† **Electronic Supplementary Information (ESI) available:**

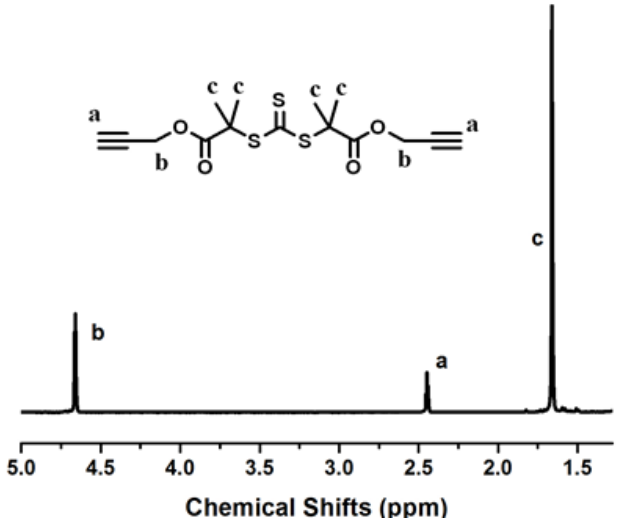

Fig. S1 ^{1}H NMR spectrum of dialkynetrithiocarbonate in $CDCl_3$.

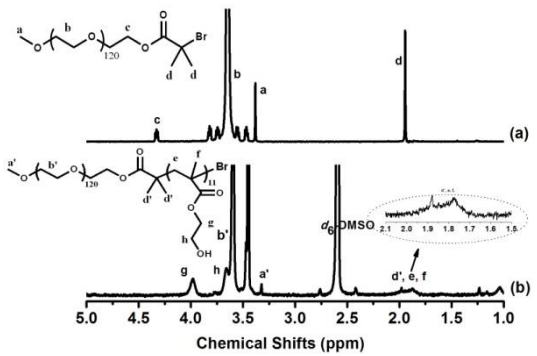

Fig. S2 ^{1}H NMR spectra of (a) PEG-Br in $CDCl_3$, (b) PEG-*b*-PHEMA in d6-DMSO.

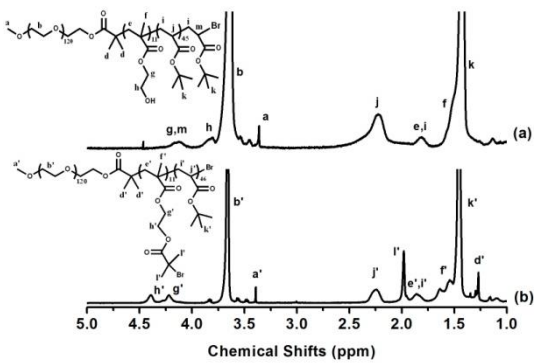

Fig. S3 ^{1}H NMR spectra of (a) PEG-*b*-PHEMA-*b*-PtBA and (b) PEG-*b*-PBIEM-*b*-PtBA in $CDCl_3$.

Weight percentage of nitrogen in the polymeric micelles was measured by elemental analysis, and the value is about 10.09 %.

The weight percentage of PNIPAM was calculated using the following formula:

$$W_{PNIPAM} = \frac{M_{NIPAM}}{14}(W_{N1} - W_{N2}) \qquad (1)$$

Where, M_{NIPAM} is molecular weight of NIPAM monomer, 14 is atomic weight of nitrogen, W_{N1} is weight percentage of nitrogen in micelles after RAFT polymerization of NIPAM as determined by elemental analysis and W_{N2} is weight percentage of nitrogen before RAFT polymerization. Assuming all the repeating units of PBIEM block were grafted by azide groups, the value of W_{N2} can be calculated. Based on the above formula, the weight percentage of PNIPAM in the micelles was calculated to be about 76%.

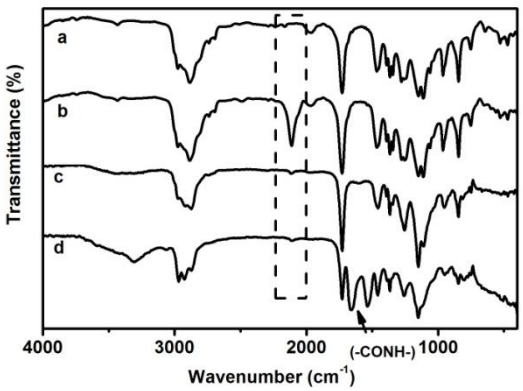

Fig. S4 FTIR spectra of (a) PEG-*b*-PBIEM-*b*-PtBA, (b) PEG-*b*-(PBIEM-g-N_3)-*b*-PtBA, (c) interface cross-linked micelles, and (d) micelles after in situ RAFT polymerization of NIPAM.

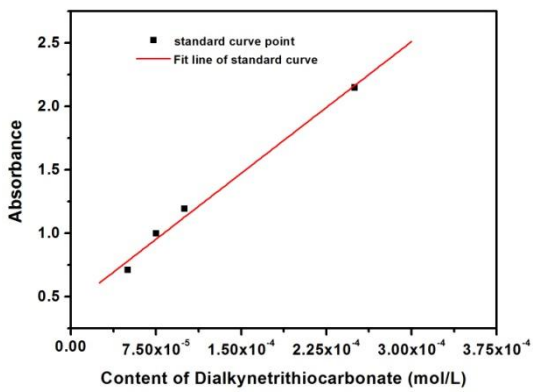

Fig. S5 The standard absorption curve of RAFT CTA recorded at 300 nm, which was made by measuring known amount of RAFT CTA in THF.