Research Article

Received: 18 October 2017 Revised: 20 January 2018 Accepted article published: 31 January 2018 Published online in Wiley Online Library: 2 March 2018

(wileyonlinelibrary.com) DOI 10.1002/pi.5543

Structural and optical properties of soluble melanin analogues with enhanced photoluminescence quantum efficiency

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Abstract

Melanin is a functional material of growing interest for bioelectronics. Several melanin analogues have been employed in order to fully explore its potential; in this work melanin was synthesized using dimethylsulfoxide (DMSO) and O_2 under pressure as oxidizing agent. It is shown that the products have similar functional groups and solubility; however, O_2 pressure produces more carboxylated structures and improves the synthesis reaction rate. The photoluminescence of all sulfonated melanin analogues was studied. It is shown that the material synthesized in DMSO has photoluminescence in the visible region (487 nm) with a quantum yield of (2.12 ± 0.02)%. This good quantum yield compared to natural and synthetic melanin may open new perspectives for its use in optoelectronics applications. The origin of this effect is discussed in terms of the polymer structure.

Supporting information may be found in the online version of this article.

Keywords: melanin; DMSO; O_2 pressure; photoluminescence; optoelectronics

INTRODUCTION

Present throughout fauna and flora, melanin is an important pigment that has interesting physicochemical properties which enables a wide range of technological applications, especially for bioelectronics.[1,2] Not all properties are adequate for electronic device fabrication, such as its low solubility, and thus over the past few years various strategies have been proposed for controlling the structure of melanin and consequently its optical and electronic properties.[1–5] Our group has developed various synthetic approaches to tune the chemical structure of soluble melanin analogues.[3,6–8]

Very recently, we have proposed a new route for the synthesis of melanin under O_2 pressure in water.[8] In this procedure, O_2 under mild pressure induces a faster polymerization with higher content of carboxylated (DHICA, 5,6-dihydroxyindole-2-carboxylic acid) over non-carboxylated (DHI, 5,6-dihydroxyindole) structures, similar to natural melanin. DHICA-rich pigments should have higher oxidant capacity and improved chelating properties, improved protonic conductivity and solubility in water.[1,8] Since 2004, we have studied the synthesis of melanin in dimethylsulfoxide (DMSO) instead of water.[3,6,7,9] The main difference between water and DMSO is that the synthetic chemical environment can also oxidize DMSO to form sulfonate by-products which are incorporated in the melanin structure (Fig. 1).[6] In DMSO, the synthesis is more controlled producing a homogeneous derivative with higher thermal stability,[3] biocompatibility,[10] proton transport properties[11] and solubility in DMSO which enables the production of homogeneous thin films with good substrate adhesion.[3,9,11,12] In the study presented here, we extended our previous work synthesizing melanin in DMSO under O_2 pressure and evaluated the photoluminescence of the derivatives.

EXPERIMENTAL

Synthesis

The traditional derivative, called from now on DMel, was made with a mixture of 1.50 g of L-DOPA and 0.73 g of benzoyl peroxide dissolved in 200 mL of DMSO. This solution was maintained at room temperature (±27 °C) under magnetic stirring in a sealed flask to avoid air humidity. A sequence of solvent evaporation, dissolution in acetonitrile, centrifugation (2500 rpm for 15 min) and precipitate drying (at 90 °C) was used for extraction and purification.[3,6] For synthesis under O_2 pressure, 0.45 g of L-DOPA was dissolved in 60 mL of DMSO in a stainless steel reactor with a capacity of 150 mL. After sealing the reactor, oxygen was introduced until the internal pressure reached 4 or 8 atm. The extraction

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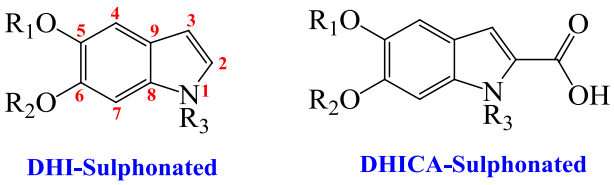

Figure 1. Basic structures proposed for melanin monomers synthesized in DMSO.

and purification process was the same described previously. The product obtained is referred to as DMel-*p*P, where *p* is the O_2 pressure in atm.

