Electronic Supplementary Material (ESI) for Soft Matter
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SUPPLEMENTARY INFORMATION

for

"Mesoscopic simulations for the molecular and network structure of a thermoset polymer"

by

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General procedure for bond and angle parameterization

To derive the bond potential and angle potential parameters for DPD, we initially run Molecular Dynamics (MD) simulations for each six bond pairs (A – B, B – C, B – F, D – E, A – D, A – E) and five dihedral angle types (A – B – C, B – F – B, C – B – F, B – C – B, D – E – D). Fully atomistic structures corresponding to these sequences are simulated in the canonical ensemble (*NVT*). For the MD simulations, simulation boxes for each bead sequences are formed with the Accelrys Discover Module[*]. The average densities in the simulation boxes are set to represent gas phase for each sequence. In all of the simulations, the temperature is 298 K and the total simulation time is 1.0 nanoseconds after a geometry optimization of 50,000 steps with Steepest Descent, Conjugate Gradient and Newton minimization algorithms. Data is collected for the last 200 picoseconds of the simulation. The center-of-mass coordinates for each sequence section representing one bead are calculated to obtain the distance and angle values. The bond length and angles are based on the center-of-mass coordinates of the first and the last bead. Then, we compute the bond length and angle histograms that show probabilities. Boltzmann inversion is used to obtain bond and angle potential values from these probabilities. Harmonic functional form of the potentials are fitted to the energy curves. In the bond potential parameter calculations, the angstrom unit is scaled to the DPD unit length before the spring potential functions are fitted. We use the value that 1 DPD unit length corresponds to 7.15 Å from Eq. (2) in the main text.

Determination of the bond potential parameters

[*] *Materials Studio,* Accelrys Software Inc.: San Diego, CA., 2002.

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As a first step, we calculate the distances between the center-of-mass of the beads to get the bond length as to represent the connectivity between the DPD beads. After all bond lengths are calculated, the histograms are obtained. The Boltzmann inversion is applied to obtain the bond potentials in units kT by the relation, $V_{\mathrm{B},ij}(r) = -\ln\left(\mathrm{P}(r)\right)kT$, where P($r$) is the bond length probability from the histograms. A harmonic potential function of the form, $V_{\mathrm{B},ij}\left(r\right) = k_{ij}\left(r - r_{0,ij}\right)^2 + c$ is fitted to the each set of the bond potentials. Finally, we determined the constants for each bond in the epoxy and hardener chains, as well as the cross-linking bonds (i.e. $A-D$ and $A-E$).

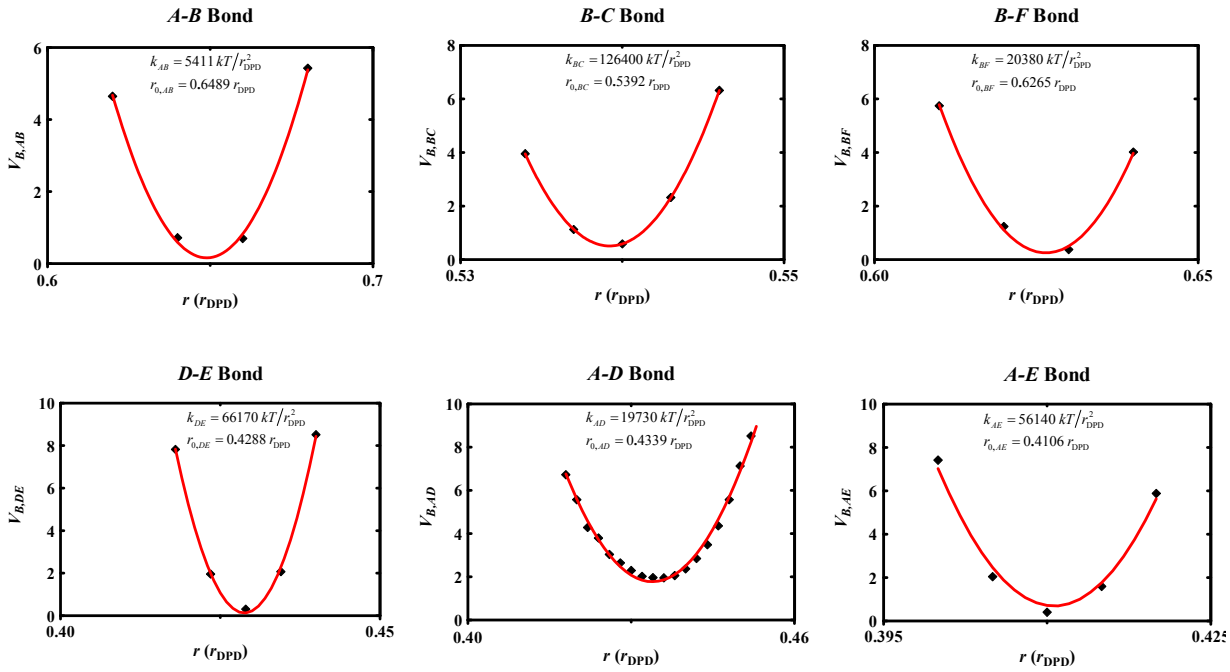

Fig. 1. The plots for the actual bond potentials (black dots) and fitted (red lines) curves as well as the constants for the harmonic spring constant and the equilibrium angle values.

