Tuning interaction parameters of thermoplastic polyurethanes in a binary solvent to achieve precise control over micro-phase separation

Supporting Information

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List of Supplementary Sections

DPD parameters used in this study were calculated using Equations S1-S3.

$$\delta = \sqrt{\frac{E_{coh}}{V}} = \sqrt{CED} \quad (1)$$

$$\chi_{ij} = \frac{V_m}{K_B T}(\delta_i - \delta_j)^2 \quad (2)$$

$$\alpha_{(\rho = 3)} = 25 + 3.25\,\chi \quad (3)$$

Tables S-1 and S-2 list the details of properties calculated via MD simulations.

Table S1 Molecular weights, calculated Cohesive Energy Densities (CED), Solubility Parameters and molar volumes of beads employed in this study.

Beads	Molecular Weight of bead (g mol^{-1})	CED (MJ m^{-3})	Solubility parameter (J m^{-3})$^{0.5}$	V_m (cm^3 mol^{-1})
THF	72.1	360±7	19.01±0.18	79.70
DMF	73.1	588±9	24.23±0.18	82.60
PEO	90.1	347±10	18.59±0.27	107.20
PPO	118.2	347±6	18.60±0.17	140.60
PTMO	74.1	277±11	16.59±0.32	100.90
PBA1	102.1	339±8	18.38±0.20	114.50
PBA2	102.1	346±6	18.59±0.16	114.50
PCL	116.2	340±6	18.43±0.17	131.00
PDMS	76.2	246±10	15.62±0.30	92.20
PIB	114.3	209±6	14.45±0.16	161.00
PEB	86.2	215±8	14.63±0.25	127.90

Table S-2 Average molar volumes, Square differences of solubility parameters, Interaction parameters and DPD parameters for each bead pair employed in this study.

Bead Pairs	V_m average (cm^3 mol^{-1})	$(\delta_1 - \delta_2)^2$ (J cm^{-3})	Interaction Parameter	DPD parameter
THF-DMF	81.15	27.21	0.89	**27.91**
PEO-THF	93.45	0.18	0.01	**25.02**
PEO-DMF	94.90	31.75	1.22	**28.98**
PPO-THF	110.15	0.17	0.01	**25.02**
PPO-DMF	111.60	31.69	1.43	**29.67**
PTMO-THF	90.30	5.85	0.21	**25.70**
PTMO-DMF	91.75	58.29	2.16	**32.06**
PBA1-THF	97.10	0.40	0.02	**25.05**
PBA1-DMF	98.55	34.22	1.36	**29.45**
PBA2-THF	97.10	0.18	0.01	**25.02**

PBA2-DMF	98.55	31.81	1.27	**29.14**
PCL-THF	105.35	0.34	0.01	**25.05**
PCL-DMF	106.80	33.59	1.45	**29.74**
PDMS-THF	85.95	11.51	0.40	**26.31**
PDMS-DMF	87.40	74.10	2.61	**33.55**
PIB-THF	120.35	20.79	1.01	**28.30**
PIB-DMF	121.80	95.57	4.70	**40.36**
PEB-THF	103.80	19.21	0.80	**27.63**
PEB-DMF	105.25	92.14	3.91	**37.80**
THF-A	61.50	85.90	2.13	**31.97**
THF-B	103.05	0.12	0.01	**25.02**
THF-C	107.50	25.99	1.13	**28.69**
DMF-A	62.95	16.14	0.41	**26.34**
DMF-B	104.50	31.36	1.32	**29.33**
DMF-C	108.95	0.02	1.03E-03	**25.00**
THF-PPO	110.15	0.17	7.58E-03	**25.02**
DMF-PPO	111.60	32.08	1.45	**29.73**
THF-PTMO	90.30	5.85	0.21	**25.70**
DMF-PTMO	91.75	58.83	2.18	**32.12**
THF-PEB	103.80	19.21	0.80	**27.63**
DMF-PEB	105.25	92.81	3.94	**37.89**
A-PPO	91.95	93.72	3.48	**36.37**
B-PPO	133.50	0.00	2.21E-04	**25.00**
C-PPO	137.95	30.37	1.69	**30.53**
A-PTMO	72.10	136.59	3.97	**38.00**
B-PTMO	113.65	4.28	0.20	**25.64**
C-PTMO	118.10	56.51	2.69	**33.81**
A-PEB	85.60	186.35	6.44	**46.05**
B-PEB	127.15	16.27	0.84	**27.73**
C-PEB	131.60	89.89	4.77	**40.61**
A-B	84.85	92.49	3.17	**35.36**
A-C	89.30	17.39	0.63	**27.05**
B-C	130.85	29.67	1.57	**30.12**
THF-DMF	77.35	27.57	0.86	**27.81**
PCL-A	87.15	96.98	3.41	**36.16**
PCL-B	128.70	0.05	0.00	**25.01**
PCL-C	133.15	32.24	1.73	**30.67**
PBA-A	78.90	98.05	3.12	**35.21**
PBA-B	120.45	0.08	0.00	**25.01**
PBA-C	124.90	32.86	1.66	**30.42**
PDMS-A	67.75	160.28	4.38	**39.33**
PDMS-B	109.30	9.26	0.41	**26.34**
PDMS-C	113.75	72.08	3.31	**35.82**
PIB-A	102.15	191.21	7.88	**50.78**
PIB-B	143.70	17.73	1.03	**28.36**

