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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1994

Link to publication in University of Groningen/UMCG research database

Mixed mono- and multilayers of poly(isocyanide)s with non-linear optically active side chains*

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Abstract

The properties and structure of Langmuir–Blodgett mono- and multilayers of several poly(isocyanide)s with non-linear optically active side-chains were studied. These polymers formed very rigid layers or layers which appeared to be unstable. To circumvent this problem they were mixed with other poly(isocyanide)s or with amylose-butyrate. Transmission electron microscopy studies of the polymeric mixtures revealed that phase separation occurred in all cases and that only poly(isocyanide)s substituted with hydrophilic side chains formed monomolecular layers. Depending on the nature of the polymer which was used for mixing, the dye polymers could be deposited with Y- or Z-type transfer. Second-harmonic intensities generated from these films were small in the case of the Y-type multilayered films and moderately high in the case of the Z-type films.

1. Introduction

The Langmuir–Blodgett (LB) technique offers the possibility of organizing molecules into highly ordered monolayers and producing multilayer films with desired architectures. Owing to stronger intra- and intermolecular interactions, polymeric LB films tend to have better thermal and mechanical stability than those of low molecular weight compounds. In spite of their lower degree of order, in some cases polymeric LB films might have great potential for applications in the field of sensors, optonics and electronics.

Many types of polymer have already been studied as monolayers at the air–water interface. Two general types have been successfully used for the preparation of LB films: comb-like polymers which resemble low molecular weight amphiphiles [1–4] and rigid rod polymers [5–8]. Recently, a number of studies have appeared dealing with polymeric non-linear optical (NLO) materials.

NLO active functions have been incorporated in polymer matrices in the form of low molecular weight compounds [9, 10] or have been introduced in the backbone [11] and side groups [12, 13] of polymers.
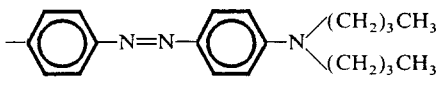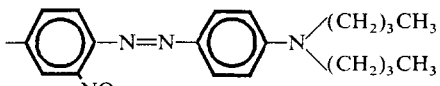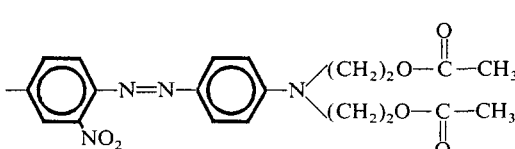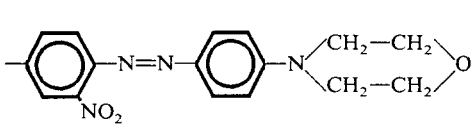
In this study we report on poly(isocyanide)s $[R–N=C<]_n$, with pendant NLO active groups. The formation, structure and transfer of these monolayers onto solid substrates are discussed. Poly(isocyanide)s have a very stable helical structure. A tightly coiled 4_1 helical backbone is formed during polymerization [14]. Polymerization of one enantiomer of a chiral isocyanide gives rise to the formation of polymer helices with an excess of one particular screw sense. Since a helix is a chiral species, this should lead to non-centrosymmetric structures. Attachment of NLO active groups to these helices might result in polymers which can exhibit second-harmonic generation.

2. Experimental details

The synthesis and characterization of the polymers (see Table 1) will be published elsewhere [15]. The experimental procedures have been outlined in previous papers [8, 16].

