Interfacial Polymerization of Monomolecular and Langmuir–Blodgett Films of ((Butoxycarbonyl)methyl)urethane Diacetylenes

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ABSTRACT: Monomolecular films of 3-BCMU, 4-BCMU, and 9-BCMU at the air–water interface were studied by measuring their surface pressure (π) vs surface area per molecule (A) isotherms as well as by the visible absorption spectra of their polymerized Langmuir–Blodgett (L–B) films. The π–A isotherms of all three n-BCMU monomers displayed a phase transition between an expanded state and a condensed state resembling that of their corresponding polymers. The expanded-state surface areas of 9-BCMU, together with a Corey–Pauling–Koltun (CPK) molecular space-filling model of 9-BCMU, suggest that appreciable diacetylenic–subphase interaction may cause kinking in the looped portions of the side chains. Visible absorption spectra of L–B films of 4-BCMU and 9-BCMU UV polymerized at the air–water interface revealed both a red and a blue form for the former, while the latter was composed of the blue form alone. Horizontally transferring in situ polymerized films of 4-BCMU and 9-BCMU to hydrophobic substrates produced a shift of λ_{max} values to longer wavelengths. Polymerization after transfer to solid substrates resulted in only a blue form polymer for both 4-BCMU and 9-BCMU. The reversibility of the conformational coil to rod transition at the air–water interface was shown to depend on the natue of the side group (i.e., the value of n). Poly-4-BCMU showed 100% conversion back to the coil form after expansion to zero surface pressure, poly-3-BCMU showed only partial conversion, and poly-9-BCMU showed essentially no conversion. In situ polymerized 4-BCMU (blue form and red form) converted completely to the red form after expansion to zero surface pressure, while in situ polymerized 9-BCMU essentially remained in its initial blue form. Polymerization of a six-layer multilayer of 4-BCMU was compared to one having five intervening layers of arachidic acid and revealed a significant decrease in the percent polymerization of the latter. A possible explanation is that polymerization is taking place between adjacent layers as well as within a given layer in multilayers of 4-BCMU.

Introduction

Previously, we have shown that the ((butoxycarbonyl)methyl)urethane diacetylenes poly-4-BCMU[1] and poly-3-BCMU[2] can be spread and compressed at the air–water interface to form stable monomolecular films. Furthermore, these monolayers exhibited a phase transition from a monomolecular amphipathic yellow coil form to a bimolecular nonamphipathic red or blue rod form. The intramolecular disorder–order transition (coil to rod) is similar to that observed in solution and solution-cast films of these same polymers.[3-8] The coil to rod transition has been interpreted as being due to the formation of intramolecular hydrogen bonding beween adjacent n-BCMU side groups along the polymer chain, brought about either by a decrease in solvent polarity or by a decrease in temperature. The simultaneous yellow to red or blue color change is postulated to be a result of the creation of an extended π-electron overlap along the conjugated polymer backbone.

In this paper we will report and compare the monomolecular film behavior of the n-BCMU monomers 3-BCMU, 4-BCMU, and 9-BCMU with regard to their surface pressure (π) vs surface area per molecule (A) isotherms, as well as their polymerization with ultraviolet radiation both at the air–water interface (in situ) and after transfer to solid substrates (Langmuir–Blodgett films). We will see that the π–A isotherms of all three monomers show evidence of a phase transition at surface areas and transition pressures (π_t) greater than that of their corresponding polymers. The polymerization behavior of these interfacial monomer films will be shown to be strongly dependent on both the length of the hydrophobic portion of the side chains (i.e., the value of n) and the physical state of the film (i.e., expanded, transition region, or condensed). Increasing the length of the hydrophobic portion of the side chain ($n = 3$ to $n = 4$ to $n = 9$) will be seen to facilitate the polymerization process. In addition, the nature of the resulting polymer formed after UV exposure at the air–water interface is demonstrated to be dependent on the value of n.

