Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting Information: Combined computational and experimental approach for bio-sourced monomers to design green pressure-sensitive adhesives

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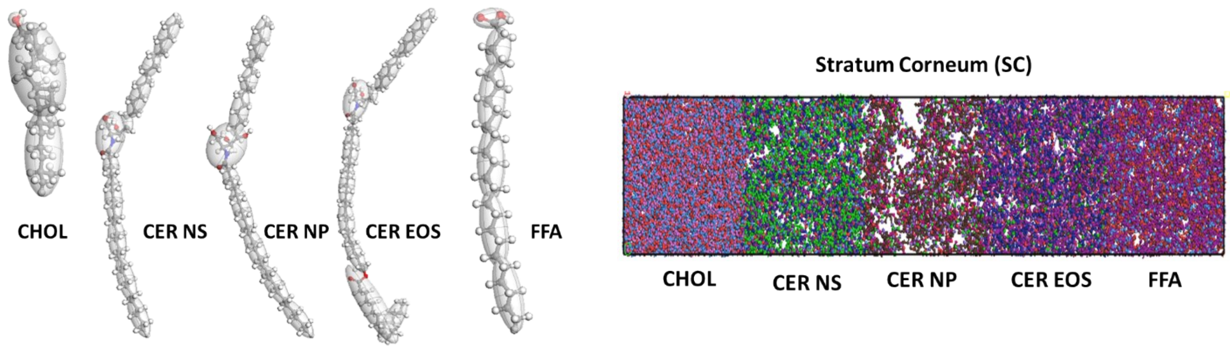
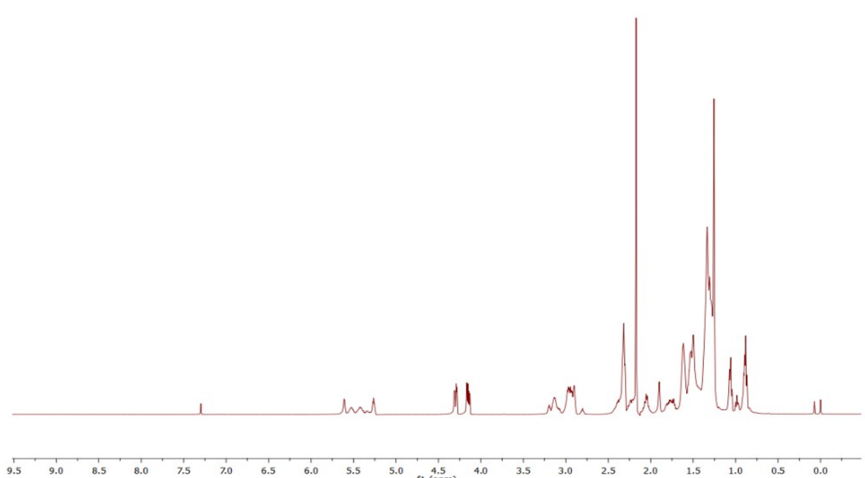
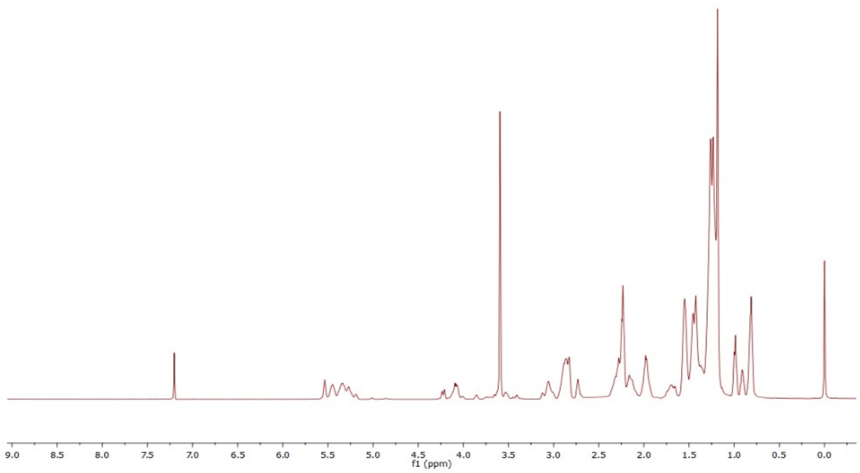


