Amphiphilic Nonlinear Optical Bis-chromophores and Their Mixtures with Amphotropic Copolymers: Preparation of Monolayers and Langmuir—Blodgett Multilayers

Donald Lupo, Helmut Ringsdorf,*,‡ Andreas Schuster,‡ and Markus Seitz‡

Contribution from Hoechst AG, 65926 Frankfurt am Main, Germany, Institut für Organische Chemie, Johannes-Gutenberg-Universität, 55099 Mainz, Germany

Received June 13, 1994[®]

Abstract: A new type of bis-chromophores containing two successive, covalently linked, nonlinear optical (NLO) dyes has been synthesized. For their preparation, α-cyanocinnamates or dinitrophenylhydrazones have been combined with an 4'-alkoxybiphenyl-4-carboxylate acting both as a hydrophobic, mesogenic moiety and as the second NLO dye. The self-organizing properties at the air—water interface as well as the monolayer and LB multilayer transfer of these new NLO amphiles has been investigated. Furthermore, stable and homogeneous mixed films with an amphotropic matrix polymer were obtained due to the enhanced miscibility of the mesogenic dye with the mesogenic side chains of the polymer. Second harmonic generation (SHG) measurements have been carried out, showing the complex behavior of the molecules.

Introduction

Langmuir—Blodgett (LB) films prepared from preformed amphiphilic polymers are of interest due to their improved homogeneity and thermal stability.[1–5] For many possible technical applications, a functionalization of the polymers is desired, e.g., for dyes with nonlinear optical or optoelectronical properties.[6–9] Unfortunately, dye-containing polymers with chemically sensitive functional groups are often difficult to synthesize. As an alternative approach, mixed LB films prepared from matrix polymers and functional low molecular weight compounds were proposed.[10–12]

In this context, side chain polymers combining amphiphilic and mesogenic elements via a flexible spacer were found to stabilize guest compounds that do not self-organize at the air—water interface (Figure 1a).[13] These so-called *"amphotropic polymers"*[14,15] form thermally stable LB films that exhibit a

reversible phase transition to a less-ordered, "liquid crystalline" state on heating.[4,16]

Mixed monolayers of amphotropic copolymer **1** (Scheme 1) and several low molecular weight compounds, such as a non-amphiphilic disubstituted biphenyl **2** or NLO dyes **3** and **4** (Scheme 2) were transferred onto solid supports and demonstrate SHG activity comparable to pure dye monolayers.

Although for the guests **2** and **3** high-quality monolayers were obtained, in some cases (e.g., compound **4**) poor miscibility and phase separation of polymer and NLO dyes was observed (Figure 1b).[13] To enhance the miscibility, and thus further improve the film quality, a different molecular architecture for the dyes was chosen. As already reported for bulk mixtures of liquid—crystalline side chain polymers with dyes,[17] an enhanced miscibility was expected for the series of guest compounds **5–8**, where the long alkyl chains of the amphiphilic NLO units were substituted with mesogenic units, such as biphenyl structures (Figure 1c).

Furthermore, by choosing a suitable donor—acceptor substitution pattern within these mesogenic units (see also Figure 2), a second NLO unit may be introduced in the hydrophobic part of the molecules to enhance the molecular hyperpolarizability (β) of the system while avoiding a red shift in the UV/vis absorption spectra. In addition, the replacement of long hydrocarbon chains by a relatively smaller orienting mesogenic unit can increase the density of NLO active moieties in a single layer, and thus the overall second-order susceptibility ($\chi^{(2)}$) of the film. Such systems may be called "bis-chromophores" or "covalently poled dipoles",[18] schematically shown in Figure 2.

Here we report on the synthesis of the bis-chromophores **5–8** (Scheme 3), which fulfill the described structural concept and hence represent a new class of amphiphilic NLO dyes.

* To whom correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts,* October 15, 1994.

(1) Laschewsky, A.; Ringsdorf, H.; Schmidt, G.; Schneider, J. *J. Am. Chem. Soc.* **1987,** *109,* 788.

(2) Jones, R.; Tredgold, H.; Hoorfar, A.; Allen, R. A.; Hodge, P. *Thin Solid Films* **1985,** *134,* 57.

(3) Erdelen, C.; Laschewsky, A.; Ringsdorf, H.; Schneider, J.; Schuster, A. *Thin Solid Films* **1989,** *180,* 153.

(4) Penner, T. L.; Schildkraut, J. S.; Ringsdorf, H.; Schuster, A. *Macromolecules* **1991,** *24,* 1041.

(5) Embs, F.; Funhoff, D.; Laschewsky, A.; Licht, U.; Ohst, H.; Prass, W.; Ringsdorf, H.; Wegner, G.; Wehrmann, R. *Adv. Mater.* **1991,** *3,* 25.

(6) Carr, N.; Goodwin, M. J.; McRoberts, A. M.; Gray, G. W.; Marsden, R.; Scrowston, R. M. *Makromol. Chem. Rapid Commun.* **1987,** *8,* 487.

(7) Penner, T. L.; Willand, C. S.; Robello, D. R.; Schildkraut, J. S.; Ulman, A. *Photochemistry and Photoelectrochemistry of Organic and Inorganic Molecular Thin Films SPIE*; SPIE: Bellingham, WA, **1991**; Vol. 1436, pp 169–178.

(8) Hsiung, H.; Rodriguez-Parada, J.; Bekerbauer, R. *Chem. Phys. Lett.* **1991,** *182,* 88.

(9) Takahashi, T.; Chen, Y. M.; Rahaman, A. K.; Kumar, J.; Tripathy, S. K. *Thin Solid Films* **1992,** *210/11,* 202.

(10) Stroeve, P.; Srinivasan, M. P.; Higgins, B. G.; Kowel, S. T. *Thin Solid Films* **1987,** *146,* 209.

(11) Hayden, L. M.; Anderson, B. L.; Lam, J. Y.; Higgins, B. G.; Stroeve, P.; Kowel, S. T. *Thin Solid Films* **1988,** *160,* 379.

(12) Duda, G.; Wegner, G. *Makromol. Chem. Rapid. Commun.* **1988,** *9,* 495.

(13) Laschewsky, A.; Paulus, W.; Ringsdorf, H.; Schuster, A.; Frick, G.; Mathy, A. *Thin Solid Films* **1992,** *210/11,* 191.

(14) (a) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *J. Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 113–158.

(15) Decher, G.; Ringsdorf, H. *Liq. Cryst.* **1993,** *12,* 57.

(16) Schuster, A. Ph.D. Thesis, Universität Mainz, 1992.

(17) Sigaud, G.; Archard, M. F.; Hardouin, F.; Gasparoux, H. *Mol. Cryst. Liq. Cryst.* **1988,** *155,* 443–456.

(18) This definition has to be told apart from the term "poled NLO polymers" in which a noncentrosymmetric structure is achieved and maintained via the simultaneous poling and chemical crosslinking of NLO chromophores in the presence of an electrical field.
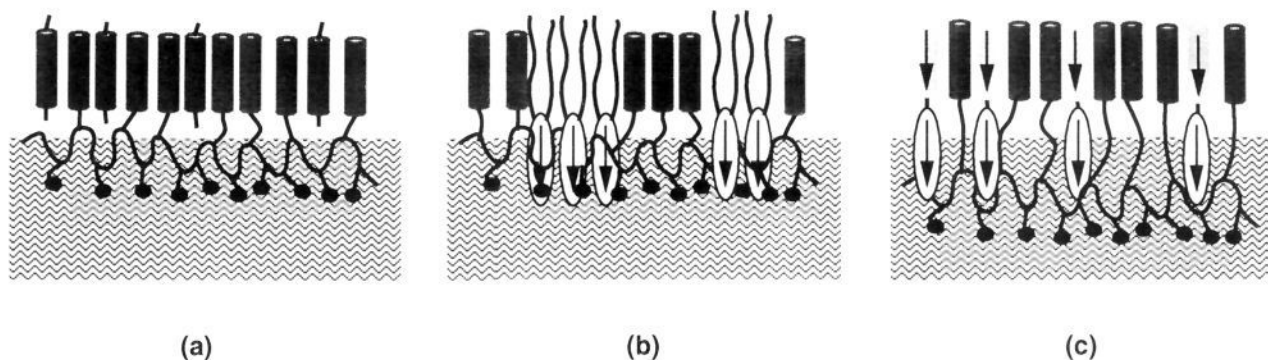
(a)   **(b)**   **(c)**

Figure 1. Mixed monolayers with low molecular weight guest compounds: (a) nonamphiphilic biphenyl derivative inserts into nondensely packed mesogenic side groups of the polymeric monolayer, (b) long chain-substituted NLO dyes are stabilized by amphotropic polymer, but tend to crystallize and phase separate, (c) "mesogenic substitution" leads to enhanced miscibility of low molecular weight dyes with polymeric film.

