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Ordered Polymer Microstructures Synthesized from Dispersions of Liquid Crystal Mesogens

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We have manufactured highly ordered polymer spheres, rods and fibrils from reactive mesogens using a template synthesis approach. The structures were fabricated by photo-polymerizing reactive mesogens in confining templates (spherical and cylindrical) while in the nematic phase. The spheres were produced from suspensions of a mesogen in glycerol and the rods and fibrils by a confining template method. The dielectric and optical anisotropy of the liquid crystalline monomer is captured by photo-polymerization. The balls are Electro-Mechano-Optical (EIMO) in nature undergoing a mechanical reorientation in the presence of an applied electric field, and therefore may be useful for electro-optic applications. The fibrils possess unusual properties due to their anisotropy and can be used to produce mesoscopic structures by self assembly. We present a number of these novel structures and methods for their fabrication.

Keywords: reactive mesogens; liquid crystals; optical texture

INTRODUCTION

The fabrication of oriented polymer structures is attractive for producing structures with highly anisotropic materials properties [1]. The polymerization of monomers with a liquid crystal phase has been used to produce both very strong materials such as aramid fibres [2].

and highly birefringent polymer films [3]. Broer and co-workers have demonstrated the manufacture of highly ordered films from reactive mesogens [4] and Chien and co-workers have utilized reactive mesogens in polymer-stabilized liquid crystal composites [5]. Curing reactive mesogens while they are in a liquid crystal phase can result in highly ordered films. In effect the liquid crystalline orientational order is 'locked in' by photo-polymerization. We present a study of oriented polymer structures fabricated from reactive mesogens, with a nematic liquid crystal phase, that are constrained to curved templates and subsequently polymerized. A rich variety of structures are possible. We have successfully fabricated ordered spheres in a fluid and ordered rods and tubes using a template approach. In addition to these basic structures we present examples of self-assembled structures from oriented polymer fibrils.

In 1904 Lehmann observed optical texture in liquid crystal droplets suspended in a fluid [6]. This early work foreshadowed the development of polymer dispersed liquid crystals (PDLC) materials [7]. In a PDLC material, liquid crystal filled cavities are dispersed within a polymer matrix. A variety of optical textures can be observed in PDLC droplets depending on the configuration of the liquid crystal molecules within the droplet [8]. The configuration within each droplet depends on the size of the cavity, the nature of the molecular anchoring at the liquid crystal polymer interface and the elastic properties of the liquid crystal [9]. The surface interactions can be modified by the use of surfactants and hence the configuration can be modified [10]. The effects of surface interactions and confinement of liquid crystals have been studied extensively for spherical and cylindrical geometries [11]. We have been able to capture the order of low molecular weight liquid crystals in confined geometries by photopolymerization and thus produce highly oriented solid polymer structures that are very different from their low molecular weight counterparts in PDLC droplets.

EXPERIMENTAL

The underlying principle employed in this study for the fabrication of ordered microstructures is template synthesis. We have manufactured ordered spheres by suspending low molecular weight reactive mesogens in glycerol and photo-polymerizing the suspended droplets while in the nematic phase. In addition we have fabricated rods and tubes using a ceramic filter membrane (Anopore) as a template.

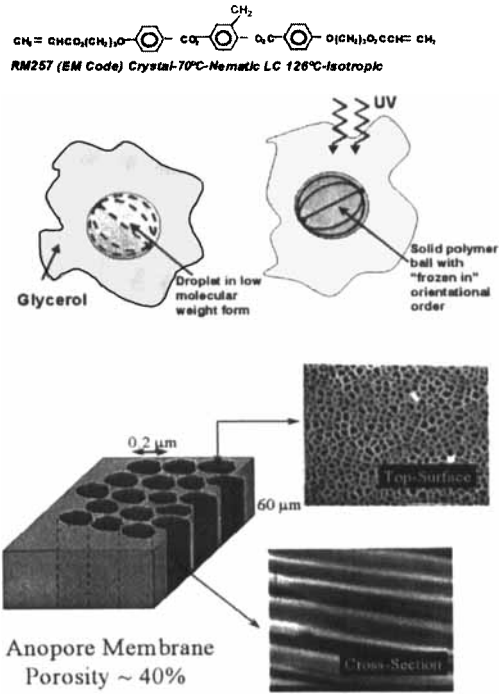

FIGURE 1 Liquid crystal monomer and templates. Chemical structure of EM Industries RM257 liquid crystal monomer (a). Droplets of monomer suspended in glycerol form the template used to polymerize ordered spheres (b). Schematic representation of anopore membrane used to produce ordered rods, toroids, tubes and yarn balls.

