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Mixed polymeric monolayers and Langmuir–Blodgett multilayers with functional low molecular weight guest compounds

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Abstract

Mixed monolayers and Langmuir–Blodgett multilayers of functional low molecular weight guest compounds, especially nonlinear optical (NLO) dyes, within the matrix of an amphotropic spacer polymer have been prepared. The polymer matrix enabled the transfer of guest compounds not capable of self-organizing at the air-water interface by themselves. The structure of the LB multilayers and the transfer process were studied by small angle X-ray scattering and UV-visible spectroscopy. Good NLO coefficients were found in the mixed films.

1. Introduction

The search for stable and functional LB multilayers resulted in the use of functionalized preformed polymers [1–5]. However, polymers with chemically sensitive functional groups, *e.g.* nonlinear optical (NLO) dyes [6, 7], are often difficult to synthesize. A more flexible approach would be the preparation of mixed LB films made from matrix polymers and functional low molecular weight compounds.

The principle is well known for mixed monolayers and LB multilayers of ionic lipids which are stabilized by complexation with oppositely charged polyelectrolytes [3, 5]. First attempts to codeposit functional guest molecules within a nonionic polymer matrix like poly(methyl methacrylate) [8], poly(octadecyl methacrylate) [9] or polyglutamate copolymers [10] have also been reported. A basic disadvantage of these systems is the rather limited miscibility of the guests within the polymeric host.

Recently spacer polymers with good self-organization properties have been introduced combining amphiphilic and mesogenic elements [2–4, 11]. These so called amphotropic polymers [3–5] form thermally stable LB films which exhibit a reversible phase transition to a less ordered "liquid-crystalline" state on heating [4].

Here we want to demonstrate that in fact amphotropic spacer copolymers are powerful host polymers for functional low molecular weight guest molecules of different chemical nature such as, *e.g.* NLO dyes, both in monolayers and LB multilayers.

2. Experimental details

The statistical liquid-crystalline biphenyl copolymer **1** [3, 12] was synthesized in analogy to refs. 1 and 4. Its composition was determined by microanalysis and ¹H NMR spectroscopy. The weight average molecular weight ($M_w = 16\,300$ g mol^{-1}) was estimated by GPC in THF (polystyrene standards).
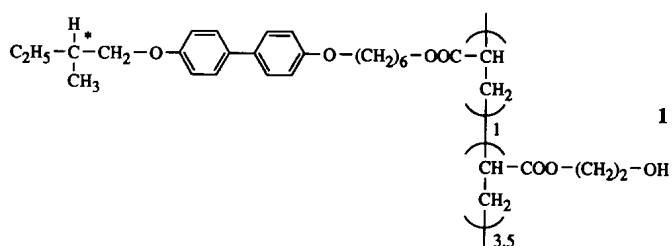
Monolayer experiments were performed with a computer-controlled film balance [13] on pure Milli-Q water (Millipore Corp.). Mixtures of polymer **1** and compounds **2–9** (Table 1) were spread as chloroform solutions in concentrations of 0.2–0.5 mg ml^{-1}. Compression rates varied from 0.01 to 0.05 nm² (repeat unit min)$^{-1}$.

LB multilayers were prepared with the film balance FW 1 (Lauda) from pure aqueous subphase at 20 °C (Table 1). Various substrates were used such as polyester foil. (Hostaphan RE3,0; Kalle), hydrophilic glass and quartz slides, and hydrophobized silicon wafers (Si 100; Wacker) [4]. Prior to deposition, the monolayers were equilibrated for 30 min at deposition

TABLE 1. Mixed polymeric and LB multilayers with functional low molecular weight guest compounds

No.	Low molecular weight (LMW) compound	Synthesis ref.	Composition of mixed films, mole fraction (X_{LMW})	Deposition pressure, π_{dep} (mN m^{-1})	Deposition speed, $v\downarrow/v\uparrow$ (cm min^{-1})	Bragg-spacing[a] (nm)	$\chi^{(2)}_{zzz}$ ($\times 10^9$/esu)	$\dfrac{\beta_{zzz}}{X_{LMW}}$ ($\times 10^{28}$/esu)
2	$CH_2{=}CH{-}COO{-}(CH_2)_{11}{-}O{-}$[biphenyl]$-OH$	14	0.43	30	2.3/1.8	4.13	—	—
3	$HO{-}(CH_2)_6{-}O{-}$[biphenyl]$-O{-}(CH_2)_6{-}OH$	14	0.52	30	2.3/1.8	2.32	—	—
4	$CH_3{-}(CH_2)_5{-}O{-}$[biphenyl]$-O{-}(CH_2)_5{-}CH_3$	12	0.46	30	9.3/1.8	5.89	—	—
5	$CH_2{=}C(CH_3){-}COO{-}(CH_2)_6{-}O{-}$[biphenyl]$-N{=}N{-}$[phenyl]$-CN$	12	0.45	25	2.3/1.8	4.19	—	—
6	$CH_3{-}(CH_2)_6{-}N^+{-}$[phenyl]$-CH{=}CH{-}$[phenyl]$-N(CH_3)CH_3$, Br^-	6	0.50	29[b]	—	—	—	—
7	$CH_3{-}(CH_2)_{15}$, $CH_3{-}(CH_2)_{15}$ $N{-}$[phenyl]$-CH{=}CH{-}$[pyridinium]$^+N{-}CH_3$, I^-	6	0.29	30	2.3/1.8	4.24	220	2.4
8	$CH_3{-}(CH_2)_{15}$, $CH_3{-}(CH_2)_{15}$ $N{-}$[phenyl]$-CH{=}N{-}NH{-}$[phenyl]$-NO_2$	6	0.50 / 0.33	17 / 27	1.2/0.7 / 1.2/0.7	4.16 / 4.20	150 / 130	1.2 / 1.5
9	$CH_3{-}(CH_2)_{15}$, $CH_3{-}(CH_2)_{15}$ $N{-}$[phenyl]$-CH{=}N{-}NH{-}$[phenyl](NO_2)$-NO_2$	6	0.50 / 0.33	8 / 10	1.2/0.7 / 2.3/1.8	— / 3.92/3.31[c]	80 / 60	0.7 / 0.9

