Tactoidal shell defects in poly (γ-benzyl-D-glutamate) liquid crystals

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TACTOIDAL SHELL DEFECTS IN POLY (γ-BENZYL-D-GLUTAMATE) LIQUID CRYSTALS

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Résumé. — Une mésophase de poly (γ-benzyl-D-glutamate) orientée par un champ magnétique peut présenter, dans certaines conditions, des défauts tactoïdaux en forme de coquille (*tactoidal shell defect* ou *TSD*). La forme de ces défauts rappelle certaines gouttelettes de cristal liquide, ou *tactoïdes*, rencontrées dans des systèmes colloïdaux biphasés et dans des solutions de virus de plantes. Toutefois, à la différence de ces tactoïdes, les TSD forment une surface fermée limitant deux régions de la même phase dans lesquelles les structures sont identiques. Bien qu'ils soient métastables, ils peuvent persister plusieurs jours pourvu que la masse de l'échantillon reste sous l'influence du champ magnétique. On peut expliquer la plupart des résultats expérimentaux en utilisant la configuration moléculaire proposée autrefois par Pryce et Frank pour des sphérolites cholestériques, c'est-à-dire pour une configuration $S = +2$ encastrée dans une paroi de torsion.

Abstract. — Under certain conditions, tactoidal shell defects (TSD's) can be produced in magnetically oriented samples of poly (γ-benzyl-D-glutamate) liquid crystals. Their shape is reminiscent of liquid crystalline droplets or *tactoids* found in various biphasic colloidal systems and solutions of plant viruses. In contrast to tactoids, however, TSD's form a boundary surface which separates two regions of identical structure of the same phase. They are metastable in nature and may persist for many days as long as the bulk of the sample remains oriented by the field. A tentative model for their structure is a twist-wall of the sort proposed by Pryce and Frank for cholesteric spherulites.

1. **Introduction.** — The average local orientation of molecular axes in a uniaxial liquid crystal is a director-field conveniently described in terms of a unit vector field $\mathbf{n}(\mathbf{r})$. Departures from regularity in $\mathbf{n}(\mathbf{r})$ may be called defects. The most common types of defects found in liquid crystals are dislocations of rotation or *disclinations*, a term derived from *disinclination* introduced by F. C. Frank [1]. All disclinations are characterized by a singularity in $\mathbf{n}(\mathbf{r})$, either at a point or along a line. Defects need not contain singularities, however. Continuous defects can occur when topological constraints such as boundary surfaces or applied fields impose a preferred orientation on the sample. For example, structures in which a reversal of $\mathbf{n}$ occurs over a boundary layer separating two uniformly oriented regions have been discussed by Helfrich [2] and observed by Nehring and Saupe [3]. These *alignment inversion walls* can exist in closed form as loops [4-8], but to the author's knowledge, no example of a wall defect closing upon itself to form a shell has previously been reported. The purpose of this article is to report the formation of tactoidal shell defects in liquid crystalline solutions of poly (γ-benzyl-D-glutamate).

2. **Experimental.** — Poly (γ-benzyl-D-glutamate) (PBDG) was taken from the same batch used in previous studies [9] and had a molecular weight of 217 000 as determined from its intrinsic viscosity in dichloroacetic acid. Reagent grade dichloromethane was filtered through a sintered glass funnel prior to use. Solutions were prepared in either a 1 × 1 cm or a 1 × 0.2 cm quartz spectrophotometric cell equipped with a teflon stopper. The sample cells were not specially treated but were rinsed with solvent and dried with nitrogen just prior to use. Experiments were performed on liquid crystalline solutions which had been matured for approximately a year from the time of their formation. Concentrations (w/w %) of the solutions were determined gravimetrically before and after an experiment and found to increase by only a few tenths of a percent over the course of a month due to solvent evaporation.

Magnetic fields were produced by a Varian electromagnet equipped with a Hall probe for field stabilization. Field strengths were measured with a RFL Industries 750 DR gaussmeter which had been calibrated with standard magnets to an accuracy of ± 1.5 % up to 25 kilogauss (kG). Field homogeneity was better than ± 0.4 % over the dimensions

of the sample being observed. No attempt at thermo-stating was made since variations in room temperature in the vicinity of the sample were only about $\pm$ 1 °C from day to day.

