



# Synthesis and characterization of liquid molecular brush binder for coating applications



Mapoloko Mpho Phiri<sup>1</sup>, Waled Hadasha, Rueben Pfukwa\*, Bert Klumperman\*

Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag X1, Matieland 7602, South Africa

## ARTICLE INFO

### Keywords:

Anhydrides  
Alternating copolymers  
*n*-BVEMAh  
Molecular brush  
Coating

## ABSTRACT

This report documents the facile synthesis of molecular brushes, via a grafting onto approach, with potential application as coating binders. Firstly, alternating copolymers of *n*-butyl vinyl ether (*n*-BVE) and maleic anhydride (MAh), i.e. *n*-BVEMAh, were synthesized via conventional radical polymerization. The anhydride reactive handle was subsequently utilised to access molecular brushes, via a grafting onto method, by imidizing the MAh repeat units with amine end-functional poly(ethylene glycol) oligomers, with 12 repeating units (PEG<sub>12</sub>-NH<sub>2</sub>). The product *n*-BVEMI-PEG<sub>12</sub> brushes were viscous liquids at room temperature, hence we termed them liquid molecular brushes (LMBs). The LMBs displayed Newtonian flow behaviour at shear rates below 1000 s<sup>-1</sup>. We evaluated the applicability of this molecular brush system as coating binder, by grafting varying fractions of linoleamide (Lin) side chains, which has oxidative crosslinking ability, along with the PEG<sub>12</sub> onto *n*-BVEMAh, to access *n*-BVEMI-PEG<sub>12</sub>/Lin. The *n*-BVEMI-PEG<sub>12</sub>/Lin binders underwent oxidative crosslinking at 50 °C in the presence of a drier. The challenges associated with the current binder system are highlighted.

## 1. Introduction

Typical coating formulations include volatile organic compounds (VOC) as solvents to reduce the viscosity of the binder, and aid in coating application. Due to increasing environmental and health concerns, however, there is a drive to lower the VOC content of paint formulations, to prevent harm to human health and the environment [1–3]. Two approaches for limiting solvent use in coatings, include the use of waterborne coatings [4–8], and the use of high-solids coatings [3,9,10]. High solids coatings can be obtained by using low molar mass oligomers, however this leads to coatings with poor drying properties [9]. An alternative strategy to reduce the resin viscosity, is to use resins with special topologies, e.g. hyperbranched polymers [10–12] and brush-type polymers (brushes) [5,13,14], which due to their physical properties, have lower viscosities than linear polymers of similar molar mass. Lower viscosity coatings are desirable because they require lower quantities of VOC ‘thinners’, hence present formulations with lower VOC contents [11,14]. Brushes, in particular, can be accessed by a broad range of synthetic approaches, presenting structures that cannot be accessed by a single technique [15,16]. Molecular brushes are prepared by either grafting a side chain from, or onto, a polymer backbone, or by polymerizing (grafting through) the polymerizable endgroup of an already made linear chain [17]. Sometimes, combinations of these

approaches are utilized [17]. Recently, in our group, we facilely prepared molecular brushes, based on a poly(styrene-*alt*-maleic anhydride) (SMA) backbone, by capitalizing on the nucleophilic susceptibility of the anhydride rings of the maleic anhydride (MAh) repeat units [18], which we imidized with mono-amine functional polyethylene glycol (PEG) side chains to access the brushes [19]. Furthermore we combined grafting through and grafting onto approaches by copolymerizing styrene-PEG<sub>12</sub> macromers with MAh, before imidizing the MAh rings with dodecyl amine. Therefore, in the final brush structure, each styrene unit was appended with a PEG<sub>12</sub> side chain, and each maleimide repeat unit with a dodecyl side chain, presenting densely grafted alternating hetero-arm molecular brushes [19]. We observed that these specific molecular brushes were viscous liquids at room temperature. It has been shown that solvent-free densely grafted polymer brushes behave like linear polymer chains, without side chains, but with added diluent [20,21]. This is caused by the brush-like character, which prevents entanglements, without significantly increasing stiffness [20]. We rationalized these LMBs, based on alternating copolymers with PEG<sub>12</sub> side chain functionalised maleimides, can be applicable in coating formulations with high solid contents (hence low VOC). Herein we show that molecular brushes based on alternating copolymers of *n*-butyl vinyl ether (*n*-BVE) and MAh, i.e. *n*-BVEMAh, when imidized with PEG<sub>12</sub> side chains, also form LMBs. We tested their applicability as

\* Corresponding authors.

