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# Thermal stability of melanin

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**Abstract**

DSC of melanin displays well-defined phase transitions as compared to TG. The homopolymer melanin-a katatype aromatics is thermally stable up to about 31°C, and loses a unit of indole-5,6-quinone with a release of heat of 120.2 J $g^{-1}$. A second transition (a broad exotherm) occurs with heat evolution of 42.56 J $g^{-1}$; then with a heat absorption of 40.39 J $g^{-1}$, the residual organic mass is converted into gases.

From the thermal chemistry of melanin, aspects of the colour-imparting structure and the aetiology of vitiligo have been inferred.

*Keywords:* DSC; Melanin; Phase transition; Pigment; Stability; TG; Vitiligo

## 1. Introduction

Vitiligo, which is a pigmentary disturbance of acquired type and a global health problem, affects approximately 1% of the population worldwide. Its aetiology is far from clear, although much effort [1–9] has gone into its study. Treatment is only possible following a complete understanding of the aetiology of vitiligo. Turner and Lerner [10] studied the physiological changes in vitiligo and recorded that there is increased temperature (>37°C) and prolonged bleeding time in vitiligo skin. This prompted the author to analyse thermally the basic pigment melanin-a katatype aromatics [11], and to determine the skin conditions that predispose it to vitiligo lesions, a problem that has yet to be solved.


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## 2. Experimental

Synthetic melanin (M 8631, prepared by persulphate oxidation of tyrosine) was supplied by Sigma. For TG analysis, a V 5.0A analyser was used. The heating rate was 10 K $min^{-1}$. A sample size of 4.910 mg and a calibration constant of 1.000 in an atmosphere of air were used. DSC thermograms were recorded using a Du Pont 9900 thermal analyser at a heating rate of 5 K $min^{-1}$. The sample size was 2.1000 mg and the cell constant 1.2359.

## 3. Results

Thermal analysis shows that the melanin molecule is thermally stable up to 30.89°C, displaying no structural transitions. Its molecular structure begins to degenerate with increasing temperature to 106.36°C, when the weight loss is 11.9%. The plateau stretches over a small temperature range (106.36–114.30°C) on the TG curve, suggesting an intermediate of definite composition. When the temperature is further increased, the intermediate molecule decomposes progressively up to 298°C. Beyond this temperature, the weight loss is abrupt and becomes very slow after 332°C. The weight loss at 396°C is 8.66% which shows incomplete combustion.

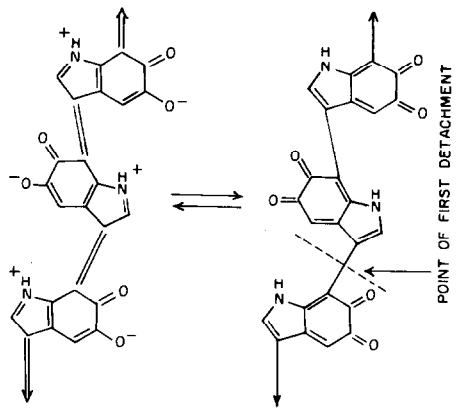
DSC displays three well-defined phase transitions. The first phase transition (a broad exotherm) with 31.27°C as the initiation point and 73.11°C as the temperature at which the sample is brought back to equilibrium, occurs with the release of 120.2 J $g^{-1}$ of heat. The first transition is complete at 36.84°C. The second exotherm is also broad (peak temperature, 114.49°C), with evolution of 42.56 J $g^{-1}$. The third transition (a sharp endotherm), with peak temperature 342.24°C and 40.39 J $g^{-1}$ heat absorption, begins at 291.98°C and ends at 375.49°C.

## 4. Discussion

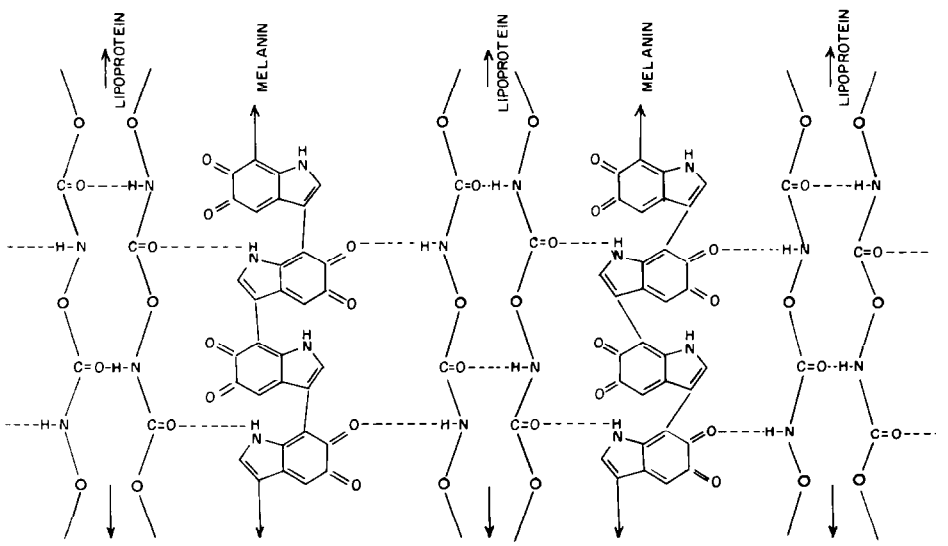
Thermal analysis of the homopolymer complex structure of melanin may help to draw conclusions regarding the often debated problems of skin colour and aetiology of vitiligo, and offers a possibility of choosing the correct therapy to be applied.

