Electronic Supplementary Information for "A molecular dynamics investigation on the cross-linking and physical properties of epoxy-based materials"

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1.   Derivation, parameters validation and potential function of the three forcefields used in the simulations of SU-8 photoresist

The original CVFF potential is derived for small organic crystals, such as amides[1] and carboxyl acids,[2] and further optimized for the simulations of organic, polymeric and biological materials.[3]   CVFF has been parameterized against a large range of experimental measurements for peptides, proteins, water and a variety of organic systems.[4, 5]   The potential function in CVFF is represented by the superposition of valance and non-bonded interactions.   The valance terms are the bonded interactions consisting of two-body bond stretching, three-body angle bending, four-body dihedral angle torsion and four-body improper out-of-plane terms, while non-bonded interactions consist of van der Waals (vdW) and Coulombic terms.   The bond stretching term is represented by a Morse functional form in the CVFF derivation.[3, 5]   But if the total energy of the simulated model is high, the Morse function will cause the bonded atoms to move far apart unrealistically, which is not desirable during the modeling process. Therefore, a harmonic term is used in the bond stretching interaction instead.[6]   In addition, the harmonic terms are also used for the angle bending, dihedral angle torsion and improper out-of-plane interactions, and the energy expression of the improper term is the same of the torsion term.   The potential function in CVFF is described in eqn (1).

$$
\begin{aligned}
U &= U_{bonded} + U_{non-bonded} \\
&= \sum_{bond} \frac{K_b}{2}\left(b-b_0\right)^2 + \sum_{angle} \frac{K_a}{2}\left(\theta-\theta_0\right)^2 + \sum_{torsion} \frac{K_t}{2}\left[1+s\cos\left(n\phi_t\right)\right] + \sum_{out-of-plane} \frac{K_{oop}}{2}\left[1+s\cos\left(n\phi_i\right)\right] \\
&\quad + \sum_{i,j} D_{ij}\left[\left(\frac{r_{ij}}{r}\right)^{12} - \left(\frac{r_{ij}}{r}\right)^6\right] + \sum_{i,j} C\frac{q_i q_j}{\varepsilon r_{ij}}
\end{aligned}
\tag{1}
$$

where K_b, K_a, K_t and K_{oop} denote the force constants; b_0, θ_0, ϕ_t and ϕ_i denote the equilibrium bond length, bond angle, torsion angle and improper angle, respectively; b and θ is the bond length and bond angle; D_{ij} is the well depth of vdW term and r is the vdW length that is equivalent to the distance at which vdW term reaches its minimum state; r_{ij} is the distance between the atoms i and j with charges q_i and q_j, respectively.

Dreiding forcefield is developed for the study of biological, organic and some inorganic molecules with a moderate accuracy on the predictions of their structures and physical properties.[7]   The forcefield parameters of Dreiding are derived from some simple hybridization rules, which adopt general force constants and geometric parameters in the terms of bonded interactions.   Similar to the CVFF, the potential function in Dreiding forcefield is made up of valence and non-bonded interactions, and is shown in eqn (2). A CHARMM[8]-like energy expression is used for the torsional term, and an umbrella functional form is used for the out-of-plane interaction.   In particular, the vdW interaction during the MD simulations is represented by a Buckingham function, which is preferred for Dreiding forcefield and is better than the LJ 12-6 function in describing the short-range repulsive interactions, which act on the pair of non-boned atoms whose distance is less than the value of vdW length.[7]

$$
\begin{aligned}
U &= U_{bonded} + U_{non-bonded} \\
&= \sum_{bond} \frac{K_b}{2}\left(b-b_0\right)^2 + \sum_{angle} \frac{K_a}{2}\left(\theta-\theta_0\right)^2 + \sum_{torsion} \frac{K_t}{2}\left\{1-\cos\left[n\left(\phi-\phi_0\right)\right]\right\} + \sum_{out-of-plane} K_{oop}\left[1-\cos\omega\right] \\
&\quad + \sum_{i,j}\left[A_{ij}e^{-B_{ij}r} - \frac{C_{ij}}{r^6}\right] + \sum_{i,j} C\frac{q_i q_j}{\varepsilon r_{ij}}
\end{aligned}
\tag{2}
$$

PCFF is a second generation potential improved from CFF91 forcefield,[9, 10] which is originally derived for investigating the alkyl functional group and alkane models, and further developed for computation of polycarbonates[11] and aromatic polyesters.[12]   Apart from these applications based on CFF91 forcefield, PCFF is also applicable for the computer simulation of polysilanes.[13]   The PCFF has been parameterized and validated for various compounds and functional groups covering a wide spectrum of organic, polymeric, and some inorganic materials, such as polycarbonates, melamine resins, metals and zeolites.[11-14]   The potential

function in PCFF is given in eqn (3).   The first four terms are bonded interactions of internal coordinates, while several cross-coupling terms are used in this forcefield, including bond-bond, bond-angle, angle-angle, bond-torsion, angle-torsion, and angle-angle-torsion coupling terms, respectively.   The non-bonded interactions consist of a vdW term represented by a LJ 9-6 function and a Coulombic term similar to CVFF and Dreiding forcefield.

