

Figure 8. Geometry of silicon and diamond tips integrated with AFM cantilevers.

Table 1. Load (F), penetration depth (h) and computed and bulk volumes of the modulus of elasticity (E) in the elastic range

Material	F	h	E (Computed)	E^{12} (Bulk)
Silicone elastomer	500	220	90.6 MPa	15–25 MPa
Mica	4500	40	5.6 GPa	15–20 GPa
Graphite (HOPG)	12000	59	10.1 GPa	5–25 GPa
GaAs	16150	45	17.8 GPa	70–90 GPa

The indentation plots show that the variation of load with penetration depth can be taken nearly linear for the loads in the elastic range of the materials. The relation between load (F) and penetration depth given by Snedden¹¹, is:

$$F = 2 E r h / (1 - \mu^2) \text{ (for cylindrical flat ended indenter),}$$

wherein E is Young's modulus of elasticity, r is radius of contact area (taken as tip radius), h is penetration depth, and μ is Poisson's ratio.

It is not necessary to have an accurate value of μ to get a reasonable value of E .

The silicon tips used in this study have much higher aspect ratio compared to diamond tips. The shape of silicon tip penetrating into the sample approximates a cylinder (Figure 8) and as such it is safe to use the above relationship.

Referring to Figure 6 (for silicone elastomer) and Figure 7 (for mica, HOPG and GaAs) for load vs penetration depth, the values of Young's moduli for these materials can be computed using Snedden's relationship.

In the elastic range, the values of load (F) and penetration depth (h), and the computed values of E have been listed in Table 1. In computing the values of E , a value of r equal to 9 nm is used. The values of μ used are 0.48 for silicone elastomer and 0.33 for the other materials.

AFM indenter tip may encounter layers of contamination and oxide layers which may have significant effect on mechanical properties; it may be a convolution of the properties of all the layers in contact with the tip. Actual dimensions of the tip and cantilever (which are taken from the commercial data) may be different from the values used. Hence the E (computed) values and E (bulk) reported in the literature differ widely.

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Langmuir–Blodgett films of poly alkyl thiophenes: Preparation and characterization of multilayers

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The interfacial behaviour of poly alkyl thiophene monolayers formed at air/water interface have been studied using π -A isotherms. These formed stable condensed monolayers on water and could be transferred by the Langmuir–Blodgett (LB) technique. The UV visible spectra of the LB films showed that the polythiophenes form well-defined aggregates with their long axes nearly vertical to the layer plane. Optical microscopy in the Brewster angle set-up showed rigid striated structures in the case of hexyl-substituted polymer while the cyclohexyl derivative showed a less oriented monolayer. In the case of hexyl-substituted polymer (LB) films, the planar polythiophene main chains lie roughly edge-on parallel to the substrate while side chains are approximately orthogonal to the substrate.

In the last two decades, increasing demand for new polymers has been evidenced in the area of functional materials, designed for specific applications often in the electronic and communication technologies system¹.

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π -stacking of π -conjugated polymers is a subject of recent interest and formation of π -stacked state is important for better performance² (e.g. large optical third-order non-linear susceptibility) of the conjugated polymer. Thiophene-based polymers are the subject of considerable interest due to the chemical versatility of the thiophene that lead to macromolecules with various structures and modulated physical and electronic properties³. Significant recent progress in the synthesis of thiophene-based polymers has resulted in enhanced processability and stability. The incorporation of relatively long and flexible side chains is a common technique for preparing soluble polymers having a stiff backbone⁴. The insolubility and infusibility of polythiophenes has been overcome by the controlled introduction of flexible side groups in the 3rd position^{5,6}. The relationship between chemical structure, solid state organization and physical properties in this family of polymers thus seems highly significant⁷⁻⁹. In this regard, influence of molecular weight, regio regularity, polymorphism in octyl, decyl, and dodecyl derivatives of poly(3-alkyl thiophenes) have been well documented¹⁰⁻¹². The use of LB film technique provides a well-defined arrangement of π -electron system in the layered structure and such organized monolayer assemblies containing quinque thiophene were reported with respect to their conductive properties^{13,14}. However, the orientation of the functional molecules even in such arrangements is still controversial. A large number of studies using the LB film technique have been carried out with preformed polymers to achieve the necessary material property and strength¹⁵⁻¹⁷.

