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Supplementary Information

Synthesis and properties of poly(DEX-GMA/AAc) microgel particle as a hemostatic agent

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Experimental Section

^{1}H Nuclear magnetic resonance

^{1}H Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 400 mHz NMR (Bruker, Rheinstetten, Germany) in D_2O. The chemical shifts were expressed as parts per million (ppm).

Fourier transform infrared spectroscopy

The dry nanoparticles were mixed with potassium bromide (KBr) and pressed into pellets. For each Fourier transform infrared spectroscopy (FTIR) (Thermo Nicolet Avetar 370, USA) measurement, the sample was scanned 30 times in the wave number range from 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

Screen out synthesis conditions

Dosages of crosslinker, initiator, monomer's mole ratio and drying methods were studied to increase the swelling ratio of poly(DEX-GMA/AAC) microgel particles. First of all, only dosage of crosslinker was changed (0, 0.5, 1, 3, 5 %) with constant another conditions (10% of initiator, 1:1 of monomer's mole ratio and drying by lyophilization). Then the swelling ratio of samples with different crosslinker content was measured. Similarly, dosages of initiator, monomer's mole ratio and drying method were studied one by one. For example, dosage of initiator was changed (0, 0.5, 1, 3, 5%) with constant another conditions (0.5% of crosslinker, 1:1 of monomer's mole ratio and drying by lyophilization). Next, monomer's mole ratio of AAc to DEX-GMA was changed (0:0, 1:1, 2:1, 3:1, 4:1, 5:1, 1:0) with constant another conditions (0.5% of crosslinker, 0.5% of initiator, lyophilization). Last, drying method was changed with constant another conditions (0.5% of crosslinker, 0.5% of initiator, 4:1 of monomer's mole ratio).

Relative molecular weight

Poly(DEX-GMA/AAc) dissolved neither in tetrahydrofuran nor in dimethylformamide. Therefore, molecular weight of poly(DEX-GMA/AAc) couldn't be measured precisely through gel permeation chromatography (GPC). And then, Photon correlation spectroscopy (PCS) and Viscosity test method were used to confirm relative molecular weight.

Method 1: Photon correlation spectroscopy was followed as user manual of Dynamic light scattering (DLS) (Beckman coulter Delsa^{TM} Nano C Particle Analyzer). The molecular weight (M_W) was calculated according to empirical formula as following:

$M_W=(\alpha/D_T)^{1/\beta}$

α represents structure effect of particles' translational motion, β represents solvent effect, and D_T is translational diffusion coefficient which can be measured by DLS. α and β can be got through reference or calculation. M_W of poly(DEX-GMA/AAc) obtained through calculation in which Dextran (M_W=40000) and Chitosan(M_W=30000) were used as standard samples. D_T of standard Dextran, standard Chitosan and poly(DEX-GMA/AAc) was measured through DLS under same temperature (25℃) and concentration (20mg/mL). Then the graph of logarithm function was constructed by standard M_W and their D_T. α and β were calculated as following:

$\alpha=10^{(-\text{intercept}/\text{slope})}$, $\beta=-1/\text{slope}$

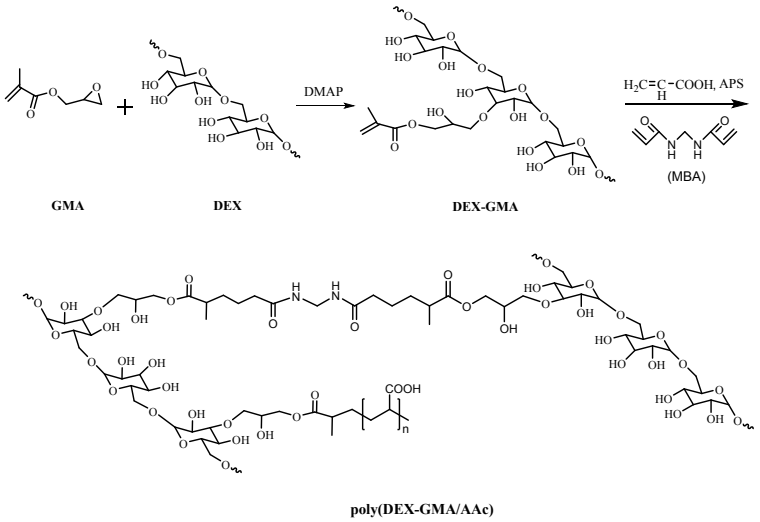
The measured D_T of standard Dextran, standard Chitosan and poly(DEX-GMA/AAc) was 5.104×10^{-9}, 8.592×10^{-9}, and 1.653×10^{-9}, respectively. After calculating, α=1.095, β=1.810, and M_W(poly(DEX-GMA/AAc))=74563.

Method 2: Viscosity test method was followed as book of physicochemical experiment[1]. Theory: The viscosities of solution and solvent are measured by viscometer in the same condition. The relative viscosity (η_r) is the ratio of the efflux time of solution to the time of solvent. Then specific viscosity can be calculated ($\eta_{sp}=\eta_r-1$). Intrinsic viscosity ([η]) can be expressed by the following equation which is $\lim_{c\to0}\eta_{sp}/c=[\eta]$. According to Mike nonlinear equation ($[\eta]=KM^{\alpha}$), the relative molecular mass of sample would be calculated.

