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Synthesis and characterization of polythioetheramide from allylamine

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Summary

A novel polythioetheramide was synthesized from allylamine and 3-mercaptopropionic acid with a free-radical initiator. The thioether and amide linkages are formed from the free-radical addition of -SH group to double bond and the condensation between $-NH_2$ and -COOH, respectively. The free-radical addition gives almost exclusively anti-Markovnikov product. The resulting polymer has a glass-transition temperature of 8.5 °C and a melting point of 145 °C. Though the introduction of the thioether linkages increases flexibility, the polymer retains good solvent resistance.

Introduction

It is well known that a thiol. group, -SH, can add to an ethylenic double bond with a trace amount of free-radical initiator or under UV light [1-2]. The free-radical addition gives almost an exclusively anti-Markovnikov adduct [3,4]. This reaction has been used to make polysulfide and polythioether from dithiols and diolefins [5-10]. We combined the $-SH/CH_2=CH-$addition and -OH/HOCO- condensation, and made a polythioetherester from allyl alcohol and 3-mercaptopropionic acid [11].

Most commercial polyamides or nylons are made from diacids and diamines, amino acids, etc. In this research [12], we combined the $-SH/CH_2=CH-$ addition and $-NH_2/HOCO-$ condensation, and synthesized a novel sulfer-containing polyamide, or polythioetheramide from allylamine and 3-mercaptopropionic acid.

Experimental

Materials:

Allylamine (Aldrich, 99+%), 3-mercaptopropionic acid (Aldrich, 99+%) and 2,2'-azobisisobutyronitrile (AIBN, Polyscience Inc.) were used as received.

Instrumentation:

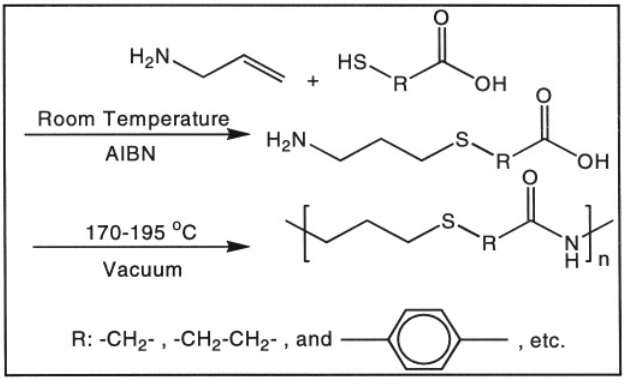
Proton NMR spectra were taken in deuterated dimethyl sulfate solution on a Varian 200 MHZ FT-NMR spectrometer with TMS as internal standard. The melting and thermal behaviors of the polymers were studied on a Perkin-Elmer 7500 DSC-7 scanning calorimeter. Sample weights between 4 and 8 mg were used and scans were run between -40 °C and 220 °C at a 20 °C/min heating or cooling rate. The polymer thermal stability was studied on a Perkin-Elmer 7500 TGA-7 thermogravimeter. The scans were run from 30 °C to 500 °C at a 20 °C/min heating rate under nitrogen or air.

Synthesis of Sulfer Containing Polyamide:

3-Mercaptopropionic acid was added dropw¡se into an equimolar amount of allylamine containing 0.1 wt.% AIBN. The addition speed was controlled at such a rate that the mixture temperature was below the boiling point of allylamine (53 °C). The mixture was stirred at room temperature overnight. The mixture would solidify in the absence of agitation due to the formation of the ammonium salt ($-NH_3^+ \, ^-OCO-$). The resulting viscous mixture was heated at 180-195 °C, first under nitrogen for 2 hrs, then under vacuum. (12 mm Hg) for 4 hrs. A yellowish polymer liquid was obtained. It solidified when it was cooled to below 100 °C. The solidified polymer was ground and washed with methanol 5 times. It was dried in a vacuum oven at 80 °C overnight.

Results and Discussion

When allylamine and 3-mercaptopropionic acid are mixed with a trace amount of free-radical initiator, the -SH group adds to the double bond and forms an intermediate adduct, i.e. $H_2N-CH_2-CH_2-CH_2-S-CH_2-CH_2-COOH$. The reaction proceeds well even at room temperature. The adduct has a high boiling point and will not evaporate at high temperature. When it is heated at 180-195 °C, the amine group reacts with the acid group and forms an amide linkage. In the late stage of the reaction, applying vacuum helps to drive the reaction going further by removing the water generated during the reaction. The thioether polyamide is formed as illustrated in **Scheme 1**.



