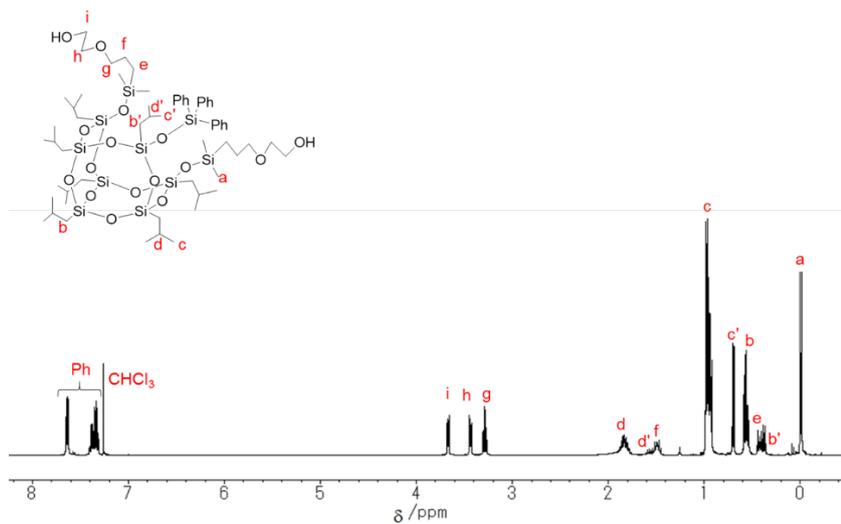


**Supporting information for**

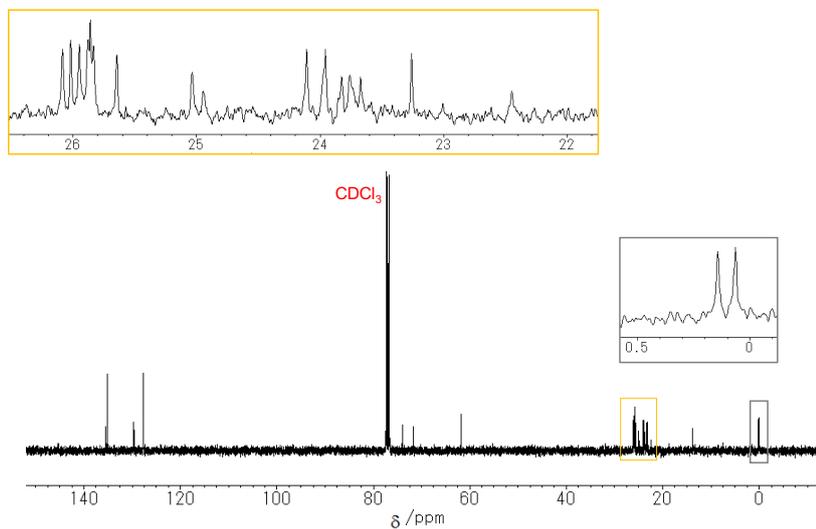
**Hybrid polyurethanes composed of isobutyl-  
substituted open-cage silsesquioxane in the main  
chains: Synthesis, properties, and surface segregation  
in a polymer matrix**

*Yukiho Ueda, Hiroaki Imoto, Arifumi Okada, Huaizhong Xu, Hideki Yamane, Kensuke Naka*

(a)



(b)



(c)

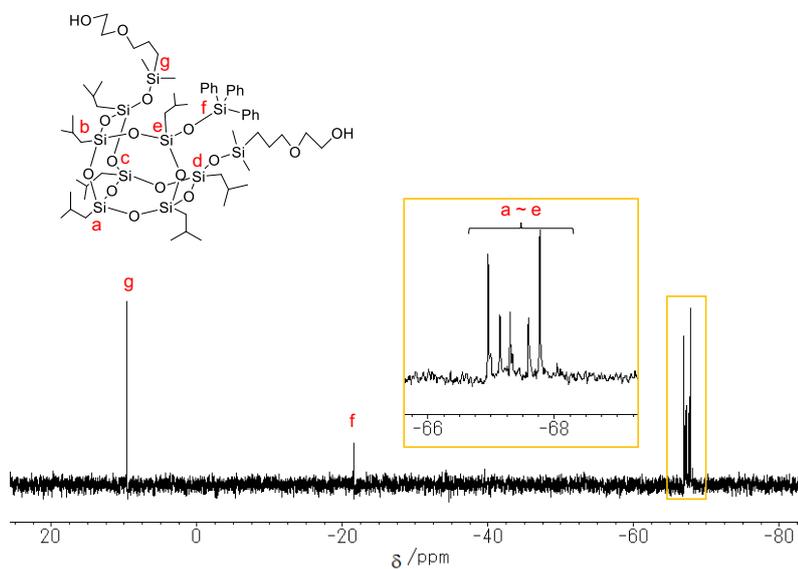
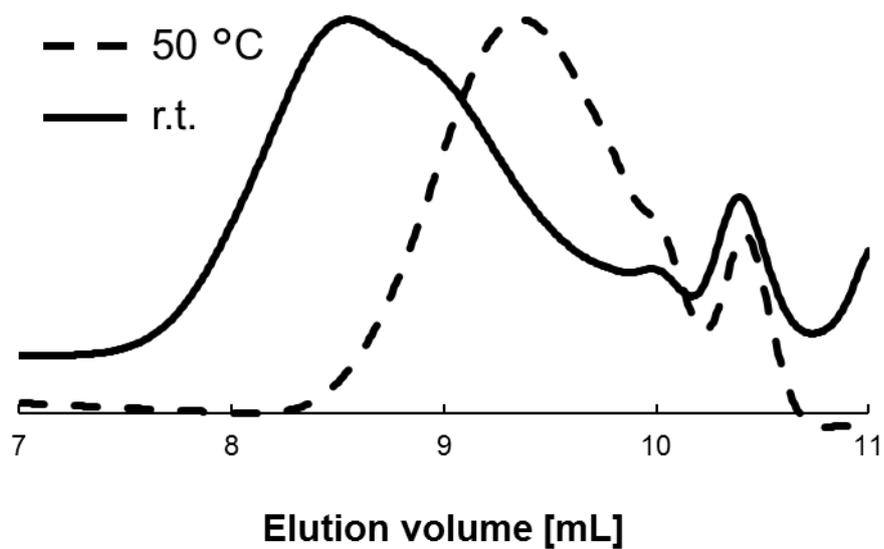
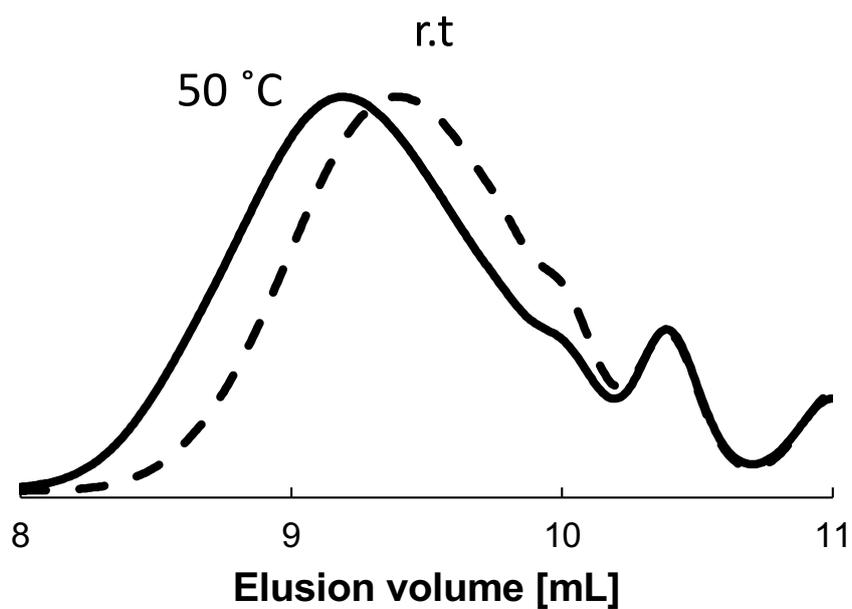


