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A cardanol-based surface-active dithiocarbamate and its application in emulsion polymerization

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Abstract: A surface-active dithiocarbamate is synthesized in three steps from the renewable cardanol. Structures of the intermediates are characterized and confirmed by ¹H-NMR spectra. This functional cardanol-based dithiocarbamate is further used in RAFT emulsion polymerization of vinyl acetate without adding any other emulsifier.

1. Introduction

Since the energy and resource crisis appeared in the late of last century, exploration of other substitutes for unsustainable fossil resources is of great importance^[1]. Research and application of renewable resources from plants and animals have attracted remarkable attention both from scientists and industrial engineers^[2-4]. These sustainable resources can be used to prepare both useful or interesting small molecules and polymers. Cardanol, a main component of CNSL, is a cheap and sufficient waste in cashew-processing industry^[5-6]. Therefore, use of cardanol to synthesize functional molecules and polymers will be benefit to both environment and chemical industry. As a matter of fact, some interesting molecules derived from cardanol were constantly reported in recent years^[7-10]. For instance, Eksik and his colleagues prepared nanocomposites from grapheme platelets (GPL) together with an epoxy thermoset derived from CNSL. Analytical results indicated that addition of grapheme platelets enhanced all measured thermal and physical properties of the CNSL derived epoxy resin^[11].

Design and preparation of macromolecules with controllable molecular mass and polydispersity index (PDI) are everlasting pursuit of chemists. Controlled polymerization techniques, especially controlled living radical polymerization (CRP), have been remarkably researched in the past years thanks for some pioneering work of scientists^[12,13]. Among various CRP methods, reversible addition-fragmentation chain transfer (RAFT) polymerization is probably one of the most studied approaches due to its manifest merits such as adaption to most monomers and metal catalyst-free^[14]. Design and synthesis of proper chain-transfer agents, such as dithiocarboxylic acid esters, trithiocarbonates, and dithiocarbamates, are very crucial in realizing controlled and living properties of RAFT reactions^[15,16]. What's more, some RAFT polymerizations have been successfully conducted under aqueous emulsion polymerization conditions, which is a greener technique because of use of water as the reaction medium.

Herein, we designed a functional dithiocarbamate. This new small molecule has at least three advantages: (i) it is derived from renewable cardanol and possible post-curing or crosslinking using unsaturated side chain of cardanol moiety; (ii) it may act as a RAFT agent; (iii) it is surface-active and can be an emulsifier in emulsion polymerizations.



2. Experimental

2.1. Reagents and Characterization

2-Chloroacetamide, K_2CO_3 , acetone, $LiAlH_4$, tetrahydrofuran (THF), CS_2 , 1,3-propanesultone, $K_2S_2O_8$, dichloromethane (DCM), and vinyl acetate are AR grade, and cardanol is industrial grade. All the related reagents are utilized straightly without any further treatment.

1H -NMR spectra were measured on a Bruker AV spectrometer, with tetramethylsilane (TMS) as the internal standard. Gel permeation chromatography (GPC) was obtained on an HP 1100 HPLC. THF was used as the eluent.

2.2. Synthesis of aminocarbonylmethyl cardanol ether (1)

Cardanol (0.30 g, 1 mmol), potassium carbonate (0.55 g, 4 mmol) are suspended in acetone (10 mL) and argited at ambient temperature for 30 min, followed by adding 2-chloroacetamide (0.187 g, 2 mmol). The mixture is refluxed overnight. Access water is poured into the reaction mixture, and the aqueous layer is extracted with dichloromethane for 3 times. The organic layer is combined, dried with Na_2SO_4 , concentrated to give crude oil. Purification on silica-gel column using PE/EA (5 : 1) as eluent affords product **1** as an oil (0.26 g, 72.8%). 1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.22 (m, 1H), 6.77–6.75 (m, 1H), 6.72–6.69 (m, 2H), 6.55–6.50 (s, *br*, 1H), 6.27–6.23 (s, *br*, 1H), 5.77–5.73 (m, 0.35 H), 5.41–5.25 (m, 3H), 5.11–4.90 (m, 0.69H), 4.43 (s, 2H), 2.79–2.72 (m, 2H), 2.59–2.48 (m, 2H), 2.05–1.82 (m, 3H), 1.66–1.49 (m, 2H), 1.40–1.18 (m, 12H), 0.88–0.75 (m, 2H).

