

*Electronic Supplementary Information*

# **Porous polycaprolactone and polycarbonate poly(urethane urea)s via emulsion templating: Structures, properties, cell growth**

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**Dedicated to Prof. Yusuf Yagci in honour of his 70th birthday and in recognition of the light that he has shone on macromolecularly complex porous polymer systems.**

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## 1. Synthesis of Reference Polymers

Table S1 lists the recipes for the six reference polymers, four based on one of the four different polyols, one based on the reaction between water and HDI, and one based on the reaction between PGPR and HDI. The recipes for the polyol-containing polymers maintain a stoichiometric 1/1 ratio of polyol hydroxyl groups to isocyanate groups.

Table S1. Recipes of the reference polymers.

Amount, wt %	L2-R	L3-R	C5-R	C10-R	W-R	PGPR-R
HDI	16.9	26.2	17.7	9.7	60.3	15.5
Polyol	53.0	46.8	52.5	57.9	---	---
H <sub>2</sub> O	---	---	---	---	6.5	---
PGPR	---	---	---	---	---	54.4
DBTDL	3.5	3.6	3.5	3.4	3.0	3.5
Toluene	26.6	23.4	26.3	29.0	30.2	26.6

## 2. Results

The FTIR spectra of the polyols, of PGPR, of the reference polymers, and of the polyHIPEs are compared for each system (as applicable) in Figure S1. The first and second heat DSC thermograms from the polyHIPEs and from the reference polymers are compared in Figure S2. The DMTA  $E'$ ,  $E''$ , and  $\tan \delta$  curves are presented for the polyHIPEs in Figure S3 and for the reference polymers in Figure S4. The transition temperatures from the DSC and DMTA results in Figure S2, Figure S3, and Figure S4 are listed in Table S2.

