Supporting Information for Structure and dynamics of small polyimide oligomers with silicon as a function of aging

Mary K. Burdette-Trofimov*,†, Beth L. Armstrong*,‡, Luke Heroux¶, Mathieu Doucet¶, Robert L. Sacci†, and Gabriel M. Veith*,†

†Chemical Sciences Division, Oak Ridge National Laboratory

‡ Materials Science and Technology Division, Oak Ridge National Laboratory

¶Neutron Scattering Division, Oak Ridge National Laboratory

E-mail: burdettekk@ornl.gov, armstrongbl@ornl.gov, veithgm@ornl.gov

ORCID
Mary K. Burdette-Trofimov: https://orcid.org/0000-0003-2395-2867
Beth L. Armstrong: https://orcid.org/0000-0001-7149-3576
Luke Heroux: https://orcid.org/0000-0001-8993-3904
Mathieu Doucet: https://orcid.org/0000-0002-5560-6478
Robert L. Sacci: https://orcid.org/0000-0002-0073-5221
Gabriel M. Veith: https://orcid.org/0000-0002-5186-4461

Rheology coupled USANS (rheo-USANS) was employed to investigate the aggregation and agglomeration behavior of silicon/PI binder slurries as a function of UV cure time. The rheo-USANS scattering curves were fit with a correlation length model described by Equation S1 and schematically depicted in Figure S1 where Q is the magnitude of the wave vector transfer of scattered neutrons.[1-2] A represents the number of agglomerates (length scale: 1-10 μm) where an increase in the number of agglomerates is represented by a smaller A value.[1-2] The n parameter is the Porod scattering exponent which characterizes the shape of the aggregate or the mass fractal. The n parameter has values of n=1-4 where an n=1 is characteristic of a rod; n=2-3 is an ellipsoid, and n=4 is a hard sphere.[1-3] The C parameter characterizes the number of aggregates (length scale: 200 nm-1 μm) where an increase in the C parameter characterizes an increase in the number of aggregates.[1-2] The L parameter corresponds to correlation, or cluster, length.[1-2] The m parameter

is the Lorentzian exponent, which relates to the density of the packing of the clusters.[1-2] Generally, in a colloidal system containing polymers in solution, the m parameter relates to the packing of polymer chains. However, since the PI chains are small and on the order of oligomers, the packing of the chains is likely too small for the USANS instrument to detect. Therefore, in the silicon/PI slurries, the m parameter is more likely representative of the packing density of Si-Si, Si-PI, or PI-PI clusters. In terms of how all the parameters relate to one another, a cluster is the building block of an aggregate where two or more clusters comprise an aggregate. An aggregate is the building block of an agglomerate where two or more aggregates make up an agglomerate (Figure S1).