Scheme 1

1
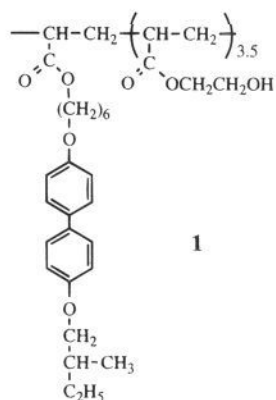
Scheme 2
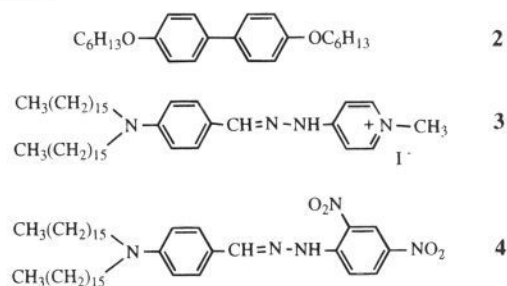
Their spreading behavior and the LB films of pure dyes and their mixtures with amphotropic copolymer **1** were investigated, and first results of second harmonic generation (SHG) measurements on transferred monolayers are reported.

Experimental Section

Synthesis. ω-Hydroxy-substituted *p*-(*N*-alkylamino)benzaldehydes were synthesized in one step from *p*-fluorbenzaldehyde and the appropriate secondary ω-hydroxyalkylamine giving the aldehydes **Ia/b**. The chromophores **IIa/b** were obtained by a Knoevenagel condensation (Scheme 4).

It should be noted that the synthesis of the ethyl analogue of compound **IIa** is described,[19a] but as a more complicated process starting from a substituted aniline via benzoylation of the ω-hydroxy group, followed by a Vilsmeier formylation, cleavage of the benzoate, and the final Knoevenagel condensation.
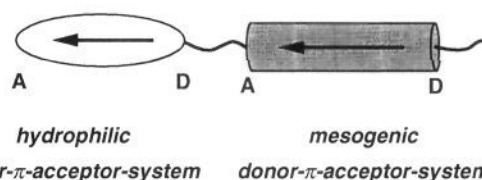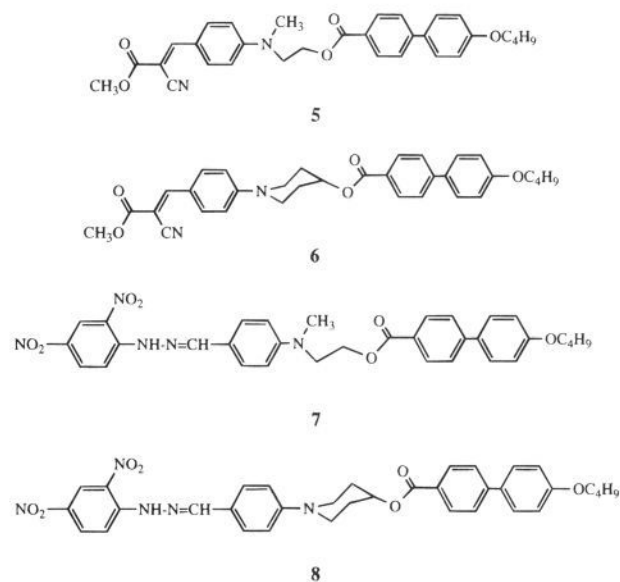
(19) (a) Stenger-Smith, J. D.; Fischer, J. W.; Henry, R. A.; Hoover, J. M.; Nadler, M. P.; Nissan, R. A.; Lindsay, G. A. *J. Polym. Sci., A: Polym. Chem.* **1991**, *29*, 1623. (b) In this context, NLO main chain polymers were reported on the basis of the (ω-hydroxyalkyl)amino substituted cyanocinnamates.

hydrophilic   *mesogenic*
donor-π-acceptor-system   *donor-π-acceptor-system*

Figure 2. "Bis-chromophores" by covalent poling of two donor−π-acceptor systems.
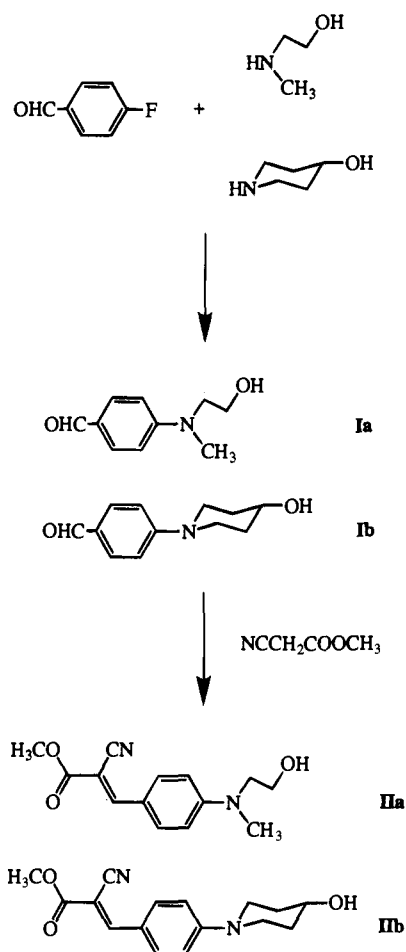
Scheme 3

5

6

7

8

The condensation of the two chromophores was carried out in the last step to avoid a transesterification under the basic conditions of the Knoevenagel condensation, whereas the hydrophilic chromophore does not disturb the esterification of the hydroxygroup with an acid chloride. In addition, (ω-hydroxyalkyl)amino-substituted cyanocinnamates are interesting intermediates for a linkage of more than two NLO phores (dipoles) in polymeric systems.[19b]

In the case of the dinitrophenylhydrazones, the condensation of the chromophores by esterification in the last step of the synthesis was not successful perhaps because the reaction seems to be disturbed by the acidic NH proton. For that reason, the dinitrophenylhydrazone dye was created in the last step (Scheme 5). The synthesis of the amphotropic copolymer **1** is described elsewhere.[4]

4-[*N*-(2′-Hydroxyethyl)-*N*-methylamino]benzaldehyde (Ia). *p*-Fluorbenzaldehyde (37.7 g, 0.305 mol), 34.3 g (0.457 mol) of (*N*-methylamino)ethanol (37 mL), and 53 g of dry, pulverized potassium carbonate were stirred for 5 days in 60 mL of dry DMSO at room temperature. After being heated to 60 °C for 5 h (significant formation of side products is observed at higher temperatures), the cooled solution

10500 *J. Am. Chem. Soc., Vol. 116, No. 23, 1994*

Lupo et al.

Scheme 4

Scheme 5

was diluted with 800 mL of water and kept in the refrigerator overnight. A red oil was formed which was separated by repeated extraction with chloroform. After evaporation of the solvent and two recrystallizations from ethyl acetate (the crude product forms yellow crystals by addition of ethyl acetate), 35.5 g of a white solid (65%) were obtained: mp 68 °C.

