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Quench-induced nematic textures of wormlike micelles

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Results are reported of a light scattering study of the ordering of aqueous solutions of wormlike tetradecyldimethylaminooxide micelles after a temperature quench from the isotropic into the nematic phase. Strongly anisotropic small-angle scattering is observed immediately after the quench. The scattered intensity exhibits a power-law dependence at high momentum transfer q: $I \propto q^{-n}$. We find a Porod-like scaling consistent with $n=4$, crossing over to $n=2$ at later stages. The latter is thought to mainly arise from director fluctuations. An explanation of the former is given in terms of a coarsening mechanism involving wall defects, separating nematic domains with different properties.

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I. INTRODUCTION

When a system of nematogens is quenched from the isotropic into the uniaxial nematic state, a phase with a high density of defects is generated. These defects often belong primarily to the class of type-$\frac{1}{2}$ disclination lines [1–6]. After the quench the defect density decreases with time, i.e., the system "coarsens." The reason is that defects interact and that oppositely charged defects are in principle able to annihilate each other. (For detailed studies of the dynamics of defect tangles in low-molecular-weight nematic liquid crystals, see Ref. [2] and references cited therein.)

Coarsening of the quenched nematic can be investigated by light scattering techniques, because the defects tend to scatter light strongly. Recent theoretical work by Bray *et al.* [7] indicates that, within the so-called equal constant approximation, the structure factor should (in three dimensions) develop a q^{-5} tail, attributed to the predominance of the half-integer disclination lines or "string defects" [8]. Results from quench experiments on solutions of stiff polymers and solutions of disklike micelles by Wong *et al.* [9] are not inconsistent with the theoretical predictions of [7]. Although these authors extract from their scattering data a q^{-6} scaling at high q, inspection of the figures presented in [9] reveals that a q^{-5} tail provides a good fit to the data. Bray *et al.* argued that experiments over too limited a q range tend to overestimate the exponent and showed that the experimental data are indeed consistent with the predicted asymptotic exponent of 5 [7].

Here we present results of a light scattering study of the temperature quench-induced nematic ordering of aqueous solutions of tetradecyldimethylaminooxide (hereafter referred to as C_{14}DMAO). C_{14}DMAO is a zwitterionic surfactant that forms wormlike micelles in aqueous solution [10]. Wormlike micelles are known to continually break and recombine, the kinetics of which couples to other dynamic processes such as diffusion and flow [11]. Our scattering measurements do *not* support the theoretical predictions by Bray *et al.* [7] nor the measurements of Wong *et al.* [9]. This implies that not all quenched nematics belong to the same dynamic universality class, as suggested in [9]. We put forth that for C_{14}DMAO in water nematic texture coarsening must involve wall defects rather than string defects. A microscopy study appears to confirm this. Eventually a single-phase nematic liquid crystal remains, exhibiting scattering consistent with what one would expect from director fluctuations. Either string defects are absent altogether or their concentration is too low to influence the scattering.

II. EXPERIMENT

The purified surfactant C_{14}DMAO was obtained in crystalline form as a gift from Dr. S. Hofmann and Professor H. Hoffmann (University of Bayreuth, Germany). Purification entailed freeze drying of the starting material [a 27% (wt./wt.) solution donated by HOECHST AG], two times recrystallization from acetone A. R. (MERCK), and drying in ultravacuum [12]. A phase diagram of aqueous solutions of C_{14}DMAO has been determined by Hoffmann *et al.* and can be found in [10].

Experiments were performed on solutions of about 32% (wt./wt.). Samples (at room temperature) were pipetted into planar sapphire sample holders (crucibles) of 1 mm depth. The sample was put on a heating-cooling stage and kept at 80 °C, where the solution is isotropic, during a settling time of a few minutes. Next, a sample was quenched deeply into the nematic part of the phase diagram by a fast temperature drop to 40 °C, crossing a biphasic *I-N* region about 10 °C wide. The cooling rate was 90 °C/min.

