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Monolayers and Langmuir–Blodgett multilayer films of a conjugated azo polymer

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Abstract

A black π -conjugated azo polymer was synthesized by oxidative coupling of 3,5-diamino-1-octadecylbenzoate. The polymer, with a number average molecular weight of about 16 000, was soluble in chloroform. Monolayer formation was studied by transmission electron microscopy and the structure of the deposited Langmuir–Blodgett multilayer film was investigated with small angle X-ray diffraction and Fourier transform IR spectroscopy. A smooth monolayer was obtained when, after spreading, the material was allowed to disintegrate without any applied surface pressure for 18 h at 20 °C and 1 h at 40 °C. Monolayers could be transferred successfully onto different substrates at high temperature (40 °C) and high pressure (30 mN m⁻¹). The deposition was of the Y type with transfer ratios of 1 on both the downstroke and the upstroke. It was concluded that the aliphatic side chains are not able to crystallize and therefore form amorphous layers.

1. Introduction

Over the last ten years researchers have shown a great interest in the processability of electrically conductive polymers. The Langmuir–Blodgett (LB) technique is a promising tool to prepare thin films of highly ordered conjugated polymers [1]. In general this can be done in three different ways. One method is to make the polymer soluble in common organic solvents, *e.g.* by attaching long aliphatic side chains to the π -conjugated backbone [2–10]. Monolayers of these polymers can be transferred directly onto a solid substrate using the vertical or horizontal dipping method. In this way polymers can be processed directly. Another method is to use a precursor polymer with a flexible backbone [11–13]. The LB multilayer films are made conductive in the final stage. The last method to prepare a conductive LB film is to form a monolayer of a surface-active monomer at the air–water interface. The polymerization, resulting in a π -conjugated polymer, takes place in this monolayer [14–25]. Subsequently, the monolayer can be transferred onto a solid substrate. Polymerization can take place in LB multilayers as well [2, 26]. In this paper, we report on the monolayer behaviour of a conjugated azo polymer made by oxidative coupling of 3,5-diamino-1-octadecylbenzoate.

2. Experimental details

2.1. Materials

Details about the monomer synthesis will be reported separately [27]. Copper (I) chloride was synthesized according to the method of Stathis [28]. Pyridine (Merck) was distilled before use.

2.2. Polymerization

Details of the polymerization will be reported separately [27]. The reaction conditions for the oxidative coupling were as follows: $T = 50$ °C; $[\text{Cu}] = 0.03$ mol l⁻¹; $[\text{3,5-diamino-1-octadecylbenzoate}] = 0.06$ mol l⁻¹; reaction volume, 150 ml [29]. The oxygen consumption was followed with an automatic isobaric gas burette. After an oxygen consumption of about 0.045 mol l⁻¹ the reaction mixture was precipitated in a saturated aqueous solution of ethylenediaminetetraacetic acid (EDTA) disodium salt to remove the copper catalyst. The black material was filtered off and washed with a saturated aqueous solution of EDTA disodium salt. Then the reaction product was washed carefully with pure water and dried in a vacuum desiccator. The reaction product was dissolved in chloroform (*p.a.*), filtered (0.45 μm pore size of the filter), precipitated in acetone (*p.a.*), washed with acetone and dried in a vacuum desiccator. This procedure was repeated three times to remove low molecular weight components.

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2.3. Characterization

Monomer and polymer were characterized by elemental analysis (monomer: found, 74.23% C, 10.97% H, 6.79% N; calculated, 74.23% C, 10.96% H, 6.92% N; polymer: found, 69.84% C, 9.31% H, 7.03% N, 2.88% Cu, 0.31% Cl; calculated, 74.95% C, 10.77% H, 6.99% N) and the molecular weight of the polymer was determined by size exclusion chromatography (SEC) (PSS Gel type $10^3 + 10^5$ Å columns, Viscotek viscometer H502 detector, tetrahydrofuran as eluent). Further details about the characterization of the polymer will be reported separately [27].

Small angle X-ray diffraction measurements were performed with a PW 1830 generator and PW 1820 diffractometer. Cu K α radiation ($\lambda = 1.54$ Å) was used.

