High-Pressure Optical Absorption Studies of Poly(4BCMU)

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ABSTRACT: The changes with pressure in the optical absorption spectra of poly(4BCMU) films, gels, and solutions were measured by using a diamond anvil cell. For red phase gels and films, the electronic absorption band slightly broadened and red-shifted at a rate of ~0.010 eV/kbar. While the pressure-induced shifts were reversible for gel samples, the low-energy absorption edge of spin-cast films sharpened following cycling from low to high pressure. Yellow phase solutions of poly(4BCMU) in chloroform and toluene/methanol mixtures underwent a phase transition at ~4 kbar pressure, converting from the disordered yellow phase to a more ordered red phase. Unlike typical gels and films, the optical absorption spectrum of the pressure-induced red phases showed no exciton at the absorption edge. From these results, we infer that the pressure-induced yellow–red phase transition corresponds to the formation of a more planar conformation with a smaller specific volume than the coiled conformation of the polymer in the yellow phase. These results are best explained by a wormlike chain model for the local chain conformation of poly(4BCMU) in yellow phase solutions.

Introduction

Conjugated polymers are currently under intense investigation largely because their nonlinear optical properties suggest potential applications in all-optical switching schemes.[1,2] Of the many conjugated polymers, the polydiacetylenes are particularly promising nonlinear optical materials since they have large third-order optical nonlinearities,[3,4] and are available as large-area single crystals[5] or as low-defect thin films deposited from solution.[6,7] Significant advances have been made toward evaluating polydiacetylenes in prototype optical device formats. For example, waveguiding,[7–9] the fabrication of channel waveguides,[6,10–12] and optical switching phenomena[13] in thin films of soluble polydiacetylenes were recently reported. By understanding the solution properties of polydiacetylenes, improved methods for depositing low-loss films might be devised. Improvements in the optical properties of polydiacetylene films would significantly accelerate their applications in nonlinear optics.

Much interest in the solution properties of polydiacetylenes centers on their solvatochromic and thermochromic phase transitions.[14] There is general agreement that these chromic transitions correspond to changes in the optical coherence length of the conjugated backbone that are related to changes in the backbone contour. The poly(nBCMU)'s (n = 2, 3, 4, 5, ...) (Figure 1) are perhaps the most widely studied of the chromic polydiacetylenes and exemplify the various chromic transitions that have been observed. Topotactic polymerization converts single crystals of monomer to polymer crystals with a golden luster. The as-polymerized polymers are blue in transmitted light but often convert to an intermediate red phase on heating[15] and at high temperatures form a yellow disordered phase. On cooling, the polymer returns to either a blue (odd-numbered members of the series) or red phase (even-numbered derivatives). Similar chromic behavior has also been observed for solutions of poly(nBCMU)'s. For example, chloroform solutions of poly(3BCMU) are yellow, but the addition of hexane, a nonsolvent, drives the polymer to a blue phase.[16,17] Similarly, poly(4BCMU) converts from a soluble yellow phase to a red gel,[18] and poly(nBCMU) derivatives with long side chains (n = 9, for example) can exist in a combination of red and blue phases.[19]

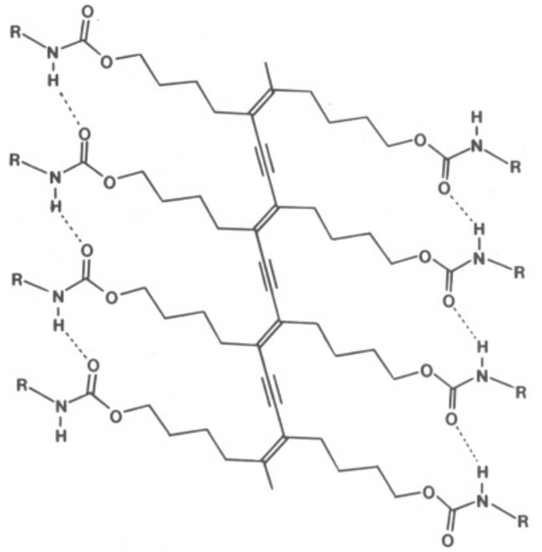

Figure 1. Poly(4BCMU) structure. R corresponds to $CH_2COOCH_2CH_2CH_2CH_3$. The members of the nBCMU family differ in the number of carbon atoms between the polymer backbone and the urethane linkage.

