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Monomolecular and Langmuir–Blodgett Film Behavior and the Spectral Properties of Films of Poly-9-BCMU

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ABSTRACT: Monomolecular films of poly(dibutyl 4,29-dioxo-5,28-dioxa-3,30-diaza-15,17-dotriacontadiynedioate) (poly-9-BCMU) were studied at the air–water interface by measuring their surface pressure (π) vs surface area per reside (A) isotherms as well as by the visible absorption spectra of monolayer and Langmuir–Blodgett (L–B) films. Poly-9-BCMU displays a phase transition between an expanded and a condensed state similar to those previously reported for poly-3- and poly-4-BCMU. In the case of poly-9-BCMU, however, both the expanded and the condensed states occupy larger areas per residue than either poly-3- or poly-4-BCMU. The larger areas are postulated to be due to the increased number of methylene groups per residue. None of the poly-9-BCMU isotherms, in contrast to those of poly-4-BCMU, show a metastable transition peak on being compressed from the expanded to a condensed state, indicating that the more expanded state facilitates the transition. The visible absorption spectra indicate that the expanded state consists primarily of a yellow coil form while the condensed state primarily has a red rod structure.

Introduction

Studies of the diacetylenic [(butoxycarbonyl)methyl]-urethane (poly-*n*-BCMU) polymers and monomers have revealed many fascinating aspects of these unique materials. One such aspect is the remarkable correspondence between the behavior in solution and solution-cast films[1-6] and that in mono- and multimolecular films.[7-10] In particular, the polymers exhibit a similar transition from a monomolecular amphipathic yellow coil form to a pseudo bimolecular nonamphipathic red or blue rod form, which parallels one that occurs in solution due to a change in either the nature or temperature of the solvent. In both environments the yellow to red or blue change has been postulated to be due to the creation of an extended π-electron overlap along the conjugated polymer backbone.

We have already[9] provided a preliminary report of the polymerization of 9-BCMU and a brief description of the behavior of poly-9-BCMU as it compares with that of poly-3-BCMU and poly-4-BCMU. In this paper we will provide a more detailed description of the film behavior of poly-9-BCMU. This will include a description of the temperature dependence of the surface pressure (π)/area per residue (A) compressional isotherms, leading to a thermodynamic analysis of the expanded/condensed transition via a modified two-dimensional Clapeyron equation. In addition, the visible absorption spectra are reported for transferred films as a function of compression. On the basis of a comparison of all data reported with those of poly-3- and poly-4-BCMU, it is clearly seen that poly-BCMU behavior is very much dependent on the number of methylene groups per residue. For poly-9-BCMU the increased number of methylene groups results in an expansion of both the expanded and condensed states. In turn, this provides for a greatly increased ease of transition from an expanded to condensed state. The results demonstrate that the film, electronic and presumably nonlinear optical behavior can be tailored by altering the number of methylene groups per residue.

Experimental Section

Surface pressure (π) vs area per residue (A) isotherms were measured by using a Langmuir trough as described previously.[11] Film spreading was carried out by using dilute solutions of the film sample in chloroform (approximately 1.0 mg in 10.0 mL). A compressional rate of 10 Å^2/residue min was used for all π–A isotherms. The temperature of the subphase water and that of the gaseous phase above it were controlled by a circulating heating/cooling water bath (Ultra Kryomat TK 30 D), which allowed the temperature to be varied between 2.0 and 40.0 °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.

All glass slides used as substrates were cleaned by 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 approximately 5 min in an argon plasma prior to use. Subphase water was first distilled and 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.

The samples of poly-9-BCMU used in this study were obtained from Dr. D. Bloor of Queen Mary College, London, England.

The 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

***π–A* Isotherms.** The surface pressure (π) vs area per residue (A) isotherms for poly-9-BCMU are shown in Figure 1. All the isotherms display a highly compressible expanded state lifting off at about 175 Å^2/residue, a horizontal transition region, and a condensed state of low compressibility over the entire temperature range studied (3.4–36.2 °C). The condensed state displays a small condensation with increasing temperature, while the expanded state shows a slight expansion. The onset of the transition is seen to shift from A_t = 119 Å^2/residue at 3.4 °C to A_t = 136 Å^2/residue at 36.2 °C. The absence of a peak or maximum at the transition onset is in contrast to the isotherm of the 9-BCMU monomer[10] and also in contrast to that of poly-4-BCMU,[9] both of which display a distinct maximum in their π–A isotherms at the transition onset when compressed with comparable rates of compression. The transition pressure (π_t), defined by the point of transition onset, is seen to have a negative temperature dependence that is nonlinear as shown in Figure 2. That is, the transition takes place more easily at higher tem-

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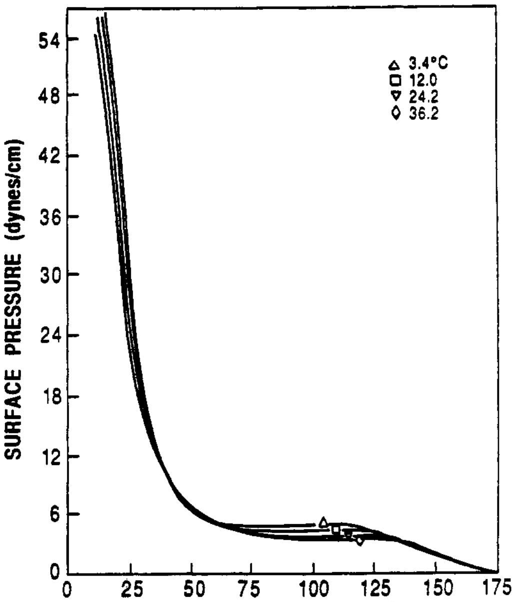

Figure 1. Surface pressure (π) versus area per residue (A) isotherms of poly-9-BCMU over the temperature range indicated.

