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Reversible Mechanochromism of a Luminescent Elastomer

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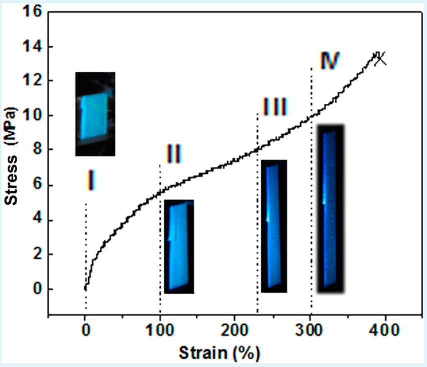
ABSTRACT: A novel mechanochromic elastomer was manufactured by doping bis(benzoxazolyl)stibene (BBS) into a thermoplastic polyurethane. Both solution casting and melt compounding approaches were tried with a range of BBS concentrations, and an optimal concentration of 0.5% was selected to investigate the mechanochromic mechanism in detail. When the blend film was stretched up to 100%, its emission peaks at 475 and 413 nm changed in intensity ratio from 6.3 to 1.8. When it was released, both the film size and emission peaks largely recovered. By a short annealing at 120 °C, their full recovery was achieved. Its reversion mechanism was proposed and proved by X-ray diffraction. In comparison to previous mechanochromic materials, this smart elastomer is easy to prepare, highly sensitive to stress, facilely renewable in usage, and totally based on biocompatible materials, having potential applications like stress sensors, intelligent devices, and alarming packages.



KEYWORDS: *mechanochromism, luminescence, elastomer, X-ray diffraction, stress sensor*

■ INTRODUCTION

Smart chromatic response to external stimuli is attracting growing interest from material researchers.[1−6] Mechanochemical transduction enables an extraordinary range of physiological processes, which has inspired the development of mechanically sensitive materials. Novel mechanochromic materials have been creatively synthesized by a few groups. In Davis group, spiropyran mechanophores were incorporated into elastomeric poly(methyl acrylate) (PMA) or plastic poly(methyl methacrylate) (PMMA) as a chain unit or a cross-linker, by which evident color changes were achieved under both tension and compression.[7] In Chen group, a bis(adamantyl)-1,2-dioxetane unit was incorporated into PMA as a chain unit or a cross-linker. The resultant materials showed a temporal visible luminescence upon stretching activation, and their luminescence intensity and color were finely adjusted by energy transfer to suitable acceptors.[8]

However, the chemical synthesis route requires special skills and critical conditions. Physical doping was developed as an easier route to manufacture mechanochromic materials. A few crystalline plastics were doped with special dyes, like oligo(*p*-phenylene vinylene) and stilbene derivatives, and demonstrated strain-responsive color change.[9,10] These special dyes were termed as aggregachromic dyes, because their fluorescence peaks moved to longer wavelengths upon aggregation.[11,12] The mechanochromic response of these plastics only started upon yielding, and increased with further elongation, because the rupture of dye aggregates greatly depended on the deformation and breakage of polymer crystallites.[11,12] The higher polymer crystallinity supported the more pronounced chromatic response. Competing with traditional covalent linking method, this physical blending approach has prevailed as a more facile route for the industrial scale-up. However, all the success is still limited in plastic materials with a high crystallinity, such as polyethylene, polypropylene, and poly(vinylidene fluoride), which chromatic response is irreversible.[12−14]

Here we report a reversibly mechanochromic elastomer with an aggregachromic dopant. In this case, a strong association between dye and polymer molecules is a prerequisite to obtain the desired mechanochromic property. Otherwise, the rearrangement of polymer chains would not rupture the preexistent dye aggregates. Therefore, a highly aromatic dye, bis(benzoxazolyl)stibene (BBS), was selected to associate with a thermoplastic polyurethane (TPU), Estane 2103−90AE from Lubrizol Inc. (chemical structures are shown in Scheme 1). Both of them are biocompatible and commercially available materials, allowing safe applications in wide range of products.[10,15]

