Electronic Supporting Information

Mechanochromic and thermochromic shape memory photonic crystal films based on core/shell nanoparticles for smart monitor

Pan Wu, Xiuqing Shen, Christian G. Schäfer, Jian Pan, Jia Guo, and Changchun Wang*

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, and Laboratory of Advanced Materials, Fudan University, 220 Handan Road, Shanghai 200433, China

Corresponding author E-mail: ccwang@fudan.edu.cn (Changchun Wang)

Video S1 (In a separated file)

Sample	e Name	Z-ave / nm	PDI	d _{TEM} / nm
	S	70	0.02	56
	С	237	0.01	214
CI3-R	CI	257	0.03	228
	CIS	308	0.01	248
	S	65	0.07	46
	С	193	0.01	186
C13-G	CI	212	0.01	198
	CIS	251	0.01	219
	S	55	0.03	41
	С	183	0.01	158
CI3-D	CI	196	0.01	178
	CIS	231	0.01	191

Table S1. Average particles diameters determined by DLS measurements and TEM images: monodisperse seed (S), core (C), core-interlayer (CI) and core-interlayer-shell (CIS) particles of red, green and blue films.



Fig. S1 TEM of seed, core, core-interlayer (CI) and core-interlayer-shell (CIS) particles of red, green and blue films, scale bar 100 nm.



Fig. S2 FESEM images of the surface and cross-section of ordered RGB SMPC films. Scale bar is 2 $\mu m.$



Fig. S3 Photographs of a typical red SMPC film, original, stretching and recovered state taken in the dark environment with flash light. Transparent adhesive tape was used on both ends to fix the stretched film. The effective stretch length was attributed to the middle portion.



Fig. S4 DSC curves of SMPC films with transform temperature (T_g of shell material) at 12, 4 and -11 °C, respectively.



Fig. S5 Photograph of a typical red SMPC films.



Fig. S6 Photographs of a typical red film under different strains in the white background.

Table S2. Effective reflective index $\binom{n_{eff}}{(111)}$ plane distances $\binom{d_{SEM}}{d_{c}}$ determined from SEM images and d_c by calculations), reflected $\binom{\lambda_R}{n}$ and calculated $\binom{\lambda_c}{0}$ peak position of the red, green and blue films with various CIS diameters (D) and deviation (δ) between λ_R and λ_c .

Sample	D [nm]	n _{eff}	d _{SEM} [nm]	<i>d_C</i> [nm]	λ_R [nm]	$^{\lambda_{C}}$ [nm]	δ [%]
Red	248	1.510	205	202	635	619	2.6
Green	219	1.488	183	179	559	545	2.6
Blue	191	1.529	153	156	487	468	4.1

 n_{eff} is calculated according to Equation (1) mentioned below; d_c is calculated by $\sqrt{\frac{2}{3}}D$, and matches well with d_{SEM} ; λ_R is measured from reflected spectra at normal incidence angle; λ_c is calculated according to the Bragg's diffraction equation; δ is calculated by Equation (3).

Table S3. Calculated strains along thickness direction $\binom{\varepsilon_Z}{}$ and (111) plane distance (d), reflected ($\binom{\lambda_R}{}$) and calculated $\binom{\lambda_C}{}$ peak position of the red film with various tensile strains $\binom{\varepsilon_X}{}$ and the deviation $\binom{\delta}{}$ between $\binom{\lambda_R}{}$ and $\binom{\lambda_C}{}$.

^ɛ x [%]	0	5	10	15	20	25	30	35	40	45	50
^ε z [%]	0	1.8	3.6	5.4	7.2	9	10.8	12.6	14.4	16.2	18
d [nm]	208	204	201	197	193	189	186	182	178	174	171
λ_R [nm]	662	645	634	622	610	594	585	575	563	547	545
λ_{c} [nm]	637	625	614	603	591	580	568	557	545	534	522
δ [%]	3.9	3.2	3.3	3.2	3.2	2.4	3.0	3.2	3.3	2.4	4.4

 ε_{Z} is calculated from ε_{X} assuming a Poisson ratio of 0.36 typically observed for similar polymer PMMA; d is calculated using $\varepsilon_{Z'}$ and the initial (111) plane distance with 0 % tensile strain is 208 nm which can be estimated from $\sqrt{\frac{2}{3}}$, the diameter of CIS nanoparticles (D=255 nm); λ_{R} is determined from reflected spectra at normal incidence angle; λ_{C} is calculated according to

Equation (2), n_{eff} is 1.532 calculated by Equation (1); δ is calculated by Equation (3).

