

# Isothiocyanate Derivatives of Soybean Oil Triglycerides: Synthesis, Characterization, and Polymerization with Polyols and Polyamines

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**ABSTRACT:** In this article, a novel two step synthesis of soy oil based isothiocyanate is described. Allylically brominated soybean oil (ABSO) was reacted first with ammonium thiocyanate in tetrahydro furan to form allylic thiocyanates. These compounds were then converted to isothiocyanated soybean oil (ITSO) by a thermal rearrangement. Conversion was found to be 70%. The structure of the ITSO was characterized by IR and  $^1\text{H-NMR}$  techniques. Then ITSO was reacted with ethylene glycol, glycerol, and castor oil to produce polythiourethanes and ethylene diamine and triethylene tetra amine to produce polythioureas. Thermal properties of the products were determined by DSC and TGA techniques. DSC traces showed  $T_g$ 's for ethylene glycol polythiourethane at  $-39$  and  $58^\circ\text{C}$ , for glycerol polythiourethane at  $-39$  and  $126^\circ\text{C}$ , for castor oil polythiourethane at  $-38^\circ\text{C}$  and  $-17^\circ\text{C}$ , for ethylene diamine polythiourea at  $-45^\circ\text{C}$ , and for triethy-

lene tetra amine poly thiourea at  $-39^\circ\text{C}$ . Additionally, DSC analysis of polythioureas showed an endotherm at around  $100^\circ\text{C}$ . All of the polymers started to decompose around  $200^\circ\text{C}$ . Tensile properties of the polymers were determined. Polythiourethanes showed higher tensile strength and lower elongation when compared with their urea analogs. Stress at break values of the polymers were 1.2 MPa for glycerol polythiourethane, 0.6 MPa for ethylene glycol polythiourethane, 0.5 MPa for ethylene diamine polythiourea, and 0.9 MPa for triethylene tetra amine polythiourea polymers. Unfortunately, polymers synthesized showed poor solvent resistance. All polymers swelled and disintegrated in  $\text{CH}_2\text{Cl}_2$  in 5 h. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 125–131, 2010

**Key words:** soybean oil; polythiourethanes; polythioureas; biopolymers

## INTRODUCTION

Isothiocyanates are valuable intermediates that are used in many areas from cosmetics to polymer industries. Isothiocyanates are also biologically active materials and are used in cancer research. Sulfur containing polymers have attracted much attention in polymer industry because of their high thermal stability and high refractive index.<sup>1,2</sup>

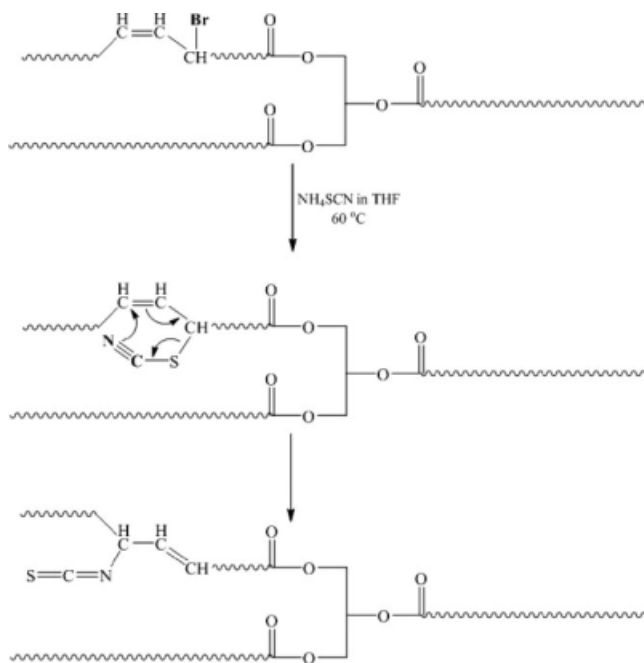
Classically, the most widely used method for the preparation of isothiocyanates is the condensation of amines with carbon disulphide in the presence of a base. The second common method is the condensation of amines with thiophosgene. Decomposition of mono substituted thioureas also gives the corresponding thiocyanates. All of these approaches involve toxic and dangerous chemicals. Another approach to synthesize isothiocyanates is the reaction of alkyl halides with ambient thiocyanate anion. Unfortunately, reaction between alkyl halides with thiocyanate anion gives the alkyl thiocyanates

instead of alkyl isothiocyanates.<sup>3</sup> Luckily, if the thiocyanate anion is reacted with allylic halides, the intermediate thiocyanate compounds rearrange to allylic isothiocyanates. Several published examples of this rearrangement can be found in the literature.<sup>4–8</sup>

