Supporting Information

Lithium Polysulfide Radical Anions in Ether-Based Solvents

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I. UV-vis Spectra Peak Fitting and Parameters

UV-vis spectra obtained for polysulfide solutions were fit using a series of Gaussian functions in Igor Pro's MultipeakFit peak fitting program. An example of the peak fitting is shown below in Figure S1, where the raw spectrum of the TEGDME, x_{mix} = 4, 50 mM sample is plotted along with the calculated fit and the individual Gaussian functions comprising the calculated fit.

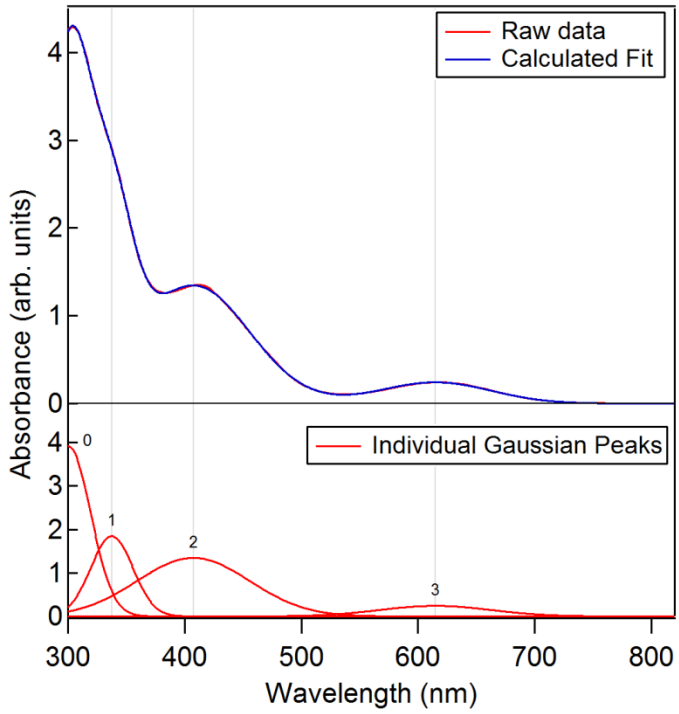

Figure S1: Peak fitting for the TEGDME, x_{mix} = 4, C_S = 50 mM UV-vis spectrum

The parameters pertaining to each solution's UV-vis spectrum are shown in Tables S1-S15 below.

Table S1. UV-vis peak fitting parameters for TEGDME x_{mix} = 4, C_S = 10 mM

TEGDME x_{mix} = 4, C_S = 10 mM			
	Location	Amplitude	Area
Peak 0	297.93	0.77	42.88
Peak 1	339.16	0.44	19.65
Peak 2	410.92	0.32	42.74
Peak 3	472.20	0.01	0.24
Peak 4	617.00	0.10	12.05

Table S2. UV-vis peak fitting parameters for TEGDME x_{mix} = 4, C_S = 50 mM

TEGDME x_{mix} = 4, C_S = 50 mM			
	Location	Amplitude	Area
Peak 0	300.72	3.95	191.84
Peak 1	338.28	1.77	78.23
Peak 2	407.32	1.35	164.09
Peak 3	617.00	0.24	28.19

Table S3. UV-vis peak fitting parameters for TEGDME x_{mix} = 4, C_S = 100 mM

TEGDME x_{mix} = 4, C_S = 100 mM			
	Location	Amplitude	Area
Peak 0	321.76	6.44	409.40
Peak 1	411.54	2.70	316.65
Peak 2	617.00	0.39	45.07

Table S4. UV-vis peak fitting parameters for TEGDME x_{mix} = 6, C_S = 10 mM

TEGDME x_{mix} = 6, C_S = 10 mM			
	Location	Amplitude	Area
Peak 0	291.01	0.48	24.28
Peak 1	337.24	0.32	14.91
Peak 2	334.99	0.22	54.49
Peak 3	442.37	0.13	13.52
Peak 4	617.00	0.05	6.04

Table S5. UV-vis peak fitting parameters for TEGDME x_{mix} = 6, C_S = 50 mM

TEGDME x_{mix} = 6, C_S = 50 mM			
	Location	Amplitude	Area
Peak 0	292.43	3.85	216.60
Peak 1	335.76	2.30	128.79
Peak 2	418.34	1.50	218.79
Peak 3	617.00	0.21	24.52

Table S6. UV-vis peak fitting parameters for TEGDME x_{mix} = 6, C_S = 100 mM

TEGDME x_{mix} = 6, C_S = 100 mM			
	Location	Amplitude	Area
Peak 0	345.13	3.65	175.41
Peak 1	417.63	3.24	455.74
Peak 2	617.00	0.39	45.09

