## Supplementary Information

## The Simplest Method for Fabrication of High Refractive Index Polymer-Metal Oxide Hybrid Based on Soap-Free Process

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## 1. Materials and Generals

12-tungstophosphoric acid ( $[H_3PW_{12}O_{40}]$  nH<sub>2</sub>O) and 12-tungstosilicic acid ( $[H_4SiW_{12}O_{40}]$  26H<sub>2</sub>O) were purchased from Wako Chemical. Polymethylmethacrylate (Mw: ~280,000), poly(2-hydroxyethylmethacrylate) (Mw: ~300,000), polyacrylate (Mw: ~25,000), poly(vinyl phenol) (Mw: ~25,000), and polystyrene (Mw: ~280,000) were purchased from Aldrich. Refractive index was measured by using prism coupler (Sairon Technology, Inc., model SPA-4000) equipped with a He-Ne laser (wavelength: 632.8 nm) and GGG prism (*n* = 1.965). Transmission and FT-IR spectra were measured with V-560 (JASCO) and FT/IR-4100. TEM, AFM and EDX images were observed with JEM-1400 plus (JEOL), di-Inova (Bruker), and FE-SEM SU-8000 (Hitachi), respectively. X-Ray diffraction (XRD) patterns were recorded with a RINT-2500HV diffractometer (Rigaku) equipped with a thin film attachment. And radiation was generated from a copper target (Cu-K $\alpha$  1.54060 A) using X ray generator operated at 40 kV and 200 mA. The concentration of heteropoly acids as WO<sub>3</sub> were measured by using TG/DTA-6200 (Hitachi-hitec) when heating from room temperature to 550 °C at 5 °C/min under air at a flow rate of 200 mL/min. The WO<sub>3</sub> concentration was detected by the residual weight. Surface hardness of film on glass substrate was measured by using pencil hardness test (ISO 15184) (COTEC) with 750 g load. Weight fraction (wt%) of SiW12 (or PW12) in composite was obtained by equation (1),

$$wt\% = w_{\rm H}/(w_{\rm H} + w_{\rm P}) \ x \ 100 \tag{1}$$

w<sub>H</sub>: weight of SiW12 (or PW12) and w<sub>P</sub>: weight of polymer.

The theoretical refractive indexes of the heteropolyacid/polymer composites are calculated by the Lorentz-Lorenz equation  $(2)^1$ ,

$$(n^{2} - 1)/(n^{2} + 2) = \varphi_{P} (n_{P}^{2} - 1)/(n_{P}^{2} + 2) + \varphi_{H}(n_{H}^{2} - 1)/(n_{H}^{2} + 2)$$
<sup>(2)</sup>

n: refractive index of the hybrid,  $\varphi_P$ , H: volume fraction of component polymer and heteropoly acid,  $n_P$ , H: refractive index of component polymer and heteropoly acid. For example, the refractive indexes of WO<sub>3</sub>, PMMA and PHEMA were used as 2.2, 1.4881 (measured) and 1.5053 (measured), respectively.

1. J. V. Herráez, R. Belda, J. Solution Chem. 2006, 35, 1315.



**Figure S1.** Transmission spectra of (a) PMMA/PW12 and (b) PHEMA/SiW12 hybrid films. Film thickness = c.a. 3 µm.



**Figure S2.** Transmission spectra of polymer/SiW12 hybrid films. Film thickness = c.a. 3 µm.



**Figure S3.** Refractive indexes of (a) PHEMA/SiW12 and (b) PMMA/PW12 hybrid films versus SiW12 and PW12 concentration. Solid circles: measured refractive index. Dotted line: calculated refractive index as  $H_4SiW_{12}O_{40}$  or  $H_3PW_{12}O_{40}$ . Dashed line: calculated refractive index as  $[H_4SiW_{12}O_{40}]$  6H<sub>2</sub>O or  $[H_3PW_{12}O_{40}]$  6H<sub>2</sub>O.



**Figure S4.** EDX spectra of (a) PHEMA/SiW12 (20 wt%) and (b) PHEMA/SiW12 (80 wt%) films on glass plate.



Figure S5. AFM images of PHEMA/SiW12 (80 wt%) film on glass plate.



Figure S6. FT-IR spectra of (a) PMMA/PW12 and (b, c) PHEMA/SiW12 hybrid films.



Figure S7. XRD spectra of (a) PMMA/PW12 and (b) PHEMA/SiW12 hybrid films.



**Figure S8.** Photo image of PHEMA/SiW12 (55 wt%) hybrid films (a) before and after thermal treatment for 30 min at (b) 200 °C and (c) 250 °C.