Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting information for

Dye immobilization in halochromic nanofibers through blend electrospinning of a dye-containing copolymer and polyamide-6

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^{1}H-NMR spectra and SEC traces

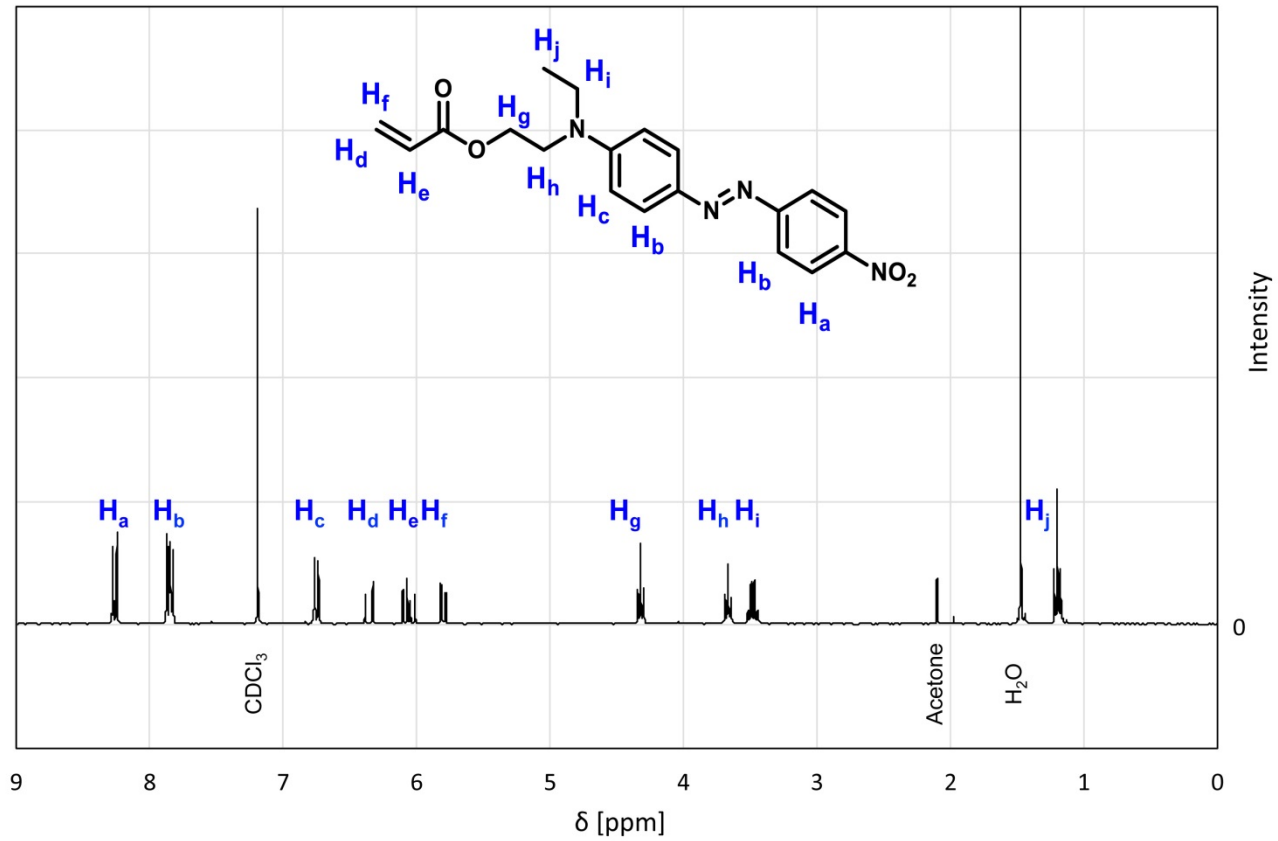

Fig A. ^{1}H-NMR spectrum (300 MHz) of Disperse Red 1 – acrylate in $CDCl_3$.