[a]Bragg-spacing of pure copolymer 1 multilayers on hydrophobized silicon wafer: 4.64 nm; 2–5, 7 multilayers deposited on hydrophobic PET foil; 8, 9 multilayers deposited on hydrophobized silicon wafer.
[b]No codeposition of 6 with polymer 1.
[c]Two independent populations of Bragg reflections.

pressure. Between subsequent dipping cycles, the samples were pulled out of the subphase, and were allowed to dry in air (≥ 15 min) to avoid retransfer of previously deposited monolayers during the next downward dip.

Small angle X-ray (SAXS) diffractograms were obtained with nickel-filtered Cu Kα radiation (λ = 0.1541 nm) on a Siemens D-500 diffractometer. UV-visible spectra were recorded with a Perkin–Elmer Lambda 5 spectrophotometer using quartz supports. Second harmonic generation (SHG) properties of monolayers deposited on glass were investigated as previously described [7].

3. Results and discussion

3.1. Monolayers

Table 1 summarizes the compounds studied. Surface pressure–area diagrams of copolymer 1 and its mixtures with different functional low molecular weight compounds (4, 7–9) at 20 °C are presented in Fig. 1. Polymer 1 exhibits a condensed and a broad expanded phase which are attributed to the hydrophilic main chain spacer. Its monolayer properties are discussed in more detail elsewhere [11]. Noteworthy, out of the low molecular weight compounds (Table 1), only hemicyanine 7 [6] (Fig. 1A) and nitrophenylhydrazone 8 (Fig. 1B) are able to form stable monolayers.

In contrast, stable monolayers were obtained from binary mixtures of 2–5 and 7–9 with polymer 1 at room temperature. This was tested up to a molar fraction of 0.5 of the functional component. Only experiments with mixtures of 1 and the water soluble hemicyanine 6 were unsuccessful since large amounts of the dye dissolved in the subphase. Generally the fluidity of the monolayer is reduced by addition of the low molecular weight compound. This effect is particularly
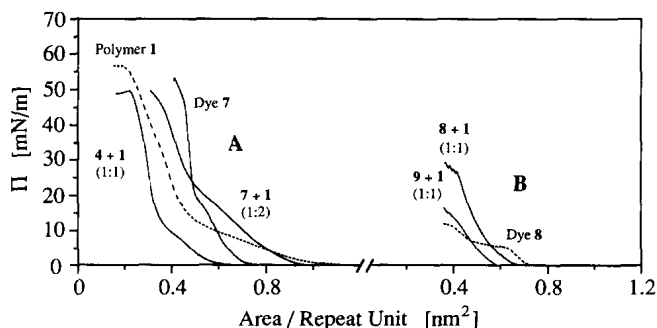
obvious for the double chain amphiphiles 8, 9 (Fig. 1B).

Despite the different structures of the single chain guest compounds, the isotherms of 1:1 molar mixtures of 1 with 2–5 are very similar in shape, and vary only in collapse pressure and in the onset of the expanded phase. Remarkably, the mixed polymeric monolayer with the non-amphiphilic biphenyl derivative 4 yields the highest collapse pressure within this series although 4 alone is not surface active (Fig. 1A).

Mixed monolayers with the double chain NLO dyes 7–9 reveal a strong influence of the headgroup. Whereas mixtures with the phenylhydrazones 8, 9 display solely condensed phases with a drastically reduced collapse pressure (Fig. 1B), an expanded and a condensed phase up to about 45 mN/m are observed for mixtures with hemicyanine 7 (Fig. 1A). Further, mixed monolayers of 1 and the dinitrophenylhydrazone 9 seem to be phase separated (see discussion of the X-ray characterization of the LB multilayers below).

Hence, despite certain limitations, the amphotropic copolymer 1 proved to be a powerful matrix for the stabilization of a variety of different non-self-organizing functional guest components at the air–water interface.

