

Erbium(III)-Doped Polyurethaneureas: Novel Broadband Ultraviolet-to-Visible Converters

Huseyin Cankaya,¹ Reyhane Kilci,¹ Alphan Sennaroglu,¹ Emel Yilgor,² Iskender Yilgor²

¹Laser Research Laboratory, Department of Physics, Koc University, Rumelifeneri yolu, Sariyer 34450, Turkey

²Polymer Research Laboratory, Department of Chemistry, Koc University, Rumelifeneri yolu, Sariyer 34450, Turkey

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ABSTRACT: Novel, polymeric UV-to-visible converters were prepared by doping elastomeric poly(ether-urethaneurea) copolymers with 5–25% by weight of $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, corresponding to Er^{3+} concentrations of 2.19 to 10.86% by weight. When excited in the UV at 355 nm, the doped films generated a very broad, continuous visible luminescence between 400 and 750 nm. Preparation and spectroscopic characterization of the samples are discussed in detail. The color coordinates, color temperature, color rendering index of the samples, and the degree of overlap of their emission bands with the spectral response of the eye were determined.

The color rendering index of samples is in the 57–70 range. The sample containing 2.19% by weight of Er^{3+} was found to give the color coordinates closest to the white-source region and the highest color rendering index. The color temperatures of the samples were in the 5093–5540 K range. Overlap between the emission bands and the spectral response of the eye improved with increasing erbium concentration. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 378–383, 2010

Key words: rare earth ions; polyurethane; UV-to-visible conversion; organic UV-to-visible converters

INTRODUCTION

There has been a great deal of interest in the development of white-light sources for applications in color displays and solid-state lighting. To date, numerous device architectures have been proposed and demonstrated. Among these, one approach uses active sources such as organic light-emitting diodes (OLEDs), which can produce broadband visible light whose spectral characteristics can be controlled by varying the layer composition and/or the applied bias.^{1–3} Alternatively, converters can be used together with an excitation source to produce visible fluorescence. For example, thin films of Group II–VI compounds, such as ZnSe, can be excited by electron beam to produce tunable visible fluorescence.⁴ As a second example, CdSe/ZnS fluorescent nanocrystals have been pumped with blue LEDs to generate different color bands in the visible region.⁵ Here, color tunability is achieved by using nanocrystals of different sizes. In other studies, nanoparticles or organic compounds doped with trivalent rare-earth ions have been used to produce upconversion⁶ or downconversion^{7,8} luminescence in the visible range. Several important merits are sought in the development of versatile systems for UV-to-visible conver-

sion. These include ease of fabrication, flexibility, repeatability, low cost, and potential for mass production.

This communication reports the preparation and properties of novel, polymeric broadband UV-to-visible converters based on segmented, thermoplastic poly(ether-urethaneurea) (PUU) copolymers doped with trivalent erbium ions. Chemical structure of a PUU consists of alternating soft and hard segments along a linear polymer backbone. Soft segments are usually aliphatic polyether or polyester oligomers with number average molecular weights in the 1000–3000 g/mol range. Hard segments are short urethane, urea or urethaneurea moieties, obtained by the reactions of diisocyanates and diols or diamines, respectively.⁹ PUUs can display properties ranging from very soft thermoplastic elastomers to strong and rigid thermoplastics depending on their chemical compositions, hard/soft segment types, hard/soft segment ratios, and equilibrium microphase morphologies or nanostructures. Versatility of PUU technology stems from the commercial availability of a very large number of starting materials for their synthesis and their flexible polymerization methods.^{10,11}

In this study, a novel water chain extended¹² PUU based on an aromatic diisocyanate (MDI) and poly(tetramethylene oxide) (PTMO-2000) was prepared. Polymer produced was doped with erbium trichloride hexahydrate ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$), ranging from 5–25% by weight (corresponding to Er^{3+} concentrations of

Correspondence to: I. Yilgor (iyilgor@ku.edu.tr).