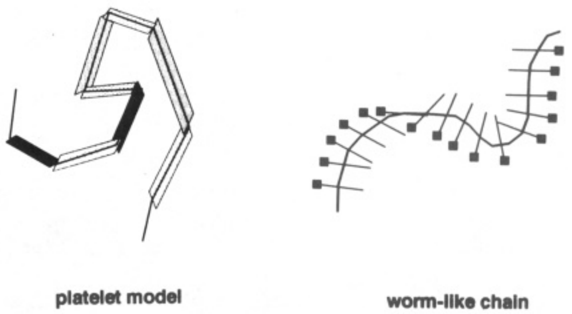

Figure 2. Models for the local conformation in yellow phase solutions of poly(nBCMU)s.

There is an extensive literature about the chromic transitions in the poly(nBCMU)s. While there is general agreement that the red (or blue) to yellow chromic transitions correspond to the polymer backbone converting from an extended conformation to a coiled conformation, there is still controversy over two aspects of the problem.

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First, what is the proper description for the local backbone contour, and second what is the mechanism for the "coil-rod" transitions. There are two competing models for the backbone conformation (Figure 1). The first is to build the polymer from platelike segments joined by freely rotating units. The length of the plates corresponds to the coherence length of the polymer, and for large numbers of segments such a model corresponds to a random coil. The wormlike chain model, however, describes the local backbone contour in terms of a gently twisting ribbon, with the collective small deviations from planarity between adjacent monomer units defining the correlation length.

A variety of light and neutron scattering experiments have probed the changes in the coherence lengths that accompany the chromic changes in the polymer solutions in an effort to understand the polydiacetylene conformation changes during the solvatochromic phase transition. The original work was described in terms of the platelet model for the local chain conformation;[18,20-23] however, Wenz et al. argued that a wormlike chain is a more realistic description for the yellow phase.[24-26] While they agreed that the chromic changes (yellow-red) corresponded to an increase in the correlation length for the polydiacetylene chains, they favored a cooperative mechanism that involved more than one chain.[26,27] Since many of the spectroscopic data reported to date can be interpreted by either model, additional information is needed to choose between the two models for local chain conformation.

Recently, high-pressure experiments have been used to probe the electronic structure and phase transitions of several π-[28,33] and σ-conjugated[34,35] polymers. For some polymers, pressure was found to drive solvatochromic and piezochromic phase transitions, and thus we carried out a series of high-pressure experiments on solutions and gels of poly(4BCMU), to try to learn how pressure affects the optical spectrum of the polymer, and by implication the conformation of the polymer. In particular, we were interested in the possibility of observing phase transitions in solutions of poly(4BCMU) that would correspond to the conversion of the disordered yellow phase to the more ordered red phase and whether a blue phase analogous to as-polymerized monomer might form at high pressures.

Experimental Section

The 4BCMU monomer was prepared as previously described.[36] After grinding 1.00 g of monomer to a fine powder, it was added under a blanket of nitrogen to a 1-L Ace photochemical reactor half-filled with deionized water. Nitrogen was bubbled through the resulting slurry, and the monomer was photopolymerized by using a 450-W medium-pressure mercury lamp as the source. After 30 min, the polymerized crystals were collected by filtration and were washed with acetone until the washings became clear. The resulting green-gold polymer (0.42 g, 42% yield) was dissolved in hot acetone, filtered, and precipitated into methanol. The purified polymer was collected, dried in vacuo, and stored in the dark at -10 °C until used. Typical weight-average molecular weights for the polymer (versus polystyrene standards, $CHCl_3$) were 2×10^5.

A gasketed Merrill-Bassett diamond anvil cell was used for the pressure measurements, with the pressure measured in situ by the ruby fluorescence method.[37] For studies involving gels of poly(4BCMU), thin films were deposited by spin casting from a 1 wt % solution of poly(4BCMU) in cyclopentanone onto a silicon wafer substrate. The films were removed from the substrate and were placed in the pressure cell with 2-propanol as the pressure medium. Solutions of poly(4BCMU) were made in the appropriate solvents and were filtered through 0.2-μm filters before use. The absorption spectra were measured on a Cary 2300 spectrometer.