(a) (b)

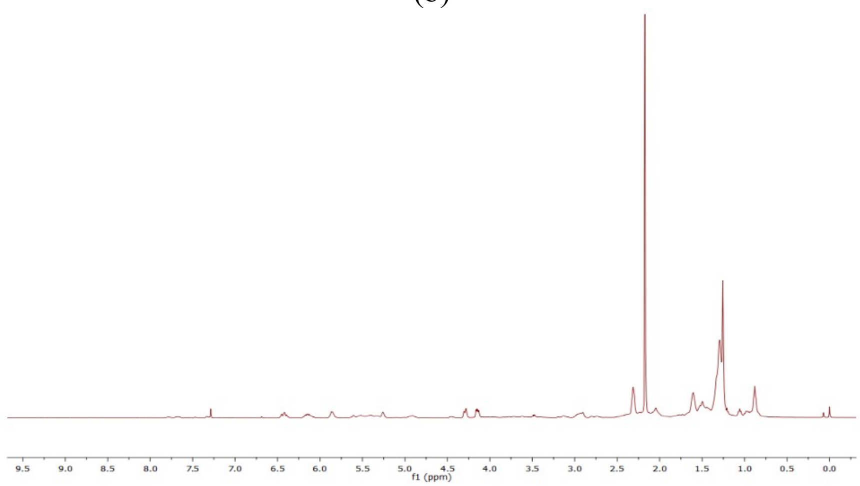
Fig. S1. Illustration of (a) mesoscale beads of components of lipid matrix of stratum corneum and (b) mesostructured stratum corneum



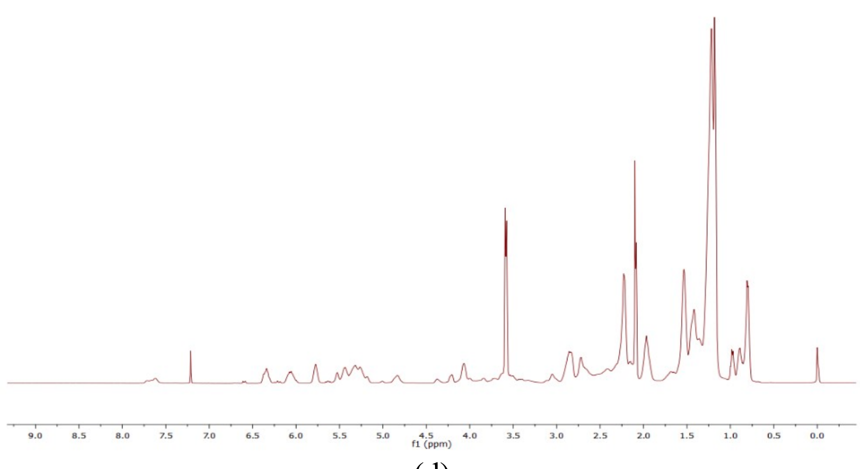
(a)



(b)



(c)



(d)

Fig. S2. ^{1}H NMR of synthesized (a) ELO, (b) EME, (c) AELO and (d) AEME

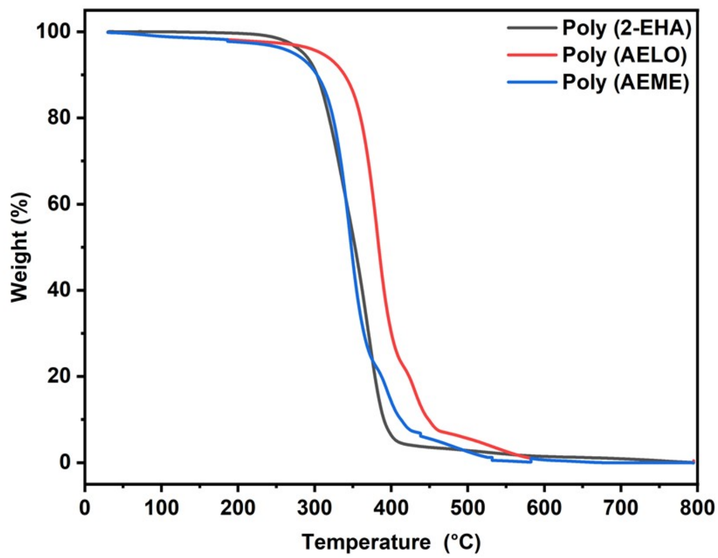


Fig. S3. TGA curves of all the cured homopolymers of 2-EHA, AELO and AEME.

