Self-Assessing Photoluminescent Polyurethanes

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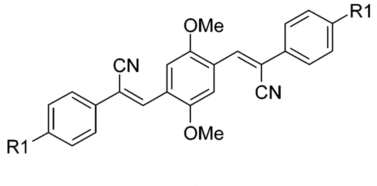
ABSTRACT: Due to excimer formation upon self-assembly, the photoluminescence (PL) spectra of isolated and aggregated cyano-substituted oligo(*p*-phenylene vinylene) (cyano-OPV) molecules can be very different. With the objective to create self-assessing elastomers, which reversibly change their PL color as a function of applied strain, cyano-OPVs were used here as built-in deformation sensors in thermoplastic polyurethanes (TPUs). Binary blends of a commercial TPU and 0.05−0.4% w/w of various cyano-OPVs were prepared by melt processing. The phase behavior and emission characteristics of these materials were strongly influenced by the chromophore's chemical structure, the blend's composition, and the processing protocol. However, only a modest PL color change was observed upon deformation of these blends. Also investigated was the covalent incorporation of 1,4-bis(α-cyano-4-(12-hydroxydodecyloxy)styryl)-2,5-dimethoxybenzene into TPUs based on poly(tetramethylene glycol), butanediol, and 4,4′-methylene-bis(phenyl isocyanate). The TPU composition was systematically varied, and the composition was related to the material's PL response. This approach afforded TPUs which in their relaxed state display predominantly excimer emission and exhibit a significant PL color change upon deformation. This mechanochromic response was largely reversible and mirrored the stress−strain curves of the materials.

Introduction

Chromogenic polymers exhibit a change of their absorption and/or fluorescence characteristics in response to a thermal,[1,2] mechanical,[3−9] chemical,[10] optical,[11] or other[12] stimulation and are useful for a wide range of technologies.[13] Most research efforts in this field are primarily devoted to chemical sensing, while mechanochromic polymers have received the least attention.[13] We recently reported on a new class of "self-assessing" polymers with built-in deformation sensors.[14−16] These materials are produced by blending ductile host polymers with trace amounts of excimer-forming,[17] photoluminescent (PL) chromophores. The approach relies on the initial formation of nanoscale aggregates of the sensor molecules in the polymer matrix and exploits that deformation transforms the nanophase-separated systems into molecular mixtures, concomitant with a pronounced shift from excimer- to monomer-dominated emission.[18] The excimer-forming dyes employed in our ongoing studies are cyano-substituted oligo(*p*-phenylene vinylene) derivatives (cyano-OPVs, Figure 1).[19] These chromophores are particularly attractive sensors, since they often exhibit a strong tendency toward excimer formation and the fluorescence maxima of their molecular solutions (monomer emission) and aggregates (excimer emission) display large differences (up to 140 nm).[19−23] Our previous work on polymers with built-in deformation sensors involved physical mixtures of the sensor dyes and ductile semicrystalline[14−16] and glassy amorphous[16] materials. To explore if the sensing scheme can also be exploited in elastomers, which reversibly change their PL color as a function of applied strain, we investigated thermoplastic polyurethanes (TPUs) that comprise cyano-OPVs as built-in deformation sensors. Our study involved both physical blends of a commercial TPU and small amounts of various cyano-OPVs, as well as copolymers produced by the covalent incorporation of a cyano-OPV into TPUs based on poly(tetramethylene glycol) (PTMG), butanediol (BDO), and 4,4′-methylene-bis(phenyl isocyanate) (MDI). The latter approach afforded elastomers which in their relaxed state display predominantly excimer emission but exhibit a significant PL color change upon deformation. This change was largely reversible and mirrored the stress−strain curves of the materials. The new materials appear to nicely complement the intriguing, nonfluorescent mechanochromic TPUs reported by Rubner and co-workers[3] and Kim and Reneker,[4] which comprise cross-linked diacetylenes or *cis*-azobenzene moieties, respectively.



1a: R1 = OCH_3
1b: R1 = $(OCH_2)_{17}CH_3$
1c: R1 = $(OCH_2)_{12}OH$

Figure 1. Chemical structure of the cyano-OPVs employed in this study.

Experimental Section

Materials. 1,4-Bis-(α-cyano-4-methoxystyryl)-2,5-dimethoxybenzene[19] (**1a**), 1,4-bis-(α-cyano-4-octadecyoxystyryl)-2,5-dimethoxybenzene[16] (**1b**), and 2,5-dimethoxy terephthal-dicarboxyaldehyde[24] were prepared as described previously. All solvents employed were of analytical grade. All chemicals were of highest commercial quality and were used as received unless otherwise noted. Terathane 1000 (DuPont), a hydroxy-terminated poly(tetramethylene glycol) (PTMG) with a typical M_n of 1000, was purchased from Aldrich Chemical Co. Texin 985, a TPU based on PTMG, butanediol (BDO), and 4,4′-methylenebis(phenyl isocyanate) (MDI) with a Shore A hardness of about 85, was obtained from Bayer MaterialScience. NMR analysis of Texin 985 (Supporting Information) revealed that the PTMG soft segment in this polymer has a typical M_n of around 900 and that the molar ratio of PTMG/BDO is approximately 1:1.

Instrumentation. ^1H NMR spectral data are expressed in ppm relative to internal TMS and were obtained in $CDCl_3$ or DMF-d_7

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on a Varian 600 MHz NMR spectrometer. GPC measurements were carried out on a Varian Pro Star with a Viscotec 270 dual light-scattering detector using Mesopore columns (Polymer Labs, 300 mm × 7.5 mm) and THF as solvent/eluent at a flow rate of 1 mL/min. Differential scanning calorimetry (DSC) experiments were conducted under N_2 atmosphere on a Perkin-Elmer DSC Pyris 1 at heating and cooling rates of 10 °C/min. Elemental analyses were performed by Galbraith Laboratories Inc. Visual inspections of a PL color change were conducted under illumination with a 15 W UV lamp operating at 365 nm. Unless otherwise noted, steady-state PL spectra were acquired on a PTI C720 under excitation at 435 nm and are corrected for instrument throughput and detector response. Temperature-dependent PL spectra were acquired on a SPEX Fluorolog FL3-12 spectrometer; samples were placed on a Gel Instrumente AG hotstage controlled by a TC2 temperature controller, and an optical fiber was used for the PL experiments. In situ opto−mechanical studies were carried out on an Anton-Parr rheometer equipped with an Expansion Instruments SER universal testing platform, which is described in detail elsewhere,[25] in connection with an Ocean Optics ACD1000-USB spectrometer under excitation at 480 nm; the emission spectra thus acquired were not corrected.

