Monolayers of Adipate Polyesters at Air-Liquid Interfaces [1]

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The surface pressure-area isotherms at 24.5 °C are reported for poly(ethylene adipate), poly(trimethylene adipate), and poly(propylene adipate), spread as monolayers at air-aqueous interfaces. The monolayers were spread on distilled water and 0.01 N HCl, using benzene, chloroform, and acetone as spreading solvents. Poly(propylene adiptate) was the least compressible of the three, and poly(ethylene adipate) the most. Poly(propylene adipate) did not collapse at the highest pressures studied. The spreading characteristics of both poly(ethylene adipate) and poly(propylene adipate) were independent of the amount of material used. The spreading of poly(trimethylene adipate) appeared to depend upon the spreading solvent. The effect of structure on the surface pressure—area isotherms and the specific areas for each polymer are discussed.

1. Introduction

The monolayer properties of a series of linear succinate polyesters, with a number-average molecular weight ($\overline{M}_n$) of the order of 4,500, at air-aqueous interfaces were recently reported [1]. It was shown that the monolayer of poly(ethylene succinate) was highly expanded but that it collapsed at very low surface pressures. Poly(pentamethylene succinate) monolayers were also expanded. They did not collapse with increasing pressure, but the surface compressibility went through a maximum and continued to decrease as the pressure increased. An isomer of this polymer, poly(neopentyl succinate), produced a much less expanded film which collapsed at a surface pressure higher than that observed for collapse or pressure decrease for the other two polymers. It also gave the smallest extrapolated specific area per repeating unit. Other work has been reported on polyesters by Harkins, Carmen, and Ries [2] and Moss [3].

The work reported in this paper is concerned with a surface film balance study of three linear saturated polyesters of adipic acid at the liquid-air interface.

2. Experimental Procedure

The polyesters used in this investigation were: poly(ethylene adipate) [-O(CH$_2$)$_2$OCO(CH$_2$)$_4$CO-]$_n$, poly(trimethylene adipate) [-O(CH$_2$)$_3$OCO(CH$_2$)$_4$CO-]$_n$, and poly(propylene adipate) [-OCH(CH$_3$)CH$_2$OCO(CH$_2$)$_4$CO-]$_n$. These polymers were prepared by Dr. James Farr, Jr., of the Thiokol Chemical Company and were synthesized from the melt without catalyst. They were purified by reprecipitation from chloroform solution with ethyl ether and dried in vacuum. Some of the bulk properties of these polymers are given in table 1.

The film balance used to study the monolayers of the spread films has been described previously [1]. The water used as a subphase was redistilled from an all-quartz system. The spreading solvents were twice distilled and tested for active impurities by

measurements of the surface pressure of the solvent alone. The polymer solutions were spread from micropipets and 10 min usually allowed for solvent evaporation. The average time of an experiment was 1 hr. All measurements were made at 24.5 ± 0.5 °C.

TABLE 1. *Bulk properties*

Polymer	Softening point	Molecular weight $\overline{M}_n$[a]	Bulk density at 27 °C	Physical state at 25 °C [b]
	°C		g/cm³	
Poly(ethylene adipate)	51	3900	1.3	Crystalline
Poly(trimethylene adipate)	40	4000	1.3	Crystalline
Poly(propylene adipate)		5400	1.2	Viscous liquid

[a] $\overline{M}_n$, number average molecular weight determined from supplied end group analysis.
[b] Crystallinity detected by X-ray diffraction.

3. Results

The monolayer properties of poly(ethylene adipate) spread from benzene and chloroform on the two substrates are given in figures 1 and 2. The surface pressure in dynes per centimeter is shown as a function of the specific area of the polymer (area per unit weight). All of the runs shown in figure 1 were obtained using benzene as the spreading solvent. Extrapolation of the linear portion of the curve drawn gives a limiting specific area of 2.6 m²/mg. In order to obtain the entire isotherm 30.36 × 10⁻³ mg of polymer was used for the region of high surface pressure and 5.50 × 10⁻³ mg for the region of low surface pressure and large area. Both regions were reproducible as shown by duplicated experiments. The two regions overlapped and a smooth continuous isotherm was obtained.

