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Monolayer behaviors of poly(hexamethylene adipamide) at the air/water interface

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Abstract Monolayer films on the neutral water substrate were obtained by spreading *N*-trifluoroacetic anhydride (NTF)-modified nylon 66 or nylon 612 in chloroform solutions. Alternatively, monolayer films were obtained by spreading from nylon 66 solutions in the 3:1 mixture of benzene (B) and phenol (P). The temperatures studied are 10.3°, 14.7 °C, and 19.4 °C. The isothermss of surface pressure (π), and surface moment (μ) against surface area per residue (A) were determined. The π-A isotherms of the NTF-modified nylon 66/chloroform and the nylon 66/BP were found to be an expanded type, while that of NTF-modified nylon 612/chloroform was of a condensed type. The NTF-modified nylon 66/chloroform solutions could yield well-spread films even at higher concentrations than nylon 66/BP solutions. In the μ-A isotherms at 10.3 ° and 14.7 °C, the surface moments are constant at 143 mD/residue for NTF-modified nylon 66/chloroform, and 340 mD/residue for nylon 66/BP until the surface area reaches where the π-A isotherms show a transition point. After the transition point, the surface moments for both systems drop steadily. However, the surface moment at 19.4 °C shows a maximum at the transition point. Possible configuration of the nylon 66 residue in monolayer is discussed.

Key words π-A and μ-A isotherms – monolayers – air/water interface – poly(hexamethylene adipamide) – spreading solution

Introduction

Surface films of synthetic polymers were first studied systematically by Crisp in 1946 [1, 2]. As the constitutions are generally known and can be varied as desired, synthetic polymers are well suited to investigation of surface behavior [3–14]. Furthermore, the behavior confined to monolayers at the free surface of a liquid substrate may provide valuable insights into the bulk behavior of polymers [13].

It is interesting to understand the role of the hydrogen bonds [2, 15] at an air/water interface. Nylons differ from proteins in that the former possess hydrocarbon groups in the main chain with no side chains masking the CONH groups. Hence, nylons serve as useful materials for examining the effect of the CONH group in a polymer film.

Crisp [1, 2] claims that nylons are difficult to form stable expanded films on the water substrate due to strong lattice forces. Yamashita [16] studies a series of surface films of nylons in details, and indicates that most nylons except for nylon 6 cannot be made into a stable film on the neutral water. Nylon 6 can develop an expanded film on a neutral water substrate, while nylon 4 and 5 develop an expanded film only on a 40% ammonium sulfate substrate, whereas other nylons such as nylons 8 to 11, and nylon 3 can produce condensed type films only on the substrate of 40% aqueous ammonium sulfate solution. He suggested that either a strong hydrogen bonding interaction or strong van der Waals force in nylons are the main factors influencing the film formation and behavior.

Regardless of all the work on nylons, poly(hexamethylene adipamide) (nylon 66) has been less reported [17]. Probably, similar to the lactam-based nylons mentioned above, nylon 66 is not easily obtained as a stable film on a water substrate. Shigehara [18] obtained a stable surface film of nylon 6, which was obtained by reacting nylon 6 with *N*-trifluoroacetic anhydride to become *N*-trifluoroacetyl-nylon 6. Then, the product was reverted readily to nylon 6 by reacting with water.

We believed that the Shigehara procedure could be manipulated to yield a monomolecular film. In this work two different methods were used to obtain surface films of nylon 66. One was similar to the Shigehara method, i.e., nylon 66 was modified to be *N*-trifluoroacetyl-nylon 66 and chloroform was used as a spreading solvent. The other was by directly dissolving nylon 66 in a mixture of benzene and phenol. Effects of the spreading solution and temperature on monolayer behavior were investigated.

