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Microtubule particle dispersion in liquid crystal hosts

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Microtubule particles and metal-coated microtubules were dispersed in various host liquid crystal mixtures. Dispersion effects were evaluated as a function of liquid crystal type, viscosity, dielectric anisotropy and surface interaction. Experimental results indicated that all the types of liquid crystals studied were aligned perpendicular to the microtubule surfaces, regardless of liquid crystal composition or various surface coatings used on the metal-coated microtubules. Low concentrations of the metal-coated microtubules in nematic liquid crystal hosts were aligned by flow or cell surface alignment conditions, and could be modulated by electric or magnetic fields. We observed better microtubules dispersion uniformity in high viscosity liquid crystal host mixtures and in liquid crystal-monomers than in isotropic fluids. Microtubules particles dispersed in ROTN–404 liquid crystal mixture had a much higher birefringence in the microwave region than dispersion in a paraffin oil.

1. Introduction

1.1. *Description of microtubules*

The microtubules used in this study are self-organizing microstructures formed from lipids with diacetylenic lecithin structures. The formation and properties of these microtubules were discovered in pioneering work by a group of researchers working in the Bio/Molecular Engineering Branch of the Naval Research Laboratories [1–5]. They also discovered that much greater stability and many other important properties were obtained by coating these microstructures with metal [6, 7]. The studies in this paper were made using material supplied by the NRL group, either as bulk lipid material, microtubules, or metallized microtubules.

Microtubules were grown by the Naval Research Laboratories from the diacetylenic lecithin 1,2-bis(10,12-tricosadiynoyl)-*sn*-glycero-3-phosphocholine, abbreviated as $DC_{23}PC$, whose chemical structure is shown in figure 1. Most of our studies on microtubule particle dispersions in liquid crystal hosts were made with metallized microtubules. We started our studies with copper-coated microtubules, and then used mainly ones which were coated with permalloy or nickel because these were both ferromagnetic and readily aligned by magnetic fields as well as electrical fields.

Metallized microtubules usually have the shape of a hollow cylinder, and have fairly uniform diameter (from a given batch) which is often about 0·6 μm. Their length (after metallization) was usually in the range of 5 to 100 μm, depending upon the starting microtubule sample and the handling procedures in metallization and separation. The median length of most of the microtubule samples used in our experiments was usually in the range of about 10 to 30 μm. Figure 2 shows scanning electron microscope pictures of individual permalloy-coated microtubules. These two pictures were selected

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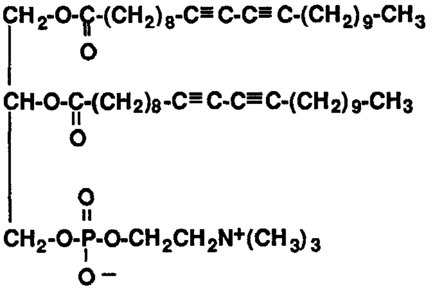


$$\begin{array}{l} CH_2\text{-}O\text{-}\overset{}{\underset{\underset{O}{\parallel}}{C}}\text{-}(CH_2)_8\text{-}C\equiv C\text{-}C\equiv C\text{-}(CH_2)_9\text{-}CH_3 \\ | \\ CH\text{-}O\text{-}\underset{\underset{O}{\parallel}}{C}\text{-}(CH_2)_8\text{-}C\equiv C\text{-}C\equiv C\text{-}(CH_2)_9\text{-}CH_3 \\ | \\ CH_2\text{-}O\text{-}\overset{\overset{O}{\parallel}}{\underset{\underset{O^-}{|}}{P}}\text{-}O\text{-}CH_2CH_2N^+(CH_3)_3 \end{array}$$

1,2-bis(10,12-tricosadiynoyl)-sn-glycero-3-phosphocholine

Figure 1. Chemical structure of microtubule lipid material, $DC_{23}PC$.