$$
\begin{aligned}
U &= U_{bonded} + U_{cross-coupling} + U_{non-bonded} \\
&= \sum_{n=2}^{4} K_{b,n}\left(b-b_0\right)^n + \sum_{n=2}^{4} K_{a,n}\left(\theta-\theta_0\right)^n + \sum_{n=1}^{3} K_{t,n}\left[1-\cos\left(n\phi-\phi_n\right)\right] + \sum_{out-of-plane} K_{oop}\left(\chi-\chi_0\right)^2 \\
&\quad + \sum_{bb} K_{bb'}\left(b-b_0\right)\left(b'-b_0'\right) + \sum_{ba} K_{ba}\left(b-b_0\right)\left(\theta-\theta_0\right) + \sum_{aa} K_{aa'}\left(\theta-\theta_0\right)\left(\theta'-\theta_0'\right) + \sum_{bt}\left[K_{bt}\left(b-b_0\right)\sum_{n=1}^{3} k_{bt,n}\cos n\phi\right] \\
&\quad + \sum_{at}\left[K_{at}\left(\theta-\theta_0\right)\sum_{n=1}^{3} k_{at,n}\cos n\phi\right] + \sum_{aat}\left[k_{aat}\left(\theta-\theta_0\right)\left(\theta'-\theta_0'\right)\cos\phi\right] \\
&\quad + \sum_{i,j} D_{ij}\left[2\left(\frac{r_{ij}}{r}\right)^9 - 3\left(\frac{r_{ij}}{r}\right)^6\right] + \sum_{i,j} C\frac{q_i q_j}{\varepsilon r_{ij}}
\end{aligned}
\tag{3}
$$

2. Parameters of the three forcefields

CVFF

ATOM TYPES

Type	Mass	Element	Connections	Comment
h	1.007970	H	1	Hydrogen bonded to C
ho	1.007970	H	1	Hydrogen bonded to O
c	12.011150	C	4	Sp3 aliphatic carbon
c3	12.011150	C	4	Sp3 carbon in methyl (CH3) group
c2	12.011150	C	4	Sp3 carbon bonded to 2 H's, 2 heavy atoms
c1	12.011150	C	4	Sp3 carbon bonded to 1 H, 3 Heavy atoms
cp	12.011150	C	3	Sp2 aromatic carbon (partial double bonds)
o	15.999400	O	2	Sp3 oxygen in ether or ester groups
oh	15.999400	O	2	Oxygen in hydroxyl (OH) group

EQUIVALENCE

Type	NonB	Bond	Angle	Torsion	OOP
h	h	h	h	h	h
ho	hn	ho	ho	ho	ho
c	cg	c	c	c	c
c3	cg	c	c	c	c
c2	cg	c	c	c	c
c1	cg	c	c	c	c
cp	c'	cp	cp	cp	cp
o	o'	o	o	o	o'
oh	o'	oh	o	o	o'

QUADRATIC BOND

I	J	R0	K2
c	o	1.4250	273.2000
c	h	1.1050	340.6175
c	c	1.5260	322.7158
cp	o	1.3700	384.0000
cp	h	1.0800	363.4164
cp	cp	1.3400	480.0000
cp	c	1.5100	283.0924
oh	ho	0.9600	540.6336
oh	c	1.4200	384.0000

QUADRATIC ANGLE

I	J	K	Theta0	K2
h	c	h	106.4000	39.5000
h	c	c	110.0000	44.4000
c	c	c	110.5000	46.6000
c	o	ho	106.0000	58.5000
o	c	h	109.5000	57.0000
c	c	o	109.5000	70.0000
cp	cp	h	120.0000	37.0000
cp	cp	cp	120.0000	90.0000
h	c	cp	110.0000	44.4000
c	cp	cp	120.0000	44.2000
c	c	cp	110.5000	46.6000
o	cp	cp	120.0000	60.0000
cp	o	c	109.5000	50.0000
cp	c	cp	110.5000	46.6000
c	o	c	109.5000	60.0000

TORSION

I	J	K	L	Kphi	n	Phi0
*	c	c	*	1.4225	3	0.0000
*	c	o	*	0.3900	3	0.0000
*	cp	cp	*	12.0000	2	180.0000
*	cp	c	*	0.0000	2	0.0000
cp	cp	c	cp	0.6750	4	0.0000
*	cp	o	*	1.5000	2	180.0000
cp	cp	o	c	1.8000	2	180.0000