For a given n-BCMU film, it will be shown that the physical–chemical nature of the substrate on which polymerization was carried out (i.e., air–water interface, hydrophilic glass slide, or hydrophobic glass slide) has a significant effect on the spectral behavior of the resulting polymerized adjacent film. Similarly, in situ polymerized films also show modification of their spectral properties after being transferred to hydrophobic rather than hydrophilic substrates. In general, the less fluid and less hydrophilic the interface, the more ordered the adjacent poly-n-BCMU film tends to be. The most ordered polymer films were obtained by the polymerization of Langmuir–Blodgett transferred monomer films, whereas less ordered polymer films were produced by in situ polymerization at the air–water interface.

The reversibility of the coil to rod transition that has previously been observed for poly-n-BCMU in solution by Patel and others[3,4] is investigated here for the case of films at the air–water interface. After compression of spread polymers and subsequent reexpansion to zero surface pressure, we can demonstrate that the degree of conversion from the rod form back to the coil form is dependent on the value of n, with poly-4-BCMU displaying complete conversion, poly-3-BCMU partial conversion, and poly-9-BCMU essentially no conversion. Similar behavior can also be observed for the in situ polymerized poly-4-BCMU and poly-9-BCMU, with the former showing a

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greater percent conversion to a less ordered form than the latter upon expansion to zero surface pressure.

Finally, we will show that a comparison of the polymerizability of a six-layer multilayer film of the 4-BCMU monomer with that of one having intervening layers of arachidic acid reveals a greater percent polymerization for the former after equal exposure to UV light.

Experimental Section

Surface pressure (π) vs surface area per molecule (A) isotherms were measured by using a Langmuir trough as described previously.[9] Surface pressure was measured via the Wilhelmy method in which a Wilhelmy plate was suspended from the arm of an R. G. Cahn automatic nulling electrobalance. The compressional isotherms were first recorded by means of an analog recorder and then digitized and plotted by computer to yield axes having the appropriate units.

Film spreading was carried out with dilute solutions of the film sample in chloroform (ca. 1.0 mg in 10.0 mL). After the desired volume of sample was slowly deposited at the water surface in dropwise fashion, 10 min was allowed for solvent evaporation before compression was begun. A compressional rate of 10 Å^2/(molecule-min) was used for all π-A isotherms. All isotherms were run at 20 °C. Langmuir–Blodgett vertical film transfer onto hydrophilic glass slides was carried out at constant surface pressure (within 0.1 dyn/cm) via a servo-driven, compressional barrier. The rate of vertical emersion of slides was approximately 3 mm/min. Horizontal transfer of films onto hydrophobic glass slides was accomplished by slowly lowering the substrate parallel to the film-covered air–water interface until contact was made. This was followed by suctioning off the surrounding film with an aspirator and finally lifting the substrate with the adherent film up from the interface.

All glass slides used as substrates were cleaned by first immersing them in hot chromic acid for 12 h. This was followed by a thorough rinsing of the slides with singly distilled water and then with quadruply distilled water. The slides to be used for vertical transfers (with an original hydrophilic surface) were then treated for ca. 5 min in an argon plasma prior to use. Those slides to be used for horizontal transfers (with a hydrophobic surface) were first cleaned as above and then alkylated by immersing them in a dilute solution of octadecyltrichlorosilane (OTS) in chloroform (0.1 mL of OTS in 50 mL of $CHCl_3$) for ca. 10 min, after which they were rinsed with chloroform and quadruply distilled water and then finally dried in a stream of nitrogen. Subphase water was first distilled then deionized to give a resistivity of at least 15.0 MΩ-cm. This water was then quadruply distilled, first from an alkaline stage, then from an acidic stage, and finally twice from an all-quartz still.

Samples of 3-BCMU and 4-BCMU were obtained from Dr. T. Prusik of Allied Chemical Corp., while the sample of 9-BCMU was provided by Dr. D. Bloor of Queen Mary College. The 3-BCMU, 4-BCMU, and 9-BCMU monomers were purified immediately before use of any trace polymer by first dissolving the sample in hexane, filtering out any trace polymer present, and finally recrystallizing the monomer from the filtrate.

Polymerization of monomer films was carried out with an ultraviolet light source having a wavelength maximum of 254 nm and an effective intensity of 80 mW/cm^2.

Visible absorption spectra were obtained on a Shimadzu UV 260 spectrophotometer. All films were transferred and spectra obtained at temperatures between 20 and 25 °C.