The main application of isothiocyanates is to synthesize polythioureas and polythiourethanes. Although polythioureas are not used as widely as polythiourethanes, some members of aliphatic thioureas show ferroelectric behavior and they are used for production of shaped articles.<sup>9</sup> Polythioureas are synthesized by the condensation reaction between diisothiocyanates and diamines. Literature search showed that condensation of diisothiocyanates with dithiols and cationic ring opening polymerizations of cyclic thiourethanes are the main synthetic routes of synthesizing polythiourethanes.<sup>10–12</sup>

In this work, a simple two step method for the synthesis of isothiocyanate derivative of soybean oil triglyceride is reported. First, soybean oil triglyceride is brominated at the allylic positions with *N*-bromo succinimide. Second, the allylic bromide is substituted by thiocyanate anion, which then converts to an isothiocyanate by an allylic rearrangement upon heating (Fig. 1). Using this chemistry, we report here the first example of an isothiocyanate functionalized

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**Figure 1** Synthesis of allylic isothiocyanates of soybean oil (positional isomers are not shown).

plant oil triglyceride and its polymers with polyols and polyamines. We also report the synthesis of isothiocyanate derivative of methyl oleate which was used as an NMR and IR model compound.

## EXPERIMENTAL

### Materials and methods

Methyl oleate was synthesized by a previously published method.<sup>13</sup> Soybean oil used was degummed, decolorized, deodorized, and deacidified (food grade) and dried under vacuum before use. NBS (*N*-bromo succinimide),  $\text{CCl}_4$  (carbon tetra chloride)  $\text{NH}_4\text{SCN}$  (ammonium thiocyanate), THF (Tetrahydrofuran), glycerol, ethylene glycol, and ethylene diamine were purchased from Merck (Darmstadt, Germany). Triethylene tetra amine was purchased from Aldrich (Milwaukee, USA). Castor oil was obtained from Aklar Kimya (Ankara, Turkey). All materials were used as received.

IR characterization of compounds was performed by PerkinElmer FTIR 1600 series spectrometer using KBr windows. The  $^1\text{H-NMR}$  spectra was recorded on a Varian 400-MHz NMR instrument (Varian Associates, Palo Alto, CA) operating at a frequency of 399.986 MHz for proton. The spectra were recorded as ppm ( $\delta$ ) with  $\text{CDCl}_3$  as a solvent. DSC characterizations were performed by "Thermal Analyses" Q 200 instrument (New Castle, DE) with a heating rate  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere from  $-70$  to  $120^\circ\text{C}$ . TGA characterizations were performed by "Thermal Analyses" Q 50 instrument (New Castle,

DE) with a heating rate  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere from room temperature to  $600^\circ\text{C}$ . Strain tests were performed by Devotrans DVG 32 Model tester with a  $20\text{ mm}/\text{min}$  elongation rate.

### Allylic brominated of methyl oleate (ABMO)

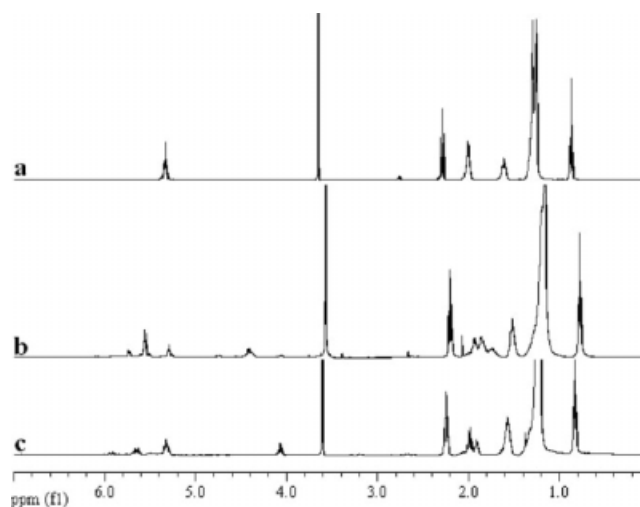
This compound was synthesized by using a previously reported procedure.<sup>14</sup> IR and  $^1\text{H-NMR}$  spectra were identical with the published results (Fig. 2).

