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Generation of Anisotropic Emission by Light-Induced Orientation of Liquid Crystalline Polymers

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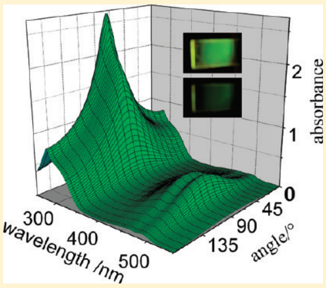

ABSTRACT: Functionalized polymers containing mesogenic, photosensitive, and fluorescent side groups were synthesized for all-in-one films with anisotropic absorption and emission. Aligned films were prepared by a two-step bulk-alignment procedure combining a photochemical step at room temperature and a thermal aligning step at temperatures of the mesophases. The irradiation with linearly polarized light results in small values of anisotropy via angular-selective photoreactions of cinnamates, stilbenes, and anthracene moieties. The photoinduced anisotropy was significantly amplified by annealing above the glass transition temperature of the liquid crystalline polymers, resulting in a cooperative alignment of all side groups leading to dichroism values up to 0.7 (dichroic ratio up to 6.7) and ratios of anisotropic fluorescence up to 8. The irradiation conditions for the induction of anisotropy were optimized concerning wavelength and dose with respect to the absorption of photosensitive groups and the limited photostability of the dyes. Depending on the distribution of the photoproducts, alignment parallel or perpendicular to the electric field vector of the incident light was induced in dependence on the polymer composition and irradiation conditions.

I. INTRODUCTION

The alignment of reactive liquid crystals (LC) and liquid crystalline polymers (LCP) is the key step for the preparation of anisotropic optical elements, such as anisotropic polarizers, retarders, anisotropic emitters, or polarization gratings.[1] The surface aligment of LCs has advantages concerning efficiency, but it requires two layers and has disadvantages in the precise adjustmet of the order and resolution and shows shrinkage upon the photopolymerization. A new way to achieve macroscopically aligned films is the light-induced orientation of photochromic polymers. Advantages of such processes are the defined control of orientational direction, tilt angle, order parameter, and their pixelwise modification at room temperature. Using LC polymer, the photoinduced order can be significantly increased by self-organization due to annealing.[2−7] Remarkable is the fact that both ordering principles—the light-induced generation of anisotropy and the thermal amplification process—work cooperatively for photochromic and nonphotochromic, co-mesogenic side groups.

Photoorientation of azobenzene is the most prominent example for the photoinduction of anisotropy. Upon linearly polarized irradiation, a photoorientation process takes place in the steady state of the E/Z photoisomerization process via a large number of photoselection events and rotational diffusion resulting in anisotropy perpendicular to the electric field vector of incident light. Recently, we had shown that a cooperative orientation of dye side groups perpendicular to the E-field vector can be also generated in azobenzene-containing polymers, but the fluorescence was totally quenched caused by the azobenzene moieties.[8] This polymer composition offers the opportunity for the preparation of anisotropic color filters but cannot be used to create films with anisotropic emission. Moreover, disadvantages of azobenzenes are their absorption in the visible range, the photoinduced oblate order, and the quenching of the emission of fluorophores.

Anisotropic fluorescent films have been obtained by Contoret et al. due to photoalignment and subsequent photopolymerization of reactive luminophores on a coumarine-containing polymeric layer[9] and by Sainova et al. due to alignment of a liquid crystalline polyfluorene on an azobenzene-containing photoaligning layer.[10] However, these are two-layer approaches requiring an additional aligning layer.

Cinnamic esters are widely investigated as photoaligning layer for liquid crystals. A one-layer solution for the generation of anisotropic films due to photoinduction of anisotropy and amplification in the bulk of polymer films containing cinnamoyl groups was shown for the first time by Kawatsuki et al.[11] Upon irradiation cinnamates undergo simultaneously E/Z photoisomerization establishing a steady state between both isomers and bimolecular [2 + 2] photocycloaddition. The ratio of both reactions depends on the concentration of the photochromic moiety and matrix effects. Different groups have shown that the irradiation of spin-coated cinnamate containing films with LP UV

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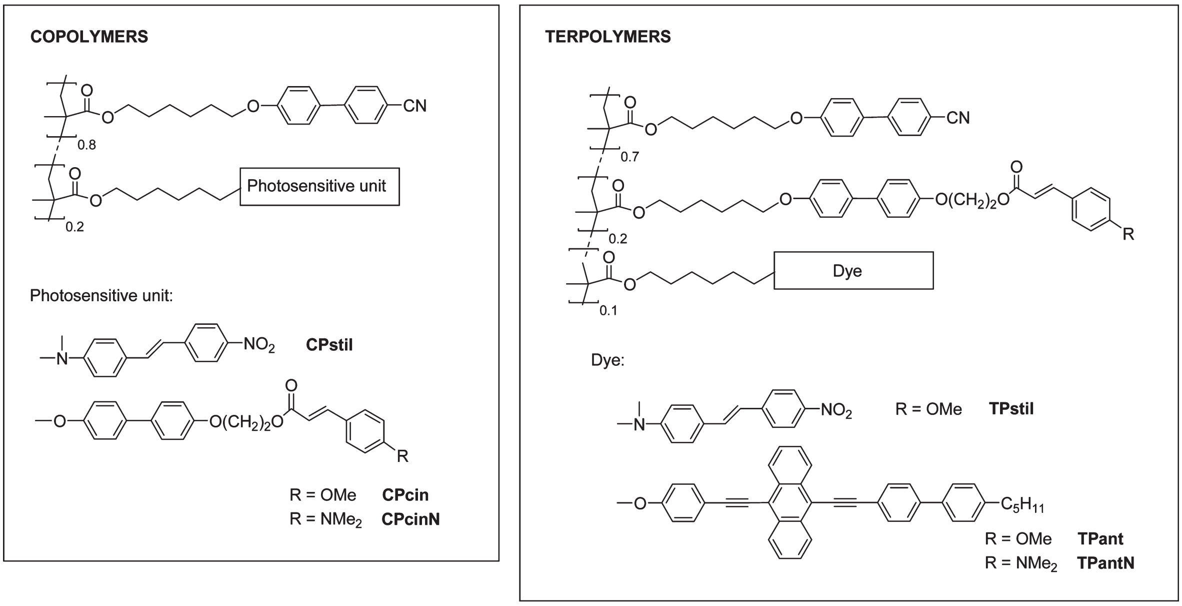

Figure 1. Structure of the investigated polymers.

light generates anisotropy, mainly caused by the angular-selective photocycloaddition of the E isomer.[12−16] Nevertheless, there is a controversy discussion whether the aligning properties at the interface is mainly caused by the photocycloaddition products or by the photoisomerization.[17,18] With respect to the aligning direction the photocycloaddition reaction is the dominating process in closed packed matrices. The [2 + 2] photocycloaddition in polymer films of cinnamates[19,20] converts the E isomers irreversibly to truxillic or truxinic esters as photoproducts, which differ with respect to head-to-head or head-to-tail arrangement.[21] Moreover, this is connected with the cross-linking of the film. The alignment of LCs or LC side groups can be mainly caused by molecules with anisotropic shape such as the truxillic ester. But unfortunately in films of poly(vinylcinnamate) the photoproduct is mainly formed as a head-to-head truxinic ester in a ratio of 10:1. To overcome this problem, specially designed cinnamate containing LC polymers were created by Kawatsuki et al.[22,23] in which the cinnamic ester moiety was connected to a 4,4′-biphenyl group via a ethylene spacer. It was shown that the UV irradiation results in the preferred formation of the head-to-tail photoadduct. The photoproduct works as aligning group for the whole LCP upon annealing in the liquid crystalline (LC) phase establishing an orientation parallel to the electric field vector. More recently, we have shown that a polymer with cinnamoyl groups orients fluorescent anthracene groups parallel to the E field vector after LP exposure and annealing, resulting in an anisotropic emission.[24]

The aim of this study is to orient fluorescent side groups in the bulk of spin-coated polymer films without using an additional aligning layer, resulting in anisotropic emission of red, green, and blue (RGB). As azobenzene side groups show a fluorescence quenching effect, new photosensitive groups should be used for the bulk photoalignment. For this purpose several multifunctional polymers were synthesized containing moieties with fluorescent, photosensitive, and mesogenic properties (Figure 1). These polymers should be designed in such a way that they combine photosensitivity in order to generate anisotropy, liquid crystallinity for the alignment of the whole system, and anisotropic absorption and emission. The anisotropic films should be generated based on all-in-one polymers due to photoinduced anisotropy and bulk alignment.