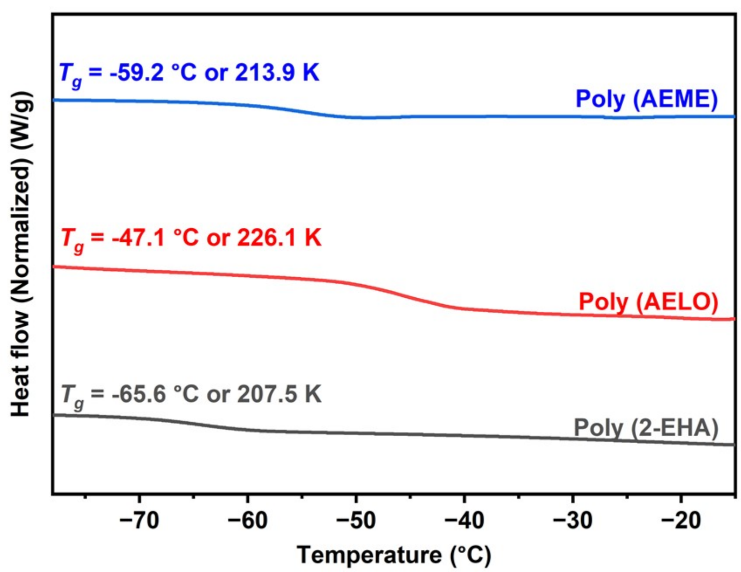
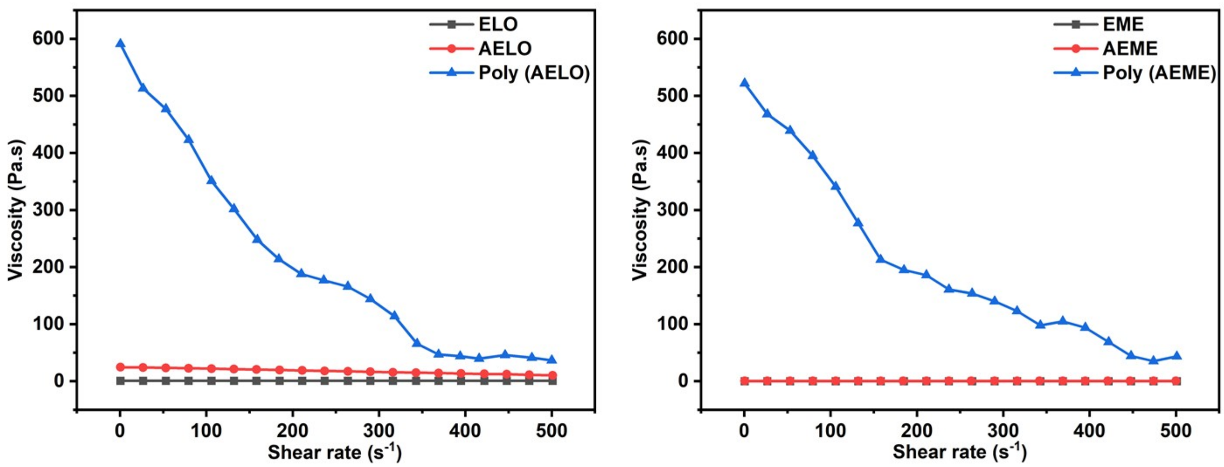
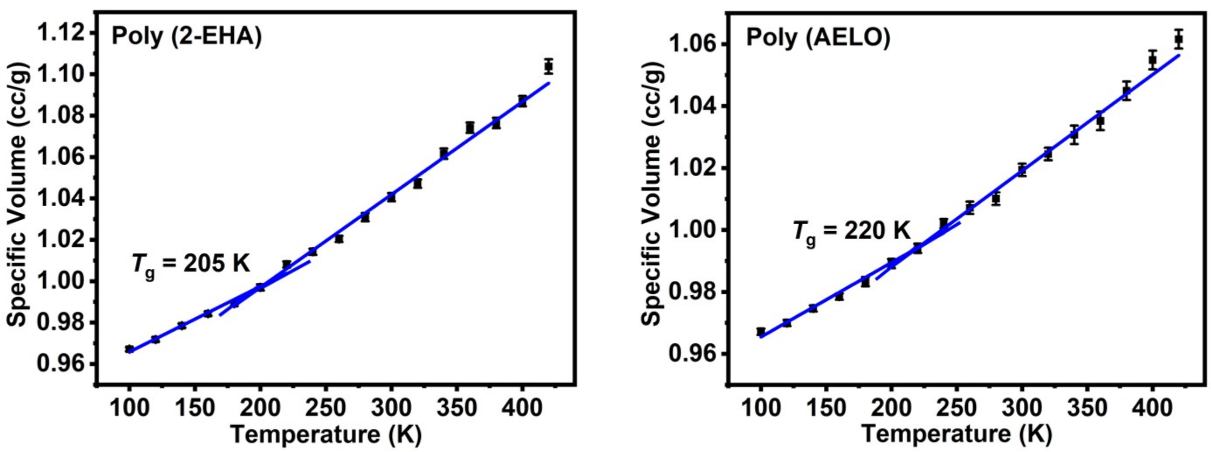


