Electronic Supplementary Information

Anthracene functionalized thermosensitive and UV-crosslinkable polymeric micelles

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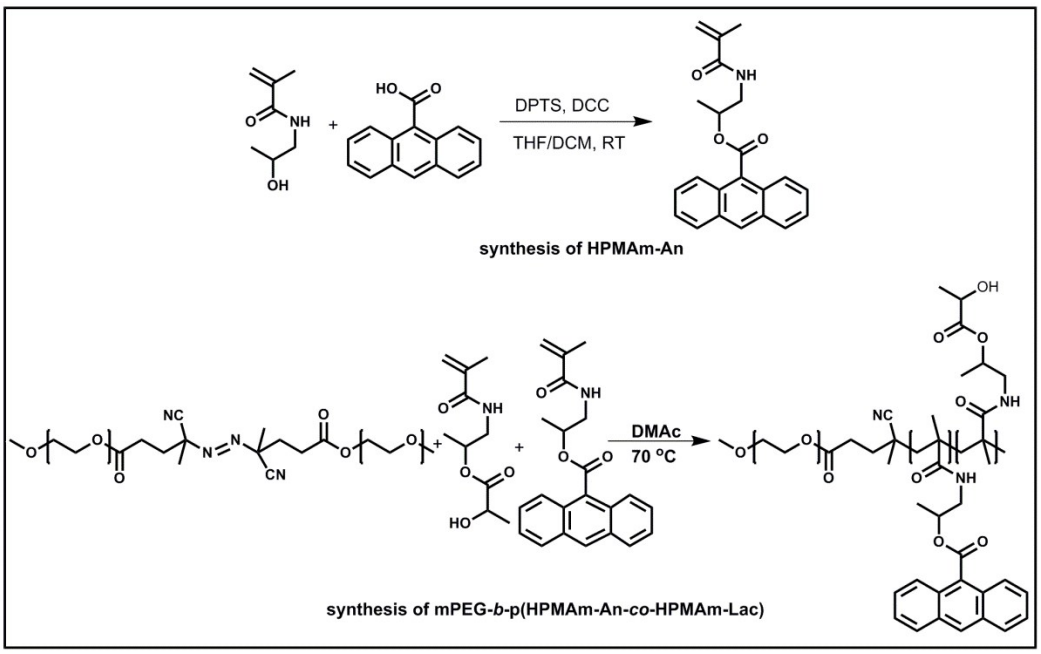
1. Synthesis and characterizations of *N*-(9-anthranoyloxypropyl) methacrylamide (HPMAm-An).



Scheme 1 Synthesis of HPMAm-An and mPEG-b-p(HPMAm-An-co-HPMAm-Lac).

The melting point of the compound was 182 °C, which was measured by differential scanning calorimetry (Discovery, TA Instruments) (Fig. 1)