E-mail addresses: [rueben@sun.ac.za](mailto:rueben@sun.ac.za) (R. Pfukwa), [bklump@sun.ac.za](mailto:bklump@sun.ac.za) (B. Klumperman).

<sup>1</sup> Current address: Nelson Mandela University, Port Elizabeth, South Africa.

solvent-free binders for coating materials, by incorporating varying fractions of linoleamide (Lin) chains, to impart crosslinking ability, using similar chemistry as employed in traditional alkyd resins [9,12].

## 2. Experimental

### 2.1. Materials

*n*-BVE (Sigma-Aldrich, > 99%) was purified by distillation under reduced pressure. 1,4-Dioxane (Sigma-Aldrich > 99%) was dried over anhydrous magnesium sulphate (MgSO<sub>4</sub>) for 24 h and stored over 3 Å molecular sieves (Sigma-Aldrich, 4–8 mesh). *N,N'*-Azobisisobutyronitrile, AIBN (donation from Freeworld Coatings) was recrystallized from methanol. Poly(ethylene glycol) monomethyl ether (PEG<sub>12</sub>-OH, from Sigma-Aldrich) was used as received and the amine derivative (PEG<sub>12</sub>-NH<sub>2</sub>) was synthesized according to literature [22]. THF was distilled over sodium and benzophenone. MAh (Merck, 98%), deuterated dimethyl sulphoxide, DMSO-*d*<sub>6</sub> (Sigma-Aldrich, 99.8%), *N,N*-dimethyl formamide, DMF (Sigma-Aldrich > 99%), diethyl ether (Sigma-Aldrich), toluene (Sigma-Aldrich, > 99%), ethylene diamine (Sigma-Aldrich, > 98%), ethanol, *N,N*-dicyclohexyl carbodiimide, DCC (Sigma-Aldrich, > 99%), *N*-hydroxy succinimide (Fluka, > 97%), and linoleic acid (Sigma-Aldrich, > 98%) were used as received. Snake skin dialysis tubing (molecular weight cut-off, MWCO = 3500 g/mol) was purchased from Thermo Scientific.

### 2.2. Measurements

**NMR:** NMR spectroscopy experiments were performed on a Varian Inova 300 MHz spectrometer, at 25 °C.

**Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR):** ATR-FTIR spectra were recorded on a Thermo Nicolet iS10 spectrometer (Thermo Scientific, Waltham, MA) fitted with a germanium crystal. Spectra were recorded at a resolution of 8 cm<sup>-1</sup> where 16 scans were averaged for each spectrum. Thermo Scientific OMNIC software (version 8.1) was used for data collection and processing.

**Size exclusion chromatography (SEC):** All SEC experiments were carried out on an Agilent 1260 Infinity series HPLC instrument (Agilent Technologies, Waldbronn, Germany) with a refractive index detector (DRI).

For SEC-MALLS, a Wyatt DAWN Heleos II, 8-angle laser light scattering detector was added. A mobile phase of THF/acetic acid (95/5 (v/v)) was used with two PLgel Mixed-B columns, average particle diameter 10 μm, with the following dimensions 300 × 8 mm i.d. (Polymer Laboratories, UK). The flow rate was 1 mL/min and the column oven temperature was set to 35 °C. Sample concentrations of 2.5 mg/mL and an injection volume of 100 μL were used.

For standard SEC the system was calibrated using narrow dispersity polystyrene (PS) standards with molar masses ranging from 580 to 6 035 000 g/mol.

For SEC-MALLS, the MALLS detector was calibrated using pure toluene assuming a Rayleigh ratio of 3.4985 × 10<sup>-5</sup> cm<sup>-1</sup> at a wavelength of 658 nm. The RI detector was calibrated using NaCl of varying concentrations i.e. 0.002–0.02 M, assuming a dn/dc value of 0.174 mL/g at a wavelength of 658 nm. The refractive index increments (dn/dc) for the samples were determined from the quantitatively recovered samples.

Data was acquired using ASTRA version 6.0 (Wyatt Technology, Goleta, Santa Barbara, CA, USA) and PSS WinGPC Unichrom (PSS Polymer Standards Service GmbH (Mainz, Germany)).