Process: Efflux time of solvent (distilled water) and solution (c(poly(DEX-GMA/AAc)=1mg/mL) were measured by Ubbelohde Viscometer. After plotting and calculating, the intrinsic viscosity of poly(DEX-GMA/AAc) was obtained ([η]=341.22). α and K of microgel particles were referenced from konjac glucomannan's, because they showed similar structure and property. And then, the numerical value of [η] (341.22) , K(5.06) and α (0.0506) were substituted into the equation

$[\eta]=KM^{\alpha}$. After calculating, the molecular weight of poly(DEX-GMA/AAc) was obtained (M_{η}=119700).

Supplemental Figures



Scheme S1. Synthesis of poly(DEX-GMA/AAc) microgel particles.

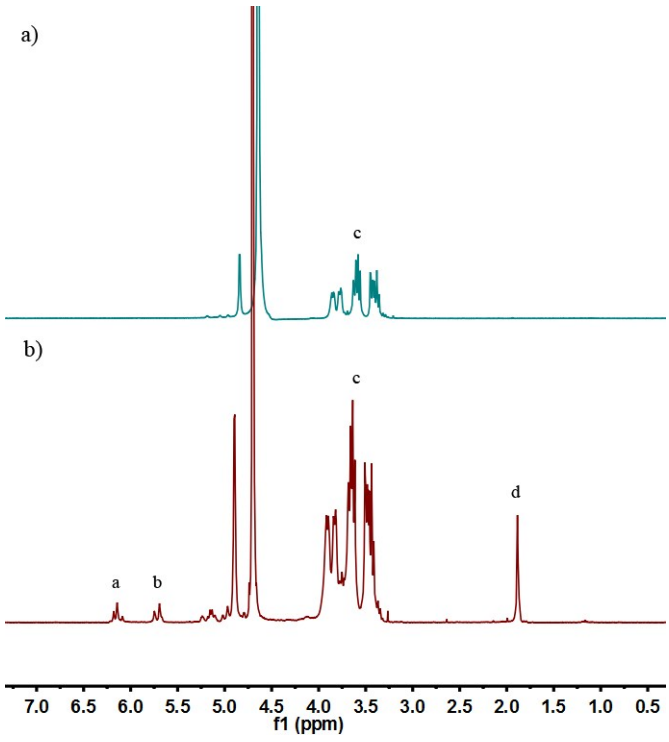


Fig. S1 ^{1}H-NMR spectra (400MHz, D_2O) of DEX (a) and DEX-GMA (b)

Fig. S2 FTIR spectra of (a) DEX-GMA and (b) poly(DEX-GMA/AAc)

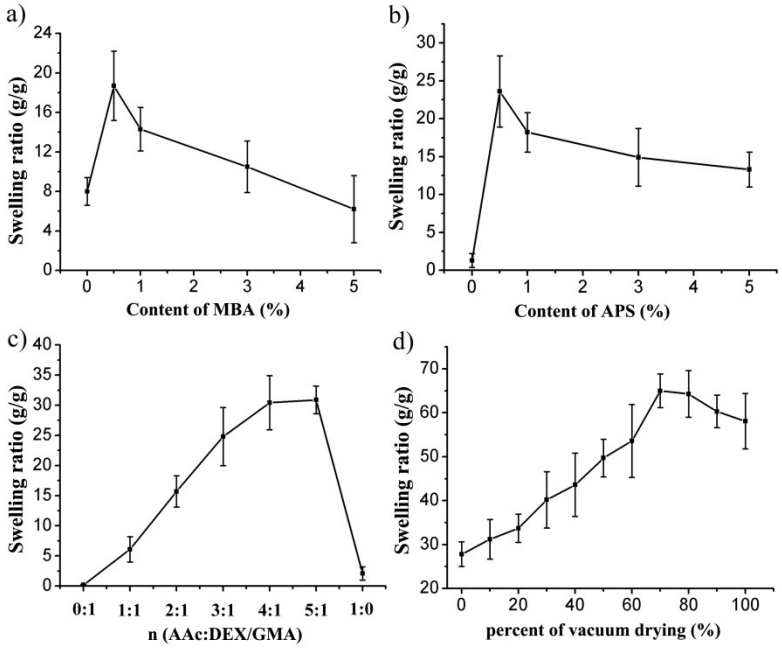


Fig. S3 The change of swelling ratio synthesized at different conditions. (n=5) (a) different content of MBA (APS 10%, AAc: DEX-GMA=1:1, lyophilization). (b) different content of APS (MBA 0.5%, AAc: DEX-GMA=1:1, lyophilization). (c) different mole ratio of AAc and DEX-GMA (MBA 0.5%, APS 0.5%, lyophilization). (d). different percent of vacuum drying (MBA 0.5%, APS 0.5%, AAc: DEX-GMA=4:1).

References:

1. H. Xia, *physicochemical experiment*, Press of Nanjin university, China, 2006.