Experimental

Experimental section

Commercially available nylon 66 and nylon 612 for laboratory use (Janssen Chemical) were used. The intrinsic viscosity of nylon 66 measured in *m*-cresol at 25 °C was 0.85. L.C. grade chloroform and benzene (Alps Chem.) were used without further purification. Phenol and *m*-cresol for analysis, and trifluoroacetic anhydride for synthesis (Ferak) were used as received. The substrate water was purified by double distillation and subsequent filtration through a Milli-Q purification system, *N*-Trifluoroacetyl-nylon 66 (NTF-nylon 66) was obtained by the method described elsewhere [19, 20]. This was dissolved in chloroform to obtain a spreading solution, which unless otherwise stated had a concentration of 0.92 mg NTF-nylon 66/ml, corresponding to 0.5 mg nylon 66/ml. In addition, nylon 66 was dissolved directly in a benzene/phenol (3/1 by volume) mixture to prepare a second spreading solution (0.50 mg nylon 66/ml).

Methods

A commercially available LB 5000 Langmuir–Blodgett apparatus (KSV Instruments; Finland) with a computerized control was used. A Pt-Wilhelmy balance was used as a surface pressure sensor. The surface pressure (π) and the surface moment (μ) at various surface areas (A) were monitored and recorded automatically. A poly(tetrafluoroethylene) (PTFE) trough and polyoxymethylene (Delrin) barriers were used. The initial surface area of the trough was 85000 mm^2. The surface potential ΔV, which is the difference in the potentials of the substrate and the film-covered substrate, was determined by the vibrating capacitor method. The vibrating electrode of the capacitor was placed above and near the water surface. Another electrode of the capacitor was placed under the surface of the substrate. Using the Helmholtz equation, $\Delta V = 4\pi n\mu$, where n is the reciprocal of surface area, the surface moment was determined from the obtained data ΔV. The temperature control of water in the trough was carried out by passing thermostatted water into the jacket at the bottom of the trough. The temperature near the surface of the water was measured by means of a thermistor. The three substrate temperatures investigated were 10.3°, 14.7°, and 19.4 °C. The spreading solution of nylon 66 was slowly applied by a microsyringe onto the surface at the initial spreading area of about 250 Å^2/residue (250 Å^2/repeat unit). After 30 min, determination of the isotherms was conducted under compression at a constant speed 600 mm^2/min. The surface pressure was determined with an accuracy of $\pm 4\ \mu N/m$, the surface moment $\pm 8\ mD$/residue, the area $\pm$ 0.3 Å^2/residue, and the temperature $\pm$ 0.1 °C.

Results and discussion

π-A isotherms

In the study the nylon 66 obtained by exposing NTF-nylon 66 to air for 5 minutes was examined using the IR spectra. In the spectrum of the recovered nylon 66, we do not find the absorption peak of 1715 cm^{-1} for the C=O of the CF$_3$CO group, but rather the absorption peaks of the characteristic function groups of nylon 66, which are 3300 and 3080 cm^{-1} for the stretching of the NH group as well as 1640 and 1540 cm^{-1} for the amide-I and -II-band, respectively, are observed. It is just the same as that of the ordinary nylon 66 [19, 21]. It indicates that the nylon 66 had been recovered completely from NTF-nylon 66. In this work the determination of isotherms was conducted after standing the films on the water surface for 30 minutes. Hence, it could be safely assumed that the films studied were completely composed of nylon 66.

Figure 1 shows the π-A isotherms for NTF-nylon 66 spreading from chloroform (NTF-nylon 66/chloroform), and Fig. 2 for nylon 66 directly spreading from the 3:1 mixture of benzene and phenol (nylon 66/BP) at 10.3 °, 14.7 °C, and 19.4 °C, respectively. The isotherms indicate