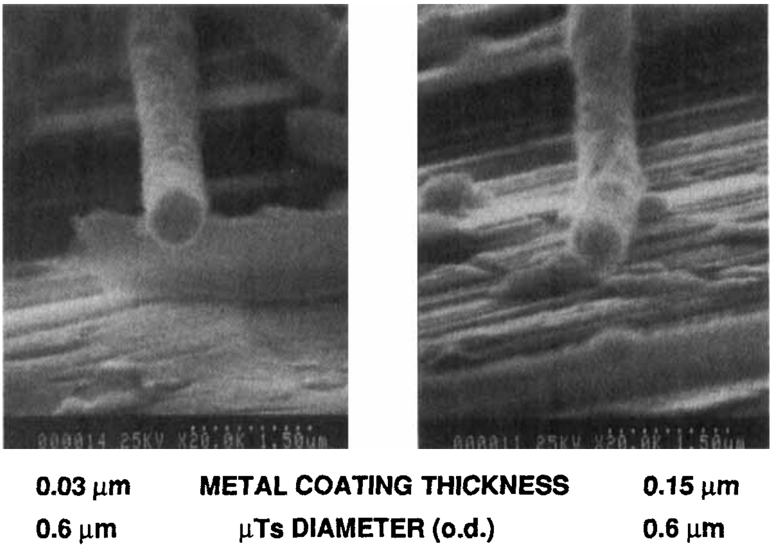


Figure 2. Scanning electron microscope pictures of permalloy-coated microtubules.

from the same batch to illustrate the variation that occurs in the thickness of the metallization. Both microtubules were about 0·6 μm in diameter, but the metal coating thickness was 0·03 μm for one and 0·15 μm for the other. The metal coating is on the inside as well as the outside of the microtubule, with a thin layer of lipid structure in between. The thickness of the metal coating was usually more uniform in the Ni-coated microtubules, particularly when polyvinylpyrrolidone was used in the plating solution.

1.2. *Microtubules dispersion in fluids*

Small particles often disperse poorly in liquid media. In low viscosity media, both in a highly polar fluid such as water and in a non-polar fluid such as FC-77 fluorocarbon (from 3 M), the metallized microtubules tend to aggregate loosely. However, both permalloy and nickel coated microtubules dispersed well in many viscous liquid media without the undesirable effect of aggregations, particularly when the microtubules had been surface treated. Our experiments utilized some isotropic and anisotropic liquid media to disperse and suspend metallized microtubules, and compared the dispersion effect in paraffin wax oil (Fluka PW76234) to liquid crystal mixtures, such as ROTN-404.

Because the metallized microtubules have a high specific density, of about 4, they settle out in nearly all common fluids. When dispersed in a high viscosity ($>100\,\mathrm{cP}$) media, their suspension time can be increased to the order of hours. Our experiments on settling rates demonstrated that a uniformly distributed suspension of metallized microtubules in paraffin oil has at least two orders of magnitude longer settling time than calculated for a layer of microtubules in this media.

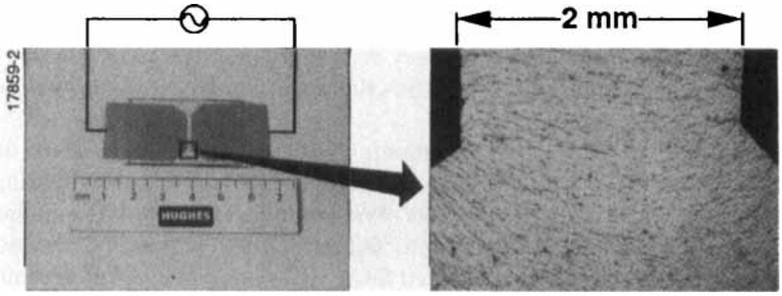
1.3. *Electric-field alignment of microtubules in isotropic liquids*

Electric fields alignment of metallized microtubules in fluid dispersions is readily observed in thin cells under a microscope. For example, Cu-coated microtubules (about 10 to 60 μm in length) dispersed in an optical cement fluid (Norland NOA-65) and placed in a 25 μm layer between glass slides were aligned by a lateral electrical field of 100 V (60 Hz) across a 2 mm gap between parallel metal shim electrodes. An overall view of this cell is shown in figure 3, which also has another microscope picture showing the curved alignment pattern of the microtubule in the inhomogeneous region at the edge of the electrodes. Under these conditions the microtubules were aligned mostly perpendicular to the electrode surface and into strings containing filament-like groups about 200 to 800 μm long.