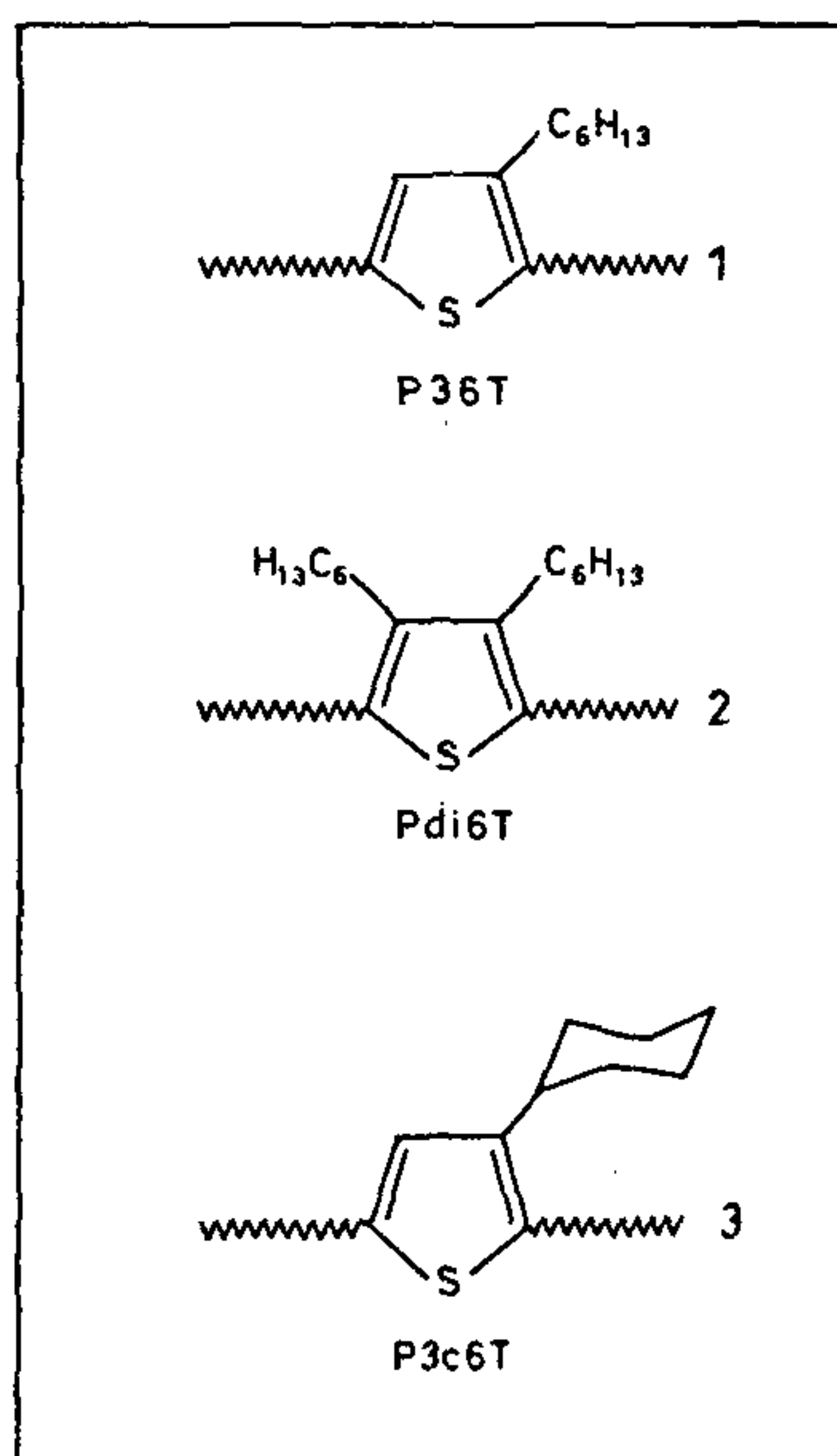


Figure 1. Structure of poly alkyl thiophene repeat units: 1, P3HT; 2, PdiHT; and 3, P3cHT.