Synthesis of 4-(12-Hydroxydodecyloxyphenyl)acetonitrile. A suspension of K_2CO_3 (10.0 g, 72.4 mmol) in *N*,*N*-dimethylformamide (DMF, 50 mL) was purged with Ar for 20 min, heated to 75 °C, and 4-hydroxyphenylacetonitrile (4.78 g, 35.9 mmol) was added. After stirring for 5 min, 12-bromododecanol (10.0 g, 37.7 mmol) was slowly added, and the suspension was stirred at 75 °C under Ar for 30 h. After this time a pale yellow precipitate had formed. The reaction was terminated by pouring the suspension into ice water (250 g), the product was filtered off and dried under vacuum. Recrystallization from EtOH (100 mL) afforded 4-(12-hydroxydodecyloxyphenyl)acetonitrile in the form of white crystals (9.07 g, 80%). ^{1}H NMR: δ = 7.21 (d, 2 H, ArH), 6.87 (d, 2 H, ArH), 3.93 (t, 2 H, CH_2-OAr), 3.68 (s, 2 H, CH_2-CN), 3.93 (m, 2 H, CH_2-OH), 1.77 (m, 2 H, CH_2), 1.57 (m, 2 H, CH_2), 1.44 (m, 2 H, CH_2) 1.4−1.2 (m, 14 H, 7 × CH_2). Anal. Calcd for $C_{20}H_{31}NO_2$: C, 75.67; H, 9.84; N, 4.41. Found: C, 75.39; H, 10.44; N, 4.35.

Synthesis of 1,4-Bis(α-cyano-4-(12-hydroxydodecyloxy)styryl)-2,5-dimethoxybenzene (1c). 2,5-Dimethoxy-terephthaldehyde (1.00 g, 5.15 mmol) and 4-(12-hydroxydodecyloxyphenyl)acetonitrile (3.35 g, 10.56 mmol) were dissolved at 50 °C in a mixture of *t*-BuOH (300 mL) and THF (100 mL). *t*-BuOK (1.03 mL of a 1 M solution in THF, 1.03 mmol) and *n*-Bu_4NOH (20.6 mL of a 1 M solution in MeOH, 20.6 mmol) were added quickly, and an orange precipitate started to form immediately. The mixture was stirred for 15 min at 50 °C, cooled to room temperature, and poured into acidified methanol (300 mL containing ca. 0.2 mL conc acetic acid). The resulting precipitate was filtered off, excessively washed with MeOH, and dried under vacuum at 50 °C to yield **1c** (3.03 g, 74%) in the form of orange crystals. Mp: 145−155 °C. ^{1}H NMR: δ = 7.89−7.87 (2 × s, 2 × 2 H, ArH + CH=CCN), 7.64 (d, 4 H, ArH), 6.96 (d, 4 H, ArH), 4.00 (t, 4 H, CH_2-OAr), 3.95 (s, 6 H, CH_3-O), 3.65 (t, 4 H, CH_2-OH), 1.81 (m, 4 H, CH_2), 1.58 (m, 4 H, CH_2), 1.47 (m, 4 H, CH_2) 1.4−1.2 (m, 28 H, 7 × CH_2). Anal. Calcd for $C_{50}H_{68}N_2O_6$: C, 75.72; H, 8.64; N, 3.53. Found: C, 75.21; H, 8.82; N, 3.49.

General Procedure for Melt Polymerization of TPUs. MP6 was prepared as follows: poly(tetramethylene glycol) (PTMG, 4.00 g, 4.00 mmol), **1c** (0.79 g, 1.00 mmol), and butanediol (BDO, 0.65 g, 7.25 mmol) were combined in a glass vial and dried at 100 °C for 1 h. 4,4′-Methylenebis(phenyl isocyanate) (MDI, 3.18 g, 12.70 mmol, NCO/OH molar ratio ca. 1.04) was dried at 60 °C for 1 h. The MDI was added to the diol mixture under vigorous mechanical mixing, and the mixture was stirred for ∼30 s until the viscosity began to increase. The mixture was poured into a Teflon dish, placed in an oven at 100 °C for an additional 30 min, and subsequently stored overnight at ambient. The resulting rubbery polymer was cut into pieces, fed into a corotating, recycling twin-screw miniextruder (DACA Instruments, Santa Barbara, CA) and mixed for 5 min at 200 °C. Subsequent extrusion resulted polymer **MP6** in the form of an orange, rubbery solid. ^{1}H NMR: δ = MDI residue 9.55 (s, 2H, NH), 9.52 (s, 2H, NH), 7.51 (d, 4H, ArH), 7.17 (d, 4H, ArH), 3.87 (s, 2H, CH_2-Ar); PTMG residue 4.12 (t, 4H, CH_2-OOC), 3.39 (s, 52H, CH_2-O), 1. 1.69 (s, 4H, CH_2), 1.58 (s, 52H, CH_2); BDO residue 4.13 (d, 4H, CH_2-O), 1.73 (s, 4H, CH_2); **1c** residue 8.02 (2H, ArH *obstructed*), 7.88 (s, 2 H, CH=CCN), 7.78 (d, 4 H, ArH), 7.13 (4 H, ArH *obstructed*), ∼4.12 (4H, CH_2-OOC *obstructed*), 4.11 (4H, CH_2-OAr *obstructed*), 4.00 (s, 6 H, CH_3-OAr), 1.8 (m, 4 H, CH_2), 1.5 (m, 4 H, CH_2) 1.4−1.2 (m, 32 H, 16 × CH_2); end groups 6.90 (d, 2H, ArH), 6.60 (d, 2H, ArH), 4.97 (s, 2H, NH_2). Anal. Calcd for (MDI$_{12.70}$PTMG$_{4.00}$-BDO$_{7.25}$**1c**$_{1.00}$)$_n$: C, 67.87; H, 8.31; N, 4.45. Found: C, 67.85; H, 8.67; N, 4.34.

MP1−**MP5** and **MP7** were prepared by the same procedure as **MP6**. Details can be found in the Supporting Information.

General Procedure for Solution Polymerization of TPUs. SP4 was prepared as follows: PTMG was dried under vacuum at 100 °C for at least 2 h, and BDO and MDI were vacuum-distilled over molecular sieves and stored under N_2 at 4 °C prior to use. **1c** (0.396 g, 0.499 mmol) was charged into a reaction vessel equipped with mechanical stirrer, septum, and nitrogen inlet and was purged with N_2 for 30 min. PTMG (1.996 g, 1.996 mmol), BDO (0.333 g, 3.695 mmol), dibutyltin dilaurate (DBTDL, 0.039 g, 0.062 mmol), and dry DMF (20 mL, Acros Organics, <50 ppm water) were added via syringe under N_2, and the system was brought to 60 °C. A mixture of MDI (0.317 g, 1.266 mmol, NCO/OH molar ratio ca. 1.04) and DMF (10 mL) was added dropwise via syringe over the course of 1 h. The reaction mixture was then heated to 70 °C for 1 h and subsequently to 80 °C for an additional 1 h. The very viscous solution was diluted with an equal volume of DMF (30 mL) and finally precipitated into a methanol/water mixture (150 mL, 1:1 v/v) yielding an orange rubbery material. The product was collected by filtration and immediately dissolved in THF (30 mL). The resulting solution was filtered through a 0.8 μm filter, precipitated into methanol/water (150 mL, 1:1 v/v), and the product was dried over night at 80 °C under vacuum to yield polymer **SP4** in the form of an orange rubbery solid. ^{1}H NMR: δ = MDI residue 9.55 (s, 2H, NH), 9.52 (s, 2H, NH), 7.51 (d, 4H, ArH), 7.17 (d, 4H, ArH), 3.87 (s, 2H, CH_2-Ar); PTMG residue 4.12 (t, 4H, CH_2-OOC), 3.39 (s, 52H, CH_2-O), 1.69 (s, 4H, CH_2), 1.58 (s, 52H, CH_2); BDO residue 4.13 (d, 4H, CH_2-O), 1.73 (s, 4H, CH_2); **1c** residue 8.02 (2H, ArH *obstructed*), 7.88 (s, 2 H, CH=CCN), 7.78 (d, 4 H, ArH), 7.13 (4 H, ArH *obstructed*), ∼4.12 (4H, CH_2-OOC *obstructed*), 4.11 (4H, CH_2-OAr *obstructed*), 4.00 (s, 6 H, CH_3-OAr), 1.8 (m, 4 H, CH_2), 1.5 (m, 4 H, CH_2) 1.4−1.2 (m, 32 H, 16 × CH_2); end groups 6.90 (d, 2H, ArH), 6.60 (d, 2H, ArH), 4.97 (s, 2H, NH_2). Anal. Calcd for (MDI$_{6.251}$PTMG$_{1.996}$BDO$_{3.695}$**1c**$_{0.499}$)$_n$: C, 67.83; H, 8.34; N, 4.41. Found: C, 67.37; H, 7.89; N, 4.38.

