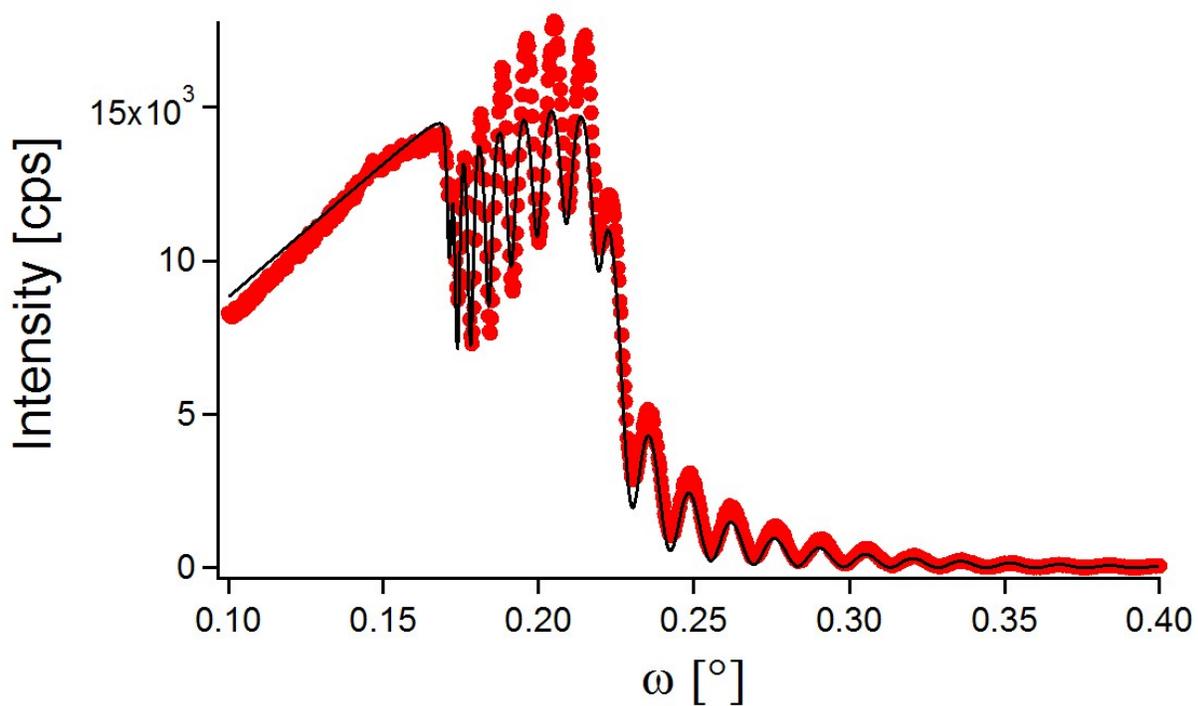


## Development of Polycarbonate-containing Block Copolymers for Thin Film Self-assembly Applications

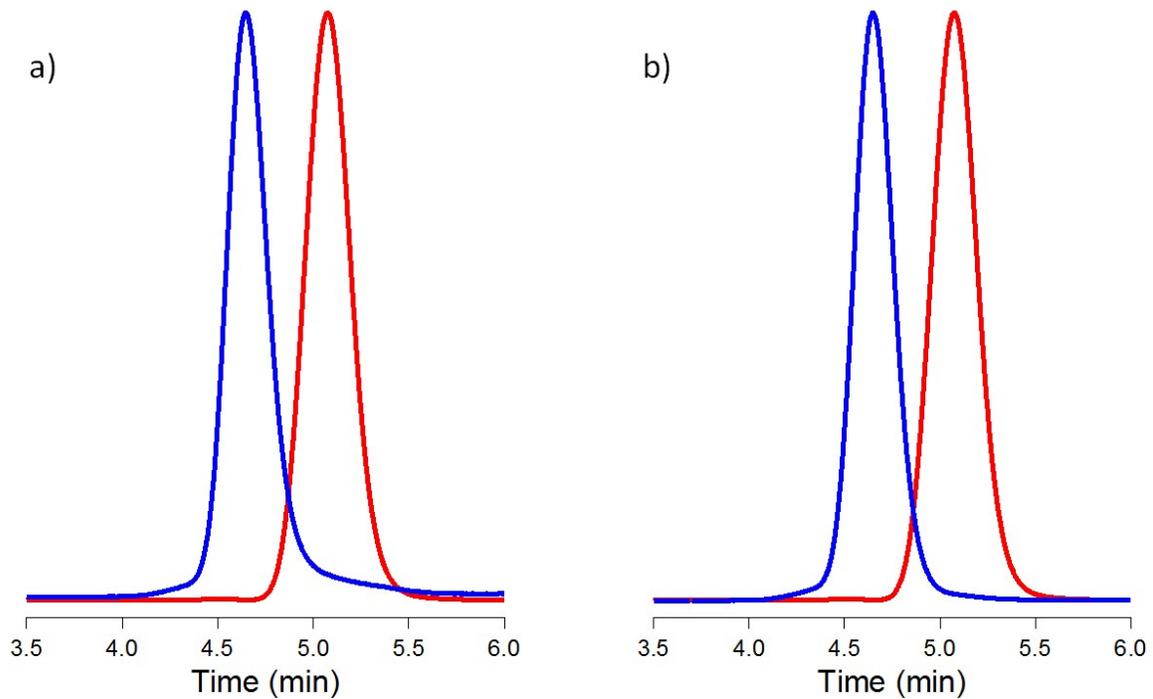
Ankit Vora\*, Rudy J. Wojtecki, Kristin