Results and Discussion

(a) π–A Isotherms. The surface pressure (π) vs area per molecule (A) isotherms for the monomers 3-BCMU, 4-BCMU, and 9-BCMU at 20 °C are shown in Figure 1. Both 4-BCMU and 9-BCMU display an expanded, a transition, and a condensed region not unlike their corresponding polymers,[1,10] whereas the isotherm of 3-BCMU exhibits a much narrower transition region and has expanded-state areas well below those corresponding to an interfacially located monolayer. In addition, while both 4-BCMU and 9-BCMU were able to maintain surface pressures at $\pi < \pi_t$ with only minimal relaxation at constant area (<0.5 dyn/cm in 10 min), 3-BCMU showed significant relaxation in the expanded state while held at constant area (2–3 dyn/cm in 10 min). Both observations indicate an enhanced instability, most likely due to a lower crystallinity or greater solubility, in the case of 3-BCMU. Such an increased solubility is not unreasonable since the decrease in the number of methylene groups (CH_2) on going from $n = 9$ to $n = 4$ to $n = 3$ should result in a significantly more hydrophilic molecule with an increased affinity for the water subphase. We will therefore restrict much of our discussion to a comparison of the behavior of 4-BCMU and 9-BCMU, since only these monomers form stable monomolecular films at the air–water interface.

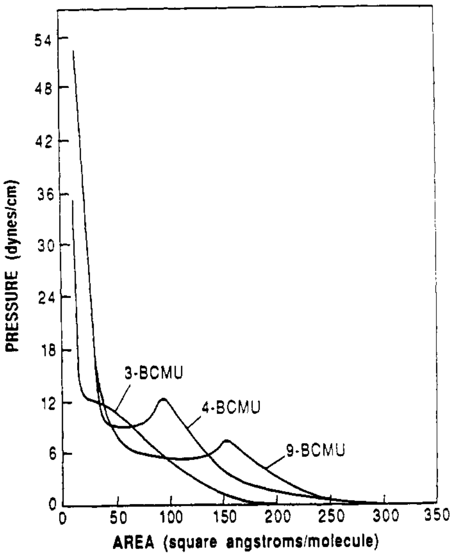


Figure 1. π-A isotherms at 20 °C of the monomers 3-BCMU, 4-BCMU, and 9-BCMU.

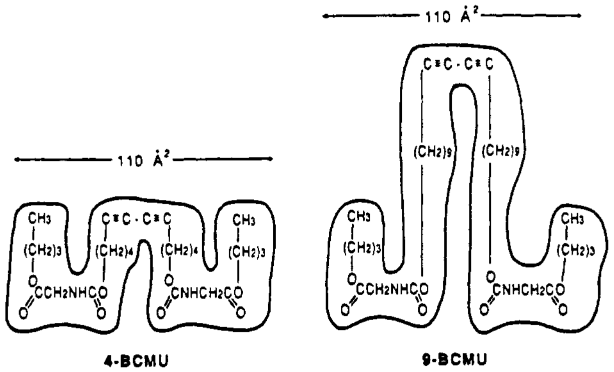
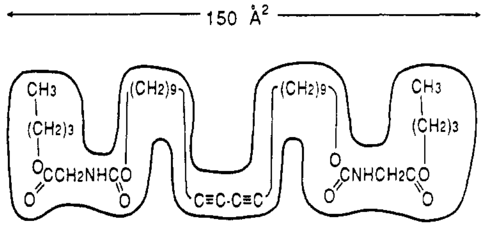


Figure 2. Schematic illustration of the molecular shape of equivalent amphipathic conformations of 4-BCMU and 9-BCMU based on Corey–Pauling–Koltun (CPK) models.

