Supporting Information

Mesoscopic simulations of hydrophilic cross-linked polycarbonate polyurethane networks: structure and morphology

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SI-1. MD simulations

All MD simulations were done using the software package Materials Studio with the Compass force field under NPT (constant number of particles, pressure and temperature) conditions with periodic boundary conditions. The cut-off value used for the van der Waals interactions was 12.5 Å. The box was typically of linear size larger than 3.2 nm, so that self-interactions are avoided, and contained typically 100 molecules at a density of about 1.0 g/cm^3, as constructed by the amorphous builder of Materials Studio package. After static energy minimization, 5.0 ps of dynamic equilibration followed. Equilibrium was assessed by evaluating both the kinetic and potential energy. Thereafter a production run of 1.0 ps was used to calculate the bond and angle distributions according to the procedure as described before[1]. The resulting MD configurations are then used for calculating average bond lengths and bond angles between beads (fragments of molecules) by reducing each fragment to a point particle located at the center of mass of the respective fragment. The distributions were

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[1] Kacar, G.; Peters, E. A. J. F.; de With, G., A generalized method for parameterization of dissipative particle dynamics for variable bead volumes. *EPL-EuroPhys Lett* **2013**, *102* (4).

fitted with a Gaussian to estimate the mean value and standard deviations. The data obtained are given in Tables S1 and S2, respectively.

Table S1.: Bond lengths and spring constants for all the connected bead pairs. For the labelling of the beads we refer to Scheme 1.

Bead pair	Spring constant ($k_\mathrm{B}T/r_\mathrm{DPD}^2$)	Bond length (DPD units)
D1-D2	151.34	0.567
D2-D2	1202.08	0.422
D2-D3	1202.082	0.422
T-P2	164.1	0.672
P2-P2	35.98	0.810
P2-P1	43.0	0.533
B-C	43.0	0.602
C-R	253.98	0.602
R-P1	54.0	0.561
R-D3	108.0	0.433

Table S2: Angle parameters and force constants for valence angles for connected beads. For the labelling of the beads we refer to Scheme 1.

Angle	Force constant ($k_\mathrm{B}T/\theta^2$)	Angle (θ)
D1-D2-D2	0.0005	95.97
D2-D2-D2	0.0005	95.14
D2-D2-D3	0.0003	93.14
P2-T-P2	0.0003	93.14
T-P2-P2	0.0005	98.50
P2-P2-P2	0.0004	98.60
P2-P2-P1	0.0004	98.60
C-B-C	0.0003	93.14
B-C-R	0.0005	98.50
C-R-P1	0.0004	98.60
P2-P1-R	0.0004	97.50

SI-2. DPD parameters used

Table S3: Pair interaction parameters for beads used in the DPD calculations. All parameters are given in units of $k_\mathrm{B}T$. For the labelling of the beads we refer to Scheme 1.

	T	P2	P1	B	C	R	D1	D2	D3
T	107.75	91.51	103.48	128.5	80.44	48.65	75.89	63.04	63.04
P2		57.33	59.34	78.55	72.38	25.08	46.43	33.85	33.85
P1			56.28	74.81	86.18	29.87	49.71	36.27	36.29
B				99.21	104.19	38.49	65.37	47.88	47.88
C					60.00	41.67	60.65	53.08	53.08
R						10.85	20.18	15.10	15.10
D1							37.49	27.55	27.55
D2								19.96	19.96
D3									19.96

SI-3. Correlation between off-stoichiometry and cross-linking rate

Figure S1 shows the correlation between the off-stoichiometry and cross-linking rate between R and P1 beads, as estimated from the maximum slope of the conversion curves. For sub-stoichiometric systems the rate is determined by the P1 beads, while for super-stoichiometric systems the rate is determined by the R beads. An approximately linear increase in rate with respect to the stoichiometric system is observed.
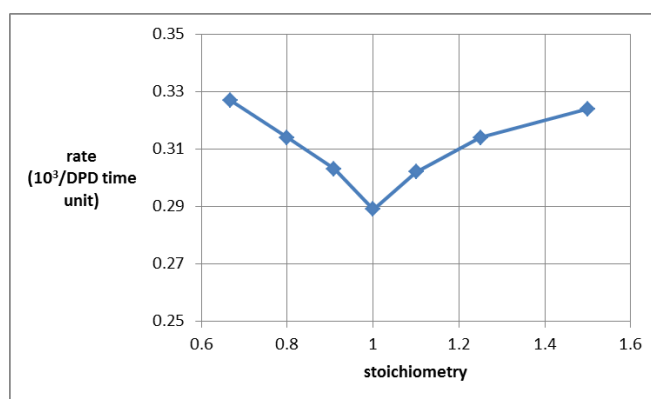

Figure S1. Cross-linking rate (10^3/DPD time unit) as a function of stoichiometry.