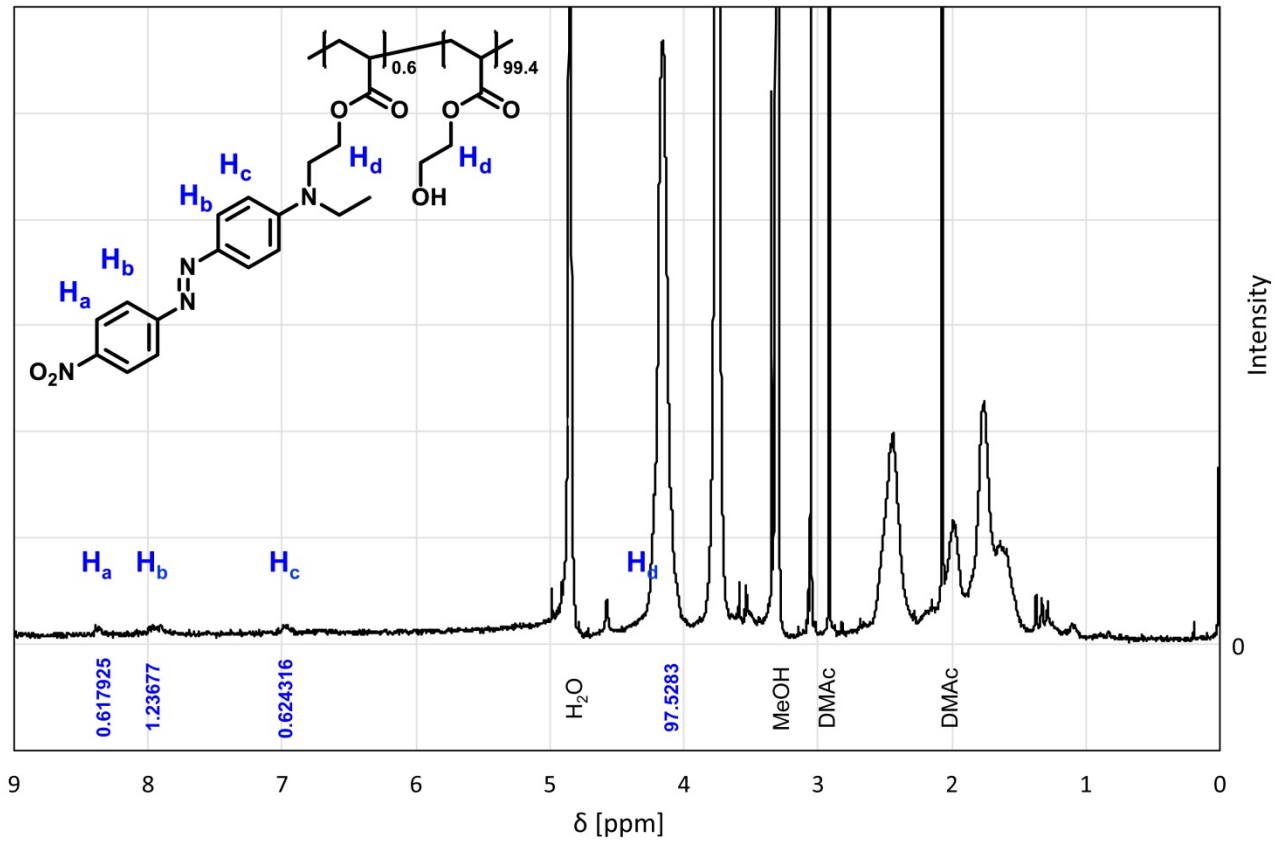

Fig B. ^{1}H-NMR spectrum (300 MHz) of precipitated P(HEA-co-DR1-A) (P1) in MeOD-4d and integrations (in blue) used for the determination of the DR1 content.

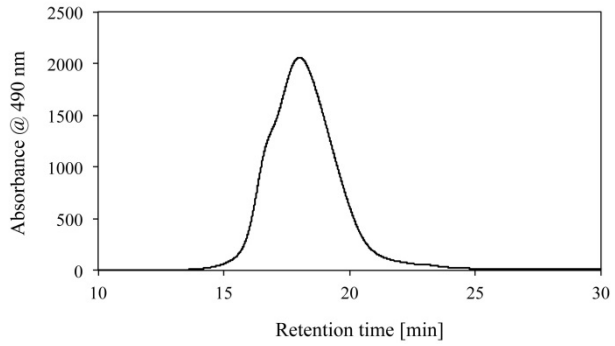

Fig C. SEC-trace @ 490 nm of purified P(HEA-co-DR1-A) (P1).

