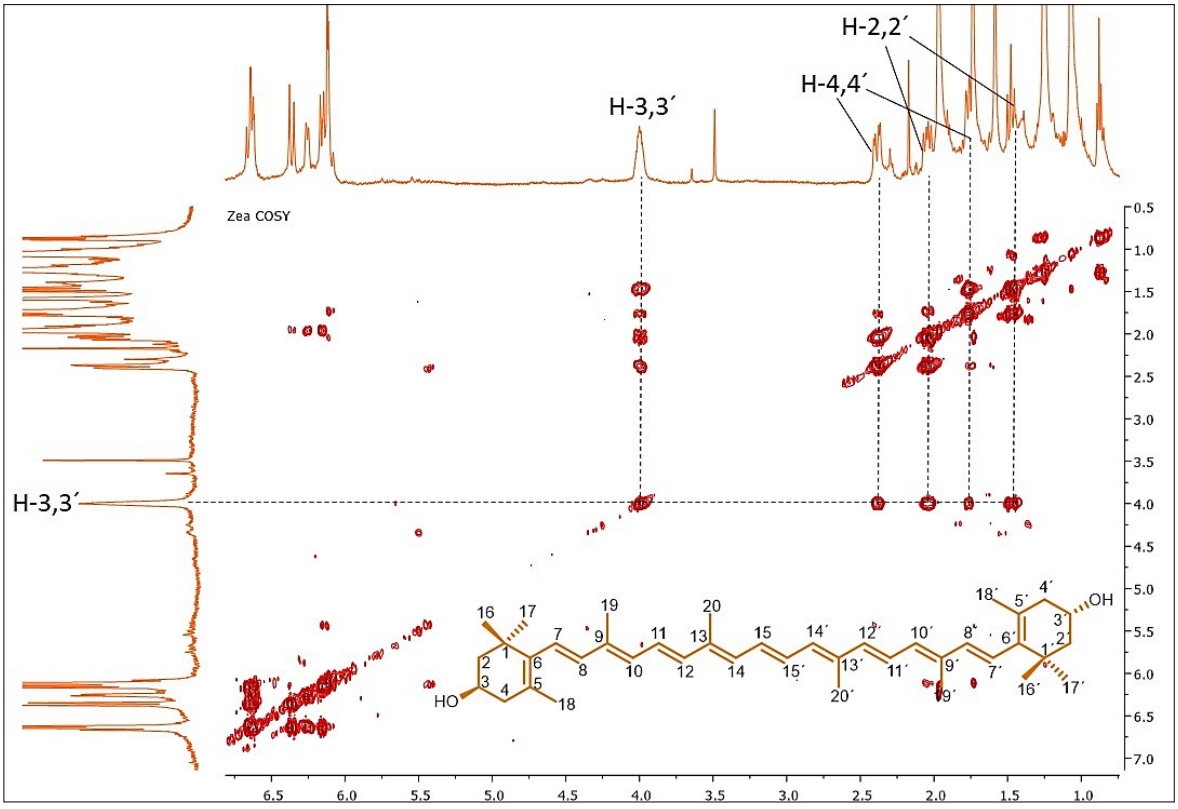

Fig. S9. ^{1}H-^{1}H COSY of (3*R*,3´*S*)-Zeaxanthin (**2**) (500 MHz, $CDCl_3$).

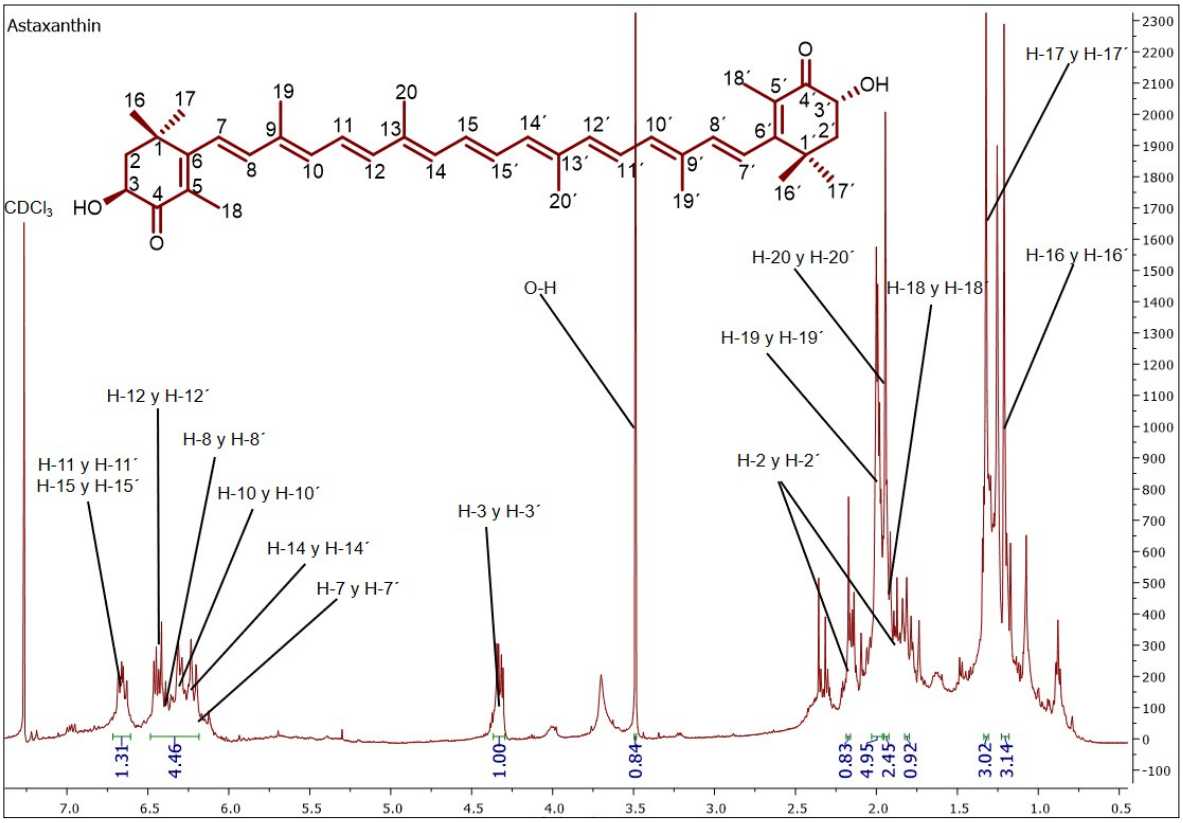

Fig. S10. ^{1}H NMR spectrum of (3*R*,3´*S*)-Astaxanthin (**3**) (500 MHz, $CDCl_3$).

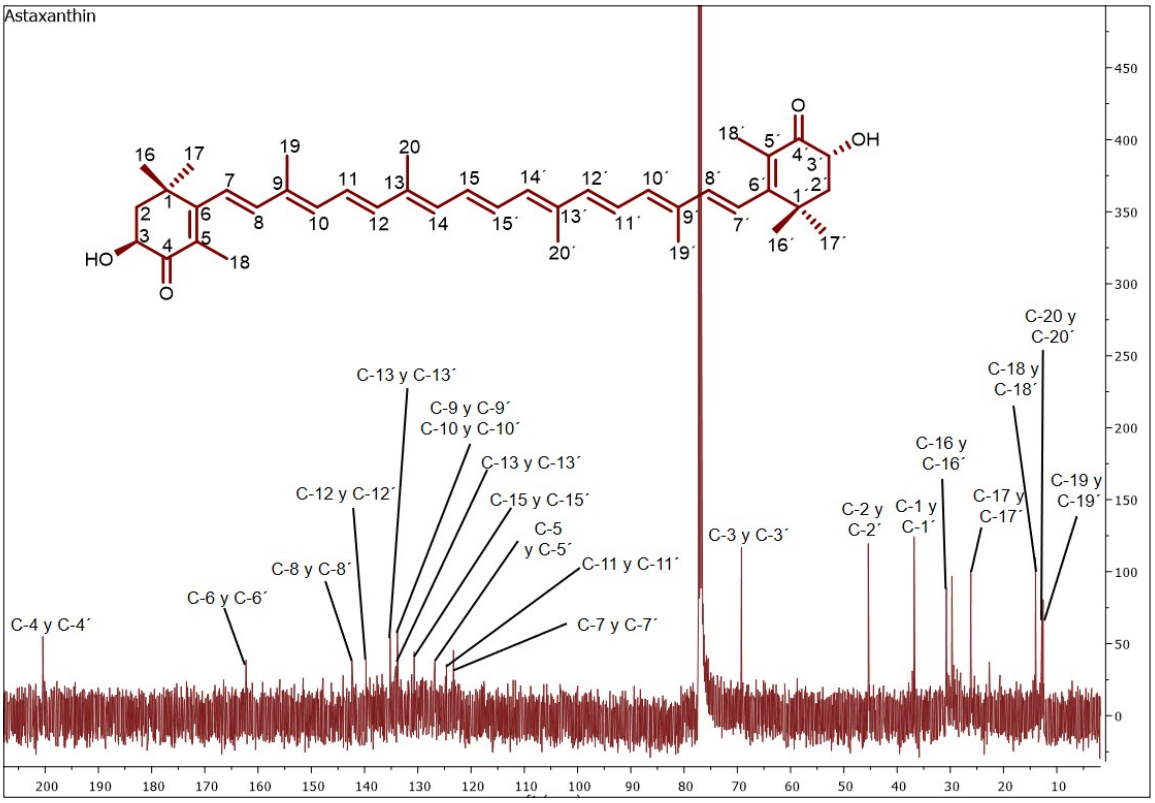

Fig. S11. ^{13}C NMR spectrum of (3*R*,3´*S*)-Astaxanthin (**3**) (125 MHz, $CDCl_3$).