OUT-OF-PLANE

I	J	K	L	Kchi	n	Chi0
cp	cp	cp	h	0.3700	2	180.0000
cp	cp	cp	c	0.3700	2	180.0000
cp	cp	cp	cp	0.3700	2	180.0000
cp	cp	cp	o'	0.0000	2	180.0000

NON-BOND (LJ 12-6)

I	A	B
h	7108.4660	32.87076
hn	0.00000001	0.00000
cg	1790340.7240	528.48190
c'	2968753.3590	1325.70810
o'	272894.7846	498.87880

BOND INCREMENTS

I	J	DeltaIJ	DeltaJI
oh	ho	-0.3500	0.3500
c	c	0.0000	0.0000
c	cp	0.0000	0.0000
c	o	0.1500	-0.1500
c	oh	0.0300	-0.0300
c	h	-0.1000	0.1000
cp	cp	0.0000	0.0000
cp	o	0.0282	-0.0282
cp	h	-0.1000	0.1000

Dreiding Forcefield

ATOM TYPES

Type	Mass	Element	Connections	Comment
H_	1.0080000	H	1	Normal Hydrogen
H___A	1.0080000	H	1	Hydrogen capable of hydrogen bonding, i.e. bonded to N, O and S
C_3	12.011000	C	4	sp3 Carbon
C_R	12.011000	C	3	Resonant Carbon, i.e. in benzene
O_3	15.999400	O	2	sp3 Oxygen
O_R	15.999400	O	2	Resonant Oxygen, i.e. in furan

QUADRATIC BOND

I	J	R0	K2
C_R	C_3	1.4600	350.0
C_3	H_	1.0900	350.0
C_R	C_R	1.3900	525.0
O_R	C_R	1.3500	525.0

O_3	C_3	1.4200	350.0
C_R	H_	1.0200	350.0
C_3	C_3	1.5300	350.0
O_R	C_3	1.4200	350.0
O_3	H___A	0.9800	350.0

QUADRATIC ANGLE

I	J	K	Theta0	K2
*	C_3	*	109.471	50
*	C_R	*	120	50
*	O_3	*	104.51	50
*	O_R	*	120	50

TORSION

I	J	K	L	Kphi	n	d
*	C_3	C_3	*	1	3	0
*	C_3	C_R	*	1	3	0
*	C_3	O_3	*	1	3	0
*	C_3	O_R	*	1	3	0
*	C_R	C_R	*	12.5	2	180
*	C_R	O_R	*	12.5	2	180

OUT-OF-PLANE

I	J	K	L	Kchi	Chi0
*	*	*	C_R	40	0
*	*	*	O_R	40	0

NON-BOND (X6)

I	R	D
H_	3.195	0.0152
H___A	3.195	0.0152
C_3	3.8983	0.0951
C_R	3.8983	0.0951
O_3	3.4046	0.0957
O_R	3.4046	0.0957

PCFF

ATOM TYPES

Type	Mass	Element	Connections	Comment
hc	1.007970	H	1	Hydrogen bonded to C
ho	1.007970	H	1	hydrogen bonded to oxygen
c	12.01115	C	4	generic SP3 carbon
c1	12.01115	C	4	sp3 carbon with 1 H 3 heavies
c2	12.01115	C	4	sp3 carbon with 2 H's, 2 Heavy's
c3	12.01115	C	4	sp3 carbon with 3 hHs 1 heavy
c3h	12.01115	C	4	sp3 carbon in 3-membered ring with hydrogens
cp	12.01115	C	3	sp2 aromatic carbon
o3e	15.99940	O	2	sp3 oxygen in three membered ring
oc	15.99940	O	2	sp3 oxygen in ether or acetals
oh	15.99940	O	2	oxygen bonded to hydrogen

EQUIVALENCE

Equivalences

Type	NonB	Bond	Angle	Torsion	OOP

-----	-----	-----	-----	-------	-----
hc	h	h	h	h	h
ho	h*	h*	h*	h*	h*
c	c	c	c	c	c
c1	c	c	c	c	c
c2	c	c	c	c	c
c3	c	c	c	c	c
c3h	c	c	c	c	c
cp	cp	cp	cp	cp	cp
o3e	o	o	o	o	o
oc	o	o	o	o	o
oh	o	o	o	o	o

