Electronic Supplementary Material (ESI) for ChemComm.

# Electronic Supplementary Information

# Synthesis of supramolecular gels based on electron-transfer reactions between clay nanotubes and styrene

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## Experimental details:

### 1. Materials

Halloysite nanotubes (HNTs) were purchased from Guangzhou Runwo Materials Technology Co., Ltd., China. HNTs were purified according to the reference to remove the impurities.[1] Styrene (St) was obtained from Tianjin Damao Chemical Reagent Co., Ltd, China. Other chemicals used in the experiment were supplied by Aladdin Industrial Co., China.

### 2. Sample preparation

HNTs were added to St and they were mixed by shaking. Then, the mixture was placed in an ultrasonic cleaner for sonication for a certain time to obtain gel. Mixture of St and HNTs was denoted as St@HNTs with St and HNTs weight ratio. For example, St@HNTs 100-20 meant the weight ratio between St and HNTs was 100: 20. St@HNTs meant 5 kinds of mixtures: St@HNTs 100-1, St@HNTs 100-2, St@HNTs 100-5, St@HNTs 100-10 and St@HNTs 100-20. Additionally, α-methyl styrene@HNTs and ethyl benzene@HNTs were prepared with a weight ratio between corresponding organic substance and HNTs was 100: 20.

HNTs masked by sodium tripoly phosphate were prepared as follows. HNTs and sodium tripoly phosphate were added in ultrapure water in proportion of 0.05 mol sodium tripoly phosphate per 100 g HNTs. The suspension was stirred for 6 h. Then, HNTs in the suspension were centrifuged and washed three times with ultrapure water. After drying under 60$^{o}$C, HNTs masked by sodium tripoly phosphate were obtained.

### 3. Characterization

*Zeta potential.* The samples were diluted to 0.5 wt% aqueous suspensions for testing, which were tested by a Nano ZS zeta-potential analyzer (Malvern Instruments Co., U.K.).

*Dynamic light scattering (DLS).* The samples were prepared by diluting HNTs or St@HNTs to 0.045wt% suspension with ultrapure water, which were tested by a nanoparticle size and zeta potential analyzer (Omni, Brookhaven Instruments Co., USA).

*Electron paramagnetic resonance (EPR).* The test method of EPR test was based on the relevant literature.[2] St (300 μL) and HNTs (54 mg) were placed in a Pyrex EPR tube (i.d. 3.8 mm). The solution in tube was degassed through repeated freeze and thaw cycles. Then, the tube was saturated with argon. After being sealed, it was placed in the cavity of the EPR spectrometer (JES FA300, JEOL Ltd., Japan) to test. Spectra were recorded repeatedly until the spectral pattern showed no further change.

*Polarized optical microscopy (POM).* St@HNTs gels were coated to a glass slide and covered with another piece of glass to get the samples which were observed under a polarized optical microscope (BX51, Olympus, Japan).

*The rheological behavior.* The dynamic viscosity was measured by a hybrid rheometer (TA Discovery HR-2, USA) using a parallel plate model with a diameter of 40 mm at 25°C. The shear rate of the shear stress and the dynamic viscosity was from $10^{-1}$ $s^{-1}$ to

$10^2$ $s^{-1}$. The strain scan range of St@HNTs 100-20 was from $10^{-4}$% to $10^3$%.

*Transmission electron microscopy (TEM).* The HNT dispersion (in St solvent or ultrapure water) was dropped on carbon film supported by a copper grid. After evaporation of the solvent, the samples were characterized by TEM (JEM-2100F, JEOL Ltd., Japan).

*Scanning electron microscopy (SEM).* St@HNTs 100-20 and water dispersion of HNTs (20 wt%) were coated on the glass and the solvent were fully volatilized. The images were taken through SEM (Ultra-55, Carl Zeiss Jena Ltd., Germany) with an accelerating voltage of 5 kV. The cross sections of HNTs@polystyrene (HNTs@PS) to be observed were obtained after being broken in liquid nitrogen.

*Fourier transform infrared spectroscopy (FTIR).* The FTIR spectra were characterized by a Thermo FTIR (Nicolet iS50, Thermo Fisher Scientific Ltd., USA). The wavenumber ranged from 4000 $cm^{-1}$ to 500 $cm^{-1}$.