### Methyl oleate isothiocyanate (ITMO)

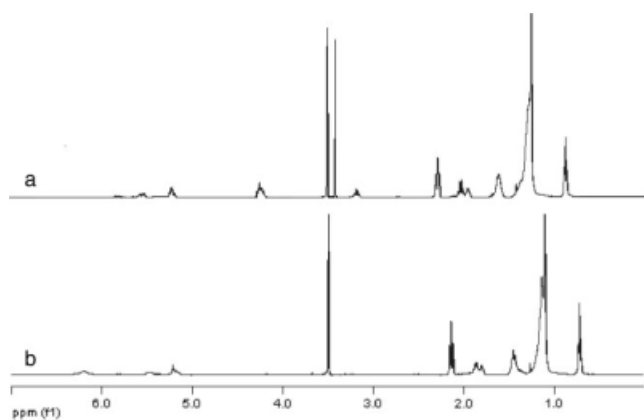
A total of 5.0 g of ABMO (0.013 mol) was dissolved in 20 mL dry THF and 1.98 g of  $\text{NH}_4\text{SCN}$  (0.026 mol) was dissolved separately in 20 mL of dry THF. These two solutions were mixed at room temperature and refluxed for 5 h.  $\text{NH}_4\text{Br}$  precipitate was observed in the first 30 min. Then the crude product was filtered and THF was partially evaporated and the remainder was centrifuged and decanted in order to remove excess  $\text{NH}_4\text{SCN}$ . The rest of THF was evaporated to give reddish-brown oil. IR spectrum: A new strong and broad peak was appeared at  $2074\text{ cm}^{-1}$  due to  $\text{N}=\text{C}=\text{S}$  group (Fig. 4).  $^1\text{H-NMR}$ : ( $\text{S}=\text{C}=\text{N}-\text{CH}-\text{CH}_2-$ ) 1.5 ppm, ( $\text{CH}=\text{CH}-\text{CH}-\text{N}=\text{C}=\text{S}$ ) 3.8–3.9 ppm, ( $\text{S}=\text{N}=\text{C}-\text{CH}-\text{CH}=\text{CH}-\text{CH}-\text{N}=\text{C}=\text{S}$ ) 4–4.1 ppm, ( $\text{CH}=\text{CH}-\text{N}=\text{C}=\text{S}$ ) 5.4 ppm, ( $\text{CH}=\text{CH}-\text{CH}-\text{N}=\text{C}=\text{S}$ ) 5.6 ppm, ( $\text{S}=\text{C}=\text{N}-\text{CH}-\text{CH}=\text{CH}-\text{CH}-\text{N}=\text{C}=\text{S}$ ) 6.1 ppm are the peaks that differ from allylic brominated methyl oleate. Also the peaks at 4.2–4.4 ppm and 4.8 ppm which belong to ABMO disappeared (Fig. 2).

### Methyl carbamate of ITMO

A total of 2.0 g of ITMO was mixed with 20 mL of dry methanol in presence of one drop of pyridine. The



**Figure 2**  $^1\text{H-NMR}$  of (a) methyl oleate, (b) allylic brominated methyl oleate, and (c) isothiocyanated methyl oleate as a model compounds.