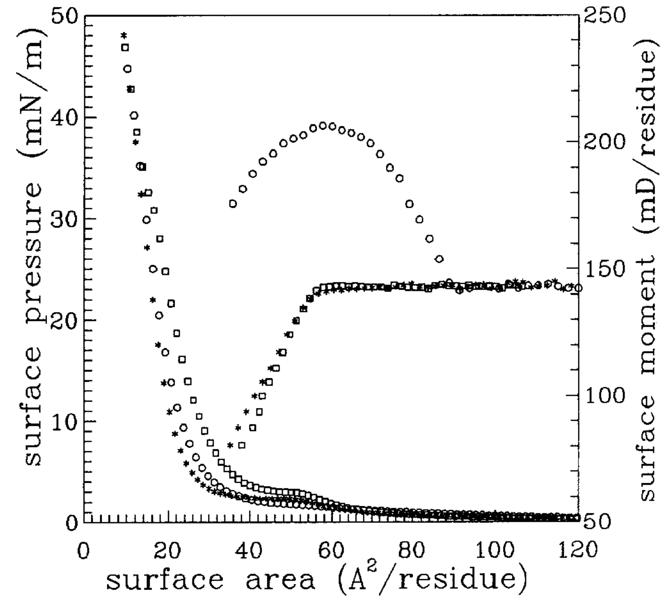


Fig. 1 Surface pressure and surface moment versus surface area isotherms of NTF-nylon 66/chloroform: (□) = at 10.3 °C; (∗) = at 14.7 °C; (○) = at 19.4 °C.

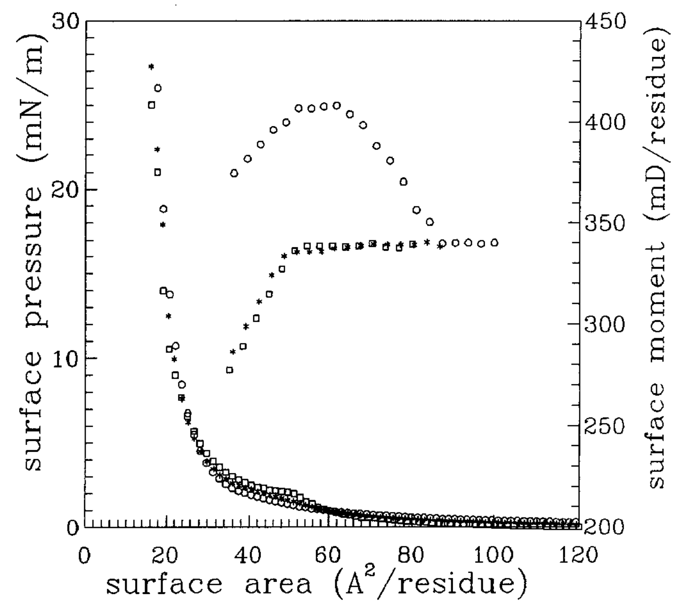


Fig. 2 Surface pressure and surface moment versus surface area isotherms of nylon 66/BP: (□) = at 10.3 °C; (∗) = at 14.7 °C; (○) = at 19.4 °C.

that the films apparently experienced a change of states during the course of compression. From the initial surface pressure (π_i) to the surface pressure where the isotherms show a transition point (π_p) the film was highly compressible. After attaining the transition point, the surface pressure became nearly independent of the surface area, i.e., the isotherm in this region reached a plateau. Across the plateau region the films became low compressible. Table 1 summarizes the surface areas A_p and surface pressures π_p at the transition point. A_p is nearly independent of the temperature. However, the higher the temperature, the lower the π_p. Moreover, it was found that the nylon 66/BP gave a lower π_p at any given temperature than the NTF-nylon 66/chloroform did. The former showed an A_p of 48.1 Å^2/residue, and the latter gave 52.6 Å^2/residue. The results will be discussed in more detail below.