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The coarsening process was followed by time-resolved static light scattering with an apparatus described in detail elsewhere [13]. Two-dimensional (2D) scattering patterns were recorded at regular time intervals with a charge coupled device camera and stored digitally on a computer. The resolution of the patterns in momentum transfer space is about 6%. The sampling time of each image was 10 ms, more than sufficient to render the noise level in the signal negligible. The time evolution of the scattered intensity has been investigated in both the polarized and the depolarized mode and was followed up to 36 h.

Light microscopy studies of the quench induced ordering were performed with a Zeiss Axioplan Microscope with crossed polars. The microscope was fitted with an Olympus OM4 camera.

III. RESULTS AND DISCUSSION

After the quench a four lobe scattering pattern with distinct intensity maxima appears, both in the polarized and the depolarized mode. Figure 1 shows the depolarized scattering almost immediately following the quench. The main axes of the lobes coincide with those of the (crossed) polarizers; rotating the sample does not change this. In the polarized mode the four lobes are rotated 45° with respect to the axes of the depolarized pattern. One pair of lobes is stretched relative to the other, distorting the fourfold symmetry observed in the depolarized mode. In the following discussion, the focus will be on scattering in the depolarized mode.

Scattering patterns of this kind have been observed not only in films of nematic liquid crystalline polymers [3–5,14] and polymerized solutions of linear micelles [15], but also in thin films of crystalline polymers [16]. The scattering of polymer spherulites in these materials is more or less understood in terms of the anisotropic polarizabilities and structure of the spherulites. Such is not yet the case for the scattering from a quenched nematic. What is known is that scattering by a collection of noninteracting half-integrally charged string defects alone is not sufficient to produce the characteristic lobes [3]. There have been attempts to calculate the scattering from pairs of perfectly parallel, oppositely charged disclination lines [3,17]. The theory of Greco [17] indeed yields a four-leaf-clover scattering pattern, although it does not recover the power law tail we find at high momentum transfer. (At high q the numerical data of Greco [18] exhibit strong oscillations that prevent an unambiguous determination of the scaling behavior.) The theory is anyway unlikely to apply to the defect tangles one expects to be generated in macroscopically thick samples (see below). As will become clear below, we may in fact not have a nematic liquid crystal dominated by defects of the string type.

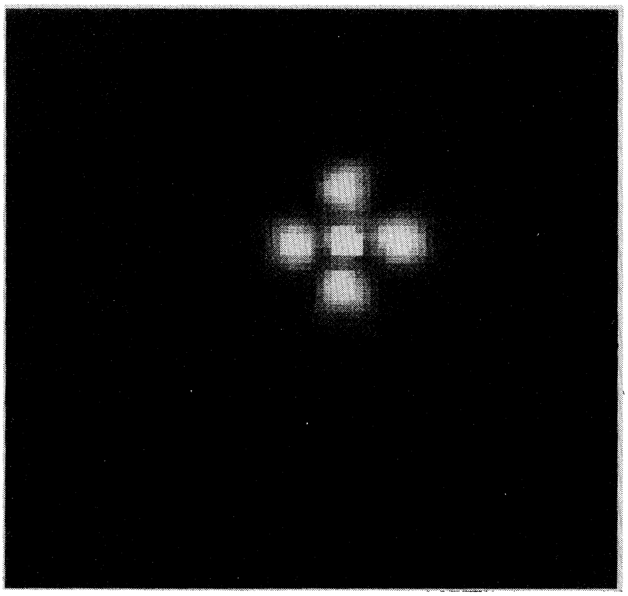


FIG. 1. Depolarized scattering pattern of the C_{14}DMAO solution, immediately after a quench from the isotropic into the nematic phase. (Here a beam-stop was not used; the central maximum is due to a weakly transmitted incident beam.) The main axes of the lobes coincide with those of the polarizers.

Figure 2 gives a cut through the axis of one of the lobes and the center of the depolarized scattering pattern. There is a clear maximum, indicating the existence of a characteristic length scale. The position of the maximum shifts to lower values of q with time, indicating a coarsening process. We have not been able to sample the time dependence of the position of the maximum sufficiently fast to obtain an indication of the time evolution of the characteristic length scale. After about 200 s the intensity peak disappears behind the beamstop. From then on the fourfold symmetry of the scattering pattern becomes less obvious: the scattering becomes increasingly isotropic with time. This is probably a consequence of the formation and growth of polarizing inhomogeneities that randomize the polarization of both the incident and scattered light well within the 1-mm-thick sample. For the same reason, the difference between the polarized and depolarized intensities reduces as a function of time.