SP1−**SP3** and **SP5** were prepared by the same procedure as **SP4** but the solvent volume was adjusted to maintain a 15% w/v ratio. Details can be found in the Supporting Information.

Film Preparation. All TPUs were dried at 80 °C under vacuum for at least 2 h prior to processing. Blends of Texin 985 and **1a** or **1b** were prepared by combining Texin 985 with the appropriate amount of dye in a DACA twin-screw miniextruder, mixing for 5 min at 200 °C, and extruding the resulting blend. Films were prepared by compression molding the polymer (blend) between two Teflon films using 100 μm spacers in a Carver press at 200 °C for approximately 1 min. Unless otherwise noted, the samples were immediately quenched after removal from the hot press to 0 °C by immersion into ice water. In some cases (as indicated in the text and/or figure caption), the samples were slowly cooled to room temperature (21 ± 4 °C); in this case the cooling time was ca. 15 min. The resulting films had a homogeneous thickness of ca. 100 μm.

Results and Discussion

Blends of Conventional TPUs with Sensor Dyes. Our initial efforts to create mechanochromic PL elastomers involved the preparation of blends of commercially available TPUs and

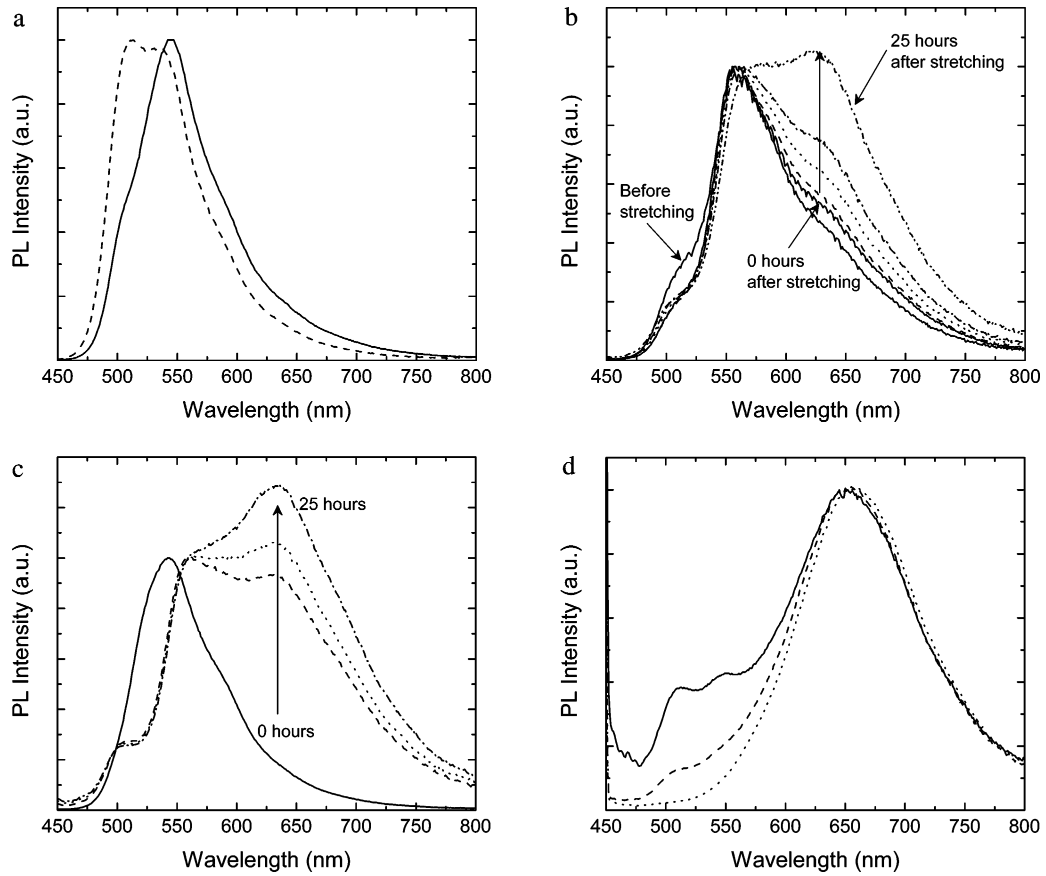


Figure 2. PL emission spectra of blend films of TPU Texin 985 and cyano-OPVs as a function of composition and thermo−mechanical history. (a) Quenched blend containing 0.2% w/w (dashed) and 0.4% w/w (solid) **1a** immediately after quenching. (b) Quenched blend containing 0.4% w/w **1a** stored for 11 days before stretching and at 0, 1, 3, 7, and 25 h after being stretched to $\lambda = 500\%$ and released. (c) Slowly cooled (15 min) blend containing 0.4% w/w **1a** and stored at ambient for 0, 6, 11, and 25 h. (d) Quenched blends containing 0.05% w/w **1b** (solid), 0.1% w/w **1b** (dashed), and 0.4% w/w **1b** (dotted) immediately after quenching.

