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A novel thioether polymer with pendent ester groups from a readily available acrylate derivative

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Summary

A thioether polymer with pendent ester groups was synthesized via nucleophilic substitution and Michael addition. Williamson ether synthesis conditions led to nucleophilic substitution at the α-methylene carbon of ethyl α-(chloromethyl)acrylate (ECMA, **1**) and Michael addition at the activated vinyl group. Polymerization was rapid at room temperature to give a highly viscous, sticky product with intrinsic viscosity of 0.15 dL/g in chloroform at 24° C. ^{13}C solid-state and solution NMR were used to characterize the polymer and a model compound of the nucleophilic substitution product.

Introduction

Thioether polymers containing pendent ester groups have potential for metal complexation similar to ether\thioether copolymers. Our group has previously synthesized copolymers of this type via Michael-type polyadditions of dithiols to activated divinyl monomers (1). Similar Michael addition polymers have been synthesized containing carboxylic acids and hydrolyzable backbone moieties (2). Liquid alkyl polysulfides are also used as sealants in the shipping, building, automotive and aerospace industries (3), suggesting additional applications for the polymer described here.

A method for producing thioether polymer **2** combines Michael addition and nucleophilic attack of thioanions on a readily available alkyl acrylate derivative **1** (4). The polymer obtained has two sulfur atoms per ester group, both situated three atoms away from the ester oxygens, which should facilitate six-membered ring chelation. Here we describe synthesis of the polymer and a related monomer **3** used as a model compound.

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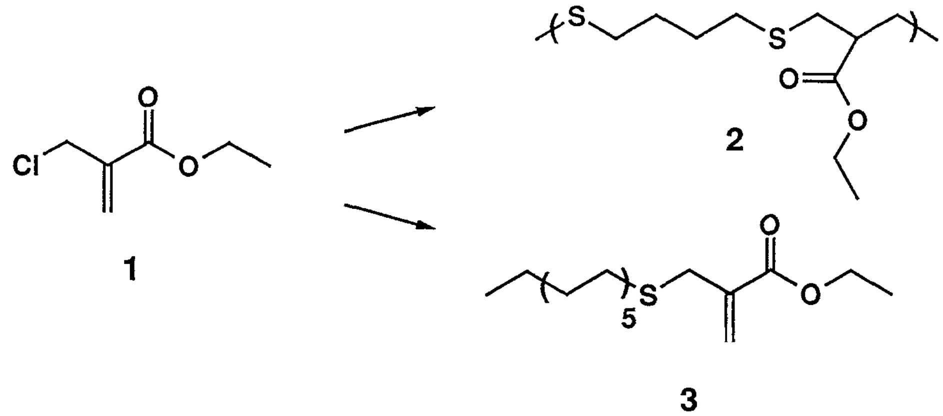

Experimental

Ethyl α-(chloromethyl)acrylate (ECMA, **1**) was synthesized from ethyl α-(hydroxymethyl)acrylate (EHMA) as described in a previous communication (4). 1,4-butanedithiol and 1-dodecanethiol were used as received from Aldrich Chemical Company. Potassium hydroxide (87.3 assay, from Fisher Scientific), and solvents were used as received. ^{13}C solid-state magic angle spinning and solution spectra were acquired on Bruker MSL-200 and AC-300 spectrometers, respectively, and processed using an in-house NMR module based on the Spectra Calc software package (5). The intrinsic viscosity was determined by extrapolating n_{sp}/c values to zero concentration. Viscosity measurements were taken at 24° C in chloroform using a Cannon-Ubbelohde #50 micro-viscometer.

Synthesis of Polymer **2**

A 1.1:1 mole-ratio of dithiol to ECMA was used with cyclohexane as solvent. The dithiol (4.91 g, 0.040 mol) was added to a saturated solution of potassium hydroxide in deionized water (10 mL) with stirring via magnetic stir bar. The vessel was open to room air. ECMA (5.43 g, 0.036 mol) in 15 mL cyclohexane was then added in one portion to the vessel. Rapid evolution of heat with concurrent formation and precipitation of polymer followed. The polymer was filtered, washed with water and methylene chloride, and dried (1.46 g, 15.2% conversion) Low yields are typical for this type of polymerization (1).

Synthesis of Model Compound **3**

The procedure that follows is general for thioanion substitution at the α-methylene carbon of ECMA. To a 5% w/w potassium hydroxide/deionized water solution (125 mL) was added ECMA (5 g, 0.034 mol), 1-dodecanethiol (6.8 g, 0.034 mol) and 20 mL methylene chloride. The reaction was monitored by gas chromatography. ECMA disappeared faster than the dodecanethiol, perhaps due to hydrolysis, and should be added during the reaction to maintain stoichiometry.