A top view of the experimental setup is shown schematically in figure 1. Light from a 100 watt tungsten light source (L) was diffused by a piece of translucent plastic (D) and polarized parallel to the horizontal magnetic field direction (H) by a polarizer (P_1). The light then passed through the sample (S) situated between the magnet poles (M) and a second polarizer (P_2) which was crossed with P_1. Quarter-wave plates (Q_1 and Q_2) were added as shown and oriented at + 45° and − 45° to P_1 and P_2, respectively, for observation of the sample between crossed circular polarizers. Photographs of the sample were made with a 35 mm camera (C) equipped with a telephoto lens and bellows.
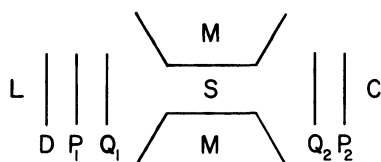

FIG. 1. — Schematic representation of experimental setup (top view). See text for meaning of symbols.

3. **Results and Discussion.** — In solvents such as dichloromethane which favor the formation of intra-molecular hydrogen bonds, poly (γ-benzyl glutamate) molecules adopt the α-helical conformation and are essentially rodlike in shape [10, 11]. Above a critical concentration of polymer [12, 13], solutions of PBG form an anisotropic liquid crystalline phase. Except under certain special conditions, such as particular solvent mixtures [14] or a racemic mixture of the D and L enantiomorphs [15, 16], the PBG helices spontaneously arrange themselves into a cholesteric structure [12, 15] over the course of several hours or days. Changes in the state of orientation of the polypeptide molecules during this time are apparent from visual inspection of the sample. For example, a 17 % solution of PBDG is translucent and scatters light strongly immediately after it has been mixed by pouring the solution from one end of the cell to the other. As the solution ages, however, its translucent character begins to clear noticeably in about half an hour and has essentially disappeared after a few hours. Retardation lines or *fingerprints* made visible by the Becke line effect can eventually be seen in natural light (i.e., unpolarized, white light) as the cholesteric structure forms [13].

The different states of orientation of the PBG molecules in freshly mixed and aged liquid crystalline solutions are also evident from their behavior in a strong magnetic field. It is well known [17, 18] that the long (optic) axis of the polypeptide tends to align

itself parallel to H forming a nematic-like structure. This orientation process can be monitored visually using the setup of figure 1 without the quarter-wave plates. If a 17 % sample is mixed and immediately placed in a magnetic field of 23.5 kG, the initially bright white appearance between the crossed polarizers begins to darken in patches after about 20 mn. In less than an hour the sample is well oriented and appears completely and uniformly dark. Such a magnetically oriented sample is quite transparent and behaves optically like a linear retarder whose optic axis lies in a plane parallel to the surface of the cell and is parallel to H. The *high-order white* interference color [19] observed off the four extinction positions is consistent with the reported average birefringence of 0.025 v_2 for PBG liquid crystals in various solvents [14], since for a volume fraction of polymer $v_2 = 0.17$ the retardation of a 2 mm cell would be about 8 500 mμ.

The magnetic orientation of a sample that has been aged for two days subsequent to mixing exhibits quite a different appearance when placed in a magnetic field and observed under the same conditions as described in the previous paragraph. The orientation seems to proceed more slowly than in a freshly mixed sample in a field of the same strength, and many white defect lines can be seen. Most of these defects disappear in a few hours, but other structures which have a spindle-like shape persist for many days as long as the bulk of the sample remains oriented by the magnetic field. One of these *football* defects as seen perpendicular to the horizontal magnetic field is shown in figure 2. The three-dimensional nature of these defects is easily recognizable in natural light by observing their parallax at various angles.
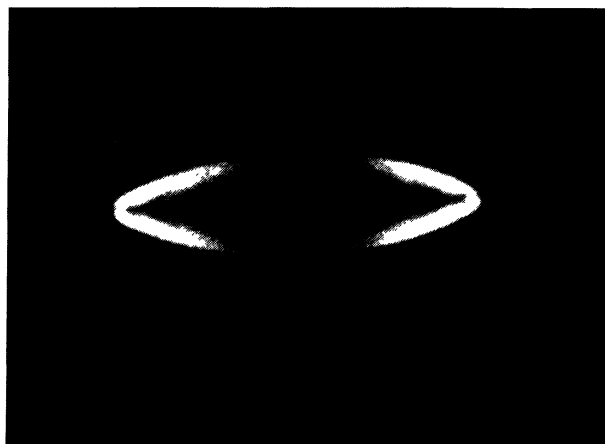

FIG. 2. — A tactoidal shell defect (TSD) in a horizontal magnetic field of 23.5 kg. Actual length of the TSD is 2.4 mm. Crossed linear polarizers are horizontal and vertical.

