



Lightly branched comb polyesters: Application in fast drying solvent-borne coating formulations

Ge Cheng^a, Barnaby W. Greenland^a, Chris Lampard^b, Neal Williams^b, Malkit S. Bahra^b, Wayne Hayes^{a,*}

^a Department of Chemistry, University of Reading, Whiteknights, Reading, Berkshire RG6 6AD, UK

^b AkzoNobel Ltd., Wexham Road, Slough, Berkshire SL2 5DS, UK

ARTICLE INFO

Article history:

Received 17 October 2012

Received in revised form 8 January 2013

Accepted 12 January 2013

Available online 22 January 2013

Keywords:

Oxazoline

Fatty acid

Comb polymers

Polyester

Alkyd coatings

ABSTRACT

Novel oxazoline-based comb-polymers possessing linoleyl or oleic side chains have been synthesized and used to produce low viscosity coatings. Inclusion of the polymers in model paint formulations results in coatings that exhibit faster drying times than commercially available alkyd resin formulations. The comb polymers were produced from diol substituted oxazoline monomers that were synthesized through a scalable, solvent free protocol and purified by simple recrystallisation. Co-polymerisation of the oxazolines with adipic acid at 160 °C in the bulk resulted in the targeted polyester comb type polymers. The polymers were soluble in a range of organic solvents and compatible with commercial alkyd resins. Model paint formulations containing up to 40 wt% of the linoleyl-based comb polymers exhibited a dramatic reduction in viscosity (from 35 to 13 Poise at 25 °C) with increasing quantities of polymer added. Dynamic mechanical analysis (DMA) studies revealed that the drying rate of the model paint formulations containing the comb polymers was enhanced when compared with that of commercial alkyd resins.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Reducing emissions of volatile organic compounds (VOCs) from paint formulation has received increasing attention in recent years, as a consequence of environmental concerns and the potential risks to human health assigned to prolonged exposure [1,2]. For example, recent legislation concerning VOC (in Europe 2010) requires a maximum level of 300 g/L [3], effectively eliminating many generations of solvent borne coatings from the market place. Therefore, there is a strong demand for new air drying resins to improve upon more conventional alkyd resin technologies which are now reaching, or have indeed reached the end of their product lifecycle.

Advances in polymer synthesis in the previous three decades have resulted in robust strategies to produce polymers with controlled molecular weights and branched structures on an industrial scale. Notable advances in coating applications include the synthesis of branched polymers (BPs) [4,5]. The compact nature of BPs results in high numbers of surface functional groups along with lower viscosity compared to conventional linear polymers [6,7]. These unique structural attributes make branched structures intriguing candidates as coating additives as they may serve to reduce the viscosity of the product formulation which, in turn, could lower the quantity of VOC thinner required whilst promoting effi-

cient crosslinking during curing by reaction of their numerous of surface functional groups [7–15]. Within the family of branched polymers, numerous specific structures including combs [16], comb-on-comb [17] and arborescent polymers [18–23] also exhibit similar advantageous physical properties.

In this study, comb-type polymers were targeted that contain repeat units with reactive fatty acid side-groups. These polymers, which consist of a linear backbone with numerous lengthy side chains, exhibit rheological properties that are more comparable to hyperbranched polymers rather than conventional linear analogues [24–26]. As a consequence of this useful property, comb-shaped polymers have been employed in developing low viscosity and rapid drying organic coatings. Recent studies by Athawale et al. produced comb-type acrylic copolymers for surface coatings applications that exhibited lower viscosities and reduced drying times when compared to linear acrylic copolymers [27].

Another possible strategy based on comb polymer technology is blending commercial alkyds with comb polymers. Talroze et al. demonstrated that comb polymers can be used as flow modifiers for thermoplastic polymers [28]. It was shown that a dramatic decrease in blend viscosity could be achieved if the length of the side chains of comb polymers were less than the critical entanglement limit.

In this study, easily accessed lightly branched comb-structured polyesters containing oxazoline units as linker groups to reactive fatty acid side chains have been synthesized and fully character-

* Corresponding author. Tel.: +44 118 378 6491; fax: +44 118 378 6331.

E-mail address: w.c.hayes@reading.ac.uk (W. Hayes).

ised. Blending studies of these materials with commercial alkyd resins has resulted in new formulations that exhibit more rapid drying than comparable commercial coating formulations.

