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Synthesis and characterization of glycerol-adipic acid hyperbranched polyesters

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ABSTRACT

The structure and molecular weight of the hyperbranched polyesterification of adipic acid and glycerol were characterized by ^{13}C NMR spectroscopy and size-exclusion chromatography as a function of reaction time and reaction stoichiometry. The glycerol substitution patterns and the extent of reaction of both glycerol and adipic acid were determined by NMR. The glycerol species concentrations determined by NMR were used with a Macosko–Miller conditional probability model to predict the hyperbranched polyester weight-average molecular weight. The model accommodated the difference in primary and secondary –OH reactivity and any substituent effects to glycerol –OH reactivity. In all cases, the predicted weight-average molecular weights were in excellent agreement with the absolute molecular weights determined by size-exclusion chromatography with light scattering detection.

1. Introduction

Hyperbranched polyesters (HBPE) have attracted renewed interest because many of their monomeric building blocks can be obtained from renewable sources and are biodegradable, opening new areas of application. HBPEs have been synthesized from many different biobased monomeric building blocks, including those from multifunctional aliphatic alcohols such as pentaerythritol, xylitol, and erythritol, and multifunctional acids such as sebacic, aconitic, succinic, adipic, citric, glutaric and azelaic [1–5] and specifically, several from glycerol and difunctional acids [6–15]. Many of the applications targeted for these biobased HBPEs include the delivery of actives such as pharmaceuticals, pesticides and antimicrobials [16–25].

Hyperbranched polymers (HBP) are synthesized from mutually reactive multifunctional monomers, A_x and B_y, where x and y are the functionality of the molecule. The simplest of these multifunctional monomers is the $A_2 + B_3$ system, such as adipic acid with glycerol, which is the system described in this work. This $A_2 + B_3$ system forms a HBPE by a step-growth polymerization reaction, which if performed in equimolar quantities of functional groups, forms a gel at high conversions. However, by proper choice of monomer stoichiometry, one can produce soluble polymers at high conversions, with the ability to synthesize polymers of targeted molecular weight (MW). This is the basis of bimolecular nonlinear polymerization (BMNLP) methodology [26].

The endgroup composition for BMNLP is dependent on the monomer stoichiometry and the extent of reaction, the endgroup functionality primarily being that of the excess component at high extent of reaction. This reaction strategy enables design of HBPs with either A or B endgroups. The ability to easily control endgroup functionality is a valuable attribute for HB systems since many polymer properties depend on it including solubility, solution and melt viscosity, and thermal properties. The endgroups are also available for subsequent reaction such that actives can be covalently attached or the polymer can be crosslinked into networks [27–30]. Scheme 1 shows the structure of a HBPE from glycerol and a diprotic acid such as adipic acid (AA) with glycerol in excess such that the endgroups are alcohols at high extent of reaction. The polymers are composed of polar ester groups which enable host–guest interactions with active agents facilitating their encapsulation. Encapsulated actives are released by diffusion which is often significantly more rapid than release of covalently bonded actives.

The versatility and simplicity of the BMNLP approach enables the use of biobased polyfunctional alcohols and acids for the preparation of HBPEs which are able to degrade to their monomeric building blocks either by chemical or enzymatic hydrolysis. Since

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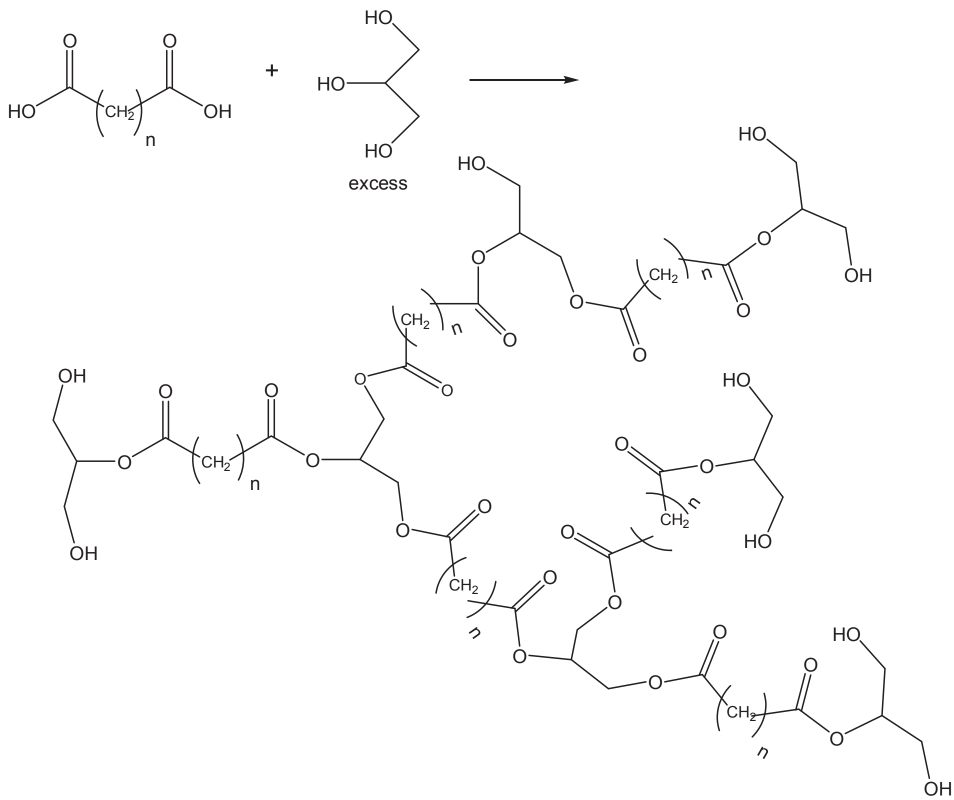