## 2.1 Macromolecular Structures

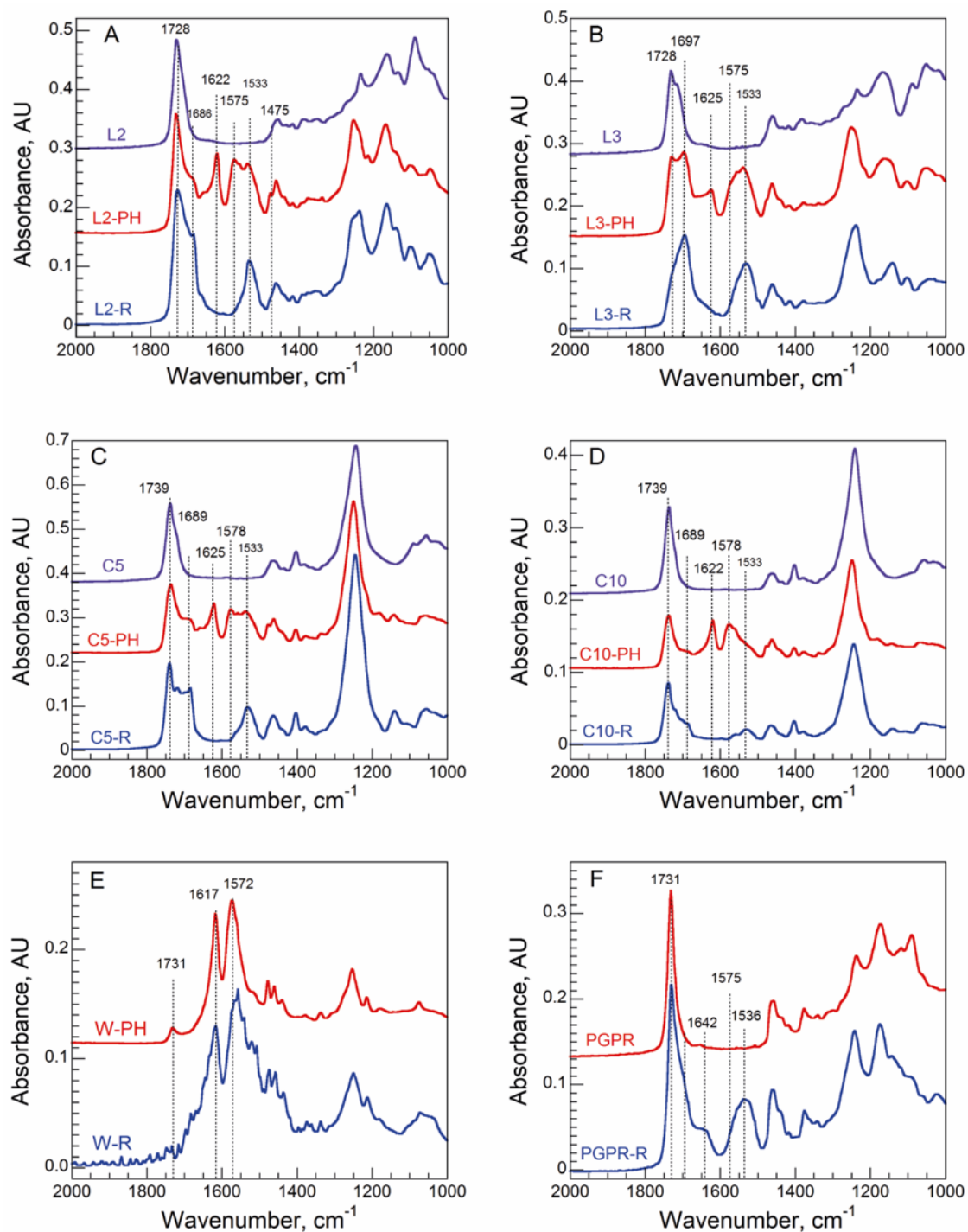


Figure S1. Sets of FTIR spectra. (A-D) The polyols, the PUU polyHIEPs, and the reference PURs: (A) L2; (B) L3; (C) C5; (D) C10. (E) W-PH and W-R. (F) PGPR and PGPR-R.