In this approach different photosensitive groups are used (4-methoxycinnamate, 4-(*N*,*N*-dimethylamino)cinnamate, or 4-amino-4′-nitrostilbene), a mesomorphic unit (4-cyanobiphenyl), and different fluorescent dyes: 4-cyanobiphenyl (blue), 9-phenylethynyl-10-biphenylethynylanthracene (green), and 4-amino-4′-nitrostilbene (red). Especially, the combination of the different photoreactions as well as the competition between photoprocessing and the photostability of the dyes will be discussed and optimized.

II. EXPERIMENTAL SECTION

II.1. Materials. Polymers were synthesized in solution by radical polymerization of the corresponding methacrylic monomers (6-(4′-cyanobiphenyl-4-yloxy)hexyl methacrylate,[25] 6-{4-[10-(4′-pentylbiphenyl-4-ylethynyl)anthracene-9-ylethynyl]phenoxy}hexyl methacrylate,[26] 6-(4′-nitrostilbene-4-yloxy)hexyl methacrylate,[27] 6-{4′-[2-(4-methoxycinnamoyloxy)ethoxy]biphenyl-4-yloxy}hexyl methacrylate), and 6-{4′-[2-(4-(*N*,*N*-dimethylaminocinnamoyloxy)ethoxy]biphenyl-4-yloxy}hexyl methacrylate). A general procedure for the synthesis of the cinnamate polymers is as follows. A mixture of the methacrylic monomers (molar ratio as indicated in Figure 1) were dissolved in freshly distilled tetrahydrofuran (THF) (∼10% w/v) under an argon atmosphere in a Schlenk tube. The solution was heated to 60 °C, and 1−2 mol % of azobis(isobutyronitrile) (AIBN) was added. The solution was stirred at this temperature for 48−96 h, and the reaction mixture was poured into cold diethyl ether and the solid filtered out, washed, and air-dried. Purification was carried out by dissolving the polymer in the minimum amount of dichloromethane or chloroform and precipitation over cold diethyl ether or by Soxhlet extraction with diethyl ether until complete removal of unreacted monomers. Experimental details for CPstil[28] and TPant[24] have been previously described.

CPcin. Purified by reprecipitation over cold diethyl ether. Yield 67%. $M_w = 36\,440$. PI = 1.9. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.72−7.30, 7.00−6.73, 6.35−6.25, 4.55−4.40, 4.28−4.10, 4.08−3.70, 2.10−1.18, 1.18−0.65. IR (KBr): ν (cm^{-1}) = 2223 (C≡N), 1723 (C═O), 1629 (C═C), 1602, 1513, 1492 (arC−C), 1247 (C−O). Anal. Calcd for $C_{25.2}H_{27.6}N_{0.8}O_{3.8}$: C, 75.25; H, 6.86; N, 2.78. Found: C, 74.95; H, 6.13; N, 2.76.

CPcinN. Purified by reprecipitation over cold diethyl ether. Yield 73%. M_w = 45 573. PI = 2.2 (bimodal). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 7. 85−7.30, 7.00−6.75, 6.38−6.20, 4.62−4.43, 4.30−4.12, 4.10−3.75, 3.10−2.93, 2.92−2.80, 2.10−1.15, 1.14−0.70. IR (KBr): ν (cm^{-1}) = 2223 (C≡N), 1723 (C=O), 1601, 1523, 1494 (arC−C), 1246 (C−O). Anal. Calcd for $C_{25.4}H_{28.2}NO_{3.6}$: C, 75.33; H, 6.96; N, 3.46. Found: C, 75.31; H, 6.38; N, 3.46.

TPstil. Purified by Soxhlet extraction with diethyl ether. Yield 53%. M_w = 34 978. PI = 1.9. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 8.10−8.00, 7.70−7.30, 7.20−7.02, 6.98−6.75, 6.65−6.52, 6.35−6.23, 4.57−4.43, 4.26−4.15, 4.00−3.75, 3.35−3.15, 2.90, 2.02−1.50, 1.49−1.15, 1.12−0.98, 0.98−0.75. IR (KBr): ν (cm^{-1}) = 2223 (C≡N), 1722 (C=O), 1631 (C=C), 1603, 1578, 1513, 1494 (arC−C), 1247 (C−O). Anal. Calcd for $C_{25.4}H_{27.9}N_{0.9}O_{3.9}$: C, 74.75; H, 6.83; N, 3.09. Found: C, 74.36; H, 6.28; N, 3.03.

TPantN. Purified by reprecipitation over cold diethyl ether. Yield 47%. M_w = 10 764. PI = 1.2. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 8.75−8.58, 7.90−7.30, 7.00−6.75, 6.70−6.58, 6.30−6.08, 4.60−4.38, 4.30−4.10, 4.10−3.70, 3.05−2.95, 2.70−2.53, 2.18−0.62. IR (KBr): ν (cm^{-1}) = 2223 (C≡N), 1724 (C=O), 1631 (C=C), 1602, 1524, 1494 (arC−C), 1246 (C−O). Anal. Calcd for $C_{28.2}H_{30.5}N_{0.9}O_{3.6}$: C, 77.11; H, 6.94; N, 2.87. Found: C, 76.92; H, 6.45; N, 2.98.

II.2. Techniques. Elemental analysis was performed with a Perkin-Elmer 240C microanalyzer. FTIR spectra were measured on an ATI Matson Genesis Series FTIR from KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity or a Bruker ARX spectrometers operating at 300 MHz. Gel permeation chromatography (GPC) was carried out on a Waters liquid chromatography system equipped with a 600E multisolvent delivery system and a 996 photodiode array detector, using a combination of two Ultrastyragel columns with pore sizes ranging from 500 to 10^4 Å, THF as the mobile phase at 0.8 mL/min flow rate, and calibration using polystyrene standards. Mesogenic behavior and transition temperatures were determined using an Olympus BH-2 polarizing microscope equipped with a Linkam THMS hot-stage central processor and a CS196 cooling system. Differential scanning calorimetry (DSC) was performed using a DSC 2910 from TA Instruments with samples sealed in aluminum pans and a scanning rate of 10 °C/min under a nitrogen atmosphere. Temperatures were read at the maximum of the peak. Thermogravimetric analysis (TGA) was performed using a TA Instruments STD 2960 simultaneous TGA-DTA at a rate of 10 °C/min under a nitrogen atmosphere.

Spin-coated films (2000 rpm, 30 s) were prepared from THF solutions (0.10−0.15 mmol) of the polymers (Figure 1). The films were stored at least for 1 day at room temperature. The irradiation was carried out using the linearly polarized (LP) light of a HeCd laser (Kimmon Electronics) at 325 nm using 15 mW/cm^2 and an Ar$^+$ laser (Innova 4, Coherent) at 488 nm using 100 mW/cm^2. The irradiation at 365 nm was carried out using a 100 W mercury lamp and a Glan-Thomson prism at a power density of 14.2 mW/cm^2. After different times of exposure the films were annealed ∼5 °C below T_i in the mesophase of the polymers up to 3 days.

