Supporting Information

Micellar-Cluster Association of Ureidopyrimidone Functionalized Monochelic Polybutadiene

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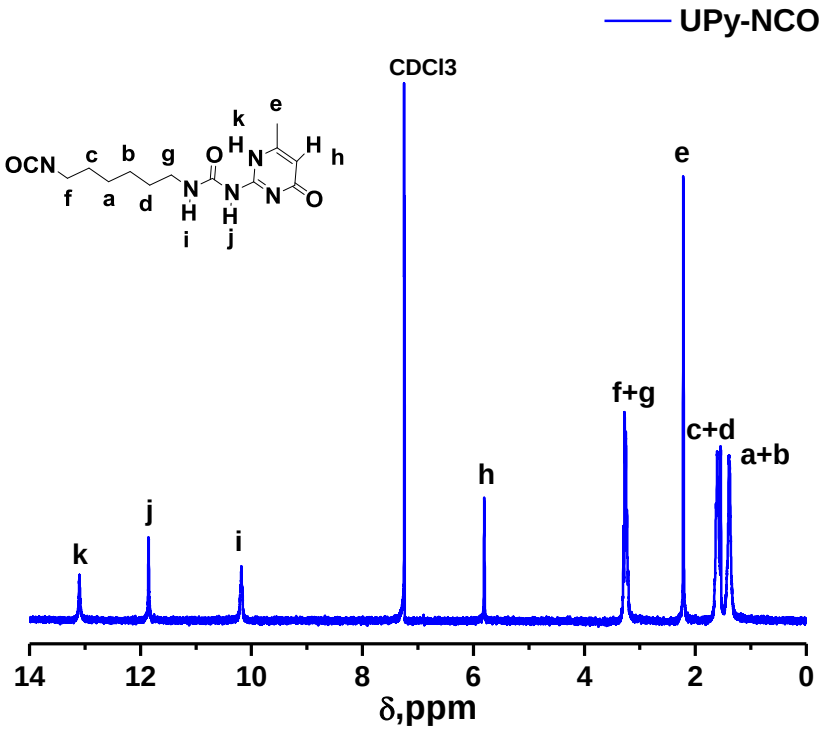

Figure S1: ^{1}H NMR spectrum of UPy-Synthon

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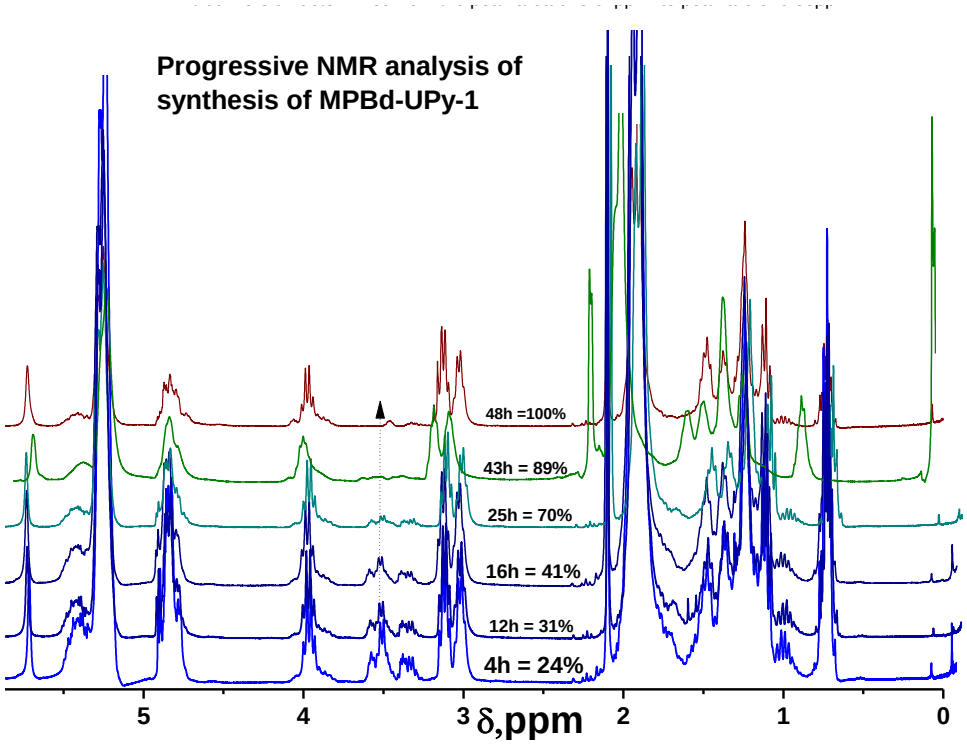

