

ARTICLE

## A novel soft matter composite material for energy-saving smart windows: from preparation to device application

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### Materials

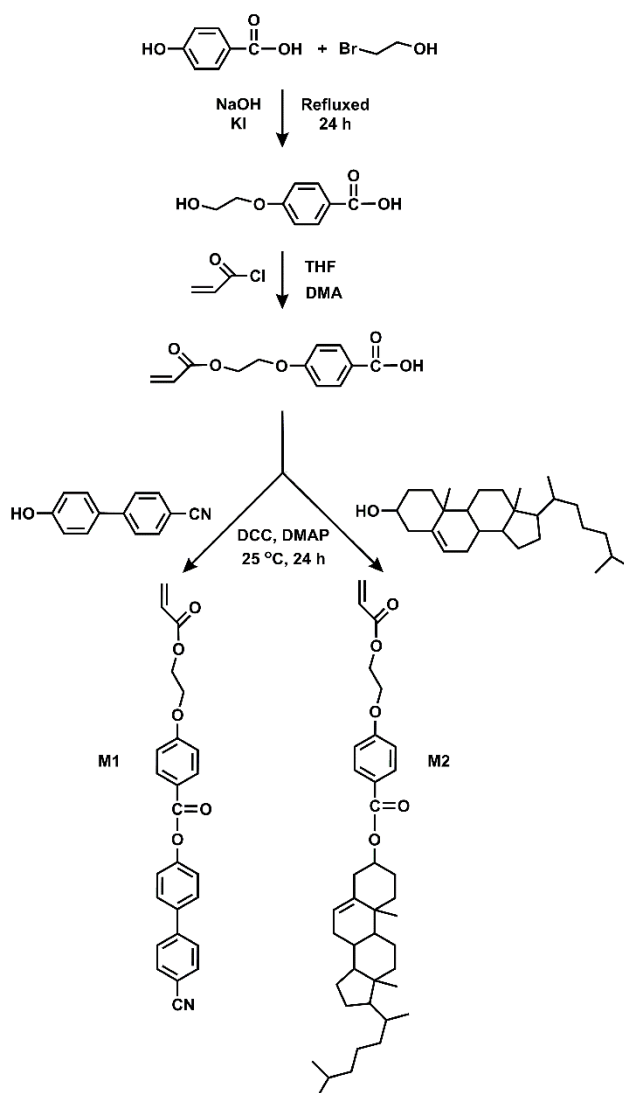
Tetrahydrofuran (THF, Beijing Chemical Works, AR) was refluxed over sodium and distilled. Methylene chloride ( $\text{CH}_2\text{Cl}_2$ , Beijing Chemical Works, AR) was dried with calcium hydride and distilled. Azobisisobutyronitrile (AIBN, Tianjin Jinke Fine Chemical Research Institute, CP) was recrystallized from ethanol and stored at  $-18\text{ }^\circ\text{C}$  before use. 4-hydroxybenzoic acid (Beijing Dominant Technology Co., Ltd., 99%), 2-bromoethanol (Beijing Dominant Technology Co., Ltd., 95%), acryloyl chloride (Beijing Dominant Technology Co., Ltd., 99%),  $N,N'$ -dicyclohexyl carbodiimide (DCC, Energy Chemical, 99%), 4-dimethylaminopyridine (DMAP, Energy Chemical, 99%), cholesterol (Beijing Chemical Co., Ltd., 99%), 4-hydro-4'-cyanobiphenyl (Beijing Dominant Technology Co., Ltd., 99%) and other reagents and solvents were commercially available and used without further purification.

### Characterization and Measurements

$^1\text{H-NMR}$  (400 MHz) spectra were recorded on a Bruker Avance III 400 spectrometer at room temperature.  $\text{CDCl}_3$  was used as the deuterated solvents and tetramethylsilane was the internal standard. Fourier transform IR spectroscopy (FT-IR) was conducted on a Nicolet Magna-IR 750 Fourier transform IR spectrometer with the method of IR microscopy. Six scans were conducted for each spectrum in the wavenumber range of  $400\text{-}4000\text{ cm}^{-1}$ .