■ RESULTS AND DISCUSSION

Fourier-transformed infrared spectra (FTIR) of blend films and pure TPU were measured and shown in Figure 1. Both the solution-cast and the melt-compounded blends showed obvious and similar changes. Upon doping BBS, the TPU N−H peak at 3334 $\mathrm{cm^{-1}}$ shifted to a lower wavenumber 3300 $\mathrm{cm^{-1}}$; the TPU C−H peak at 2940 $\mathrm{cm^{-1}}$ shifted to 2915 $\mathrm{cm^{-1}}$; the benzene peaks at 1600 and 1531 $\mathrm{cm^{-1}}$ changed much in intensity ratio. All these changes in FTIR peaks supported the $\pi-\pi$ coupling and hydrogen bonding interaction between the conjugated planar BBS molecules and the aromatic benzene and carbamate groups of TPU.[16] The melt-compounded TPU/BBS was stretched by 100% and relaxed, then measured again by

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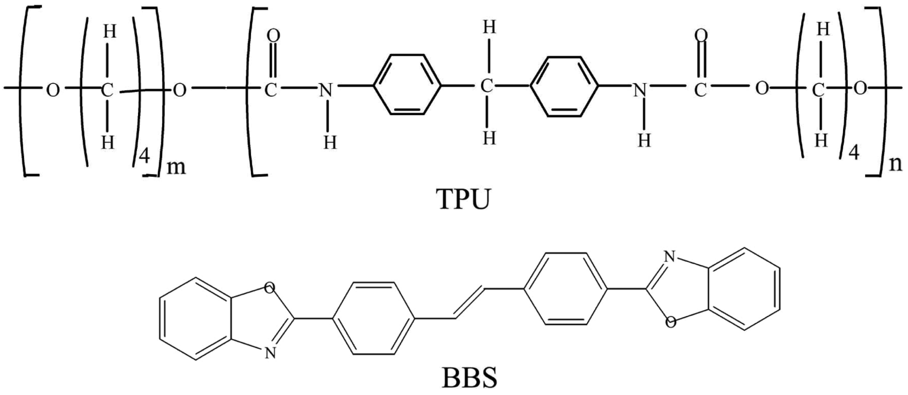
Scheme 1. Chemical Structures of Molecules TPU and BBS



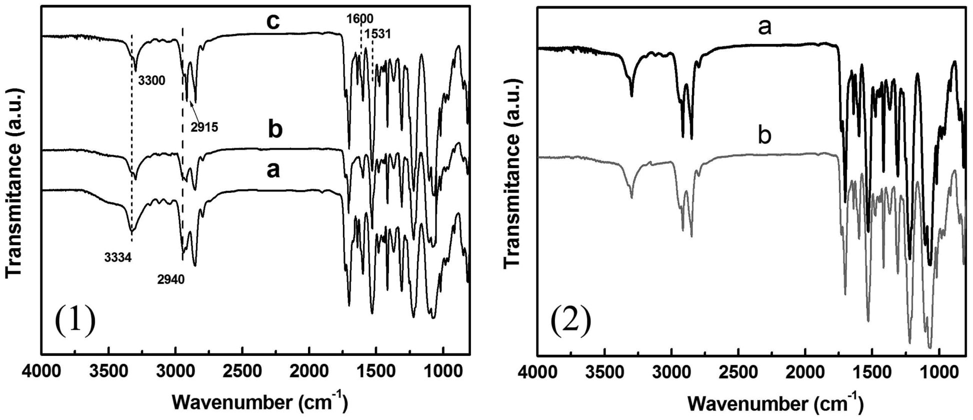


Figure 1. FTIR spectra of (1a) pure TPU, (1b) TPU/0.5%BBS prepared by solution casting, or (1c, 2a) melt compounding, and (2b) the melt-compounded TPU/0.5%BBS after a 100% stretch−relax cycle.