2.19 to 10.86 weight percent). Doped films were transparent and strong. When excited in the UV at 355 nm, the doped films generated very broad, continuous visible luminescence between 400 and 750 nm. Rare-earth ion-doped segmented poly(ether-urethaneurea) copolymers could provide a simple technique for the realization of UV-Vis converting materials and may find applications as novel hybrid white light sources. Furthermore, the host polyurethaneurea materials are elastomeric and fiber forming, which may enable their use in the production of UV-protective clothing.

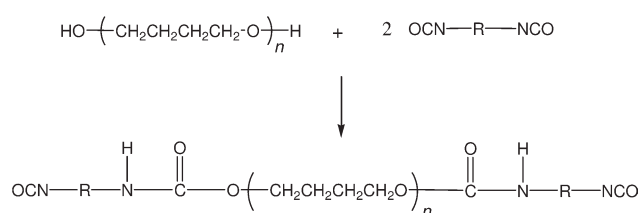
EXPERIMENTAL

Materials

4,4'-Diphenylmethane diisocyanate (MDI) with purity greater than 99.5% was kindly supplied by Bayer, Germany. Poly(tetramethylene oxide)glycol (PTMO-2000) oligomer with number average molecular weight $\langle M_n \rangle$ of 2040 g/mol was provided by DuPont. Erbium(III) chloride hexahydrate ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$) with a purity of 99.9% was obtained from Alfa Aesar and used as received. Dimethylformamide (DMF) (Aldrich) was used as the reaction solvent without purification. Triple distilled water was prepared in our laboratories.

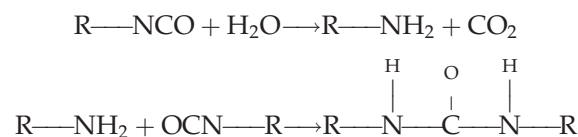
Synthesis of poly(ether-urethaneurea) (PUU) copolymer

Polymerization reactions were conducted in a three-neck, round-bottomed 500 mL Pyrex flask equipped with an overhead stirrer, addition funnel, and thermometer, using the two-step "prepolymer" method. Reactions were carried out at 50°C. In the first step to prepare the isocyanate terminated prepolymer, 15.70 g PTMO-2000 (7.70 mmol) and 3.85 g MDI (15.40 mmol) ($[\text{NCO}]/[\text{OH}] = 2.0$) were introduced into the flask, dissolved in 28.2 g of DMF, stirred and reacted. Formation of the isocyanate end capped PTMO prepolymer (shown below, where R indicates diphenylmethane group in MDI) was completed in about 30 min, which was monitored by FTIR spectroscopy.

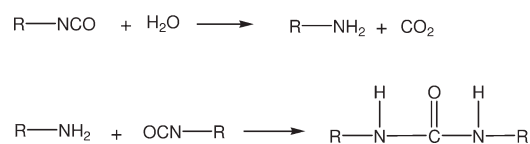


For the chain extension, 0.138 g water (7.66 mmol) was mixed with 15.8 g DMF, introduced into the addition funnel and slowly added into the reactor over a period of 2 h. Reaction mixture was diluted

with a total of 66.0 g of DMF as the viscosity increased because of the formation of high molecular weight polymer. As shown below, water reacts with the isocyanate group and converts it into an amine, which immediately reacts with another isocyanate, resulting in the formation of a urea linkage.¹²



As a result of the two-step reactions discussed above and the stoichiometry used; $([\text{MDI}]/[\text{PTMO}]/[\text{H}_2\text{O}] = 2/1/1)$, expected (ideal) chemical structure of the water chain-extended, MDI and PTMO based poly(urethaneurea) (PUU) copolymer is given below:



From the stoichiometry of the reaction system, urethaneurea hard segment content of this copolymer is 20.2% by weight and the average molecular weight of the urethaneurea hard segments is calculated to be 504.5 g/mol.