4-(4'-Hydroxypiperidino)benzaldehyde (Ib). A mixture of 10 g (80 mmol) of *p*-fluorobenzaldehyde, 12 g (120 mmol) of 4-hydroxy-piperidine, and 14 g (85 mmol) of pulverized, dried potassium carbonate was heated to 90 °C in 15 mL of DMSO for 48 h. After cooling, the viscous reaction mixture was diluted with 200 mL of water. An orange precipitate was separated and recrystallized from a chloroform/cyclohexane mixture; 13.3 g (81%) of a red crude product was obtained (mp 105 °C). The aldehyde was purified by flash chromatography from ethyl acetate to give 8.4 g (51%) of a pale yellow powder: mp 116 °C.

4-[4'-(Butyloxy)phenyl]benzoyl Chloride. 4-[4'-(Butyloxy)phenyl]-benzoic acid (4.05 g, 15 mmol) was refluxed with a 15-fold excess of thionyl chloride (17 mL = 26.8 g, 225 mmol) and a few drops DMF for 4 h. Nonreacted thionyl chloride was removed by distillation under reduced pressure at room temperature. The crude acid chloride was stored under nitrogen in the refrigerator and used for the next syntheses without further purification.

Methyl α-Cyano-4-[*N*-(2'-hydroxyethyl)-*N*-methylamino]cin-namate (IIa). Methyl α-cyanoacetate (1.35 g, 14 mmol) was dissolved in 15 mL of methanol with 0.3 mL of piperidine. Then 2.44 g (14 mmol) of the aldehyde Ia in 15 mL methanol was added, and the color of the solution changed from yellow to orange. The solution was cooled in the refrigerator overnight, and the orange precipitate formed was filtered off and washed with cold methanol to give 2.9 g (82%) of IIa: mp ~124 °C.

Methyl α-Cyano-4-(4'-hydroxypiperidino)cinnamate (IIb). The synthesis was carried out in analogy to IIa; 3.2 g (76%) of IIb were obtained: mp 98–99 °C.
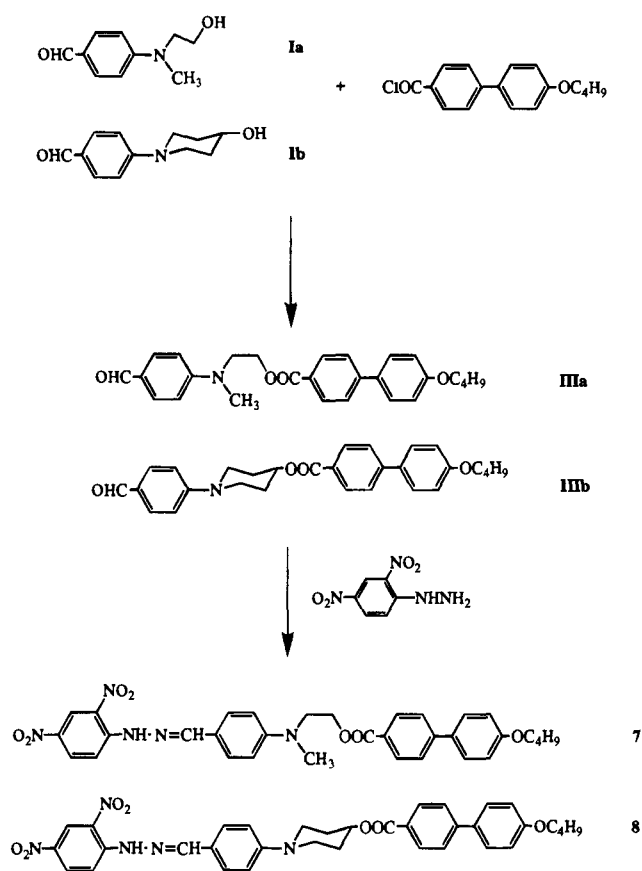
Methyl α-cyano-4-[*N*-methyl-*N*-[2'-[[4''-(4'''-(butyloxy)phenyl]-benzoyl]oxy]ethyl]amino]cinnamate (Bis-chromophore 5). The α-cyanocinnamate IIa (0.86 g, 3.3 mmol) was mixed with 0.4 g (3.3 mmol) of (*N,N*-dimethylamino)pyridine (DMAP) and 30 mL of dichloromethane. The crude 4'-(butyloxy)biphenyl-4-carboxylic acid chloride (0.95 g, ~3.3 mmol) in 10 mL of dichloromethane was added dropwise, and the reaction mixture was stirred for 16 h at room temperature. The solvent was evaporated, and the product was purified by 2-fold flash chromatography with ethyl acetate (R_f = 0.86) and dichloromethane (R_f = 0.16) to give 1.0 g (59%) of the bis-chromophore 5: mp ~126 °C; ¹H NMR (CDCl₃, 200 MHz) δ 0.98 (t, 3 H, CH₃-(CH₂)₃O), 1.51 (m, 2 H, CH₃CH₂(CH₂)₂O), 1.80 (m, 2 H, CH₃CH₂CH₂-CH₂O), 3.17 (s, 3 H, NCH₃), 3.87 (t, 5 H, CH₃OOC and NCH₂CH₂-OOC), 4.02 (t, 2 H, OCH₂CH₂CH₂CH₃), 4.54 (t, 2 H, NCH₂CH₂OOC), 6.81 (d, 2 H, Ar H-3,5), 6.97 (d, 2 H, Ar H-3''',5'''), 7.56 (t, 4 H, Ar H-3'',5'' and Ar H-2''',6'''), 7.95 (t, 4 H, Ar H-2'',6'' and Ar H-2,6), 1 H, Ar-C*H*=C); IR (film on NaCl plate) 2215 (ν, CN) cm⁻¹; mass spectrum, *m/e* 511.4; UV (CHCl₃) λ_max = 418 nm. Anal. Calcd for C₃₁H₃₂N₂O₅ (M_r = 512.62): C, 72.64; H, 6.29; N, 5.47. Found: C, 72.23; H, 6.27; N, 5.35.

Methyl α-Cyano-4-[4'-[[4''-[4'''-(butyloxy)phenyl]benzoyl]oxy]-piperidino]cinnamate (Bis-chromophore 6). The synthesis was carried out in analogy to the synthesis described for bis-chromophore 5. After a reaction time of 4 days, 1.2 g (58%) of 6 was obtained: mp ~158 °C; ¹H NMR (CDCl₃, 200 MHz) δ 0.98 (t, 3 H, CH₃(CH₂)₃O), 1.50 (m, 2 H, CH₃CH₂(CH₂)₂O), 1.79 (m, 2 H, CH₃CH₂-CH₂CH₂O), 1.97 and 2.10 (m, 4 H, NCH₂CH₂ ring ax/eq), 3.49 and 3.77 (m, 4 H, NCH₂CH₂ ring ax/eq), 3.89 (s, 3 H, CH₃OOC), 4.00 (t, 2 H, OCH₂(CH₂)₂CH₃), 5.29 (m, 1 H, CHOOC ring), 6.95 (q, 4 H, Ar H-3''',5''' and Ar H-3,5), 7.58 (q, 4 H, Ar H-2''',6''' and Ar H-3'',5''), 7.95 (d, 2 H, Ar H-2'',6''), 8.07 (d, 3 H, Ar H-2,6 and Ar-C*H*=C); IR (film on NaCl plate) 2218 (ν, CN) cm⁻¹; mass spectrum, *m/e* 538.4; UV (CHCl₃) λ_max = 417 nm. Anal. Calcd for C₃₃H₃₄N₂O₅ (M_r = 538.66): C, 73.58; H, 6.36; N, 5.20. Found: C, 73.16; H, 6.31; N, 5.10.

