

# Hyperbranched polymers containing oxazoline monomers and succinic anhydride: Applications in fast drying, low solvent coating formulations



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## ABSTRACT

Melt-polycondensation of succinic acid anhydride with oxazoline-based diol monomers gave hyperbranched polymers with carboxylic acid terminal groups. <sup>1</sup>H NMR and quantitative <sup>13</sup>C NMR spectroscopy coupled with DEPT-135 <sup>13</sup>C NMR experiment showed high degrees of branching (over 60%). Esterification of the acid end groups by addition of citronellol at 160 °C produced novel white spirit soluble resins which were characterized by Fourier transform-infrared (FTIR) spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Blends of the new hyperbranched materials with commercial alkyd resins resulted in a dramatic, concentration dependent drop in viscosity. Solvent-borne coatings were formulated containing the hyperbranched polymers. Dynamic mechanical analysis studies revealed that the air drying rates of the new coating systems were enhanced compared with identical formulations containing only commercial alkyd resins.

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## 1. Introduction

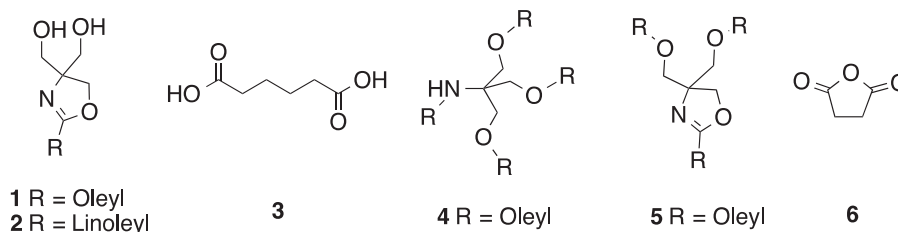
The negative impact of volatile organic compounds (VOC) to the atmosphere and human health has led to research focussed on the reduction of VOC levels in coatings and paints. Europe-wide legislation currently restricts the upper level of VOC in paint products to a value of 300 g/l, [1–3] thus eliminating many long-standing solvent borne coating formulations from the market place. These legislation changes have led to an increase in interest in producing new coating formulations in recent years with the target to produce low viscosity, fast drying products even at high weight contents of solids. One of the most attractive approaches to overcoming this problem has been to study the possibility of using branched polymers in solvent-borne coatings [4–7]. Since branched and hyperbranched materials were first synthesised and rigorously characterised, it has been recognised that high levels of branching can increase solubility and lower viscosity in solution or in molten states [8]. Moreover, branched materials contain more reactive and accessible end-groups than their linear polymer analogues and, therefore,

provide a greater number of reactive chain-end which can facilitate efficient cross-linking (curing) in coatings formulations [8–9]. Thus, macromolecular architectures including comb-like polymers [10,11], centipede typed polymers [12], barbwire typed polymers [13], and dendritic polymers [14] have been investigated within prototype solvent-borne coating formulations with potential fast drying characteristics.

Previous studies in our group have shown that polycondensation of diol functionalised oxazoline-based monomers [15] (1, 2) with adiacid monomer, adipic acid (3) results in polymers with architectures that were dependent on the feed ratio of the monomers (Fig. 1) [16,17]. Molar ratios between 3:4 and 1:1 (1 or 2–3, respectively) resulted principally in comb polymer formation, whereas increasing the molar feed-ratio to 2:1 generated hyperbranched materials that exhibited statistical degrees of branching (ca. 50%) with branch points occurring as a consequence of an acid catalysed oxazoline ring opening reaction [16,17]. Branching was confirmed readily by comparison of the <sup>1</sup>H NMR spectrum of the polymers with spectra of the model compounds 4 and 5, which are structural analogues of the branching and linear residues, respectively, in the polymer backbone.

Herein we describe our investigations into the melt-polycondensation of a latent diacid monomer succinic acid

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**Fig. 1.** Structures of oxazoline based diol monomers (1, 2), adipic acid (3), model compounds 4 and 5 used to determine the degree of branching in the polymers by comparison of characteristic signals in  $^1\text{H}$  NMR spectra. Succinic anhydride (6) was used in the synthesis of the new polyesters reported in this paper.

anhydride (6) with oxazolidiols 1 and 2 and their end-group modification to produce new materials for fast drying coatings formations.