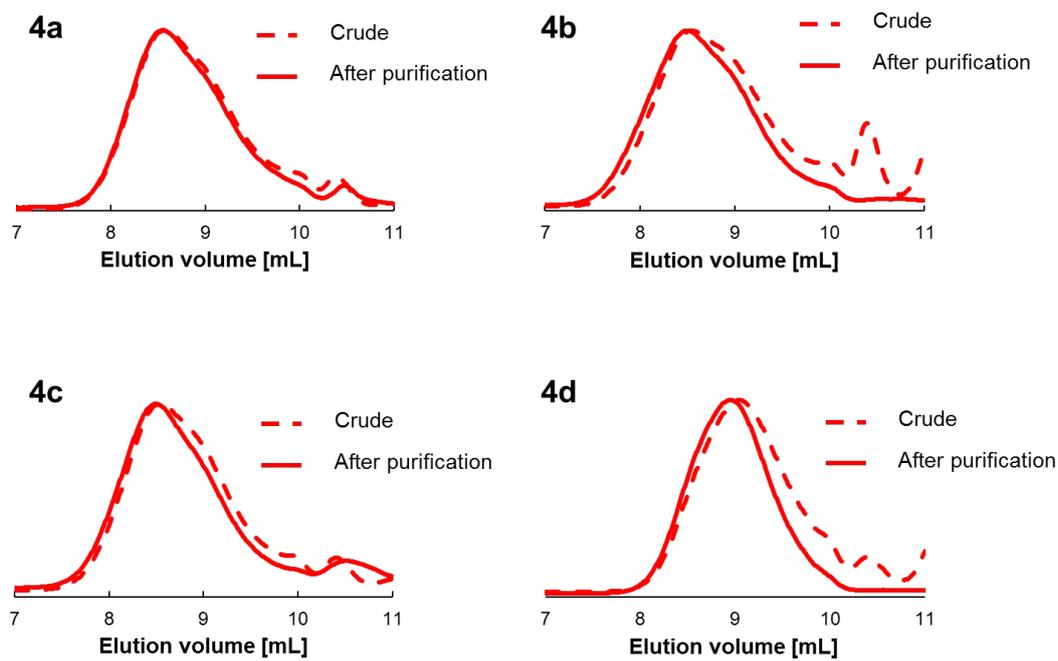
Figure S1 (a) <sup>1</sup>H-, (b) <sup>13</sup>C-, and (c) <sup>29</sup>Si-NMR spectra of **2** in CDCl<sub>3</sub>.