Schmidt, Anindarupa Chunder, Joy Y. Cheng, Alshakim

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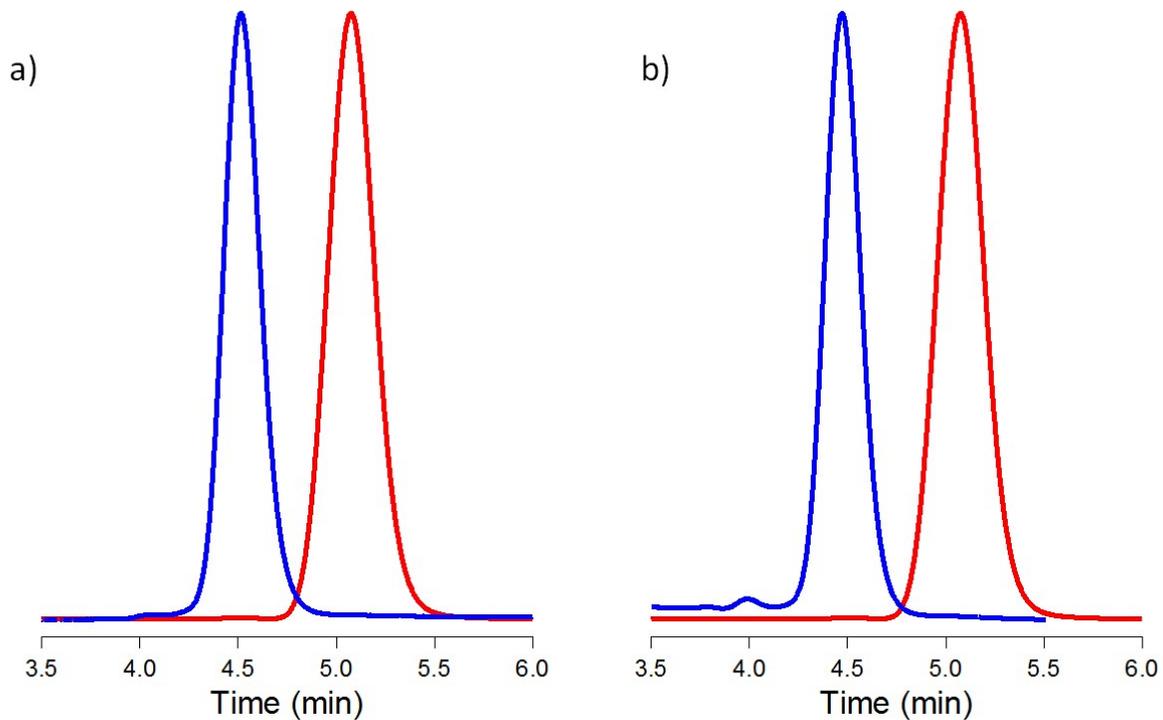
IBM Research – Almaden, 650 Harry Rd., San Jose, California 95120