## 2. Experimental

### 2.1. Materials

Oleic acid, linoleic acid, succinic anhydride, and *N,N'*-dimethylformamide (DMF) were purchased from Aldrich. Monomers 1, 2 plus model compounds 4 and 5 were prepared according to procedures described in previous studies [16,17]. Tetrahydrofuran (THF), DMSO,  $\text{CH}_2\text{Cl}_2$ , MeOH, acetone, and 2-propanol were purchased from Fisher. Low odour white spirit, the anti-skinning agent, methyl ethyl ketone oxime (MEKO), and driers including Octa-soligen 10 (cobalt carboxylate 58%, naphtha40% and methoxypropoxy propanol 2%), Octa-soligen calcium 10 (calcium carboxylate 45% and naphtha 55%) and Octa-soligen zirconium10 (zirconium 2-ethyl hexanoate 56% and naphtha 44%) were used as supplied by OMG Borchers. The commercially available alkyd used (a soy oil based alkyd with 70 wt% in low odour white spirit) was obtained from Cray Valley Ltd.

### 2.2. Measurements

$^1\text{H}$  NMR spectra were recorded on Bruker AC250 (250 MHz) spectrometer.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC250 (62.5 MHz) spectrometer. Infrared (IR) spectroscopic analyses were performed on a PerkinElmer 1720-X infrared Fourier transform spectrometer on KBr disks using thin film. Gel permeation chromatography (GPC) was conducted using one of two chromatographic instruments: - for the polymers with high polarity, a Polymer Laboratories PL-GPC 120 with PL-AS-MT autosampler fitted with columns (PL PolarGel guard plus 2  $\times$  PolarGel-M, 30 cm, 8  $\mu\text{m}$ ) in conjunction with refractive index detector was employed with *N,N'*-dimethylacetamide with 0.01 M lithium bromide as the eluent at 80  $^\circ\text{C}$  (flow rate: 1 mL  $\text{min}^{-1}$ ) (in this case, Polymer Laboratories polymethyl methacrylate standards were used as calibrants). For the polymers soluble in chloroform, a Viscotek TDA model 301 (with associated pump and autosampler fitted with columns PLgel guard plus 2  $\times$  mixed bed-D, 30 cm, 5  $\mu\text{m}$ ) in conjunction with refractive index (with differential pressure and light scattering) detector was employed with chloroform as the eluent at 30  $^\circ\text{C}$  (flow rate: 1 mL  $\times$   $\text{min}^{-1}$ ) and the chromatograph calibrated using Polymer Laboratories polystyrene standards. In both GPC analyses, the data were acquired and analysed using Polymer Laboratories 'Cirrus' software. Modulated differential scanning calorimetry (MDSC) measurement was performed on Instrument 2920 MDSC V2.6A. Thermal gravimetric analysis was carried out on Instrument AutoTGA 2950HR V5.4A and the samples (5–15 mg) were heated from room temperature up to 600  $^\circ\text{C}$  under dry nitrogen gas at a heating rate of 5  $^\circ\text{C}/\text{min}$ . MDSC and TGA data were collected and processed on Universal Thermal Analysis Software.

### 2.3. Synthesis of hyperbranched polymers

Into a three-armed flask was added the calculated amount of succinic acid anhydride 6(3.00 g, 30 mmol) and 1 or 2 (5.48 g, 15.00 mmol) in the molar ratio of 2:1. The flask was first purged with nitrogen and then transferred into an oil bath held at 130  $^\circ\text{C}$ . After the mixture was in a molten state it was then vigorously stirred for 8 h under a high rate flow of nitrogen to remove the water formed during the reaction. The product was then subject to reduced pressure for 30 min at 100  $^\circ\text{C}$  to distil off any residual traces of water and then citronellol (2.66 g, 17 mmol) was added. This end-capping reaction was held at 160  $^\circ\text{C}$  for 8 h to finally afford a yellow-coloured oil.