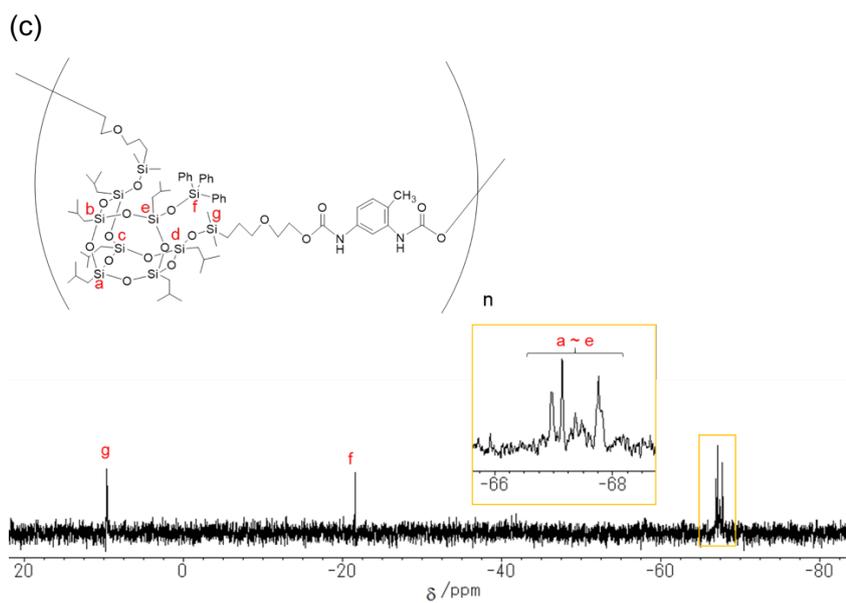
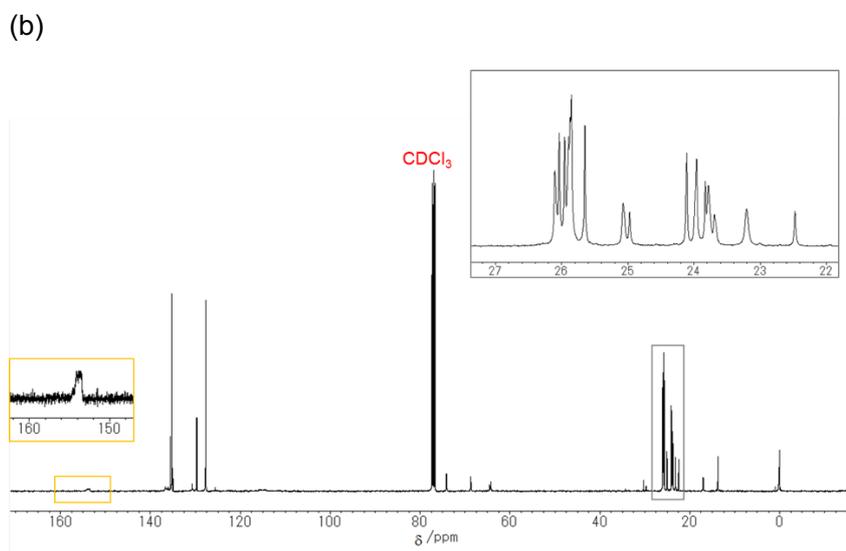
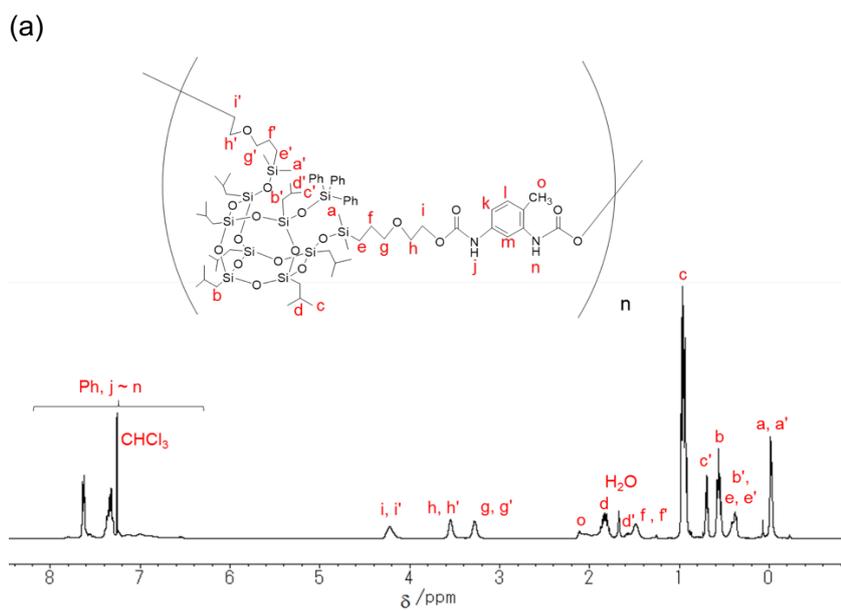
**Figure S2** SEC traces of crude **4b** polymerized at 50 °C and r.t.



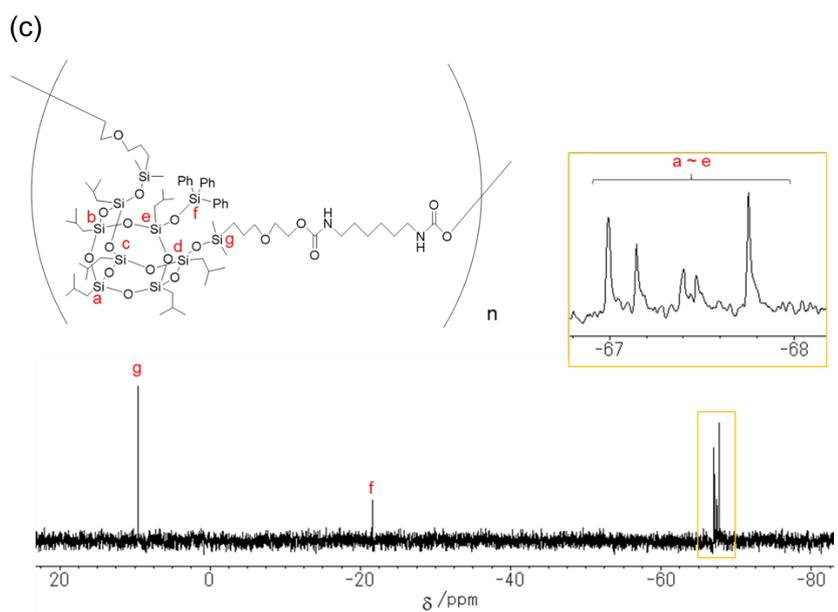
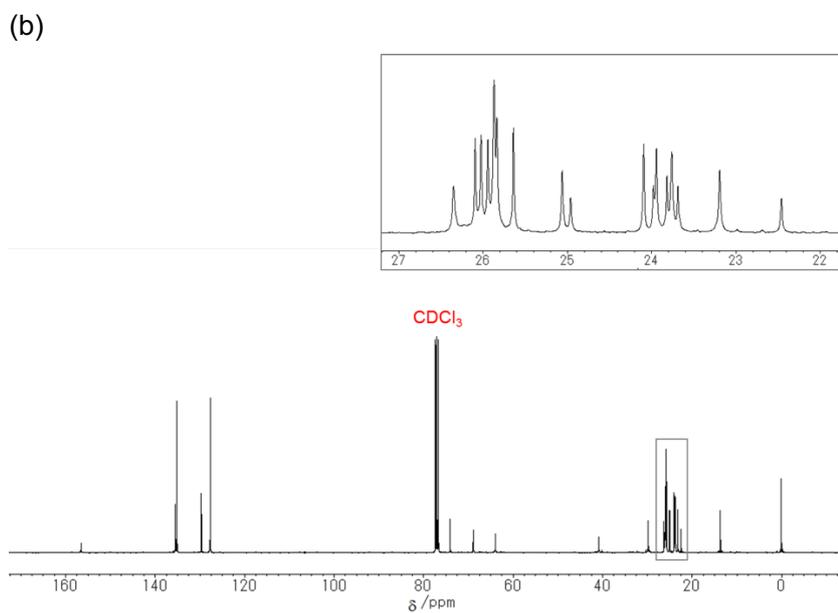
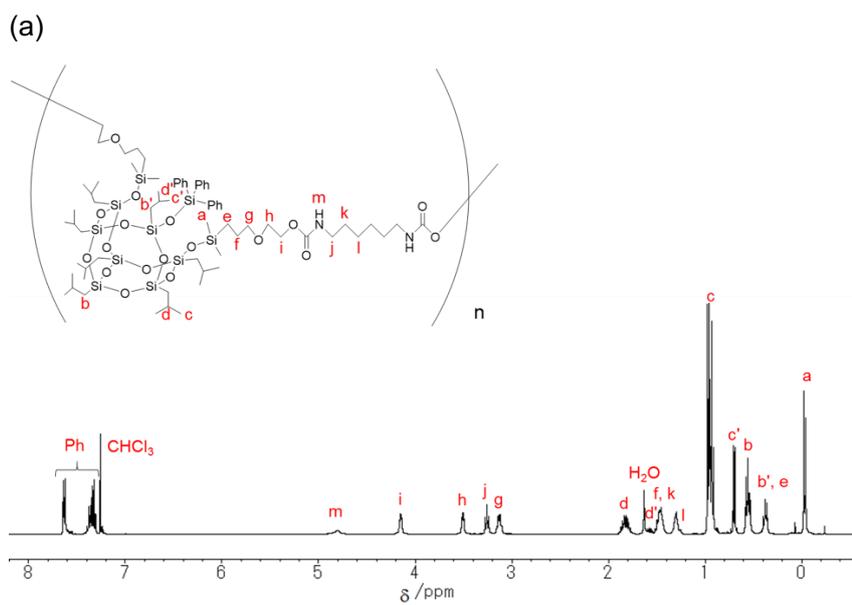
**Figure S3** SEC traces of crude **4a** polymerized at 50 °C and r.t.