In Fig. 3 we have plotted on double logarithmic axes the scattering intensity versus q about 83 min after the quench. It reveals that the intensity obeys a power-law scaling at high q; the curve has a slope very close to -4. One in fact expects a q^{-4} tail in quenched systems with a conserved scalar order parameter (Porod's law [19]). But in nematic liquid crystals the (orientational) order parameter is tensorial, not a scalar, and also not conserved. Bray *et al.* [7] find in a theoretical study of power of -5 a value that is confirmed by experimental results on two very different lyotropic systems, although only for samples of sufficient thickness [7,9]. When reducing the sample thickness, Wong *et al.* find a crossover to a Porod-type power law. This was interpreted in terms of a crossover from a three-dimensional to a (quasi-) two-dimensional coarsening. Two dimensional coarsening was reported to occur for sample thicknesses of less than 50 μm for the micellar system and less than 100 μm for the polymer system. Our sample thickness is an order of magnitude greater, 1000 μm, so we rule out the possibility of a 2D morphology. (This is confirmed by a microscopy study, where we find no evidence for a quasi-2D

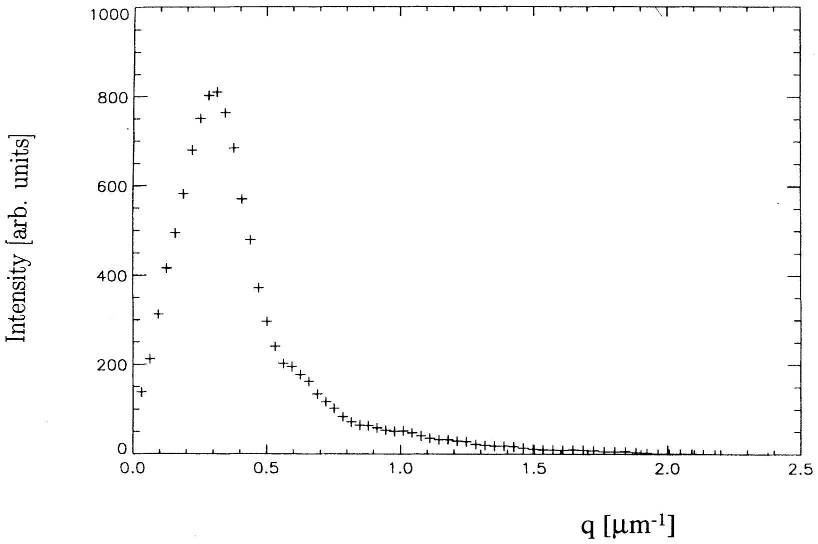


FIG. 2. Cross section along the main axis of one of the lobes of Fig. 1. Note the presence of the higher-order maxima.

coarsening.)

We are inclined to interpret the scattering as arising from wall defects, not string defects, because of the Porod tail [20]. It is usually thought that wall defects in single-phase (thermotropic low molecular weight) nematic liquid crystals are highly unstable and can be smeared out efficiently in favor of a gradual variation of the director field [22]. Tentatively assuming that this is also true for our lyotropic system (see, however, [23]), we must have a coarsening process involving two coexisting (nonequilibrium) phases separated by an interface. The emergence of two phases may have something to do with the fact that a coexistence region is crossed during the quench. But in the experiments of [9] isotropic-nematic biphasic regions were also crossed and yet these quenches gave a completely different type of behavior. Besides, it is important to note that due to our high quench rate, the amount of time spent in the biphasic gap, 7 s, is considerably less than in the study presented in [9]. It seems unlikely that a stay in the biphasic region of such a short duration will influence our results in any dramatic way, because of the much longer time scales involved in the coarsening process. (These time scales are of the order of hours, not seconds.)