**Figure S1.** XRR data for PTMC homopolymer (red trace). This data was fitted (black trace) using a single layer with a density of  $1.3\text{g}/\text{cm}^3$ , thickness of 243nm and roughness of 2.7nm.



**Figure S2.** GPC traces for PS-OH (red),  $M_n = 6600$  g/mol, PDI = 1.04 and PS-*b*-PTMC (blue) BCP using DBU catalyst with 50% conversion of TMC monomer (Table 1, Example 3), (a) before purification,  $M_n = 11,700$ , PDI = 1.06 and (b) after fractionation in 60:40 (v/v) MeOH:MeCN  $M_n = 12,500$ , PDI = 1.03



**Figure S3.** GPC traces for PS-OH (red),  $M_n = 6600$  g/mol, PDI = 1.04 and PS-*b*-PTMC (blue) BCP using DPP catalyst with 50% conversion of TMC monomer (Table 1, Example 4), (a) before fractionation,  $M_n = 15,200$ , PDI = 1.02 and (b) after fractionation with 60:40 (v/v) MeOH:MeCN  $M_n = 16,400$ , PDI = 1.02.

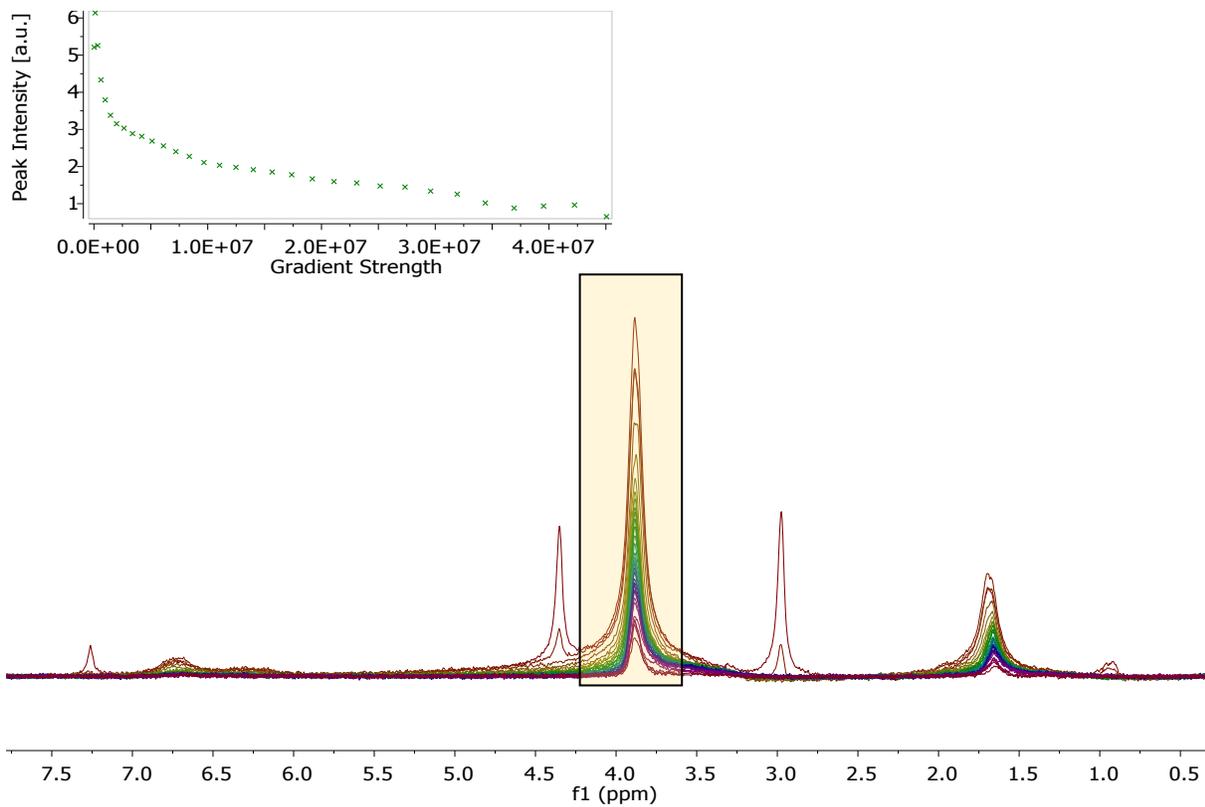
## **CEDOSY – Experimental Procedure and Control Experiments**

