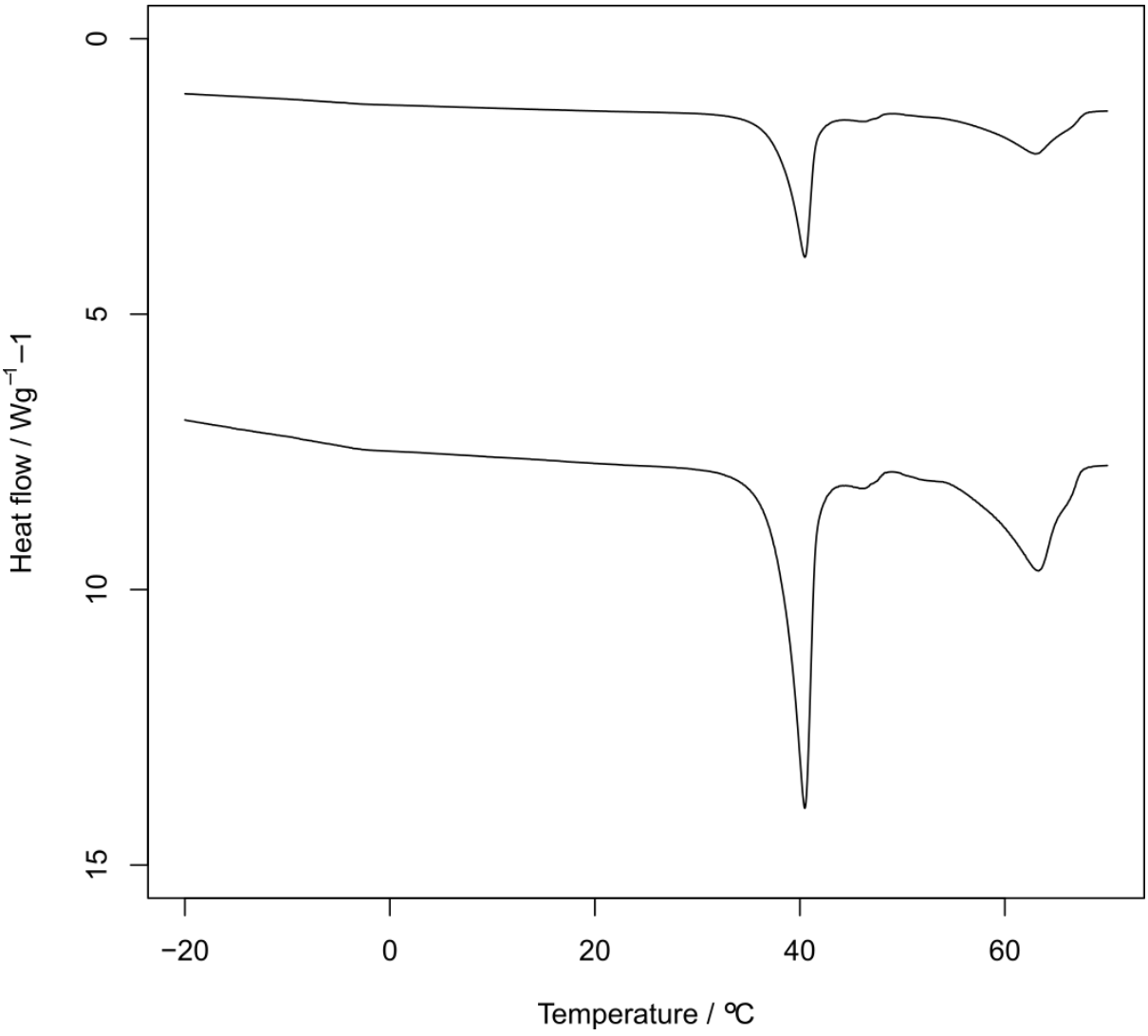


Figure SI1. Two thermograms of PGAS85 in the range between -20 and 70 °C. The two main melting transitions are present in both the thermal cycles.

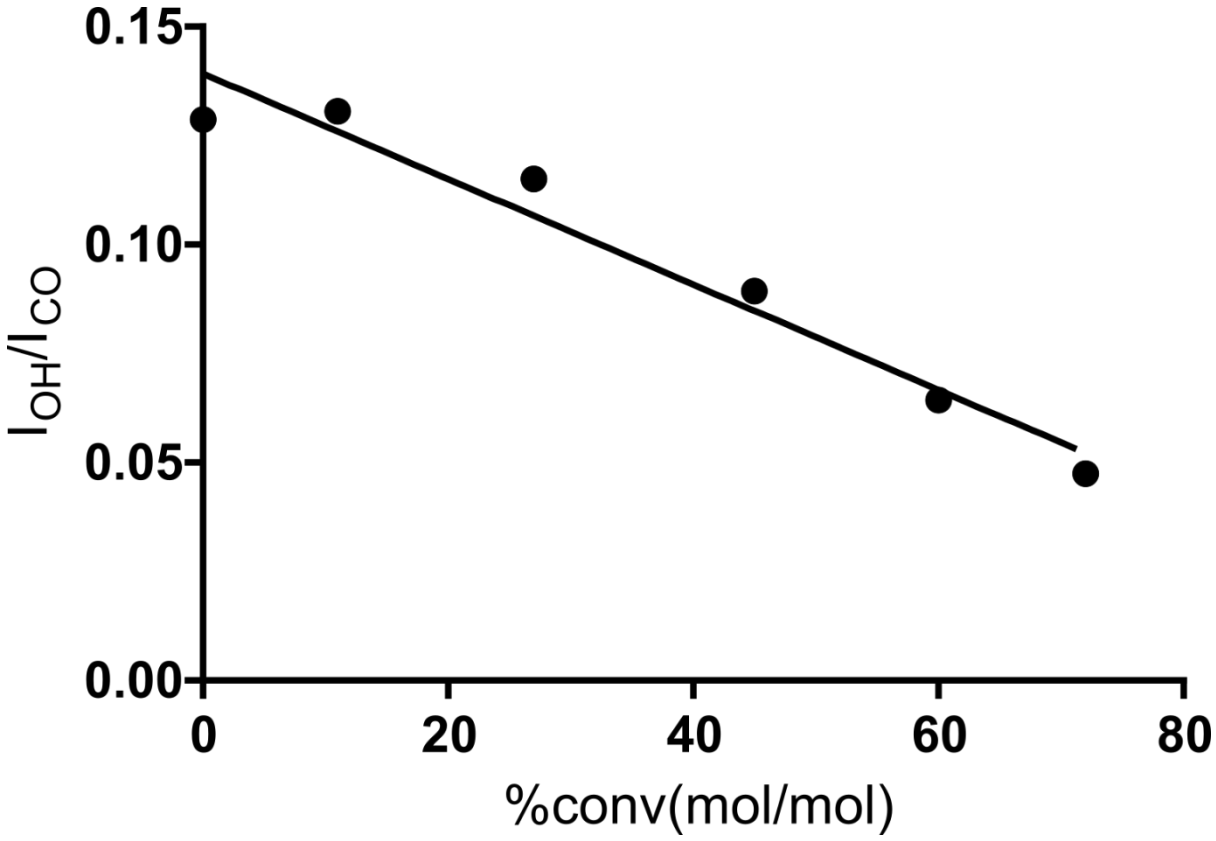


Figure SI2. Ratio between the intensity of hydroxyl group stretching and the carbonyl group stretching decreases with the degree of functionalization. This particular graph depicts PGAB polymer set trend.