Figure S2: Progress of coupling reaction between UPy-NCO and MPBd-OH-1 in the presence of trace amounts of co-distilled stabilizer ethanol in chloroform. The arrow points to the disappearance of terminal $–CH_2-$ group of MPBd-OH via coupling.

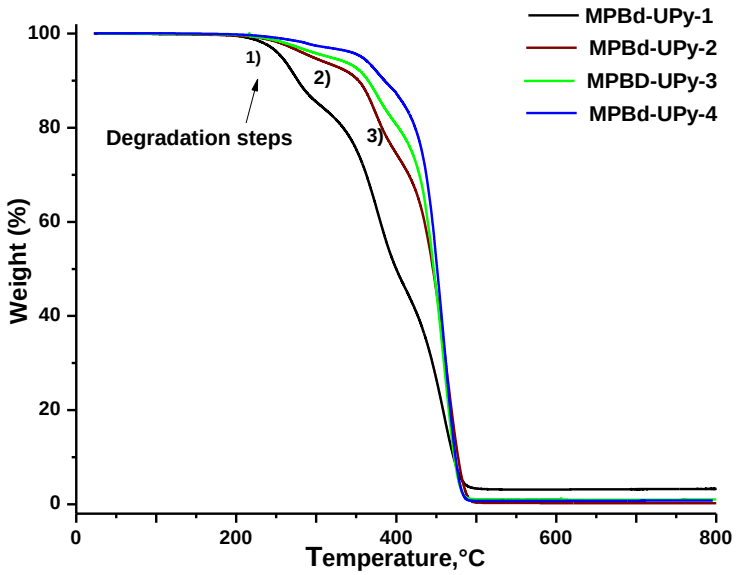

Figure S3: Thermogravimetric analysis of MPBd-UPy-1-4. Different steps (1-3) are indicative of end-group and main segment cleavage and decompositions.

