Supporting Information for

Investigating the effect of supramolecular gel phase crystallization on gel nucleation

Arnab Dawn, [a] ‡ Marzieh Mirzamani,[a] ‡ Christopher D. Jones, [b] Dmitry S. Yufit,[b] Shou Qian,[c] Jonathan W. Steed *[b] and Harshita Kumari *[a]

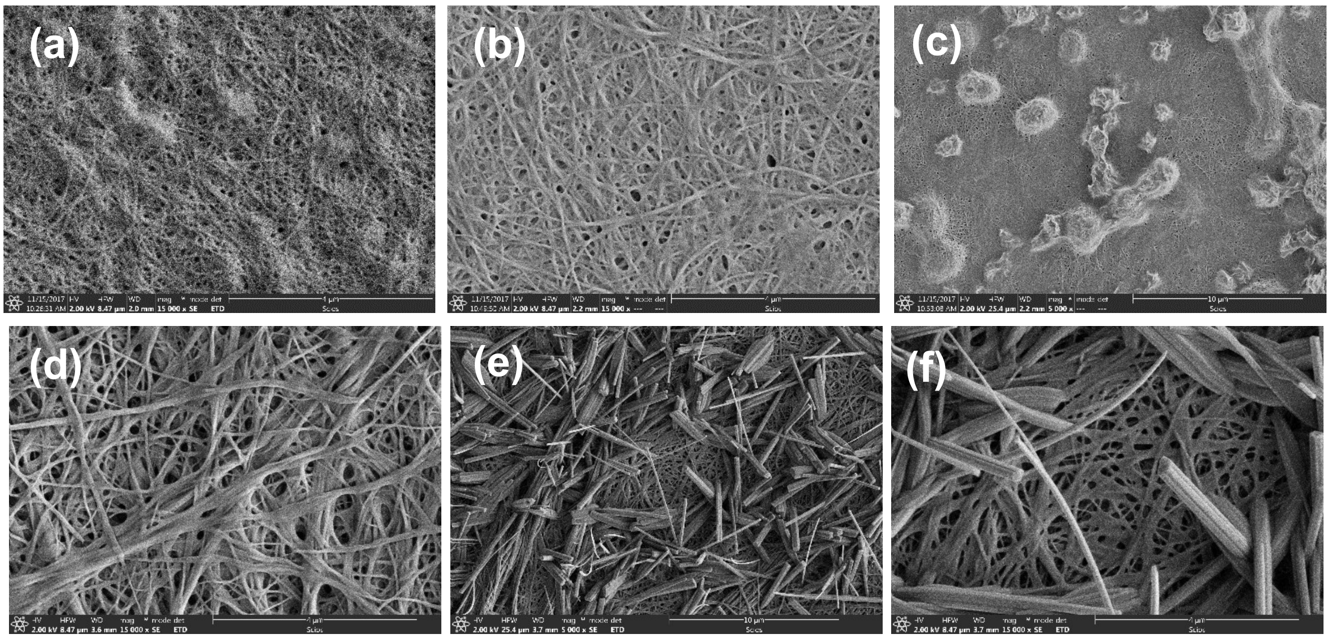


Figure S1. SEM images of the xerogel samples prepared from toluene: (a) 0.06% (w/v) gel of **G**, (b) and (c) 0.06% (w/v) of **G** in presence of 0.2 % (w/v) CBZ, (d) 0.25% (w/v) gel of **G**, (e) and (f) 0.25% (w/v) gel of **G** in presence of 0.2 % (w/v) CBZ.

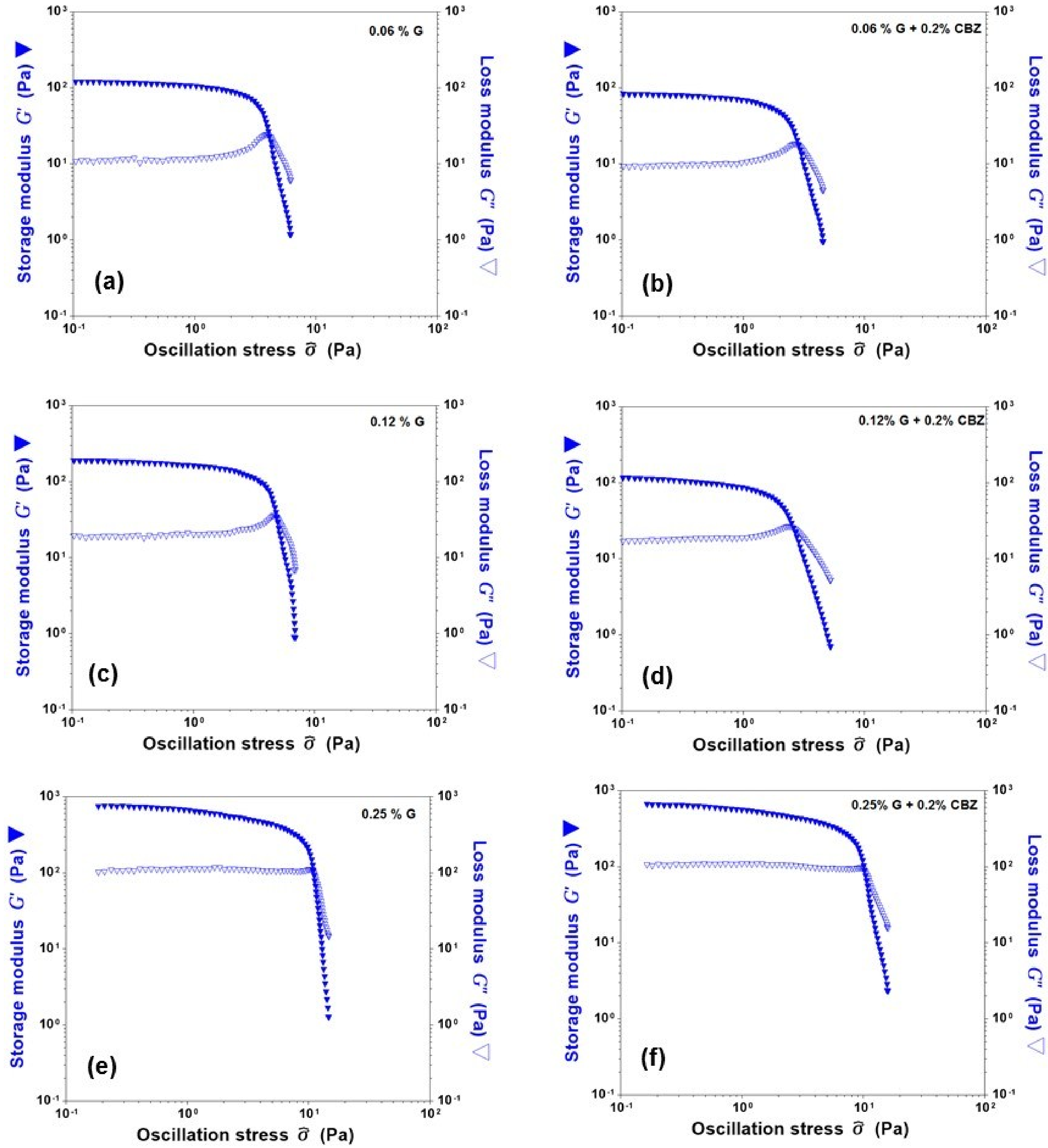


Figure S2. Stress sweep experiments performed at a constant frequency of 1 Hz: Gel samples (a, c, e), and gel samples with CBZ (b, d, f), prepared in toluene, at 25 °C (concentrations are expressed in % w/v).