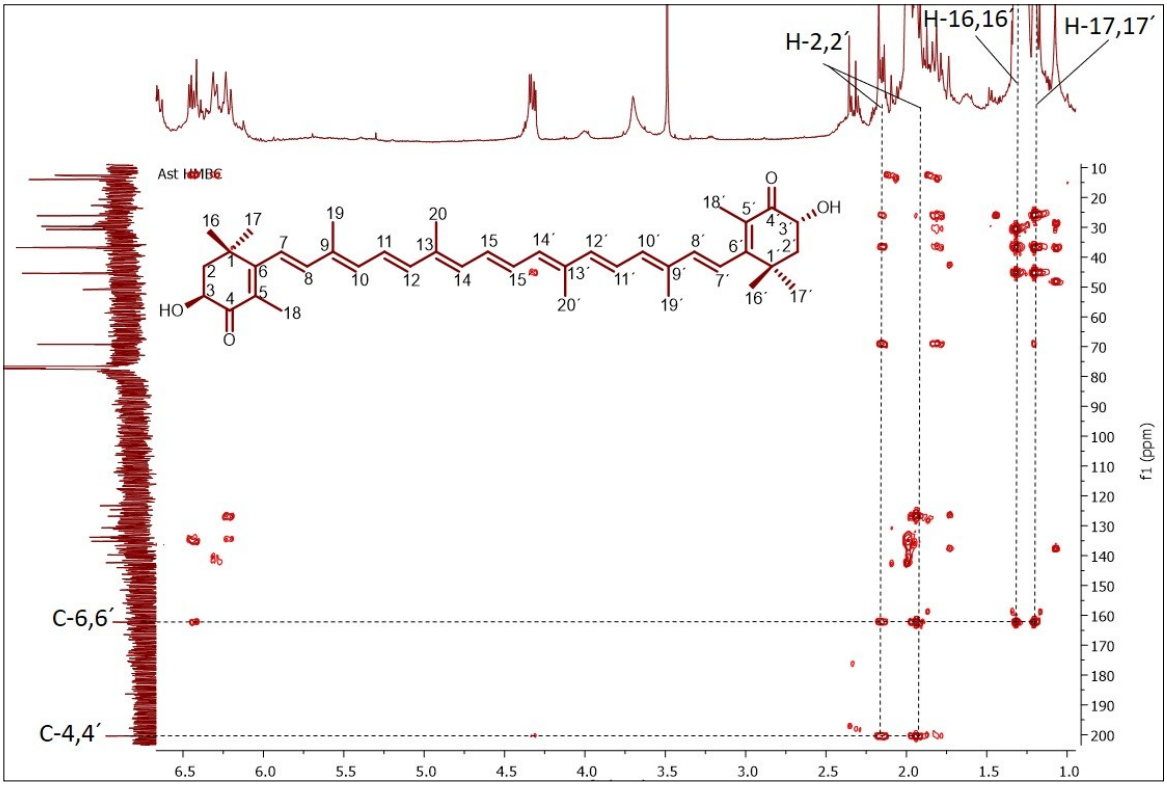

Fig. S12. HMBC of (3*R*,3´*S*)-Astaxanthin (**3**).

Table S2. NMR data of compounds **2** and **3**.

	Zeaxanthin (2)		**Astaxanthin (3)**	
Position	δ_C, type	δ_H (*J* values in Hz)	δ_C, type	δ_H (*J* values in Hz)
1 & 1´	37.1, C	–	36.8, C	–
2 & 2´	48.4, CH_2	1.77 m, 1.48 t, *J* = 12 Hz	45.4, CH_2	1.81 m, 2.17*
3 & 3´	65.1, CH	4.00 m	69.2, CH	4.33 dd, *J* = 14.0, 5.5 Hz
4 & 4´	42.6, CH_2	2.39 dd, *J* = 16.5, 5 Hz 2.04 dd, *J* = 16.5, 5 Hz	200.4, C=O	–
5 & 5´	126.2, C	–	126.8, C	–
6 & 6´	137.8, C	–	162.3, C	–
7 & 7´	125.6, CH	6.12*	123.3, CH	6.20 m
8 & 8´	138.6, CH	6.15*	142.4, CH	6.43*
9 & 9´	135.7, C	–	134.8, C	–
10 & 10´	131.3, CH	6.17 m	135.2, CH	6.31 m
11 & 11´	124.9, CH	6.64 m	124.6, CH	6.66 m
12 & 12´	137.6, CH	6.37 d, *J* = 14.5 Hz	139.7, CH	6.45 d, *J* = 7.5 Hz
13 & 13´	136.4, C	–	136.7, C	–
14 & 14´	132.6, CH	6.26 m	133.8, CH	6.29 m
15 & 15´	130.1, CH	6.62 m	130.7, CH	6.68 m
16 & 16´	28.7, CH_3	1.07 s	30.7, CH_3	1.21 s
17 & 17´	30.3, CH_3	1.07 s	26.2, CH_3	1.32 s
18 & 18´	21.6, CH_3	1.74 s	14.0, CH_3	1.94 s
19 & 19´	12.8, CH_3	1.97 s	12.6, CH_3	2.00*
20 & 20´	12.8, CH_3	1.97 s	12.8, CH_3	1.99*

* Overlapped

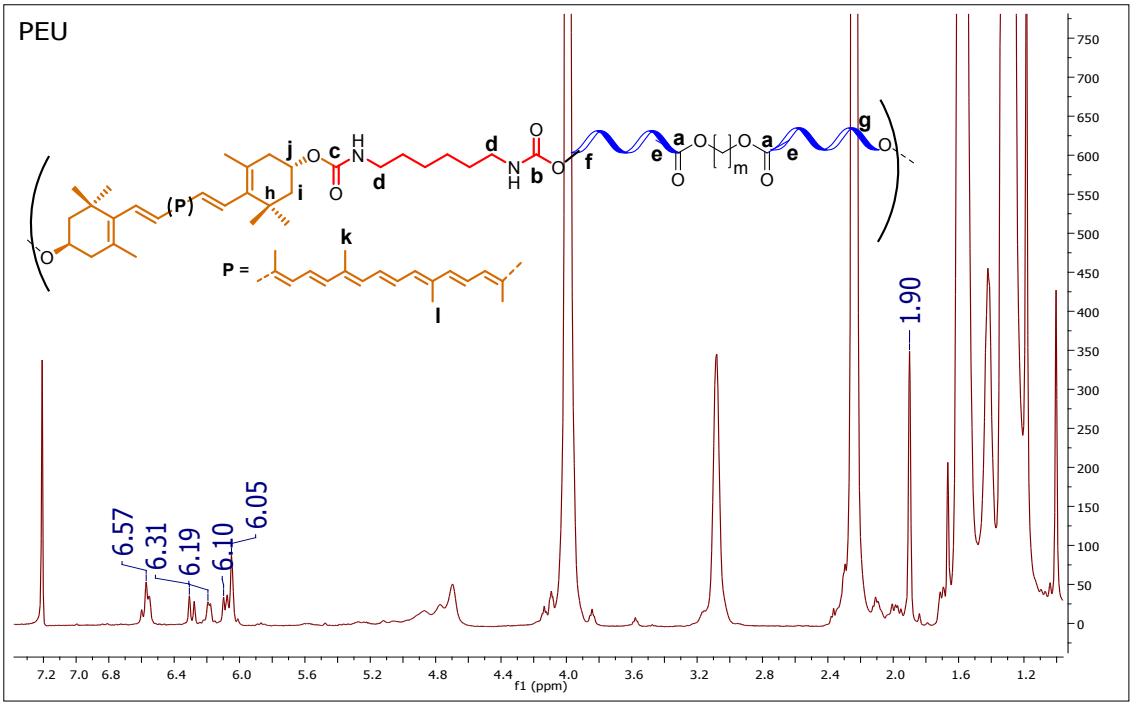

Fig. S13. ^{1}H NMR spectrum of PEU with **2** as chain extender (500 MHz, $CDCl_3$).

Photographs of PEUs synthesized using 1, 2, and 3 as chain extenders

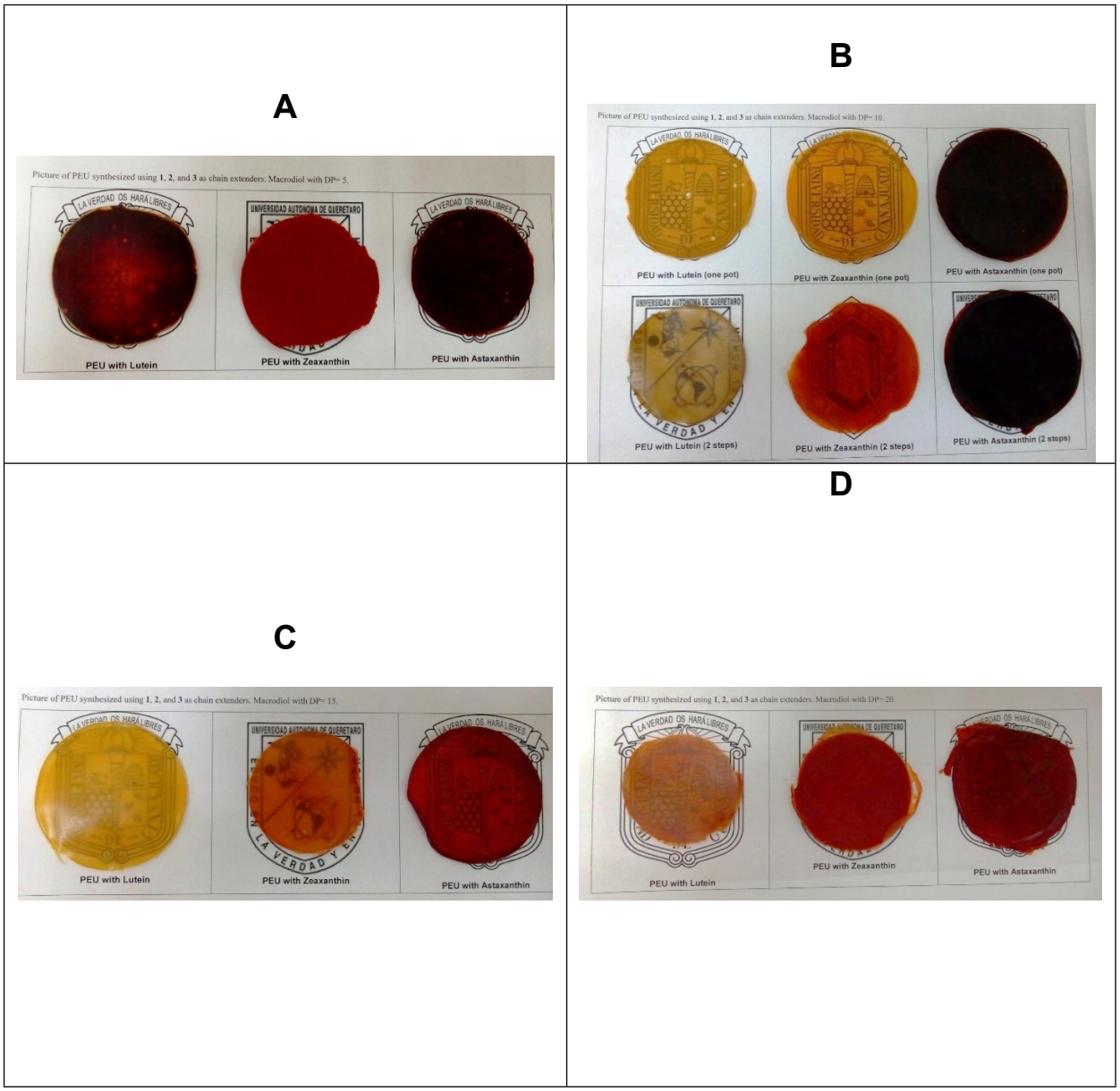

Fig. S14. Photographs of PEU synthesized using **1**, **2**, and **3** as chain extenders and macrodiol with DP = 5 (**A**), DP = 10 synthesized in a one pot way (**B up**) and synthesized in a two steps (**B down**), DP = 15 (**C**), and DP = 20 (**D**).

