Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Crystallization Behavior of Organic Compound Mixed with Polymers by Hidden Liquid Phase Domains

Gagan N. Kangovi and Sangwoo Lee*

Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy,
New York 12180, United States

E-mail: lees27@rpi.edu.

*Corresponding author

Electronic Supplementary Information (ESI)

Table S1. Thermal characterization data of the binary mixtures of pyrene and the model polymers measured from the DSC technique.

Polystyrene

ϕ_{PS}[a]	T_{m} (°C)[b]	T_{c} (°C)[c]			
		5 °C/min[d]	10 °C/min[d]	20 °C/min[d]	30 °C/min[d]
0.00	154 ± 1	112 ± 2	113 ± 2	113 ± 2	111 ± 1
0.12	154 ± 1	112 ± 1	114 ± 2	113 ± 1	112 ± 1
0.23	152 ± 1	115 ± 1	116 ± 1	118 ± 1	114 ± 2
0.34	150 ± 1	112 ± 1	112 ± 1	111 ± 1	111 ± 1
0.45	147 ± 1	111 ± 1	109 ± 3	111 ± 1	112 ± 1
0.55	143 ± 1	105 ± 2	101 ± 2	100 ± 1	101 ± 1
0.65[e]	137 ± 1	-	-	-	-
0.74[e]	127 ± 2	-	-	-	-

Poly(ethylene-*alt*-propylene)

ϕ_{PEP}[a]	T_{m} (°C)[b]	T_{c} (°C)[c]			
		5 °C/min[d]	10 °C/min[d]	20 °C/min[d]	30 °C/min[d]
0.00	154 ± 1	112 ± 2	113 ± 2	113 ± 2	111 ± 1
0.07	154 ± 1	114 ± 3	116 ± 6	116 ± 7	114 ± 6
0.25	153 ± 1	123 ± 2	123 ± 1	122 ± 1	123 ± 2
0.39	153 ± 1	115 ± 1	115 ± 2	115 ± 3	116 ± 2
0.50	153 ± 1	116 ± 2	116 ± 3	115 ± 1	115 ± 3
0.60	151 ± 1	113 ± 3	111 ± 2	110 ± 2	112 ± 2
0.69	149 ± 1	111 ± 1	111 ± 1	112 ± 3	111 ± 5
0.78	146 ± 1	99 ± 3	98 ± 2	97 ± 3	94 ± 4

Poly(2-vinylpyridine)

ϕ_{P2VP}[a]	T_{m} (°C)[b]	T_{c} (°C)[c]			
		5 °C/min[d]	10 °C/min[d]	20 °C/min[d]	30 °C/min[d]
0.00	154 ± 1	112 ± 2	113 ± 2	113 ± 2	111 ± 1
0.10	154 ± 1	116 ± 2	116 ± 1	116 ± 2	113 ± 3
0.21	151 ± 1	117 ± 3	117 ± 3	116 ± 5	112 ± 2
0.32	148 ± 1	130 ± 3	124 ± 9	119 ± 2	126 ± 5
0.41	145 ± 1	117 ± 7	118 ± 7	114 ± 9	120 ± 8
0.48	141 ± 1	90 ± 2	99 ± 8	93 ± 4	90 ± 1
0.62[e]	136 ± 1	-	-	-	-
0.71[e]	127 ± 1	-	-	-	-

[a] Volume fraction of polymer. [b] Melting temperatures of the pyrene crystals reported in our earlier work.[1] [c] Crystallization temperatures of pyrene characterized by cooling sequences. [d] Cooling rates. [e] Thermograms do not show noticeable crystallization signatures.[1]