An indication of the time scales involved in the coarsening dynamics can in principle be obtained by determining the time dependence of the portion of the scattering curves that exhibit the q^{-4} scaling. This produces a prefactor presumably proportional to the defect density, plotted as a function of time in Fig. 4. Apparently the coarsening process is very slow for some time, after which it accelerates and approaches a power law. A precise power is difficult to ascertain because of the scatter in the data, but it is definitely quite smaller than unity. Note that for the systems described in [9], a stronger time dependence was found in agreement with a $t^{-3/2}$ scaling

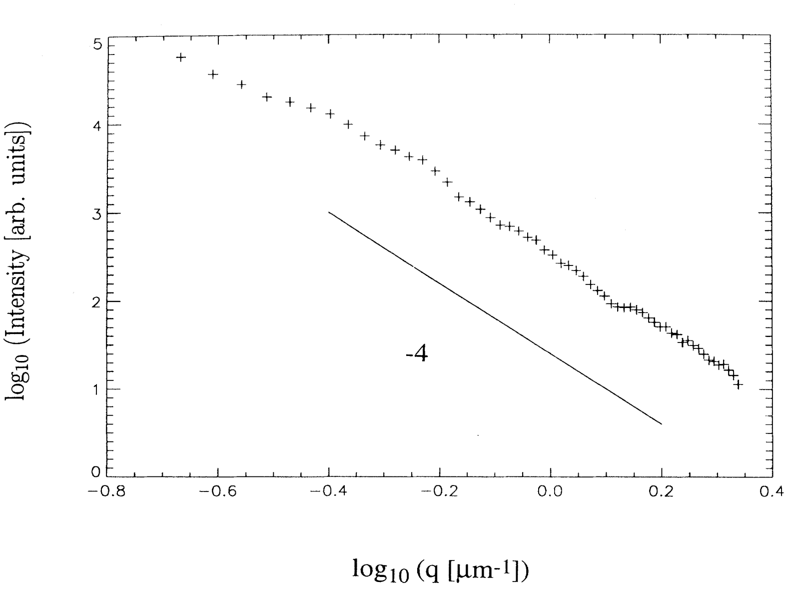


FIG. 3. Logarithm of the intensity (in arbitrary units) versus the logarithm of the momentum transfer (in reciprocal micrometers), 83 min after the quench. The wiggles in the power-law tail of the intensity are due to higher-order maxima (see also Fig. 2). A slope of −4 is indicated.

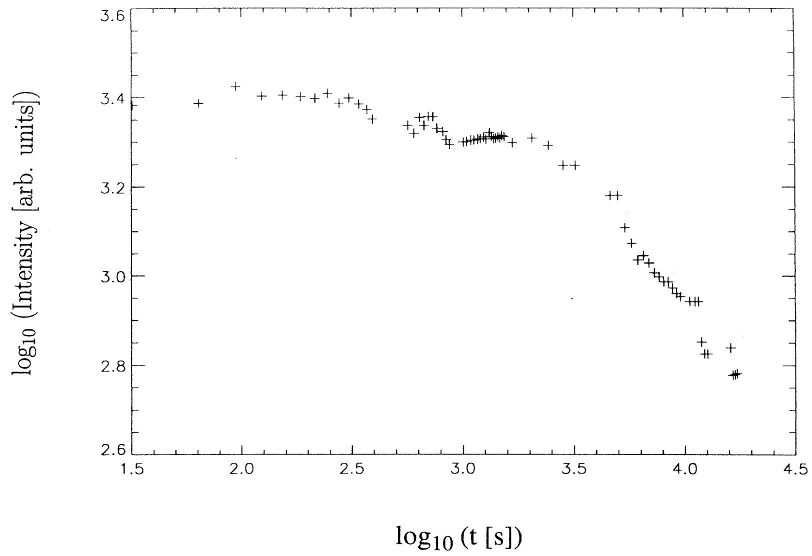


FIG. 4. Time dependence of the intensity at $q = 0.62\ \mu\mathrm{m}^{-1}$, radially averaged over an angle of about 18°. At this value the intensity scales like q^{-4} for a long period of time before it crosses over to the q^{-2} found in the late stage scattering (see Fig. 5). The time evolution of the intensity in the q^{-4} tail, proportional to the defect density, is an indicator of the coarsening dynamics.

for the thick samples and with a t^{-1} scaling for the thin ones. This again shows that the coarsening of our nematic solution of self-assembled worms must proceed via a different mechanism.