Thermal properties of PCL Macrodiols (HOPCLOH) and segmented poly-(ester-urethanes) (PEUs) obtained by DSC

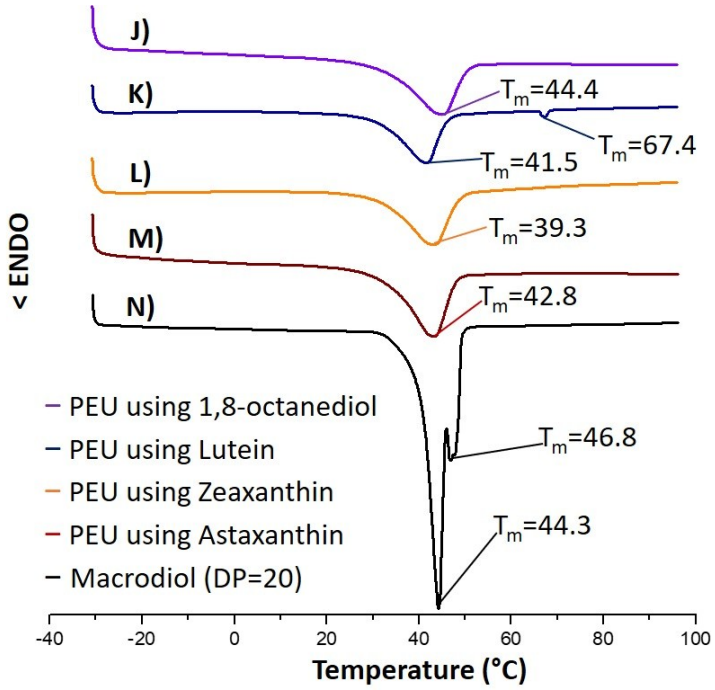

Fig. S15. DSC of PEUs derived from macrodiol with DP = 20 and the different chain extenders.

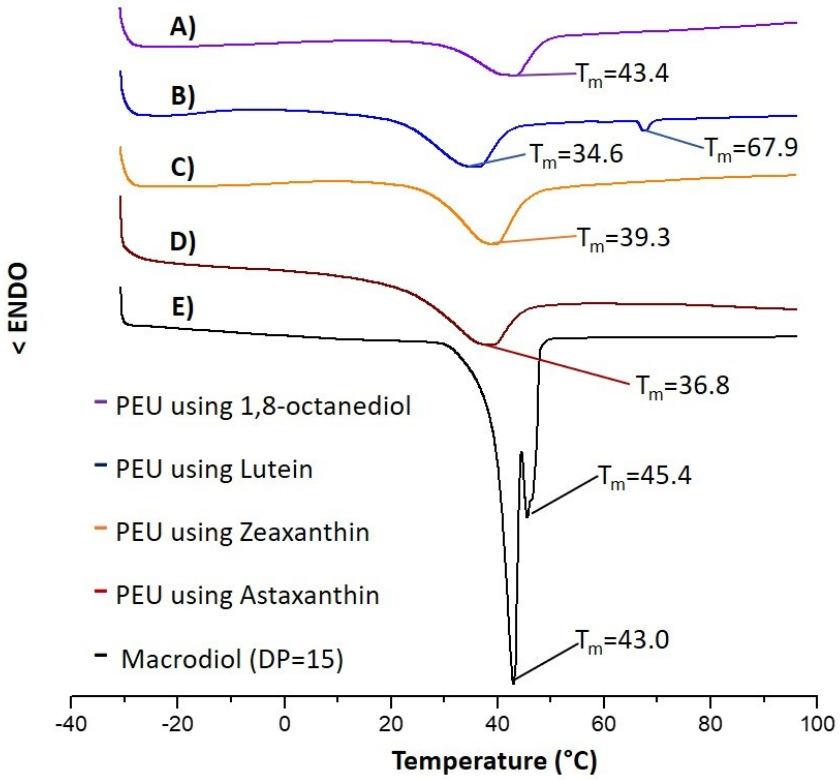

Fig. S16. DSC of PEUs derived from macrodiol with DP = 15 and the different chain extenders.

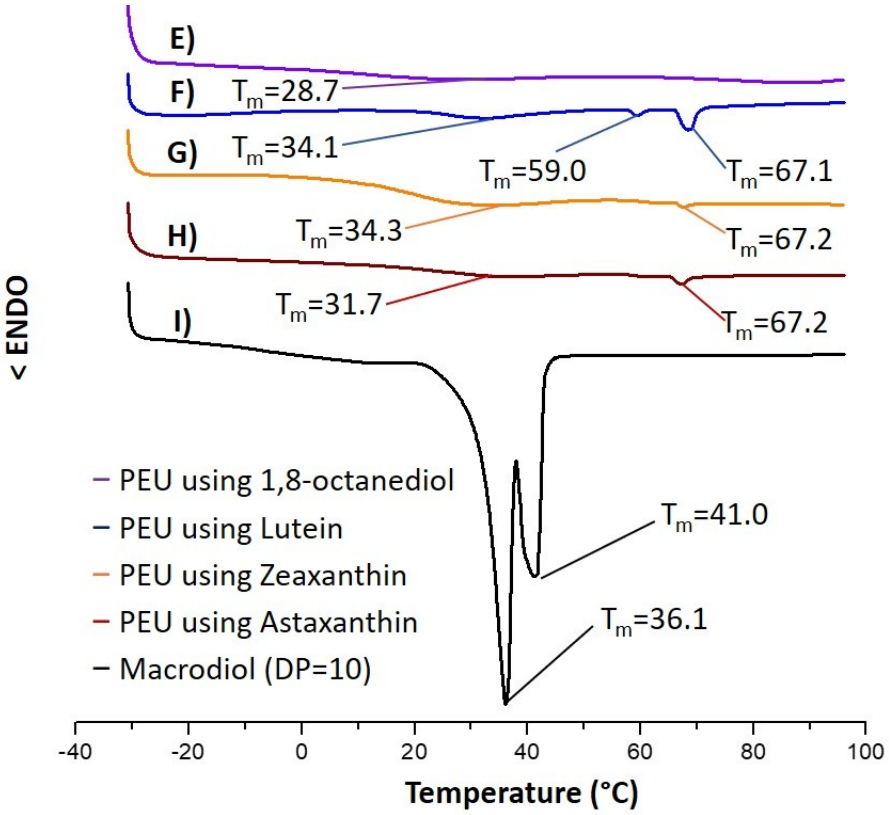

Fig. S17. DSC of PEUs derived from macrodiol with DP = 10 and the different chain extenders.

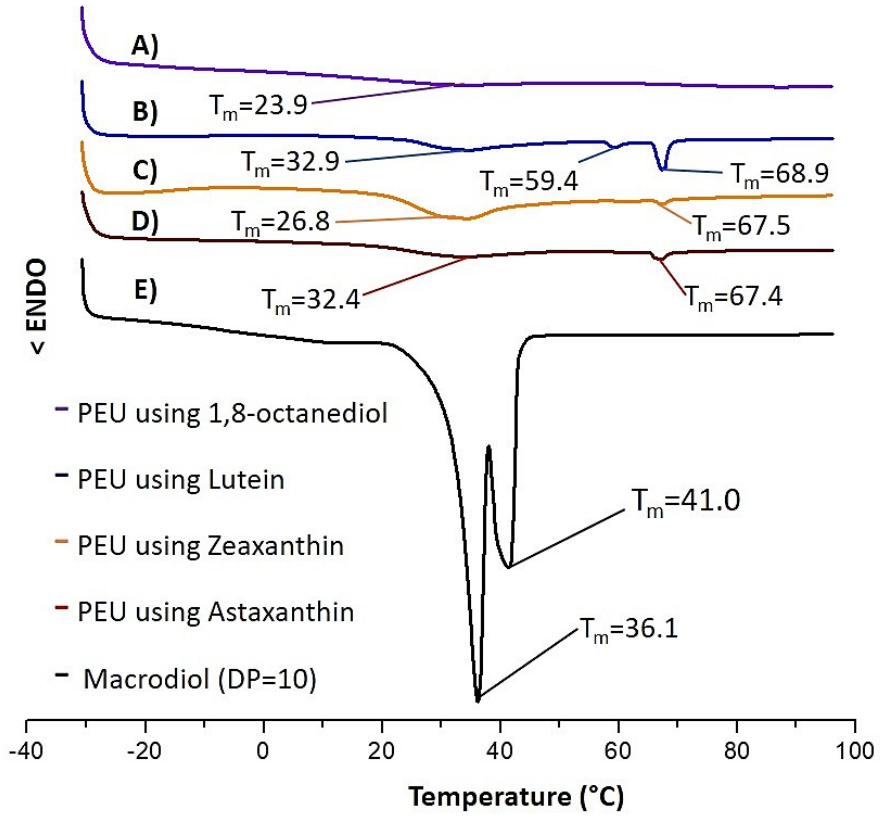

Fig. S18. DSC of PEUs synthesized in a one pot way and derived from macrodiol with DP = 10 and the different chain extenders.

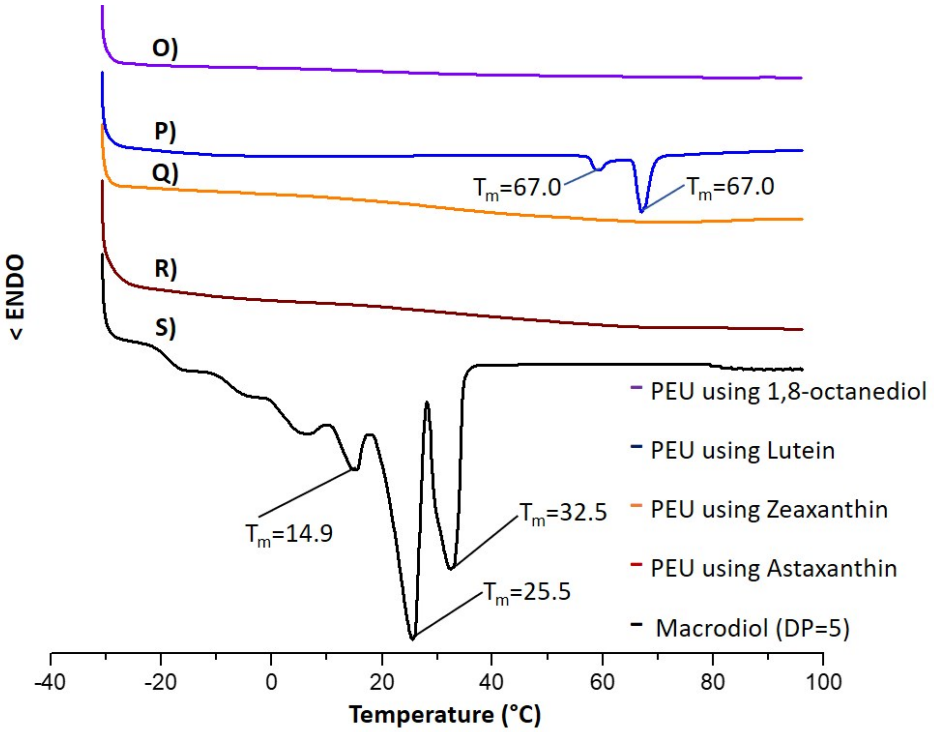

Fig. S19. DSC of PEUs derived from macrodiol with DP = 5 and the different chain extenders.