Concentration of spreading solution effect

The effect of the concentration of spreading solution on the π-A isotherms of nylon 66 films were investigated. In the study all the films were made to contain the same amount of nylon 66, in spite of different concentrations of the spreading solution being used. For the NTF-nylon 66/chloroform solution six concentrations of spreading solution, 0.92, 1.90, 2.43, 3.05, 3.26, and 4.00 mg NTF-nylon 66/ml were studied. Nearly identical π-A isotherms for all the concentrations were obtained. It means that in the concentration range studied the configuration of nylon 66 in the surface film was independent of the concentrations. Unlike the NTF-nylon 66/chloroform solution, the nylon 66/BP spreading solution could yield the identical π-A isotherms only for the low concentrations, 0.22, 0.44, and 0.50 mg nylon 66/ml. As the concentration was increased to 0.65 and 0.80 mg nylon 66/ml, the isotherms showed a similar trend for the change of surface pressure with surface area. However, the surface pressure at any given surface area and the transition area A_p were smaller than those obtained in the lower concentrations. It was found that the higher the concentration, the lower the surface pressure and the smaller the A_p. Davey [22] and Crisp [1] indicated that if the specific area varied with experimental conditions, the film was only partially spread. According to this, the nylon 66/BP could not develop a well-spread film as the concentration was larger than 0.65 mg nylon 66/ml. Evidently, the NTF-nylon 66/chloroform could yield a well-spread film at larger concentrations than the nylon 66/BP. It may be attributed to the fact that in the NTF-nylon 66 system the hydrogen in the amide group of nylon 66 is substituted by N-trifluoroacetyl, which prevents the intermolecular hydrogen bondings among nylon 66. Thus, the molecules of NTF-nylon 66 in chloroform are in a more expanding state than that of nylon 66 in BP (3/1) solution. Further, the NTF-nylon 66 reacting first with water upon spreading also hinders the intermolecular hydrogen bondings among the recovered nylon 66.

Table 1 Film characteristics for NTF-nylon 66/chloroform and nylon 66/BP

Spreading solution	Temperature (°C)	A_p (Å^2/residue)	π_p (mN/m)	A_o (Å^2/residue)	μ (mD/residue)
NTF-nylon 66/ chloroform	10.3	52.6	2.9	166	143 (μ_c)
	14.7	52.6	2.3	166	143 (μ_c)
	19.4	52.6	1.7	174	205 (μ_m)
nylon 66/BP	10.3	48.1	2.1	162	340 (μ_c)
	14.7	48.1	1.7	163	340 (μ_c)
	19.4	48.1	1.5	170	410 (μ_m)

Properties of monolayers with π lower than ca. 0.2 mN/m

As the π vs. $1/A$ isotherm was plotted, a linear relationship could be obtained for all the isotherms at surface pressures smaller than ca. 0.2 mN/m (Figs. 3 and 4). The linear relationship can be represented by the following empirical equation,

$$[\pi - (\pi_i - K/A_i)]A = K\,, \tag{1}$$

where π_i denotes the initial surface pressure depending on temperature and spreading solution, A_i denotes the initial surface area, and $K \doteqdot 50$ for NTF-nylon 66/chloroform and 60 for nylon 66/BP. Obviously, even though Eq. (1) is apparently similar to a special van der Waals equation, the constant K is not a function of the absolute temperature. This behavior is quite different from the equations of state described elsewhere [23–25] for polymer monolayers. The specific area where the π vs. $1/A$ isotherm begins to deviate from the linear line (A_0) was determined. It was found that A_0 varied with the temperature and the kind of spreading solutions and that the films at 10.3° and 14.7 °C had almost same A_0, while those at 19.4 °C showed a larger A_0. The results are shown in Table 1. In the other studies, the hysteresis test for the films was done. No hysteresis is

Fig. 3 Surface pressure versus reciprocal of area isotherms for NTF-nylon 66/chloroform: (□) = at 10.3 °C; (∗) = at 14.7 °C; (○) = at 19.4 °C