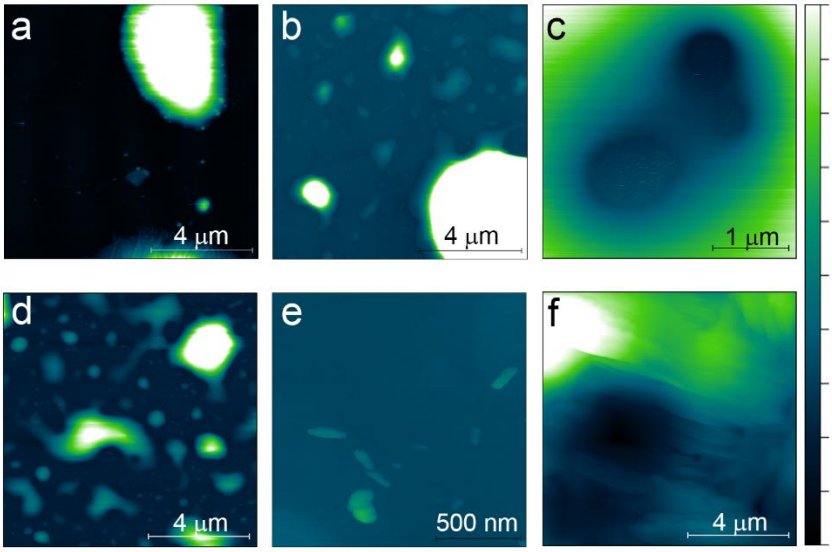


Figure SI3. AFM height images [with scale bars: x, z] of (a) PGA [4 µm, 100 nm], (b) PGAB 11% [4 µm, 100 nm], (c) PGAB 60% [1 µm, 100 nm], (d) PGAB 75% [4 µm, 100 nm], (e) PGAO 65% [500 nm, 100 nm], and (f) PGAS 65% [4 µm, 800 nm].

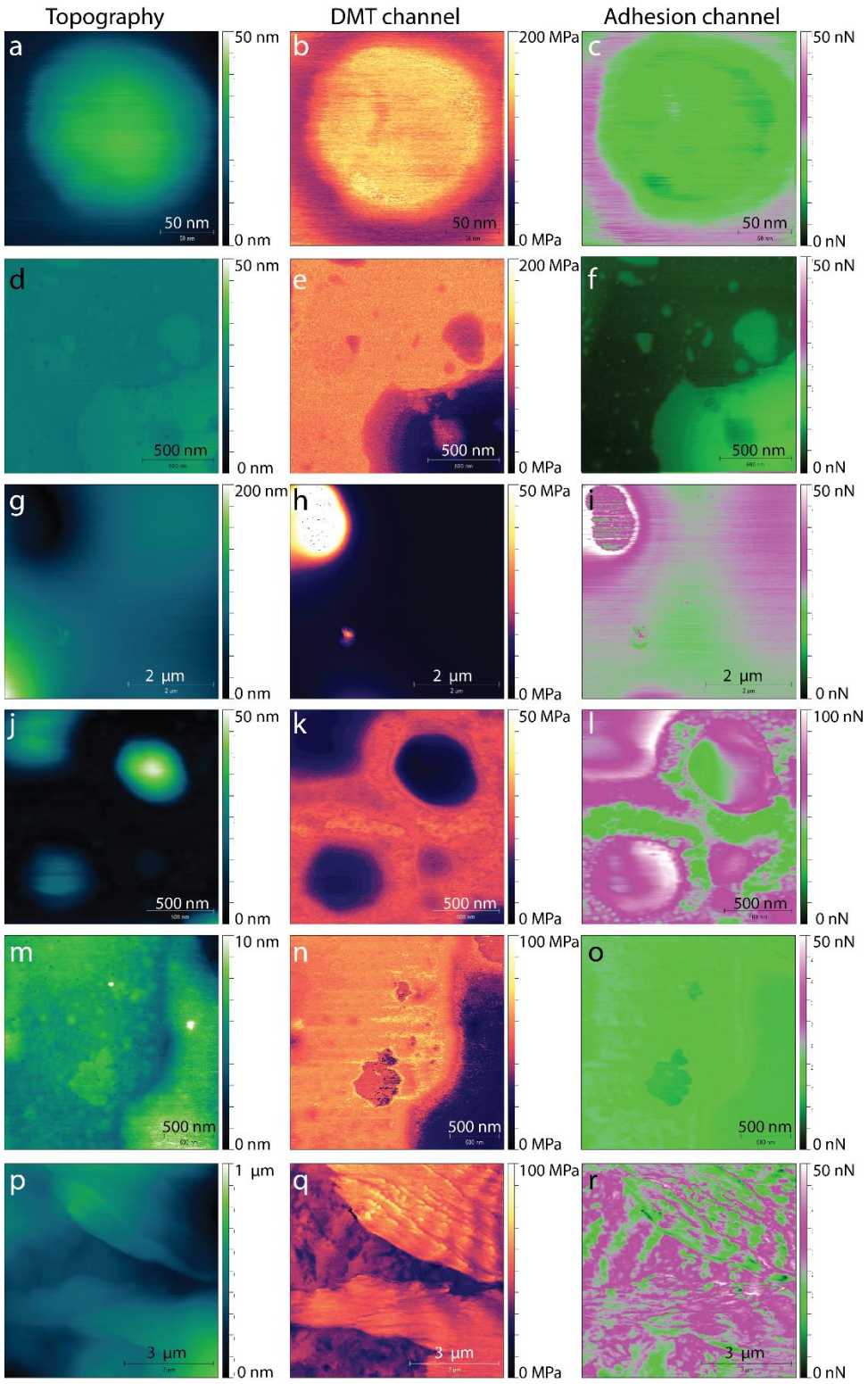


Figure SI4. AFM images of (a - c) PGA, (d - f) PGAB 11%, (g - i) PGAB 60%, (j - l) PGAB 75%, (m - o) PGAO 65%, and (p - r) PGAS 65%, with left-most column from height channel, central column from DMT (stiffness) channel, and right-most column from adhesion channel.