A freely suspended dispersion of metal particles would be expected to form aggregates in the presence of a non-uniform external electric field E (or magnetic field B) due to the resultant attractive force F acting on a dipole moment p in the presence of the field gradient $\mathrm{d}E/\mathrm{d}x$ (where x is the displacement along maximum field gradient), as indicated in equation (1).

$$F = -p(\mathrm{d}E/\mathrm{d}x). \qquad (1)$$

Thus, some filamentation effects might be expected in the inhomogeneous field region shown in figure 3. The metallized microtubules themselves may contribute to local field inhomogeneity which cause this effect. Such field induced clustering is detrimental to the reversible operation of active composite media consisting of metallized microtubule suspensions.



GLASS CELL WITH 25 μm THICK METAL ELECTRODES. MICROTUBULES IN OPTICAL CEMENT

ALIGNED WITH 100 V (60 Hz). UV CURED JUST AFTER REMOVAL OF FIELD

Figure 3. Lateral electric field cell for Cu-coated microtubules, and alignment patterns in an inhomogeneous field region.

2. Microtubules dispersion in liquid crystal

2.1. *Flow alignment*

Liquid crystals were studied as possible hosts for the dispersion of metallized microtubules, mainly to investigate the possibility of using the liquid crystals to assist in controlling the alignment direction of the microtubules. Although the microtubule dimensions are enormous compared to the size of liquid crystal molecules, the collective interaction of groups of liquid crystal molecules normally extends over a range of about 0·1 μm even without surface and field interactions which can be used to order liquid crystals over distances larger than the length of microtubules. We also considered the possibility that if the liquid crystals were aligned surface-parallel on the microtubules themselves, then even a modest concentration of microtubules might act as a sort of internal alignment surface within the bulk of the liquid crystal. If this were the case, then we would expect cooperative interaction between liquid crystals and the microtubules. However, we found that, in fact, all the liquid crystals we studied aligned themselves perpendicular to the surface of the metallized microtubules (even those treated with silanes). This observation was clearest when we examined applied field effects under a polarizing microscope for microtubules in liquid crystals of positive dielectric anisotropy (for example 0·01 per cent of Cu-coated microtubules in BDH-E7 with 10 V of 10 kHz applied across a 50 μm thick cell). Here the microtubules and the bulk of the liquid crystal were both strongly aligned in the field direction, perpendicular to the surfaces of the cell, but a halo of misaligned liquid crystal much larger than the microtubule diameter was observed around the end-on view of each microtubule. In any case, when this type of microtubule/liquid crystal dispersion was used in cells with surface-parallel liquid crystal alignment (for example, rubbed cell surfaces) the metallized microtubules did not follow the liquid crystal back to the surface-controlled alignment state when the field was turned off.

Alternate liquid crystal mixtures tested as hosts for microtubules suspension included more viscous positive dielectric anisotropy ($\Delta\varepsilon$) nematic liquid crystal mixtures, such as ROTN-404 (commercial liquid crystal mixture by Hoffmann–La Roche, Switzerland), cholesteric to nematic phase transition mixture, dual frequency liquid crystal mixtures, and dynamic scattering mode liquid crystal mixtures. Cu coated microtubules were dispersed in a Hughes prepared dual frequency liquid crystal mixture with 6 kHz crossover frequency. At 0·1 kHz low frequency the microtubules and the positive dielectric anisotropy liquid crystal director aligned parallel to the electric field, whereas in the high frequency regime (10–40 kHz) the Cu microtubules were still aligned in the field direction, but the negative $\Delta\varepsilon$ liquid crystal realigned orthogonal to the field direction.

Liquid crystal induced flow alignment effects were observed with oxidized microtubules which did not respond to applied electric fields. (Permalloy coatings were oxidized with hydrogen peroxide.) These oxidized microtubules were studied in a crossover liquid crystal (ROTN-3421) in a 50 μm thick cell between indium tin oxide electrodes overcoated with angle-deposited SiO_2. Although birefringent domains were still observed around each tubule, and they disrupted the uniform surface alignment of the liquid crystal, some of the shorter microtubules were observed to follow the field-induced liquid crystal alignment directions: namely, surface-perpendicular at low frequency (100 Hz) and surface-parallel at high frequency (10 kHz). The table shows some approximate response times for these effects.