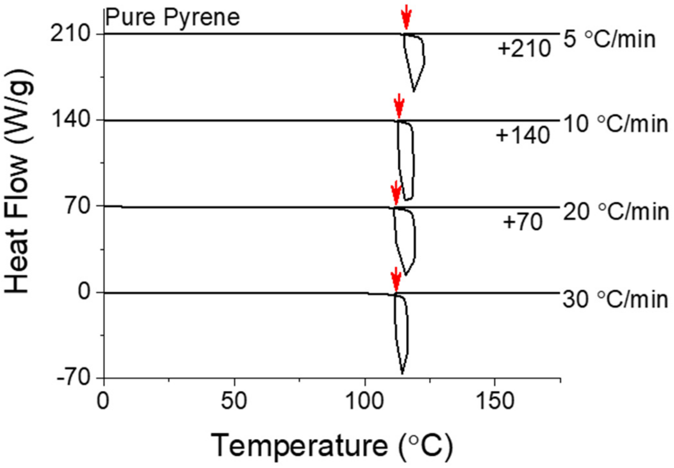

Figure S1. Cooling DSC thermograms of pyrene in endo-up form. The initiation temperatures of crystallization are marked with red arrows. Thermograms are shifted for clear representations.

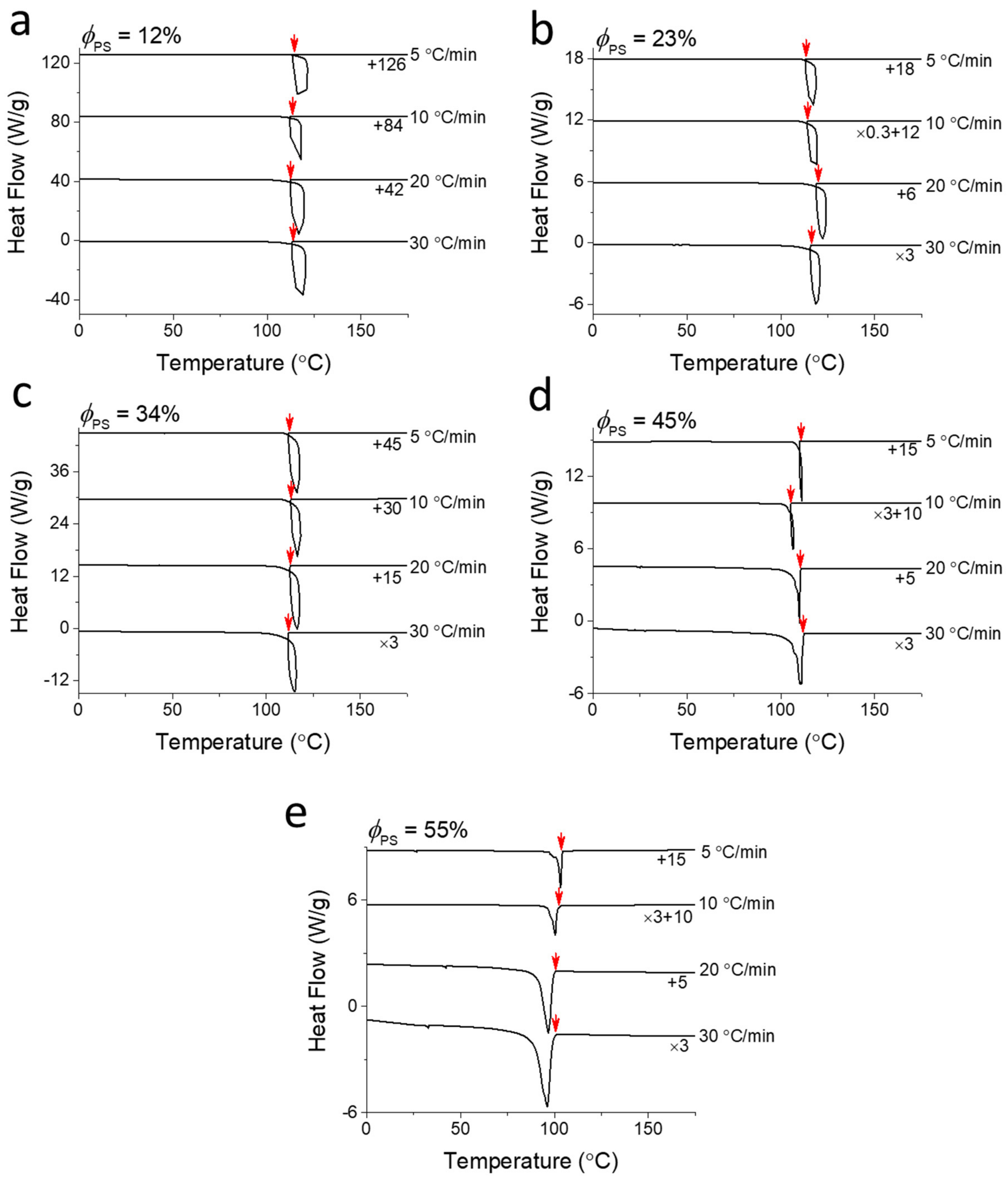

Figure S2. Cooling DSC thermograms of polystyrene (PS, M_n = 23.4 kg/mol) and pyrene mixtures at ϕ_{PS} = (a) 12 vol. %, (b) 23 vol. %, (c) 34 vol. %, (d) 45 vol. %, (e) 55 vol. % in endo-up forms. The commencement temperatures of crystallization are marked with red arrows. Thermograms are shifted for clear representations.