Samples for transmission electron microscopy (TEM) were prepared by transferring the monolayer onto grids covered with Formvar, Formvar-carbon or Parlodion by a manual horizontal lifting method. The samples were Pt shadowed at an angle of 20°. Transmission electron micrographs were recorded on Agfa Scientia 23D56 film in a Jeol JEM 1200EX microscope at a magnification of $10\,000\times$.

For IR measurements a standard procedure was followed [30].

2.4. Langmuir–Blodgett measurements

Monolayer properties were studied using a computer-controlled Lauda Filmbalance FW2. The water used to prepare the subphase was purified with an Elgastat reverse osmosis system coupled with a Milli-Q purification system. Monolayers were spread from chloroform solutions with a typical concentration of 0.7–0.9 mg of total solute ml^{-1} . Surface pressure–area isotherms were measured with a standard compression speed of 5 Å^2 (repeating unit) $^{-1}\text{ min}^{-1}$. Transfer experiments were carried out by a vertical dipping method after stabilization of the monolayer on the water surface (about 2 h) at constant temperature and pressure. Unless mentioned otherwise, a dipping speed of 3 mm min^{-1} was used for the down and upstroke transfer. For the preparation of glass slides, gold and ZnS substrates a standard method was used [31].

3. Results and discussion

SEC measurements revealed a number average molecular weight \bar{M}_n of 16 000 and a weight average molecular weight \bar{M}_w of 52 000 (for the azo polymer) ($D = 3.25$).

From ^1H nuclear magnetic resonance and SEC measurements it was also deduced that partial hydrolysis of the ester groups takes place during the oxidative polymerization or during the precipitation procedure. As-

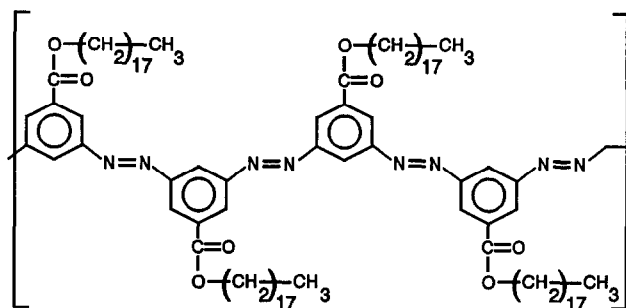


Fig. 1. Structure of the azo polymer.

suming that each repeating unit in the azo polymer has two nitrogen atoms, an averaged molecular weight for the repeating unit of 389 can be calculated from the amount of nitrogen determined by elemental analysis. From the carbon content it was calculated that about 13% of the aliphatic side chains were removed as a result of hydrolysis. Elemental analysis also revealed that the polymer contains a substantial amount of copper, bound to the π -conjugated backbone in an as-yet unknown way. Indications for this will be a subject of another paper [27].

Because of the 1,3,5-trisubstitution of the benzene ring and the probably trans conformation of the azo group, steric hindrance of the aliphatic side chains will be reduced (Fig. 1). In this way the conjugation might not be disturbed by torsion of the planar backbone [32]. The general idea was that, because of the trans conformation of the azo group and the interaction of the hydrophilic ester groups with the water phase, the backbone is forced to lie flat on the water surface. The aliphatic side chains, whose first function was to make the polymer soluble in chloroform, can now have a second function, namely stabilization of the monolayer.

Figure 2 shows the surface pressure–area isotherm of the azo polymer at 40 °C (curve A), recorded directly after the chloroform solution had been spread onto the water surface. Variation of the temperature between 15 and 45 °C had no effect on the isotherm. The apparent area per repeating unit of approximately 24 Å^2 , calculated from the isotherm, is not consistent with the presumed orientation of the polymer on the water surface. From Corey–Pauling–Kolton models it was calculated that a repeating unit, of a pure azo polymer, without defects, should have an area of about 35 Å^2 , when the benzene ring lies flat on the water surface.

