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Linear and macrocyclic water soluble polyacylhydrazones and their utilisation in coatings

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ABSTRACT

Water soluble polyacylhydrazones have been generated that contain a high proportion of renewable materials. The polyacylhydrazones were found to be present simultaneously as linear and macrocyclic species, the latter being favoured at higher concentrations and in certain combinations of levulinoyl ester/acyldihydrazide. Levulinoyl esters with multiple ketone reactive sites were targeted as building blocks for the backbone. Reaction of these species in aqueous media with commercially available acyldihydrazides afforded a series of high solids-content water soluble polyacylhydrazone solutions. Evaporation of the water from the solutions reproducibly generated films with differing and useful characteristics. One of the polyhydrazones was successfully formulated into two different types of resin bases of commercial coating systems, producing paint products with renewable content.

1. Introduction

Hydrazones and oximes have been utilised in a variety of applications ranging from the generation of combinatorial libraries [1–3] to organic polymers [4–6] and coatings [7,8]. Because hydrazone formation is reversible, and since much about the equilibrium [9] and rate of reaction [10] is now understood, a certain level of control over the position of this equilibrium in solution can be achieved. The effects of pH, catalysis [11] and the nature of the parent carbonyl or hydrazide/amine containing molecule on these factors has been discussed in detail [10,12,13]. The reversible nature of the hydrazone formation give rise to a dynamic system in which the hydrazones can be manipulated post-preparation, giving rise to 'dynamers' [4,5,14,15].

The use of ketones in the synthesis of polyacylhydrazones is rare, and in most previous studies aldehydes have been used as substrates, likely due to anticipated higher reactivity [4,6,17]. Polyketone species have been previously employed in the preparation of hydrogels, but these were formed using oxime chemistry, not utilising hydrazones [16]. In the present investigation, we utilised ketones as the carbonyl functionality, with interesting outcomes, as detailed below, especially relating to the nature of the species formed in solution.

Cross-linking of polymers by formation of a hydrazone linkage *via* the incorporation of adipic acid dihydrazide (ADH) into commercial formulations is widely utilised in the coatings industry. Here, ketone groups are incorporated into the polymer particles of the resin by co-polymerisation of a keto-functionalised monomer, such as diacetone acrylamide [17]. Evaporation of water from the waterborne coating leads to coalescence of the emulsion droplets and the formation of a film. During this process, the particles are brought into contact with the water soluble ADH, which leads to crosslinking upon late-stage evaporation of the water and film formation. It would be valuable to the coatings industry if film-forming polyhydrazones could be directly prepared from systems that are wholly water soluble. This represents an interesting scientific challenge given the known reversibility of hydrazone formation in aqueous media. Whilst the reaction has been investigated in organic solvents, significant issues exist with the solubility of the raw materials in the organic solvents, and the process is complicated by the near-insoluble nature of the polymeric polyhydrazone material so generated in organic solvents [4,6,18,19]. We have been interested for some time in the production of waterborne coatings with improved environmental footprints over their petrochemical-derived counterparts [20–22]. Accordingly, we have chosen monomers for the present study which are not only largely renewable but also soluble in aqueous systems. Our vision was to develop sufficient understanding of

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the behaviour of the polyhydrazones in aqueous media to allow us to successfully incorporate them into various commercial coatings.

Here we investigate the preparation of a series acylhydrazone species from ketone functionalised monomers in reactions with dihydrazides, probing the effectiveness of di- or tri-ketones in the formation of acylhydrazones in aqueous solution. We investigate their solution properties, film forming ability and their usefulness for incorporation into coatings.

2. Materials and methods

2.1. Materials

All commercially available chemicals were used as received unless otherwise stated. Glycerol, ethylene glycol and diethylene glycol were sourced from Sigma Aldrich, triethylene glycol was sourced from Acros Organics and triethanolamine from Riedel-de Haën. Levulinic acid was supplied by SAFC, adipic acid dihydrazide (ADH) from Nuplex Resins Ltd and oxalyl dihydrazide, isophthalic dihydrazide and carbohydrazide from AK Scientific, Inc.