The shape of these structures closely resembles that of liquid crystalline droplets or *tactoids* found in various biphasic colloidal systems [20, 21] and solutions of plant viruses [22, 23]. According to

Wulf's theorem [24], the equilibrium shape of a particle is functionally related to the directional dependence of its specific surface free energy [25] (γ). The three-dimensional representation of γ, a γ-plot, is defined to be the polar plot of γ in which the distance from the origin along the direction of the unit surface normal is proportional to γ. If the γ-plot is a sphere, as in isotropic liquids, then the equilibrium shape is also a sphere. For anisotropic liquids in which no translational order exists and the structure is uniform, it can be shown that as the anisotropy of the γ-plot increases, the equilibrium shape will become ellipsoidal or tactoidal [25]. In contrast to *tactoids*, however, tactoidal shell defects (TSD's), like the one shown in figure 2, are believed to form a boundary surface which separates two regions of identical structure of the same phase. On both the interior and exterior of this shell, the structure is nematic with n parallel to H and the long axis of the TSD.

The internal structure of TSD's can be probed by examining them with polarized light. Under the conditions described in figure 2, the incident plane-polarized light is propagated without alteration through the sample until it reaches the defect surface. Wherever the TSD appears extinct, the light has emerged from it essentially plane-polarized and orthogonal to P_2. There are two instances in which such extinction effects occur : (1) the light travels parallel to the surface normal (s); (2) the light travels perpendicular to s, and s is parallel to the preferred direction of one of the crossed polarizers. Case (1) prevails near the center of a TSD where the light travels normal to two surfaces. Case (2) is important along the outline of a TSD, the effect being most clearly exemplified in the vicinity of its meridian where the radius of curvature is the greatest. The extinction at the tips of a TSD is much less obvious and is not complete. The intensity of the transmitted light between extinction positions in case (2) apparently reaches maxima halfway between the minima. Unfortunately, the polarization form of the transmitted light cannot be observed directly, since the nematic material between the TSD and the front of the cell has sufficiently large retardation to make the bright regions appear as a high-order white.

When observing TSD's parallel to the magnetic field direction, however, the surrounding nematic bulk does not contribute to the birefringence since the light is propagating along its optic axis. Such an observation is made possible, using the setup shown in figure 1, by turning off the magnetic field and rotating the sample by 90°. The high viscosity of the sample prevents any visible changes to occur due to relaxation of the nematic structure for a minute or more, which is ample time to take photographs. Figures 3 and 4 show negative prints of the end view of a large number of TSD's in a 2 mm cell between crossed linear and crossed circular polarizers, re-
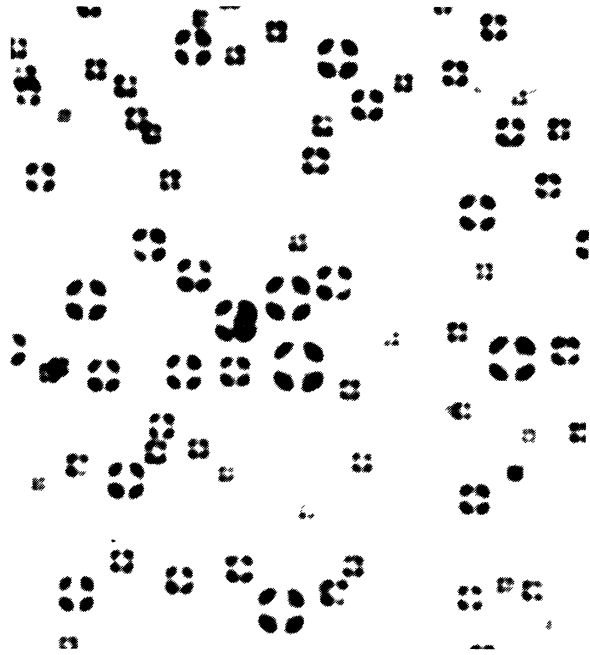