### **Data Normalization:**

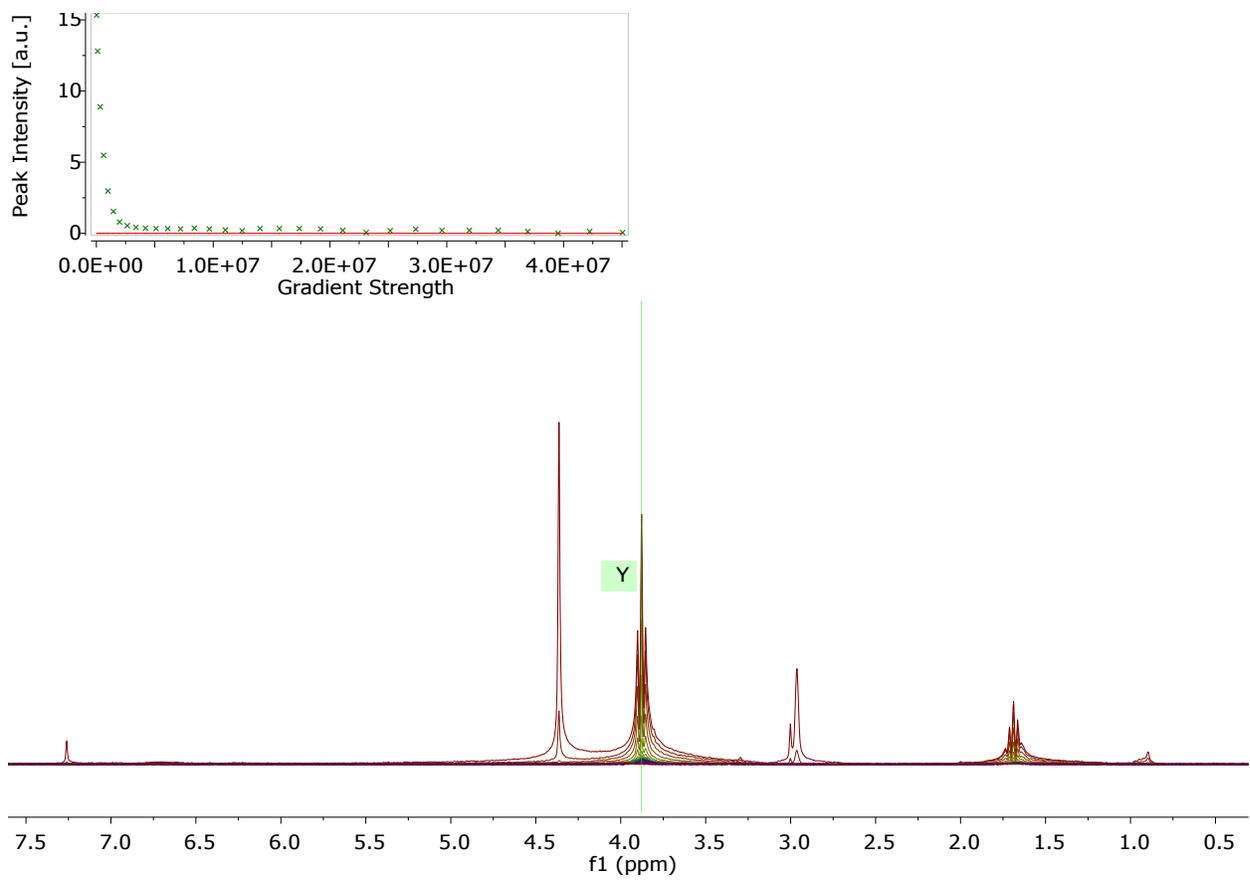
The procedure for data normalization involved first plotting peak intensity data vs. gradient strength for the resonance **a** after a CEDOSY experiment. There are two distinct slopes in the data. The point in which these slopes change, the inflection point, is used to normalize peak intensity values. Therefore all the raw data is divided by the peak intensity at the inflection point, which is defined as one. This is a reasonable method of data treatment as it ensures that the larger diffusing aggregate is the same initial peak intensity value.