### Synthesis of the Monomers

The synthetic routes of the monomers are present in **Scheme S1**. These compounds were prepared according to the synthetic routes similar to those reported in literatures with minor modifications.<sup>[1,2]</sup> Detailed synthesis of the intermediates and monomers were described below.



**Scheme S1.** Synthetic routes of the nematic monomer (M1) and cholesteric monomer (M2).

### Synthesis of 4-(2-hydroxyethoxy)-benzoic Acid

KOH (250.0 mmol, 14.00 g), KI (34.9 mmol, 5.80 g), p-hydroxybenzoic acid (100.0 mmol, 13.80 g), and water (100 mL) were successively added into a 250 mL three-necked round-bottom flask, stirred and heated to 110 °C. Then, 2-bromoethanol (120.0 mmol, 15.00 g) was added dropwise, and the mixture was refluxed overnight. After cooled to ambient temperature, HCl (12 mol L<sup>-1</sup>) was added dropwise to the mixture and white precipitation appeared. The mixture was filtrate, and the obtained white solid was recrystallized from ethanol twice to get the product (14.74 g, 81%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 3.71 (t, 2H, CH<sub>2</sub>), 4.15 (t, 2H, CH<sub>2</sub>), 4.90 (s, 1H, CH<sub>2</sub>OH), 7.05 (d, 2H, Ar H), 7.88 (d, 2H, Ar H), 12.68 (s, 1H, COOH).

### Synthesis of 4-(2-acryloyloxy-ethoxy)-benzoic Acid

4-(2-hydroxyethoxy)-benzoic acid (50 mmol, 9.10 g) and DMA (100 mmol, 12.10 g) was dissolved in 20 mL of dried THF, stirred and heated to 60 °C. An amount of (60 mmol, 5.43 g) was added dropwise to the mixture and refluxed at 60 °C for 4 h. Then the solution was poured into ice water (300 mL) immediately and the crude solid product of 4-(2-acryloyloxy-ethoxy)-benzoic acid (9.77 g, 69%) was collected by air pump filtration, followed by recrystallization from ethanol and isopropanol (V/V = 3/7).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 4.27 (t, 2H, CH<sub>2</sub>); 4.53 (t, 2H, CH<sub>2</sub>); 5.85 (dd, 1H, CH<sub>2</sub>=CH); 6.17 (dd, 1H, CH<sub>2</sub>=CH); 6.45 (dd, 1H, CH<sub>2</sub>=CH); 6.96 (d, 6H, Ar H); 8.09 (d, 6H, Ar H); 12.66 (s, 1H, COOH).

### Synthesis of 4-cyanobiphenyl 4-(2-acryloyloxy-ethoxy)-benzoate (M1)

DCC (20.0 mmol, 4.12 g) dissolved in 20 mL of  $\text{CH}_2\text{Cl}_2$  was added dropwise to a mixture of 4-(2-acryloyloxy-ethoxy)-benzoic acid (20.0 mmol, 4.72 g), 4-hydro-4'-cyanobiphenyl (20.0 mmol, 3.90 g), DMAP (2.0 mmol, 0.24 g), and 100 mL of dichloromethane. The solution was stirred at 25 °C under magnetic stirred for 24 h. After filtration of the precipitation, the excessive dichloromethane was removed at reduced pressure by evaporation. The residue (5.78 g, 70%) was purified by silica gel column chromatography with dichloromethane as the eluent.

IR (KBr): 2945, 2867 ( $\text{CH}_3$  and  $\text{CH}_2$ ), 2225 ( $\text{C}\equiv\text{N}$ ), 1733 ( $\text{C}=\text{O}$ ), 1636 ( $\text{C}=\text{C}$ ), 1605, 1509 (Ar), 1298, 1258 ( $\text{CO}$  Ar), 1198, 1167 ( $\text{COC}$ ).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 4.31 (t, 2H,  $\text{CH}_2$ ); 4.55 (t, 2H,  $\text{CH}_2$ ); 5.90 (dd, 1H,  $\text{CH}_2=\text{CH}$ ); 6.20 (dd, 1H,  $\text{CH}_2=\text{CH}$ ); 6.48 (dd, 1H,  $\text{CH}_2=\text{CH}$ ); 7.05 (d, 2H, Ar H); 7.32 (d, 2H, Ar H); 7.65–7.76 (d, 6H, Ar H); 8.21 (d, 2H, Ar H).