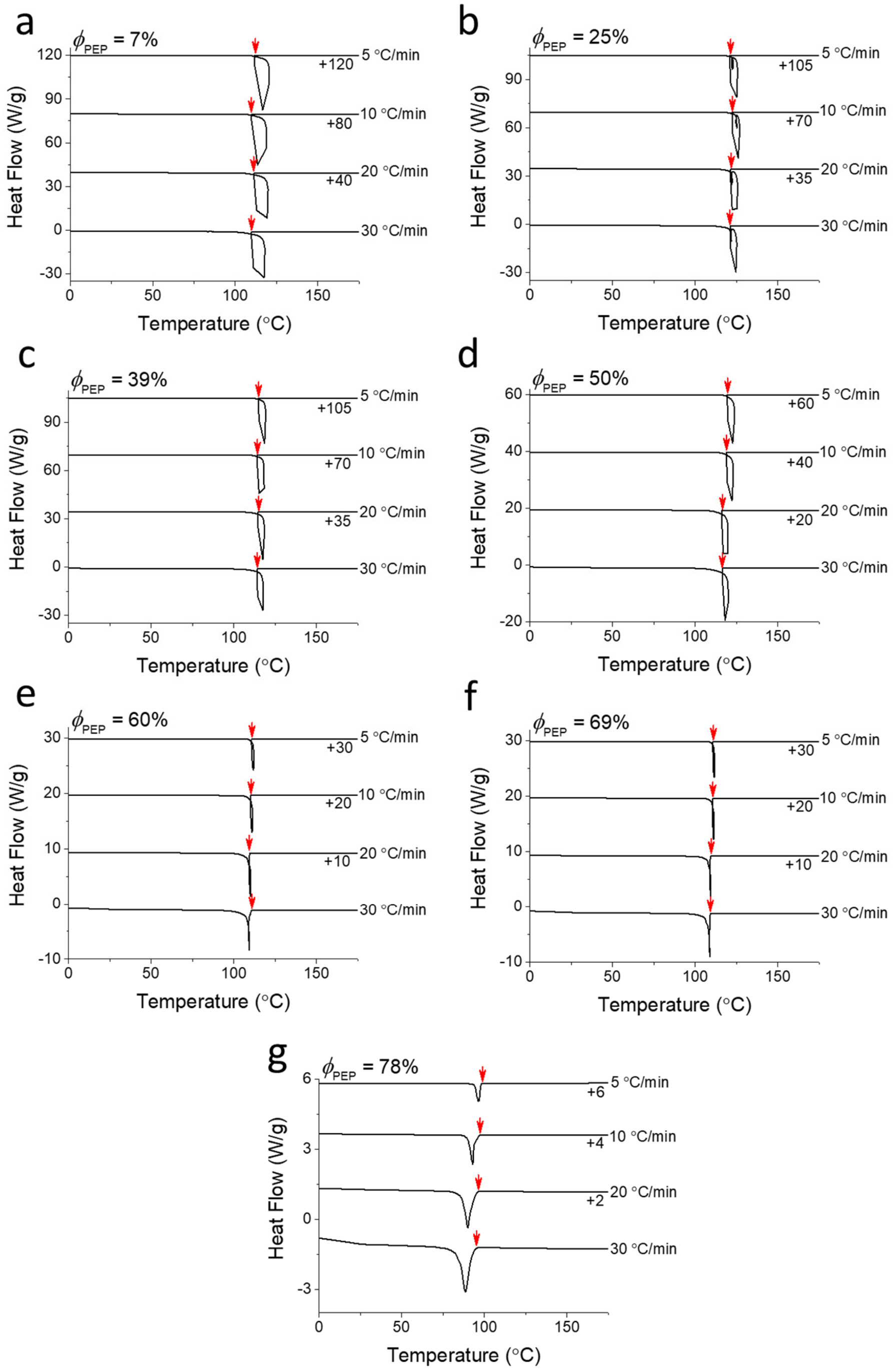

Figure S3. Cooling DSC thermograms of poly(ethylene-*alt*-propylene) (PEP, M_n = 25.5 kg/mol) and pyrene mixtures at ϕ_{PEP} = (a) 7 vol. %, (b) 25 vol. %, (c) 39 vol. %, (d) 50 vol. %, (e) 60 vol. %, (f) 69 vol. %, (g) 78 vol. % in endo-up forms. The commencement temperatures of crystallization are marked with red arrows. Thermograms are shifted for clear representations.