Scheme 1. Synthesis of Sulfer Containing Polyamide

In addition to 3-mercaptopropionic acid, many other mercapto acid compounds may be used to synthesize polythioetheramides with different structures and properties. Obviously, a small amount of diamine, such as 1,6-hexanediamine, may be added to control the average molecular weight and make an amine-terminated polythioetherester that may be cured with an isocyanate or an epoxy. Similarly, a small amount of diacid, such as adipic acid, may be added to make carboxyl-terminated polythioetherester, which may be cured with an epoxy.

Figure 1 shows the ^{1}H NMR spectrum of the polymer. All of the hydrogens from the polymer chain are identified. The small peak at 1.30 ppm is assigned to the -SH end group. The absence of a strong -CH_3 peak in the NMR spectrum demonstrates that the addition of -SH to double bond forms mainly anti-Markovnikov adduct.

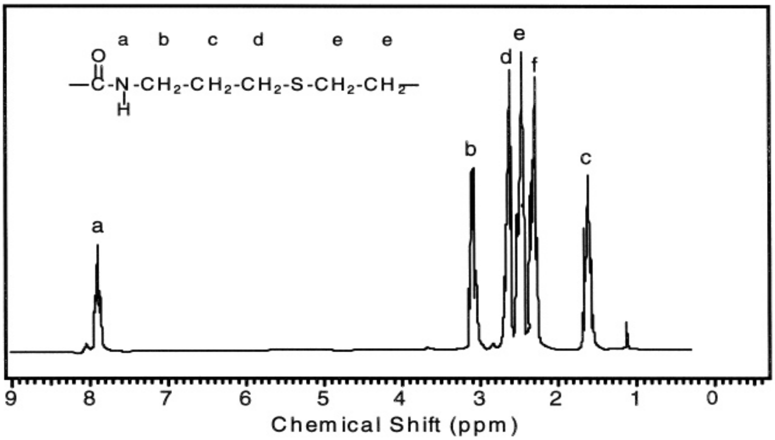


Figure 1. 200 MHZ ^{1}H NMR spectrum of the thioether polyamide.

The polythioetherester crystallizes at about 92 °C and melts at 144-147 °C as shown in

Figure 2. The melting point is much lower than that of nylon-6 (223 °C). The polymer has a glass-transition temperature of 8.5 °C, which is also much lower than that of nylon-6 (40 °C). The low values in melting point and glass-transition temperature are due to the presence of the flexible thioether linkage in the polyamide. As in nylon-6, the hydrogen bonding also forms in the polythioetheramide as illustrated in **Figure 3**. The intermolecular hydrogen bonding makes the polymer insoluble in most organic solvents. Only some strong polar solvents, such as phenols and dimethyl sulfate, can dissolve it. This is quite different from a similarly structured polythioetherester [11], which does not form intermolecular hydrogen bonding. The polythioetherester is soluble in many organic solvents and has a much lower melting point (47 °C) than that of the polyamide.

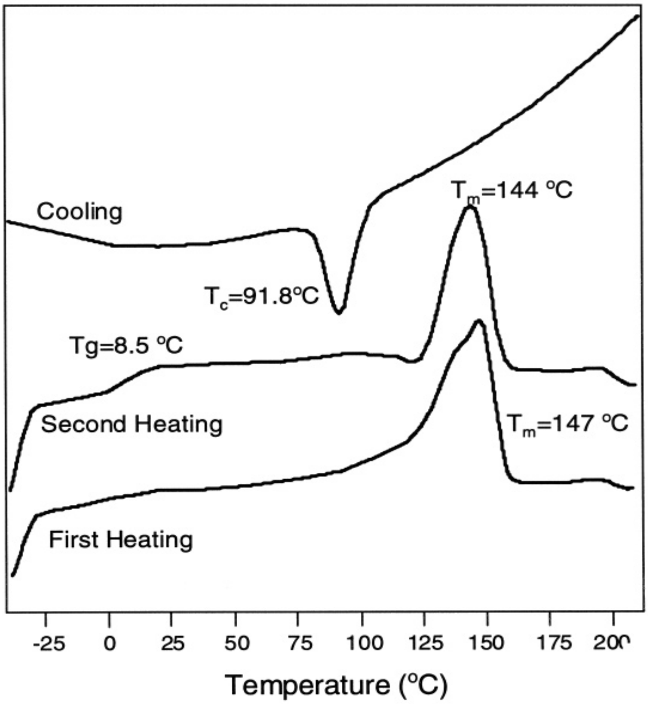


Figure 2. DSC traces of polythioetheramide at a 20 °C/min heating rate.