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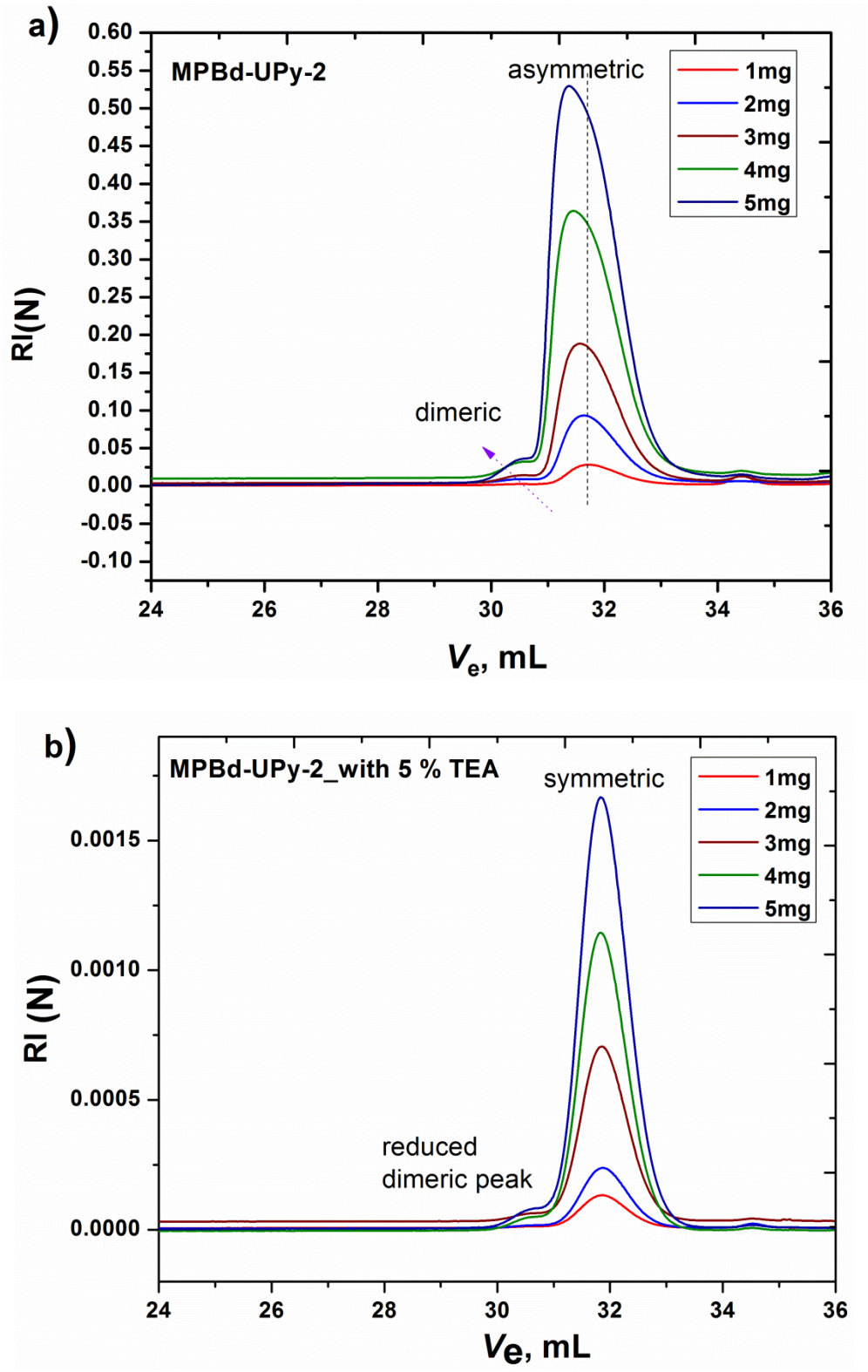

Figure S4: Normalized concentration dependent (1-5 mg/mL) GPC eluograms of MPBd-UPy-2 (a) and in presence of 5% triethylamine (b).

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Table S1: Concentration dependent GPC of the MPBd-UPy-2 and MPBd-OH –2

Sample concentration (mg/mL)	MPBd-OH			MPBd-UPy		
	$M_{n\ SEC,}$ (g/mol)	$M_{n(max)}$ (g/mol)	M_w/M_n	$M_{n,\ SEC}$[c] g/mol	$M_{n,\ NMR}$[d] g/mol	M_w/M_n
1	1,720	1,810	1.048	1,890	2,120	1.064
2	1,700	1,780	1.049	1,920	2,240	1.074
3	1,680	1,760	1.050	1,980	2,330	1.068
4	1670	1,750	1.051	2,020	2,470	1.077
5	1670	1,750	1.052	2,590	2,590	1.077

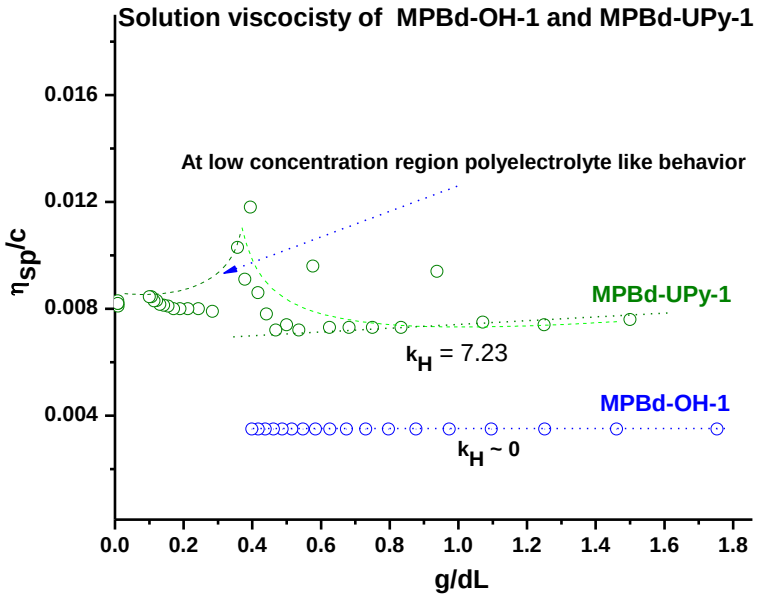

Figure S5: Solution viscosity of the MPBd-UPy-1 in toluene. A linear region at higher concentration and non-linear region at lower concentration can be seen. An upward increase of viscosity at low concentration shows behavior like polyelectrolyte in water.