A monolayer of the azo polymer, stabilized at extreme conditions ($T = 40$ °C, $\pi = 30\text{ mN m}^{-1}$) is more or less stable in time (Fig. 3, curve A). When the monolayer is deposited onto a substrate (glass, ZnS or gold) under these conditions, Y-type transfer is ob-

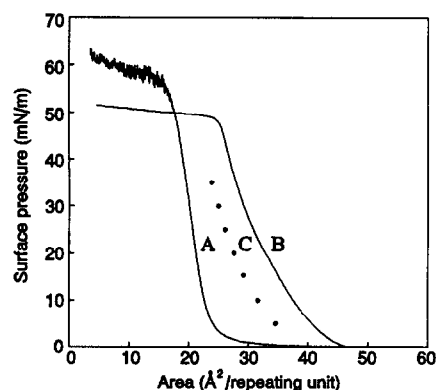


Fig. 2. Surface pressure–area isotherms at 40 °C of the azo polymer compressed directly (curve A), and compression after 18 h at 20 °C and 1 h at 40 °C without pressure (temperature increase from 20 to 40 °C in $\frac{1}{2}$ h) (curve B). Points C representing the area found after stabilization of the monolayer at 40 °C and 5, 10, 15, 20, 25, 30 and 35 mN m^{-1} for 45 min each. After spreading, the material was allowed to disintegrate overnight (18 h) at 20 °C and for 1 h at 40 °C without pressure (temperature increase from 20 to 40 °C in $\frac{1}{2}$ h).

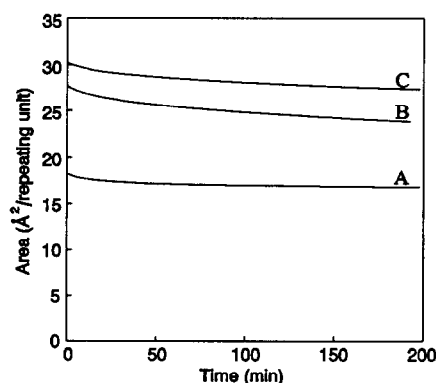


Fig. 3. Stabilization curves of the monolayer, compressed directly at 40 °C and 30 mN m^{-1} (curve A), and of monolayers, compressed at 40 °C and 30 mN m^{-1} , after 18 h at 20 °C and 1 h at 40 °C (temperature increase from 20 to 40 °C in $\frac{1}{2}$ h) without pressure (curve B) and at 30 °C and 20 mN m^{-1} , after 18 h at 20 °C and 1 h at 30 °C (temperature increase from 20 to 30 °C in $\frac{1}{2}$ h) without pressure (curve C).

served, with transfer ratios of 0.9 on the downstroke and 1 on the upstroke.

The X-ray diffraction pattern of 30 layers, deposited onto glass, is shown in Fig. 4 (curve A). A broad peak is observed, representing the bilayer distance.

A monolayer, stabilized at a temperature of 15 °C and a pressure of 25 mN m^{-1} , gave a deposition onto glass with transfer ratios of 0.5 on the downstroke and 1 on the upstroke (dipping speed, 1 mm min^{-1}). The X-ray diffraction pattern of 26 layers prepared in this way is shown in Fig. 4 (curve B). The reduction in the transfer ratio on the downstroke to 0.5 disturbs the regular layer pattern in such a way that the peak almost disappears.

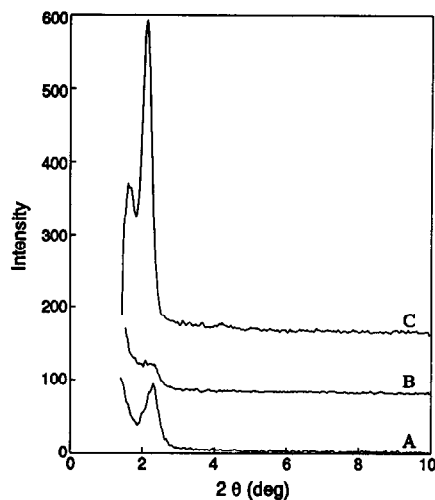


Fig. 4. Small angle X-ray diffraction patterns: curve A, direct compression of the monolayer, stabilization at 40 °C and 30 mN m^{-1} , deposition of 30 layers; curve B, direct compression of the monolayer, stabilization at 15 °C and 25 mN m^{-1} , deposition of 26 layers; curve C, after spreading, 18 h at 20 °C and 1 h at 40 °C (temperature increase from 20 to 40 °C in $\frac{1}{2}$ h) without pressure, stabilization at 40 °C and 30 mN m^{-1} , deposition of 14 layers.