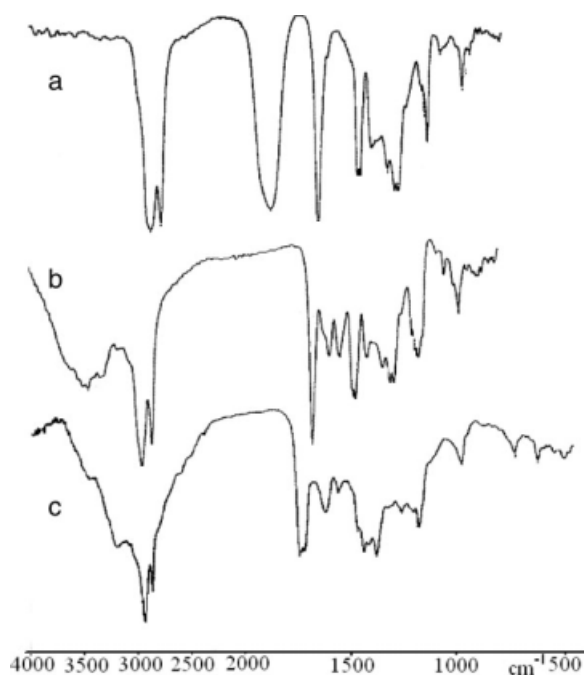


**Figure 3**  $^1\text{H-NMR}$  of (a) methyl thiocarbamate and (b) ammonia thiourea of isothiocyanated methyl oleate.

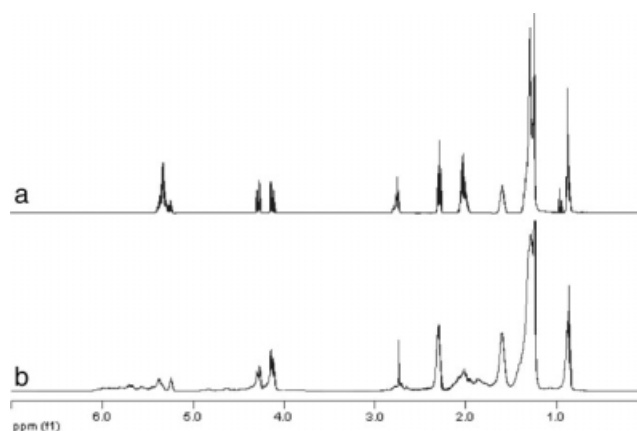
mixture was refluxed overnight. Methanol was evaporated. Methyl thiourethane of ITMO was obtained as oily brownish liquid. The product was characterized by IR and  $^1\text{H-NMR}$ . The peak at  $2074\text{ cm}^{-1}$  disappeared. At  $1739\text{ cm}^{-1}$ , a new peak was observed due to carbonyl group of thiocarbamate. Two new peaks were observed at  $1500\text{--}1400\text{ cm}^{-1}$  due to the NH groups of the urethane functionality (Fig. 4).  $^1\text{H NMR}$ : ( $\text{CH}_3\text{OC}=\text{ONH}-$ )  $3.3\text{ ppm}$ , ( $\text{CH}=\text{CH}-\text{CH}-\text{NH}-$ )  $4.27\text{ ppm}$ , ( $\text{CH}=\text{CH}-\text{CH}-\text{NH}-$ )  $3.1\text{ ppm}$ , (Fig. 3).

#### Thio urea of ITMO

Two grams of ITMO was mixed with  $50\text{ mL}$   $7\text{N}$   $\text{NH}_3$  in methanol solution. Mixture was stirred at



**Figure 4** IR spectra of (a) isothiocyanated methyl oleate (ITMO), (b) methanol thiocarbamate, and (c) ammonia thiourea of ITMO.



**Figure 5**  $^1\text{H-NMR}$  spectra of (a) soybean oil and (b) isothiocyanated soybean oil (ITSO).

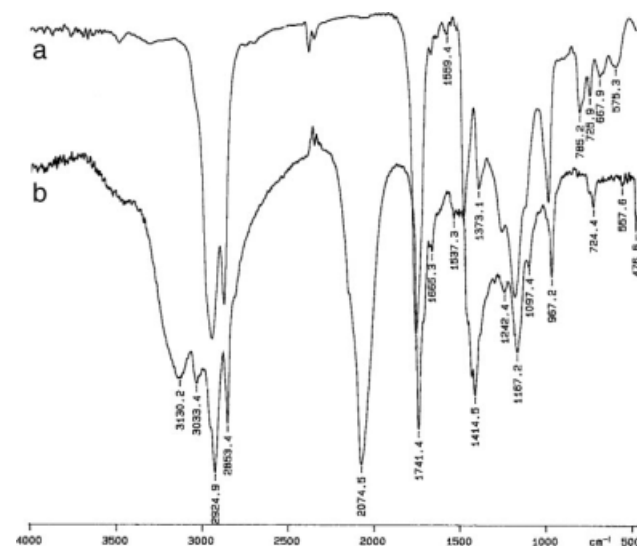
room temperature for  $10\text{ h}$ . Then methanol was evaporated and the product was characterized by IR and  $^1\text{H-NMR}$ . IR peaks:  $3180\text{ cm}^{-1}$  N—H stretching,  $1742\text{ cm}^{-1}$  and  $1713\text{ cm}^{-1}$  carbonyl groups;  $1660\text{ cm}^{-1}$  and  $1560\text{ cm}^{-1}$  C—N stretching (Fig. 4).  $^1\text{H-NMR}$  is similar to thiocarbamate of methyl oleate a peak appeared at  $6.2\text{ ppm}$  due to the presence of  $\text{NH}_2\text{C}=\text{ONH}-$  group (Fig. 3).

#### Allylic brominated soybean oil (ABSO)

This compound was synthesized by a previously reported procedure. IR and  $^1\text{H-NMR}$  spectra were identical to the published results<sup>14</sup> (Figs. 5 and 6).