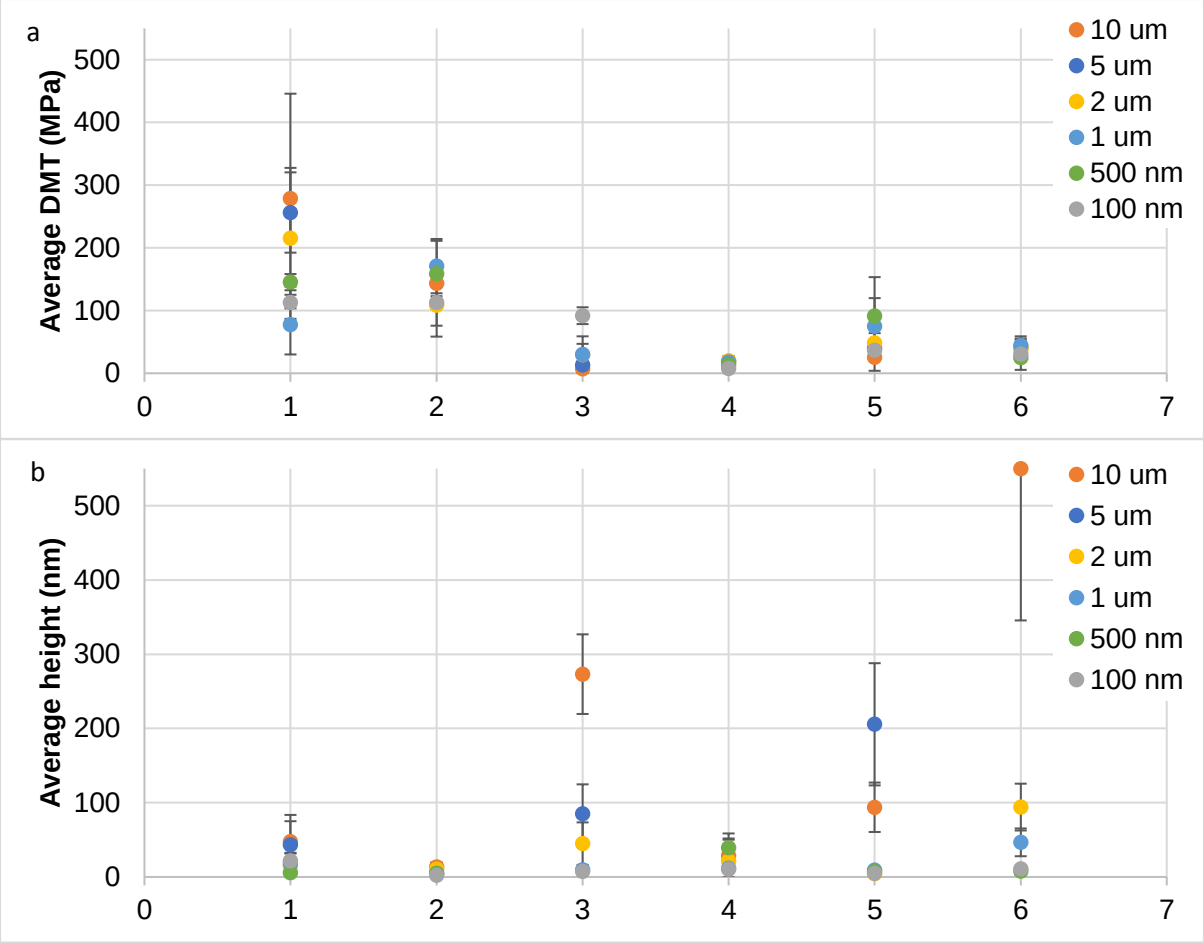


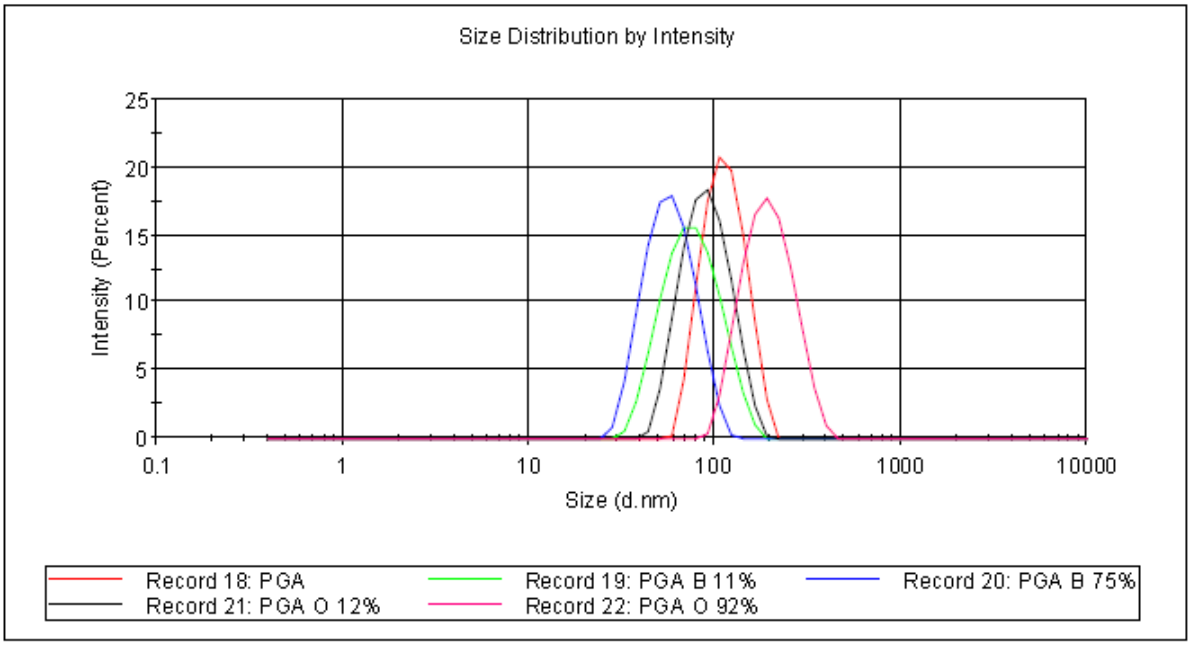
Figure SI5. DMT (stiffness, a) and height (topography, b) and values extracted from QNM images of varying image area size. Each data point is an average of the entire scan area, with the RMS (rq) used for standard deviation. Samples 1– 6 are PGA, PGAB 11%, PGAB 60%, PGAB 75%, PGAO 65%, and PGAS 65%, respectively.

AFM statistical analyses:

AFM images were analysed using freeware Gwyddion (v2.41, http:/gwyddion.net). For height data, plane subtraction and line correction were carried out, and minimum height was set to zero. For adhesion and DMT data, no data correction was applied. Samples showing a strong topographical artefact were excluded. The 'statistical quantities' function was utilised to obtain the average and RMS (rq) values across entire images (512 x 512 pixels) and exported to Excel. Where multiple images of one scale were available, data was averaged and the error was calculated as the square root of the average variance. These data are tabulated as follows where N = number of images used:

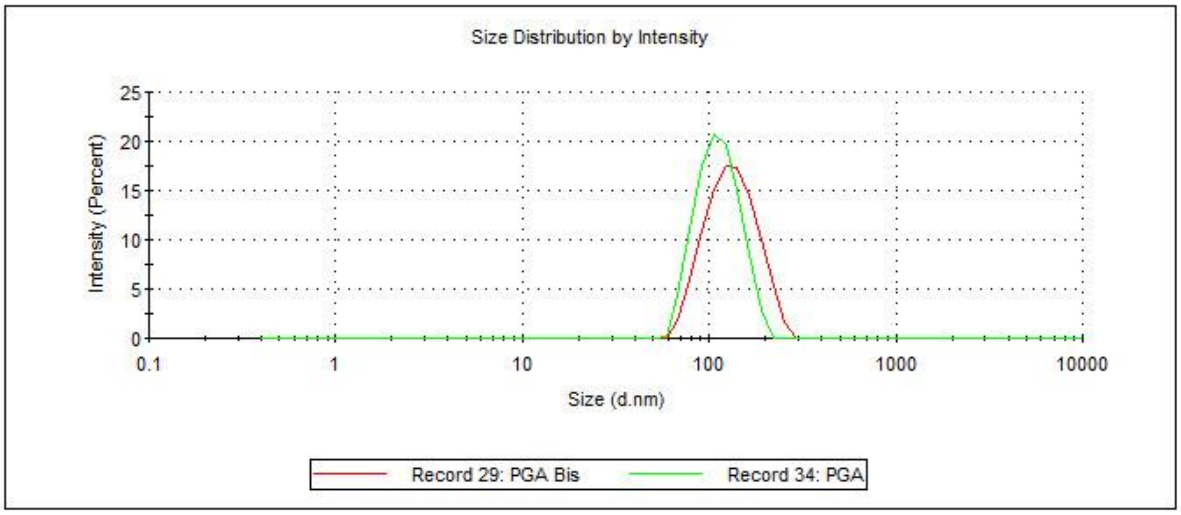
		10000 nm			5000 nm			2000 nm		
		height (nm)	DMT (MPa)	Adhesion (nN)	height (nm)	DMT (MPa)	Adhesion (nN)	height (nm)	DMT (MPa)	Adhesion (nN)
PGA	mean	47.49	278.97	29.59	43.41	256.41	28.50	15.08	215.59	23.07
	deviation	36.1	166.9	8.3	41.4	64.0	5.9	9.4	112.0	8.4
	N	2			2			3		
PGAB 11%	mean	13.55	143.61	7.01				10.33	108.88	6.86
	deviation	6.8	67.7	4.7				11.1	50.4	4.4
	N	3						3		
PGAB 60%	mean	273.15	7.13	27.82	84.93	13.12	28.42	44.91	29.38	22.44
	deviation	53.9	11.3	4.8	40.5	15.8	7.5	28.6	29.6	4.8
	N	2			2			1		
PGAB 75%	mean	28.52	19.23	59.84				21.32	20.09	62.01
	deviation	30.1	7.6	14.2				30.5	7.2	14.0
	N	1						3		
PGAO 65%	mean	93.85	25.79	17.19				4.62	48.47	14.84
	deviation	41.1	21.8	3.8				2.4	15.6	2.1
	N	2						3		
PGAS 65%	mean	549.90	41.26	20.27	205.63	39.77	20.12	94.14	38.39	24.35
	deviation	204.4	12.2	6.0	82.3	10.0	7.0	33.2	9.0	5.3
	N	1			1			2		