4-[*N*-methyl-*N*-[2'-[[4''-[4'''-(butyloxy)phenyl]benzoyl]oxy]ethyl]-amino]benzaldehyde (IIIa). 4-[*N*-Methyl-*N*-(2'-hydroxyethyl)amino]-
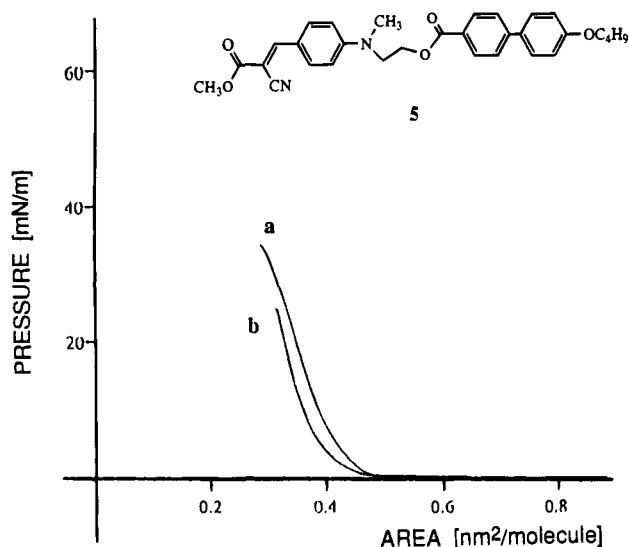
Figure 3. Spreading behavior of "bis-chromophore" **5** containing a flexible ethylene linkage: (a) $T = 20$ °C, (b) $T = 37$ °C.
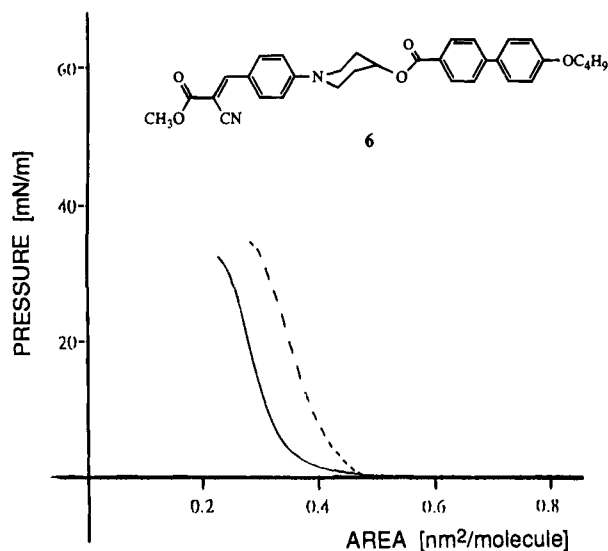

Figure 4. Comparison of flexible and stiff connection between α-cyanocinnamate and biphenyl system: π-A isotherms of bis-chromophore **5** (flexible linkage, dotted line) and **6** (stiff linkage, straight line) at T = 20 °C.

benzaldehyde **Ia** (0.9 g, 5 mmol), 4′-(butyloxy)biphenyl-4-carboxylic-acid (1.35 g, 5 mmol), and 30 mg of DMAP were mixed in 50 mL of dichloromethane and cooled to 0 °C. A solution of 1.2 g DCCI in 20 mL of dichloromethane was added dropwise to the stirred suspension, and the mixture was allowed to reach room temperature overnight. After the mixture was stirred for 2 days the precipitated N,N'-dicyclohexylurea was separated; 1.34 g (62%) of the product was isolated by flash chromatography with dichloromethane as eluent ($R_f = 0.09$): mp 106—108 °C.

4-[4′-[[4″-[4‴-(Butyloxy)phenyl]benzoyloxy]piperidino]-benzaldehyde (IIIb). The synthesis was carried out in analogy to the benzaldehyde derivative **IIIa** with a yield of 0.86 g (77%): mp 118—121 °C.

4-[N-Methyl-N-[2′-[[4″-[4‴-(butyloxy)phenyl]benzoyl]oxy]ethyl]-amino]benzaldehyde 2′,4′-Dinitrophenylhydrazone (Bis-chromophore 7). Benzaldehye **IIIa** (0.65 g, 1.5 mmol) was diluted in 25 mL of dichloromethane. A solution of 2,4-dinitrophenylhydrazine (0.3 g, 1.5 mmol) in 70 mL of ethanol and 1.5 mL of HCl (concentrated) was added. Immediately, a deeply red precipitate was formed which was separated and purified by flash chromatography (eluent: dichloromethane, $R_f = 0.51$). After washing with hot ethyl acetate, 710 mg (77%) of pure bis-chromophore **7** was obtained: mp 201—202 °C dec; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.97 (t, 3 H, CH_3(CH$_2$)$_3$O), 1.51 (m, 2 H, CH$_3$CH_2(CH$_2$)$_2$O), 1.78, 2 H, CH$_3$CH$_2$CH_2CH$_2$O), 3.13 (s, 3 H, NCH_3), 3.83 (t, 2 H, NCH$_2$CH$_2$OOC), 3.97 (t, 2 H, OCH_2(CH$_2$)$_2$CH$_3$), 4.53 (t, 2 H, NCH$_2$CH_2OOC), 6.80 (d, 2 H, Ar H-3,5), 6.92 (d, 2 H, Ar H-3‴,5‴), 7.45—7.65 (m, 6 H, Ar H-3″,5″ and Ar H-2‴,6‴ and Ar H-2,6), 7.98 (q, 5 H, Ar H-2″,6′ Ar-CH=N and Ar H-2,6), 8.25 (q, 1 H, Ar H-5′), 9.11 (d, 1 H, Ar H-3′), 11.21 (s, 1 H, Ar-NHN=CH-Ar); IR (film on NaCl plate) 1508 (ν_a, N=O), 1328, 1307 (ν_s, N=O), 1275 (ν, N—O) cm^{-1}; UV (CHCl$_3$) $\lambda_{max} = 426$ nm. Anal. Calcd for C$_{33}$H$_{33}$N$_5$O$_7$ ($M_r = 611.68$): C, 64.80; H, 5.44; N, 11.45. Found: C, 64.79; H, 5.57; N, 11.56.

4-[4′-[[4″-[4‴-(Butyloxy)phenyl]benzoyl]oxy]piperidino]-benzaldehyde 2′,4′-Dinitrophenylhydrazone (Bis-chromophore 8). The synthesis was carried out in analogy to bis-chromophore **7**. Bis-chromophore **8** (175 mg, 36%) was formed as a red powder: mp 227 °C dec; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.97 (t, 3 H, CH_3(CH$_2$)$_3$O), 1.53 (m, 2 H, CH$_3$CH_2(CH$_2$)$_2$O), 1.78 (m, 2 H, CH$_3$CH$_2$CH_2CH$_2$O), 1.98 and 2.11 (m, 4 H, NCH$_2$CH_2 ring ax/eq), 3.34 and 3.65 (m, 4 H, NCH_2CH$_2$ ring ax/eq), 4.02 (t, 2 H, OCH_2(CH$_2$)$_2$CH$_3$), 5.27 (m, 1H, CHOOC ring), 6.96 (d, 4 H, Ar H-3‴,5‴ and Ar H-3,5), 7.50—7.67 (m, 6 H, Ar H-3″,5″ and Ar H-2‴,6‴ and Ar H-2,6), 8.05 (q, 4 H, Ar H-2″,6″ a′ and Ar-CH=NNH-Ar), 8.30 (q, 1 H, Ar H-5′), 9.12 (d, 1 H, Ar H-3′), 11.25 (s, 1H, Ar-NHN=CH-Ar); UV (CHCl$_3$) $\lambda_{max} = 415$ nm. Anal. Calcd for C$_{35}$H$_{35}$N$_5$O$_7$ ($M = 637.72$): C, 65.92; H, 5.53; N, 10.98. Found: C, 65.85; H, 5.59; N, 10.95.