FIG. 3. — Many TSD's viewed parallel to their long axis in a 2 mm cell. Actual width of the figure is 4.3 mm. Crossed linear polarizers are horizontal and vertical (negative print).
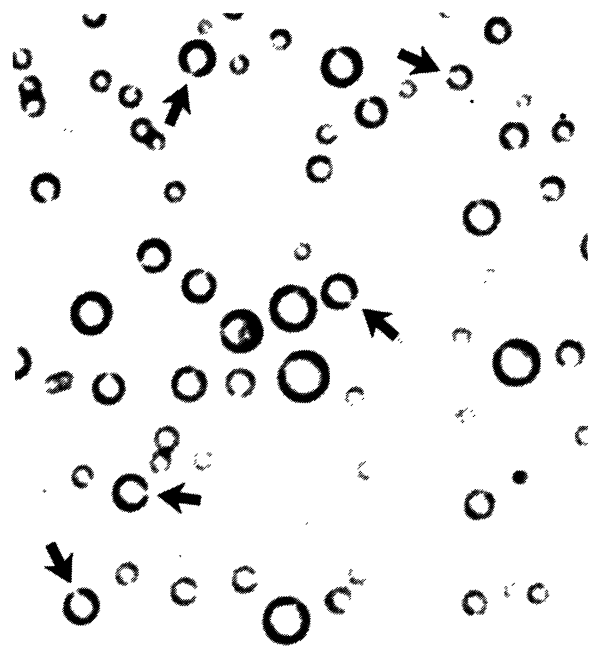

FIG. 4. — Same as figure 3 except as seen between crossed circular polarizers. Arrows point to lines of nearly zero birefringence (negative pritnt).

spectively. The extinction cross produced between linear polarizers has its arms parallel to the preferred directions of the polarizers. By inserting a unit retardation plate (a *first-order red*) between the sample and P_2 in the setup of figure 3, the diametrically opposed quadrants of each TSD image show either the blue addition or yellow subtraction colors corresponding to a tangential orientation of the

polymer molecules, as in PBG spherulites. The extinction pattern produced with crossed circular polarizes is confined to a central circular spot with one important qualification. Careful examination of figure 4 reveals that many, but not all, of the dark circles show a radially directed line of partial extinction (see arrows). This asymmetry of the extinction pattern is an important clue in determining the structure of TSD's and will be discussed later in more detail.

Any proposed model for the structure of these shell defects must be capable of explaining both their optical properties and their metastable nature. One possible model which satisfies both these criteria is similar to that proposed for the cholesteric spherulitic texture by H. L. Pryce and F. C. Frank [26]. According to the Pryce-Frank model, a spherulite can be described as a succession of concentric spherical subshells, much like the layers of an onion. The thickness of each subshell would correspond to the diameter occupied by a PBG molecule in the liquid crystal. (Of course, there is no evidence that such subshells actually exist per s.) Consider a line PQ which is tangent to the family of circles generated by the intersection of all planes passing through PQ with the surface of one of these subshells. Except close to the singular point P, every PBG molecule is nearly parallel to its neighbors in the same subshell. The tangent line PQ associated with each subshell is rotated by an angle β with respect to the preceeding subshell creating a radially directed twist along the singular radius OP. This model has been shown to be capable of explaining the radial disclination line and the double-spiral structure observed in PBG spherulites [16].

By analogy, a TSD could be subdivided into a series of tactoidal subshells. Within any one subshell, the PBG molecules would lie along a family of curves (no longer circles) which are all tangent to each other at some point P. The observed optical properties of TSD's can now be compared with this modified Pryce-Frank model ([1]). For example, consider the side view of a TSD as shown in figure 2. According to the proposed model, s is parallel to the torsion axis of the twist-wall so that along the outline of the TSD, where s is in the plane of the page, the PBG molecules would behave as linear retarders. Parts of the outline which are extinct would therefore be due to a zero-amplitude effect in which the preferred vibration directions in the PBG molecules are parallel to those of the polarizers. In the center of the TSD, where the light is traveling parallel to the surface normal, a twisted wall should have the characteristics

of a circular retarder and rotate the plane of polarization of the incident light.