#### Synthesis of soybean oil isothiocyanate (ITSO)

In  $20\text{ mL}$  of dried THF,  $14.0\text{ g}$  of ABSO ( $0.01\text{ mol}$ ) was dissolved. In  $20\text{ mL}$  of dry THF,  $1.52\text{ g}$  of



**Figure 6** IR spectra of (a) allylic bromine of soybean oil and (b) allylic isothiocyanate of soybean oil.

**TABLE I**  
Amounts of Reagents and Reaction Conditions for ITSO Polymers

Reagent	Reagent weight (g)	ITSO weight (g)	Reaction time (h)	Reaction temperature (°C)
Castor oil	2.1	2.5	5	140
Ethylene glycol	0.11	2.5	5	140
Glycerol	0.163	2.5	5	140
Ethylene diamine	0.11	2.5	5	140
Triethylene teramine	0.26	2.5	5	140

$\text{NH}_4\text{SCN}$  (0.02 mol) was dissolved. The two solutions were mixed, stirred, and refluxed for 5 h. Then the crude product was filtered and THF was partially evaporated and the remainder was centrifuged and decanted in order to remove excess  $\text{NH}_4\text{SCN}$ . The rest of THF was evaporated to give reddish-brown oil. A new peak was observed at  $2074\text{ cm}^{-1}$  due to allylic isothiocyanate and also new peaks were observed at  $3300\text{ cm}^{-1}$  probably due to partial hydrolyzation of isothiocyanate groups (Fig. 5). The  $^1\text{H-NMR}$  spectrum of ITSO was very similar to ABSO spectrum as expected (Fig. 6). The yields were calculated from the amount of precipitated  $\text{NH}_4\text{Br}$ .

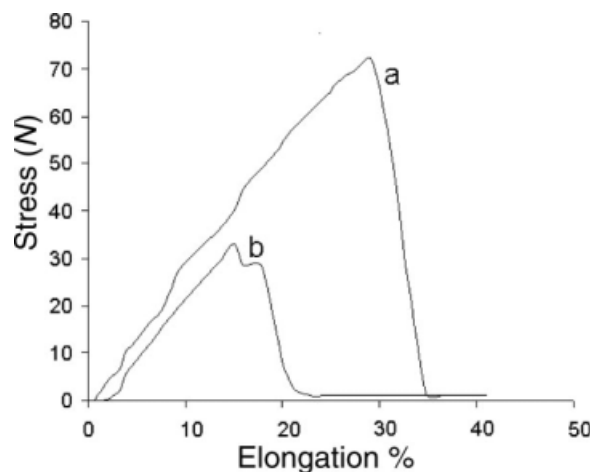
#### General procedure for polymerization of ITSO with polyols and polyamines

In a typical example, ITSO, 2.5 g, (0.0018 mol) was mixed well with a prescribed amount of polyamine or polyol. The viscous mixture was poured into a Teflon mold and placed in a vacuum oven and the pressure was reduced to 5 mmHg for 1 h. Then the pressure was increased to 300 mmHg and the sample was gradually heated to  $140^\circ\text{C}$  and kept at this temperature for 5 h. This procedure gave thermoset, insoluble polythiourea or polythiourethane samples that were free of gas bubbles and suitable for mechanical property measurements. Amounts of reagents and reaction conditions for all ITSO polymers are given in Table I.

## RESULTS AND DISCUSSIONS

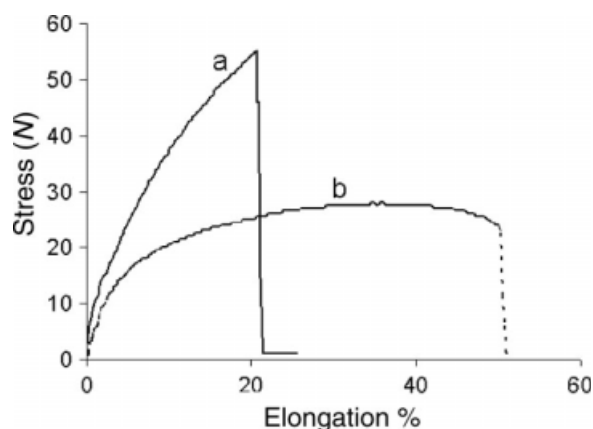
### Synthesis of monomers

Allylic isothiocyanates were obtained in 50–70% yields as a mixture of positional isomers. The yields were measured by two ways. In the first method, yields were calculated by simply weighing the precipitated  $\text{NH}_4\text{Br}$  at the end of the reaction. In the second method, ITSO was reacted with *n*-butyl amine and excess amine then was titrated with a standardized HCl solution to calculate the yields according to a literature procedure.<sup>15,16</sup> The results