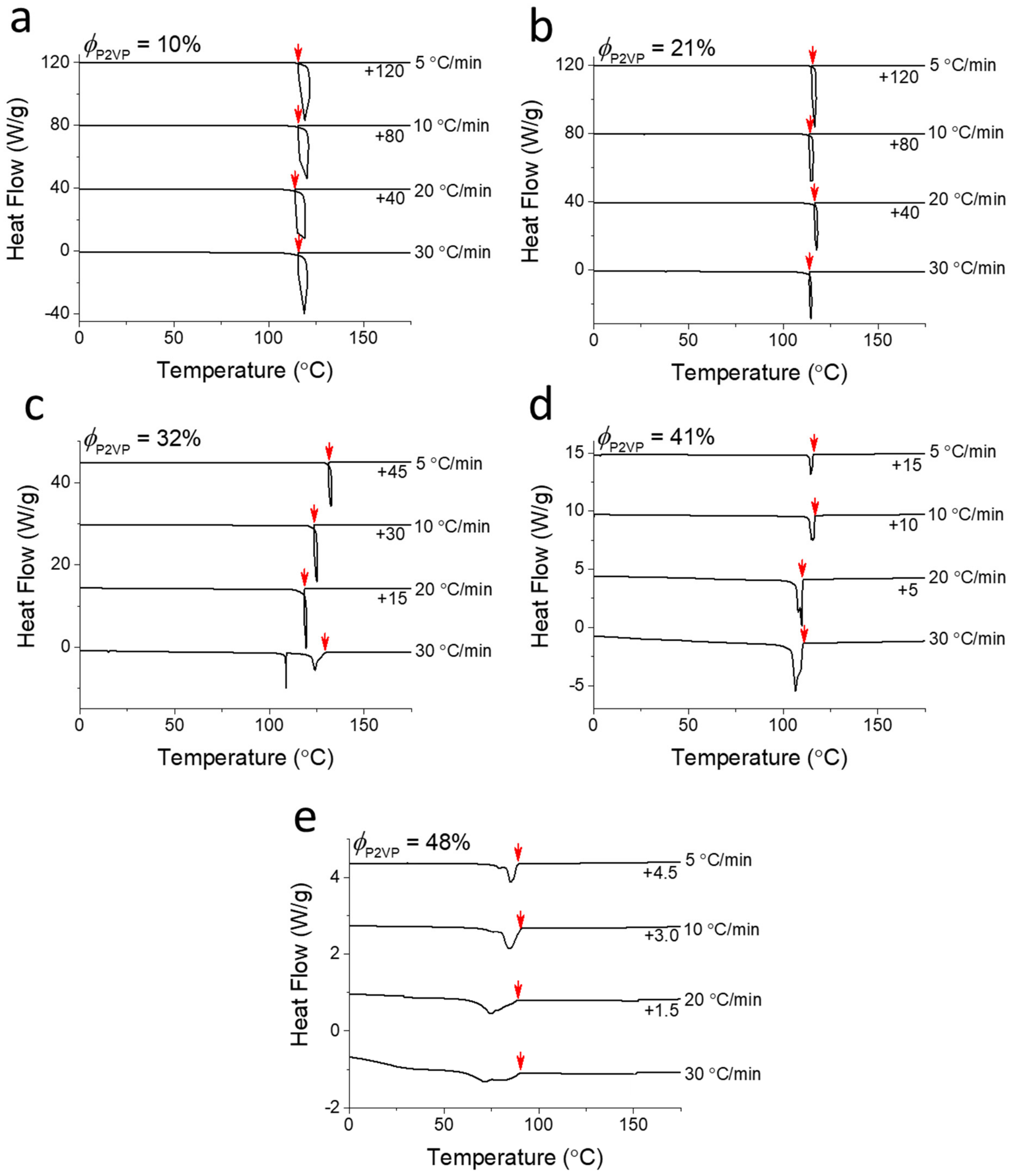

Figure S4. Cooling DSC thermograms of poly(2-vinylpyridine) (P2VP, M_n = 20.3 kg/mol) and pyrene mixtures at ϕ_{P2VP} = (a) 12 vol. %, (b) 23 vol. %, (c) 34 vol. %, (d) 45 vol. %, (e) 55 vol. % in endo-up forms. The commencement temperatures of crystallization are marked with red arrows. Thermograms are shifted for clear representations.

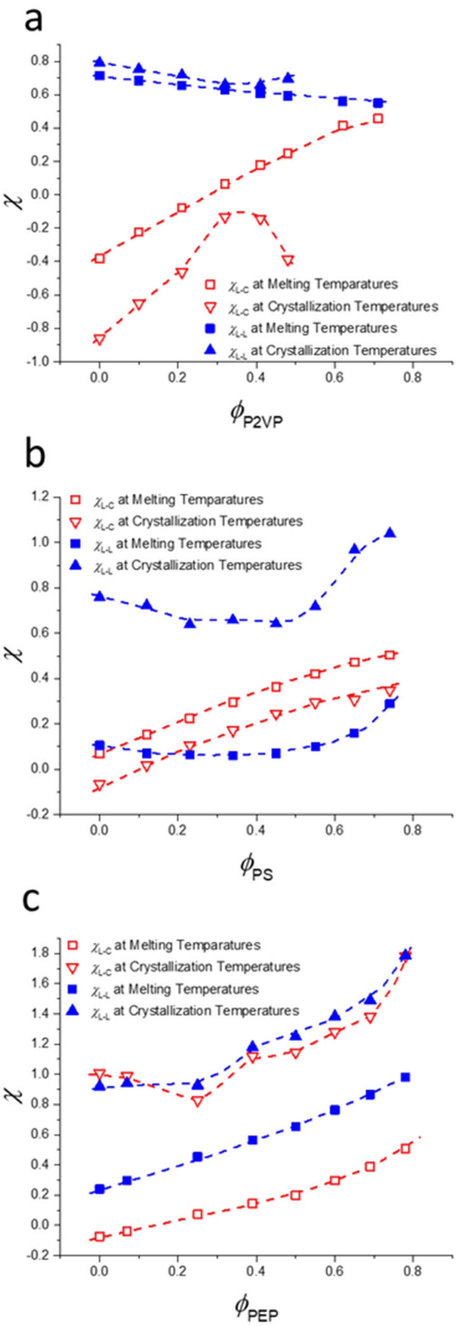

Figure S5. Effective interaction parameters of pyrene and (a) Poly(2-vinylpyridine), (b) Polystyrene, or (c) Poly(ethylene-*alt*-propylene) at the binodal and crystallization temperatures and compositions based on the parameters extracted from the melting and crystallization temperatures in Figure 6 of the main text. The effective interaction parameters extracted at different temperatures and by the different experimental methods are inconsistent with each other.