Fig. S4. DSC thermograms of cured polymer resins of 2-EHA, AELO, AEME indicating their respective T_g.

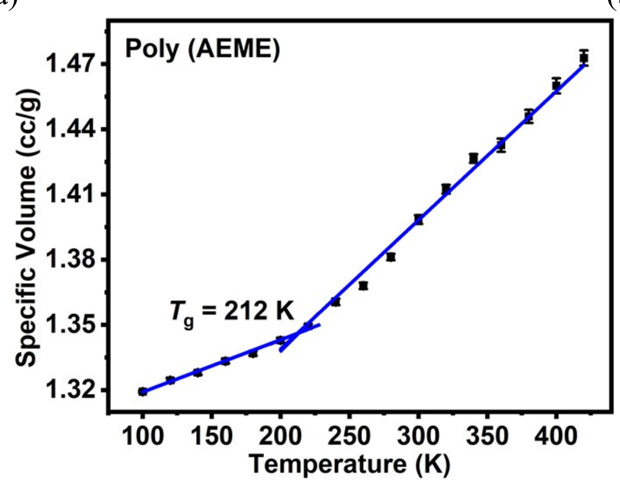


(a) (b)

Fig. S5. Representation of viscosity *versus* shear rate curves of (a) ELO and (b) EME and compared with their respective acrylates and polymer resins.

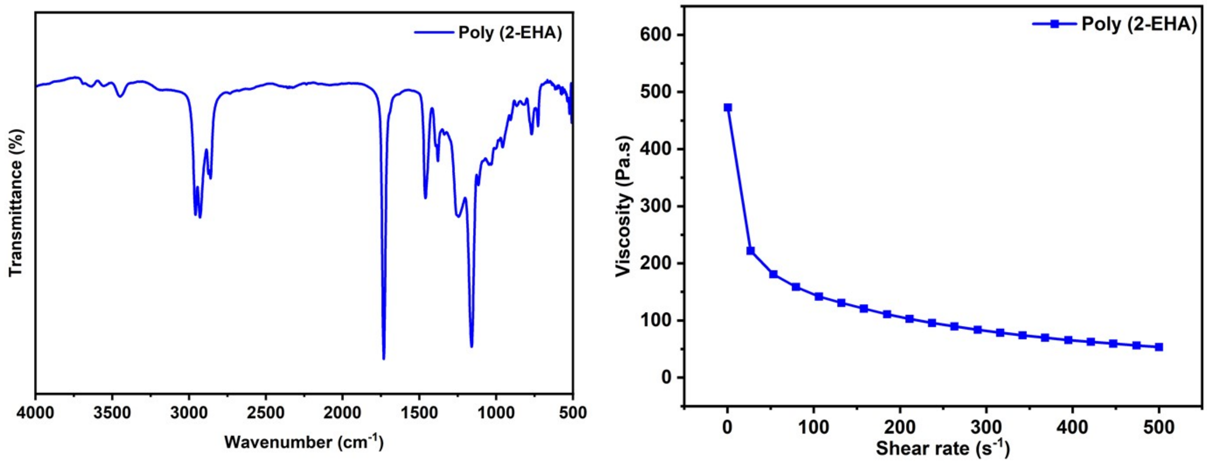


(a) (b)



