

# Self-Sorting of Guests and Hard Blocks in Bisurea-Based Thermoplastic Elastomers

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ABSTRACT: Self-sorting in thermoplastic elastomers was studied using bisurea-based thermoplastic elastomers (TPEs) which are known to form hard blocks via hierarchical aggregation of bisurea segments into ribbons and of ribbons into fibers. Self-sorting of different bisurea hard blocks in mixtures of polymers to give separate ribbons was established by studying exciplex formation between fluorescent pyrene and dimethylaniline (DMA) functionalized bisurea probes. If both probes had the same spacing between the bisurea units as the matrix hard segments, exciplex bands were observed in the fluorescence emission spectra, whereas exciplex intensities were strongly reduced when DMA and pyrene probes with different spacer lengths were incorporated in a mixed matrix that provided matching host segments for each guest separately. Probes with butylene spaced bisurea groups showed the highest degree of self-sorting. Self-sorting was further improved by annealing of the polymer films leading to a degree of self-sorting of more than 95%. Self-sorting at the fiber level of aggregation was studied by fluorescence resonance energy transfer (FRET) between naphthalene (donor) and pyrene (acceptor) bisurea guests. Large differences in FRET behavior for matching and nonmatching probes showed that significant self-sorting takes places between ribbons to give separate fibers.

## Introduction

Self-sorting is the ability of an entity to distinguish between self and nonself. This principle is found in nature in the replication of DNA and in the crystallization of racemates into conglomerates (mixtures of enantiomerically pure crystals of one enantiomer and its opposite), but also in phase separation of oil and water. On the molecular level, Isaacs and co-workers have investigated the self-sorting capacity of several synthetic host-guest complexes in organic solvents and water.<sup>1-5</sup> They showed that each guest molecule in these studies can bind to its own host in a complex mixture of hosts and guests. Others have extended this approach to self-sorting in (block) copolymers $^{6-14}$  and on surfaces.<sup>15</sup> Weck et al. synthesized polynorborenes with host groups that can complex different guest molecules based on metal-ligand interactions, hydrogen bonding, and ion-dipole interactions. Association was observed to occur preferentially between the established host-guest complexes in a mixture having different hosts and guests. Also, functionalization of polynorbornene with two similar hydrogen-bonding hosts led to selective binding of the guest molecules to the best matching hosts.<sup>11</sup> Schalley and co-workers have reported self-sorting behavior based on 11 tetraurea-substituted calix[4]arenes having wide rim substitutents.<sup>16</sup> Dimerization of equimolar mixtures of these 11 calix[4]arenes in nonpolar solvents exclusively led to the formation of six structures out of 35 possible different homo- and heterodimers. In a simple four-component self-sorting system based on crown ethers and ammonium ions, using ESI-MS and tandem mass spectrometry, they were able to study distinctly different pseudorotaxane assemblies formed upon mixing. Self-sorting has also been studied on surfaces by assembling molecules of different bisurea spacings. In these studies, the

bisurea molecules selectively formed 2D crystals with bisurea molecules having identical spacer length.<sup>17</sup> Recently, Khan et al. showed with a series of biscarbamates that length of the total molecule also plays a role in the self-sorting of small molecules.<sup>18</sup>