The available area of the balance for initial spreading of the film was of the order of 800 cm². Using the specific surface area, the larger quantity of polymer corresponds to an area of approximately 790 cm² and the smaller to an area of approximately 145 cm². The isotherm was, therefore, independent of the quantity of material used over this relatively
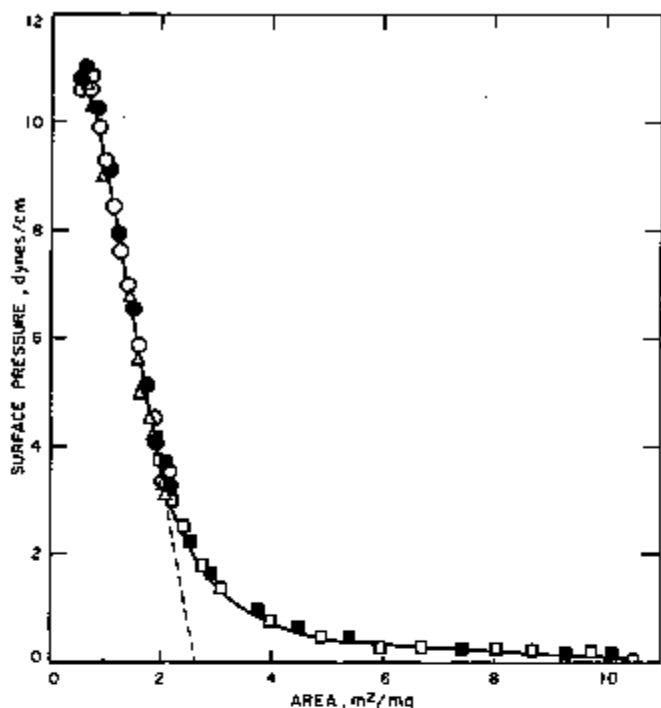
FIGURE 1. *Surface pressure-area isotherm of poly(ethylene adipate) spread from benzene at 24 ± 0.5 °C.*

Distilled water subphase ○, ● 30.38×10⁻² mg.
□, ■ 5.50×10⁻² mg.
0.01 N HCl subphase △ 30.38×10⁻² mg.

FIGURE 2. *Surface pressure-area isotherm of poly(ethylene adipate) on distilled water at 24 ± 0.5 °C.*
Spread from benzene □ 17.51×10⁻² mg.
Spread from chloroform ○, ● 12.12×10⁻² mg.

wide range, which included a quantity near the maximum capacity of the balance. The absence of any change in the isotherm with quantity of material spread suggests that the films were completely spread and existed as monolayers. The use of 0.01 N HCl with a pH of 2 resulted in the same isotherm as the use of distilled water with a pH of 6.5. The collapse pressure of the films spread from benzene was 11.1 dynes per cm, as shown by figure 1. A quantity of polymer intermediate between the two amounts described above also resulted in the same isotherm as those spread from benzene, as shown in figure 2. Films spread from chloroform on distilled water also yielded the identical isotherm, but the collapse pressure was slightly higher, 12 dynes per cm.

The isotherm of poly(propylene adipate) spread from chloroform on distilled water is shown in figure 3. The properties for very dilute surface concentration were not studied for this film. The extrapolated specific area at zero surface pressure was 2.2 m²/mg. Films of this polymer did not collapse. Two quantities were again used to obtain different portions of the isotherm. These two sections overlapped and a smooth isotherm resulted. The spreading characteristics were, therefore, not dependent on the quantity of material deposited, within this range. The larger quantity, 29.94×10⁻² mg, corresponded to an area of approximately 660 cm² at zero surface pressure, while the smaller quantity corresponded to one-half this amount.
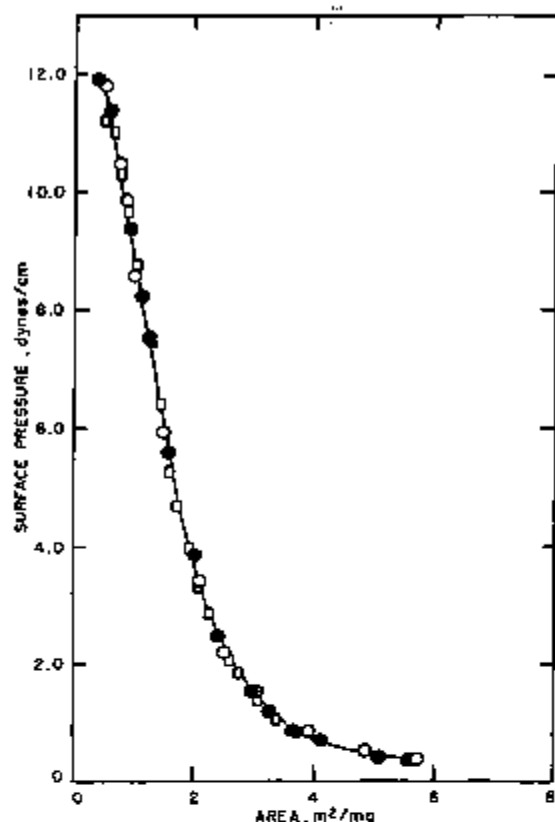
This independence on the amount of polymer suggests that the films were monolayers.

