Communications to the Editor

An Unusual Conformational Transition in Monomolecular and Langmuir–Blodgett Films of the Poly(diacetylene) Poly-4-BCMU, Poly(dibutyl 4,19-dioxo-5,18-dioxa-3,20-diaza-10,12-docosadiynedioate)

The phase transition of poly(dibutyl 4,19-dioxo-5,18-dioxa-3,20-diaza-10,12-docosadiynedioate), a soluble poly(diacetylene) commonly known as poly-4-BCMU, has been of considerable recent interest.[1-5] This occurs in the solution-cast film as a transition from a room-temperature red form to a high-temperature yellow form. In solutions, the red-to-yellow phase transition can be induced either by increasing the temperature or by changing the solvent composition. One model suggests that the phase transition in solution involves the disruption of intramolecular hydrogen bonds along the polymer chain, leading to a conformational transition from an extended rigid-rod conformation, in the red form, to a random-coil conformation, in the yellow form.[2-4]

In this paper, we report the observation of an unusual transition from the yellow-to-red forms in monomolecular/bimolecular films of poly-4-BCMU, induced by an increase in surface pressure. Although a first-order phase transition, going from a monolayer to a bilayer, has already been reported for films of polypeptides, to our knowledge, this is the first observation of a conformational change (affecting π-electron conjugation and hence the shift of the $\pi-\pi^*$ electronic transition) in a monolayer/bilayer film. This is a specific feature only of the polymer film, since no phase transition is observed in the monomer monolayer of 4-BCMU.

The isotherms were obtained on a film balance that has been described elsewhere.[6] The polymer and monomer samples were spread from chloroform solutions while the surface pressure was measured by the Wilhelmy plate method using a Cahn, R.G. automatic-nulling electrobalance. The temperature of the water subphase was controlled to ±0.1 °C. Subphase water used was quadruply distilled and had a pH of 5.6 and a resistivity of at least 15.0 MΩ cm. Films were transferred to glass microscope cover slides by the Langmuir–Blodgett technique by vertically lifting the glass sides through the film-covered subphase.

The Π–*A* isotherms of both 4-BCMU and poly-4-BCMU at 20 °C are shown in Figure 1. The compression rate for both isotherms was 10 Å^2 molecule^{-1} min^{-1}. The monomer isotherm is featureless, characteristic of an expanded state of high compressibility, collapse initiating at about 10 dyn/cm and 110 Å^2/residue. By contrast, the polymer isotherm shows both an expanded and a condensed region with a well-defined transition. Collapse for this latter film occurs above 40 dynes/cm.

An examination of Corey–Pauling–Koltun (CPK) molecular space-filling models (see Figure 2) suggests that a close-packed monomolecular film of poly-4-BCMU molecules oriented at the air–water interface would occupy an area of approximately 110 Å^2/residue (the term residue refers to one repeating unit in the polymer chain). Interestingly, this is almost exactly the area per molecule at which the monomer isotherm shows an onset of collapse and the polymer isotherm shows the onset of the plateau. It appears that while compression of the monomer monolayer below 110 Å^2/molecule results in a film collapse, the polymer monolayer, at an equivalent packing, begins to undergo a first-order transition. The flatness of the plateau indicates the considerable stability of the new phase being formed. In the polymer monolayer, it is to be expected that film hydrophilic/aqueous substrate interactions will play a major role. In subsequent layers, however, this would not be the case and other conformations, including intrapolymer, hydrogen-bonded conformations, will become possible. The monolayer conformation depicted in Figure 2 will lack such intrapolymer hydrogen bonds. It may then resemble, to some degree, the yellow conformation obtained in polar solvents.