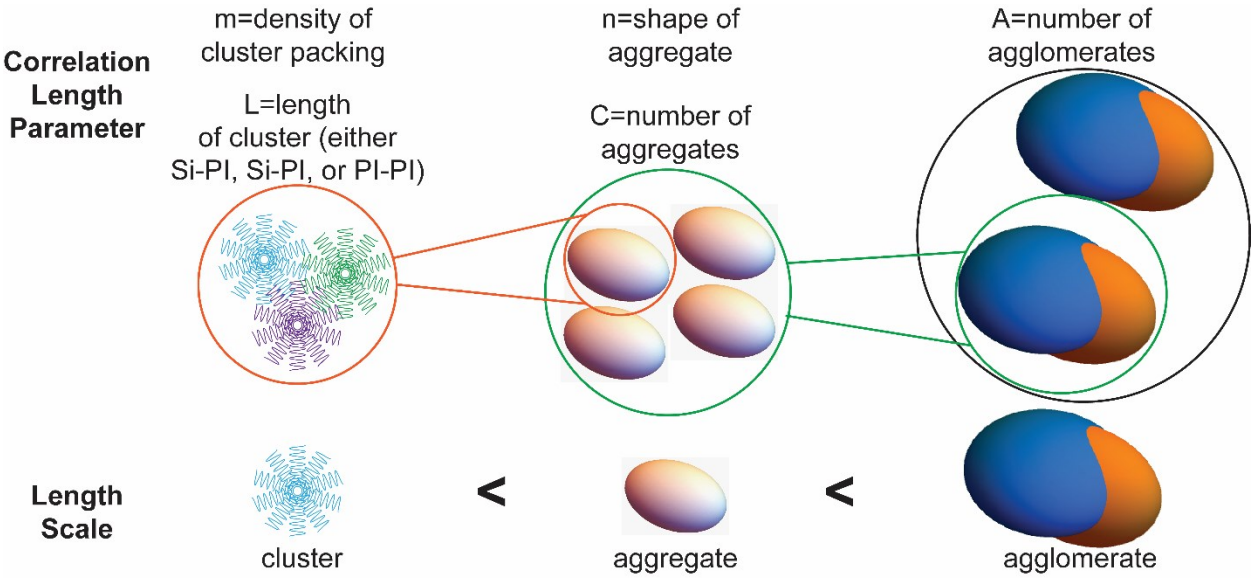


Figure S1: Schematic representation of the correlation length model used to fit the rheo-USANS data. The m parameter represents the density of cluster packing and L represents the length of the cluster; C characterizes the number of aggregates and the n parameter represents the shape of the aggregate; A represents the number of agglomerates. An agglomerate is comprised to aggregates, while aggregates are made of clusters.

Figure S2 presents the full FTIR spectrum of 10 min UV cured PI solution, 30 min UV cured PI solution, 60 min UV cured PI solution, and uncured PI binder solution.

