Effect of the disulfide bond and polyethylene glycol on the degradation and biophysicochemical properties of polyurethane micelles

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Dissipative particle dynamics (DPD) simulation

The dissipative particle dynamics (DPD) method is a mesoscopic simulation technique suitable for complex fluids, proposed by Hoogerbrugge and Koelman[1-2], and revised by Espanol and Warren[3]. The components used in this simulation comprise of polyurethane micelles (containing LDI, GQA, PDO, CYSD, PCL and mPEG) and water.

The force between each pair of beads comprises of a conservative force F^C, a dissipative force F^D and a random force F^R obeying the following equation:

$$f_i = \sum_{j \neq 1} (F_{ij}^C + F_{ij}^D + F_{ij}^R) \quad (1)$$

We can obtain Flory–Huggins parameters from solubility parameters[4]:

$$X_{ij} = (\delta_i - \delta_j)^2 V_{ref}/RT \quad (2)$$

where δ_i and δ_j are the solubility parameters of a pair of interacting particles, V_{ref} is the average molar volumes of two particles, which could be calculated using discover and amorphous cell modules in Materials Studio software with the COMPASS force field at 298K and under atmospheric pressure, and R is gas constant, T is temperature. Groot and coworkers[5-6] proposed the relationship between α_{ij} and the Flory-Huggins parameters (x_{ij}) to determine the conservative force:

$$F_{ij} = \begin{cases} \alpha_{ij} + 3.27x_{ij} & \rho = 3 \quad (3) \\ \alpha_{ij} + 1.45x_{ij} & \rho = 5 \quad (4) \end{cases}$$

Where α_{ij} is the interaction parameter between particles of the same type, and can be calculated according to the follow Equation, and ρ is the density.

$$\alpha_{ij} = 75K_bT/\rho \quad (5)$$

The bead density of the system is close to that of water with $\rho = 3$, and the cut-off radius is $r_C = k_BT = 1$. Therefore, from Equations (3) and (5), α_{ij} can be obtained:

$$\alpha_{ij} \approx 25 + 3.27x_{ij} \quad (6)$$

The calculated interaction parameters of polyurethane micelles systems (298 K, atmospheric pressure) according to Equations (1)-(5) are given in Table S2. It is worth noting that the x-parameter between mPEG and water was taken as 0.30 proposed by Groot and Rabone[7]. The simulation systems contained polyurethane micelles and water in a cubic simulation box of size $30 \times 30 \times 30\, r_c^3$ with a periodic boundary condition. The total beads were 24,000, the spring constant C was set as 4.0. To obtain the result, 100,000 DPD steps

adopted were sufficient for achieving simulation equilibrium and steady results, and the time step was chosen as 0.05. All the computational works were performed using DPD program incorporated in the Materials Studio software (Accelrys) installed on a DELL PowerEdge SC430 server.

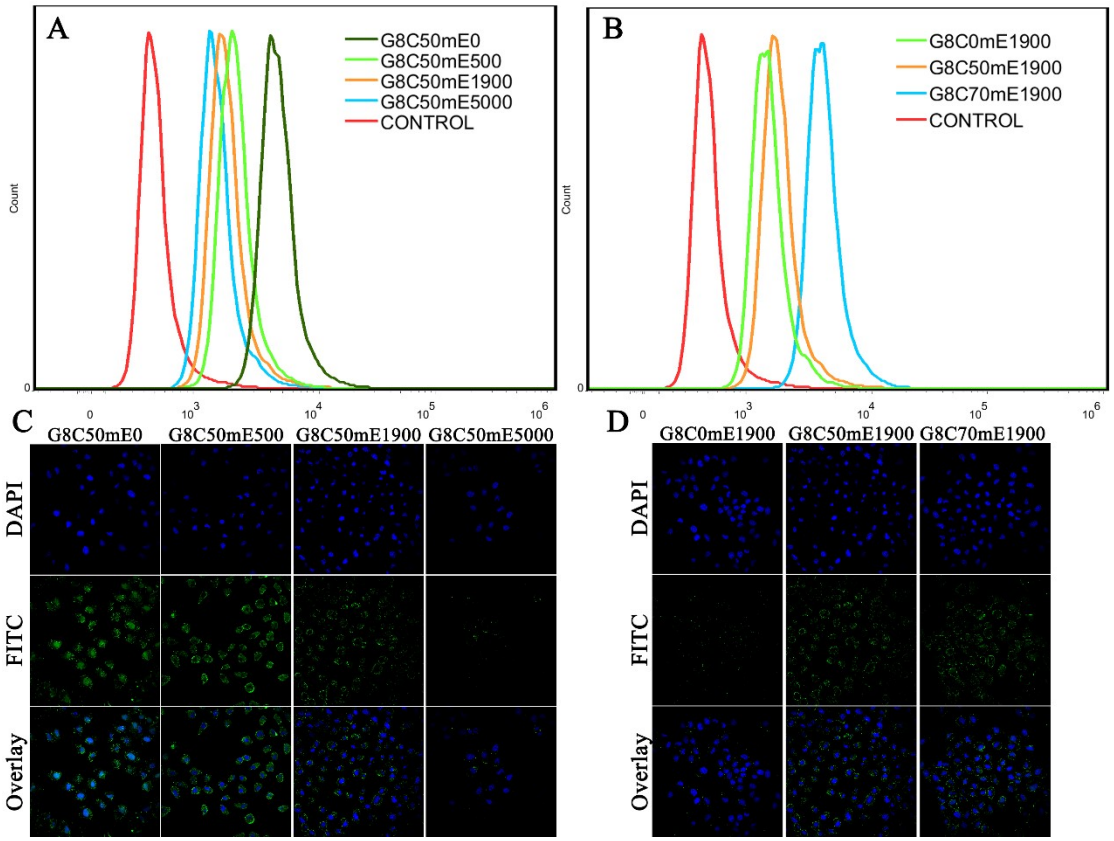

Figure S1. Flow cytometry histogram profiles (A, B) and CLSM images (C, D) of Hela cells incubated with polyurethane micelles containing different PEG lengths (A, C) and different CYSD content (B, D) for 1 h of incubation.

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