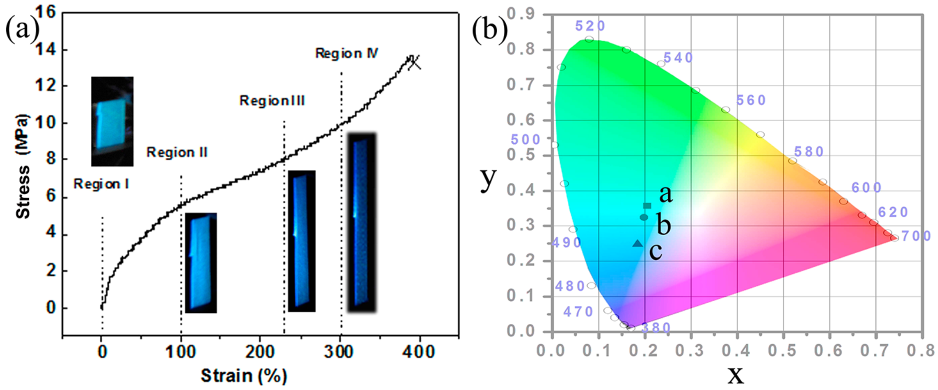


Figure 2. (a) Typical stress−strain curve of the solution-cast film TPU/0.5%BBS together with its photos under a UV light corresponding to different strain values; (b) Representative colors of the film at different strains (a, 0; b, 10%; c, 100%) are located in the CIE chromaticity diagram.

FTIR. The obtained IR spectrum showed no difference from that of original film. This result supported that the stretch deformation of TPU matrix did not break significantly the association between TPU chains and BBS molecules.

To check its mechanochromic property, the solution-cast TPU/0.5%BBS film was stretched on a tensile machine and observed under a 365 nm UV light. At the beginning, the film gave a cyan image. Upon stretching, its color gradually turned blue, and reached a dark blue before its failure (shown in Figure 2a). To locate the changing colors in a CIE chromaticity diagram, the fluorescent film was precisely measured with a 2D color analyzer in a standard light booth. As shown in Figure 2b, the color of the initial TPU/0.5%BBS was located in a cyan region ($x = 0.205$, $y = 0.357$). During a tensile deformation, its CIE coordinates moved to a blue region ($x = 0.198$, $y = 0.324$) at a 10% strain, and further to the point ($x = 0.184$, $y = 0.248$) at a 100% strain. Apparently, this composite showed a cyan-to-blue shift in the CIE diagram with its tensile strain increasing. To record the color change more precisely, we also operated the stretching within a fluorescence spectrometer (FLS 920P, Edinburgh Instruments, UK), where only a few steps were achieved due to the limitation of our sample holder attached in the spectrometer.

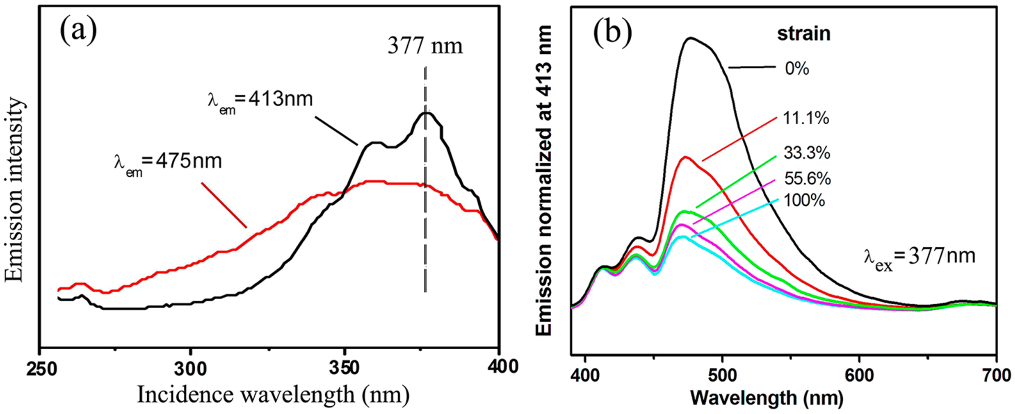


Figure 3. (a) Excitation spectra of the solution-cast TPU/0.5%BBS film with emission detected at 413 and 475 nm, respectively; (b) emission spectra of the film at various strains.

