Supporting Information

for

Effect of Solvent Quality toward the Association of Succinimide Pendants of a Modified Ethylene-Propylene Copolymer in Mixtures of Toluene and Hexane

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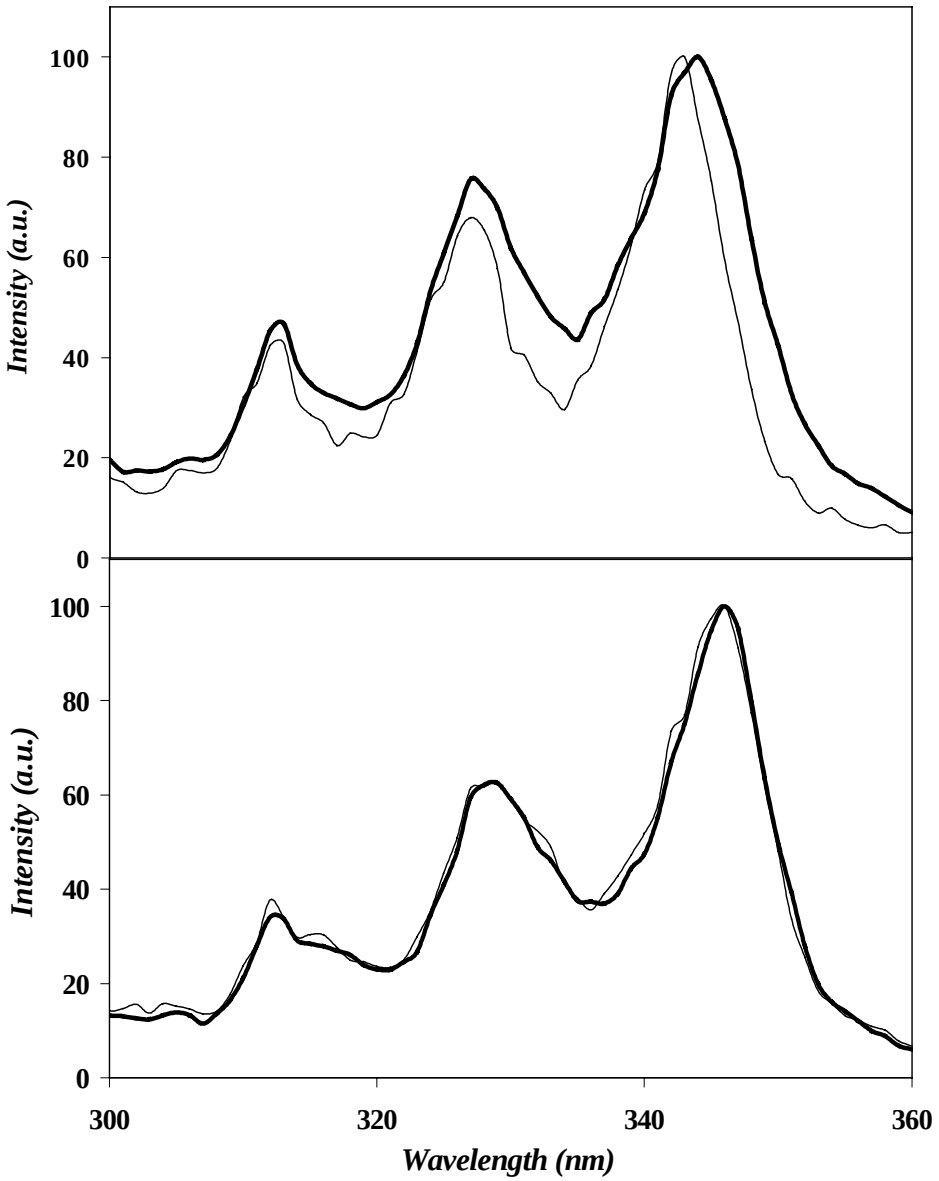

Figure SI.1. Excitation spectra of Py–EP in A) hexane and B) toluene. λ_{em} = 375 nm (──), λ_{em} = 500 nm (▬) ([Py–EP] = 2.5×10^{-6} M).

Table SI.1A. Parameters obtained from the tetra-exponential fit of the monomer fluorescence decays of the Py–EP in hexane/toluene mixtures at various volume fractions of hexane

Hexane%	τ_{m1} (ns)	a_{m1}	τ_{m2} (ns)	a_{m2}	τ_{m3} (ns)	a_{m3}	τ_{m4} (ns)	a_{m4}	χ^2
100	11	0.31	54	0.31	159	0.24	350	0.14	0.99
95	10	0.32	36	0.32	129	0.22	348	0.15	1.08
90	12	0.27	31	0.34	128	0.25	345	0.14	1.07
85	10	0.38	41	0.27	123	0.21	342	0.14	1.16
80	11	0.31	35	0.27	103	0.24	340	0.18	1.10
60	12	0.24	25	0.26	105	0.30	325	0.20	1.11
50	16	0.37	55	0.25	137	0.20	316	0.19	1.07
40	13	0.29	36	0.32	125	0.24	305	0.14	1.13
20	10	0.29	40	0.30	111	0.22	296	0.19	1.01
0	12	0.33	39	0.29	118	0.25	282	0.13	1.13

