Polymer nanospheres are useful drug delivery techniques. The nanospheres are formed by molecular self-assembly, which is a process where molecules spontaneously assemble into stable structures. The ability for a nanosphere to undergo conformational changes is a beneficial characteristic for drug delivery techniques. Recently, a special type of polymer nanosphere was developed by Xiao et al. The particles were able to transform from a spherical conformation to an oblong conformation due to the photo-deformability of azo-dyes.[1] The azo-dye component is toxic to the human body and could not be used in drug delivery. Retinoic acid is a biocompatible molecule and shows very cis- and trans-conformational changes as the azo-dyes, which suggests a photo-deformable characteristic. The polymer PAN-stat-P4VP was synthesized and coupled with retinoic acid (RA). Also, a complex was formed between PAN-stat-P4VP and the azo-dye-metanil yellow (MY) to use as a comparison in the PAN-stat-P4VP/RA complex. The nanospheres were exposed to a polarized laser and characterized using Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) analysis, and scanning electron microscopy (SEM). The data from this experiment shows the polymer may have been too small, or the polymer chain itself was too short. Furthermore, the complex did not self-assemble into a sphere. The lack of a spherical conformation is further evidence that the molecular weight of the polymer may have been too small, or the polymer chain itself was too short. The SEM images of the PAN-stat-P4VP/MY self-assembly post laser treatment (Figure 8) shows that the particles are slightly deformed. We expect the more apparent deformation will be observed with the increase of exposure time.

Preparation of PAN-stat-P4VP polymers

RAFT of 4-vinylpyridine and acrylonitrile was performed using cumyl dithiobenzoic acid (CDB) as a macroRAFT agent and 2.2’-azobisisobutyronitrile (AIBN) as an initiator. The molar ratio was [CDB:RAFT]: [AIBN] = 4 : 1. A dry three-neck flask was filed with 150 mL of dimethylformamide (DMF) and purged with nitrogen gas for 15 minutes. The CDB macroRAFT agent was added to the flask. DMF was used to dissolve the AIBN, and the solution was added to the addition funnel. In a 10 mL graduated cylinder the acrylonitrile and 4-vinylpyridine were mixed, and five drops of the solution was added to the solution in the addition funnel. The solution in the three-neck flask was heated to 60°C, and the solution in the addition funnel was slowly added drop by drop to the addition funnel. The solution was reacted at 70°C for 30 minutes. After 30 minutes, the 4-vinylpyridine and acrylonitrile solution was put into the addition funnel and added very slowly drop wise to the three-neck flask. The solution was reacted at 70°C for overnight. The DMF was evaporated using the Rotavapor® and the remaining solution was poured into copious amounts of deionized water. The precipitate was filtered and dried for two days at 60°C in a vacuum oven.

Fabrication of hollow polymer nanospheres

PAN-stat-P4VP was neutralized by deionized water. A 10 M solution was prepared using a 5% ethanol. A 10 M solution of retinoic acid was prepared by neutralizing the retinoic acid with 0.1 M NaOH and dissolving it in 75% ethanol. The retinoic acid solution was added drop wise to the polymer solution. The Rotavapor® was used to evaporate the ethanol, and the remaining solution was cooled to room temperature and filtered via vacuum filtration. The filtrate was left to air dry overnight and then dried at 60°C in a vacuum oven. The polymer/retinoic acid precipitate was dissolved in a couple drops of DMF. A few drops of deionized water were then added to the DMF mixture to form the colloid. Ethanol was also used as a solvent to prepare the colloid.

Characterization and conformational change of polymer nanospheres

The particles were exposed to a polarized laser light of 800nm and 1.35mWatts of power for five minutes. The polymer nanospheres were characterized using Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) analysis, and scanning electron microscopy (SEM).

Discussion

The data suggests that a complex between the PAN-stat-P4VP polymer and the retinoic acid was formed. However, the complex self-assemble into a spherical shape instead of the spherical conformation. The IR spectrum of the self-assembled shown in figure 5 provides evidence for the presence of retinoic acid in the complex but no evidence of polymer in the complex. This could suggest that the molecular weight of polymer was too small to be accurately detected by the IR instrument. The carbon-13 NMR spectrum of the complex does show evidence for the presence of retinoic acid and polymer in the complex. Since the NMR instrument was able to detect the presence of polymer in the complex, it could be a more sensitive instrument.

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The Fabrication of Photo-Deformable Polymer Nanostructures Using Biocompatible Molecules

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