**DOSY NMR:** DOSY analysis was performed on an Agilent Inova spectrometer operating at 600 MHz for the <sup>1</sup>H Larmor frequency with a 5-mm two-channel inverse detection probe optimized for <sup>1</sup>H detection and equipped with an actively shielded Pulsed Field Gradient z-gradient coil. The temperature was regulated at 25 °C with an air flow of 10 L min<sup>-1</sup> to avoid temperature fluctuations due to sample heating

during the gradient pulses. The samples were prepared by dissolving the individual polymers in DMSO-*d*<sub>6</sub> (30 mg mL<sup>-1</sup>), before transferring the solution (0.75 mL) to the NMR tubes. Additional experimental details and conditions are identical to those reported in reference [23].

**Rheology:** An Anton Paar MCR302 rheometer fitted with an H-TPD200 oven and a 25 mm diameter parallel plate at 22 °C and 60 °C and a gap of 0.2 mm was used to characterize the rheological behavior of the LMBs. The shear rates were varied from 10<sup>-2</sup> to 10<sup>4</sup> s<sup>-1</sup>. The sample was placed on the bottom plate set at 60 °C and the oven hood was lowered for about 1 min to allow the softening of the sample before resuming the analysis.

**Electron Spray Ionization Mass Spectroscopy (ESI-MS):** A Waters Synapt G2 instrument was used with ESI positive (H<sup>+</sup> ionization) as a source, cone voltage 15 V, lock mass: leucine encephalin. Introduction: ESI probe injected into a stream of acetonitrile.

### 2.3. Synthetic work

#### 2.3.1. Alternating copolymerization of *n*-BVE and MAh

*n*-BVE (1.50 g, 150 mmol), MAh (1.49 g, 150 mmol), and AIBN (0.082 g, 0.500 mmol) were weighed into a 50 mL round bottom flask, dissolved in 1,4-dioxane (15 mL) and then degassed by purging with argon gas for 30 min. The mixture was then immersed into an oil bath preheated to 60 °C, and the reaction ran for 24 h. The resulting polymer was isolated by precipitation from cold diethyl ether, and dried under reduced pressure at 60 °C, overnight. Total monomer to AIBN ratios (mol:mol), and total monomer concentrations were varied to synthesize copolymers with various molar masses (Table 1).

#### 2.3.2. Grafting onto, by imidization of *n*-BVEMAh copolymer with PEG<sub>12</sub>-NH<sub>2</sub>

A typical procedure is described: *n*-BVEMAh (entry 1, Table 1) (0.50 g, 2.47 meq MAh) was dissolved in DMF (15 mL), in a two-neck round bottom flask fitted with a reflux condenser and a dropping funnel containing a DMF solution (15 mL) of PEG<sub>12</sub>-NH<sub>2</sub> (2.77 g, 4.94 mmol), 2 mol equivalents to the MAh unit. Thereafter the round bottom flask was immersed in an oil bath preheated to 120 °C. The PEG<sub>12</sub>-NH<sub>2</sub> solution was added drop-wise over 30 min. The reaction was allowed to run for 48 h then the mixture was purified by dialysis. Afterwards, the solvent was evaporated, and the liquid product obtained further dried under reduced pressure at 100 °C, for 16 h. Details of other grafting onto experiments are in Table 2.

#### 2.3.3. *N*-hydroxysuccinimide linoleate

A solution of linoleic acid (20.0 g, 0.071 mol) in anhydrous chloroform (50 mL) was added to a dry 250 mL three-neck round-bottom flask. To this solution, a mixture of *N*-hydroxysuccinimide (8.21 g, 0.713 mol) and DCC (14.7 g, 0.713 mol), dissolved in anhydrous chloroform (50 mL), was quickly added in one step. The reaction flask was sealed with a rubber septum and the mixture degassed for 30 min, by purging with argon, and left to stir at room temperature for 24 h. The solution was filtered and chloroform removed by rotatory evaporator. Residual *N,N'*-dicyclohexylurea byproduct (white

**Table 1**  
Results of copolymerization of *n*-BVE and MAh.

#	<i>n</i> -BE:MAh:AIBN	[M] <sub>total</sub>	M <sub>n</sub> (kg/mol)	M <sub>w</sub> (kg/mol)	Đ
1	<i>n</i> -BVEMAh 1 30.4:30:1	2.0	186	248	1.3
2	<i>n</i> -BVEMAh 2 63.1:62.9:1	3.32	736	1149	1.6
3*	<i>n</i> -BVEMAh 3 60:60:1	2.0	657	843	1.3

[M]<sub>total</sub> = total monomer concentration, in organic solvent.

SEC-MALLS analysis in THF-Acetic acid, at 30 °C.

\* Copolymerization was carried out in methyl ethyl ketone, for entries 1 & 2 polymerizations were in dioxane.

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