Transmission electron microscopy (TEM) was performed on monolayers in two different ways. In order to image the film side facing the water surface, the monolayers were picked up from the water surface by touching the monolayer with a Formvar–carbon-coated grid, at $\pi = 15$ mN m^{-1} and $T = 18\,°$C. To observe the air-facing side of the layer, the grids were

TABLE 1. Polymers

Polymer	Configuration at C*	R in $\overset{\uparrow}{\underset{\downarrow}{C}}=N-\overset{*}{C}H(CH_3)-CH_2O-\overset{O}{\overset{\|}{C}}-R \Big]_n$
1	(S)	$-CH_3$
2	(R, S) or (S)	⬡$-N=N-$⬡$-N\overset{(CH_2)_3CH_3}{\underset{(CH_2)_3CH_3}{<}}$
3	(S)	⬡$-N=N-$⬡$-N\overset{(CH_2)_3CH_3}{\underset{(CH_2)_3CH_3}{<}}$ with NO₂
4	(S)	⬡$-N=N-$⬡$-N\overset{(CH_2)_2O-\overset{O}{\overset{\|}{C}}-CH_3}{\underset{(CH_2)_2O-\underset{O}{\underset{\|}{C}}-CH_3}{<}}$ with NO₂
5	(R, S)	⬡$-N=N-$⬡$-N\overset{CH_2-CH_2}{\underset{CH_2-CH_2}{<}}O$ with NO₂

submerged to the bottom of the trough prior to film formation. After application and stabilization of the film, the grids were carefully removed from the bottom of the trough by passing the interface nearly horizontally. The specimens were blotted dry by touching the edge of the grid with filter paper and were subsequently shadowed with platinum at an angle of 20°. The electron micrographs were recorded on a JEOL 1200EX microscope at 80 kV using a magnification of 10 000 times.

3. Results and discussion

3.1. Monolayer behaviour and transfer

Poly(isocyanide) 1 forms stable, Z-type transferable, monolayers probably because its side chains are hydrophilic and interact strongly with the water subphase [8]. Replacement of the ester methyl function of 1 with large hydrophobic groups results in polymers 2 and 3, which do not form stable monolayers, probably because of lack of interaction of the side chains with the water subphase. The polar parts of these polymer molecules are completely shielded from the water surface by the hydrophobic substitute groups. However, upon mixing 2 or 3 with amylose-ester derivatives, i.e. amylose-acetate or amylose-butyrate (AB), stable and transferable films were formed. Isotherms of films of AB mixed with increasing concentrations of poly(isocyanide)s 2 and 3 show a decreasing area A_0, which is the area found by extrapolating the linear increase in the pres-
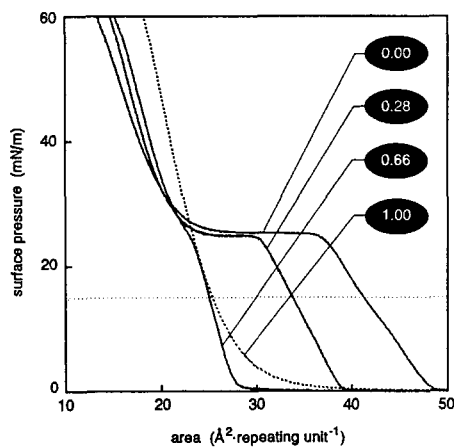

Fig. 1. Surface presssure–area isotherms of mixtures of 3 and AB. The base mole fraction of 3 is indicated. The temperature was 15 °C and the speed of compression was 5 Å² min⁻¹ per repeating unit.

sure–area isotherm to $\pi = 0 \text{ mN m}^{-1}$ (Fig. 1). Moreover, in the entire range A_0 is smaller than the value given by the additivity rule

$$A_{0, \text{mixture}} = f_{\text{polymer}} A_{0, \text{polymer}} + (1 - f_{\text{polymer}}) A_{0, \text{AB}} \qquad (1)$$

in which f_{polymer} and $A_{0, \text{polymer}}$ denote the (base) mole fraction and the specific area of the corresponding poly(isocyanide) respectively. Figure 2 shows the area A_0 of 2 and 3 as a function of the (base) mole fraction of these polymers in mixtures with AB.