excimer-forming sensor dyes. The chromophores employed in this study are based on the cyano-OPV motif, which we used previously for deformation sensing in polyolefins[14,15] and polyesters[16] (Figure 1). We here employed 1,4-bis-(α-cyano-4-methoxystyryl)-2,5-dimethoxybenzene (**1a**, Figure 1)[19] and 1,4-bis-(α-cyano-4-octadecyloxystyryl)-2,5-dimethoxybenzene (**1b**),[16] which display virtually identical photophysical characteristics and change their PL color from green (emission maxima, $\lambda_{\max}$, ≈ 506, 538 nm) to red ($\lambda_{\max} \approx 644$ nm) upon self-assembly from a dilute $CHCl_3$ solution. Due to the long alkyl substituents, **1b** displays a much lower solubility in polar polymers than **1a**.[16] After screening experiments with a number of different TPUs,[26] binary blends of Texin 985, an aromatic polyether-based polyurethane based on PTMG, BDO, and MDI, and between 0.05 and 0.4% w/w **1a** or **1b** were prepared by melt mixing. The resulting blends were compression-molded at 200 °C to produce films having a thickness of ca. 100 μm. The films were either rapidly quenched to 0 °C or slowly cooled to room temperature. Upon excitation with UV light, freshly quenched blend films comprising up to 0.2% w/w **1a** displayed green fluorescence ($\lambda_{\max} \approx 512$, 535 nm) characteristic of monomer emission (Figure 2a). The emission spectra of similarly prepared samples containing 0.4% w/w **1a** displayed only one peak with a maximum at 545 nm due to internal absorption in the high-energy portion of the spectrum. Over the course of 11 days we observed a shift of the peak maximum to 558 nm along with the appearance of a shoulder around 625 nm, indicative of some phase separation and excimer formation (Figure 2b). After this initial change the emission spectra of the quenched blend films containing **1a** remained essentially unchanged over a period of 1 year. However, rather surprisingly, if a quenched blend containing 0.4% w/w **1a** was strained to a draw ratio, $\lambda = l/l_0 - 1$, of ca. 500%, released, and subsequently stored at ambient, the emission spectrum rapidly developed a dominant, unstructured red band centered at 625 nm within a few hours after stretching (Figure 2b). This band is characteristic of excimer emission and reflects phase separation and the formation of ground-state aggregates of **1a** after stretching. This deformation-triggered aggregation is most intriguing, and such materials may find use in "one-time-stretch" sensing applications. If a blend film containing 0.4% w/w **1a** was *cooled slowly* (ca. 10 °C/min) to room temperature, the material's initial fluorescence was green, but very much like the quenched/stretched samples, the emission spectrum rapidly developed a dominant, unstructured red band centered at 635 nm, and within 24 h the emission spectrum was dominated by excimer emission (Figure 2c). These results suggest that quenching the blend rapidly to room temperature leads to kinetic trapping of the chromophore molecules in a thermodynamically unstable state, in which a significant portion of the dye remains molecularly dispersed or dissolved. Noting that the whereabouts of subpercent concentrations of additives in phase-separated polymer matrices are extremely difficult to establish by conventional analytic means, we conducted a solubility study with model compounds to support this interpretation. We established that the solubility of **1a** in (unreacted) PTMG (ca. 0.03% w/w at 35 °C) and dibutyl-4,4′-methylenebis(phenylcarbamate)[27] (ca. 0.01% at 35 °C), which was synthesized as a model compound for the hard segment, is much lower than the concentration of the dye in the blends investigated (0.4% w/w).[28] These data support that

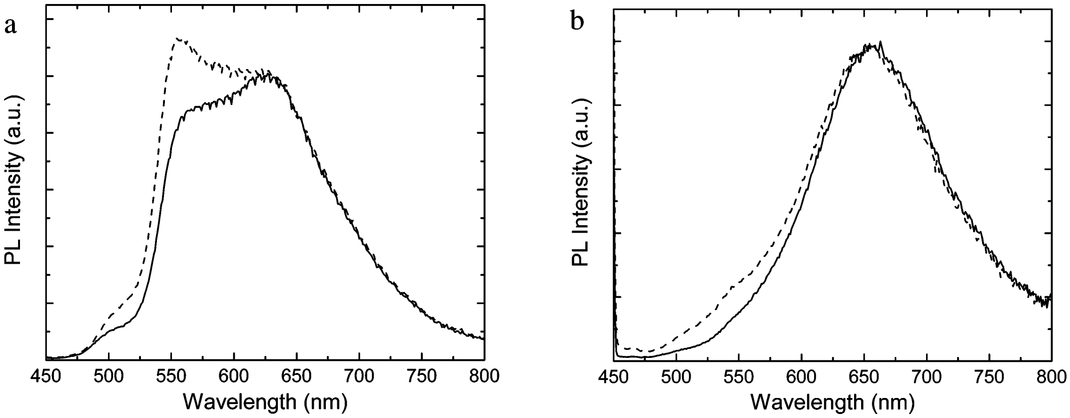
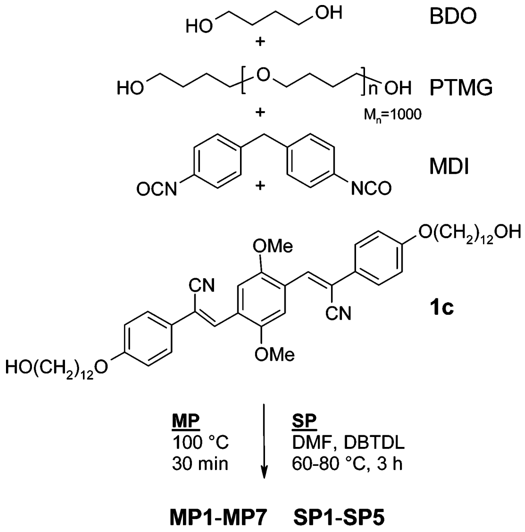


Figure 3. PL emission spectra of appropriately conditioned (see text) blend films of Texin 985 containing 0.4% w/w **1a** (a) or 0.1% w/w **1b** (b) relaxed (solid line) and strained to 300% (dashed line).

the dye must be kinetically trapped in the polymer, presumably in a phase predominantly consisting of polar hard-blocks. Although the molecular mechanism is at this point unclear, mechanical deformation appears to express the dye into soft-segment-rich domains, where high translational mobility and low solubility lead to rapid phase separation. Blends of Texin 985 and 0.2% w/w **1a** display a similar behavior to those of higher concentration, although the extent of excimer emission was lower and phase separation ensued much more slowly. (cf., Supporting Information). As expected, cyano-OPV **1b** displayed a much lower solubility in Texin 985 than **1a**, and rapid phase separation was observed in both quenched and slow-cooled blends comprising up to 0.4% w/w dye (Figure 2d). This was evidenced by the fact that the emission spectra of these blends displayed almost exclusively excimer emission immediately after quenching the samples from the melt, even at dye concentrations as low as 0.05% w/w.

The effect of solid-state tensile deformation of phase-separated blends of Texin 985 and either 0.4% w/w **1a** (quenched, stretched, and stored for 1 day at room temperature) or 0.1% w/w **1b** (quenched and stored 2 days at room temperature) is illustrated in Figure 3. The thermo−mechanical history of these samples was designed to cause the sensor molecules to self-assemble. Indeed, the PL emission spectrum of films comprising 0.4% w/w **1a** shows a strong excimer contribution, and the emission of films comprising 0.1% w/w **1b** is virtually exclusively related to excimers. Unfortunately, however, the emission spectra of these samples displayed only minor changes upon deformation, and the increase of monomer to excimer emission ratio (I_M/I_E) was rather small (Figure 3). This reflects that either the stress experienced by the dye aggregates in these blends is insufficient for their dispersion or that the aggregate size is simply too large to allow for effective dispersion. Indeed, large-scale phase separation in the form of dye sweating (optical microscopy identified dye crystals with a size of the order of 10−50 μm) was eventually observed in the case of all excimer-forming blend compositions investigated here. We reported before that dye aggregates of such dimensions are not suitable for the targeted deformation-sensing approach.[15] Similarly small changes of the emission spectra upon deformation were observed in a separate study focused on blends of cyano-OPVs and an ethylene−octene copolymer with a very low degree of crystallinity and large free volume (unpublished). Thus, it appears that large free volume, low crystallinity, and the absence of nucleation sites favor the formation of large sensor dye aggregates and thus stifle adequate strain-induced dispersion of these sensor molecules if they are incorporated through physical blending.