TEM samples of a monolayer compressed directly after spreading were taken after 3 h of stabilization at a temperature of 40 °C and a pressure of 30 mN m^{-1} . TEM revealed a monolayer with above or underneath this monolayer a large amount of domains of different sizes of the order of 0.05–1 μm (Figs. 5(A) and 5(B)). Usually, grids covered with Formvar–carbon were used. Grids covered with other films (Formvar without carbon or Parlodion) exhibited the same image. From these electron micrograph, it is clear why too small an area per repeating unit was found from the isotherms. It appears that during the spreading and evaporation of the chloroform solution the polymer forms aggregates on the water surface. From centrifugation and filtration experiments we concluded that no aggregation takes place in the chloroform solution itself.

The isotherm shown in Fig. 2 (curve B) was recorded when, after spreading of the chloroform solution on the water surface, the material was left at the air water interface for 1 night (18 h) at 20 °C and subsequently, after increasing the temperature to 40 °C ($\frac{1}{2}$ h), for 1 h at 40 °C. It is seen that the area per repeating unit has increased strongly. Longer waiting times at 20 or 40 °C had no further effect on the isotherm. This procedure was used now for each of the following experiments.

The points in Fig. 2 (points C) represent the areas found after stabilization of a monolayer at 40 °C, using the above-described procedure, at 5, 10, 15, 20, 25, 30 and 35 mN m^{-1} for 45 min each. Figure 3 shows the stabilization curves of monolayers at 40 °C and 30 mN m^{-1} , after 18 h at 20 °C and 1 h at 40 °C (temperature increase from 20 to 40 °C in $\frac{1}{2}$ h) without

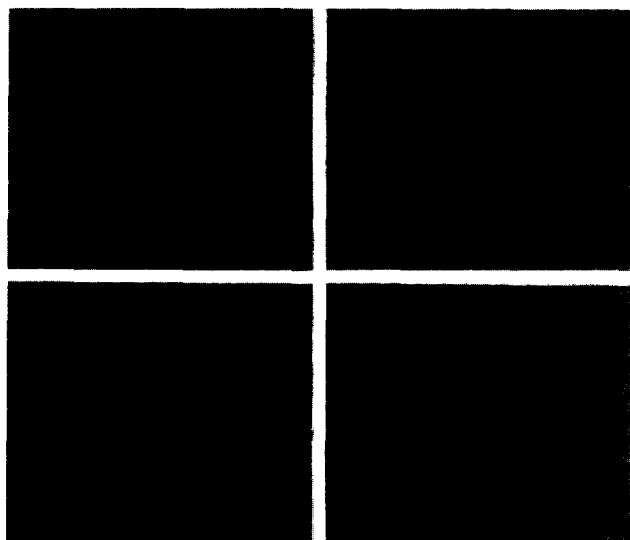


Fig. 5. Transmission electron micrographs: (A), (B) the directly compressed monolayer after 3 h of stabilization at 40 °C and 30 mN m⁻¹; (C), (D) the monolayer at 40 °C, compressed after 18 h at 20 °C and 1 h at 40 °C (temperature increase from 20 to 40 °C in $\frac{1}{2}$ h) without pressure, (C) during compression at 15 mN m⁻¹ and (D) after 3 h of stabilization at 40 °C and 30 mN m⁻¹. The scale bar corresponds to 0.5 μ m.

pressure (curve B) and at 30 °C and 20 mN m⁻¹, after 18 h at 20 °C and 1 h at 30 °C (temperature increase from 20 to 30 °C in $\frac{1}{2}$ h) without pressure (curve C). From these experiments it was obvious that the area per repeating unit decreases in time. This effect is discussed subsequently.

Deposition of the monolayer onto a substrate (glass, ZnS, gold) gave transfer ratios of 1 on the down- and upstrokes. The X-ray diffraction pattern of 14 layers deposited onto glass is shown in Fig. 4 (curve C). The bilayer structure of the LB film, with a repeat distance of about 42 Å, appears to be greatly improved.