*X-ray diffraction (XRD).* The XRD patterns were recorded through an X-ray diffractometer (MiniFlex-600, Rigaku Co., Japan). The scanning angle was from $5^o$ to $60^o$ while the scanning speed was $5^o$/min.

*UV-vis spectrum*. St@HNTs gel was diluted to 500 ppm with alcohol and scanned in 200-800 nm by an ultraviolet spectrophotometer (UV-2550, Shimadzu Instrument Ltd., Japan).

**Supporting figures:**

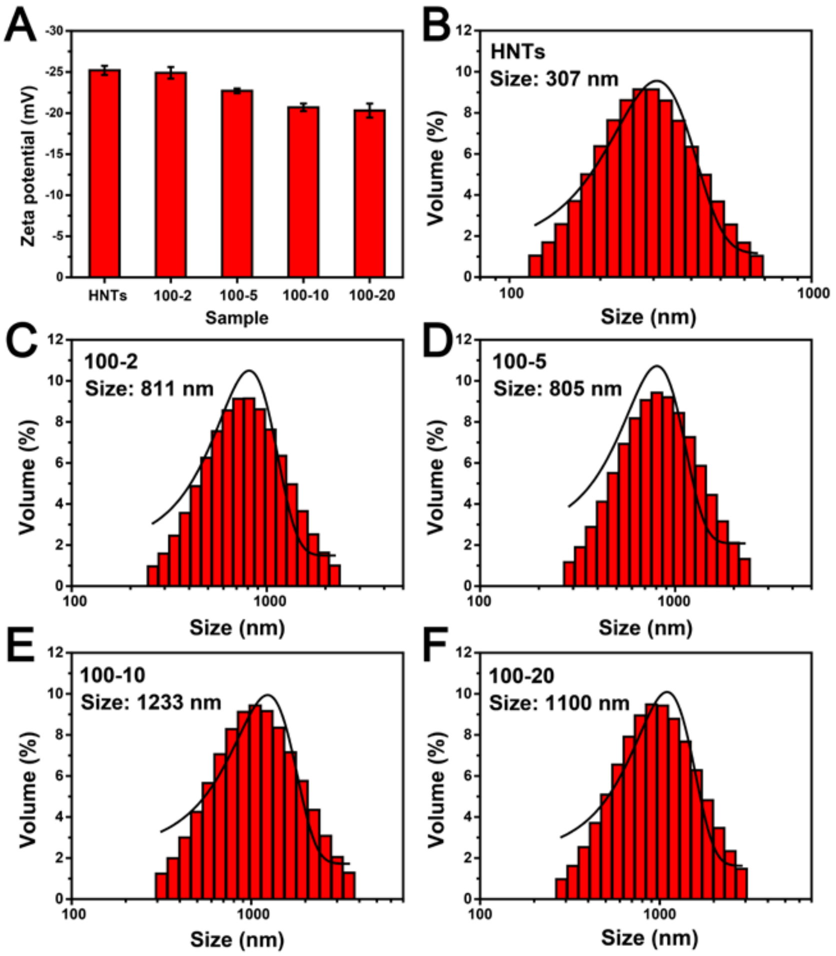

**Fig. S1** Zeta potential of HNTs and St@HNTs (A); DLS results of HNTs and St@HNTs (B: HNTs; C: St@HNTs 100-2; D: St@HNTs 100-5; E: St@HNTs 100-10; F: St@HNTs 100-20).