		1000 nm			500 nm			100 nm		
		height (nm)	DMT (MPa)	Adhesion (nN)	height (nm)	DMT (MPa)	Adhesion (nN)	height (nm)	DMT (MPa)	Adhesion (nN)
PGA	mean	18.32	77.62	31.60	5.84	145.37	18.39	21.90	112.60	20.23
	deviation	14.2	47.6	9.4	21.0	12.9	2.4	9.7	25.8	4.2
	N	1			3			1		
PGAB 11%	mean	5.11	170.91	5.89	4.87	158.89	3.65	2.14	113.05	4.68
	deviation	1.2	43.3	2.3	0.5	12.4	1.0	0.9	9.9	1.2
	N	1			2			1		
PGAB 60%	mean	9.51	29.88	22.96				7.30	91.90	33.15
	deviation	4.1	17.1	2.7				2.3	13.4	5.4
	N	2						3		
PGAB 75%	mean	11.60	18.02	59.62	39.24	13.11	50.43	10.71	7.65	46.13
	deviation	12.3	5.8	15.1	11.5	4.8	11.2	2.5	0.5	2.1
	N	2			2			1		
PGAO 65%	mean	9.24	74.89	12.18	7.34	91.38	14.23	5.04	36.62	11.45
	deviation	3.8	45.0	2.1	3.9	62.0	3.1	1.9	13.2	1.7
	N	3			1			2		
PGAS 65%	mean	46.64	44.67	7.91	7.73	24.87	38.78	11.07	30.49	1.47
	deviation	20.6	14.3	2.0	5.1	5.6	4.4	3.3	25.0	0.4
	N	4			1			1		



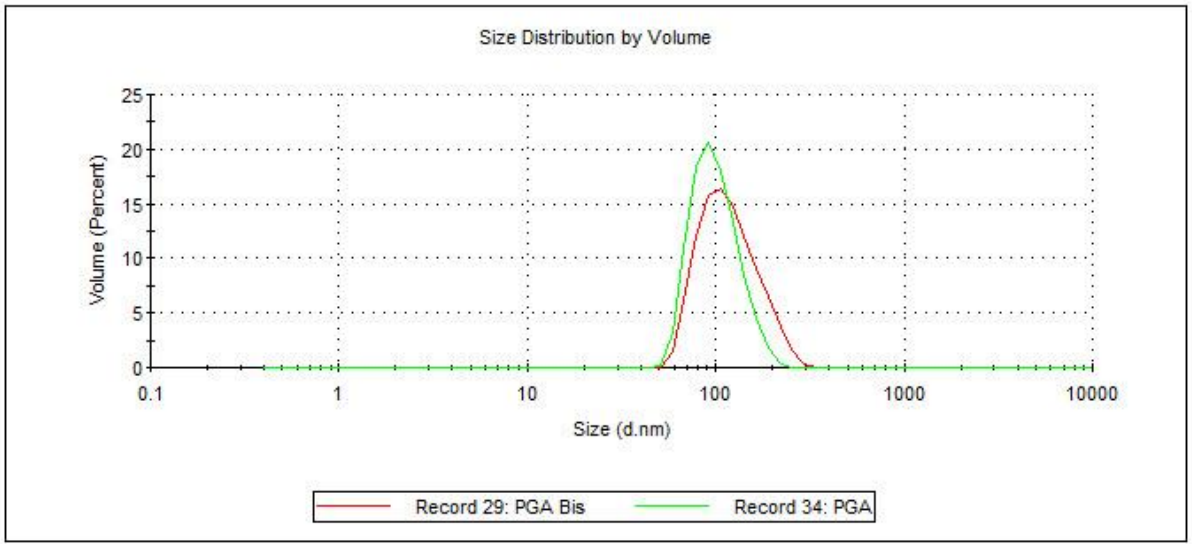
PGA

		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 108.0	Peak 1:	114.6	100.0	29.21
PdI: 0.043	Peak 2:	0.000	0.0	0.000
Intercept: 0.917	Peak 3:	0.000	0.0	0.000
Result quality : Good				



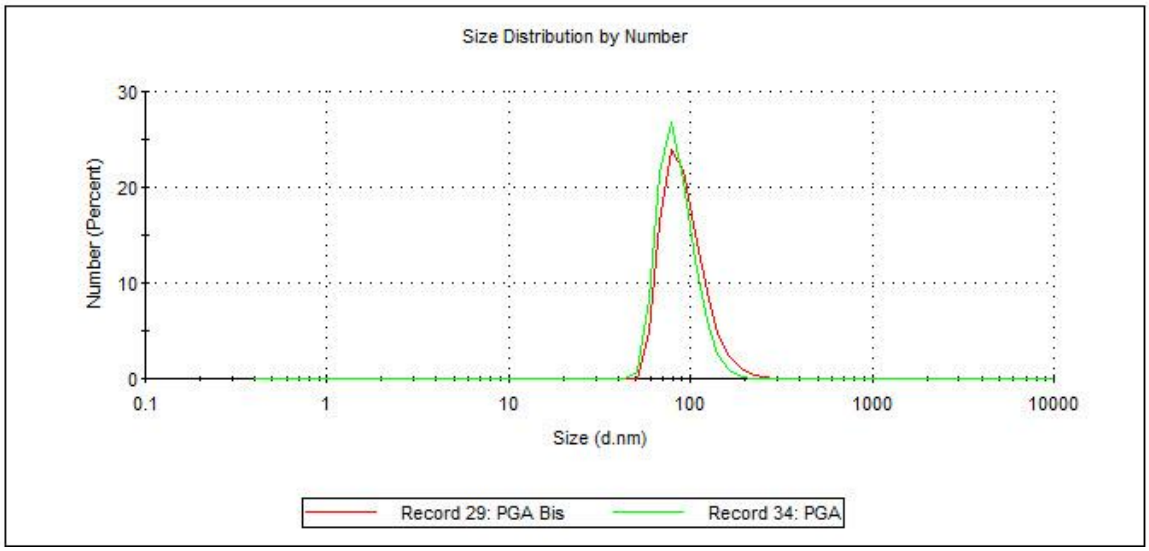
		Size (d.nm):	% Volume:	St Dev (d.nm):
Z-Average (d.nm): 108.0	Peak 1:	102.0	100.0	29.63
PdI: 0.043	Peak 2:	0.000	0.0	0.000
Intercept: 0.917	Peak 3:	0.000	0.0	0.000