## 2.2 Thermal Behavior

### 2.2.1 Differential Scanning Calorimetry

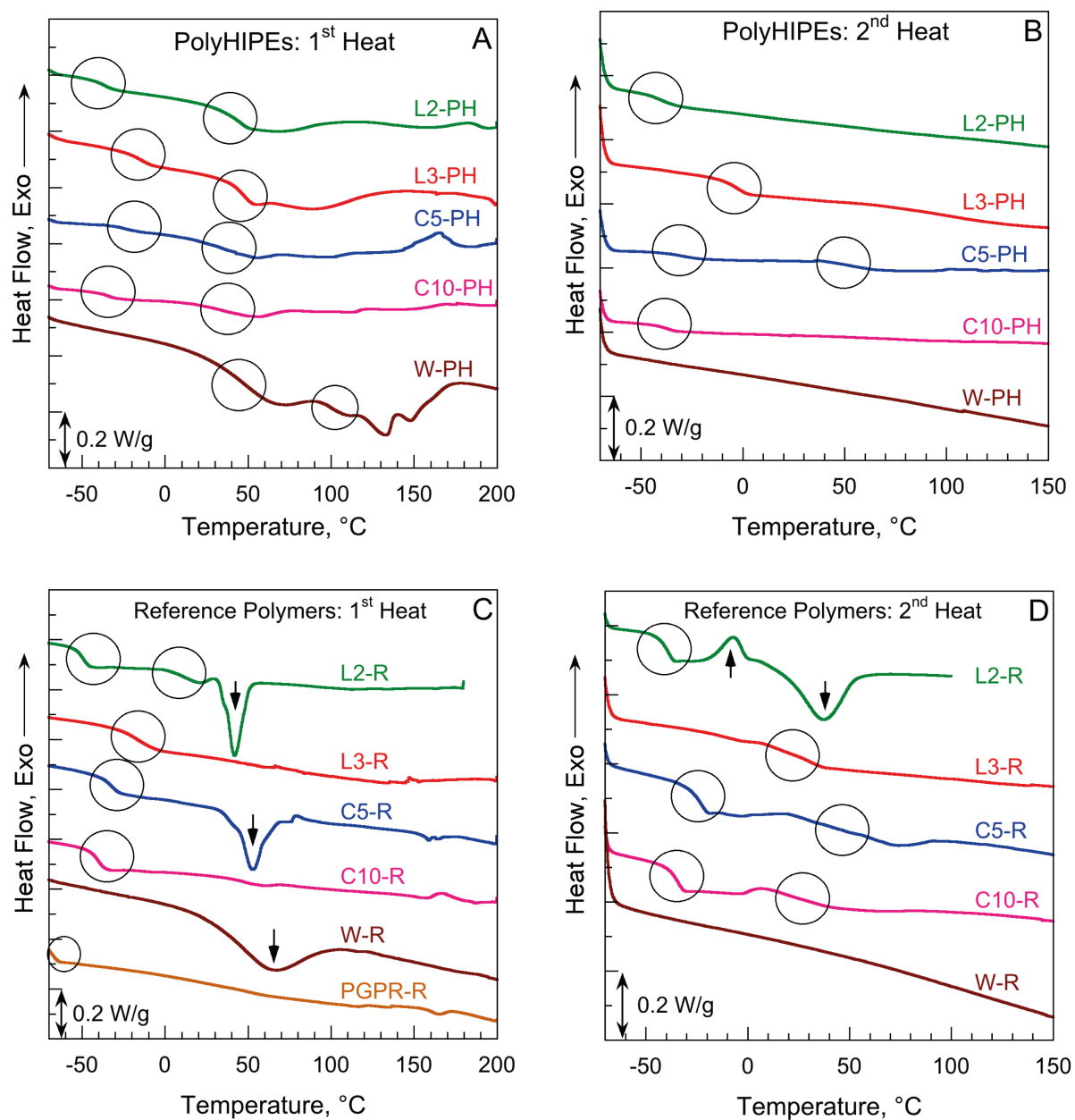


Figure S2. Sets of DSC thermograms: (A) the polyHIPEs, first-heat; (B) the polyHIPEs, second-heat; (C) the reference polymers, first-heat; (D) the reference polymers, second-heat.