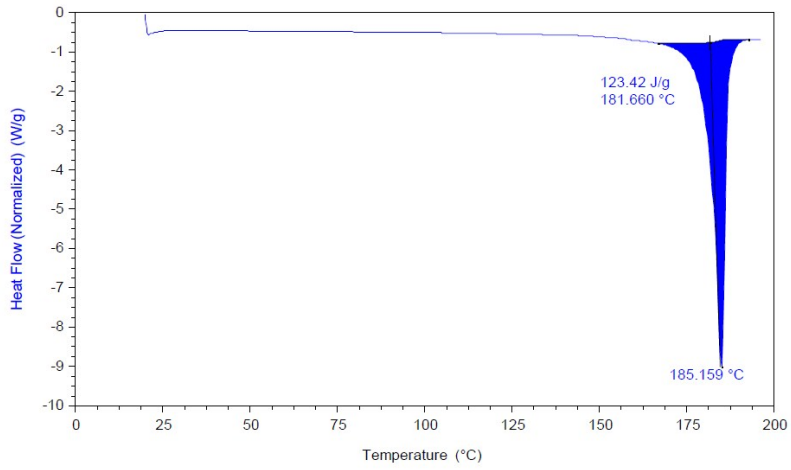


Fig. 1 Thermogram of HPMAm-An

The chemical structure of the compound was examined by ^{1}H NMR spectroscopy on a Varian Mercury 300 MHz spectrometer in DMSO-d_6. δ (ppm): 8.8 (s, 1 H, aromatic CH), 8.2 (t, CO-N<u>H</u>-CH_2), 8.1 (q, 2H, aromatic CH), 7.9 (q, 2H, aromatic CH), 7.6 (q, 4H, aromatic CH), 5.7 and 5.4 (s, C<u>H$_2$</u>=C), 5.6 (m, CH_2-C<u>H</u>(CH_3)-O), 3.4 (t, NH-C<u>H$_2$</u>-CH), 1.8 (s, C<u>H$_3$</u>-C=C), 1.5 (d, CH_2-CH(C<u>H$_3$</u>)-O). The purity of HPMAm-An was assayed by HPLC (Waters Alliance HPLC system. Eluent A: ACN/water = 5/95 (v/v) with 0.1% perchloric acid; eluent B: 100% ACN with 0.1% perchloric acid). A solvent gradient was run with the volume fraction of eluent B increasing from 0-100% in 10 minutes. A Sunfire C18 column was used and detection was done at 254 nm.

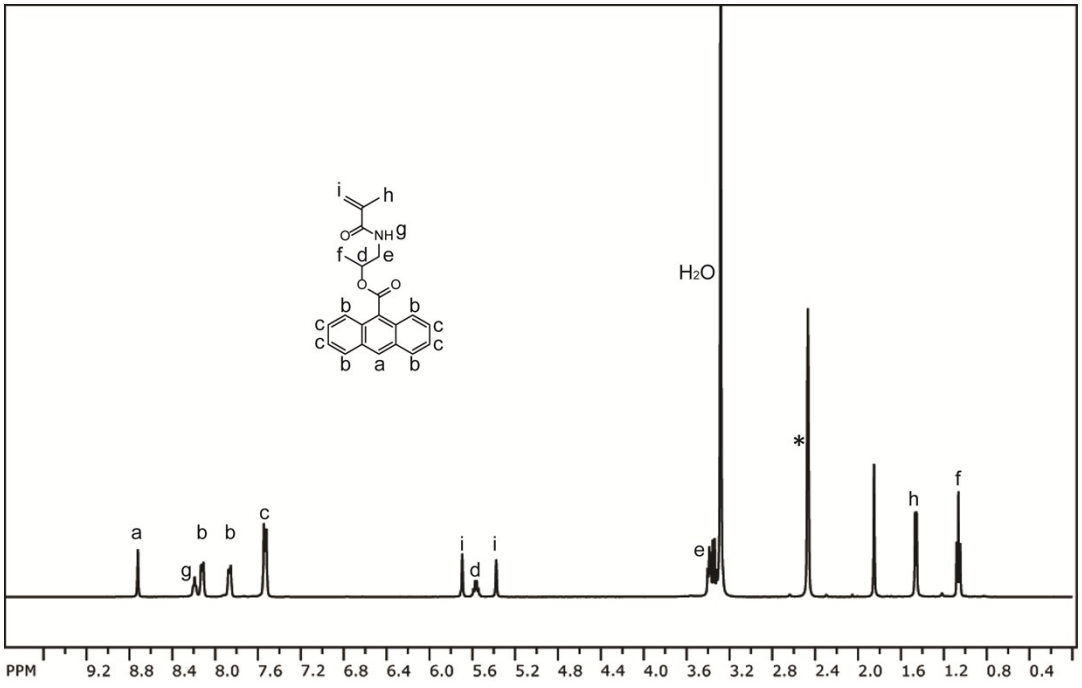


Fig. 2 ^{1}H NMR spectrum of HPMAm-An. * indicates the solvent (DMSO-d_6) peak.