Preparation of erbium doped polyurethaneureas

Depending on the level of doping, calculated amount of $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in DMF to produce a dilute solution containing about 10% by weight of dopant. The solution was sonicated for 5 min at room temperature to obtain complete dissolution. $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ solution was then mixed with the polymer solution and further sonicated for 5 more minutes. Clear solution obtained was poured into a Teflon mold and solvent was evaporated in an air oven at 60°C, overnight. Complete removal of DMF was obtained in a vacuum oven at 60°C, until constant weight is achieved. Table I gives a list of the $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ doped PUU samples prepared and their compositions. The integer numbers in the polymer code that follow PUU indicate the weight percent concentration of Er^{3+} in the samples. Undoped PUU designated as PUU-0 was also used as control or reference.

Spectroscopic characterization of the samples

FTIR spectra were recorded on a Nicolet Impact 400D spectrometer with a resolution of 2 cm^{-1} , using thin films cast on KBr disks. Completion of the prepolymer formation reaction was determined by following the disappearance of strong and broad

TABLE I
Compositional Characteristics of ErCl₃ Doped Poly(ether-urethaneurea) Copolymers

Sample code	Polymer (g)	t (mm)	HS (mmol)	ErCl ₃ 6H ₂ O (g) (mmol)		ErCl ₃ 6H ₂ O (wt %)	Er ³⁺ (wt %)	[Er ³⁺]/[HS]
PUU-0	1.50	0.50	0.59	0	0	0	0	0
PUU-2	1.50	0.60	0.59	0.079	0.207	5.00	2.19	0.35
PUU-4	1.50	0.48	0.59	0.160	0.419	9.64	4.22	0.71
PUU-6	1.50	0.76	0.59	0.261	0.684	14.82	6.49	1.16
PUU-11	1.50	0.90	0.59	0.503	1.318	24.78	10.86	2.23

(t) and (HS) denote the film thickness and hard segment content (wt %) of PUU, respectively.

O—H absorption peak centered around 3460 cm⁻¹ and formation of N—H peak at 3305 cm⁻¹. Chain extension reaction with water was monitored by the disappearance of strong isocyanate absorption peak at 2270 cm⁻¹.

In the spectroscopic characterization experiments, samples with film thicknesses in the 0.5–0.9 mm range were used. Absorption spectrum of each sample was recorded on a Shimadzu, model 3101 PC UV-VIS-NIR spectrometer in the 300–1200 nm range. In the luminescence measurements, the triple harmonic of a pulsed Nd:YAG at 355 nm was used to excite the samples. The repetition frequency of the source was 1 kHz and pulses with energy up to 14.2 μJ were used. The emitted fluorescence was then collected with a concave gold mirror and imaged to the entrance slit of a 1/2-m, Czerny-Turner type monochromator (CVI, model DK 480). The luminescence signal was then detected with a photomultiplier tube.

To determine the white color parameters of the sample films, we calculated the chromaticity coordinates (x,y) of each luminescence spectrum by using the color matching functions of the CIE 1964 standard. According to this standard, an ideal white light source has the chromaticity coordinates (1/3, 1/3). By using the 8 standard targets, the color rendering index (CRI) of each sample was also evaluated. The color temperature was further estimated from Wien's displacement law by using the relation

$$\lambda_0 T = 2.8978 \times 10^6 \text{ K}\mu\text{m} \quad (1)$$

Here, λ_0 is the center wavelength of the emission band.

To quantify the degree of overlap between the emission spectrum of the samples and the eye response curve, we further introduced an overlap factor η , defined according to:

$$\eta = \frac{\int_0^\infty I_s(\lambda)R_e(\lambda)d\lambda}{\sqrt{\int_0^\infty I_s^2(\lambda)d\lambda} \sqrt{\int_0^\infty R_e^2(\lambda)d\lambda}} \quad (2)$$

In eq. (2), $I_s(\lambda)$ is the spectral intensity distribution of the sample, $R_e(\lambda)$ is the spectral responsivity of the eye, and λ is the wavelength. When $I_s(\lambda)$ and $R_e(\lambda)$ are identical, η becomes unity. η was calculated for each sample as discussed in the next section.