Spreading Experiments, LB Transfer, and NLO Measurements. Monolayer experiments were performed with a film balance using a Wilhelmy system (stiff films were measured with a Langmuir system). For the control and evaluation of the experiments, a Commodore computer CMB 4032 GR was used.[20] The films were spread from dichloromethane solutions in concentrations of $\sim$5 × 10^{-4} mol/L on pure Milli-Q water (Millipore Corp.). Compression rates varied from 0.01 to 0.05 nm^2 (repeat unit min)$^{-1}$.

Monolayers and LB multilayers were transferred onto hydrophilic glass substrates with a FW 1 (Lauda) film balance from pure aqueous subphase at 20 °C. The transfer conditions are listed in Tables 1 and 2. Prior to deposition, the monolayers were equilibrated for at least 30 min at deposition pressure. Between subsequent dipping cycles, the samples were pulled out of the subphase and allowed to dry in air to avoid retransfer of previously deposited monolayers during the next downward dip.

UV—visible spectra were recorded with a Perkin-Elmer Lambda 5 spectrophotometer. The detailed experimental set up for the second harmonic generation (SHG) measurements of monolayers deposited on glass, and the evaluation of data obtained are described elsewhere.[21,22]

Results and Discussion

Monolayer experiments. 1.1. Spreading Behavior of Bis-chromophores. Figures 3 and 4 show the spreading behavior of the bis-chromophores **5** and **6** which form films of rather low viscosity.

In the case of densely packed biphenyl moieties on the air—water interface, one might expect an area of about 0.25 nm^2 per molcule.[23] At $T = 20$ °C the observed values are 0.3 nm^2/molecule for **5** and 0.24 nm^2/molecule for **6**, respectively. A dense packing of the mesogens in the solid-analogous phase can therefore be assumed. Nevertheless, the influence of the more flexible ethylene linkage between the two chromophores in compound **5** can be seen: it requires more space than chromophore **6**. By introducing the rather stiff piperidine linkage between the two chromophores, mobility is reduced, bending of the molecule is excluded, and the area per molecule is less.

(20) Albrecht, O. *Thin Solid Films* **1983**, *99*, 227.

(21) Lupo, D.; Prass, W.; Scheunemann, U.; Laschewsky, A.; Ringsdorf, H.; Ledoux, I. *J. Opt. Soc. Am. B* **1988**, *5*, 300.

(22) Bubeck, C.; Laschewsky, A.; Lupo, D.; Neher, D.; Ottenbreit, P.; Paulus, W.; Prass, W.; Ringsdorf, H.; Wegner, G. *Adv. Mater.* **1991**, *3*, 54.

(23) Albrecht, O.; Cumming, W.; Kreuder, W.; Laschewsky, A.; Ringsdorf, H. *Colloid Polym. Sci.* **1986**, *264*, 659.
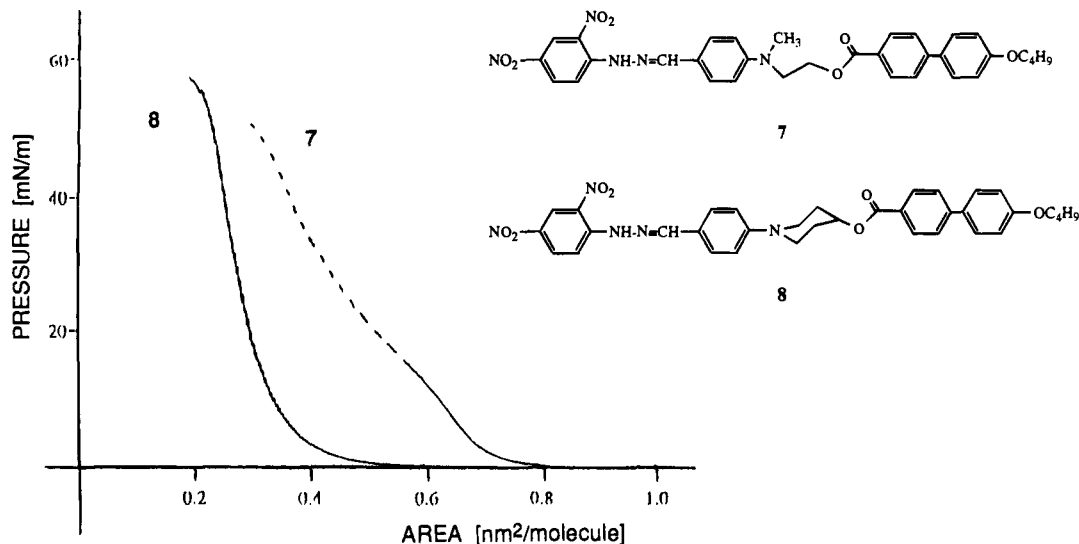
Figure 5. π-A isotherms of dinitrophenylhydrazones 7 (flexible linkage) and 8 (stiff linkage) at *T* = 20 °C.

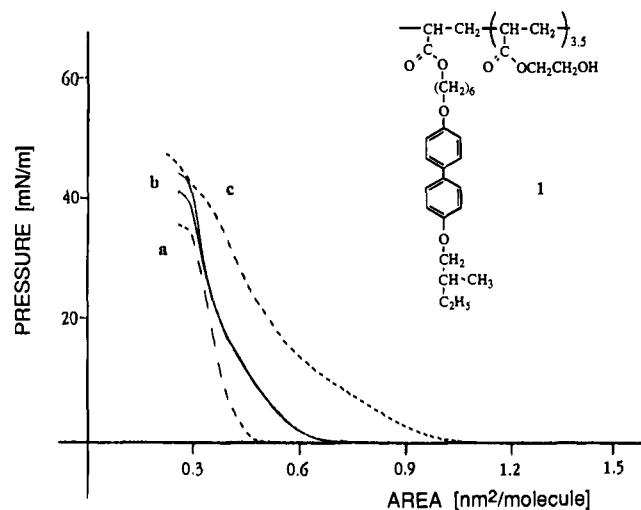**Figure 6.** π-A isotherms: (a) pure bis-chromophore 5 at *T* = 20 °C, (b) 1:1 mixture of dye 5 with polymer 1 at *T* = 20 °C and *T* = 37 °C, (c) pure polymer 1 at *T* = 20 °C.

In contrast to the cyanocinnamates 5 and 6, both dinitrophen-ylhydrazones 7 and 8 give rather stiff films on the water surface. The measured isotherms are shown in Figure 5.

The difference between a flexible and a stiff connection between chromophores is more pronounced in this case. The flexible ethylene unit between the two chromophores in compound 7 leads to an interaction between the molecules at a much larger area. The surface pressure increases at 0.8 nm²/mol which correlates with the calculated area of one dinitro-phenylhydrazone head lying flat on the water surface.