3.2. LB multilayers

Although LB multilayers could not be prepared from any of the pure compounds 2–9, their polymeric mixtures were successfully transferred onto a variety of solid supports, except those containing hemicyanine 6. Deposition always occurred in both dipping directions. Mixed films thicker than 30 layers built on silicon exhibited optically homogeneous interference colours and were totally transparent on glass, thus indicating
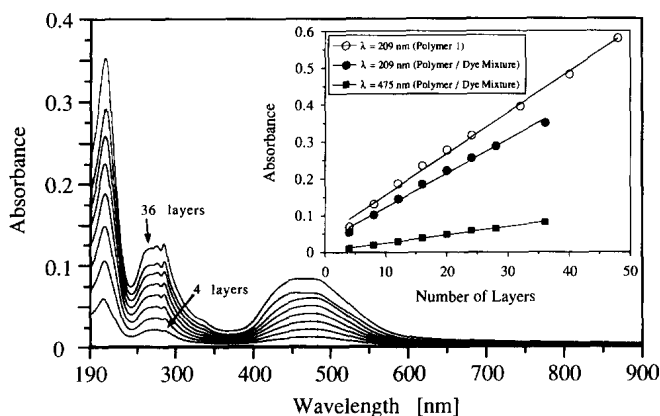

Fig. 1. Surface pressure–area isotherms at 20 °C on pure water subphase. A, Monolayers of pure copolymer 1 and pure NLO dye 7; mixed polymeric monolayers of 4 + 1 (1:1) and 7 + 1 (1:2). B, Monolayers of pure NLO dye 8; mixed polymeric monolayers of 8 + 1 (1:1) and 9 + 1 (1:1).

Fig. 2. Cotransfer of NLO dye 7 within polymer 1 matrix monitored by UV-visible spectroscopy. Absorbance spectra of mixed film and linear increase of UV absorbance with number of LB multilayers on quartz: 4–48 layers of pure polymer 1 (λ_{max} = 209 nm); 4–36 layers of a 2:1 molar mixture of polymer 1 and NLO dye 7 (polymer 1, λ_{max} = 209 nm; dye 7, λ_{max} = 475 nm).

film homogeneity. This was confirmed by UV-visible spectroscopy as shown for LB films of hemicyanine 7 and polymer 1 in Fig. 2. The incorporation of 7 is manifested by the absorption band centered at 475 nm [6]; copolymer 1 itself absorbs below 340 nm. The absorption intensity increases linearly with the number of layers deposited for LB films of the pure polymer as well as for the polymer/dye mixture, thus corroborating a reproducible and well defined codeposition (Fig. 2, polymer 1, $\lambda_{max} = 209$ nm; dye 7, $\lambda_{max} = 475$ nm).

The layer structure of the mixed LB films was proven by SAXS (Table 1). The deviation of the repeat distances of the mixed multilayers from the value of 4.64 nm, measured for the pure copolymer, gives additional proof of the successful incorporation of the guest molecules. Generally a reduced d-spacing of about 4.2 nm was found for mixed multilayers of compounds 2, 5, 7, 8 with a regular amphiphilic structure suggesting a more tilted arrangement of the hydrocarbon chains within the layers. About half the polymeric repeat distance was observed for mixed films with 3 bearing headgroups on both ends of the hydrocarbon chain. This can be explained either by a monolayer arrangement, or by the extinction of the first order Bragg reflection. A d-spacing of 5.89 nm close to the theoretical repeat distance of about 6.4 nm for the fully extended polymer bilayer was found in mixtures with 4. These films also showed more and narrower Bragg reflections than the pure polymer multilayers pointing to an improved layer structure. Obviously, the admixture of the nonamphiphilic biphenyl compound 4 structurally similar to the polymeric side chain leads to an enhanced self-organization. The observation of two populations of Bragg reflections in the X-ray diffractograms of mixed LB films in case of dinitrophenylhydrazone 9 points to a phase separated structure. In agreement, eye-examination of these films revealed numerous small dark islands scattered isotropically all over a homogeneously coloured surface.

High nonlinear optical coefficients $\chi^{(2)}$ and β were determined for transferred monolayers of the polymer/NLO dye mixtures on glass by SHG measurements (Table 1). The molecular hyperpolarizabilities β of 8 and 9 in the mixed films exceed those measured previously for pure amphiphilic nitrophenylhydrazone monolayers with a less favourable substitution pattern [6, 7]. Most interestingly, the β-value of 2.4×10^{-28} esu for hemicyanine 7 in the mixed monolayer with 1 is close to the value published for a monolayer of the pure dye (3.0×10^{-28} esu) [7].

4. Conclusions

The mixing of low molecular weight guest molecules with amphotropic spacer polymers offers a suitable way to prepare functional polymeric LB multilayers. The polymer matrix is particularly useful to stabilize guests not capable of self-organizing at the air-water interface by themselves. Such mixed monolayers can be transferred on to solid supports to form high quality LB multilayers which cannot be obtained otherwise. By incorporation of NLO dyes, mixed LB films are built which exhibit high SHG activity comparable to the pure dye monolayers.

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