Table S7. UV-vis peak fitting parameters for TEGDME x_{mix} = 8, C_S = 10 mM

TEGDME x_{mix} = 8, C_S = 10 mM			
	Location	Amplitude	Area
Peak 0	275.30	0.69	55.44
Peak 1	337.99	0.24	12.72
Peak 2	418.26	0.20	29.60
Peak 3	617.00	0.03	3.45

Table S8. UV-vis peak fitting parameters for TEGDME x_{mix} = 8, C_S = 50 mM

TEGDME x_{mix} = 8, C_S = 50 mM			
	Location	Amplitude	Area
Peak 0	283.30	3.96	326.05
Peak 1	341.47	1.07	59.53
Peak 2	405.33	1.25	264.77
Peak 3	617.00	0.08	8.95

Table S9. UV-vis peak fitting parameters for TEGDME x_{mix} = 8, C_S = 100 mM

TEGDME x_{mix} = 8, C_S = 100 mM			
	Location	Amplitude	Area
Peak 0	268.74	11.93	1901.30
Peak 1	440.64	0.71	54.73
Peak 2	457.16	1.72	342.99
Peak 3	617.00	0.12	15.67

Table S10. UV-vis peak fitting parameters for TEGDME x_{mix} = 10, C_S = 10 mM

TEGDME x_{mix} = 10, C_S = 10 mM			
	Location	Amplitude	Area
Peak 0	278.26	0.67	50.54
Peak 1	337.39	0.23	12.45
Peak 2	416.51	0.18	27.42
Peak 3	617.00	0.02	2.64

Table S11. UV-vis peak fitting parameters for TEGDME x_{mix} = 10, C_S = 50 mM

TEGDME x_{mix} = 10, C_S = 50 mM			
	Location	Amplitude	Area
Peak 0	259.19	4.61	833.28
Peak 1	442.92	0.45	37.09
Peak 2	482.41	0.46	80.51
Peak 3	617.00	0.06	7.29

Table S12. UV-vis peak fitting parameters for TEGDME x_{mix} = 10, C_S = 100 mM

TEGDME x_{mix} = 10, C_S = 100 mM			
	Location	Amplitude	Area
Peak 0	255.63	11.81	2102.40
Peak 1	444.38	0.52	38.15
Peak 2	464.25	1.56	313.01
Peak 3	617.00	0.08	9.98

Table S13. UV-vis peak fitting parameters for PEO x_{mix} = 4, C_S = 10 mM

PEO x_{mix} = 4, C_S = 10 mM			
	Location	Amplitude	Area
Peak 0	305.33	0.75	68.44
Peak 1	345.67	0.42	13.79
Peak 2	428.60	0.26	34.66
Peak 3	617.00	0.06	7.38

Table S14. UV-vis peak fitting parameters for PEO x_{mix} = 6, C_S = 10 mM

PEO x_{mix} = 6, C_S = 10 mM			
	Location	Amplitude	Area
Peak 0	299.13	0.56	53.20
Peak 1	344.48	0.20	6.87
Peak 2	425.35	0.17	22.55
Peak 3	617.00	0.03	3.94

Table S15. UV-vis peak fitting parameters for PEO x_{mix} = 8, C_S = 10 mM

PEO x_{mix} = 8, C_S = 10 mM			
	Location	Amplitude	Area
Peak 0	296.63	0.41	18.07
Peak 1	336.83	0.35	17.93
Peak 2	416.55	0.14	19.78
Peak 3	617.00	0.02	2.71

II. EPR Spectra Fitting and Parameters

EPR spectra were fit using a first derivative Tsallian function as described by Weir et al.[1] and shown in Equation S1:

$$y = a\frac{\left(2^{(b-1)}-1\right)}{(b-1)}\frac{2}{d^2}(x-c)\left[1+(2^{b-1}-1)\left(\frac{x-c}{2d}\right)^2\right]^{\left(\frac{-b}{b-1}\right)} \qquad \text{(Equation S1)}$$

Here, four parameters (*a*, *b*, *c*, and *d*) were fit for each spectrum. The spectra were fit using Igor Pro's Curve Fitting program. An example fitting is shown in Figure S2, for the TEGDME, x_{mix} = 6, 100 mM spectrum.