The isotherm of 7 shows a bend at 0.6 nm²/mol. Below this area the isotherm could not be reproduced, indicating a collapse of the monolayer at this point. The isotherm of bis-chromophore 8 looks similar to that of the α-cyanocinnamate 6 which also contains the stiff piperidine connection. For the dinitrophenyl-hydrazone, however, a very stiff film is obtained and long-term measurements reveal that the monolayer is not stable over a long time period. Presumably, aggregates are formed in the gas-analogous state which are pushed together during compression. Thus, although reproducible Π-A isotherms can be measured, neither of the two dinitrophenylhydrazones (7, 8) form stable multilayers at the air—water interface. This is in good agreement with earlier results obtained for long-chain-
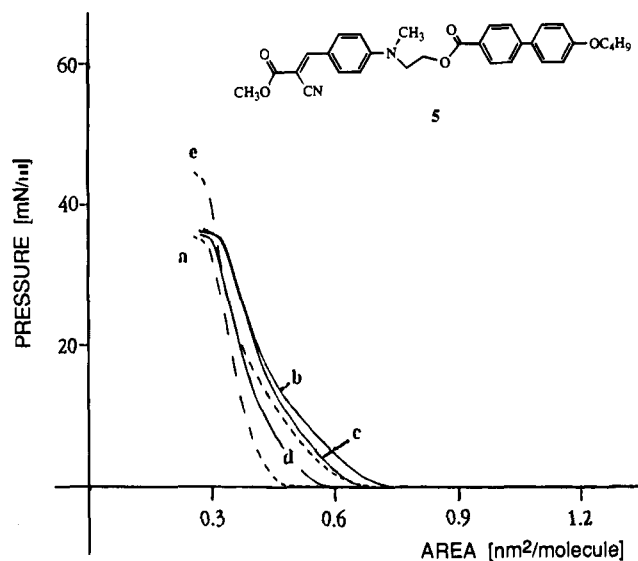

Figure 7. π-A isotherms of mixtures polymer 1/dye 5 (spread from separate solutions): (a) pure 5 (dotted), (b) ratio 1:1, (c) ratio 1:2, (d) ratio 1:3, (e) ratio 1:1 spread from premixed solution (dotted).
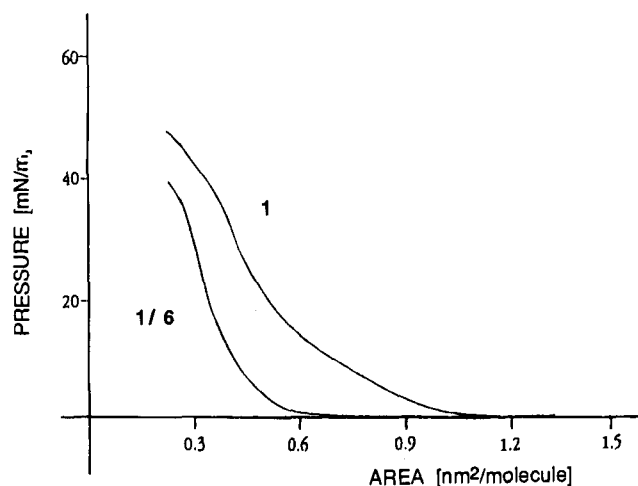

Figure 8. π-A isotherm of polymer 1 and polymer/dye 6 mixture (1: 1) at *T* = 20 °C.

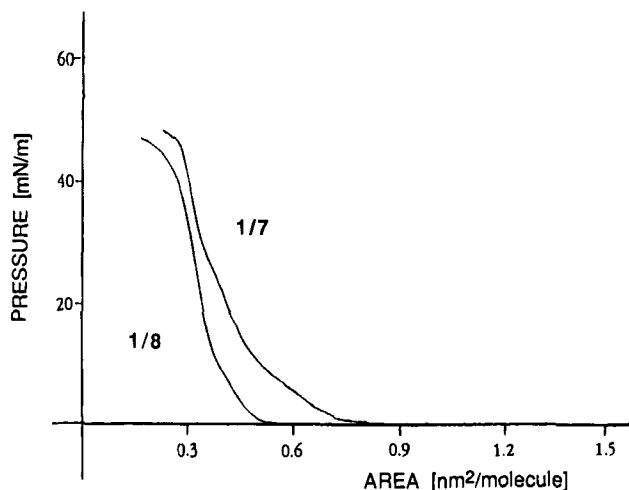substituted dyes and is probably caused by the high crystallization tendency of the dinitrophenylhydrazone headgroup.

Figure 9. π-A isotherms of 1:1 mixtures polymer 1/dinitrophenylhydrazones **7, 8** at T = 20 °C.

1.2. Mixed Monolayers of Amphotropic Polymer with Low Molecular Weight Bis-chromophores. Figure 6 shows the isotherm of a 1:1 mixture of amphotropic polymer **1** and α-cyanocinnamate **5** at 20 °C and 37 °C. The dotted lines are the curves obtained for pure dye and for pure polymer.

The mixed films are of low viscosity and are more thermally stable than the pure dye films: The two curves for 20 °C and 37 °C are practically identical. The collapse area is the same in both cases ($\sim$0.3 nm²/mol) and corresponds to the value for the pure low molecular weight compound. Nearly ideal mixing behavior is found in the condensed monolayer as indicated by the change of the collapse pressure with dye concentration in the mixed film.

It should be noted that the spreading process itself is decisive for the miscibility of the films. The same collapse pressure as that of the pure dye is observed after spreading the two components from two different solutions for the compositions **1/5** = 1:1, 1:2, and 1:3, as shown in Figure 7. This may indicate a separation of the dye and polymer domains in the film.

Considering the diffusion of dye molecules within a two-dimensional, expanded polymer layer at the air—water interface, such behavior can be explained. At the air—water interface this process is limited to two dimensions and thus proceeds much more slowly than in a three-dimensional, highly diluted solution of both components. It is therefore necessary to mix the two components in one solution before spreading in order to form a homogeneous and stable film.

Thus, mixed solutions of amphotropic polymer **1** and chromophores **6–8** (molar ratio 1:1) in dichloromethane were used for all further spreading experiments. The isotherms are shown in Figures 8 and 9.
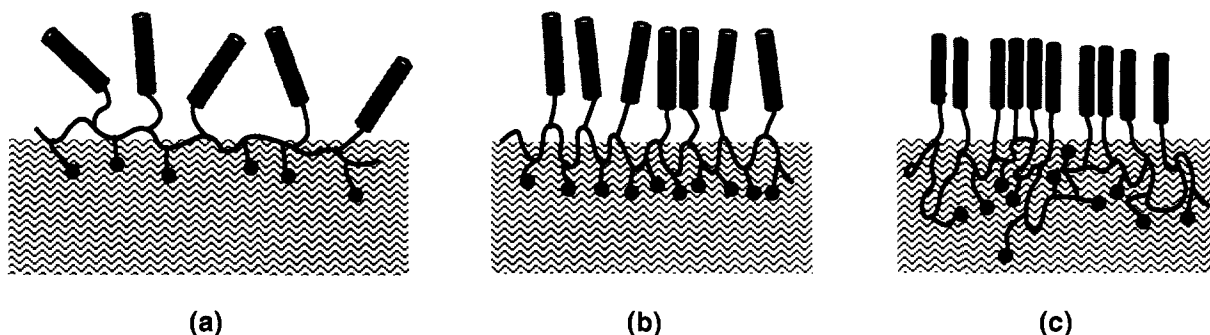
The mixtures with the "stiff" bis-chromophores **6** and **8** show behavior similar to that observed for the flexible compound **5**. The films are fluid and homogeneous. Therefore, by mixing bis-chromophore **8** with an amphotropic polymer, the first stable but also the first sufficiently fluid monolayer of an amino-substituted dinitrophenylhydrazone was obtained which allows an improved quality in the transferred films (as shown later).

As observed for monolayers of pure bis-chromophores, the surface pressure of dinitrophenylhydrazone **7** in the mixture increases at much higher areas, and an expanded state like that of the pure amphotropic polymer (see Figure 8) is observed.[24]

The isotherm of pure polymer **1** (Figure 8) shows a bend at $\sim$0.37 nm²/repeat unit which corresponds to a completely condensed polymer main chain (Figure 10b).[16] This point was considered to be the real collapse of the monolayer, since for lower areas parts of the main chain are pressed out of the interfacial region into the water or even into the hydrophobic monolayer where the biphenyl units are not yet densely packed (see Figure 10c). In mixtures, the required space of the main chain—not finding its equivalent packing density in the pure polymer monolayer—is compensated by the low molecular weight compounds which insert into the loose side chain packing and hence stabilize the film (Figure 1).

