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# Electronic Supplementary Information for

## UV Gelation of Single-Component Polyacrylate Bearing Dinitrobenzoate Side Groups

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### Materials and Methods.

**Materials.** 4-(chloromethyl) styrene (90%, TCI Reagent Co.), 2-bromo-2-methylpropanoyl bromide (95%, Aladdin Reagent Co.), 1-ethyl-3-(3-dimethylaminopropyl) carbodiiehydrochlide (98.5%, Aladdin Reagent Co.), 4-dimethylaminopyridine (98%, Aladdin Reagent Co.), sodium acetate (99.5%, Guoyao Reagent Co.), carbazole (96%, Aladdin Reagent Co.), sodium hydride (95%, Aldrich Reagent Co.), ethyl bromoacetate (98%, Aladdin Reagent Co.), 3,5-dinitrobenzoyl chloride (98%, Aladdin Reagent Co.) were used as received. Azo-diisobutyronitrile (AIBN) (99%, Aladdin Reagent Co.) was recrystallized from ethanol (2×) and vinyl carbazole (99%, Puyang Reagent Co.) was recrystallized from methanol (2×) and both were stored at low temperature before use. Hydroxyethyl methacrylate (96%, Aladdin Reagent Co.) and styrene (99%, Aladdin Reagent Co.) were passed through a basic alumina column, then distilled under reduced pressure to remove the inhibitor, and both were stored at low temperature. Water was deionized with a Milli-Q SP reagent water system (Millipore) to a specific resistivity of 18.2 MΩcm. All other solvents and reagents were purchased from Aladdin Reagent and were used as received or purified as previously described methods when preparing the corresponding published compounds.

**Methods.** $^1$H NMR (300 MHz) spectra were recorded on a Bruker AV300 NMR spectrometer operated in the Fourier transform mode. NMR chemical shifts were reported in standard format as values in ppm relative to deuterated solvents. Mass spectral data (ESI/MS) were obtained on a Micromass auto spec spectrometer. Fluorescence microscopy images of the solid samples were obtained from an Olympus DP72 color camera mounted on a BX51 microscope excited by a mercury lamp for wide-band UV excitation. Dynamic laser light scattering (LLS) measurements were conducted on a commercial spectrometer (ALV/DLS/SLS-5022F) equipped with a multitau digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser ($\lambda_0$ = 632 nm) as the light source. Scattered light was collected at a fixed angle of 90° for duration of ~5 min. Distribution averages and particle size distributions were computed using cumulants analysis and CONTIN routines. UV/vis absorption spectra were recorded on a Beijing Persee TU-1901 UV-Vis spectrometer. Excitation and steady-state fluorescence emission spectra were recorded on a FluoroMax-4 spectrofluorometer (Horiba Scientific) and analyzed with an Origin integrated software FluoroEssence (v2.2). Fluorescence lifetime data were acquired with a 1MHz LED laser with the excitation peak at 369 nm (NanoLED-370). Lifetime data were analyzed with DataStation v6.6 (Horiba Scientific). Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with Waters 1515 pump and Waters 2414 differential refractive index detector (set at 30 °C). The detectioncomponents used a series of two linear Styragel columns (HR2 and HR4) at an oven temperature of 45 °C. The eluent was DMF at a flow rate of 1.0 mL/min. Melting point was recorded on a SGW-X4 (Shanghai Precision and Scientific Instrument Co., Ltd.) illuminated microscope melting point apparatus. The conductivity in the solution was measured using a DDS-307 conductivity meter (CSDIHO, China). Density functional theory (DFT) calculations were performed by the software package of GAUSSIAN09.[1] The hybrid functional B3LYP and the 6-31G basis was selected to calculate all the molecules.[2] Time-dependent DFT (TDDFT) method[3] was used to simulate the optical properties, and the polarizable continuum model (PCM)[4] was chosen to consider the solution effect.