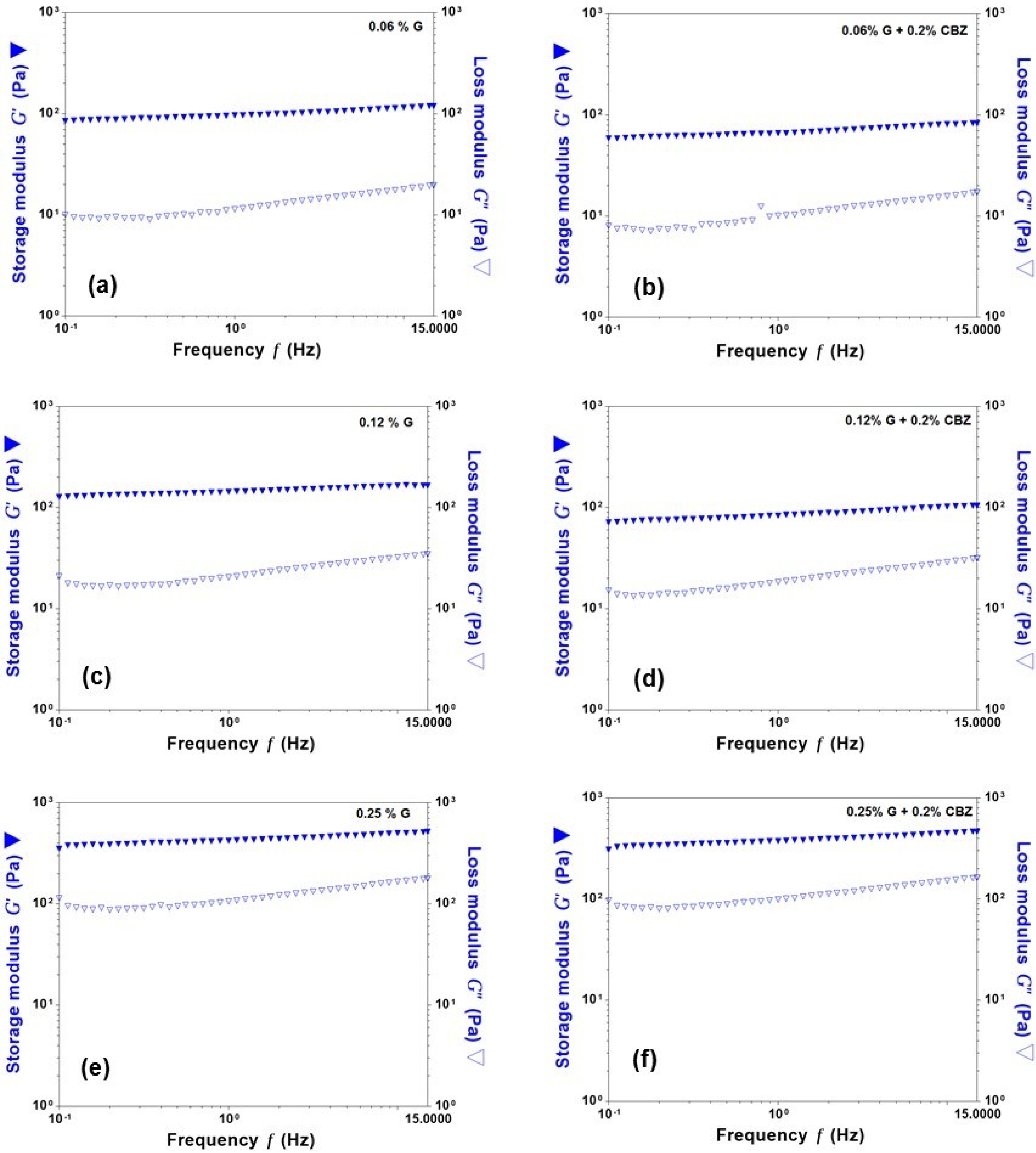


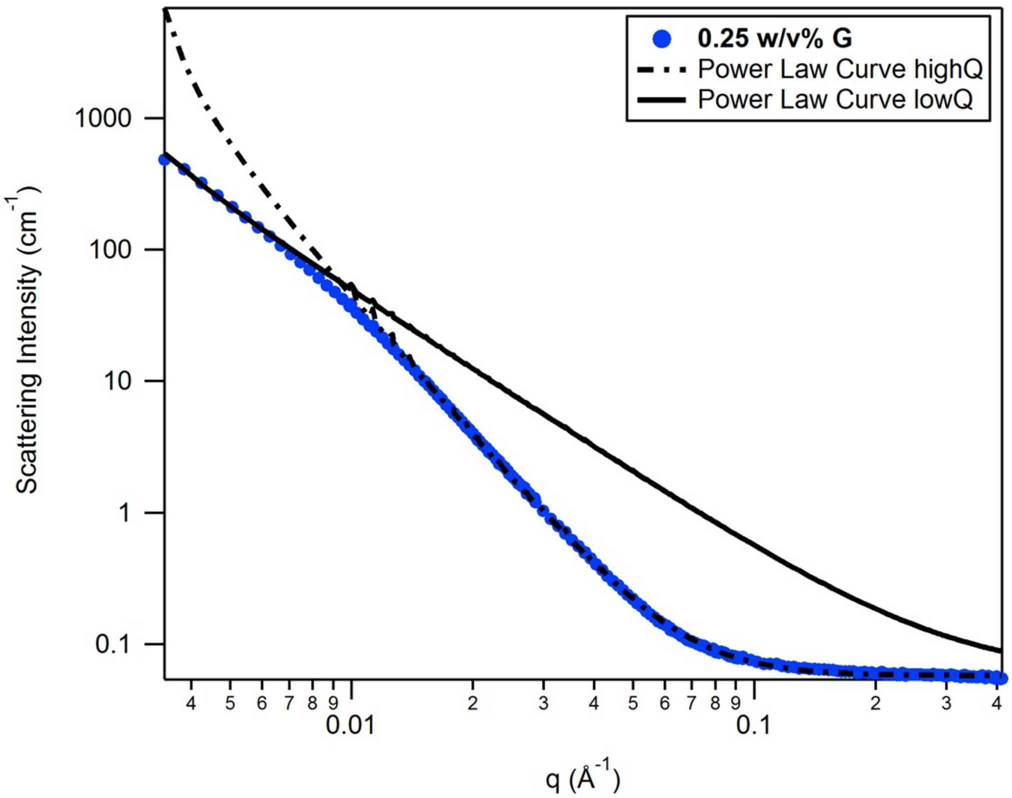
Figure S3. Frequency sweep experiments performed at a constant strain of 1%: Gel samples (a, c, e), and gel samples with CBZ (b, d, f), prepared in toluene, at 25 ^{o}C (concentrations are expressed in % w/v).

SANS

Table S1: Scattering length densities for the individual components and gelator with drug mixtures for the SANS analyses. Calculated using NIST's neutron activation and scattering calculator, https://www.ncnr.nist.gov/resources/activation/

Sample	Scattering Length Density (Å^{-2})
G	8.2e-07
CBZ	2.023e-6
0.06% G + 0.2% CBZ	1.745e-06
0.12% G + 0.2% CBZ	1.572e-06
0.25% G + 0.2% CBZ	1.355e-06
D8-toluene	5.664e-06

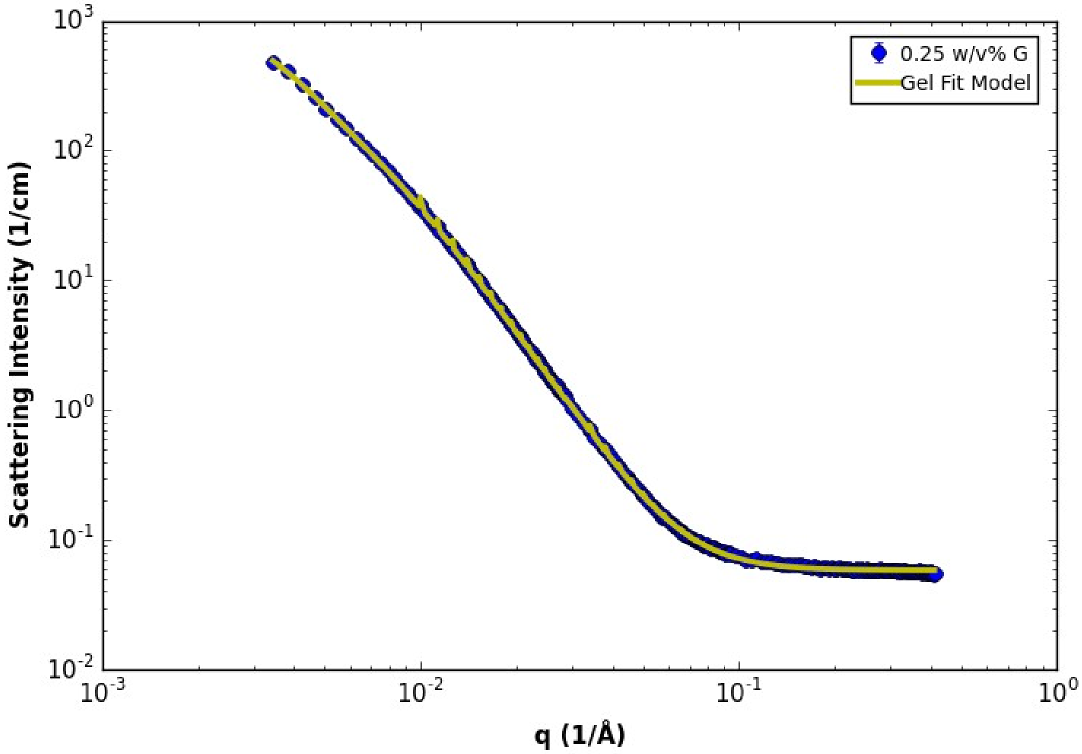
Power Law Analysis of 0.25 w/v% G:



	Low *Q*			High *Q*		
Coefficient, A =	0.00521294	±	0.000563395	5.20767e-6	±	3.88441e-8
(-)Power =	1.98222	±	0.0199313	3.44543	±	0.00195882
Bkgd (cm^{-1}) =	0.0577534	±	0	0.0577534	±	6.09244e-5
Fitted Range =	0.003433	$< Q <$	0.006261	0.01555	$< Q <$	0.4121

The Power Law model was used to determine the slopes (the (-)Power parameter) of the high and low *Q* regions, with the respective fitted ranges kept within the straight portions of the curve. Based on the error bars and how closely each fit follows the data over its fitted range, the fits are good. The background value for the low *Q* fit was held constant and equal to the background value obtained from the high *Q* fit to prevent overfitting.

