Phase behavior of novel triacylglycerols derived from metathesis modified plant oils

CrossMark

Prasanth K.S. Pillai, Athira Mohanan, Laziz Bouzidi, Suresh S. Narine*

Trent Centre for Biomaterials Research, Departments of Physics & Astronomy and Chemistry, Trent University, 1600 West Bank Drive, Peterborough, Ontario K9J 7B8, Canada

A B S T R A C T

The cross-metathesis of vegetable oils containing a finite amount of unsaturation with small olefins such as ethylene or 1-butene results in the production of important platform chemicals. However, a largely unused portion of the original triacylglyceride molecule is left unused: a metathesis modified triacylglyceride or MTAG. The byproduct MTAGs are very interesting precursors for many materials; particularly for the synthesis of polyols and polyurethanes because of their shortened acyl chain and terminal double bond structure. The liquid-solid phase behavior of five metathesis modified triacylglycerols (MTAGS) produced when, for instance, canola, soy and palm oils are cross metathesized with ethylene or 1-butene; namely propane-1,2,3-triyl tris dec-9-enoate (DDD), 3-(stearoyloxy) propane-1, 2-diyl bis dec-9-enoate (DDS), 2-(stearoyloxy) propane-1, 3-diyl bis dec-9-enoate (DSD), 1,2-(stearoyloxy) propane-3-diyl bis dec-9-enoate (SSD) and 1,3-(stearoyloxy) propane-2-diyl bis dec-9-enoate (SDS), was comprehensively examined with DSC and XRD.

The differences observed in the thermal transition behavior, melting temperatures and polymorphism between these MTAGs and their unmodified natural stearic-oleic TAG counterparts were well correlated with the number of terminal double bonds, number of shortened fatty acid chains, and number and positions of saturated fatty acid chains. The competition between the effects of unsaturation and position of the short moieties explained the distinctive phase trajectories of the MTAGs. The role of the large chain length mismatch (CLM) between the stearic and decenoic moieties was particularly highlighted in the chain length packing. The structure-function relationships established for MTAGs have never been reported before, and are important to the utilization of this feedstock which is growing in volume due to the commercial utilization of olefin cross metathesis of vegetable oils in the manufacture of oleochemicals.

© 2016 Published by Elsevier B.V.

1. Introduction

Current research efforts for the production of sustainable materials and energy are targeted at selecting the most suitable natural sources, improving existing synthesis routes, developing new chemistries, particularly so-called "green chemistries" such as metathesis and one-pot solvent free syntheses, and optimizing processing conditions (Behr and Gomes, 2010; Yao and Tang, 2013). Vegetable oils are a sustainable renewable feedstock that is widely used for the production of fine chemicals and as substrates for materials traditionally made from petroleum (dos Santos et al., 2014; Gandini and Lacerda, 2015). For example, most of the bio-based polyols for polyurethanes are synthesized from vegetable oils (Desroches et al., 2012).

Vegetable oils are particularly suitable for chemical transformation because of their triacylglycerol (TAG) structure which offers ready chemical modification sites such as at the double bond and ester linkages (Biermann et al., 2011; Desroches et al., 2012).

Olefin metathesis is a very powerful but still relatively benign approach, which is presently used to produce fine chemicals, substrates and materials from vegetable oils (Chikkali and Mecking, 2012; Malacea and Dixneuf, 2010; Rybak et al., 2008; Stoianova et al., 2015). Self-metathesis (forward reaction in Scheme 1) is the process in which the same olefin molecules react to produce two different olefin products; whereas, cross metathesis (backward reaction in Scheme 1) is the process in which two different olefins are involved to produce a new olefin product. The actual composition of a metathesis product is dependent on the reaction

$$2\ R\text{-}CH\text{=}CH\text{-}R' \rightleftharpoons R\text{-}CH\text{=}CH\text{-}R\ +\ R'\text{-}CH\text{=}CH\text{-}R'$$
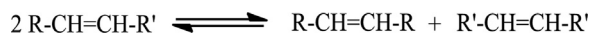
Scheme 1. Representation of olefin metathesis reaction.

conditions, such as starting materials, temperature, type of catalyst, etc. (Biermann et al., 2010; Li et al., 2012; Pillai et al., 2014; Tian and Larock, 2002), providing the possibility of controlling the product composition and ultimately its physical properties.

The cross-metathesis of natural oils with small olefins produces a modified triacylglycerol (MTAG) which includes shortened structures with terminal double bonds, not present in the parent oil (Malacea and Dixneuf, 2010; Mol and Buffon, 1998). However, the commercial potential of these derivatives of the metathesis of vegetable oil is not fully exploited because little is known about the properties of the MTAG components and their specific interactions. The ability to study the properties and phase behavior of individual MTAGs is hindered by challenging separation and purification techniques (Mol, 2004; Montero de Espinosa and Meier, 2011). An approach to avoiding costly and maybe impossible separation procedures is to synthesize pure model MTAGs by conventional chemistry routes. Such an approach has already been used to synthesize in very high purity several oligomers which are products of the self-metathesis of vegetable oils (Li et al., 2013, 2014).

The present work reports on the phase behavior of propane-1,2,3-triyl tris (dec-9-enoate) (DDD), 3-(stearoyloxy) propane-1, 2-diyl bis (dec-9-enoate) (DDS), 2-(stearoyloxy) propane-1, 3-diyl bis (dec-9-enoate) (DSD), 1,2-(stearoyloxy) propane-3-diyl bis (dec-9-enoate) (SSD), and 1,3-(stearoyloxy) propane-2-diyl bis (dec-9-enoate) (SDS). These MTAGs can be obtained for example by the cross metathesis of ethene or 1-butene with triolein (OOO), 1,2-dioleoyl-3-stearoyl-sn-glycerol (OOS), 1,3-dioleoyl-2-stearoyl-sn-glycerol (OSO), 1,2-distearoyl-3-oleoyl-sn-glycerol (SSO), and 1,3-distearoyl −2-oleoyl-sn-glycerol (SOS), respectively, or generally of high oleic − high stearic vegetable oils such as soybean oil. The sample abbreviation, molecular weight, IUPAC names and structures of the MTAGs are listed in Table 1.