PIB-C	148.15	93.28	5.58	**43.24**

Table S-3 PEB-DMF interaction parameters and error margins from repeated runs with boxes containing 20 and 100 beads, and for simulation lengths of 100 and 200 ps.

Bead Pairs A-B	**Number A**	**Number B**	**MD Duration (ps)**	**$(\delta_1 - \delta_2)^2$ (J cm^{-3})**	**Interaction Parameter**	**DPD parameter**
PEO-DMF	10.00	10.00	100.00	31.75	**1.22**	**28.98±0.03**
PEO-DMF	10.00	10.00	200.00	31.99	**1.23**	**29.01±0.00**
PEB-DMF	10.00	10.00	100.00	92.14	**3.91**	**37.80±0.02**
PEB-DMF	20.00	20.00	100.00	96.63	**4.10**	**38.42±0.01**
PEB-DMF	100.00	100.00	100.00	92.93	**3.95**	**37.91±0.02**

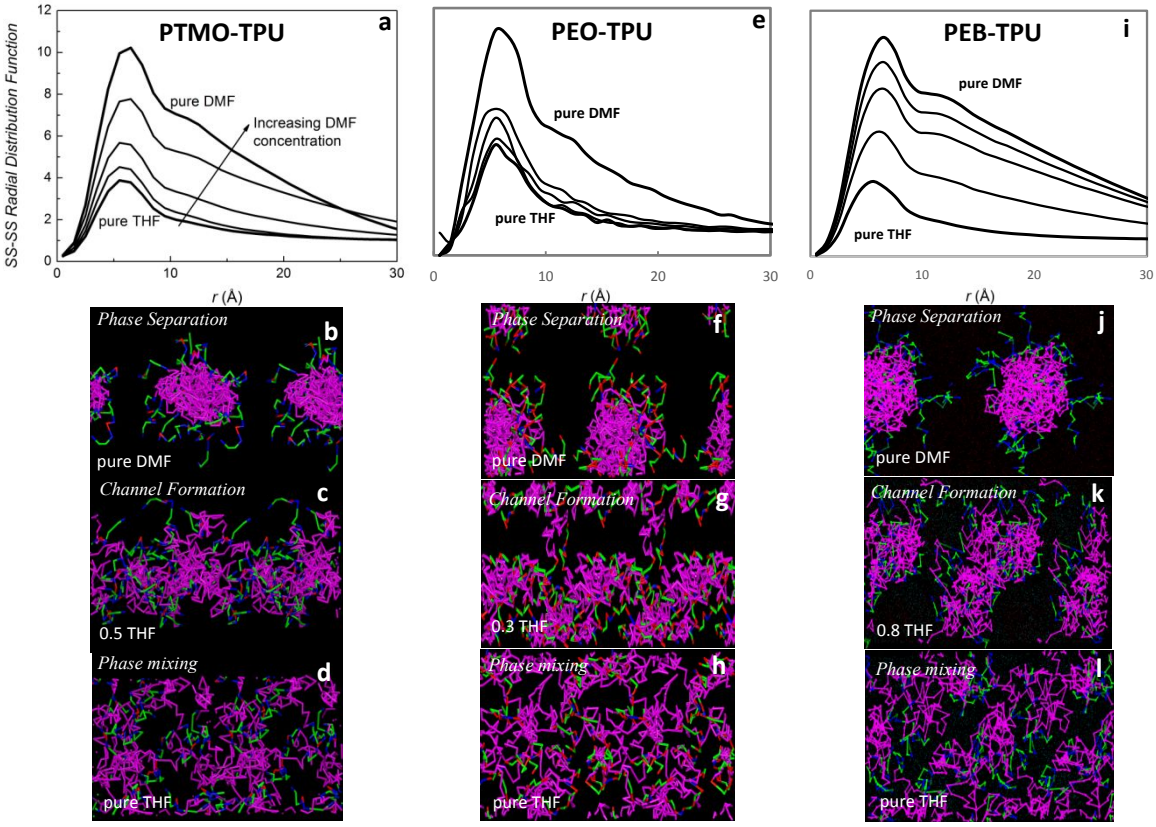

Figure S-1 RDFs between SS beads of the PTMO-TPU (a), PEO-TPU (f) and PEB-TPU (j) copolymer at different solvent ratios. Copolymers-pure solvents RDFs are shown in bold lines. Representative conformations of multiple chains of PTMO-TPU (b-d), PEO-TPU (f-h) and PEB-TPU (j-l) obtained from the final DPD snapshots at varying THF fractions (given in insets). Here, SS (magenta), A (blue), B (green) and C (red) beads of the copolymer are displayed and solvent molecules are turned off.