In the present work, using three poly alkyl thiophenes (Figure 1), the molecular organization in LB films has been studied by forming monolayers at air/water interface. Poly alkyl thiophenes with different substituents at the 3rd and 4th positions have been already tested for their mechanical stability using conventional thick films^{18,19}. The mono layers formed from the poly alkyl thiophenes have been characterized by the surface pressure isotherms and the UV visible spectra of the films then transferred on to solid substrates by the LB technique have been analysed. The morphology of these layers has been studied by a Brewster angle microscope set-up.

Preparation of monomers and subsequent chemical polymerization have been done using reported procedures¹⁹⁻²¹ and the three poly alkyl thiophenes were obtained. The purities were checked by spectroscopic and chemical analysis and were found to be 99% pure. The weight-average molecular weights of these substances found using GPC are between 90,000 and 1,50,000 and the polydispersity of P3cHT is (9.81) very high when compared to polymer 1 (P3HT) (3.87) and polymer 2 (PdiHT) (5.37).

The monolayers were formed by spreading chloroform solution on to distilled water or aqueous subphase containing 5×10^{-5} M KHCO_3 (pH 6.3). A NIMA trough (model 611) with a Wilhelmy-type balance was used for the measurement of the surface pressure-molecular area (π -A) isotherms. The LB films were built upon quartz substrates cleaned by the usual procedure (washing with $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ (7:3) and rinsing with double distilled water). The films were transferred at $\pi = 15$ mN/m and the transfer ratios were about 0.9. The UV visible spectra were recorded on a Shimadzu 160A spectrophotometer with a special set-up for the LB films. The optical micrographs were taken with a Brewster angle microscope set-up very similar to that of the Nanofilm Technologie, Gottingen, FRG.

Figure 2 shows the π -A isotherms for the compounds P3HT (1), PdiHT (2) and P3cHT (3) on KHCO_3 subphase at $T = 22^\circ\text{C}$. The area/repeating unit at $\pi = 15$ mN/m for compound 1 is 11 \AA^2 while that for compounds 2 and 3 is around 16 and 18 \AA^2 respectively, suggesting that the planar poly thiophene main chains lie, roughly edge-on parallel to the water surface while the side chains are all perpendicular to the subphase. These monolayers are stable up to 18 mN/m above which they seem to collapse to form stacks of multimeric structures. Compared to compound 1 the other compounds seem to form condensed monolayers with smaller molecular areas. Both compounds 1 and 2 show a liquid expanded (up to 30 \AA^2) to liquid condensed state (15 \AA^2) without any other phase transition, while compound 3 shows a fairly large plateau of low compressibility (between 18 and 10 \AA^2). This may suggest that the polymer 3 with a cyclohexyl group^{21,22} introduces in addition to a steric effect, a more hydrophobic character to the monomer units.