Nickel coated microtubules dispersed with sonication in the high viscosity ROTN-404 liquid crystal mixture (120 cP at 22°C), showed initial alignment in the liquid

Alignment response of oxidized permalloy-coated microtubules in a crossover liquid crystal.

Signal applied to cell	Liquid crystal responses	µT responses	Comments†
On (0 to 25 V, 100 Hz)	15	2	µTs aligned faster than liquid crystal‡
Off (25 to 0 V, 100 Hz)	10	25	Liquid crystal aligned faster than µTs§
Frequency switch at 25 V (from 100 Hz–10 kHz)	4	7	Liquid crystal aligned faster than µT‖

† Visually observed response times of a crossover liquid crystal and some shorter microtubules. The changeable microtubules aligned in the same direction as the liquid crystal, namely surface-perpendicular at low frequency and surface-parallel at high frequency.

‡ Presumably the microtubules responded quickly to the initial realignment of the liquid crystal.

§ The microtubules followed the liquid crystal realignment to surface-parallel, induced by the cel surface.

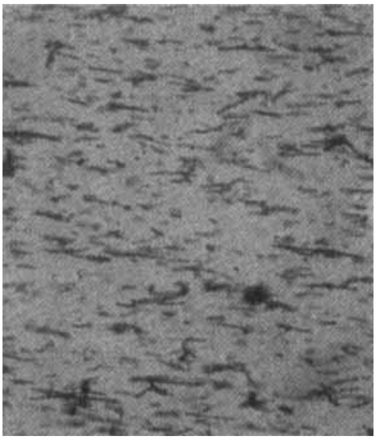
‖ The microtubules followed the liquid crystal field realignment to surface-parallel.

crystal flow direction, good alignment parallel to the electric field, and relaxation to a random state, as shown in figure 4. Approximate one second response time was observed under the microscope for a 50 µm thick test cell (0·95 mg µTs/300 µl liquid crystal) with 20 volts activation (4 kv cm^{-1}), and about 5 s decay time to the random alignment.

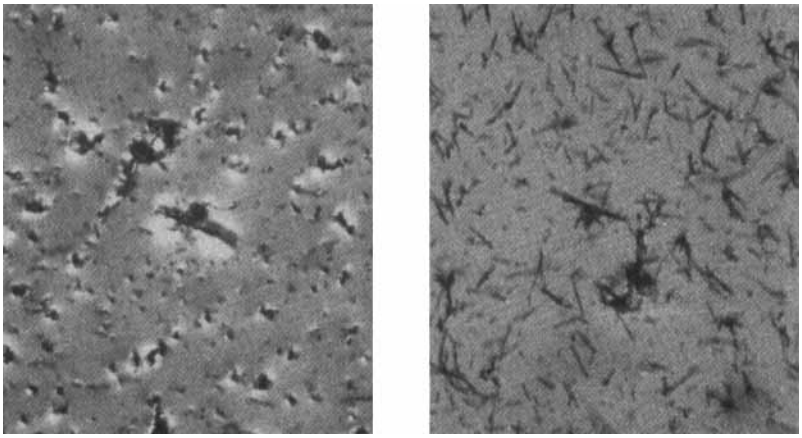
Because we had observed strong flow alignment effects of microtubules in various fluids, we attempted to use the turbulent flow of liquid crystals in their dynamic scattering mode to randomize microtubules previously field aligned. We first aligned the microtubules with a high frequency electrical field (no dynamic scattering mode), and then switched to the dynamic scattering mode with a low frequency field. The dynamic scattering mode caused the microtubules to move all around the cell, but due to their strong interaction with the field the microtubules stayed field aligned all the time. When the signal was removed the dynamic scattering mode turbulence decayed much faster than the microtubule relaxation from the field alignment, so there was no net alignment change despite the dynamic flow effects.