The observed form optical rotation of PBG cholesteric liquid crystals has been explained by Robinson [14] using the theory of Mauguin [30] as extended by de Vries [31]. The theory predicts that for light propagating along the helical z-axis of a uniformly twisted dielectric medium in which $4(\lambda')^2/\alpha^2 \gg 1$, the emerging electromagnetic wave will be nearly linearly polarized and rotated by an amount

$$\frac{d\theta}{dz} = -\frac{2\pi}{P}\frac{\alpha^2}{8(\lambda')^2[1-(\lambda')^2]} \qquad (3.1)$$

radians per unit length. In equation (3.1), P is the pitch of the helicoidal structure; $\alpha \equiv (\varepsilon_2 - \varepsilon_1)/2\varepsilon$ is a measure of the birefringence, where ε_1 and ε_2 are the dielectric constants normal to the cholesteric axis and $\varepsilon \equiv 1/2(\varepsilon_1 - \varepsilon_2)$; $\lambda' \equiv \lambda/P\varepsilon^{1/2}$ is a reduced wavelength, where λ is the wavelength in vacuo. By making several approximations [14], equation (3.1) can be simplified to

$$\frac{d\theta}{dz} \simeq -\frac{45 n^2 P}{\lambda^2} \qquad (3.2)$$

degrees per unit length, where n is the birefringence of the untwisted material. Using typical values for PBG liquid crystals [14], $n = 0.005$, $P = 40\,\mu m$, and choosing $\lambda = 0.6\,\mu m$, the form optical rotation is calculated to be about 0.13 degree per micron, or 5 degrees per pitch. If the defect surface is a 180° twist-wall, then light passing through the center of a TSD must traverse two wall thickness or one pitch. The value of 40 μm represents a typical pitch for the cholesteric structure in the absence of any magnetic field, so the quantity $\theta = 5$ degrees would be an upper limit of the form optical rotation for two 180° twist-walls. Since the intensity of transmitted light is proportional to $\cos^2(90 - \theta)$, this model predicts that less than 1 percent of the light would be transmitted in the central region of a TSD, in agreement with observation. For regions of the surface between the center and edge of a TSD, the calculation of the transmitted intensity becomes more difficult, but the optical properties of the defect surface should vary continuously between that of a circular and linear retarder.

The explanation of the extinction patterns in figures 3 and 4 follows similar arguments. The disappearance of the arms of the extinction crosses when the crossed quarter-wave plates are inserted demonstrates that the extinction in those areas is due to the zero amplitude effect, whereas the remaining central extinction spots are due to a lack of linear birefringence. The radial lines of partial extinction shown in figure 4, however, still need to be rationalized. Either the continuous or discontinuous χ ($S = 2$) type of structure should not appear extinct between crossed circular polarizers if observed in a direction

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([1]) According to the proposed model, the fault line has a structure analogous to a radial screw disclination of χ type with $S = 2$ [27]. As Y. Bouligand has shown, however, a discontinuous $S = 2$ is unnecessary and may be replaced by a continuous adaptation [28]. The latter is necessary if the twist-wall is to be continuously joined with the surrounding nematic material [29].

perpendicular to its twist axis. It seems likely, however, that an applied magnetic field would distort the molecular arrangement so that the PBG helices would tend to be aligned more nearly parallel to the field. The birefringence perpendicular to the fault (and parallel to **H**) would therefore be expected to decrease as the field increases, but to remain non-zero as long as the structure does not disintegrate because some molecules will always be orthogonal to the direction of light propagation, as required by continuity.

The variation in the degree of extinction from one fault to another could be explained by considering that, in general, the fault would not be perpendicular to **H**, but could be parallel to any surface normal, s_0. For the purposes of discussion, consider a Cartesian coordinate system with its z-axis parallel to the long axis of a TSD. The orientation of any s_0 in this system can be defined in terms of two polar angles : ω is the angle between s_0 and the xy-plane, and φ is the angle between the projection of s_0 in the xy-plane and the x-axis. The condition $\omega = 0°$ would then correspond to the case of perpendicular observation which has just been discussed. As ω increases from $0°$ to $90°$, the fault would become progressively less noticeable, and beyond a certain angle would no longer be visible. For reasons of symmetry, there should be no preferred value of φ for any given ω, so that the distribution of faults about the field direction should be random. All these qualitative predictions seem to be realized in figure 4.

No direct determination of the *thickness* of a TSD wall has yet been made, but it is possible to at least make an order of magnitude estimate using data from the literature. The PBG molecules in the twist-wall structure of a TSD would not be *unwound* by the magnetic field if the wall thickness were of an order less than twice the magnetic coherence length, $\xi(\mathbf{H}) = H^{-1}(K/\chi_a)^{1/2}$, where K is an elastic constant and χ_a is the anisotropy of the diamagnetic susceptibility [32]. When the twist axis is essentially orthogonal to **H**, use of the *twist* elastic constant [1] (K_{22}) is appropriate. Using the measured value of K_{22}/χ_a for PBLG in dichloromethane [33], an approximate minimum value for the thickness of a 180° twist-wall is calculated to be about 7 μm for a field strenght of 23.5 kG. If the thickness of the shell defect varies with the angle between **s** and **H**, then the thickest part of a TSD wall would be at the tips, where the PBG molecules would be orthogonal to **H** and the magnetic torque would vanish. At these two points the shell thickness might correspond more closely to the natural periodicity of the cholesteric structure.