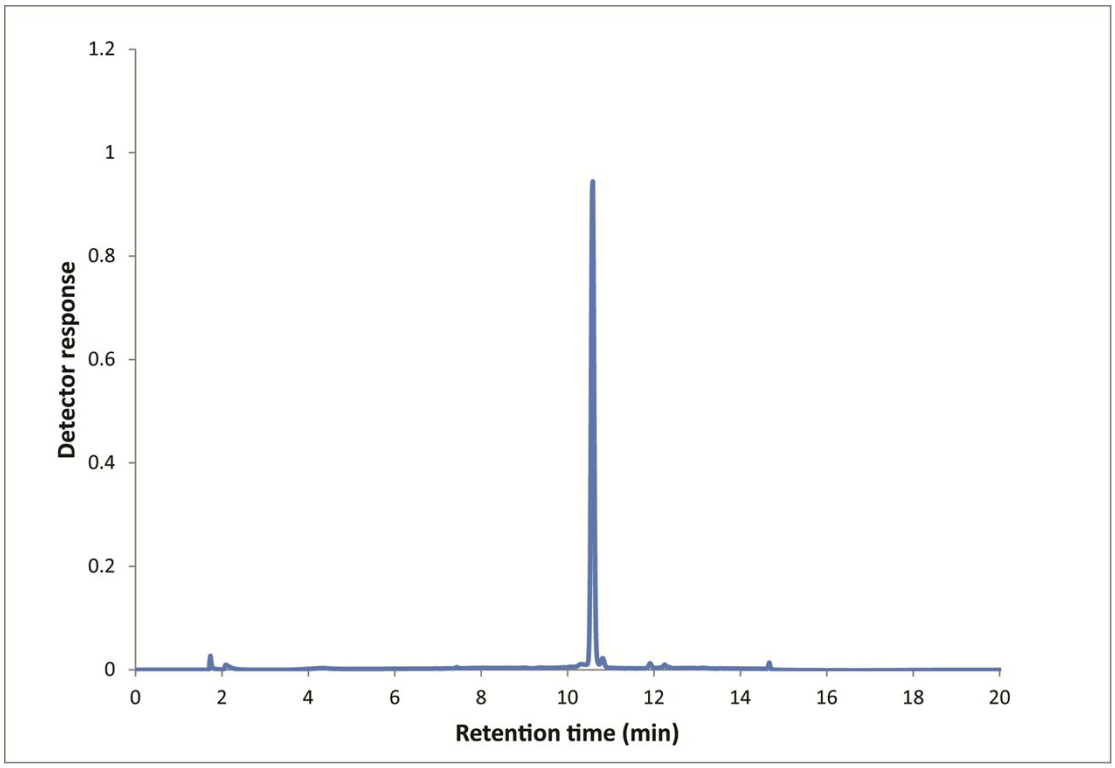


Fig. 3. HPLC chromatogram of HPMAm-An.

2. Characterizations of *ω*-methoxy poly(ethylene glycol)-*b*-(*N*-(9-anthranoyloxypropyl) methacrylamide)-*co*-(*N*-(2-lactoyloxypropyl) methacrylamide) (mPEG-*b*-p(HPMAm-An-*co*-HPMAm-Lac)).

The structure of the obtained mPEG-b-p(HPMAm-An-co-HPMAm-Lac) was confirmed by ^{1}H NMR spectroscopy on a Varian Mercury 300 MHz spectrometer in DMSO- DMSO-d_6. δ (ppm): 8.8 (b, 1H, aromatic CH), 8.1 (b, 2H, aromatic CH), 7.9 (b, 2H, aromatic CH), 7.7-7.0 (b, CO-N<u>H</u>-CH_2 and 4H, aromatic CH), 5.3 (d, CH(CH_3)-O<u>H</u>), 5.1 (b, NH-CH_2-C<u>H</u>(CH_3)-O-(Bz)), 4.8 (b, NH-CH_2-C<u>H</u>(CH_3)-O-(Lac)), 4.1 (b, C<u>H</u>(CH_3)-OH), 3.40-3.60 (b, $mPEG_{5000}$ methylene protons, O-C<u>H_2</u>-C<u>H_2</u>), 3.2 (b, NH-C<u>H_2</u>-CH), 0.6-2.2 (b, the methyl and backbone CH_2 protons).

