Polymer 92 (2016) 189–200

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Spectral and thermal studies on the synthesis and catalyzed oligomerization of novel cardanol-based benzoxazines

Lloyd Ryan Viana Kotzebue [a], Francisco Wanderson Moreira Ribeiro [a], Venícios Gonçalves Sombra [a], Judith P.A. Feitosa [a], Giuseppe Mele [b], Selma Elaine Mazzetto [a], Diego Lomonaco [a], *

[a] Department of Organic and Inorganic Chemistry, Federal University of Ceará, 60440-900, Fortaleza, Brazil
[b] Department of Engineering for Innovation, University of Salento, Via Arnesano, 73100, Lecce, Italy

ARTICLE INFO

Article history:
Received 23 February 2016
Received in revised form
1 April 2016
Accepted 3 April 2016
Available online 4 April 2016

Keywords:
Cardanol
Benzoxazines
Thermal polymerization

ABSTRACT

The aim of this study was to synthesize novel cardanol-based benzoxazines, using different primary amines, and evaluate their influences on the synthesis and polymerization process. The monomers were characterized using NMR (^1H and ^{13}C), FT-IR, DSC and TGA. It was demonstrated how the amines structures influence on the stability of the oxazine ring, which relates to the onset polymerization temperature (T_e). Aniline-type benzoxazines provided higher T_e than aliphatic ones. Since at this elevate temperature (230–295 °C) the alkyl chain of cardanol could degrade, the use of a new catalyst was also evaluated, showing the innocuous $MgCl_2$ as an efficient alternative. The polymerization of these monomers with $MgCl_2$ (1%) were studied using FT-IR, DSC and GPC, showing that under mild temperatures it is possible to obtain polybenzoxazines completely soluble and with high polydispersity.

1. Introduction

Polybenzoxazines has drawn a lot attention due its unique advantages when compared with traditional phenolic resins, like: low dielectric constant; low water absorption; good thermal stability and chemical resistance; high mechanical properties; and no release of byproducts during its thermal ring-opening polymerization (ROP) [1,2]. Another advantage of this class of polymers is the great molecular design flexibility of its monomer, benzoxazine, which can be synthesized from a phenolic compound, a primary amine and aldehydes, enabling to vary other properties of the polymer. Even though it is possible to use different aldehydes for benzoxazine synthesis [3], the use of formaldehyde has been reported extensively [1,4–12]. Looking forward for “green” benzoxazines, the use of renewable phenolic compounds has been reported, such as urushiol, eugenol, guaiacol, vanillin and also cardanol, a constituent found in the cashew nut shell liquid [13–16].

Cashew nut shell liquid (CNSL) is the main byproduct of the cashew nut (*Anacardium occidentale* L.) industries. Found in the honeycomb mesocarp of the cashew nutshell, this dark viscous liquid has a chemical composition of four phenolic compounds: anacardic acid, cardanol, cardol and 2-methylcardol (Fig. 1). Due the rough thermal processes to obtain the cashew nut almond, the CNSL is now called as “technical CNSL”, containing predominantly cardanol from the decarboxylation of anacardic acid [17].

Aware that CNSL represent around 25 wt% of the nut, it was estimated that in 2013 more than 1.000.000 tonnes of CNSL could be produced from the world production of cashew nuts, 4.439.960 tonnes [18]. Besides the biodegradability and its low cost, this enormous amount of natural phenolic compounds showed to be a very promising renewable feedstock for a variety of applications in the polymer industries where usually the fossil based phenols are used.

Rao and Pathak [19] used cardanol to synthesize a phenylalkamine curing agent for the preparation of a copolymer network system with epoxide and a bis-benzoxazine. Caló and co-workers [20] developed the first cardanol-based benzoxazine and polybenzoxazine. Since then, cardanol was used as a fine bio-chemical for synthesis of other novel polybenzoxazines, proving that this phenolic compound shows to be very promising for this class of polymers [21–24].

In this paper, we studied the thermal and spectral behaviours of

---

* Corresponding author.
E-mail address: lomonaco@ufc.br (D. Lomonaco).

http://dx.doi.org/10.1016/j.polymer.2016.04.005
0032-3861/© 2016 Elsevier Ltd. All rights reserved.