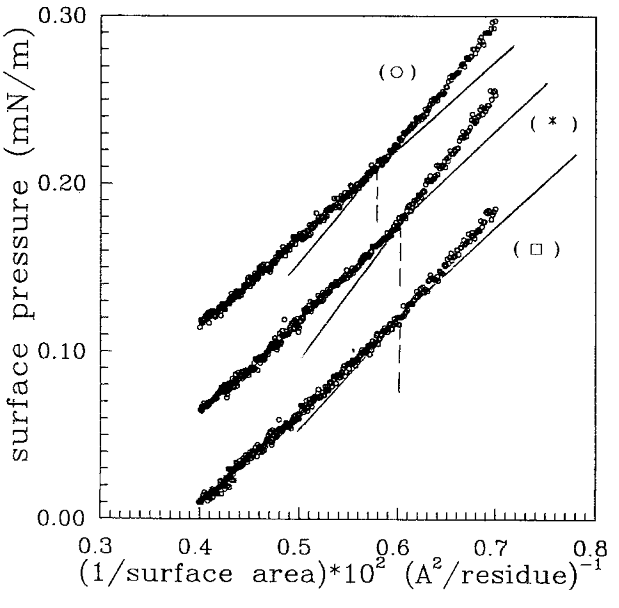
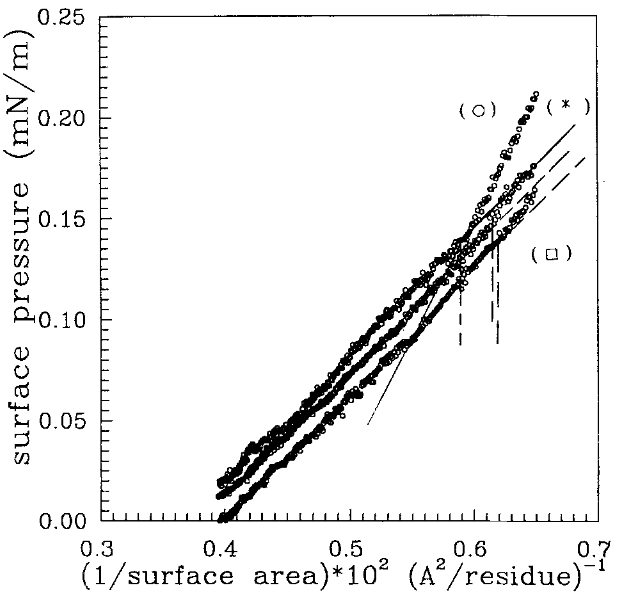


Fig. 4 Surface pressure versus reciprocal of area isotherms for nylon 66/BP: (□) = at 10.3 °C; (∗) = at 14.7 °C; (○) = at 19.4 °C

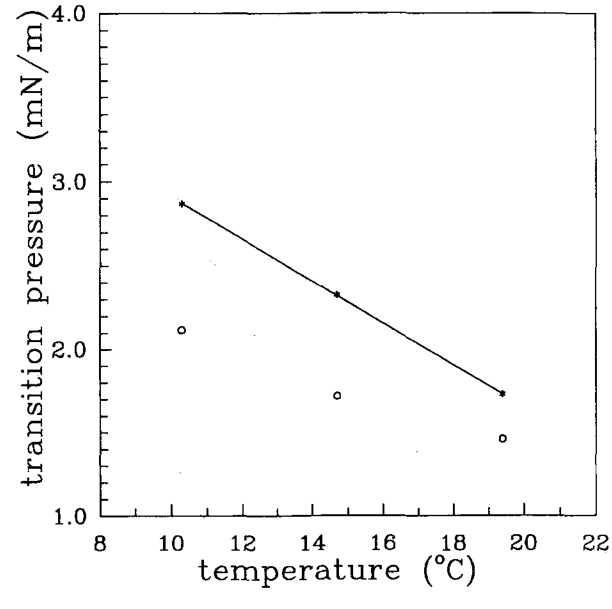


observed as the target surface area is larger than A_0. It reveals that the molecules of the films behave like ordinary gaseous molecules in this region. As the target surface area is below A_0, the pressure, during re-expansion, becomes lower than the pressure of the compression. The monolayer compression is not instantaneously reversible. Therefore, the specific area A_0 is the limit in which the monolayer can exhibit a reversible compression.