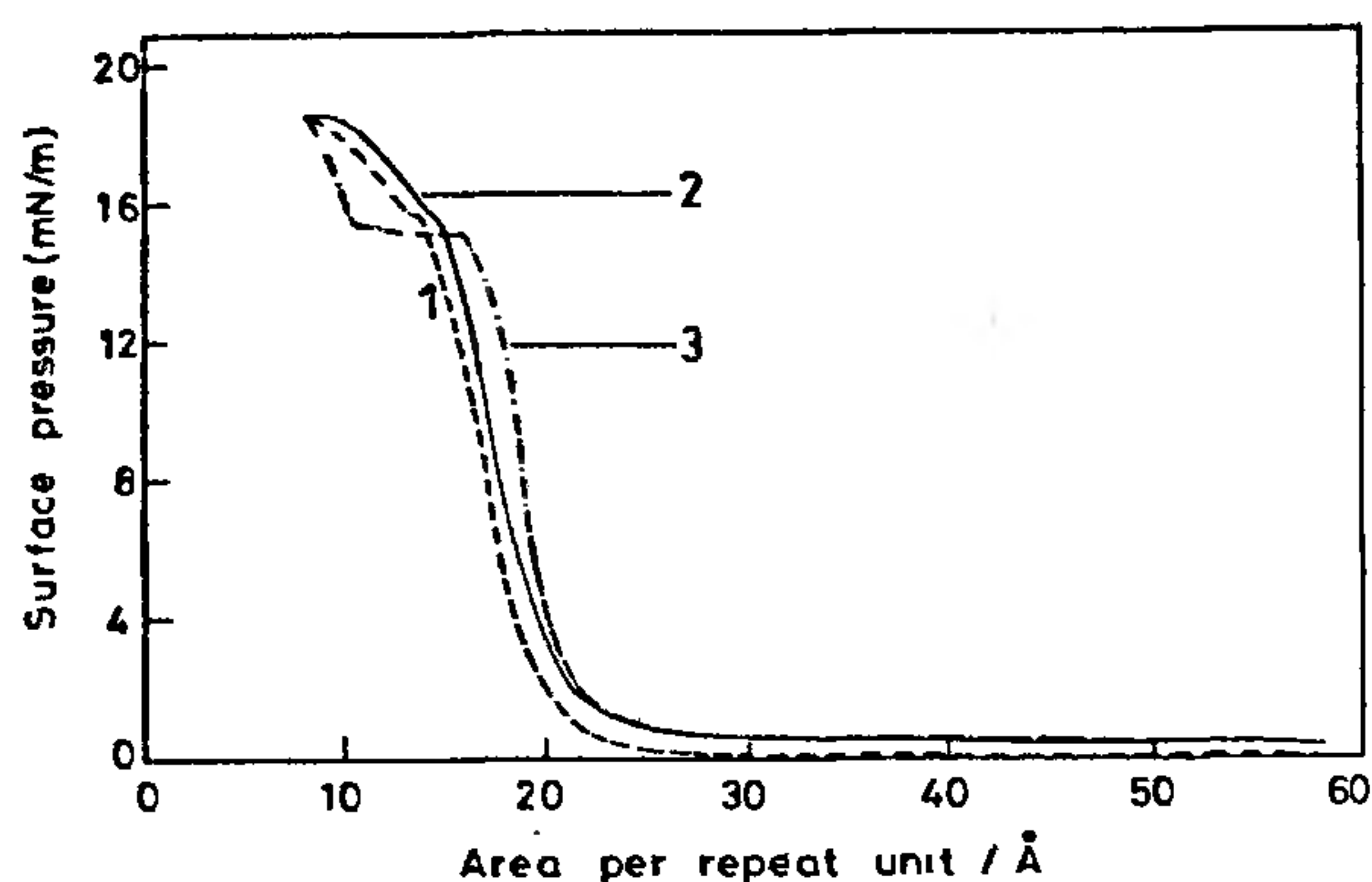


Figure 2. Surface pressure area isotherms for polymers at $T = 22^\circ\text{C}$, 1, P3HT; 2, PdiHT; and 3, P3cHT.

