



Desorption electrospray ionisation mass spectrometry of stabilised polyesters reveals activation of hindered amine light stabilisers



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ARTICLE INFO

Article history:

Received 11 September 2013

Received in revised form

14 October 2013

Accepted 31 October 2013

Available online 14 November 2013

Keywords:

Mass spectrometry

Polyester

Hindered amine light stabiliser

Mechanism

ABSTRACT

The use of hindered amine light stabilizers (HALS) to retard thermo- and photo-degradation of polymers has become increasingly common. Proposed mechanisms of polymer stabilisation involve significant changes to the HALS chemical structure; however, reports of the characterisation of these modified chemical species are limited. To better understand the fate of HALS and determine their *in situ* modifications, desorption electrospray ionisation mass spectrometry (DESI-MS) was employed to characterise ten commercially available HALS present in polyester-based coil coatings. TINUVIN[®] 770, 292, 144, 123, 152, and NOR371; HOSTAVIN[®] 3052, 3055, 3050, and 3058 were separately formulated with a pigmented, thermosetting polyester resin, cured on metal at 262 °C and analysed directly by DESI-MS. High-level *ab initio* molecular orbital theory calculations were also undertaken to aid the mechanistic interpretation of the results. For HALS containing *N*-substituted piperidines (*i.e.*, *N*-CH₃, *N*-C(O)CH₃, and *N*-OR) a secondary piperidine (*N*-H) analogue was detected in all cases. The formation of these intermediates can be explained either through hydrogen abstraction based mechanisms or direct *N*-OR homolysis with the former dominant under normal service temperatures (*ca.* 25–80 °C), and the latter potentially becoming competitive under the high temperatures associated with curing (*ca.* 230–260 °C).

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1. Introduction

Many contemporary synthetic polymers require one or more chemical additives to enable them to carry out an intended function effectively. In the surface coatings sector, for example, the polymer provides the binder for a coating and the pigment for the aesthetic, but several types of functional additive are also required for a successful formulation. Thus, additives for rheology control, pigment dispersion, wetting, levelling *etc.* are commonly found in a wide range of coating types. Many of these additives have performed the role for which they were designed after the coating has been applied and dried (or cured). However, additives such as UV-absorbers and the so-called hindered amine light stabilisers (HALS) function during the service lifetime of the coating, and their role is to retard the degradation of the coating caused by the continuous barrage of

environmental insults which can lead to compromised performance. HALS have been commonly employed in automotive, wood and plastic coatings for decades [1–6], and the last 10 years has seen an increase in their use in coil coatings. Coil coating is a large-scale process for continuous painting of steel strip at speeds of up to 200 m min⁻¹. The pre-painted steel strip thus produced is used in many different applications, the most severe of which is that employed in roofing, where the product needs to retain good appearance in service for 20 years or more. In turn, this places considerable emphasis on HALS to preserve the aesthetic and functional roles of the surface coating by protecting the polymer from degradation. Therefore, the optimisation of these compounds for such applications is of considerable interest; however, this first requires a thorough understanding of the chemistry associated with the protection of polymers by HALS. It is widely believed that HALS operate as chain-breaking antioxidants, undergoing oxidation of a heterocyclic amine to an aminoxyl radical, although the exact mechanisms by which this occurs is still the subject of investigation. It is this persistent aminoxyl radical that acts as a free radical

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scavenging intermediate and is thought to be involved in converting deleterious free radicals to less harmful even-electron species. As a result, regeneration of the aminoxyl radical occurs, theoretically allowing the process to repeat indefinitely [7–16]. However, empirical evidence suggests that the protective effects are finite and the use of HALS only delays the failure of polymers rather than denying it. Thus stabilisation *via* HALS must consist of a more complex mechanism.

Recently, Hodgson and Coote [17] deployed high-level quantum chemical calculations to compare the kinetics and thermodynamics of a dozen different reaction pathways comprising over 30 individual reactions. This allowed critical assessment of all the previously suggested mechanisms. Hodgson and Coote's analysis shows most of the mechanisms are kinetically and/or thermodynamically disfavoured with even the most favourable mechanism subject to a large activation barrier (~ 150 kJ mol⁻¹) for one of its key steps [17]. Furthermore, this mechanism does not account for previous experimental observations that suggest *in situ* conversion of an alkoxyamine functional group (*N*-OR) – analogous to an intermediate expected in an aminoxyl radical regenerative mechanism – to a secondary piperidine (*N*-H). This phenomenon was observed following high temperature curing of the polymer-based coating as well as subsequent exposure of the coating to accelerated weathering conditions [18]. Concordant results have also been reported in the literature for the decomposition of 2,2,6,6-tetramethylpiperidine-based HALS under thermo- and photo-oxidative conditions [19,20].