Th expanded-state areas per molecule at the onset of the transition for 4-BCMU and 9-BCMU are approximately 106 and 162 Å^2, respectively. These areas/molecule reflect the greater area required to accommodate the five additional methylenes in the two longer 9-BCMU side chains. This is equivalent to a 56 Å^2 increase in area; however, CPK models indicate both monomers would have an area/molecule of ca. 110 Å^2 for equivalent amphipathic conformations provided the diacetylene group is located well above the air–water interface as is shown in Figure 2. This discrepancy, along with the known affinity of triple bonds for the air–water interface,[11,12] suggests that 9-BCMU may assume a more expanded conformation with at least some of the diacetylene groups located at the water



9-BCMU

Figure 3. Schematic illustration of a CPK model of 9-BCMU assuming a somewhat more expanded amphipathic conformation with appreciable diacetylenic–subphase interaction.

surface as is shown in Figure 3. The longer, more flexible, alkane chains of 9-BCMU make such a conformation more possible. This would result in a less than perpendicular orientation of the $(CH_2)_9$ segments and would probably give rise to gauche conformers (i.e., prevent the formation of all-trans chains). A CPK model of 9-BCMU with both an interfacially located diacetylene group and close-packed adjacent hydrophobic chains would occupy about 150 Å², a 44 Å² increase in area compared to the conformation with no diacetylenic groups in the interface. Presumably the additional 12 Å² required to match the observed 162 Å² arises through the presence of gauche conformers in the looped portion of the side chains.

Both 4-BCMU and 9-BCMU have a distinct maximum in their π–A isotherm just at the onset of the transition as did poly-4-BCMU at low temperatures.[1] The monomer maxima, however, appear to be much more pronounced. As was previously pointed out, these maxima represent unstable regions of the isotherm and are compression rate dependent. Even with extremely slow stepwise compression techniques, waiting each time for "equilibrium", such maxima can still persist, though they are reduced in magnitude.[2] The π_t values in these cases are obtained by extrapolation of the near-horizontal transition plateau to the expanded state. A comparison of transition pressures reveals that all three monomers have π_t values greater than those of their corresponding polymers, indicative of the increased stability of the expanded monolayer state of the monomer. The decrease in the magnitude of π_t of the monomers on going from $n = 3$ to $n = 4$ to $n = 9$ also reflects the increasing stability of their condensed state with increasing chain length.

(b) Polymerization and Spectra. The ability of monomolecular and multilayer films of all three monomers to be polymerized by irradiation with UV light, both at the air–water interface and after transfer onto solid substrates, was also studied. No measurable polymerization at the air–water interface was observed after 1-h exposure to UV light to 3-BCMU in the expanded, the transition, or the condensed region. The instability of 3-BCMU at the air–water interface (i.e., the inability to maintain a given surface pressure over time) prevented the transfer of good-quality films onto solid substrates for subsequent UV exposure. Because of this we did not include 3-BCMU in this polymerization study.

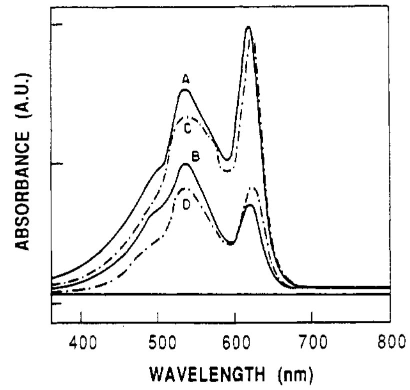


Figure 4. Visible absorption spectra of single-layer films of 4-BCMU polymerized at the air–water interface at 20 °C: (A) condensed state, π_t + 5.0 dyn/cm, hydrophilic substrate; (B) transition region, π_t, hydrophilic substrate; (C) condensed state, π_t + 5.0 dyn/cm, hydrophobic substrate; (D) transition region, π_t hydrophobic substrate.

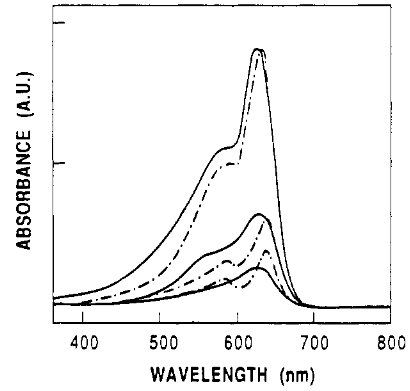


Figure 5. Visible absorption spectra of single-layer films of 9-BCMU polymerized at the air–water interface at 20 °C. Hydrophilic substrate, solid lines; hydrophobic substrate, dashed lines. Top to bottom: condensed state, π_t + 5.0 dyn/cm; transition region, π_t; expanded state, π_t − 1.0 dyn/cm.