Our recent results showed that a polythioetheramide made from mercaptoacetic acid instead of 3-mercaptopropionic acid has a melting point very close to room temperature. This is because only 50% of the amide groups in the resulting polythioetheramide may form hydrogen bonding even under ideal conditions.

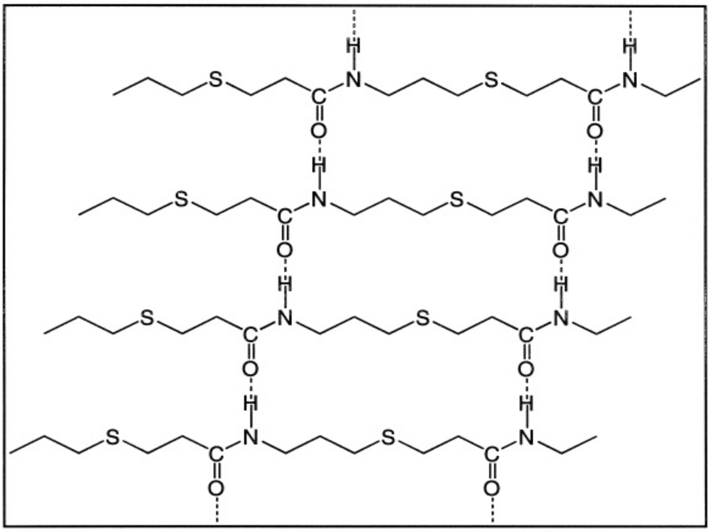


Figure 3. Hydrogen bonding in the thioether polyamide.

The presence of the -S- linkage in a polymer chain usually decreases its thermal stability. However, the thioether linkage in the polythioetheramide, like polythioetherester [11], is quite thermally stable. In fact, the thermogravimetric (TGA) traces under both nitrogen and air are almost identical. There was no noticeable weight loss below 250 °C as shown in **Figure 4**. The polymer started to decompose at 300 °C.

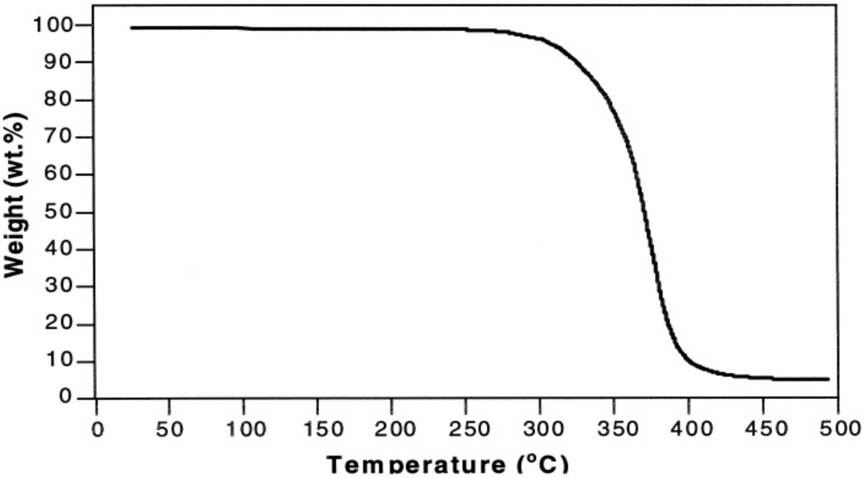


Figure 4. Thermogravimetric (TGA) traces of the thioether polyamide running under air at a 20 °C/min heating rate.

In conclusion, we demonstrated that polythioetheramide can be readily synthesized from allylamine and 3-mercaptopropionic acid or a similar acid with a trace amount of free-radical initiator. The polythioetheramide forms hydrogen bonding similar to what is observed in a typical nylon polymer. Due to the presence of the flexible thioether linkage, the polymer has a lower melting point than a similar polyamide without the thioether linkage.

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