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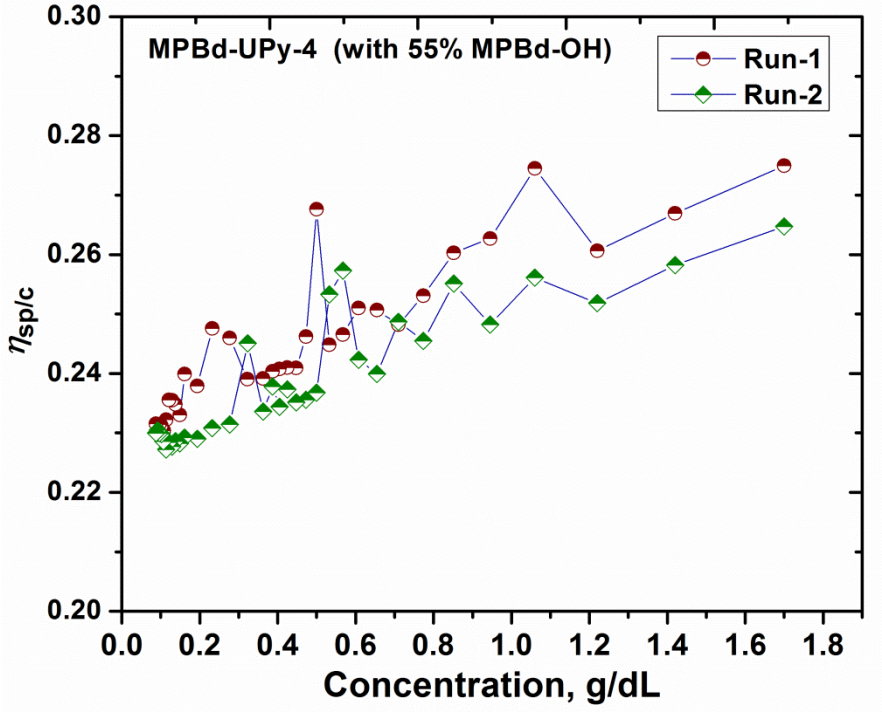

Figure S6: Repetition experiments of the mixture of MPBd-UPy-4 with MPBd-OH (55 wt. %) in toluene as an attempt to find error limits as requested by the reviewer #2 during the revision. The sample which was stored in a refrigerator over 6 months was measured again for this purpose.

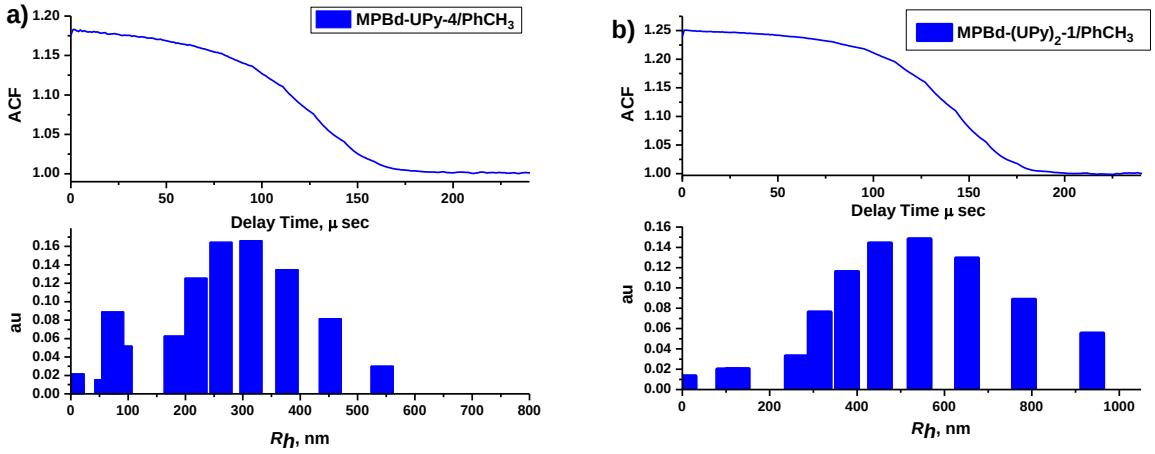

Figure S7: Representive histograms of the a) MPBd-UPy-4 and b) MPBd-$(UPy)_2$-1 at 25°C