UV–visible spectroscopy was used to monitor melanin polymerization following a procedure described elsewhere.[7] Reproducible optical and structural properties were obtained; for each material, at least three independent syntheses were done. Commercially available chemicals were purchased from Acros or Sigma-Aldrich and used without further purification.

Characterizations

Fourier transform infrared (FTIR) measurements in the region between 4000 and 500 cm^{-1} were performed with a Bruker Vertex 70 spectrometer at room temperature in attenuated total reflectance mode. Spectral deconvolutions were implemented at the carbonyl and C—C=C region of the spectra, following a procedure described elsewhere[7] using OriginPro version 9 (OriginLab Corp., MA, USA). An X-ray photoelectron spectroscopy (XPS) instrument (Thermo Scientific ESCALAB 250 Xi) with Al Kα monochromatic X-ray radiation ($h\nu$ = 1486.6 eV) and 650 µm beam size was used for acquiring core-level spectra (C 1s, N 1s, O 1s and S 2p). Atomic ratios were calculated from peak intensities using Scofield's sensitivity factors. Curve-fitting analysis of the C 1s, N 1s, O 1s and S 2p spectra was made using a product algorithm from Gaussian and Lorentzian functions after subtraction of a Shirley-type background performed using Thermo Avantage v.5.956 software. ^{1}H NMR and ^{13}C NMR spectra were measured with a Bruker Avance III spectrometer (600 MHz) using DMSO-d_6 as solvent at room temperature. For XRD, a Rigaku RINT2000 diffractometer with Cu Kα radiation was used (40 kV, 20 mA).

For optical characterization, a stock solution of 5 mg mL^{-1} in DMSO was prepared and left to magnetically stir for 1 h. UV–visible measurements were made in triplicate with concentration ranging from 2.0 to 7.0 µg mL^{-1} and the Beer–Lambert law was used to calculate the molar absorption coefficient. For photoluminescence (PL) measurements, solutions of 17 µg mL^{-1} were used. Quantum yields (ϕ) were obtained following a standard procedure[13] using equation 1

$$\phi_M = \phi_S \left(\frac{g_M}{g_S}\right)\left(\frac{n_M}{n_S}\right)^2 \quad (1)$$

where g is the gradient of the integrated emission *versus* absorbance plots and n is the solvent refractive index. Subscript 'S' refers to the standard sample and 'M' to melanin. Fluorescein in 0.1 mol L^{-1} NaOH solution ranging from 0.16 to 0.50 µg mL^{-1} (λ_{Ex} = 490 nm, ϕ_S = 0.92 and n_S = 1.33) was used as standard. For the melanin samples, λ_{Ex} = 425 nm and n_M = 1.48 were used. The measurements of absorbance and PL were made, respectively, using a Shimadzu UVmini-1240 and a Varian Cary Eclipse with a quartz cuvette of 1 cm optical length.

RESULTS

Figure 2 shows C 1s, N 1s, O 1s and S 2p high-resolution XPS spectra for DMel-4P and the corresponding fitting analysis. Similar features are observed for the other samples (Figs S1 and S2 in the supporting information). Table 1 presents the peak positions and the atomic concentrations of the functional groups. There are seven contributions assigned to the C 1s spectrum, C=C, C—C, C—N/C—S, C—O, C=O, COOH and shake-up satellite, that are related to the basic indole structure of melanin. The O 1s XPS spectrum shows C—O and C=O groups from catechol and quinone and O—C=O structures of DHICA. Note that C—O is the major structure containing oxygen due the presence of sulfonated groups attached to the oxygen at position 5-C and 6-C (Fig. 1). The presence of —SO_2— refers to sulfonated groups. The N 1s photoemission signals are assigned to five groups, =N—, —N—H/—N—S, —NH—, —N^+— and =N^+—, that are related to the cyclic structure, as expected, since L-DOPA is cyclized to form melanin. The smaller contributions from =N— are related to oxidized structures, and —N^+— and =N^+— suggest spontaneous proton transfer from the hydroxyl or carboxyl group towards the indole nitrogen. Notice that the N 1s signal other experimental evidence that indicates that N-sulfonation occurs in DMel as proposed in our synthesis mechanism.[6] Peaks of —S—, —SO— and —SO_2— corresponding to S 2p signal are assigned to sulfonated groups. The signal related to SO_4^{2-} observed for DMel-8P can be understood as trapped molecules within the macromolecule obtained by the oxidation of the by-products derived from DMSO oxidation as a consequence of the synthesis under pressure. The assigned functional groups are in good agreement with the literature.[8,14–16]