The inability to account for these observations by any of the commonly accepted mechanisms sparked a follow-up computational study by Coote and co-workers in which a new mechanism was proposed to explain the catalytic free radical scavenging by HALS in organic materials [21]. In this proposed cycle, an aminoxyl radical traps a carbon-centred substrate radical to form an alkoxyamine, and is then regenerated in a cascade of reactions triggered by hydrogen atom abstraction at the β -position of the alkoxyamine *via* another substrate-derived radical. The resulting species rapidly undergoes β -scission to form a ketone and an aminyl radical, and the aminyl radical can then either be oxidised back to the aminoxyl or abstract a hydrogen atom to form a secondary amine (see Scheme 1) [21]. This secondary amine can re-enter the catalytic cycle *via* hydrogen abstraction with any number of substrate-derived radicals, depending on the relative concentrations. In species that degrade *via* tertiary substrate-derived radicals, for which β -hydrogen abstraction is not possible, alternative catalytic cycles were proposed depending on whether direct *N*-OR homolysis was possible or not (see Scheme 1) [21]. These were shown to be much less energetically favourable, thus providing an explanation for the lower catalytic efficiency of HALS in such cases. The activation of the HALS was also studied, and shown to vary depending on whether the starting material was a secondary amine, the *N*-methyl derivative or an alkoxyamine (see Scheme 2) [21].

This recent computational study, supported by previous experimental observations suggests there may be other major repositories for HALS outside of the traditional regenerative cycles. Therefore, the aim of this work is to investigate the changing functionalisation of the piperidine nitrogen by characterising the structural changes occurring to a range of HALS compounds in polymer-based coatings. In this study, the focus is on the changes that occur specifically during curing under typical curing conditions and what impact they have on the chemical structure of the HALS. This in turn has implications for its activation (and hence protective action) under subsequent in-service conditions.

We have employed desorption electrospray ionisation mass spectrometry (DESI-MS) for the analysis of ten polyester-based coil coatings each containing a different commercially available HALS

compound (Fig. 1). The compounds selected are structurally diverse providing the four most common piperidiny moieties (*i.e.*, *N*-H, *N*-CH₃, *N*-C(O)CH₃, and *N*-OR). It is noted that basic HALS (*N*-H, *N*-CH₃; p*K*_a 7.5–9.7) are not typically used in acid-catalysed, cross-linked polyesters as they interfere with the curing process. They are included here however, to provide insight into the changes in functionality of HALS that are associated with curing conditions. HALS compounds retained within the coating after cure are detected *in situ*, characterised by tandem mass spectrometry and the results are rationalised with the aid of high-level electronic structure calculations.

2. Methods

2.1. Reagents

Methanol and formic acid were HPLC grade (Crown Scientific, Minto NSW, Australia). Chloroform and acetone were AR grade (Crown Scientific, Minto NSW, Australia). The hindered amine light stabilisers; bis(2,2,6,6-tetramethyl-4-piperidiny) sebacate (TIN770), bis(1,2,2,6,6-pentamethyl-4-piperidiny) sebacate (TIN292), bis(1,2,2,6,6-pentamethyl-4-piperidiny)-((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl)butylmalonate (TIN144), bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidiny) sebacate (TIN123), 2,4-bis(*N*-butyl-*N*-(1-cyclohexyloxy-2,2,6,6-tetramethyl-4-piperidiny)amino)-6-(2-hydroxyethylamine)-1,3,5-triazine (TIN152), and oligomers based on *N*-2-butyl-*N*-2-*N*-4-bis(2,2,6,6-tetramethyl-1-propoxy-4-piperidyl)-*N*-4-[5-(2,2,6,6-tetramethyl-1-propoxy-4-piperidyl)pentyl]-1,3,5-triazine-2,4-diamine (TIN NOR371) were supplied by Ciba Specialty Chemicals (Basel, Switzerland) now BASF (Ludwigshafen, Germany) and were used without purification. The hindered amine light stabilisers; β -alanine-*N*-(2,2,6,6-tetramethyl-4-piperidiny)-dodecyl ester and β -alanine-*N*-(2,2,6,6-tetramethyl-4-piperidiny)-tetradecyl ester (HOST3052), 2-dodecyl-*N*-(2,2,6,6-tetramethyl-4-piperidiny) succinimide (HOST3055), 7-oxa-3,20-diazadispiro[5.11.12]heneicosane-20-propanoic acid-2,2,4,4-tetramethyl-21-oxo-dodecyl ester (HOST3050), and 2-dodecyl-*N*-(1-acetyl-2,2,6,6-tetramethyl-4-piperidiny) succinimide (HOST3058) were supplied by Clariant (Huningue, France) and were used without purification.

2.2. Preparation of coated steel panels

The topcoat paint system employed in these studies was a solvent-borne, polyester topcoat paint incorporating a melamine-formaldehyde cross-linker, acid catalysed and formulated for coil paint-line application. This sample was formulated as a wet paint mixture and found to be 45% w/w resin solids by thermogravimetry (Perkin–Elmer TGA 7). The bulk paint sample was sub-sampled and weighed into small containers providing an identical matrix for comparative HALS analysis. The paints were formulated to give a final concentration of each HALS that resulted in a molar equivalent of an aminoxyl radical precursor (*N*-R) to that of TIN123 added at 2% w/w of total resin solids. The coated samples that were used in this project were laboratory prepared upon a pre-primed (commercial chromated epoxy primer) panels of a 0.6 mm thick GALVALUME®-type steel substrate. Wet paint was applied using a #28 wire-wound draw-down bar then cured for 55 s in a fan forced oven set at 262 °C. Under these conditions, 55 s equates to a peak metal temperature of 232 °C.

2.3. Desorption electrospray ionisation-mass spectrometry (DESI-MS)

Metal panels with a thermosetting polyester-based coating were cut into small sections (7 × 25 mm) using hydraulic shears

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