Pure AB forms well-defined stable monolayers in which the polymer has a helical structure. Monolayers
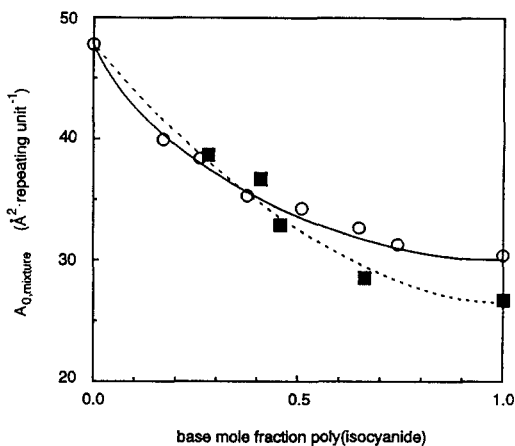
Fig. 2. Relationship between the specific area A_0 of $\underline{2}$ ($\bigcirc$, —) and $\underline{3}$ ($\blacksquare$, $\cdots$) and their base mole fraction in the mixtures with AB.
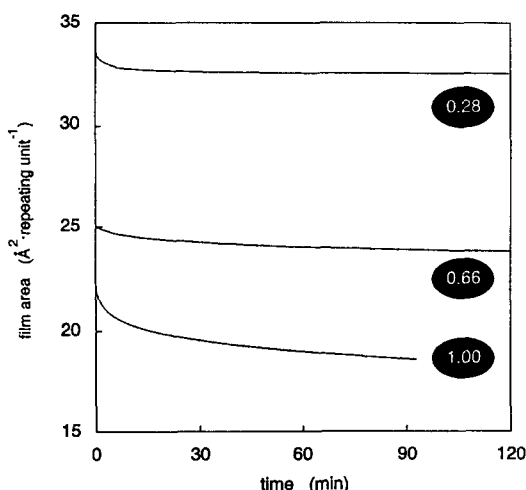
Fig. 3. Stabilization curves of mixtures of $\underline{3}$ and AB at a surface pressure of 15 mN m^{-1}. The base mole fraction of $\underline{3}$ is indicated. The temperature was 17 °C in all cases.

of AB can be deposited onto solid substrates with transfer ratios of 0.7 on the downstroke and 1.0 on the upstroke [17]. Given this fact we assume that in the mixtures with $\underline{2}$ and $\underline{3}$ this polymer is situated at the air–water interface. Consequently, the poly(iso-cyanide)s can be only partly located at the air–water interface (see Figs. 1 and 2). Figure 3 shows the effect of AB on the stability of the monolayers. The area per repeating unit for pure $\underline{3}$ is decreasing even after 1 h in contrast to the layers containing AB which are stable. Unlike the films of the pure poly(isocyanide)s the mixed films can be transferred easily. At least 100 successive layers can be deposited (Y-type) with transfer ratios of 0.75 on the downstroke and 1.00 on the upstroke. Monolayer thicknesses were calculated from ellipsome-try measurements on deposited multilayers. To this end silicon substrates were covered with 16, 32, 48, 64, 80 and 96 successive monolayers respectively, prepared
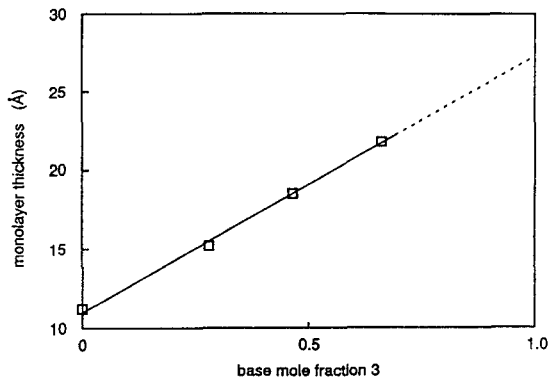

Fig. 4. Calculated monolayer thickness as a function of the base mole fraction of $\underline{3}$ in AB.