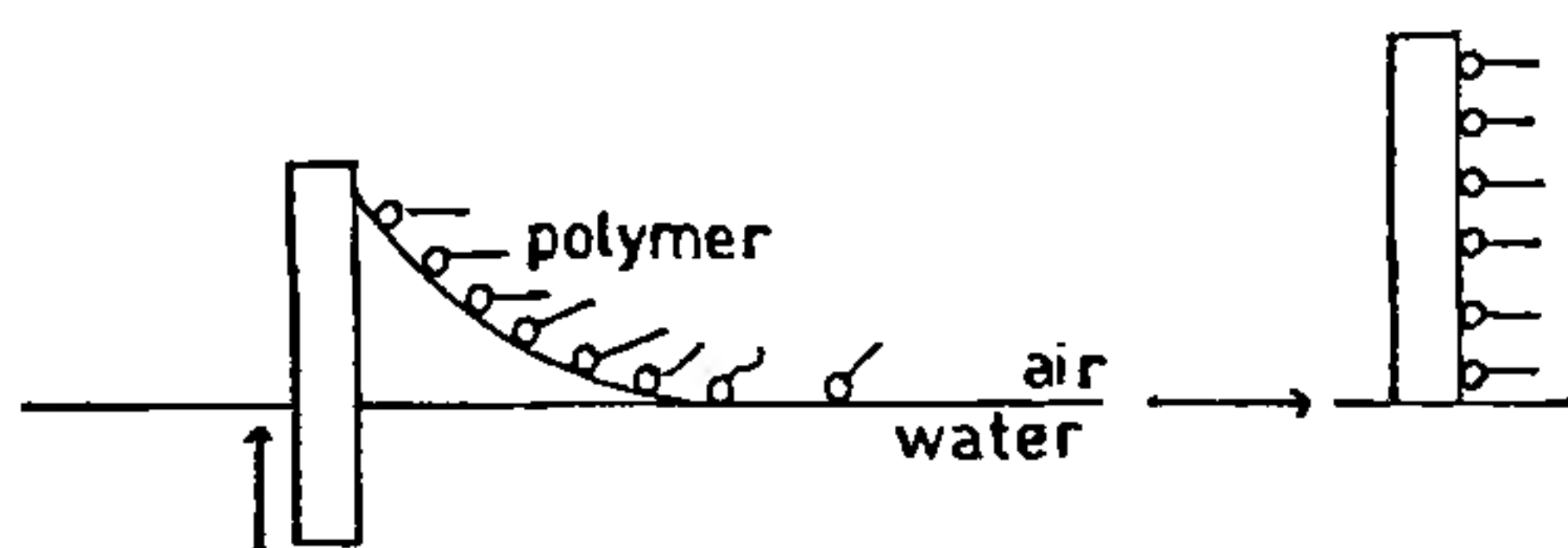


Figure 3. Schematic diagram of Y-type transfer of LB film.

These monolayers can be transferred on to solid supports at 15 mN/m to form a 'Y' type film²³ (Figure 3). However, the quality of polymer 2 in the LB film is not very homogeneous and therefore no spectra could be measured.

Figure 4 shows a representative spectra of compound P3cHT in solution and in LB films. The spectra does not show large differences for the three polymers. For the sake of brevity, they have not been shown here. It is seen that uniformly there is a shift to the red especially the 408 nm band in the solution which shifts to 430 nm. The band gap in the LB film was found to be 2.37 eV while the solution showed 2.56 eV. This long wavelength band shift may be assigned to the electronic transition along the long axis and indicate the formation of J aggregates. Further, the absorption bands at 275 nm in the solution exhibit a blue shift (268 nm) in the LB films. In a first approximation, from the dipole interactions between chromophores in the linear aggregates, it is expected that the absorption band due to the transition moment that lies flat exhibits the red shift while that standing vertically exhibits a blue shift²⁴. These agree well with the λ_{max} values of pure poly (2,5 thiophene diyl) compounds with the values ranging between 480 and 500 nm and band gap being 2.0 eV. The shorter wavelengths with high band gaps in the present study may result from steric interactions between the substituents and the polymer backbone. These steric interactions lead to a non-planar conformation and consequently reduce the effective conjugation length. Though the solution spectra of all the compounds showed similar bands, the spectra in LB films seem to reflect strongly the effect of