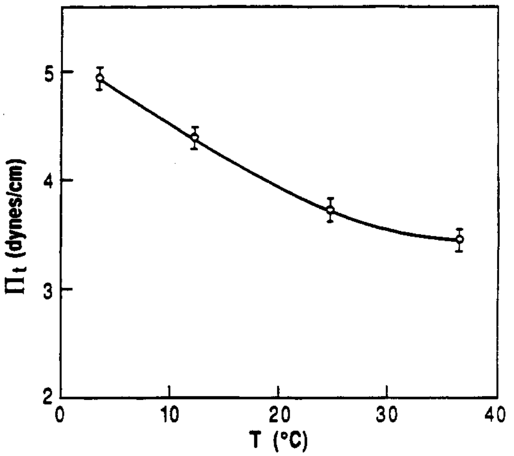

Figure 2. Temperature dependence of the pressure at the onset of the expanded–condensed transition (π_t) for poly-9-BCMU films.

peratures. The difference between a continuous compression isotherm and a stepwise or "equilibrium" isotherm of poly-9-BCMU at 19.0 °C is shown in Figure 3. Relaxation is clearly seen to take place at areas less than or equal to that of the transition onset, while the expanded state shows no appreciable relaxation. Similar observations have been made for other lipid films.[12,13] Application of the modified Claperyon equation[14]

$$\Delta H = T\Delta A(\mathrm{d}\pi_t/\mathrm{d}T - \mathrm{d}\gamma^\circ/\mathrm{d}T)$$

taking $\Delta A = -98$ Å^2/residue, gives $\Delta H = -3.9$ kcal/mol and $\Delta S = -13.4$ cal/mol·K at 19.0 °C for the transition from the expanded state to the condensed state. The above described interfacial behavior of poly-9-BCMU is similar to, and consistent with, our previous observations (i.e., for the case of poly-3-BCMU[8] and poly-4-BCMU,[7,9] where a monolayer to bilayer transition took place at the air–water interface upon compression to π_t.

Visible Absorption Spectra. The visible adsorption spectra of Langmuir–Blodgett films of poly-9-BCMU taken at five different points along the isotherm are shown in Figure 4. The yellow coil form is seen to predominate in the expanded state ($\pi < \pi_t$). Once into the transition region, the appearance of a shoulder at 504 nm is observed and proceeds to grow in magnitude with increasing pressure until it coalesces with the continually modified yellow coil peak. Clearly the monolayer to bilayer transition is coincident with an intramolecular conformational transition of poly-9-BCMU from a disordered yellow coil form to a planar, ordered red rod form, not unlike that of poly-3-BCMU[8] and poly-4-BCMU.[7,9]

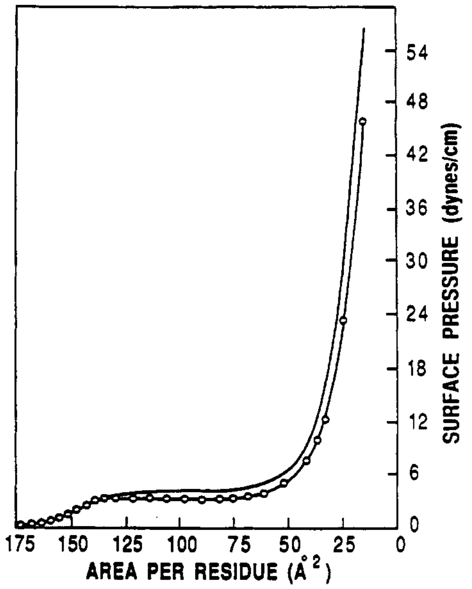

Figure 3. Comparison of a continuous compression (10 Å^2 residue^{-1} min^{-1}) and a stepwise isotherm of poly-9-BCMU at 19.0 °C. The steps in the stepwise isotherm are indicated by the area reduction between successive open circles (○), with each step being allowed to achieve a metastable equilibrium. The two isotherms are coincident in the expanded region.

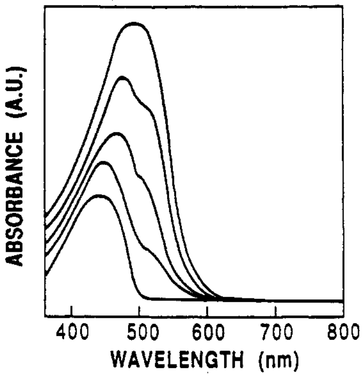

Figure 4. Visible absorption spectra of single films of poly-9-BCMU transferred at five different points onto hydrophilic glass slides. Top to bottom: condensed state, $\pi_t + 5.0$ dyn/cm; $\pi_t + 1.5$ dyn/cm; approximately the end of the transition region, π_t; the onset of the transition region, π_t; the expanded state $\pi_t - 1.0$ dyn/cm.