Table SI.1B. Parameters obtained from the tri-exponential fit of the excimer fluorescence decays of the Py–EP in hexane/toluene mixtures at various volume fractions of hexane

Hexane%	τ_{e1} (ns)	$\frac{a_{e1}}{a_{e2}+a_{e3}}$	τ_{e2} (ns)	$\frac{a_{e2}}{a_{e2}+a_{e3}}$	τ_{e3} (ns)	$\frac{a_{e3}}{a_{e2}+a_{e3}}$	χ^2
100	16	-0.28	66	0.91	149	0.09	1.05
95	15	-0.34	68	0.94	167	0.06	1.19
90	15	-0.39	67	0.92	151	0.08	1.16
85	17	-0.41	63	0.87	132	0.13	1.17
80	15	-0.48	67	0.93	162	0.07	0.94
60	15	-0.52	67	0.92	157	0.08	1.04
50	18	-0.54	63	0.87	130	0.13	1.11
40	16	-0.63	67	0.93	156	0.07	1.18
20	16	-0.60	67	0.93	165	0.07	1.18
0	16	-0.58	66	0.93	154	0.07	1.18

Table SI.2A. Parameters retrieved from the *blob* model global analysis of the pyrene monomer and excimer decays of Py–EP in hexane/toluene mixtures at various volume fractions of hexane

hexane%	f_{Mdiff}	f_{Mfree}	k_{diff} (10^7 s^{-1})	k_{ex}[blob] (10^6 s^{-1})	<*n*>	τ_M (ns)	f_{Ediff}	f_{EE0}	f_{ED}	τ_{E0} (ns)	τ_D (ns)	χ^2
100	0.83	0.17	1.7	4.9	1.4	350	0.34	0.63	0.03	64	145	1.20
95	0.85	0.15	2.0	5.2	1.5	348	0.44	0.52	0.04	63	157	1.18
90	0.86	0.14	2.2	5.5	1.5	345	0.48	0.49	0.03	62	159	1.18
85	0.85	0.15	2.7	5.7	1.5	342	0.49	0.48	0.03	59	162	1.16
80	0.81	0.19	2.2	6.2	1.6	340	0.57	0.39	0.04	54	169	1.19
60	0.80	0.20	2.2	5.5	1.5	325	0.61	0.36	0.03	53	165	1.10
50	0.80	0.20	2.1	5.2	1.5	316	0.62	0.36	0.02	55	159	1.17
40	0.83	0.17	2.0	4.8	1.5	305	0.65	0.34	0.02	53	163	1.17
20	0.79	0.21	2.1	6.2	1.5	296	0.66	0.29	0.05	56	165	1.12
0	0.76	0.24	2.1	5.2	1.5	282	0.67	0.31	0.02	52	158	1.18

Table SI.2B. Fraction of associated Py units f_{agg} (=f_{E0} + f_D)

hexane%	f_{diff}	f_{free}	f_{E0}	f_D	f_{agg}
100	0.31	0.08	0.58	0.03	0.61
95	0.41	0.07	0.47	0.04	0.51
90	0.44	0.07	0.46	0.03	0.49
85	0.45	0.08	0.44	0.02	0.46
80	0.50	0.12	0.35	0.04	0.39
60	0.52	0.13	0.31	0.03	0.34
50	0.53	0.14	0.31	0.02	0.33
40	0.57	0.12	0.30	0.02	0.32
20	0.56	0.15	0.25	0.04	0.29
0	0.55	0.17	0.26	0.02	0.27

Solubility parameter of methyl succinimide.

The Hansen parameters can be estimated as follows:

$$\delta_d = \frac{\sum F_{di}}{V} \qquad \delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \qquad \delta_h = \sqrt{\frac{\sum E_{hi}}{V}}$$

where V represents the molar volume of methyl succinimide and the values of the F_{di}, F_{pi}, and E_{hi} parameters can be found in the literature.[1] Methyl succinimide being made of 2 methylenes, 2 carbonyls, 1 methyl, and a tertiary nitrogen, the values of F_{di}, F_{pi}, and E_{hi} for each section of the molecule is listed in Table SI.3.

Table SI.3.

Structural Group i	F_{di} $J^{1/2}.cm^{3/2}.mol^{-1}$	F_{pi} $J^{1/2}.cm^{3/2}.mol^{-1}$	E_{hi} $J.mol^{-1}$	V_i $cm^3.mol^{-1}$
$-CH_2-$	270	0	0	15.55
$-CO-$	290	770	2000	17.3
$-CH_3$	420	0	0	21.55
$-N-$ |	20	800	5000	12.6

It must be noted that $\sum F_{pi}^2$ in the expression of δ_p was halved to account for the plane of symmetry of methyl succinimide. The F_{di}, F_{pi}, E_{hi}, and V_i values listed in Table SI.3 were used to calculate the parameters δ, δ_d, δ_p, and δ_h for methyl succinimide shown in Table 3.

Reference

1. Bandrup, J. ; Immergut, E. H. ; Grulke, E. A. *Polymer Handbook*, 4th ed.; John Wiley & Sons: NY, 1999, p 686-687.