2.3. Synthesis of aminoethyl cardanol ether (2)

The amide **1** (0.36 g, 1 mmol) was put in anhydrous THF (10 mL) under N_2 atmosphere. Lithium aluminum hydride (0.11 g, 3 mmol) was then suspended in the above solution. The mixture was mixed at room temperature for 5 h, then refluxed for about 2 h until completion of the reaction detected by TLC. The mixture was cooled to about 0 °C, followed by adding cautiously water and diluted aqueous HCl. The acidic mixture was extracted with DCM for three times. The organic phase was combined, and washed with aqueous Na_2CO_3 , water, brine, respectively, dried with anhydrous Na_2SO_4 . The crude oil was achieved after distilling off DCM. Silica-gel column purification by using PE/EA (3 : 1) as eluent gave product **2** as an oil (0.21 g, 61.7%). 1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.21 (m, 1H), 6.79–6.77 (m, 1H), 5.78–5.75 (m, 0.3H), 5.48–5.30 (m, 3H), 5.15–4.76 (m, 4H), 4.18–4.11 (m, 2H), 4.95–3.05 (m, 3H), 2.79–2.72 (m, 2H), 2.59–2.52 (m, 2H), 2.05–1.82 (m, 3H), 1.69–1.62 (m, 2H), 1.41–1.16 (m, 22H), 0.88–0.75 (m, 6H).

2.4. Synthesis of cardanol-based surface-active dithiocarbamate (3)

The intermediate **2** (0.34 g) was dispersed in deionized water (10 mL), followed by adding K_2CO_3 (0.55 g) and CS_2 (0.31 g). The mixture was stirred at room temperature for eight hours, then 1,3-propanesultone (0.24 g) was added. The resulting mixture was argited for additional two hours. The aqueous solution was extracted with ethyl acetate once. The aqueous layer can be used straight forward in the subsequent emulsion polymerizations (concentration of **3** is about 0.1 mol/L).

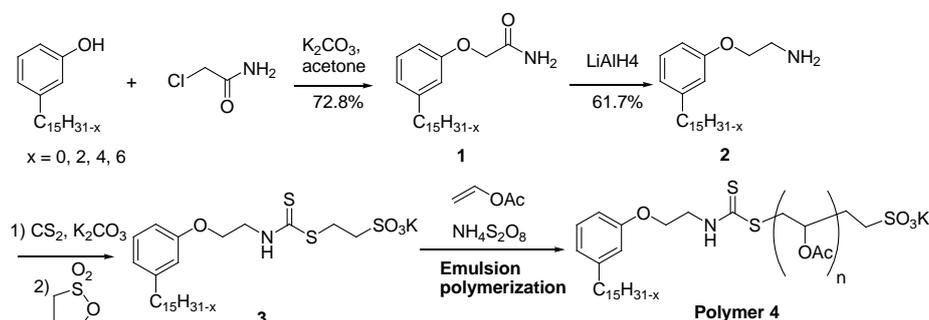
2.5. Emulsion polymerization of vinyl acetate by using 3 as both an emulsifier and RAFT agent

The aqueous solution of compound **3** (c.a. 0.5 mmol of pure **3**, 10 mL) is mixed with deionized water (10 mL) to form a solution, followed by adding monomer vinyl acetate (4.3 g, 50 mmol). The mixture is pre-emulsified by vigorous agitation for 30 min. When the temperature of the mixture is raised to 80 °C, $NH_4S_2O_8$ (0.1 g) is added to initiate the polymerization reaction. After 6 hours, heating is ceased, and the latex is cold to room temperature. Excess methanol is added to precipitate the bulky polymer product, which is weighed 2.9 g after being dried. Conversion is about 61%.

3. Results and discussion

3.1. Synthesis of cardanol-based surface-active dithiocarbamate **3**

The ether intermediate **1** is conveniently synthesized in 72.8% yield from cardanol and 2-chloroacetamide under basic conditions (Scheme 1). Structure of **1** is confirmed by $^1\text{H-NMR}$ spectrum (Fig. 1). A typical singlet peak at about 4.40 ppm proves formation of ether bond of compound **1**. Then, the amide **1** is reduced by LiAlH_4 to give primary amine **2**. The $^1\text{H-NMR}$ spectrum of **2** is shown in Figure 2. According to a report of Li's group, primary amines can react with CS_2 and sultones to provide organic sulfonic acids^[17]. Thus, our compound **2** reacts with CS_2 and 1,3-propanesultone to afford compound **3**. Note that **3** can act as a functional molecule in the subsequent reactions: a) as an emulsifier because it has a hydrophobic chain and a hydrophilic head; b) as the RAFT chain transfer agent; c) as a pre-oligomer for UV-curing because it has an unsaturated alkyl chain.



