

Tuning mechanical properties of liquid crystalline nanoparticles

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ABSTRACT

We report the synthesis of colloidal nanoparticles with an internal structure forming a gel-like matrix. These nanoparticles are composed of low molecular weight liquid crystal (LC) 4-pentyl-4-cyanobiphenyl (5CB) encapsulated in an LC-based polymer network. Using nanoscopic mechanical analysis, we demonstrate the ability to independently tune the shape anisotropy and stiffness by varying, respectively, the 5CB concentration and the extent of the polymer cross-linking. Based on these data, a model is introduced to account for the effect of the polymer network on the mechanical properties, thus providing novel insight into the nanomechanics of these soft particles.

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1. Introduction

Liquid crystals (LCs) are well known for their inherent self-assembly, rich phase behavior and diverse anisotropic properties. Their electrooptical properties have been exploited extensively in display technology. Recently, polymeric nanoparticles containing LC molecules (LC nanoparticles) have also attracted interest as a new class of nanomaterial [1–5]. Conventional polymeric nanoparticles consist of random coils and are isotropic in both their shape and their properties. With the incorporation of liquid crystal molecules, it is possible to introduce internal molecular order and diverse responsive properties in a nanoparticle. For example, birefringence, dielectric and diamagnetic anisotropy in these molecules provide opportunities for the LC materials to be responsive to external stimuli, such as light, electric and magnetic fields. These active properties add another dimension to a wide range of applications, including photonics, sensing and controlled release.

The development of functional LC nanoparticles continues to progress. The synthesis of LC nanoparticles has been well established with a mini-emulsion procedure [1–3]. Since then, our group has developed a polymerizable surfactant that significantly improved the stability of the LC nanoparticles [1]. A few studies have also addressed an important question: How does the molecular composition of the LC nanoparticles affect their physical properties and functionalities? Yang et al. fabricated intrinsically non-spherical

nanoparticles due to the nematic alignment of main-chain LC [4]. A shape memory effect was observed when these nanoparticles went through thermal phase transitions. Another study from our group reported the synthesis of LC nanoparticles doped with fluorescent dye [1]. We demonstrated the ability of the LC to control dye aggregation, leading to tunable fluorescence over a significant part of the visible spectrum.

In this work, we fabricate nanoparticles composed of a gel-like network and examine the effect of the molecular composition on their mechanical properties. In addition, we propose a model to account for the effect of the internal polymeric chains on the shape and stiffness of immobilized nanoparticles.

2. Material and methods

2.1. Chemicals

The liquid crystal 4-pentyl-4-cyanobiphenyl (5CB) was purchased from EMD (Licristal K15 IS-1143). The polymerizable LC acrylic acid 8-(4'-cyano-biphenyl-4-yloxy)-octyl ester (AC8CB), the cross-linking agent DACTP11 and the polymerizable surfactant AC10COONa were synthesized as previously reported [1]. The thermal initiator α,α' -azoisobutyronitrile (AIBN) was purchased from Sigma-Aldrich.

2.2. Synthesis of nanoparticles

Gel-like LC nanoparticles were synthesized using a mini-emulsion process [1–3]. In brief, 15 mg of surfactant AC10COONa was dissolved in 10 ml of water. The LC components 5CB, AC8CB and

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DACTP11 at various molar ratios were mixed with 2 wt% AIBN in 500 μl of chloroform. The solution was added dropwise to the surfactant solution, stirred for 1 h and then sonicated in an ice bath for 2 min at 90% amplitude with an Ultrasonic Processor (ACE Glass, Inc) and probe (Model LV261). The resulting mini-emulsion was stirred under nitrogen at room temperature for 15 min to remove oxygen and then heated in an oil bath at 64 $^{\circ}\text{C}$ for 6 h to evaporate the chloroform and promote polymerization. The nanoparticle suspension was centrifuged to reduce the polydispersity (see [Supporting Information](#)) and deposited on silicon and gold substrates for further characterization. Scanning electron microscopy (SEM) of the LC nanoparticles was performed using a Leo Supra 55 (Carl Zeiss SMT AG). Hydrodynamic diameters of the nanoparticles suspended in water were measured and analyzed using Nanoparticle Tracking System (LM-10, NanoSight Ltd.).

2.3. Nanoparticle deposition on solid substrates

The nanoparticles were deposited on acid-cleaned Si wafers for SEM observation. The nanoparticle suspension was diluted, and nanoparticles were deposited by slow vertical pulling from the suspension using an Apt Microstepping dip-coater (Thorlabs) at 250 nm/s. This deposition method produced monolayers of nanoparticles on the wafers.

Isolated nanoparticles were adsorbed onto gold substrate for morphology and mechanical studies with SEM and AFM. Gold-coated mica substrate was first functionalized with primary amine by immersion into 1 mM aqueous solution of cystamine for 1 h. The amine-functionalized gold substrate was then rinsed with water and immersed into a diluted nanoparticle solution for 10 min. The substrate was rinsed with water and blown dry with N_2 gas.