The angular-dependent UV/vis measurements were carried out using a diode array spectrometer (Polytec X-dap-04 V 2.3) and for the angular-dependent UV/vis measurements of oriented pixels were used a microscope−spectrometer (Photomikroskop 3, Carl Zeiss Oberkochen). The angular-dependent IR measurement of the CN stretching vibration was carried out using an RS1 IR spectrometer (Mattson Instruments). The dichroism D was calculated from maximum and minimum values of the absorbance A_{max} and A_{min}, obtained by measurements of the absorbance perpendicular and parallel to the electric field vector of the incident light (eq 1).

$$D = \frac{A_{max} - A_{min}}{A_{max} + A_{min}} \qquad (1)$$

Polarized excited fluorescence was measured by a linear setup of a TIDAS fluorimeter (J&M) using cutoff filters. The dichroic ratio of absorbance (R_{abs}) of fluorescence (R_f) and of the CN stretching vibration (R_{CN}) was calculated by division of the maximum (X_{max}) and the minimum (X_{min}) of the angular-dependent value of UV/vis absorption (A_{max} and A_{min}), IR stretching vibration of the CN group (VibCN_{max} and VibCN_{min}), or of the fluorescence (F_{max} and F_{min}), respectively (eq 2).

$$R = \frac{X_{max}}{X_{min}} \qquad (2)$$

III. RESULTS AND DISCUSSION

III.1. Design and Synthesis of the Polymers. Three LC side group copolymers containing mesomorphic 4-cyanobiphenyl unit and either a cinnamate or a stilbene as photosensitive unit were synthesized. On the basis of it, also three terpolymers containing the mesomorphic 4-cyanobiphenyl unit, the photosensitive cinnamate unit, and a fluorescent dye, either stilbene or anthracene unit (Figure 1), were developed. All the units are connected to a polymethacrylate backbone via hexamethylene spacers. Cinnamate units (4-methoxycinnamate for three polymers and 4-(*N,N*-dimethylamino)cinnamate group for two other polymers) were chosen with respect to their photoalignment properties.[24] The different fluorophores were selected regarding their photostability, rodlike structure, and emission properties.[26] The dye groups should have a high photostability in order to get fluorescent films with acceptable lifetimes of fluorescence. One way to enhance the photostability of stilbenes is the introduction of a strong donor−acceptor substitution.[29] Compared to non-substituted and donor−donor substituted stilbenes, the donor−acceptor substituted 4-amino-4′-nitrostilbene has a 43 times higher photostability. The degradation of about 10% of the last one requires an energy dose of 6.3 J/cm^2 upon nonpolarized irradiation at 436 nm in a PMMA matrix.[30] In the case of the anthracene unit the substitution in the 9,10-position has a stabilizing effect.

The feed ratio in the copolymers and terpolymers was selected according to previous studies carried out with this kind of photoorientable copolymers.[7,8,24]

In detail, the copolymers CPcin and CPcinN contain mesogenic 4-cyano-4′-hexyloxybiphenyl and photosensitive 4-methoxycinnamate or alternatively (*N,N*-dimethylamino)cinnamate side groups connected via an ethylene linker to a 4′-hexyloxybiphenyl moiety. The side groups are introduced with a ratio of 9:1. These copolymers with the photosensitive cinnamate groups are used as reference systems in order to investigate the irradiation conditions of the fluorophore-containing terpolymers. Moreover, the blue fluorescence of the cyanobiphenyl groups was investigated as well.

The terpolymer TPstil contains three side groups: a cyanobiphenyl unit, 4-methoxycinnamate unit, and 4-nitro-4′-(*N*-hexyl-*N*-methyl)aminostilbene fluorescent side group. In this case two moieties are photosensitive: the cinnamic ester and the stilbene group. The ratio of mesogenic, cinnamate ester, and fluorescent stilbene side groups is 7:2:1.

The copolymethacrylate CPstil contains 4-cyanobiphenyl and 4-nitro-4′-aminostilbene side groups in a ratio of 9:1. The 4-amino-4′-nitrostilbene group of the copolymer CPstil combines two functionalities—photosensitivity and fluorescence—in the same group.

The terpolymers TPant and TPantN have a similar composition as TPstil containing the mesogenic 4-cyanobiphenyl group and either the photosensitive 4-methoxycinnamate or 4-(dimethylamino)cinnamate side groups. The fluorophore was incorporated as a 9-(4-hexyloxyphenylethynyl)-10-(4′-pentylbiphenylethynyl)anthracene side group. The ratio of the side groups was the same as for TPstil.

All polymers were synthesized by free-radical polymerization of the methacrylate monomers in solution using AIBN as the initiator. Their physical characterization was undertaken by IR, ^{1}H NMR, and GPC, and the data were consistent with the expected structures. The actual composition of the copolymers CPcin and CPstil was calculated by integration of the signals in the ^{1}H NMR spectra obtaining good agreement with the monomeric feed ratio. In the case of the terpolymers a calculation was not possible due to signal overlapping.

III.2. Properties of the Materials. *Thermal Properties.* All investigated polymers are glassy polymers at room temperature and show liquid crystalline behavior in the range between the glass transition temperature, T_g (54−63 °C), and the isotropic state, T_i (98−108 °C). Transition temperatures and mesophases are collected in Table 1. The cinnamate polymers CPcin, CPcinN, TPstil, and TPant show a SmC mesophase, whereas CPstil and TPantN show only nematic mesophases. All polymers exhibit a good thermal stability, and the thermal decomposition detected by TGA starts at temperatures above 315 °C. There are no significant differences in stability depending on the constitution of the polymers.

Table 1. Thermal Properties of the Investigated Polymers[a]

polymer	TGA	DTGA	T_g	T_i	mesophase
CPcin	352	309, 398	54	106	SmC
CPcinN	359	326, 399	58	102	SmC
CPstil	324	350, 397	57	109	N
TPstil	347	352, 399	56	98	SmC
TPant	349	316, 401	63	108	SmC
TPantN	359	330, 402	61	94	N

[a] Temperatures are given in °C. TGA: onset of the weight loss curve; DTGA: first derivative of the weight loss curve; T_g: glass transition temperature; T_i: isotropization temperature. Transition temperatures were determined by DSC during the second heating scan.

Optical Properties. Absorption and emission spectra of the polymers have been measured in THF solutions and in thin films. The data are summarized in Table 2. All polymers form films of good optical quality by spin-coating. UV/vis spectra of the investigated copolymer films and terpolymer films are shown in parts a and b of Figure 2, respectively. The spectrum of copolymer CPcin is characterized by only one absorption band at 293 nm, which includes the absorbance of all three chromophores (4-cyano-4′-hexyloxybiphenyl, 4-methoxycinnamate, and 4-ethoxy-4′-hexyloxybiphenyl). To separate the absorption band by shifting the cinnamate absorption to longer wavelengths, another cinnamate cinN unit was introduced, resulting in the copolymer CPcinN. The substitution of the methoxy group by the strong donor *N,N*-dimethylamino results in an bathochromic shift of the absorbance of the cinnamic group from 293 to 371 nm in the case of the CPcinN film. The functionalization of the copolymers by additional chromophoric side groups (stilbene or anthracene moieties) results in the terpolymers TPstil, TPant, and TPantN and in a variation of the corresponding absorption spectra, respectively. The spectra of the terpolymer films are characterized by the overlapping of the $\pi\pi^*$ absorbance of the copolymer CPcin at 293 nm and CPcinN at 293 and 371 nm, respectively, and the $\pi\pi^*$ transition of the fluorophores at 456 nm for the stilbene unit (TPstil) and 462 and 489 nm for the anthracene unit (TPant and TPantN). The copolymer CPstil shows an absorbance of the cyanobiphenyl

Table 2. UV−Vis Absorption and Emission Containing Polymers[a]

polymer	absorbance (THF sol) λ_{max}/nm	emission (THF sol) λ_{max}/nm	absorbance (film) λ_{max}/nm	emission (film) λ_{max}/nm
CPcin[a]	292		293	455
CPcinN	296, 364		293, 371	—[b]
CPstil	296, 444	601	278, 452	643
TPstil	296, 444	605	295, 456	655
TPant	292, 452, 476	495, 523	283, 293, 462, 489	557
TPantN	292, 362, 453, 477	494, 523	283, 293, 371, 462, 489	—[b]

[a] The cyanobiphenyl group shows a blue fluorescence in the film. [b] No emission observed in films; the emission appears only in diluted polymers.

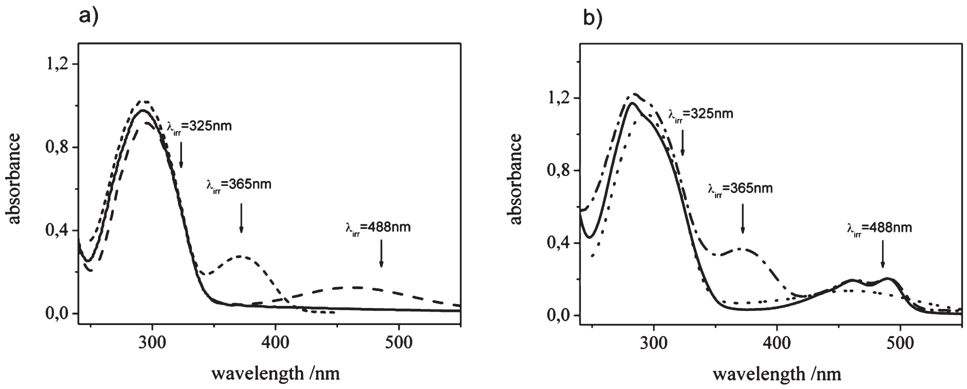

Figure 2. Absorption spectra of films of (a) the copolymers CPcin (—), CPcinN (· · ·), CPstil (− −) and (b) the terpolymers TPstil (· · ·),TPant (—), and TPantN (− · −).