SI-4. Snapshot of the crosslinked structure

Figure 3 shows the crosslinked structure with all the crosslinker beads in red and the polymer beads in white. Figure S2 shows the same snapshot but now with only the center beads of the crosslinker molecules in red.
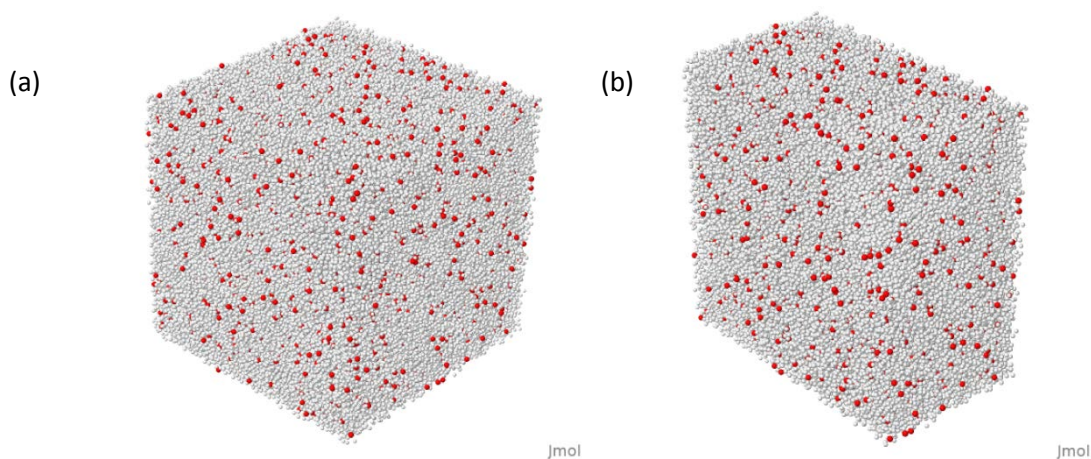

Figure S2. The same snapshot as in Figure 3, but with only the center beads of the crosslinker molecule in red.

SI-5. Radial distribution functions of B-B bead pairs

Figure S3 shows the B-B beads RDFs for the various stoichiometries used.
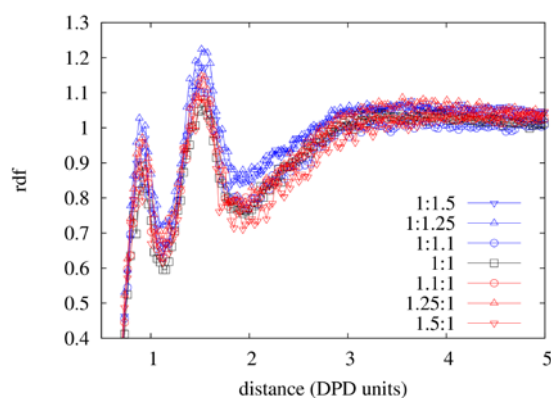
Figure S3. RDF of the cross-linking points (B-beads) for systems with different stoichiometric ratios without dangling chains, as given in Table 1. The *y*-axis is cut off at 0.4 for clarity.

Table S1. Peak positions and areas of the RDF peaks as given in Figure S-1.

System	First peak position	Area	Second peak position	Area	First minimum	Second minimum
1:1.5	0.94	1.26	1.51	25.07	1.12	2.02
1:1.25	0.88	1.37	1.51	26.31	1.09	1.87
1:1.1	0.94	1.22	1.48	23.93	1.12	1.96
1:1	0.91	1.14	1.54	22.83	1.12	1.99
1.1:1	0.88	1.21	1.48	23.64	1.12	1.90
1.25:1	0.91	1.32	1.51	24.37	1.12	1.99
1.5:1	0.97	1.21	1.51	22.74	1.12	1.93