#### 2.3.1. Acid terminated hyperbranched polymer 9

Yield: 6.74 g (80%);  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.88 (t,  $J=7.5$  Hz), 1.29 (br), 1.59(br), 2.02 (m), 2.32 (m), 2.77 (m), 4.16 (br), 4.42 (br), 4.70(m), 5.34 (m);  $^{13}\text{C}$  NMR (62.8 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 13.9, 22.5, 23.7, 25.4, 27.0, 28.9, 29.1, 29.3, 29.6, 31.7, 33.8, 57.8, 59.7, 62.3, 127.7, 127.9, 129.5, 129.8, 171.4, 171.9, 172.5, 173.0, 173.2, 173.5, 175.8, 178.3, 178.6; FTIR (KBr,  $\text{cm}^{-1}$ ): 3350, 2926, 2855, 1739, 1655, 1544, 1458, 1378, 1244, 1171, 1062, 1020, 917, 727; GPC:  $M_n=5000$ ,  $M_w=44,000$ , PDI=8.8.

#### 2.3.2. Acid terminated hyperbranched polymer 10

Yield: 6.54 g (77%);  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.89 (t,  $J=7.5$  Hz), 1.35 (br), 1.60 (m), 2.03 (m), 2.32 (t,  $J=7.5$  Hz), 2.77, (t,  $J=7.5$  Hz), 4.16(br), 4.42 (br), 4.73(m), 5.36 (m);  $^{13}\text{C}$  NMR (62.8 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 13.9, 22.4, 24.6, 25.4, 26.5, 28.0, 28.9, 29.2, 29.4, 31.3, 33.8, 57.8, 60.1, 62.4, 63.9, 65.6, 71.8, 127.7, 127.9, 129.8, 130.0, 171.3, 171.8, 173.2, 175.9, 176.1, 178.1, 178.7; FTIR (KBr,  $\text{cm}^{-1}$ ): 3335, 3075, 2926, 2855, 1739, 1654, 1544, 1463, 1378, 1244, 1171, 1062, 1021, 917, 722; GPC:  $M_n=2700$ ,  $M_w=35,000$ , PDI=13.

#### 2.3.3. Citronellol terminated polymer 11

Yield: 9.40 g(84%);  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.90–0.92 (m), 1.11–1.30 (m), 1.39–1.73 (m), 1.89–2.02 (m), 2.25–2.35 (m), 2.61–2.62(m), 4.12–4.24 (m), 4.44 (br, s), 4.73 (br, s), 5.05–5.11(m), 5.30–5.38 (m);  $^{13}\text{C}$  NMR (62.8 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 13.8, 17.3, 19.1, 22.4, 22.9, 24.5, 24.7, 25.1, 25.4, 26.9, 27.7, 28.7, 28.8, 29.0, 29.1, 31.6, 33.7, 34.0, 35.1, 36.7, 59.6, 62.4, 62.9, 63.0, 65.8, 71.6, 72.0, 124.3, 129.4, 129.6, 130.8, 168.8, 171.1, 171.5, 171.8, 171.9, 172.1, 172.9, 173.5, 174.6, 176.4, 177.9; FTIR (KBr,  $\text{cm}^{-1}$ ): 2926, 2855, 1739, 1655, 1544, 1458, 1378, 1244, 1171, 1062, 1020, 727; GPC:  $M_n=1980$ ,  $M_w=6570$ , PDI=3.3;  $T_g=-29^\circ\text{C}$ .

#### 2.3.4. Citronellol terminated polymer 12

Yield: 9.20 g(82%);  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.90–0.92 (m), 1.11–1.31 (m), 1.35–1.71 (m), 1.92–2.08 (m), 2.22–2.32 (m), 2.61–2.63(m), 2.74–2.79, 4.10–4.24 (m), 4.44 (br, s), 4.73 (br, s), 5.05–5.11(m), 5.26–5.40 (m);  $^{13}\text{C}$  NMR (62.8 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 13.8, 17.3, 19.1, 22.3, 22.9, 24.5, 24.7, 25.1, 25.4, 25.7, 27.6, 28.6, 28.8, 29.0, 29.1, 29.3, 31.2, 33.6, 34.0, 35.1, 36.7, 56.1, 59.6, 62.3, 62.8,

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