# Spontaneous Nematic Alignment in Conjugated-Polymer Gels

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We report observations of optical birefringence indicative of spontaneous, long-range, nematic alignment in gels of polydiacetylene 4BCMU in toluene. The results indicate that an order parameter with magnitude of only $\sim 10^{-2}$ is maintained over macroscopic distances in an otherwise random system.

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Competing tendencies in polymer solutions restrict the types of polymers for which lyotropic liquid-crystalline phases can form. On the one hand, a rigid rodlike polymer will produce an ordered phase at a lower concentration than will a flexible polymer.[1] On the other hand, a rigid polymer is generally less soluble than a flexible one,[2] which makes it difficult to achieve even the reduced concentrations necessary to produce the ordered phase. Polydiacetylene (PDA) 4BCMU (4-butoxycarbonyl-methylurethane)[3] is known to have a rodlike conformation with a large axial ratio (length/diameter) in certain solvents,[4,5] which makes it a likely candidate for a lyotropic polymer. However, it has low solubility in those solvents and no liquid-crystalline phase has been observed. A rod-to-coil conformational transition can be induced in the PDA 4BCMU by a change of the solvent quality[4] (e.g., by an increase of temperature) with a marked increase in polymer solubility. Cooling a sufficiently concentrated solution ( > 0.06% by weight) from the high-temperature, high-solubility, coil phase back to the low-temperature, low-solubility, rod phase produces a gel,[3,6] a random network of the rodlike polymer molecules embedded in the solvent.[7] One might suspect, for such a polymer, that it would be possible to prepare a solution in the (isotropic) coil phase which, on cooling to the rod phase, would form an orientationally ordered gel.

We report, in this Letter, observations of macroscopic optical birefringence in PDA 4BCMU gels that indicate spontaneous, long-range, nematic alignment in these gels. Orientational order has been observed in polymer gels previously and is of considerable technological importance.[2] However, orientation is produced in those gels either by the stretching of the gel network or the shearing of the polymer solutions prior to gelation. In contrast, PDA 4BCMU gels exhibit *spontaneous* birefringence, i.e., without our subjecting them to external fields. We know of no previous reports of the spontaneous formation of a nematic gel phase.

Gels are produced by dissolving solid PDA 4BCMU in toluene at 100 °C and then cooling the solution to room temperature.[6,7] The gel-sol (and rod-coil) transition is reversible. Gelation is essentially complete after several hours at room temperature, although slow changes in the optical properties are observed up to 24 h later. The gels are stable over several months.

The gels exhibit phenomena characteristic of birefringent media. Figure 1 demonstrates birefringent double refraction in the gel. A single, well-collimated, linearly polarized He-Ne laser beam (5 mW, 6328 Å) passes through a PDA 4BCMU gel ($c = 1.7 \times 10^{-2}$ g/ml) at a small angle to the gel surface and strikes a screen several meters away. The front and back surfaces of the gel are not parallel in order to enhance the separation of the two refracted beams. In Fig. 1(a), we see that the single beam has been decomposed into two separate beams. A polarizer is placed in these beams and rotated until one of the beams vanishes [Fig. 1(b)]. When the polarizer is rotated 90°, the second beam vanishes, and the first reappears [Fig. 1(c)]. It is also possible to rotate the incident polarization so that only one spot appears on the screen. By rotation of the incident polarization by an additional 90°, that spot vanishes and the other appears. This birefringence indicates net orientational order in the gel; i.e., the polymers are aligned, on average, along some preferred direction. The net alignment, coupled with the anisotropic molecular polarizability[3b,8] of the rodlike molecules, produces the birefringence. Moreover, this double refraction implies net orientational order over *macroscopic* lengths. If the orientation occurred only over microscopic domains, the net birefringence would average to zero.