In the first stage of decomposition (sigmoid, 30.89–106.36°C), a unit of indole-5,6-quinone (shown by dotted lines in Scheme 1) is lost from the complex structure of eight repeat units of indole-5,6-quinone.

The status of the melanin molecule under body conditions is assessable in the light of its thermal chemistry. Melanin (a biomolecule) is synthesised in melanocytes and transferred through the dendritic network to keratinocyte cells. The thermal degeneration of melanin after about 31°C, which is less than body temperature (37°C), suggests that this molecule cannot exist as such under physiological conditions. In order to survive under body conditions it probably associates with the inherently available complementary peptide-type structures, namely lipoprotein in the keratinocyte cells, through an extensive network of hydrogen bonds.




Scheme 1. Resonating structure of melanin-a homopolymer.




Scheme 2. Melanoprotein colour-imparting structure in skin. –CHR groups are represented by bold spheres; hydrogen bonds are dashed; conjugated molecules in protein not shown.

The resulting thermally stable complex structure (melanolipoprotein) at body temperature, exfoliates the keratinocytes and shades the stratum corneum. Skin colour is thus traceable to the viable state of melanolipoprotein in the epidermis. Scheme 2 illustrates the colour-imparting structure, displaying hydrogen bond interaction in binding melanin molecule to lipoprotein.

Turner and Lerner [10] have demonstrated the increased temperature in vitiligo skin. The physiological environment is changed. The complex structure of melanolipoprotein may degenerate, precipitating depigmentation. The author agrees with

Breathnach [12], who reported a case of a young girl who developed vitiligo overnight after being hit by gunfire, that this rare phenomenon cannot be a direct result of melanocytes suddenly ceasing to produce melanin pigment. On the contrary the disappearance of the preformed skin colour might have resulted due to the acquired thermal instability of the binding forces (hydrogen bonds) of these biomolecules (melanin and lipoprotein) and the subsequent thermal degeneration of melanin resulting from the increased temperature ($>37°C$) of skin consequent to the forces let loose by the head injuries.

Melanolipoprotein on further association at the available hydrogen-acceptor group (carboxyl or charged carboxyl groups) with the complementary structures, namely hydroquinone, *p*-(benzyloxy) phenol and *p*-hydroxypropiophenone having the hydrogen-donor group (–OH), results in a new thermally stable structure under body conditions but devoid of the potential to shade the skin. It has been observed that these hydroxy derivatives on application depigment the skin. The infection normalises when the inbuilt purging mechanism sweats off the applied chemical. The infection stays if the environmental factors in the skin wear out, and the chemical settles down into the skin.

## 5. Conclusions

The thermal chemistry of melanin pigment may clarify its colour-imparting structure and the aetiology of vitiligo, including the trigger mechanism of vitiligo, its spread and extension of lesions, and other unresolved properties. This study also offers a possibility of choosing the correct therapy to be applied to rehabilitate the acquired pigmentary disturbance.

## References

[1] A.B. Lerner and G.S. McGuire, Proc. Int. Dermatol. Congr., 1 (1962) 128.
[2] A.M. El Mofty, Vitiligo and Psoralens, Pergamon, Oxford, 1967, p. 147.
[3] M. Mojamdar, N. Puri and A. Ramaih, J. Biosci., 11 (1987) 399.
[4] A.B. Lerner, J. Invest. Dermatol., 32 (1959) 285; Am. J. Med., 51 (1971) 141.
[5] M. Levai, Arch. Dermatol., 78 (1958) 372.
[6] A.B. Lerner, R.S. Shell, M.L.C. Turner and J.S. McGuire, Arch. Dermatol, 94 (1986) 269.
[7] A.S. Breathnach, D. Goodwin and L.M.A. Wyllie, J. Anat., 99 (1965) 445.
[8] A.S. Breathnach, T.B. Fitzpatrick and L.M.A. Wyllie, J. Invest. Dermatol., 45 (1965) 28.
[9] P.N. Behl, R.S. Agarwal and G. Singh, Indian J. Dermatol., 6 (1961) 101.
[10] M.L.C. Turner and A.B. Lerner, Arch. Dermatol., 91 (1965) 390.
[11] Teh Fu Yen, Wen Hhu Wu and G.V. Chilingar, Energy Sources, 7(3) (1984) 203.
[12] A.S. Breathnach, Ann. N.Y. Acad. Sci., 100 (1963) 58.