The polymer spheres were fabricated by mixing a 2% by weight solution of photoinitiator (Darocur 1173) in 98% of EM Industries reactive monomer RM257 (see Figure 1(a)). The solution was heated to 90°C (RM257 has a stable nematic phase for T>70°C and T<126°) and mixed for approximately 30 seconds using a hand shaker. A few drops of the liquid crystal monomer were then placed in a test tube and five ml of hot 90°C glycerol (Aldrich

Spectrophotometric grade) was poured into the same tube. At this temperature, the nematic phase is stable for the RM257 reactive monomer. The mixture was maintained at 90°C, in a NuArc 26-1KS ultra violet exposure system for eight minutes to cure the reactive monomer. It should be noted that the final UV photo-polymerization must be carried out when the RM257 is in its nematic phase to achieve highly ordered structures. The fabrication of the polymer spheres is shown schematically in Figure 1(b).

In an analogous technique we have fabricated rods and tubes using a solid template of Anopore membrane (see Figure 1(c)). A 1% by weight solution of Darocur in 99% by weight of RM257 was prepared. The mixture was heated to 120°C on a glass slide and an Anopore membrane place on the top of the mixture. The membrane filled by capillary action and the filled template was then cured as described for the spheres above. Fibrils were also fabricated in this way using a diluted mixture of the mesogen in chloroform. A variety of structures were produced depending upon the concentration of mesogen in chloroform and surface treatment of the membrane template.

We have fabricated fibrils in an Anopore membrane from solutions of RM257 in chloroform. For example, 20% of RM257 in chloroform is permeated into Anopore membranes, and the chloroform is then evaporated off leaving behind the RM257 on the cavity walls. The membrane sample is then heated to the nematic phase and polymerized with UV. When the membrane was removed by etching in a 0.4 molar solution of NaOH we observed mesoscopic structures formed by self-assembly.

Three distinct structures were produced depending on the concentration of mesogen and the use of a surface treatment. Tubes were produced by filling the Anopore with a 12% and 20% by weight solution of RM257 in chloroform (see Figure 2(c) and (d)). Toroids (Figure 4(a) and (b)) and yarn balls (Figure 4(c) and (d)) were produced using a 25% and 12% solution of RM257 in chloroform respectively, for these two structures the membrane was also treated with lecithin. Lecithin is well known to promote alignment of low molecular weight liquid crystals perpendicular to the treated surface. The only difference between the preparation of toroids (Figure 4(a)) and yarn balls shown in Figure 4(c) is the initial concentration of RM257 in chloroform.

ORDERED POLYMER MICROSTRUCTURES

It was possible to fabricate a range of structures using the template approach. Three of these structures are shown in Figure 2: solid polymer sphere, solid cylinders and tubes. The spheres were the largest structures produced and have a diameter of approximately 10 μm, this is large enough to observe ordering with optical polarizing microscopy. This is shown in Figure 3. The optical texture is consistent with a bipolar configuration previously reported in PDLCs [8]. This is a consequence of the nematic ordering being captured by photo-polymerization.

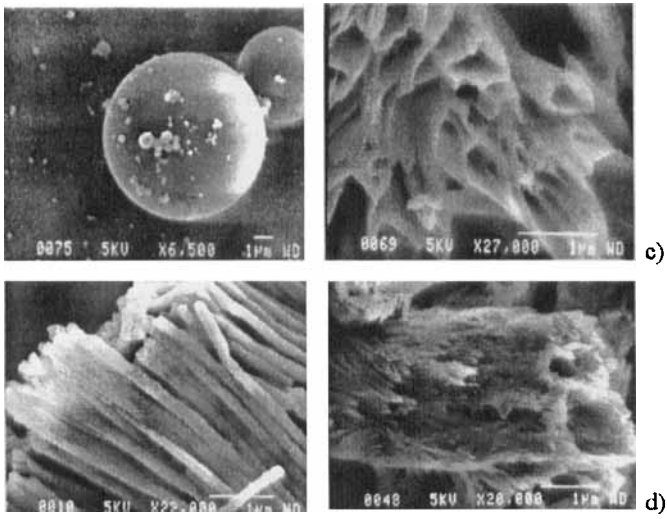

FIGURE 2 Scanning Electron Micrographs of solid microstructures from reactive mesogens. Sphere fabricated in glycerol (a), rod from RM257 in an uncoated Anopore membrane (b), self assembled tubes from uncoated Anopore membrane 20% RM257 (c) and 12% RM257 (d).