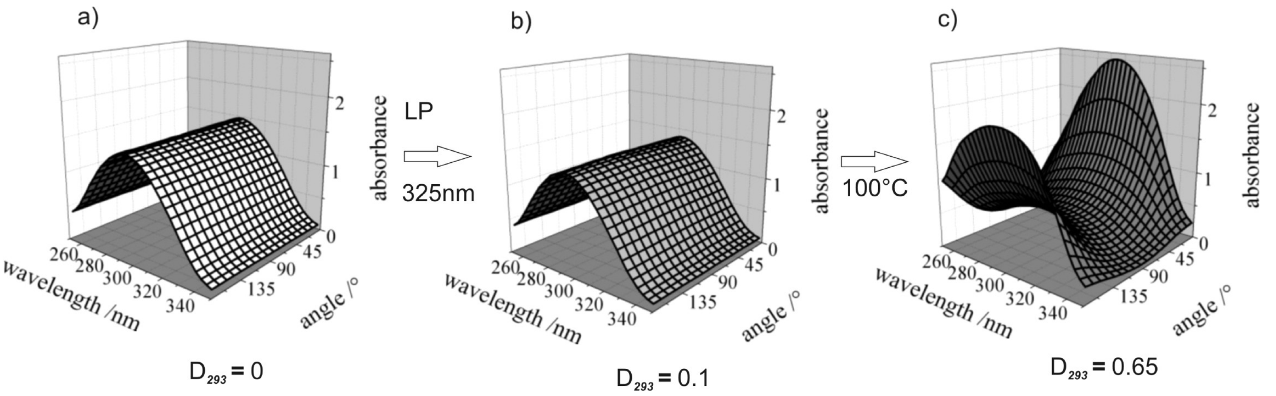

Figure 3. Angular-dependent UV/vis spectra of CPcin: (a) initial spin-coated film; (b) film after induction of anisotropy by LP irradiation at 325 nm; and (c) aligned film by annealing at 100 °C for 23 h and related dichroism at 293 nm.

group at 293 nm and an absorbance of the stilbene group at 452 nm.

Stilbene-containing polymers CPstil and TPstil displayed a red luminescence in THF solution and in films. The anthracene-containing polymers TPant and TPantN showed luminescence in the green region in solution. In thin films, whereas TPant was clearly emissive, almost no emission was observed for the TPantN terpolymer. This fact could be related to quenching effects by the 4-(dimethylamino)cinnamate unit. Films of the copolymer CPcin were also luminescent in the blue region due to the cyanobiphenyle unit.

The dichroic properties of the dyes (0.01 mol/kg) were characterized in a nematic 1:1 mixture of the low molecular weight liquid crystals K15 and ZLI1132 (supplied by Merck, Darmstadt). As seen from our former pulication[8] both dyes show high dichroism values, indicating that the transition moment is parallel to the long molecular axis. Nevertheless, for the monomeric anthracene derivative with a smaller length-to-width ratio, the dichroism of about D_{462} = 0.88 is higher than that of the stilbene monomer with D_{452} = 0.73.

III.3. Preparation of Anisotropic Fluorescent Polymer Films. *Bulk Photoalignment of Blue-Emitting Copolymers.* The liquid crystalline copolymers CPcin and CPcinN were investigated as model polymers for the dye-containing terpolymers in order to optimize the irradiation conditions and the aligning procedure. The polymer CPcin containing 4-methoxycinnamate as photosensitive group and the mesogenic fluorophor cyanobiphenyl was irradiated using LP UV light and annealed 6 °C below T_g. This two-step orientation procedure of CPcin results in anisotropic films that do not absorb in the visible range. Figure 3 shows the angular-dependent UV spectra of the isotropic spin-coated film (a), the same film after linearly polarized irradiation (b), and after subsequent annealing (c).

The photosensitive groups parallel to the E-field vector are preferably converted by angular selective photocycloaddition, whereas the moieties perpendicular to the E-field vector are not excited and do not undergo any photoreaction. In this way, the LP irradiation results in a small dichroism with a maximum absorbance perpendicular to the E-field vector (Figure 3b). Thus, dimeric head-to-tail and head-to-head photocycloadducts are preferably formed parallel to the E field vector indicated by a loss of the absorbance due to the degradation of the cinnamic ester. Exclusively, the head-to-tail cycloadduct has a prolongated anisometric shape with significant aligning capability to the mesogenic units, whereas the bulky head-to-head cycloadduct has a less pronounced anisometric shape compared to the truxillic photoproduct and the nonreacted cinnamic ester group. The subsequent annealing of the irradiated CPcin film at 100 °C for 23 h causes preferred alignment of the side groups parallel to the head-to-tail cycloadduct or with other words parallel to the E-field vector, resulting in a dichroism value of D_{293} = 0.65 (Figure 3c). The change of the orientational direction from perpendicular (after irradiation) to parallel (after annealing) indicates that the polymer is aligned by the photocycloadduct. This behavior is typical for light-induced alignment caused by angular selectively formed photoproduct with anisometric shape. The formation of photoproducts is characterized by a decrease of the absorbance parallel to the E-field vector, and the photoproducts are formed with the long axis perpendicular to the direction of the E-field vector which gives the orientational direction for the mesogenic units.

Very short irradiation times using linearly polarized light of 325 nm, related to a small absorbed energy[31] below 3 J/cm^2 result in a decrease of the initial absorbance at 293 nm of about 10% (Figure 4a). In comparison to the irradiation at shorter wavelength, higher irradiation doses are required for the irradiation at 365 nm in order to achieve the same amount of photoconversion, caused by the lower absorbance of only 0.02 at this wavelength. Nevertheless, irradiation at 365 nm allows a better control of the photoreaction compared to the irradiation at 325 nm.

Investigating the influence of the photoconversion on the aligning process, two ranges were found. While small doses corresponding to a decrease of absorbance up to 10% result in an efficient parallel alignment of the polymer, higher doses cause no or only a small anisotropy perpendicular to the electric field vector. In dependence on the dose there is a reduction of the photoinduced anisotropy upon annealing. This behavior should be related to the pronounced photo-cross-linking which results in a loss of the mesogenic properties. The irradiation using LP light of 365 nm up to a photoconversion between 4 and 6.5% results after annealing in the same dichroism as found for the LP irradiation with 325 nm (Figure 4b).

With respect to the overlapping of the absorbances of the different side groups, it is not possible to differentiate between the cinnamoyl and the biphenyl groups using UV/vis spectroscopy. Nevertheless, with respect to the high order parameter, one can assume that all groups are oriented in the same direction. As shown in Figure 5a, the same orientational direction as observed from the UV/vis measurements was found for the angular

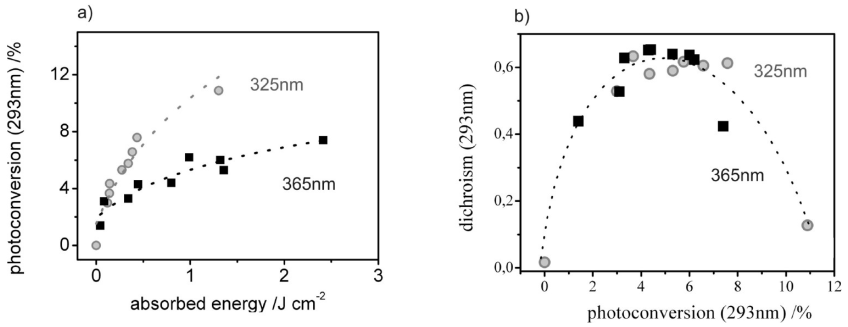

Figure 4. Influence of irradiation dose on photoconversion and dichroism in films of CPcin upon LP irradiation at 325 nm (●) and 365 nm (■). (a) Photoconversion in dependence on the absorbed energy calculated from the film absorbance and irradiation dose.[32] (b) Dichroism after LP irradiation and thermal treatment in dependence on the photoconversion.