Approximately $1\frac{1}{2}$ h after the quench, a crossover from a q^{-4} to a different power law appears at the highest q accessible in our light scattering setup. The crossover q moves to smaller values with time. In Fig. 5 we have plotted the logarithm of the scattered intensity versus the logarithm of the momentum transfer q, 5 h after the quench. The tail has a slope of -2. When we wait long enough, the remnant of q^{-4} scaling is no longer noticeable and we are left with q^{-2} behavior over the entire accessible q range. This tail can be explained in terms of the director fluctuations [22,26]. At late stages in the coarsening process the defect density becomes so low that scattering due to director fluctuations begin to dominate, at least for q's much greater than the inverse of the typical domain size. The domains grow and hence the crossover q must shift to smaller values. Eventually a single domain nematic liquid crystal remains. Throughout the process we have no indication that string defects are present. If they are, the concentration must be quite low.

A conformation of the suggested coarsening of nematic domains is found in Fig. 6, where a 3D representation is given of the evolution at high q of the scattering after the quench. The development of the q^{-2} tail is accompanied by a modest increase in scattering intensity (compare also Figs. 3 and 5). This may be explained in terms of suppressed director fluctuations when the domains are very small. Director fluctuations of wavelengths larger than the domain size are frozen out, but those at smaller wavelengths are possibly affected by the system size as well. The fluctuation suppression becomes less effective

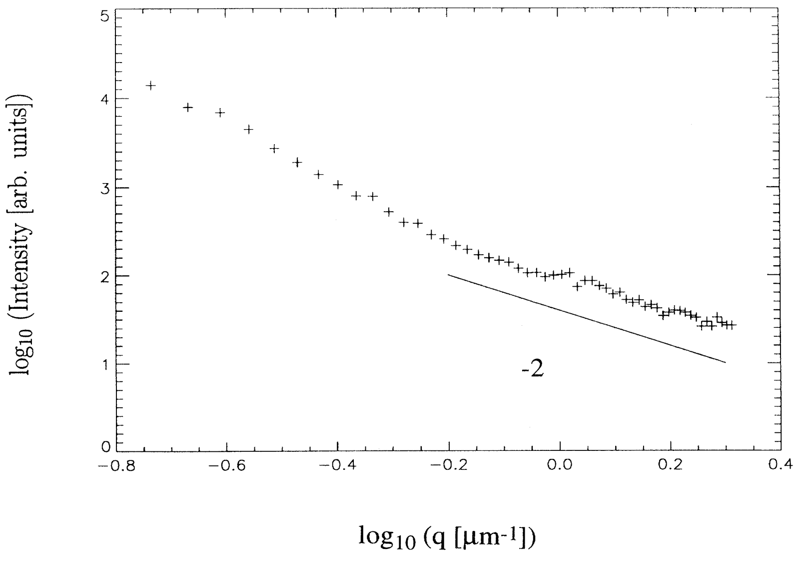


FIG. 5. Same as Fig. 3, 5 h after the quench. A slope of -2 is indicated. We expect a q^{-2} tail due to scattering from director fluctuations.