### **Control Experiments:**

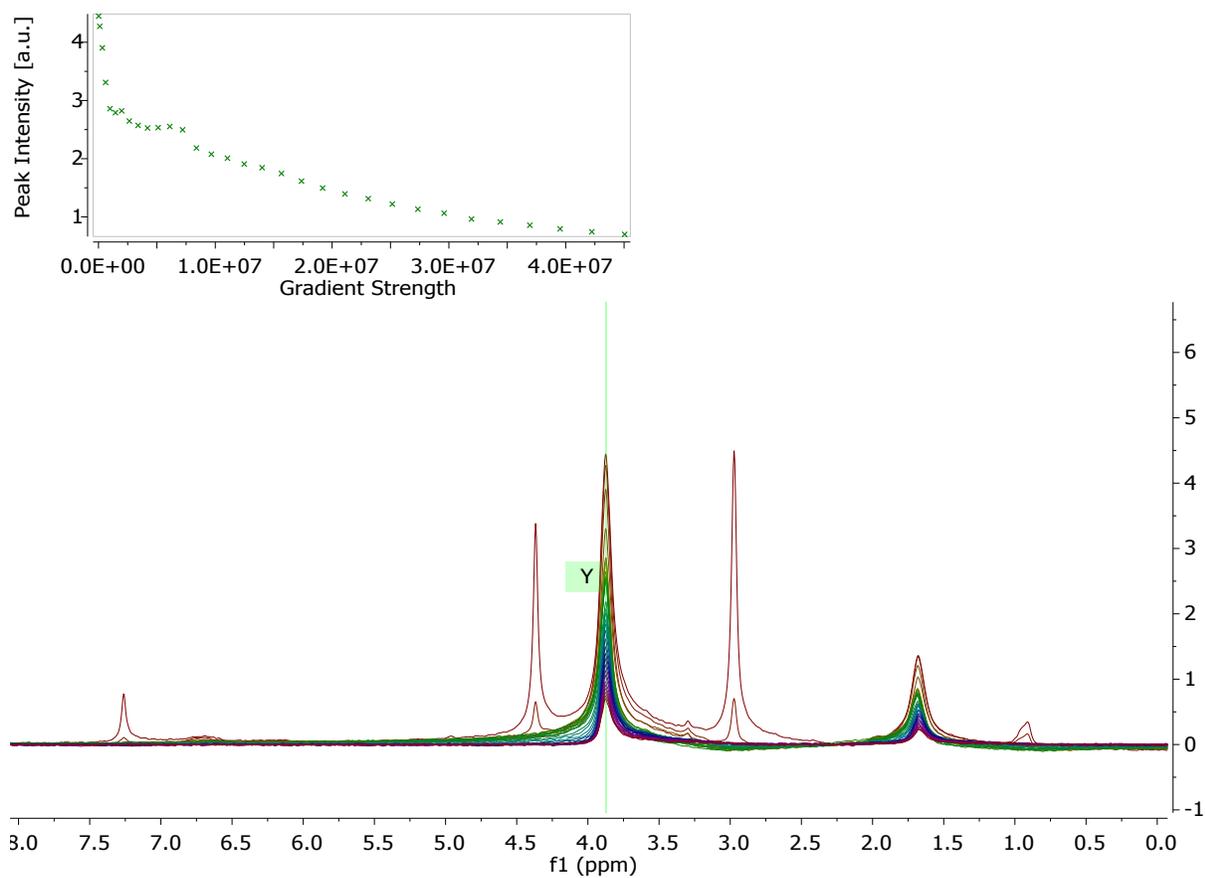
While the results from Figure 5c is consistent with two distinct polymeric species being present in solution (free PTMC and PS-*b*-PTMC aggregates) the observed data may also be the observation of a dynamic process where dissolved polymers (quick diffusing) exchange with or are being incorporated into the slower diffusing aggregate. To distinguish between these two processes CEDOSY was used to analyze: (i) the isolated BCPs (no homopolymer PTMC) (ii) the isolated impurity (homopolymer PTMC only) and (iii) PS-*b*-PTMC after subsequent fractionation steps. Gratifyingly, data from a sample containing pure PS-*b*-PTMC and a sample containing the isolated homopolymer PTMC both exhibit a single exponential decay, multiple slopes were not observed in either sample. Furthermore, examining PS-*b*-PTMC samples after subsequent fractionations reveal a decreasing signal intensity from the first CEDOSY increment and a smaller number of data points that are part of the quickly decaying regime. These results strongly support the explanation that two distinct polymeric species are present in solution: a quickly diffusing PTMC unimer and slowly diffusing PS-*b*-PTMC aggregate.