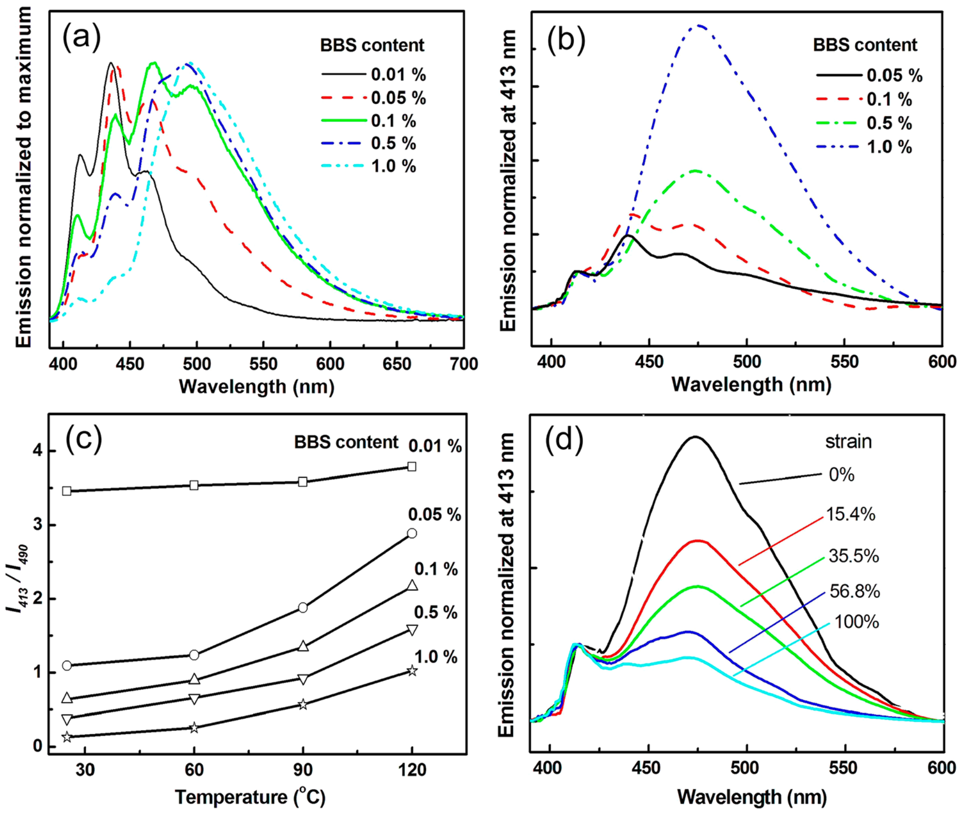


Figure 4. (a) Emission spectra of solution-cast TPU/BBS films excited at 377 nm; (b) emission spectra of melt-compounded TPU/BBS films excited at 377 nm; (c) ratio I_{413}/I_{490} of solution-cast TPU/BBS films at different temperatures; (d) emission spectra of the melt-compounded TPU/0.5%BBS film at various strains.

As shown in Figure 3b, excited at 377 nm, the solution-cast TPU/0.5%BBS film annealed at 120 °C gave three emission peaks at 413, 436, and 475 nm. The peak at the shortest wavelength was attributed to isolated BBS molecules (monomers), while the peaks at longer wavelengths were assigned to suitable aggregation units (excimers) of BBS.[11,12] The excitation spectra of original film were also recorded by monitoring the emissions at 413 and 475 nm, respectively. As shown in Figure 3a, they supported 377 nm as a suitable excitation wavelength for both isolated molecule and aggregation unit. Upon stretching, the blend film gave a series of fluorescence spectra with constant peak wavelengths and changing intensity distribution. For comparison, all the fluorescence spectra were normalized by the 413 nm peak. Regarding the excimer band at 475 nm, its relative intensity continuously reduced with the film extension increasing, indicating the rupture of BBS aggregates during the TPU stretch.

The effect of BBS concentration on the blend fluorescence property was also investigated, to analyze the solubility of BBS in TPU matrix. The tried BBS content covered a range of 0.01−1.0% on weight of TPU, and all the samples had been annealed at 100 °C before measurement (Figure 4a). At low BBS contents of 0.01, 0.05, and 0.1%, four emission peaks were clearly observed at 413, 436, 465, and 490 nm, indicating the complexity of the fluorescent species in the blends. When BBS