Poly(trimethylene adipate) was sensitive to the spreading solvent. Films spread from benzene on 0.01 N HCl subphase exhibited the surface characteristics shown by curve A in figure 4. A limiting area of 3.1 m²/mg was obtained from this isotherm. The quantity of polymer spread, 5.47×10⁻³ mg, corresponds to an area of approximately 170 cm², and because of the small quantity should represent a completely spread film.

The effect of the spreading solvent on the characteristics of the film is shown by isotherm B in figure 4. Polymer was spread from acetone solution in two different quantities onto a distilled water subphase. In one case 50λ ($λ=10^{-3}$ cm³) and in the other, 100λ were spread, using the same concentration of solution. Within the experimental error, both quantities resulted in the same isotherm, with a smaller specific area. The isotherm showed no signs of expansion to higher specific areas for the smaller quantity of solution spread. Repeat runs for both quantities resulted in the reproducible isotherm shown in figure 4. The fact that the maximum spreading area for the isotherm with the smaller amount of polymer was twice as large as that for the larger amount of polymer appears to indicate the spreading of the polymer with this solvent was complete.
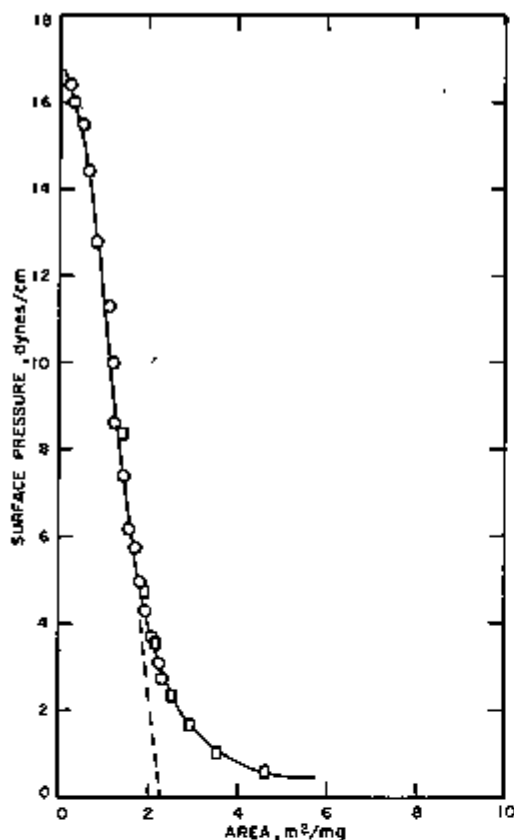
FIGURE 3. *Surface pressure-area isotherm of poly(propylene adipate) on distilled water spread from chloroform at 24.5 ±0.5 °C.*

○, 29.94×10⁻⁴ mg.
□, 14.95×10⁻⁴ mg.

FIGURE 4. *Surface pressure-area isotherm of poly(trimethylene adipate) at 24±0.5°C.*

Curve A Spread from benzene on 0.01 N HCl subphase
○, ● 5.47×10⁻⁴ mg.
Curve B Spread from acetone solution on to distilled water subphase
□, ● 23.29×10⁻⁴ mg.
■, △ 11.70×10⁻⁴ mg.

