Supporting Information for

Exploring the influence of poly(4-vinyl pyridine) segment on solution properties and thermal phase behaviors of oligo(ethylene glycol) methacrylate-based block copolymers: the different aggregation processes with various morphologies

*Yalan Dai and Peiyi Wu**

The State Key Laboratory of Molecular Engineering of Polymers, Collaborative Innovation Center of Polymers and Polymer Composite Materials,Department of Macromolecular Science, and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, China.

Materials. 2-(2-Methoxyethoxy)ethyl methacrylate(MEO$_2$MA) (Mn=188g/mol, 95%), oligo(ethylene glycol) methacrylate(OEGMA) (Mn=475g/mol) and 4-vinylpyridine (4VP) were purchased from Sigma-Aldrich and purified by passing them through a column filled with neutral alumina prior to use. 2,2-Azobis(isobutyronitrile) (AIBN, Aladdin reagent Co.) was purified by recrystallization from methanol. 4-Cyano-4-(thiobenzoylthio) pentanoic acid (CTA) was obtained from Sigma-Aldrich and used as received. N, N-Dimethylformamide (DMF, Aladdin reagent Co.) was dried with CaH$_2$ for 24 h and distilled under vacuum. All other regents were used as received without further purification.

Synthesis of P(MEO$_2$MA-*co*-OEGMA)-*b*-P4VP block copolymers

Typically, the copolymer P(MEO_2MA-*co*-OEGMA) (Molar ratio of the comonomers in the feed was 92/8) was first synthesized as macro-CTA. Polymerization of 4VP from the macro-CTA was as follows: macro-CTA (0.169 g, 0.015 mmol), 4VP (0.079 g, 0.75 mmol), and AIBN (1.3 mg, 0.008 mmol) were added into a reaction tube with 1 mL DMF. The solution was degassed by three freeze–evacuate–thaw cycles and placed in a preheated oil bath maintained at 70^{o}C for 3h. The polymerization reaction was quenched by rapid exposing the flask to liquid nitrogen. After three times precipitation by cold diethyl ether, the product was further vacuum-dried for 24 h.

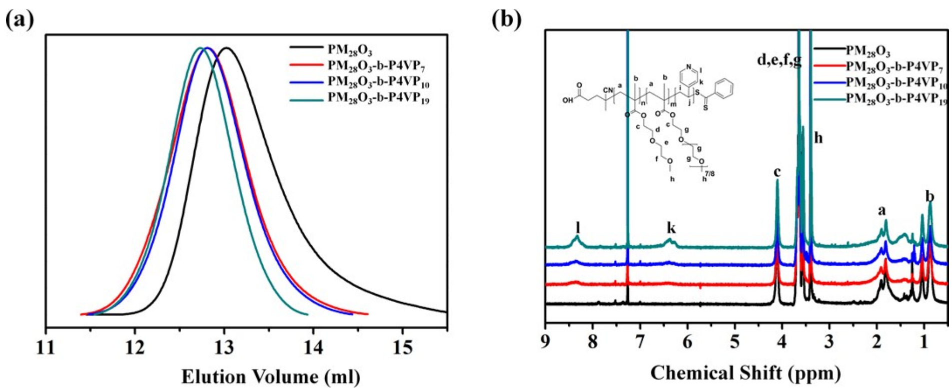

Figure S1. (a) GPC (DMF) results of three different composition copolymers and (b) ^{1}H NMR of P(MEO_2MA-*co*-OEGMA)-*b*-P4VP copolymers in $CDCl_3$.

Perturbation Correlation Moving Window (PCMW).

PCMW is a newly developed technique which was originally proposed by Thomas and Richardson[1] and later improved into much wider applicability through introducing the perturbation variable into correlation equation by Morita et al.[2] Together with its ability to determine transition points as conventional moving window did, PCMW can also monitor the sophisticated spectral changes along the perturbation direction, additionally. PCMW synchronous spectra can provide information about transition points of different chemical groups, and asynchronous spectra offer details about the transition temperature region.