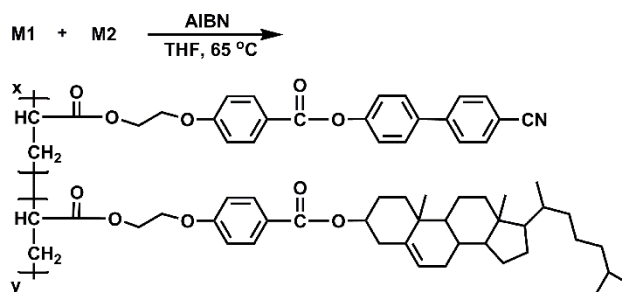
### Synthesis of Cholesteryl 4-(2-acryloyloxy-ethoxy)-benzoate (M2)

The synthesis of M2 (8.71 g, 72%) used the same method as described for the preparation of M1.

IR (KBr): 2943, 2866 ( $\text{CH}_3$  and  $\text{CH}_2$ ), 1724, 1700 ( $\text{C}=\text{O}$ ), 1636 ( $\text{C}=\text{C}$ ), 1604, 1509 (Ar), 1273, 1250 ( $\text{CO}$  Ar), 1183, 1170 ( $\text{COC}$ ).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.68 (s, 3H, cholesteryl H); 0.8–2.1 (m, 38H, cholesteryl H); 2.45 (m, 2H, cholesteryl H); 4.25 (t, 2H,  $\text{CH}_2$ ); 4.32 (t, 2H,  $\text{CH}_2$ ); 4.51 (m, 1H, cholesteryl H); 5.43 (m, 1H,  $=\text{CH}$ ); 5.95 (dd, 1H,  $\text{CH}_2=\text{CH}$ ); 6.15 (dd, 1H,  $\text{CH}_2=\text{CH}$ ); 6.44 (dd, 1H,  $\text{CH}_2=\text{CH}$ ); 6.92 (d, 2H, Ar H); 7.98 (d, 2H, Ar H).

### Synthesis of the Polymers

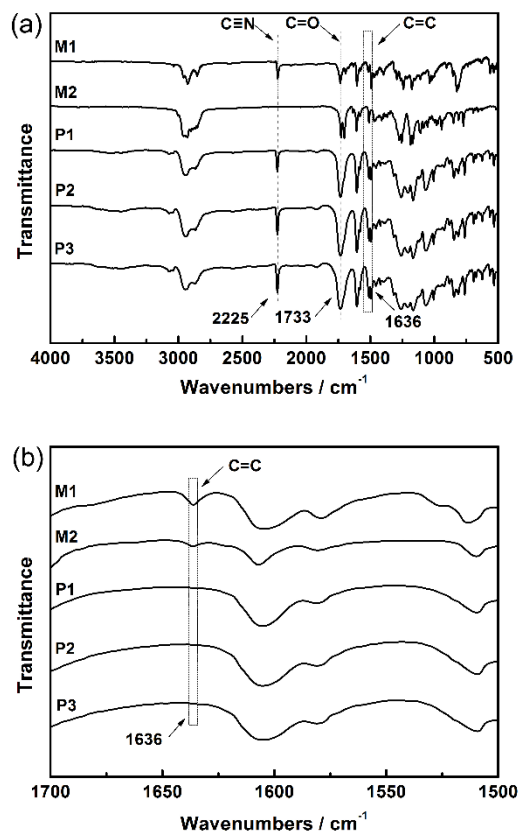
The polymers were obtained via conventional free radical polymerization in solution as shown in **Scheme S2**. Take the synthesis of P1 as an example, a typical polymerization procedure is summarized as the following. M1 (1.65 g, 4.0 mmol), M2 (0.61 g, 1.0 mmol), AIBN (163 mg), and the freshly distilled THF (30 mL) were added into a three-neck round-bottom flask. The copolymerization reaction was carried out under nitrogen and anhydrous conditions at 65 °C for 48 h. After being quenched to room temperature, the polymerization mixture was added dropwise into methanol (500 mL) under stirring. After filtration, the residue was dissolved in THF and re-precipitated in methanol repeatedly until no monomer was detectable by thin layer chromatography. Finally, the copolymer was dried under vacuum for 48 h. Yield: 84%.