Because of the large refractive-index difference between the polymer and the solvent, the size of the polymer, and the random nature of the gel network, PDA 4BCMU gels scatter light strongly. This property makes possible a novel technique for monitoring the birefringence when observations are

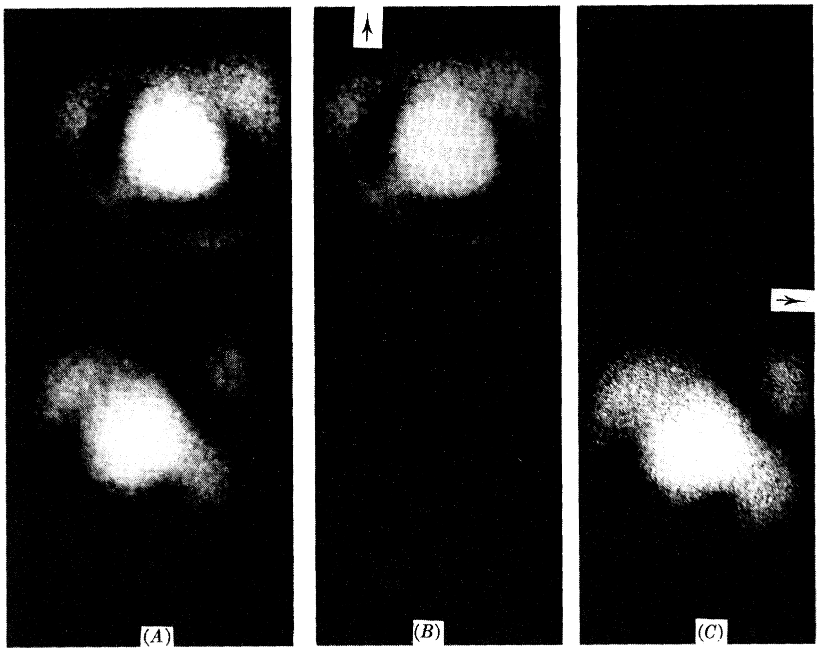

FIG. 1. A linearly polarized He-Ne laser beam is decomposed into two beams on passing through the gel. The photographs show the two beams as they strike a screen: (a) two beams resulting from double refraction by the gel; (b) a polarizer after the gel is rotated to extinguish one beam (polarization indicated by arrow); (c) an additional rotation of the polarizer by 90° extinguishes the other beam.

made *transverse* to the direction of light propagation. In Fig. 2, we present photographs of a He-Ne laser beam (6328 Å) as it passes through a PDA 4BCMU gel with concentration $5\times10^{-3}$ g/ml. The viewing direction is normal to the direction of beam propagation and the incident beam is normal to the front surface of the gel. In Fig. 2(a) the laser is linearly polarized; in Fig. 2(b), unpolarized. That the striae seen in Fig. 2(a) are not found in Fig. 2(b) rules out periodic density variations in the gel as their cause. Rather, the striae result from the interference of the light scattered from the ordinary wave with that scattered from the extraordinary wave. When linearly polarized, monochromatic light is incident normally on a birefringent medium, it can be considered as two superimposed waves, the ordinary ($o$) and the extraordinary ($e$) waves, propagating with orthogonal polarizations at two different velocities. At any point in the medium, the two waves differ in phase by $\delta=2\pi\Delta nx/\lambda$, where $|\Delta n|=|n_0-n_e|$ is the difference in the refractive indices, $\lambda$ is the wavelength of the light *in vacuo,* and $x$ is the distance traveled by the light in the medium. The waves scattered by fluctuations in the dielectric constant retain this same phase shift. The total scattered electric field, $\vec{E}_s$, at a given point along the beam is then $\vec{E}_s=\vec{E}_{so}+\vec{E}_{se}\exp(i\delta)$, where $\vec{E}_{so}$ and $\vec{E}_{se}$ are the fields scattered from the ordinary and extraordinary waves, respectively. The scattered intensity, $I_s$, is proportional to $|E_s|^2$ or $I_s\propto E_{so}^2+E_{se}^2+2E_{so}E_{se}\cos\delta$. Therefore, $I_s$ is modulated as a result of the birefringence of the gel. This explanation can be tested by rotation of the polarization of the incident beam. We find two orientations, separated by 90°, for which the dark striae vanish. These orientations are the same as those for which the double refraction in Fig. 1 disappears and correspond to the incident polarization being parallel to one of the optical axes.