The degree of self-sorting in any system is limited by mixing entropy and will only proceed up to the point where this term is compensated by the difference between the  $\Delta G_{\text{self-recognition}}$  and  $\Delta G_{\text{recognition}}$  ( $\Delta \Delta G$ ). Hence, self-sorting is optimal when a high value of  $\Delta G_{\text{self-recognition}}$  and a low value for  $\Delta G_{\text{recognition}}$  are combined. Urea groups are known to self-associate via hydrogen bonding, and this strong association has been used in the development of gelating agents.<sup>19-26</sup> Segmented poly-(THF)-bisurea polymers have been shown to be thermoplastic elastomers with excellent mechanical properties due to the high degree of phase separation between the soft poly(THF) and the hard bisurea segments.<sup>27a</sup> The bisurea segments aggregate via the well-known hydrogen-bonding motif of urea groups to form ribbons (Figure 1a), which further aggregate in a hierarchical fashion to form fibers consisting of stacks that are estimated to contain 4-6 ribbons (Figure 1b). The segmented copolymers 1a-1c (Scheme 1) used here as matrix in the self-sorting study are highly elastic materials, which show Hookean behavior upon elongation up to 100%, with plastic deformation at higher strains and a strain at break of 1000%.<sup>27b</sup> The selectivity of the binding of bisurea guests in a thermoplastic elastomer with bisurea hard blocks has been studied extensively in our group because it enables an easy, modular approach for the functionalization of these polymers leading to materials with useful properties.<sup>28-30</sup> Previously, we have shown that the amount of bisureafunctionalized dyes that was extracted by a detergent solution from bisurea-poly(tetrahydrofuran) polymers is much lower for dyes that match the spacing between urea units of the matrix than for dyes that are mismatched by a single methylene unit. Furthermore, upon elongation of elastomer films, strong differences in

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alignability of matching and nonmatching dyes were observed.<sup>28</sup> We have also shown that pyrene-based fluorescent probe molecules provided with "matching" bisurea moieties, which have the same number of methylene units between urea groups as the host, are specifically bound to the fibrous hard blocks of these polymers, while probe molecules with "nonmatching" bisurea units are not incorporated in the hard blocks of the host.<sup>30–32</sup> The observed selectivity of guest binding in these matrices provides opportunities to form interpenetrating networks of fibrous hard blocks with multiple types of functionality in separate domains. Such features are useful when one type of functionality has to be kept spatially separate from another within a single matrix.



**Figure 1.** (a) Aggregation motif of bisurea as displayed in the X-ray structure of a model compound.<sup>28</sup> (b) Aggregation of bisurea hard segments into ribbons (left) and subsequent stacking of ribbons to form fibers (right).

Microphase separation in tri- and multiblock copolymers is known to give rise to materials with multiple phases and can be considered as a form of self-sorting.<sup>33</sup> However, self-sorting of hard blocks in segmented copolymers that have much smaller hard segment dimensions of around 1 nm requires strong and directional interactions to prevent mixing. Here, we describe the result of self-sorting experiments in mixed thermoplastic matrices with bisurea polymers having minimal structural differencesvariation of the spacer length by one or a few methylene units between the urea groups. Self-sorting in blends of these polymers is probed with fluorescent bisurea guests. With these experiments we obtain an insight into the following questions: Do hard segments with different bisurea spacings aggregate into separate ribbons in a mixture of polymers (Figure 2)? Do these ribbons aggregate into mixed fibers, or do fibers contain a single type of hard segment? Do bisurea guest molecules selectively bind to the fibers of the matching hard segment, so-called "narcissistic" selfsorting (Figure 3a)? Self-sorting of bisurea guest molecules in pTHF-bisurea polymer matrix was studied using fluorescent probe molecules based on pyrene and dimethylaniline (DMA) which form exciplex upon excitation if they are in direct contact. The information obtained from these studies was utilized to investigate whether the guest molecules reside in the same type of ribbon. Fluorescence resonance energy transfer (FRET)



Figure 2. Cartoon of perfect self-sorting in a bisurea thermoplastic elastomer. In a mixture of pTHF-bisurea segmented copolymers with varying spacer length between urea groups, the hard blocks phase separate.







**Figure 3.** Proposed inclusion behavior of fluorescent guest molecules in the poly(tetrahydrofuran) bisurea-based polymer matrix. The poly(tetrahydrofuran) soft blocks are omitted, and only hard blocks of the polymer matrix are shown for clarity. (a) Poly(tetrahydrofuran)-bisurea polymer matrix and bisurea probe molecules all have identical spacing (C6) between the bisurea group resulting in molecular contacts between dimethylaniline and pyrene molecules. (b) Poly(tetrahydrofuran)-bisurea polymer matrix and fluorescent probe molecules dimethylaniline and pyrene with different spacing (C4 and C7) between the bisurea groups are bound to separate hard blocks with little molecular contact of the chromophores.

between chromophores typically occurs up to distances of several nanometers. FRET between naphthalene- and pyrene-labeled bisurea probes was used to investigate self-sorting at the level of aggregation of ribbons into fibers in order to establish whether indeed separate networks of fibers consisting of one type of ribbons are formed in pTHF-bisurea polymers, as depicted in Figure 2.