SI-3. Non-crosslinked structure

Figure S4 shows the molecule distribution for the system with mPEG dangling chains. Comparing this figure with Figure 8 shows the effect of cross-linking on the phase separation. In Figure S5 cross-sections of the mPEG distribution at various heights in the simulation box are shown. These images illustrate the varying shape of the cylinder-like phase-separated region after cross-linking.
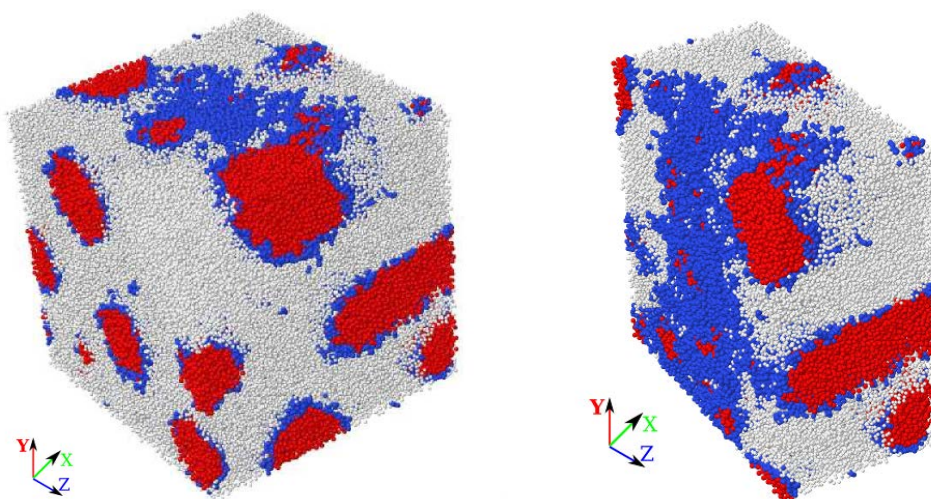
Figure S4. Simulation snapshot after equilibration but before cross-linking for the system with mPEG dangling chains (ratio of reactive beads is 1:1). White beads = Polymer precursor molecules, red beads = cross-linker molecules and blue beads = dangling chains. (a) Snapshot of the entire box (45×45×45 DPD units). (b) Snapshot of a cross-section of the box (22×45×45 DPD units).
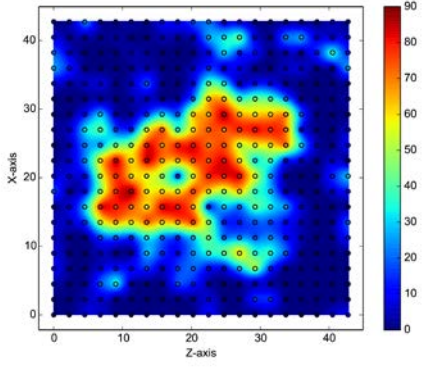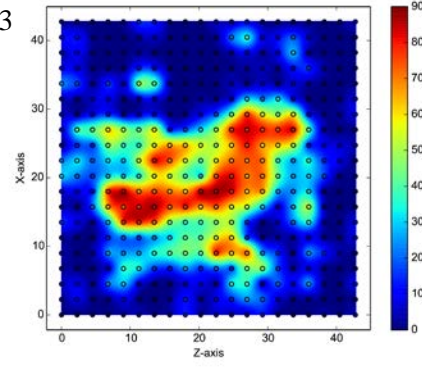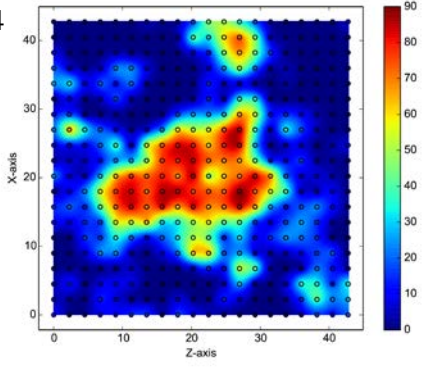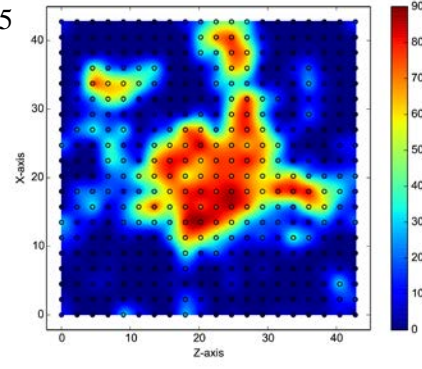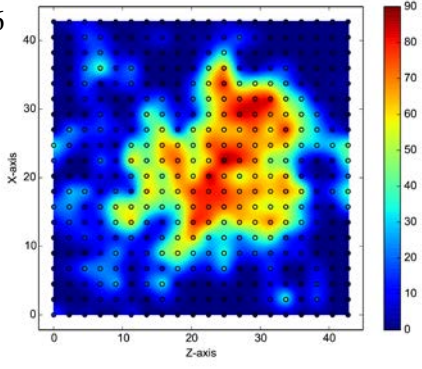
y = 0
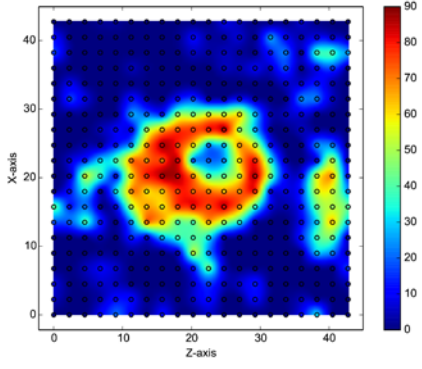
y = 4.1
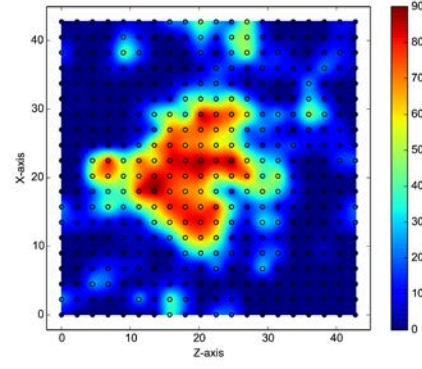
y = 8.2
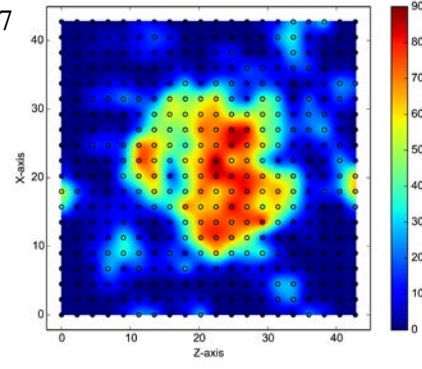
y = 12.3

