## Supporting Information

## Self-Assembly and -Cross-Linking Lamellar Films by Nanophase Separation with Solvent-Induced Anisotropic Structural Changes

Kohei Amada<sup>†</sup>, Manabu Ishizaki<sup>‡</sup>, Masato Kurihara<sup>‡</sup> and Jun Matsui<sup>‡\*</sup>

<sup>†</sup>Graduate School of Science and Engineering, <sup>‡</sup>Faculty of Science Yamagata University, 1-4-12 Kojirakawa -machi, Yamagata 990-8560, Japan

**Table S1.** Synthesis condition of copolymer and composition, molecular weight, polydispersity

 and thermal property

run	copolymer	molar ratio DDA/TMSPA in feed	molar ratio DDA/TMSPA in product	$M_n$ / 10 <sup>4</sup>	$M_w/M_n$	<i>T<sub>g</sub></i> / °C	$T_M / °C$	<i>T<sub>5d</sub></i> / °C
1 p(	DDA/TMSPA13) <sup>a)</sup>	74:26	87:13	2.52	2.06	39.6	-37.8	328

a) Polymerized at 60 °C for 12 h.

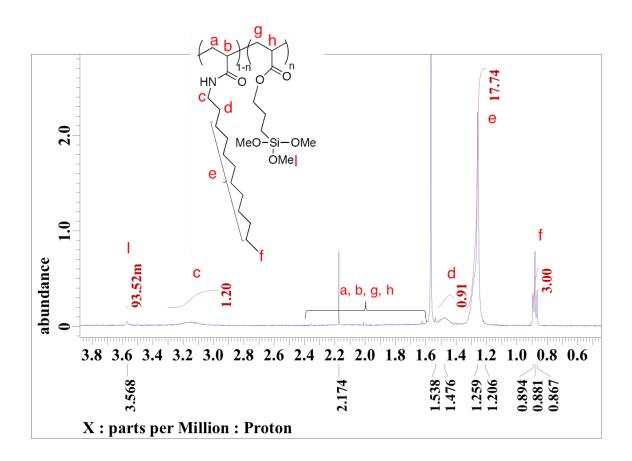
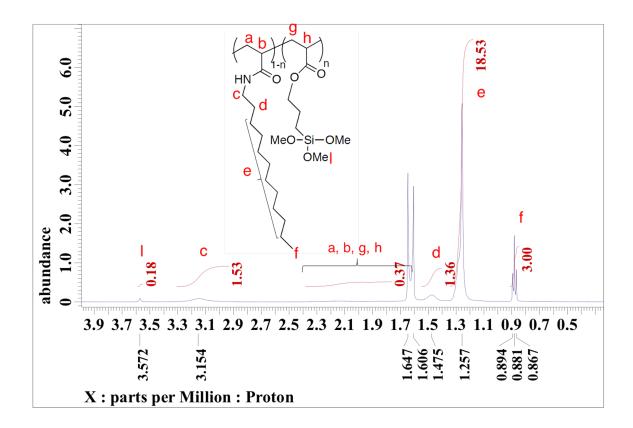
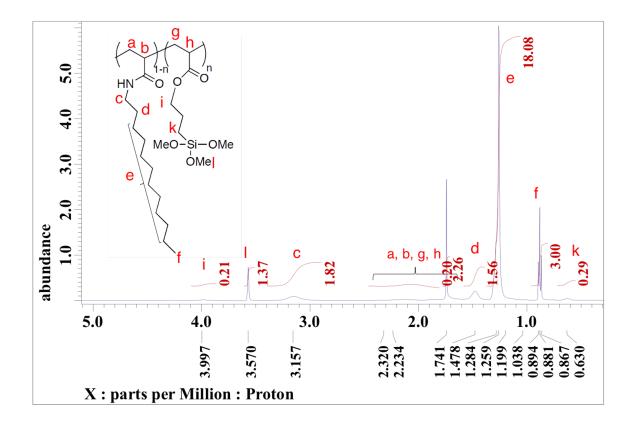


Figure S1. <sup>1</sup>H NMR spectrum of p(DDA/TMSPA1).