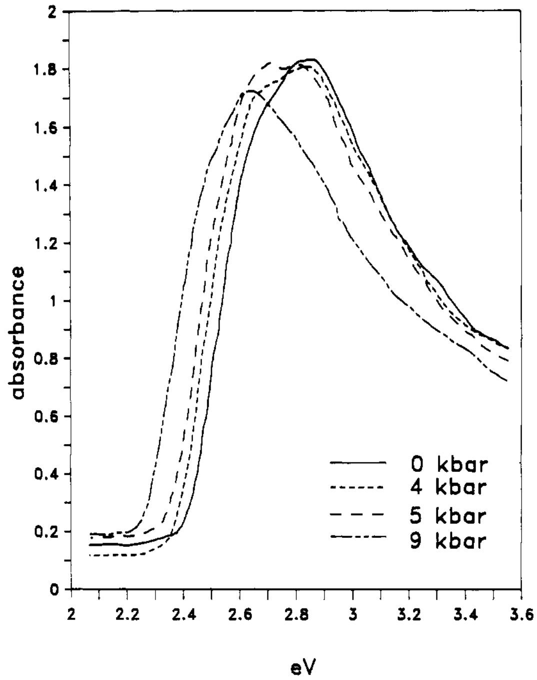

Figure 3. Shift with pressure of the absorption spectrum of poly(4BCMU) with pressure. Conditions: $\approx 5 \times 10^{-4}$ g/cm^3 poly(4BCMU) in $CHCl_3$.

Results

Pressure-Driven Yellow-Red Transitions. We first examined chloroform solutions of poly(4BCMU) and found that the absorption spectrum for poly(4BCMU) red-shifted with pressure (Figure 3). These results are similar to those from solvatochromism induced by adding nonsolvent to chloroform solutions of poly(4BCMU),[17] since the changes do not correspond to a simple rigid shift of the absorption band from yellow to red but rather reductions in the yellow phase intensity are matched by increases in that for the red phase. At intermediate pressures, we observed an apparent isosbestic point, but it was more poorly defined than typically seen in studies of the solvatochromic behavior of poly(nBCMU)'s.[14] This was not surprising since pressure was expected to induce shifts in the absorption spectrum as well as drive the phase transition. Optical measurements at pressures beyond 10 kbar become problematic because the solvent became glassy and readily fractured. In a second set of experiments, we examined solutions of poly(4BCMU) in mixtures of toluene and methanol. The results of this pressure study are shown in Figure 4. Again, a pressure-driven phase transition was seen, with the yellow to red phase conversion occurring at ≈ 5 kbar. In this mixed solvent system, the isosbestic point was sharper than when chloroform was used as solvent.

The data for these two sets of absorption curves were plotted on a linear energy scale and the low-energy edge of the absorption band was extrapolated to its baseline value. The extrapolated edge and the corresponding pressures are plotted in Figure 5. In well-behaved systems with no phase transitions over the range of pressures studied, plots such as Figure 3 are often linear with little scatter in the data.[28,30,32] Not surprisingly, our data gave a poor linear fit since the modest pressure range includes a phase transition.

Red Phase Samples. We also examined the pressure dependence of the optical absorption spectrum for red phase poly(4BCMU). Two types of red phase materials were examined: a gel prepared by cooling a warm toluene solution of poly(4BCMU) and a spin-cast film. Since spin-

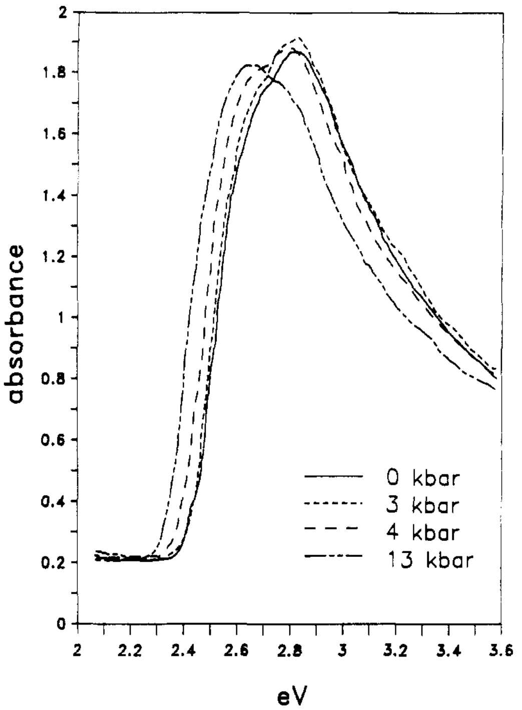

Figure 4. Shift of the absorption spectrum with pressure for poly(4BCMU) dissolved in 1:1 methanol/toluene mixtures. Conditions: ≈5 × 10^{-4} g/cm^3 poly(4BCMU) in 1:1 methanol/toluene.