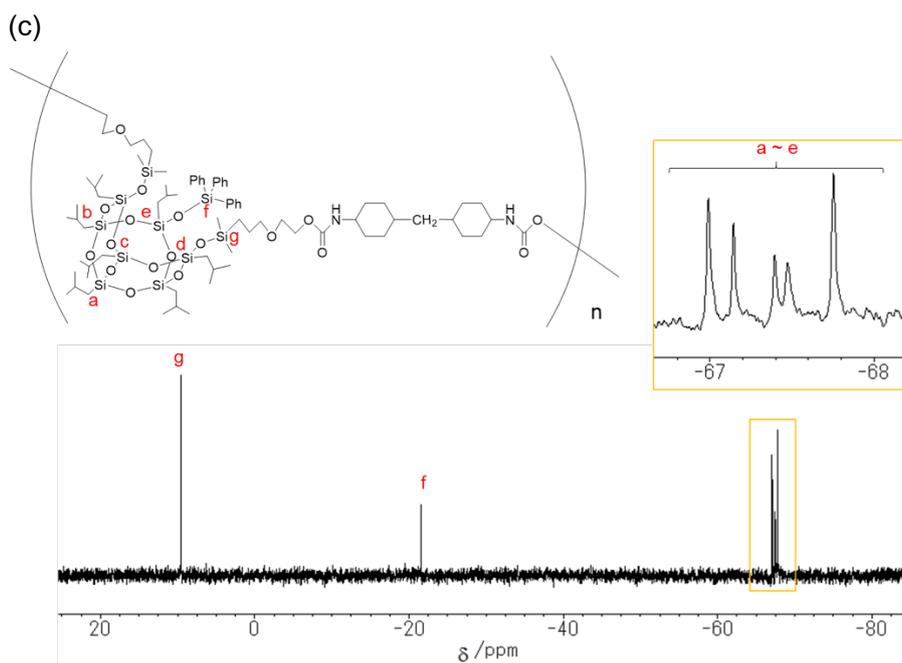
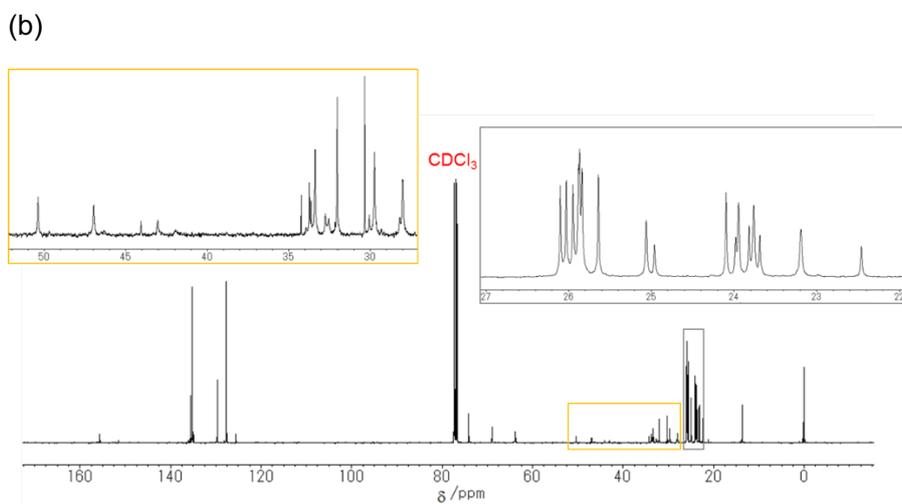
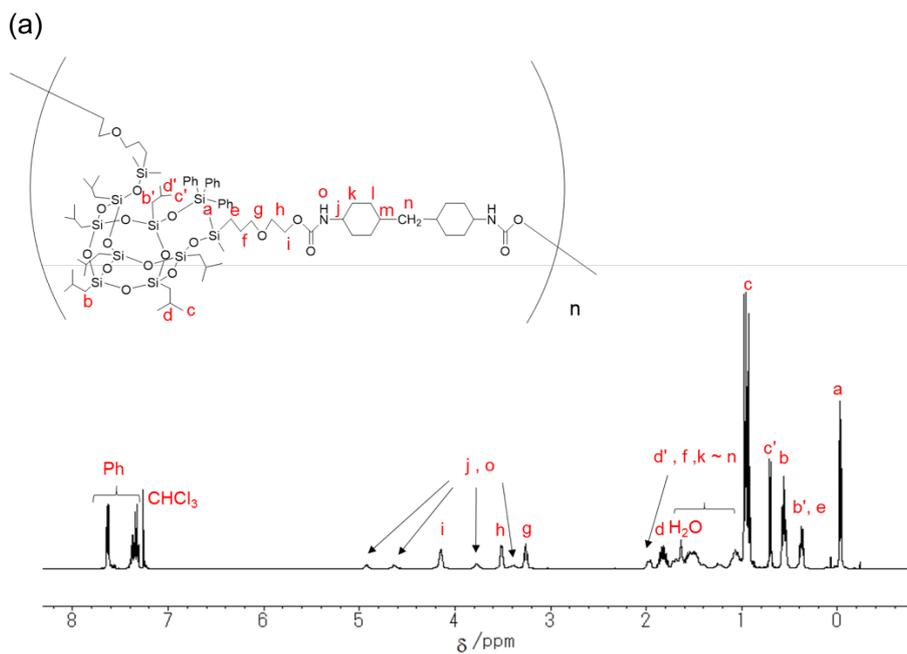
**Figure S4** SEC traces of **4a**, **4b**, **4c**, and **4d** before and after the purification.