RESULTS AND DISCUSSION

Novel, high strength, elastomeric poly(urethaneurea) (PUU) copolymers were prepared by using an aromatic diisocyanate (MDI), poly(tetramethylene oxide)glycol (PTMO-2000) and water as the chain extender. PUU was synthesized using a two-step reaction procedure as discussed in synthesis of poly(ether-urethaneurea) (PUU) copolymer section. Polymers obtained were doped with varying amounts (5 to 25% by weight) of ErCl₃ 6H₂O in DMF solution and strong films were obtained after the evaporation of the solvent. Level of Er³⁺ incorporation changed between 2.19 and 10.86% by weight, as shown in Table I. In addition to the weight percent compositions, the molar ratio of erbium ions to urea hard segments [Er³⁺]/[HS] are also provided in Table I. Doped polymers showed excellent elastomeric properties as the virgin PUU, similar to other Er³⁺ doped polyurethanes reported in the literature.¹³ They were transparent with a pale purple color depending on their Er³⁺ contents. Previous studies^{14–16} carried out using infrared spectroscopy have shown that when poly(urethaneureas) are doped with transition metal salts, although interaction with both polyether and urea segments are possible, the metal ions mainly interact with the hard (urethane and urea) segments. Others have also investigated Er³⁺ doped polyurethane systems, where interaction between Er³⁺ and C=O of the urethane groups was reported.¹³ Selected regions of comparative (normalized) FTIR spectra of thin films cast on KBr discs for host PUU-0 and PUU-11, doped with about 25 weight percent of ErCl₃ 6H₂O are reproduced in Figures 1(a–c). Figure 1(a) shows 3700–2800 cm⁻¹ region, which contains absorption bands because of N—H and C—H stretching. As expected, there is no difference in the C—H peaks

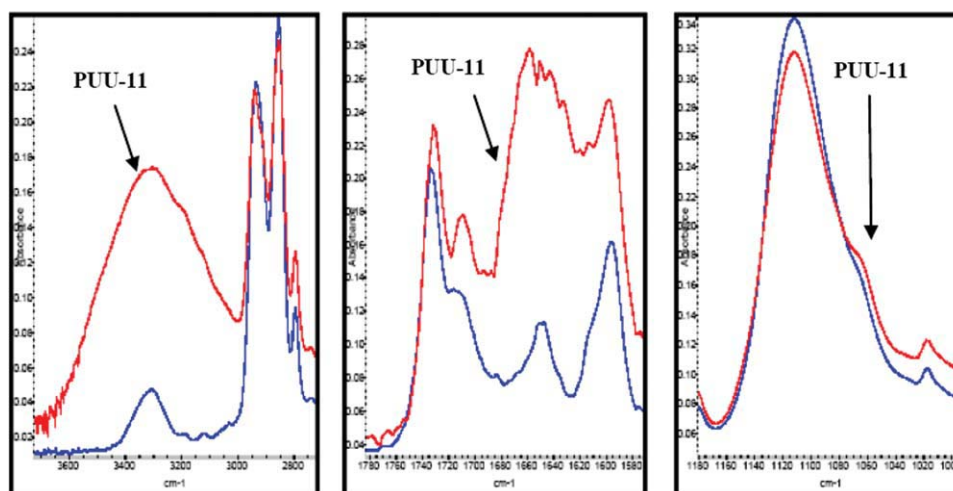


Figure 1 Comparative FTIR spectra of undoped (PUU-0) and 24.78% by weight Er^{3+} doped (PUU-11). (a) $3700 - 2800 \text{ cm}^{-1}$ (N–H) region, (b) $1780 - 1580 \text{ cm}^{-1}$ (C=O) region, and (c) $1180 - 1100 \text{ cm}^{-1}$ (C–O–C) region. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