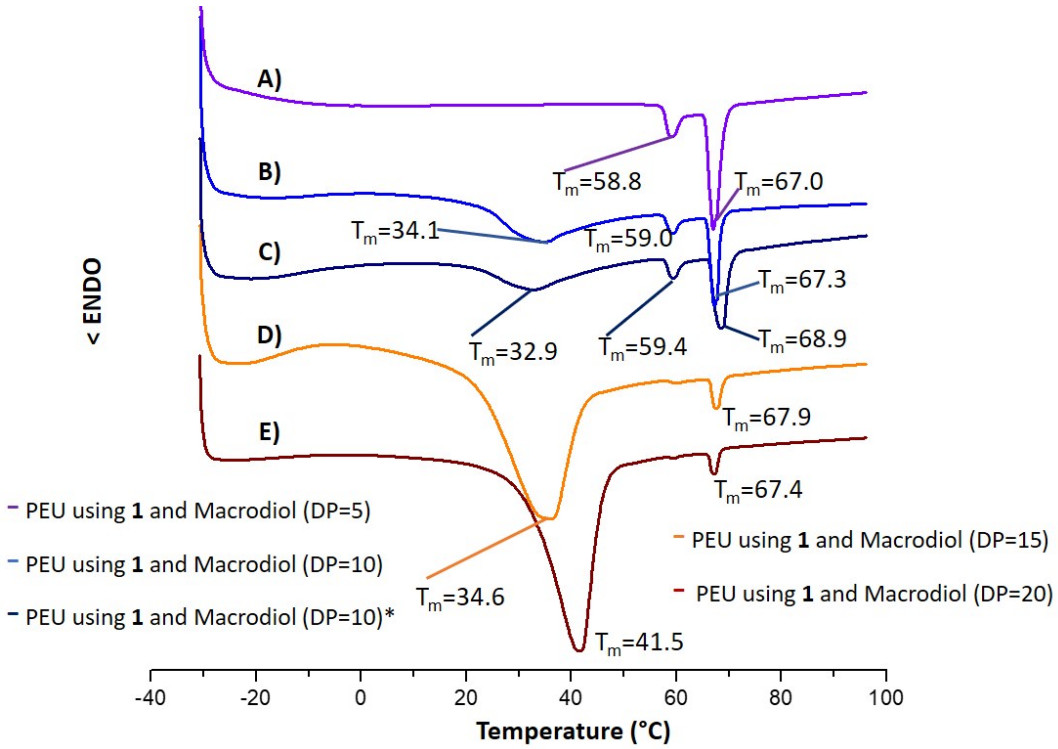

Fig. S20. DSC of PEUs derived from **1** and the different macrodiols.

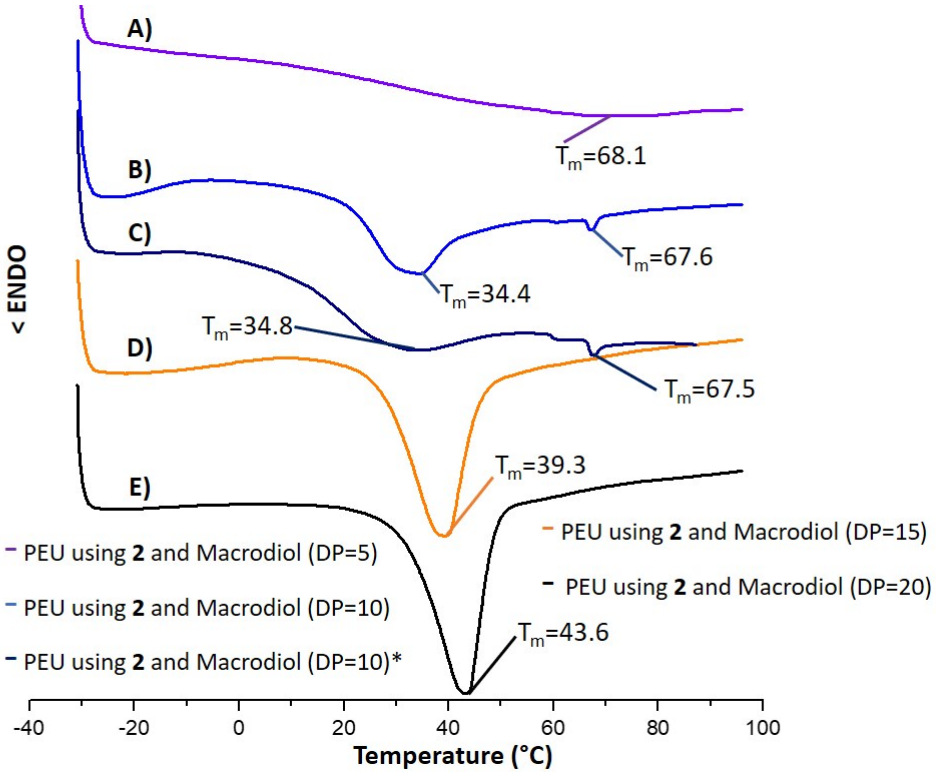

Fig. S21. DSC of PEUs derived from **2** and the different macrodiols.

Table S3. Thermal properties of macrodiols.

Macrodiol (DP)	T_m (°C)	ΔH_m (J/g)
HOPCLOH (5)	5.6, 14.9, 25.6, 32.5	108.5
HOPCLOH (10)	36.2, 41.0	89.62
HOPCLOH (15)	43.0, 45.4	92.71
HOPCLOH (20)	44.3, 46.8	91.77

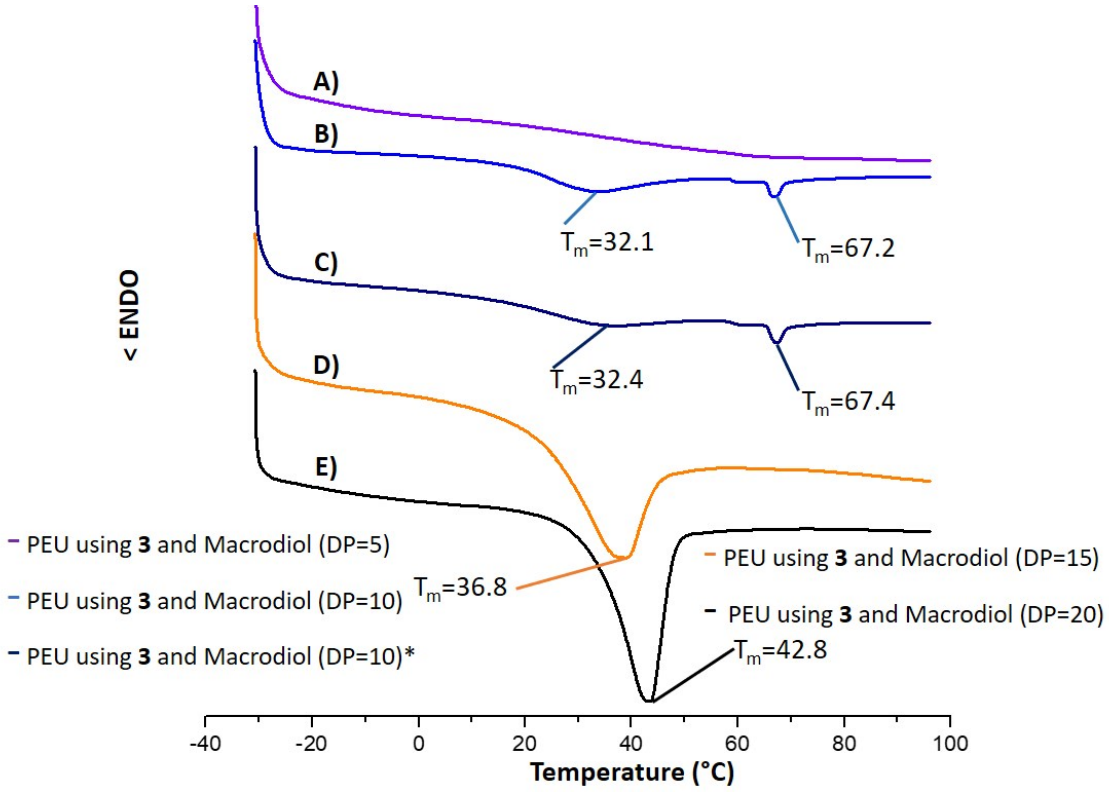

Fig. S22. DSC of PEUs derived from **3** and the different macrodiols.

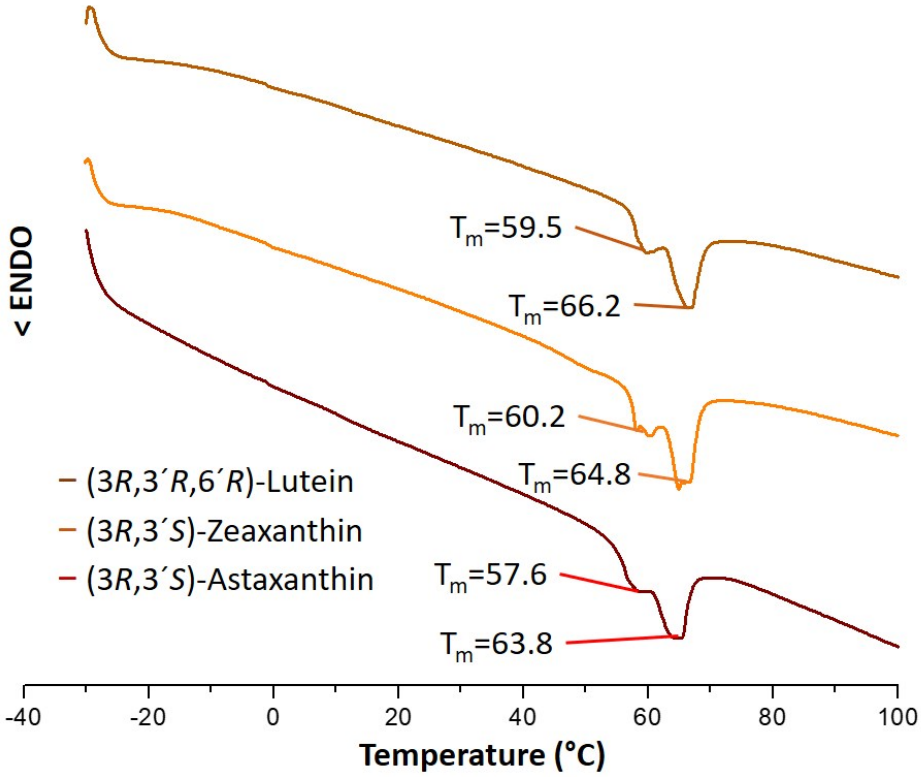

Fig. S23. DSC of the three different hard segments.

