

## Supplementary Information

**Table S1.** Densities and molar volumes for the healing monomer library.

Chemical <sup>a</sup>	Density (g/ml) <sup>b</sup>	Molar Volume (ml/mole) <sup>c</sup>
Norbornane	0.845	113.80
-H	0.844	111.42
-CH=CH-CH <sub>2</sub> -	0.985	134.07
-CH=CH <sub>2</sub>	0.840	142.91
=CH-CH <sub>3</sub>	0.892	134.59
-COOEt	1.022	162.42
-CH <sub>2</sub> -OH	1.025	120.92
-COOH	1.128	122.37
-COCH <sub>3</sub>	1.004	135.51
-CHO	1.029	118.60
-CH <sub>2</sub> -Cl	1.050	135.71
-CH <sub>2</sub> -Br	1.300	143.77
-CH <sub>2</sub> -O-CH <sub>3</sub>	0.931	148.22
-CON(CH <sub>3</sub> ) <sub>2</sub>	1.150	143.45

<sup>a</sup>with the exception of the first chemical (norbornane), the functional group listed refers to a derivative of 2-norbornene functionalized with this group at the 5-position.

<sup>b</sup>reported density values of all monomers are the average of 10 measurements

<sup>c</sup>molar volume was determined from each monomer's density and molecular weight

## Calculation of Norbornene's Group Contributions

The four Beerbower "group contributions" of norbornene are identical to the four corresponding cohesive energies of norbornene ( $E_T$ , total cohesive energy;  $E_D$ , cohesive energy related to dispersion forces;  $E_p$ , cohesive energy related to fixed dipole forces; and  $E_H$ , cohesive energy related to hydrogen bonding forces), which were determined using previously established methods [1]. Their calculation is detailed in the subsections below:

### Calculation of $E_T$ for norbornene

Total cohesive energy,  $E_T$ , is defined as the energy of vaporization ( $\Delta E_{\text{vap}}$ ), which can be calculated from enthalpy of vaporization ( $\Delta H_{\text{vap}}$ ) at room temperature using equation S1 (where  $R$  is the ideal gas constant and  $T$  is room temperature, taken as 25 °C).

$$E_T = \Delta E_{\text{vap}} = \Delta H_{\text{vap}} - RT \quad (\text{S1})$$

Enthalpy of vaporization ( $\Delta H_{\text{vap}}$ ) was measured with a differential scanning calorimeter (DSC, Model Q20, TA instruments). All DSC experiments were conducted under a flow of nitrogen gas at a constant rate of 50 ml/min. In a typical experiment approximately 10 mg of solid monomer was loaded into a DSC sample pan, and the pan was covered and pressed with a sample lid containing a pinhole-sized puncture. A dynamic scan was performed on the sample at a heating rate of 40 K/min over a temperature range of 50 °C – 175 °C. The average of 5 experiments yielded a  $\Delta H_{\text{vap}}$  for norbornene of  $292 \pm 13.2$  J/g. Then,  $E_T$  was determined from equation S1 to be  $28.55 \pm 1.4$  kJ/mole.

### Calculation of $E_D$ for norbornene

The cohesive energy related to dispersion forces for a chemical is defined as the total cohesive energy for that chemical's homomorph (saturated, hydrocarbon analogue). Hence, the same DSC measurements outlined above for calculating the total cohesive energy for norbornene was applied to

norbornene's homomorph—norbornane (Aldrich, used as received). For norbornane,  $\Delta H_{\text{vap}}$  was measured as  $268 \pm 4.0$  J/g, and  $E_D$  for norbornene was then determined to be  $26.85 \pm 0.4$  kJ/mole. A typical DSC plot showing the vaporization of norbornene and norbornane is shown in Figure S1.

### Calculation of $E_p$ for norbornene

$E_p$  of a chemical is conveniently calculated by the Hansen-Beerbower equation:

$$E_p = 1398.76 \cdot \mu^2 \quad (\text{S2})$$

where  $\mu$  is the chemical's dipole moment and the constant 1398.76 gives the parameter in SI units.

With a dipole moment of 0.396 D [2],  $E_p$  for norbornene was calculated to be 0.22 kJ/mole.

### Calculation of $E_H$ for norbornene

There is no way to directly measure  $E_H$  for a chemical. Instead,  $E_H$  is generally determined by first calculating the other three cohesive energy densities ( $E_T$ ,  $E_D$ , and  $E_p$ ) and using equation S3.

$$E_T = E_D + E_p + E_H \quad (\text{S3})$$

$E_H$  was determined to be 1.47 kJ/mole.

### Summary

$E_x$	Equation	Value (kJ/mole)	$E_x/V$ (MPa)	$\delta_T$ (MPa <sup>1/2</sup> )
$E_T$	$E_T = \Delta E_{\text{vap}} = \Delta H_{\text{vap}} - RT$	$28.55 \pm 1.4$	256.2	16.0
$E_D$	$E_D = \Delta E_{\text{vap,norbornane}} = \Delta H_{\text{vap,norbornane}} - RT$	$26.85 \pm 0.4$	241.0	15.5
$E_p$	$E_p = 1398.76 \cdot \mu^2$	0.22	2.0	1.4
$E_H$	$E_T = E_D + E_p + E_H$	1.47	13.2	3.7

## References

- [1] Hansen, C.M. *Hansen Solubility Parameters: A User's Handbook*, 2nd ed.; CRC Press: Boca Raton, FL, 2007
- [2] TOPAS Advanced Polymers Technical Datasheet for norbornene

**Figure S1.** Vaporization of norbornene and norbornane measured by DSC. The enthalpy of vaporization ( $\Delta H_{\text{vap}}$ ) is defined as the area under the endothermic vaporization peak, denoted by arrows.