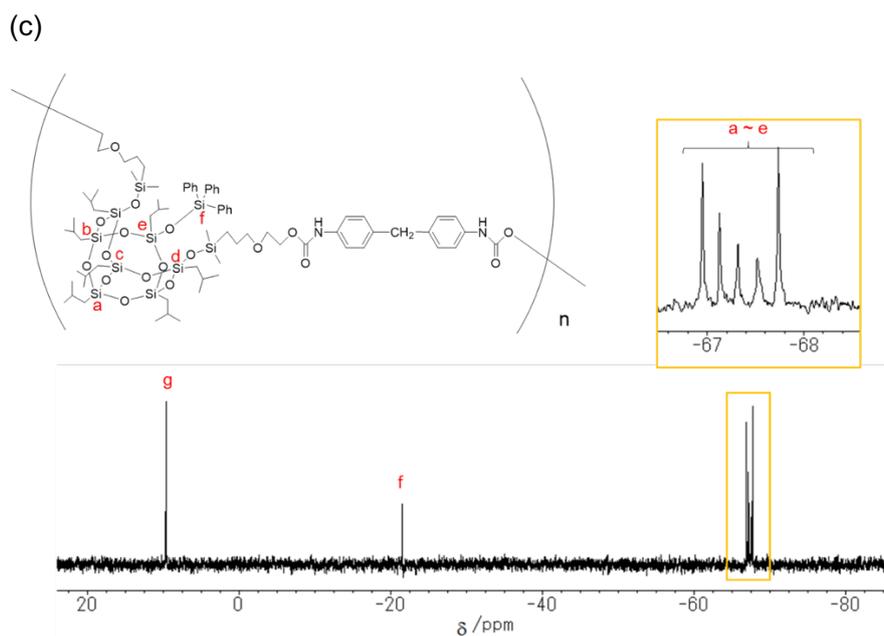
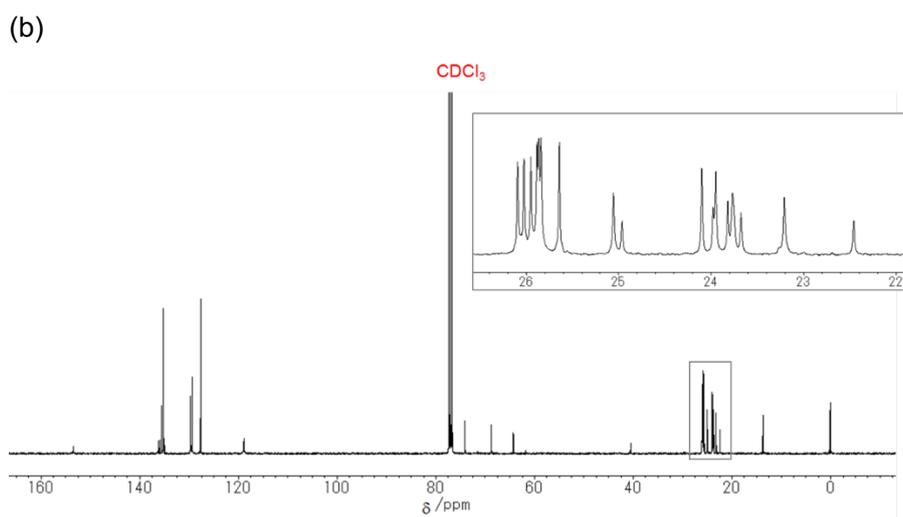
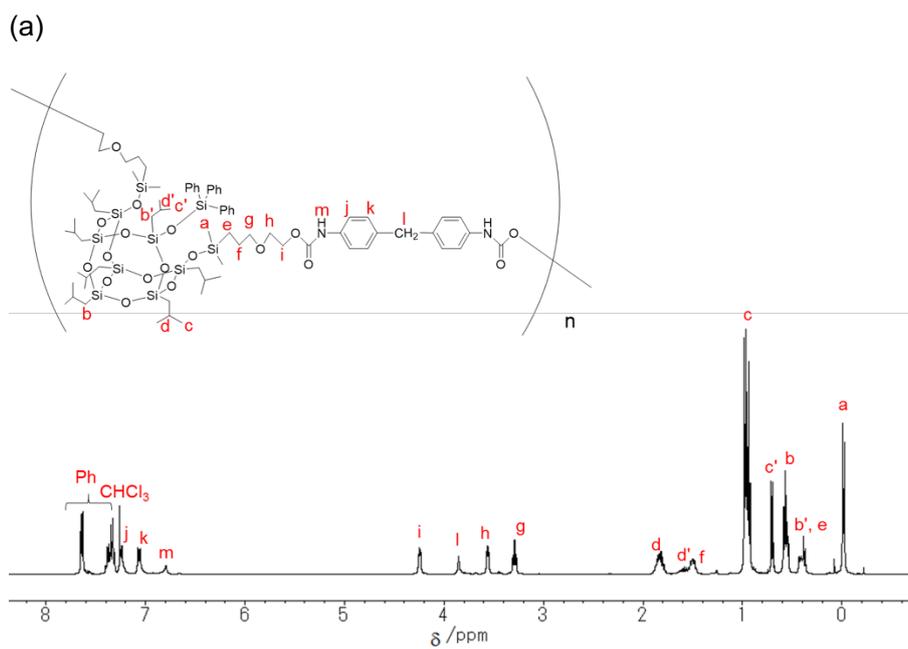
**Figure S5** (a)  $^1\text{H}$ -, (b)  $^{13}\text{C}$ -, and (c)  $^{29}\text{Si}$ -NMR spectra of **4a** in  $\text{CDCl}_3$ .