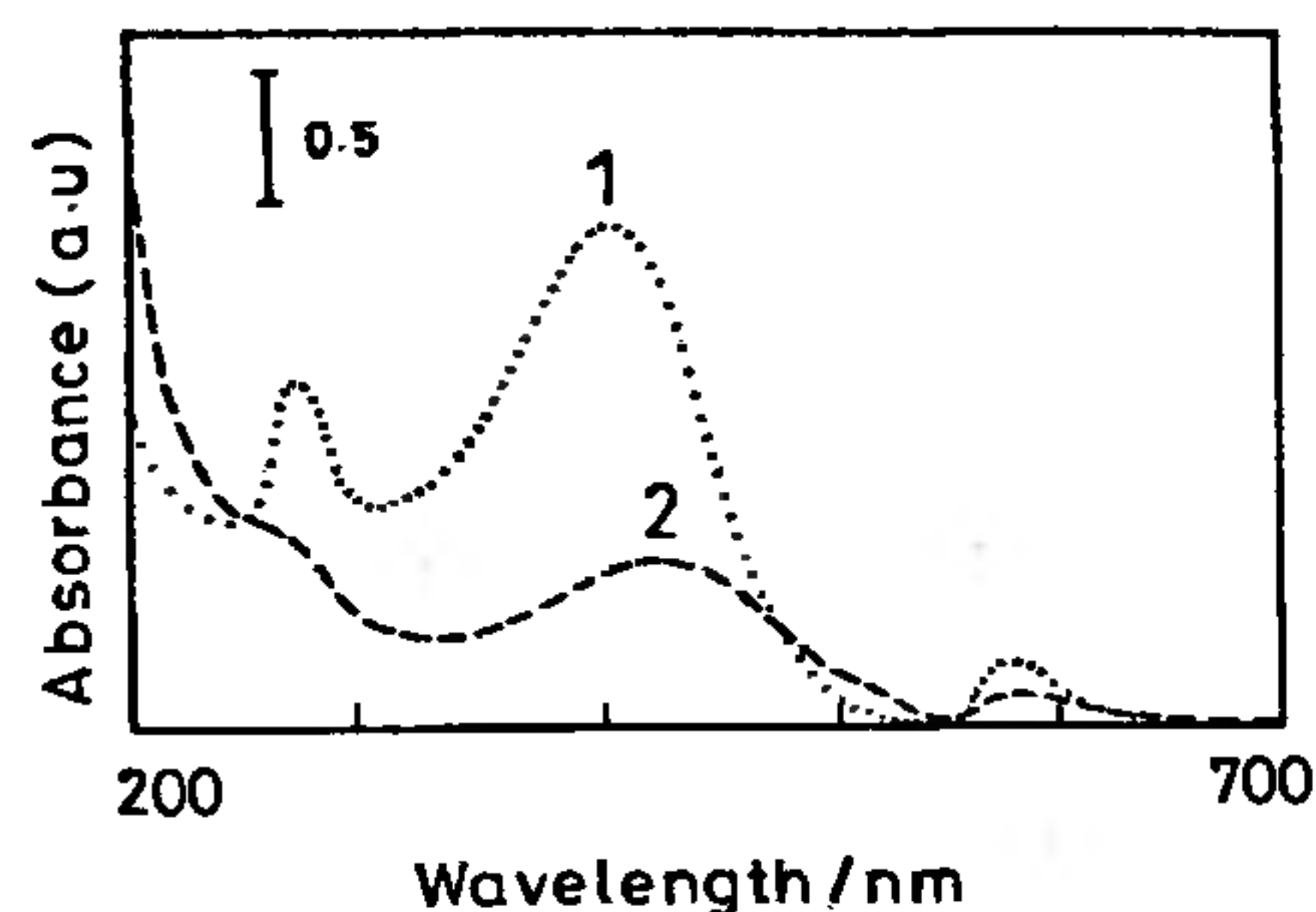


Figure 4. UV visible spectra of solution (1) and LB film (2) of P3cHT.