^{1}H NMR and ^{13}C NMR spectra are presented in Fig. 3. The regions of the observed signals are in agreement with our previous work and the literature.[6,7,17–19] In Fig. 3(a) the signal between 6 and 8.5 ppm is assigned to the protons of the indole structure; the broad signal at 3.5 ppm to the sulfonated groups bonded to oxygen at 5-C and 6-C and to protons of methyl groups bounded to nitrogen. Note that the amine, hydroxyl and carboxylic acid proton signals are not observed, in agreement with previous work.[17] Moreover, Fig. 3(b) has peaks related to carbons from the carboxyl group at 167 ppm and aromatic carbons from the indole structure between 155 and 110 ppm; the peaks at 40.8 and 42.6 ppm are related to sulfonated groups. Although similar, there are clear changes in the spectra for the different synthesis conditions used.

Figure 4(a) shows the molar absorption coefficient of the various samples. Although the optical characteristic of the samples are similar to those reported in the literature, there are small changes that indicate structural differences.[7,20] Note that for higher energies DMel has the lowest absorption coefficient compared with the samples synthesized under O_2 pressure. On the other hand, Fig. 4(b) shows the PL spectra of the samples characterized by a broad signal with emission maximum at 487 nm for DMel. PL quantum yields with excitation at 425 nm were calculated for DMel to be (2.12 ± 0.02)%, for DMel-4P to be (0.22 ± 0.01)% and for DMel-8P to be (0.19 ± 0.02)%. These results are one or two orders of magnitude greater than those reported in the literature for non-functionalized synthetic melanin.[13]