QUARTIC BOND

I	J	R0	K2	K3	K4
-----	-----	-------	--------	--------	--------
c	c	1.5300	299.6700	-501.7700	679.8100
c	cp	1.5010	321.9021	-521.8208	572.1628
c	h	1.1010	345.0000	-691.8900	844.6000
c	o	1.4200	400.3954	-835.1951	1313.0142
cp	cp	1.4170	470.8361	-627.6179	1327.6345
cp	h	1.0982	372.8251	-803.4526	894.3173
cp	o	1.3768	428.8798	-738.2351	1114.9655
h	h	0.7414	414.0000	0.0000	0.0000
h*	o	0.9650	532.5062	-1282.9050	2004.7658

QUARTIC ANGLE

I	J	K	Theta0	K2	K3	K4
-----	-----	-----	--------	--------	--------	--------
c	c	c	112.6700	39.5160	-7.4430	-9.5583
c	c	cp	108.4000	43.9594	-8.3924	-9.3379
c	c	h	110.7700	41.4530	-10.6040	5.1290
c	c	o	111.2700	54.5381	-8.3642	-13.0838
cp	c	cp	111.0000	44.3234	-9.4454	0.0000
cp	c	h	111.0000	44.3234	-9.4454	0.0000
h	c	h	107.6600	39.6410	-12.9210	-2.4318
h	c	o	108.7280	58.5446	-10.8088	-12.4006
c	cp	cp	120.0500	44.7148	-22.7352	0.0000
cp	cp	cp	118.9000	61.0226	-34.9931	0.0000
cp	cp	h	117.9400	35.1558	-12.4682	0.0000
cp	cp	o	123.4200	73.6781	-21.6787	0.0000
c	o	c	104.5000	35.7454	-10.0067	-6.2729
c	o	cp	102.9695	38.9739	-6.2595	-8.1710
c	o	h*	105.8000	52.7061	-12.1090	-9.8681
cp	o	h*	108.1900	53.1250	-8.5016	0.0000

TORSION

I	J	K	L	V(1)	Phi1(0)	V(2)	Phi2(0)	V(3)	Phi3(0)
-----	-----	-----	-----	--------	-------	--------	-------	--------	-------
c	c	c	c	0.0000	0.0	0.0514	0.0	-0.1430	0.0
c	c	c	h	0.0000	0.0	0.0316	0.0	-0.1681	0.0
c	c	c	o	0.7137	0.0	0.2660	0.0	-0.2545	0.0
h	c	c	h	-0.1432	0.0	0.0617	0.0	-0.1083	0.0
h	c	c	o	-0.1435	0.0	0.2530	0.0	-0.0905	0.0
o	c	c	o	-0.1820	0.0	-0.1084	0.0	-0.7047	0.0
c	c	cp	cp	-0.2802	0.0	-0.0678	0.0	-0.0122	0.0
cp	c	cp	cp	-0.2802	0.0	-0.0678	0.0	-0.0122	0.0
h	c	cp	cp	-0.2801	0.0	-0.0678	0.0	-0.0122	0.0
c	c	o	c	-0.5203	0.0	-0.3028	0.0	-0.3450	0.0
c	c	o	h*	-0.6732	0.0	-0.4778	0.0	-0.1670	0.0
h	c	o	c	0.5302	0.0	0.0000	0.0	-0.3966	0.0

h	c	o	cp	0.9513	0.0	0.1155	0.0	0.0720	0.0
h	c	o	h*	0.1863	0.0	-0.4338	0.0	-0.2121	0.0
c	cp	cp	cp	0.0000	0.0	4.4072	0.0	0.0000	0.0
c	cp	cp	h	0.0000	0.0	1.5590	0.0	0.0000	0.0
cp	cp	cp	cp	8.3667	0.0	1.1932	0.0	0.0000	0.0
cp	cp	cp	h	0.0000	0.0	3.9661	0.0	0.0000	0.0
cp	cp	cp	o	0.0000	0.0	4.8498	0.0	0.0000	0.0
h	cp	cp	h	0.0000	0.0	1.8769	0.0	0.0000	0.0
h	cp	cp	o	0.0000	0.0	1.7234	0.0	0.0000	0.0
cp	cp	o	c	0.0000	0.0	1.5000	0.0	0.0000	0.0
cp	cp	o	h*	-0.6900	0.0	0.5097	0.0	0.0095	0.0
cp	c	c	h	-0.0228	0.0	0.0280	0.0	-0.1863	0.0

OUT-OF-PLANE

I	J	K	L	KChi	Chi0
c	cp	cp	cp	7.8153	0.0000
cp	cp	cp	cp	7.1794	0.0000
cp	cp	cp	h	4.8912	0.0000
cp	cp	cp	o	13.0421	0.0000