y = 16.4
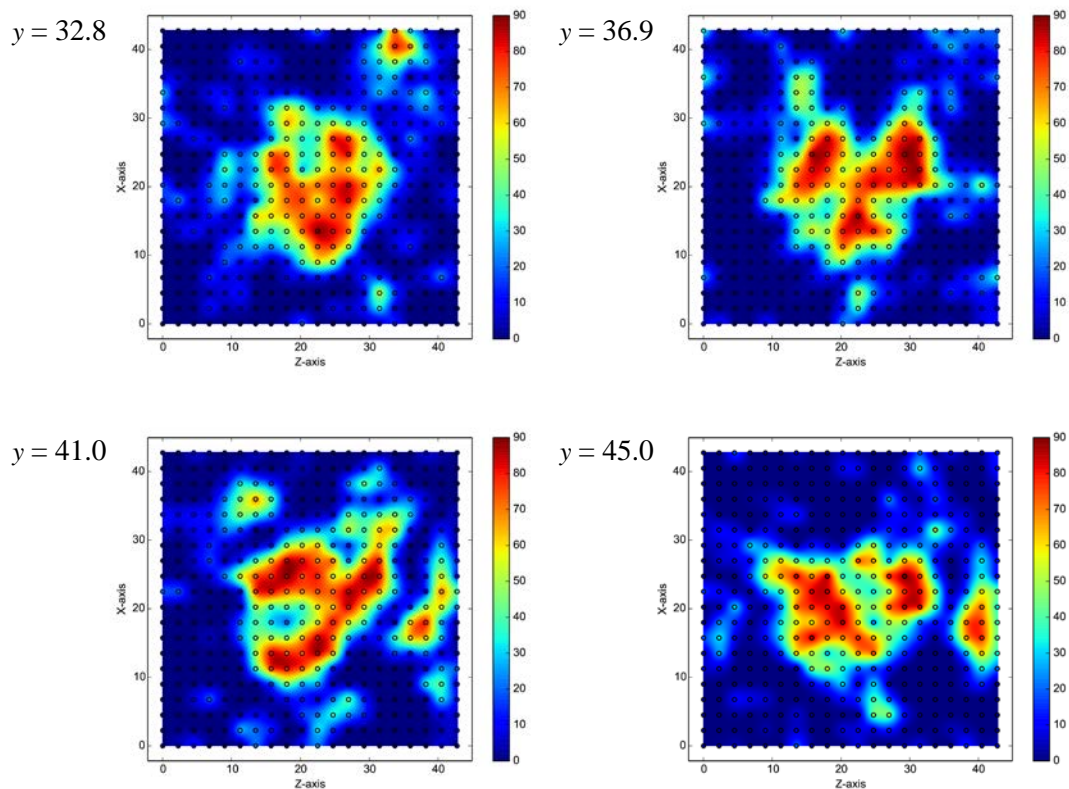
y = 20.5

y = 24.6

y = 28.7

Figure S5. (Color online) Number density distributions of the mPEG dangling chains (D1-, D2- and D3-beads) at various cross-sections through the simulation box for a stoichiometric ratio of 1:1 = cross-linker (*R-beads*)/[polymer(*P1-beads*)+dangling chains (*D3-beads*)]. The cross-sections are from $y = 0$ L_{DPD} (bottom) to $y = 45$ L_{DPD} (top). The color scale indicates the mPEG chain density per grid point.