2.2. Analysis

Preparative chromatography utilised a Grace Reveleris system equipped with a pre-packed column of silica gel. All NMR spectra, including ^{1}H, ^{13}C, COSY, HSQC and HMBC experiments, were recorded on a Bruker Avance 500 spectrometer at 27 °C, in $CDCl_3$ for the monomers and in D_2O for the polymeric products, unless otherwise specified, using an inverse-detection probe. NMR spectra in $CDCl_3$ were referenced to TMS and those in D_2O to the solvent peak (δ 4.7 ppm). High temperature NMR experiments were carried out as above in DMSO-d_6 at a temperature of 90 °C. Differential scanning calorimetry was completed on a Mettler DSC1 STAR^{e} system equipped with a GC200 gas controller and autosampler. Samples (0.5–1.5 mg) in pierced aluminium crucibles (40 µL, PN ME-26763) were assessed using three contiguous repeat cycles from −20 to 160 °C at a ramp rate of 5 °C min^{-1} under a constant flow of nitrogen (30 mL min^{-1}).

Mass spectrometric analysis was carried out on a Q-TOF Premier mass spectrometer (Micromass, UK) with the MassLynx operating system (version 4.1). Samples were dissolved in water or aqueous methanol (containing a trace amount of formic acid to assist positive-ion mode ionisation) and infused directly into the ESI source. Tandem mass experiments were carried out with an optimised collision energy and helium as the collision gas. The instrument was calibrated with an aqueous solution of sodium formate prior to accurate mass measurements.

Molecular modelling calculations were carried out in Chem 3D Pro 14.0 using the MM2 forcefield.

2.3. Preparation of ketone monomers

Monomers with multiple ketone-functionality were prepared in esterification reactions by heating (135 °C) the relevant polyol, *p*-toluenesulfonic acid (0.003 equiv.) and levulinic acid (1.4 equiv. *per* hydroxyl) under reduced pressure (10 mmHg) to remove water in solventless reactions. Reaction completion was determined as the point where no additional water was generated (approximately 2.5 h). The reaction mixture was cooled to room temperature before being diluted with chloroform, washed with water (2 × 300 mL) and the product recovered by evaporative concentration.

Dilevulinoyl ethylene glycol (**1**) (112.3 g, 0.44 mol) was recovered from the reaction of ethylene glycol (30 g, 0.48 mol) in 92% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.28 (s, 4H), 2.76 (t, J = 6.7 Hz, 4H), 2.60 (t, J = 6.7 Hz, 4H), 2.19 (s, 6H); ^{13}C NMR (125 MHz $CDCl_3$): δ 206.4, 172.5, 62.2, 37.8, 29.8, 27.8. ESI-HRMS: calcd for $C_{12}H_{18}O_6$ $[M+Na]^+$ 281.1001; found 281.0994.

Dilevulinoyl diethylene glycol (**2**) (411 g, 1.36 mol) was prepared from diethylene glycol (180 g, 1.70 mol) and recovered as a thin, pale-yellow oil in 80% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.23 (t, J = 4.9 Hz, 4H), 3.69 (t, J = 4.9 Hz, 4H), 2.76 (t, J = 6.5 Hz, 4H), 2.61 (t, J = 6.5 Hz, 4H), 2.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.5, 172.7, 69.0, 63.6, 37.9, 29.8, 27.9. ESI-HRMS: calcd for $C_{14}H_{22}O_7$ $[M+Na]^+$ 325.1263; found 325.1263.

Dilevulinoyl triethylene glycol (**3**) (12.46 g, 34 mmol) was prepared from triethylene glycol (6.00 g, 38 mmol) in 90% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.23 (t, J = 4.9 Hz, 4H), 3.70 (t, J = 4.9 Hz, 4H), 3.66 (s, 4H), 2.76 (t, J = 6.7 Hz, 4H), 2.60 (t, J = 6.7 Hz, 4H), 2.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.7, 172.6, 70.4, 68.9, 63.6, 37.8, 29.7, 27.8. ESI-HRMS: calcd for $C_{16}H_{26}O_8$ $[M+Na]^+$ 369.1525; found 369.1520.