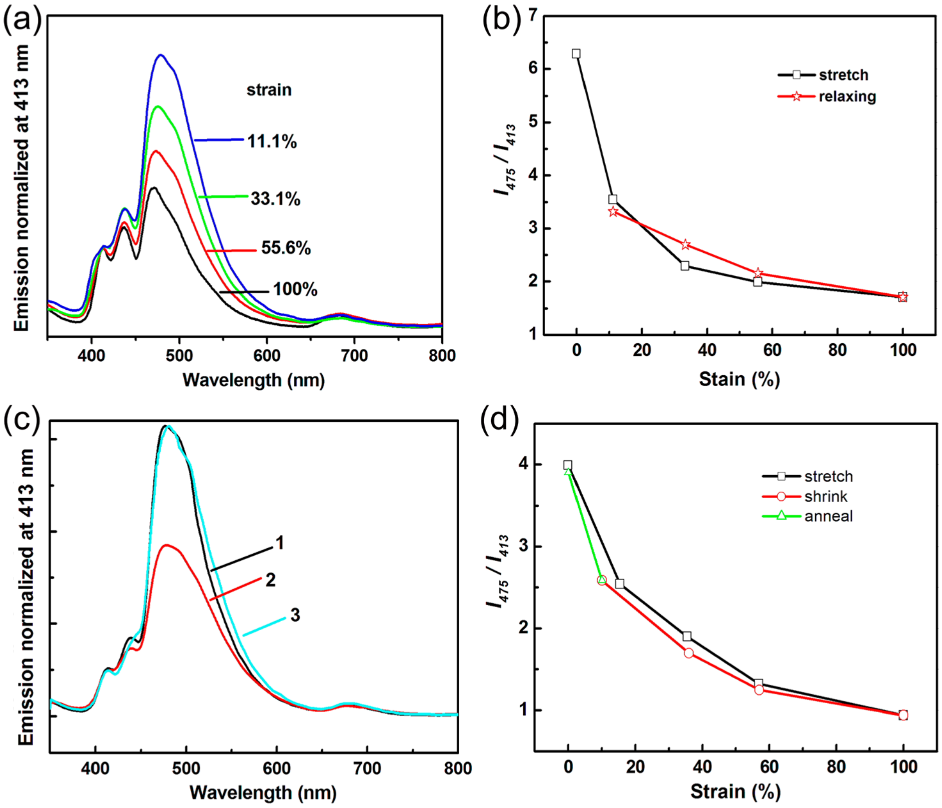


Figure 5. Solution-cast TPU/0.5%BBS film: (a) its emission spectra at various strains during shrink process; (b) its emission ratio I_{475}/I_{413} vs strains during a cycle of stretch and shrink; (c) its emission spectra before stretch (1), after a cycle of stretch and shrink (2), and after a further post treatment at 120 °C for 1 min (3). The melt-compounded TPU/0.5%BBS film: (d) its emission ratio I_{475}/I_{413} vs strains during a full cycle.

content reached up to 0.5 and 1.0%, the emission at 490 nm became the predominant feature. So, our tension experiments mainly focused on the TPU/0.5%BBS blend. In comparison to the previous TPU/0.5%BBS film annealed at 120 °C, annealing at 100 °C gave discernible peaks at 465 and 490 nm and relative intense emissions at 413 and 436 nm. In contrast, annealing at 120 °C caused conversion from monomers (413 nm) to excimers (465 and 490 nm) and fusion of 465 and 490 nm peaks into the 475 nm peak. The excimer emission at 490 nm was observed for all the concentrations, showing higher area percentage for more BBS content. A clear solubility limit cannot be deduced from these data, since multiemissions were produced even at the lowest BBS concentration of 0.01%. To quantitatively assess the population ratio between BBS monomer and excimer, we calculated the ratios between film luminescence intensities at 413 and 490 nm (I_{413}/I_{490}) for all the blends at several temporal temperatures, as illustrated in Figure 4c. It monotonically decreased with the BBS content increasing. At the lowest concentration 0.01%, the ratio was almost unaffected by the temperature change. At higher concentrations, the ratio showed evident increase with increasing temperature from 25 to 120 °C, at which monomer emission became the predominant peak. For the TPU/0.5% BBS blend, I_{413}/I_{490} increased from 0.38 up to 1.58. It should be noted that this temporal heating treatment gives an effect much different from that of long-term annealing. Considering that these temperatures were much lower than the BBS T_m (over 300 °C) and the TPU has a T_g of −34 °C and a T_m of 190 °C,[12,18] we attribute the ratio increment to the volume expansion of amorphous phase rather than melting of crystallites or molecular solubility.