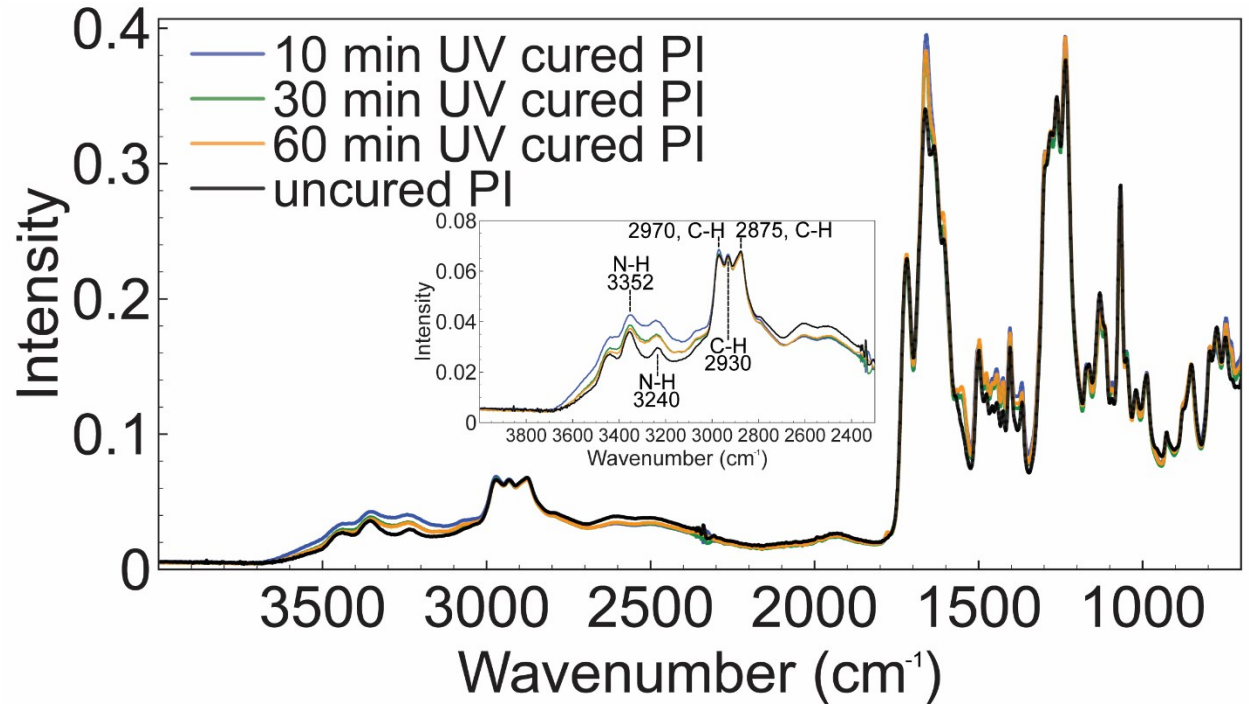


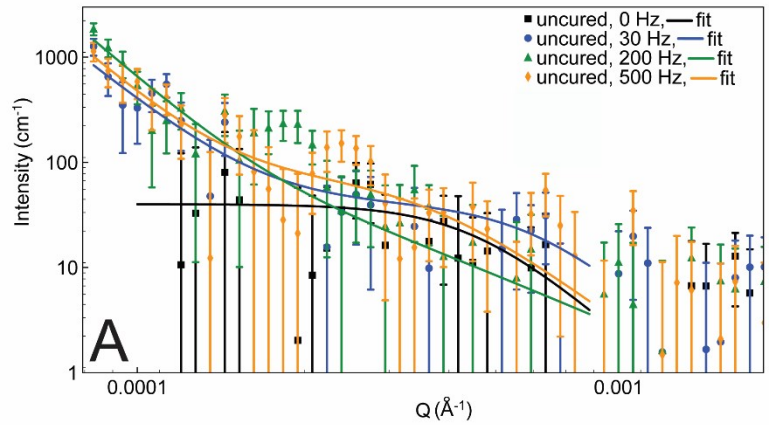
Figure S2: Full Fourier transform infrared (FTIR) spectra plotted as intensity versus wavenumber for 10 min UV cured PI solution (blue), 30 min UV cured PI solution (green), 60 min UV cured PI solution (orange), and uncured PI solution (black). The black dashed lines indicate important peaks. The inset is a zoomed view of the region from 4000-2400 cm^{-1}.

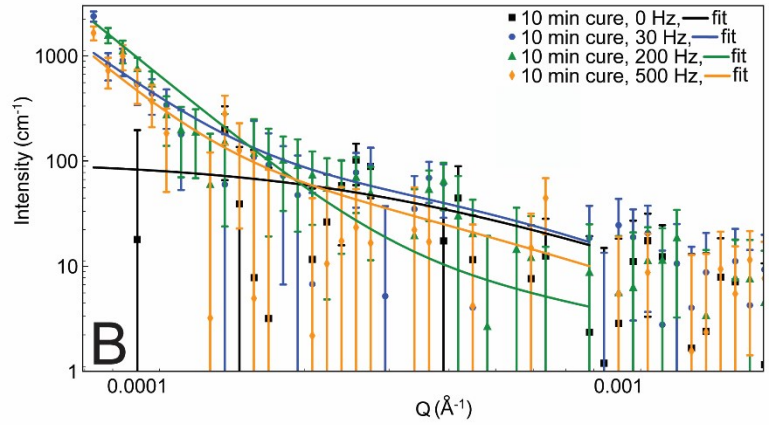
Table S1 presents the weight average molecular weight and polydispersity index of the uncured, 10, 30, and 60 min UV cured PI.

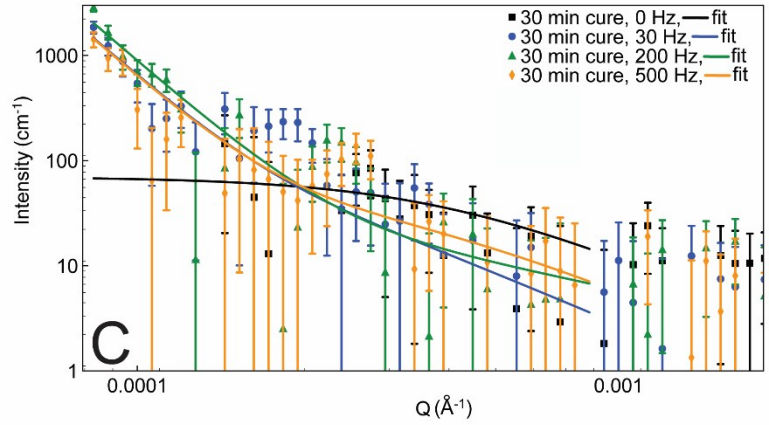
Table S1: Weight average molecular weight and polydispersity index of uncured, 10, 30, and 60 min cured PI.

Sample	Weight Average Molecular Weight (M_w)	Polydispersity Index (PDI)
Uncured PI	6240 g/mol	1.08
10 min UV cured PI	6190 g/mol	1.10
30 min UV cured PI	6380 g/mol	1.14
60 min UV cured PI	7050 g/mol	1.24

Figure S3 are the neutron scattering curves plotted as neutron scattering intensity versus the neutron wavevector, Q for the neat PI solutions.


uncured, 0 Hz, fit
uncured, 30 Hz, fit
uncured, 200 Hz, fit
uncured, 500 Hz, fit
Intensity (cm-1)
1000
100
10
1
A
0.0001
0.001
Q (Å-1)


10 min cure, 0 Hz, fit
10 min cure, 30 Hz, fit
10 min cure, 200 Hz, fit
10 min cure, 500 Hz, fit
Intensity (cm-1)
1000
100
10
1
B
0.0001
0.001
Q (Å-1)


30 min cure, 0 Hz, fit
30 min cure, 30 Hz, fit
30 min cure, 200 Hz, fit
30 min cure, 500 Hz, fit
Intensity (cm-1)
1000
100
10
1
C
0.0001
0.001
Q (Å-1)