4. Discussion

4.1. Physical Properties

In table 2 are given values for the thickness of the monolayers, the energies of compressing the films to collapse or the point of inflection, and compressibilities. The approximate thicknesses of the films were calculated from the bulk density and the limiting specific area of the completely spread film. As seen in table 2 they are within the range of 3 to 4 Å and are of a reasonable thickness for monolayers. They fall in approximately the same range as did the succinate polyesters [1], and indicate that these polyesters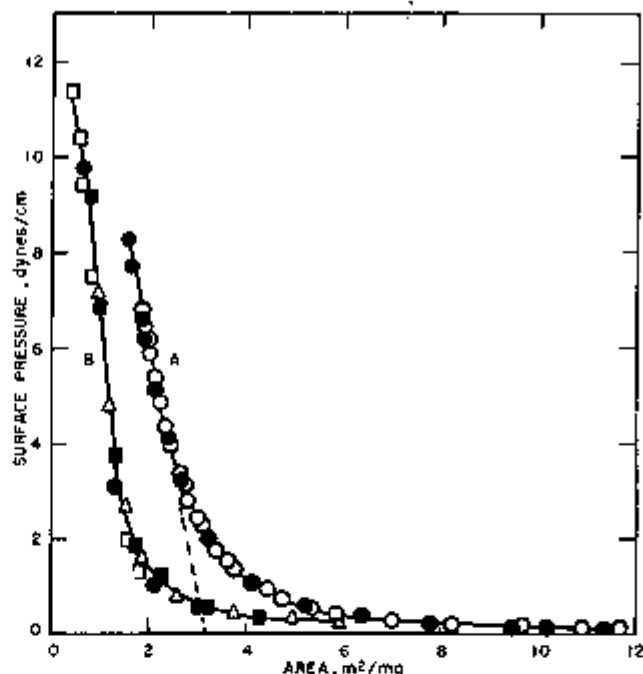 lie relatively flat on the surface. Integra-tion of the area under the isotherms from very large segment areas to the point of collapse for poly-(ethylene adipate) and to the point of inflection for poly(propylene adipate) gives the energy to compress the film to a position of unstability. The energies shown in table 2 are rather high, one being of the order of 700 and the other 800 cal/mole/segment. For the succinate polyesters studied previously [1], only poly(neopentyl succinate) gave an energy above 700, as shown in table 2. Poly(ethylene succinate) gave an energy of 349, and poly(pentamethylene succinate) an energy of 568 cal/mole/segment. The compressibilities given in table 2 were calculated from the equation:

$$K=\frac{A_0-A_1}{A_0\pi_1}$$

where K is the compressibility, A_0 the extrapolated specific area at zero surface pressure, and A_1 the specific area at surface pressure π_1.

TABLE 2

| Polymer | Extrap- olated specific area | Area per segment | | Energy to compress film to collapse, cal mole⁻¹ segment⁻¹ | Compres- sibility | Thickness at π=0 |
		Calculated	Observed			
	m²/mg	A²	A²		cm/dyne	A
Poly(ethylene adipate)	2.6	67	75	716	0.067	3.0
Poly(propylene adipate)	2.2	67	68	807	.048	3.3
Poly(trimethylene adipate)	3.1	74	28	------	.038	2.7
Poly(ethylene succinate) *	2.3	55	60 to 70	349	.11	3.1
Poly(pentamethylene succinate) *	2.9	74	90	568	.056	2.9
Poly(neopentyl succinate) *	2.0	60	63	734	.028	3.9

* Reference [1].

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4.2. Compressibility

The compressibility values for all the polyesters studied, except for poly(ethylene succinate) [1], are in the range observed for linear polyesters, such as the self ester of the hydroxydecanoic acid studied by Harkins, Carmen, and Ries [2], and poly(vinyl acetate) films studied by Ries, Ahlbeck, and Gabor [4]. The latter polymer contains the ester groups as side chains.

The compressibility data for the adipate monolayers and the succinate monolayers, as reported previously, point to the general observation that the compressibility of the monolayer decreases with the number of carbon atoms in the glycol and acid groups and also with the arrangement of these groups.