Scheme 1. Synthesis of TPUs MP1−MP7 and SP1−SP5



Covalent Incorporation of Cyano-OPVs in TPUs. In order to increase the forces experienced by the dye residues during strain and to decrease the chromophore's translational mobility, we elected to incorporate the sensor dyes covalently into the polymer backbone. For this purpose we synthesized 1,4-bis-(α-cyano-4-(12-hydroxydodecyloxy)styryl)-2,5-dimethoxybenzene (**1c**, Figure 1), which through the 12-hydroxydodecyloxy groups can readily be incorporated into a polyurethane. This PL dye was prepared in good yield through the Knoevenagel reaction of (4-(12-hydroxydodecyloxy)-phenyl)acetonitrile with 2,5-dimethoxy-terephthaldehyde (see Experimental Section for details). The emission properties of **1c** (see Supporting Information) are similar to those of **1a** and **1b** and are characterized by green monomer emission in dilute chloroform solution ($\lambda_{max} \approx$ 506, 538 nm) and red excimer emission in the solid state ($\lambda_{max} \approx$ 644 nm). To develop a predictive understanding of how the hard segment content influences the emission characteristics of cyano-OPV-containing TPUs, a first series of polymers was synthesized by the conventional melt polymerization[29] of MDI, PTMG, BDO, and **1c** (Scheme 1). The hard segment (formed by reaction of MDI and BDO) to soft segment (formed by reaction of MDI and PTMG) molar ratio (HS/SS) was systematically varied between 0:1 and 2:1, and the PTMG/**1c** molar ratio was kept constant at 9:1 (**MP1**−**MP5**, Table 1); this led to materials comprising between 6.4% w/w (**MP1**, no hard segment) and 4.0% w/w (**MP5** HS/SS $\approx$ 2:1) of the dye. With the objective to create a TPU that exhibits high toughness and significant excimer emission at the same

Table 1. Composition of the Monomer Feed and Molecular Weights of the TPUs Synthesized

	molar equivalents used[a]				wt %[b]			
polymer	PTMG	**1c**	BDO	MDI	**1c**	HS/SS[c]	M_n[d]	M_w/M_n
MP1	1.8	0.2	0.00	2.08	6.4	0:1	24000	1.6
MP2	1.8	0.2	0.96	3.07	5.6	0.5:1	20000	1.6
MP3	1.8	0.2	1.90	4.05	5.0	1.0:1	87000	1.3
MP4	1.8	0.2	2.83	5.02	4.6	1.4:1	50000	3.2
MP5	1.8	0.2	4.14	6.38	4.0	2.1:1	31000	1.6
MP6	4.0	1.0	7.25	12.7	9.2	1.5:1	47000	1.6
MP7	5.0	0	7.25	12.7	0	1.5:1	55000	1.7
SP1	1.122	0.085	0.000	1.266	4.5	0:1	13700	2.1
SP2	1.122	0.112	1.239	2.564	4.5	1:1	35300	1.4
SP3	1.125	0.125	1.930	3.247	4.5	1.5:1	26400	1.5
SP4	2.000	0.500	3.690	6.250	9	1.5:1	40100	1.8
SP5	2.502	0	3.643	6.329	0	1.5:1	24100	1.3

[a] PTMG = poly(tetramethylene glycol); BDO = butanediol; MDI = 4,4′-methylenebis(phenyl isocyanate). [b] Weight fraction of **1c** in the monomer feed. [c] Molar ratio of the hard and soft segments. [d] M_n = number-average molecular weight determined by GPC. Data reported for the MP series are for the THF-soluble portions.

time (vide infra), a polymer with a similar HS/SS ratio as **MP4** (1.5:1), but twice the dye concentration (9.2% w/w), was synthesized (**MP6**). A reference polymer containing no dye with an HS/SS ratio of 1.5:1 was also synthesized (**MP7**). The reaction conditions employed here are widely used since they readily afford polymers with good mechanical characteristics; however, they are known to lead to branching and/or cross-linking on account of the formation of allophanate, biuret, and isocyanurate groups.[30] Indeed, the melt-polymerized polymers were only partially soluble in common solvents for polyurethanes (DMF, THF), indicative of partial cross-linking due to the slight excess of diisocyanate used and the high reaction temperature. ^{1}H NMR spectra of the soluble portions confirm the chemical structure of the polymers and reveal amine end groups and a small amount of urea linkages (δ = 8.66), both indicative of (partial) isocyanate hydrolysis, which is typical when conducting the reaction under ambient conditions. Gel permeation chromatography (GPC) data of the soluble portions reveal number-average molecular weights, M_n, between 20 000 and 87 000 and polydispersity indices (PDI) between 1.3 and 3.2 (Table 1). In order to also investigate better-defined, linear (non-cross-linked) polymers and to further investigate the influence of the HS/SS ratio at a constant dye concentration on the emission characteristics, a second series of TPUs was synthesized via solution polymerization in DMF with dibutyltin dilaurate (DBTDL) as a catalyst. In this case, HS/SS was varied between 0:1 and 1.5:1 and the weight fraction of **1c** was kept constant at a level of 4.5% w/w (**SP1**−**SP3**, Table 1). A polymer similar to **MP6** having the same HS/SS ratio as **SP3** (1.5:1) but twice the dye concentration (9.0% w/w) was also synthesized (**SP4**) as well as a reference polymer with no dye (**SP5**). All polymers from this series were completely soluble in DMF and THF. ^{1}H NMR spectra confirm their chemical structure, reveal amine end groups, and indicate the presence of some urea linkages (δ = 8.66). GPC data reveal slightly lower M_n (13 700−40 000) and PDI (1.3−2.1, Table 1) than the representatives of the **MP** series, indicating that the higher structural purity of the members of this series comes at the expense of a somewhat lower molecular weight.

The phase behavior of the new TPUs was studied by means of differential scanning calorimetry (DSC). A comparison of first (see the Supporting Information) and second heating scans of pressed, quenched TPU films for the entire series of polymers reveals that, not surprisingly, the heat flow observed in the DSC experiments is dependent on the sample's thermal history. DSC traces of the second heating scans of both polymer series, acquired after first heating the polymers to 250 °C and cooling them to 0 °C at a rate of 10 °C/min, are shown in Figure 4. The traces of the reference polymers containing no dye (**SP5**, **MP7**) show broad endothermic peaks around 160 and 190 °C, respectively, which are characteristic for TPUs based on MDI and BDO and in the light of previous studies can be assigned to the melting or disordering of MDI−BDO hard segments.[31] The DSC scans of the polymers containing no BDO chain extender (**SP1**, **MP1**) display a broad endothermic peak at 104 and 107 °C, respectively; these transitions can also be observed in the first heating scans (see Supporting Information), although at slightly different temperatures. Previous studies have shown that TPUs based on MDI and PTMG without chain extender do not display any thermal transitions above ca. −40 °C, where a glass transition is observed.[32,33] Thus, the broad endotherms observed in the case of **SP1** and **MP1** appear to reflect the melting or disordering of domains of hard segments formed by the reaction of MDI and **1c**. This interpretation was confirmed by temperature-dependent optical experiments (vide infra). All polymers comprising dye **1c** and chain extender BDO (**SP2**, **SP3**, **SP4**, **MP2**, **MP3**, **MP4**, **MP5**, and **MP6)** show a broad endothermic transition (with occasional shoulders) that is between the ones observed for the polymers without MDI and without dye. The temperature at which this transition occurs generally increases with the HS/SS ratio, presumably on account of the formation of larger and/or better organized hard segments. The **MP** polymers generally display somewhat lower transition temperatures than the corresponding **SP** polymers, consistent