Trilevulinoyl triethanolamine (**4**) (134.8 g, 0.30 mol) was prepared from triethanolamine (48.8 g, 0.33 mol) in 93% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.12 (t, J = 6.0 Hz, 4H), 2.84 (t, J = 6.0 Hz, 4H), 2.75 (t, J = 6.7 Hz, 4H), 2.60 (t, J = 6.7 Hz, 4H), 2.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.5, 172.6, 62.8, 53.3, 37.9, 29.8, 27.9. ESI-HRMS: calcd for $C_{21}H_{33}O_9$ $[M+Na]^+$ 466.2053; found 466.2047.

Trilevulinoyl glycerol (**5**) (18.9 g, 49 mmol) was prepared from glycerol (5.00 g, 54 mmol) in 90% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.23–5.27 (m, 1H), 4.27 (dd, J = 11.9, 4.2 Hz, 2H), 4.18 (dd, J = 11.9, 6.0 Hz, 2H), 2.75–2.78 (m, 6H), 2.58–2.61 (m, 6H), 2.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.3 (×2), 172.2, 171.9 69.2, 62.2, 37.8, 29.7, 27.7. ESI-HRMS: calcd for $C_{18}H_{26}O_9$ $[M+Na]^+$ 409.1475; found 409.1468.

1,2-Dilevlinoyl-1,2-benzenedimethanol (**6**) was prepared from the reaction of 1,2-benzenedimethanol (500 mg, 3.6 mmol), levulinic acid (1.18 g, 10.2 mmol, 1.4 equiv.) and *p*-toluenesulfonic acid (6 mg). The mixture was heated for 1.5 h at 115 °C under reduced pressure. The reaction mixture was diluted with $CHCl_3$ (10 mL) and washed with water (2 × 5 mL). The organic phase was concentrated under reduced pressure to afford **6** as a yellow oil (1.13 g, 93% containing 11% starting material); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31–7.41 (m, 4H), 5.20 (s, 4H), 2.76 (t, J = 6.7 Hz, 4H), 2.61 (t, J = 6.7 Hz, 4H), 2.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.5, 172.4, 134.4, 129.7, 128.7, 64.0, 37.9, 29.8, 27.9. ESI-HRMS: calcd for $C_{18}H_{22}O_6$ $[M+Na]^+$ 357.1314; found 357.1306.

1,4-Dilevulinoyl-1,4-benzenedimethanol (**7**) was prepared in a similar fashion to **6** above by the reaction of 1,4-benzenedimethanol (500 mg, 3.6 mmol) and levulinic acid (1.04 mL, 10.2 mmol) to afford a yellow oil (810 mg, 67% containing 5% starting material): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (s, 4H), 5.11 (s, 4H), 2.76 (t, J = 6.7 Hz, 4H), 2.63 (t, J = 6.7 Hz, 4H), 2.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.6, 172.6, 135.9, 128.3, 66.1, 37.9, 29.8, 28.0. ES-HRMS: calcd for $C_{18}H_{22}O_6$ $[M+Na]^+$ 357.1314; found 357.1310.

2.4. Acylhydrazone test reactions

The simple acyldihydrazone test compounds were synthesised following the procedure of Zha and You [23]. ADH was added to a methanol solution containing 2–2.3 equivalents of the aldehyde or ketone. For compound **8**, glacial acetic acid was also added to the flask dropwise to achieve a pH of 4–5. The reaction mixture was heated at reflux temperature to yield a white precipitate, which was washed with methanol (2 × 5 mL) and isolated by vacuum filtration. The acyldihydrazones were soluble in DMF and DMSO. In the ^{1}H NMR data below for molecules that display rotamers in solution, we list the two signals demonstrating the rotameric forms, then their multiplicity and the *total* value for which they integrate (e.g. δ 11.14 & 11.02 (d, J = 5.8 Hz, J = 5.0 Hz, 2H)). Where one rotameric form predominates, the signals for the major isomer are shown in bold type.

Compound **8** was synthesised by stirring ADH (406 mg, 2.26 mmol) and vanillin (714 mg, 4.55 mmol) in methanol (140 mL) at reflux temperature for 40 h, providing the product as a white solid (820 mg,

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