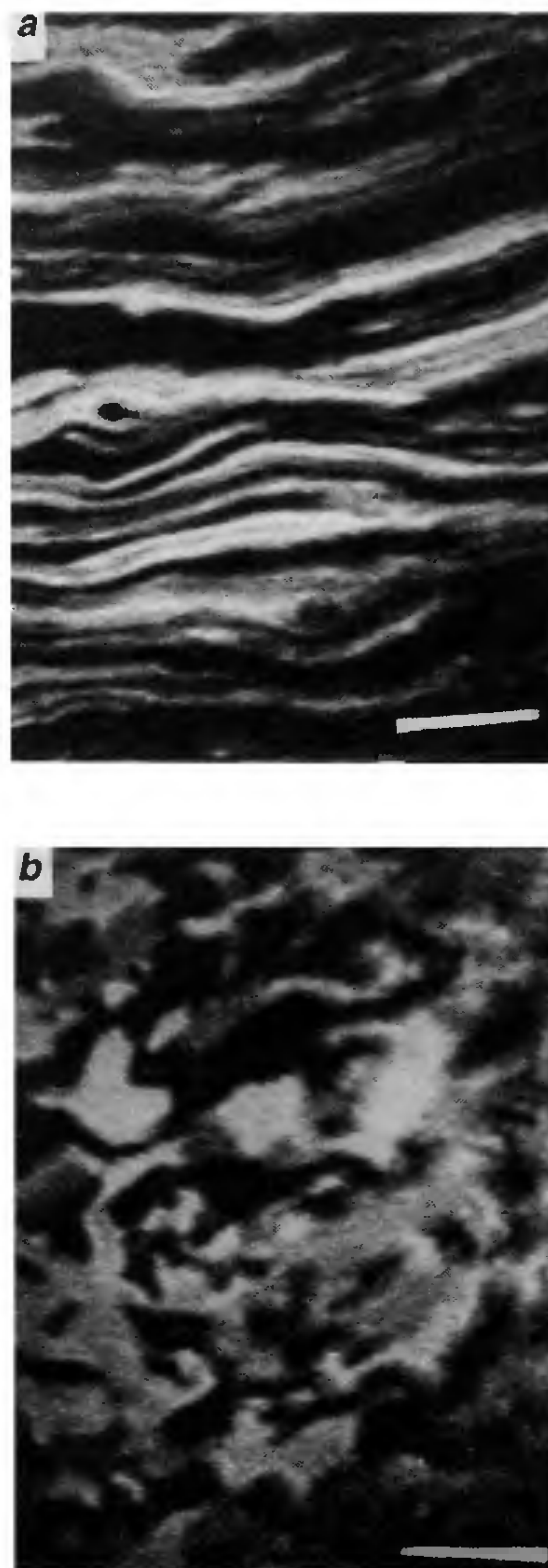


Figure 5. Optical micrograph of *a*, polymer 1 and *b*, polymer 3 at $\pi = 15 \text{ mN/m}$ (scale bar is 20 μm).

the different substituents. Such an effect should be related to inter-molecular effects (i.e. better packing)²⁵.

The optical micrographs of these LB films at Brewster angle set-up for compounds 1 and 3 are shown in Figure 5a and b. Polymer 1 shows a fairly rigid structure with striations running parallel to the dipping direction. The micrographs also indicate that the rigidity leads to more disorganized domain formation with different orientations in the case of polymer 3. This compares well with the mechanical studies carried out on these polymers which showed that the anisotropy in polymer 3 would decrease as the substituents increased in size.

This work shows that these pure alkyl-substituted thiophenes form stable monolayers at air/water interface and can be transferred to solid substrates by the LB technique. It is also seen that a possible change in orientation and packing of polymeric LB films can be obtained which can find applications in conductivity²², nonlinear optical and electronic properties, especially in light emission³, when the polymer was fabricated into light emitting diodes.

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Expression of *nptII* marker and *gus* reporter genes and their inheritance in subsequent generations of transgenic *Brassica* developed through *Agrobacterium*-mediated gene transfer

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NptII marker and *gus* reporter genes were introduced in *Brassica juncea* through *Agrobacterium*-mediated transformation showing a transformation frequency of 3–5% in the best responsive medium. Seventy-one per cent regeneration from hypocotyl explants was obtained on MS medium containing 0.01 mg/l 2,4-D and 2.0 mg/l BA supplemented with 20 μ M AgNO₃ and 0.7% agarose as the gelling agent. The presence of transgenes (*nptII* and *gus*) in T₀, T₁ and T₂ generations was confirmed by dot blot analysis, using *nptII* gene as the probe, and by histochemical assay for the *gus* gene, respectively. Mendelian inheritance of the transgene (*nptII*) was observed in the T₁ and T₂ generations. Both the marker and reporter genes co-segregated in the T₁ and T₂ generations. The kanamycin-resistant plants in the T₁ progeny were either homozygous or heterozygous for the transgene.

AMONG the various approaches for integrative transformation, *Agrobacterium*-mediated technique is most widely used. This method of transformation has been used previously by Mathews *et al.*¹, Barfield and Pua²,

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