between 2800 and 3000 cm^{-1} for undoped PUU-0 and heavily doped PUU-11, while there is a dramatic difference in the N–H region. Fairly narrow and symmetrical N–H stretching peak between 3200 and 3470 cm^{-1} , with peak maxima at 3305 cm^{-1} , observed in undoped PUU-0, becomes much stronger and broader after doping with $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$. The N–H peak in PUU-11 extends from 3700 to 3000 cm^{-1} and the peak maxima shifts to 3345 cm^{-1} . Water of hydration present in ErCl_3 may also be contributing to the broadening of the peak in this region. Figure 1(b) provides the comparative FTIR spectra in the carbonyl region, where clear differences between the peak positions and peak shapes of undoped and doped samples, especially in the strongly hydrogen bonded C=O peak observed. H-bonded C=O peak in undoped sample is centered at 1650 cm^{-1} and it is fairly symmetrical and sharp. In the doped material (PUU-11) it becomes very strong and broad and shows several maxima. Figure 1(c) shows the strong ether (C–O–C) peaks

between 1180 and 1000 cm^{-1} . Interestingly, there is no noticeable difference in the shape and the absorption maxima of the ether peaks for the undoped and doped material. These FTIR results indicate that $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ seems to interact mainly with the urea hard segments and there seems to be no significant interaction with the polyether soft segments.

We believe these results are important, because they indicate that it is possible to prepare rare-earth ion (REI) doped luminescent¹⁶ thermoplastic polyurethane and polyurea systems with controlled nanostructures, where hard segment morphology determines the location of the REI in the system. Polyurethane or polyurea hosts also offer other benefits over conventional glasses typically used in UV-to-visible converters. These include ease of preparation, possibility of incorporation of large amounts of dopant, toughness and elasticity.

Figure 2 shows the absorption spectra of the undoped (PUU-0) and 6.49% by weight Er^{3+} doped film samples (PUU-6), where characteristic

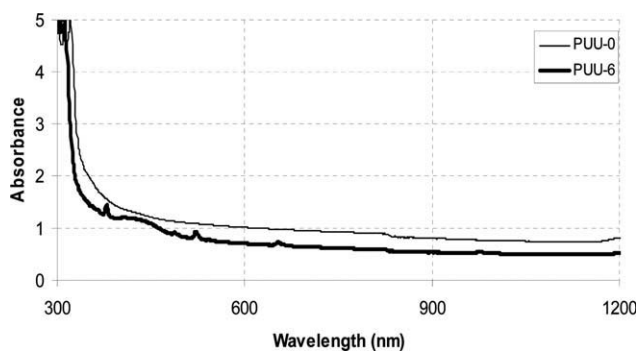


Figure 2 Absorption spectra of undoped (PUU-0) and 6.49% by weight Er^{3+} doped (PUU-6) samples. Characteristic absorption bands of the trivalent erbium ion are visible in the PUU-6 spectrum.

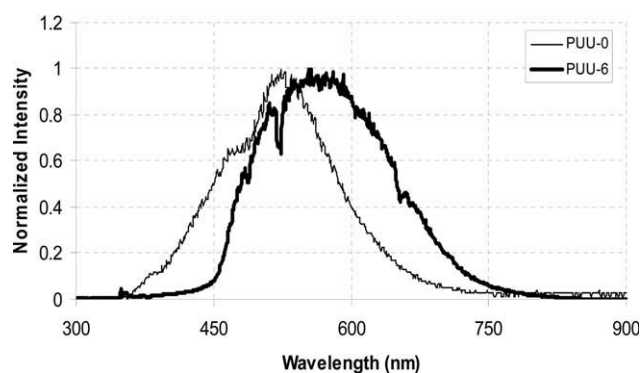


Figure 3 Emission bands of PUU-0 and PUU-6. Doping with erbium red shifts the band and covers the whole visible spectrum.