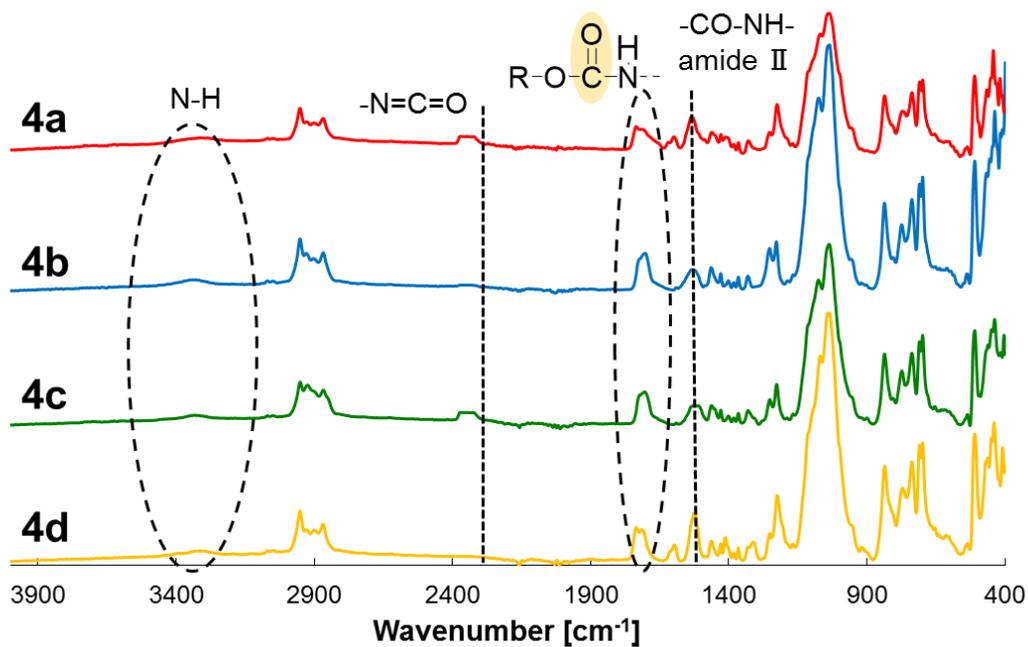
**Figure S6** (a)  $^1\text{H}$ -, (b)  $^{13}\text{C}$ -, and (c)  $^{29}\text{Si}$ -NMR spectra of **4b** in  $\text{CDCl}_3$ .



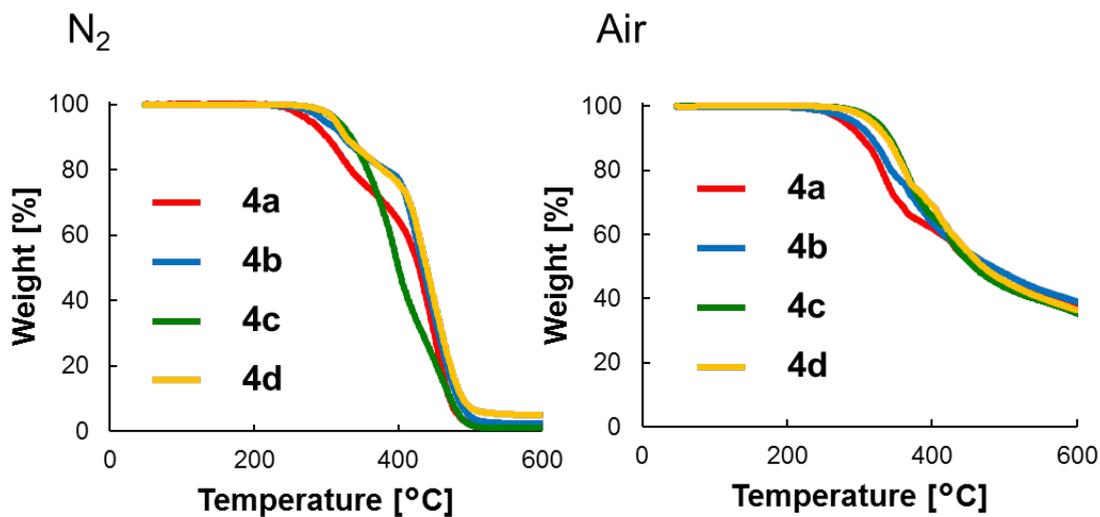
**Figure S7** (a)  $^1\text{H-}$ , (b)  $^{13}\text{C-}$ , and (c)  $^{29}\text{Si-}$ NMR spectra of **4c** in  $\text{CDCl}_3$ .



**Figure S8** (a)  $^1\text{H}$ -, (b)  $^{13}\text{C}$ -, and (c)  $^{29}\text{Si}$ -NMR spectra of **4d** in  $\text{CDCl}_3$ .



**Figure S9** FT-IR spectra of **4a**, **4b**, **4c**, and **4d**.



**Figure S10** TGA thermograms of the polymers under N<sub>2</sub> and air, 10 °C/min. No residue remained under N<sub>2</sub> due to sublimation, but high residual weights corresponding to SiO<sub>2</sub> were remained under air.

Table S1 Static water contact angles of the films of PMMA and PMMA containing **4**.

Polymer	Static water contact angles [°]						
	100 wt%	0.5 wt%	1 wt%	2 wt%	5 wt%	10 wt%	20 wt%
<b>4a</b>	105.0 ± 1.0	101.5 ± 1.0	101.8 ± 1.6	102.9 ± 1.7	102.0 ± 1.3	102.1 ± 1.3	102.8 ± 1.1
<b>4b</b>	121.4 ± 2.4	105.3 ± 1.2	106.2 ± 0.8	106.2 ± 1.8	110.4 ± 1.2	110.9 ± 1.0	113.8 ± 2.1
<b>4c</b>	104.4 ± 1.7	101.3 ± 0.8	101.6 ± 1.2	102.7 ± 1.2	101.6 ± 0.7	101.9 ± 1.6	102.4 ± 1.5
<b>4d</b>	106.1 ± 0.7	102.0 ± 0.3	101.8 ± 1.2	103.2 ± 1.3	102.9 ± 0.5	101.3 ± 1.1	102.5 ± 0.7