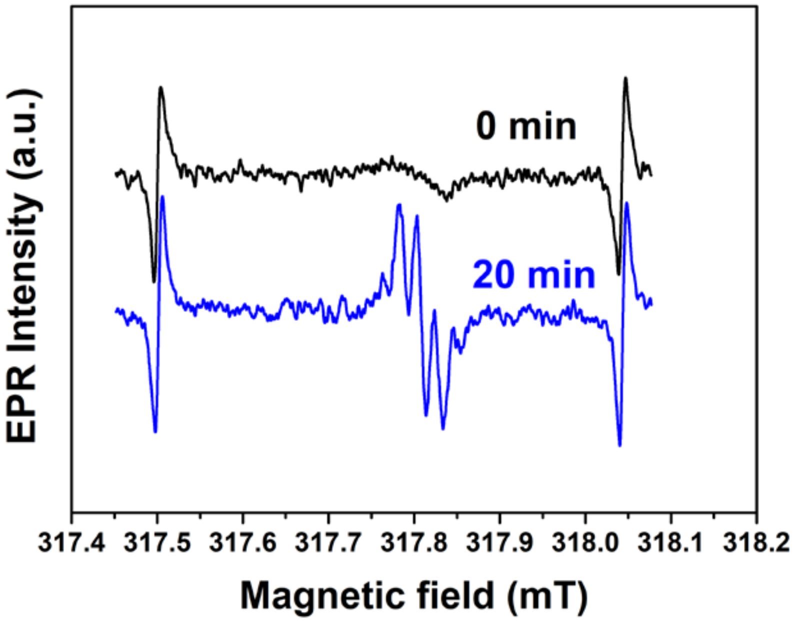

**Fig. S2** EPR curves of St@HNTs 100-20 at different time.

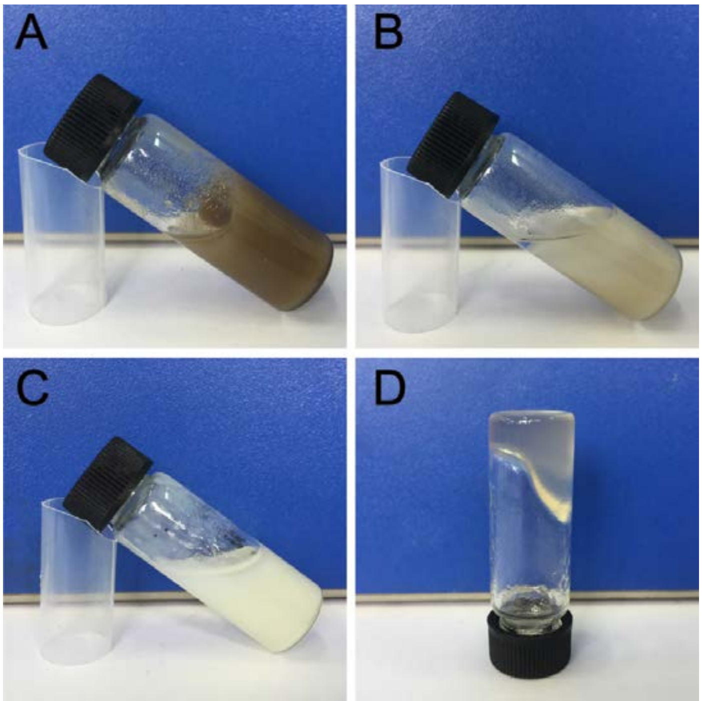

**Fig. S3** The appearance of mixture of St and clay minerals with ultrasound treatment for 30 min (A: attapulgite; B: montmorillonite; C: kaolin; D: HNTs masked by the polyphosphate).

