



Styrenated urethane oil synthesis via CuAAC “click” chemistry approach



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ABSTRACT

In this study, a novel route for the modification of sunflower oil-based partial triglycerides with styrene (St) was described. For this purpose, in the first step, copolymers of St and 4-chloromethyl styrene (P(St-co-CMS)) were synthesized by free radical polymerization (FRP) and controlled/living radical polymerization (nitroxide mediated radical polymerization (NMRP)) methods. In the second step, chloro groups of these samples were transformed into azido groups by using NaN_3/DMF and then azido groups were coupled with propargyl alcohol to achieve hydroxyl functional polystyrene chain (PSt-OH) via Cu(I)-catalyzed 1,3-dipolar azide-alkyne cycloaddition (CuAAC) “click” chemistry approach. Finally, alcohol groups of PSt-OH and the partial glyceride (PG) were combined by the reaction with toluene 2,4-diisocyanate (TDI). As a result, styrenated urethane oil (PG-TDI-PSt) was obtained as an oil-based binder. The structures were determined by FT-IR, ^1H NMR and GPC analyses, and film properties of the products were examined according to the related standards. (PG-TDI-PSt) gave good film properties, and therefore could be considered as an applicable oil-based binder.

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1. Introduction

Triglyceride oils have been substantially utilized for the production of organic coatings, biomaterials, paints, inks, lubricants, plasticizers, agrochemicals and polyurethane foams [1–5]. Even though triglyceride oils cannot be directly used in coating applications, they can be successfully used after applying various modification methods in this field [1–14]. One of the most popular modification techniques is the copolymerization of triglyceride oils with vinyl monomers, most extensively with styrene (St). In the classical styrenation process, the formation of homopolystyrene leads to weak film properties. A number of studies were previously carried out in our laboratory with respect to avoidance of homopolymer formation in order to improve the film properties of oil-based binders [6–14]. In our previous studies, different strategies were employed to insert St segment into the oil structure. One of these strategies was the macromonomer technique and the other one was the use of macroinitiator having large oil portion as a soft segment [7–12]. Moreover, in addition to vinyl polymer segments, inorganic domains such as vinyl trimethoxysilane, 3-aminopropyltriethoxysilane and titanium isopropoxide

were also inserted into the final polymer structure [13,14]. The nanohybrid composite film prepared by curing the oil modified products through the sol-gel process, showed good film properties with improved thermal stability [13,14]. It should be emphasized that oil portion of the polymeric structure imparts the flexibility characteristic to the film to overcome the brittleness drawback. Moreover, the combination of oil segment with polystyrene and polyurethane polymers improves the film properties such as short drying time, good alkali, acid and, water resistances [6–14].

As a continuation of these studies, in the present study “click” chemistry strategy was applied as a new route for the preparation of styrenated urethane oil using triglyceride oil, styrene and urethane linkage without homopolystyrene formation. Sharpless and Meldal groups have great contribution to the remarkable development of “click” chemistry strategy that provides quantitative yields, high tolerance of functional groups, insensitivity of the reaction to solvents, moderate reaction temperatures, possibility of working under both homogeneous and heterogeneous systems, short reaction time and high selectivity [15–19]. Several types of “click” reactions have been identified such as, nucleophilic substitution/ring-opening reactions, non-aldol type carbonyl reactions, addition to carbon-carbon multiple bonds, cycloaddition reactions (Cu(I)-catalyzed 1,3-dipolar azide-alkyne cycloaddition (CuAAC) and [4 + 2] cycloaddition–Diels Alder reaction) [19].

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CuAAC which is an important member of “click” reactions, occurs between terminal alkyne and azide groups in the presence of catalytic system at moderate reaction conditions [15–19]. During the CuAAC reaction, formed 1,2,3-triazole ring is chemically very stable and high conversion of functional groups can be achieved [15,20–23]. Additionally, 1,2,3-triazole ring could establish hydrogen bonding with –NH part of the urethane linkage and be in a dipole–dipole interaction with other 1,2,3-triazole ring because of 1,2,3-triazole’s high polarity nature in the molecule [21–23]. It was mentioned that highly stable aromatic structure of 1,2,3-triazole part has an advantage of being resistant to acidic, basic and oxidative mediums [21–23]. Numerous applications of CuAAC introduce new routes in product design that have been recently studied for functionalization of polymers [22–32].

In the recent years, the combination of CuAAC and controlled living radical polymerization (CLRP) methods is a robust and favourable strategy for the synthesis of novel materials since CLRP which are nitroxide mediated radical polymerization (NMRP), atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer polymerization (RAFT) methods have powerful advantage on the structure control of polymer chain comparing to the conventional free radical polymerization (FRP) method [8]. The product with the controlled structure and molecular weight, end group and low polydispersity can be obtained by means of CLRP methods. There have been a various studies concerning this combination in the literature. For instance, Lutz et al. prepared the end-functionalized polystyrene via ATRP together with CuAAC method [20]. In their study, the bromine chain ends of polystyrene formed by ATRP, were easily transformed into azido group moieties and these chain ends were transformed into ω -hydroxy, ω -carboxyl and ω -methyl-vinyl functional end-groups in the presence of CuBr/4,4'-di-(5-nonyl)-2,2'-bipyridine catalytic system [20]. In another research, azide end-functional poly(oligo(ethylene glycol) acrylate) was synthesized and then it was used to prepare potential biocompatible polymers having functional end-groups such as ω -amino and ω -hydroxy [24]. Likewise, NMRP and CuAAC combination having CuBr/PMDETA system was an efficient way to prepare semi-conductors carrying pendant groups [32]. NMRP method ensures highly controlled structure and narrow molecular weight distribution for the final polymer in the presence of thermally stable free radical, 2,2',6,6'-tetramethylpiperidinyl-1-oxy (TEMPO) that provides dormant chains during the polymerization process by acting as a reversible terminating agent [8,9,32]. TEMPO is one of the hindered amine light stabilizers that protect coatings against photo-oxidative degradation [8]. Styrenated oil coating samples produced by NMRP method contain TEMPO moieties at the chain ends and these samples have significantly longer life [8,9].

