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Molecular characterization of biodegradable natural resin acid-substituted polycaprolactone

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ABSTRACT

Renewable resin acid-substituted polycaprolactone is prepared for characterization of physical properties of polymers. Six samples of dehydroabietic acid-substituted polycaprolactone (PCL-g-DAPE) with various molecular weight were synthesized by a combination of ring-opening polymerization and click chemistry. These polymers were characterized by on-line two angle light scattering and differential pressure viscosity. The values of *dn*/*dc*, average molecular weight, intrinsic viscosity, hydrodynamic radius, and radius of gyration were determined. Mark-Houwink double logarithmic relations of intrinsic viscosity and weight average molecular weight as well as Stockmayer–Fixman plots were established to scale the dimensions and conformation of PCL-g-DAPE chains related to their molar mass. The results indicated that PCL-g-DAPE is a flexible-coil polymer, similar to poly(methyl acrylate). Such properties were somewhat unexpected, considering the bulky group in the polymer side chains.

1. Introduction

Biodegradable polymers have gained much attention due to their potential applications in biomedical areas and utility as environment-friendly disposable packaging materials [1,2]. One important source of these polymers comes directly from natural biomass or can be synthesized by microorganisms [3]. Another scope of biodegradable polymers is classified as petroleum-derived synthetic polymers such as polycaprolactone [4]. By combining degradability of synthetic polymers and sustainability of renewable resources, biodegradable polymers based on natural resources have been developed, with new emerging properties originating from renewable resources [5].

Rosin is a renewable natural resource from the exudation of pine and conifer trees or from waste pulp in paper industry [6]. Its major components are resin acids, which have a bulky hydrophenanthrene group that can render hydrophobicity to any substrates it attaches. We have recently developed a platform of sustainable polymers and composites based on renewable rosin [7,8]. These materials include (meth)acrylic polymers by controlled polymerization [9], semi-degradable [10] or degradable polyesters by ring-opening polymerization [11], and lignin, cellulose composite polymers by surface-initiated polymerization [12,13].

These materials exhibit interesting properties including enhanced hydrophobicity, good thermal stability, fluorescent property and antimicrobial activities [12,14–16]. All polymers with rosin at the side chain are amorphous. However, most polymers are brittle, most likely due to the presence of the bulky hydrophenanthrene, which could result in

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a high entanglement molecular weight of polymers. One of intuitive questions is whether these polymers adopt a rigid conformation due to the bulky group or still exhibit a random-coil conformation. An in-depth understanding of their conformation would facilitate macromolecular design toward favorable mechanical properties. The influence of side chain groups on the physical properties of polyethylene chains is well documented [17]. In the case of polyacrylates, interests have been focused on the changes induced by altering the length of alkyl ester group [18] or identity of the ester linkage such as phenyl with alkyl substituent in various positions [19]. The methods of evaluating configurational properties are usually sought after two parameters theories, such as Mark-Houwink-Kuhn-Sakurada (MH) and Stockmayer–Fixman (SF) [20,21] relationships to viscosity and molar weight to estimate conformational properties including Flory's characteristic ratio (C_∞) [22–24].

Herein we present a case of model study to investigate some physical properties of a rosin-containing polyester by intrinsic viscosity and molar mass relationship based on MH and SF methods. We hope this study could shed light on many other types of polymers containing rosin moiety. This polyester is based on rosin-substituted polycaprolactone. Specifically, we prepared six samples of dehydroabietic acid-substituted polycaprolactone (PCL-g-DAPE) with different molecular weight via a click reaction between propargyl ester of dehydroabietic acid (DAPE) and an azide-substituted PCL.

All samples were characterized via a combination of online measurement of intrinsic viscosity, refractive index, and two-angle light scattering in a size exclusion chromatography [25]. The advantage of this method is that a single measurement could simultaneously yield characteristic parameters of macromolecules including weight-average molecular weight (M_w), number-average molecular weight (M_n), polydispersity (M_w/M_n), intrinsic viscosity [η], radius of gyration (R_g), hydrodynamics radius (R_h), and dn/dc of samples in solution.

2. Experimental

2.1. Materials

Standard calibration samples of polystyrene with narrow molecular mass distribution were purchased from Sigma–Aldrich; tetrahydrofuran (THF) was purchased from Fisher Scientific. Other solvents and reagents were purchased from the above mentioned companies and used without further treatment.

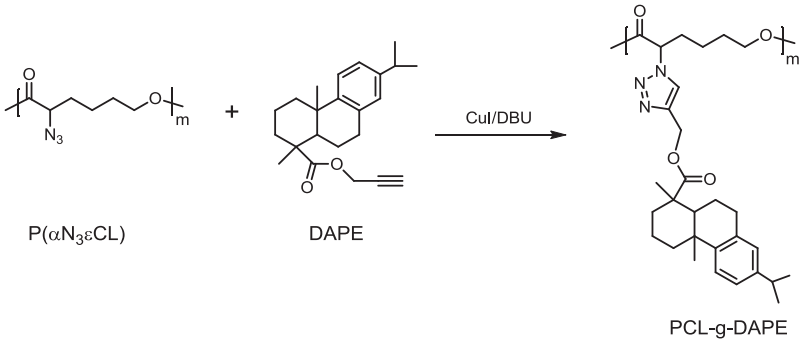
2.2. Synthesis of PCL-g-DAPE polymers

PCL-g-DAPE samples with different molecular weight were prepared according to our previous report [11]. The synthetic route is shown in Scheme 1. Propargyl ester of dehydroabietic acid (DAPE) and α-azide substituted poly(caprolactone) (P($\alpha N_3\varepsilon$CL)) with different molecular weight were first prepared. Through a copper-catalyzed (with CuI/DBU (1,8-diazabicyclo[5.4.0]undec-7-ene)) cycloaddition reaction between the azide group and the alkyne group, DAPE was grafted onto P($\alpha N_3\varepsilon$CL), resulting PCL-g-DAPE as our sample. The product was first purified by passing through a basic aluminum oxide column. The concentrated solution was then precipitated into a solution of ethylenediaminetetraacetic acid tetrasodium salt (EDTA) in a mixture of H_2O/CH_3OH, and washed with methanol before drying under vacuum. ^{1}H NMR spectra (Fig. 1) confirmed the successful preparation of the polymers. Using P($\alpha N_3\varepsilon$CL) with different molecular weight, six samples of PCL-g-DAPE with various molecular weight were prepared and named as samples A–F, in the trend of decreasing molecular weight.

2.3. Characterization

^{1}H NMR (300 MHz) spectra were recorded on a Varian Mercury spectrometer with tetramethylsilane (TMS) as an internal reference. The dilute solution viscosities were measured by Viscotek (Houston, TX) GPC-MAX 303 using various volume of the solution (15, 25, 35, 75, 95, 110, 130, 150 μL) of a given sample of PCL-g-DAPE in THF prepared a day before use. The solutions were prepared gravimetrically by measuring mass of solvent and solute using a Mettler-Toledo XS205 Dual-Range analytical balance with an uncertainty of 0.02 mg.

The Viscotek (USA) TDA consists of a 18 μL cell with a laser light at 760 nm, two-light scattering detectors, one at right angle and the other at low angle (~7°), a refractive index deflection type detector with reference cell volume 12 μL and light emitting diode (LED) at 660 nm wavelength, and a four capillary, differential Wheatstone bridge configuration viscometer with bridge volume about 72 μL.



Scheme 1. Synthesis of PCL-g-DAPE polymers.