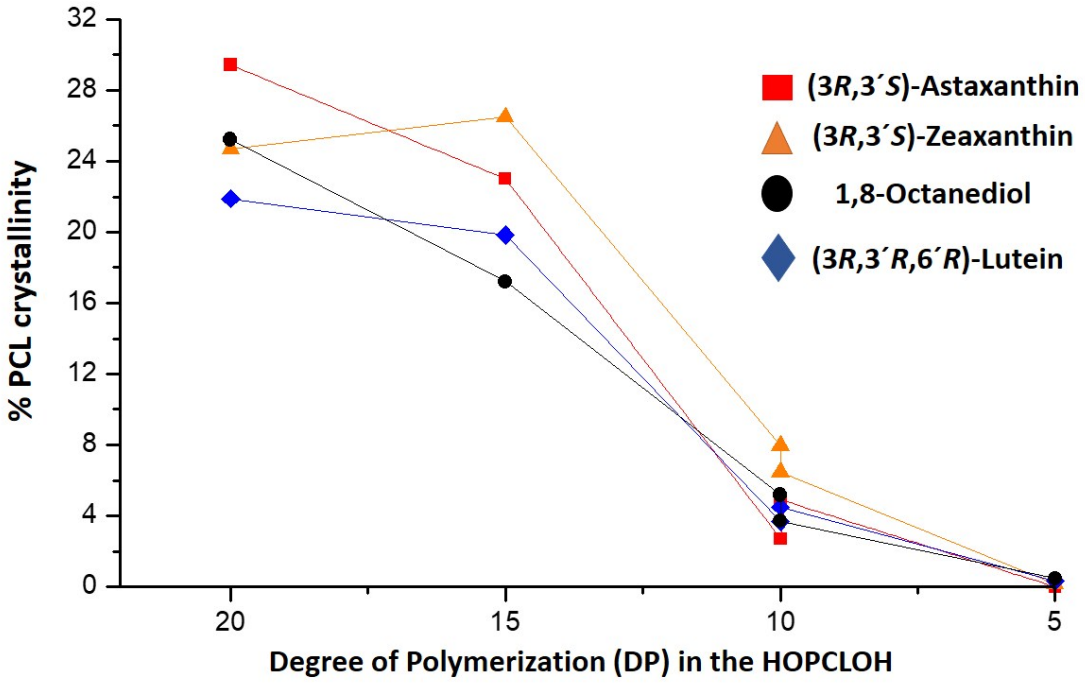

Fig. S24. Effect of HOPCLOH (DP) on the crystallinity of PCL on PEUs.

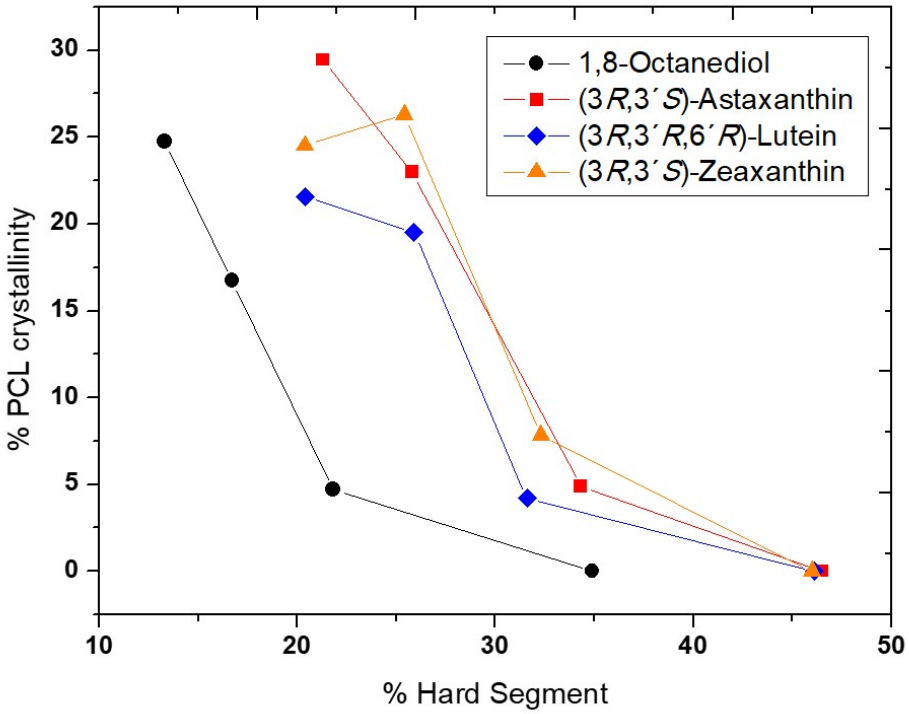

Fig. S25. Effect of HS percent on the crystallinity of PCL on PEUs.

IR spectra

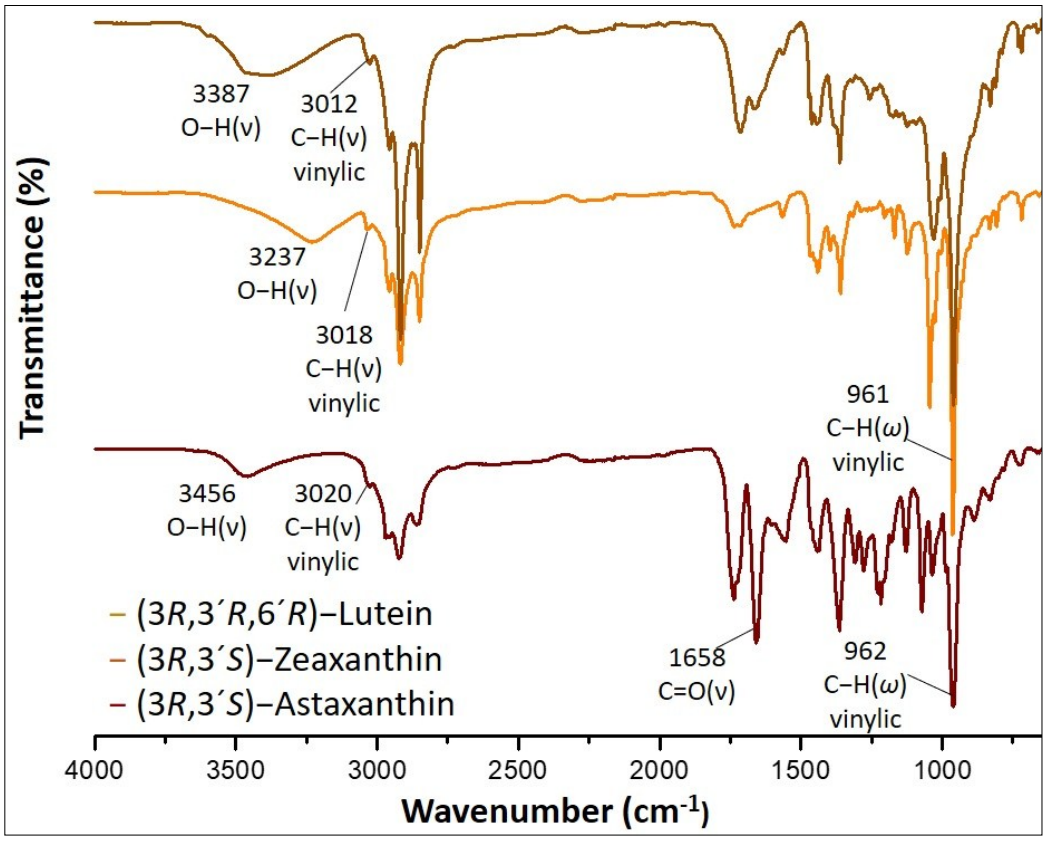

Fig. S26. FTIR spectra of the three xanthophylls.

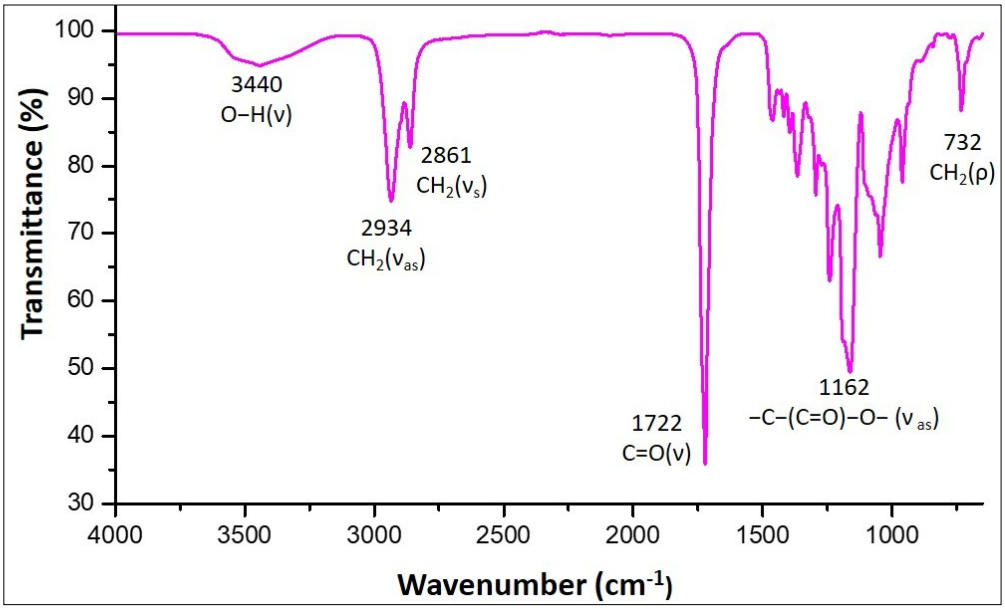

Fig. S27. FTIR spectrum of the macrodiol (HOPCLOH, DP = 5).