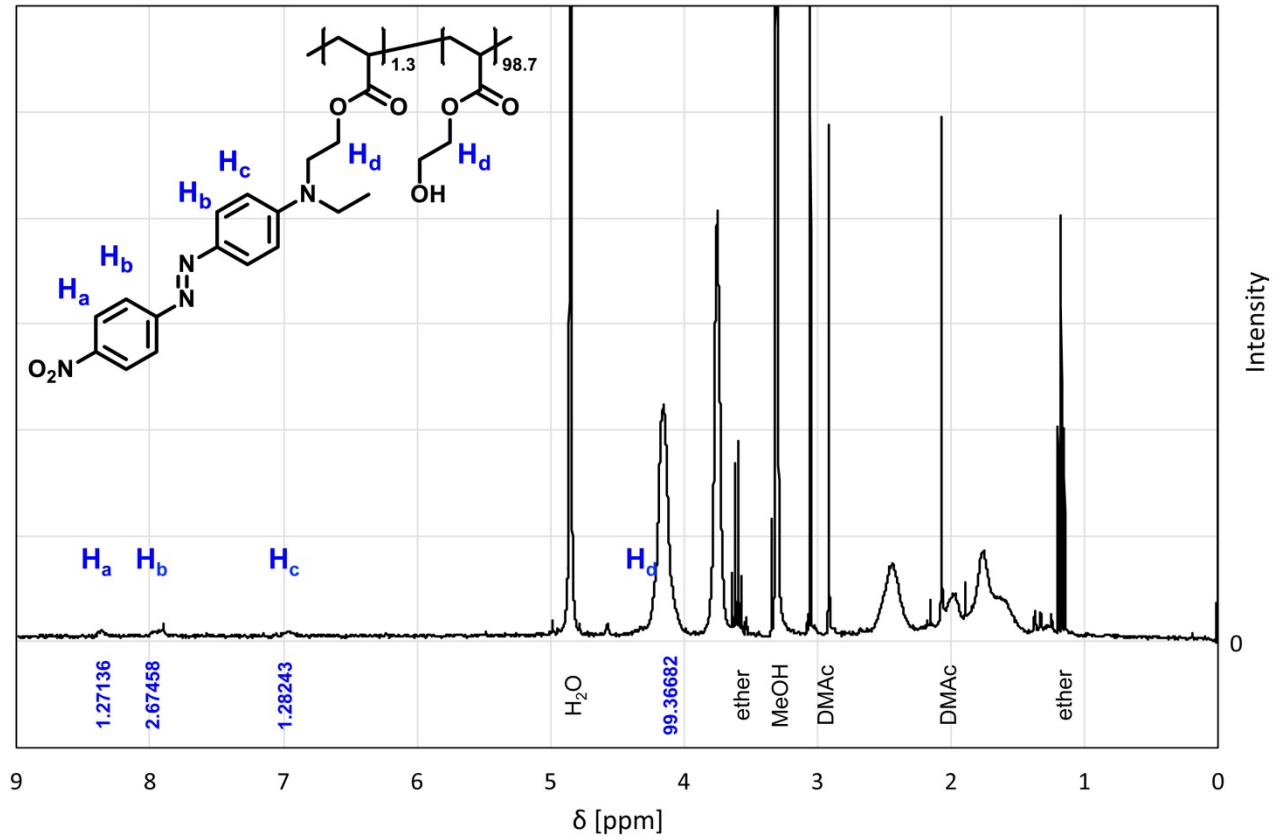

Fig D. ^{1}H-NMR spectrum (300 MHz) of precipitated P(HEA-co-DR1-A) (P2) in MeOD-4d and integrations (in blue) used for the determination of the DR1 content.

Hydrolysis of P(HEA-co-DR1-A)

The water bath leaching experiments shows hydrolysis under basic improving the solubility of the dyed polymer.

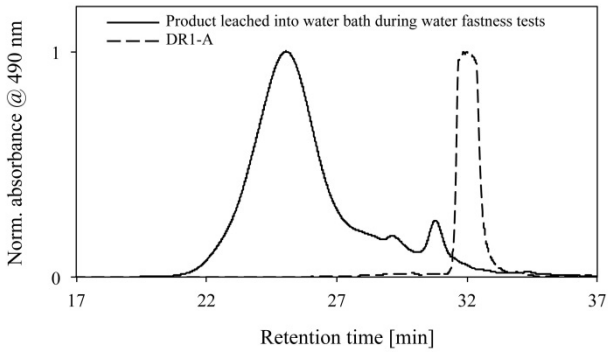

Fig E. Normalized SEC-trace @ 490 nm of DR1-A and the residue of a water bath after the water fastness test at pH 13.

