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Synthesis of hemoglobin-conjugated triblock copolymer for oxygen carrying and specific recognition of cancer cells

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Polymers were also characterized by FTIR, as shown in Fig. S1. Fig. S1(A) displays the FTIR spectrum of PMAG-b-PMAA. The typical stretching vibration of C=O in PMAA could be clearly observed at 1730 cm^{-1}. The peak appeared at 1640 cm^{-1} attributed to the amide Ⅰ band of PMAG. The FTIR spectrum of PMAG-b-PMAA-b-PBMA is shown in Fig.S1(B). It was found that the intensity of the peak at 1730 cm^{-1} attributed to the stretching vibration of C=O becomes stronger in contrast to the one of the typical amide Ⅰ band. Taking the introduction of BMA units into consideration, the amounts of C=O increased significantly.

CMC of PMAG-b-PMAA-b-PBMA was determined by fluorescence probe technique. Pyrene, as a hydrophobic probe, is initially dissolved in water, whereas tends to exist in the hydrophobic core of micelles, which forms when the concentration of polymer is above the CMC. The ratio between the intensities of absorptions at 375 (I_1) and 386 (I_3) nm depends greatly on the microenvironmental polarity, the variation of which could result in the corresponding variation of I_1/I_3 ratio. The emission spectra of pyrene at different copolymer concentrations in phosphate buffer solution were acquired. And then, I_1/I_3 ratio versus logarithmic of polymer concentration was plotted (Fig. S2). As shown in Fig. S2, the ratio is almost constant when polymer concentrations are relatively low. After the polymer concentration reaches a critical value, ratio begins to decrease dramatically with the increasing concentration. This is due to the forming of micelles as well as the simultaneous transfer of pyrene from water into the hydrophobic core of the micelles. Thus, the CMC of PMAG-b-PMAA-b-PBMA is 5×10^{-4}g/L.

The diameter and PDI of micelles after stored at 4°C for 30 days is shown in Fig. S3.