PCMW synchronous and asynchronous spectra

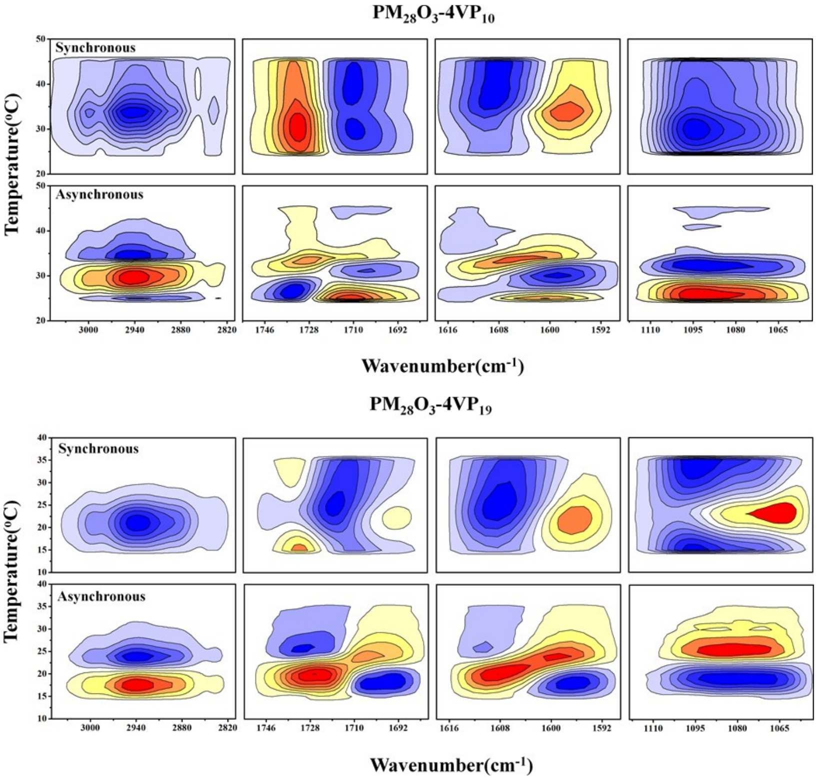

Figure S2. PCMW synchronous and asynchronous spectra of P(MEO_2MA-*co*-OEGMA)-*b*-$P4VP_{10}$ and P(MEO_2MA-*co*-OEGMA)-*b*-$P4VP_{19}$ upon heating. Warm colors (red) denote positive intensities, while cool colors (blue) denote negative intensities.

Two-Dimensional Correlation Analysis (2Dcos).

As a widely employed mathematical method, 2Dcos has been considerably used to investigate spectroscopic intensity fluctuations of different chemical groups under external perturbations (e.g., temperature, pressure, time, concentration, electromagnetic), originally proposed by Noda in 1986.[3, 4] Based on spreading the original spectra along a second dimension, many complex or overlapped IR bands not readily visible in the conventional 1D spectrum can be extracted and spectral resolution enhancement can be attained, hence. Moreover, useful information about molecular motions or conformational changes can be deduced from specific sequence order of different chemical groups under a certain physical or chemical variation through 2Dcos analysis.

Noda's rule: when the cross-peaks of $v1$ and $v2$ ($v1 > v2$) in synchronous and asynchronous spectra have the same symbol (both positive or negative), then the change at peak $v1$ has an earlier response than that at peak $v2$, and vice versa.[5]

Table S1. Final results of multiplication on the signs of each cross-peak in the synchronous and asynchronous spectra of P(MEO_2MA-*co*-OEGMA)-*b*-$P4VP_{10}$ from 20 to 50 ^oC.

1079	-	-	-	-	-	-	-	-	-	+	-	-	-	+	
1099	-	-	-	-	-	-	-	-	-	+	-	-	-		
1598	-	-	-	-	-	-	-	-	-	+	+	-			
1608	+	+	+	+	+	+	+	+	-	+	+				
1710	-	-	-	-	-	-	-	-	-	+					
1727	-	-	-	-	-	-	-	-	-						
2825	+	+	+	+	+	+	+	+							
2838	-	-	-	-	-	-	-								
2879	+	+	+	+	+	+									
2894	+	+	+	+	+										
2927	+	-	+	-											
2939	+	-	+												
2952	+	-													
2987	+														
3002															
	3002	**2987**	**2952**	**2939**	**2927**	**2894**	**2879**	**2838**	**2825**	**1727**	**1710**	**1608**	**1598**	**1099**	**1079**

Table S2. Final results of multiplication on the signs of each cross-peak in the synchronous and asynchronous spectra of P(MEO_2MA-*co*-OEGMA)-*b*-$P4VP_{19}$ from 10 to 40 ^{o}C.

1079	+	+	+	+	+	+	+	+	+	+	-	+	+	+	
1099	+	+	+	+	+	+	+	+	+	-	-	+	+		
1598	+	+	+	-	-	-	-	-	-	-	-	-			
1606	+	+	+	+	+	+	+	+	+	-	-				
1704	+	+	+	+	+	+	+	+	+	+					
1716	+	+	+	+	+	+	+	+	+						
1729	+	+	+	+	+	+	+	+							
2827	+	+	+	+	+	+	+								
2836	+	+	+	+	+	-									
2877	+	+	+	+	+										
2890	+	+	+	+											
2923	+	+	+												
2954	-	-													
2994	+														
3000															
	3000	**2994**	**2954**	**2923**	**2890**	**2877**	**2836**	**2827**	**1729**	**1716**	**1704**	**1606**	**1598**	**1099**	**1079**

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