3.2. *Liquid crystal viscosity effect on dispersion*

Studies were made on the preparation of various mixtures of liquid crystals, liquid crystal monomers, liquid crystal polymers, and other polymerizable monomers to use in seeking improved electrical field alignment of microtubules. Several liquid crystal monomers were synthesized and purified, with alkylphenyl acryloyloxybenzoate and alkoxyphenyl acryloyloxybenzoate structures. Two room-temperature nematic liquid crystal monomer eutectic mixtures were prepared, and their measured clearing points were in good agreement with the calculated values. Photopolymerization of the liquid crystal monomer mixtures gave high clearpoint liquid crystal polymers. Lower clearpoint polymers were obtained by ultra-violet polymerization of the liquid crystal monomer mixtures dissolved in a nematic liquid crystal. For example, a 1 : 3 mixture of liquid crystal monomer/BDH-E7 showed a clearing point of 147°C after polymerization. Some qualitative studies indicated that the field alignment of metallized microtubules during ultra-violet polymerization was maintained better in our liquid crystal monomers than in isotropic optical cements. A dilute concentration (about 0·1 per cent) of Cu-coated microtubules was studied in a 25 : 5 : 1 solution of liquid crystal monomer/BDH-E7/diethoxyacetophenone. Polymerization with and without an



(*a*)
LC FLOW ALIGNMENT



(*b*)
E = 20 V, 20 kHz

(*c*)
E = 0 V

Figure 4. Nickel coated microtubules electric field alignment and relaxation in ROTN-404 liquid crystal; (*a*) flow alignment prior to electric field; (*b*) 20 V 10 kHz electric-field, (*c*) random alignment 2 minutes after electric field turned off.

applied field showed some visual transmission difference between two halves of a thin cell, where the liquid crystal monomer and liquid crystal polymer were field-aligned in the same direction as the microtubules.

4. Microwave phase modulations

For most applications of active composites it is important to have a large birefringence. The birefringence of an active composite medium consisting of suspended aluminium particles was reported [8] by previous investigators to be as high as $\Delta n = 0{\cdot}08$. We have shown that microtubule-based composites in isotropic fluids yield a birefringence of about $\Delta n = 0{\cdot}05$. Attempts to increase the birefringence by increasing the concentration of microtubules often resulted in rapid aggregation effects.

Another way to increase the birefringence of a composite medium is to disperse metallized microtubules in a liquid crystal host. We had discovered, in the course of another research project, that liquid crystals had surprisingly high birefringence values (typically $\Delta n = 0{\cdot}15$) in the millimeter wave region [9, 10]. We found that the metallized microtubules dispersed well in liquid crystals and that this host reduced the field induced aggregation of the particles. We used a modified sample cell with electrodes in the 30 GHz microwave phase bridge. The experimental phase bridge set up for the 30 GHz phase shift studies has been described in detail [10] and is shown in figure 5. Samples of Ni-coated microtubules in ROTN-404 liquid crystal were aligned parallel to the microwave electric field vector by the application of 300 V (60 Hz) at the electrodes, and were aligned perpendicular to the microwave electric field vector by a pair of 3 kG permanent magnets. Figure 6 shows the birefringence phase shifts versus optical path lengths of two samples: (1) a pure liquid crystal, ROTN-404, and (2) a 0·2 wt% dispersion of Ni-coated microtubules (10 μm average length) in the ROTN-404. From this experiment, the 30 GHz birefringences of the liquid crystal and the microtubule/liquid crystal composite were found to be 0·151 and 0·233 respectively. In this way, a high birefringence was obtained for a microtubule composite medium at a relatively low concentation of microtubules. In fact, the birefringence of this composite medium was higher than expected from the individual components. A 0·2 wt% dispersion of the same microtubules in the isotropic fluid Fluka PW76234 had

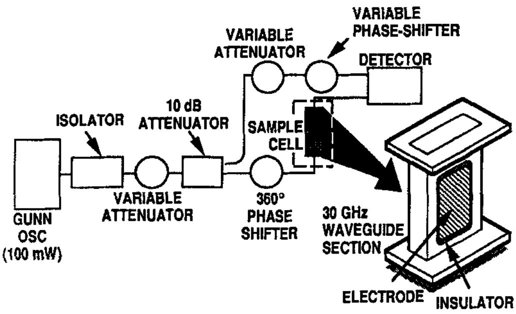


Figure 5. Experimental phase bridge set up for 30 GHz phase shift studies, including modified waveguide cell with electrodes to orient microtubule dispersions.

