

Solventless synthesis and free-radical photopolymerization of a castor oil-based acrylate oligomer

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ABSTRACT

A simple, low environmental impact procedure for preparing acrylated castor oil (ACO) was developed using a hybrid acrylate isocyanate monomer. The photopolymerization of neat ACO and the copolymerization of ACO with common low molecular weight acrylate monomers were rapid and reached high conversions, as monitored by real-time FT-IR spectroscopy. The mechanical properties of the ACO polymers and copolymers were determined by dynamic mechanical analysis of the thin polymer films. The resulting copolymers ranged from highly flexible, low glass transition materials to rigid, high glass transition materials depending on the functionality and secondary functional groups of the commercial monomers used. The ACO oligomer was compatible with a variety of acrylate monomers and produced transparent films regardless of co-monomer used. The glass transition temperatures of the copolymers can be coarsely estimated *a priori* using the Fox correlation. ACO-based materials provide a promising route to introduce renewable materials in many acrylate-based coating applications.

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1. Introduction

The fabrication of protective organic coatings can be done in many ways. Historically, organic solvents used either as a polymerization medium or simply as a resin carrier were evaporated, leaving a thin polymeric film as a protective coating over the substrate [1]. The solvent evaporation technique is clearly environmentally deleterious and is a health hazard to coating applicators and other individuals near the application area. The development of waterborne and so-called 100% solids systems has provided significant decreases in volatile organic compound (VOC) emissions in coatings production processes [2–4].

Photo-induced polymerization of 100% solids resins is particularly efficient in that considerably lower energy input is required to produce polymeric films in comparison to thermal curing schemes. In order to increase the environmental benefits of photopolymerization, renewable materials can replace petroleum-derived monomers as feedstock [5–7]. Triglycerides, derived from seed oils, are especially attractive starting materials for photopolymerization for two reasons: intrinsically high molecular weight and high functionality.

Castor oil triglycerides offer a promising route to synthesize reactive oligomers [8] for photopolymerization [9–11] and exhibit numerous advantages. For example, the high molecular weight would mitigate polymerization-induced shrinkage [12,13], which causes internal stresses and surface deformations in the polymer film [14–16]. In addition to lower shrinkage, the high molecular weight would render the resin non-volatile, which simplifies the processing of the resin and reinforces the low to no VOC quality often associated with photopolymerizable resins. The fatty acid composition in castor oil triglycerides differs from most other triglycerides, which are typically high in saturated fatty acids, as well as mono- and di-unsaturated fatty acids. About 90% of the acid residues in castor oil triglycerides are ricinoleic acid. Ricinoleic acid is singly unsaturated and bears one hydroxyl group, see Fig. 1 [17]. The hydroxyl group allows for direct modification of the triglycerides, resulting in a multifunctional, renewable oligomer accomplished in a single modification reaction step.

Hydroxyl groups can couple readily with esters, epoxides, and isocyanates. The coupling with isocyanates is the most rapid and thermodynamically favorable of these reactions and has no secondary reaction products, as shown in Scheme 1 [18,19]. The reaction can take place without solvent or catalyst, but a simple tertiary amine catalyst accelerates the reaction and reduces the reaction temperature. A solventless modification can then be carried out if both reactants are compatible and in the liquid state when combined. In this work, a unique hybrid monomer that has

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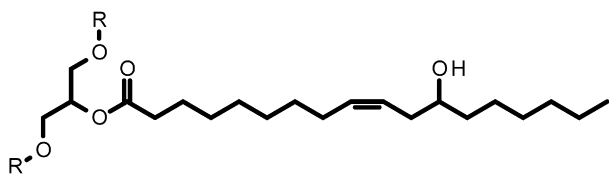
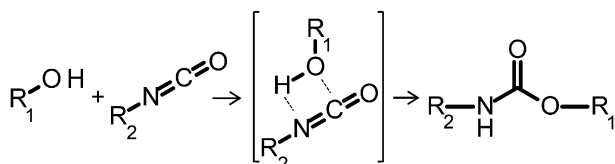


Fig. 1. Chemical structure of ricinoleic acid in triglyceride form.



Scheme 1. Isocyanate and alcohol functional groups readily couple. The hydrogen-bonded complex is shown as the intermediate.

both acrylate and isocyanate functional groups (AOI) is used to functionalize the castor oil.

The functionalization of castor oil using AOI is an efficient technique that can be used to prepare oligomers for polymerization in a facile way and facilitates the transition from pure petroleum-based feeds to a combination of petroleum and renewable ones. The synthesis of acrylated castor oil (ACO), the photopolymerization behavior, and the material properties of the resulting polymer in both neat- and co-polymerizations are detailed in this work.