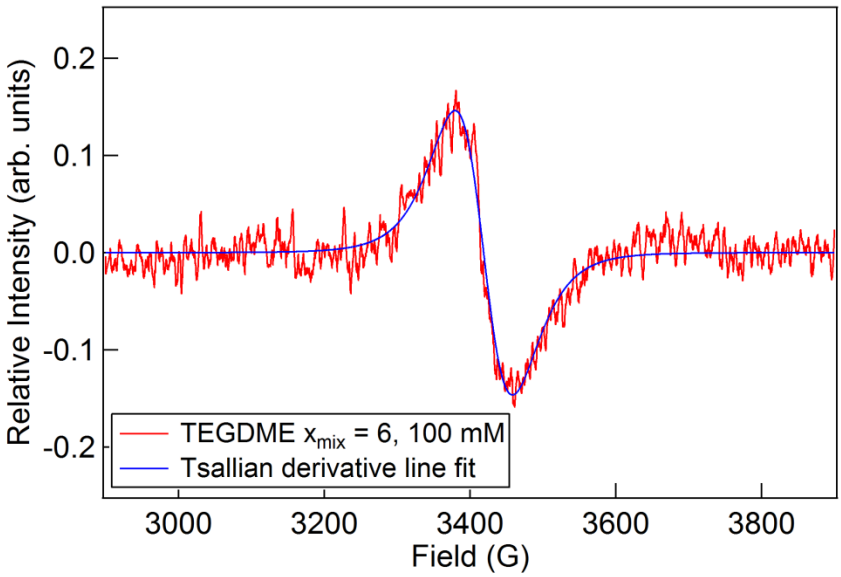

Figure S2: Peak fitting for the TEGDME, x_{mix} = 6, C_S = 100 mM EPR spectrum

After fitting the EPR spectra with the Tsallian first derivative line functions, the fits were then integrated using Igor Pro's built-in Integration function (using a trapezoidal integration algorithm). The areas of the resulting integrated Tsallian curves were then obtained using Igor Pro's "areaxy" code. The g-factors ('g') for each solution were obtained using Equation S2:

$$g = \frac{B\mu_B}{h\nu} \qquad \text{(Equation S2)}$$

Here, h represents Planks constant; ν is the microwave frequency of the given EPR experiment; B is the center of the EPR spectrum (the field strength at which the EPR spectrum intersects y = 0), which for each spectrum was parameter c determined from fitting of Equation S1 above; and μ_B the Bohr magneton.

The fitting parameters, g-factors, and integrated areas for each EPR spectrum are shown below in Tables S16 and S17.

Table S16: EPR peak fitting parameters for TEGDME polysulfide solutions

TEGDME EPR Spectra Fit Parameters										
x_{mix}	C_S	a	±	b	±	c	±	d	±	g-factor
4	10	0.91	0.01	1.68	0.06	3424.3	0.35	25.9	0.4	2.0280
	50	1.52	0.01	1.35	0.03	3420.5	0.23	26.55	0.2	2.0298
	100	3.18	0.02	1.59	0.02	3420.3	0.12	27.76	0.13	2.0307
	300	6.18	0.02	1.49	0.01	3420.1	0.08	27.81	0.08	2.0302
6	10	0.22	0.01	1	0	3435.1	0.08	15.77	0	2.0221
	50	1.47	0.01	1.34	0.03	3422.4	0.23	26.66	0.19	2.0294
	100	2.96	0.02	1.39	0.02	3418.7	0.14	27.26	0.13	2.0305
	300	7.24	0.02	1.8	0.01	3418.9	0.07	29.84	0.09	2.0308
8	10	0.18	0.01	1.21	0.16	3438.4	0.97	16.74	0.7	2.0203
	50	0.52	0	1	0	3425.8	0.03	22.46	0	2.0274
	100	1.39	0.02	1.37	0.03	3421.1	0.26	25.6	0.22	2.0302
	300	3.35	0.02	1.69	0.02	3420.7	0.13	26.41	0.15	2.0298
10	10	0.13	0.01	1.01	0.15	3442	1	14.62	0.61	2.0176
	50	0.56	0.05	1	0	3424.3	0.04	21.43	0.86	2.0280
	100	0.97	0.01	1.18	0.04	3423.2	0.34	24.7	0.24	2.0288
	300	2.67	0.02	1.52	0.02	3419.6	0.16	26.29	0.16	2.0299

Table S17: EPR peak fitting parameters for PEO polysulfide solutions

PEO EPR Spectra Fit Parameters										
x_{mix}	C_S	a	±	b	±	c	±	d	±	g-factor
4	10	0.62	0.01	1.43	0.06	3421.7	0.3	17.03	0.27	2.0315
	300	7.98	0.02	2	0.01	3418.4	0.03	19.99	0.05	2.0318
6	10	0.27	0.01	1	0.07	3423.6	0.55	15.32	0.36	2.0289
	300	1.6	0.02	2	0.04	3414.1	0.14	18.11	0.22	2.0327
8	10	0.126	0.01	1.56	0.27	3413.2	0.74	10.98	0.76	2.0351
	300	1.03	0.01	1.8	0.05	3413	0.17	16.7	0.22	2.0340

References

(1) Weil, J. B., James *Electron Paramagnetic Resonance Elementary Theory and Practical Applications*; Second Edition ed.; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2007.