2. Experimental

2.1. Materials and physico-chemical characterisation

Oleic acid, linoleic acid, dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), triethyl amine, tris(hydroxymethyl)aminomethane (THAM), adipic acid, and *N,N'*-dimethylformamide (DMF) were purchased from Aldrich. Tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dichloromethane (CH_2Cl_2), methanol, acetone and 2-propanol were purchased from Fisher. Low odour white spirit (Exxsol D40 ex-Total), anti-skinning agent, methyl ethyl ketone oxime (MEKO ex-Elementis Pigments), and driers including Octa-soligen 10 (cobalt carboxylate 58%, naphtha 40% and methoxy propoxy propanol 2%), Octa-soligen calcium 10 (calcium carboxylate 45% and naphtha 55%) and Octa-soligen zirconium 18 (zirconium 2-ethyl hexanoate 56% and naphtha 44%) were used as supplied by OMG Borchers. The alkyd used (a soy oil based alkyd with 70 wt% in low odour white spirit) was obtained from Cray Valley Ltd. Melting points were carried out with Stuart Melting Point Apparatus (SMP10) (UK). 250 MHz ^1H and 62.5 MHz ^{13}C NMR spectra were recorded on Bruker AC250 spectrometer. Infrared (IR) spectroscopic analyses were performed on a Perkin Elmer 1720-X Infrared Fourier Transform spectrometer on KBr discs using thin film. GPC was performed with Polymer Laboratories PL-GPC 120 with PL-AS-MT autosampler fitted with columns (PLgel guard plus 2 \times mixed bed-D, 30 cm, 5 μm) in conjunction with refractive index (with differential pressure and light scattering) detector using THF as the eluent at 30 $^\circ\text{C}$ (flow rate 1 mL min^{-1}). Polymer molecular weight data is quoted with respect to polystyrene calibrants. For each GPC sample, a single solution was prepared by accurately adding 10 mL of solvent to an accurately known mass of ca. 20 mg of sample. The solutions were left for 2 h to dissolve/disperse and were then thoroughly mixed before being filtered through a 0.2 μm polyamide membrane. Modulated differential scanning calorimetry (MDSC) measurement was performed on a TA Instruments 2920 MDSC V2.6A. Thermo-gravimetric analysis was carried out on a TA Instruments 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 $^\circ\text{C/min}$. MDSC and TGA data were collected and processed on Universal Thermal Analysis Software.

2.1.1. Viscosities studies

The comb polymers were diluted to 70 wt% solid by addition of white spirit at room temperature and stirred vigorously for 10 min in order to give an homogeneous pale yellow oil. These comb polymer solutions were mixed with commercial alkyd resins (a soy oil based alkyd with 70 wt% in low odour white spirit) at increasing comb polymer concentrations (from 5 to 50 wt% solid) and these mixtures were stirred vigorously for 10 min to give homogenous blends. This procedure ensured that the total solids content remained at 70 wt%. Viscosity data was collected using a cone and plate viscometer at both 25 $^\circ\text{C}$ and 50 $^\circ\text{C}$.

2.1.2. Drying studies

Coating samples for drying studies were prepared by addition of these three drying agents (Octa-soligen 10, 0.5 wt%; Octa-soligen calcium 10, 2.0 wt%; Octa-soligen zirconium 18, 2.8 wt%) and MEKO into the blends and vigorously stirred for 10 min. Each sample (100 μl) was taken by capillary glass tube and coated on a rectangular glass braid substrate (size: 15.700 mm (*l*) \times 10.000 mm

(*w*) \times 0.310 mm (*h*)). Dynamic mechanical analysis was conducted with DUPONT DMA 983 DMA (with fixed frequency: 1 Hz) operating in a shearing mode (isotherm 30 $^\circ\text{C}$ for 3 days). All the DMA data were collected and processed on Universal Thermal Analysis Software.