Properties of monolayers with π between ca. 0.2 mN/m and π_p.

As the surface pressure was increased to above ca. 0.2 mN/m, the π vs. $1/A$ isotherms did not follow a straight line. For the earlier stage of this region, the surface pressure increases with increasing temperature (Figs. 1 and 2). However, approaching the transition point, the surface pressure begins to decrease with increasing temperature. The transition pressure, π_p, is seen to have a negative temperature dependence that is linear for NTF-nylon 66/chloroform, but is approximately linear for nylon 66/BP (Fig. 5). Therefore, the transition takes place more easily at high temperatures. Similar results were also reported by other investigators [10, 14, 26–28]. They considered that the transition was to a large extent controlled by the mobility of the segments and thus by a transport term (kinetical control) rather than by the free energy gain upon transition (thermodynamic control). It is reasonable to expect that increasing the substrate temperature tends to weaken the hydrogen bondings between the surface film and water, which allows the polymer chains to move more freely, and then enhances the interaction between the nylon 66 segments.

Fig. 5 Temperature dependence of the transition pressure: (*) = NTF-nylon 66/chloroform; (○) = nylon 66/BP

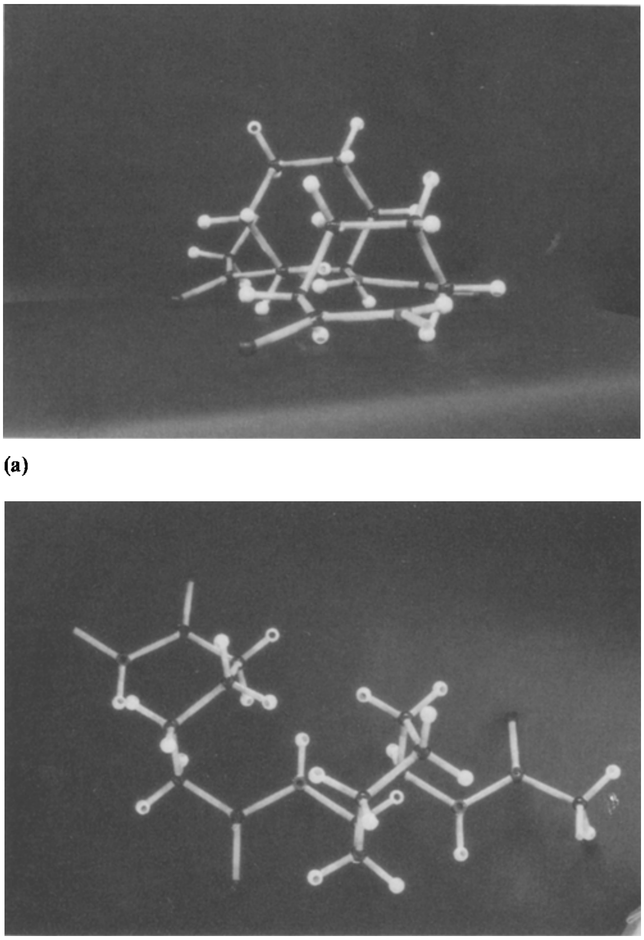


The test of the surface moment (μ) against surface area is a powerful method to study the orientation of a molecule with a permanent dipole during the course of compression. As reported in literature [1, 29–30], a reliable surface moment could not be obtained before some specific surface pressure. In this study, this surface moment can be obtained as the surface pressure of the film reaches ca. 0.4 mN. Figures 2 and 3 show the reliable μ-A isotherms. It is noted that at 10.3° and 14.7°, the films show a nearly constant surface moment (μ_C) until the transition point is reached. As shown in Table 1, the μ_C is independent of temperature, but depends on the kind of spreading solutions. The μ_C for NTF-nylon 66/chloroform is 143 mD/residue, while for nylon 66/BP is 340 mD/residue. The constant surface moment suggest that the molecular chains in the monolayer assume a stable configuration and that the work consumed in the range simply serves to orient the molecules in a perpendicular position to the compression direction and to shorten the distance between the molecules without altering the orientation of the polar groups. Similar results have been found elsewhere [1, 15, 16, 29–31]. However, at 19.4 °C the values of μ_C start to rise sharply at ca. 0.75 mN/m for NTF-nylon 66/chloroform and at 0.51 for nylon 66/BP. The increases reach a maximum (μ_m) at the transition point. Similar results have been reported for polyorganosiloxanes [32].