Result quality : Good



		Size (d.nm):	% Number:	St Dev (d.nm):
Z-Average (d.nm): 108.0	Peak 1:	85.93	100.0	21.38
PdI: 0.043	Peak 2:	0.000	0.0	0.000
Intercept: 0.917	Peak 3:	0.000	0.0	0.000

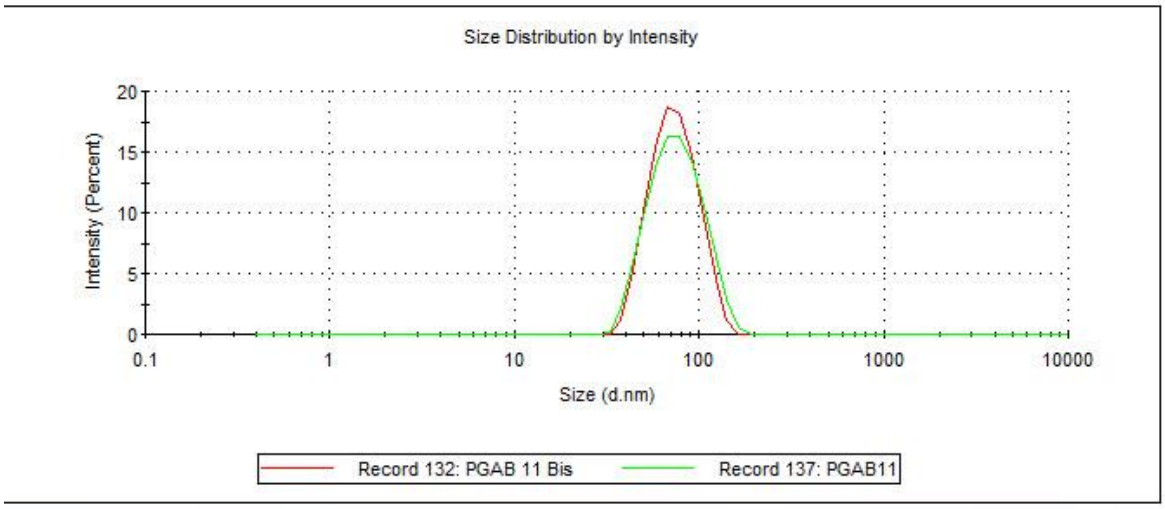
Result quality : Good



PGAB11

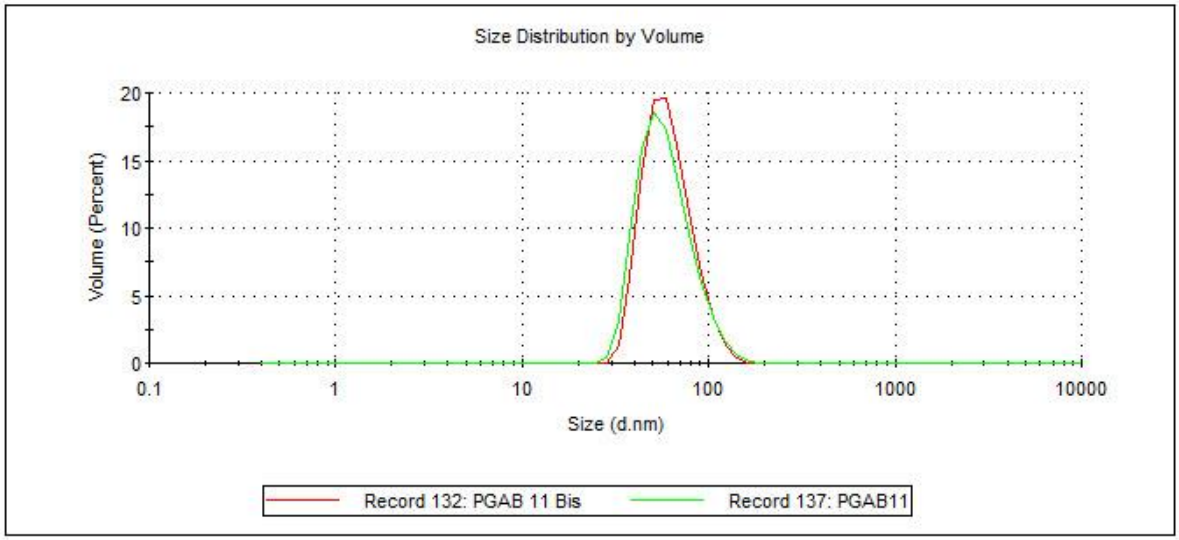
		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 70.35	Peak 1:	77.96	100.0	25.38
PdI: 0.089	Peak 2:	0.000	0.0	0.000
Intercept: 0.935	Peak 3:	0.000	0.0	0.000

Result quality : Good



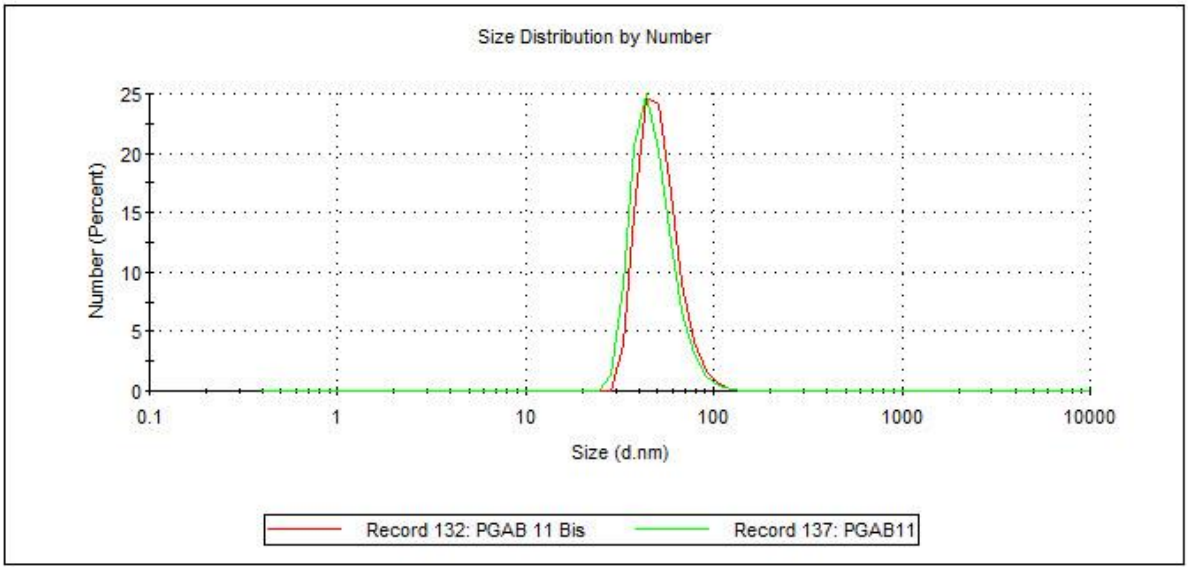
		Size (d.nm):	% Volume:	St Dev (d.nm):
Z-Average (d.nm): 70.35	Peak 1:	60.44	100.0	20.71
PdI: 0.089	Peak 2:	0.000	0.0	0.000
Intercept: 0.935	Peak 3:	0.000	0.0	0.000