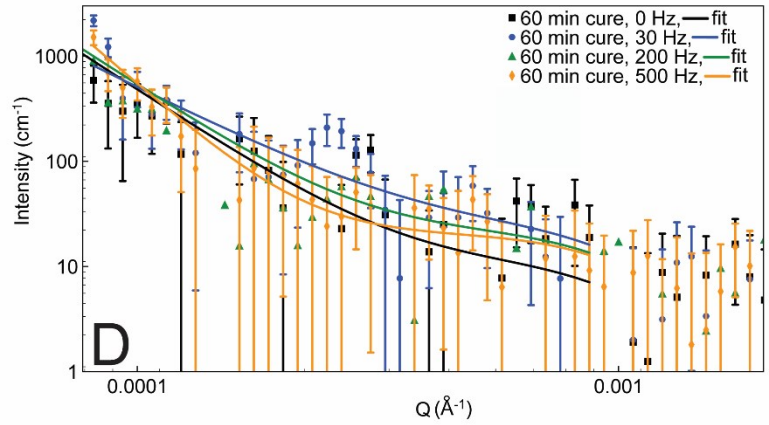

60 min cure, 0 Hz, fit
60 min cure, 30 Hz, fit
60 min cure, 200 Hz, fit
60 min cure, 500 Hz, fit
Intensity (cm-1)
1000
100
10
1
D
0.0001
0.001
Q (Å-1)

Figure S3: USANS scattering curves plotted as intensity versus the neutron wavevector, Q, of A) uncured PI, B) 10 min cure PI, C) 30 min cure PI, and D) 60 min cure PI neat solutions at 0 (black), 30 (blue), 200 (green), and 500 Hz (orange).

Figure S4 presents the neutron scattering curves of Si+uncured PI, Si+10 min UV cure PI, Si+30 min UV cure PI, Si+60 min UV cure PI slurries at 0 Hz, 30 Hz, 200 Hz, and 500 Hz plotted as scattering intensity as a function of the neutron wave vector, Q.