**Figure S2.** <sup>1</sup>H NMR spectrum of p(DDA/TMSPA2).



**Figure S3.** <sup>1</sup>H NMR spectrum of p(DDA/TMSPA13).

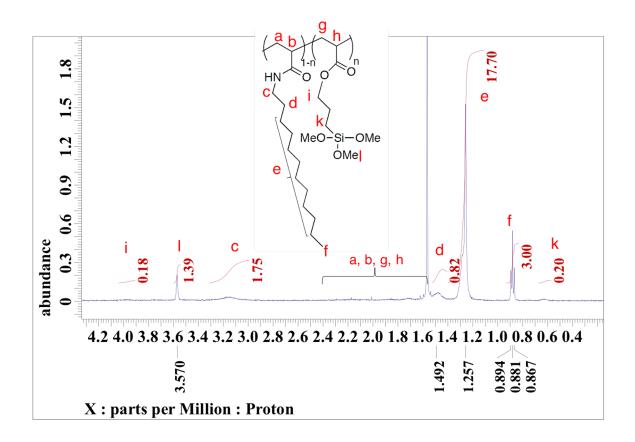
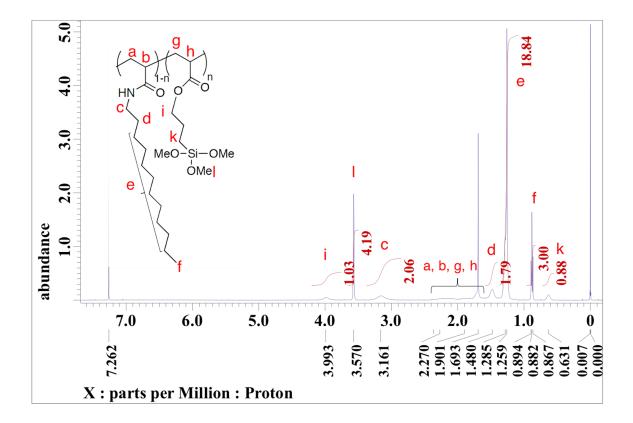
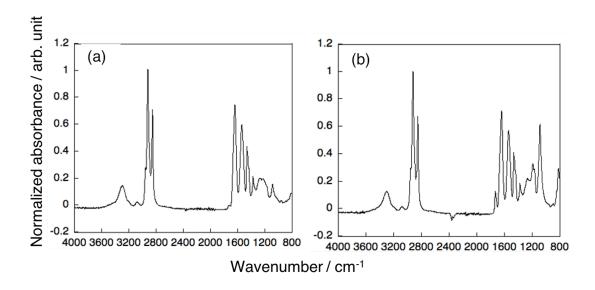


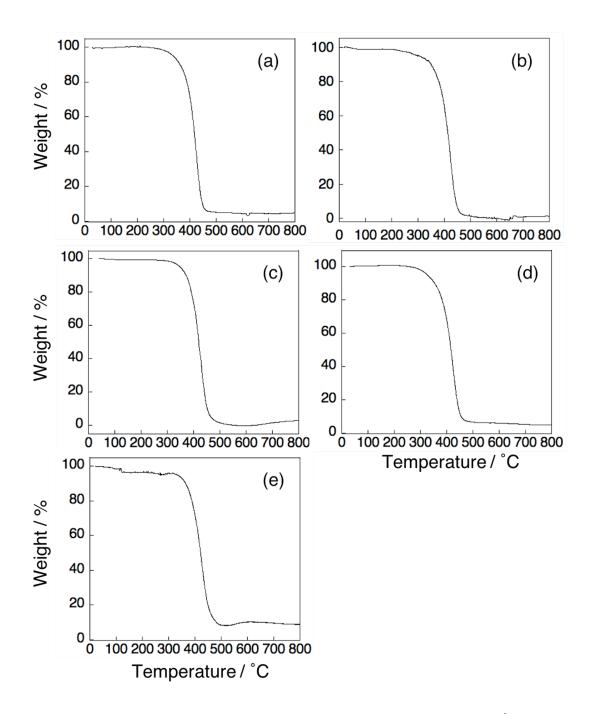
Figure S4. <sup>1</sup>H NMR spectrum of p(DDA/TMSPA13) synthesized by run 1 of Table S1.