Result quality : Good



		Size (d.nm):	% Number:	St Dev (d.nm):
Z-Average (d.nm): 70.35	Peak 1:	48.36	100.0	13.23
PdI: 0.089	Peak 2:	0.000	0.0	0.000
Intercept: 0.935	Peak 3:	0.000	0.0	0.000

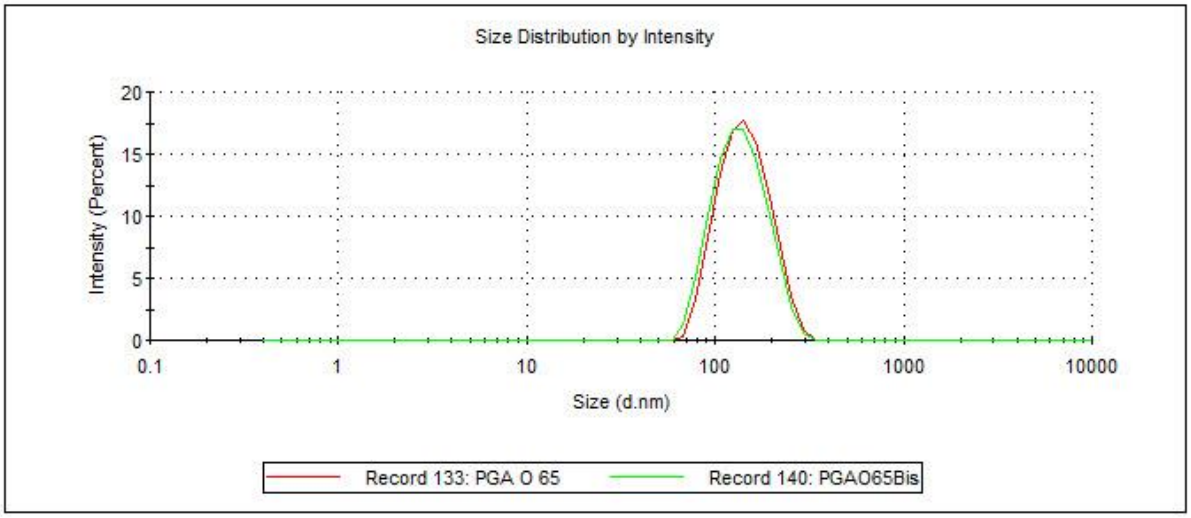
Result quality : Good



PGAO65

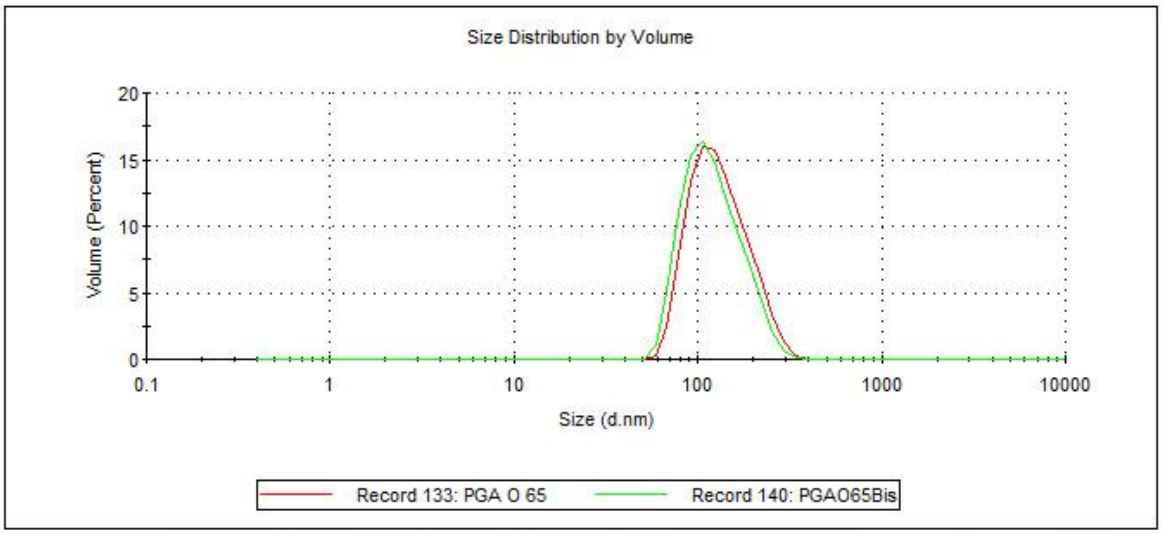
		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 128.7	Peak 1:	141.6	100.0	44.63
PdI: 0.094	Peak 2:	0.000	0.0	0.000
Intercept: 0.948	Peak 3:	0.000	0.0	0.000

Result quality : Good



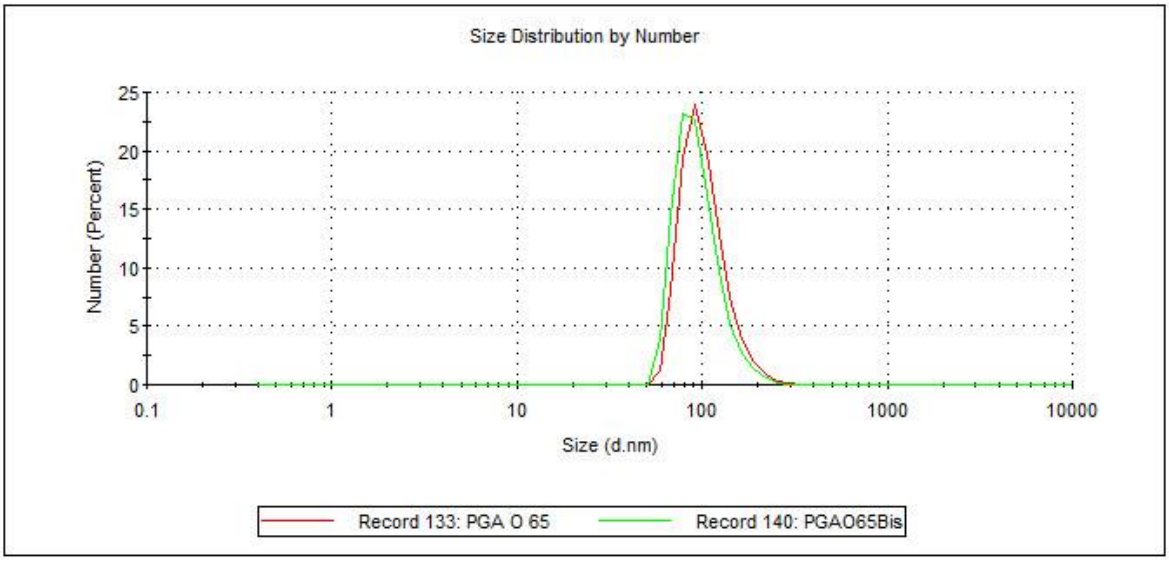
		Size (d.nm):	% Volume:	St Dev (d.nm):
Z-Average (d.nm): 128.7	Peak 1:	126.3	100.0	46.57
PdI: 0.094	Peak 2:	0.000	0.0	0.000
Intercept: 0.948	Peak 3:	0.000	0.0	0.000