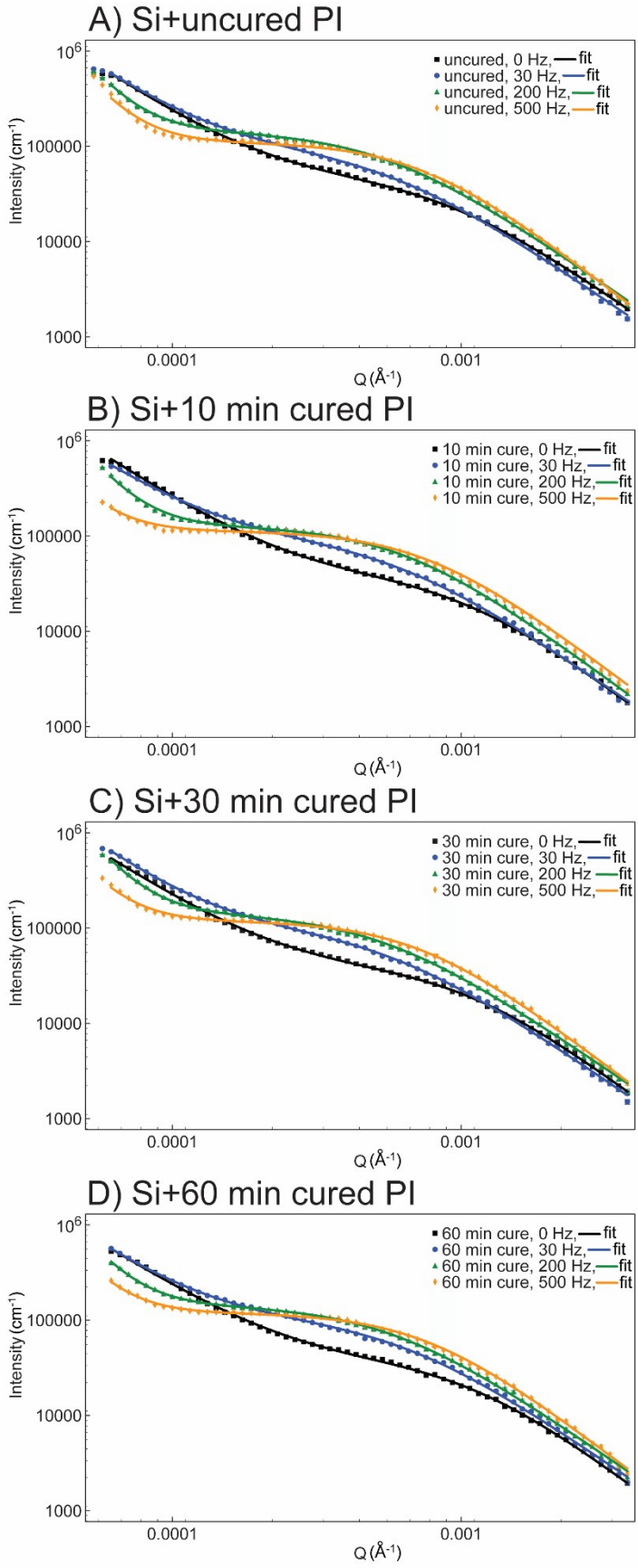

A) Si+uncured PI
uncured, 0 Hz, fit
uncured, 30 Hz, fit
uncured, 200 Hz, fit
uncured, 500 Hz, fit
B) Si+10 min cured PI
10 min cure, 0 Hz, fit
10 min cure, 30 Hz, fit
10 min cure, 200 Hz, fit
10 min cure, 500 Hz, fit
C) Si+30 min cured PI
30 min cure, 0 Hz, fit
30 min cure, 30 Hz, fit
30 min cure, 200 Hz fit
30 min cure, 500 Hz, fit
D) Si+60 min cured PI
60 min cure, 0 Hz, fit
60 min cure, 30 Hz, fit
60 min cure, 200 Hz, fit
60 min cure, 500 Hz, fit
Intensity (cm-1)
Q (Å-1)
10^6
100000
10000
1000
0.0001
0.001

Figure S4: USANS scattering curves plotted as intensity versus the neutron wavevector, Q, of A) Si+uncured PI, B) Si+10 min cure PI, C) Si+30 min cure PI, and D) Si+60 min cure PI at 0 (black), 30 (blue), 200 (green), and 500 Hz (orange).

Tables S2, S3, S4, and S5 present the correlation length model fit parameters for the Si+uncured PI, Si+10 min UV cure PI, Si+30 min UV cure PI, Si+60 min UV cure PI slurries at 0 Hz, 30 Hz, 200 Hz, and 500 Hz, respectively. The physical interpretation of the fit parameters is also provided in each table.

Table S2: Tabulated USANS correlation length model parameters and their physical meaning for the Si+uncured PI, Si+10 min UV cure PI, Si+30 min UV cure PI, Si+60 min UV cure PI slurries at 0 Hz.

Parameter	Sample	Value	Error	Physical Meaning
0 Hz				
C	Si+uncured PI	4.4×10^{4}	849	Number of aggregates decreases as cure time increases to 30 min. Number of aggregates decreases as cure time increases from 30 min to 60 min
	Si+10 min cure PI	3.4×10^{4}	704	
	Si+30 min cure PI	3.5×10^{4}	794	
	Si+60 min cure PI	3.4×10^{4}	701	
A	Si+uncured PI	1.3×10^{-3}	1.7×10^{-4}	Number of agglomerates decreases as cure time increases to 10 min. Number of agglomerates increases as cure time increases to 30 min. Number of agglomerates decreases as cure time increases to 60 min.
	Si+10 min cure PI	2.4×10^{-3}	2.5×10^{-4}	
	Si+30 min cure PI	2.2×10^{-3}	2.8×10^{-4}	
	Si+60 min cure PI	4.2×10^{-3}	5.0×10^{-4}	
L	Si+uncured PI	111 nm	2 nm	Cluster length decreases as cure time increases
	Si+10 min cure PI	98 nm	2 nm	
	Si+30 min cure PI	95 nm	2 nm	
	Si+60 min cure PI	93 nm	2 nm	
n	Si+uncured PI	2.05	0.01	Aggregate shape becomes more ellipsoidal as cure time increases
	Si+10 min cure PI	2.00	0.01	
	Si+30 min cure PI	1.98	0.01	
	Si+60 min cure PI	1.92	0.01	
m	Si+uncured PI	2.15	0.02	Cluster packing increases as cure time increases
	Si+10 min cure PI	2.30	0.03	
	Si+30 min cure PI	2.30	0.03	
	Si+60 min cure PI	2.32	0.03	

Table S3: Tabulated USANS correlation length model parameters and their physical meaning for the Si+uncured PI, Si+10 min UV cure PI, Si+30 min UV cure PI, Si+60 min UV cure PI slurries at 30 Hz.