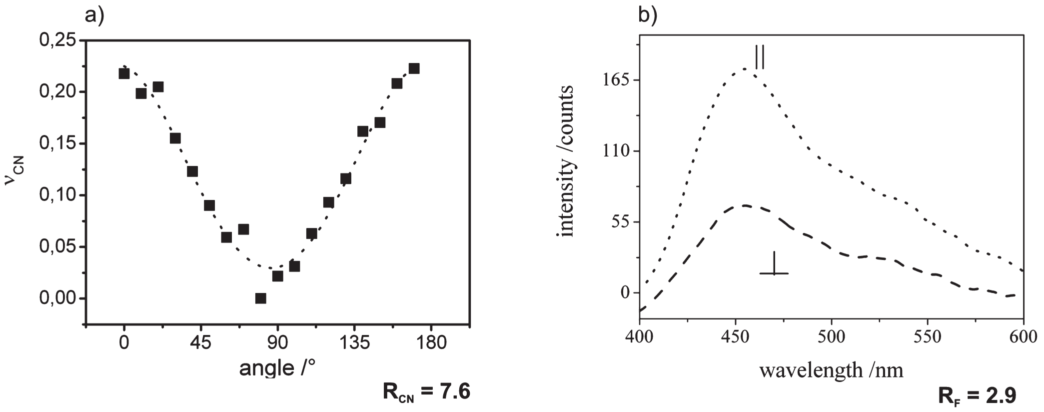

Figure 5. Characterization of the anisotropic properties of the mesogenic group in an oriented film of CPcin by IR and fluorescence spectroscopy. (a) Angular-dependent stretching vibration of the cyano group. (b) Fluorescence spectra upon excitation at 311 nm parallel (· · ·) and perpendicular (— —) to the orientational direction.

dependence of the CN-stretching vibration of the mesogenic cyanobiphenyl unit. A dichroic ratio of about R_{IR} = 7.6 was obtained.

Angular-dependent excitation at 311 nm of the cyanobiphenyl groups results in a blue fluorescence with a dichroic ratio of R_F = 2.9 (Figure 5b), indicating a parallel alignment of the units as well. So, this polymer is not only interesting as reference system; moreover, it is suitable as blue-emitting polymer. Nevertheless, the quantum yield of fluorescence is low.

The value of fluorescence anisotropy is significantly lower compared to the value indicated by the IR measurement. In contrast to the anisotropy of the CN stretching vibration and the UV dichroism, the value of angular-dependent fluorescence is not a direct measure for the degree of orientation in the films; it depends strongly from the optical density of the film. If the optical density is high, the passing light will be attenuated and not all of the chromophores can be excited, whereas at low optical densities almost all fluorophores contribute to the fluorescence. This situation is found in the oriented cinz films, there the absorbance at 311 nm contains the absorbance of the nonfluorescent methoxycinnamate and the fluorescent cyanobiphenyl groups. The overall absorbance at 311 nm parallel to the E field vector is around 2.2, perpendicular to E only an absorbance of 0.45 was detected. This results in an internal filter effect only parallel to E, and the measured fluorescence intensity (LP excitation parallel to E) is much lower as expected. The optical density of the oriented films strongly depends on the orientation direction. This filter effect also causes a lower fluorescence anisotropy in oriented samples.

For CPcin it has to be stated that the spectral overlapping of all chromophores causes a filter effect regarding the fluorescence anisotropy. Moreover, the irradiation at an absorption wavelength of the biphenyl groups can result in a degradation of the mesogenic units. Finally, the photochemical and thermal behavior of the different side groups cannot be investigated in detail by UV/vis spectroscopy. For this reasons we prepared a new cinnamate group containing the strong donor *N*,*N*-dimethylamino with an absorbance at 371 nm. So, all side groups of the regarding copolymer CPcinN are characterized by an individual absorbance in the UV/vis spectrum (Figure 2a).

The irradiation of films of CPcinN up to a conversion of 40% of the (*N*,*N*-dimethylamino)cinnamate side group results in an anisotropy with a maximum absorbance perpendicular to the E-field vector. As in the case of CPcin, the thermal treatment developes an anisotropy parallel to the E-field vector. As an example the photoalignment of a film irradiated up to a conversion of 13.6% is shown in Figure 6.

The LP irradiation for 2 min at 365 nm results in a dichroism of D_{371} = 0.05 at 371 nm due to the photocycloaddition. This value is significantly higher compared to films of CPcin using the same irradiation dose. As we have a spectral separation of the cinnamic group the anisotropy was only detected for this group. As expected, after irradiation the absorbance of the biphenyl groups at 292 nm does not show any change in the absorbance.

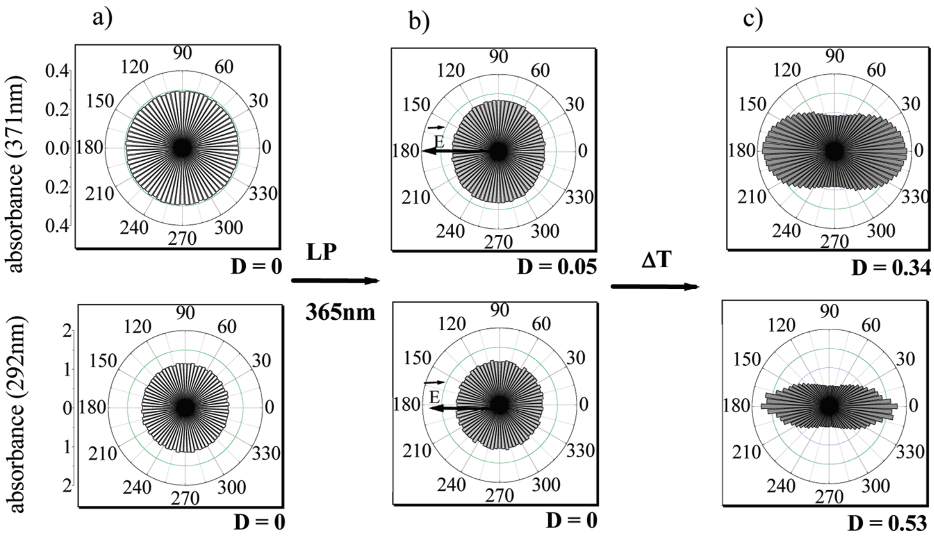

Figure 6. Angular-dependent UV/vis spectra of CPcinN: (a) initial spin-coated film, (b) film after induction of anisotropy by LP irradiation with 365 nm, and (c) aligned film by annealing at 92 °C and related dichroism at 292 and 371 nm.

Annealing results in the establishment of dichroism in both typs of groups. For the mesogenic biphenyl groups a dichroism of $D_{292} = 0.56$ and for the photosensitive cinnamate a dichroism of $D_{371} = 0.34$ were found (Figure 6). So, we can state, that the two-step bulk-photoalignment results in a cooperative orientation of both side groups.

The photoinduced order of CPcin is long-term stable (room temperature) at least for 14 months without any change of dichroism and absorbance. Moreover, annealing at 33 °C above the clearing temperature T_i for 1 h does not result in any change of anisotropy. By postirradiation with nonpolarized light of 365 nm, the absorbance of the oriented units parallel to the E-field vector decreases, whereas the units perpendicular to it remain at the same level. The oriented units undergo a photo-cross-linking by subsequent irradiation which leads to a decrease of the order of the film. In this way it is possible to adjust the order in the film by a subsequent irradiation step with nonpolarized light (Figure 7).

The polymer film CPcin can be patterned using a mask for LP irradiation. After subsequent annealing anisotropic pixels are formed. In this way pixels of different directions can be obtained by irradiation with LP light. Figure 8 shows the angular-dependent absorbance at 296 nm of orthogonal oriented pixels with a dichroism of $D_{296} = 0.55$ and $D_{296} = 0.59$.

The bulk orientation of methoxycinnamate and (*N*,*N*-dimethylamino)cinnamate containing polymers (CPcin and CPcinN) using LP light of 325 and 365 nm results in quite highly ordered films. CPcin shows additionally anisotropic blue emission due to the oriented cyanobiphenyl groups; CPcinN does not emit. The films can be oriented pixelwise and stabilized by an additional irradiation step with nonpolarized light.

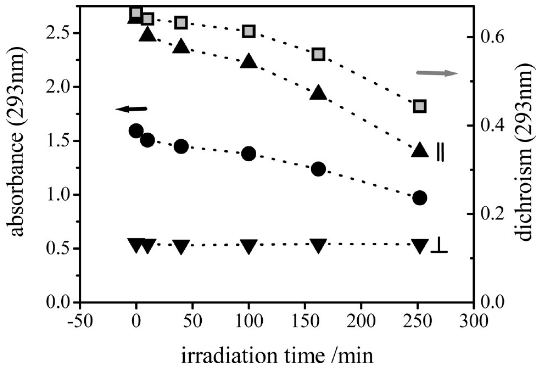

Figure 7. Development of the measured average absorbance of CPcin (●), absorbance parallel (▲), and perpendicular (▼) to the E-field vector and the dichroism (■) at 293 nm of an oriented CPcin film upon nonpolarized irradiation at 365 nm.