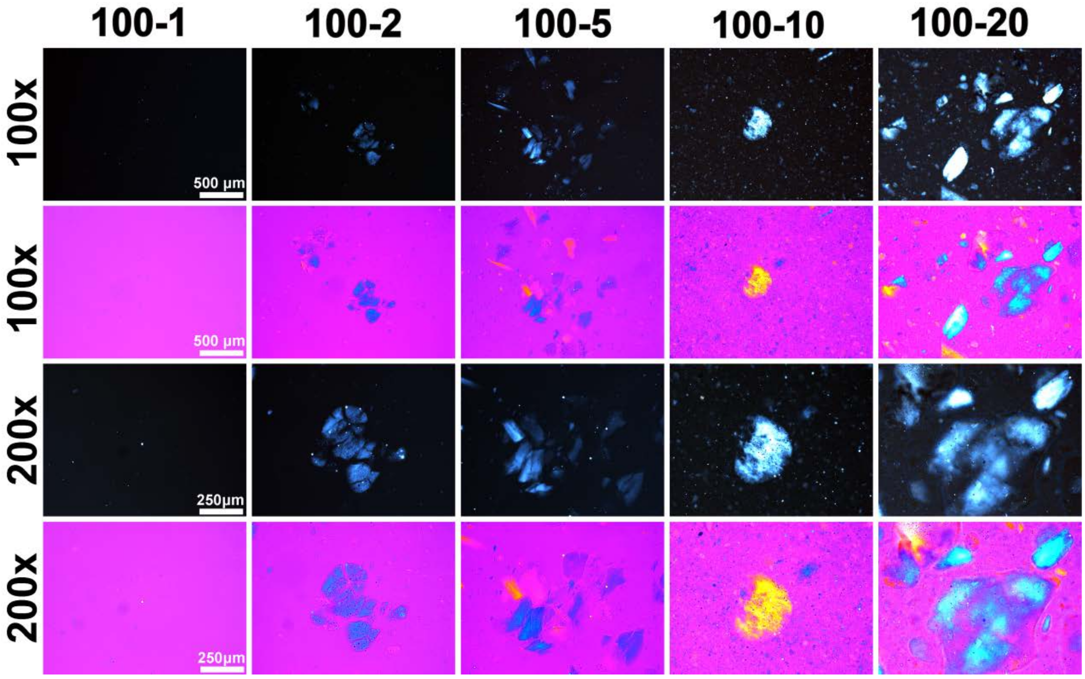

**Fig. S4** Polarized optical micrograph of St@HNTs with different magnification.

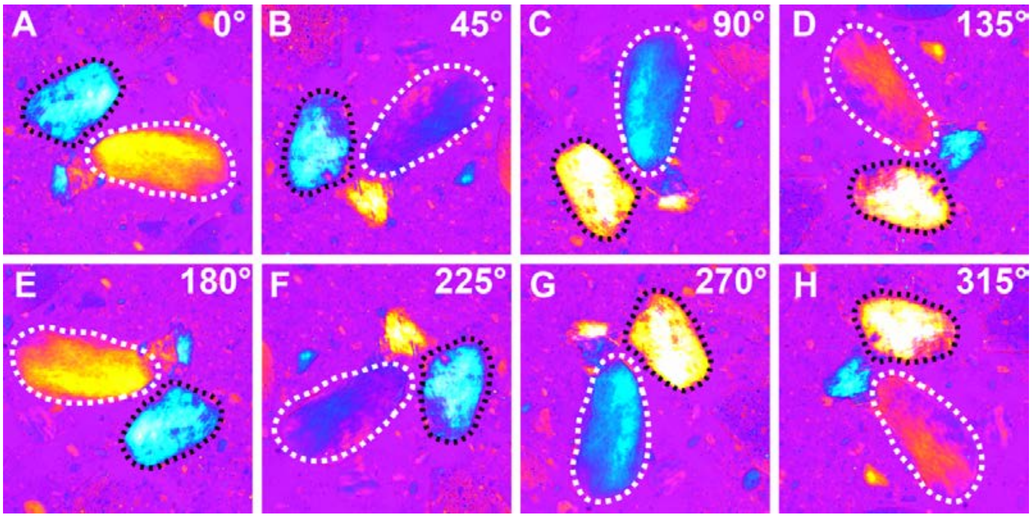

**Fig. S5** Polarized optical micrograph of St@HNTs 100-20 in the same area by rotating different angle.

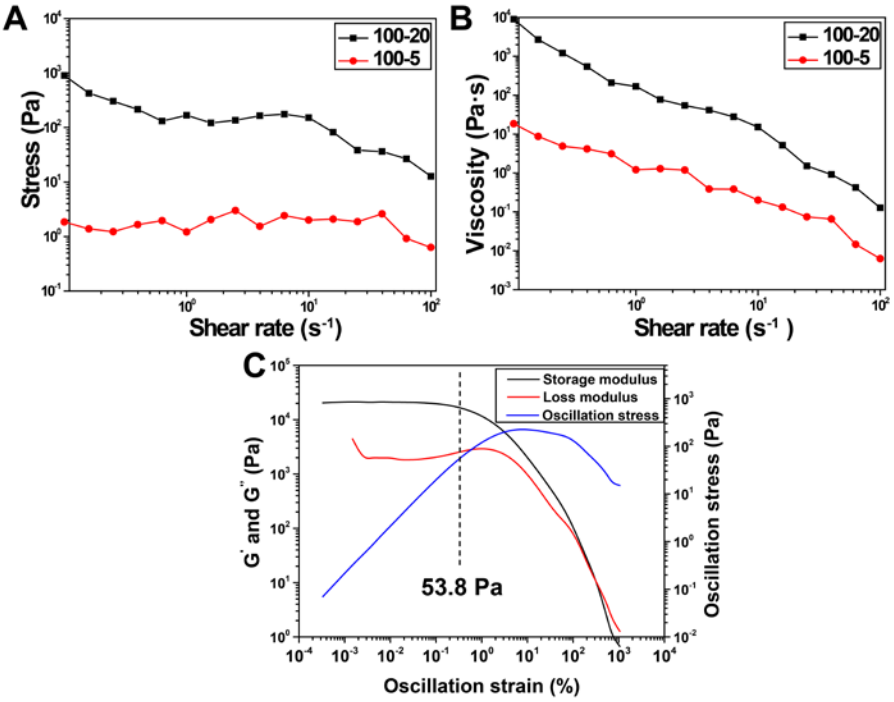

**Fig. S6** Shear stress vs shear rate curves (A) and shear viscosity vs shear rate curves (B) of St@HNTs gel (St@HNTs 100-20 and St@HNTs 100-5); strain scanning curves (C) of St@HNTs 100-20.