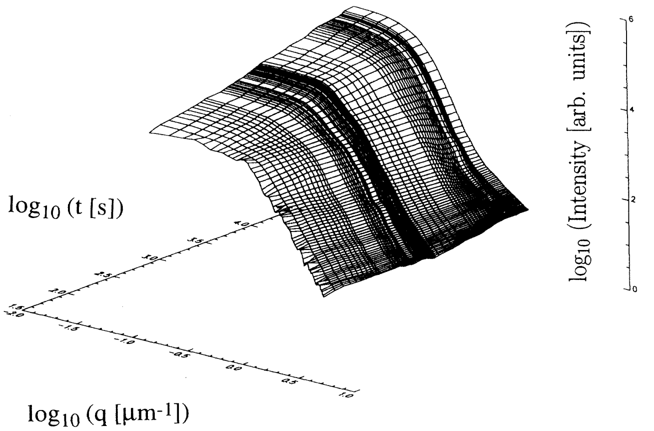


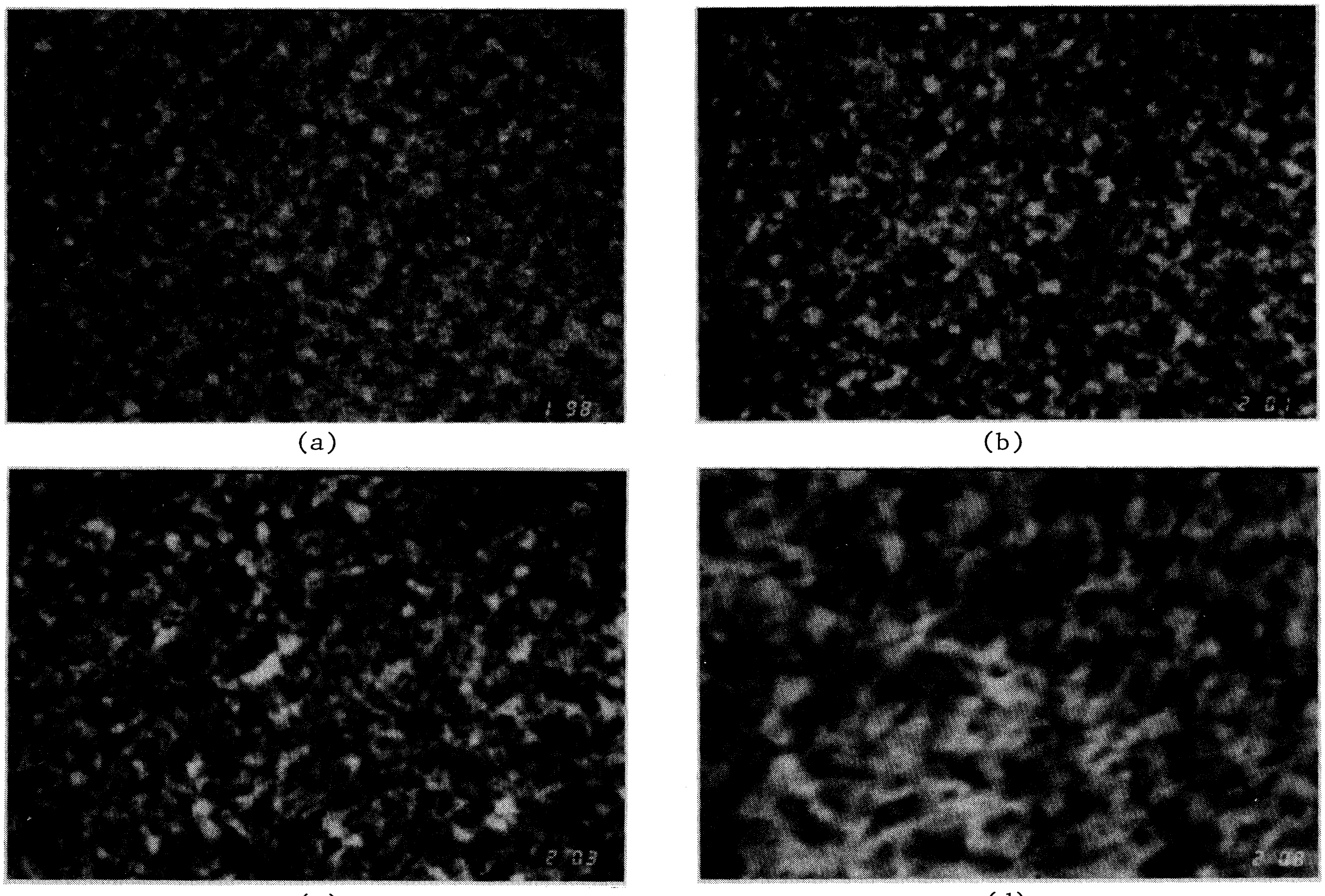
FIG. 6. Three-dimensional plot of the scattered intensity (in arbitrary units) versus the magnitude of the scattering vector ($\mu\mathrm{m}^{-1}$), as a function of time after the quench (in seconds). Initially the intensity has a q^{-4} scaling at high q. This crosses over to a q^{-2} at later stages. Notice the increase in intensity of the scattering at low and high q.

when the domains grow, leading to an increase (by a factor of order unity) in the scattered intensity.