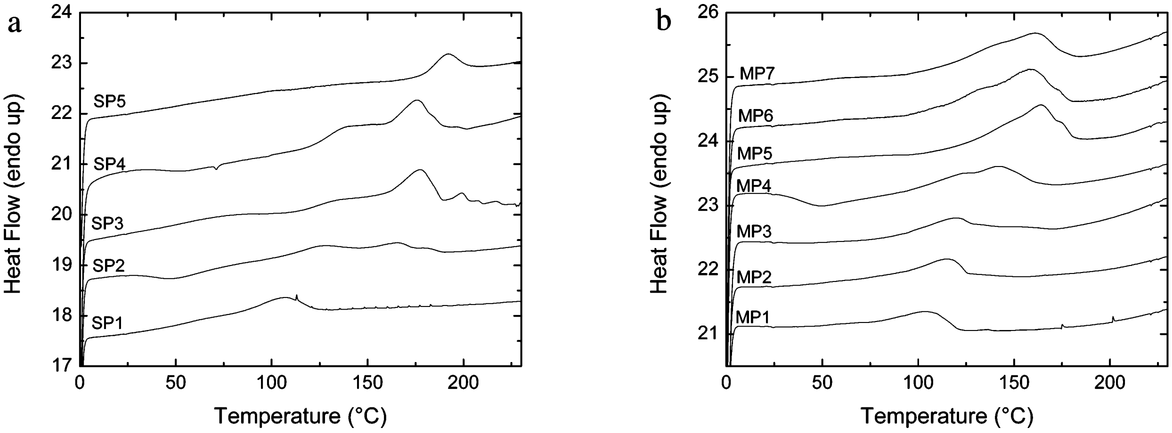


Figure 4. DSC traces showing the second heating of **SP1**−**SP5** (a) and **MP1**−**MP7** (b). All experiments were conducted under N_2 at a heating rate of 10 °C/min.

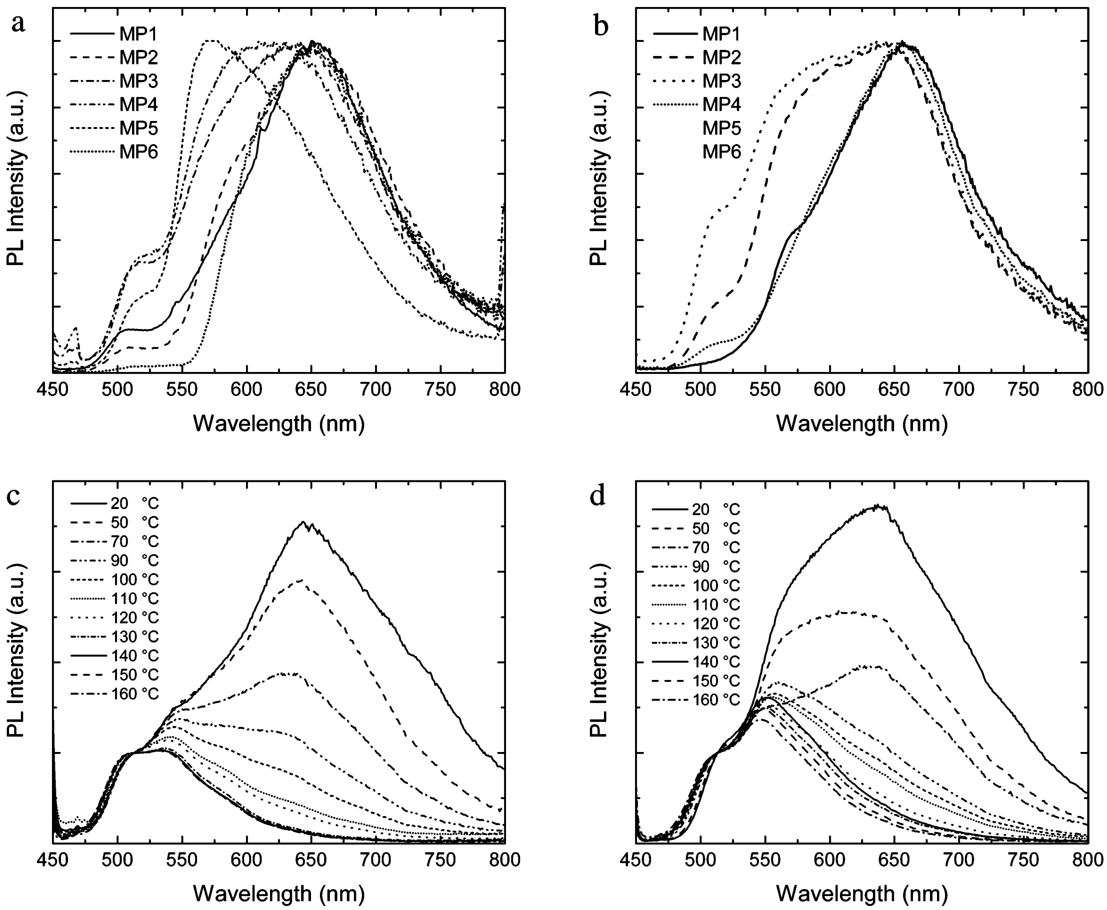


Figure 5. Steady-state PL emission spectra of freshly quenched films of cyano-OPV-comprising TPUs **MP1**−**MP6** (a) and **SP1**−**SP4** at room temperature (b). Steady-state PL emission spectra of **MP1** (c) and **MP6** (d) as a function of temperature; samples used for the variable temperature experiments had previously been cooled from 200 °C to room temperature at a rate of 10 °C/min.

with the slightly cross-linked/branched nature of the former, which reduces the hard segments' degree of organization.

Due to the optical absorption of the cyano-OPV chromophore ($\lambda_{\max} \approx 435$ nm in $CHCl_3$ solution),[19] all TPUs comprising **1c** were orange. Steady-state PL spectroscopy of compression-molded, quenched films of both melt-polymerized (**MP1**−**MP6**) and solution-polymerized (**SP1**−**SP4**) TPUs reveals that all of the new polymers (except **MP5**, vide infra) display a combination of monomer and excimer emission (Figure 5, parts a and b). Expectedly, polymers of the same composition prepared by the two different protocols (e.g., **MP4** vs **SP3**) exhibit very similar optical properties. **MP5** features the lowest dye content (4.0% w/w) and the highest HS/SS ratio (2.1:1) of the polymers synthesized and displays an emission spectrum that is based virtually exclusively on monomer emission. The spectra shown in Figure 5, parts a and b, reveal that I_M/I_E of freshly prepared films decreases, as expected, with increasing dye concentration (e.g., **MP6** vs **MP4**, **SP4** vs **SP3**) and increases with the HS/SS ratio (e.g., **MP5** vs **MP1**, **SP3** vs **SP1**). The observed increase of I_M/I_E at higher HS content is consistent with the stifled aggregation of the dye molecules due to the reduced translational mobility of these moieties that arises from their covalent incorporation in the polymer backbone. This effect can, however, be compensated by an increase of the dye concentration (e.g., **MP6** vs **MP4**, **SP4** vs **SP3**). Only minor changes in the emission spectra were observed for all films upon storage at room temperature over a period of several months (cf., the Supporting Information).