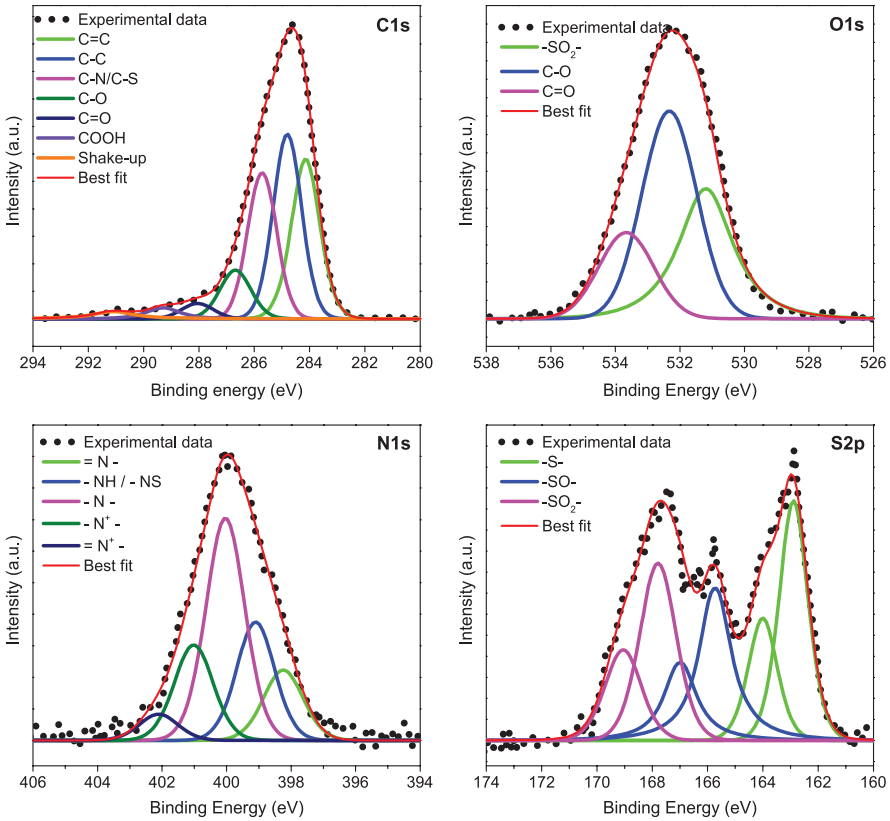

Figure 2. High-resolution XPS spectra of C 1s, N 1s, O 1s and S 2p core levels of DMel-4P. Experimental data are shown as solid dots, while the fitting is shown as solid lines.

DISCUSSION

As mentioned above, melanin analogues synthesized in DMSO have good technological potential; however, the reaction takes 57 days to be completed.[7] Thus, we propose O_2 pressure to accelerate the reaction. The results show that, similarly to the synthesis in water,[8] the reaction time in DMSO under O_2 pressure decreases considerably. For instance, on increasing the pressure to 4 atm the synthesis takes six days to be concluded and to 8 atm only three days. Notice that when pressure is introduced the synthesis does not use benzoyl peroxide, and thus we have tested the oxidation of L-DOPA at atmospheric pressure without benzoyl peroxide. Melanin is formed (Figs S3–S5 in the supporting information); however, the reaction time is extremely long.

Solubility tests based on the literature found that all samples are soluble in DMSO, *N*-methyl-2-pyrrolidone and dimethylformamide.[3] The solubility in more than one solvent is an interesting feature from a technological point of view, since it is known that different solvents may produce different film morphologies.[12] Not only that, the fact that all derivatives have similar solubility suggests that they have similar structures. This idea is reinforced by the small variation in the concentrations of functional groups in Table 1. Table 1 also indicates that the highest concentration of carboxylic groups was obtained for DMel-4P and the lowest for DMel in agreement with our previous work.[8] This effect is confirmed on analyzing the FTIR spectra in the region of 1050 and 1750 cm^{-1} (Fig. S5).[7] Note that, although there is a slight decrease in DHICA/DHI ratio in DMel-8P in comparison to DMel-4P, it is still higher than in DMel in agreement with our proposed model. This decrease in DMel-8P is also obtained for sample synthesized in water.[8]

However, it is interesting to note that the synthesis under oxygen pressure causes changes in melanin polymerization (Fig. 3). In the absence of a radical initiator, benzyl peroxide in our case, the interaction between carboxylic groups and phenolic hydroxyls of melanin monomeric structures can give rise to the formation of alkoxy groups. ^{13}C NMR spectra confirm alkoxy groups (peaks at 145.37 ppm) in DMel-4P and DMel-8P that are not observed in DMel. Therefore, a more detailed investigation of the aromatic region suggests that the polymerization in DMSO under oxygen pressure is based on the esterification of different functional groups as shown in Fig. 5. For DMel the similarity of the ^1H NMR spectra to natural melanin[17] indicates that the polymerization process preferentially occurs on 2-C, 3-C, 4-C and 7-C, as broadly reported in the literature.[8,21]

Normalizing the signals of the carboxylic group (167 ppm) (Fig. 3(b)), with respect to the sum of all aromatic signals, a similar pattern is observed when compared to XPS and FTIR, supporting the idea that the synthesis under oxygen pressure favors carboxylated structures (Table 2). It is worth mentioning that the integration of carbon signals is not usual; however, this procedure may be used for a qualitative analysis, in our case, of the DHICA/DHI ratio on melanin samples, as reported elsewhere.[7,8,19,22]