## **Experimental Section**

Materials and Methods. Polymers 1a-1c were synthesized as reported in the literature.<sup>27a</sup> Solvents used in the synthesis were reagent grade. The reagents 1,4-diisocyanatobutane, 1,6-diisocyanatohexane, 1-pyrenemethylamine hydrochloride, 2-naphthalenemethylamine, 4-(dimethylamino)benzylamine dihydrochloride, N-Boc-1,4-butanediamine, N-Boc-1,6-hexanediamine, 2-ethylhexyl isocyanate, and bis(3-aminopropyl)poly(tetrahydrofuran),  $M_{\rm n} = 1100$  g/mol, were purchased from Aldrich and used without additional purification. The NMR spectra were acquired on a 400 MHz Varian Mercury Vx (400 MHz for <sup>1</sup>H NMR, 100 MHz for <sup>13</sup>C NMR) or a 300 MHz Varian Gemini-2000 (300 MHz for <sup>1</sup>H NMR, 75 MHz for <sup>13</sup>C NMR) spectrometer. Proton and carbon chemical shifts are reported in ppm downfield of tetramethylsilane using the resonance of the deuterated solvent as internal standard. Splitting patterns are designated as singlet (s), doublet (d), triplet (t), and multiplet (m). Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with a Universal ATR sampling accessory. MALDI-TOF was performed on a Perseptive DE PRO Voyager MALDI-TOF mass spectrometer using  $\alpha$ -cyano-4-hydroxycinnamic acid as the calibration matrix. UV/vis spectra were recorded on a Perkin-Elmer Lambda 900. Fluorescence spectra were recorded on an Edinburgh Instrument FS920 double-monochromator spectrometer with a Peltier-cooled red-sensitive photomultiplier.

**Preparation of Polymer Films for Fluorescence Measurements.** Quartz substrates ( $3 \times 3$  cm) were cleaned by ultrasonic treatment in acetone (10 min), rubbing with SDS soap solution, sonication in SDS soap solution (10 min), rinsing in a stream of demineralized water (15 min), sonication in isopropranol (5 min), and finally UV/ozone treatment (30 min). Solutions for spin-coating were freshly prepared by mixing different stock solutions, reaching a final polymer concentration of 12 mg/mL. Stock solutions for pTHF-bisureas were always 20 mg/mL in MeOH/CHCl<sub>3</sub> (1:9 v/v). Stock solutions for pyrene-bisurea guests were always 20 mg/mL in TFA/CHCl<sub>3</sub> (15:85 v/v). Stock solutions for DMA-bisurea guests were 10 or 20 mg/mL in MeOH/CHCl<sub>3</sub> (1:9 v/v). The mol % of bisurea guest was calculated with respect to the number of bisurea groups in the polymer, assuming a molecular weight of a polymer repeating unit of 1400 g/mol for all polymers. The stock solutions were freshly prepared prior to spin-coating, and the pyrene stock solutions were used within 30 min to prevent degradation of the compounds by the TFA. The solutions were spin-coated at 1500 rpm for 2 min.

**Fluorescence Measurements.** Fluorescence spectra were recorded on an Edinburgh Instrument FS920 double-monochromator spectrometer with a Peltier-cooled red-sensitive photomultiplier. The dwell time was set to 0.2, the number of scans to 3, and the step size to 1 nm. The emission and excitation slit sizes were set to 4 nm. Emission spectra were recorded after excitation at 290 nm (FRET) or 347 nm (exciplex). Excitation spectra were recorded at emission wavelengths of 377 and 487 nm.