The spatial period, $d$, of the intensity modulation is related to $\Delta n$ by $d=\lambda/\Delta n$, while $\Delta n$ is related to the degree of orientational order in the gel and can be used to estimate the order parameter, $\bar{S}=(3\cos^2\theta-1)/2$. In Fig. 2(a), we measure $d\simeq1.5$ mm, which yields $\Delta n\simeq4\times10^{-4}$. Measurement of the reflectivity of PDA 4BCMU crystals[8] gives $\Delta n\simeq3.8$ at $\lambda=6328$ Å. If we let the crystal represent complete alignment in a system of unit density, then our value of $\Delta n$ implies $\bar{S}\simeq0.02$. The striae are uniformly spaced along the 15-mm path of the beam, which implies a constant order parameter over the sample along that direction. This value for $\bar{S}$ is approximate since $\Delta n$ should be measured along the principal axes of gel (the orien-

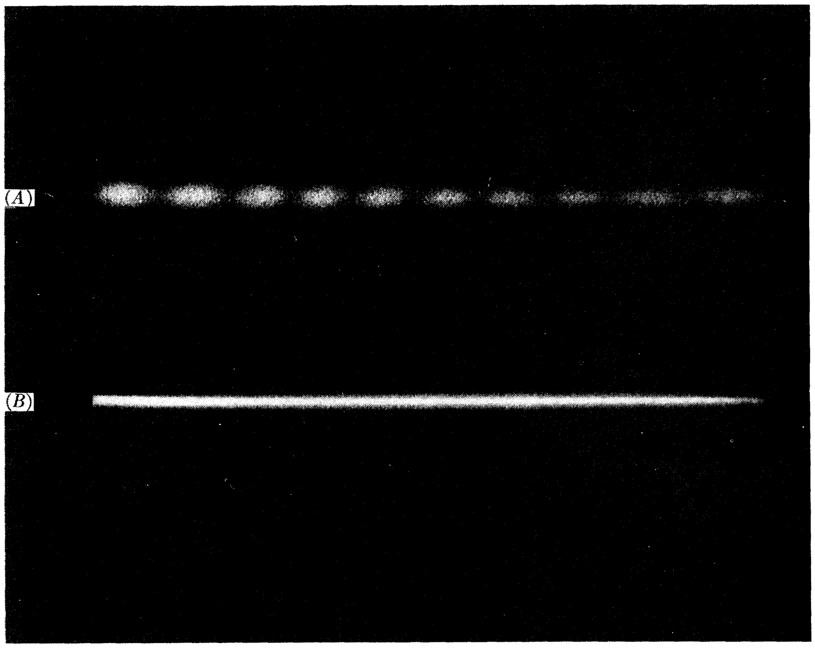

FIG. 2. Photograph of He-Ne laser beam as it passes through the PDA 4BCMU gel; viewing direction is normal to propagation direction. The gel is viewed through a circular window on the top of the cell with the center one-third of the path being visible. The laser is (a) linearly polarized or (b) unpolarized. The dark fringes in (a) are separated by 1.5 mm. The brightness decreases along the path as a result of scattering and absorption.

tation of the principal axes relative to the propagation direction is unknown). However, examination of several samples prepared independently and in different sample cells gave about this value in every case. Since significant error would be involved only in the singular case where the beam propagated at a very small angle with respect to the principal axes, we expect the inferred value of $\bar{S}$ to have the correct magnitude.