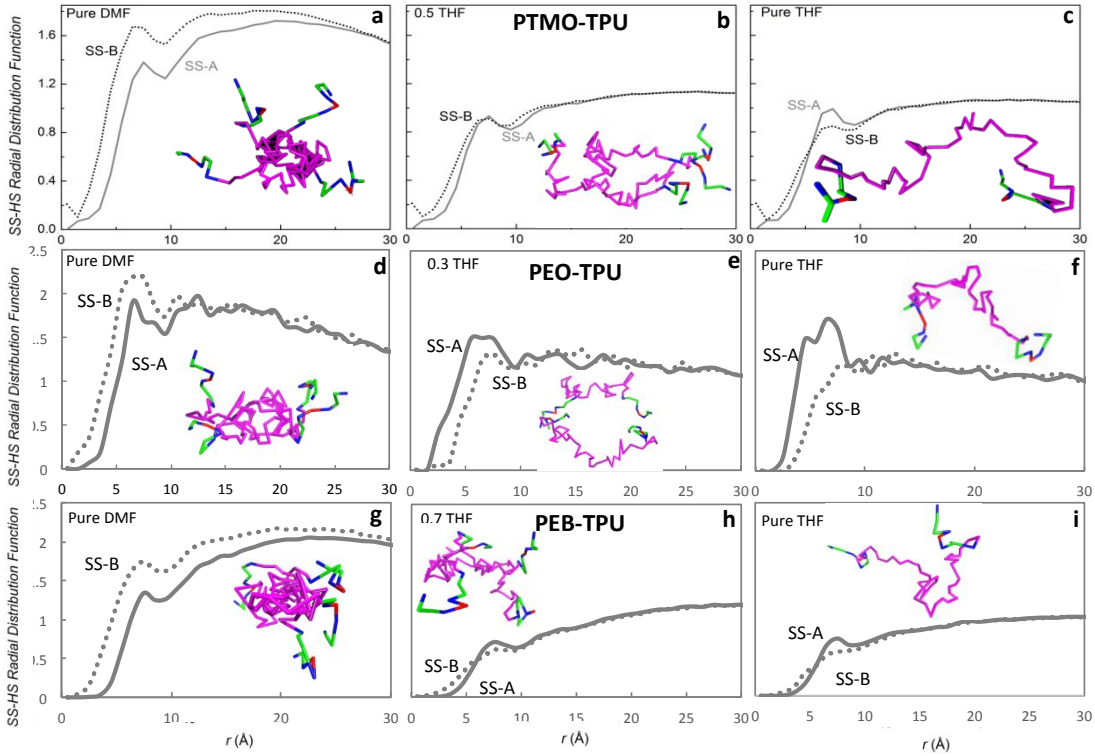

Figure S-2 RDFs of SS beads of PTMO-TPU (a-c), PEO-TPU (d-f) and PEB-TPU (g-i) plotted against A (___) and B (_ _ _) types of beads of HS for phase-separated (a, d, g), channel-formed (b. e. h) and phase-mixed (c, f, i) structures. Molecular conformations of copolymers are given as insets. 3D molecular structures of TPUs in corresponding solvent ratios are given in line representation; SS (pink), A (blue), B (green) and C (red).

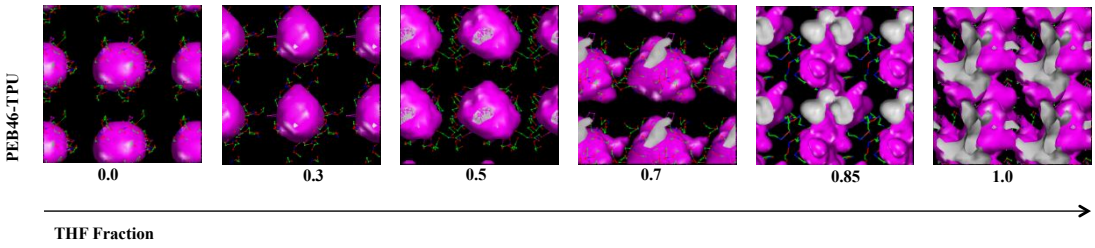

Figure S-3 Density fields of SS obtained from DPD trajectories PEB-TPU. SS density fields of PEB-TPU are represented in magenta. Solvent beads are turned off, and HS beads are in line representation for better visualization. The white regions represent cross-section profiles of density fields where 2x2x2 expansion of periodic images intersects the density field. In HS, A, B, and C beads are shown in red, green and blue, respectively.