**Figure 7** Stress strain curves of ITSO (a) glycerol and (b) ethylene glycol polythiourethanes.

of the two methods were consistent with each other. In  $^1\text{H-NMR}$ , the proton on the carbon bearing the NCS group gave a peak at 4.2 ppm. Peaks of the glycerol moiety also appear in the same region. This unpleasant coincidence made the yield calculation by  $^1\text{H-NMR}$  impossible. Depending on the reaction time, temperature, and freshness of the ABSO, yields may vary between 50% and 70%. Higher temperatures, such as,  $60^\circ\text{C}$  and longer reaction times increased the yields. When freshly prepared ABSO was used, the yield of the reaction reached to 70% at room temperature in 4.5 h. In the case of the older ABSO samples, yields never exceeded 50% and a new peak was observed at  $2150\text{ cm}^{-1}$  as a shoulder due to the formation of thiocyanate groups. We had previously observed that allylic brominated triglycerides sometimes behave in unexpected ways. Bromination conditions convert some of the polyunsaturated fatty acid chains into their conjugate isomers and these are capable of various reactions among themselves.



**Figure 8** Stress strain curves of ITSO (a) triethylene diamine (b) ethylene diamine polythiourethanes.

**TABLE II**  
**Mechanical and Thermal Properties of Polymers Synthesized**

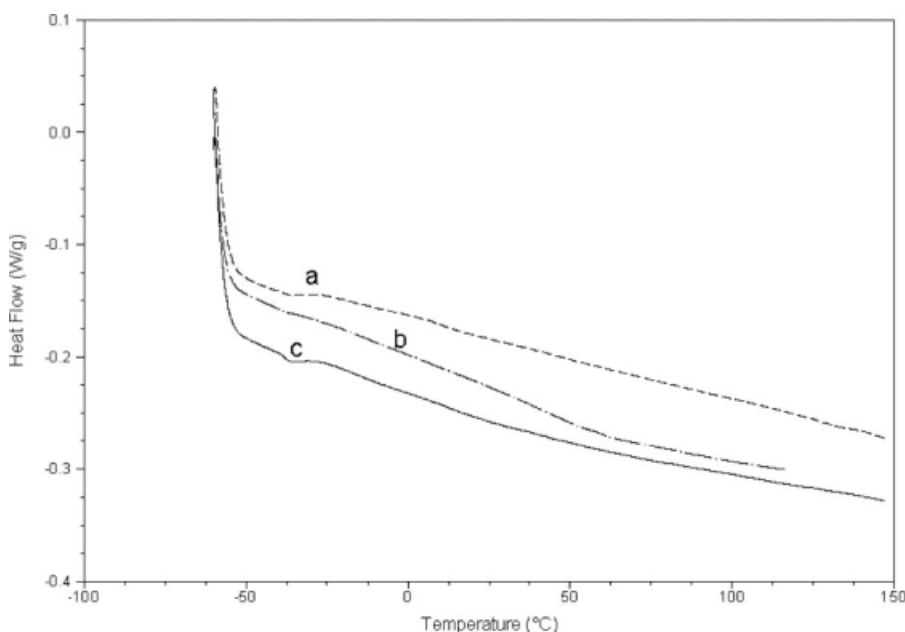
Polymer	Tensile strength	% Elongation at break	$T_g$	5 % Weight lost temperature
ITSO ethylene diamine polythiourea	500 KPa	22	-45°C	215°C
ITSO triethylene tetramine polythiourea	900 KPa	50	-39°C	194°C
ITSO ethylene glycol polythiourethane	600 KPa	22	-39°C	197°C
ITSO glycerol polythiourethane	1200 KPa	35	-39 and 58°C	248°C
ITSO castor oil polythiourethane	NA	NA	-38°C	255°C

Allylic bromination and substitution of bromine with isothiocyanate were easily monitored by observing the changes of the peaks of soybean oil in the IR spectrum. A peak at  $965\text{ cm}^{-1}$  was attributed to allylic  $\text{HC}=\text{CHCHBr}$  stretching and a peak at around  $640\text{ cm}^{-1}$  was attributed to  $\text{C}-\text{Br}$  deformation. When isothiocyanate substitution occurred, a new peak at  $2070\text{ cm}^{-1}$  was observed due to  $-\text{NCS}$  group. If the substitution occurred at S side, thiocyanate group gave a peak at  $2150\text{ cm}^{-1}$ . In a separate experiment, benzyl chloride was used as an IR model compound. Benzyl chloride reacts with thiocyanate ion to give benzyl thiocyanate easily but the product is incapable of rearranging to the isothiocyanate and it was observed by IR spectroscopy that the S end was bound to benzyl group preferentially. In the IR spectrum, a sharp and intense peak at  $2152\text{ cm}^{-1}$  due to formation of  $-\text{SCN}$  group and at  $2063\text{ cm}^{-1}$  a small and broad peak due to the formation of  $-\text{NCS}$  group were observed. When compared with the other isothiocyanate synthesis methods, allylic bromination and the subsequent substitution reaction with  $\text{NH}_4\text{SCN}$  were simple reactions. Allylic bromination was complete in 4.5 h. Substitution reac-