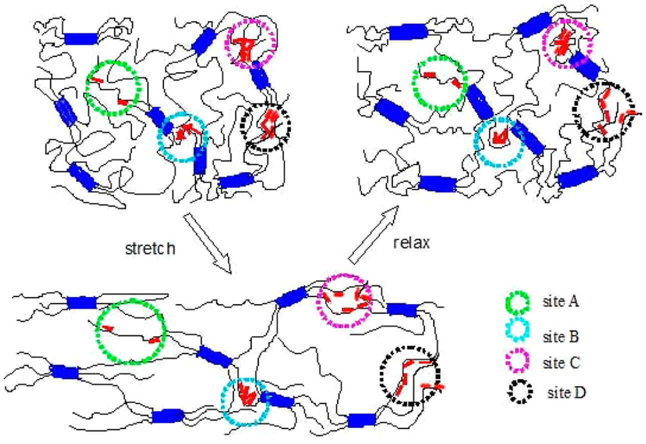
Melt-compounded TPU/BBS blends were also assessed in fluorescence properties (Figure 4b). The blends with 0.05% and 0.1% BBS showed three obvious emissions at 413, 436, and 465 nm, whereas blends with 0.5% and 1.0% BBS showed only a weak peak at 413 nm and a intense peak at 475 nm. The TPU/0.5% BBS film was further studied by stretching. Upon stretch, the excimer peak at 475 nm also monotonically reduced in intensity, as shown in Figure 4d. It presented a similar trend to that of solution-cast films.

Being different from previous mechanochromic plastics, this TPU can spontaneously shrink back after removing the tension force. This reversion in dimension might lead to a reversion of its fluorescence property. By stepwise controlling the film shrink, the fluorescence spectra of shrank film were recorded in several stages (Figure 5a). Clearly, the excimer band gradually recovered to higher intensity along with the film shrink. This is an attractive advantage over the previous composite.[11,12] Although a reversible mechanochromic material has been reported, it required critical synthesis conditions and specially designed monomers, thus was not as facile as this doping method.[17] In that report, the dyes cyano-substituted oligo(*p*-phenylene vinylene) derivatives (cyano-OPVs) were incorporated into thermoplastic polyurethanes (Texin 985 and self-synthesized) by melt blending and covalent bonding, respectively. For the physical blends of Texin 985 and cyano-OPVs, their mechanically induced fluorescence change was very little and irreversible. In contrast, self-synthesized TPUs containing cyano-OPVs units showed obvious and reversible fluorescence change. However, the covalent incorporation of dye molecules into TPU backbones limited the size of dye aggregates resultant from self-assembly in TPU matrix. During a cyclic triangular strain, the fluorescent signals correlated with the strain changes in some degree, which was mainly limited in the high strain regions. In comparison with the Texin 985 with T_g of −71 °C, our TPU (Estane 2103−90AE) has a higher T_g of −34 °C,[18] indicating that Estane product has a higher content of 4,4′-methylene-bis(phenyl isocyanate) (MDI), which provides more coupling sites for conjugated dyes. Compared to the cyano-OPVs, our dye BBS can form additional hydrogen bonding with TPU. Therefore, this dope system Estane/BBS had a better performance than the previous Texin/cyano-OPVs.

The film luminescence intensity ratios I_{475}/I_{413} were calculated and drawn against film strains in Figure 5b. Upon stretching to 100%, the I_{475}/I_{413} value reduced from original 6.3 to 1.8, indicating the rupture of BBS aggregates into isolated molecules. After the elastic shrink of released film, the value recovered to 3.3 at a residual strain of 11%, which indicated the reaggregation of BBS molecules in TPU matrix. However, the film shrink stopped at a strain of 11% rather than fully recovered, and the ratio I_{475}/I_{413} also did not return to its initial level.