BOND-BOND

I	J	K	K(b,b')
c	c	c	0.0000
c	c	cp	0.0000
c	c	h	3.3872
c	c	o	11.4318
cp	c	h	2.9168
h	c	h	5.3316
h	c	o	23.1979
c	cp	cp	12.0676
cp	cp	cp	68.2856
cp	cp	h	1.0795
cp	cp	o	48.4754
c	o	c	-7.1131
c	o	h*	-9.6879

BOND-BOND-13

I	J	K	L	K(b,b')
h	c	cp	cp	-3.4826
c	cp	cp	cp	2.5085
c	cp	cp	h	0.8743
cp	cp	cp	cp	53.0000
cp	cp	cp	h	-6.2741
cp	cp	cp	o	-2.2436
h	cp	cp	h	-1.7077
h	cp	cp	o	2.0517
cp	cp	o	h*	1.1590

BOND-ANGLE

I	J	K	K(b,theta)	K(b',theta)
c	c	c	8.0160	
c	c	cp	0.0000	0.0000
c	c	h	20.7540	11.4210
c	c	o	2.6868	20.4033
cp	c	h	26.4608	11.7717
h	c	h	18.1030	
h	c	o	4.6189	55.3270

c	cp	cp	47.0579	31.0771	
cp	cp	cp	28.8708		
cp	cp	h	20.0033	24.2183	
cp	cp	o	58.4790	107.6806	
c	o	c	-2.8112		
c	o	h*	28.5800	18.9277	
cp	o	h*	53.8614	23.9224	

ANGLE-ANGLE

I	J	K	L	K(theta,theta')
c	c	c	c	-0.1729
c	c	c	h	-1.3199
c	c	c	o	-0.8330
cp	c	c	h	-1.8202
h	c	c	h	-0.4825
h	c	c	o	2.5926
c	c	h	c	0.1184
c	c	h	cp	1.0827
c	c	h	h	0.2738
c	c	h	o	3.9177
cp	c	h	h	2.3794
h	c	h	h	-0.3157
h	c	h	o	2.4259
c	c	o	c	-3.5744
c	c	o	h	0.1689
h	c	o	h	2.1283
cp	cp	c	cp	0.0000
c	cp	cp	cp	0.0000
cp	cp	cp	cp	0.0000
cp	cp	cp	h	0.0000
cp	cp	cp	o	0.0000
cp	cp	h	cp	0.0000
cp	cp	o	cp	0.0000

END-BOND-TORSION

				LEFT			RIGHT		
I	J	K	L	F(1)	F(2)	F(3)	F(1)	F(2)	F(3)
c	c	c	c	-0.0732	0.0000	0.0000			
c	c	c	h	0.2486	0.2422	-0.0925	0.0814	0.0591	0.2219
c	c	c	o	-0.3190	0.4411	-0.7174	1.1538	0.8409	-0.9138
h	c	c	h	0.2130	0.3120	0.0777			
h	c	c	o	0.9681	0.9551	0.0436	0.5903	0.6669	0.8584
o	c	c	o	1.0165	0.7553	-0.4609			
c	c	cp	cp	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
h	c	cp	cp	1.3997	0.7756	0.0000	-0.5835	1.1220	0.3978
c	c	o	c	-0.2456	1.0517	-0.7795	0.4741	1.2635	0.5576
c	c	o	h*	-0.5800	0.9004	0.0000	0.0000	0.5343	0.9025
h	c	o	c	-0.6054	1.3339	0.9648	-0.1620	0.1564	-1.1408
h	c	o	h*	-1.7554	1.3145	0.2263	0.2493	0.6803	0.0000
c	cp	cp	cp	0.0000	0.2421	0.0000	0.0000	-0.6918	0.0000
c	cp	cp	h	0.0000	-1.7970	0.0000	0.0000	-0.4879	0.0000
cp	cp	cp	cp	-0.1185	6.3204	0.0000			
cp	cp	cp	h	0.0000	-6.8958	0.0000	0.0000	-0.4669	0.0000
cp	cp	cp	o	0.0000	0.2655	0.0000	0.0000	4.8905	0.0000
h	cp	cp	h	0.0000	-0.6890	0.0000			
h	cp	cp	o	0.0000	-1.5867	0.0000	0.0000	4.2641	0.0000
cp	cp	o	h*	0.9000	-1.3456	1.1900	3.4132	0.5873	-0.1323