Both 4-BCMU and 9-BCMU were capable of being polymerized in the condensed state and the transition region, both at the air–water interface and after transfer to solid substrates. Only 9-BCMU, however, was capable of polymerization while in the expanded state. The visible absorption spectra of monolayer films of 4-BCMU and 9-BCMU polymerized at the air–water interface and then transferred to hydrophilic substrates are shown in Figures 4 and 5, respectively. The resultant poly-4-BCMU shows two distinct absorption peaks near 530 and 610 nm for the transition region and near 535 and 620 nm for the condensed state. Similar results have been reported by Prock et al.[13] The shorter wavelength peak corresponds to the red conformer and the longer wavelength peak to the blue conformer. While the transition region is seen to favor the red form over the blue form, the opposite is true of the condensed state. This is consistent with a more ordered nature for the blue form. On the basis of the low areas/molecule in the condensed state it would also seem that the blue form predominates in condensed multilayers while the red form is favored at higher areas/molecule.

Poly-9-BCMU, however, displays only one dominant peak, but with a shorter wavelength shoulder, for the case of condensed state, transition region, and expanded state. The λ_{max} near 625 nm for the expanded state is seen to shift to 627 nm in the transition region and to remain at 627 nm in the condensed state. In each case the polymer formed is a more uniform blue form. Presumably the more ordered molecular packing arrangement in the case of poly-9-BCMU is due to the increased hydrocarbon side chain length ($(CH_2)_9$) since this should give rise to greater chain–chain intra- and intermolecular forces of attraction. The shoulder on the main peak could represent the monolayer equivalent of the intermediate form cited by Bloor et al.[14] for solution polymerization.

For 4-BCMU, with much shorter side chains ($(CH_2)_4$), polymerization only occurs in the condensed state and the transition region where all or some of the molecules are already close-packed. In addition to a resultant less tightly bound blue form, due to the shorter side chain, a slightly less ordered red conformation is also found. The fact that the two peaks corresponding to red and blue forms are separate and distinct from each other and the fact that the areas per molecule at which the polymerizations were carried out (25 $\AA^2$ for the condensed state and 50 $\AA^2$ for the transition region) are well below that corresponding to a close-packed monomolecular film of 4-BCMU (i.e., 106 $\AA^2$/molecule) indicate that these polymerized films are multimolecular and/or achieve a much more condensed conformation than that shown in Figure 2. This will be discussed further in a subsequent publication.

It was found (Figures 4 and 5) that, by using a hydrophobic substrate and horizontally lifting polymerized films of 4-BCMU and 9-BCMU from the air–water interface, the λ_{max} of each spectrum was shifted to a longer wavelength. This indicates an increase in the order and therefore in the effective π-electron conjugation length of the polymer backbone. For polymerized 4-BCMU the shifts in λ_{max} were as follows: the transition region, 530 → 535 nm and 610 → 625 nm; the condensed state, 535 → 545 nm and 620 → 625 nm. The shift of the blue-form peak is less in the condensed state (Δ5 nm) than in the transition region (Δ15 nm), with both attaining the same final value of 625 nm. This behavior presumably reflects the already more ordered condensed-state blue form. The larger shift of the red-form peak from the condensed state (Δ10 nm) as compared to that from the transition region (Δ5 nm) may reflect a greater ordering or nucleating effect on the red form by the more closely packed blue. The conversion of the red form to the blue form, however, is seen to occur to a greater extent in the transition region than the condensed state. By comparing the relative intensity (I_{blue}/I_{red}) ratio for the case of hydrophilic and hydrophobic substrates for both the transition region and the condensed state of 4-BCMU polymerized on water, one observes the following values: transition region, 0.73 → 1.04 (15%); condensed region, 1.33 → 1.44 (4.5%).