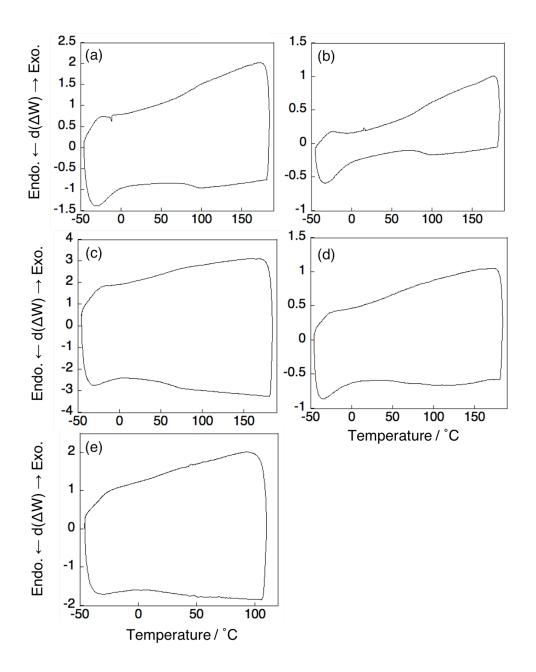
**Figure S5.** <sup>1</sup>H NMR spectrum of p(DDA/TMSPA32).



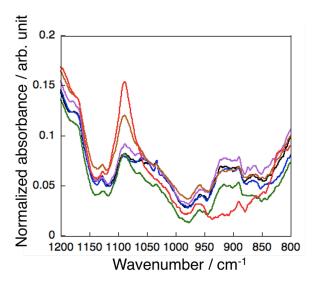
**Figure S6.** FT-IR spectra of (a) p(DDA/TMSPA2) and (b) p(DDA/TMSPA13). The spectra were normalized using the asymmetric stretching vibration of CH<sub>2</sub>.



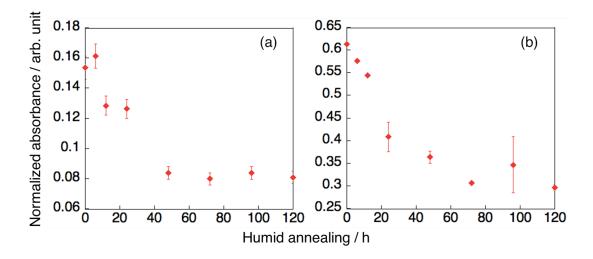
**Figure S7.** TGA curves of p(DDA/TMSPA) at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. (a) p(DDA/TMSPA1), (b) p(DDA/TMSPA2), (c) p(DDA/TMSPA13), (d) p(DDA/TMSPA13) which was run 1 of Table S1 and (e) p(DDA/TMSPA32).



**Figure S8.** DSC curves of p(DDA/TMSPA) for the third heating and cooling process at a rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. (a) p(DDA/TMSPA1), (b) p(DDA/TMSPA2), (c) p(DDA/TMSPA13), (d) p(DDA/TMSPA13) which was run 1 of Table S1 and (e) p(DDA/TMSPA32).



**Figure S9.** Normalized FT-IR spectra of p(DDA/TMSPA2) powder. Before humid annealing (red), humid annealed for 24 h (brown), 48 h (green), 72 h (purple), 96 h (blue) and 120 h (black). The spectra were normalized using the asymmetric stretching vibration of CH<sub>2</sub>.



**Figure S10.** Plots for normalized absorbance of Si-OMe as humid annealing time. (a) p(DDA/TMSPA2) and (b) p(DDA/TMSPA13) powders. The absorbance was normalized using the asymmetric stretching vibration of CH<sub>2</sub>.

