Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Towards a Predictive Model for Polymer Solubility Using the NCI Index: Polyethylene as a Case Study

Supporting Information

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S1. Plot of dictane's solvent accessible surface area in anisole and methanol vs. the simulation time starting from a slightly bended coil

In the figure below (Figure S1), it is seen that the system immediately evolves towards its most stable state, as opposed to what is seen in Figure 2 and 3 (main text) for the extended coils. It should be noted that the chain in methanol solvent immediately evolves to its collapsed state as discussed in the text, and, importantly, the bended coil in anisole immediate evolves towards its more stable extended state.

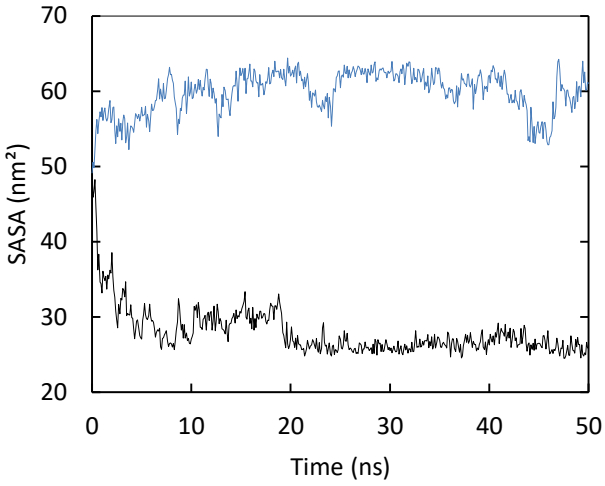

Figure S1: Plot of dictane's solvent accessible surface area in anisole (blue) and methanol (black) vs. the simulation time starting from a slightly bended coil.

S2. Conformational analysis of dictane in methanol

Figure S2 shows the evolution of the radius of gyration, R_g, in different simulations of dictane in methanol starting from differently bended chains (green, light green, yellow, light yellow), whereby three chains were bended manually, while one was bended via a 50 ps NPT simulation in vacuum, in comparison with simulations that started from an extended chain (red and orange), in analogy with what is shown in Figure 4 for the SASA (main text). The radius of gyration was computed as the root

mean squared distance of each point on the coil from its centre of mass, thus representing the size of the polymer coil in the solution

$$R_{\mathrm{g}} = \left(\frac{\sum_{\mathrm{i}} \|\mathbf{r}_{\mathrm{i}}\|^2 m_{\mathrm{i}}}{\sum_{\mathrm{i}} m_{\mathrm{i}}} \right)^{1/2} \tag{S1}$$

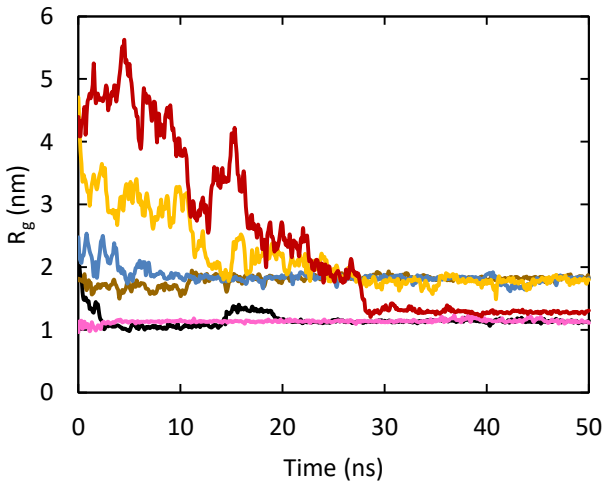

Figure S2: Plot of dictane's radius of gyration, starting from fully extended coils (red and orange) and randomly bended coils (blue, black, brown and pink) in methanol vs. the simulation time.

S3. Numerical values for the SASA and I_{NCI} in anisole and methanol

Table S1: Summary of the calculated integrated NCI density (in a.u.) and solvent accessible surface area (in nm²) at equilibrium.