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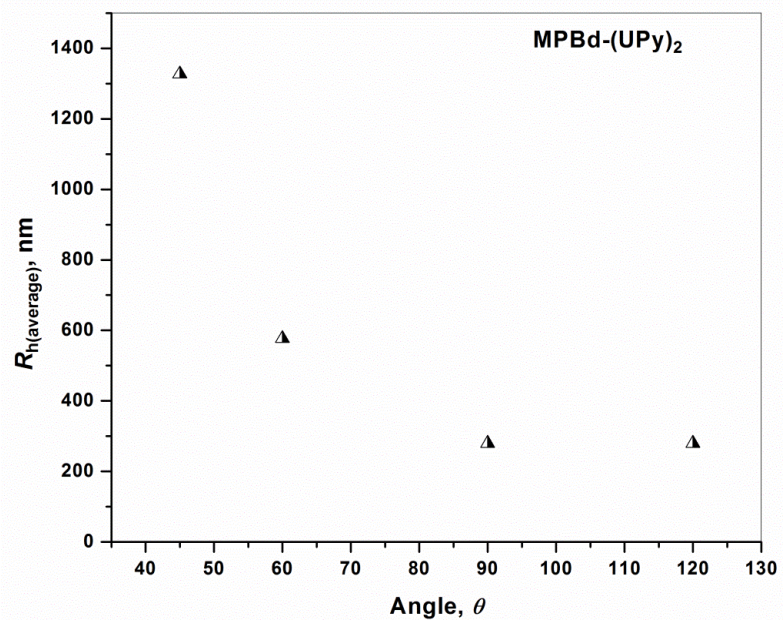

Figure S8: Average population of larger size micelles ($R_{h,average}$) in a toluene solution of MPBd-$(UPy)_2$ at different angles. Sample concentration was 35 mg/mL, and analyzed at 25 °C

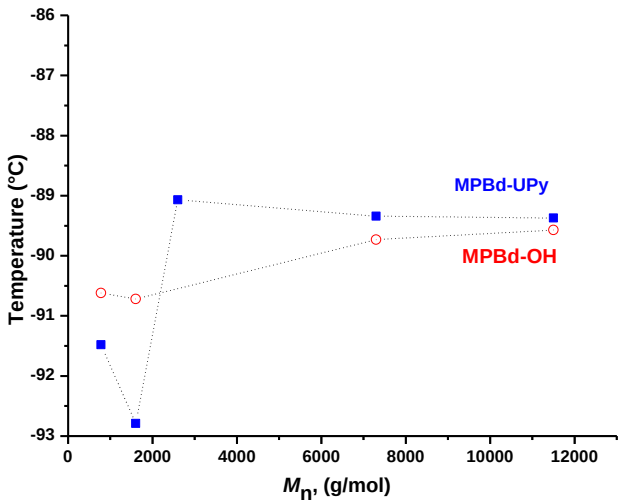

Figure S9: Plot of glass transition (T_g) temperature v_s molecular weight of polybutadiene