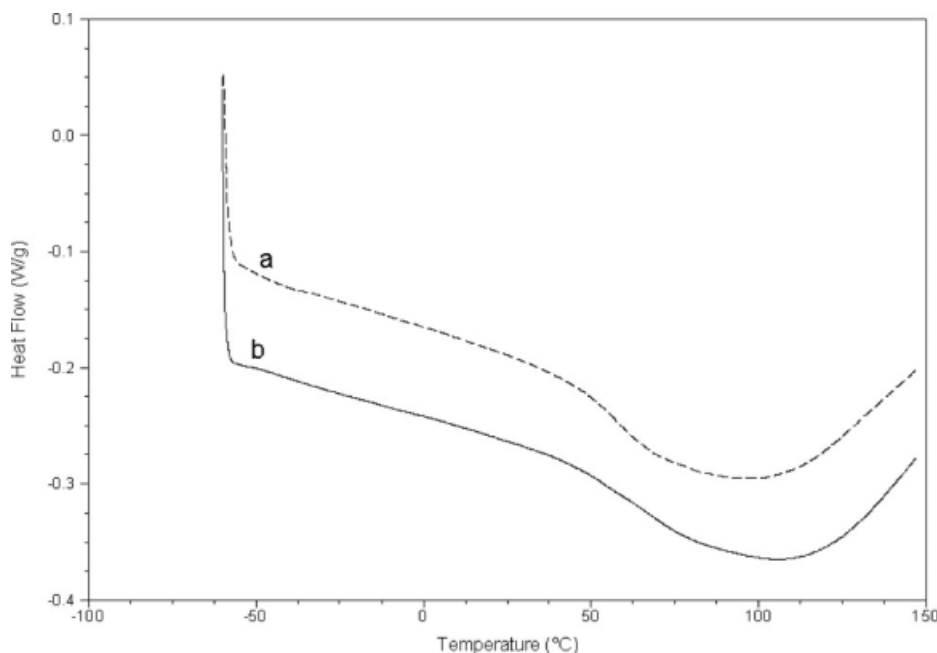
tion with  $\text{SCN}^-$  required mild reaction conditions and reaction was nearly complete in 30 min at  $60^\circ\text{C}$ . At room temperature, 5 h were required to complete the reaction. The average number of isothiocyanate group per triglyceride could not be measured directly with  $^1\text{H-NMR}$  technique but precipitation and titration methods described earlier indicated between 2.0 and 2.2 isothiocyanate groups per triglyceride on the average. The fact that the products polymerized to thermoset polymers with diols and diamines supports this.

### Synthesis of polymers

Polymerization of ITSO with ethylene glycol, glycerol, and castor oil were generally completed in 5 h at  $140^\circ\text{C}$ . ITSO was conveniently miscible with all the other monomers and reacted fast with triethylene tetra amine (TETA) and ethylene diamines (EDA) even at room temperature. Reaction with polyols gave the corresponding polythiourethane and reaction with polyamines gave the corresponding polythioureas. Polymerization reactions of ITSO were slower than corresponding isocyanated



**Figure 9** DSC traces of (a) ITSO castor oil, (b) ITSO glycerol, and (c) ITSO ethylene glycol polythiourethanes.



**Figure 10** DSC traces of (a) ITSO ethylene glycol polythiourea and (b) ITSO triethylene tetramine polythiourea.

soybean oil.<sup>14</sup> Thus, longer reaction times and higher temperatures were required. With dry monomers, no gas evolution was observed and the reaction could be carried out in an open Teflon mold, under a dry atmosphere, quite easily.