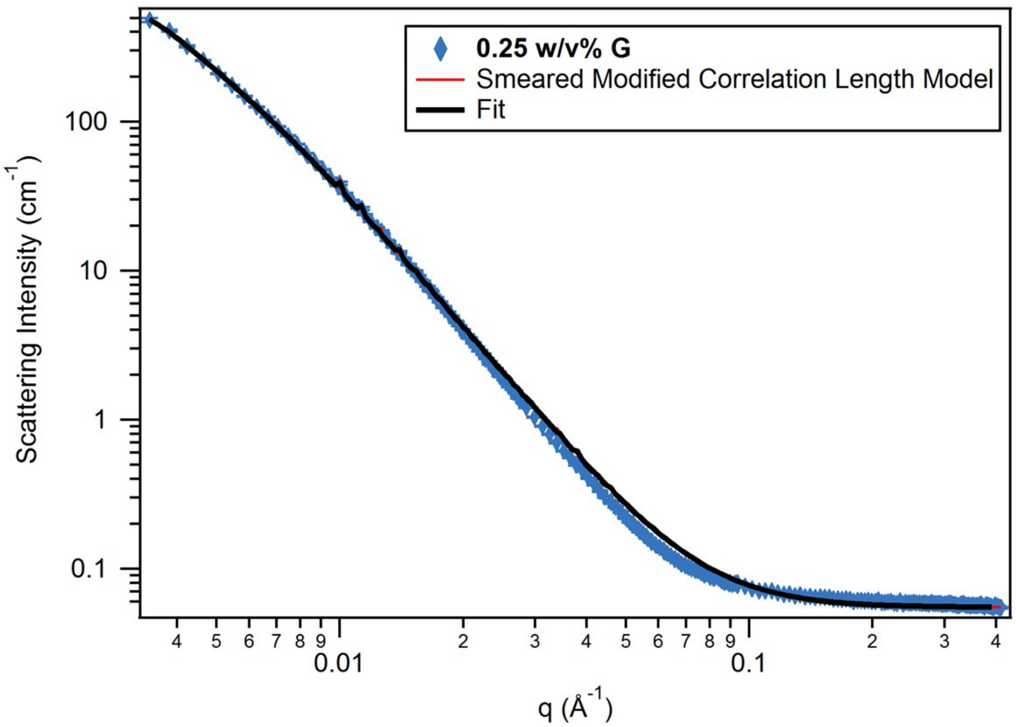
Gel Fit Model to 0.25 w/v% G:



FractalExp (D) =	3.5886	±	0.0030842
Guinier Scale ($I(0)_G$) =	1012	±	86.649
Radius (R_g) =	745.8	±	17.804
Lorentzian Scale ($I(0)_L$) =	586.9	±	7.4303
Correlation Length (a_1) =	160.23	±	0.85071
Bkgd (cm^{-1}) =	0.058262	±	6.1319e-5
Sqrt(χ^2/N) =	2.8912		
Fitted Range =	0.003433	$< Q <$	0.4121

The fit follows the data closely, the error bars are small compared to their respective fitting parameter, and the sqrt(χ^2/N) value is small, suggesting a good fit. Furthermore, the fractal dimension D parameter is also sufficiently close to the high Q slope determined from the Power Law fitting to suggest that these analyses do not contradict. The model is general enough to be able to apply to different types of gels while still describing the basic characteristics of the gel structure, thus reducing the risk of overfitting the data. For these reasons, this model was chosen in conjunction with the Power Law analysis.

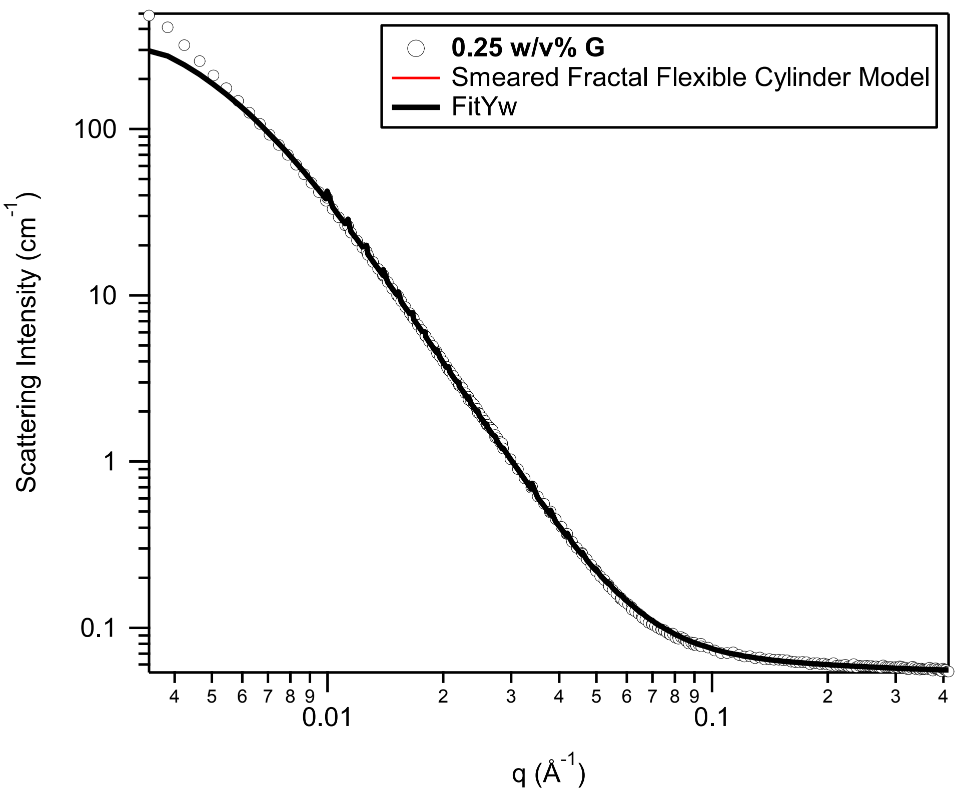
Modified Correlation Length Model to 0.25 w/v% G:



Dimensionality (s) =	1.25967	±	2.84
High-Q Scale =	0.482988	±	96.2
Screening Length (Å) =	194.09	±	0
High-Q Porod Exponent =	2.02461	±	5.97e-157
Bgd (cm^{-1}) =	0.055	±	8.05e-158
Sqrt(χ^2/N) =	0.8653		
Fitted Range =	0.003433	$< Q <$	0.4121

This model is similar to the Correlation Length model, except it incorporates a stretching term $1/Q^s$. The parameter s is a stretching factor, where $s = 0$ indicates an unstretched mass fractal network and $s = 1$ means the network is fully stretched. Here, $s > 1$ which is not feasible given this definition. The error bars are large for s and the scaling factor. The high-Q Porod exponent also does not agree with that found from the Power Law fitting. The model also does not fit the $0.02 < Q < 0.1$ region as well as the other models. For these reasons, this model was not chosen.

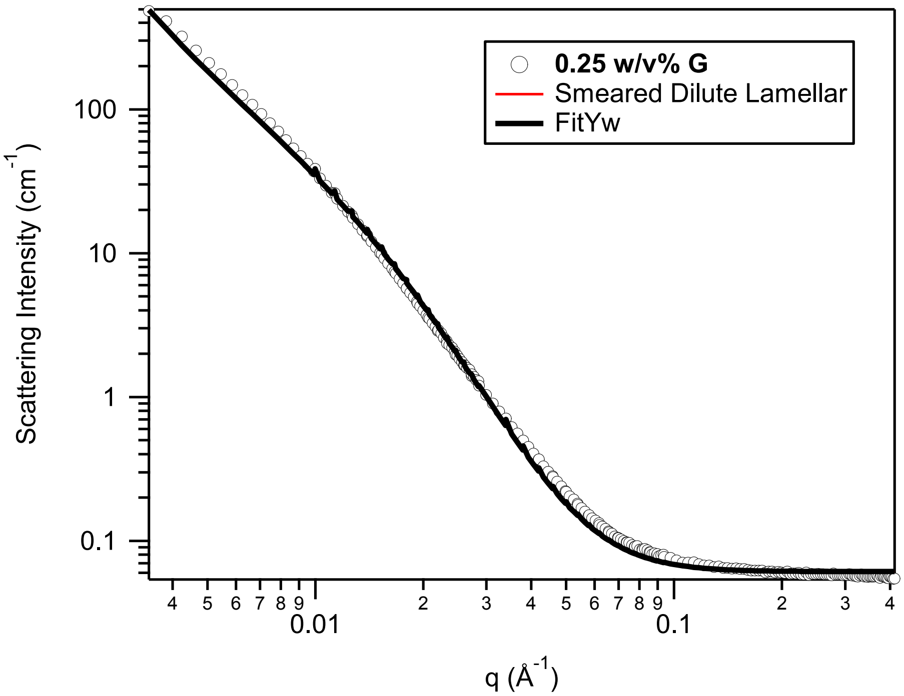
Fractal Flexible Cylinder fit to 0.25 w/v% G:



Volume Fraction (scale) =	0.00159859	±	0.000725494
fractal dimension =	2.90567	±	0.00090077
correlation length (Å) =	190.089	±	0.494126
SLD block (Å^{-2}) =	8.2e-07	±	0
SLD solvent (Å^{-2}) =	5.664e-06	±	0
Contour Length (Å) =	23.5656	±	0.0239447
Kuhn Length, b (Å) =	11.5796	±	0.0149754
Cylinder Radius (Å) =	5.13415	±	1.17028
bkgd (cm^{-1}) =	0.0549175	±	0.000600213
Sqrt(χ^2/N) =	3.8653		
Fitted Range =	0.003433	$< Q <$	0.412

Although this model is consistent with the morphology depicted in the SEM images and the error bars for the individual variables and the sqrt(χ^2/N) value are small, the model does not fit the data well over the low Q region. The fractal dimension parameter does not agree well with either of those determined from the Power Law analysis, suggesting that these methods contradict each other. This model was also incapable of producing a unique solution; it was fitted to the data multiple times (one example shown here), and each time yielded different contour length, Kuhn length, and cylinder radius results. Many times, the Kuhn length was reported as being larger than the contour length, which does not make physical sense. There is also the risk of this model overfitting the data due to the lack of scattering features such as peaks. For these reasons, this model was not chosen as the best model to analyze the data.

