Polymer-Based Systems for Advanced Optical Applications

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Abstract. Displays, in many different variations and for a multitude of uses, continue to be an evermore attractive area for industrial activity and academic development. Here, we address the development of polymer-based systems for application in advanced optical devices. More specifically, we report the fabrication and characterisation of photoluminescent polarizers based on uniaxially oriented, conjugated polymers and their application in a new family of photoluminescent liquid-crystal displays with substantially increased brightness, contrast, and efficiency. In another development, we show that efficient 'color polarizers' can be produced on the basis of oriented polymer-inorganic nano-composites. It is anticipated that these polarizers enable the fabrication of another new family of LCDs in which multiple colors can be displayed on the same pixel.

Introduction

The role of polymers in the area of optics traditionally has been associated with passive elements, e.g., in lenses, optical fibers or packaging materials and other, e.g. structural components[1]. However, in the past two decades, functionalized polymer systems have attracted a considerable interest and opened a variety of advanced applications for optical systems. For example, the development of nonlinear optical polymers[2] has led to concepts for a variety of active elements ranging from electrooptic switches and modulators to devices for the protection of eyes or sensors based on a two-photon absorption process[3]. Another major recent development has been the discovery of polymer-based light-emitting diodes (LEDs)[4] which have been extensively studied over the last decade and are expected to result in first commercial applications in short time[5]. Optical polymers now also play an increasingly important role in liquid-crystal displays (LCDs) which, despite the growing progress in electroluminescent devices and other alternative techniques, have maintained their dominant position in the field of flat-panel displays[6]. However, LCDs exhibit severe limitations in brightness and energy efficiency caused by the use of absorbing polarizers and color filters which convert a major amount (i.e., > 85%) of the incident light into thermal energy[6].

In this paper, we review part of our activities in the area of advanced optical systems. Specifically, we describe the fabrication of photoluminescent (PL) polarizers based on uniaxially oriented, conjugated polymers and their application in a new family of PL liquid-crystal displays with substantially increased brightness, contrast, and efficiency. PL polarizers exhibit highly anisotropic absorption and/or emission properties and efficiently combine two separate features: the polarization of light and the generation of bright color. A new photophysical effect – polarizing energy transfer – can be used to drive the efficiency of these elements to the theoretical limit: it enables to produce PL polarizers which optimally harvest incident light by isotropic absorption and emit the absorbed energy in highly linearly polarized fashion.

In another development, we have demonstrated that efficient 'color polarizers' can be made on the basis of oriented polymer-inorganic nano-composites. It is anticipated that these polarizers enable the fabrication of another new family of LCDs in which multiple colors can be displayed on the same pixel.

Polarizing Light with Polymers

Uniaxially oriented PL materials usually exhibit anisotropic, i.e., linearly polarized absorption and emission. This phenomenon has been known for inorganic crystals for more than a century[7] and was reported for oriented blends of ducite polymers and low-molecular weight PL materials as early as the 1930s[8]. Since, the effect has been shown in a variety of materials and using a diversity of orientation method[9] including, e.g., PL liquid-crystal systems[10] or low-molecular PL materials uniaxially grown onto orienting substrates, such as oriented poly(tetrafluoroethylene)[11]. Direct deposition through friction or rubbing[12] or the Langmuir-Blodgett technique[13], as well as mechanical deformation of pure conjugated polymer films[14] have also been demonstrated to yield films which exhibit anisotropic optical properties. However, the degree of orientation and, hence, the dichroic ratios obtained with these methods are usually only modest, typically well below 10. By contrast, the tensile deformation of guest-host systems, in which the guest molecules adopt the orientation of the host, was found to be a most promising technique for the production of films with highly anisotropic optical properties. This concept has been used in the past by different research groups for the preparation of oriented films based on blends of various form-anisotropic low-molecular and oligomeric compounds and a variety of matrix polymers such as polystyrene or polyethylene[9][15][16]. Rather surprisingly, this method has only recently been adapted for blend films of conjugated polymers; a blend of poly(2-methoxy-5-(2'-ethylhexyloxy)-p-phenylenevinylene (MEH-PPV) and ultrahigh-molecular weight polyethylene (UHMW-PE) was used in the initial experiment[17].

