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Supporting Information

Effect of Solvent on the Emulsion and Morphology of Polyfluorene Films: All-atom molecular dynamics approach

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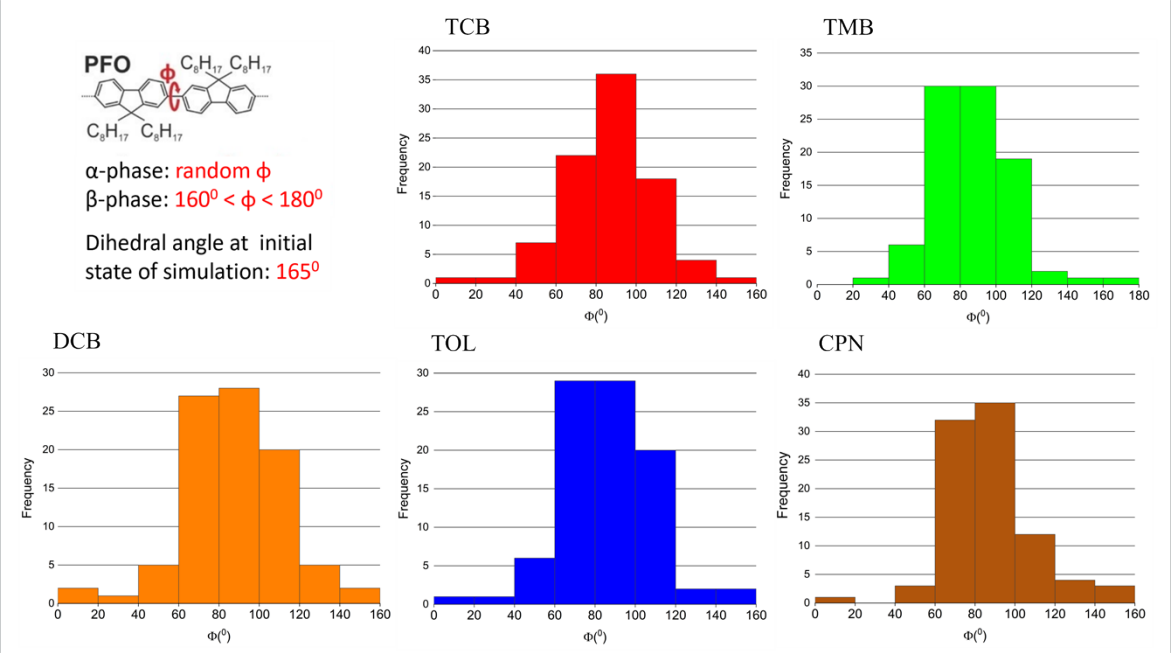

Figure S1 Histogram of backbone dihedral angle at final state for all the chains in the systems with different solvents.

Materials

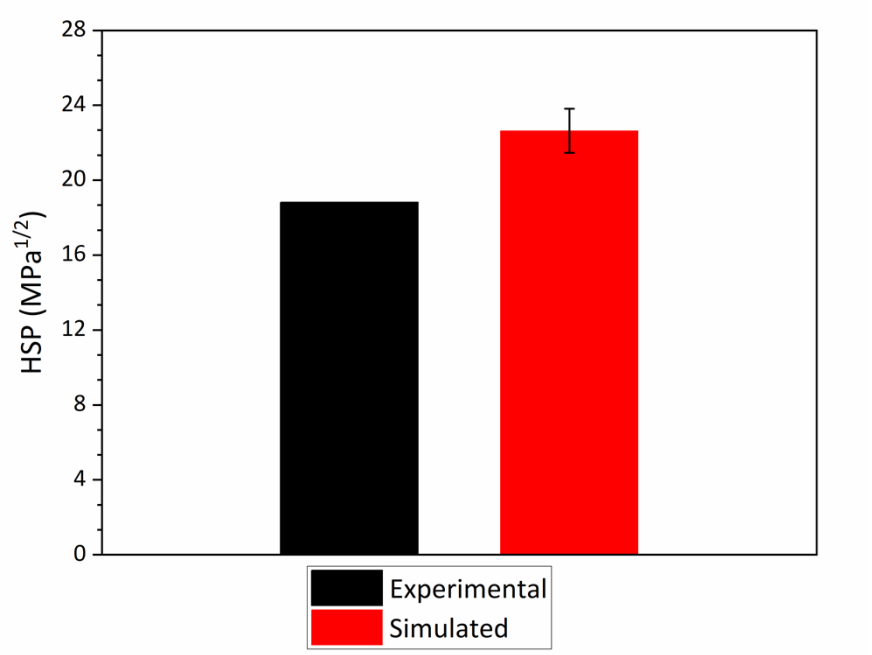

Figure S2 Total Hansen Solubility Parameter (HSP) for a pure PFO polymer system simulated using the GAFF2 force field (10 x 10-mer chains, 300 K, 1 atm) compared to an experimental reference value for PFO based on an average of total HSPs for chloroform and tetrahydrofuran from Grell et. al.[1]