Parameter	Sample	Value	Error	Physical Meaning
30 Hz				
C	Si+uncured PI	8.5×10^{4}	1800	Number of aggregates is unchanged

	Si+10 min cure PI	$8.5x10^{4}$	2012	as cure time increases to 10 min. Number of aggregates increases as cure time increases to 60 min.
	Si+30 min cure PI	$9.1x10^{4}$	1951	
	Si+60 min cure PI	$9.7x10^{4}$	1864	
A	Si+uncured PI	$7.0x10^{-3}$	$1.5x10^{-4}$	Number of agglomerates increases as cure time increases
	Si+10 min cure PI	$1.5x10^{-3}$	$3.6x10^{-4}$	
	Si+30 min cure PI	$2.6x10^{-4}$	$6.1x10^{-5}$	
	Si+60 min cure PI	$4.8x10^{-4}$	$1.2x10^{-4}$	
L	Si+uncured PI	175 nm	3 nm	Cluster length decreases as cure time increases to 10 min. Cluster length increases as cure time increases to 30 min. Cluster length decreases as cure time increases to 60 min.
	Si+10 min cure PI	168 nm	3 nm	
	Si+30 min cure PI	177 nm	3 nm	
	Si+60 min cure PI	160 nm	3 nm	
n	Si+uncured PI	2.10	0.02	Aggregate shape becomes more ellipsoidal as cure time increases to 10 min. Aggregate shape becomes more spherical as cure time increases to 30 min. Aggregate shape becomes more ellipsoidal as cure time increases to 60 min.
	Si+10 min cure PI	2.01	0.02	
	Si+30 min cure PI	2.21	0.02	
	Si+60 min cure PI	2.13	0.03	
m	Si+uncured PI	2.10	0.02	Cluster packing remains constant as cure time increases
	Si+10 min cure PI	2.09	0.02	
	Si+30 min cure PI	2.09	0.01	
	Si+60 min cure PI	2.10	0.02	

Table S4: Tabulated USANS correlation length model parameters and their physical meaning for the Si+uncured PI, Si+10 min UV cure PI, Si+30 min UV cure PI, Si+60 min UV cure PI slurries at 200 Hz.

Parameter	Sample	Value	Error	Physical Meaning
200 Hz				
C	Si+uncured PI	$1.4x10^{5}$	700	Number of aggregates decrease as cure time increases to 10 min. Number of aggregates increase as cure time increases to 60 min.
	Si+10 min cure PI	$1.3x10^{5}$	619	
	Si+30 min cure PI	$1.4x10^{5}$	794	
	Si+60 min cure PI	$1.4x10^{5}$	744	
A	Si+uncured PI	$4.2x10^{-12}$	$3.2x10^{-14}$	Number of agglomerates increase as cure time increases to 10 min. Number of agglomerates decreases as cure time increases to 30 min. Number of agglomerates increases as cure time increases to 60 min.
	Si+10 min cure PI	$4.1x10^{-12}$	$3.1x10^{-14}$	
	Si+30 min cure PI	$5.4x10^{-12}$	$3.7x10^{-14}$	
	Si+60 min cure PI	$3.8x10^{-12}$	$3.4x10^{-14}$	
L	Si+uncured PI	183 nm	1 nm	Cluster length decreases as cure time increases to 10 min. Cluster length increases as cure time increases to 30 min. Cluster length decreases as cure time increases to 60 min.
	Si+10 min cure PI	160 nm	1 nm	
	Si+30 min cure PI	188 nm	2 nm	
	Si+60 min cure PI	176 nm	1 nm	
n	Si+uncured PI	4.00	$3.5x10^{-9}$	Aggregate shape is a hard sphere at all cure times.
	Si+10 min cure PI	4.00	$3.8x10^{-9}$	

	Si+30 min cure PI	4.00	$4.0x10^{-9}$	
	Si+60 min cure PI	4.00	$3.6x10^{-9}$	
m	Si+uncured PI	2.11	0.01	Cluster packing increases as cure time increases to 10 min. Cluster packing decreases as cure time increases to 60 min.
	Si+10 min cure PI	2.24	0.01	
	Si+30 min cure PI	2.09	0.01	
	Si+60 min cure PI	2.11	0.01	

Table S5: Tabulated USANS correlation length model parameters and their physical meaning for the Si+uncured PI, Si+10 min UV cure PI, Si+30 min UV cure PI, Si+60 min UV cure PI slurries at 500 Hz.