Recently, we have systematically investigated the structure-property relations of oriented films based on blends of poly(2,5-dialkoxy-p-phenylene ethynylene)(PPE, Fig. 1)derivatives and UHMW-PE[18]. PPEs exhibit an ideal matrix of properties with respect to the preparation of such PL polarizers[18–22], including large PL quantum efficiencies in solution
We have recently demonstrated that PL polarizers, such as the uniaxially orientated PL films described above, can combine and directly replace the standard polarizer and color filter in conventional LCDs and, using an appropriate, e.g., blue or ultraviolet (UV) backlight, result in efficient, colored PLLCDs [23]. Of course, a variety of device configurations can be envisioned [23]. Depending on the selected configuration, the predominantly relevant polarization characteristic of the PL polarizer is either a high degree of anisotropy in absorption or PL emission. As one relevant example, here, we describe a backlight twisted nematic (TN) configuration, in which light emitted from the polarized PL film (a yellow-green light-emitting 2% w/w EHO-OPPE/UHMW-PE blend film, draw ratio = 80, \( d = 2 \mu m \)) is switched (Fig. 3). The arrangement consists of a linear polarizer (here, used as analyzer), an electrooptical (EO) light valve (here, a standard twisted nematic cell), the PL polarizer, and a UV light source, emitting at 365 nm.

In this device configuration, the light emerging from the light source is at least partially absorbed by the PL polarizer, from where subsequently polarized light is emitted. The light emitted in the direction of the viewer either passes the combination of EO light valve and polarizer ('bright') or is blocked ('dark'). Maxi-
mum contrast is obtained when i) the PL polarizer is characterized by a high dichroic ratio for PL emission, and ii) the portion of light visible to the human eye that is emitted by the light source but not absorbed by the polarized PL film – and thus exits the device in the direction of the viewer – is minimal. This can be achieved by different means; e.g., by using an additional cutoff filter or employing an UV light source. In the latter case, the portion of UV light that is not absorbed by the PL polarizer may be absorbed by the EO light valve and the polarizer, since both these elements are usually absorbing in the UV regime. The device investigated in this work comprised a PPE-based PL polarizer and a UV light source emitting at 365 nm. Of course, the emission wavelength of the light source is by no means optimized for the absorption of the PPE-based polarized PL layer, as is evident from the PPE's absorption spectrum shown in Fig. 3. The switching of the device yielded a significant change in brightness that was perceived by the human eye as a change from a very bright yellow-green to almost completely dark. The outstanding contrast and the absolute brightness of the 'on' and the 'off' state were quantified with a standard luminance meter: a brightness of 30 ("bright") and 4 cd/m² ("dark"), respectively, was measured for the respective switching states. These values for brightness and contrast compare favorably with those of a similar, commercial, direct-view LCD (17 vs. 7 cd/m²) that was analyzed under identical ambient conditions.

Many other device configurations based on PL polarizers can be designed [23], including devices where the excitation light is switched, and the PL polarizer, positioned between the EO light valve and the viewer, functions as an analyzer. In this arrangement, a significantly improved

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Fig. 3. Schematic structure of a PL liquid-crystal display device

Fig. 4. Polarized absorption (a) and photoluminescence (b) spectra of a uniaxially oriented film of a 2% w/w EHO-OPPE/2% w/w DMC/UHMW-PE ternary blend film (draw ratio = 80). Spectra were recorded with polarizers oriented parallel (p, solid line) and perpendicular (s, dashed line), respectively, to the orientation direction of the film.
Polarizing Energy Transfer

The efficiency of PL polarizers is chiefly limited by the luminophore's quantum yield which, ultimately, can approach unity. However, when used in a standard PL LCD configuration (see above), only ca. 50% of light incident from the light source is used, since the absorption of these PL polarizers is also anisotropic [9–18]. We recently have demonstrated a new concept for polymer-based PL polarizers which overcome this limitation and can be used in PL LCDs with, in principle, an ultimate efficiency of unity [24]. These PL polarizers comprise a nearly randomly oriented sensitizer that maximally harvests light by isotropic absorption, efficiently transfers the energy to a uniaxially oriented PL polymer which subsequently emits highly linearly polarized light. Key step is a polarizing energy transfer which, to a certain extent, mimics the concept used by nature in photosynthesis to optimally use optical energy [25].

While the reverse effect, i.e., PL depolarization, is well-known [25], the polarizing energy transfer exhibited by the new materials is not only of technological relevance but also manifests a new photophysical phenomenon.