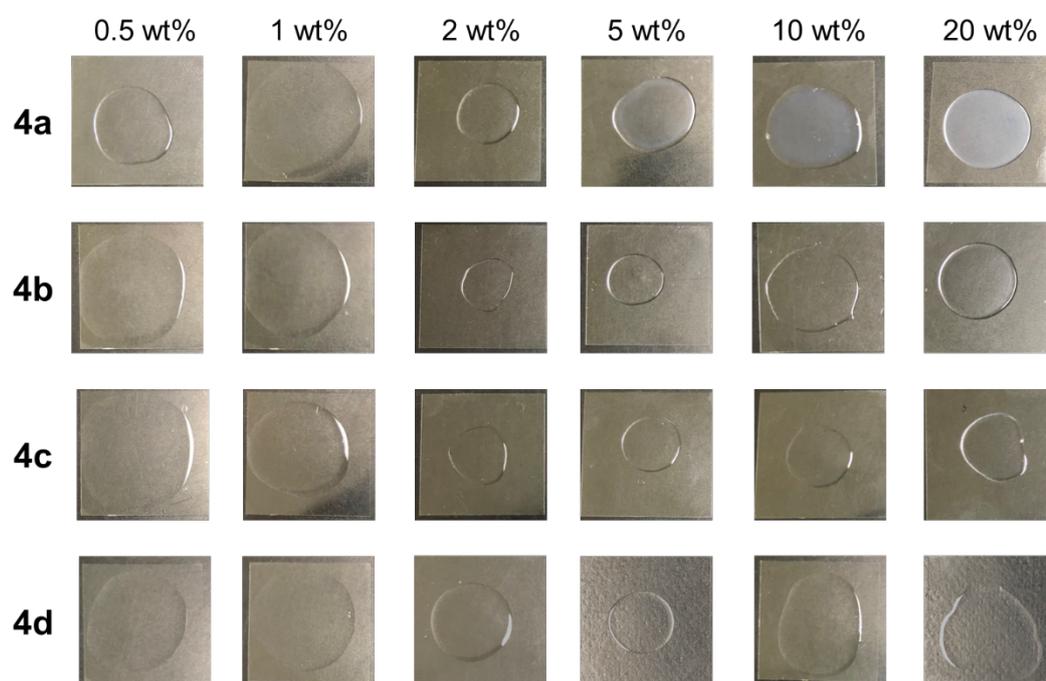
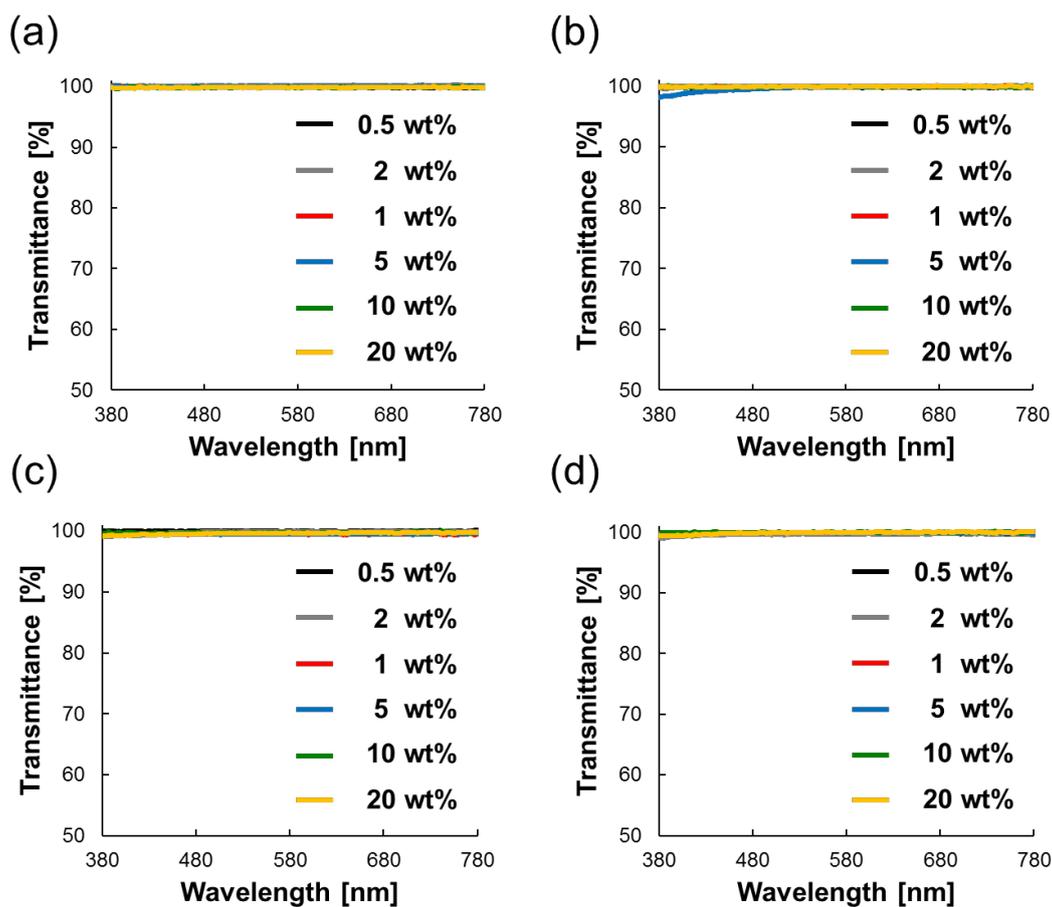
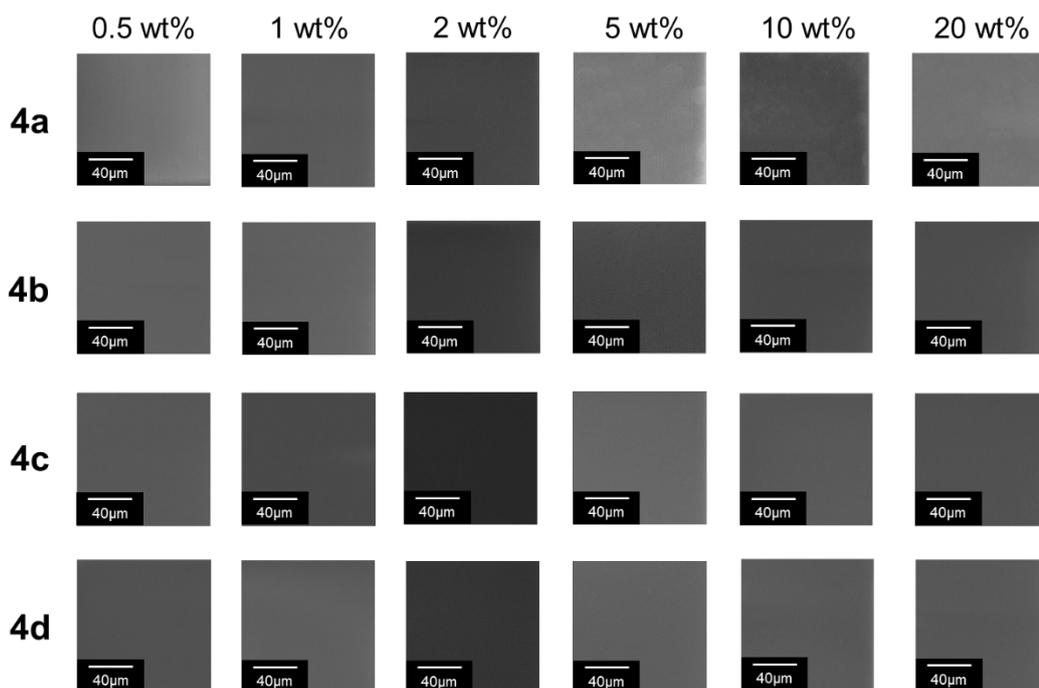