Parameter	Sample	Value	Error	Physical Meaning
500 Hz				
C	Si+uncured PI	$1.1x10^{5}$	468	Number of aggregates increases as cure time increases.
	Si+10 min cure PI	$1.1x10^{5}$	475	
	Si+30 min cure PI	$1.2x10^{5}$	567	
	Si+60 min cure PI	$1.2x10^{5}$	545	
A	Si+uncured PI	$3.0x10^{-12}$	$2.7x10^{-14}$	Number of agglomerates increases as cure time increases to 10 min. Number of agglomerates decrease as cure time increases to 30 min. Number of agglomerates increases as cure time increases to 60 min.
	Si+10 min cure PI	$1.2x10^{-12}$	$2.4x10^{-14}$	
	Si+30 min cure PI	$2.1x10^{-12}$	$2.9x10^{-14}$	
	Si+60 min cure PI	$1.9x10^{-12}$	$2.8x10^{-14}$	
L	Si+uncured PI	136 nm	1 nm	Cluster length decreases as cure time increases to 10 min. Cluster length increases as cure time increases to 30 min. Cluster length decreases as cure time increases to 60 min.
	Si+10 min cure PI	130 nm	1 nm	
	Si+30 min cure PI	139 nm	1 nm	
	Si+60 min cure PI	132 nm	1 nm	
n	Si+uncured PI	4.00	$3.5x10^{-9}$	Aggregate shape is a hard sphere at all cure times.
	Si+10 min cure PI	4.00	$4.8x10^{-9}$	
	Si+30 min cure PI	4.00	$3.6x10^{-9}$	
	Si+60 min cure PI	4.00	$3.8x10^{-9}$	
m	Si+uncured PI	2.36	0.01	Cluster packing remains relatively constant as cure time increases.
	Si+10 min cure PI	2.31	0.01	
	Si+30 min cure PI	2.26	0.01	
	Si+60 min cure PI	2.33	0.01	

Figure S6 shows the refractive index calibration curve of uncured and 60 min cured PI (black squares), respectively, as a function of mass of the PI. The orange circles on Figure S6 represent the PI mass in the supernatant, and the blue numbers represent the weight percent of PI initially added to the silicon slurry. Figure S7 shows the adsorption of uncured PI on the C45 carbon black.

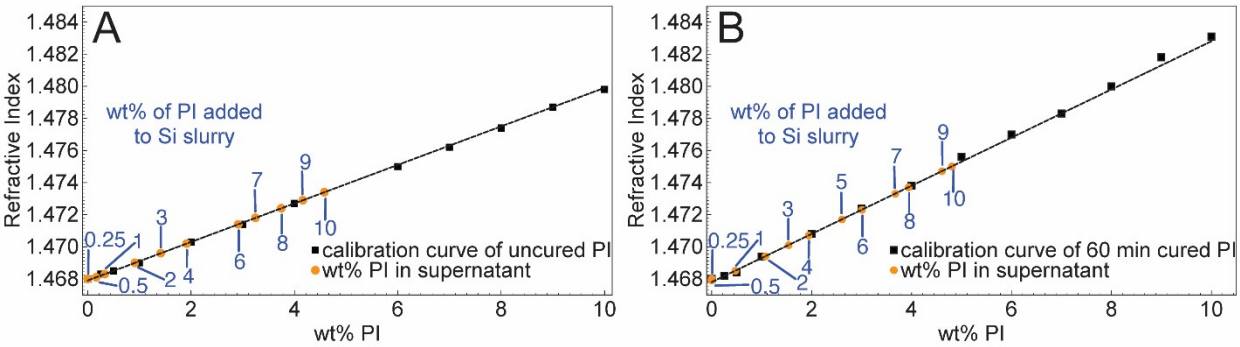


Figure S6: A) Refractive index of neat uncured PI solution (black squares) and supernatant of the silicon+uncured PI slurry (orange circles) as a function of mass of PI present in the NMP solution or supernatant, respectively. B) Mass (wt%) of uncured PI adsorbed onto silicon as a function of PI mass (wt%) added to the silicon slurry. The blue numbers correspond to the actual mass of uncured or 60 min UV cured PI added to the silicon slurry. Error bars are smaller than the data points.