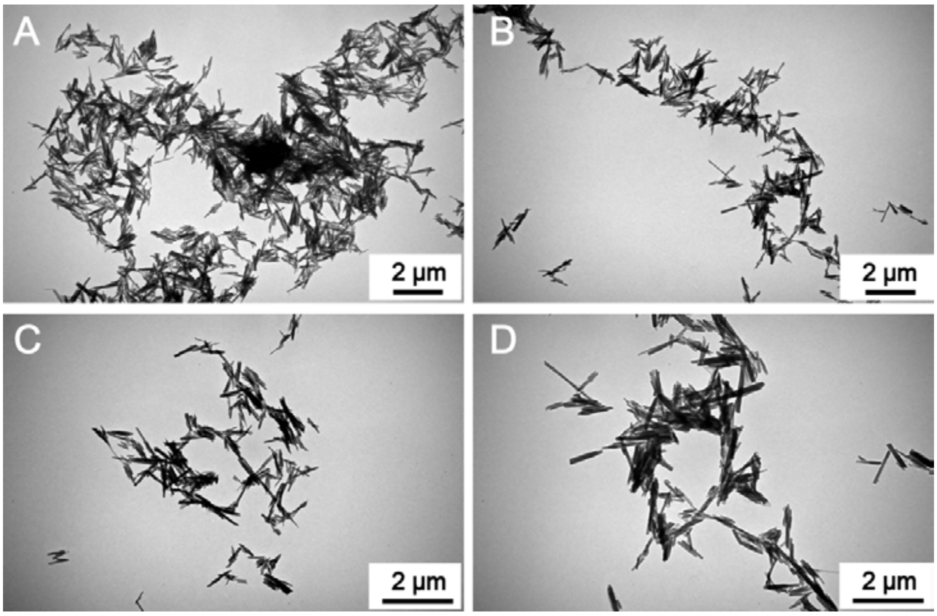

**Fig. S7** TEM image of HNTs dispersed in St with different magnification.

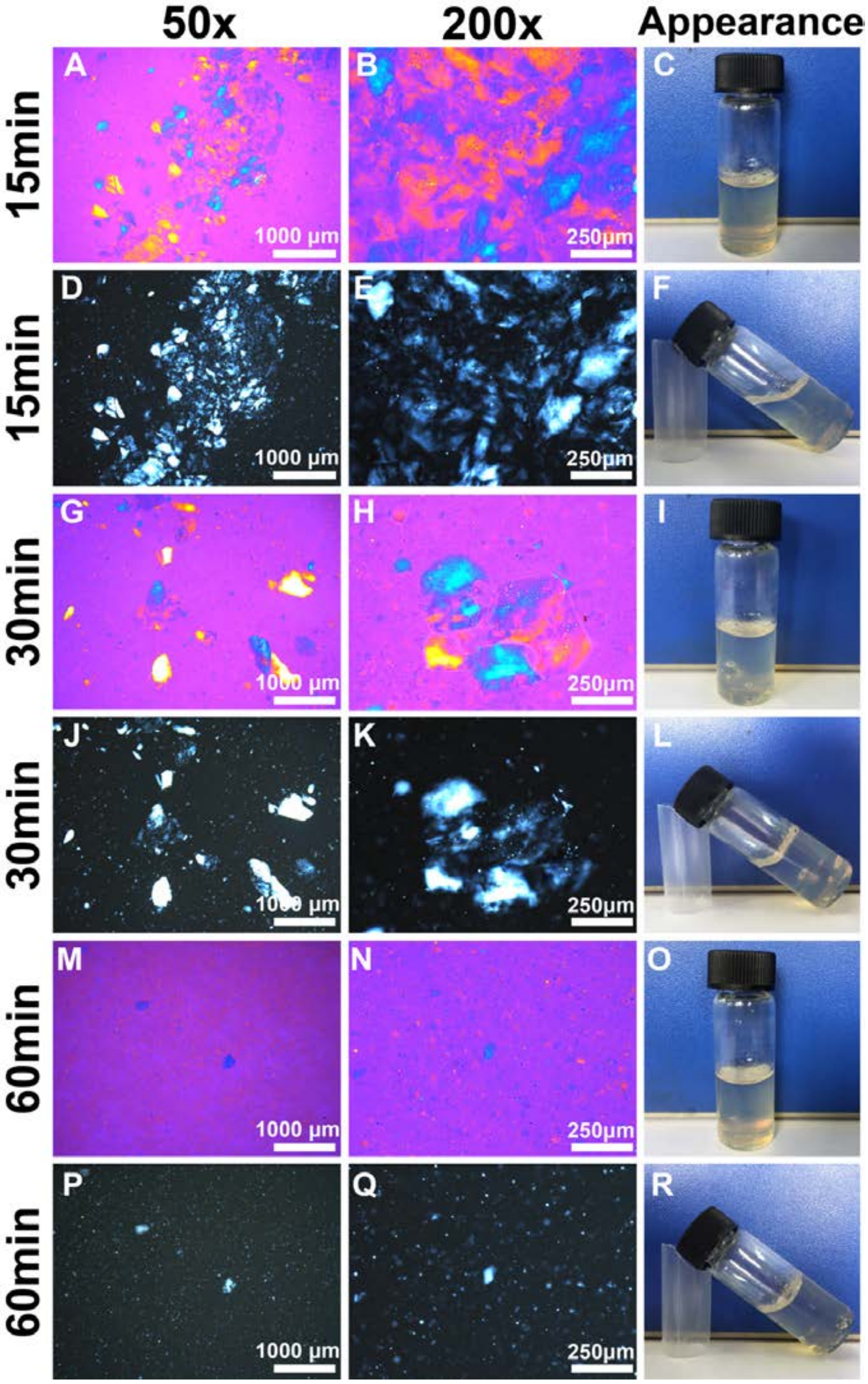

**Fig. S8** Effect of ultrasonic time on St@HNTs 100-20 (15 min: A, B, C, D, E, F; 