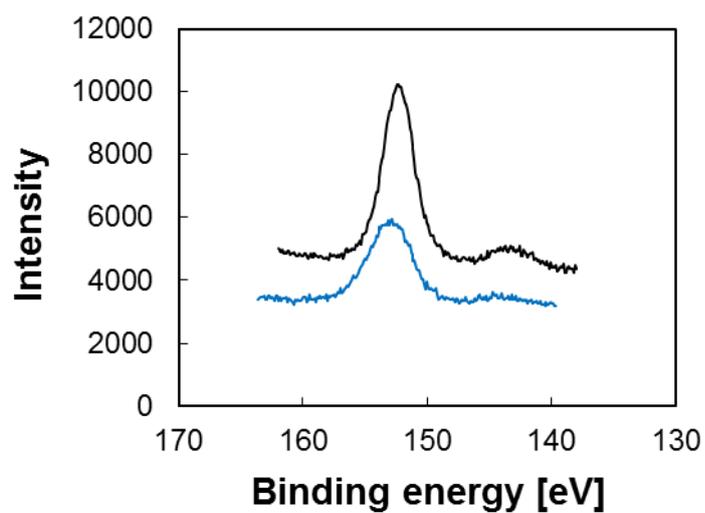
Figure S11 Photographs of PMMA films containing 0.5, 1, 2, 5, 10, and 20 wt% **4**.



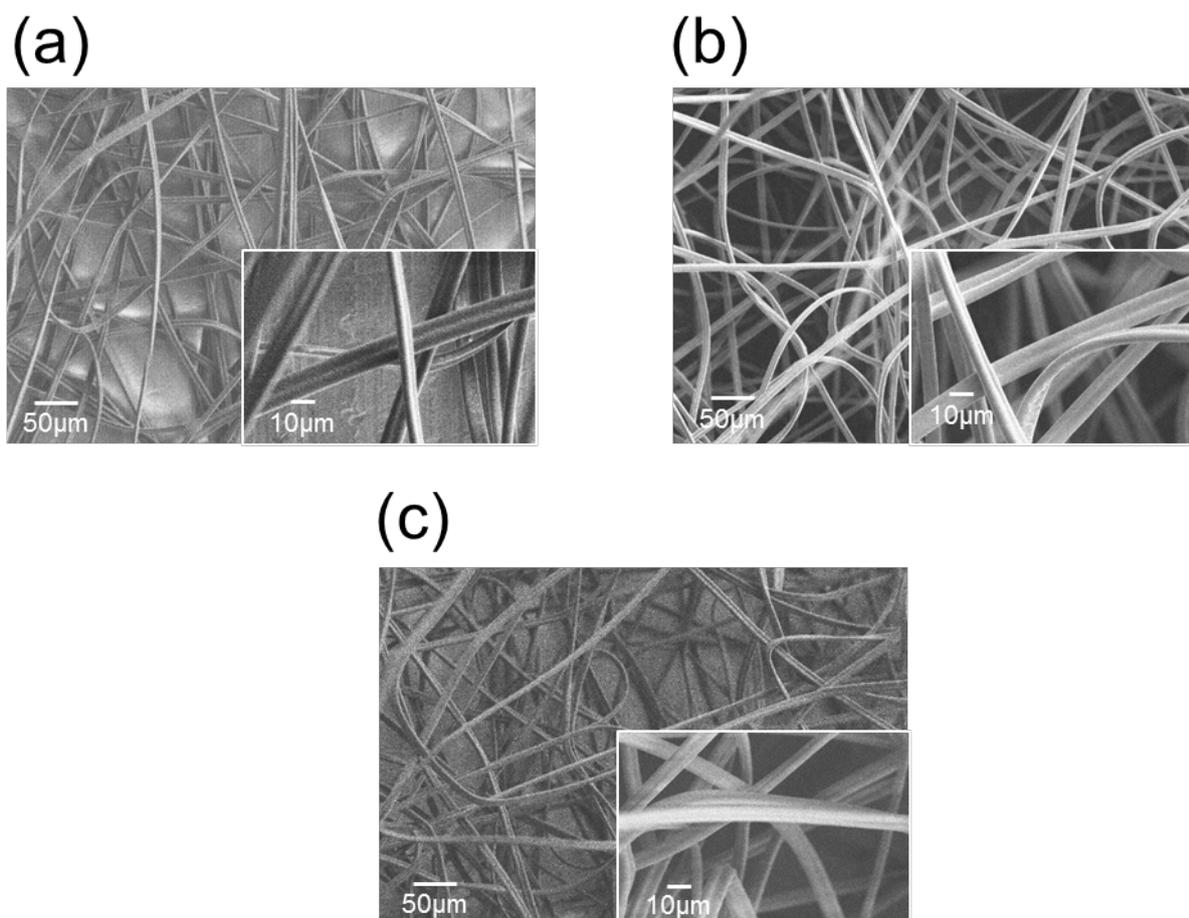
**Figure S12** Transmittance spectra of PMMA films containing 0.5, 1, 5, 10, and 20 wt% of (a) **4a**, (b) **4b**, (c) **4c**, and (d) **4d**.



**Figure S13** SEM images of PMMA films containing 0.5, 1, 2, 5, 10, and 20 wt% **4**.



**Figure S14** Si 2p spectra of the PMMA film containing 5 wt% **4a** before and after the argon ion sputtering.



**Figure S15** SEM images of (a) PMMA nanofiber, (b) PMMA with 2 wt% **4a**, and (c) PMMA with 5 wt% **4a**.