9-BCMU monolayers polymerized at the air-water interface also show the λ_{max} value shifting to longer wavelengths for films horizontally lifted onto hydrophobic substrates. The actual increases in λ_{max} were as follows: expanded state, 625 → 645 nm; transition region, 627 → 640 nm; condensed state, 627 → 637 nm. The largest increase occurred for the expanded-state film (Δ20 nm), while the smallest increase was that of the condensed-state film (Δ10 nm). This is not unreasonable since the single layer present in the expanded state should be more easily modified by the hydrophobic substrate than the presumably multilayer type arrangement present in the condensed state.

It was found that, by first transferring either 4-BCMU or 9-BCMU from the air–water interface onto hydrophilic solid substrates and then polymerizing with UV light, only the blue form of the polymer was obtained (see Figures 6 and 7) with no well-defined red form. There is, however, a peak at 570–590 nm intermediate between red and blue forms indicating that there are no well-defined "pure" forms but rather a continuous but nonuniform distribution.[14] In contrast, 4-BCMU polymerized on water showed clearly defined red and blue forms of the polymer. The hydrophilic substrate λ_{max} values for both polymers were the highest of any of the polymerized single-layer films obtained, namely, 625 nm for poly-4-BCMU and 645 nm for poly-9-BCMU. In addition, the same value for λ_{max} (i.e., 625 nm) was obtained for the polymer obtained from both the transition region and the condensed state of 4-BCMU. Similar results were obtained for the expanded, transition, and condensed states for 9-BCMU (i.e., 645 nm) when polymerized after transfer. The absence of a distinguishable red conformer in the case of poly-4-BCMU shows that this particular substrate favors the more ordered blue form. The near invariance in the λ_{max} values for different states of compression further demonstrates the major influence the nature of the interface can have in determining the amount of intramolecular order or disorder in these amphipathic diacetylenic polymers.

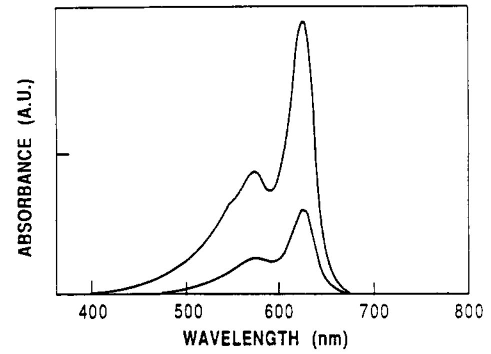


Figure 6. Spectra of 4-BCMU polymerized after transfer to a hydrophilic substrate. Top to bottom: π_t + 5.0 dyn/cm; π_t; π_t − 1.0 dyn/cm (no spectrum detected).

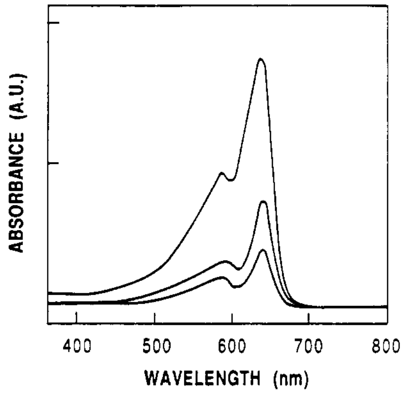


Figure 7. Spectra of 9-BCMU polymerized after transfer to a hydrophilic substrate. Top to bottom: π_t + 5.0 dyn/cm; π_t; π_t − 1.0 dyn/cm.

Similar results were obtained when a hydrophobic substrate was used in place of the hydrophilic substrate. Although the value of λ_{max} was found to be identical with those observed when using a hydrophilic substrate (i.e., 625 nm for poly-4-BCMU and 645 nm for poly-9-BCMU), polymerization was detected only for the condensed state of 4-BCMU and only for the transition region and condensed state of 9-BCMU. Since the hydrophobic surface of the alkylated glass substrate interacts with the hydrophobic portions of the monomer molecules, including the methylenes directly adjacent to the diacetylene group, this type of interfacial interaction may weaken the intermolecular attraction between adjacent diacetylene groups. Since close packing of this polymerizable segment with its neighbors is essential for effective polymerization, those monolayer states that possess the greatest intermolecular attraction between molecules (i.e., the most condensed) should be the most easily polymerized. More expanded states (i.e., the transition region for 4-BCMU and the expanded state for 9-BCMU) with weaker intermolecular attractive forces are more easily affected and are less easily polymerized.