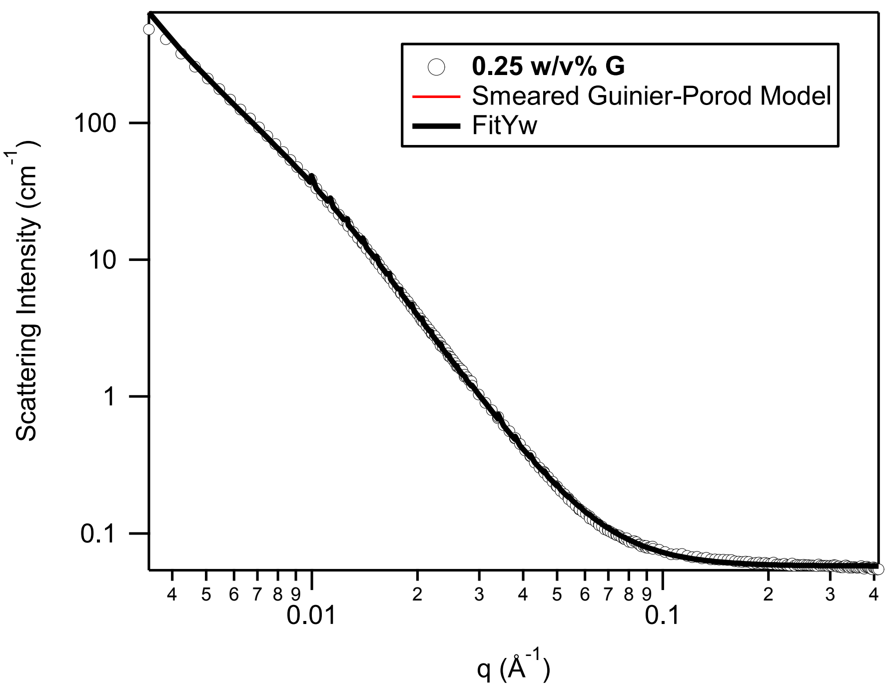
Dilute Lamellar fit to 0.25 w/v% G:



Scale =	0.000812575	±	0.000216977
Bilayer Thick (delta) (Å) =	33.5592	±	9.0087
polydisp of thickness =	3.14579	±	0.930426
SLD bilayer (Å^{-2}) =	8.2e-07	±	0
SLD solvent (Å^{-2}) =	5.664e-06	±	0
Incoherent Bgd (cm^{-1}) =	0.0610335	±	5.82968e-05
Sqrt(χ^2/N) =		11.1755	
Fitted Range =	0.003433	$< Q <$	0.4121

Visually, the model does not fit well to the data. The model also has a large sqrt(χ^2/N) value, further supporting the conclusion that this model is not a good choice for this data. Lastly, when the SEM images were obtained showing that the gel structure was a fibrous network, it was clear that a lamellar structure was not a relevant form factor. For these reasons, this model was not chosen.

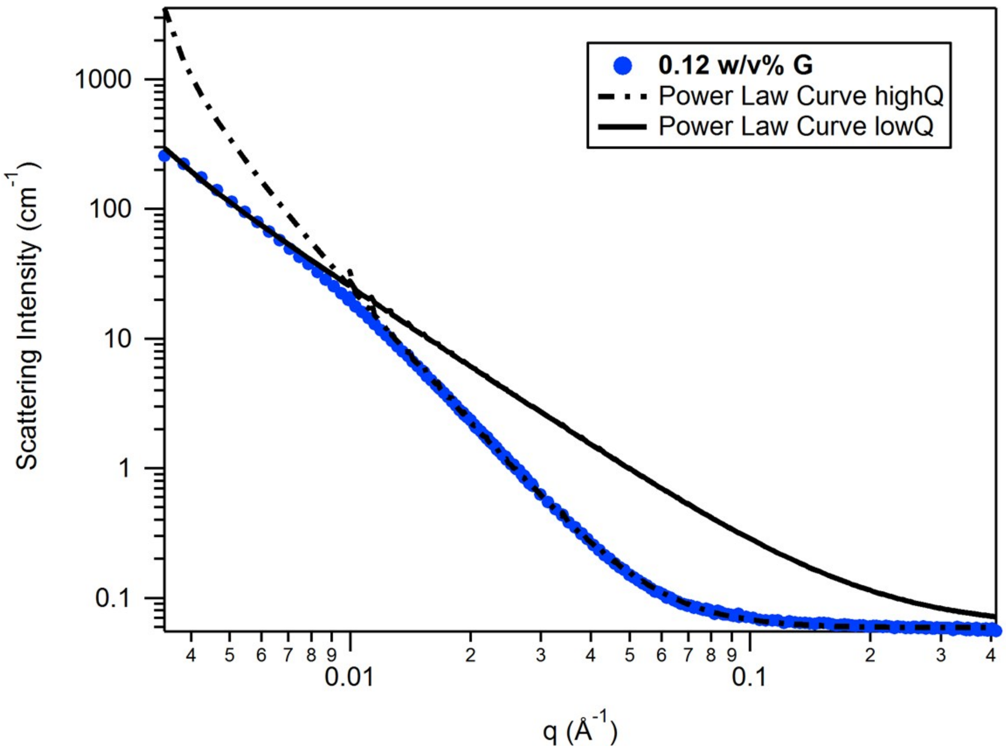
Guinier-Porod fit to 0.25 w/v% G:



Guinier Scale =	0.00230462	±	8.62179e-05
Dimension Variable, **s** =	2.14749	±	0.0072268
Rg (Å) =	49.3515	±	0.502803
Porod Exponent =	3.4447	±	0.00205459
Bgd (cm^{-1}) =	0.0577553	±	6.10797e-05
Sqrt(χ^2/N) =	3.35675		
Fitted Range =	0.003433	$< Q <$	0.4121

The model looks like it fits well to the data, which is further supported by the low sqrt(χ^2/N) value and small error bar for each variable. However, the model suggests that the slope of the data when $Q < 0.01$ is 2.14 (the dimension variable **s**) and the slope for $Q > 0.01$ is 3.44 (the Porod exponent). Close examination of the data shows that the slopes do not differ so noticeably, which means that the **s** and Porod exponent values returned by the model do not make sense. Additionally, an **s** value of 2 suggests that the structure is plate-like, which is contradicted by the SEM images. For these reasons, this model was not chosen.

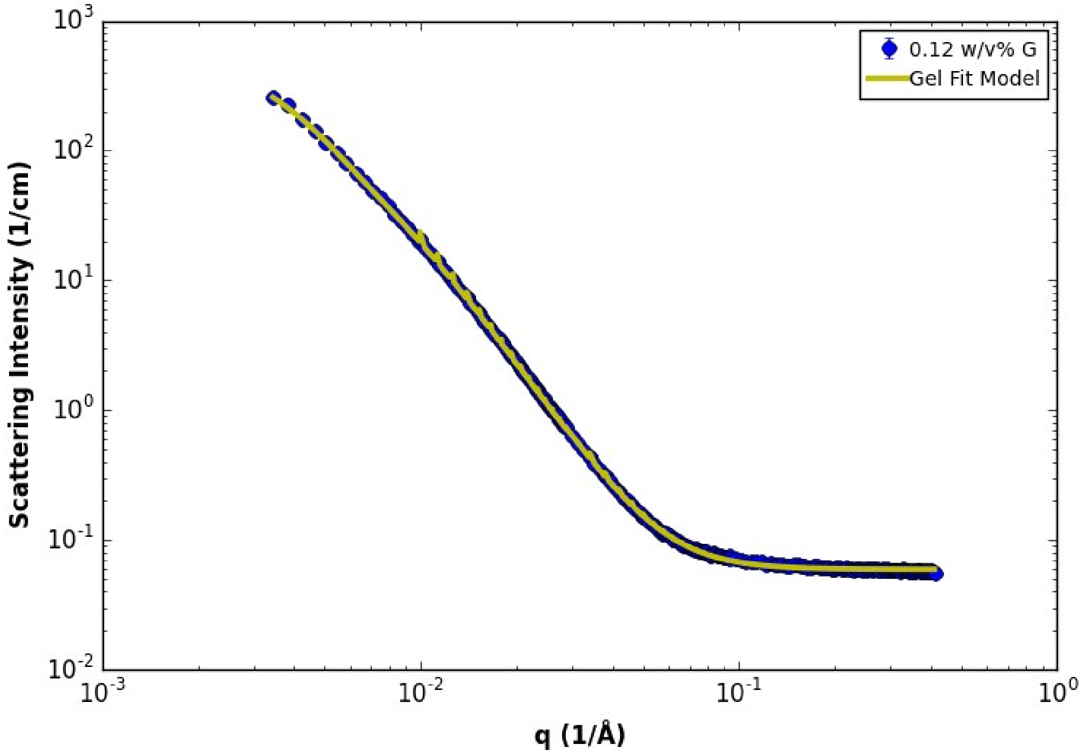
Power Law Analysis of 0.12 w/v% G:



	Low Q			High Q		
Coefficient, A =	0.00206433	±	0.000154097	3.40483e-6	±	3.76737e-8
(-)Power =	2.03578	±	0.0139882	3.41134	±	0.00291469
Bkgd (cm^{-1}) =	0.0588715	±	0	0.0588715	±	6.11913e-5
Fitted Range =	0.003433	$< Q <$	0.006665	0.01393	$< Q <$	0.4121

The Power Law model was used to determine the slopes (the (-)Power parameter) of the high and low Q regions, with the respective fitted ranges kept within the straight portions of the curve. Based on the error bars and how closely each fit follows the data over its fitted range, the fits are good. The background value for the low Q fit was held constant and equal to the background value obtained from the high Q fit to prevent overfitting.