### Mechanical properties of polymers

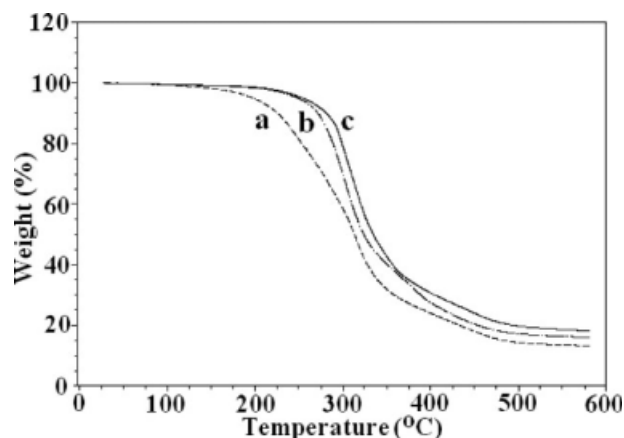
Unexpectedly, both the thiourethanes and thiourea polymers were not rubbery. They were hard solids. Polythiourethanes were stronger than polythioureas. Stress strain curves of polyurethanes and polyureas synthesized are shown in Figures 7 and 8. Stress at break values of the polymers were 1.2 MPa for glycerol polythiourethane, 0.6 MPa for ethylene glycol polythiourethane, 0.5 MPa for ethylene diamine polythiourea, and 0.9 MPa for triethylene tetra amine polythiourea polymers. These values are quite high when one considers that the weight fraction of the triglyceride component in these polymers is around 90%. It was obvious that mechanical properties of the polythiourethanes and ureas were higher than their nonsulfur analogs.<sup>14</sup> We observed a general trend in tensile strength that when the functionality of polyols and polyamines increased the tensile strength of material also increased. All materials also showed low elongation at break (See Table II). Almost all polythiourethanes and ureas showed poor solvent resistance. They swelled and fractured in  $\text{CH}_2\text{Cl}_2$  in 5 h.

### Thermal properties of polymers

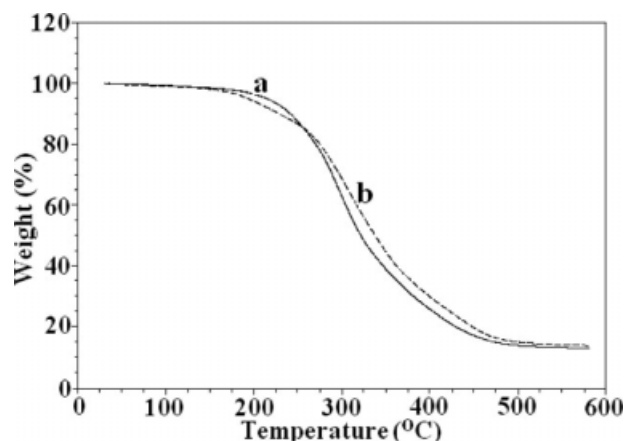
Thermal characterizations of the materials were determined by DSC (Fig. 9).  $T_g$  values of the poly-

mers are shown in the Table I. All materials showed more than one  $T_g$ . Generally, they showed a segmental motion at  $-40^\circ\text{C}$  probably due to the presence of triglyceride alkyl groups. Surprisingly, polythiourethanes made with glycerol showed two  $T_g$  transitions at  $-39$  and  $58^\circ\text{C}$ . It was found that  $T_g$  values appeared at higher temperatures when the functionality of the alcohol was higher. Polythioureas showed heat absorption at around  $100^\circ\text{C}$ . The amount of absorbed heat was nearly  $35 \text{ J/g}$  for both thioureases (Fig. 10), this behavior can be attributed to crystallization of the urea segments of the polymers.

For the evaluation of the thermal stability TGA is one of the most favored techniques. All polythioureas and polyurethanes lost 5% of their weight around  $200^\circ\text{C}$  (Figs. 11 and 12). Weight lost data is



**Figure 11** TGA traces of (a) ethylene glycol, (b) glycerol, and (c) castor oil polythiourethanes.



**Figure 12** TGA traces of (a) ethylene diamine and (b) triethylene tetramine polythioureas.

given in the Table I. The highest weight lost temperature belonged to ITSO glycerin polyurethane. The 5% weight lost temperatures of polythioureas were generally lower than polyurethanes.

### CONCLUSIONS

In this article, a novel synthesis of plant oil based isothiocyanates is described. Using those monomers with polyols and polyamines, thermoset polymers with a variety of main structures could be synthesized by one-pot reactions. Castor oil, glycerin, and ethylene glycol polythiourethanes and ethylene diamines and triethylene tetra amine polythioureas were synthesized and characterized, and the poly-

thioureas were found to be more rigid than the polythioureas.

Polythiourethanes and polythioureas showed high mechanical strength and low elongation when compared with isocyanated soybean oil based polyurethanes and polyureas. Heat resistance of the polymers synthesized was higher than the nonsulfur analogs. Possibility of preparing molded articles by a RIM (reaction injection molding) process with the new monomer is under investigation.

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