The equilibrium bond length values are used as they are calculated. On the other hand, the harmonic spring constants for all bonds are found to be very large because of their very stiff

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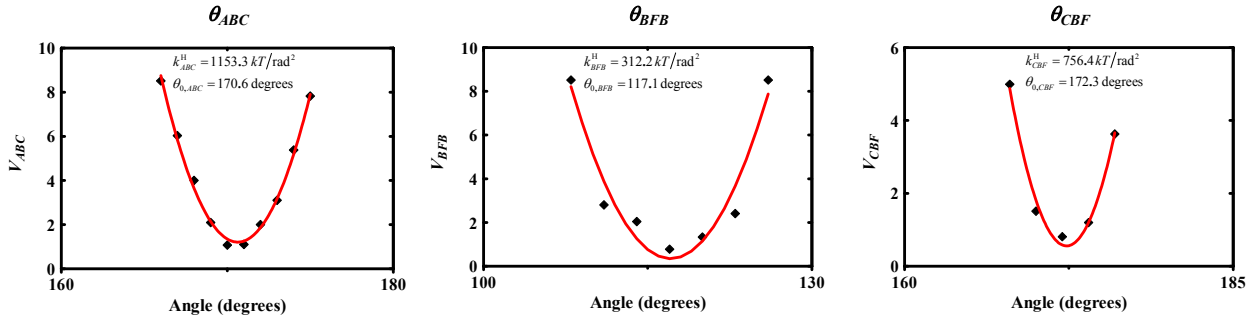
nature. These values are unpractically high to be used in the DPD simulations. Hence, we used $500\,kT/r_{\mathrm{DPD}}^2$ as lower but still representing the stiff bonds instead of the calculated values.

Determination of the angle potential parameters

We can obtain the dihedral angle energy, $V_{\mathrm{A},ijk}\left(\theta_{ijk}\right)$, in kT units by again taking the inverse Boltzmann factor of the probability, $V_{\mathrm{A},ijk}(\theta) = -\ln\left(\mathrm{P}(\theta_{ijk})\right)kT$ where $\mathrm{P}(\theta_{ijk})$ is the probability value of the angle for the bead sequence $i-j-k$.

An angle potential with the form of a spring potential $V_{\mathrm{A},ijk}\left(\theta\right) = k_{ijk}^{\mathrm{H}}\left(\theta-\theta_{0,ijk}\right)^2 + c$ is used in the fitting in which k_{ijk}^{H} is the force constant in dimensions kT/rad^2 in the simulations and $\theta_{0,ijk}$ is the equilibrium angle value.

Figures below show the angle potential plots with their corresponding fitted lines as well as the angle constants used in the simulations.



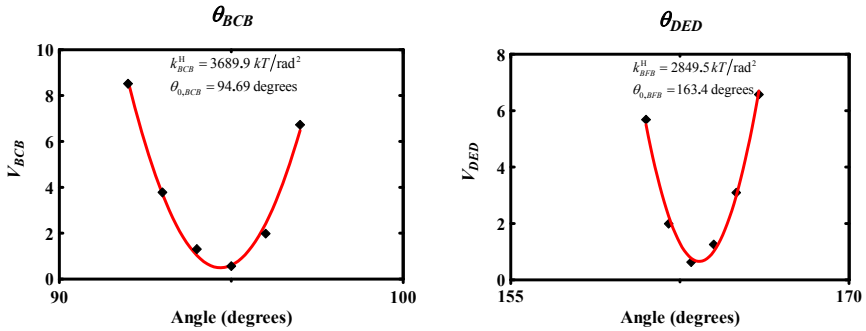


Fig. 2. The plots for the actual dihedral angle potentials (black dots) and fitted (red lines) curves as well as the constants for the harmonic spring constant and the equilibrium angle values. Red lines show the fit in the form of a spring potential, and the black lines show actual potential values.

We found all bead sequences form highly stiff angles. Therefore, we used the equilibrium angle values as they were obtained and did not use the calculated spring potential values because of the very high numerical values. We employed the spring constant value as $50\ kT/\text{rad}^2$ in the simulations representing stiff angles.

Bond and Angle Parameters

Table 1. Sets of (a) bond and (b) angle constants calculated from MD, and used in the DPD simulations.

(a)

Bond type	MD		DPD		
	k_{ij} [kJ/mol/Å^2]	$r_{0,ij}$ [Å]	k_{ij} [kT/r$_{DPD}^2$]	$k_{ij}^{\ddagger}$ [kT/r$_{DPD}^2$]	$r_{0,ij}^{\ddagger}$ [r$_{DPD}^2$]
A-B	0.88	4.64	5411	500	0.649
B-C	20.55	3.85	126400	500	0.539
B-F	3.31	4.48	20380	500	0.627
D-E	10.76	3.07	66170	500	0.429
A-D	3.21	3.10	19730	500	0.434
A-E	9.13	2.94	56140	500	0.411

(b)

Angle type	MD	DPD		
	k^{H}_{ijk} [kJ/mol/deg^2]	k^{H}_{ijk} [kT/rad^2]	$k^{H\ddagger}_{ijk}$ [kT/rad^2]	$\theta_{0,ijk}^{\ddagger}$ [deg]
A-B-C	$2.9\cdot10^{-3}$	1153	50	170.6

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B-F-B	$1.6 \cdot 10^{-3}$	312	50	117.1
C-B-F	$1.9 \cdot 10^{-3}$	756	50	172.3
B-C-B	$9.3 \cdot 10^{-3}$	3689	50	94.7
D-E-D	$7.2 \cdot 10^{-3}$	2849	50	163.4

Values in DPD columns are converted from physical units calculated from MD.

‡ Values used in the DPD simulations.