Hotta [29] and Yamashita [16] indicate that the surface moments of nylons are mainly contributed by the C=O dipoles. Alexander and coworkers [33] show that the surface moment for the C=O dipole will attain a maximum value of 360 mD as the C=O becomes vertical to the interface. Referring to this, the angles of the C=O of NTF-nylon 66/chloroform and nylon 66/BP vertical to the interface were estimated to be 78.5° and 61.8° from the calculated $\mu_C = 71.5$ and 170 mD/amide group. The calculated μ_C's were obtained by dividing the measured μ_C by 2 because one residue of nylon 66 contains two amide groups. In view of the process of film forming from the spreading solutions, the NTF- nylon 66/chloroform forms the monolayer film through the step of replacing *N*-trifluoroacetyl group with the hydrogen of water, however, the step does not occur for nylon 66/BP. It is known that the pre-existing *N*-trifluoroacetyl group is much bulkier than the usual N-H group. It causes the carbonyl group to position more horizontally to the water interface. Consequently, the NTF- nylon 66/chloroform exhibits a smaller surface moment than the nylon 66/BP. The fact that the NTF-nylon 66/chloroform gives a larger surface pressure than nylon 66/BP does at the same surface area is also attributed to this reason.

It is noted that the surface moments begin to decrease tremendously at the transition area A_p. As mentioned above, the surface moment is a measurement of the configuration of the amide group of nylon 66 on the water surface. Thus, a drop of μ_c reflects some change about the configuration of the amide groups in the film, probably resulting from the formation of microfibrils [31]. Therefore, the film at the transition point is the limit of monolayer to exist, and the residues assume a certain type of closest packing configuration. It is well known that the primary structure of nylon 66 is composed of hydrophilic amide groups as well as hydrophobic polymethylene groups. Accordingly, the amide groups would remain at the water surface through the hydrogen bonding interaction, but the polymethylene groups are, presumably, pushed outwards from the interface [16, 17].

Fig. 6 Illustration for the configuration of nylon 66 at the air/water interface: a) = viewed along the chain; b) = top view of chain

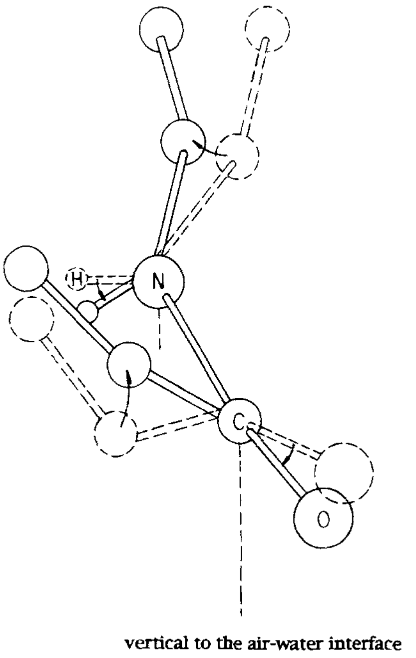

(a)

(b)

From the above discussions and using the calculated angles for C = O bond vertical to the interface, one attempts to propose a possible configuration of nylon 66 residue. Figure 6 shows the configuration in the region of constant moment, which is represented by Sigma M-4534 molecular model orbit set. The gauche configuration of polymethylene groups was used. According to this configuration, the co-areas [34] per residue were estimated to be 36.1 and 32.6 Å^2/residue for NTF-nylon 66/chloroform and nylon 66/BP, respectively. Further, the closest distance between two neighboring chains was assumed to be 2.4 Å [1]. By using these two pieces of information, the close packing area per residue at 10.3 ° and 14.7 °C was calculated. The results were 53.1 and 48.5 Å^2/residue for NTF-nylon 66/chloroform and nylon 66/BP, respectively, which are in good agreement with the experimental A_p's.