## 2.2.2 Dynamic Mechanical Thermal Analysis

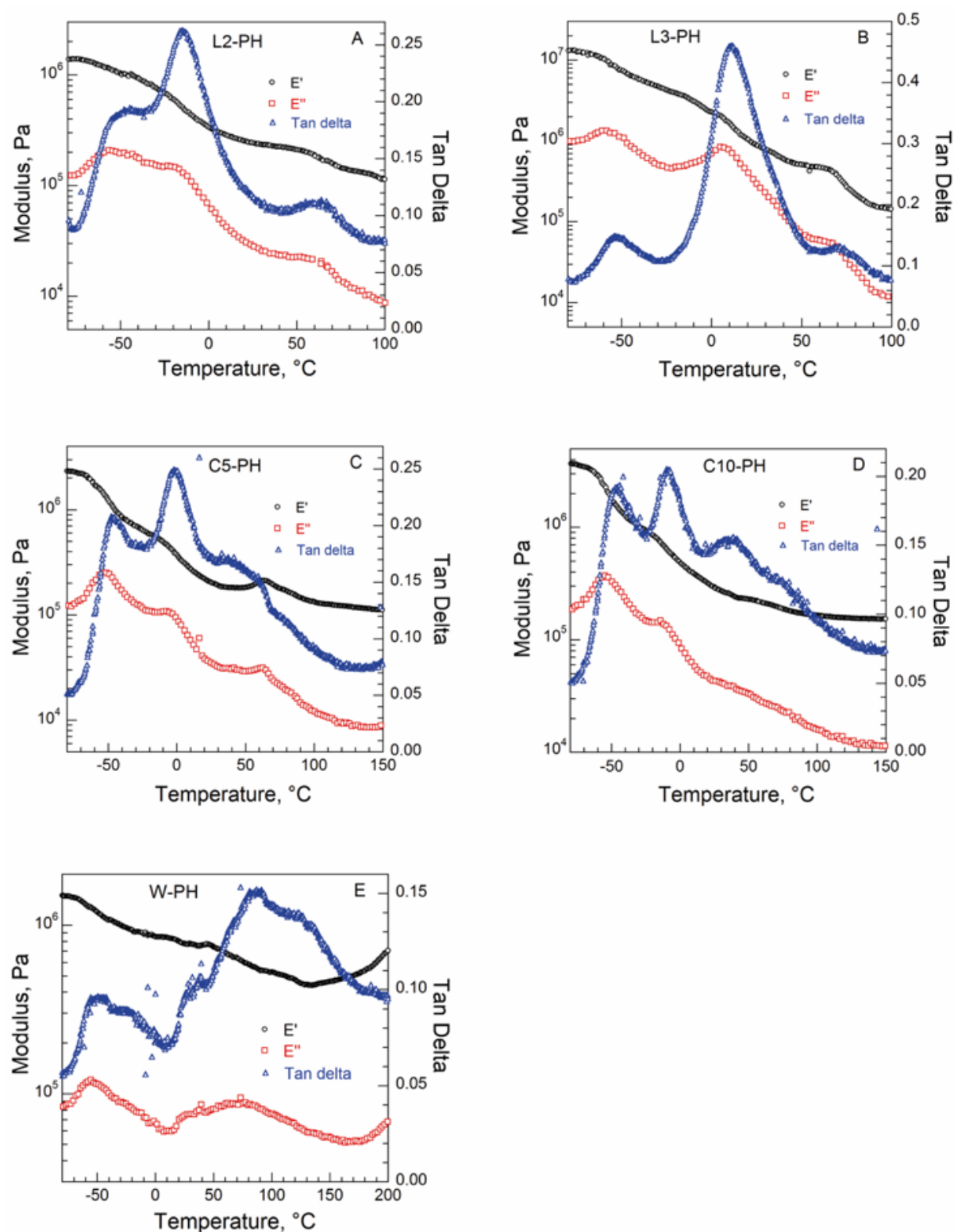


Figure S3. Sets of DMTA  $E'$ ,  $E''$ , and  $\tan \delta$  curves: (A) L2-PH; (B) L3-PH; (C) C5-PH; (D) C10-PH; (E) W-PH.