30 min: G, H, I, J, K, L; 60 min: M, N, O, P, Q, R).

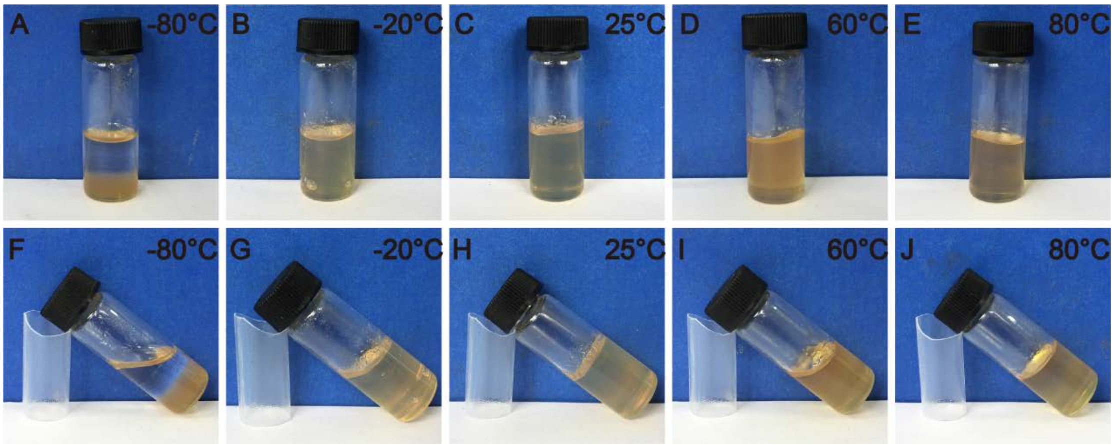

**Fig. S9** Effect of temperature on St@HNTs 100-20 (-80$^o$C: A, F; -20$^o$C: B, G; 25$^o$C: C, H; 60$^o$C: D, I; 80$^o$C: E, J).