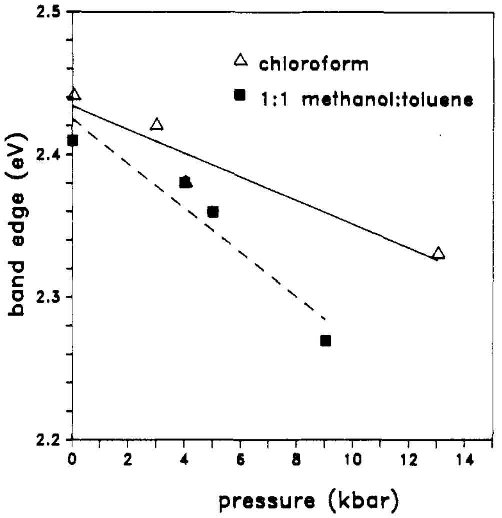

Figure 5. Changes in the extrapolated absorption edge as a function of pressure. The solid and broken lines are least-square fits to the data from chloroform and methanol/toluene solutions, respectively.

cast films are kinetic products of the spinning process,[38] they are more disordered than gels,[39] with the signature of disorder being the reduced intensity of the exciton at the low-energy edge of the absorption spectrum. In contrast to yellow phase solutions of poly(4BCMU), the shape of the optical absorption spectra for gel samples did not change appreciably with pressure but instead simply shifted to lower energies with increases in pressure (Figure 6). Some broadening accompanied the shift of the absorption envelope, but the gel never converted to a distinct blue phase that would be analogous to the optical absorption of polydiacetylene single crystals. In several runs a poorly defined knee appeared on the low-energy edge of the spectrum (not shown), but we were unable to identify with confidence the additional feature as the onset of the blue phase.

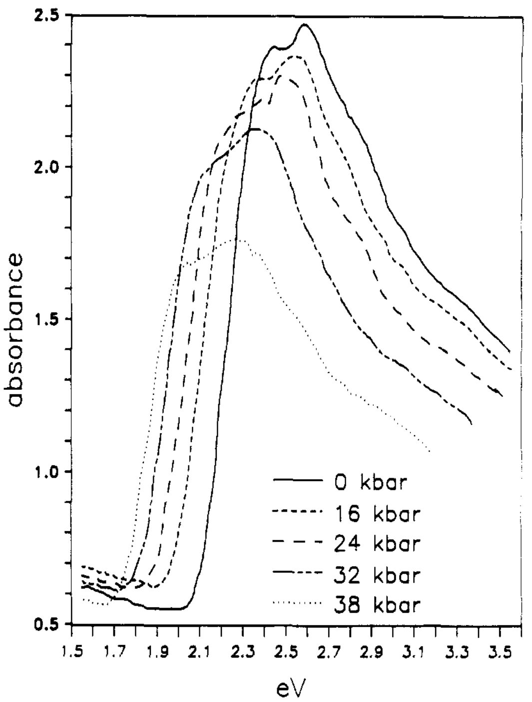

Figure 6. Shift of the absorption spectra with pressure for poly(4BCMU) gels.

While the pressure dependence of the spectrum for red phase gels was completely reversible, spin-cast films exhibited hysteresis. After cycling spin-cast films from low to high and back to low pressure, we found that the ambient pressure absorption spectrum had shifted slightly to lower energies and sharpened. We believe that these effects are caused by ordering of spin-cast poly(4BCMU) films under isotropic pressure, the pressure equivalent to thermal annealing. Other data support this interpretation. For example, spin-cast poly(4BCMU) films held just above room temperature develop sharper absorption edges,[38] and prism coupling experiments have detected flow in spun films of poly(4BCMU) under pressure.[7] These observations are also consistent with recent reports of the formation of ordered domains in polysilanes under pressure.[34,35]

As with the previous data, the energy at the onset of absorption was determined and the results are plotted in Figure 7. For the extrapolations, the slight "knee" seen at the highest pressures was ignored. The linear fit of the data is good, with a slope of 10 meV/kbar. The value is similar to the values observed for polyacetylene[30] (≈11 meV/kbar) and single crystals of PTS[28] (7.3 meV/kbar).

