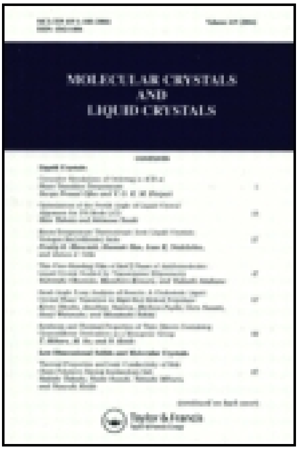

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Novel Microstructures from Confined Reactive Mesogens

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Novel Microstructures from Confined Reactive Mesogens

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Novel supramolecular self-organized microstructures with high degrees of captured mesogenic order and well-defined non-planar symmetry are presented. The molecular self-assembly of reactive mesogens is profoundly modified when constrained to non-planar templates with either spherical or cylindrical symmetry. Multi-dimensional, ordered configurations are created and indefinitely captured by photopolymerization forming solid polymer microspheres or microfibrils on the submicrometer or micrometer scale. Sophisticated microstructures and details on their structural, electrical, optical, and dynamic properties are presented, as well as the ways in which these self-organized structures can be manipulated and modified by imposed external constraints *(e.g.* interfaces, finite size effects, external fields, and constraining geometry). Scanning electron microscopy and optical microscopy studies will be presented.

Keywords: reactive mesogens; microstructures; captured mesogenic order

INTRODUCTION

Supramolecular architectures with three-dimensional control over their molecular profile are of fundamental and practical importance because of their strong anisotropic properties. Such structures can possess highly anisotropic optical, electrical, and thermo-mechanical properties which are desirable for various passive optical applications; for example, polarizers, wave-plates, optical filters, and wave-guides.[1,2]The methods to produce these ordered supramolecular polymer architectures are limited in number and no generic algorithm exists which enables complete and unrestricted control over the position of molecules in all dimensions. A method that approaches this ideal situation is the photoinitiated polymerization of liquid crystalline reactive monomers in pre-designed configurations forming dense networks with captured mesogenic order[3] or photoinitiated polymerization of small concentrations of reactive monomers in a low molecular weight non-reactive liquid crystal ordering medium for low concentration ordered polymer networks.[4,5,6]

The history of polymer networks with mesogenic order dates back to the late 1960's when researchers suggested polymerizing and cross-linking liquid crystals in their mesophases targeting highly ordered polymer systems.[7,8] Early attempts to thermally initiate bulk polymerization (thermosetting) of liquid crystal diacrylates resulted in ordered networks with strong anisotropies; however, the high processing temperatures to start polymerization were incompatible with the temperature ranges of the mesogenic phase. In addition, cross-linking and polymerization began prior to the desired phase resulting in defects. In the presence of small amounts of polymerization inhibitors, liquid crystal reactive monomers can be processed into their mesogenic state until their desired order is obtained. Now the molecular order arrangement can be captured very rapidly by exciting the dissolved photoiniator with light of the appropriate wavelength. The early studies on bulk photopolymerization of reactive mesogens were performed on monoacrylates forming linear side chain polymers.[9,10,11] In these situations, fixation of mesogenic order typically does not occur and the formed polymer still exhibits various mesophases, each at different temperatures than the low molecular weight monomer. For this reason, the photopolymerization of poly-functional liquid crystal monomers became so important. For example, free radical based photopolymerization of monolithically ordered nematic diacrylates resulted in stable polymers with the same texture and degree of order as the reactive mesogen prior to photopolymerization.[12] Other demonstrations of diepoxides[13] and liquid crystal divinylethers[14,15] polymerized by photocationic mechanisms led to analogous results. The photo-fixation of low concentrations of diacrylates[16,17] in non-reactive liquid crystals were also reported. Their intriguing electro-optic properties lead to a broad interest in these composite materials for modern optical applications.[18]

The many candidates of liquid crystal configurations and phases of the low molar mass reactive mesogens provide diversity in molecular orientation and order, all being accessible to 'capture' via the polymerization process. The established methods and techniques to induce monolithic order in liquid crystals are applicable and compatible with reactive mesogen materials to create thin films of complicated molecular architectures that are optically homogeneous and free of defects. The monomers allow a large degree of freedom in their molecular structure to tailor optical and mechanical properties of the films. Moreover, versatility in the properties of the monomeric state, for example, elastic constant constants, indices of refraction, viscosity, transition temperatures, etc., can all be manipulated by preparing mixtures of various monomers. When reactive mesogens, or mixtures thereof, with a higher functionality are polymerized in the bulk or in thin film configurations, ordered supramolecular networks are produced which exhibit stable molecular organization up to the degradation temperature of the polymer.