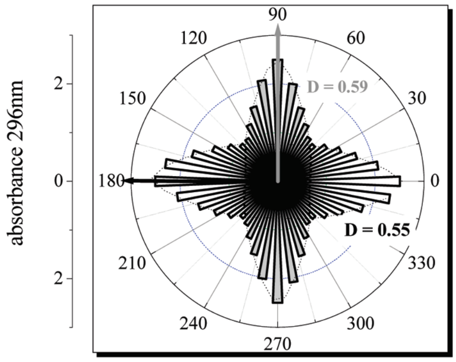

Figure 8. Angular-dependent absorbance at 296 nm of oriented pixels of a CPcin film measured by the microscope–spectrometer.

Orientation of the Red-Emitting Copolymer. In order to get anisotropic films with red fluorescence, the bulk orientation of the stilbene-containing copolymer CPstil was investigated. The stilbene group itself combines fluorescent and photosensitive properties. Like azobenzene and cinnamic ester, stilbene is able to undergo photoisomerization, but as in the case of cinnamates the thermal back-reaction is restricted.[31] Moreover, upon irradiation [2 + 2] photocycloaddition and a ring-closing reaction are the dominating processes, whereas the last one leads to dihydrophenanthrene, which reacts with oxygen to phenanthrene. In general, using UV/vis spectroscopy, one cannot differentiate between these photoreactions; all reactions are characterized by a decrease of the stilbene absorbance as a result of the photodegradation of the *E*-stilbene unit.

Upon LP irradiation at 325 nm an angular selective photoprocess occurs which results after a photoconversion of 27% of

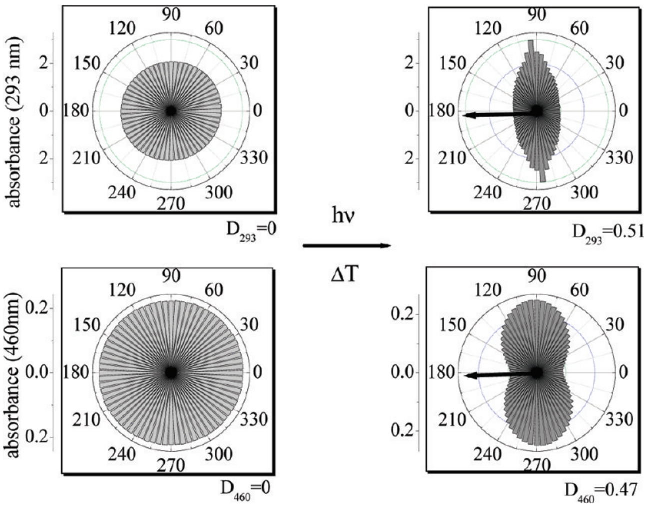

Figure 9. Angular-dependent absorbance of CPstil (cinnamate/cyanobiphenyl and the dye group) at 293 and 460 nm of the initial spin-coated film (left) and after induction of anisotropy by LP irradiation with 325 nm and annealing at 93 °C for 3 days (right).

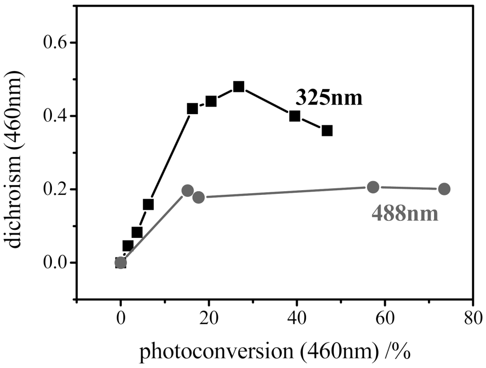

Figure 10. Dichroism of LP irradiated and annealed films of CPstil at different degrees of photoconversion using irradiation wavelengths of 488 nm (●) and 325 nm (■).

the stilbene absorption in a dichroism of D_{460} = 0.03 with a maximum absorbance perpendicular to the E-field vector. Annealing at 92 °C for 3 days results in an amplification of this order by a factor of 16 up to a value of D_{460} = 0.47 with a maximum absorbance perpendicular to the E-field vector as well (Figure 9). The cyanobiphenyl units, characterized by an absorption at 278 nm, are aligned cooperatively as well, and a dichroism of D_{293} = 0.51 was found.

As seen from Figure 10, the dichroism after LP irradiation and subsequent annealing depends on the amount of photoconversion and the used irradiation wavelength. Increasing the doses of UV light results in a higher photoconversion and causes an increase of dichroism resulting in a maximum value of D = 0.5. Using higher irradiation doses, the induced dichroism after irradiation and annealing decreases due to photodecomposition of the stilbene unit. Upon UV irradiation the stilbene and the cyanobiphenyl moieties are excited; using visible light irradiation the stilbene moiety is exclusively. Moreover, assuming a photoorientation mechanism for the stilbene, irradiation at longer wavelengths results in a less efficient steady state of the photoorientation and so in a lower dichroism.

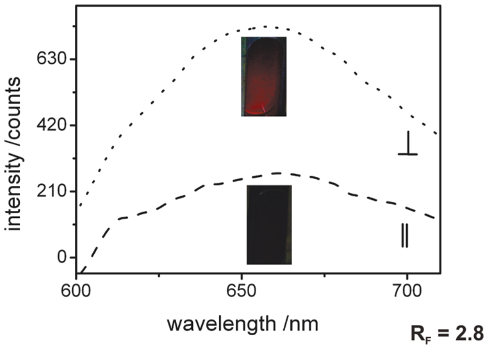

Figure 11. Red emission and fluorescence spectra of an oriented film of CPstil upon excitation at 463 nm perpendicular (···) and parallel (— —) to the orientational direction and the related ratio of fluorescence at 662 nm.

In fact, the irradiation with LP visible light at 488 nm results in a significantly lower dichroism after annealing compared to the UV irradiation. Remarkably, the irradiation with higher doses does not cause a decrease of the dichroism after irradiation and annealing. On the basis of these findings, we exclude a photocycloaddition process and a photoorientation mechanism as it is known for azobenzene should be taken into account.

Such a E/Z isomerization of the monomeric stilbene compound was observed in PMMA during UV irradiation. But the absorbance could not fully rebuild, neither by an additional thermal nor by photochemical treatment.[32] So, we have to consider that at least one additional angular selective irreversible photoprocess takes place which causes a significant decrease of the absorbance of the stilbene units.

Moreover, the decrease of the dichroism at higher irradiation doses is connected with the loss of the mesogenic properties due to the formation of non-rod-like photoproducts. The fact that the film was less soluble after the two-step orientation procedure confirms this point. But in contrast to the cinnamate polymer CPcin the cross-linking photoproduct does not contribute to an alignment in CPstil films. The alignment was observed perpendicular to the E-field vector due to a photoorientation process and the remaining rodlike side groups after the angular-dependent photodecomposition.

Simplifying, we can state that a complex angular selective photodegradation process of a donor–acceptor substituted stilbene takes place, and the remaining stilbene units cause an alignment of the mesogenic polymer film. Based on a photodegradation process, an efficient bulk photoalignment was obtained.

The oriented films of CPstil show anisotropy of fluorescence upon angular selective excitation. The fluorescence reaches maximum values in the film excited at 463 nm perpendicular to the E-field vector of the irradiation light and minimum values if the excitation was parallel. In this way the fluorescence anisotropy shows a perpendicular orientation regarding the E-field vector of the incident light. The anisotropy ratio of fluorescence (see eq 2) was detected of about R_F = 2.8 (Figure 11).

Orientation of the Red-Emitting Terpolymer. In order to know which photoreaction dominates, the red-emitting terpolymer TPstil containing two different photosensitive side groups, the cinnamic ester and the stilbene group, was investigated.