Result quality : Good



		Size (d.nm):	% Number:	St Dev (d.nm):
Z-Average (d.nm): 128.7	Peak 1:	96.14	100.0	28.63
PdI: 0.094	Peak 2:	0.000	0.0	0.000
Intercept: 0.948	Peak 3:	0.000	0.0	0.000

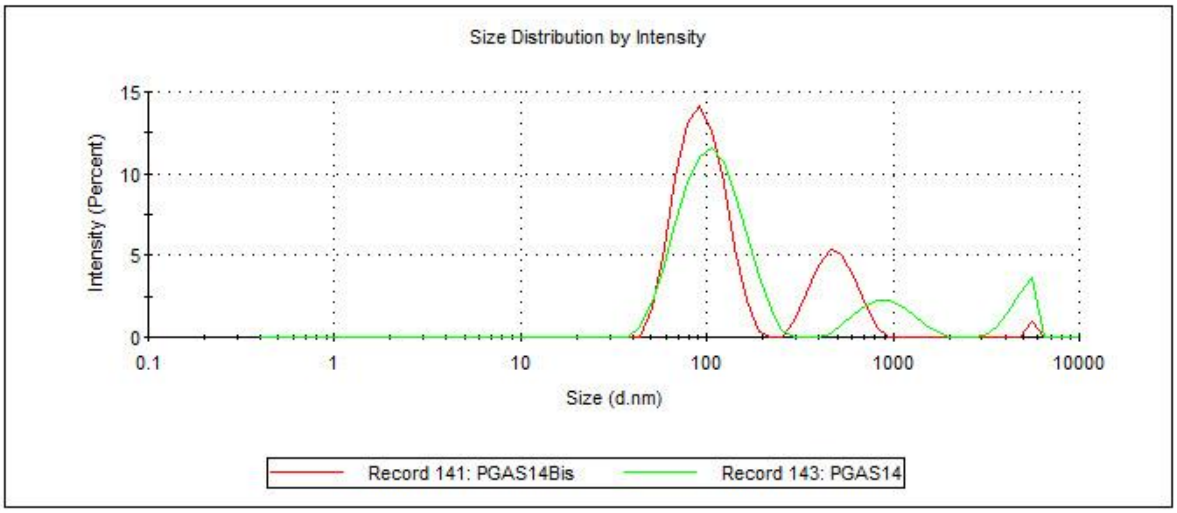
Result quality : Good



PGAS14

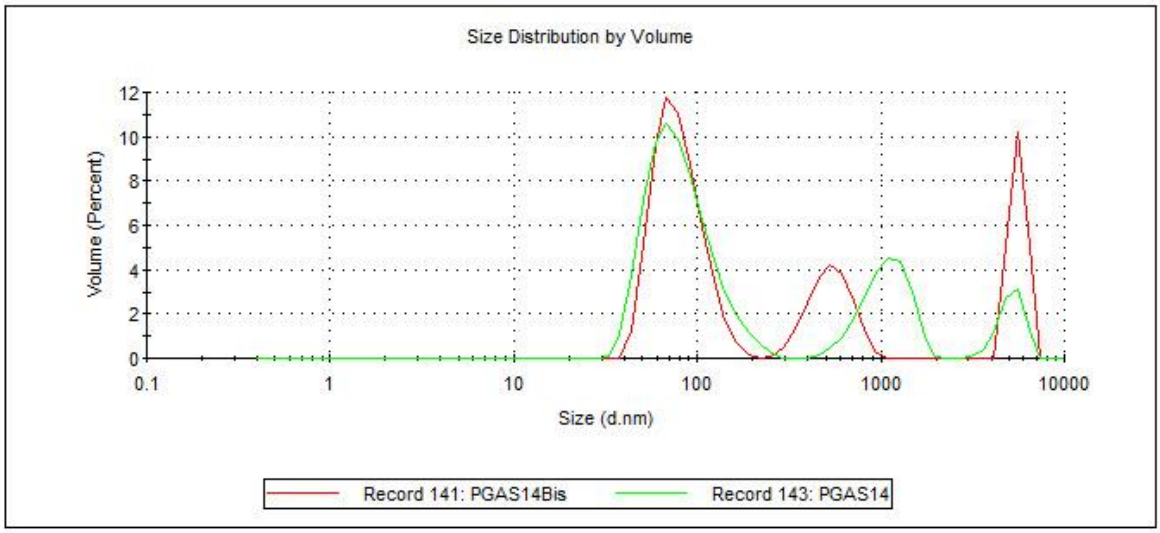
		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 140.1	Peak 1:	110.9	78.0	40.95
PdI: 0.467	Peak 2:	935.7	13.4	293.4
Intercept: 0.891	Peak 3:	4883	8.6	688.9

Result quality : Good



		Size (d.nm):	% Volume:	St Dev (d.nm):
Z-Average (d.nm): 140.1	Peak 1:	84.54	68.2	36.33
PdI: 0.467	Peak 2:	1093	23.0	298.1
Intercept: 0.891	Peak 3:	5137	8.8	807.8

Result quality : Good



		Size (d.nm):	% Number:	St Dev (d.nm):
Z-Average (d.nm): 140.1	Peak 1:	60.87	100.0	19.31
PdI: 0.467	Peak 2:	861.2	0.0	275.5
Intercept: 0.891	Peak 3:	0.000	0.0	0.000

Result quality : Good

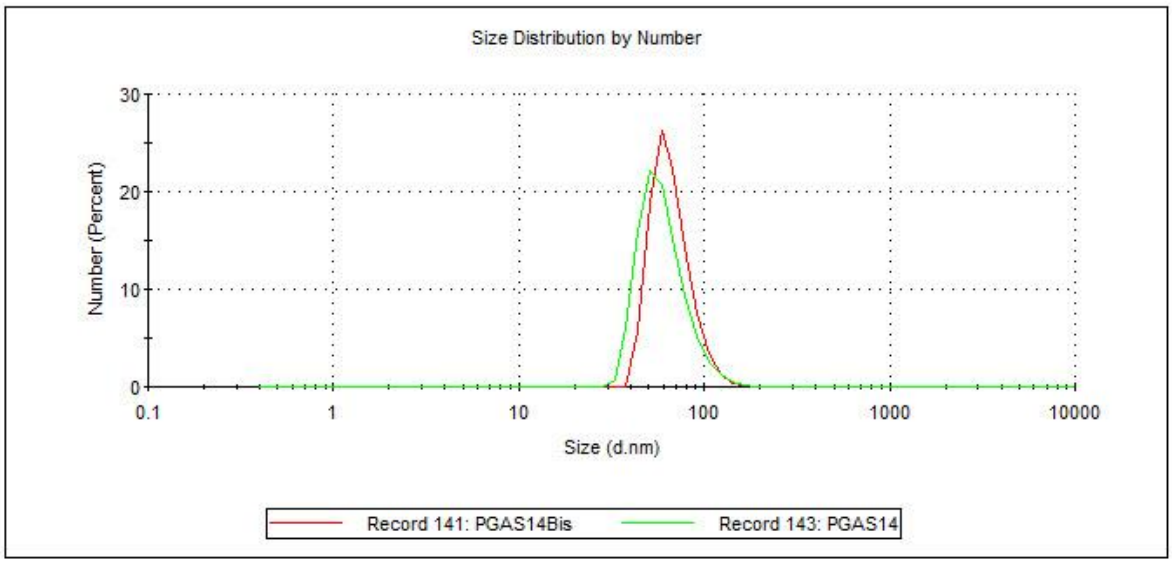


Figure SI6a DLS traces of PGA, PGAO12, PGAB11, PGAO92 and PGAB75, PGAS14 and PGAO65. Intensity, volume and number traces.