## Synthesis

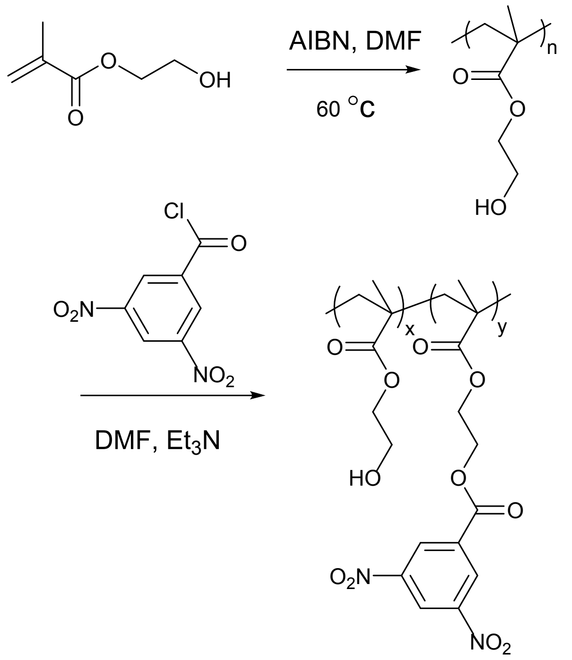
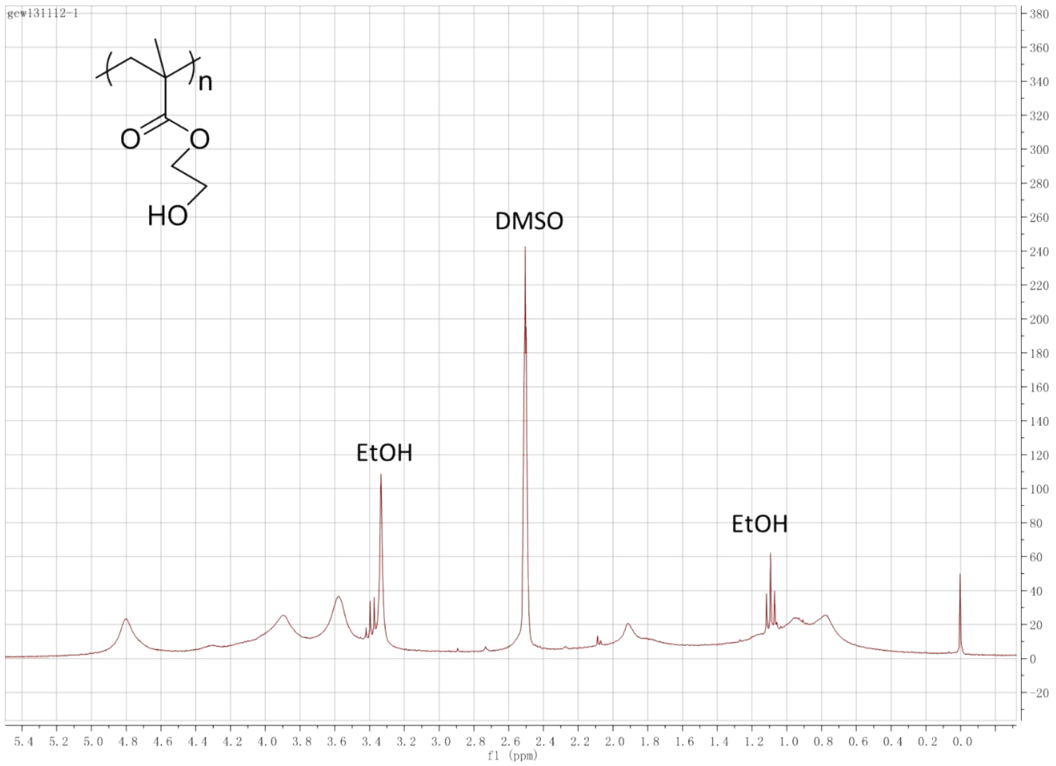
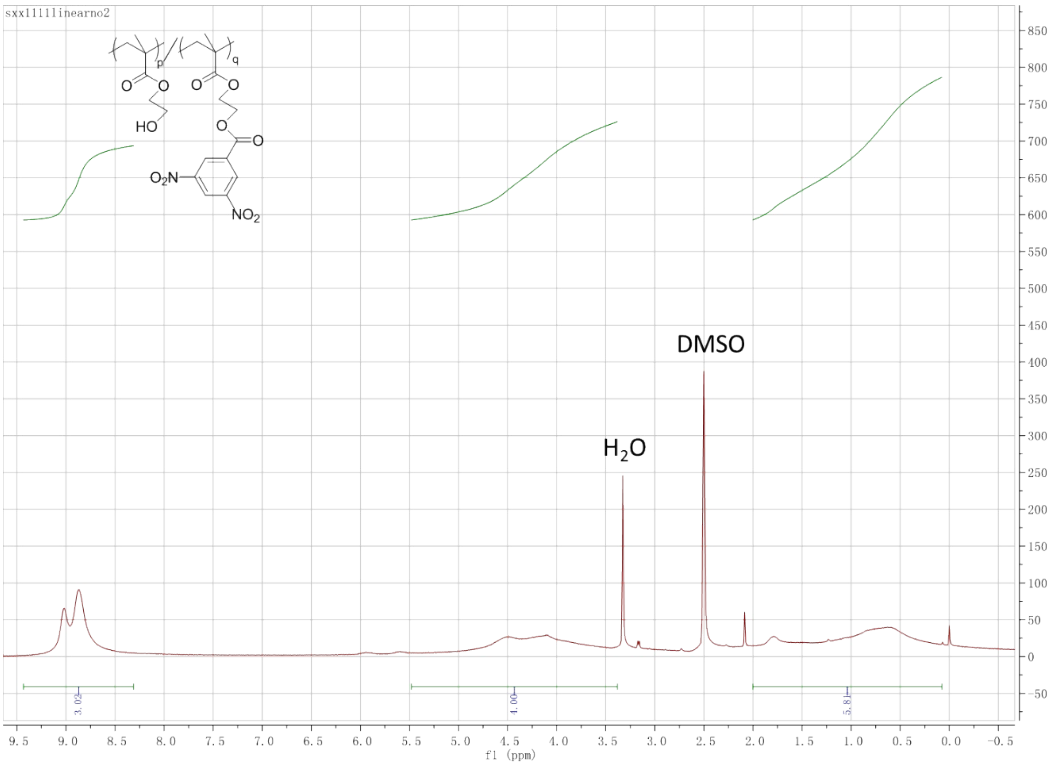