(c) Conformational Reversibility. As we have previously shown, spread samples of poly-3-BCMU[5] and

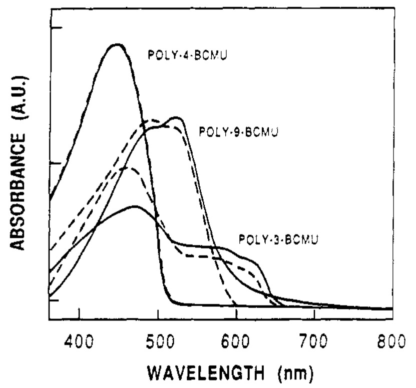


Figure 8. Spectra of *n*-BCMU polymers compressed to $\pi_t + 5.0$ dyn/cm, expanded to $\pi = 0$ for (—) 1 h or (- - -) 18 h, compressed to $\pi_t - 1.0$ dyn/cm, and transferred to hydrophilic substrate.

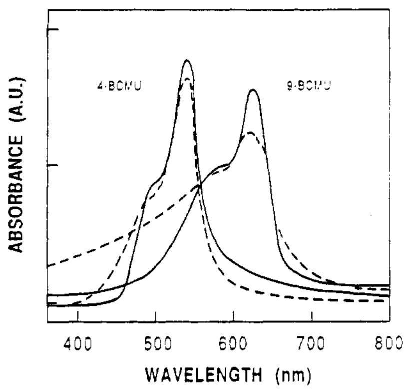


Figure 9. Spectra of *n*-BCMU monomers polymerized in the condensed state, expanded to $\pi = 0$ for (—) 1 h or (- - -) 18 h, compressed to $\pi_t - 1.0$ dyn/cm, and transferred to a hydrophilic substrate.

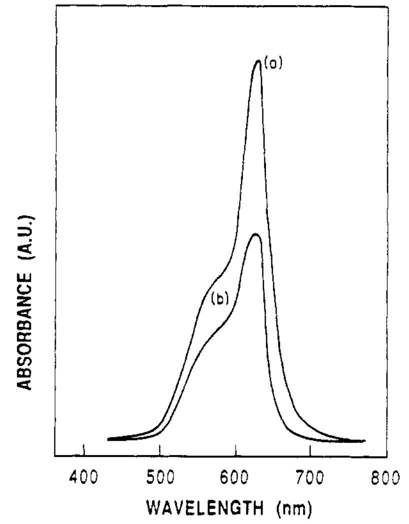


Figure 10. Spectra of 4-BCMU multilayers: (a) six layers (adjacent) and (b) six layers (each separated by a single layer of arachidic acid) after 60 min of exposure to UV light. 4-BCMU layers were transferred at $\pi_t - 1.0$ dyn/cm. Arachidic acid layers were transferred at 20 dyn/cm. Both multilayers were transferred by using a hydrophilic substrate.

poly-4-BCMU[1] form stable monomolecular films at the air–water interface and upon compression undergo a yellow to blue and yellow to red conformational transition, respectively. We have just recently found[10] that films of poly-9-BCMU show a similar behavior, going from yellow to red upon compression at the air–water interface. In solution it has been shown by Patel and others[3-8] that the conformational transition from a disordered yellow to an ordered red (poly-4-BCMU) or more ordered blue (poly-3-BCMU) form is reversible via either an increase in temperature or an increase in solvent polarity. It was therefore of interest to see if upon expansion to zero surface pressure whether the red or blue conformers favored in the condensed state of the spread polymer would return to the more disordered yellow form favored by the expanded state.

The visible absorption spectra of single-layer films of poly-3-BCMU, poly-4-BCMU, and poly-9-BCMU obtained after compression to their condensed states ($\pi_t + 5$ dyn/cm), expansion to $\pi = 0$ for the indicated time, and then recompression to $\pi_t - 1$ dyn/cm and transference to a hydrophilic substrate are shown in Figure 8. After the first 30 min at $\pi = 0$ poly-4-BCMU is seen to convert completely to the yellow form, with poly-3-BCMU showing only a partial conversion to the yellow ($I_{\text{yellow}}/I_{\text{blue}} = 2$) and poly-9-BCMU showing no conversion. When left for 18 h at zero surface pressure, poly-3-BCMU is seen to further convert to the yellow form ($I_{\text{yellow}}/I_{\text{blue}} = 3$) but the conversion is still not complete, while poly-9-BCMU still shows only slight conversion to a modified red form.