The studies to date on these supramolecular architectures have been limited to planar environments where the 'captured' deformation typically propagates along one dimension.[1] This paper focuses on novel ways to fabricate non-planar supramolecular structures with deformations being fixed by polymerization in two and three dimensions. This new class of polymer materials may have far reaching applications in which the supramolecular ordered network assembly is the principal active optical element.

EXPERIMENTAL

To accomplish the fabrication of supramolecular microstructures with spherical symmetry, the photoreactive mesogenic materials are emulsified in a glycerin matrix and maintained at a temperature where the nematic liquid crystal phase is stable. We procured the reactive mesogen RM257 from EM Industries (Hawthorne, NY). The RM257 material has a nematic phase temperature range of 70°C to 126°C. The dispersion is then agitated thereby forming spherical droplets suspended in the glycerin matrix. The time span and degree of agitation governs the size of the suspended droplets. The dispersion is then photopolymerized by exposing it to UV radiation which locks-in the mesogenic order indefinitely. The droplets are now robust ordered polymer 'balls' that can easily be separated from the binder and washed with compatible solvents. The ordered microstructures can then be re-dispersed into other binders for investigation.

To fabricate microfibrils with well-defined cylindrical symmetry, a membrane based synthesis route was used. The method entails the permeation of the reactive mesogen within the channels of a microporous membrane. The microporous membrane serves as an ordering template of the reactive liquid crystal. Because the porous membranes contain cylindrical pores of uniform diameter, monodispersed microfibrils of the desired material, whose dimensions can be carefully controlled, are obtained. Surface modification of the microporous template results in various molecular profiles of the reactive mesogen, which is then, exposed to UV to lock-in the mesogenic order.

A commercially available porous alumina membrane (Anopore Corp.) with 0.2 mm diameter cylindrical channels was used.[19] The membranes are permeated with the reactive liquid crystal mesogen. The molecular profile of the reactive mesogen strongly depends on the surface boundary condition of the template; for example, the Alumina membranes induce uniform homogeneous alignment (axial) along the cylinder axis for low molecular weight liquid crystals thereby stabilizing an axial structure. [20,21] The permeated template membrane is subsequently exposed to UV radiation to capture the mesogenic order within the tube. The membranes are then dissolved by immersing the composite in a solution (NaOH for alumina) yielding an ensemble of isolated fibrils.

RESULTS

A series of scanning electron microscopy (SEM) experiments were performed on both spherical and cylindrical microstructures described above. The photographs are shown in Figure 1. The spherical microstructures are depicted in Figure 1 (a) and (b). In order to extract the spheres from the glycerin for SEM viewing, a few drops of the solution were mixed with approximately 10 ml reagent alcohol and then vacuum filtered using an Anopore membrane. Deionized water was also tried as a medium in which to process the spheres but the low viscosity did not allow them to remain suspended for long periods of time. Figure 1(a) and (b) show that the spheres coagulated after polymerization. From these SEM photographs, there is no clear evidence that these structures are ordered. Later, optical polarizing microscopy will be presented which confirms captured mesogenic order.

The cylinders are shown in Figure 1 (c) and (d). Notice the well defined cylindrical diameter and diameter distribution. Again there is no clear evidence of mesogenic order within the tube from the SEM photograph. Studies using higher magnifications are planned in the future. The cylindrical fibrils shown in Figure 1(c) and (d) are connected at the bottom with a common polymer 'skin'. During the capillary fill process of the membrane with the mesogenic monomer, a thin layer of the mesogen is subsequently polymerized on the bottom surface of the membrane. A polymer 'skin' therefore remains after the NaOH etch. We have been investigating ways in which this polymer skin can be removed after fabrication or ways in which to avoid its formation but to date we have been unsuccessful.