By way of illustration we give in Fig. 6 photographic images of various stages of the phase ordering of the micellar nematic, taken through a microscope in differential interference contrast mode with crossed polarizers. At no instance during the monitoring of the coarsening process were line defects observed. Notice the dropletlike structures, especially in Fig. 7(b). The images support our suggestion that domains, separated by interfaces, are involved in the process.

IV. CONCLUDING REMARKS

The nematic ordering of aqueous solutions of the surfactant C_{14}DMAO, induced by a rapid temperature drop, does not seem to conform to the current paradigm of nematic phase ordering, i.e., the nucleation of string defects and subsequent coarsening by defect annihilation. We have presented evidence, based on light scattering experiments and light microscopy, that for this system, the nematic phase formation proceeds via a process in which wall defects are involved, separating nematic domains.


(a) (b)

(c) (d)

FIG. 7. Microscopic images (taken with crossed polarizing lenses) of the coarsening of the micellar nematics: (a) 40 s, (b) 7 min, (c) 17 min, and (d) 4 h after the quench. The photographs represent regions of approximately 420 μm×600 μm. Dropletlike structures are clearly visible in (b). Color prints of the photographs can be obtained from the authors upon request.

The precise nature of these domains is unknown. We may have domains of two nematics liquid crystals with different properties or possibly a "nematic foam" in which domains are separated by thin films of, for example, isotropic phase. Quench-induced nucleation and growth of nematic droplets can in principle explain the generation of such a nematic foam. Why such should arise here and not in other systems is unclear. Theoretical considerations indicate that in nematic solutions of hard wormlike chains wall defects may not be as unstable as in the usual thermotropic nematic liquid crystals, provided they are sufficiently stiff [23]. Eventually a single-phase nematic liquid crystal remains, which is probably (virtually) defect free.

We have no explanation for the peculiar type of nematic coarsening found in this study. The possibility cannot be excluded that it is somehow connected to the crossing of the biphasic region during the quench, although arguments have been given why we think this is unlikely.

It is important to realize that a nematic liquid crystal of wormlike micelles differs in an important way from the usual lyotropic or thermotropic nematics: self-assembling worms to not have a constant size. Their mean length depends not only on the chemical structure of the constituent surfactant molecules, temperature, concentration, etc., but also on the particular phase these micelles are in. According to recent theoretical work wormlike micelles grow considerably upon going from the isotropic to the nematic phase [27–29]. Liquid crystalline solutions of self-assembling linear objects simply cannot be described by an orientational order parameter alone (nor can, as a matter of fact, any lyotropic system). A theory for nematic coarsening in this type of system must also somehow deal with the scission and recombination kinetics of the micelles [30]. For these reasons wormlike micellar nematics may well belong to a different dynamic universality class.

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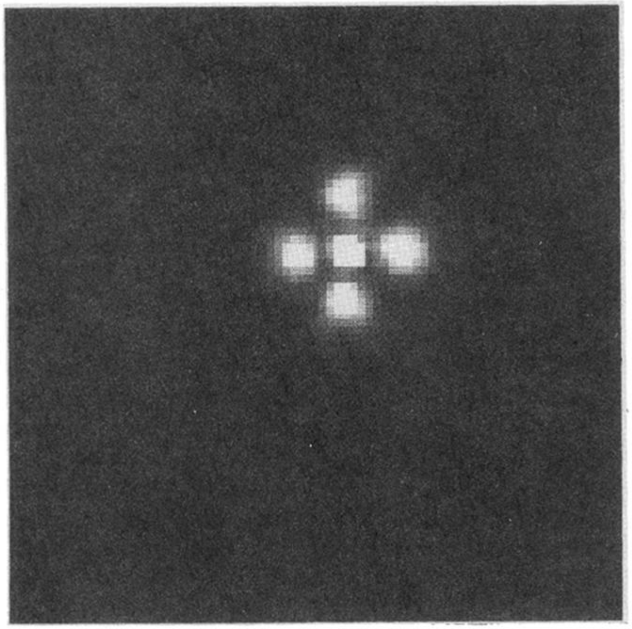