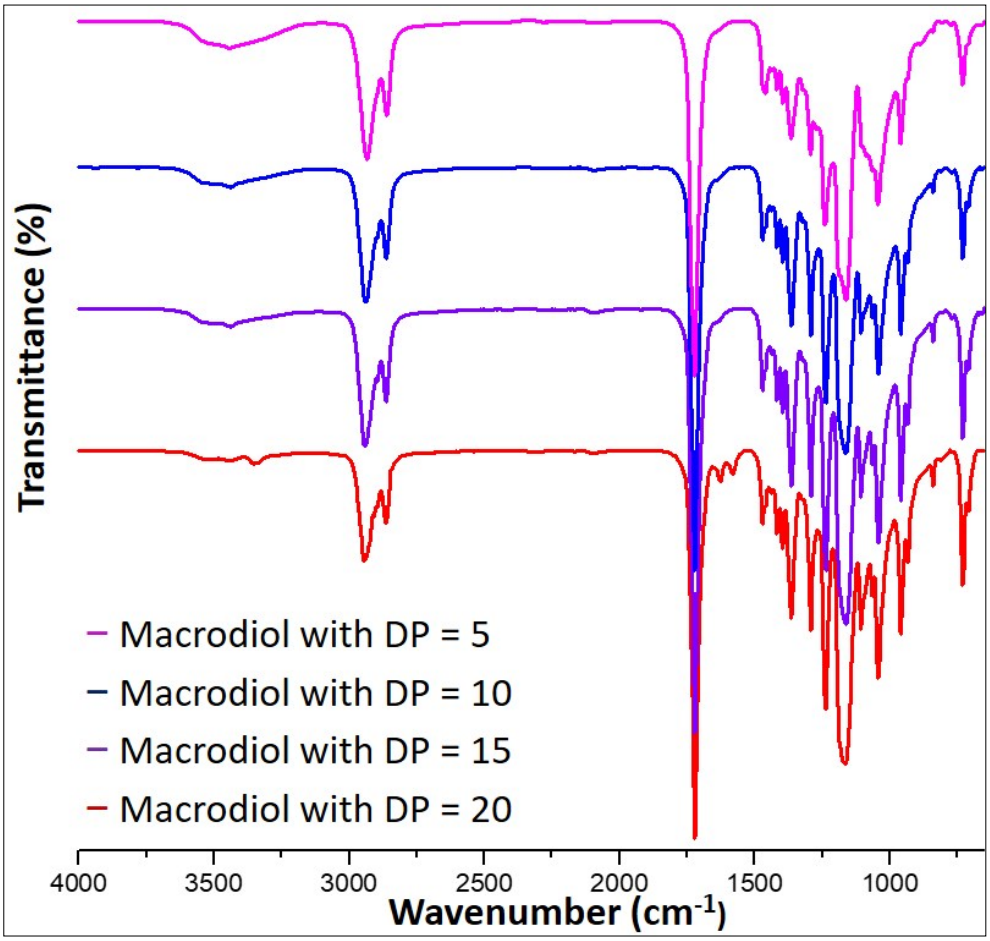

Fig. S28. FTIR spectra of the four PCL macrodiols (HOPCLOH).

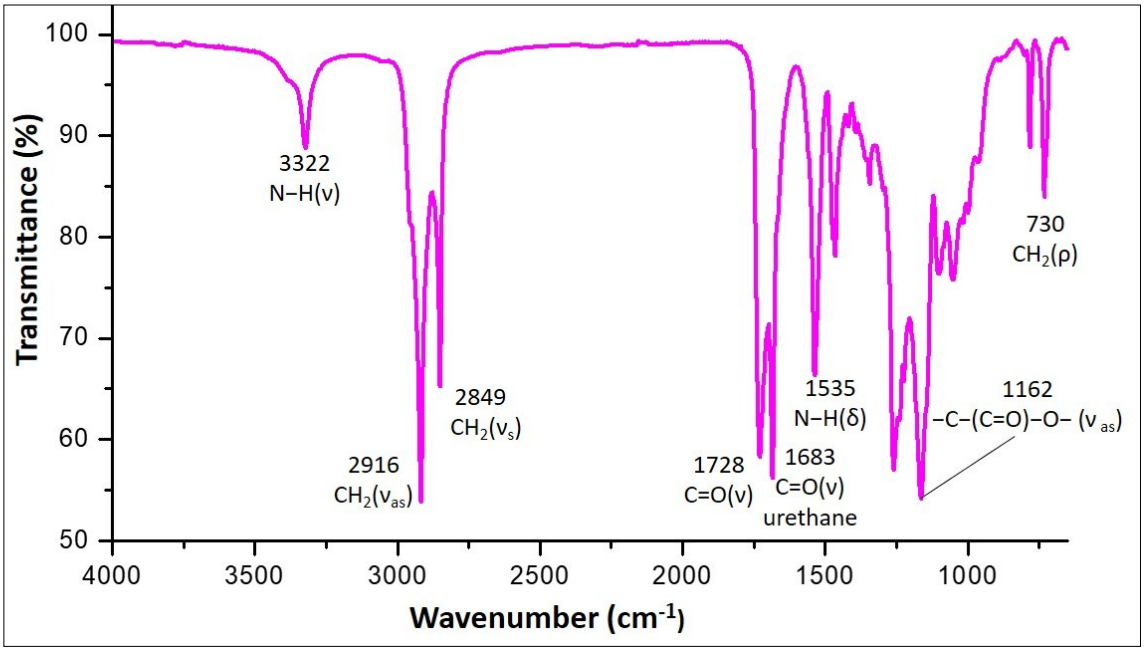

Fig. S29. FTIR spectrum of PEU synthesized from macrodiol (DP = 5) and **Oct** as chain extender.

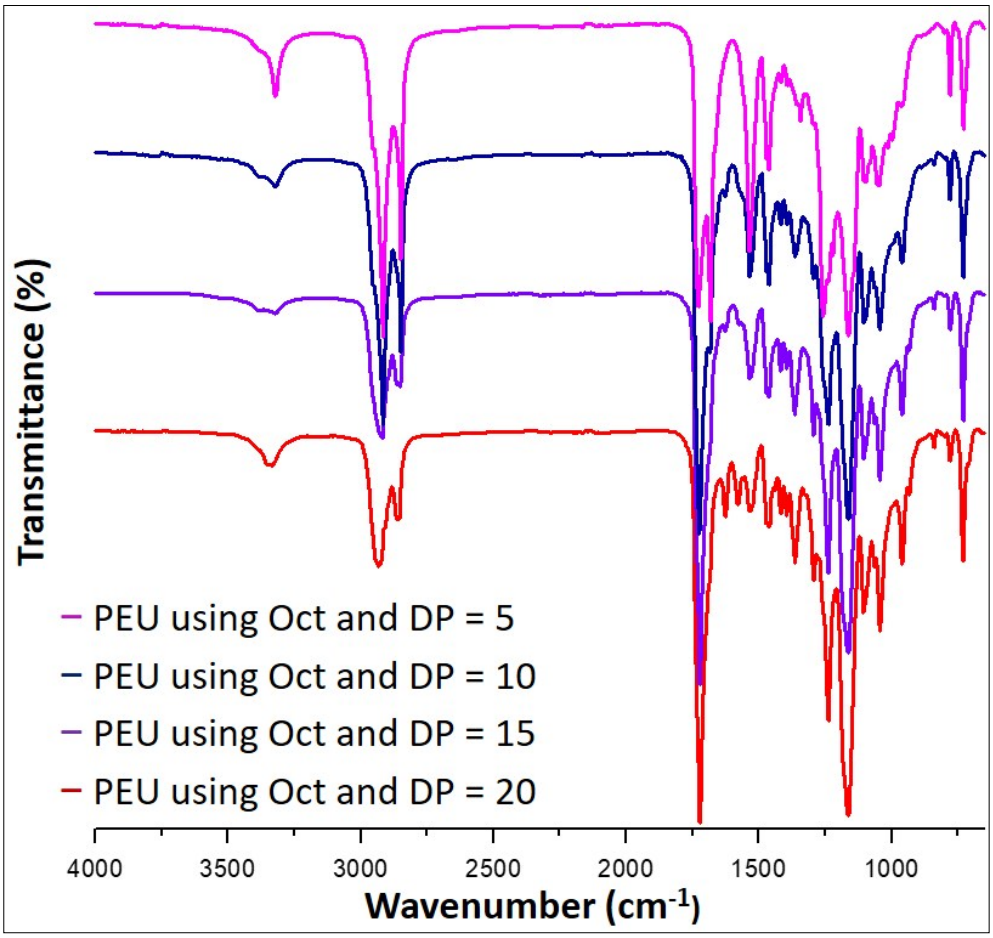

Fig. S30. FTIR spectra of PEUs synthesized from different macrodiol and **Oct** as chain extender.

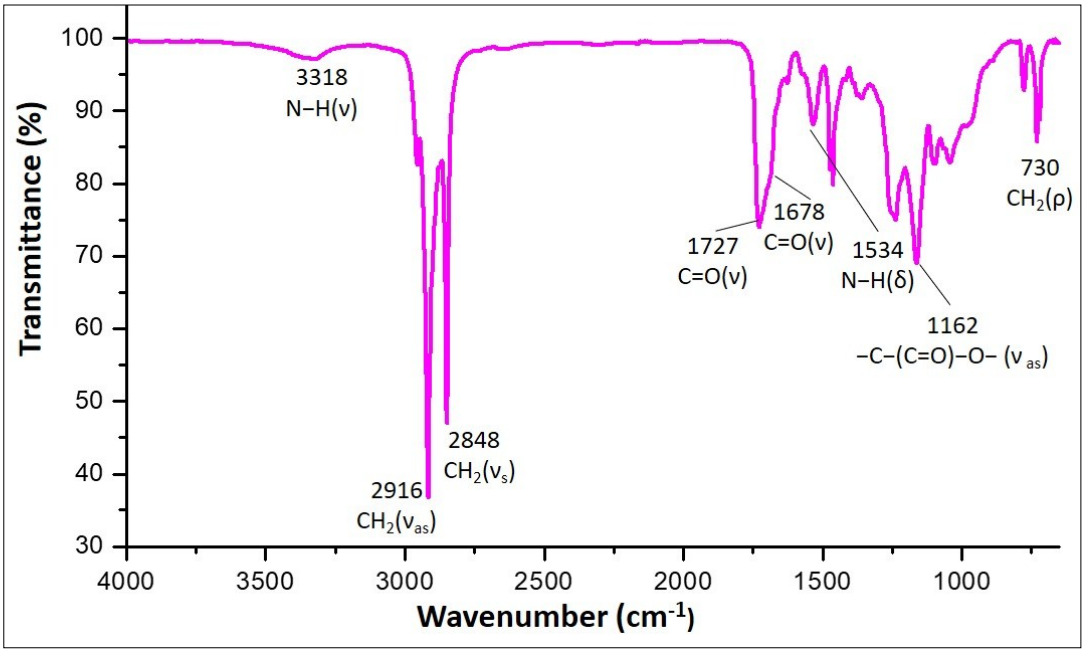

Fig. S31. FTIR spectrum of PEU synthesized from the different macrodiol (DP = 5) and **1** as chain extender.