This could be explained by the hydrolysis of the HEA monomer producing ethylene glycol and partially transforming the polymer into poly(acrylic acid). The latter would be deprotonated at pH > 7 increasing the overall solubility of the copolymer. This hydrolysis mechanism was already partially proven by the presence of dyed copolymer in the water bath as measured with SEC. Further quantification of the hydrolysis speed and extent was determined by measuring the amount of ethylene glycol produced in time in a buffered copolymer solution at pH of 13 using gas chromatography.

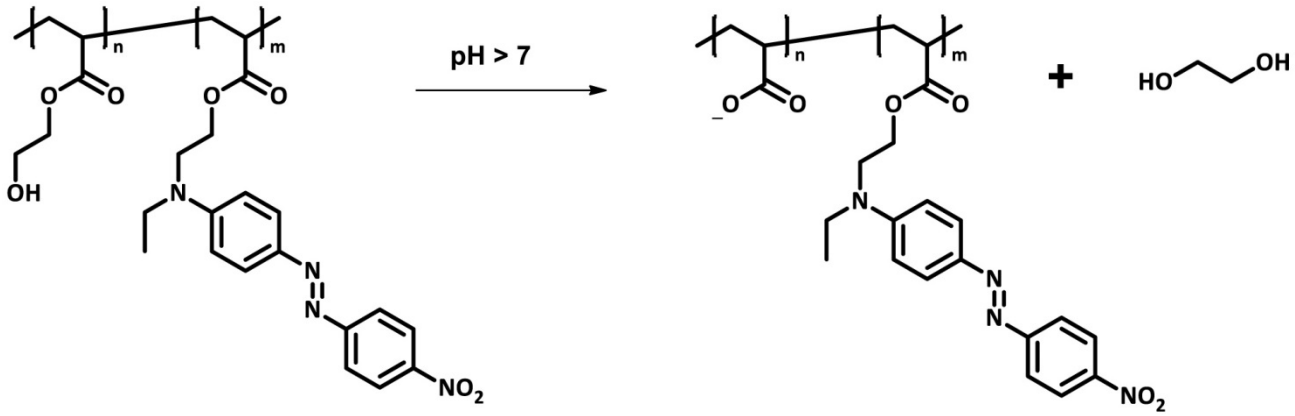

Fig. F: Proposed hydrolysis mechanism of P(HEA-co-DR1-A) under basic conditions.

100 mg of P(HEA-co-DR1-A) was dissolved in 2 ml pH 13 buffer solution and stirred at room temperature. The mixture was sampled in time and analyzed with gas chromatography. The calibration test on the left in Fig. G shows a linear dependence of the peak area (t = 1.6 min) and the concentration of ethylene glycol both of the pure mixture and a 50 µl sample diluted in 450 µl MeOH. The latter was used to calculate the percentage hydrolysis in the sample based on the peak area in the unknown samples.

A second batch of P(HEA-co-DR1-A) was used for these follow-up tests characterized by a HEA conversion of 77 % and a 98/2 ratio of incorporated HEA/DR1-A as calculated based on ^{1}H-NMR. Using these data we can calculate the absolute molecular weight of the polymer as 9825.15 Da and estimate the maximum concentration of ethylene glycol (EG).

$50\ {}^{mg}/_{ml}\ polymer\ solution$	$\Rightarrow$	$25.86\ {}^{mg}/_{ml}\ EG\ (100\%\ hydrolysis)$
$\downarrow\ in\ 2\ ml$		$\uparrow\ in\ 2\ ml$

$$1.0177\ 10^{-5}\ mol\ polymer \xrightarrow{100\ \%\ hydrolysis} 7.837\ 10^{-6}\ mol\ EG$$

The large increase shown in Fig. G proves the production of ethylene glycol through hydrolysis of hydroxyethyl acrylate as proposed in Fig. F. The initial large increase is slowed down due to neutralization of the buffer by the formed acrylic acid until it reaches a plateau around 44 % hydrolysis corresponding with a pH of 8.12.