In the absence of a preferred direction in the gel, one would expect nematic alignment only in microscopic domains oriented randomly with respect to one another. Since the principal axes are found to be parallel and perpendicular to the container walls, we believe that the walls impose this preferred direction. Moreover, the striae in Fig. 2 are always more closely spaced when the laser beam passes close to one of the container side walls. As the beam is translated away from the wall, $\bar{S}$ decreases (by a factor of 2–3 on going $\sim 0.5$ cm from the wall). Once the beam passes the middle of the container and approaches the opposite side wall, $\bar{S}$ again increases. This enhanced ordering near the side walls leads one to suspect convection-induced shear as the mechanism for alignment. We rule this out on the basis of light-scattering observations. Laser light scattered by the solution at temperatures above the gel point produces a time-varying, swirling speckle pattern characteristic of convection. With the onset of gelation, the speckle pattern becomes stationary, which signifies the suppression of convective motion. It is only well after convection stops that the birefringence appears.

Since x-ray scattering does not indicate the presence of microcrystals[3a] in the PDA gels, we suggest a picture based on a gel network of interconnected rods[6,7] to account for the oriented gel. Steric interactions among the rodlike polymers would tend to produce an aligned solution phase. An additional, attractive, short-ranged interaction (possibly hydrogen bonding, in this case),[9] insensitive to the orientation of neighboring rods, would produce the essentially random gel network. Whether this system exhibits orientational order then depends on the relative kinetics of gelation and orientation. Estimates show that the minimum concentration needed to form a nematic solution phase[1] of PDA 4BCMU in its rod conformation and the minimum concentration needed for gelation[6] are both of order 0.05%. Thus, any solution of this polymer concentrated enough to form a nematic phase also will form a gel. If nematic alignment of the initially isotropic solution occurs in a short time compared to the time required for the solution to gel, then the final state of the system would be a nematic phase with many of the polymers linked to one another (a nematic of "sticky" polymers). In the limit of fast gelation and slow alignment, the gel would be isotropic.

A more microscopic picture can be developed based on measurements of the relevant time scales. The characteristic time ($\tau_r$) for orientational alignment of a PDA 4BCMU molecule is known from studies of transient electric-field–induced birefringence[5]; $\tau_r \simeq 0.1$ s. If two molecules (each of length $L$) are separated by a distance greater than $\sim L/2$, there would be no tendency for alignment. Thus, the degree of orientation should be at most $\tau_t/\tau_r$, where $\tau_t$ is the time needed for translational diffusion over a distance of order $L/2$. Consequently, an estimate for the orientational order parameter would be $\bar{S} \sim \tau_t/\tau_r$. Since $\tau_t \simeq 500$ $\mu$s (from quasielastic light scattering[4]), $\bar{S} \sim 10^2$. A more precise theory must take into account the effect of random connectivity (two molecules "stick" whenever they make contact) in the presence of an orientation-dependent interaction.

Gelation of solutions of another rodlike macromolecule, PBLG, has been explained[10,11] in terms of the spinodal decomposition of a homogeneous solution phase into a dilute isotropic solution phase and strands of a dense nematic solution phase that form the gel network. Although there is some evidence for regions of orientational order within the PBLG gels,[10] they do not exhibit macroscopic birefringence.

A nematic gel is an intriguing system from a materials point of view. The combination of the optical properties of a nematic liquid crystal with the structural properties of a gel results in a system with rather unique acousto-optic characteristics. A distortion of the gel network in response to some external force produces a change in the gel's birefringence.[7] Because of the elastic stiffness of the network, the gel (hence, the birefringence) returns to its initial equilibrium state when the external force is removed. Birefringent crystalline solids respond in a similar manner but with an elastic modulus many orders of magnitude greater than in the PDA 4BCMU gels.[7] In addition, the coupling of the gel birefringence to an applied electric field via interactions with the polymer network[7] along with the low optical attenuation at wavelengths above 5800 Å[3] makes this gel suitable for electro-optic applications.

Currently, we are investigating the effect of external fields on the alignment in gels. Preliminary results show a significant enhancement of the orientational ordering ($\bar{S} \sim 0.1$) when the gel forms in the presence of an electric field. Studies of the concentration dependence of the birefringence are also underway.