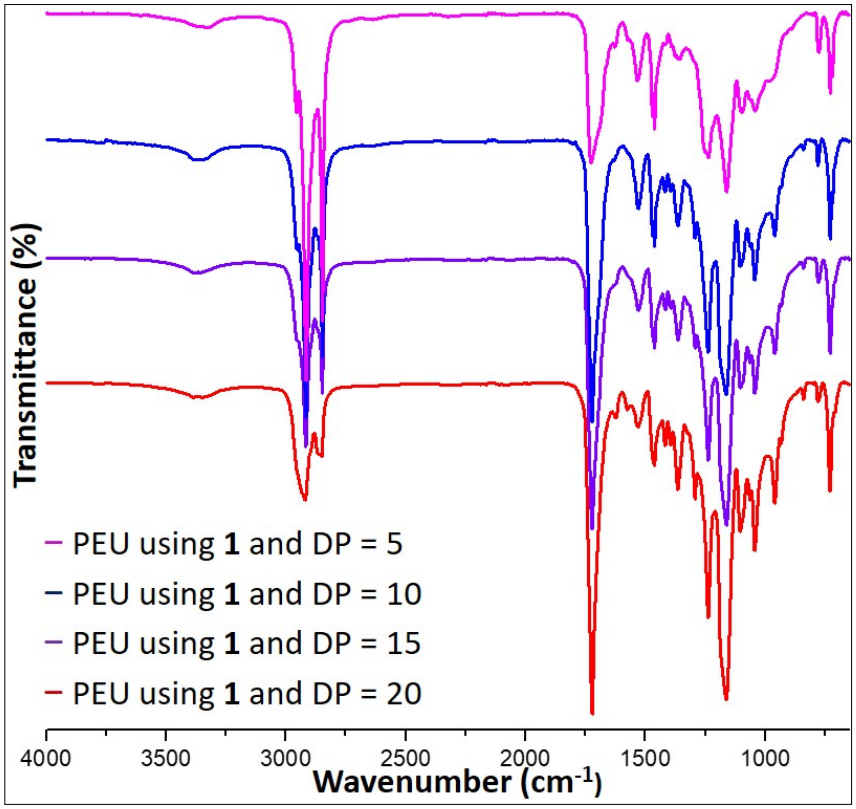

Fig. S32. FTIR spectra of PEUs synthesized from the different macrodiols and **1** as chain extender.

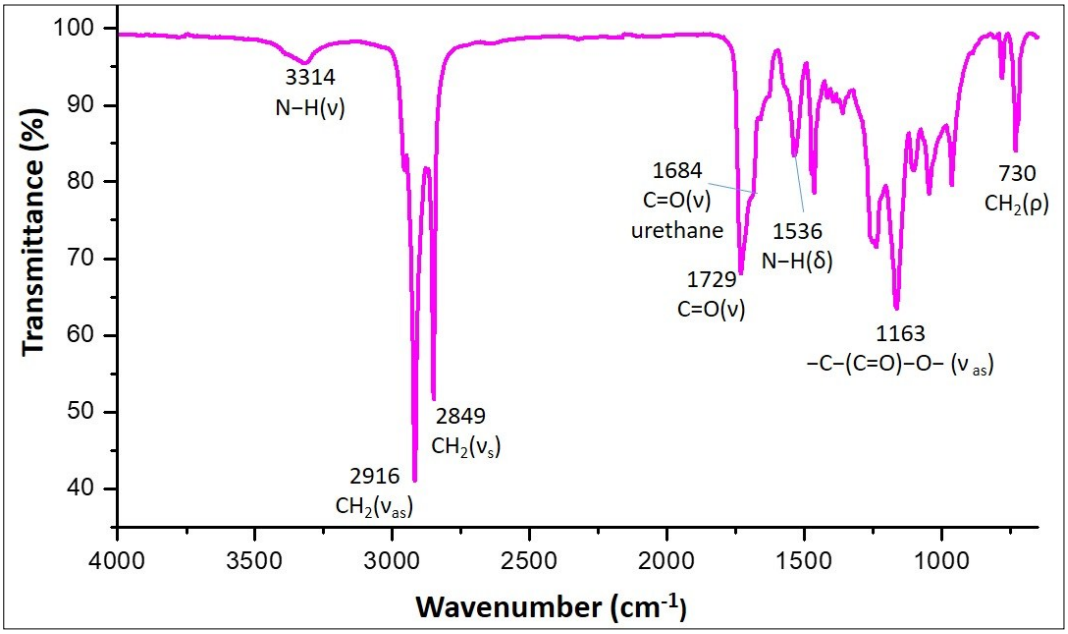

Fig. S33. FTIR spectrum of PEU synthesized from the different macrodiol (DP = 5) and **2** as chain extender.

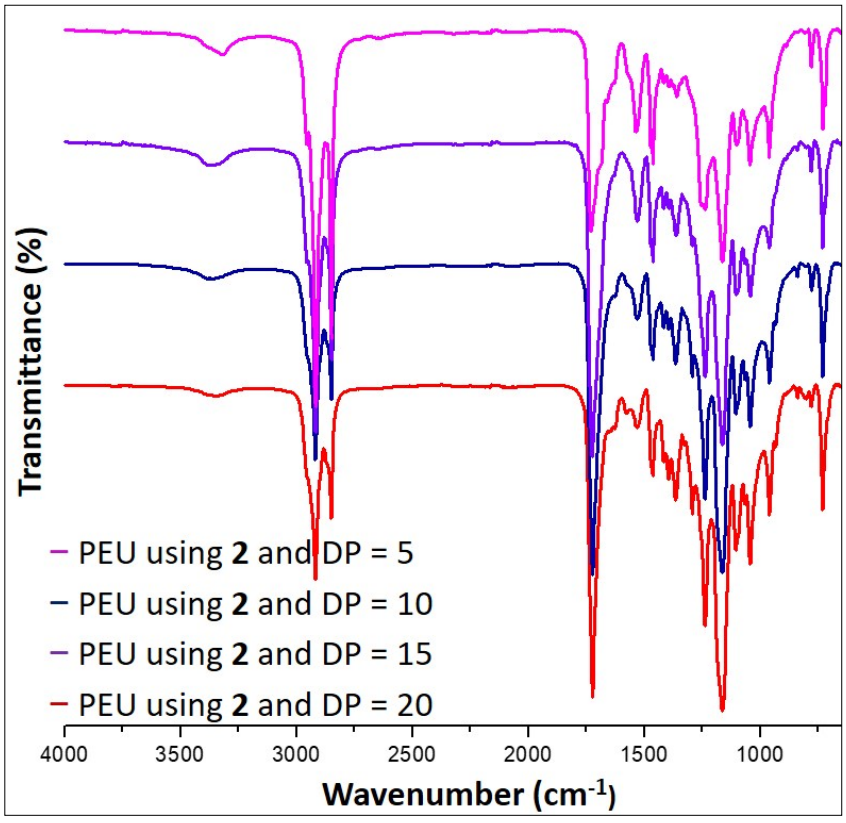

Fig. S34. FTIR spectra of PEUs synthesized from the different macrodiols and **2** as chain extender.

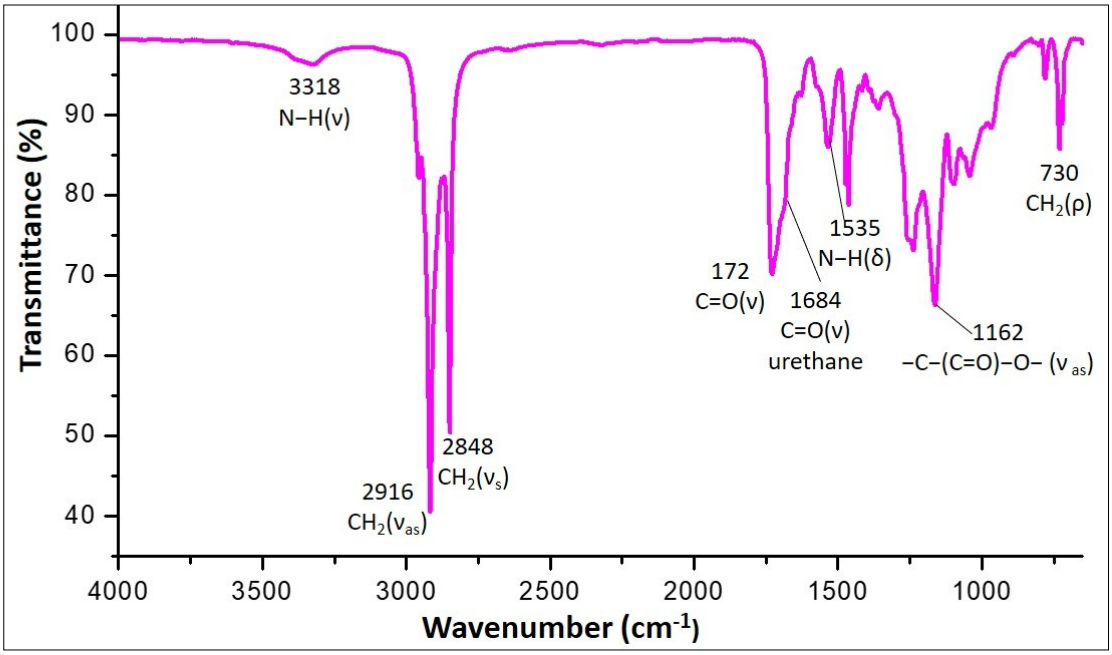

Fig. S35. FTIR spectrum of PEU synthesized from the different macrodiol (DP = 5) and **3** as chain extender.

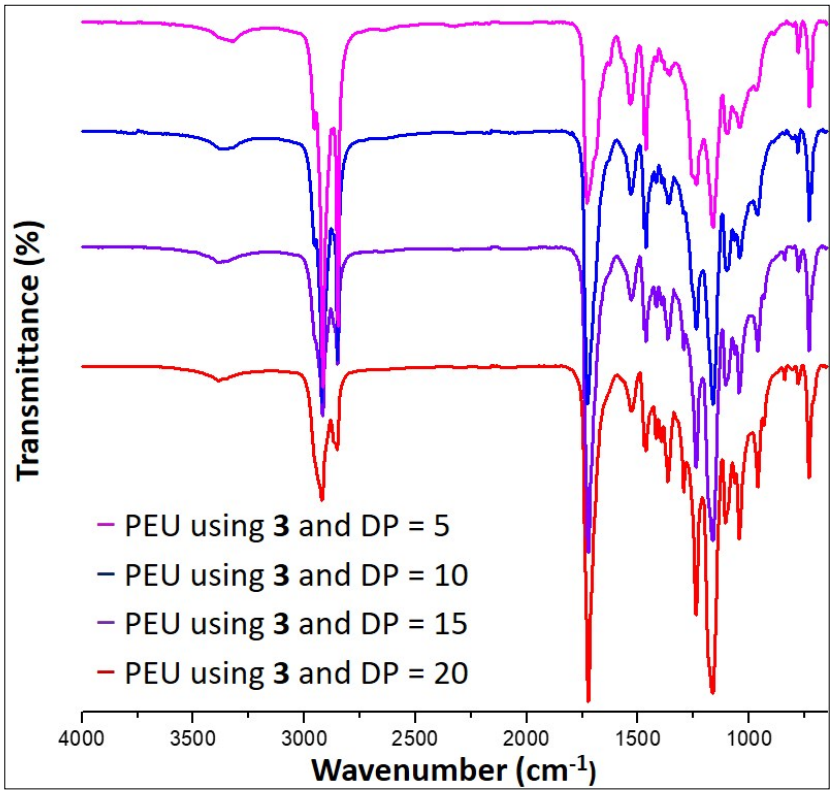

Fig. S36. FTIR spectra of PEUs synthesized from the different macrodiols and **3** as chain extender.