2.4. Atomic force microscopy (AFM)

MultiMode AFM with a Nanoscope IIIa controller (Digital Instruments) was used to obtain topographic images of LC nanoparticles and force–distance curves. All images were recorded in ambient conditions (24 $^{\circ}\text{C}$, 40% relative humidity). For tapping mode imaging, a silicon SPM sensor with Pt/Ir coating (NanoWorld AG) was used. The typical resonance frequency of the cantilever was 75 kHz, and the force constant was about 2.8 N/m.

Nanoscale indentation measurements were taken on LC nanoparticles adsorbed on amine-functionalized gold substrates. A Si cantilever (FMR, NanoWorld AG) with tip radius of ~ 10 nm and spring constant of 2.3 N/m (calibrated by manufacturer) was used for all five nanoparticle samples. The calibration of the spring constant was precise within 10%; however, this precision was better than the spread in the Young's modulus measured from different nanoparticles within a single sample (r.m.s. $\sim 20\%$), and hence, uncertainty in the spring constant was neglected. Force–distance curves (32×32) were recorded in force–volume mode to map a $2 \mu\text{m} \times 2 \mu\text{m}$ region containing a number of nanoparticles. Height topography of the same region was simultaneously recorded at each position where the force–distance curves were obtained. A small triggering parameter for tip deflection was set to ensure that the indentations into the nanoparticles were less than 10%; in this method, the approaching curve was stopped as soon as a pre-set deflection of the cantilever was detected. For data analysis, ten nanoparticles in each image were selected and only the force–distance curves located on top of the nanoparticles were used. The approaching force–distance curves were then translated into force–indentation curves, thus allowing calculation of the Young's modulus.

3. Results and discussion

The gel-like LC nanoparticles were composed of diacrylate cross-linker DACTP11, monoacrylate liquid crystal monomer AC8CB and nonreactive liquid crystal 5CB and capped with monoacrylate surfactant possessing a carboxylate head group, AC10COONa (Fig. 1). The acrylate components were thermally polymerized to create a polymer network, while the nonreactive 5CB was encapsulated in the matrix via hydrophobic and π – π interactions. The surfactant AC10COONa acted as an interface allowing the hydrophobic nanoparticles to be dispersed in water with the carboxylate head group providing a negative charge on the nanoparticle surface.

In order to investigate the effect of composition on the nanoparticle morphology and stiffness, systematic variation of the cross-linking density and mole percent of low molecular weight (non-polymerizable) LC was carried out to produce five nanoparticle populations. All samples had polydisperse size distributions with particles that were stable in both aqueous and dry conditions. The molecular components and average hydrodynamic diameter are listed in Table 1. Each nanoparticle population is expected to exhibit a LC phase based on Larentovich's model for LC droplets [6] and the fact that they are predominantly composed of the well-known nematic 5CB and the monoacrylate AC8CB, which also has a nematic phase at room temperature [7]. Due to the small size of the nanoparticles, light microscopy could not be used to observe the phase behavior, though bulk mixtures similar to the ratios used for the nanoparticle populations showed nematic textures under polarized light (data not shown).

The morphology of nanoparticles was assessed by dispersion and immobilization of samples on both Si and gold substrates. Over the range of cross-linking densities, SEM images reveal a distinct variation in the spreading of the nanoparticles on the surface. Specifically, as the cross-linking was decreased, the nanoparticles appeared to flatten on the substrate to a much larger extent than particles with higher cross-linking densities (Fig. 2). To quantify the shape of the nanoparticles, the lateral diameter, d , of 100 individual nanoparticles immobilized on a gold substrate was measured from the SEM image. The same substrate was used to record the AFM topography image and determine the height, h , of different 100 nanoparticles. The AFM images were not used to assess d because of a significant tip broadening effect. In this manner, corresponding distributions of height and diameter were obtained for each sample (Fig. S2, Supporting Information). We note that for each population comparison of the average volume of a nanoparticle calculated from the hydrodynamic diameter in

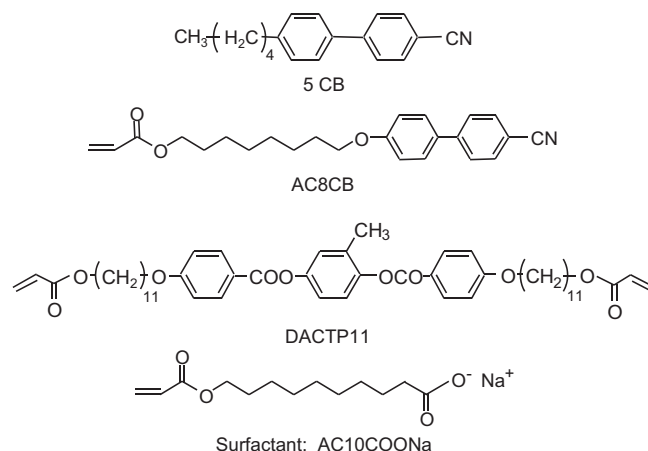


Fig. 1. Chemical structures of molecules composing the nanoparticles.

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