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Mesoscale Chiroptics of Rhythmic Precipitates

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Rhythmic precipitation is a well-established consequence of diffusion controlled crystallization giving rise to Liesegang rings in gels,[1] agates in geochemical systems,[2] and banded spherulites in melts of high polymers.[3] Rhythmic precipitation is also common from simple, rapidly evaporating solutions[4] such as aqueous potassium dichromate ($K_2Cr_2O_7$, PD) first studied by Miers[5] or phthalic acid (C_6H_4-1,2-$(CO_2H)_2$, PA) first described by Gaubert.[6] We show the formation of large chiral fields of centrosymmetric crystallites that emanate from a PA nucleus (space group $C2/c$, point group C_{2h}) with our recently constructed square-wave, mechanically modulated, circular-extinction imaging microscope (CEIM).[7] The chiroptical properties inform the growth mechanisms of structured polycrystalline mesoscale aggregates[8] and suggest a general mechanism for the local amplification of chirality via dendritic growth.

Phthalic acid (0.12 M) was precipitated by evaporation of single drops of 20% ethanol/water solution on glass slides. Concentric polycrystalline rings (established as the $C2/c$ structure[9] by powder XRD) were observed spreading over several square millimeters. Growth proceeds rapidly (5−10 μm/s) once nucleation occurs. Between crossed polarizers, these rings showed “Maltese cross” extinction characteristic of organized radial bodies. The ring spacing was 29 μm ($\pm$15) with height differences of 150−250 nm between troughs.

Analysis of the aggregates by atomic force microscopy (AFM) revealed that PA is a type-2 spherulite[10] in which the nucleus is a needle rather than a point source. The ends of the needle branch dendritically, filling space as they fold around the nucleus to approximate a circular shape. Banding presumably occurs because of oscillations in nutrient concentration although the etiology of these oscillations has yet to be established.

When rhythmic PA precipitates were imaged at low magnification (4× objective) on the CEIM at 550 nm, they showed division into two large heterochiral fields (Figure 1) one of which passed right-handed light more effectively than left-handed light and vice versa. The average difference in circular transmission ($(I_R - I_L)/(I_R + I_L)$) for 0.1 mm^2 sections was $\pm$3.5%. PA is mirror symmetric in the *ac* plane, with a 2-fold axis parallel to [010]. In accordance with the Neumann−Curie principle, the division of spherulites into homochiral fields is consistent with a vertical (010) mirror. Any such crystal lying with its *b*-axis parallel to the substrate would have C_s symmetry when the crystal is considered in relation to the surface. Birefringence imaging indicated that the slow axis was always oriented in the radial direction for banded PA spherulites.[11] The largest refractive index (1.756, $\Delta n = 0.300$) of PA is along [010].[12] Thus, on average the radii of the branching dendrites are parallel to [010], the slow axis of the crystal (Figure 2).

What is the origin of the differential circular extinction? AFM revealed (Figure 3) that the heterochiral optical domains did indeed have heterochiral microtextures. It is well-established that large chiral objects differentially scatter left and right circularly polarized light.[13] The contrast in Figure 1 diminishes as the magnification increases, suggesting that the differences are recorded only when some of the scattered light is not captured by the objective. Light scattering from spherulites has long been observed and referred to as pseudopolychroism.[14] We are currently building a Stokes microscope with laser illumination to collect and analyze the scattered light and thereby characterize the scattering matrix. The contrast in Figure 1 was almost twice as great at 700 nm than at 400 nm. Therefore, the contrast is likely a confluence of circular differential Raleigh scattering, Bragg scattering from a chiral grating, and circular differential reflection.[15]

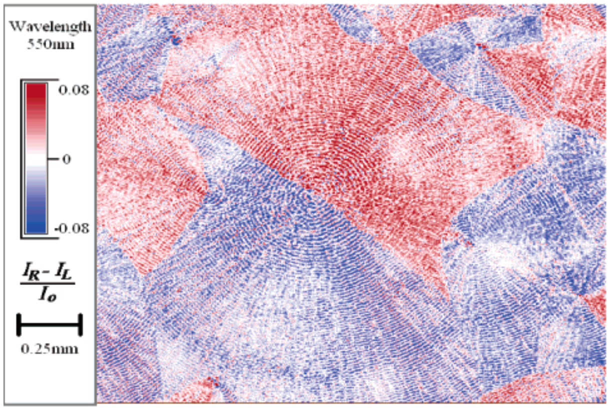

Figure 1. Circular extinction micrograph of a phthalic acid (PA) spherulite showing heterochiral bisection.