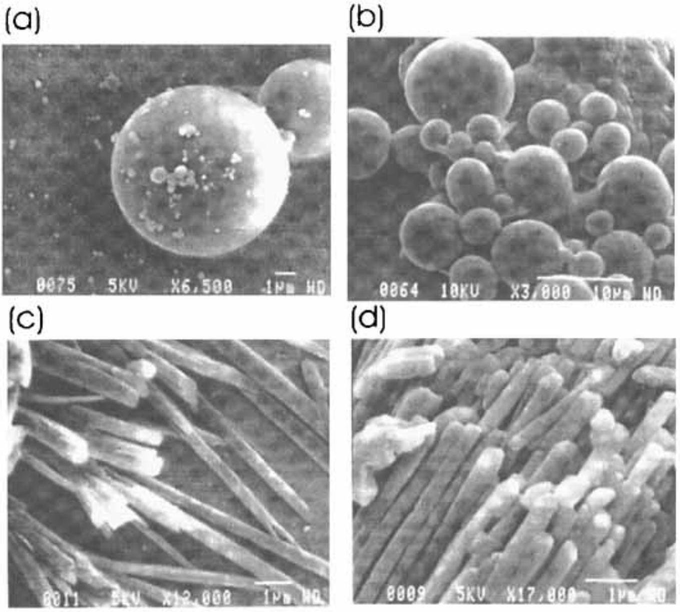

FIGURE 1 Scanning electron microscope photographs of microstructures with captured mesogenic order. Spheres are shown in (a) and (b) and cylinders in (c) and (d).

The proof of mesogenic order within the microstructures is shown in Figure 2. The ordered supramolecular network spheres are viewed between crossed polarizers of an optical microscope. The strong interference pattern depicts the optical anisotropy confirming highly ordered supramolecular ordered microstructures. Figure 2 (a) depicts a radially aligned network, (b) and (c) depict the axial structure that was formed under two different electric field strengths and therefore are highly aligned, and (d) shows the bipolar structure. Doping the glycerin matrix with a small percentage of Lecithin formed the structures that have radial (homeotropic) alignment. Lecithin is a known surfactant that induces homeotropic alignment. The diversity in structures presented in Figure 1 are brought about by modifying the gylcerin binder, which supported the microstructures during photopolymerization, thereby altering the surface boundary conditions prior to polymerization. If one were to observe a pure low molecular weight nematic liquid crystal droplet configuration between crossed polarizers, it would be strikingly reminiscent of those shown in Figure 2 for reactive mesogens. This is because the optical interference pattern of the spherical supramolecular microstructure unambiguously show that the microstructure has captured the low molecular weight mesogenic order and anisotropy, and remains indefinitely after photopolymerization.

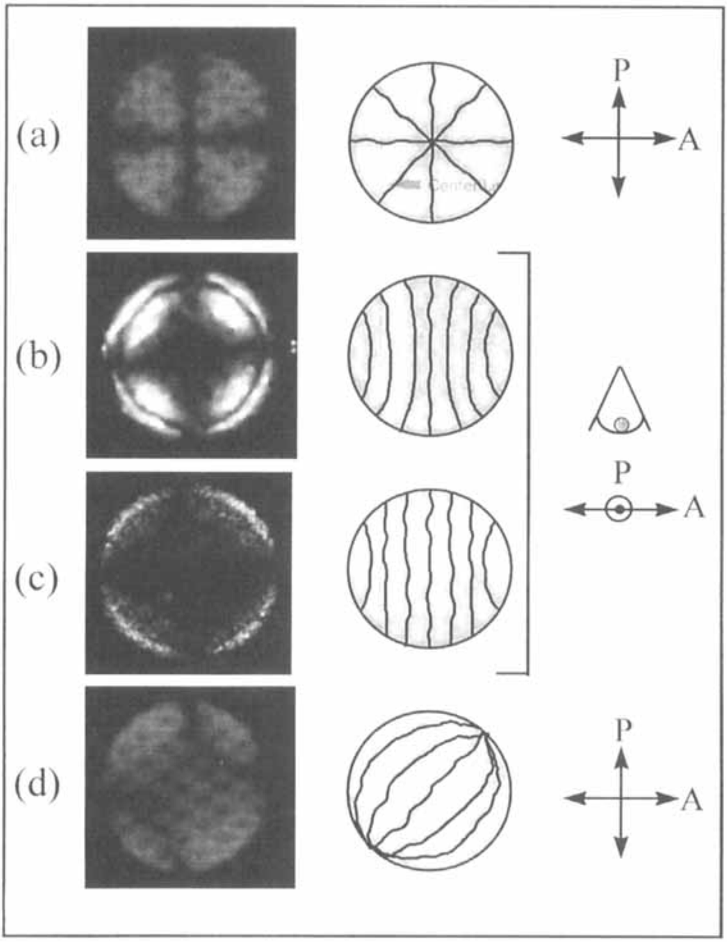

FIGURE 2 Spherical microstructures that were formed from reactive mesogens: (a) radial; (b) low field axial; (c) high field axial; and (d) bipolar. Although these resemble low molecular weight droplets, they are solid polymer spheres. The

spheres are approximately 25 mm in diameter.