MIDDLE-BOND-TORSION

I	J	K	L	F(1)	F(2)	F(3)
c	c	c	c	-17.7870	-7.1877	0.0000
c	c	c	h	-14.8790	-3.6581	-0.3138
c	c	c	o	-21.8842	-7.6764	-0.6868
cp	c	c	h	0.0000	0.0000	0.0000
h	c	c	h	-14.2610	-0.5322	-0.4864
h	c	c	o	-16.7975	-1.2296	-0.2750
c	c	o	c	-5.9288	-2.7007	-0.3175
c	c	o	h*	1.2472	0.0000	0.7485
h	c	o	c	-6.8007	-4.6546	-1.4101
h	c	o	h*	0.0000	0.9241	-0.5889
c	cp	cp	cp	0.0000	9.1792	0.0000
c	cp	cp	h	0.0000	3.9421	0.0000
cp	cp	cp	cp	27.5989	-2.3120	0.0000
cp	cp	cp	h	0.0000	-1.1521	0.0000
cp	cp	cp	o	0.0000	4.8255	0.0000
h	cp	cp	h	0.0000	4.8228	0.0000
h	cp	cp	o	0.0000	5.5432	0.0000
cp	cp	o	h*	1.1580	3.2697	3.5132

ANGLE-TORSION

I	J	K	L	LEFT			RIGHT		
				F(1)	F(2)	F(3)	F(1)	F(2)	F(3)
c	c	c	c	0.3886	-0.3139	0.1389			
c	c	c	h	-0.2454	0.0000	-0.1136	0.3113	0.4516	-0.1988
c	c	c	o	0.5623	-0.3041	-0.4015	0.9672	-0.7566	-1.2331
cp	c	c	h	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
h	c	c	h	-0.8085	0.5569	-0.2466			
h	c	c	o	2.3668	2.4920	-1.0122	-0.1892	0.4918	0.7273
o	c	c	o	0.5511	0.9737	-0.6673			
c	c	cp	cp	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
h	c	cp	cp	4.6266	0.1632	0.0461	0.2251	0.6548	0.1237
c	c	o	c	-2.7466	1.4877	-0.8955	0.5676	0.9450	0.0703
c	c	o	h*	-3.5903	2.5225	0.4888	0.8726	-0.3577	0.3888
h	c	o	c	-1.8234	1.6393	0.5144	-0.7777	0.4340	-0.6653
h	c	o	h*	-3.4060	1.6396	0.0737	0.0000	-0.2810	-0.5944
c	cp	cp	cp	0.0000	-4.4683	0.0000	0.0000	3.8987	0.0000
cp	cp	cp	h	0.0000	2.5014	0.0000	0.0000	2.7147	0.0000
cp	cp	cp	o	0.0000	10.0155	0.0000	0.0000	1.7404	0.0000
h	cp	cp	h	0.0000	2.4501	0.0000			
h	cp	cp	o	0.0000	1.8729	0.0000	0.0000	2.5706	0.0000
c	cp	cp	h	0.0000	-0.1242	0.0000	0.0000	3.4601	0.0000
cp	cp	o	h*	-5.1360	-1.0122	0.0000	4.6852	0.0230	-0.5980

ANGLE-ANGLE-TORSION

I	J	K	L	K(Ang,Ang,Tor)
c	c	c	c	-22.0450
c	c	c	h	-16.1640
c	c	c	o	-29.0420
cp	c	c	h	0.0000
h	c	c	h	-12.5640
h	c	c	o	-20.2006
o	c	c	o	-14.0484
c	c	cp	cp	0.0000
h	c	cp	cp	-5.8888
c	c	o	c	-19.0059

c	c	o	h*	-12.1038
h	c	o	c	-16.4438
h	c	o	h*	-10.5093
c	cp	cp	cp	-14.4097
c	cp	cp	h	4.4444
cp	cp	cp	cp	0.0000
cp	cp	cp	h	-4.8141
cp	cp	cp	o	-21.0247
h	cp	cp	o	4.2296
cp	cp	o	h*	-4.6072

NON-BOND (LJ 9-6)

I	r	eps
c	4.0100	0.05400
cp	4.0100	0.06400
h	2.9950	0.02000
h*	1.0980	0.01300
o	3.5350	0.24000

BOND INCREMENTS

I	J	DeltaIJ	DeltaJI
c	c	0.0000	0.0000
c	cp	0.0000	0.0000
c	h	-0.0530	0.0530
c	o	0.1330	-0.1330
cp	cp	0.0000	0.0000
cp	h	-0.1268	0.1268
cp	o	0.0265	-0.0265
h*	o	0.4241	-0.4241