(c)

Fig. S6. Illustration of simulated specific volume versus temperature curves to estimate T_g of (a) poly (2-EHA), (b) poly (AELO) and (c) poly (AEME).



(a) (b)

Fig. S7. (a) FTIR spectra and (b) viscosity of cured poly (2-EHA).

S1. Molecular weight, gel content and crosslinking density of low T_g resins

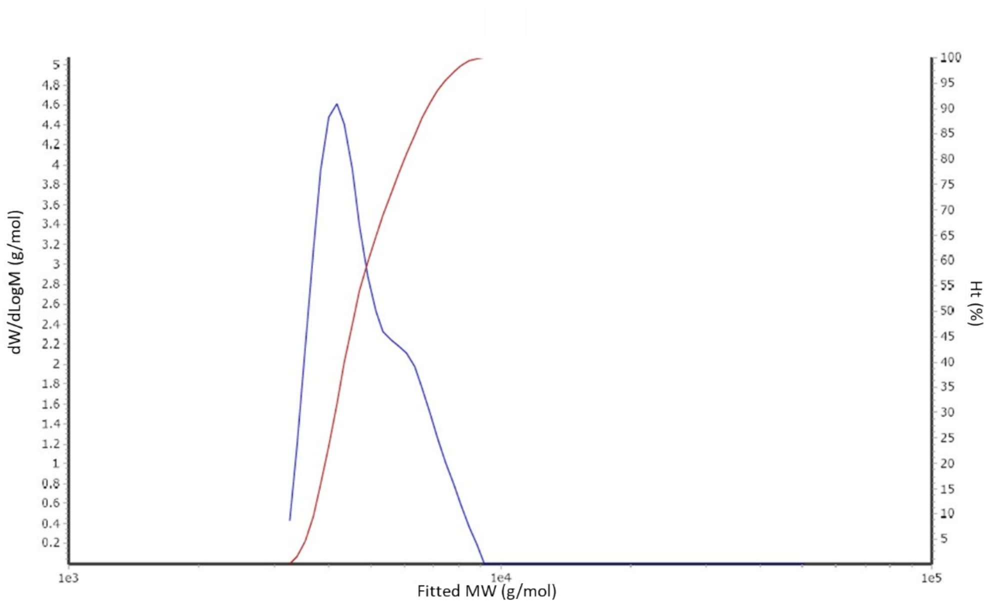


Fig. S8. Illustration of distribution plot of molecular weight of poly (2-EHA).

Gel content for low T_g resins has been measured using the following equation.

Gel content (%) = $\frac{w_1 \times 100}{w_0}$ --------------**(1)**

Where w_1 is the weight of the sample before immersion (in g) in THF and w_0 corresponds to the dried weight after immersion (in g).

Cross-link density was calculated from the volume fraction of the swollen polymer. From the weights of the swollen (w_s) and de-swollen (w_{ds}) specimens, the swell ratio (Q) is given by the following equation.

$Q = {}^{w_s}/_{w_{ds}} - 1$ --------------**(2)**

The swell ratio (Q) was obtained experimentally by placing the specimens (1cm×1cm) in THF for 24 h. The solvent absorbed was driven off by keeping it in a vacuum oven for 2 h at 100 °C, and the weight of the de-swollen specimen was determined. The weight fraction of the polymer (w_2) and the solvent (w_1) can then be calculated by the relation,

$w_2 = 1 / (1+Q)$ and $w_1 = (1 - w_2)$ --------------**(3)**

The volume fraction of the polymer (v_2) in the swollen specimen was given by,

$$v_2 = \frac{\frac{w_2}{\rho_2}}{\frac{w_2}{\rho_2} + \frac{w_1}{\rho_1}} \quad \text{----------} \quad \textbf{(4)}$$

where ρ_1 and ρ_2 were the densities of the solvent and the polymer, respectively. From the volume fraction data, the cross-link density (ϑ_e) were calculated by the Flory-Rhener relation.