The PL films investigated were based on uniaxially oriented, ternary blends of UHMW-PE, EHO-OPPE (2% w/w), and 7-diethylamino-4-methylcoumarin (DMC) (2% w/w) as the sensitizer and were prepared according to the methods outlined above. DMC was selected as the sensitizer because of its low form anisotropy, suitable photophysical prerequisites, and particularly beneficial phase behavior. The melting temperature of 74°C makes DMC compatible with the orientation process which requires mobility of the guest molecules during deformation; in addition, DMC and EHO-OPPE are miscible at elevated temperatures, which enables a most favorable morphology of the oriented blends (see below). The absorption of DMC around 364 nm optimally overlaps with the emission of common UV lamps that may be used as excitation source in PL LCDs [23]. Importantly, DMC seems not to quench emission of EHO-OPPE and, mandatory for energy transfer [25], exhibits an own emission that favorably overlaps with the absorption of EHO-OPPE.

The ternary blend exhibits high absorption dichroic ratios $D_{RA}$ of up to 13 at
440 nm, resulting from a high degree of orientation of EHO-OPPE (Fig. 4). By contrast, the absorption at 365 nm is essentially isotropic (DR$_\text{a}$ = 1.5) and reflects the nearly random orientation of the sensitizer within the oriented UHMW-PE matrix. Polarized emission spectra (Fig. 4), obtained under isotropic excitation at 365 nm and polarized detection in either p- or s-mode, show that the DMC emission is almost fully suppressed, while the emission from EHO-OPPE is highly polarized (DR$_\text{p}$ = 16) and of significantly enhanced intensity when compared to binary UHMW-PE/EHO-OPPE films. Further, the intensity of p-polarized emission from the ternary blend was found to be only weakly depending on the polarization of the incident light (when excited at 365 nm). In fact, the ratio of the emission intensities for excitation with s- and p-polarized light (1.5) is in gratifying agreement with the slightly dichroic absorption of the film at 365 nm (DR$_\text{a}$ = 1.5). Thus, the ternary blend unambiguously exhibits the phenomenon of polarizing energy transfer: optical energy is isotropically absorbed by DMC, with similar efficiency for both absorption (excitation) polarizations transferred to EHO-OPPE which subsequently emits polarized light. In the most unfavorable limit, the new material converts fully s-polarized into highly p-polarized light.

The polarizing energy-transfer process observed in the new PL materials may, principally, originate from either radiative (trivial), long-range coulombic (Förster), or short-range electron-exchange (Dexter) energy transfer between the DMC sensitizer as donor and the oriented EHO-OPPE as acceptor [25]. The fact that energy is transferred between donor molecules that have been excited with s-polarized light and acceptor molecules which subsequently emit p-polarized light implicates a depolarization of the donor excited state, unless Dexter-type coupling is involved [25]. This depolarization can derive from randomizing energy migration or orientational relaxation of the donor and is indeed observed when exciting the binary DMC reference blend with polarized light. While the low optical density of the samples excludes a radiative energy transfer [25], a nonradiative energy transfer might point to a very particular phase behavior of the oriented blends. As discussed elsewhere, it was found that in binary blends, EHO-OPPE forms an apparent molecular dispersion in the UHMW-PE matrix[18]. Thus, the incompatibility of DMC and UHMW-PE, and the affinity of DMC and EHO-OPPE make the formation of DMC/EHO-OPPE aggregates very likely, in which a nonradiative energy transfer is enabled by the close proximity of donor and acceptor molecules.

**Oriented Polymer-Metal Nano-Composites as 'Color Polarizers'**

Inorganic particles are frequently added to polymers in technical applications, e.g., to increase the polymer's stiffness, abrasion resistance, or electrical conductivity. The diameters of the particles in such systems are typically at least several 100 nm, or the particles are present as agglomerates of such sizes. If the diameters are below 100 nm in at least one direction, the materials are included in the class of nano-composites. Such systems can exhibit particular optical properties, such as markedly reduced light scattering. Hence, nano-composites are of considerable interest in the field of optics [26-34].

Polymer-inorganic nano-composites of high optical quality can be prepared only in rare cases with the common procedures of composite fabrication, i.e., mixing of the components in the polymer melt or in presence of a solvent. In these cases, the inorganic particles typically agglomerate due to their high surface energies, and the forces acting at those aggregates during common processing methods are not sufficient to separate the particles from each other and to homogeneously disperse them in the polymer matrix. To avoid the formation of aggregates, generally, the inorganic particles have to be covered with a strongly bound substance of low surface...
energy, or they have to be prepared in situ. The latter preparation is usually performed in homogeneous solutions in the presence of or by subsequent addition of the polymer. Nano-composites are then obtained, e.g. by co-precipitation, spin coating, or solvent casting.