The bipolar configuration is particularly suited for electro-optic applications because the net dielectric anisotropy of the structure allows the sphere to be reoriented as a whole by an applied electric field and reorientation of the structure results in a change in optical

texture when viewed through crossed-polarizers. This is in contrast to a radial configuration that would be invariant to an applied electric field. A cavity filled with a low molecular weight liquid crystal in this configuration has a net electric dipole moment, when an electric field is applied the liquid crystal molecules reorient such that the net dipole moment aligns with the applied field. Our ordered polymer spheres also have a net dipole moment and will thus interact with an applied electric field. However, in this case the polymer sphere reorients as a whole. We have rotated a sphere using an in-plane electrode configuration (see Figure 3). The optical texture, as viewed between crossed polarizers, was observed to change as the sphere was rotated. Hence, the ordered spheres are Electro-Mechano-Optical (ElMO) in nature – they experience a mechanical reorientation in an electric field resulting in a change in optical texture.

The solid rods and tubes are also ordered on the molecular level. The possible microstructures are limited only by the templates available. It is possible to capture the orientational order of almost any confined liquid crystal system using the template approach.

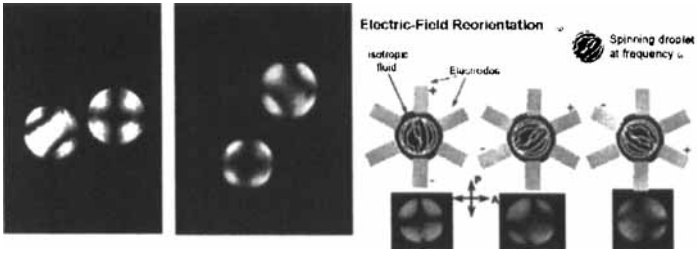

FIGURE 3 Optical polarizing microscope images of spheres fabricated from reactive mesogens in a reference position (a) and rotated by 90° (b). Rotation of an ordered sphere by an applied electric field (c) showing the change in optical texture as viewed through crossed-polarizers.

MESOSCOPIC SELF ASSEMBLY

The toroid and yarn balls shown in Figure 4 can be seen to be composed of fibrils. The cause of this self assembly is not clear, however, it is clear that the fibrils fabricated in the lecithin coated

pores tend to curl when the supporting membrane is removed while the untreated pores result in stretched out fibrils and self assembly results in tubes. It is reasonable to assume that the alignment within the fibrils is different for the treated and untreated pores and that in the former the ordering is along the length of the fibril and in the latter in the radial direction. This will be an area of future study. The self assembly reported here is very sophisticated and it is surprising how many diverse mesoscopic structures can be fabricated using the template approach.

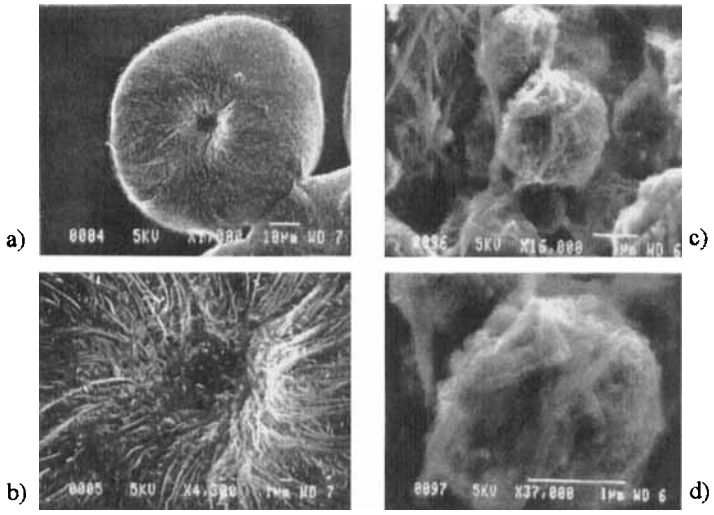

FIGURE 4 Scanning Electron Micrographs of self assembled microstructures from reactive mesogens. The toroid in (a) and (b) was produced from a 25% solution of RM257 in chloroform the Anopore membrane was coated with lecithin. The yarn balls (c) and (d) were produced in a lecithin coated Anopore membrane from a 12% solution of RM257 in chloroform.

CONCLUSIONS

We have successful fabricated a number of ordered polymer microstructures from reactive mesogens using a template approach.

These solid-microstructures retain the order of the monomer in its low molecular weight form and therefore have highly anisotropic materials properties. It may be possible to utilize these anisotropic materials properties in novel device systems. In addition we report the self-assembly of ordered fibrils on a mesoscopic scale to produce tubes, toroids and yarn balls.

ACKNOWLEDGEMENTS

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