A similar bend in the isotherm at $\sim$0.4 nm²/repeat unit is found for mixed films with dinitrophenylhydrazone **7**. We have no explanation for this observation at this time. For the most unfavorable case one would assume a demixing of the components, but one can also expect that the dinitrophenylhydrazone head group lies flat on the water surface. Nevertheless, the alignment of the mesogens seems to be achieved due to the flexible linkage. The collapse area of less than 0.28 nm²/repeat unit suggests a dense packing of the mesogens, but it cannot be excluded that—as in the case of the pure polymer system—some molecules are pressed out of the monolayer. It was not possible to transfer more than one single monolayer onto a glass substrate of this particular mixture (see below) which supports this assumption.

LB Transfer on Glass Supports. 1. Transfer of Monolayers. The quality of transferred monolayers is determined by several parameters including temperature, surface pressure, and viscosity of the monolayer. In general, stiff films are of poor quality after deposition, and often a collapse of the monolayer during the transfer is observed. Table 1 shows the transfer conditions for pure dyes and dye/polymer mixtures and the UV/ vis absorption maxima of the monolayers on glass. The optical quality of the films was verified by the reproducibility of UV/ vis spectra at different "spots" of the film.

The pure α-cyanocinnamates **5** and **6** and all dye/polymer mixtures are transferable onto glass substrates. Better film

       (a)   **(b)**   **(c)**

Figure 10. Phase transitions in monolayers of amphotropic copolymers: (a) expanded phase, (b) condensed phase: closely packed main chain, loose packing of mesogens, (c) condensed phase: tightly packed mesogens, disturbed main chain packing (distortion of ordered monolayer).

Table 1. Experimental Details for Monolayer Transfer on Glass Substrates and UV/vis Absorption Maxima of Deposited Films (T = 20 °C in All Cases)

	π (mN/m)	deposition speed (cm/min)	optical quality	λ_{max} (nm)
		Pure Dyes		
5	20	0.20	opaque	417
6	20	0.35	opaque	407
7				
8				
		Dye/Polymer Mixtures 1:1		
1/5	30	0.20	transparent	423
1/6	30	0.13	transparent	414
1/7	25	0.18	opaque	428
				~580
1/8	25	0.23	transparent	413
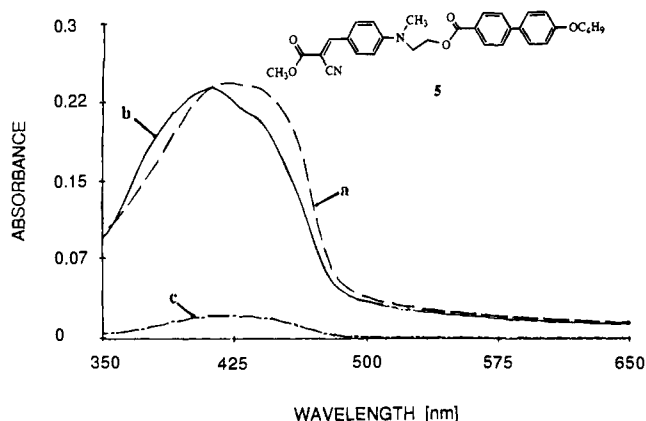
Figure 11. UV/vis spectra of LB multilayer of pure dye **5**: (a) new film (9 layers), (b) same, aged film, (c) monolayer of **5**.

quality was achieved in the mixed systems due to the improved fluidity of the mixed films. This is most important for the dinitrophenylhydrazones where no stable monolayers were found for pure dyes.
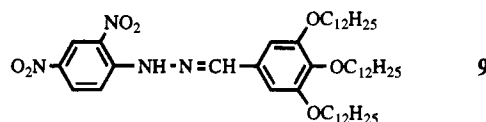
The absorption maxima of all transferred mixed films lie around λ_{max} = ~420 nm. Therefore, frequency doubling may be carried out using a Nd^{3+}:YAG-laser (λ = 1064 nm) without film destruction. An additional effect is found if one compares the UV/vis spectra of the two dinitrophenylhydrazones **7** and **8**. Besides the absorption at λ = 428 nm, an additional band is found at ~580 nm for the dye **7** with a flexible link between the two chromophores whereas for the stiff linkage in compound **8** only the normal dinitrophenylhydrazone absorption at λ = 413 nm is observed. This additional absorption is found in the transferred monolayer only and cannot be detected in the solution spectra of either the pure compound or the dye/polymer mixture. These observations could indicate an aggregation in

Scheme 6

the film which might be due to a back-folding of the molecule which is only possible in the case of a flexible linkage. For dyes with a strong crystallization tendency, the desired structure of the mixed film as shown in Figure 1c can only be achieved if a back-folding of the molecule is avoided by stiff linkage.

The transferred, mixed monolayer of polymer **1** and bis-chromophore **8** is the first stable monolayer of an amino substituted dinitrophenylhydrazone. Classical long-chain substitution did not provide stable monolayers of these compounds.[25]

2. Transfer of LB Multilayers. The transfer of LB multilayers was investigated for pure cinnamates **5** and mixtures of polymer and dyes **5–7**. The buildup of LB multilayers of pure dye **5** was achieved. The transferred films are translucent, but aging is observed and the films become very inhomogeneous after a few days. This process can be followed by UV/vis spectroscopy. A splitting of the absorption band and a shift to shorter wavelengths can be seen which indicates an aggregation of the chromophores (see Figure 11).

The mixed LB multilayers of the cinnamate dyes **5** and **6** with polymer **1** have improved homogeneity and long-term stability, e.g., no changes were observed in the UV/vis spectra of 31 consecutive layers after several weeks. In the case of dinitrophenylhydrazone **7**, no reproducible transfer of more than three layers could be achieved. Furthermore, a transfer of the monolayer is only possible at the upstroke of the substrate giving a Z-type layer structure. This supports the results found for the monolayer of this system, indicating an undesired back-folding and crystallization of the dyes in the mixture which leads to stiff layers and a significant hydrophilicity of the layer surface. The multilayer transfer of dye/polymer mixture **8/1** has yet to be investigated. The conditions and results for the multilayer transfer are shown in Table 2.

Mixed LB multilayers of NLO dyes with amphotropic polymer **1** are homogeneous and of high optical quality. It has to be pointed out that in bulk mixtures of dye **5** with polymer **1** a phase separation and crystallization of the dye is observed at a dye content of ~10–15%. This is a high content compared to other LC side chain polymer/dye mixtures and is, we believe, due to the mesogenic structure of the hydrophobic dye. The remarkable miscibility in LB multilayers (~50% of dye) is a striking feature of these systems.

Second Harmonic Generation measurements. The NLO activity of transferred monolayers was determined by measuring

Table 2. Transfer Conditions for LB Multilayers at T = 20 °C

	π (mN/m)	deposition speed [cm/min] down	up	drying pause (min)	deposition type	no. of layers	optical quality
5	20	0.54	0.35	13	Y	9	opaque after several days
1/5 1:1	30	0.99	0.74	9	Y	17	transparent
1/6 1:1	30	0.75	0.35	7	Y	31	transparent
1/7 1:1	25	0.62	0.29	11	(Y/Z)	5	opaque

Table 3. Evaluated Second Harmonic Generation (SHG) Data of Transferred Monolayers