3. Maximum reaction radius and cross-linking degree in the modeling of SU-8 photoresist

It is believed that a longer equilibration before the cross-linking reaction can enhance the atom diffusion and thus it can result in a more relaxed structure.   The influence of equilibration on the maximum reaction radius and cross-linking degree is investigated by alternating the equilibration scheme before the cross-linking reaction.   The final cross-linked structure from the CVFF simulation is chosen as an illustration.   The cross-linked structure undergoes a 10 ns equilibration (5 ns NVT + 5 ns NPT) before the cross-linking process at a larger reaction radius.   Another set of cross-linking process is performed using the original equilibration scheme (5 ps NVT+ 5 ps NPT).   It is found that the cross-linking process can be successfully performed at a maximum reaction radius of 11 Å for both cases.   At a reaction radius larger than 11 Å, there increase a large amount of atom pairs whose distance is smaller than the reaction radius.   The computational power required in searching the potential reactive atoms from those recognized atom pairs exceeds our available computational resource.   And the cross-linking process can only succeed at a maximum reaction radius of 11 Å.   The obtained cross-linking degree for both cases is plotted in Fig. S1.   It can be seen that at the extended reaction radius, new cross-links are formed slowly for both cross-linking process.   The final cross-linking degree of the model after 10 ns equilibration is 85%, while the original model is 84%.   It is noted that a longer equilibration enhances the formation of cross-links, but it demands more computational power than the proposed equilibration scheme.   Considering a large computational consumption and a limited improvement in terms of the cross-linking degree, current reaction radius range and equilibration process can be considered reasonable.
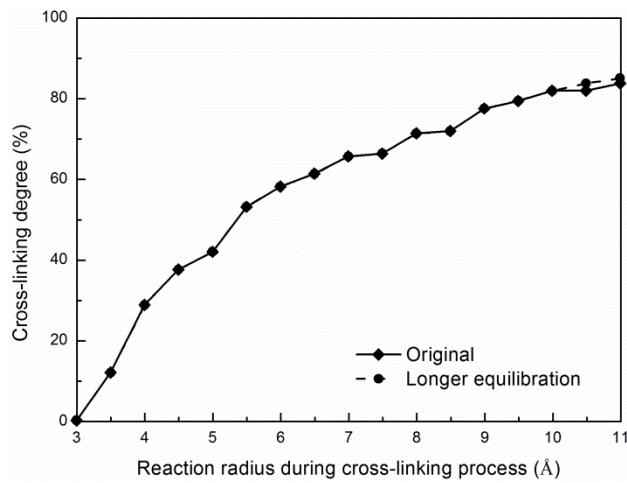

Fig. S1 Cross-linking degree of SU-8 photoresist as a function of reaction radius under CVFF forcefield.

4.   Potential energy and density of the cross-linked SU-8 photoresist

The potential energy and density of the cross-linked SU-8 epoxy network as a function of the simulation time is shown in Fig. S2. Data are recorded at the last 5 ns NPT equilibration run as indicated in TABLE 1 shown in the paper.   The variation of potential energy in the cross-linked system is small along the simulation time, which implies that the cross-linked structure is close to an equilibrium state.   In addition, the density at the last 2 ns simulation is relatively stable for the three cases, which indicates the equilibrium state is reached in the three systems.
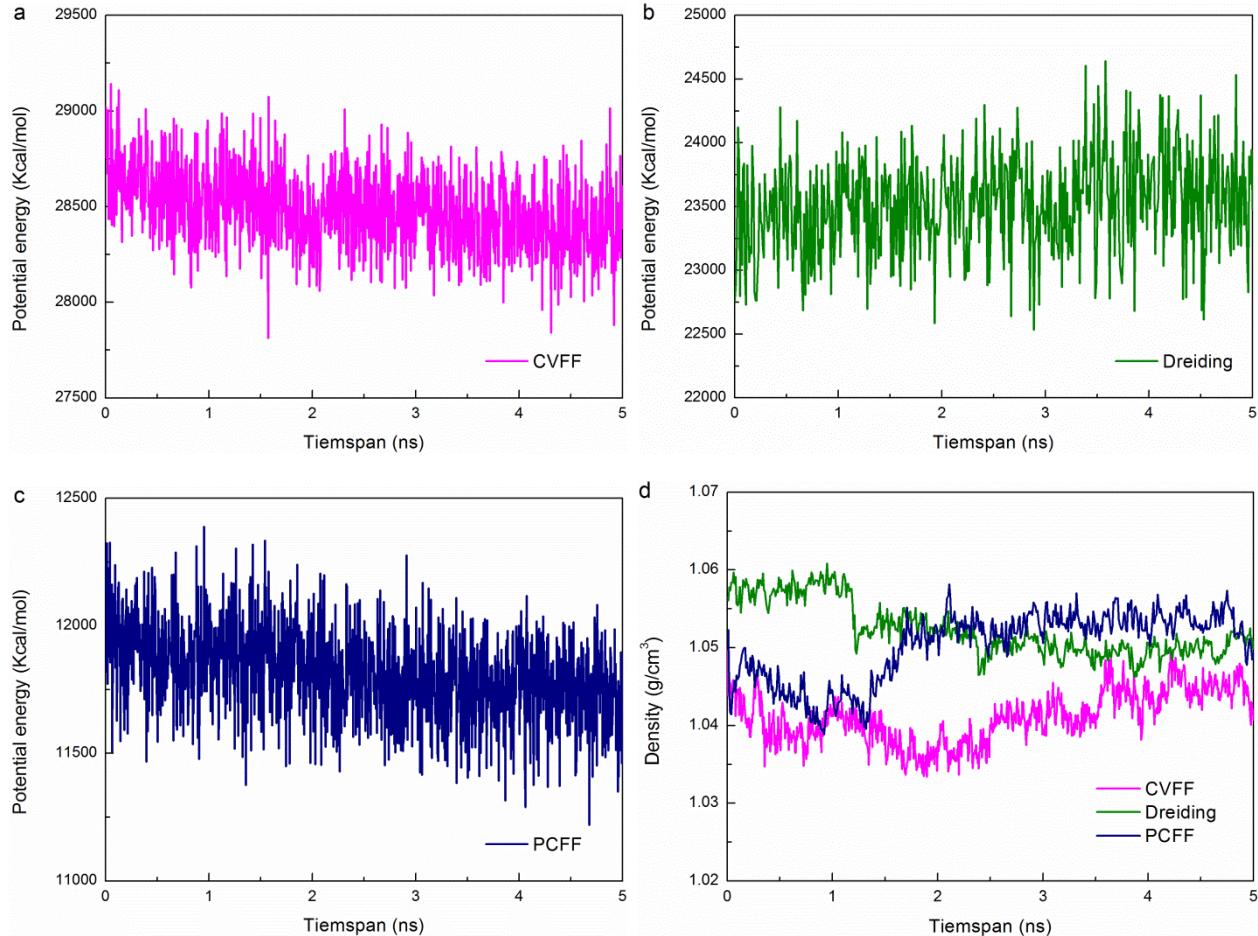
Fig. S2 Evolution of (a, b, c) potential energy and (d) density in the 5 ns NPT equilibration run under three forcefields.