XRD analysis was performed in order to investigate the macromolecular structure. As expected it is characterized by a broad peak centered at about 22.5 ± 0.1° (Table 2; and Fig. S6 in supporting information). This peak corresponds to $\pi-\pi$ stacking of parallel planar layers.[23,24] Considering the first-order diffraction from the Bragg equation we have interlayer spacing (*d*) similar to the values obtained for natural melanin (4.0 Å) and it is greater than that of synthetic melanin (*ca* 3.5 Å)[24] (Table 2). Using the

Table 1. Atomic percentage of melanin synthesized in DMSO

Signal	Assignment		Binding energy (eV)	DMel (at%)	DMel-4P (at%)	DMel-8P (at%)
C 1 s	C=C		284.10	19.43	19.02	18.65
	C—C		284.81	22.21	23.5	21.52
	C—N; C—S		285.75	17.69	15.8	11.68
	C—O		286.76	6.37	6.54	8.64
	C=O		288.11	2.03	1.89	4.75
	COOH		289.29	1.74	2.18	1.93
	Shake-up		290.98	1.73	0.63	0.93
O 1 s	$—SO_2—$		531.19	8.33	6.37	7.56
	C—O		532.44	7.68	8.96	9.76
	C=O		533.62	4.07	3.71	3.30
N 1 s	=N—		398.27	0.41	0.70	0.81
	—NH/—NS		399.15	0.72	1.12	1.67
	—N—		400.09	1.3	2.15	2.11
	$—N^+—$		401.15	1.81	0.93	1.21
	$=N^+—$		402.43	0.42	0.25	0.28
S 2p	—S—	$2p_{3/2}$	163.06	0.99	0.85	0.56
		$2p_{1/2}$	164.24	0.00	0.00	0.00
	—SO—	$2p_{3/2}$	165.82	0.69	0.72	0.56
		$2p_{1/2}$	167.04	0.00	0.00	0.00
	$—SO_2—$	$2p_{3/2}$	167.83	1.40	0.75	1.02
		$2p_{1/2}$	169.07	0.00	0.00	0.00
	SO_4^{2-}	$2p_{3/2}$	170.48	–	–	0.34
		$2p_{1/2}$	171.54	–	–	0.00

Debye–Scherrer equation, the estimated average grain size (*D*) is 8.0 ± 0.2 Å (Table 2) which suggests two-layer stacking, in disagreement with the literature that reports stacking of three to four layers.[23,24] This is attributed to the sulfonated groups; they increase the interlayer distance due to topological hindrance reducing the stability of non-covalent bonds. This can also explain the enhancement of the solubility of the sulfonated derivatives, since a combination of higher π-stacking and hydrogen bonding is responsible for melanin insolubility.[25] Notice that DMel-4P has the lowest grain size, which can be related to the higher DHICA/DHI ratio since it is known that DHICA monomers form smaller and more elongated aggregates.[8,21] Previous AFM results reported a similar effect in DMel.[10,11] The higher values of *d* and *D* for DMel-8P on the other hand can be assigned to SO_4^{2-} trapped inside the macromolecule.

The same reasoning can be applied to the differences in absorption spectra observed in Fig. 4(a). We have observed previously that increasing the amount of decarboxylated oligomers (that is, DHI) results in a decrease in the absorption intensity.[7] Thus from Fig. 4, DMel-4P has a higher concentration of carboxylated structures followed by DMel-8P and DMel in agreement with what has been discussed so far.

One of the most characteristic properties of melanin is its low PL intensity; typically photoexcited electronic states decay through non-radiative decay, with PL yields lower than 0.07%.[13] Yet, in the case of DMel, the yield is higher. Several PL quenching mechanisms propose that the non-radiative processes occur due to proton transfer,[26–29] so the presence of sulfonated groups decreases the protonation in the catechol structure and increases, as a consequence, the radiative emission. In addition, PL quenching is also induced by $\pi-\pi$ stacking,[30] which as discussed earlier is reduced in DMel. On the other hand, it is well established that carboxylic acid can quench the fluorescence of indole structures[31]