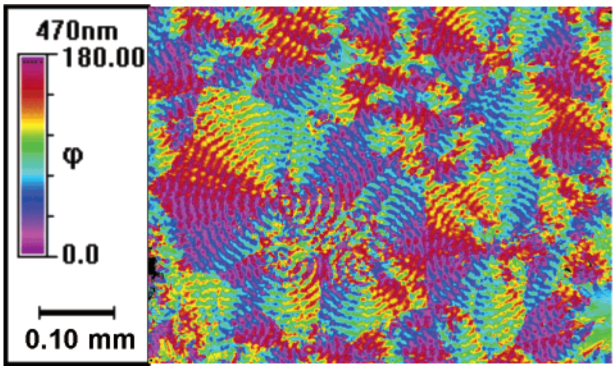

Figure 2. Optical extinction[11] image of phthalic acid (PA) spherulites. Slow axis is counterclockwise (ϕ, deg) from the horizontal

If the chiral texture of polycrystalline fields of PA is responsible for the circular differences, any system that is presumed to grow likewise should also show characteristic left and right handed domains in our microscope. In a recent reinvestigation of $K_2Cr_2O_7$, Imai and Oaki described type 2 spherulites whose radii twist helically and turn in heterochiral directions from the site of nucleation.[16] Their work was distinguished from that of the earliest researchers[5] in that they added 10 wt.% gelatin to their solutions in order to encourage the formation of rhythmic precipitates, a strategy borrowed from Bernauer.[17] This is not essential; we prepared spherulites with and without gelatin. The $P\bar{1}$ phase[18] of

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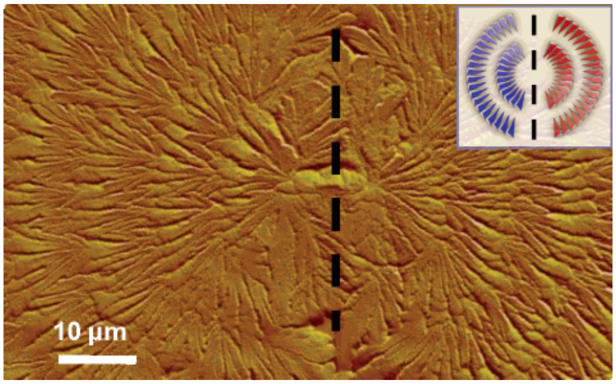

Figure 3. AFM image of a banded phthalic acid (PA) spherulite showing the difference in handedness of the "red" (right) and "blue" (left) sectors referred to Figure 1. Dashed line highlights the mirror symmetric relationship between sectors. Inset shows schematically the banding and chiral microtexture in the disposition of wedge-shaped crystallites. Colors refer to circular extinction contrast as shown in Figure 1.

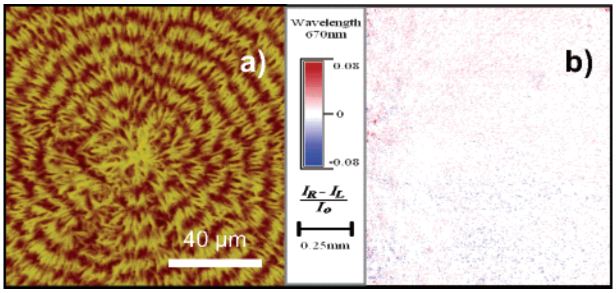

Figure 4. $K_2Cr_2O_7$ (PD) spherulites: (a) AFM; (b) lack of contrast in CEIM.

PD was confirmed by powder XRD. The growth of banded PD spherulites is much faster than that of PA reaching 1 mm/s. The rhythmic PD spherulites showed 23 μm band spacings ($\pm$10 μm) and a height variation of 200−500 nm.

Curiously, when the PD spherulites (grown with or without gelatin) were examined with the CEIM, there was no signal above the background (Figure 4b). Though scanning electron microscopy (SEM) showed evidence of twinning and twisting, the arrangement of plates showed no persistent helices and no large scale chiral microtexture. This observation is surely consistent with the lack of circular differential scattering. In other words, in the two patterned polycrystalline structures examined, circular intensity differences were associated with chiral microtexture.

Our achiral ensembles were strikingly different from those of Imai and Oaki.[16] Nevertheless, our results do not contradict theirs, in our view. It is likely that there is more than one banded PD morphology, and under highly nonequilibrium conditions our groups are accessing different polycrystalline structures, one of which is chiral on the mesoscale and another that is not. This dichotomy is consistent with the long-standing and puzzling symmetry breaking that has been observed in PD single crystals, known as the Shubnikov effect.[19]

The etiology of biomolecular homochirality is one of the outstanding problems in origin of life science,[20] and it has focused attention on processes in which random fluctuations, followed by autocatalysis, give rise to macroscale chirality. Classic examples of such systems include the homochirality of sodium chlorate crystals precipitated from disturbed solutions and 1,1′-binaphthyl grown from the melt.[21] Here, even centric crystallites constrained to grow unidirectionally in conditions far from equilibrium can show chiral amplification—though this phenomenon is qualitatively distinct from those aforementioned in that the chiral fields are deterministically linked to the chirality of the facets through which the dendrites are related to the nucleus. This is an unanticipated manifestation of Shubnikov's insight that all crystal growth emanating from a single face must be dissymmetric[22] and highlights the utility of chiroptical light scattering in assaying mesoscale polycrystalline structure.[23] We have recorded many other characteristic circular extinction images that underscore our assertion that differential scattering is a productive method for interrogating structured polycrystals.

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Supporting Information Available: Additional AFMs and SEMs (S1−S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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