Discussion

Red Phase Samples. The effects of pressure on electronic absorption spectra are often interpreted in terms of contributions from both intramolecular and intermolecular interactions.[40] Since the excited states of a molecule are usually more polarizable than the ground state, pressure is thought to increase the strength of the van der Waals interactions between the components of molecular solids and cause a stabilization of the excited state. This is manifested as a red shift of the optical absorption spectrum, and for materials without significant intermolecular electronic coupling, it is expected to be the dominant contribution to pressure-induced spectral shifts. The results of high-pressure studies on molecular crystals and conjugated polymers are in accord with such a model. For polyacetylene,[30,31] polyphenylene,[32] the polydiacetylene PTS,[28] and the molecular crystals NTCDA and

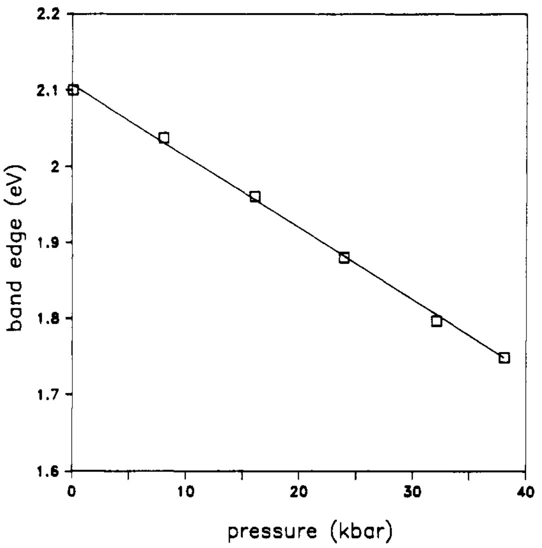

Figure 7. Changes in the extrapolated low-energy absorption edge of poly(4BCMU) gels as a function of pressure. The line is a least-squares fit to the data.

PTCDA[41] reversible linear shifts of the absorption edge were found for pressures less than 40 kbar, with nonlinear shifts observed at higher pressures. Our pressure data for the red phase gels of poly(4BCMU) are linear and reversible and thus can be interpreted similarly.[42]

We did not observe the transition of the red-phase gel to a blue phase that would be comparable to that of as-polymerized crystals of 4BCMU monomer. Recent optical polarization measurements showed that the blue–red transition is a solid-state disordering of as-polymerized crystals that largely preserves the optical anisotropy and linear arrangement of chains.[43] We attribute the inability to form a blue phase from red phase gels to disorder, since the near-perfect order of poly(4BCMU) single crystals is unlikely to be attained by starting with an ensemble of disordered chains with limited mobility. In the few experiments where hints of a blue phase were seen, we found that the results were sample dependent and often irreproducible. Perhaps these results corresponded to the local formation of the blue phase within the poly(4BCMU) aggregates.

Yellow Phase Samples. From previous work on the thermal disordering and solution properties of polydiacetylenes, it is known that hydrogen bonding associated with urethane linkages in the side chains of the polymer plays an important role in the phase transitions.[20,44,45] IR studies showed that the intramolecular hydrogen bonding network melts when poly(4BCMU) films are heated to 110 °C.[44] This is a single-chain phenomena since disordering of the polymer is largely associated with a second endothermic transition near 160 °C. Intramolecular hydrogen bonding also plays an important role in the solvatochromic behavior of polydiacetylenes, since the polymers are in their soluble yellow phase as long as the hydrogen-bonding network is disrupted. An experimental illustration of this effect is that poly(4BCMU) dissolves in neither toluene nor methanol but forms stable yellow solutions in mixtures of the two solvents. Competition by methanol for hydrogen bonding apparently disrupts the intramolecular hydrogen bond network, allowing the polymer to dissolve in toluene. Trifluoroacetic acid reportedly causes similar effects.[20]

How then does pressure modulate the polymer–polymer (intramolecular hydrogen bonding) and polymer–solvent interactions? Most pressure data are explained by proposing that, at high pressures, ensembles with lower specific volumes are favored relative to less dense arrangements. For an isolated poly(4BCMU) chain without chain folding, the conformation with the lowest specific volume corresponds to a perfectly flat ribbon with all intramolecular hydrogen bonds intact.[46] This arrangement, comparable to the chain conformation in the polymer crystal structure, is apparently inaccessible via pressure when starting with a disordered yellow solution. Less dense arrangements for a poly(4BCMU) chain correspond to twisted ribbons having some of the hydrogen bonds intact and the least dense conformation corresponds to a random coil with no intramolecular hydrogen bonding. Thus the differences in specific volumes favor the pressure-induced change from the yellow to red phase.