The hypothesis that a TSD is composed of a twist-wall implies that TSD's should be more readily produced under conditions which favor the creation of twisted structures. In aged samples the spontaneous formation of the cholesteric helix provides such a situation. A much more efficient procedure for creating

TSD's, however, involves the magnetic reorientation of the polypeptide molecules. If a well-oriented sample is rotated by 90° in the magnetic field and observed between crossed circular polarizers, the entire sequence of standard interference colors can be seen, beginning with the first order and ending in a high-order white. The same reorientation observed between crossed linear polarizers is entirely different in appearance, showing many vividly colored patches of unequal size. The various hues, some of which are pure while others are almost pastel, gradually lose intensity as the reorientation proceeds toward completion. Since the effects of optical rotation are eliminated by crossed circular polarizers, much of the color seen during a magnetic reorientation between crossed linear polarizers must be due to the dispersion of optical rotation. The magnitude of the form optical rotation of PBG liquid crystals was measured by Robinson [14]. He found that the optical rotation parallel to the cholesteric axis varies by more than 90° over the visible spectrum for a 1 mm sample. Since the intrinsic optical activity of the PBG α-helices is negligible (an oriented sample appears extinct between crossed linear polarizers when viewed parallel to the optic axis), any significant optical rotation must indicate the formation of twisted domains.

There is evidence from nuclear magnetic resonance studies [34] that even at equilibrium with the field, the PBG molecules form a finite angular distribution about **H**, and that after a 90° rotation of the sample, half of the α-helices rotate clockwise (CW) and the other half rotate counterclockwise (CCW). The process in which some of the PBG molecules reorient in the opposite direction from the remainder is called *counterrotation*. If there is no net macroscopic transfer of material from one part of the sample to another during reorientation, then the bulk of the sample must divide itself into many regions such that in any one region the PBG helices will all be rotating in unison. Whenever a CW region and a CCW region are adjacent, there is an opportunity for an inversion wall to form along their common border. Counterrotation, therefore, appears to play an important role in the formation of TSD's.

Although very few TSD's are formed after one 90° rotation of an oriented sample, a second 90° rotation back to the sample's original orientation with respect to the field can produce about an order of magnitude more TSD's than by the orientation of an aged sample. The number of TSD's created per unit volume varies with the number of 90° rotations and the time between successive rotations under any given set of conditions. For a 15.5 % sample at 28 °C, this density peaks at about 2.5 min. between two 90° rotations in a field of 23.5 kG, and 10.2 mn at 11.7 kG (Fig. 5). Note that the times of maximum density in the curves vary inversely as the square of magnetic field strength. Although the density of TSD's produced at 11.7 kG is smaller
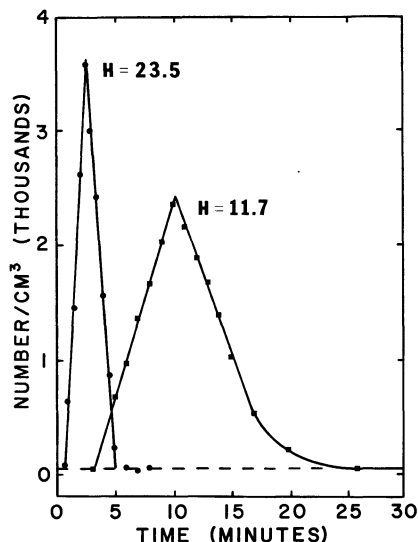
FIG. 5. — Number of TSD's per cm^3 remaining 48 hours after two 90° rotations of a 15.5 % sample vs time between rotations. Only one set of data points is represented so that no error bars could be drawn. The precision is estimated to be about ± 15 % (H = 23.5 and 11.7 kG, T = 28 °C, 2 mm cell).

than at the corresponding point on the 23.5 kG curve, the average size of the TSD's formed during the reorientations at the lower field strength is greater than at the higher field.