from mixed films of $\underline{3}$ and AB. As can be seen in Fig. 4 the monolayer thickness depends on the mole fraction of $\underline{3}$. Extrapolation of the curve yields a monolayer thickness of 27.4 Å for pure $\underline{3}$. TEM pictures of the mixed films show separate domains of $\underline{3}$ and AB. Pure $\underline{3}$ (see Fig. 5(a)) forms a layer which is smooth over large areas but which also contains thicker domains. These domains are visible as dark circular patches with a cross-section of about 250 nm. The wrinkles on the micrograph are probably caused by collapse of the unstable layer. Figure 5(B) shows a mixed film of 66% $\underline{3}$ in AB. The AB domains have a bumpy surface. The poly(isocyanide)s form irregularly shaped domains of
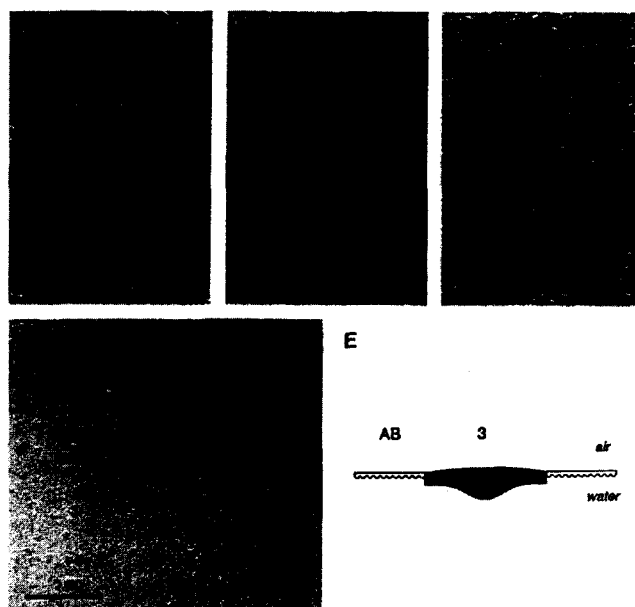

Fig. 5. (A)–(D) Transmission electron micrographs of (A) pure $\underline{3}$ (water-side view), (B) 66% $\underline{3}$ in AB (water-side view), (C) 28% $\underline{3}$ in AB (water-side view) and (D) 28% $\underline{3}$ in AB (air-side view). (E) Schematic representation of the mixed layers of $\underline{3}$ with AB. Surface pressure was 15 mN m^{-1} and the temperature was 18 °C. The scale bar represents 500 nm.

about 1 μm. The thick areas of 3 are still present. The surface of the thin areas of 3 is lying higher than the AB domains, as can be seen at the boundary lines of the different phases. The collapse wrinkles are not as pronounced as in the films of pure 3. In the mixed film of 28% 3 in AB (Fig. 5(C)) the domains of 3 have become smaller (< 100 nm). Moreover, the collapse is completely suppressed.

The mixed films were also observed from the air side. Figure 5(D) shows such a film composed of 28% 3 in AB. The AB matrix shows no bumpy surface but gives the impression of being rather smooth. The dark domains of 3 are only slightly higher than the domains of AB. From the foregoing results we may conclude that mixed films of 3 and AB can be represented schematically as depicted in Fig. 5(E). Polymer 3 is present as lenticular domains which are thinned out to a monolayer thickness at their edges. The AB phase is clearly asymmetric, being rough at the water side but very smooth at the air side of the layer.