#### **Results and Discussion**

Synthesis of Bisurea-Based Guest Molecules. The bisureapoly(tetrahydrofuran) polymers (1a-1c) and bisurea-based fluorescent guest molecules (6a-6c, 7a-7c, and 8a,8b) used for the self-sorting experiments are depicted in Scheme 1. The synthesis of the guest molecules (6a-6c, 7a-7c, and 8a,8b) included the following steps: (a) monoBoc protection of 1,7-diaminoheptane by reaction with di-tertbutyl dicarbonate followed by (b) reaction of monoBocprotected diaminobutane (3a), diaminohexane (3b), and diaminoheptane (3c) with 2-ethylhexyl isocyanate, yielding intermediates with one urea group (4a-4c). In the third step, the Boc protecting group was removed using trifluoroacetic acid (TFA) to yield the free amine groups (5a-5c) which were coupled in the last step to isocyanate-functionalized probe molecules, resulting in the formation of monofunctionalized bisurea molecules (6a-6c, 7a-7c, and 8a,8b). All compounds were purified via column chromatography. The detailed synthetic procedure and characterization of the intermediates and final products are provided in the Supporting Information.

Self-Sorting Monitored via Exciplex Formation between Pyrene and Dimethylaniline. Fluorescence emission of pyrene is quenched by the complexation with dimethylaniline (DMA) in the excited state in a so-called exciplex with a band in the fluorescence emission spectrum at 487 nm.<sup>34–37</sup> The formation of the exciplex requires molecular contact between pyrene and DMA. Therefore, observation of exciplex emission from a film containing a mixture of pyrene and DMA-bisurea guests indicates that the guest molecules are assembled in the same fiber (Figure 3a). However, if the two



Figure 4. Fluorescence emission spectra of polymer films containing (a) bisurea guest molecules Py-U6U (6b) and DMA-U6U (7b) that match with the polymer matrix pTHF-U6U (1b) and (b) bisurea guest molecules Py-U7U (6c) and DMA-U4U (7a) in a mixed polymer matrix pTHF-U4U (1a) and pTHFU7U (1c). The excitation wavelength used was 347 nm. Spectra are normalized to the peak at 377 nm for comparison. Insets show magnifications of the spectrum between 440 and 600 nm, all drawn to the same intensity scale.

guests are assembled in different fibers, molecular contact between pyrene and DMA is not possible, and no exciplex will be observed (Figure 3b). Exciplex emission intensity is therefore a good measure for the degree of self-sorting of these bisurea compounds into their matching bisurea ribbons. The fact that monofunctional pyrene-bisurea guests (6a-6c) are less prone to aggregate into fibrous structures than the bisfunctional pyrene-bisurea guests prompted us to use monofunctional guest molecules for our study.<sup>32</sup> Furthermore, in order to prevent the formation of pyrene excimer, a very low concentration (1 mol %) of guest molecule (Py-U6U (6b)) was used.

Atomic force microscopy (AFM) performed on films with the highest concentration of the guest molecule (10 mol % of DMA-U6U (7b)) indicated normal pTHF-bisurea fiber morphology with no phase separation. Furthermore, fluorescence studies of the solutions used for spin-coating of the films showed that self-sorting does not take place in solution (see Supporting Information). Fluorescence spectra of polymer films spin-coated from polymer matrix pTHF-U6U (1b) and matching guests (1 mol % pyrene-U6U (6b) with 0, 1.5, and 5 mol % DMA-U6U (7b)) and 1:1 ratio of pTHFU4U (1a) and pTHF-U7U (1c) polymer matrices and guests molecules (1 mol % Py-U7U (6c) with 0, 1.5, and 5 mol % DMA-U4U (7a)) were recorded (Figure 4a,b). The spectra were normalized to the emission at 377 nm to enable comparison. As can be seen from Figure 4a, the polymer films prepared using matching guest molecules



Figure 5. Fluorescence emission spectra of polymer films containing bisurea guest molecules Py-U7U (6c) and DMA-U6U (7b) or DMA-U7U (7c) in the polymer matrix pTHF-U6U (1b) and pTHF-U7U (1c). The excitation wavelength used was 347 nm, and spectra are normalized to the peak at 377 nm for comparison. Insets show magnifications of the spectrum between 440 and 600 nm, all drawn to the same intensity scale.