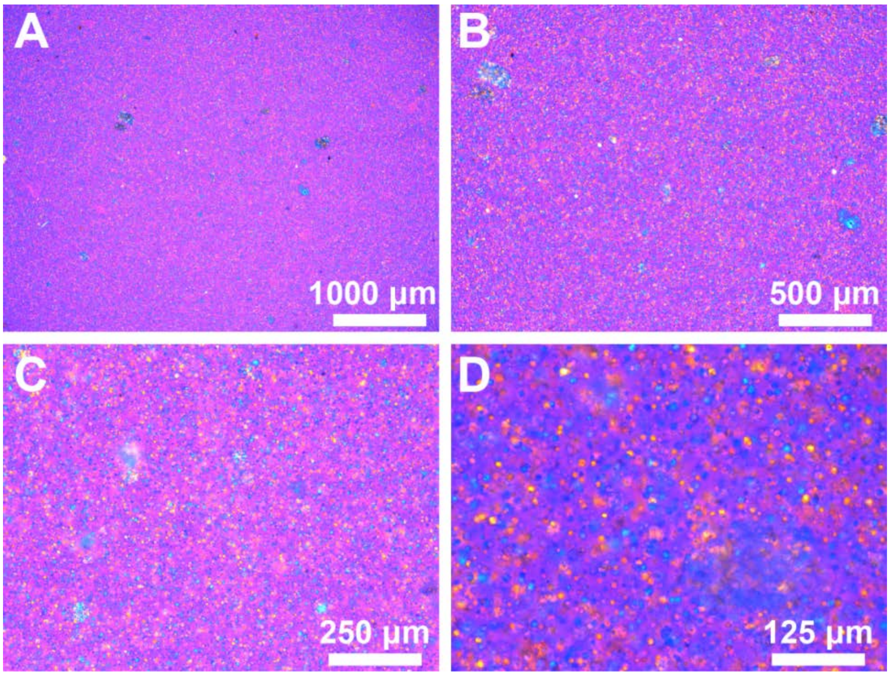

**Fig. S10** Polarized optical micrograph of St@HNTs 100-20 placed under 60$^{o}$C for 14 days with different magnification.

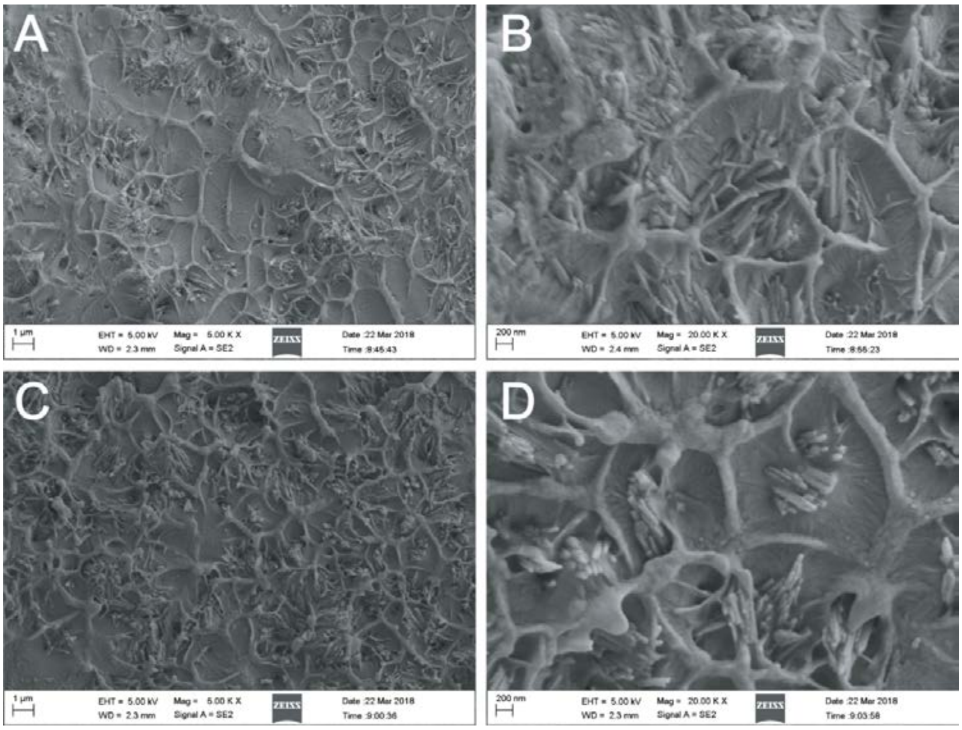

**Fig. S11** SEM image of the cross section of HNTs@PS polymerized at 60$^{o}$C (A, B) and polymerized at 80$^{o}$C (C, D).