Little attention has been paid to inorganic particles that are oriented in a polymer matrix, although old and widely forgotten experiments [35–39] indicated that such materials may be useful as color polarizers. We aimed at the preparation and investigation of these materials, and present two routes to produce filters through which transmitted light has a polarization-direction-dependent color, herein referred to as ‘color polarizers’.

In the first route, we prepared gold colloids in situ in aqueous solution by reduction of tetrachloroaurate(III) with citrate [40][41]. This method allows synthesis of colloidal gold particles of controlled size: we produced particles of an average diameter of 16 nm. The particle-size distribution is shown in Fig. 5. Films of gold-poly(vinyl alcohol) (PVAI) nano-composites were obtained by addition of an aqueous PVAI solution to the colloidal gold suspension, followed by casting and drying. After drawing of the films at 120° to five times their initial length, the samples were found to contain linear arrays of gold particles and agglomerates that were oriented in the drawing direction (cf. Fig. 6). As a consequence of the anisotropic, uniaxial arrangement of the gold-colloidal particles, the color of the resulting materials varied when observed through a linear polarizer, depending on the angle (φ) between the polarization axis and the drawing direction. The absorption maximum shifted to higher wavelengths as φ decreased. For example, the color of light transmitted through the nano-composites shifted from red to blue when φ was varied from 90° to 0° (Fig. 7). In principle, it is expected that these results can be transferred also to other polymer-metal systems, which may result in a variety of materials which can change the color of transmitted light simply by variation of φ and, therefore, can act as ‘color polarizers’.

In addition to the above system, we also dispersed dodecanethiol-coated gold particles [42] in poly(ethylene) (PE). The surface energy of an alkanethiol layer is 1–2 orders of magnitude below that of gold, i.e., the agglomeration tendency of dodecanethiol-coated gold particles is little pronounced. The dodecanethiol-coated gold colloids form in the isolated state a waxy product that readily disperses in organic solvents. The average size of the gold particles was 2.2 nm (Fig. 8). Optically transparent suspensions of dodecanethiol-modified gold particles and dissolved PE were heated at 130° in p-xylene. At this temperature, alkanethiol molecules begin to desorb, i.e., gold particles begin to agglomerate, manifested in a color shift from red to blue. Films of gold-PE nano-composites were again prepared.
by solvent casting and drying. The films thus obtained were stretched to 45 times their initial length. As in the case of the gold-poly(vinyl alcohol) nano-composites, the color of light transmitted through these drawn films switches from red to blue when $\phi$ is varied from 90 to 0°. Transmission electron microscope (TEM) pictures show the presence of elongated agglomerates oriented in the drawing direction, similar to the structure presented in Fig. 6. Before drawing, globular gold aggregates were present in the PE matrix. Hence, the elongated gold features are most likely formed by shearing during tensile deformation which simultaneously orients the aggregates in the drawing direction.

The UV/VIS spectra of polarized light for different values of $\phi$ are presented in Fig. 9 for the gold-PE nano-composites. An isosbestic point is evident at 630 nm. At this wavelength, the absorption is independent of $\phi$. The color of colloidal gold is mainly dominated by absorption and not by scattering [43]. Hence, the color shifts in the nano-composites with the uniaxially oriented linear aggregates can be described in the simplest case by an approximation with two extinction coefficients $\varepsilon_{pp}$ and $\varepsilon_{pe}$ for parallel and perpendicular orientation, respectively, between the polarization and drawing axis. At the isosbestic point, $\varepsilon_{pp}$ is equal to $\varepsilon_{pe}$, i.e., the absorption remains constant for all values of $\phi$.

With the above model systems we have demonstrated that ‘color polarizers’ can be developed on the basis of oriented polymer-inorganic nano-composites. In the examples presented here, color shifts from red to blue were observed, depending on $\phi$. It is anticipated that the color depends on the inorganic compound and the size of its particles and aggregates. Therefore, we expect that it will be possible to select desired colors by choosing the proper nano-composite system.

Conclusions

In summary, we have shown that advanced functional polymeric materials may play an increasingly important role in optical devices and enable a variety of novel display configurations. For example, we have demonstrated that PL polarizers can efficiently combine two separate features, i.e., the polarization of light and the generation of bright color. In addition, we have shown a new photophysical effect — polarizing energy transfer — that can bring the efficiency of these elements to the theoretical limit. Hence, photoluminescent display devices based on such polarizers can offer a substantial increase in device brightness and efficiency. In another development, we have also demonstrated that efficient ‘color polarizers’ can be made on the basis of oriented polymer-inorganic nano-composites, and it is anticipated that these polarizers enable the design of another new family of LCDs in which multiple colors can be displayed on one pixel.

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