Results

			Size (d.n...	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	140.1	Peak 1:	110.9	78.0	40.95
PdI:	0.467	Peak 2:	935.7	13.4	293.4
Intercept:	0.891	Peak 3:	4883	8.6	688.9
Result quality	Good				

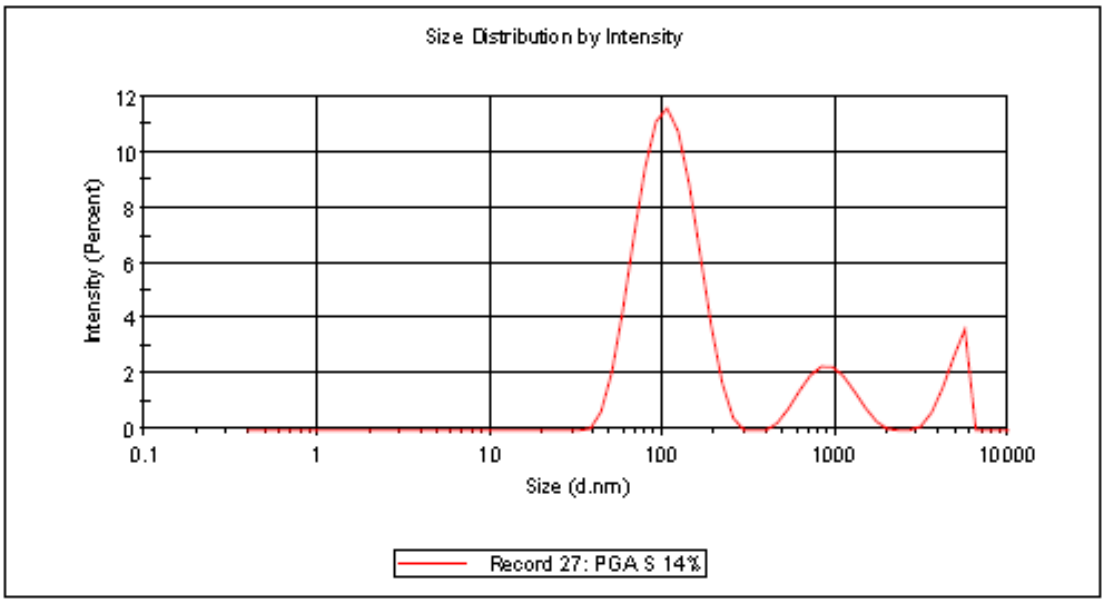


Figure SI6b. DLS intensity trace of PGAS14

Results

			Size (d.n...	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	127.7	Peak 1:	116.7	94.2	38.96
PdI:	0.348	Peak 2:	5163	5.8	497.8
Intercept:	0.930	Peak 3:	0.000	0.0	0.000
Result quality	Good				

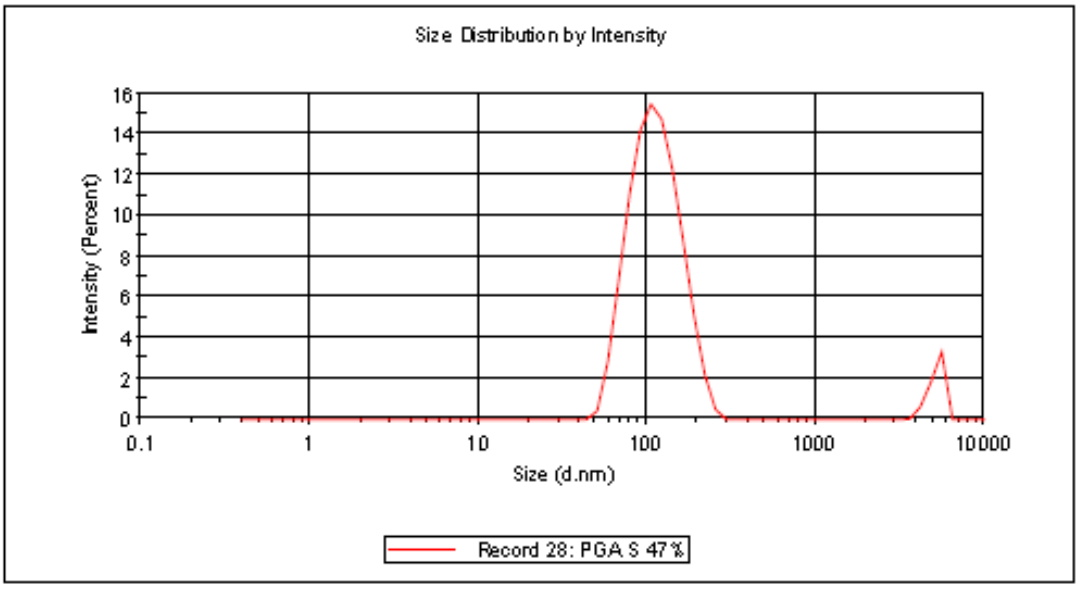


Figure SI6b. PGAS47 DLS trace.

Results

			Size (d.n...	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	136.0	Peak 1:	144.3	100.0	36.65
PdI:	0.045	Peak 2:	0.000	0.0	0.000
Intercept:	0.946	Peak 3:	0.000	0.0	0.000
Result quality	Good				

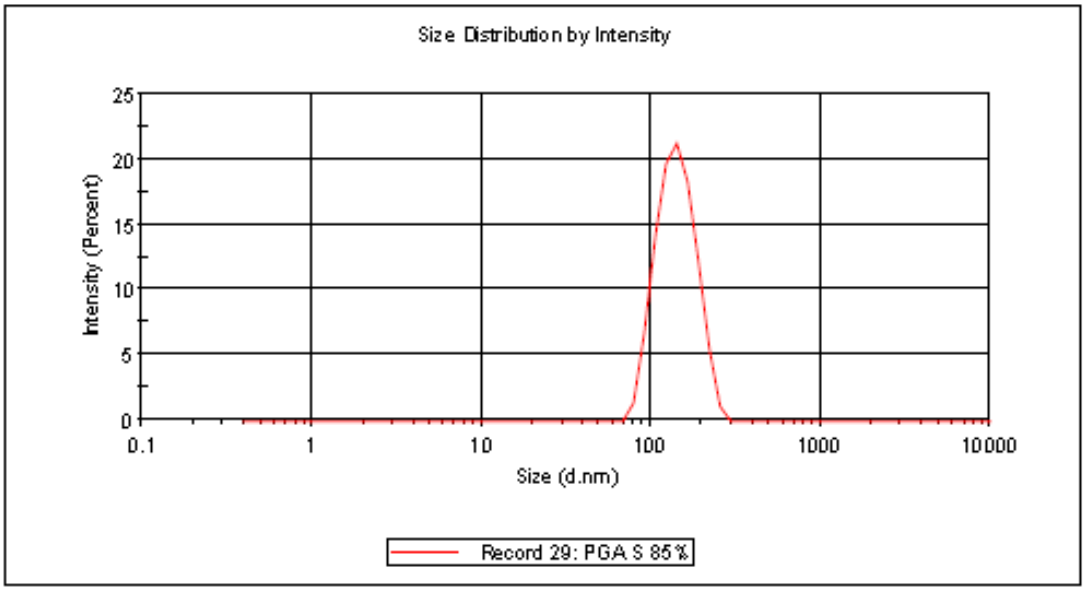


Figure SI6b. DLS Intensity trace of PGAS85.