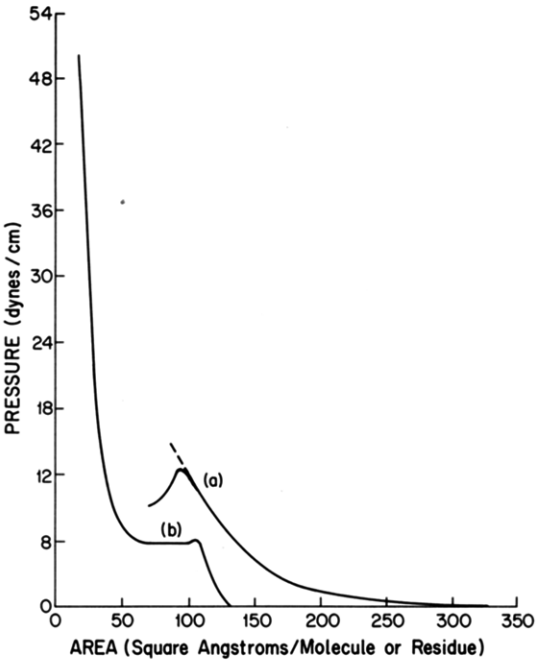

Figure 1. Surface pressure (Π in dyn/cm) vs. area (Å^2) isotherms at 20 °C (a) per molecule of 4-BCMU and (b) per residue of poly-4-BCMU. The broken line shows the conformational isotherms of the monomer 4-BCMU where we believe the onset of a collapsed phase occurs.

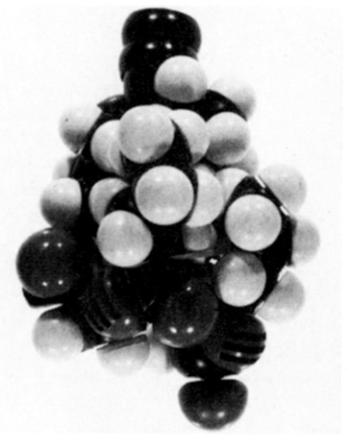

Figure 2. CPK model of a poly-4-BCMU residue in the assumed conformation at the air–water interface. Poly-4-BCMU has the structure $(=CR-C\equiv C-CR)_n=$, where R is $(CH_2)_4OOCNHCH_2COO(CH_2)_3CH_3$. The conformation shown has an excellent hydrophilic–hydrophobic segregation with the polar groups available to the air–water interface and the hydrophobic backbone well removed. The area/residue is approximately 110 Å^2.

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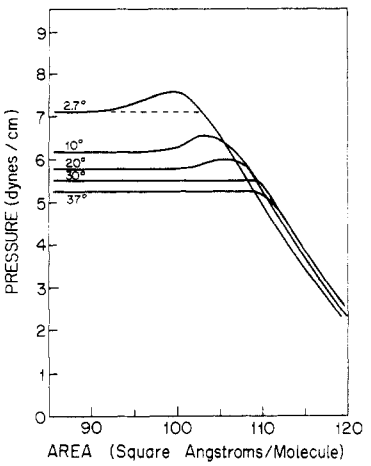

Figure 3. The temperature dependence of a segment of the surface pressure/area per molecule isotherm shown in Figure 1. The segment includes the onset of the monolayer/bilayer transition Π_t as defined by the extension of the plateau (broken line) to meet the expanded region. These isotherms were obtained by continuous compression at a compression rate of 10 Å^2 molecule^{-1} min^{-1} at the temperatures indicated. The metastable peak, due to delayed nucleation of the bilayer phase, becomes more prominent as the temperature decreases while the surface pressure of the plateau increases. $d\Pi_t/dT$ is −0.048 dyn cm^{-1} deg^{-1}.[8]

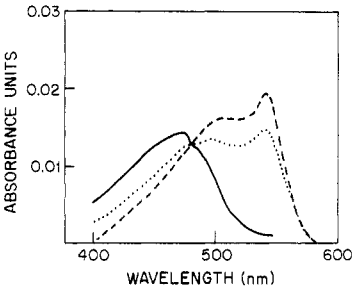

Figure 4. Absorption spectra of Langmuir–Blodgett transferred films at 23 °C: (—) film transferred at areas/residue in excess of those of the isotherm plateau (see Figure 1); (···) film transferred while in the plateau; (- - -) film transferred at areas/residue less than those of the plateau region.

The eventual increase in Π at the low-area end of the plateau represents the compression of this now completely formed new phase, which, because of its stability, can attain a much higher pressure before its collapse. It was observed that this condensed state of high stability appeared quite rigid while being compressed, actually moving the Wilhelmy plate out of its vertical position in the direction of film compression. Clearly, the areas per residue, both observed and calculated, suggest that the plateau observed for poly-4-BCMU represents a heterogeneous two-phase region consisting of monolayer and bilayer domains. This type of film behavior is in fact quite similar to that observed by Malcolm[7] for polypeptides at the air–water interface.