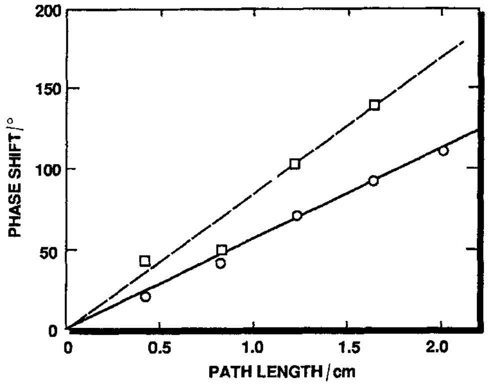


Figure 6. $E\|$ to $H\perp$ phase shifts at 30 GHz of ROTN-404, ○, and a 2 per cent dispersion of Ni-coated microtubules in ROTN-404, represented by □.

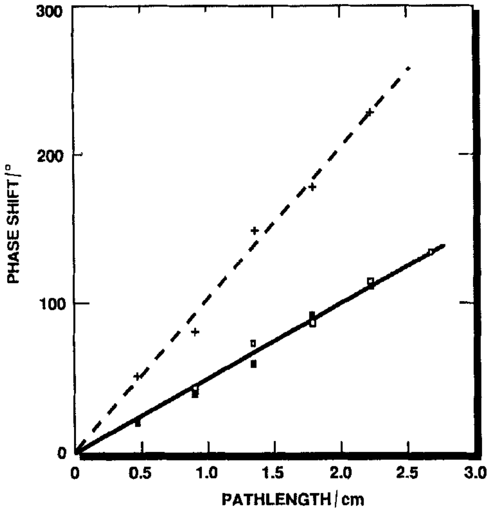


Figure 7. Phase shift and birefringence at 30 GHz of magnetic field aligned 0·6 per cent microtubule dispersion in the liquid crystal ROTN-404, +, and of the pure liquid crystal, ■ and □. For the microtubule dispersion in ROTN-404 $\Delta n = 0{\cdot}28$ and for the pure liquid crystal $\Delta n = 0{\cdot}14$.

$\Delta n = 0{\cdot}04$. The sum of the birefringences of the liquid crystal ($\Delta n = 0{\cdot}151$) and of 0·2 wt% of microtubules in the isotropic fluids is 0·191, while a larger birefringence of $\Delta n = 0{\cdot}233$ was measured for the liquid crystal composite with the same concentration of microtubules.

Similar experiments were performed on these materials using H-field alignment in both directions (transverse-‖ and transverse-⊥) to determine the phase shifts. Results as a function of path length are shown in figure 7 for the liquid crystal alone and for 0·6 per cent concentration of the Ni-coated microtubules in this liquid crystal. A very high microwave birefringence of 0·28 was found for this composite with 0·6 per cent microtubules.

5. Conclusion

Microtubules particles and metal-coated microtubules were dispersed in various host liquid crystal mixtures. The microtubules were typically hollow tubes about 0·6 μm in diameter, 10–40 μm in length, and when metallized had copper or nickel coatings of about 0·05–0·1 μm thickness both inside and outside. Dispersion effects were evaluated as a function of liquid crystal type, viscosity, dielectric anisotropy, and surface interaction. Experimental results indicated that all the types of liquid crystals studied were aligned perpendicular to the microtubule surfaces, regardless of liquid crystal composition or various surface coatings used on the metal-coated microtubules. Low concentrations of the metal-coated microtubules in nematic liquid crystal hosts were aligned by flow or cell surface alignment conditions, and could be modulated by electric or magnetic fields. In 50 μm thick cells, the electric field alignment of metal-coated microtubules were faster than that of the liquid crystal host, while the off-field realignment was much slower. The realignment was not speeded up by the turbulent motion of dynamic scattering liquid crystals or by use of dual frequency operation of crossover liquid crystals. We observed better microtubules dispersion uniformity in high viscosity liquid crystal host mixtures and in liquid crystal monomers than in isotropic fluids. Microtubules particles dispersed in ROTN-404 had a much higher birefringence in the microwave region than dispersions in a paraffin oil, despite the surface-perpendicular alignment of the liquid crystal on the microtubule surface.

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