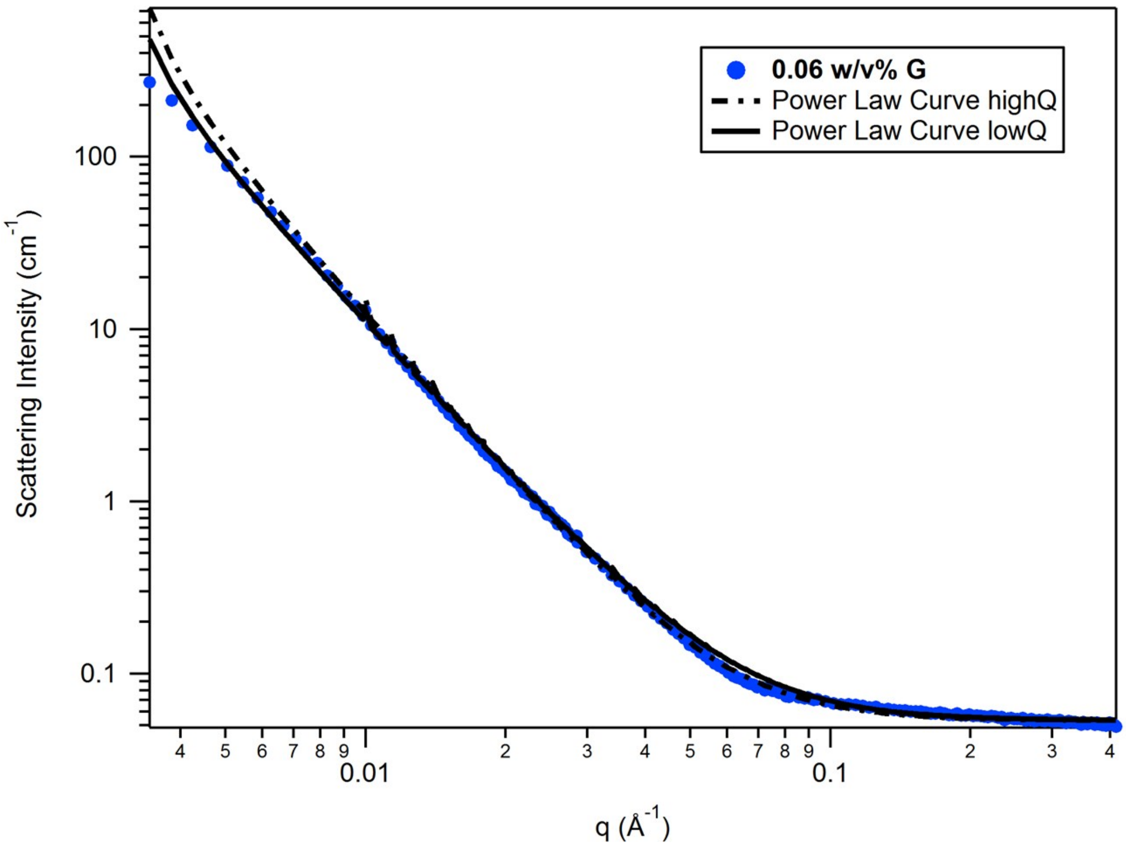
Gel Fit Model to 0.12 w/v% G:



FractalExp (D) =	3.5751	±	0.0047714
Guinier Scale ($I(0)_G$) =	441.21	±	21.574
Radius (R_g) =	631.56	±	9.9053
Lorentzian Scale ($I(0)_L$) =	247.71	±	4.1604
Correlation Length (a_1) =	147.5	±	1.0954
Bkgd (cm^{-1}) =	0.059259	±	6.1633e-5
Sqrt(χ^2/N) =		2.6364	
Fitted Range =	0.003433	$< Q <$	0.4121

The fit follows the data closely, the error bars are small compared to their respective fitting parameter, and the sqrt(χ^2/N) value is small, suggesting a good fit. Furthermore, the fractal dimension D parameter is also sufficiently close to the high Q slope determined from the Power Law fitting to suggest that these analyses do not contradict. The model is general enough to be able to apply to different types of gels while still describing the basic characteristics of the gel structure, thus reducing risk of overfitting the data. For these reasons, this model was chosen in conjunction with the Power Law analysis.

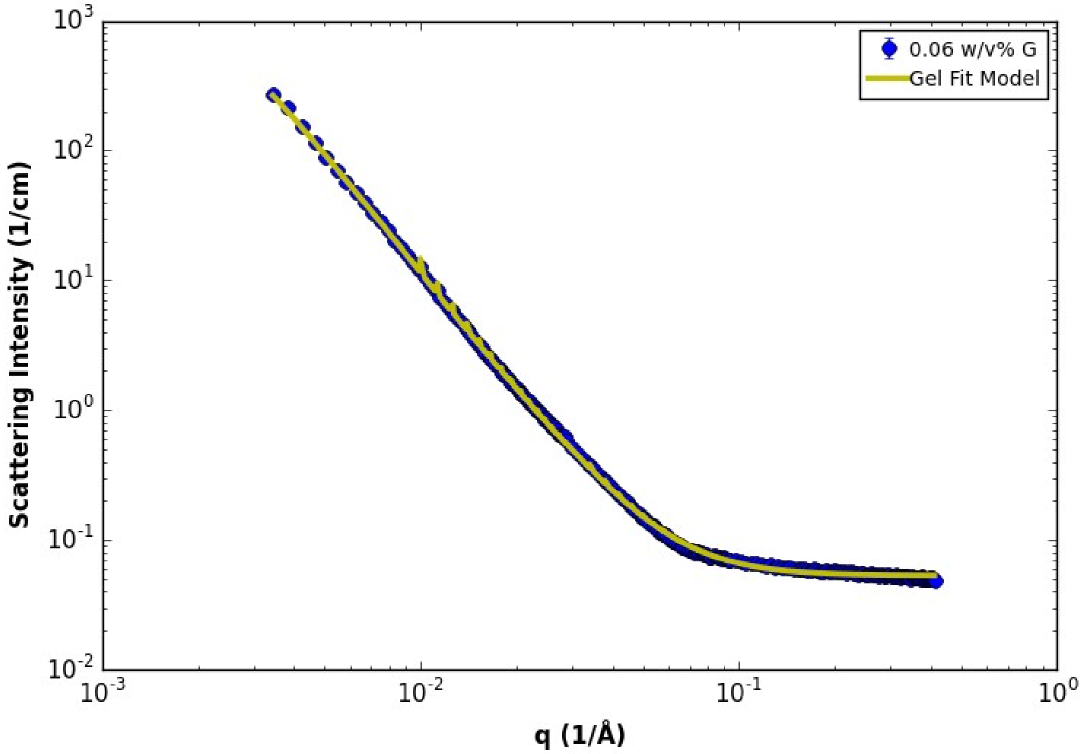
Power Law Analysis of 0.06 w/v% G:



	Low Q			High Q		
Coefficient, A =	2.32864e-5	±	2.93524e-7	1.21037e-5	±	2.03846e-7
(-)Power =	2.82423	±	0.002739	2.98818	±	0.00482327
Bkgd (cm^{-1}) =	0.0534047	±	0	0.0534047	±	6.46391e-5
Fitted Range =	0.003433	$< Q <$	0.01232	0.02194	$< Q <$	0.4121

The Power Law model was used to determine the slopes (the (-)Power parameter) of the high and low Q regions, with the respective fitted ranges kept within the straight portions of the curve. Based on the error bars and how closely each fit follows the data over its fitted range, the fits are good. The background value for the low Q fit was held constant and equal to the background value obtained from the high Q fit to prevent overfitting.

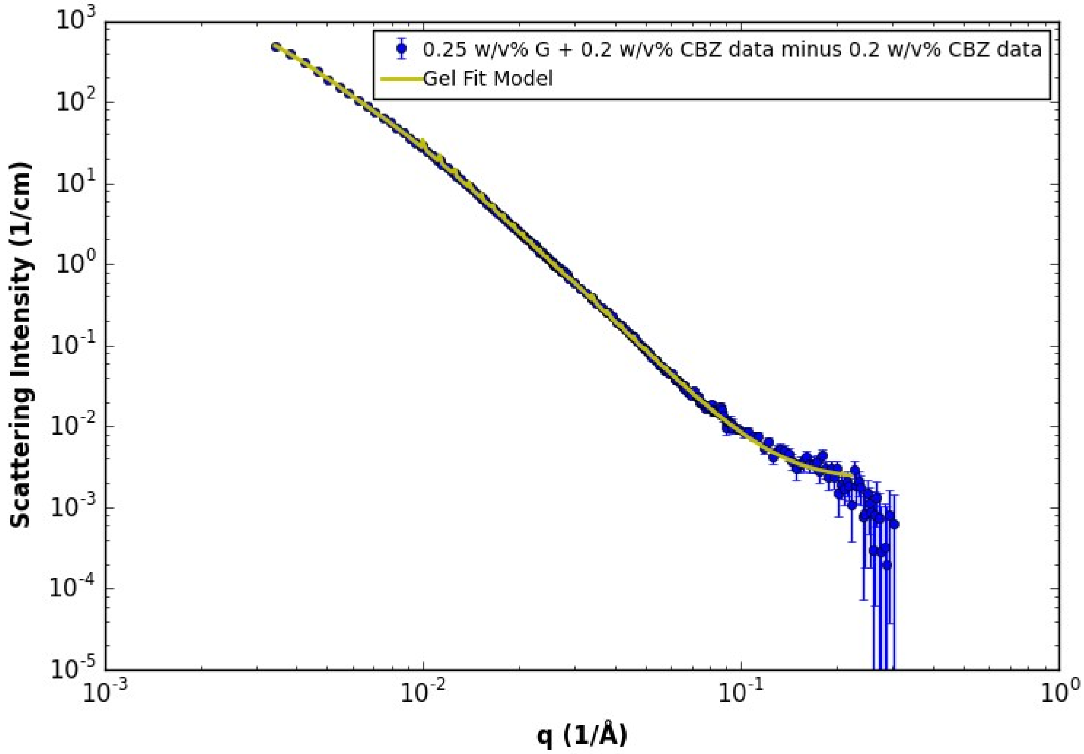
Gel Fit Model to 0.06 w/v% G:



FractalExp (D) =	2.9216	±	0.0031011
Guinier Scale ($I(0)_G$) =	13.387	±	1.3882
Radius (R_g) =	329.82	±	7.6135
Lorentzian Scale ($I(0)_L$) =	2088.2	±	100.89
Correlation Length (a_1) =	535.74	±	9.8641
Bkgd (cm^{-1}) =	0.053112	±	6.2987e-5
Sqrt(χ^2/N) =	3.8333		
Fitted Range =	0.003433	$< Q <$	0.4121

The fit follows the data closely, the error bars are small compared to their respective fitting parameter, and the sqrt(χ^2/N) value is small, suggesting a good fit. Furthermore, the fractal dimension D parameter is also sufficiently close to the high Q slope determined from the Power Law fitting to suggest that these analyses do not contradict. The model is general enough to be able to apply to different types of gels while still describing the basic characteristics of the gel structure, thus reducing risk of overfitting the data. For these reasons, this model was chosen in conjunction with the Power Law analysis.