In the present study, the versatile root for the functional polymer synthesis was thought of worth studying in the modification of triglyceride oils and CuAAC “click” chemistry approach was applied as a new route for the styrenated urethane oil production. For this purpose, copolymers of St and 4-chloromethyl styrene (P(St-co-CMS)) having different molecular weights were prepared by both FRP and NMRP techniques separately to determine which polymerization technique is convenient to obtain coating materials with better film properties. In the next step, chloro-functional copolymer samples were converted to azido-functional polymers (PSt-N₃) via nucleophilic substitution reaction with NaN₃. These azido groups were then coupled with propargyl alcohol (PA) to generate hydroxyl groups on the polymer chains (P(St-OH)) by CuAAC in the presence of CuBr/2,2'-bipyridine catalytic system. The hydroxyl groups of P(St-OH) were combined with the PG hydroxyls by the reaction with toluene 2,4-diisocyanate (TDI) to prepare styrenated urethane oil as a final product. The structures of samples were identified by GPC, FT-IR and ¹H NMR measurements and

additionally the samples were investigated in the view of their film properties. It was successfully proved that the combination of CuAAC and NMRP approaches was a influential way for the production of the styrenated urethane oil with excellent film properties.

2. Experimental

2.1. Materials

Sunflower oil for commercial purposes was used as an oil resource. Styrene (St, 99%, Aldrich) and 4-chloromethyl styrene (CMS, 90%, Acros) were passed through columns filled with basic alumina to remove the polymerization inhibitor. Benzoyl peroxide (BPO, Sigma) and CuBr ($\geq 97.0\%$, Riedel-de Haën) were used without any further purification process. Toluene-diisocyanate (TDI, 2,4 isomer = 80% and 2,6 isomer = 20%) and tetrahydrofuran (THF) from Merck and propargyl alcohol (PA), N,N-dimethylformamid (DMF), NaN₃, and 2,2',6,6'-tetramethylpiperidinyl-1-oxy (TEMPO, 99%) and 2,2'-bipyridine (Bpy, $\geq 99\%$) from Aldrich were used as received.

2.2. Characterization

The structures of the products were characterized using Fourier-transform infrared spectroscopy (PerkinElmer FT-IR Spectrum One B spectrometer, range: 4000–650 cm⁻¹). Proton nuclear magnetic resonance spectroscopy (¹H NMR) were recorded on a Varian Unity INOVA instrument (500 MHz) using CDCl₃ as a solvent and tetramethylsilane as an internal standard. Molecular weights and polydispersities of the samples were determined by gel permeation chromatography (GPC) equipped with a Viscotek GPCmax autosampler system consisting of a pump and a Viscotek differential refractive index (RI) detector. Series of analysis were performed in THF as eluent at a flow rate of 1.0 mL/min at 35 °C and three Viscotek GPC columns (G2000HHR, G3000HHR, and G4000HHR) which were used in series, have 7.8 mm internal diameter, 300 mm length. Molecular weights were determined by polystyrene standards and results were analyzed using Viscotek OmniSEC Omni-01 software. Perkin Elmer differential scanning calorimeter (DSC400) instrument was used to determine the glass transition temperature (T_g) of the final product with a heating rate of 10 °C/min under nitrogen flow (20 mL/min).

2.3. Synthesis of partial glyceride mixture of sunflower oil

Partial glyceride (PG) was prepared by the glycerolysis reaction between triglyceride oil and glycerol. Sunflower oil (100 g) and glycerol (8.5 g) were placed into the three-necked reaction flask and heated under N₂ atmosphere. When the temperature was set at 218 °C, Ca(OH)₂ (0.1 wt% of the oil portion) was added as a catalyst. Then the temperature was increased to 230 °C and kept constant. The samples were taken from reaction medium and poured into three-fold ethanol within predetermined time intervals. Trans-esterification reaction was finalized when the alcohol solution became clear. After cooling, the reaction mixture was dissolved in diethyl ether, washed in sequence with 0.2 N H₂SO₄ and distilled water in order to remove the catalyst and unreacted free glycerol, respectively. Na₂SO₄ was poured into the flask of washed organic solution to remove water, and then the solvent was removed by using rotary evaporator. The hydroxyl and acid values of dry PG mixture were determined [33].

2.4. Synthesis of P(St-co-CMS) samples via FRP

The mixtures of St and CMS (CMS: St = 0.036: 1, CMS: St = 0.121: 1 and CMS: St = 0.170: 1, in mole) in different ratios were placed

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