Compared to the stilbene copolymer CPstil, the two-step photoalignment process in TPstil is less efficient. Only a dichroism of D_{460} = 0.21 in the range of the stilbene absorbance and of

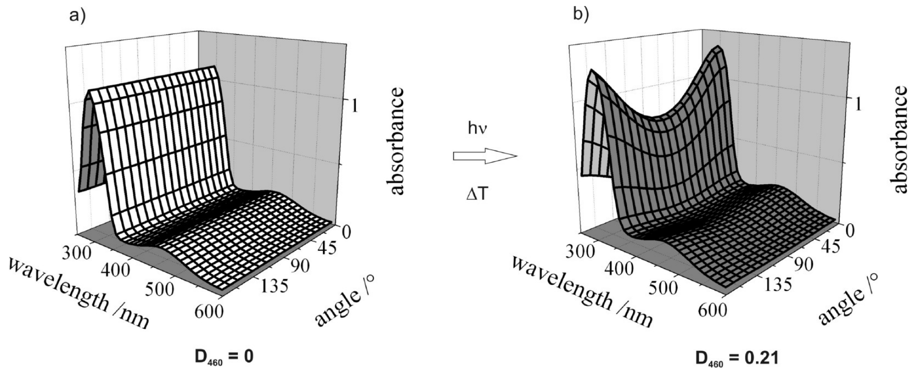

Figure 12. Angular-dependent UV/vis spectra of TPstil: (a) initial spin-coated film; (b) film after induction of anisotropy by LP irradiation with 325 nm and annealing at 92 °C for 1 day. The related dichroism was measured at 460 nm.

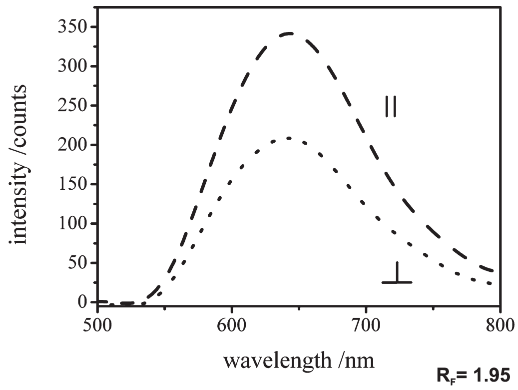

Figure 13. Fluorescence spectra of an oriented film of TPstil upon excitation at 463 nm parallel (— —) and perpendicular (· · ·) to the orientational direction and the related ratio of fluorescence at 662 nm.

about D_{293} = 0.23 for the $\pi\pi^*$ absorbance of the other chromophores were found (Figure 12). As in the case of the copolymers CPcin and CPcinN, the preferred orientational direction parallel to the E-field vector of the incident light was found for oriented films of TPstil. The dichroism could not be enhanced by optimizing the irradiation conditions regarding wavelength or irradiation dose. But, as in the case of the reference copolymer CPcin and CPcinN, the alignment is dominated by the angular selective formation of the photocycloadducts of the cinnamic ester units, resulting in an alignment parallel to the E-field vector. However, the low aligning capability indicates the appearance of competing aligning processes, i.e., perpendicular alignment for the stilbene group and parallel alignment for the cinnamate group.

The fluorescence of the aligned film shows anisotropy as well. It appears with a maximum value parallel to the electric field vector after the combined LP irradiation and annealing procedure indicating a parallel orientation of the stilbene fluorophores. A ratio of the fluorescence parallel and perpendicular excited at 463 nm of R_F = 1.95 was obtained. This is in agreement with the dichroic ratio of absorbance (Figure 13).

Orientation of the Green-Emitting Terpolymers. In order to achieve anisotropic green fluorescence, 9-phenylethynyl-10-biphenylethynylanthracene[26a] was selected as fluorophore in the terpolymers TPant and TPantN.

The irradiation of the spin-coated films with LP UV light of 325 nm and a dose of 0.90 J/cm^2 results in a small decrease of the absorbance and in the induction of a very small dichroism at 300 nm of less than 0.01. No anisotropy could be detected in the range of the fluorophore absorbance, but a decrease of absorbance at 489 nm of about 10% was observed. Subsequent annealing of the film in the mesophase at 100 °C for 24 h results in the development of a highly dichroic film. While the dichroism of the mesogenic and photosensitive units measured at 300 nm was only 0.48, the 9-phenylethynyl-10-biphenylethynylanthracene group shows a dichroism of about D_{489} = 0.7 (Figure 14a). Most surprisingly and in contrast to the basic model copolymer CPcin, the preferred orientational direction was perpendicular to the electric field vector of the incident actinic light.

However, in contrast to that, a film of the same terpolymer covered with a top layer of poly(vinyl alcohol) (PVA) results in an alignment parallel to the electric field vector establishing the same value of dichroism of about D_{489} = 0.7 as result of the same procedure applying a dose of only 0.15 J/cm^2 (Figure 14b). As a result of the exposure, there is only a very weak dichroism at 300 nm but no detectable alignment in the absorption range of the 9-phenylethynyl-10-biphenylethynylanthracene chromophore at 470 nm/490 nm. Moreover, in contrast to the first experiment, no decrease of absorbance at the anthracene band was observed. The change in the orientational direction from perpendicular to parallel was exclusively caused by the use of the PVA protection layer. As known from our former investigations regarding the photostability of organic dyes, PVA films are able to restrict the diffusion of oxygen.[34] The orientational behavior of the PVA-covered film corresponds to that of the copolymer CPcin without fluorophore side group. In this case an orientation parallel to the electric field vector and a well-established dichroism of about 0.65 were observed. As discussed for CPcin, the parallel alignment might be caused by the alignment force of the angular selectively formed anisometric photocycloadducts of the cinnamic ester in the polarization direction of the incident light. It is obvious that the unexpected perpendicular orientation in the noncovered film is caused by an oxygen-influenced photoreaction of the 9-phenylethynyl-10-biphenylethinylanthracene moiety. Probably, the alignment is caused by the remaining rodlike anthracene side groups perpendicular to the electric field vector, whereas the moieties parallel to E undergo an angular-selective photooxidation in 9,10-positions. So, the elongated chromophore degrades parallel to the polarization plane of the incident light to a less anisometric photoproduct with much lower aligning capability. In this way the absorbance is decreased, and the molecular shape of the side group is changed.

The exposure of a PVA-covered TPant film with linearly polarized blue light (488 nm) at the absorption band of the

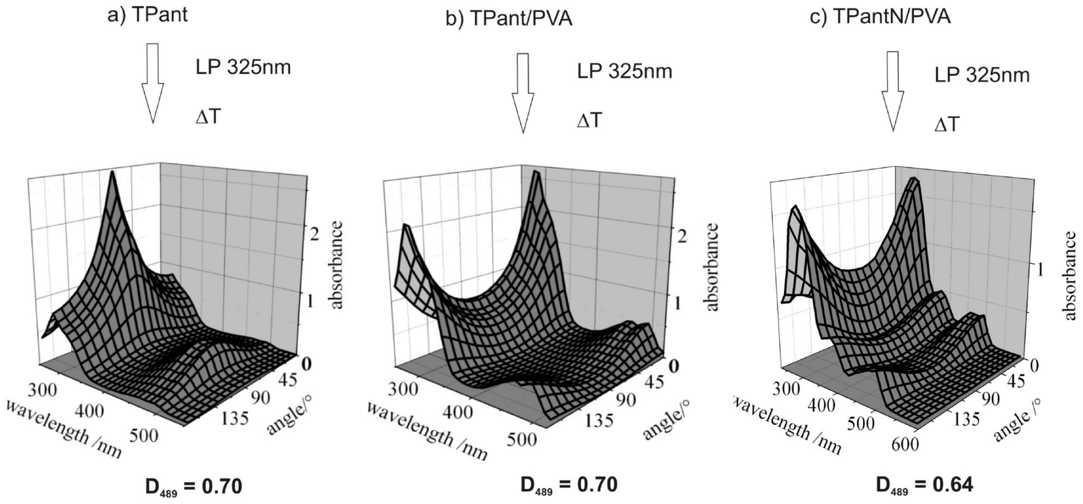

Figure 14. Angular-dependent UV/vis spectra of oriented films of cinnamate and anthracene containing terpolymers using LP UV light and thermal treatment: (a) film of TPant, (b) film of TPant covered with a PVA top layer, and (c) film of TPantN covered with a PVA top layer. The related dichroism was measured at 489 nm.

fluorophore was carried out up to a decrease of 9% of the initial absorption of the anthracene band at 489 nm, which might be caused by [4 + 4]-photocycloaddition. This change is comparable to the decrease by UV exposure of the noncovered film. But compared to that, a much higher energy dose of about 94.5 J/cm^2 was required. This indicates that the quantum yield of this photoreaction is very small compared to that of the photooxidation. Annealing of this films results in a small dichroism of about D_{489} = 0.21 with an orientation perpendicular to the E-field vector. Nevertheless, this reaction is less efficient regarding the induction of anisotropy and the subsequent alignment by annealing compared to the photooxidation reaction. Thus, we can state that the orientation by the anthracene moiety in the case of the noncovered films should be caused by an angular-selective photooxidation process, whereas the direct irradiation of the PVA-protected anthracene chromophore results in another slower angular-selective photoreaction with lower aligning capability.