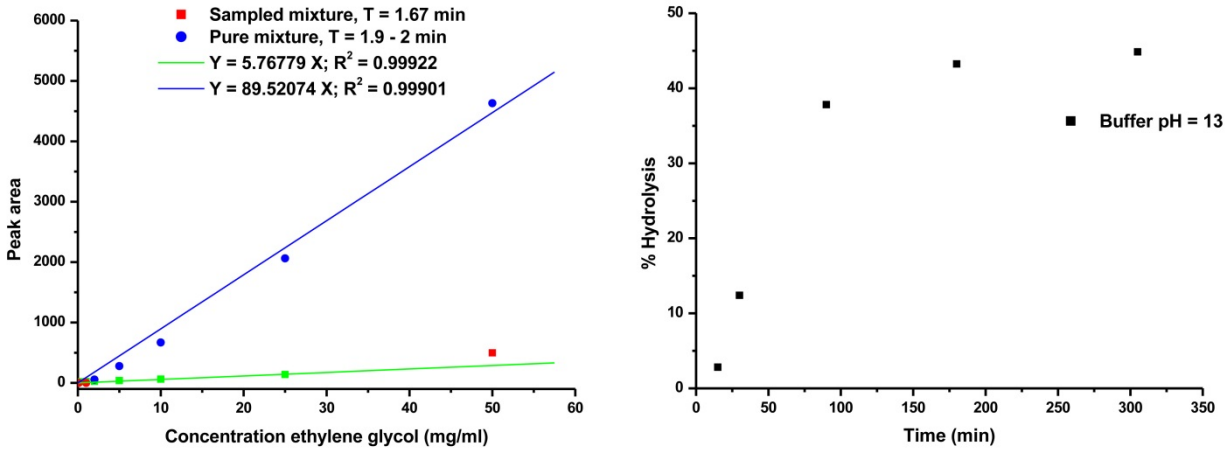

Fig. G: Left: two calibration curves correlating peak area with ethylene glycol concentration in a pH 13 buffer solution sampled directly (blue) and 50 µl sample diluted with 450 µl MeOH (green). Right: calculated hydrolysis percentage of P(HEA-co-DR1-A) dissolved in a pH 13 buffer given in time

Electrospinning of DR1-containing nanofibers

No significant differences in electrospinning behavior or fiber morphology were found for the blank, dye-doped or blend nanofibers, as illustrated by Fig. H.

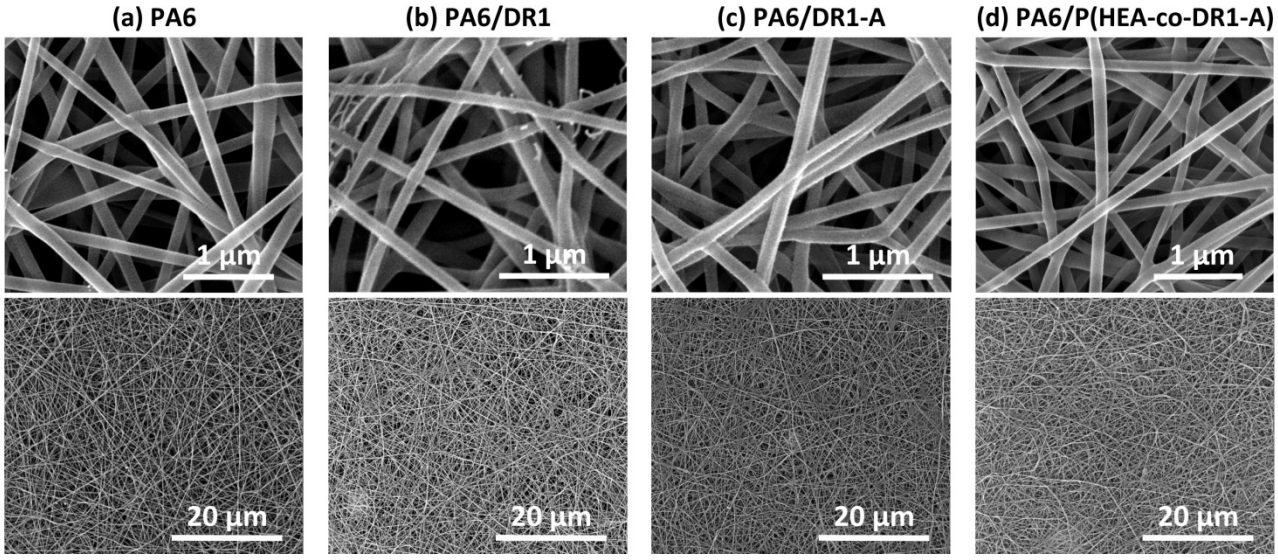

Fig. H: SEM-images of the electrospun samples: (a) PA6 – 136 ± 19, (b) PA6/DR1 – 123 ± 18, (c) PA6/DR1-A – 120 ± 14 and (d) PA6/P(HEA-co-DR1-A) – 138 ± 25