Second, it is to be observed that the polyesters with the lower number of carbon atoms between the carboxylic groups have greater compressibilities than those with large numbers, as evidenced by comparison of the compressibilities of poly(ethylene succinate) with poly(ethylene adipate). Similarly the compressibilities of polyesters containing the ethylene glycol grouping have greater compressibilities than those having segments of longer glycols. This is evidenced by a comparison of poly(ethylene adipate) with poly(trimethylene adipate) as well as a comparison of poly(ethylene succinate) with poly(pentamethylene succinate).

Third, it appears that differences in the arrangement of the carbon atoms in the glycol chain also affects the compressibility. Thus, poly(propylene adipate) and poly(trimethylene adipate) differ in their compressibilities in that the branched three carbon group has a lower compressibility than the straight chain arrangement. Similar behavior is observed in a comparison of poly(neopentyl succinate) with poly(pentamethylene succinate).

The spreading of polymer films has been shown by others [2, 5] to be independent of molecular weight. Crisp [5] has shown that polymer films are completely spread when the specific areas are reproducible and independent of the solvent or solution concentration over a moderate concentration range. The spreading of both poly(ethylene adipate) and poly(propylene adipate) were independent of the quantity of material spread, over the concentration range studied, as shown in figures 1 to 3. As completely spread films are assumed to be independent of molecular weight, the surface pressure was plotted as a function of the area of the repeating structural unit. Such isotherms for the three polyesters are given in figure 5. Experimental points from different runs are given on each curve, except those of poly(trimethylene adipate) spread from acetone.

There is a large difference in the isotherm of poly(ethylene adipate), as shown in curve C, figure 5, and that of poly(ethylene succinate) (fig. 5, ref. 1). The increase in the length of the repeating unit by the addition of two methylene groups in the acid changed the collapse pressure from approximately 4 dynes/cm for the succinate to approximately 12 dynes/cm for the adipate polymer. This is very likely due to the greater freedom of orientation of
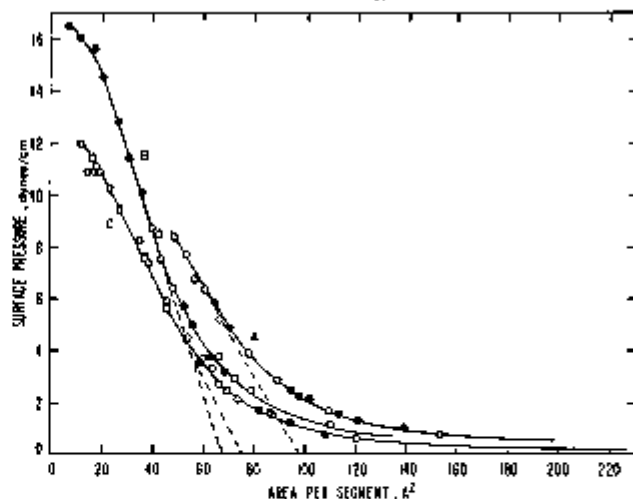

FIGURE 5. *Surface pressure-area isotherms of linear saturated polyesters on aqueous subphases at 24.5 ± 0.5 °C.*
Curve A Poly(trimethylene adipate)
Curve B Poly(propylene adipate)
Curve C Poly(ethylene adipate)

the carbonyls in the interface, resulting in a higher vertical component of the dipole. The extrapolated segment area for the adipate polymer is 75 A^2 and 60 to 70 A^2 for the succinate polymer. These values are somewhat larger than the minimum calculated from molecular models.

The monolayer properties of poly(trimethylene adipate) spread from benzene, curve A, are similar to those of poly(ethylene adipate), curve C, at moderate surface pressures. At all surface pressures studied the segment areas are larger for the poly(trimethylene adipate) than for the poly(ethylene adipate). The extrapolated segment area of 98 A^2 is 23 A^2 larger than the value obtained for the poly(ethylene adipate) which is in good agreement with the cross-sectional area of a long chain hydrocarbon, as established by monolayer measurements.

5. Summary

Differences in the surface pressure—area isotherms of the three adipate polyesters studied were found to be related to differences in the chemical structure. Large differences were also observed between these polyesters and succinate polyesters studied previously. A large difference was observed between the observed and the calculated specific area for the repeating unit of poly(trimethylene adipate). As in the case of the succinate polyesters, one of the adipate polyesters studied did not collapse at high pressures.

6. References

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