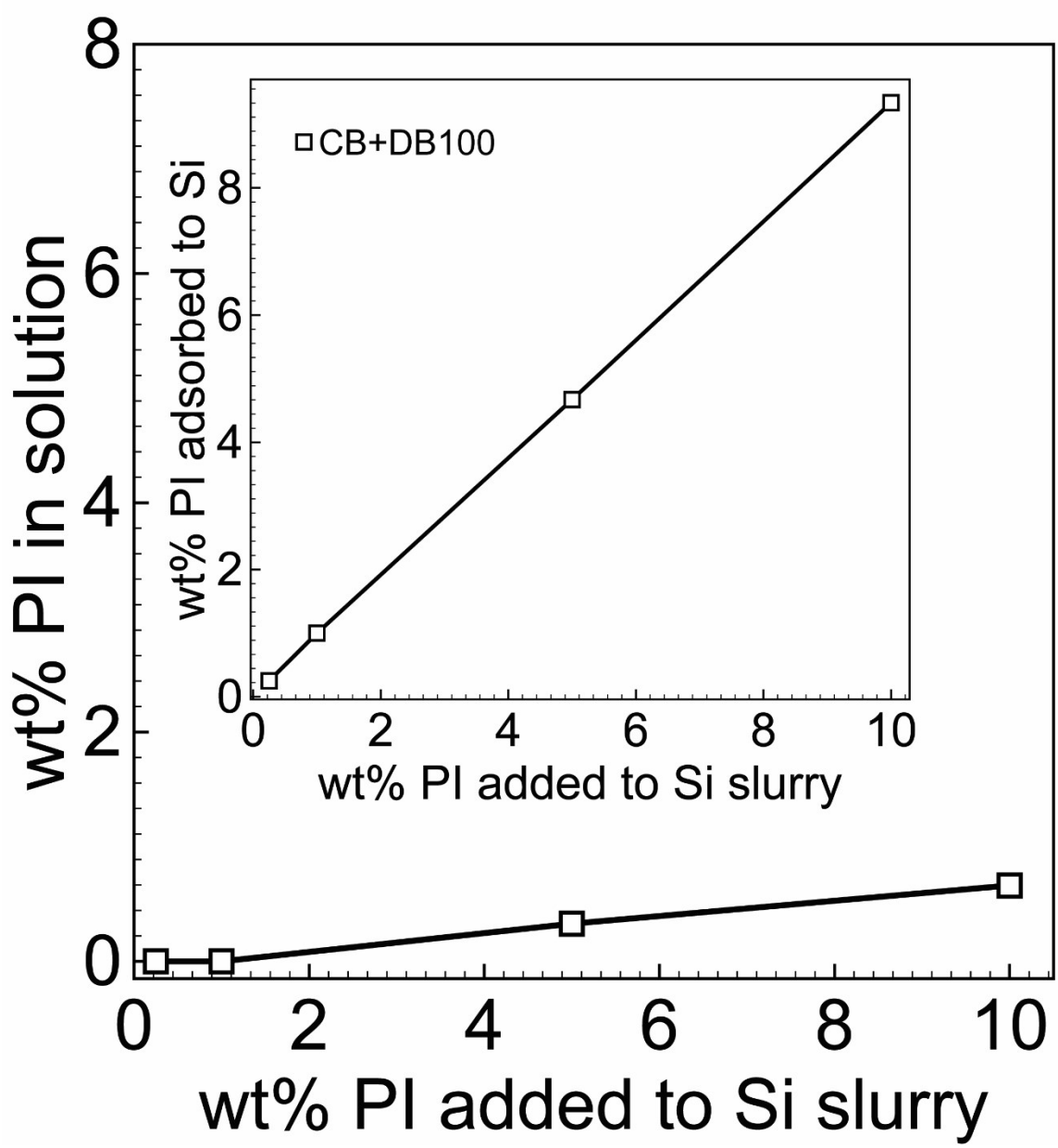


Figure S7: Weight percent of uncured PI in the supernatant as a function of weight percent uncured PI added to the Si slurry where amounts are based on refractive index measurements. Inset: Weight percent of uncured PI adsorbed to carbon black plotted as a function of weight percent uncured PI added to the Si slurry. Error bars are smaller than the points.

Table S6 shows the first cycle specific lithiation and delithiation capacities of electrodes made with Si+uncured PI, Si+10 min UV cured PI, Si+30 min UV cured PI, and Si+60 min UV cured PI.

Table S6: First cycle lithation and delithiation specific capacity of electrode slurries made from Si+uncured PI, Si+10 min UV cured PI, Si+30 min UV cured PI, and Si+60 min UV cured PI.

Electrode	First Cycle Lithiation Capacity (mAh/g)	First Cycle Delithiation Capacity (mAh/g)
Si+uncured PI	2350	350
Si+10 min cured PI	250	50
Si+30 min cured PI	750	150
Si+60 min cured PI	275	75

References

1. Hammouda, B., Solvation Characteristics of a Model Water-Soluble Polymer. *J. Polym. Sci. Pol. Phys.* **2006,** *44* (22), 3195-3199.
2. Hammouda, B.; Ho, D. L.; Kline, S., Insight into Clustering in Poly(ethylene oxide) Solutions. *Macromolecules* **2004,** *37* (18), 6932-6937.
3. Burdette-Trofimov, M. K.; Armstrong, B. L.; Murphy, R., P.; Heroux, L.; Doucet, M.; Rogers, A. M.; Veith, G. M., Probing Clustering Dynamics between Silicon and PAA or LiPAA Slurries under Processing Conditions *ACS Appl. Polym. Mater.* **2021,** *3* (5), 2447–2460.