2.2. Small molecule synthesis and characterisation

2.2.1. Monomer 1

Into a three-armed round bottomed flask was added oleic acid (86.00 g, 264 mmol) and tris(hydroxymethyl)aminomethane (THAM) (32.00 g, 264.00 mmol). The flask was degassed with nitrogen and heated slowly to 160 $^\circ\text{C}$ with vigorous stirring under a high flow rate of nitrogen to remove the water formed during the reaction. After being stirred for 48 h at 160 $^\circ\text{C}$, the mixture was cooled down to 80 $^\circ\text{C}$ and slowly poured into acetone (1500 mL) with stirring. The solution was maintained at room temperature while a white solid formed which was collected by filtration and recrystallised from acetone to afford **1** as a white powder (61.13 g, 63%). M.p.: 72–74 $^\circ\text{C}$; FTIR (KBr, cm^{-1}): 3350 (OH), 3051, 2924, 2851, 1658 (oxazoline ring), 1464 (symmetric COO-stretching), 1366, 1264, 1030, 989, 741. ^1H NMR (250 MHz, CDCl_3): δ 0.88 (t, $J = 7.5$ Hz, 3H), 1.30 (br, 20H), 1.61 (m, 2H), 2.02 (m, 4H), 2.29 (t, $J = 7.5$ Hz, 2H), 3.45 (brs, 2H), 3.63 (ABq, $J = 12.5$ Hz, 4H), 4.15 (s, 2H), 5.35 (m, 2H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 14.5, 23.1, 26.5, 27.6, 27.6, 28.7, 29.5–29.9 (6C), 30.12, 30.16, 32.3, 65.3, 72.2, 76.1, 130.1, 130.6, 171.2. CI-MS calcd. for $\text{C}_{22}\text{H}_{41}\text{NO}_3$ 367.3086, found 367.3090.

2.2.2. Monomer 2

Into a three-armed round bottomed flask was charged with linoleic acid (25.00 g, 89.00 mmol) and tris(hydroxymethyl)aminomethane (THAM) (10.80 g, 89.00 mmol). The flask was purged with nitrogen and slowly heated to 160 $^\circ\text{C}$ with vigorous stirring under a high flow rate of nitrogen to remove the water formed during the reaction. After being stirred for 48 h at 160 $^\circ\text{C}$, the mixture was cooled down to 80 $^\circ\text{C}$ and slowly poured into acetone (1500 mL) with stirring. The solution was maintained at room temperature and a white solid formed, which was collected by filtration and recrystallised from acetone to afford **2** as a white powder (26 g, 80%). M.p.: 60–62 $^\circ\text{C}$; FTIR (KBr, cm^{-1}): 3353 (OH), 3084, 3010 (*cis*- $\text{CH}=\text{CH}-\text{CH}_2=\text{CH}$), 2927, 2852, 1656 (oxazoline ring), 1464 (symmetric COO-stretching), 1428, 1367, 1328, 1270, 1223, 1182, 1140, 1088, 1030, 993, 973, 949, 724, 670. ^1H NMR (250 MHz, CDCl_3): δ 0.89 (t, $J = 7.5$ Hz, 3H), 1.31 (br, 14H), 1.60 (m, 2H), 2.06 (m, 4H), 2.28 (t, $J = 7.5$ Hz, 2H), 2.77, (t, $J = 7.5$ Hz, 2H), 3.63 (ABq, $J = 12.5$ Hz, 4H), 4.15 (s, 2H), 5.35 (m, 4H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 14.51, 23.00, 26.04, 26.53, 27.61, 27.62, 28.67, 29.53–29.58 (3C), 29.76, 30.03, 31.94, 65.49, 72.16, 76.07, 128.29, 128.49, 130.41, 130.66, 171.24. CI-MS calcd. for $\text{C}_{22}\text{H}_{39}\text{NO}_3$ 365.2930, found ($\text{M}+\text{H}^+$) 366.3001.

2.3. Comb polymer synthesis and characterisation

2.3.1. General procedure

Into a three-armed flask was added the calculated amount of adipic acid **3** and monomer **1** or **2**. The flask was purged with nitrogen and transferred into an oil bath maintained at 160 $^\circ\text{C}$. After the mixture was molten it was vigorously stirred under a high flow rate of nitrogen to remove the water formed during the reaction for a period of 8 h. After this time ^{13}C NMR and IR spectroscopic analysis revealed that the resonance of the carboxylic acid group was not evident (see Supporting Information, Figs. S1 and S2), then the reaction mixture was submitted to a reduced pressure for 30 min to distil off residual water to yield a pale-yellow viscous oil.

Download English Version:

<https://daneshyari.com/en/article/5210166>

Download Persian Version:

<https://daneshyari.com/article/5210166>

[Daneshyari.com](https://daneshyari.com)