To clearly analyze the smart mechanochromic mechanism, we illustrated several possible behaviors of BBS molecules during the TPU matrix deformation in Scheme 2. The TPU matrix consists of a few crystallites (the blue rectangles) and massive amorphous regions (the black lines), wherein the crystallites act as physical cross-links that allow the reshape of TPU above its melting point (190 °C for Estane 2103−90AE).[18] The TPU hard segments tend to form the crystallites and leave soft segments in the amorphous phase. However, TPU's crystallites are much smaller and less regular than that of common plastics, even difficult to detect by XRD (as shown in Figure 6a). Some aromatic hard units cannot enter the crystalline regions, still disperse in the amorphous phase and provide anchoring points for BBS molecules. Since alien molecules cannot be involved in the polymer crystalline phase, the added BBS molecules totally present in the amorphous phase or at the interface between crystalline and amorphous phases. Upon a stretch, the orientation of TPU chains induces the rearrangement of BBS molecules due to the strong association between BBS and TPU aromatic units, as approved by the above FTIR spectra. Four possible behaviors (A, B, C, and D) of BBS molecules are considered during the matrix rearrangement. In type A, the isolated BBS molecules remain isolated through the tension and release stages. This section is low, based on the beginning ratio I_{475}/I_{413} of 6.3. In type B, BBS exists as an aggregate through the whole deformation process. This fraction is not high too, deduced from the ratio I_{475}/I_{413} of 1.8 at the strain of 100%. In type C, the BBS aggregate ruptures into isolated molecules upon tension and reaggregates along with shrink. This group contributes to the change of I_{475}/I_{413} from 1.8 back to 3.3. In type D, the BBS aggregate breaks into monomers under tension and remains isolated even after the stress release, due because of the residual strain of TPU matrix. This group impedes a full recovery, and corresponds to difference between the start ratio 6.3 and the end ratio 3.3. Type A and B contribute nothing to the mechanochromic response.

Scheme 2. Schematic Illustration of the BBS Distribution in TPU Matrix during a Cycle of Stretch and Shrink: Big Rectangles are TPU Crystallites; Thin Lines are TPU Chains in Amorphous Area; Small Rods Represent BBS Molecules



This proposed change of BBS aggregates was approved by X-ray diffraction measurement of solution-cast TPU/0.5%BBS film (XRD, Philips Xpert XRD system). As shown in Figure 6a, diffraction peaks of BBS aggregates were clearly detected at 12, 18, and 24°, whereas diffraction peak of TPU crystallites was not observed, indicating the low crystallinity and small crystal size of TPU matrix. Upon stretching by 50 and 100%, the BBS peaks reduced and even disappeared finally. It indicated a significant reduction in BBS aggregate amount rather than exhaustion of the aggragates. The residual BBS aggregates became out of the detection limit of the XRD equipment. Once the film was released, the typical BBS peaks recovered in a large degree, although not fully restored. The reversion in BBS aggregate supported the reversion in luminescence property of the blend film.

Furthermore, full recovery was observed upon annealing of the stretched film at 120 °C for 1 min. The full recovery was verified by the fluorescence intensity. In Figure 5c, the excimer emission fully restored to its initial state, indicating that annealing is an effective treatment to restore the stretched film. The possible mechanism of this heat-induced recovery was related to the mobility of TPU hard segments (aromatic units): although this temperature 120 °C was much lower than the melting point of TPU, it made the film significantly softer, allowed the scattered hard segments to move in amorphous phase under the residual inner stress, and brought the associated BBS back to aggregate status. Here, the fully reversible change of blend fluorescence property was controlled by combination of mechanical and thermal stimuli. It was also approved by the melt-compounded blend film, as shown in Figure 5d. The start film gave a ratio I_{475}/I_{413} of 4.0, and was reduced to 0.9 by a stretch of 100%. After releasing, it stopped at a strain of 10% with a ratio I_{475}/I_{413} of 2.6. A further annealing at 120 °C fully restored the film to original size and I_{475}/I_{413} value.