The polymer isotherm shows a small peak or maximum just at the onset of the plateau (Figure 3). As the temperature is lowered, this feature becomes more prominent, as is typical of a disorder–order transition, i.e., going from a less ordered to a more ordered state.[9] In our case, the bilayer phase is more ordered than the monolayer phase. The transition pressure of the plateau is found to decrease with increasing temperature, indicating the bilayer phase becomes more stable with increasing temperature, presumably because the necessary molecular reorganization to form such a structure is much easier. This indicates that the transition from monolayer to bilayer is an endothermic process.

Visible absorption spectra from glass slide deposited monolayers and Langmuir–Blodgett multilayers were obtained on a Perkin-Elmer UV–visible spectrometer at 25 °C. Spectra were obtained with a scan rate of 60 nm/min and a slit width of 0.2 nm. An analysis of the visible absorption spectra (Figure 4) of poly-4-BCMU films transferred to glass slides at different points of compression (i.e., different points on the isotherm) reveals that in addition to bilayer formation, a conformational change is taking place in the plateau region. Films transferred at areas per residue in excess of the onset of the plateau show an absorption spectrum characteristic of the yellow coil form of poly-4-BCMU, and those transferred at the end of the plateau have a spectrum characteristic of the red rod form as reported by Lim and Heeger.[4,5] Films transferred within the plateau show an absorption spectrum characteristic of a mixture of both red rod form and yellow coil form. Therefore, it appears that a monomolecular film of poly-4-BCMU on water exists in the disordered yellow form, reported to be of random-coil conformation in solution. This is in contrast to the solution-cast film, which at room temperature is in the red form. However, once compressed beyond the area/residue of a close-packed monolayer, nucleation of a new phase results, in which an ordered red form involving a conformation with enhanced π-electron conjugation is favored. If we assume that the red form also involves a rigid-rod conformation as proposed for toluene solutions, then its rigid nature could explain the effect noted earlier of increased film rigidity once bilayer formation is complete.

Further support for the idea of bilayer formation comes from the study of successively dipped bilayer films. It is found that if a glass slide onto which one monolayer of yellow coil form of poly-4-BCMU has already been transferred is used as a substrate and a second layer of the yellow form is transferred, the resulting bilayer has a visible absorption spectrum characteristic of a mixture of the red and yellow forms of poly-4-BCMU. It will be recalled that spectra similar to these were obtained for single films transferred within the plateau region where bilayer formation is presumed to take place. Our results, therefore, provide the first evidence that the macromolecules of poly-4-BCMU in a monolayer are stable in the yellow conformation, but the preferred conformation in the bilayer and multilayers is that of the red form. Therefore, intermolecular forces tend to stabilize the ordered red conformation.

Further experiments involving a detailed study and analyses of temperature dependence as well as others involving electron microscopy and ellipsometry are currently under way.

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Registry No. Poly-4-BCMU (homopolymer), 68777-93-5; poly-4-BCMU (SRU), 76135-61-0.

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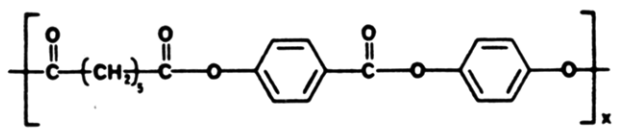
Surface-Enhanced Rate of Molecular Alignment in a Liquid Crystal Polymer

The orienting effect of surfaces on liquid crystals formed by small molecules is a well-known phenomenon.[1-5] It has been explained theoretically on the basis that orientation avoids high-energy elastic distortions in mesophases that are in contact with specific types of surfaces.[6,7] The types of surfaces that are known to have this "guiding" effect on the liquid crystal's orientation include chemically modified surfaces and also those containing topographical features such as uniaxial grooves or cavities. Should it be possible to extend these effects to macromolecular liquid crystals, many possibilities would exist for the study of solid-state properties in highly ordered thin films formed at interfaces. However, recent findings suggest that little if any orientation can be induced in high molecular weight thermotropic polymers by conventional surface treatments. Krigbaum and Lader,[8] for example, were reportedly unable to orient 10-μm-thick samples of a thermotropic polyester by standard surface-rubbing techniques. Another example is the work by Meurisse et al.,[9] in which they reported difficulties in the surface alignment of a liquid crystal polyester. In our own experience over the past 2 years we find that polymeric liquid crystals respond very slowly if at all to surface forces as revealed by optical microscopy. On the other hand, small-molecule thermotropics become completely aligned in response to surface forces in times well under 1 s.[10] In light of these observations, it has been our objective to understand the principles and limitations of surface forces affecting molecular organization in polymeric systems. We report here on the alignment kinetics that result as a consequence of coupling both magnetic and surface forces. The effect such coupling has on alignment dynamics can help us understand the equilibrium structure of polymer liquid crystals.