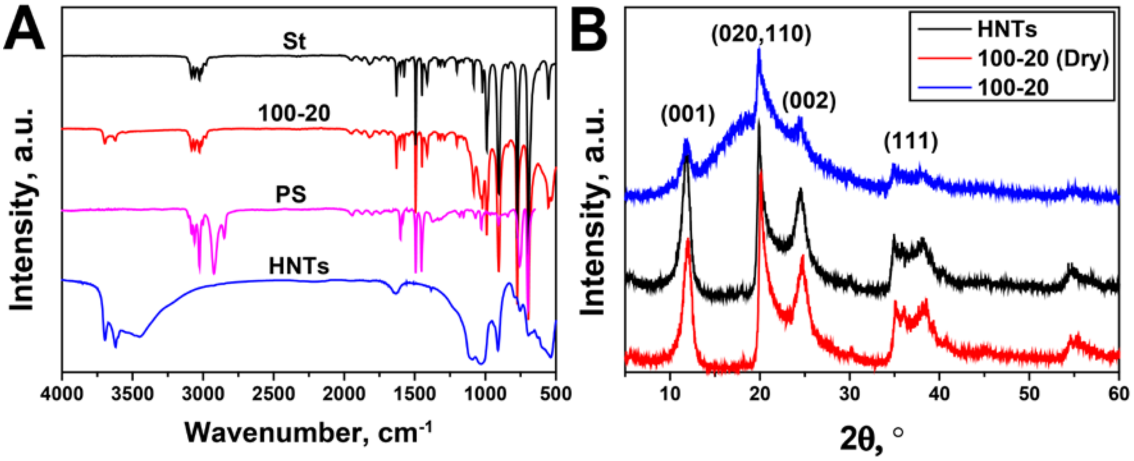

**Fig. S12** FTIR spectrum (A) of St, St@HNTs 100-20, PS and HNTs; XRD pattern (B) of HNTs, powder of dry St@HNTs 100-20 and St@HNTs 100-20.

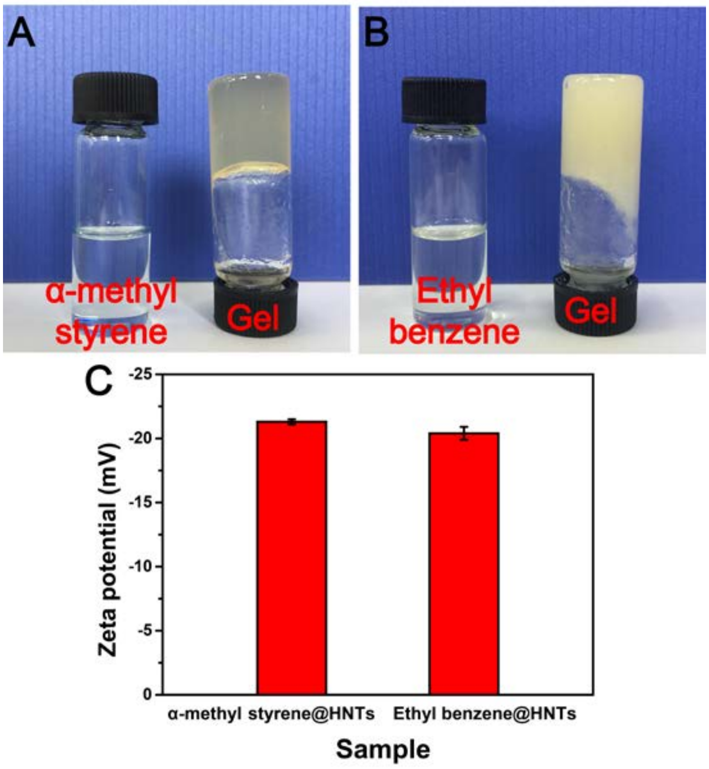

**Fig. S13** The appearance of α-methyl styrene@HNTs (A) and ethyl benzene@HNTs (B); zeta potentials of α-methyl styrene@HNTs and ethyl benzene@HNTs (C).

## Reference

1. M. Liu, B. Guo, Q. Zou, M. Du, D. Jia, Nanotechnology, 2008, 19(20):205709.
2. A. Alberti, M. Benaglia, M. Laus, D. Macciantelli, K. Sparnacci, Macromolecules, 2003, 36(3):736-740.