Comparison of Poly-9-BCMU with Poly-4-BCMU and Poly-3-BCMU. A comparison of the interfacial and spectral behavior of poly-9-BCMU with previous data of poly-4-BCMU[8] and poly-3-BCMU[7,9] reveals both similarities as well as differences, which reflect the effect of the increased length of the hydrophobic portion of the side chain (i.e., $n = 9$).

In Figure 5 the π–A isotherms of all three polymers are shown at 20 °C. The magnitude of the expanded state areas follows the same order as the value of n (i.e., $n = 3 < n = 4 < n = 9$) and is consistent with our model of an amphipathic conformation at the air–water interface. In addition, the compressibility of poly-9-BCMU's expanded state is greater than that of poly-4-BCMU, which suggests a less efficient molecular packing in the former. The

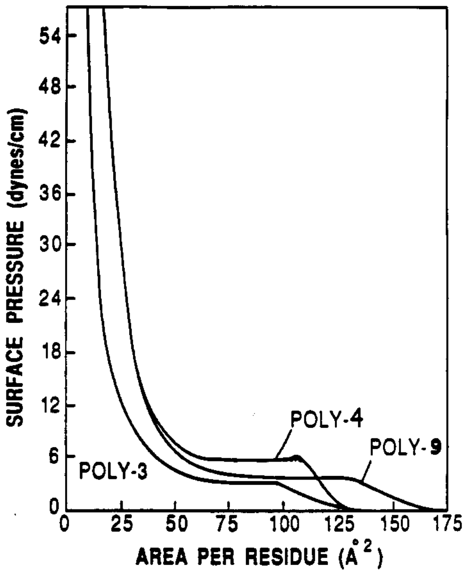

Figure 5. Surface pressure (π) versus area per residue (A) isotherms of poly-3-BCMU, poly-4-BCMU, and poly-9-BCMU at 20 °C.

compressibility of poly-3-BCMU's expanded state, which is comparable to that of poly-9-BCMU and greater than that of poly-4-BCMU, being attributed to a slight solubility and/or subphase penetration.[8] This more loosely packed film should therefore be expected to more easily undergo a transition to a more stable, condensed bilayer phase (i.e., π_t(poly-9-BCMU) < π_t(poly-4-BCMU)). The fact that the condensed state of both poly-9-BCMU and poly-4-BCMU are nearly identical in terms of their π–A isotherms suggests a similar packing efficiency of film molecules for both polymers once into the condensed state. In the case of poly-3-BCMU, the smaller areas in the condensed state probably reflect a slight solubility and/or subphase penetration by the more hydrophilic poly-3-BCMU side groups.[8]

Poly-9-BCMU displays the least amount of relaxation in the transition region of all three polymers. Thermodynamically, however, the monolayer to bilayer transition of poly-9-BCMU is seen to be the most exothermic of all three polymers, due mainly to the greater area at the transition onset for poly-9-BCMU (i.e., greater A_t value). The nine methylenes between the polymer backbone and the polar groups on poly-9-BCMU are seen to produce an expansion of the monolayer phase as compared to either poly-4-BCMU or poly-3-BCMU, thereby giving rise to a more exothermic phase transition to a condenser bilayer phase.

Spectrally, poly-9-BCMU in the expanded state is seen to display the least conformationally ordered films of all three polymers. That is, the λ_{max} value in this state (λ_{max} = 440 nm) is smaller than that of either poly-4-BCMU (λ_{max} = 465 nm) or poly-3-BCMU (λ_{max} = 475 nm). Therefore, the longest side chain ($n = 9$) polymer produces the greatest interference of the overlap of neighboring π-electrons along the polymer backbone and hence the shortest effective conjugation length or l_{EC}. Similarly in the condensed state, poly-9-BCMU is seen to be the least conformationally ordered as well (i.e., poly-9-BCMU, λ_{max} = 488 nm; poly-4-BCMU, λ_{max} = 535 nm; poly-3-BCMU, λ_{max} = 575 and 620 nm). Here also the longest side chain produces the greates interference of the overlap of π-electrons along the polymer backbone and thus the shortest l_{EC}. Interestingly, the modification of the yellow coil form with compression (shifting of λ_{max} to longer wavelength) is most pronounced for poly-9-BCMU. Here the polymer–subphase interactions of this interfacial layer are quickly replaced by polymer–polymer interactions in the forming bilayer. Since poly-9-BCMU's side chains are the least hydrophilic of the three polymers, it is not unreasonable to expect that the interfacial coil layer of poly-9-BCMU would be the most easily modified by polymer–polymer interactions with adjacent polymer molecules during bilayer formation.

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Registry No. Poly-9-BCMU (homopolymer), 105710-00-7; poly-9-BCMU (SRU), 105710-75-6.