Table S2. Contributions to the second virial coefficient by Budkov and co-workers.[2] Note that calculated quantities are estimations and not exact.

i) Contribution by the Flory-Huggins interaction parameter.

Compound	δ_s (MPa$^{1/2}$)[a]	$\chi_{FH} = \frac{v}{RT}\left(\delta_{\mathrm{PY}} - \delta_p\right)$ [b]	$v\left(\frac{1}{2} - \chi_{FH}\right)$ (m^3)[c]
Pyrene	21.7	-	
Polystyrene	18.8	0.204	7.82×10^{-28}
Poly(ethylene-*alt*-propylene)	17.6	0.407	2.44×10^{-28}
Poly-2-vinylpyridine	19.6	0.107	10.4×10^{-28}

ii) Contribution by the Keesom dipole-dipole interaction.

Compound	p (Debye)[d]	$-\frac{16\pi^3 p^4}{27(k_B T)^2 \varepsilon_s^2 v}$ (m^3)[e]
Toluene (Polystyrene)	0.375	-0.07×10^{-28}
Isobutane (Polyethylene-*alt*-propylene)	0.132	-0.01×10^{-28}
Pyridine (Poly-2-vinylpyridine)	2.2	-82.9×10^{-28}

iii) Contribution by the dielectric mismatch of solvent and polymer.

Compound	ε_r[f]	δ[g]	$\frac{8\pi^2 p^2}{9k_B T\varepsilon_s}\delta$ (m^3)[h]
Pyrene	3.10	-	-
Polystyrene	2.69	0.133	0.12×10^{-28}
Poly(ethylene-*alt*-propylene)	2.51	0.189	0.02×10^{-28}
Poly-2-vinylpyridine	2.80	0.097	3.02×10^{-28}

[a] Solubility parameters of the compounds employed in this study.[1] [b] Flory-Huggins interaction parameters of pyrene and the polymers employed in study.[3] $v = 2.64\times10^{-28}$ m^3 is the volume of a pyrene molecule in the crystalline state,[4] R is the gas constant, T is the temperature of the solution which we assume 400K, δ_{PY} is the solubility parameter of pyrene, and δ_p is the

solubility parameter of polymer. [c] First term of the right-hand side of eqn (8) in the main text which is of the Flory-Huggins interaction parameter. [d] Dipole moments of simple liquids assumed comparable to the dipole moments of the chain segments of the polymers in the parenthesis of the compound column.[5] [e] Second term of the right-hand side of eqn (8) in the main text which is of the Keesom dipole-dipole interaction. k_B is the Boltzmann constant and ε_s is the dielectric permittivity of solvent which is the permittivity of pyrene in this study. [f] Relative dielectric permittivity $\varepsilon_r = \varepsilon/\varepsilon_0 \approx \delta_s/7$ where ε is the dielectric permittivity and ε_0 is the vacuum permittivity.[6] [g] $\delta = (\varepsilon_s - \varepsilon_p)/\varepsilon_s$ where ε_p is the dielectric permittivity of polymer. [h] Third term of the right-hand side of eqn (8) in the main text which is of the dielectric mismatch between solvent and polymer.

References

1. G. N. Kangovi and S. Lee, *Macromolecules*, 2017, **50**, 8678-8687.
2. Y. A. Budkov, N. N. Kalikin and A. L. Kolesnikov, *Eur. Phys. J. E*, 2017, **40**, 47.
3. P. C. Hiemenz and T. P. Lodge, *Polymer Chemistry*, CRC Press, Boca Raton, FL, 2nd edn., 2007.
4. W.-K. Wong and E. F. Westrum, *J. Chem. Thermodyn.*, 1971, **3**, 105-124.
5. W. M. Haynes, *CRC handbook of chemistry and physics*, CRC press, 2014.
6. D. W. van Krevelen, *Properties of Polymers: Their CorrelationWith Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*, Elsevier Science, Amsterdam, Netherlands, 4th edn, 2014, p. 331.