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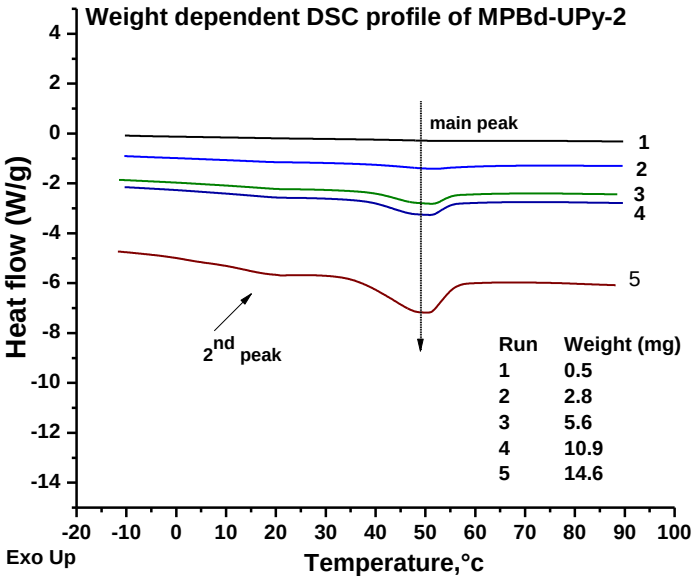

Figure S10: Effect of sample weight on the DSC endothermic peak MPBd-UPy-2

Table S2: Enthalpy values of MPBd-UPy

Sample	Heating cycle	1st peak		2nd peak	
		$T_{1deagg.}$ (°C)	Enthalpy (J/g)	$T_{2deagg.}$ (°C)	Enthalpy (J/g)
MPBd-UPy-1	1st	6.49	1.122	70.87	18.980
	2nd	6.69	1.245	70.62	18.430
	3rd	7.24	1.147	70.67	18.310
MPBd-UPy-2	1st	20.78	0.495	52.52	6.258
	2nd	19.60	0.483	51.00	5.598
	3rd	19.20	0.462	50.61	5.80
MPBd-UPy-3	1st	1.69	0.273	46.77	6.564
	2nd	-2.03	0.160	48.72	6.280
	3rd	-2.40	0.138	48.43	5.980
MPBd-UPy-4	1st	None	None	48.02	2.642
	2nd	None	None	51.55	2.730
	3rd	None	None	53.52	2.519

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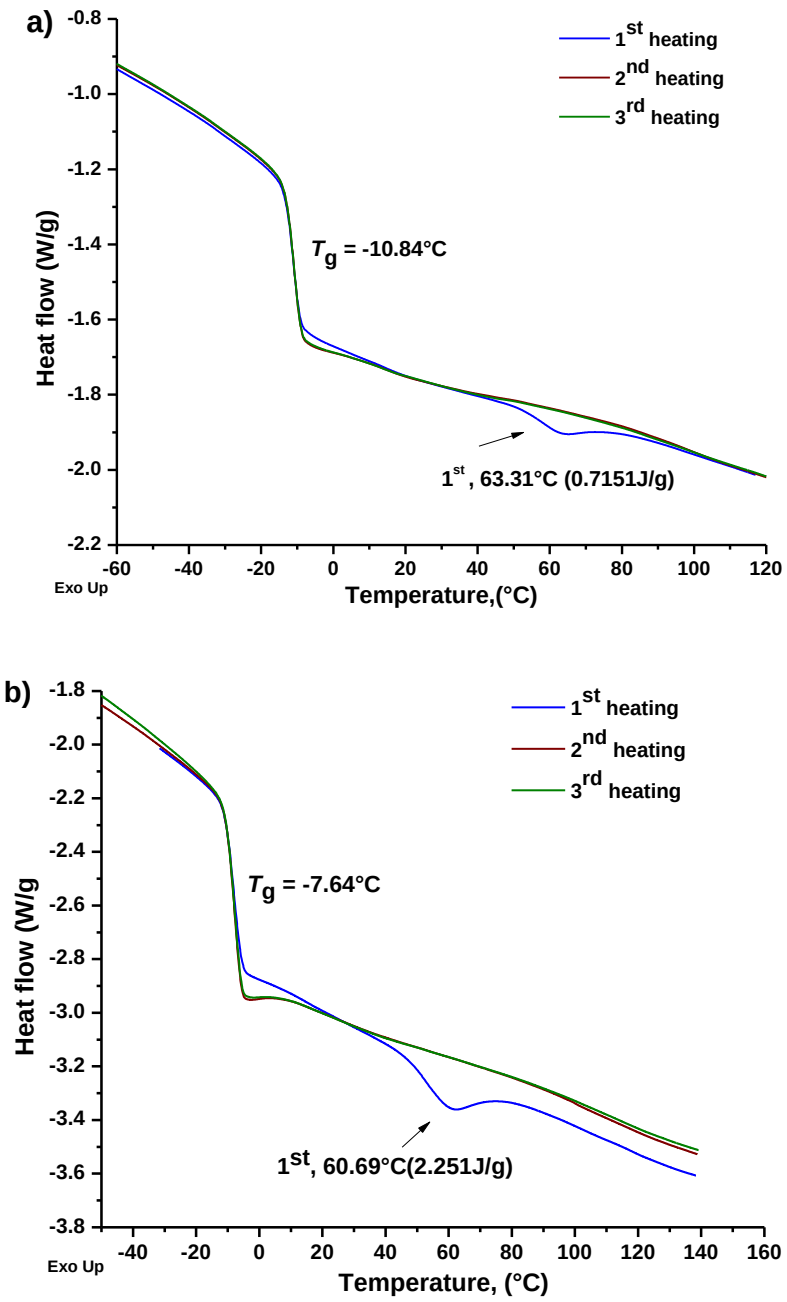