As mentioned above, the surface moments at 19.4 °C positively deviate from μ_c with decreasing surface area. This indicates that the configuration of nylon 66 residue in monolayer profoundly changes during the course of compression. As the compression increases, the C=O is positioned to be vertical to the interface. Figure 7 shows an interpretation of the configuration change. Under the condition of 19.4 °C, the nylon molecules contain sufficient thermal energy to enhance thermal motion of the flexible polymethylene groups and to reduce the hydrogen bonding effects between the amide group and water substrate.

Fig. 7 Configuration change of nylon 66 at 19.4 °C during the course of compression



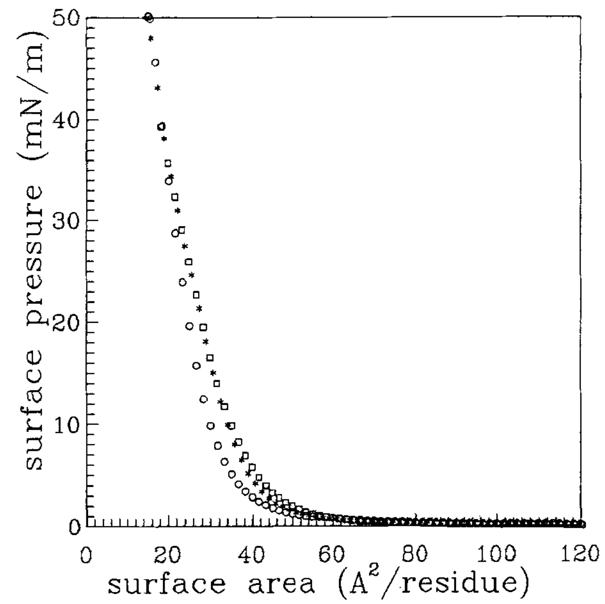


Fig. 8 Surface pressure versus surface area isotherms of NTF-nylon 612/chloroform: (□) = at 10.3 °C; (∗) = at 14.7 °C; (○) at 19.4 °C

The cooperative chain motion of the hydrophilic and hydrophobic segments tends to push polymethylene chains farther away from the water interface and to rotate C=O and N–H groups more perpendicular to the interface.

Surface films of nylon 612

Using the procedure similar to NTF-nylon 66/chloroform, we modified nylon 612 to be NTF-nylon 612, and used chloroform as the spreading solvent to obtain the surface films of nylon 612 at 10.3°, 14.7°, and 19.4 °C. As shown in Fig. 8, unlike nylon 66, the π-A isotherms belong to condensed-type films. The repeat unit in nylon 612 contains six more methylene groups than nylon 66. Therefore, the van der Waals force is expected to be the governing factor for the formation of condensed-type film.

Conclusions

N-trifluoroacetic anhydride modified nylon 66 spreading from chloroform on the neutral water substrate gives a larger surface pressure than nylon 66 directly spreading from the 3:1 mixture of benzene and phenol. It is attributed to the pre-existing bulkier *N*-trifluoroacetyl substituent, resulting in a favorable configuration of the residue to form a more expanded monolayer. However, it is not evident for *N*-trifluoroacetic anhydride modified nylon 612. There seems to be a critical temperature existing between 14.7° and 19.4 °C or at 19.4 °C. At (or above) the critical temperature, the films are relatively unstable, i.e., they easily change configuration during compression and form microfibrils when the molecules have been closely compacted.

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