The material investigated here is a main-chain thermotropic polyester synthesized in our laboratory and having the ideal chemical structure shown below.



Its synthesis was first reported by van Luyen and Strzelecki.[11] The structure is termed ideal since we believe this polymer transesterifies to a random chemical microstructure.[12] The material undergoes a solid-to-liquid crystal phase transition near 150 °C and can be oriented in magnetic fields under certain conditions. In our recent studies on magnetic field orientation dynamics of this

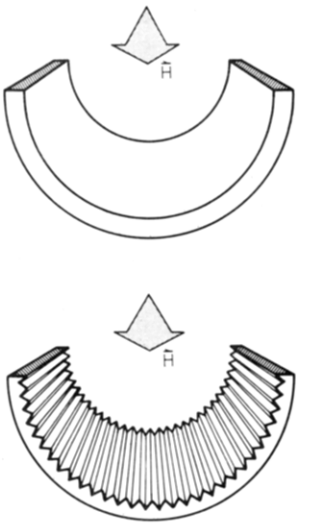


Figure 1. Schematic diagram of ungrooved (top) and grooved (bottom) NMR tubes used in orientation experiments. Note that the direction of the grooves is parallel to the external magnetic field.

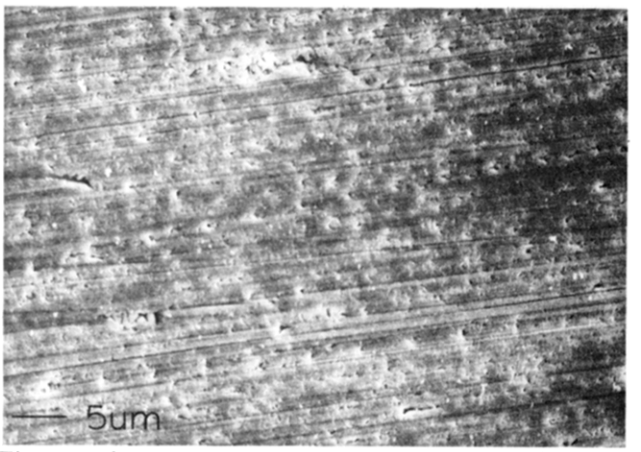


Figure 2. Scanning electron micrograph of grooved NMR tube.

polymer,[13] we identified one high molecular weight sample that responded sluggishly to the external field over periods of several hours at temperatures of 185 °C. We have used this specific sample in the present investigation.

Samples were placed in 4-mm-diameter glass tubes and exposed at 185 °C to the magnetic field of a superconducting magnet (4.7 T) in a Varian XL-200 NMR instrument. The control experiment utilized glass tubes with featureless surfaces. In other experiments we used featured surfaces containing uniaxial grooves prepared on the inner walls of similar tubes. The grooves were produced by abrasion with 1-μm diamond paste and a glass plunger over a period of 10 min. This procedure was followed by ultrasonic cleaning of the surface with water, ultrasonic cleaning solution, and then a series of reagent grade solvents (30 min with each). The solvents used were isopropyl alcohol, acetone, and methyl ethyl ketone. Finally, the surfaces were immersed in a concentrated chromic acid–sulfuric acid solution for 30 h, rinsed with distilled water, and dried at 300 °C for 3 h. As shown schematically in Figure 1, the grooving direction was parallel to the cylindrical axis of the tube and scanning electron microscopy of the inner walls revealed a groove size ranging from 0.4 to 1.25 μm in width (see Figure 2). All tubes were filled with 0.250 g of polymer, added in four equal-mass portions. After the addition of each portion, the tube was heated to 170 °C for 1 min and packed lightly with a solid glass

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