Table S1 Details of the simulation systems (PFO = polyfluorene polymer, PS = primary solvent, SS = secondary solvent, and WAT = water)

Solvent name	**No. of total atoms**	**Mass fraction**				**No. of atoms**			
		PFO	PS	SS	WAT	PFO	PS	SS	WAT
TCB	12391	0.5	0.118	0.029	0.353	6920	600	299	4572
TMB	13387	0.5	0.118	0.029	0.353	6920	1596	299	4572
DCB	12535	0.5	0.118	0.029	0.353	6920	744	299	4572
CPN	13667	0.5	0.118	0.029	0.353	6920	1876	299	4572
TOL	13276	0.5	0.118	0.029	0.353	6920	1485	299	4572

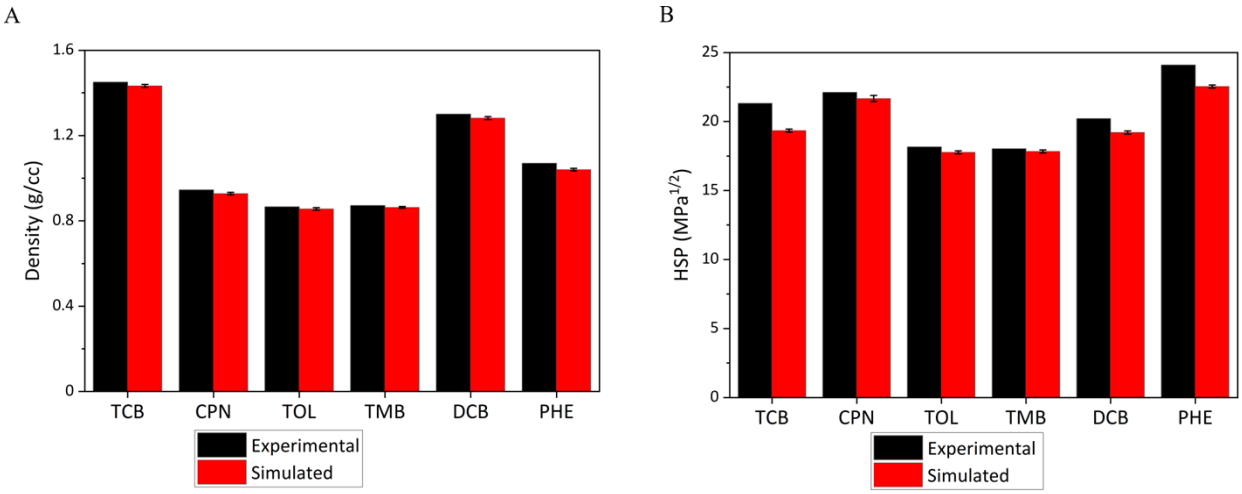

Figure S3 A) Density comparison and B) total Hansen Solubility Parameter (HSP) comparison for pure solvent systems using the GAFF2 force field. Experimental data were collected from different online sources[2,3]

Table S2 Solvent properties calculated from MD simulations.

Primary solvent	Chemical formula	Density (g/cc)	DM* (debye)	Total HSP** ($MPa^{1/2}$)
TCB	$C_6H_3Cl_3$	1.433±0.0067	1.756±0.0082	17.405±0.106
TMB	$C_6H_3(CH_3)_3$	0.863±0.0006	0.34±0.0043	16.05±0.107
DCB	$C_6H_4Cl_2$	1.28±0.0069	3.38±0.0027	17.28±0.111
TOL	$C_6H_5CH_3$	0.856±0.0058	0.32±0.0014	15.99±0.131
CPN	C_5H_8O	0.928±0.006	3.392±0.0029	19.50±0.161