Only the first 90° rotation produces brilliant colors between crossed polarizers, the sample appearing white during subsequent rotations and gradually darkening over the course of several days revealing the tactoidal defects (Fig. 6). The density of TSD's after any arbitrary time following the successive 90° rotations decreases with the number of rotations; practically none are produced by ten rotations spaced 2.5 min. apart at 23.5 kG. The largest density of TSD's is evidently achieved with a particular amount of counterrotation. Less than this optimum amount of counterrotation occurs if the time between two 90° rotations does not correspond to the peak time, as shown in figure 5. At the other extreme, a large number of 90° rotations of the sample produces too much counterrotation, which destroys the integrity of the domains to the extent that no intact shell defects remain.

4. **Summary and Conclusions.** — Under certain conditions, tactoidal shell defects (TSD's) are formed in magnetically oriented liquid crystalline solutions of poly (γ-benzyl-D-glutamate). The long axis of a TSD is aligned parallel to the magnetic field. As long as the bulk of the sample remains well-ordered by the field, TSD's are metastable and can remain intact for many days. Their shape closely resembles that of liquid crystalline droplets or *tactoids* found in
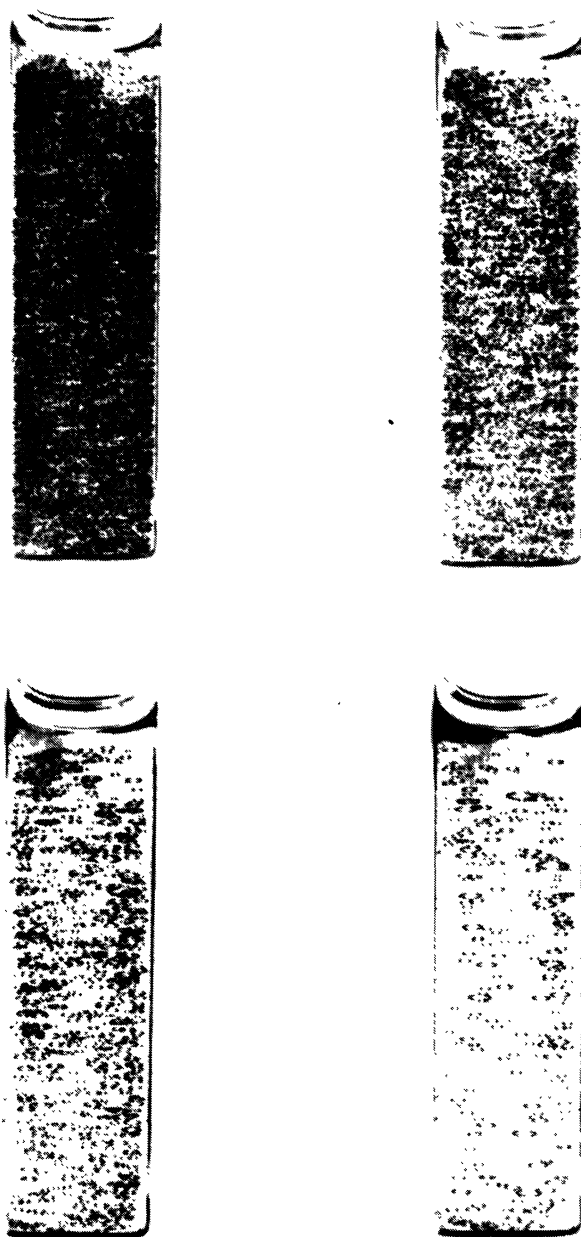

FIG. 6. — Appearance of a 17.2 % sample 24, 48, 100, and 173 hours subsequent to two 90° magnetic reorientations spaced 2 minutes apart. The magnetic field is horizontal. Crossed linear polarizers are horizontal and vertical (H = 23.5 kG, T = 28 °C, 1 × 1 cm cell, negative print).

various biphasic solutions of rod-shaped particles and reflects the anisotropy of the surface free energy of the shell defect. A tentative model for the internal structure of TSD's which can account for their observed optical properties is a twist-wall with a structure based on the Pryce-Frank spherulitic texture. TSD's are most readily formed under conditions which favor the creation of twisted domains, such as during the process of magnetic reorientation in which counterrotation occurs. Considering that TSD's

are not formed during the orientation of thoroughly mixed and unaged samples, it is not too surprising that their existence has not been previously reported. Further studies on the formation, shape, and stability of TSD's are currently in progress.

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