When we use poly(isocyanide)s with a more hydrophilic side chain, namely 4 and 5, stable monomolecular layers can be formed without the requirement of mixing the polymers with AB. The films obtained, however, are very rigid and as a consequence are not transferable by the conventional vertical dipping method. When 4 and 5 are mixed with 1, the stability of the films remains the same but vertical transfer for at least 100 successive layers becomes possible and can even be of a perfect Z-type. The transfer ratios and film stability are not affected up to a (base) mole fraction of 0.6 poly(isocyanide) in the mixtures with 1. In contrast to the mixtures described above, the mixtures of 4 and 5 with 1 show areas A_0 which follow eqn. (1) (Fig. 6). Owing to their more hydrophilic side chains the poly(isocyanide)s 4 and 5 are probably completely located at the water surface. They can form
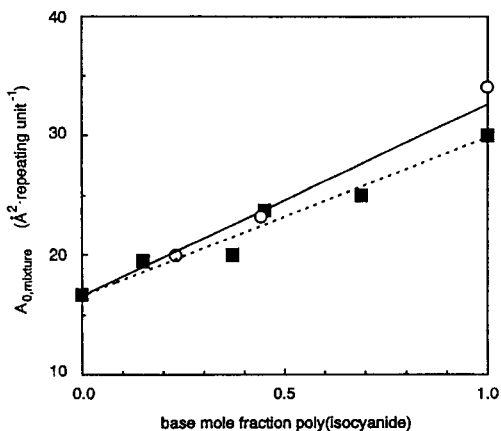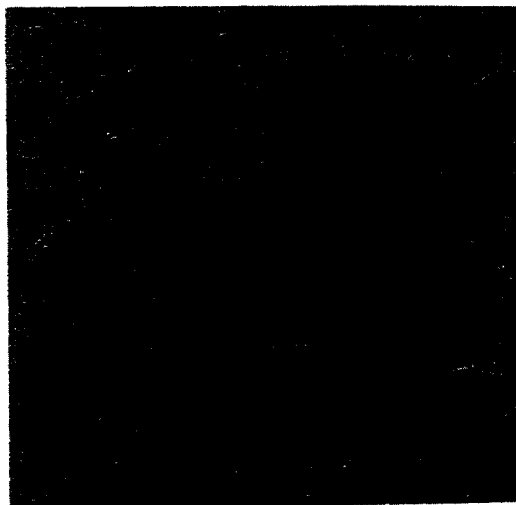

500 nm

Fig. 7. Transmission electron micrograph of a mixture of 37% 5 in 1 (water-side view). Surface pressure was 15 mN m^{-1} and the temperature was 18 °C.

H bonds with the water subphase more easily than polymers 2 and 3. In the transmission electron micrograph of a film of 37% 5 in 1 (Fig. 7) domains of the two polymers are visible. It is clear that the dark lens-shaped domains, present in the mixtures of 3 and AB, do not appear here. A smooth monolayer with only minor height differences is observed.

3.2. NLO properties

Preliminary SHG measurements were carried out according to the method of Cnossen et al. [18]. Assuming the total polymeric structure, including the side chains, to be rigid, poly(isocyanide)s prepared from racemic mixtures of monomers were not expected to generate any second-harmonic signal. However, in contrast to cast films of the polymeric mixtures, Z-type LB films appeared to be moderately active, probably because (i) there is some orientation of the chromophores at the water surface and (ii) the monolayers are transferred in the Z-mode. Multilayers of polymers 2 and 3, which were mixed with AB, and as a consequence gave more or less Y-type films, showed much lower SHG. Further research is currently being performed to calculate absolute values of $\chi^{(2)}$ at the different polarization settings, and will be published separately.

Fig. 6. Relationship between the specific areas A_0 of 4 (○, —) and 5 (■, ···) and their base mole fraction in the mixtures with 1.

Conclusion

The poly(isocyanide)s used in this study form very rigid monolayers. Mixing these polymers with other polymers results in transferable films. In these mixed

films the poly(isocyanide)s with hydrophilic substitute groups appear to be located completely as a monolayer at the water surface, whereas the poly(isocyanide)s with more hydrophobic side chains are present as thick domains.

Depending on the polymer used for mixing, it is possible to obtain Y-type of Z-type multilayers. Transfer ratios remain constant and clear films with thicknesses of over 0.3 μm can be obtained.

Acknowledgment

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