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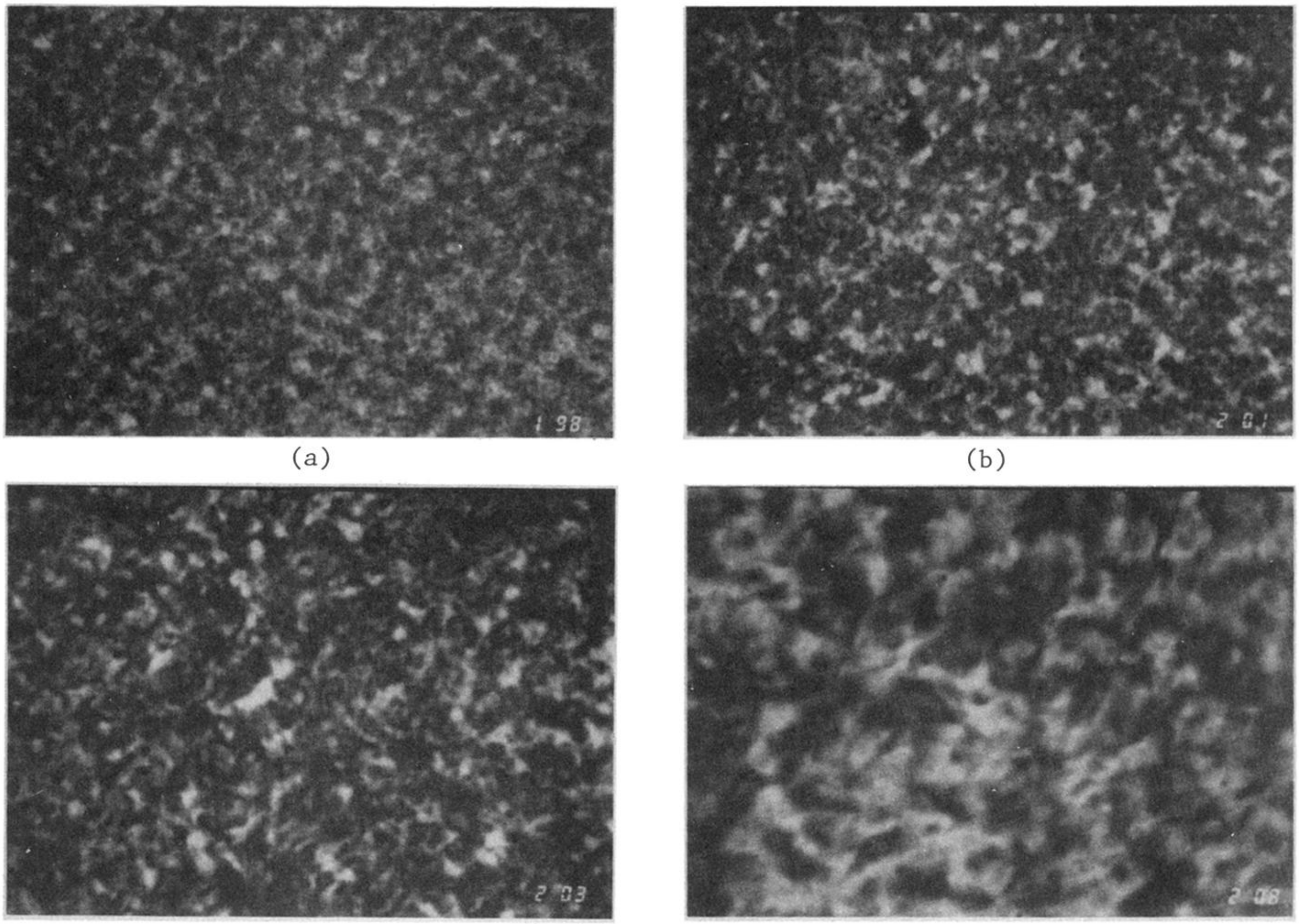

(a) (b)

(c) (d)

FIG. 7. Microscopic images (taken with crossed polarizing lenses) of the coarsening of the micellar nematics: (a) 40 s, (b) 7 min, (c) 17 min, and (d) 4 h after the quench. The photographs represent regions of approximately 420 μm × 600 μm. Dropletlike structures are clearly visible in (b). Color prints of the photographs can be obtained from the authors upon request.