TABLE II
Tristimulus Coordinates (x,y), Color Rendering Index (CRI), Color Temperature T_C , and Eye Overlap Factor (η) of the Undoped and Er³⁺ Doped PUU Samples

Sample Code	x	y	CRI	T_C (K)	η
PUU-0	0.29	0.41	61	5540	0.85
PUU-2	0.38	0.43	70	5138	0.88
PUU-4	0.38	0.44	68	5175	0.89
PUU-6	0.42	0.48	58	5212	0.92
PUU-11	0.41	0.47	57	5093	0.95

Chromaticity coordinates and CRI values were calculated according to CIE 1964 Standards.

absorption bands of trivalent erbium around 380 nm ($^4G_{11/2} \rightarrow ^4I_{15/2}$), 430 nm ($^4F_{5/2} + ^2H_{9/2} \rightarrow ^4I_{15/2}$), 490 nm ($^4F_{7/2} \rightarrow ^4I_{15/2}$), 520 nm ($^2H_{11/2} \rightarrow ^4I_{15/2}$), and 650 nm ($^4F_{9/2} \rightarrow ^4I_{15/2}$) are visible. In the emission spectrum measurements, the film samples were excited in the absorption band of the polymers by using a pulsed, frequency-tripled Nd:YAG laser at 355 nm. Emission spectra of the polymer samples were investigated as a function of Er³⁺ concentration. Figure 3 shows the emission band of PUU-0 and PUU-6 samples. The emission band of PUU-0 is in the blue-green range. We believe that the presence of the erbium absorption bands between 380 and 520 nm aids in effective energy transfer from the polymer host to the dopant ions and extend the emission band into the red region. As shown in Figure 2, the resulting emission band of PUU-6 covers the 400–750 nm range. The chromaticity coordinates, color rendering index (CRI), color temperature (T_C), and overlap factor (η) of the each PUU spectrum are shown in Table II. The calculation of chromaticity coordinates and CRI were performed according to CIE 1964 standards. Furthermore, Figure 4 shows the color coordinates of the five samples in the CIE chromaticity diagram. In general, the samples are not within but very close to the region correspond-

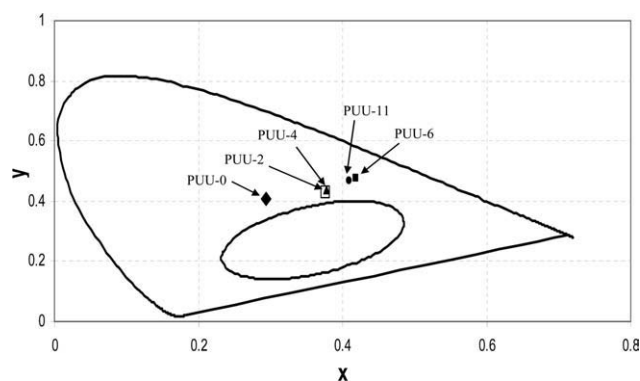


Figure 4 CIE chromaticity diagram showing the chromaticity coordinates (x,y) for PUU-0 and Er³⁺ doped PUUs with different concentrations. White-light sources fall within the region surrounded by the ellipse. The sample codes are indicated by arrows.

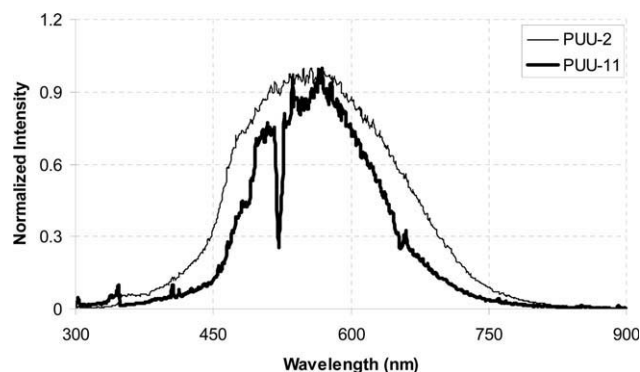


Figure 5 Emission bands of PUU-2 and PUU-11. In the emission band of PUU-2 self absorption of the erbium ions appears at 523 nm.