Superior to the previous mechanochromic plastics, this elastomer is much more sensitive to a low stress. For the plastics, a high stress was required to reach their yielding point and to trigger the mechanochromic response, e.g., ∼ 40 MPa for poly(vinylidene fluoride).[14] Even for the previous TPU synthesized by Weder group, it required more than 5 MPa to induce an observable change in fluorescence. In our elastic film, the visible change in fluorescence can be induced by a stress as low as 1.0 MPa, as shown in Figure 6b. The ratio I_{475}/I_{413} showed a striking decrement upon a gentle stress. Such a sensitive behavior is highly desired by a sensor application. This

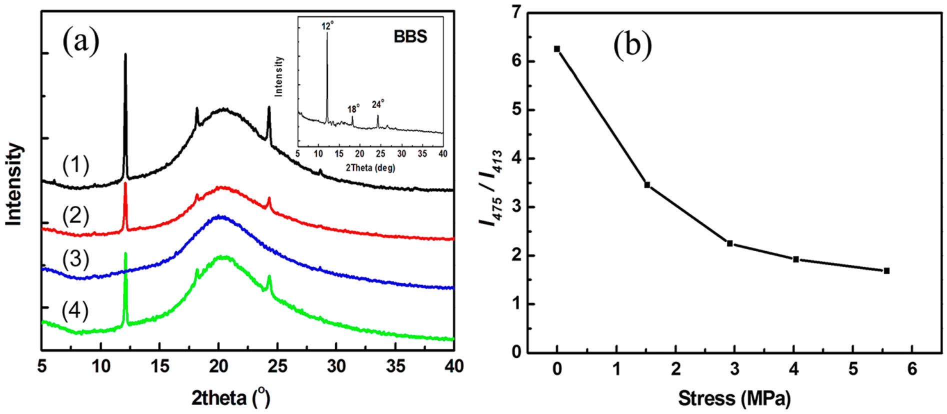


Figure 6. (a) XRD patterns of the solution-cast TPU/0.5%BBS film: (1) before stretch, (2) upon stretch by 50%, (3) upon stretch by 100%, (4) after release; the inset is XRD pattern of pure BBS powders. (b) Emission ratio I_{475}/I_{413} of the film changes with the stress during a stretching process.

advantage of our blend film is derived from the low modulus of Estane TPU in comparison to that synthesized by Weder group. It also supported our proposition that BBS mainly distributed in amorphous phase of TPU and moved together with the associated polymer chains.

■ CONCLUSION

In summary, both solution-cast and melt-compounded TPU/BBS films produced repeatable fluorescence changes upon stretch. The conversion between monomer and excimer forms of the dye BBS was easily controlled by stretching and relaxing the TPU matrix films, which directly led to the attractive mechanochromic performance. When the stretched films did not spontaneously recover fully, a simple post-thermotreatment caused the full restoration of film size and fluorescence peaks. Although only a range of strains lower than 100% was analyzed in detail by a spectrometer, the films were also visually evaluated on the tensile machine up to 400% strain and believed to follow the same mechanochropic mechanism. This reversible mechanochromic elastomer is promising for intelligent device applications.

■ EXPERIMENTAL SECTION

Chemicals and Materials. Bis(benzoxazolyl)stibene (BBS) and the thermoplastic polyurethane (TPU, Estane 2103−90AE) were purchased from Aldrich Co. and Lubrizol Inc., respectively. All materials were used as received.

Composite Film Preparations. In a solution cast preparation, TPU and BBS were dissolved in DMF at room temperature, then cast into a transparent film at 100 °C. The residual DMF was completely removed in a vacuum oven by annealing at 100 or 120 °C for 12 h. Absence of DMF was confirmed by thermogravimetric analysis. In a melt compounding preparation, TPU pellets and BBS powders were dried at 100 °C over 12 h, and premixed in a shaking bottle, then mixed at 200 °C in a Haake Minilab extruder with twin screws of 30 rpm for 15 min. The resultant extrudents were further compressed at 200 °C into thin films, and cooled in air to room temperature.

Property Measurements. Fourier-transformed infrared (FTIR) spectrum was recorded on a Perkin-Elmer System 2000 in an attenuated total reflection (ATR) mode. Film stretch was performed on an Instron 4411 tensile machine (tension rate 10 mm/min), and sample photos were taken under a UV light of 365 nm. The CIE chromaticity coordinates of composite film fluorescence were measured using a 2D color analyzer (CA-2000S, Konica Minolta) in a standard cabinet (Verivide CAC-120) equipped with 365 nm UV lamps. Film fluorescence spectra were scanned on a fluorescence spectrometer (FLS 920P, Edinburgh Instruments, UK), with an excitation wavelength at 377 nm. The X-ray diffraction (XRD) of films was measured on a Philips Xpert XRD system.

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Notes

The authors declare no competing financial interest.

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