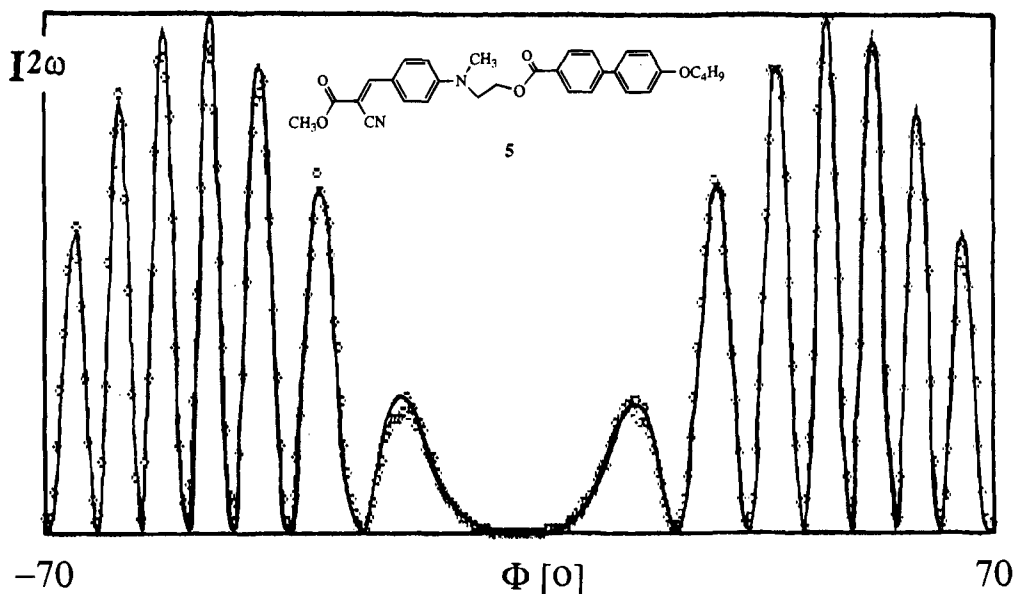|	$\chi^{(2)}_{zzz}$ (pm/V)	$\chi^{(2)}_{zxx}$ (pm/V)	$I^{2\omega}$ (au)	θ_{max} (deg)	$\chi^{(2)}_{\zeta\zeta\zeta}$ (pm/V)	$\chi^{(2)}_{\zeta\xi\xi}$ (pm/V)	$\chi^{(2)}_{\xi\zeta\xi}$ (pm/V)	$\beta_{\zeta\zeta\zeta}$ (10^{-30} esu)	λ_{max} (nm)
5	−1.02	1.89		12.46	46				
6	1.31	0.99	51.0	4.54	53	5.24	0.13	2.29	407
1/5 1:1	−0.60	1.18		8.65	46				
9[21]	2.30	2.50	56.0			13.15	0.32	13.0	407

Figure 12. SHG curve of monolayer of pure α-cyanocinnamate **5** (O) experimental data, (−) best fit curve.

the SHG efficiency ($\lambda = 1064$ nm) and evaluating the nonlinear susceptibility $\chi^{(2)}$. Table 3 shows the calculated $\chi^{(2)}$-components of transferred monolayers of α-cyanocinnamates **5**, **6** and of the 1:1 mixture polymer 1/dye **5**. The calculated average tilt angles $<\varphi>$ of the chromophores in the film and reference data of the amphiphilic dinitrophenylhydrazone **9** (Scheme 6) described in the literature[22] are also shown.

Figure 12 shows the SHG curve obtained for the bis-chromophore **5**. Its shape demonstrates a good quality film and homogeneity within the area of the laser beam as no frequency doubling is observed at an angle of 0°. Furthermore, all of the minima of the fringe pattern are close to zero which is a result of nearby complete destructive interference between light generated from the films on both sides of the substrate. Thus, a homogeneous coverage of both sides of the substrate can be assumed.[21]

Data analysis with a common fit routine[22,26−28] leads to negative values for the $\chi^{(2)}_{zzz}$ component (Table 3), and hence no tilt angles $<\varphi>$ can be calculated. Several reasons for this may be discussed:

(1) For chromophores with a high tilt toward the substrate surface, the contributions to $\chi^{(2)}_{zzz}$, perpendicular to the film plane, become very small and the component $\chi^{(2)}_{zxx}$ parallel to the film plane dominates the second-order susceptibility. The chromophore tilt may be guessed from the shape of the SHG curve. In films with a high $\chi^{(2)}_{zxx}$ component, electrical fields parallel to the substrate induce a considerable polarization perpendicular to the film plane. Therefore, high tilt angles generally cause a shift of the absolute maxima of the second harmonic intensity $I^{2\omega}$ to lower angles θ. This is the case for the monolayers investigated: Values of θ_{max} indicate a high tilt of the chromophores in the transferred films (these data are also listed in Table 3).

(24) This behavior was explained for amphiphilic copolymers by discussing a transition from a two-dimensional expanded "foam-like" state to a more condensed state of the polymer chain; see: Frey, W.; Schneider, J.; Ringsdorf, H.; Sackmann, E. *Macromolecules* **1987**, *20*, 1312.

(25) Laschewsky, A.; Paulus, W.; Ringsdorf, H.; Lupo, D.; Ottenbreit, P.; Prass, W.; Bubeck, C.; Neher, D.; Wegner, G. *Makromol. Chem. Makromol. Symp.* **1991**, *46*, 205.

(26) Sipe, J. E. *J. Opt. Soc. Am. B* **1987**, *4*, 481.

(27) Mizrahi, V.; Sipe, J. E. *J. Opt. Soc. Am. B* **1988**, *5*, 660.

(28) Neher, D. Ph.D. Thesis, Max-Planck-Institut Polymerchemie, Mainz, 1990.

(2) In the α-cyanocinnamates investigated two chromophores of practically equal strength compete with another. If the molecule takes a tilted conformation (which had been assumed from the beginning for the flexible linkage in compound **5**), the $\beta_{\zeta\zeta\zeta}$ along the "main axis" of the molecule no longer determine the hyperpolarizability β of the bis-chromophore alone. Nondiagonal elements of β have to be taken into account, and the assumptions made for the evaluation of the data no longer hold.

(3) Further interactions (electronic or charge-transfer interactions, dipole−dipole interactions) of the two chromophores may be discussed, which can influence the components of β. The magnitude of these possible interactions is difficult to analyze and not accessible by SHG measurements in monolayers. In addition, meaningful β-values are not obtainable through electrical field induced second harmonic generation (EFISH) measurements. The conformational complexity of the molecules makes accurate knowledge of the ground state molecular dipole moment (μ_o) difficult. Thus, as EFISH measurements are expressed in terms of $\mu_o\beta$, these numbers are not applicable for the determination of β.

Despite the problems in evaluating the data obtained, a qualitative comparison of hyperpolarizabilities of bis-chromophore **6** with the well-investigated dinitrophenylhydrazone **9** shows that the concept of "poled dipoles" works. The calculated $\beta_{\zeta\zeta\zeta}$ of **6** is much weaker than that of **9** and the nonlinear susceptibility of both monolayers lie in the same range (Table 3). This is due to the introduction of a second "dipole" in the hydrophobic part of the amphiphile which causes an increase of NLO active units in the monolayer and thus an increase of the macroscopically observed nonlinear susceptibility of the film. Since the intensity of the second harmonic generated from mixed films of dye **5** with amphotropic polymer **1** is nearly the same as that of the monolayer of the pure dye, a high $\chi^{(2)}$ is expected for the mixed films of the amino substituted dinitrophenylhydrazone **8**.

Conclusions

Well-known NLO chromophores have been combined with a second, "hydrophobic" donor−π-acceptor system to give new, amphiphilic bis-chromophores with two covalently—but not conjugatively—linked NLO active units. This increasing of the

density of NLO active moieties lead to an increase of macroscopic $\chi^{(2)}$ values without an undesired red shift of the UV/vis absorption. The mesogenic structure of the hydrophobic "tail" of the molecule significantly enhances the miscibility of the new bis-chromophores with amphotropic side chain polymers. Very homogeneous and stable mixed layers on the air−water interface as well as LB multilayers with a high dye content (~50%) were obtained which is a remarkable improvement compared to the bad miscibility in bulk. These results show the high potential of amphotropic polymers as a matrix for the stabilization of functional molecules in monolayers and LB multilayers.