We have also begun investigations of reorienting these microstructures in electric fields. Since the cylinders are attached to a 'skin' we have been unable to confirm alignment in electric fields. We have observed reorientations with the spherical structures in the bipolar configuration. This will be the focus of a subsequent paper.

CONCLUSIONS

Novel supramolecular, self-organized microstructures with well defined non-planar symmetry, high degrees of captured mesogenic order, and strong anisotropic optical and dielectric properties are presented. These unique attributes, in conjunction with their versatile fabrication and processing, robust thermal and mechanical stability, and responsiveness to external fields provides exciting new opportunities in polymer and liquid crystal science and technology. We have provided SEM results of well defined microstructures with spherical and cylindrical symmetry. Optical polarizing microscopy on large spheres clearly shows that the microstructures have captured the mesogenic order prior to polymerization. We are currently engaged in a number of fundamental and applied studies to understand their structure and morphology, and to look for new and innovative applications for this novel class of materials.

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References

[1] I. Heynderickx, D.J. Broer, T. Tervoot-Engelen, *J. Mater. Sci.* **27,** 4107 (1992).

[2] G.P. Crawford, T.G. Fiske, and L.D. Silverstein, *U.S. Patent 5, 726, 730* (March 10, 1998).

[3] D.J. Broer, in *Liquid Crystals in Complex Geometries Formed b Polymer and Porous Networks* (Taylor and Francis, London, 1996) edited by G. P. Crawford and S. Zumer.

[4] R.A.M. Hikment, B.H. Zwerver, and D.J. Broer, *Polymer* **33,** 89 (1992).

[5] D.K. Yang, J.L. West, L.C. Chien, and J.W. Doane, *J. Appl. Phys.* **761** 1331 (1994).

[6] G.P. Crawford, A. Scharkowski, S. Zumer, and J.W. Doane, *Phys. Rev. E* **52,** R1273 (1995).

[7] J.H. Wendorf, in *Liquid Crystal Order in Polymers* (Academic Press, New York, 1969) ed. A. Blumestein.

[8] P.G. de Gennes, *Phys. Lett.* **28A,** 725 (1969).

[9] P.J. Shannon, *Macromolecules* **17,** 1873 (1984).

[10] D.J. Broer, H. Finkelmann, and K. Kondo, *Makromol. Chem.* **190,** 19 (1988).

[11] C.E. Hoyle, C.P. Chawla, A.C. Griffin, *Mol. Cryst. Liq. Cryst.* **157,**639 (1988).

[12] D.J. Broer, G.N. Mol, and G. Challa, *Makromol. Chem.* **192,** 59 (1991).

[13] S. Jahromi, J. Lub, and G. Mol., *Polymer* **35,** 621 (1994).

[14] H. Johnson, H. Anderson, P.E. Sundell, U.W. Gudde, and A. Hult, *Polymer Bul.* **25,** 641 (1991).

[15] H. Anderson, U.W. Gedde, and A. Hult, *Polymer* **33,** 4041 (1992).

[16] R.A.M. Hikmet, *J Appl. Phys.* **68,** 4406 (1990).

[17] R. Stannarius, G.P. Crawford, L.C. Chien, and J.W. Doane, *J. Appl. Phys.* **70,** 135 (1991).

[18] G.P. Crawford and S. Zumer *in Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks* (Taylor and Francis, London, 1996) Chapter 1, ed. G.P. Crawford and S. Zumer.

[19] G.P. Crawford, L. Steele, R. Ondris-Crawford, G. Iannacchioni, J. Yeager, and D. Finotello, *J. Chem. Phys.* **98,** 7788 (1992).

[20] G.P. Crawford, R. Ondris-Crawford, J.W. Doane, and S. Zumer, *Phys. Rev. E* **35,** 3647 (1996).

[21] G.P. Crawford, R. Ondris-Crawford, J.W. Doane, and S. Zumer, *Phys. Rev. Lett* **70,** 1838 (1993).