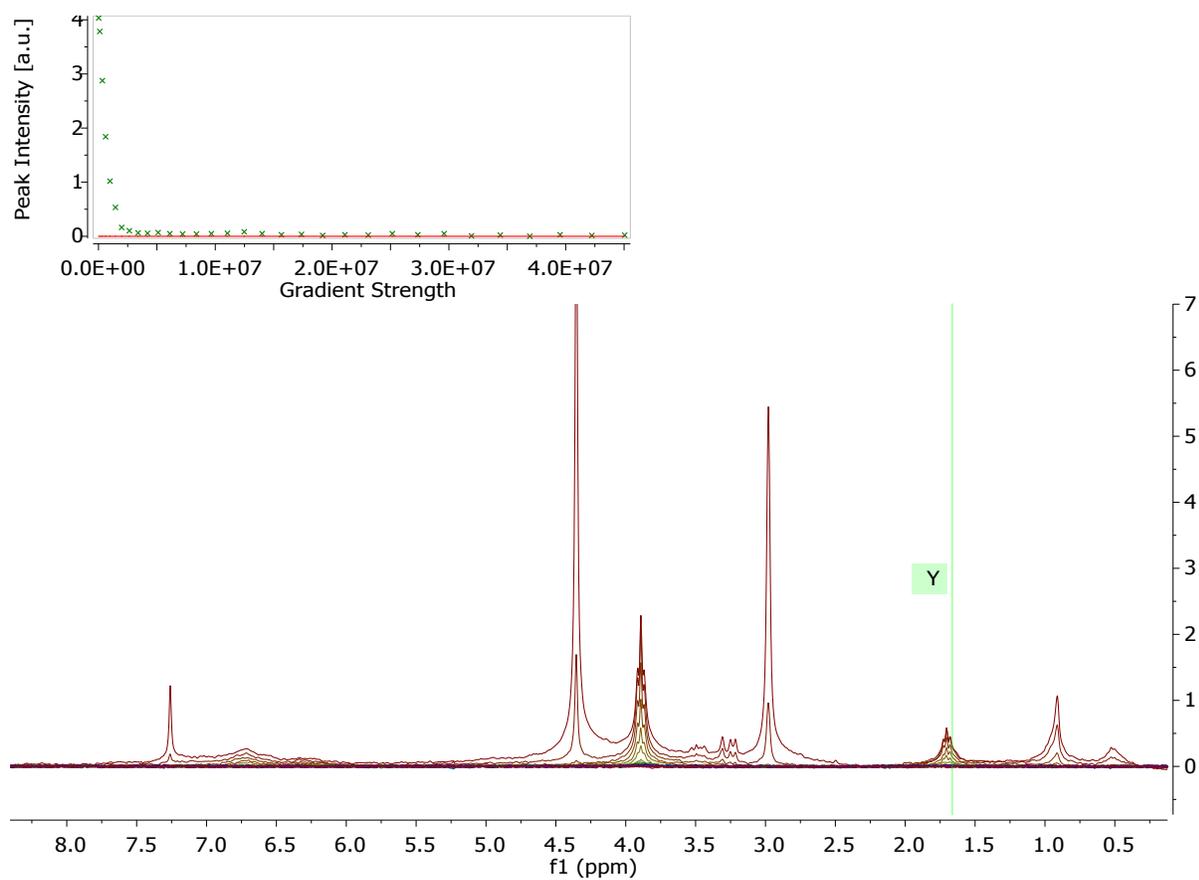
**Figure S4.** Full CEDOSY spectra for DBU catalyzed PS-*b*-PTMC precipitated twice in MeOH (Table 1, Example 1).