2. Experimental

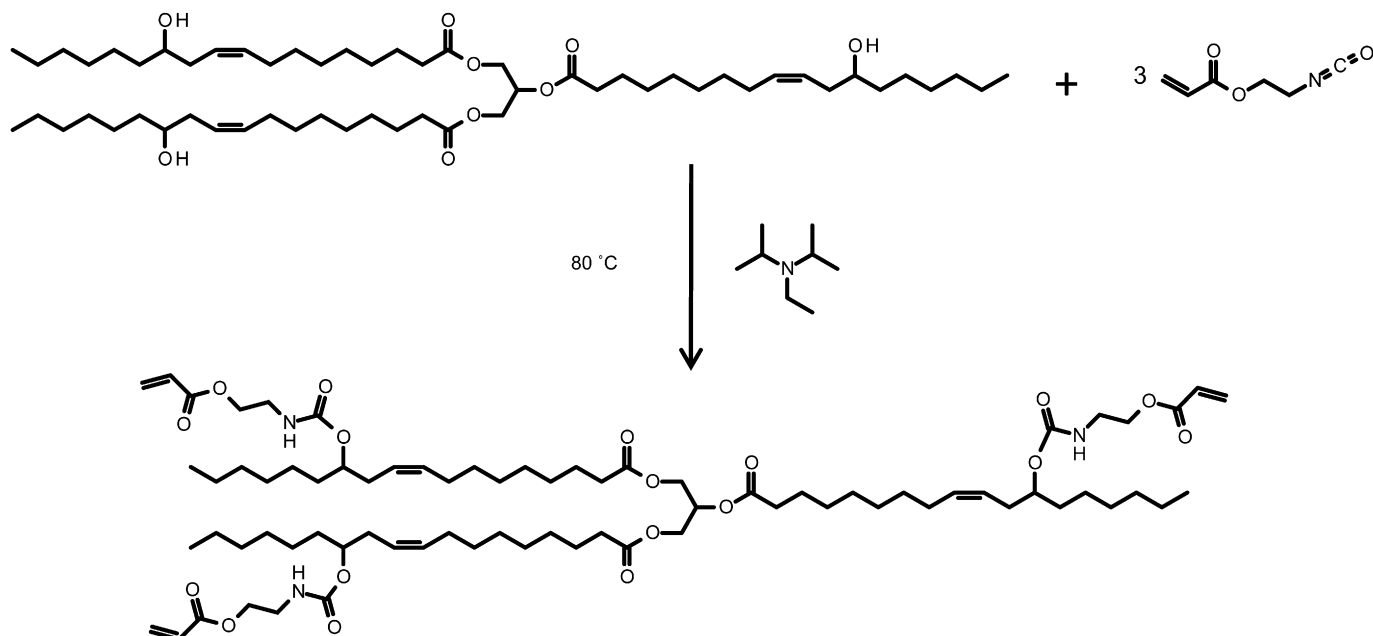
2.1. Materials

Castor oil, CVS brand (USP grade), was purchased at a local pharmacy. 2-Acryloyloxyethyl isocyanate (AOI) was donated by Showa Denko. AOI is a highly hazardous isocyanate monomer, and a thorough understanding of its toxicity and reactivity must be

obtained before handling it. The acrylate monomers used as reactive diluents were chosen to span a range of functionalities, hydrophobicity, and rigidity via secondary functional groups. These ranges of different diluent properties were explored to demonstrate the compatibility of acrylated castor oil (ACO) with various commercial acrylate monomers. Hydroxy ethyl acrylate (HEA) and hydroxy butyl acrylate (HBA) monomers were donated by BASF. Hexyl acrylate (HA) and ethylene glycol methyl ether acrylate (EGMEA) monomers were purchased from Aldrich. Isobornyl acrylate (IBA) was donated by Cytec. Tripropylene glycol diacrylate (TrPGDA) and trimethylol propane triacrylate (TrMPTra) monomers were donated by Sartomer. Hexanediol diacrylate (HDDA) was purchased from Alfa Aesar. *N,N*-diisopropylethylamine (Hünigs base) was purchased from Aldrich. Hydroquinone, which was used as a stabilizer, was purchased from Alfa Aesar. The radical photoinitiator Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-1-propanone) was donated by BASF. All materials were used as received.

2.2. Synthesis of ACO

The preparation of ACO was carried out by reacting AOI with the hydroxyl groups on castor oil in the presence of a tertiary amine catalyst, Hünigs base. Since tertiary amines are commonly used in photopolymerization and are known not to interfere with the polymerization, Hünigs base was chosen over Sn catalysts, which are more typically used in isocyanate-hydroxyl reactions. Castor oil (36.3 g, 0.10 mol OH), AOI (14.8 g, 0.10 mol), Hünigs base (1.8 g, 0.014 mol), and acrylate-stabilizing hydroquinone (0.05 g, 0.49 mmol) were added to a three-necked, round-bottom flask equipped with a reflux condenser. The reaction vessel was submerged in an oil bath, which was at a constant temperature of 83 °C, stirring at 150 rpm with a magnetic stir bar. The isocyanate-hydroxyl coupling reaction was monitored by FT-IR spectroscopy. Samples were taken from the reaction mixture, in triplicate, every 30 min and diluted by an equivalent mass of THF. The diluted samples were then placed on a ZnSe ATR crystal and FT-IR spectra collected with a Thermo Nicolet 670 Nexus spectrometer equipped with liquid nitrogen cooled MCT detector, producing spectra with



Scheme 2. Castor oil reacts with AOI monomer in the presence of a tertiary amine catalyst to form acrylated castor oil (ACO), represented by an ideal triglyceride composed of three ricinoleic acid residues.

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