Calculation of effective refractive index of opal films

Taken the green film as an example, its effective refractive index n_{eff} can be calculated with

$$n_{eff}^2 = \sum n_i^2 V_i, \quad (1)$$

Equation (1) is volume-weighted average refractive index for the whole film. The refractive indices of PS, PEA and PiBMA are 1.592, 1.469 and 1.477 respectively. The diameters of core (^{D}c), core-interlayer (^{D}cl) and core-interlayer-shell (^{D}cls) are 186, 198 and 219 nm respectively according to TEM images. Their relevant volume ratios can thus be calculated.

$$V_{C} = \frac{\frac{4}{3}\pi(\frac{D_{C}}{2})^{3}}{\frac{4}{3}\pi(\frac{D_{CIS}}{2})^{3}} = \frac{\frac{4}{3}\pi(\frac{186}{2})^{3}}{\frac{4}{3}\pi(\frac{219}{2})^{3}} = 0.613$$

$$V_{CI} = \frac{\frac{4}{3}\pi(\frac{D_{CI}}{2})^{3}}{\frac{4}{3}\pi(\frac{D_{CIS}}{2})^{3}} = \frac{\frac{4}{3}\pi(\frac{198}{2})^{3}}{\frac{4}{3}\pi(\frac{219}{2})^{3}} = 0.739$$

$$V_{I} = V_{CI} - V_{C} = 0.126$$

$$V_{S} = 1 - V_{CI} = 0.261$$

For the opal film with CIS nanoparticles, according to the recipe mentioned in the synthesis of particles part, volume ratio of each component can thus be calculated. Since the densities of all the monomers are very close, we simply chose the weight ratio as the volume ratio.

For the core,

$$V_{BDDA} = 0.1V_C = 0.061$$

 $V_{St} = 0.9V_C = 0.549$

For the interlayer,

$$V_{AMA} = 0.1V_I = 0.013$$

 $V_{EA} = 0.9V_I = 0.113$

For the shell,

$$V_{iBMA} = 0.6V_S = 0.157$$

 $V_{EA} = 0.4V_I = 0.104$

Therefore, n_{eff} can be calculated with Equation (1),

$$\begin{split} n_{eff}^{2} &= \sum n_{i}^{2} V_{i} = n_{St}^{2} V_{St} + n_{BDDA}^{2} V_{BDDA} + n_{AMA}^{2} V_{AMA} + n_{EA}^{2} V_{EA} + n_{iBMA}^{2} V_{iBMA} = 1.5467 \\ 0.061 + 1.436^{2} \times 0.013 + 1.406^{2} \times (0.113 + 0.104) + 1.42^{2} \times 0.157 = 2.214 \\ n_{eff} = 1.488 \end{split}$$

Similarly, refractive indices of red and blue films are 1.510 and 1.529.

Calculation of reflected peak position of opal films

The reflected peak position of opal films can be calculated according to Bragg's diffraction equation (Equation (2)),

$$\lambda = 2n_{eff} d\sin \alpha \qquad (2)$$

where λ represents the reflected peak wavelength of the film and d is the lattice constant and in our system is referred to (111) plane distance.

For films with different sizes of CIS nanoparticles, n_{eff} is calculated above and d is determined from the cross-section FE-SEM images of the film. Thus λ_c can be obtained by **Equation (2)** accordingly.

Taken the green film as an example, n_{eff} is 1.488 and d is 183 nm, thus

$$\lambda = 2n_{eff}d\sin\alpha = 2 \times 1.488 \times 183 \times 1 = 545 nm$$

Similarly, reflected peak positions of red and blue films are 619 and 468 nm, and the deviation (δ) between λ_R and λ_C is calculated by,

$$\delta = \frac{\lambda_R - \lambda_C}{\lambda_C} \times 100\%$$
 (3)

The estimated results of calculated peak position λ_c of the film match well with data measured from reflected spectra as the deviations are all below 5 %.

REFERENCES

[1] C. I. Aguirre, E. Reguera and A. Stein, Adv. Funct. Mater., 2010, 20, 2565-2578.

[2] Y. Xie, Y. Meng, W. Wang, E. Zhang, J. Leng and Q. Pei, *Adv. Funct. Mater.*, 2018, **28**, 1802430.