Py-U6U (6b) and DMA-U6U (7b) indeed formed exciplexes with an increase in the intensity of exciplex band upon increasing concentration of the guest molecule DMA-U6U (7b). On the other hand, polymer films prepared using nonmatching guests Py-U7U (6c) and DMA-U4U (7a) in a mixed matrix of 1a and 1c did not show exciplex emission (Figure 4b). In this mixture, exciplex intensity is reduced by more than 90%, indicating a high degree of separation between the two kinds of hard segments. A sample measured twice with a time interval of 1 day yielded two identical emission spectra, indicating that the degree of self-sorting in the films is constant over time.

The results obtained with polymer films spin-coated from pTHF-U6U (1b) and pTHF-U7U (1c) containing 1 mol % Py-U7U (6c) and 5 or 10 mol % DMA-U6U (7b) illustrate the extent of self-sorting that can be achieved with a minimal difference in structure of the hard segments. The bisurea units in this system differ by just a single methylene unit. The fluorescence emission spectrum of these polymer films is shown in Figure 5. In these samples, the exciplex band is reduced by 60% compared to the reference system containing matching guests (DMA-U7U (7c) and Py-U7U (6c)), indicating that although specificity is lower than when the bisurea units differ more in size, significant self-sorting still takes place with a difference in structure of just a single methylene unit. Since annealing of thermoplastic elastomer films leads to thermodynamically more stable fibers,<sup>38</sup> the polymer films described in Figure 5 were annealed for 1 h at 130 °C and cooled down at a rate of 20 °C/h, and the fluorescence emission spectra were recorded again. Annealing led to lowering of the intensity of exciplex band by 88% compared to the reference system, indicating an increase in self-sorting.

Self-Sorting of DMA and Pyrene Guests in Mixtures of Three Polymers. After having demonstrated the self-sorting behavior in mixtures of two polymers, we wanted to extend the principle of self-sorting to more complex mixtures. Therefore, we investigated self-sorting in a mixture of three polymers, with three different guest molecules. Nine possible combinations of polymer films were spin-coated from solution containing equal quantities of polymer matrices (pTHF-U4U (1a), pTHF-U6U (1b), and pTHF-U7U (1c)) along with 1 mol % pyrene-bisurea guest containing



**Figure 6.** Fluorescence emission spectra of polymer films containing different combinations of DMA and pyrene-bisurea guest molecules in the polymer matrix pTHF-U4U (1a), pTHF-U6U (1b), and pTHF-U7U (1c) before (a) and after (b) annealing for 1 h at 130 °C. The excitation wavelength used was 347 nm, and spectra are normalized to the peak at 377 nm for comparison. Insets show magnifications of the spectrum between 440 and 600 nm, all drawn to the same intensity scale.

either no DMA-bisurea guests, 10 mol % of the matching DMA-bisurea guests, or 5 mol % of nonmatching DMA-bisurea guests. Figure 6a, b shows two representative fluorescence emission spectra before and after annealing (see Supporting Information for comparative emission spectra of all the prepared films). A large difference in the intensity of the exciplex band was observed for matching and nonmatching systems, clearly indicating the presence of self-sorting in mixtures containing three polymers. The polymer films prepared using the mixture of Py-U4U (6a), DMA-U6U (7b), and DMA-U7U (7c) showed the best self-sorting behavior (least intensity of exciplex band), while the matching combination of Py-U4U (6a) and DMA-U4U (7a) as expected showed the highest intensity of exciplex band. The estimated degree of self-sorting was 94% for the mixture with Py-U4U (6a), DMA-U6U (7b), and DMA-U7U (7c) and 83% for the polymer films prepared using Py-U6U (6b), DMA-U4U (7a), DMA-U7U (7c), Py-U7U (6c), DMA-U4U (7a), and DMA-U6U (7b). The fact that the polymer films prepared from the mixture of Py-U4U (6a), DMA-U6U (7b), and DMA-U7U (7c) yielded the strongest reduction in exciplex intensity (94%) could be attributed to the largest difference in the spacer lengths between the pyrene and DMA guest compared to the other combinations of guest molecules used. Furthermore, the highest exciplex band is formed for the matching system having four methylene units between them (U4U system, Py-U4U 6a and