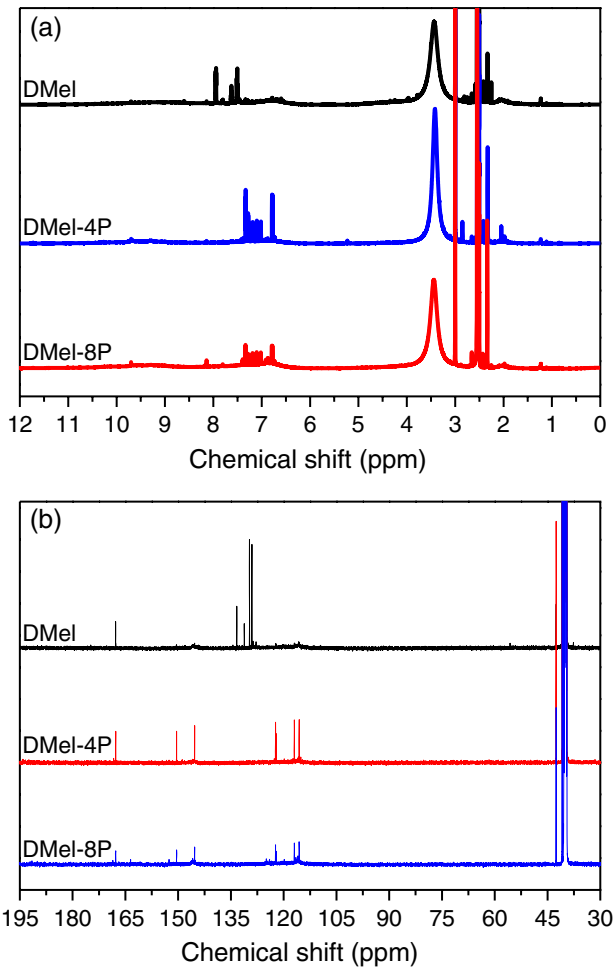

Figure 3. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of the various melanin samples in DMSO-d_6 at room temperature.

Table 2. Structural features of sulfonated melanin derivatives

Sample	COOH group (167.78 ± 0.02 ppm)	2θ (°)	*d* (Å)	*D* (Å)
DMel	0.081	22.5	3.9	8.1
DMel-4P	0.110	22.5	3.9	7.8
DMel-8P	0.102	22.4	4.0	8.2

and it has also been proposed that the intensity of PL of melanin is proportional to the conjugation of the structural backbone.[32] Thus, based on the results discussed above, the breakdown of the conjugation and the higher DHICA/DHI ratio of the samples synthesized with oxygen pressure may be the cause of the decrease in PL quantum efficiency compared to DMel.

To further understand the PL in DMel, notice that the emission spectra depend upon excitation energy (Fig. S7). In Fig. S7 it can be seen that when excited at small wavelengths the PL spectrum is composed of broad signals; however, as the excitation wavelength increases the linewidth decreases and the spectral position undergoes a red-shift. This behavior suggests that the structures responsible for the emission form large oligomers composed of different monomers.[30,33] The role of sulfonated groups and protonation can be investigated by changing the concentration of OH^- and H^+