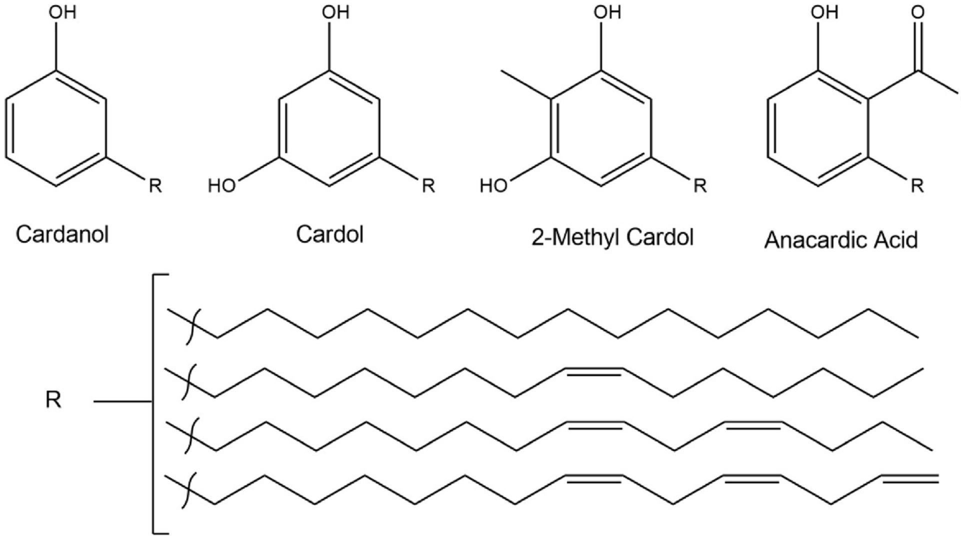

Fig. 1. Cashew nut shell liquid constituents.

novel cardanol-based benzoxazines and its oligomers by varying the amine group. The thermal study was accomplished using differential scanning calorimetry (DSC) and thermogravimetry (TGA). The spectral study was accomplished using nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared spectroscopy (FT-IR).

The purpose of this study is to obtain novel cardanol-based benzoxazines monomers and study the processes of their oligomerizations. Once in the literature the polybenzoxazines are basically studied as thermoset materials (highly crosslinked), we are focussing on the obtainment of soluble polybenzoxazines, which can be used as solution-processed polymers, widening its application range. Therefore, hydrogenated cardanol was used to minimize crosslinking between polymer chains, as the alkene groups of cardanol's side-chain are also subject to polymerize.

Another interesting point discussed here is to evaluate $MgCl_2$ as a new catalyst in order to attenuate the conditions of the ring-opening polymerization, once polybenzoxazines are commonly produced under elevate temperatures, the use of mild conditions may avoid partial degradation of the reagents and crosslinking reactions. The molar weight distributions of these oligomers were also studied using gel permeation chromatography (GPC).

2. Experimental

2.1. Materials

The hydrogenated cardanol (3-*n*-pentadecylphenol, 90–95%) was used as received from Acros Organics. Paraformaldehyde (95%), 4-chloroaniline (98%), tetrahydrofurfurylamine (97%), cyclohexylamine (99%), zinc chloride (98%) magnesium chloride (powder, 95%), *p*-toluenesulfonic acid monohydrate (98.5%) were used as received from Aldrich. Aniline (99%) and methanol (99.8%) were used from Vetec Química Fina.

2.2. General synthesis of benzoxazines

In a round bottom flask (125 mL) fitted with a condenser, 3-*n*-pentadecylphenol (2.96 mmol) and the primary amine (2.96 mmol) were heated under magnetic stirring at 70 °C. Paraformaldehyde (6.81 mmol) was added to this homogeneous molten mixture and then refluxed for 3 h at 100 °C. The progress of the reaction was followed by thin layer chromatography (TLC). After the completion of the reaction, 20 mL of methanol was added into the round bottom flask, and the mixture was stirred for 5 min. The magnetic stirring was stopped, and the supernatant was transferred to a 125 mL erlenmeyer. This procedure was repeated another four times. After collecting the supernatants, 1 mL of distilled water was added, and this mixture was put slowly to cool down till −4 °C for 90 min. After vacuum filtration, followed by washing with 5 mL of cold methanol, the obtained white product was placed inside the fumehood for 24 h for solvent evaporation.

2.3. Analytical methods

2.3.1. ^{13}C and ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR and ^{13}C NMR)

The ^{1}H NMR and ^{13}C NMR spectra were recorded on BRUKER spectrometer, model Avance DPX, operating at frequencies for ^{1}H at 300 MHz and for ^{13}C at 75 MHz. Deuterated chloroform ($CDCl_3$) was used as solvent to solubilize the samples and tetramethylsilane (TMS) was used as an internal standard.

2.3.2. Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra were obtained on a Perkin Elmer spectrometer, model FT-IR/NIR FRONTIER. Coadditions of four scans were recorded, using KBr windows with a resolution of 4 cm^{-1}, in the range of wavenumbers of 4000 to 400 cm^{-1}.

2.3.3. Mass spectrometry analysis

Mass spectrometry analysis were performed using an LC mass spectrometer Agilent 6540 Accurate-Mass Q-TOF equipped with an electrospray ionization interface working in positive ionization mode. The samples, dissolved in a chloroform/acetonitrile solution, were introduced in the mass spectrometer injected by an auto sampler using as eluent 0.1% HCOOH/acetonitrile 10:90 (v/v) aqueous solution, at a flow rate of 0.3 mL/min.

2.3.4. Differential scanning calorimetry analysis (DSC)

The DSC curves were performed in a device of Mettler-Toledo, model DSC 823e, conducted under N_2 atmosphere (flow rate of 50 mL/min). For the characterization of monomers, the non-isothermal measurements were obtained with a heating rate of 10 °C/min, in a temperature range of 30–400 °C, using