In summary, gels of PDA 4BCMU in toluene exhibit optical birefringence. This optical anisotropy results from spontaneous formation of long-range nematic order in the gel. We find it remarkable that a broken-symmetry state with order parameter of only $\sim 10^{-2}$ persists over macroscopic distance in an otherwise random system. This novel gel phase can be understood in terms of the competing tendencies in solutions of rodlike polymers to both align and gel.

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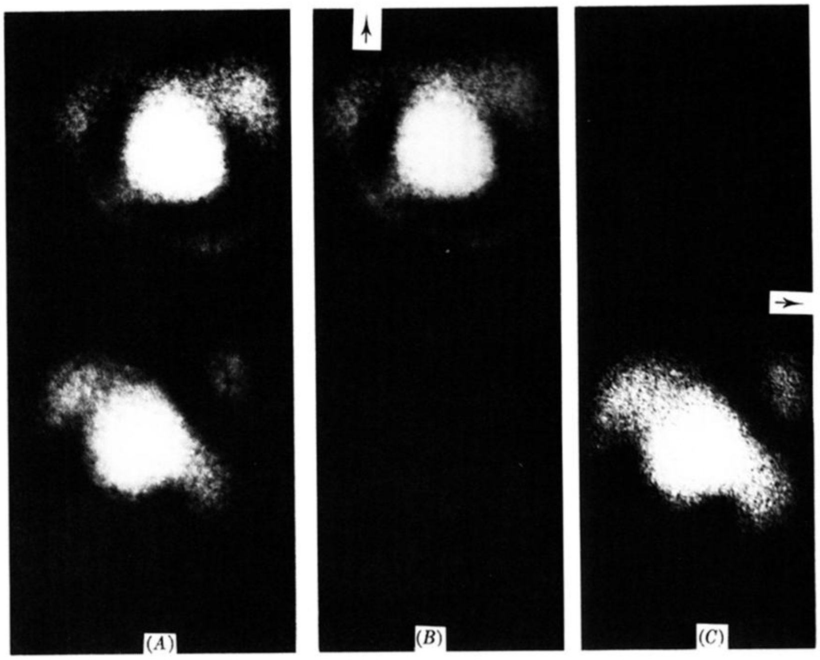

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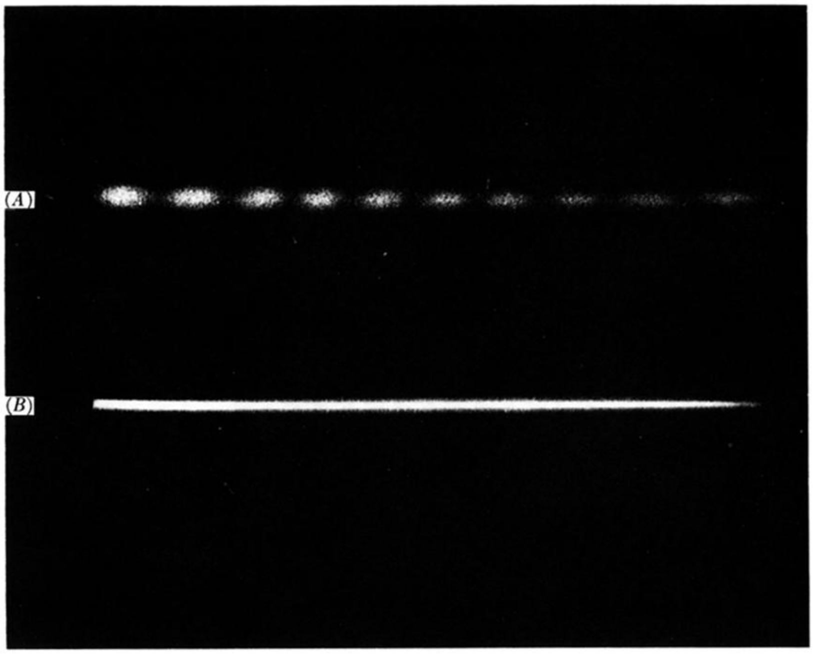

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