Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Facile Fabrication of Three-Dimensional Colloidal Crystal Film with Large-Area and Robust Mechanical Properties

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Experimental Section

Materials: Butyl acrylate (BA), styrene (St) acrylic acid (AA), methyl methacrylate (MMA), vinyl acetate (Vac), vinyl triisopropoxy silane (VTS) and allyloxy hydroxypropyl sodium sulfonate (HAPS, 40 wt% of solid content in aqueous solution) were purchased from Sinopharm Chemical Reagent Corp; Silica sol (20nm, pH=3-4, 34 wt% of solid content, zeta potential=−11.1 mV) was from Eka Chemicals Corp. (Sweden); Ammonium persulfate (APS) was purchased from Shanghai Guanghua Chemical Reagent Corp. (China) and purified by recrystallization.

Synthesis of polymer spheres: A typical surfactant-free emulsion polymerization procedure was carried out as follows: deionized water (120 g), HAPS (1.0 g), AA (1 g), BA (5 g), St (5 g), and APS (0.05 g) were added sequentially into a four-necked flask equipped with an N_2 inlet, a reflux condenser, and a mechanical stirrer at a stirring speed of 1500 rpm. The polymerization was initially performed at 75−80 °C for 30 min, and then added by a mixture of AA (1 g), BA (15 g), St (15 g), and APS (0.2 g dissolved in 15 g of water) over a period of 2 h. The reaction was allowed to proceed for another 2 h to obtain polymer latex with a solid content of 34 wt%. All formulations for the synthesis of polymer spheres with different Tg and compositions are summarized in Table 1.

Preparation of polymer/SiO_2 nanocomposite particles: The polymer latexes were further blended with various contents of colloidal silica under vigorously stirring for 2 min and ultrasonically treating for 2 min at the ambient temperature to obtain nanocomposite latexes.

Preparation of nanocomposite film: The obtained nanocomposite particles were cast on glass substrates by means of a drawdown rod and dried under 23±2 ^{o}C for 24 h with thicknesses of 100±10 μm, except where specifically noted otherwise.

Characterization: SEM images of the nanocomposite films were obtained with a Philips XL 30 field emission microscope. All samples were coated with gold by sputtering prior to observation. High-resolution TEM images of the nanocomposite particles were obtained with a JEOL 2010 microscope at an acceleration voltage of 200 kV. The particle dispersions were diluted and dried at ambient temperature onto carbon-coated copper grids before examination. The particle sizes of polymer spheres were determined by a N4 Plus dynamic light scattering particle size analyzer. The reflection spectra were recorded with a fiber-coupled spectrometer/charge-coupled device system with spectral resolution of 0.15 nm, the optical spot size of the incident beam on the samples was about 0.8 mm. The impact strength of the film was measured using an impact tester based on GB/T1732-93. Tensile properties were determined by an Instron model DXLL1000-20000 testing machine (Shanghai, China) based on the film area of 12.5 mm × 25 mm at a pulling speed of 100 mm/min. The average value of three measurements on each sample was reported. Differential scanning calorimeter (DSC) analysis was carried out on Du Pont DSC 10 detector to determin the glass transition temperature.

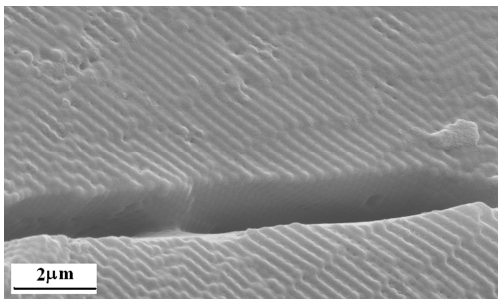


Figure S1. The large cross-sectional SEM image of film with 5 wt% of nanosilica

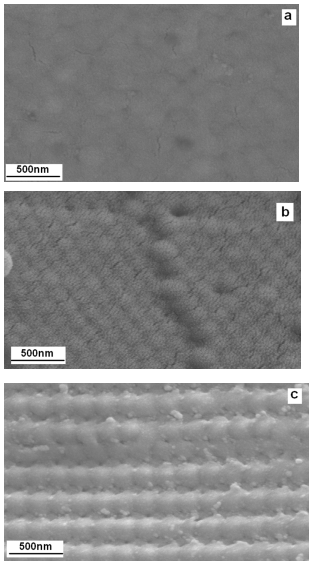
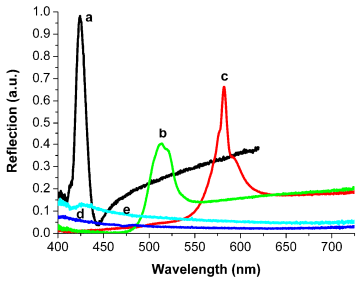


Figure S2. The cross-sectional SEM images of films with various Tg. a) -14°C (Run 1), b) 4 °C (Run 2), c) 59 °C(Run 4).

a.



b.

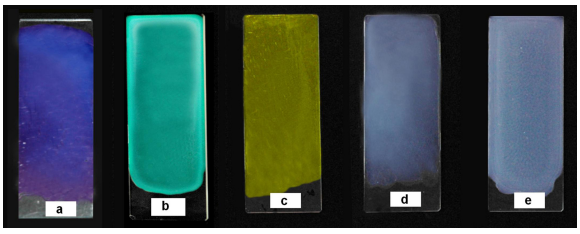


Figure S3. The reflection spectra and photographs of films with various polymer composition.
a. MMA-BA-AA (Run 5), b. Vac-BA-St-AA (Run 6), c. VTS-BA-St-AA (Run7), d. BA-St (Run 8), e. BA-St-AA (Run 9)

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Table S1. Formulations for syntheses of polymer latex*

Run	St (g)	BA (g)	MMA (g)	Vac (g)	VTS (g)	AA (g)	Tg (^{o}C)
1	30	10	/	/	/	2	-14
2	25	15	/	/	/	2	4
3	20	20	/	/	/	2	19
4	10	30	/	/	/	2	59
5	/	20	20	/	/	2	22
6	13	17	/	10	/	2	17
7	23	7	/	/	10	2	13
8	20	20	/	/	/	0	17
9	20	20	/	/	/	5	23

*Note: 1 g of HAPS solution (g), 0.25 g of APS and 80 g of water were used in all the formulations.