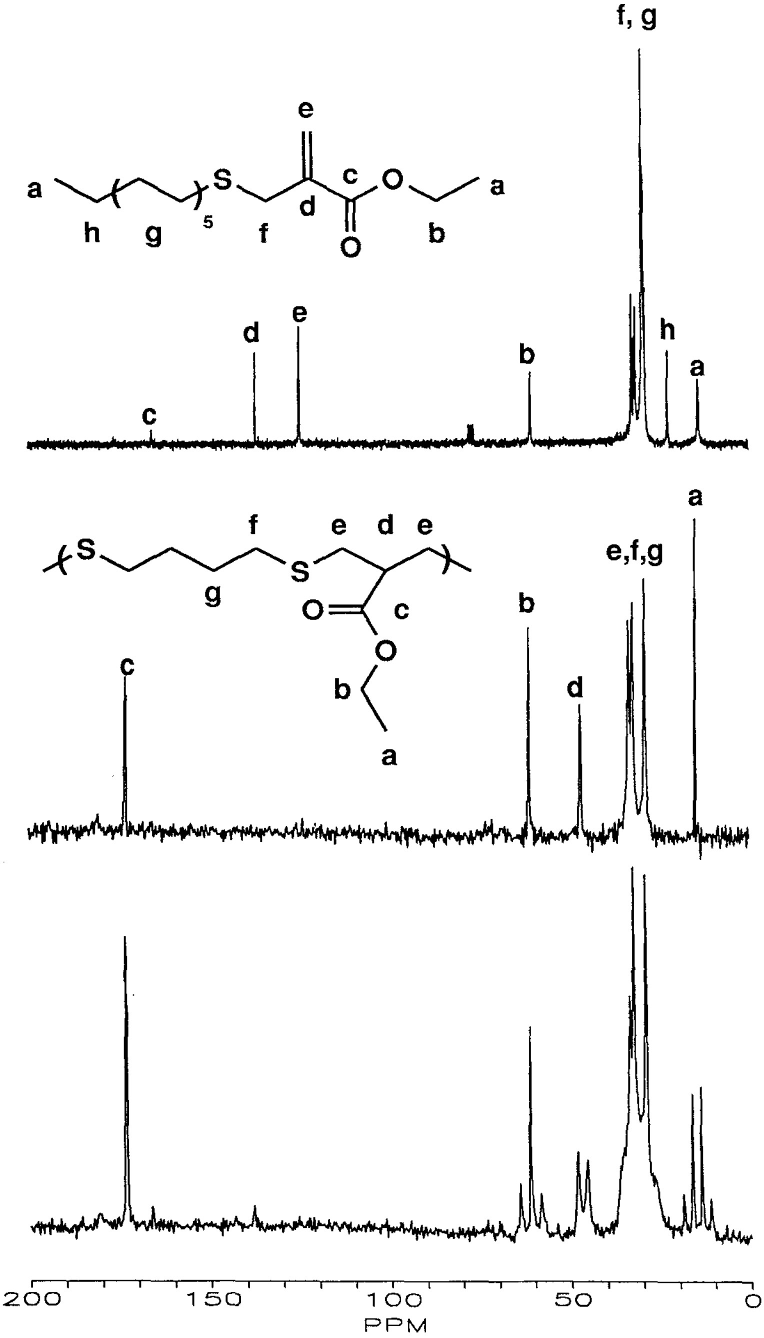

Figure 1. Solution spectrum of model compound in $CDCl_3$ (top), and solid-state MAS spectra of polymer with high-power decoupling (middle) and without decoupling (bottom).

For our purposes excess ECMA was added until the dodecanethiol was consumed. After ca 5 h a 27:70 ratio of thiol to product was obtained and just a trace of ECMA was evident. ECMA was removed under vacuum at ca 70° C.

Results and Discussion

This combination of addition and condensation polymerization techniques should be applicable to other molecules with good leaving groups and electron-withdrawing moieties next to double bonds. Substitution probably occurs first, as shown by preferential substitution under dilute base conditions (ie. the model compound synthesis gave no disubstituted product), which appears to result in a very rapid *in-situ* generation of an A-B monomer when a dithiol is used. ^{13}C NMR (Figure 1) shows disappearance of the thiol α-carbon peak at 22 ppm (similar to the peak for the model compound) and appearance of a tertiary carbon peak at ca 47 ppm resulting from Michael attack. The viscous polymer had enough molecular mobility to allow acquisition of coupled ^{13}C MAS spectrum which confirmed the identity of the 47 ppm peak as a C-H group.

While low yields of the polymer were obtained, an intrinsic viscosity of 0.15 dL/g confirms polymer synthesis. In fact, slow dissolution in chloroform supports formation of reasonable molecular weight polymer. Material balance for these types of polyadditions are difficult to achieve and maintain during the polymerization, making the results above significant.

The model compound **3** confirms order of reaction for the polymerization process. In addition, it can be used as a chain-transfer agent in the radical polymerization of typical vinyl monomers. (6)

Acknowledgements

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