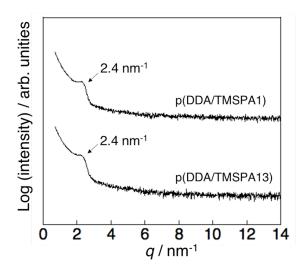
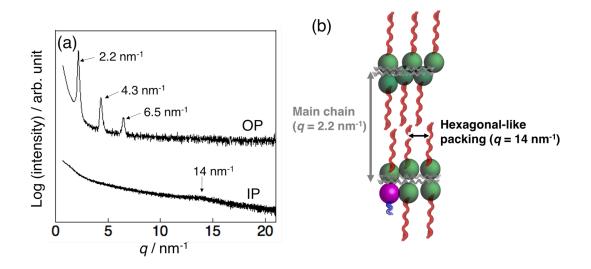
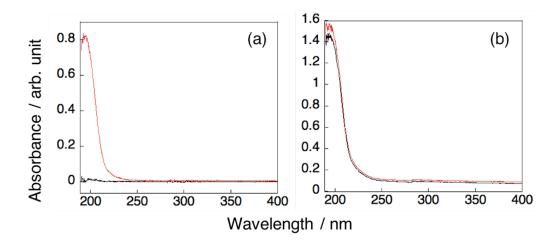


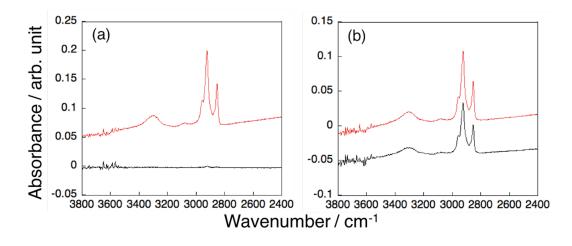
Figure S11. XRD patterns of p(DDA/TMSPA1) (top) and p(DDA/TMSPA13) (bottom) thin films annealed at 60 °C for 24 h.



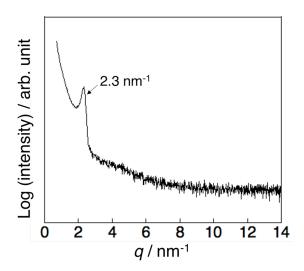
**Figure S12.** (a) XRD patterns of p(DDA/TMSPA13) thin film humid annealed at 60 °C for 96 h. In the figure, the top and bottom pattern are the pattern measured in the out-of-plane and inplane direction, respectively. (b) Schematic image of the lamellar structure of thin films of p(DDA/TMSPA). The diffraction of short axis side of dodecyl side chains assign as hexagonallike packing.



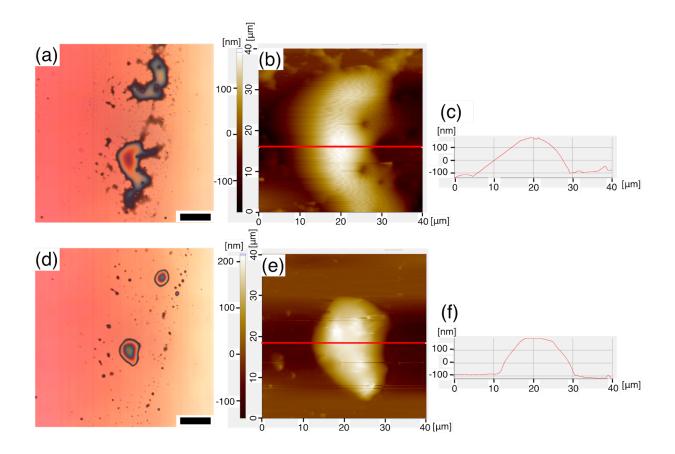
**Figure S13.** UV-vis spectra of humid-annealed p(DDA/TMSPA) thin films before (red) and after (black) dipping into toluene. (a) p(DDA/TMSPA2) and (b) p(DDA/TMSPA13) thin films.



**Figure S14.** FT-IR spectra of humid annealed p(DDA/TMSPA) thin films before (red) and after (black) dipping into toluene. (a) p(DDA/TMSPA2) and (b) p(DDA/TMSPA13) thin films.



**Figure S15.** XRD pattern for toluene dipped p(DDA/TMSPA13) thin films followed by annealed at 60 °C for 24 h.



**Figure S16.** LM images and AFM topological images of p(DDA/TMSPA13) films before (a,b) and after (d,e) humid annealing; (c,f) represent the line profiles for (b,e), respectively. (Scale bar: 25 μm).