Now we call attention to the absorption spectra of the poly(4BCMU) red phase formed by compressing yellow solutions of poly(4BCMU). The spectra are smooth with no sign of the leading-edge exciton that is characteristic of gels[39] and films[38] of poly(4BCMU). (See the 0 kbar spectrum in Figure 6 for a typical spectrum for a poly(4BCMU) film.) As noted above, the magnitude of this absorption feature has been correlated with the relative degree of disorder in poly(4BCMU) samples. Samples formed by disordering single crystals of as-polymerized monomer have the strongest excitonic absorption, with that of gels formed under near-equilibrium conditions slightly smaller. Spin-cast films have the highest degree of disorder and consequently have the weakest excitonic feature. Thermal annealing experiments on poly(4BCMU) films[38] confirm the correlation between exciton strength and disorder.

We suggest that the smooth shape of the pressure-induced red phase spectra may be related to the size of the exciton in polydiacetylenes. Calculations[47] and inferences from experiments[48] suggest that excitons in polydiacetylenes have a size of about 30 Å in crystalline samples. The size is determined by a balance of the gain in energy that accompanies the delocalization of charge over many lattice sites and the elastic forces that limit the separation of the charges. For all conformations with $l_c > l_x$, where l_c is the correlation length of the polymer chain and l_x is the equilibrium exciton size for an infinite linear chain, the exciton has a fixed size, and oscillator strength builds in at a single energy at the edge of the absorption curve. For red phase poly(4BCMU) the characteristic features appears at ≈530 nm. In contrast, when $l_c < l_x$, the size of the exciton is determined by the distribution in l_c and the corresponding absorption edge should be more diffuse. Thus we believe that the featureless absorption edge for pressure-induced red phases implies a highly disordered chain conformation with short correlation lengths. Such disorder makes sense if the chain conformation is kinetically controlled, as would be the case in a viscous solvent at high pressure.

We believe this behavior is in accord with the wormlike chain model for the local chain conformation in yellow solutions of poly(4BCMU), as depicted in Figure 8. For the wormlike chain, small increases in pressure favor intramolecular hydrogen bonding (planar structures) over polymer–solvent interactions (disordered structures), and the formation of these intramolecular bonds causes adjacent monomer units to become more planar. The overall conformation of the polymer backbone is largely retained, since adjacent monomer units need only rotate through small angles to form the intramolecular hydrogen bonds. In contrast, a platelet model for the yellow phase would be more difficult to reconcile since it would require large-scale translational movement of the polymer chain.

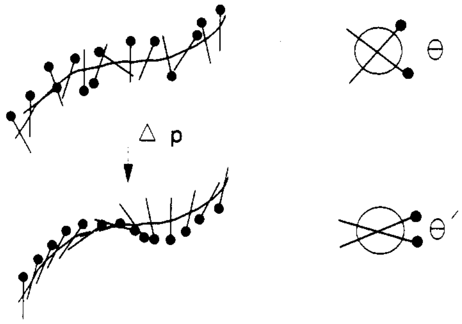

Figure 8. Model for the yellow–red phase transition. The average angle, θ, between adjacent monomer units decreases as pressure drives the transition with minimal changes in the backbone contour.

Furthermore, the smooth low-energy absorption edge is consistent with much disorder remaining in the polymer chain, and it seems unlikely that such disorder would remain if the polymer had enough mobility to convert from a coil composed of platelets to a rodlike conformation.

Summary

We examined the changes in the absorption spectra for solutions and gels of poly(4BCMU) with pressure. Gels and films show linear shifts of the absorption edge with pressure, similar to other molecular systems. For poly(4BCMU) solutions, we observed a pressure-induced phase transition from the disordered yellow phase to a more ordered red phase. To explain these observations, we propose that increased pressure favors planar structures because of their lower specific volumes. Because the smooth absorption edge of pressure-induced red phases implies considerable disorder, we believe the data are consistent with the yellow phase converting from a wormlike chain to a disordered red phase in which the side groups have increased their planarity relative to each other by small angular rotations rather than by mechanisms that require large translational motion of the polymer chain.

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