Calculation of color differences

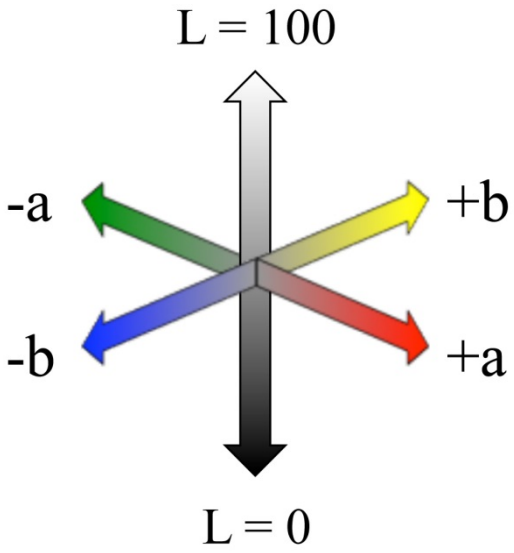

Fig. I: The CIELAB color space

Color differences can be calculated based on the Lab-values of the two samples. Lab-values are the coordinates of a color according to the CIELAB color scale. This is an approximately uniform color scale, where differences between points plotted in the color space correspond to visual differences. The L-axis represents lightness, going from 0 (black, the perfect absorber) to 100 (white, the perfect reflecting diffuser). The a- and b-axis have no specific numerical limits, representing the red-green and yellow-blue color variations, as represented in Fig. I. The overall color difference (ΔE) between two samples can thus be calculated according to [Eq-1].

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad \text{[Eq-1]}$$

Lab-values can be calculated from the UV-Vis spectrum of the sample. During this calculation, the observer (trichromatic spectral sensitivity of cone cells in the human eye) and the illuminant (light source) are taken into account. This is done through application of the color matching functions and the spectral energy distribution respectively, both described in the CIE standards[1]. Calculations were done using OptLab-SPX (Ascanis) and are based on the equations below[2]. For very dark colors, which do not fulfill the requirement for [Eq-3], other equations are necessary and can be found in literature[3].

[1] Weatherall, I.L., Coombs, B.D. (1992) Skin color measurements in terms of CIELAB color space values. *Journal of Investigative Dermatology, 99(4),* 468-473

[2] Zollinger, H. (2003) *Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments.* Germany: Wiley-VCH
Broadbent, A.D. (2001) *Basic Principles of Textile Coloration.* England: Society of Dyers and Colourists

[3] Gonnet, J.-F. (1998) Colour effects of co-pigmentation of anthocyanins revisited – 1. A colorimetric definition using the CIELAB scale. *Food Chemistry, 63(3),* 409-415

$$X = \int_{380}^{780} R(\lambda)\, E(\lambda)\, x(\lambda)\, d\lambda$$
$$Y = \int_{380}^{780} R(\lambda)\, E(\lambda)\, y(\lambda)\, d\lambda \qquad \text{[Eq-2]}$$
$$Z = \int_{380}^{780} R(\lambda)\, E(\lambda)\, z(\lambda)\, d\lambda$$

with
X, Y, Z = tristimulus values for the sample
R(λ) = reflection spectrum sample
E(λ) = spectral energy distribution illuminant (D65)
x(λ), y(λ) and z(λ) = color matching functions observer (10°)

$$L^* = 116\,(Y/Y_n)^{1/3} - 16$$
$$a^* = 500\,(X/X_n)^{1/3} - 500\,(Y/Y_n)^{1/3} \qquad \text{if } \left.\begin{matrix} X/X_n \\ Y/Y_n \\ Z/Z_n \end{matrix}\right\} > 0.008856 \qquad \text{[Eq-3]}$$
$$b^* = 200\,(Y/Y_n)^{1/3} - 200\,(Z/Z_n)^{1/3}$$

with
Xn, Yn, Zn = tristimulus values for the illuminant