		Ansiole		Methanol	
Alkane	# C atoms	I_{NCI}	SASA	I_{NCI}	SASA
Propane	3	0.77	2.14	0.41	2.13
Butane	4	0.86	2.45	0.62	2.46
Pentane	5	0.97	2.79	0.64	2.72
Hexane	6	1.04	3.03	0.82	3.07
Heptane	7	1.26	3.40	0.86	3.35
Octane	8	1.46	3.69	0.94	3.70
Nonane	9	1.61	4.00	1.09	3.96
Decane	10	1.63	4.16	1.16	4.26
Pentadecane	15	2.38	5.75	1.67	5.69
Icosane	20	3.10	7.32	2.25	7.36
Tetracontane	40	6.12	13.43	3.95	13.30
Pentacontane	50	7.41	16.25	5.18	16.65
Hexacontane	60	8.38	17.81	5.98	19.51
Octacontane	80	10.99	25.90	6.46	20.75
Hectane	100	15.07	31.84	6.96	20.02
Dictane	200	29.95	61.22	9.97	27.21

S4. Numerical values of the calculated ΔI_{NCI} value shown in Figure 8 (main text).

Table S2 : Summary of the ΔI_{NCI} values (in a.u.) for the solvation of the studied alkanes in anisole and methanol.

	Anisole	Methanol
Propane	0.76	0.40
Butane	0.82	0.60
Pentane	0.93	0.55
Hexane	0.93	0.74
Heptane	1.16	0.74
Octane	1.34	0.83
Nonane	1.46	0.91
Decane	1.32	0.97
Pentadecane	2.03	1.31
Icosane	2.66	1.89
Tetracontane	5.24	2.93
Pentacontane	6.14	4.13
Hexacontane	6.69	4.51
Octacontane	9.17	3.73
Hectane	12.82	2.02
Dictane	25.00	-4.98

S5. Numerical values for the integrated NCI densities calculated over similar 50 ps NCI trajectories as done for the calculation of the I_{NCI} values given in Table S1, but here with the solute's atomic coordinates frozen.

The figure below (Figure S3) compares the integrated NCI density values given in Table S1, $I_{NCI,free}$, to the integrated NCI density values calculated over similar 50 ps NCI trajectories but with the solute's atomic coordinates frozen, $I_{NCI,freeze}$ (numerical values in Table S3). It shows that nearly perfect correlation exists between both quantities on a 1:1 ratio. These results put confidence in using fixed coordinates for the computation of the relative integrated NCI density.

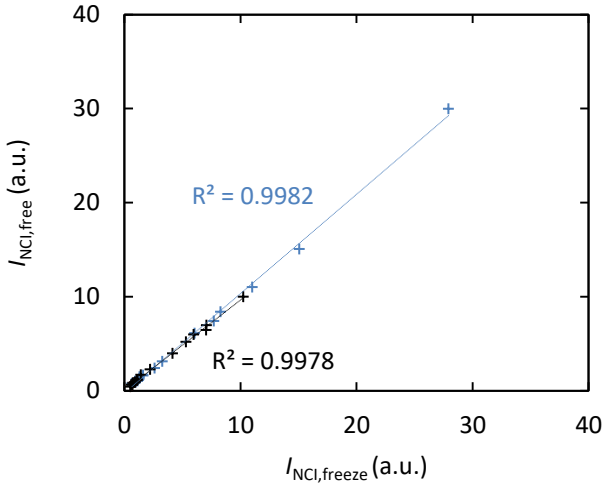

Figure S3: Correlation between the $I_{NCI,free}$ and $I_{NCI,freeze}$ values in anisole (blue) and methanol (black).

Table S3: Summary of the calculated integrated NCI density at equilibrium while keeping the solute's geometry frozen.

	Anisole	Methanol
propane	0.64	0.50
butane	0.94	0.59
pentane	0.94	0.70
hexane	1.13	0.72
heptane	1.27	0.87
octane	1.30	0.94
nonane	1.60	1.08
decane	1.58	1.14
pentadecane	2.60	1.42
icosane	3.25	2.20
tetracontane	6.05	4.13
pentacontane	7.69	5.31
hexacontane	8.27	5.97
octacontane	11.00	7.04
hectane	15.07	7.06
dictane	27.92	10.24