Scheme 1.

both glycerol and adipic acid are on the FDA's generally recognized as safe (GRAS) list, the degradation of glycerol-adipic acid HBPEs does not pose a threat to the environment. These HBPEs provide a versatile platform for achieving a variety of material properties.

HBPEs from adipic acid and glycerol are $A_2 + B_3$ systems which were synthesized in this investigation. The polycondensation reaction was monitored by NMR spectroscopy and SEC as a function of reaction time. Others have investigated glycerol-based hyperbranched polyesters and published NMR peak assignments for them [6–12]. Those investigations demonstrated that ^{13}C NMR spectroscopy is able to differentiate glycerol and the 5 ester species which are produced. However, there are some discrepancies among the chemical shift assignments previously reported. In this study, samples prepared by the esterification of glycerol with AA as a function of reaction time and stoichiometry were characterized by NMR in order to validate the chemical shift assignments.

2. Materials and methods

Glycerol, adipic acid and dibutyltin oxide were obtained from Sigma Aldrich and used without further purification.

The polyester was polymerized by melt polymerization at 140 °C with dibutyltin oxide as catalyst and driven to completion by removing the evolved water by purging the reaction vessel with a continuous stream of nitrogen. In one example, a HBPE of stoichiometry [−OH]/[−COOH] equal to 2.0 was achieved by using 23.8 g of AA, 20 g of glycerol and 0.219 g dibutyltin oxide (0.5 weight%) which were added to a 250 mL three-necked round-bottomed flask and heated to 140 °C. The reaction was blanketed with N_2. At the end of the reaction, the flask was cooled and the polymer recovered without further purification. It was a colorless, highly viscous liquid.

The series of HBPEs of varying stoichiometry was synthesized using similar methodology. The final stoichiometry of each HBPE was confirmed using ^{13}C NMR spectroscopy.

^{13}C NMR spectra of samples dissolved in DMSO-d6 were obtained using a Varian Inova 500 NMR spectrometer operating at 125.7 MHz. A 90° pulse width was used, the pulse repetition time was 10 s, gated decoupling was used without NOE, the sweep width was 31 KHz, number of points 13.1 K, 3.0 Hz line broadening, 256 scans. The relative areas of the resonances were compared to spectra obtained with a 5 s pulse repetition rate, yielding equivalent results, demonstrating that these conditions were quantitative. The ^{13}C NMR assignments were also confirmed using ^{13}C NMR APT spectra to identify the resonances belonging to the methine and methylene carbons of glycerol.

Size-Exclusion Chromatograms (SEC) were obtained using a Waters 1525 chromatograph equipped with a differential refractive index detector (dRI) and a Wyatt Dawn Helios II multiangle light scattering detector. Tetrahydrofuran was used as the mobile phase at 1 mL/min. Two PLgel mixed E columns (Agilent) were used for the separation.

3. Results

3.1. ^{13}C NMR analysis

Glycerol possesses two primary and one secondary hydroxyl unit with very different reactivity toward esterification. The five expected structures from the esterification with adipic acid (AA) are given in Table 1. They include the primary monoester, which in previously reported hyperbranched polymer terminology, is a terminal unit labeled T_G, the secondary monoester, which is also a terminal unit labeled $T_{1,3}$, the primary−primary diester linear