---------- **(5)**

$$\vartheta_e = \frac{-[\ln(1-v_2) + v_2 + \chi v_2^2]}{v_s(v_2^{1/3} - v_2/2)}$$

Table S1. Gel content and cross-link density of poly (AELO) and poly (AEME).				
Conditions	**Polymerization at 75°C for 10 hours**		**Curing at 120°C for 1 hour**	
Sample	**Gel content, GC (%)**	**Cross-link density ($\times10^{-2}$ mol/cm^3)**	**Gel content, GC (%)**	**Cross-link density ($\times10^{-2}$ mol/cm^3)**
Poly (AELO)	38 ± 3	1.17 ± 0.2	76 ± 4	1.84 ± 0.3
Poly (AEME)	23 ± 2	0.42 ± 0.05	51 ± 2	0.85 ± 0.1

Table S2. Simulated interaction energy (kcal/mol) of the low T_g homopolymers with three different substrates.

Systems	E_{Total}	E_P	$E_{Substrate}$	$IE_{P/Substrate}$
Poly (2-EHA)/Al	-64252 ± 68	-1789 ± 9	-61771 ± 72	-691 ± 11
Poly (2-EHA)/PP	-2901 ± 19	-1789 ± 9	-980 ± 5	-132 ± 5
Poly (2-EHA)/SC	-114920 ± 101	-78609 ± 85	-30214 ± 17	-6097 ± 35
Poly (AELO)/Al	-73357 ± 58	-9850 ± 11	-61771 ± 72	-1735 ± 12
Poly (AELO)/PP	-12031 ± 15	-9850 ± 11	-980 ± 5	-1200 ± 10
Poly (AELO)/SC	-49059 ± 49	-10452 ± 12	-30214 ± 17	-8392 ± 22
Poly (AEME)/Al	-81719 ± 76	-18331 ± 16	-61771 ± 72	-1616 ± 12
Poly (AEME)/PP	-18234 ± 18	-18331 ± 16	-980 ± 5	-1076 ± 15

Poly (AEME)/SC	-58499 ± 35	-21031 ± 17	-30214 ± 17	-7253 ± 26

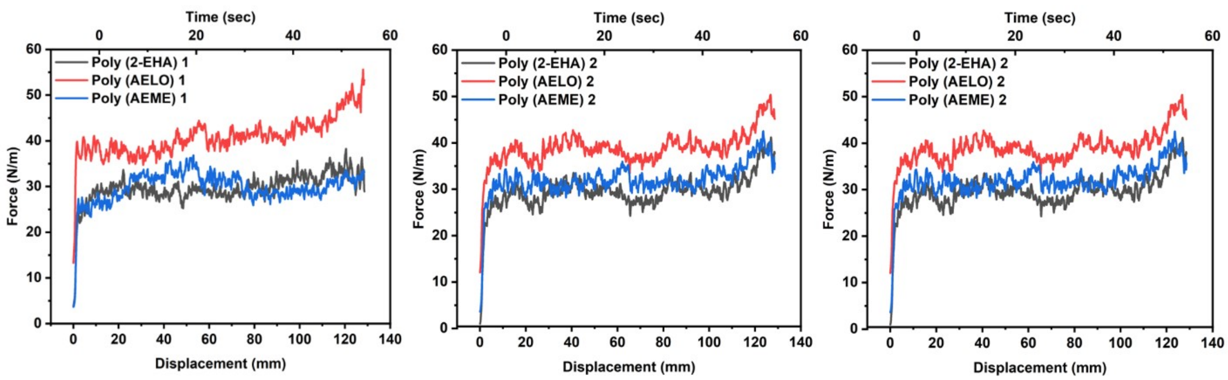


Fig. S9. Illustration of peel strength data represented as force versus displacement/time for all three samples of each low T_g resin.