Figure 7. Comparison of the relative intensity of exciplex bands before and after annealing in the polymer films containing matching and nonmatching DMA and pyrene-bisurea guest molecules in the polymer matrix pTHF-U4U (1a), pTHF-U6U (1b), and pTHF-U7U (1c). Blank indicates absence of DMA guest molecules in these samples. Nonmatching indicates presence of DMA guest molecule having a different alkyl spacer as compared to the pyrene guest molecule. Matching indicates both the pyrene and DMA guest molecules have the identical alkyl spacer between them.

DMA-U4U 7a), indicating that in the matching systems having six methylene units (U6U system, Py-U6U 6b and DMA-U6U 7b) and seven methylene units (U7U system, Py-U7U 6c and DMA-U7U 7c) some guests molecules probably are not incorporated in the bisurea fibers. Annealing (130 °C for 1 h) of the samples as described earlier had a pronounced effect in the self-sorting behavior, resulting in an increase of the estimated degree of self-sorting to 95% for all the polymer films having nonmatching guest molecules (Figure 6b). An overview of the relative intensity of the exciplex bands for all samples before and after annealing is shown in Figure 7. The influence of annealing is clearly visible as well as the differences between the self-sorting capacities of the C4, C6, and C7 spaced bisurea systems. These results clearly show that in a mixture of three polymers with different recognition units the bisurea units are able to find their analogues leading to self-sorting.

FRET as a Probe To Analyze the Stacking of Ribbons into Fibers. The hard blocks in bisurea-based thermoplastic elastomers are known to consist of fibers that consist of stacks of several hydrogen-bonded bisurea ribbons.<sup>27-29,39</sup> Although the exciplex formation between DMA and pyrene probed self-sorting behavior within ribbons, investigating self-sorting of different bisurea segments into separate fibers requires probes that allow studying interactions between bisurea guest molecules over a larger distance. For this purpose, we used the fluorescence resonance energy transfer (FRET) pair of naphthalene (as donor) and pyrene (as acceptor).<sup>40-44</sup> The structures of the FRET-based probe molecules (6a-6c, 8a, and 8b) used in our study are shown in Scheme 1. The distance dependence of the efficiency of FRET in a donor-acceptor pair is given by the Förster equation  $E = R_0^6 / (R_0^6 + r^6)$  in which *E* is the efficiency of energy transfer,  $R_0$  is the Förster radius, and *r* is the distance between donor and acceptor. For the naphthalene-pyrene FRET pair, the value of  $R_0$  is reported as 2.86 nm.<sup>45</sup> Because of the strong distance dependence, FRET is generally only observable when the donor and acceptor are separated by a distance of less than approximately  $1.5R_0$  (4.3 nm). Because the average distance between two pTHF-bisurea fibers in polymers 1 is larger than 5.5 nm,  $^{27}$  a very low (less than 2%) efficiency of FRET is expected for nonmatching donor and acceptor probes if the different ribbons aggregate in separate stacks. On the other hand, the high intensity of a FRET band in a single polymer matrix with matching donors and acceptors at low concentration may be taken as corroboration of aggregation of ribbons into fibers.



**Figure 8.** Fluorescence emission spectra of polymer films before annealing. (a) Matching donor-Naph- and acceptor-pyrene-bisurea guest molecules and (b) nonmatching donor-Naph- and acceptor-pyrene-bisurea guest molecules. The excitation wavelength used was 290 nm. The spectra were normalized to the amount of pyrene calculated from the emission spectra recorded at 347 nm and were corrected for direct pyrene excitation at 290 nm.