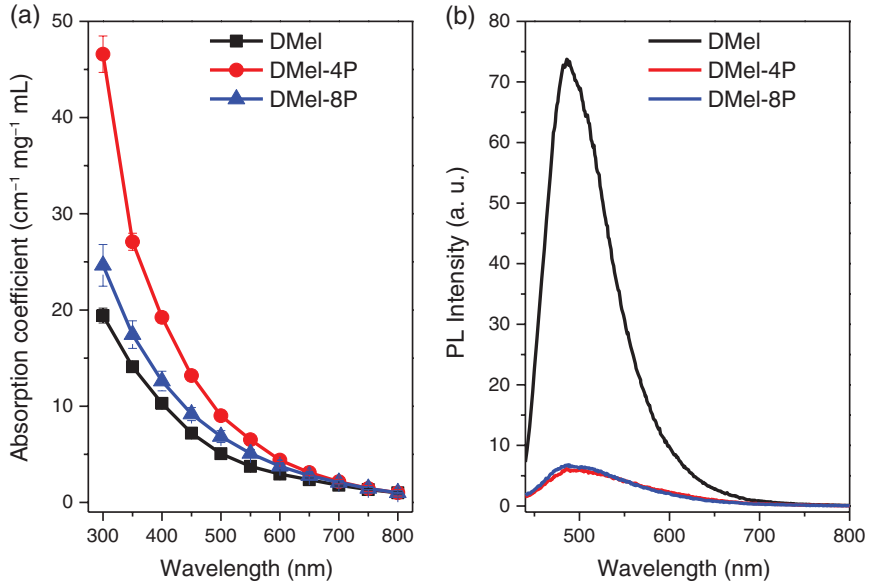

Figure 4. (a) Absorption coefficient and (b) PL spectra at $\lambda_{Ex} = 425$ nm for DMel, DMel-4P and DMel-8P.

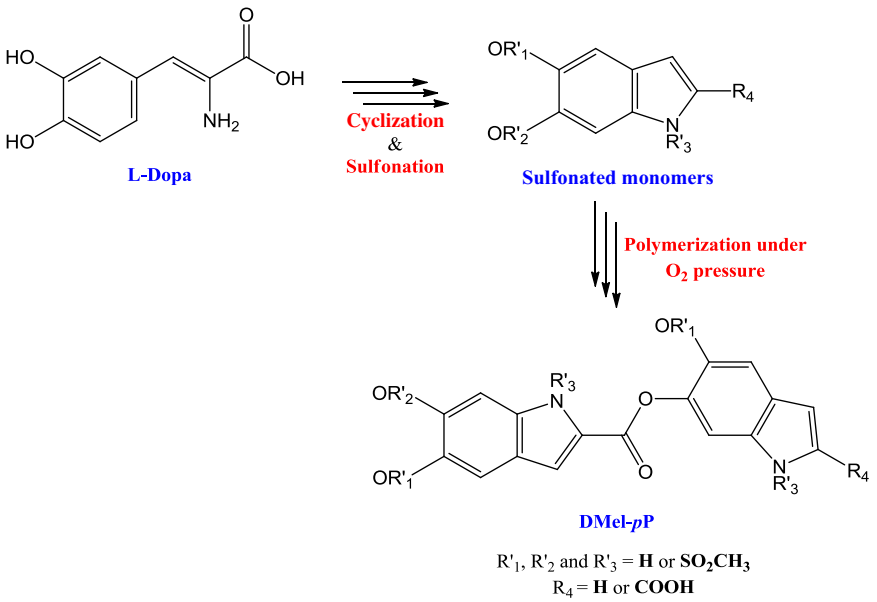

Figure 5. Scheme illustrating the possible major steps of melanin synthesis under O_2 pressure in DMSO, based on Bronze-Uhle *et al.*[6]

ions in solution. For that, a concentrated solution of ammonium hydroxide (28%) and glacial acetic acid was added to a DMel solution of 17 μg mL^{-1} ranging from 0 to 50 μL. When a small amount of NH_4OH is added to the solution, the PL intensity decreases exponentially; however, when CH_3COOH is added it decreases linearly (Fig. S8). This result can be understood, in the first case, as the removal of the sulfonate groups from the macromolecule[6] and in the latter to the quenching effect due to polymer protonation.[26–29]

Taking the kinetic process of melanization into account, the formation of compounds with higher DHI structures is expected, since decarboxylation is a spontaneous process that may be a consequence of oxidative stress that occurs in the presence of hydrogen peroxide, these compounds being formed by *o*-quinone oxidation or by reducing molecular oxygen into reactive oxygen species.[8,34,35] With DHI formation, CO_2 is released, increasing the system pressure. By the Le Chatelier principle, this reaction is prevented, resulting in a higher proportion of DHICA monomers. In our previously study, we proposed that oxygen pressure decomposes hydrogen peroxide forming H_2O and O_2 which will form an even more oxidative environment due to the increase in the concentration of oxygen dissolved in the synthesis medium.[8] Thus, the amount of hydrogen peroxide in the reaction medium will be reduced decreasing the decarboxylation process or increasing the DHICA/DHI ratio. However, this process does not explain the opposite tendency when 8 atm of O_2 was used. Our results show that in this situation the decarboxylation occurs by the decrease of COOH groups in the final product. Even though not completely understood, when one increases the oxygen pressure, the rate of hydrogen peroxide decomposition increases and consequently there is an increase in H_2O and O_2 formation in the reaction medium which will further increase the system pressure. Thus, by the Le Chatelier principle this process would be prevented, increasing