**Figure S1.** Synthesis of the polymers.

**Poly (hydroxyethyl methacrylate)**. Hydroxyethyl methacrylate (5.00 g, 38.4 mmol), AIBN (21.0 mg, 0.13 mmol) and 40 ml DMF were added to a glass tube. The tube was degassed via three freeze-pump-thaw cycles, and then sealed under vacuum. After being stirred at 60 °C for 2 h, the reaction mixture was unsealed and precipitated into an excess of cold ether. The above dissolution-precipitation cycle was repeated for three times. After drying in a vacuum oven overnight at room temperature, the product was obtained as white powders. $M_n$: 17.6 KDa, PDI: 1.55.



**Poly [hydroxyethyl methacrylate-co-(3, 5-dinitrobenzoic ethyl) methacrylate]**. Poly (hydroxyethyl methacrylate) (0.50 g), $Et_3N$ (0.78 g, 7.64 mmol) and dry DMF (20 ml) were added to a round bottom flask equipped with a magnetic stir bar. After cooling to 0 °C in an ice-water bath, 3, 5 - dinitrophenyl chloride (0.88 g, 3.82 mmol) dissolved in 5 ml dry DMF was added dropwise over ~10 min. The reaction was completed after stirring for another 12 h at 50 °C, and quenched with 50 ml $H_2O$, then extracted with $CH_2Cl_2$ (50 mL × 3). The organic phase was concentrated by rotary evaporation, then precipitated into an excess of cold ether. The dissolution-precipitation cycle was repeated for three times. After drying in a vacuum oven overnight at room temperature, the product was obtained as white powders. $M_n$: 29.4 KDa, PDI: 1.84.



## References:

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, *et al*. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

2 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

3 R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.*, 1996, **256**, 454.

4 J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.