Polymer films were spin-coated from polymer solution pTHF-U6U (1b) containing 1 mol % Py-U6U (6b) and 0, 1, 5, or 10 mol % Naph-U6U (8b) in the case of matching pairs or from a solution containing a 1:1 mixture of 1a and 1c, 1 mol % of Py-U7U (6c), and 0, 1, 5, or 10 mol % Naph-U4U (8a). Analysis of the polymer films by AFM showed Naph-U4U (8a) and Naph-U6U (8b) did not phase separate from the hard blocks, even at the highest concentrations of 10 mol %. Fluorescence emission spectra of the polymer films were recorded at the excitation wavelength of 290 nm where the donor naphthalene absorbs. To compensate for direct pyrene excitation at this excitation wavelength, the fluorescence spectrum of a polymer film with 1 mol % pyrene probe without naphthalene was recorded at the excitation wavelength of 290 nm and subtracted from all fluorescence spectra recorded for the polymer films containing pyrene and naphthalene. The results are provided in Figure 8a,b. Figure 8a shows that for the matching system (Py-U6U (6b) and Naph-U6U (8b)) the intensity of characteristic pyrene fluorescence in the wavelength region 375-430 nm increases with the amount of Naph-U6U (8b). Increased energy transfer is attributed to the increased fraction of pyrene that is within a few nanometers of naphthalene. In contrast to this, only a minimal increase in intensity of pyrene emission with increasing concentration of naphthalene donor occurs in the nonmatching system Py-U7U (6c) + Naph-U4U (8a) (Figure 8b).



**Figure 9.** A comparison of the ratios of integrated intensities between 375 and 430 nm and 320–345 nm before and after annealing of the polymer films containing matching and nonmatching naphthalene and pyrene–bisurea guest molecules.

Moreover, the intensity of characteristic naphthalene fluorescence in the wavelength region 320-345 nm is higher in the nonmatching system than in the matching system, which is also indicative of considerably lower amount of energy transfer in the nonmatching system. Annealing of the samples at 130 °C for 1 h followed by slow cooling down (20 °C/h) had a pronounced effect on the FRET ratio. For the polymer films with nonmatching probe molecules, annealing led to a significant decrease of FRET, whereas for the matching samples, the decrease was much less. An overview of the comparison of FRET ratios  $(I_{375-430}/I_{320-345})$  for the matching and nonmatching FRET pairs is shown in Figure 9. Differences in FRET ratio between matching and nonmatching systems shows that, in addition to self-sorting within ribbons, there is significant self-sorting among ribbons to give fibers containing predominantly a single type of bisurea hard segment. The FRET ratio is nearly independent of naphthalene concentration because the average distance of a naphthalene donor unit to the nearest pyrene acceptor moiety is dependent on the pyrene concentration, which is the same in all samples. However, when the concentration of both pyrene and naphthalene was lowered to 0.2 mol %, the FRET ratio of the matching system dropped to a value of 0.3, approximately the same value observed for the nonmatching systems. In principle, the number of ribbons in a fiber can be estimated from the FRET efficiency because at a constant acceptor concentration, the average number of acceptor molecules within Förster distance of a donor increases with the number of ribbons per fiber. However, the current experiments do not allow us to extract quantitative information from the data.<sup>40–42</sup>

#### Conclusions

In the present article, we have successfully demonstrated selfsorting in elastomeric matrices by using bisurea fluorescent probe molecules that bind to the hard segments of the pTHF-bisurea segmented copolymer. Since no self-sorting was observed in solution, it must be a remarkably fast process, occurring during spin-coating of the films. Annealing of the polymeric films led to improved self-sorting in all nonmatching systems and also led to an increase in exciplex ratio in the matching systems. The latter observation suggests that before annealing some of the guest molecules are present in the soft matrix and that the fraction of guest molecules present in the fibers increases upon annealing. The experiments with U6U and U7U probes demonstrate a high degree of self-sorting even when the bisurea segments differ by just a single methylene unit. FRET measurements show that ribbons aggregate predominantly into fibers containing a single type of bisurea unit. Thus, self-sorting in bisurea thermoplastic elastomers occurs at both levels of the hierarchical self-assembly

process that brings the hard segments together in ribbons that consecutively aggregate to form fibers.

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Supporting Information Available: A detailed description of the synthesis and characterization of probe molecules (6a–6c, 7a–7c, and 8a–8b), their synthetic intermediates, and addition fluorescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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