Scheme 1 Synthesis of cardanol-based surface-active dithiocarbamate **3** and its use in emulsion polymerization of vinyl acetate

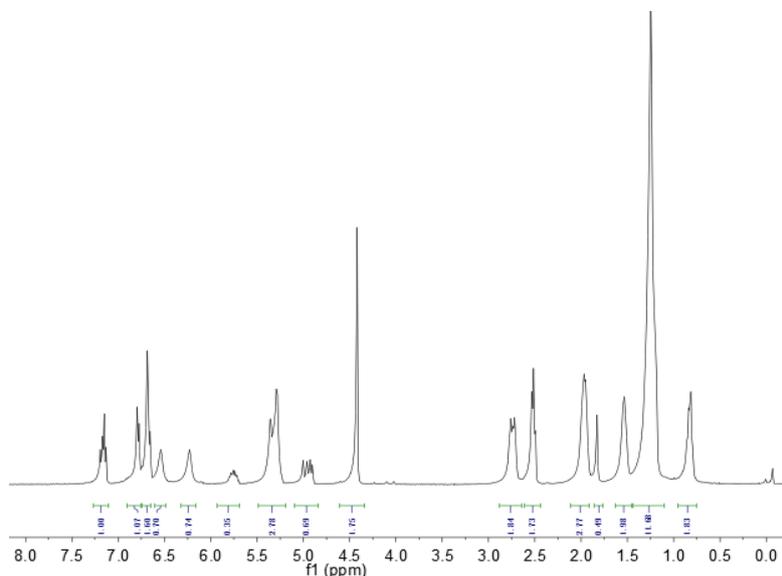


Fig. 1 $^1\text{H-NMR}$ spectrum of compound **1**

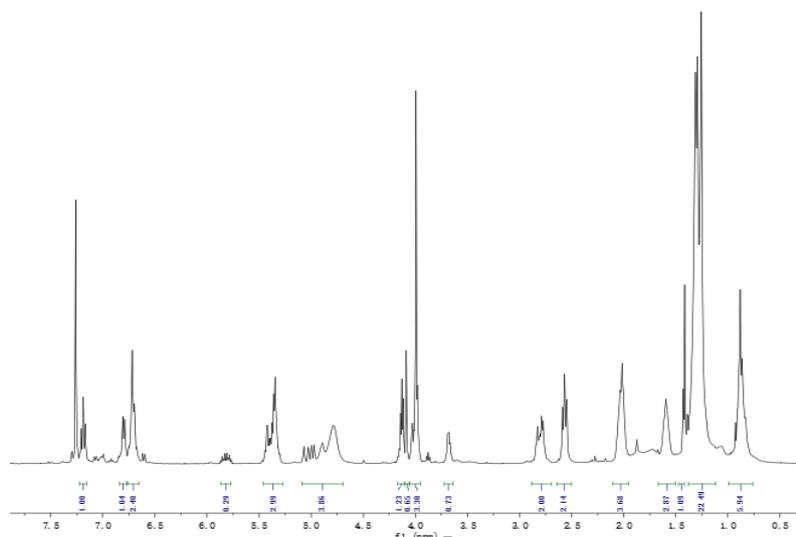


Fig. 2 $^1\text{H-NMR}$ spectrum of compound **2**

3.2. Emulsion polymerization of vinyl acetate by using **3** as both an emulsifier and RAFT agent

The dithiocarbamate RAFT agents are usually adaptable to vinyl acetate monomer. Therefore, we use this monomer in the following emulsion polymerization. Relatively stable latex is obtained after RAFT emulsion polymerization, and bulky polymer is precipitated by adding excess methanol. Furthermore, this linear polymer may be crosslinked by UV curing as there are unsaturated alkyl chains in cardanol moiety.

4. Conclusions

By using cheap and renewable cardanol, we have successfully synthesized a surface-active dithiocarbamate in three steps. The dithiocarbamate can act as both a RAFT chain transfer agent and an emulsifier in the emulsion polymerization of vinyl acetate. This work will expand the potential application of cardanol.

Acknowledgments

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