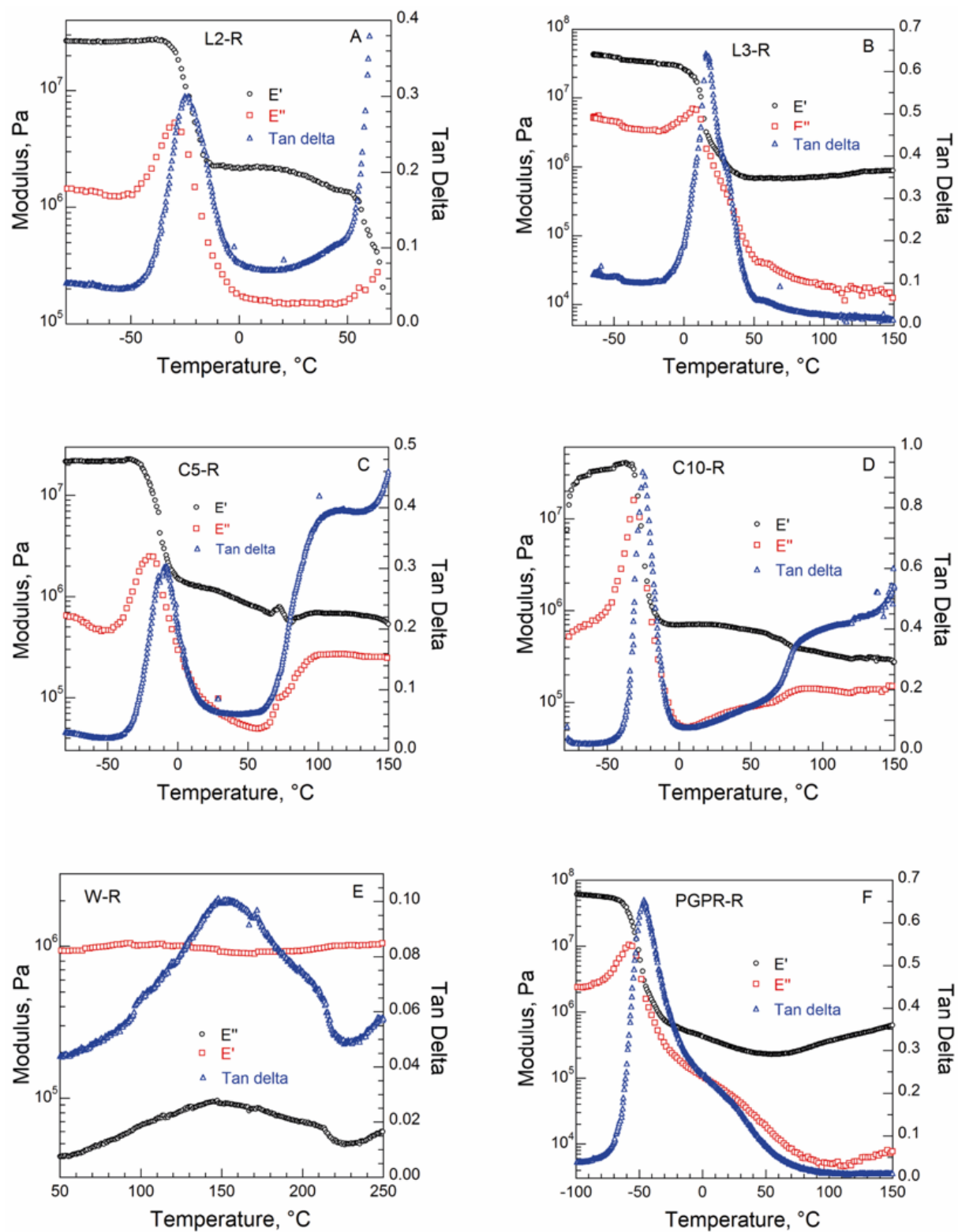


Figure S4. Sets of DMTA  $E'$ ,  $E''$ , and  $\tan \delta$  curves: (A) L2-R; (B) L3-R; (C) C5-R; (D) C10-R; (E) W-R; (F) PGPR-R.

### 2.2.3 Thermal Transitions

Table S2. Thermal transitions in the polyHIPEs and in the reference polymers: DSC glass transitions, DSC melting peaks, and DMTA tan  $\delta$  peaks.

Polymer	DSC: 1 <sup>st</sup> Heat, °C	DSC: 2 <sup>nd</sup> Heat, °C	DMTA, °C
L2-PH	$T_g$ : -38, 43, 136	$T_g$ : -40	Major: -15; Minor: 63
L2-R	$T_g$ : -50, 11; $T_m$ : 41	$T_g$ : -40; $T_m$ : 36	Major: -24; $T_m$ : 60
L3-PH	$T_g$ : -15, 47, 74	$T_g$ : -3	Major: 11; Minor: 71
L3-R	$T_g$ : -16	$T_g$ : 22	Major: 17
C5-PH	$T_g$ : -23, 34	$T_g$ : -33, 50	Major: -2; Minor: 39, 72
C5-R	$T_g$ : -33; $T_m$ : 52	$T_g$ : -24, 45; $T_m$ : 72	Major: -10; $T_m$ : 105
C10-PH	$T_g$ : -38, 34	$T_g$ : -39	Major: -9; Minor: 36, 70
C10-R	$T_g$ : -41, 45; $T_m$ : NA	$T_g$ : -35, 25; $T_m$ : 46	Major: -26; Minor: 83
W-PH	$T_g$ : 47, 101; Endotherm: 133, 148	$T_g$ : NA; Endotherms: NA	Major: 95; Minor: -25, 36, 123, 133
W-R	$T_g$ : 46	$T_g$ : NA	Major: 152; Minor: 102, 170, 200
PGPR-R	$T_g$ : -70		Major: -47; Minor: 20