As in the case of TPant, films of TPantN were covered with a protecting PVA layer. The films of TPantN can be oriented in almost the same manner like TPant changing the exposure wavelenght from 325 to 365 nm. Applying LP irradiation using a wavelength of 365 nm at the absorbance of the cinnamoyl cinN units, a small anisotropy at the absorbance of these units was introduced, and after annealing anisotropy in all side groups by cooperative bulk alignment was established. For the mesogenic units, characterized by an absorption band at 300 nm, a dichroism of D_{300} = 0.45 was found. The dichroism of the cinnamoyl unit at 371 nm was D_{371} = 0.32 and has the same value as observed in films of CPcinN. The anisotropy of the anthracene side group was detected at 489 nm with a value of D_{489} = 0.64 (Figure 14c). Noncovered TPantN-films also can be oriented applying the same irradiation dose, but the values are significantly lower, resulting in a dichroism of only D_{489} = 0.21 with the maximum of absorbance parallel to the E-field vector after the two-step orientation procedure. This behavior is different compared to TPant and can be explained by the use of the different irradiation wavelengths. The irradiation at a shorter wavelength of 325 nm (TPant films), i.e., using light with higher energy, results in the formation of a higher amount of singlet oxygen compared to the use of a wavelength of 365 nm in the TPantN films. In this way the photooxidation of the anthracene unit using 325 nm should be more pronounced compared to an irradiation at 365 nm. The photooxidation of the anthracene unit in the noncovered films can be observed by the photodegradation of the anthracene absorbance at 462 nm. Whereas the irradiation at 325 nm of the TPant results in a degradation of 19%, the degradation of the anthracene unit in TPantN was only 1.5%. As the photooxidation of the anthracene unit results in a perpendicular alignment and the formation of [2 + 2]-photoadducts of the cinnamate units causes parallel alignment, it is possible to observe a parallel alignment by a low efficiency of the photooxidation process. Nevertheless, the photooxidation process of anthracene disturbs the alignment procedure of the cinnamate units, so we observe only small values of anisotropy. As described above, a similar competitive situation was observed for TPstil.

The films of TPant show an anisotropic fluorescence upon angular-selective excitation at 463 nm. The green emission of the PVA covered film is characterized by the maximum value parallel to the director of the aligned LCP film and a minimum perpendicular to this direction. A comparatively high fluorescence anisotropy ratio of about R_F = 8.3 was found (Figure 15).

In contrast to TPant in films of TPantN, an efficient quenching of the fluorescence was observed caused by the dimethylamino group. A similar behavior was observed in a series of terpolymers containing azobenzene as photosensitive group.[8]

So, TPantN is a very interesting model system in order to investigate the cooperative bulk alignment in cinnamate-containing polymers, but the unfavorable quenching effect makes TPantN of less practical importance for any application, in which anisotropic fluorescence is desired. Nevertheless, the polymer TPant shows very good bulk-aligning properties as well as a high value of emission anisotropy, and it is the favorable candidate for possible applications. After the two-step bulk orientation films of TPant are characterized by a very high anisotropy without quenching effects, and therefore, TPant is suitable for applications as an anisotropic green-emitting material. The orientation can be triggered parallel or perpendicular to the electric field vector, governed by the use of a PVA protecting layer.

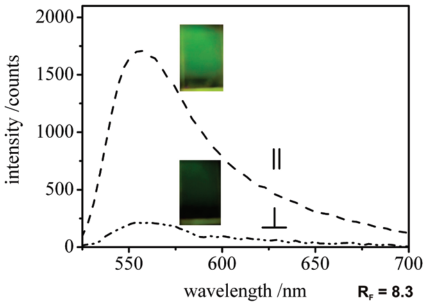

Figure 15. Green emission and fluorescence spectra of an oriented film of TPant upon excitation at 463 nm parallel (— —) and perpendicular (···) to the orientational direction and the related ratio of fluorescence at 554 nm.

IV. CONCLUSION

Films with anisotropic emission were created by all-in-one photoalignment of multifunctional LC polymers. The surface alignment of photocurable LCs has advantages concerning efficiency, but it requires two layers and it has disadvantages concerning the precise adjustment of order, the resolution, and the shrinkage. In contrast to the conventional surface alignment, the bulk alignment needs only one layer of a multifunctional polymer. For this aim, spin-coated films of LC co- and terpolymers were aligned by a two-step procedure combining the initial photoinduction of anisotropy in the glassy state with the thermotropic self-organization by subsequent annealing at temperatures of the mesophases. The multifunctional polymers were designed in such a way that they combine liquid crystalline, photosensitive, and luminescent properties in one material. So, the poly(methacrylate)s with covalently bonded side groups of cinnamic ester, cyanobiphenyl, anthracene, and stilbene type were synthesized, which differ concerning their photochemical and spectral behavior. The photosensitive stilbene, cinnamic ester, and anthracene moieties allow the generation of anisotropy upon exposure with LP light. The biphenyl side group leads in combination with the design of the other rodlike side groups to liquid crystallinity offering the bulk alignment of the polymer films by thermotropic self-organization. Thus, films with a dichroism up to a value of 0.7 and a ratio of anisotropic fluorescence of about 8 were created. The irradiation conditions were varied concerning wavelength and irradiation time or dose with respect to the photoreaction of the cinnamoyl group and the dyes in order to achieve a high efficiency of the alignment process.

Moreover, the dye groups introduce specific absorption and emission properties in the multifunctional polymers. Side groups with two functionalities are possible as well.

The variation of fluorescent chromophores and photosensitive groups demonstrates that a general approach of broad application was found. In this way films with anisotropic RGB emission were developed. But the main result is the finding that, due to the amplification by thermal self-organization, quite different photosensitive moieties can be used. In fact, a very small anisotropy photoinduced in the glassy state at room temperature is efficient enough to align the complete LCP film. Amplification factors up to 50 were found.

However, the situation becomes very complex if the dye groups undergo additional photodegradation reactions as well. In addition to the photocycloaddition of the cinnamic ester, photoreactions of the 9-phenylethynyl-10-biphenylethinylanthracene moiety (photooxidation and [4 + 4]-photocycloaddition) and of stilbene groups (isomerization, photocycloaddition, and cyclization to dihydrophenanthrene) have to be considered. The alignment depends on the distribution and aligning force of the initially photosensitive groups and the related photoproducts. In the case of angular selective photodegradation, perpendicular alignment was caused by remaining rodlike photosensitive moieties, as in the case of studied stilbenes and anthracene derivatives. Parallel alignment is caused by angular selectively formed anisometric photoproducts, for example, the head-to-tail cycloadduct of cinnamic esters.

The direction of alignment is very sensitive to the competition of different photoreactions. The study shows that bulk alignment of LCP can already be achieved by quite small anisotropies induced in the glassy state of isotropic polymer films. Thus, the direction of alignment depends on the polymer composition, the irradiation conditions, and the existence of an oxygen protecting layer. It demonstrates once more that quite different photoreactions can be used for the bulk alignment. Limitations with respect to the photoinduced anisotropy and conventional photoaligning groups such as azobenzene or cinnamic ester moieties do not exist. Moreover, bulk photoalignment works probably with a large number of dyes, but the induced anisotropy requires stabilization, such as subsequent photo-cross-linking by nonpolarized light as it is caused by cinnamic derivatives.

Pixelwise irradiation with LP light was carried out with films of the reference copolymer. Subsequent annealing of these films results in a pixelwise variation of the optical anisotropy. In the case of cinnamoyl-containing polymers polarized exposure and nonpolarized exposure after the annealing step cause an adjusting of the order and fixation of anisotropy, resulting in thermal and long-term stable films.

In summary, the two-step bulk alignment processing of multifunctional LC polymers is a quite general approach to induce anisotropic properties.

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