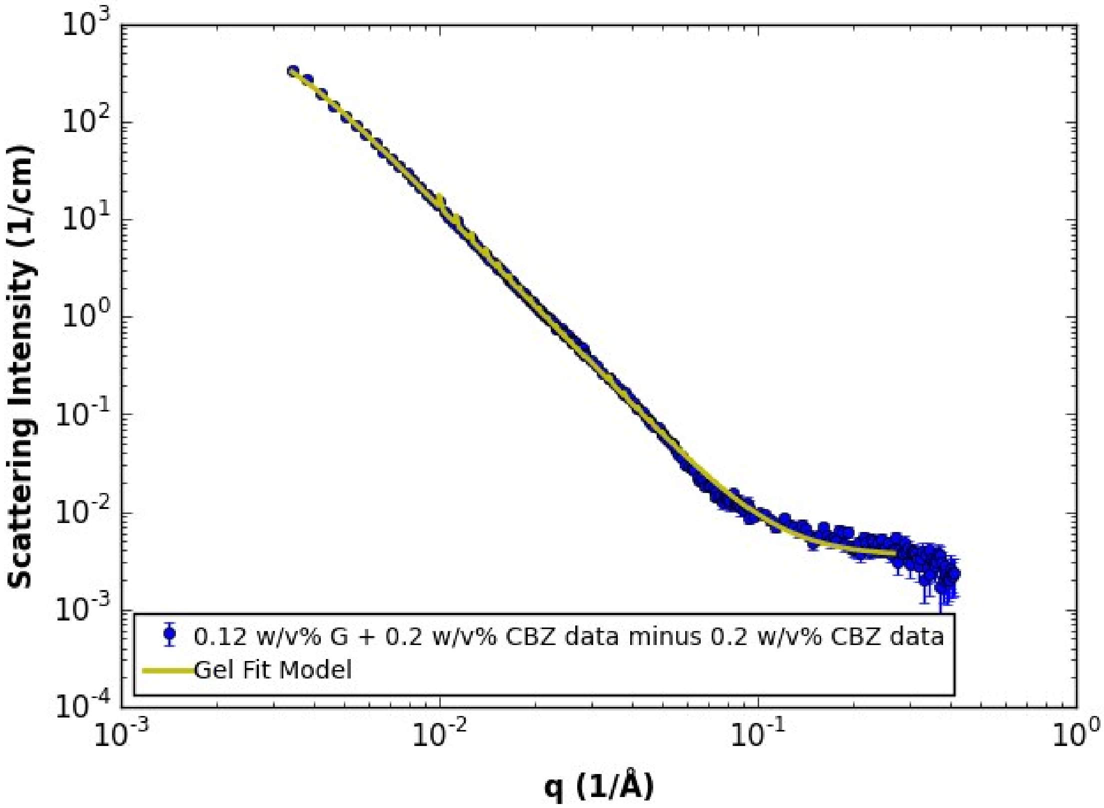
Gel Fit Model to 0.25 w/v% G + 0.2 w/v% CBZ data minus 0.2 w/v% CBZ data:



FractalExp (D) =	3.7717	±	0.004802
Guinier Scale ($I(0)_G$) =	1265.4	±	103.87
Radius (R_g) =	803.58	±	19.099
Lorentzian Scale ($I(0)_L$) =	646.76	±	10.857
Correlation Length (a_1) =	170.83	±	1.2032
Bkgd (cm^{-1}) =	0.00216	±	0.000127
Sqrt(χ^2/N) =		2.4938	
Fitted Range =	0.003433	$< Q <$	0.2222

The fit follows the data closely, the error bars are small compared to their respective fitting parameter, and the sqrt(χ^2/N) value is small, suggesting a good fit. The model is general enough to be able to apply to different types of gels while still describing the basic characteristics of the gel structure, thus reducing risk of overfitting the data.

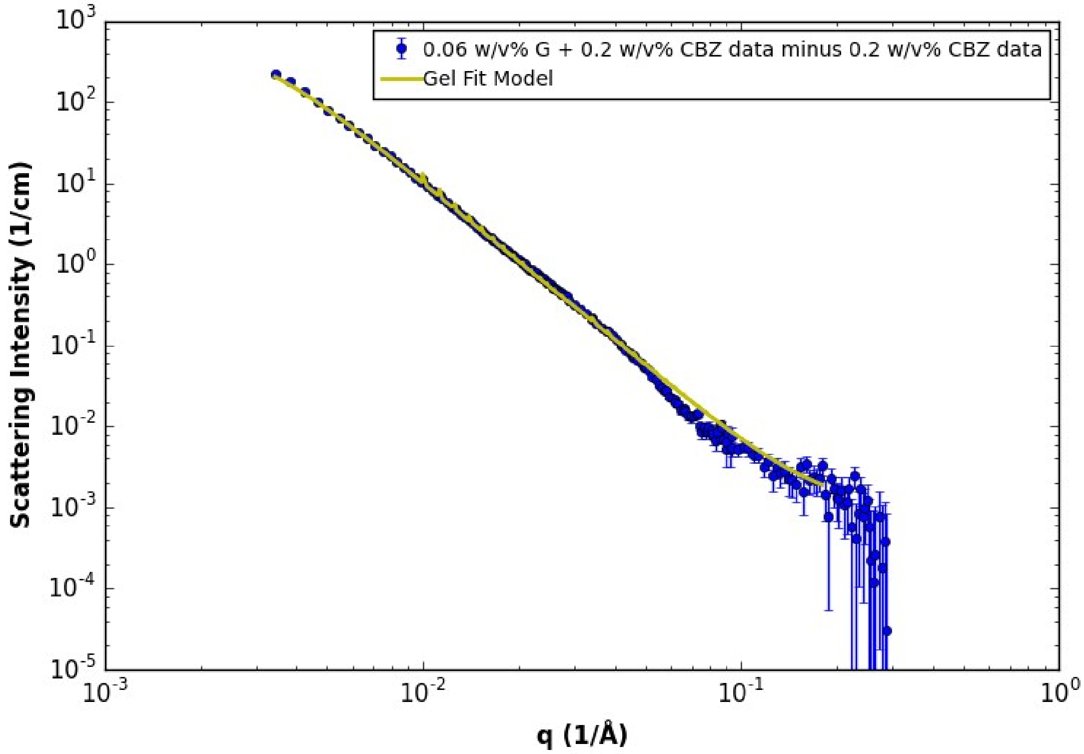
Gel Fit Model to 0.12 w/v% G + 0.2 w/v% CBZ data minus 0.2 w/v% CBZ data:



FractalExp (*D*) =	3.3481	±	0.006083
Guinier Scale ($I(0)_G$) =	5.6933	±	0.89327
Radius (R_g) =	280.33	±	10.075
Lorentzian Scale ($I(0)_L$) =	1697.3	±	53.313
Correlation Length (a_1) =	358.82	±	4.7111
Bkgd (cm^{-1}) =	0.003524	±	0.000112
Sqrt(χ^2/N) =		2.6756	
Fitted Range =	0.003433	< Q <	0.2673

The fit follows the data closely, the error bars are small compared to their respective fitting parameter, and the sqrt(χ^2/N) value is small, suggesting a good fit. The model is general enough to be able to apply to different types of gels while still describing the basic characteristics of the gel structure, thus reducing risk of overfitting the data.

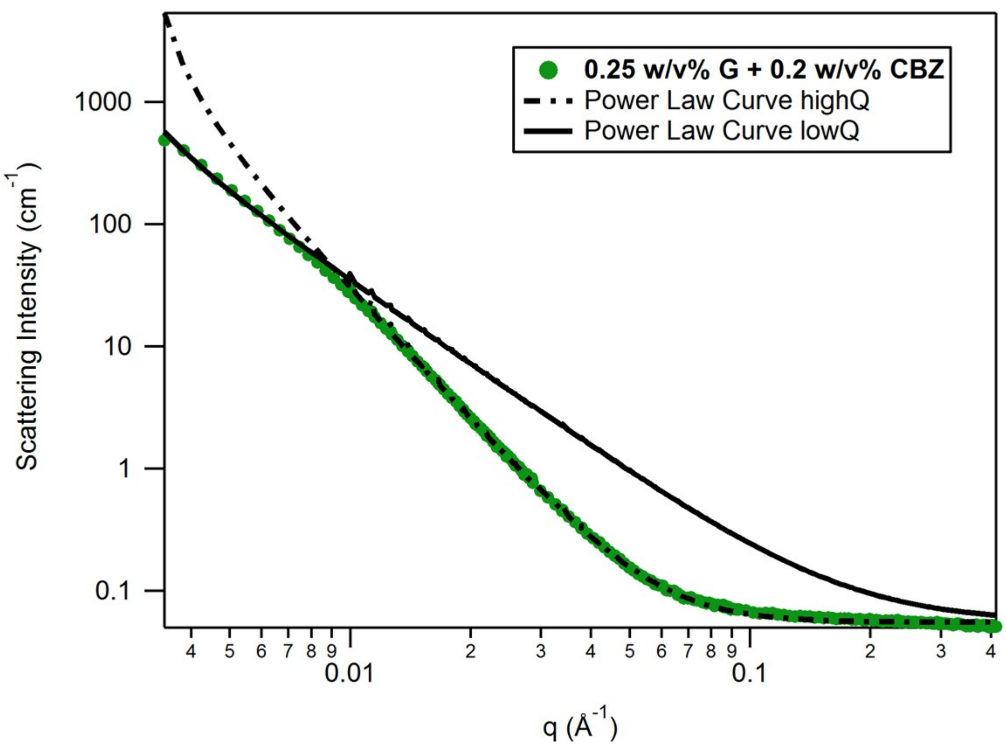
Gel Fit Model to 0.06 w/v% G + 0.2 w/v% CBZ data minus 0.2 w/v% CBZ data:



FractalExp (*D*) =	3.2256	±	0.003316
Guinier Scale ($I(0)_G$) =	1.0046	±	0.15623
Radius (R_g) =	276.65	±	10.436
Lorentzian Scale ($I(0)_L$) =	919.9	±	20.287
Correlation Length (a_1) =	343.37	±	3.0769
Bkgd (cm^{-1}) =	.001	±	0
Sqrt(χ^2/N) =		3.5128	
Fitted Range =	0.003433	< Q <	0.18

The fit follows the data closely, the error bars are small compared to their respective fitting parameter, and the sqrt(χ^2/N) value is small, suggesting a good fit. The model is general enough to be able to apply to different types of gels while still describing the basic characteristics of the gel structure, thus reducing risk of overfitting the data.
Å

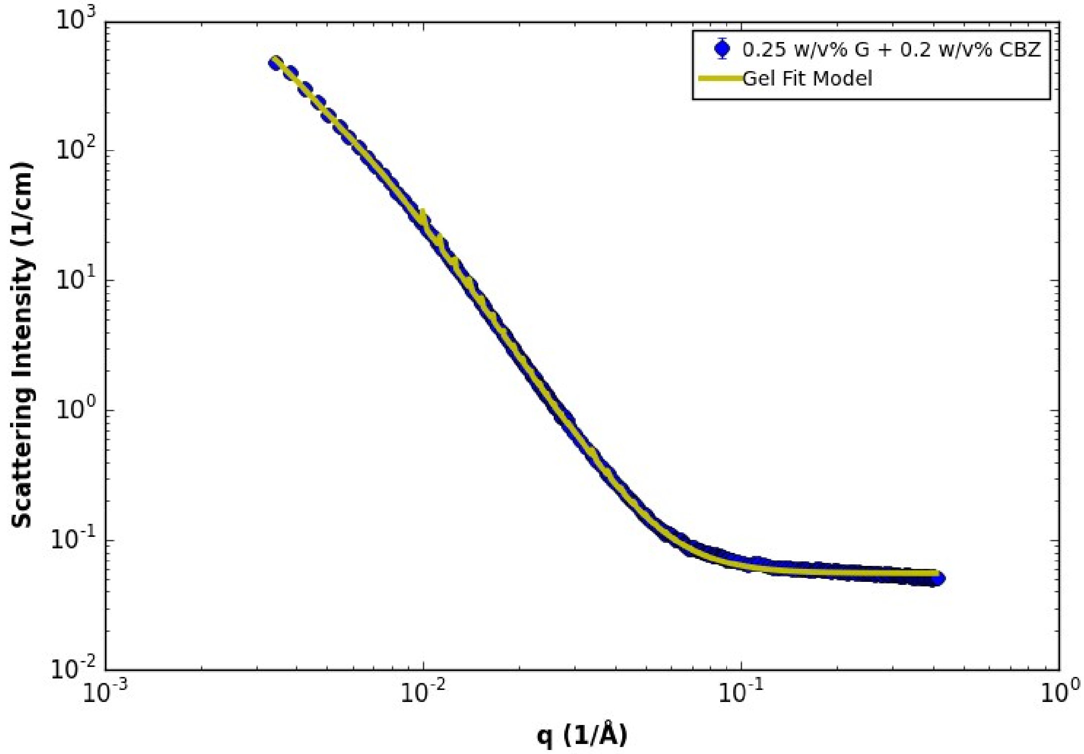
Power Law Analysis of 0.25 w/v% G + 0.2 w/v% CBZ:



	Low *Q*			High *Q*		
Coefficient, A =	0.00102944	±	5.7909e-05	2.67047e-06	±	2.70104e-08
(-)Power =	2.25524	±	0.0106801	3.50544	±	0.00264669
Bkgd (cm^{-1}) =	0.0550477	±	0	0.0550477	±	5.98028e-05
Fitted Range =	0.003433	$< Q <$	0.007069	0.01393	$< Q <$	0.4121

The Power Law model was used to determine the slopes (the (-)Power parameter) of the high and low *Q* regions, with the respective fitted ranges kept within the straight portions of the curve. Based on the error bars and how closely each fit follows the data over its fitted range, the fits are good. The background value for the low *Q* fit was held constant and equal to the background value obtained from the high *Q* fit to prevent overfitting.

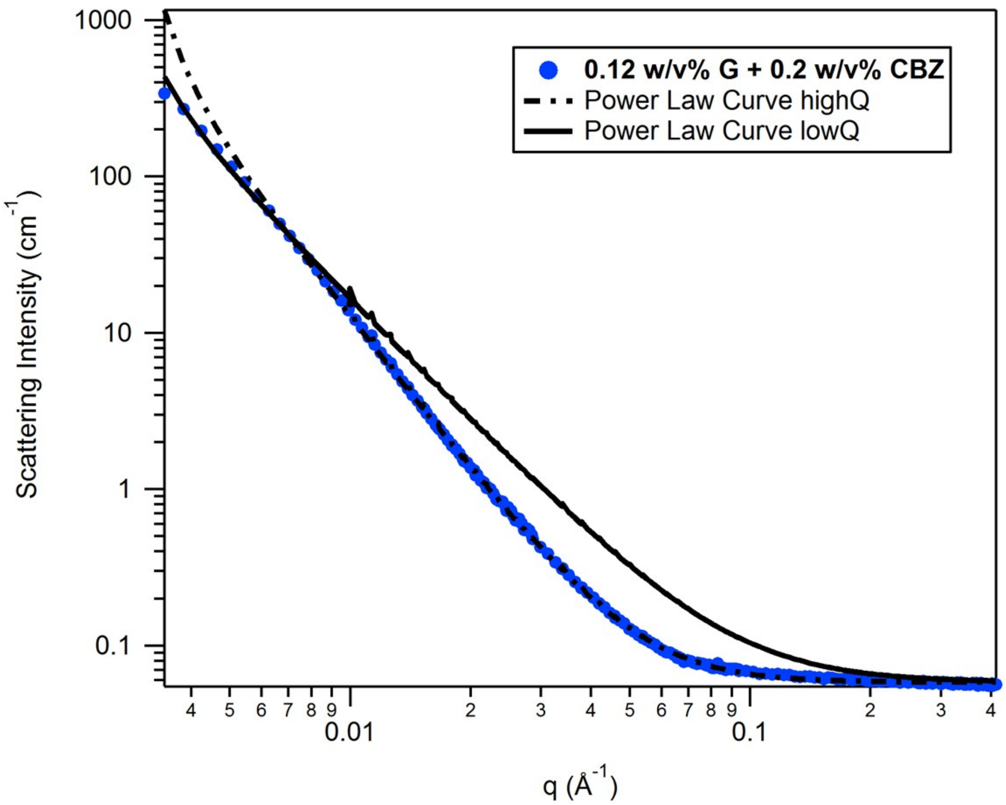
Gel Fit Model to 0.25 w/v% G + 0.2 w/v% CBZ:



FractalExp (D) =	3.6186	±	0.0032048
Guinier Scale ($I(0)_G$) =	2068.4	±	369.53
Radius (R_g) =	1056.7	±	52.662
Lorentzian Scale ($I(0)_L$) =	906.2	±	14.142
Correlation Length (a_1) =	202.98	±	1.2576
Bkgd (cm^{-1}) =	0.055365	±	5.9617e-5
Sqrt(χ^2/N) =	3.9867		
Fitted Range =	0.003433	$< Q <$	0.4121

The fit follows the data closely, the error bars are small compared to their respective fitting parameter, and the sqrt(χ^2/N) value is small, suggesting a good fit. Furthermore, the fractal dimension D parameter is also sufficiently close to the high Q slope determined from the Power Law fitting to suggest that these analyses do not contradict. The model is general enough to be able to apply to different types of gels while still describing the basic characteristics of the gel structure, thus reducing risk of overfitting the data. For these reasons, this model was chosen in conjunction with the Power Law analysis.

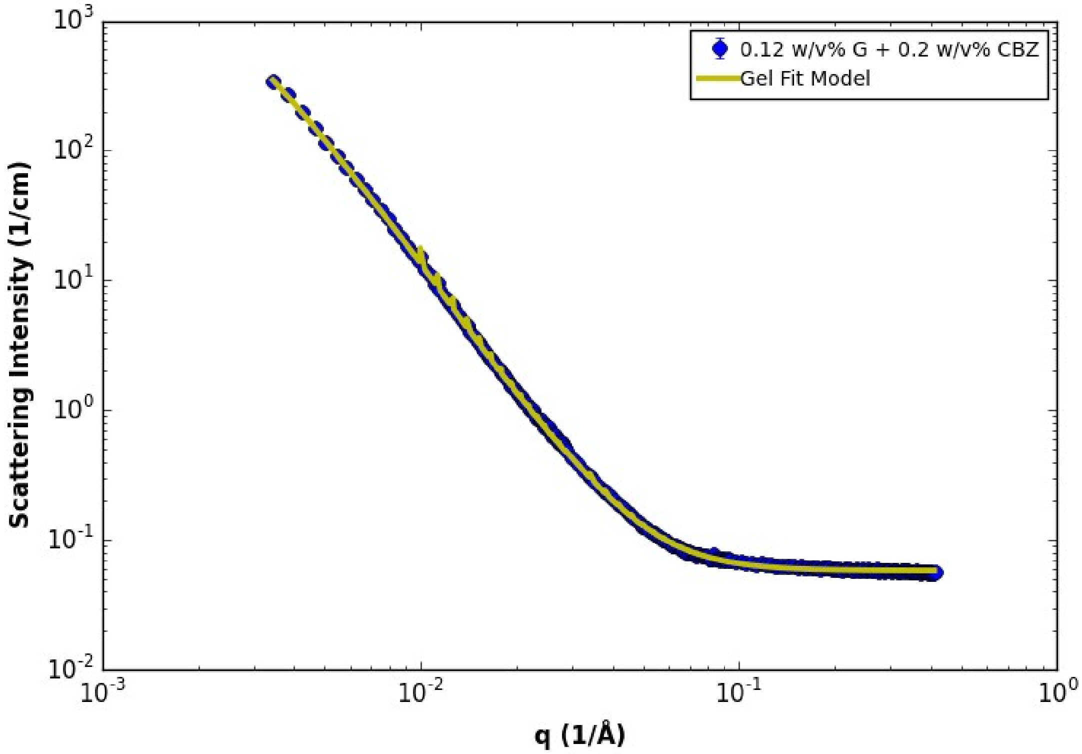
Power Law Analysis of 0.12 w/v% G + 0.2 w/v% CBZ:



	Low Q			High Q		
Coefficient, A =	0.000128405	±	5.8856e-06	4.67413e-06	±	5.61481e-08
(-)Power =	2.54375	±	0.00884791	3.20045	±	0.00308264
Bkgd (cm^{-1}) =	0.0580999	±	0	0.0580999	±	6.08108e-05
Fitted Range =	0.003433	$< Q <$	0.006665	0.01192	$< Q <$	0.4121

The Power Law model was used to determine the slopes (the (-)Power parameter) of the high and low Q regions, with the respective fitted ranges kept within the straight portions of the curve. Based on the error bars and how closely each fit follows the data over its fitted range, the fits are good. The background value for the low Q fit was held constant and equal to the background value obtained from the high Q fit to prevent overfitting.

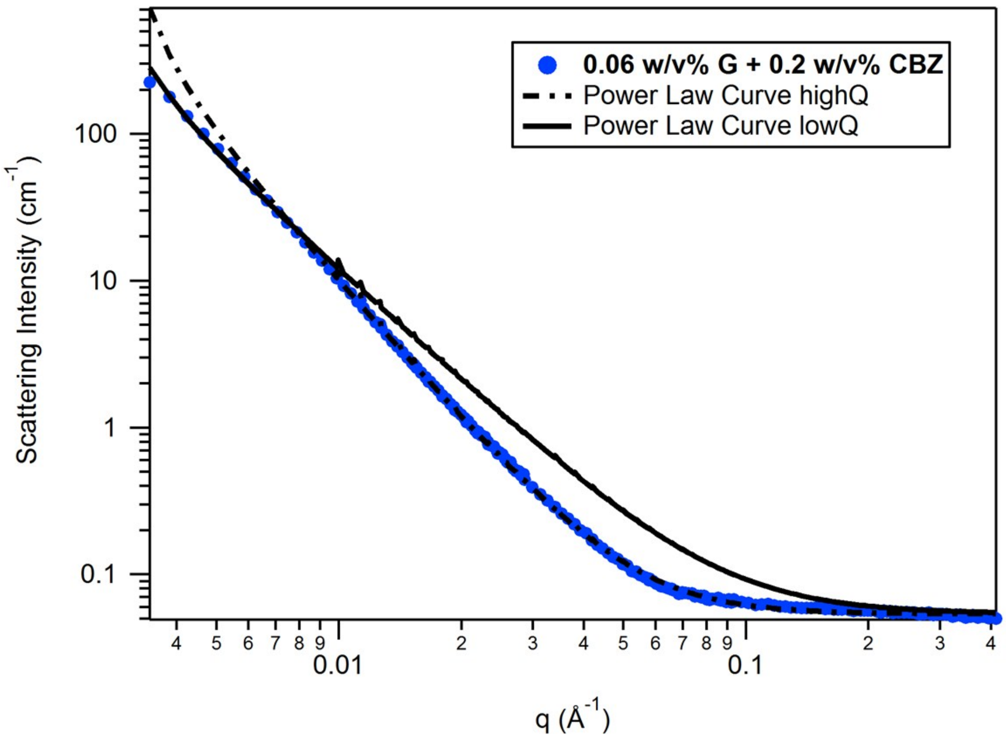
Gel Fit Model to 0.12 w/v% G + 0.2 w/v% CBZ:



FractalExp (D) =	3.1932	±	0.0043514
Guinier Scale ($I(0)_G$) =	13.437	±	0.71333
Radius (R_g) =	272.84	±	3.3554
Lorentzian Scale ($I(0)_L$) =	2470.4	±	90.923
Correlation Length (a_1) =	452.48	±	6.5172
Bkgd (cm^{-1}) =	0.058054	±	6.1822e-5
Sqrt(χ^2/N) =	2.7187		
Fitted Range =	0.003433	$< Q <$	0.4121

The fit follows the data closely, the error bars are small compared to their respective fitting parameter, and the sqrt(χ^2/N) value is small, suggesting a good fit. Furthermore, the fractal dimension D parameter is also sufficiently close to the high Q slope determined from the Power Law fitting to suggest that these analyses do not contradict. The model is general enough to be able to apply to different types of gels while still describing the basic characteristics of the gel structure, thus reducing risk of overfitting the data. For these reasons, this model was chosen in conjunction with the Power Law analysis.

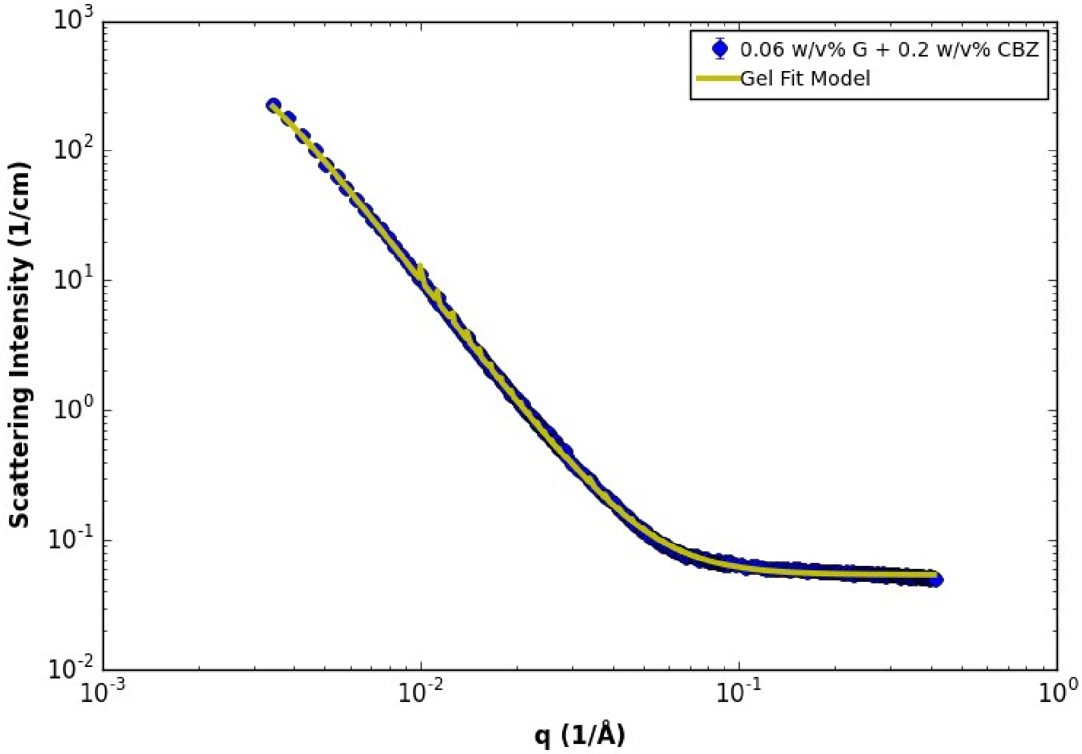
Power Law Analysis of 0.06 w/v% G + 0.2 w/v% CBZ:



	Low *Q*			High *Q*		
Coefficient, A =	0.00012659	±	5.72818e-6	6.43147e-6	±	7.42172e-8
(-)Power =	2.47755	±	0.00875341	3.08113	±	0.00293039
Bkgd (cm^{-1}) =	0.0538353	±	0	0.0538353	±	6.04923e-5
Fitted Range =	0.003433	< *Q* <	0.006665	0.01353	< *Q* <	0.4121

The Power Law model was used to determine the slopes (the (-)Power parameter) of the high and low *Q* regions, with the respective fitted ranges kept within the straight portions of the curve. Based on the error bars and how closely each fit follows the data over its fitted range, the fits are good. The background value for the low *Q* fit was held constant and equal to the background value obtained from the high *Q* fit to prevent overfitting.

Gel Fit Model to 0.06 w/v% G + 0.2 w/v% CBZ:



FractalExp (D) =	3.1082	±	0.0041266
Guinier Scale ($I(0)_G$) =	3.6473	±	1.0602
Radius (R_g) =	313.3	±	20.617
Lorentzian Scale ($I(0)_L$) =	1199.1	±	42.678
Correlation Length (a_1) =	403.3	±	5.6
Bkgd (cm^{-1}) =	0.053923	±	5.1408e-5
Sqrt(χ^2/N) =	3.1456		
Fitted Range =	0.003433	< Q <	0.4121

The fit follows the data closely, the error bars are small compared to their respective fitting parameter, and the sqrt(χ^2/N) value is small, suggesting a good fit. Furthermore, the fractal dimension D parameter is also sufficiently close to the high Q slope determined from the Power Law fitting to suggest that these analyses do not contradict. The model is general enough to be able to apply to different types of gels while still describing the basic characteristics of the gel structure, thus reducing risk of overfitting the data. For these reasons, this model was chosen in conjunction with the Power Law analysis.