The particular MTAGs of the study were selected to investigate the effect of unsaturation, positional isomerism (symmetry) and chain length mismatch (CLM) between the stearic and decenoic acids, on the phase behavior of the cross-metathesis products.

The MTAGs were synthesized by Steglich esterification and fully characterised by ^{1}H NMR and HPLC. The thermal stability, thermal transition behavior and crystal structure of SSD, SDS, DDS, DSD and DDD were examined with TGA, DSC and XRD, respectively, and compared to their oleic-stearic TAG counterparts, i.e., OSS, SOS, OOS, OSO and OOO.

2. Experimental

2.1. Materials

9-decenoic acid (>90%), glycerol (99%), DCC (*N*, *N*'-dicyclohexylcarbodiimide), DMAP (4-dimethylaminopyridine), chloroform, DCM (dichloromethane), formic acid (≥95%), and hydrogen peroxide solution (30% wt./wt.) were purchased from Sigma-Aldrich. Hydrochloric acid (36.5-38%) and perchloric acid (70%) were purchased from Fisher Scientific, and hexanes, ethyl acetate, THF (tetrahydrofuran) from ACP chemical Int. (Montreal, Quebec, Canada). The materials were used without further treatment.

2.2. Analytical methods

2.2.1. Nuclear magnetic resonance

One dimension ^{1}H NMR spectra were recorded on a Bruker Advance III 400 spectrometer (Bruker BioSpin MRI GmbH, Karl-sruhe, Germany) at a frequency of 400 MHz using a 5-mm BBO probe. The ^{1}H NMR Spectra were acquired at 25 °C over a 16-ppm spectral window with a 1-s recycle delay, 32 transients. The NMR spectra were Fourier transformed, phase corrected, and baseline corrected. Window functions were not applied prior to Fourier transformation. Chemical shifts were referenced relative to residual solvent peaks (CDCl$_3$, 7.26 ppm and DMSO-d6, 2.50 ppm).

2.2.2. Thermogravimetric analysis

TGA (thermogravimetric analysis) was carried out on a Q500 model (TA Instruments, DE, USA). Approximately 8.0–15.0 mg of fully melted and homogenously mixed sample was loaded into the TGA platinum open pan. The sample was heated from 25 to 600 °C at 10 °C/min under dry nitrogen of 40 mL/min and 60 mL/min for balance and sample purge flow, respectively.

2.2.3. X-ray diffraction

The XRD measurements were performed on a Panalytical Empyrean X-ray diffractometer (PANalytical B.V., Lelyweg, The Netherlands) equipped with a filtered Cu-K_α radiation source and a PIXcel^{3D} detector. The XRD patterns were recorded between 1 and 50° (2θ) in 0.013° steps, at 45 kV and 40 mA. The sample was thermally processed in the XRD chamber using a 700 Series Cryostream Plus cooling system (Oxford Cryosystems, Oxford, UK) fitted to the diffractometer. The temperature was controlled to better than ± 0.5 °C. The data were processed and analyzed using the Panalytical's X'Pert HighScore V3.0 software.

The subcell structure is responsible for the characteristic wide angle x-ray diffraction (WAXD, short spacing) and the hydrocarbon chain layering for the small-angle x-ray diffraction (SAXD, long spacing). Note that the first order reflection (d_{001}) of the SAXD represents the thickness of the molecular layers (Fahey et al., 1985) and the higher order reflections indicate regular periodic structures and represent the periodical sequence of electronic density differences in multiple layers (Dorset, 1995, 2002). The period of layers observed for TAG structures is usually proportional to the acyl chain length by a factor of two or three, suggesting a DCL (double-chain length) or a TCL (triple-chain length) structure (Fahey et al., 1985; Mykhaylyk et al., 2007). The polymorphic forms of TAGs are defined according to the packing of their hydrocarbon-chains (Larsson, 1986). The main subcell structures of TAGs are commonly denoted as the α-, β'- and β-forms (Larsson et al., 2006). The chain packing of the α-form is hexagonal with non-specific chain-chain interactions. The hydrocarbon chains of the β'-form are ordinarily packed in an orthorhombic perpendicular subcell, and those of the β-form parallel to each other in a triclinic or monoclinic subcell. The β-phase is the most stable, with the highest melting temperature, and the α-phase is the least stable with the lowest melting temperature (Ghotra et al., 2002; Timms, 2003).

2.2.4. Differential scanning calorimetry

DSC (differential scanning calorimetry) measurements were carried out under a nitrogen flow of 50 mL/min on a Q200 model (TA Instruments, New Castle, DE, USA) equipped with a refrigerated cooling system (RCS 90, TA Instrument). DSC cooling and heating were conducted within a range of rates to allow for the expression of all available polymorphs from the least to the most stable. The sample (5.0–6.0 (±0.1) mg) in a hermetically sealed aluminum pan was equilibrated at 90 °C for 5 min to erase thermal memory, and then cooled at different rates (0.1 °C/min − 30.0 °C/min) to −90 °C, where it was held isothermally for 5 min. The sample was then reheated to 90 °C at 5.0 °C/min to obtain the melting profile. In some instances, heating rates of 10 °C/min or 15 °C/min were used to more prominently reveal the thermal transitions occurring.