ing to white light sources (shown as the closed ellipse in Fig. 4). PUU-2 and PUU-4 containing 2.19 and 4.22 weight percent Er³⁺, display chromaticity coordinates closest to the white-source region. However, increasing the erbium concentration beyond 4.22 weight percent causes a deviation from the white region. We believe the deviation is because of self absorption by erbium, which becomes more effective at high dopant concentrations. This is also evident in Figure 5, which shows comparative plots of the emission bands for PUU-2 and PUU-11 containing 2.19 and 10.86 weight % Er³⁺, respectively. In PUU-11, self absorption of the erbium ions is clearly visible at the wavelength of 523 nm. The dopant concentration has a similar effect on the color rendering index (CRI). As can be seen from Table II, with increasing erbium concentration, CRI value first increases to 70 for PUU-2 followed by a monotonic decrease to 57 for PUU-11. CRI values of erbium doped PUUs prepared in this study are close to those reported by others. For example, CRI = 71 was reported for CdSe/ZnS nanocrystals hybridized with InGaN/GaN LEDs.⁵ In the case of OLEDs, CRI values as high as 92 have been reported.³

Color temperature (T_C) of a light source expresses the color degree of white light in comparison with a

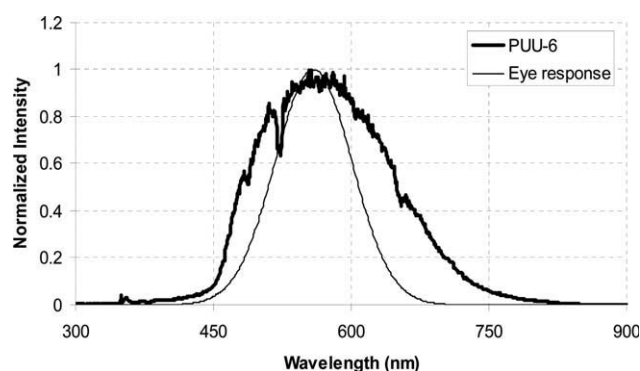


Figure 6 The emission spectrum of PUU-6 together with the spectral response function of the eye.

blackbody radiator. For illumination applications, T_C should be in the range of 3000–7500 K³. Some of the previously reported color temperature values for different white light emitters are 6400 K for OLEDs³, 4500 K for thin films of ZnSe excited by electron beam,⁴ and 5892 K for white LEDs.¹⁷ In our case, T_C was determined to be in the range of 5093–5540 K (Table II).

Figure 6 shows the emission spectrum of the PUU-6 film together with the spectral response curve for the eye. As can be seen, the emission band completely covers the visible region. In fact, there is emission beyond the visible range as well. As can be seen from Table II, as the Er^{3+} concentration is increased from 0 to 10.86 weight %, the eye overlap factor η monotonically increases from 85 to 95%. The increase in η could be due to the emergence of the self absorption bands of erbium around 660, 490, and 430 nm, which tend to narrow the emission band and produce a better match with the visible region.

CONCLUSIONS

We reported on a novel type of polymeric UV-to-visible converters, which can easily be prepared by the incorporation of Er^{3+} ions into elastomeric poly(ether-urethaneurea) copolymers (PUU). Spectroscopic properties of PUU's containing 5–25% by weight of $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (or 2.19 to 10.86% by weight Er^{3+}) were characterized by exciting them in the ultraviolet region at 355 nm. In particular the chromaticity color coordinates, color rendering index (CRI), color temperature, and the degree of overlap of the emission bands with the spectral response of the eye were determined. The chromaticity coordinates of Er^{3+} doped PUU's are very close to the region corresponding to white light sources. Furthermore, CRI values of the samples were determined to be in the range of 57–70. PUU-2, containing 2.19% by weight of Er^{3+} was found to give the chromaticity coordinates closest to the white-source region and the highest color rendering index. The color

temperatures of the samples were in the 5093–5540 K range. The overlap between the emission bands and the spectral response of the eye improved with increasing erbium concentration. In particular, PUU-11, containing 10.86 weight percent of Er^{3+} gave an overlap factor of about 95%. Novel erbium-doped PUU's, which are fairly easy to prepare, could pave the way for the development of simple, polymeric UV-to-visible converters for various applications.

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