To gain some insight about the microstructure of the new TPUs, we investigated the PL spectra of selected samples as a function of temperature. As discussed above, the DSC scan of **MP1**, which contains no BDO chain extender, displays a broad endothermic peak at 104 °C, which we tentatively assigned to the melting or disordering of hard segments formed by the reaction of MDI and **1c**. This interpretation is supported by the temperature-dependent PL spectra of **MP1** shown in Figure 5c; note that the samples used for this study were first heated to 200 °C and cooled at a rate of 10 °C/min to impart a similar thermal history as in the second heating scans of the DSC experiments. Below ca. 70 °C the PL spectra of **MP1** are dominated by excimer emission, which is indicative of the formation of ground-state aggregates of the cyano-OPV moieties. As can be seen from the temperature series, the contribution of monomer emission in **MP1** increases with increasing temperature until above ca. 110 °C the PL spectra are virtually exclusively due to monomer emission. The temperature range in which this transition occurs matches with that of the broad endothermic peak observed by DSC, suggesting a direct relation between dye deaggregation and thermal transition. A similar series of PL spectra was acquired for **MP6** (Figure 5d). Also in this case, the contribution of monomer emission increases with increasing temperature. Interestingly, the temperature regime in which a change from excimer to monomer emission is observed coincides better with that of **MP1** than the high-temperature DSC endotherm (in the range of 100−180 °C). Since the polymers were made by a one-step polymerization, the cyano-OPV and the BDO residues must be part of the same population of hard segments. Thus, the experiment seems to suggest that the OPV segments can favorably position themselves (perhaps driven by $\pi-\pi$ interactions and/or polar/

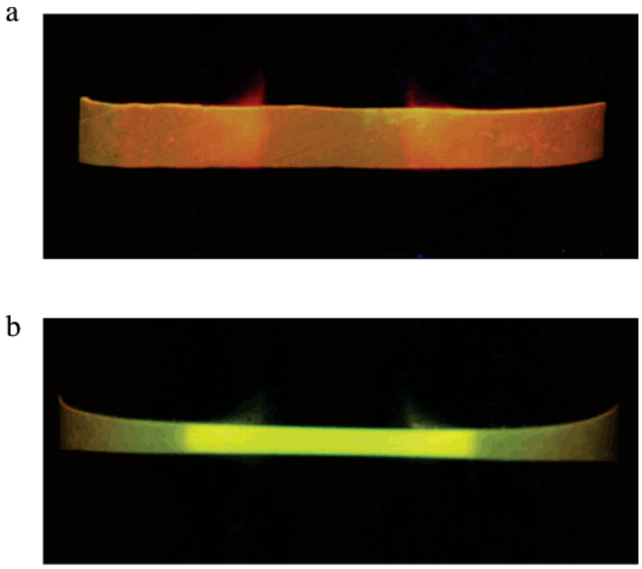


Figure 6. Pictures (taken under excitation with UV light of a wavelength of 365 nm) of a film of **MP6** in unstretched (a) and stretched (b) state.

nonpolar interactions) within domains formed by the hard segments to form ground-state aggregates that are responsible for excimer emission. These ground-state aggregates, however, can dissociate at temperatures lower than required for the melting or disordering of the hard segment domains. Gratifyingly, all of the new cyano-OPV-containing TPUs (except **MP5**, which did not display any excimer emission) changed their PL color upon mechanical treatment. **MP1** and **SP1**, which were void of MDI−BDO hard segments and appeared at room temperature as highly viscous, plastic semisolids, displayed dominant excimer emission. If these materials were sheared under extensional flow between two glass slides, the PL emission changed from red to green (not shown). After the shearing was stopped, the PL color quickly (∼2 s) turned back to red, without any mechanical relaxation of the materials. This effect reflects that the hard segments formed by the reaction of MDI and **1c** rely on comparatively weak intermolecular forces, probably a combination of hydrogen bonding and $\pi-\pi$ interactions. It is important to note that the PL spectra of **MP1** and **SP1** (Figure 5) virtually exclusively display excimer emission, indicating a high degree of phase separation between soft segment and hard segment domains in which a majority of the OPV segments can favorably position themselves to form excimers. These self-assembled aggregates of **1c** residues are readily dispersed by external mechanical forces as unequivocally demonstrated by the observed transformation from excimer- to monomer-dominated fluorescence. The rapid reaggregation reflects a rather high translational mobility of the dye residues. A detailed investigation of this reversible solid-state self-assembly process is currently under way. In case of **MP4** and **SP3** a clearly detectable PL color change from orange to green was observed when films were stretched (data not shown), but the contrast was limited due to the relatively low contribution of excimer emission in the unstretched state. The increased dye concentration in **MP6** and **SP4** led to materials which in the unstretched state displayed a significant contribution of excimer emission, similar to that observed in **MP1** and **SP1** (Figure 5, parts a and b). Deformation of both **MP6** and **SP4** resulted in a most pronounced change of the PL color from an orange-red, excimer-dominated emission to a green fluorescence that is characteristic of molecularly dispersed chromophores (Figure 6, see Supporting Information for a movie showing the mechanochromic response of **MP6**). Thus, the covalent incorporation of **1c** into the polyurethane backbone indeed allows for the production of chromogenic PL elastomers, which change their emission color as a function of applied strain. In the polymers comprising BDO the phase separation appears to be largely driven by interurethane hydrogen bonding. Within the resulting hard segment domains, some of the OPV segments are positioned to form electronic ground-state aggregates and lead to excimer emission. Large-scale phase separation of the sensor dye (as observed for the physical blends) is suppressed by the covalent integration of the chromophores into the polymer backbone. Mechanical strain pulls some of these hard segments out of the domains, thereby dispersing the ground-state aggregates of the **1c** residues and enhancing the relative magnitude of monomer emission.