the hydrogen peroxide concentration in the reaction that leads to decarboxylation process. In this way, two distinct processes based on the Le Chatelier principle will occur during the melanin synthesis under O_2 pressure depending on the oxygen partial pressure. Under 4 atm of O_2 pressure, there is a balance between these two processes in such a way that a higher DHICA/DHI ratio is obtained. On the other hand, by increasing the oxygen pressure to 8 atm this equilibrium is disturbed and an increase in hydrogen peroxide is promoted. Accordingly, the cleavage of the C—C bond of the acid group is promoted decreasing the DHICA/DHI ratio.

Another possible explanation for the increase of the carboxylic group when oxygen pressure is used during synthesis is the formation of pyrrole-2,3-dicarboxylic acid (PDCA) and pyrrole-2,3,5-tricarboxylic acid (PTCA) from melanin degradation due to nucleophilic attack of OOH^- ions.[34,36–39] Nonetheless, it is expected that this process occurs only at high concentrations of H_2O_2, as in some bleaching experiments.[34] Thus, we believe that the amount of H_2O_2 formed during our procedure will not be enough to induce catechol ring fission. Moreover, the structural characterization discussed above is not compatible with the formation of PDCA or PTCA. For instance, considering the formation of these types of structures during melanin synthesis under O_2 pressure, one may expect similar intensities of C—O, C═O and COOH in XPS spectra and only one signal in the ^{1}H NMR aromatic region at around 5.0 ppm;[17] however, this is not the case, since it is evident from Table 1 that the contribution of C—O is much higher than the others and in Fig. 3(a) there are at least four different signals in the aromatic region. Also, FTIR spectra (Fig. S5a in supporting information) show no significant differences between DMel, DMel-4P and DMel-8P that could indicate the formation of PDCA/PTCA. Therefore, based on these assumptions, we believe that the higher carboxyl content of our samples is, in fact, related to a higher DHICA/DHI ratio and not to catechol ring fission.

Finally, the main difference between the synthesis under O_2 pressure in water and in DMSO is the functionalization of the indole structure with $—SO_2CH_3$ groups. During conventional melanin synthesis in DMSO, the DMSO also participates as a reagent forming sulfonated by-products.[6] It is known that hydroxyl radicals, formed during synthesis, can oxidize DMSO in to methanesulfonic acid.[40–45] Since this acid is responsible for the functionalization of the melanin structure in the traditional synthesis,[6] it will certainly functionalize the final product with sulfonate groups in the synthesis under O_2 pressure.

CONCLUSIONS

This work presents the optical and structural properties of a melanin derivative synthesized in DMSO with O_2 pressure. It was shown that the melanin derivative has sulfonated monomers with different polymerization structures. The O_2 pressure leads to an improvement in the reaction rate by a factor of 14 and an increase of DHICA/DHI ratio up to 36%. All samples were found to be soluble in DMSO, *N*-methyl-2-pyrrolidone and dimethylformamide. DMel is found to have an enhanced PL in the visible region (487 nm) with quantum yield of (2.12 ± 0.02)% which could open new perspectives for its use in optoelectronics applications.

ACKNOWLEDGEMENTS

We thank FAPESP (2013/07296-2 and 2015/23000-1), CNPq (573636/2008-7) and CAPES for financial support. The authors also thank Prof. Luiz C Silva-Filho and Dr Erika S Bronze-Uhle for fruitful discussions; Dr Nivaldo Boralle for ^{1}H NMR and ^{13}C NMR measurements; and Prof. Paulo M Donate for lending the reactor system.

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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