These results support the conclusion that the blue rod form of poly-3-BCMU is thermodynamically more stable than the poly-4-BCMU red rod form and therefore requires a greater amount of energy to disrupt its intramolecular hydrogen bonding in order to produce the yellow coil form. The reason for the enhanced stability of poly-9-BCMU's red form compared to that of poly-4-BCMU is presumably that there is an increased stability due to the increased length of the hydrocarbon side chains. This enhanced stability may be due to increased attraction between adjacent side chains (i.e., van der Waals interactions) and/or the decreased interaction of an overall more hydrophobic side chain with the aqueous subphase.

Interestingly, solutions of rod-form poly-3-BCMU, poly-4-BCMU, and poly-9-BCMU (hexane:chloroform, 3:1 by volume) spread and compressed at the air–water interface to $\pi_t - 1$ dyn/cm (i.e., their expanded state) all gave visible absorption spectra corresponding to the yellow coil form. The dilute nature of the rod conformers spread at the air–water interface in this manner is quite different from that of the much more concentrated rod conformers present in the condensed state. This suggests that intermolecular attractions between polymer molecules also play a role in determining the reversibility of the coil to rod conformational transition at the air–water interface.

An analogous study of interfacial conversion from an ordered to a disordered form was carried out with polymer films formed after UV irradiating monomer films spread at the air–water interface. As shown above, the condensed state of 4-BCMU polymerizes at the air–water interface to give a heterogeneous film consisting of both red and blue conformers, while 9-BCMU gives a film consisting of an all-blue conformer. However, as is shown in Figure 9, after 1 h at zero surface pressure all the blue form present in the polymerized 4-BCMU film was seen to convert to the red form, while the 9-BCMU polymerized film remained in the blue form. An additional 17 h at $\pi = 0$ resulted in only marginal change. The fact that interfacially polymerized 9-BCMU maintains its rigid blue form after expansion to $\pi = 0$ reinforces the idea of a longer, more hydrophobic side chain favoring an ordered, less amphipathic conformation at the air–water interface. The shorter less hydrophobic side chain of poly-4-BCMU allows the initial highly ordered blue conformation to relax to the more favored somewhat more amphipathic red form. This red form is stable at the air–water interface at $\pi = 0$

showing no significant conversion to the yellow coil form, as did films of spread poly-4-BCMU that were first spread and compressed to the condensed state (see above). This difference in ability to convert from red rod to yellow coil must reflect a different structure between these two spectrally similar red forms of poly-4-BCMU. One possible explanation is that polymerization while 4-BCMU is in a condensed state can result in the formation of a tangled interchain network that, although able to relax to the red rod form when expanded to $\pi = 0$, is not able to fully relax to the more disordered yellow coil form. The condensed state of spread poly-4-BCMU, however, is apparently composed to red rod conformers having considerably less of an interchain network since initial solvent spreading immediately yields the loosely packed yellow coil. This idea of the formation of a polymer network during polymerization at the air–water interface is strengthened by the fact that a six-layer multilayer of 4-BCMU was found to polymerize ca. 92% more than the same number of layers separated by single intervening layers of arachidic acid (see Figure 10). This behavior is in contrast to that of diacetylenic fatty acid multilayers, which are known to polymerize within a given layer.

An equimolar mixed film of 4-BCMU and 9-BCMU polymerized while in the condensed state at the air–water interface was seen to produce only the blue form, which when left for 18 h at $\pi = 0$ did not show any conversion to red. Intermolecular interactions between the two components in the film appear to favor the blue form, perhaps by stabilizing any initially formed blue poly-4-BCMU or by allowing only blue poly-9-BCMU to be formed due to a sufficient packing disorder that inhibits the polymerization of 4-BCMU.

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