In order to investigate the deformation-induced color change in a more quantitative manner, we conducted in situ opto−mechanical studies using a modified rheometer in connection with a PL spectrometer (see the Experimental Section for details). The setup enabled us to measure the stress−strain behavior of the material while maintaining the center of the stretch zone in a fixed location and thus allowed the emission characteristics to be monitored simultaneously. Figure 7 shows I_M/I_E (measured at 540 and 650 nm) and tensile stress for films of **SP4** and **MP6** as a function of strain. A comparison of the stress−strain curves reveals that these polymers, which are of very similar composition, display the same initial modulus (40 MPa) and yield stress (7.5 MPa). **MP6**, however, is much tougher than **SP4** and reproducibly breaks at a much higher stress (∼65 MPa) than the solution-polymerized analogue which has a stress at break of ∼23 MPa. The higher toughness of **MP6** is consistent with the observed branching/cross-linking of the melt-polymerized TPUs as well as their higher molecular weight compared to that of the solution-polymerized materials. A striking correlation between emission color, expressed by I_M/I_E, and applied stress is observed in both cases. In the relaxed state, **SP4** and **MP6** feature comparable I_M/I_E values of 0.8 and 1.3, respectively. A superimposition of I_M/I_E−strain and stress−strain curves of **SP4** (Figure 7a) reveals that the mechanochromic response mirrors the stress−strain curves almost perfectly until the samples break at a strain of ∼600%. **MP6** shows the same behavior; however, due to the higher toughness of this material, the color change of this polymer (at similar strains) is much more pronounced (higher I_M/I_E) than in case of **SP4**. The reversibility of the mechanochromic PL/stress response of **MP6** was studied by subjecting samples to a cyclic triangular strain pattern where the strains was continuously varied between 100% and 500% at a frequency of 0.0125 Hz (Figure 8). In this experiment, the PL response was again found to nicely mirror the stress−strain response of the polymer. Even the maxima of both I_M/I_E and stress decreased in a similar manner as the polymer relaxed with subsequent cycles. The reversible nature of the change in emission color of the sample between stretched ($I_M/I_E = 1.3-1.7$) and unstretched ($I_M/I_E = 0.9-1.0$) states is also nicely illustrated by the return of I_M/I_E to close to its initial value of 0.8 in the unstretched state. Thus, the covalent incorporation of the π-conjugated sensor molecules into the TPU backbone appears, as targeted, to increase the forces experienced by the dye aggregates during strain, to decrease the chromophore's translational mobility, and to limit the size of the dye aggregates upon self-assembly. As a result, the new cyano-OPV-containing TPUs display a very pronounced mechanochromic photoluminescent effect in which the emission color is largely coupled to the applied strain.

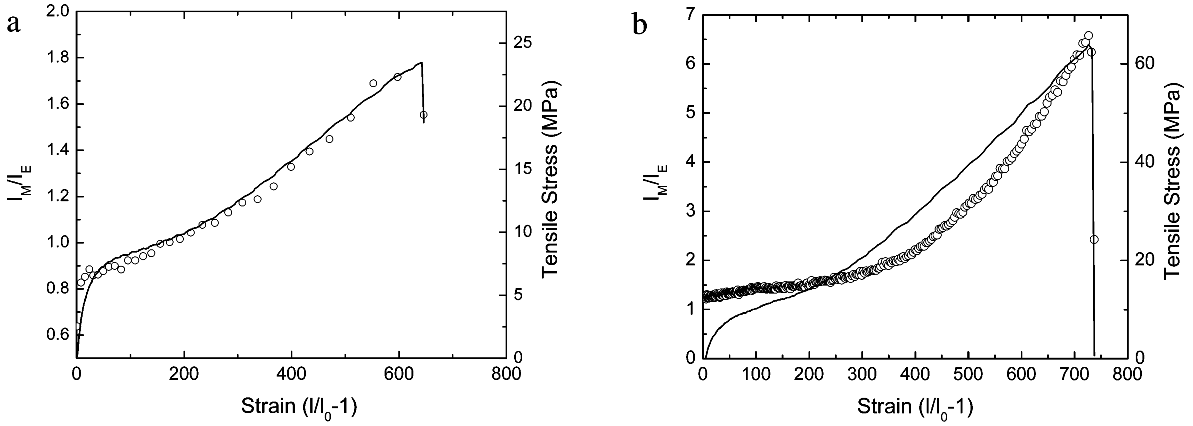


Figure 7. Ratio of monomer to excimer emission, I_M/I_E (circles, measured at 540 and 650 nm), and tensile stress (solid line) as a function of strain for films of **SP4** (a) and **MP6** (b). PL data were extracted from uncorrected emission spectra acquired under excitation at 480 nm.

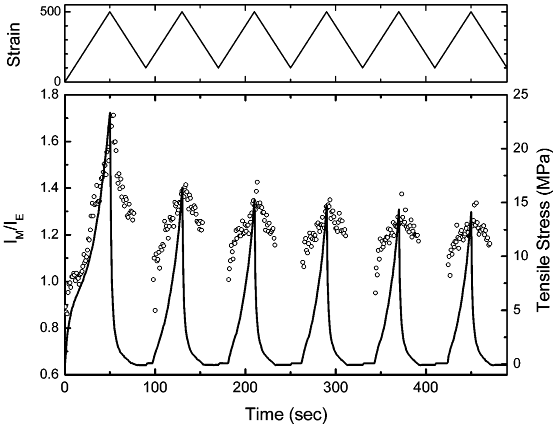


Figure 8. Ratio of monomer to excimer emission, I_M/I_E (circles, measured at 540 and 650 nm), and tensile stress (solid line) for **MP6** under a triangular strain cycle between 100% and 500% at frequency of 0.0125 Hz. PL data were extracted from uncorrected emission spectra acquired under excitation at 480 nm. Accurate I_M/I_E values could only be obtained for stresses greater than 1 MPa (at which the sample was taut and reliable spectra were obtained); data at lower stresses were omitted.

Conclusions

In conclusion, we investigated two new types of mechanochromic, photoluminescent TPUs, which comprise cyano-OPV dyes as built-in deformation sensors. Binary blends of conventional MDI/BDO/PTMG-based TPUs and small amounts (0.05−0.4% w/w) of cyano-OPVs were prepared by melt processing. The phase behavior and emission characteristics of these materials could be controlled via the composition, the substituents attached to the dyes, and the processing protocol. It was shown that the blends can be kinetically trapped so that the cyano-OPV molecules are largely molecularly dispersed. Mechanical deformation of these systems led to irreversible phase separation as evidenced by the PL color change. While this effect is useful for “one-time-stretch” sensing applications, the thermodynamic equilibrium of the investigated blends ultimately lead to large-scale phase separation, which stifles the polymer’s mechanochromic response.

The covalent integration of cyano-OPVs into the TPU’s backbone led to materials in which large-scale phase separation of the dye is prevented, while the formation of a large population of (presumably very small) ground-state dye aggregates is still allowed. Consequently, these polymers display predominantly excimer emission in the unstretched state and exhibit a pronounced fluorescence color change upon deformation. This change was largely reversible and mirrored the stress−strain curves of the material. The stimuli-responsive properties displayed by the materials systems investigated appear to bear significant potential for wide technological application, in particular the use of such dyes as “built-in” stress−strain sensors.

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Supporting Information Available: Detailed synthetic procedures of polymers **MP1**−**MP5**, **MP7**, **SP1**−**SP3**, and **SP5**; ^{1}H NMR spectra of Texin 985, **MP1**−**MP7**, and **SP1**−**SP5**; DSC traces (first heating scans) of **MP1**−**MP7** and **SP1**−**SP5**; solubility experiments of **1c** in PTMG and dibutyl-4,4′-methylenebis(phenylcarbamate); PL emission spectra of a chloroform solution and “as synthesized” crystals of **1c**; PL emission spectra of a blend film of Texin 985 containing 0.2% w/w **1a** cooled slowly from the melt; PL emission spectra of **SP1**−**SP4** and **MP1**−**MP6** after storage at ambient; movie of the mechanochromic response of **MP6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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