5.   Size effect on the physical properties of SU-8 photoresist

In order to investigate the size effect on the physical properties of SU-8 photoresist, a larger system originated from 15920 atoms (80 monomers) is simulated and compared with the original smaller system (40 monomers).   The simulation is performed using CVFF forcefield as an example.   The modeling and simulation conditions are the same as reported in the paper.   The cross-linking degree of the two SU-8 epoxy networks is shown in Fig. S3.   The trend of the two resulted curves is very similar, leading to a cross-linking degree of 78% for the larger system, while the value of the smaller system is 82%.   Meanwhile, the computed density (ρ) and Young's modulus (E) of the larger cross-linked structure are compared with the results of the smaller system, as shown in Table S1.   The densities of the two cross-linked structures are nearly the same, and the measured Young's moduli are also very close between these two systems.   In view of the computed cross-linking degree, ρ and E, a good agreement is observed between the two models with different sizes.   Thus, it indicates the size adopted in the original paper is large enough for evaluating the mechanical properties of cross-linked SU-8 photoresist.
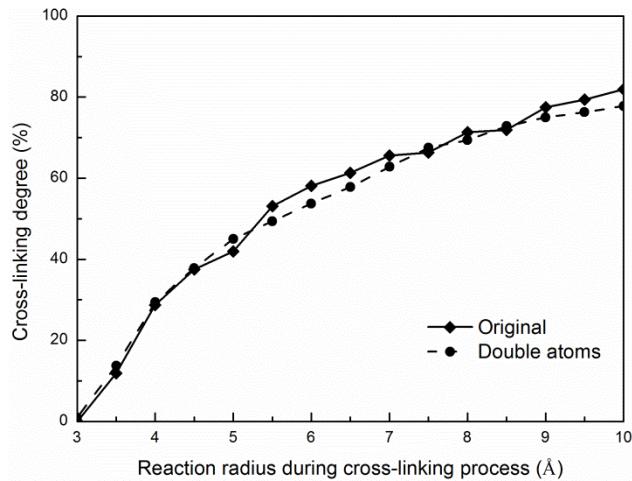

Fig. S3 Cross-linking degree of the original and larger SU-8 photoresist as a function of reaction radius under CVFF forcefield.

TABLE S1 Physical properties of original and larger SU-8 photoresist at 300 K.

	CVFF		Expt.
Monomers	40	80	
ρ (g cm^{-3})	1.044 ± 0.002	1.046 ± 0.001	$1.07 \sim 1.20$ (ref. 15)
E (GPa)	4.425 ± 0.230	4.286 ± 0.467	$2.70 \sim 4.02$ (ref. 16-19)

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