Mechanical properties

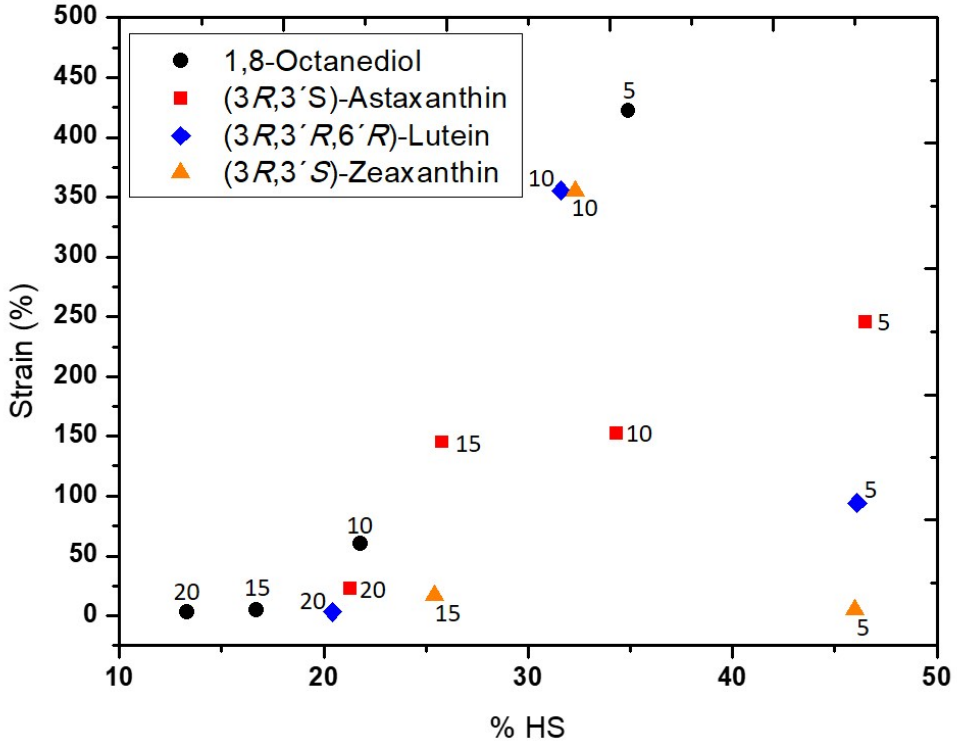

Fig. S37. Effect of HS content on the strain at break.

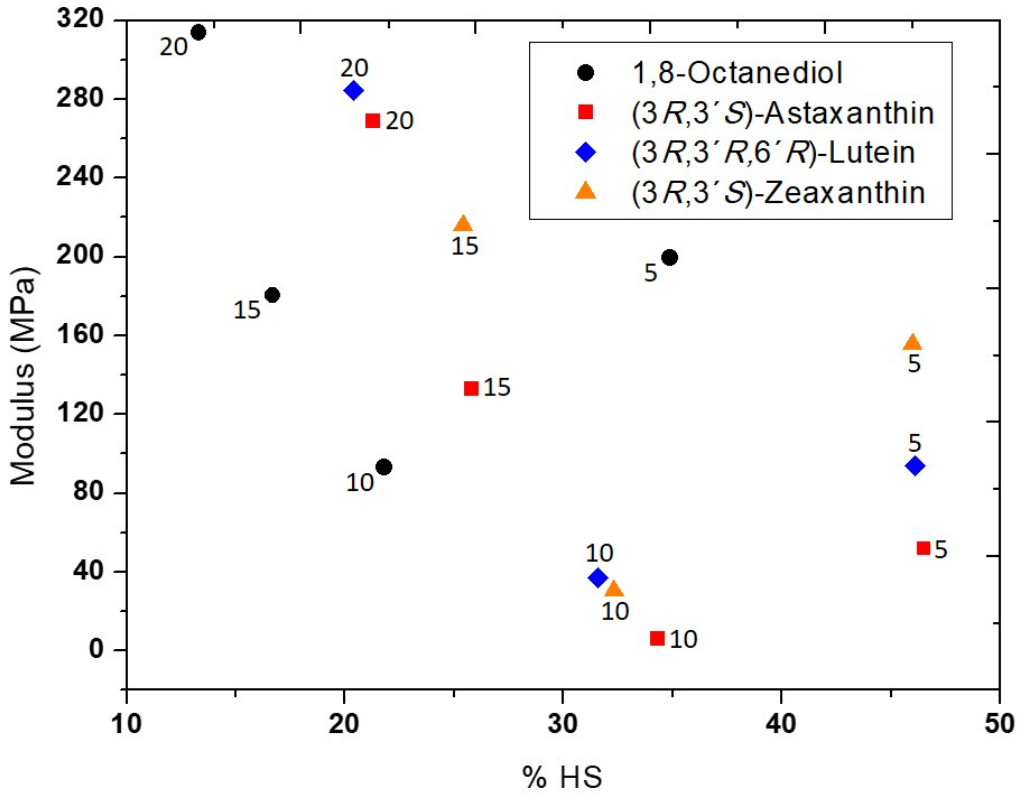

Fig. S38. Effect of HS content on the modulus.

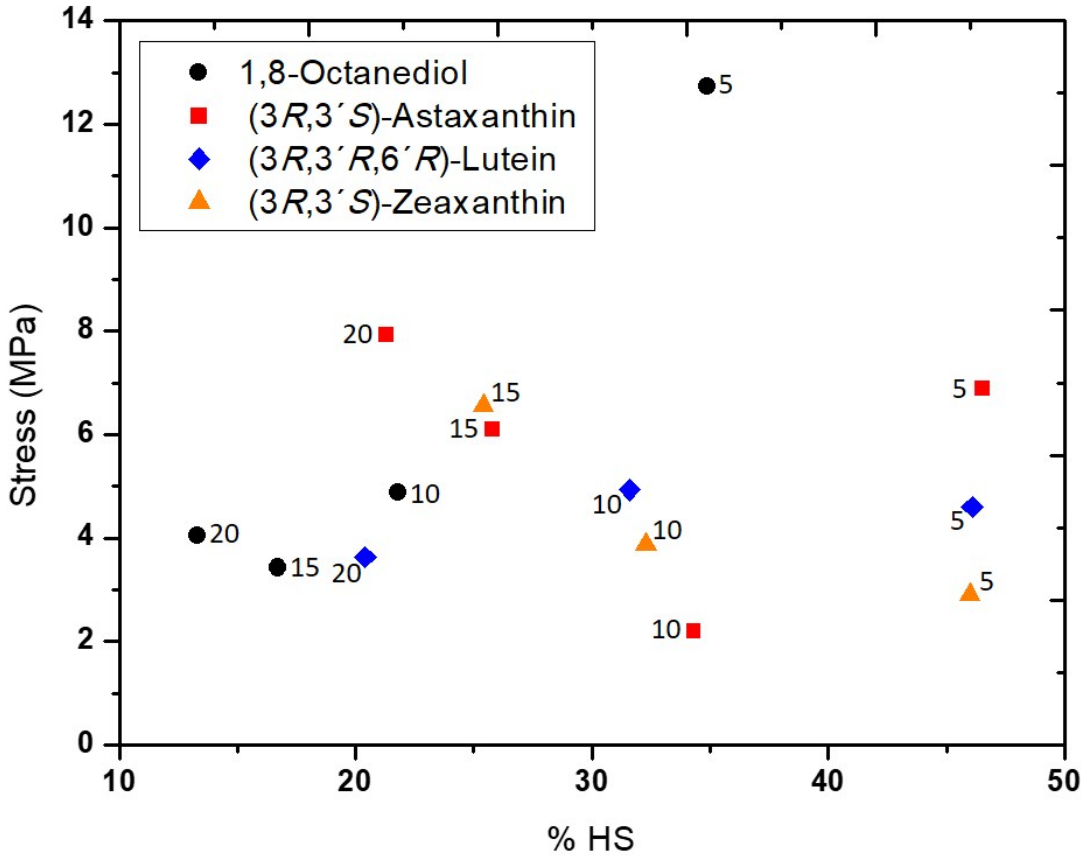

Fig. S39. Effect of HS content on the stress at break.

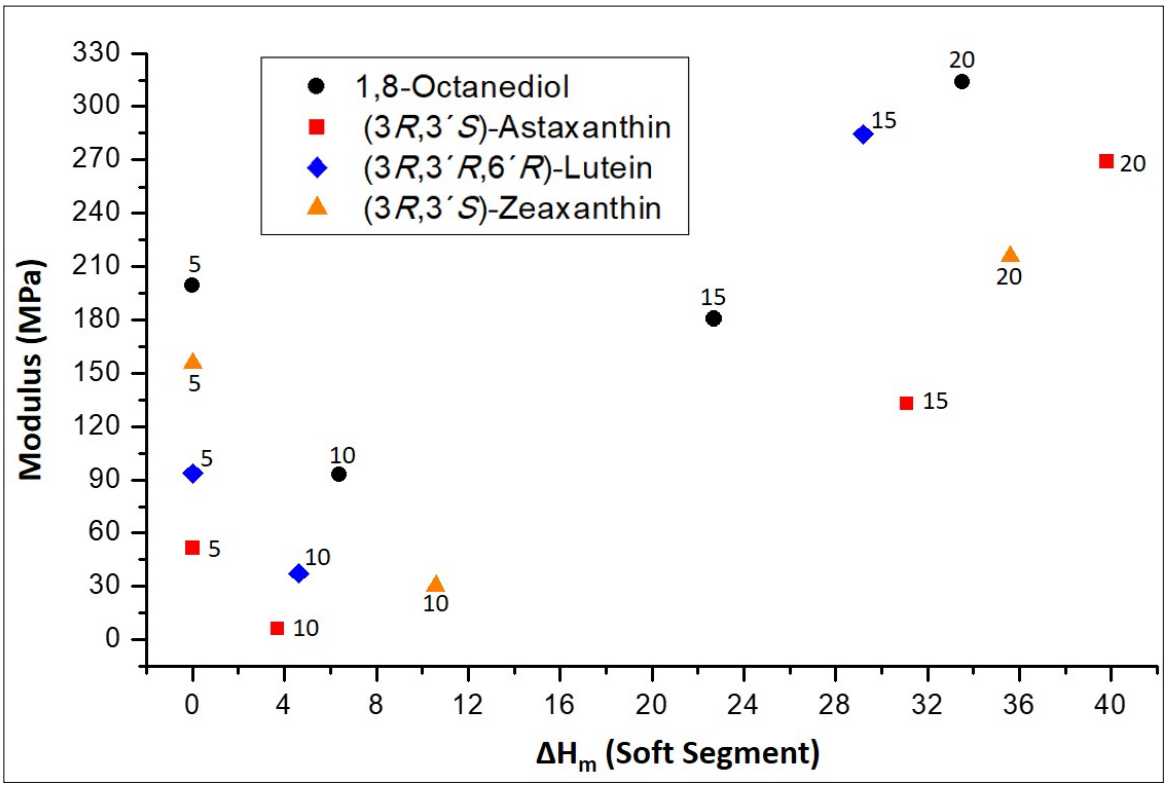

Fig. S40. Effect of the enthalpy of fusion (ΔH_m) of SS on the Modulus.