*DM is denoted for molecular dipole moment

**HSP is denoted for Hansen Solubility Parameter

Table S3 Partial charges for all the components used for emulsion systems

Components	Formula	C	H	Cl	O
TCB	C6H3Cl3	0.0557	0.1241	-0.0882	
		0.0343	0.1448	-0.0848	
		-0.0144	0.1476	-0.0916	
		0.0318			
		-0.0694			
		-0.1263			
TMB	C9H12	-0.2009	0.0632		
		-0.2160	0.0704		
		-0.1415	0.0511		
		0.1209	0.1580		
		0.0655	0.1528		
		-0.2648	0.1745		
		0.0916			
		-0.2065			
		-0.2877			
DCB	C6H6Cl2	0.0639	0.1303	-0.1054	
		-0.0903	0.1520		
		-0.1505			
CPN	C5H8O	0.5667	0.0400		-0.5623
		-0.0907	0.0164		
		-0.0243			
TOL	C7H8	-0.2576	0.0790		
		0.1247	0.1251		
		-0.1467	0.1424		
		-0.1859	0.1207		
		-0.0946			
PHE	C6H6O	0.2688	0.3786		-0.5305
		-0.1719	0.1396		
		-0.1818	0.1510		
		-0.1121	0.1214		
PFO	(C29H42)10	-0.0303	0.1428		
		-0.0799	0.1991		
		-0.4082	0.2049		
		0.2568	0.1425		
		-0.3967	0.1388		
		0.0679	0.1455		
		-0.0163	0.1319		
		-0.1759	0.0184		
		-0.1325	0.0108		
		-0.1936	0.0032		

		-0.1436	-0.0016		
		0.0923	-0.0041		
		0.0691	0.0007		
		-0.0685	-0.0038		
		-0.0030	0.0138		
		-0.0044	0.1378		
		0.0085	0.1990		
		-0.0034	0.0110		
		0.0081	0.0111		
		0.0362	0.0033		
		-0.0730	-0.0028		
		-0.0365	-0.0041		
		-0.0775	0.0015		
		-0.4059	-0.0027		
		0.2581	0.0146		
		-0.4077			
		0.0778			
		0.1020			
		-0.0503			
		0.0054			
		-0.0078			
		0.0079			
		-0.0019			
		0.0071			
		0.0335			
		-0.0748			

Table S4: Statistics of the RESP partial charge fitting for the end and middle polymer fragments using intramolecular charge constraints. These statistics are based on quantum mechanics (QM) electrostatic potential (ESP) data and ESP data calculated from the fitted atomic partial charges, after the second stage of the RESP fitting procedure. For both fragments, there were 71 atoms and 2,553 ESP grid points

Statistic	End fragment	Middle fragment
"The initial sum of squares (ssvpot)" $ssvpot = \sum_j \left(V_j^{QM}\right)^2$ V_j^{QM} = ESP at grid point *j* from QM	0.234	0.234
"The residual sum of squares (chipot)" $chipot = \chi^2 = \sum_j \left(V_j^{QM} - V_j^{calc}\right)^2$ V_j^{calc} = ESP at grid point *j* from atomic charges, q_i	0.017	0.019
"The std err of estimate (sqrt(chipot/N))" $RMS\ error = \sqrt{\frac{chipot}{N_{grid\ points}}}$ $N_{grid\ points}$ = Number of grid points (2,553)	0.00185	0.00195
"ESP relative RMS (SQRT(chipot/ssvpot))" $RRMS\ error = \sqrt{\frac{chipot}{ssvpot}}$	0.27257	0.28777
"The [squared] Pearson correlation coefficient (r^2)" $R^2 = \left(\frac{\sum_j \left(V_j^{QM} V_j^{calc}\right) - \sum_j \left(V_j^{QM}\right) \sum_j \left(V_j^{calc}\right)}{\sqrt{\sum_j \left(\left(V_j^{QM}\right)^2\right) - \left(\sum_j \left(V_j^{QM}\right)\right)^2} \sqrt{\sum_j \left(\left(V_j^{calc}\right)^2\right) - \left(\sum_j \left(V_j^{calc}\right)\right)^2} } \right)^2$	0.92316	0.91438

Table S5 Experimental and simulation data for emulsions with different primary solvents.

Primary solvent	Experimental data[25]		Simulated data		
	Solubility-in-water (g/100g)	Film roughness, R (nm)	PS-WAT interaction energy (kcal/mol)	PS-PFO interaction energy (kcal/mol)	Interaction energy ratio (PS-PFO:PS-WAT)
TCB	0.00488	15.2±3.7	-65.77±8.23	-495.76±40.66	7.537±0.17
TMB	0.0057	177.7±25.3	-113.09±14.40	-508.91±49.54	4.500±0.12
DCB	0.0156	37.6±8.5	-161.08±11.67	-836.09±51.23	5.190±0.05
TOL	0.053	250.4±32.3	-242.17±17.64	-735.56±30.26	3.037±0.02
CPN	0.9175	422±154.6	-1195.753±39.24	-610.33±37.64	0.510±0.002

References:

1 M. Grell, D. D. C. Bradley, X. Long, T. Chamberlain, M. Inbasekaran, E. P. Woo and M. Soliman, *Acta Polym.*, 1998, **49**, 439–444.

2 C. M. Hansen, *Hansen solubility parameters: a user's handbook*, CRC press, 2007.

3 C. L. Yaws, *Yaws' Critical Property Data for Chemical Engineers and Chemists*, Knovel, 2012.