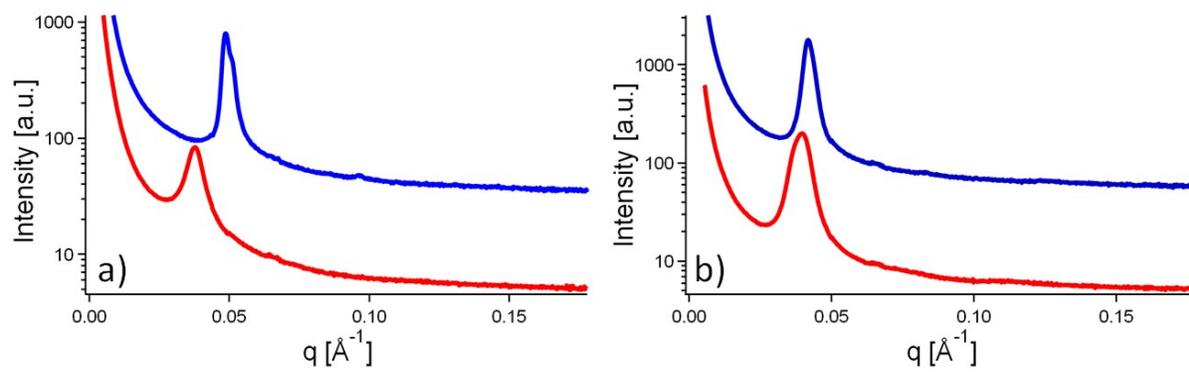
**Figure S5.** Full CEDOSY Spectrum of DBU catalyzed PS-*b*-PTMC after two precipitations in 60:40 (v/v) MeOH:MeCN (Table 1, Example 1)



**Figure S6.** Full CEDOSY Spectrum of PS-*b*-PTMC BCP obtained after 50 % conversion of TMC monomer using DPP catalyst. BCP was precipitated twice MeOH (Table 1, Example 4).



**Figure S7.** Full CEDOSY Spectrum of isolated PTMC impurity from 50% conversion DPP initiated PS-*b*-PTMC.



**Figure S8.** In-plane GISAXS profiles of (a) DBU and (b) DPP catalyzed PS-*b*-PTMC after 50% conversion before (red) and after (blue) purification.