**Scheme S2.** Synthesis of the polymers.

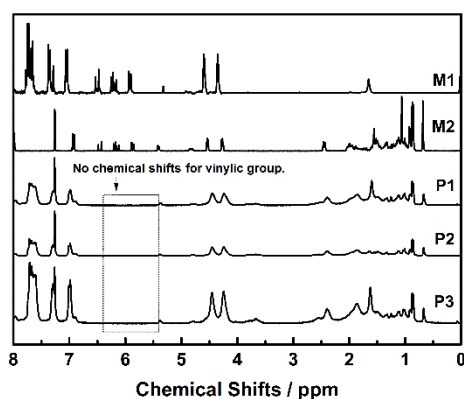
### Characterization of the Monomers and Polymers

The structures of the synthesized monomers and polymers were confirmed by FT-IR and  $^1\text{H-NMR}$  spectroscopic methods. **Figure S1** shows the FT-IR spectra of M1, M2, P1, P2, and P3. It can be seen that the vibrational bands at 2800–2900  $\text{cm}^{-1}$ , 1733  $\text{cm}^{-1}$ , 1450–1600  $\text{cm}^{-1}$  which were attributed to vibrations from aliphatic chain ( $\text{C-H}$ ), ester carbonyl ( $\text{C=O}$ ), aromatic (Ar), respectively, were presented in monomers M1 and M2 as well as in polymers P1, P2, and P3. Additionally, the vibrational band at 1636  $\text{cm}^{-1}$  assigned as the vinyl  $\text{C}=\text{C}$  stretching in monomers completely disappeared due to the polymerization (see the partial amplification of the spectra between 1700 and 1500  $\text{cm}^{-1}$  as shown in Figure S1(b)), illustrated the successful preparation of the polymers.



**Figure S1.** a) FT-IR spectra of M1, M2, P1, P2, and P3. b) Partial amplification of the spectra in (a) between 1500–1700  $\text{cm}^{-1}$ .

$^1\text{H-NMR}$  results also proved the successful synthesis of the polymers.<sup>[3]</sup> **Figure S2** presents the typical chemical shifts and peak integrations of the monomers and corresponding polymers. The spectra of M1 and M2 showed the representative resonances of the vinyl group at 6.47, 6.18, and 5.89 (dd, 3H) ppm. After polymerization, these signals totally disappeared and the chemical shifts of the polymers became quite broad, indicating the successful polymerization.



**Figure S2.**  $^1\text{H-NMR}$  spectra of M1, M2, P1, P2, and P3 in  $\text{CDCl}_3$ .

**Figure S3** presents the reflection spectra of the EVA/P1 composite films with different ratios that had been normalized regarding the reflectance of the non-reflection wavelength to show the intensity of the selectively reflection of the ChSCLCP.

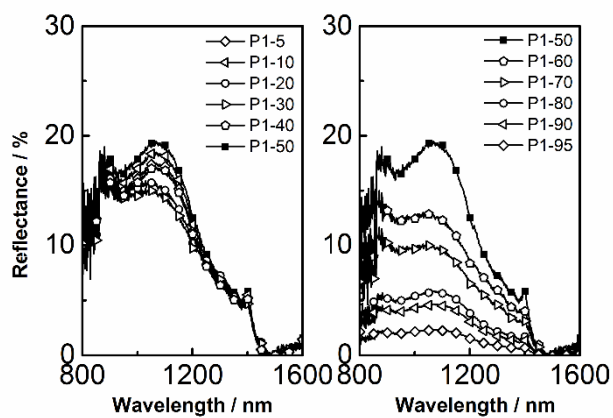


Figure S3. The reflection spectra of the EVA/P1 composite films with different ratios.

- [1] M. Portugall, H. Ringsdorf, R. Zentel, *Makromol. Chem.* **1982**, *183*, 2311–2321.
- [2] D. J. Broer, J. Boven. G. N. Mol, *Makromol. Chem.* **1989**, *190*, 2255–2268.
- [3] V. Ambrogi, M. Giamberini, P. Cerruti, P. Pucci, N. Menna, R. Mascolo, *Polymer* **2005**, *46*, 2105–2121.