TEM samples were taken at a pressure of 15 mN m⁻¹ during the compression and at 30 mN m⁻¹ after about 3 h of stabilization at 40 °C. The results are shown in Figs. 5(C) and 5(D). At a pressure of 15 mN m⁻¹ many small holes are observed in the monolayer. The slow filling of these holes with material could be a possible explanation for the decrease in the area per repeating unit in time. After 3 h of stabilization at 30 mN m⁻¹ the monolayer appears to be smooth with no domains above or underneath it. If the small cracks seen in Fig. 5(D) are formed during the preparation of the sample and therefore will not be present in the monolayer on the water surface at this point, the reason for the small decrease in the area in time cannot be understood yet. If the cracks are present in the monolayer, the filling process of these holes will continue, resulting in a small decrease in the area in time.

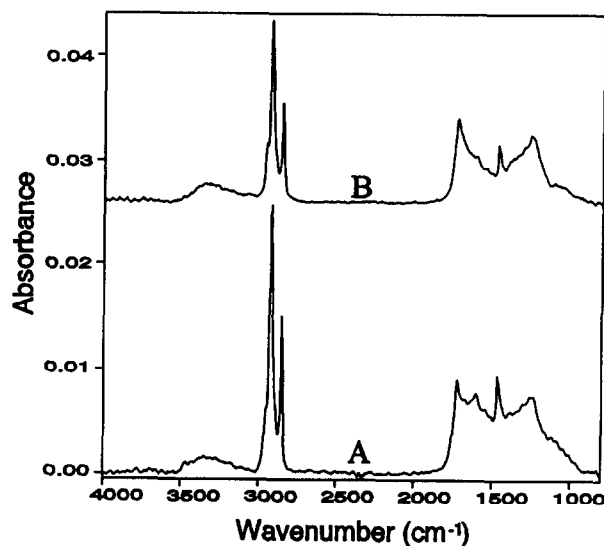


Fig. 6. IR spectra of the azo polymer: curve A, transmission spectrum of 22 layers on ZnS; curve B, grazing angle reflection spectrum of 12 layers on gold.

All experiments indicate that the aggregation, occurring after spreading, disappeared when the material was allowed to disintegrate overnight without pressure.

Figure 6 shows a grazing angle reflection IR and a transmission IR spectrum. Because of dispersion effects direct comparison of the spectra should be performed with care. However, one aspect can clearly be seen. The absorptions of the aliphatic side chains between 2800 cm⁻¹ and 3000 cm⁻¹ are very strong in both spectra. This indicates that the aliphatic side chains are oriented randomly and cannot crystallize under these conditions because they are attached to a rigid-rod backbone. The aliphatic side chains are separated too far apart and therefore form an amorphous layer. The stabilization of the monolayer therefore is probably not caused by the aliphatic side chains, because of their inability to crystallize: differential scanning calorimetry measurements of bulk samples between 20 and 200 °C revealed no melting peak and electron diffraction on transferred monolayers demonstrated no indication of a crystalline order. Together with the results of small angle X-ray diffraction and the fact that the transfer was of the Y type this results in the proposed layer structure shown in Fig. 7.

No difference was found between the transmission IR spectra taken with the polarization perpendicular and parallel to the transfer direction. Therefore, no flow induced orientation has occurred. Between 800 cm⁻¹ and 1800 cm⁻¹ a number of broad peaks were found. Because of overlap of these peaks and dispersion effects conclusions about the orientation of the conjugated backbone are difficult to draw from IR spectroscopy measurements.

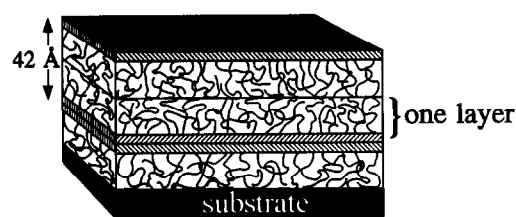


Fig. 7. Proposed multilayer structure of the azo polymer.

4. Conclusions

Smooth monolayers, of an azo polymer, prepared by oxidative coupling of 3,5-diamino-1-octadecylbenzoate, can only be formed when the material is allowed to disintegrate at the air water interface. Good Y-type deposition, with transfer ratios of 1 on both the down-stroke and the upstroke, can be achieved at a temperature of 40 °C and a surface pressure of 30 mN m⁻¹. The LB film, prepared in this way, gives a sharp X-ray diffraction peak at about 42 Å (bilayer distance). The aliphatic side chains are not able to crystallize and therefore form amorphous layers.

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