The number-average molecular weight (M_n) of the block copolymers was determined by ^{1}H NMR as follows: (a) the value of the integral of the mPEG protons divided by 448 (the average number of protons per one mPEG chain, M_n = 5000) gives the integral value for one mPEG chain, and (b) the number of HPMAm-Lac and HPMAm-An units in the polymers was determined from the ratio of the integral of the methyne protons (4.1 ppm, 1H, C<u>H</u>(CH_3)-OH) of HPMAm-Lac and aromatic protons of HPMAm-An (8.8 ppm, ^{1}H, aromatic CH) to the integral of one mPEG chain. The M_n of the thermosensitive block was calculated from the resulting number of HPMAm-Lac and HPMAm-An units. The mol % of the HPMAm-An repeating units in the thermosensitive block of the copolymer was determined by the following equation:

$$\text{Mol \% of HPMAm-An} = \frac{\text{integral (H at 8.8 ppm)}}{\text{integral (H at 8.8 ppm)} + \text{integral (H at 4.1 ppm)}}$$

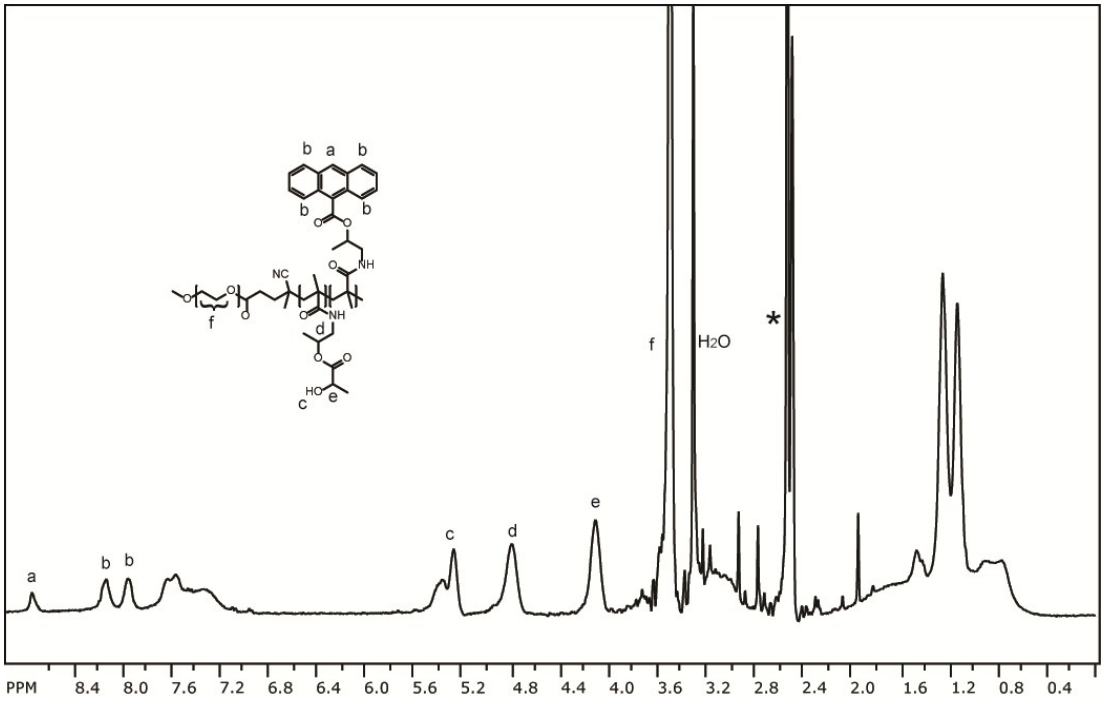


Fig. 4. ^{1}H NMR spectrum of mPEG-b-p(HPMAm-An-co-HPMAm-Lac). * indicates the solvent (DMSO-d_6) peak.

GPC was conducted to measure the number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity (PDI, or M_w/M_n) using two serial Plgel 5 μm MIXED-D columns (Polymer Laboratories) and PEGs of narrow molecular weights as calibration standards. The eluent was DMF containing 10 mM LiCl, the elution rate was 0.7 mL/min and the temperature was 40 °C.[1]

References:

1. Y. Shi, M. J. van Steenbergen, E. A. Teunissen, L. Novo, S. Gradmann, M. Baldus, C. F. van Nostrum and W. E. Hennink, *Biomacromolecules*, 2013, **14**, 1826-1837.