Figure S11: DSC profile of MPBd-UPy, 7 kg/mol with ~94 % 1,2 vinyl contents; a) after first run, b) after ~3 months at 30 °C.

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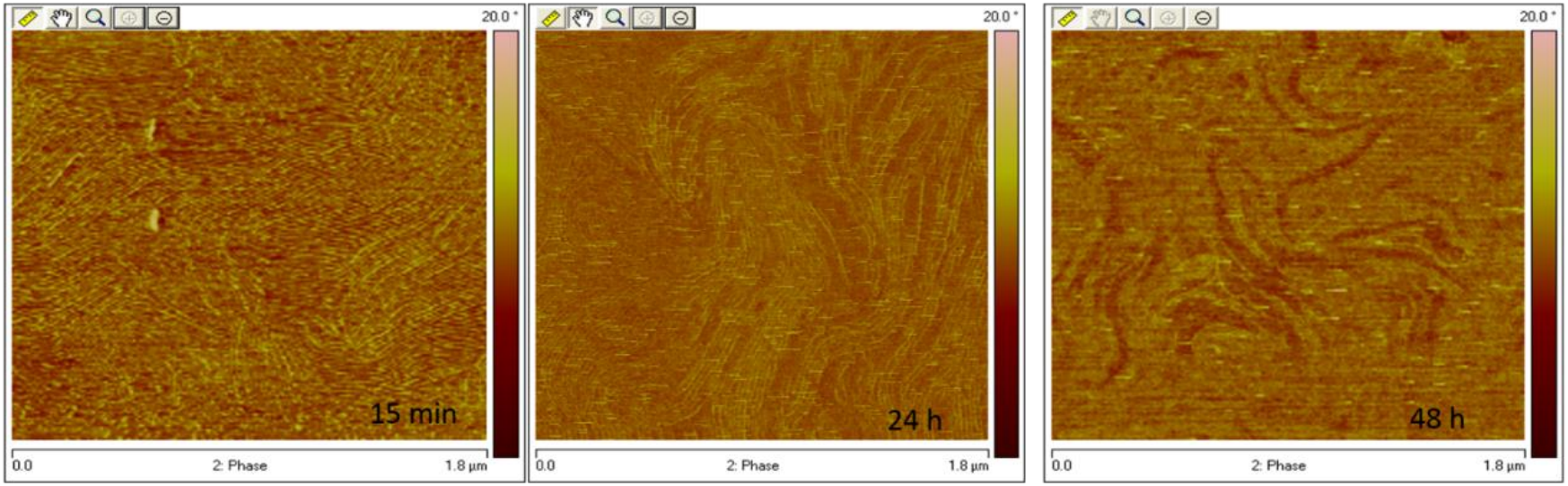

Figure S12: Time dependent morphology of MPBd-UPy-4 (from left to right, 15 min, 24 h, and 48 h after drop coating a thin film on freshly cleaved mica). The images were taken without changing the position of the sample in the AFM over 48 h. The size of the fibrous looking associated micellar clusters changes gradually over time indicating surface mobility of the associates induced by PBd segments (low T_g) at room temperature. Micellar cluster sizes are in the range of ~ 25-27 nm.

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