

Reactions of Trithiocyanuric Acid with Oxiranes. I. Synthesis of Polyetherols

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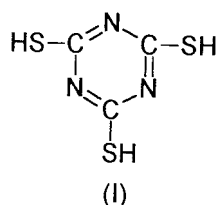
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ABSTRACT: Reactions of trithiocyanuric acid with a large excess of ethylene oxide and propylene oxide in DMF solution and in the presence of triethylamine as catalyst were carried out. Trifunctional polyetherols containing an *s*-triazine ring were prepared. The structure of the products was confirmed by using elemental analysis, ¹H-NMR and IR techniques. Some of the physical properties and thermal stability of polyetherols were analyzed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 439–445, 2000

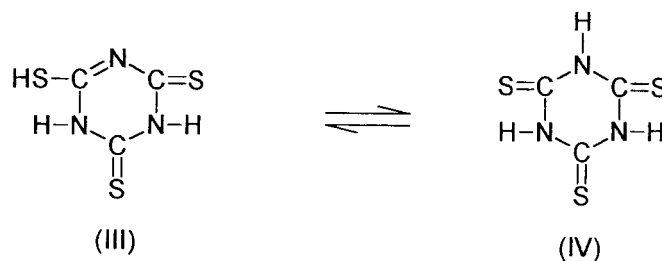
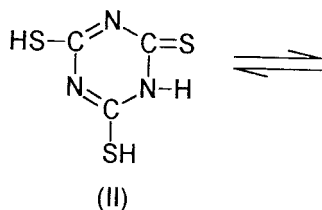
Key words: trithiocyanuric acid; ethylene oxide; propylene oxide; polyetherols

INTRODUCTION

Trithiocyanuric acid ($pK_1 = 4.96$, $pK_2 = 8.00$)¹ is a trifunctional chemical compound, of the structure:



More precisely, the structure of trithiocyanuric acid can be presented by the following tautomeric structures:



In the solid state, the trithioketonal form (IV) of trithiocyanuric acid dominates from its IR spectrum as follows.^{2,3} In solutions the fraction each tautomeric form depends on the type of a solution.³ Trithiocyanuric acid melts at more than 300°C with decomposition.⁴

Although trithiocyanuric acid has been known since 1885, information about its reactions and applications started to be published only after the 1970s.

Trithiocyanuric acid has been used as a crosslinking agent for such polymers as rubbers, poly(vinyl chloride), chlorinated or chlorosulfonated polyolefins,^{5–15} halogenated acrylic rubbers,^{16–21} some epichlorohydrin–ethylene oxide copolymer rubbers,²² and epoxy resins.^{23,24}

Trithiocyanuric acid and its salts have also been utilized as additives to natural and synthetic rubbers, resin compositions (e.g., epoxy res-

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ins) of improved adhesion to metals or alloys, such as lead, copper, nickel, brass, bronze, or steel.²⁵⁻³⁸

Trithiocyanuric acid derivatives (alkyl-, benzyl-, and aryl-substituted) as well as zinc salts of trithiocyanuric acid are used as antioxidants for polyolefins, diene polymers, fats, and waxes.^{20,39-42}

Reports on the reactivity of trithiocyanuric acid are rather scarce. The addition of ethene derivatives,^{39,43} chlorination,^{44,45} and reactions with alkyl⁴, benzyl,⁴⁶ or alkyl-, cycloalkyl-, and arylsulphenyl⁴⁷ halides are the relatively well-known reactions of this compound. Information is also available about trithiocyanuric acid complexes with an organic compound that has a basis character, such as *N*-(2-hydroxyethyl)-3-azapenthan-1,5-diol (triethanolamine),⁴⁸ 1,4-dioxan, or tetrahydrofuran (THF).¹ We have found no information on reactions of trithiocyanuric acid and oxiranes.

EXPERIMENTAL

Synthesis of Polyetherols

To a round-bottomed flask (250 cm³) equipped with a reflux condenser*, thermometer, and stirrer, 17.7 g (0.1 mol) of trithiocyanuric acid (pure, Aldrich, Germany) were introduced with 75 cm³ of DMF (pure, PPH POCh, Poland) together with an appropriate amount of triethylamine (TEA; p.a., Fluka, Switzerland) as catalyst.[†] The content was heated to 50–75°C until trithiocyanuric acid dissolved and then cooled down. A portion of oxirane (0.1 mol[‡]) was then introduced, and the reaction mixture was heated up to the boiling point.[§] The mixture was heated until no more oxirane condensed on the condenser wall, and it was then cooled down. The next portion of oxirane was introduced and heated again. This cycle was repeated until the predetermined amount of oxirane reacted.^{||} The resulting molar ratio of ox-

* When ethylene oxide (EO) was used, a salt-ice mixture was used as the cooling medium in the reflux condenser.

† A catalyst of 3.5 cm³ or 5 cm³ was used for the reaction with EO or propylene oxide (PO), respectively.

‡ EO (pure, Fluka, Switzerland) or PO (pure, Fluka, Switzerland).

§ The boiling point of the initial reaction mixture depended on the kind of oxirane: it was about 55°C or 60°C when EO or PO, respectively, was used.

|| The amounts of oxiranes used were: EO: 26.4 g (0.6 mol), 39.6 g (0.9 mol), 52.9 g (1.2 mol); and PO: 34.8 g (0.6 mol), 52.3 g (0.9 mol), 69.7 g (1.2 mol).

irane to trithiocyanuric acid was determined by weight. After introducing the last portion of oxirane, the reaction was conducted at 100°C for 1 h (ethylene oxide) or for 2 h (propylene oxide). The solvent and TEA were then removed under reduced pressure at 1.6 kPa. The product had a resinlike appearance.

Analytic Methods

Elemental analysis of the products (C, H, N, S) was performed using an EA-1108 (FISONS, Italy) analyzer. The infrared spectra were recorded on a Fourier transform IR PARAGON 1000 spectrometer (Perkin-Elmer Corp., Norwalk, CT). The samples for IR analysis were prepared in the form of capillary films or KBr tablets. The ¹H-NMR spectra of products were recorded on an 80-MHz BS-586A spectrometer (Tesla, Czechoslovakia). The solvent was d₆-DMSO with HMDSO internal standard. The thermal analysis of products was carried out using a derivatograph (MOM, Hungary) in a nitrogen atmosphere. Then 200 mg of the sample was heated in a china crucible over a temperature range of 20–1000°C. The sensitivity of the instrument was $\frac{1}{10}$ for DTA and $\frac{1}{10}$ for DTG.

Some other properties of the products were evaluated in the temperature range 20–80°C, such as refractive index, density (pycnometrically), viscosity (Höpler viscometer), and surface tension, by using the torsion balance method.

RESULTS AND DISCUSSION

At first the operating conditions of a reaction of trithiocyanuric acid with oxiranes were determined. This involved the selection of a proper solvent (i.e., a solvent in which trithiocyanuric acid dissolved sufficiently and that did not contain reactive hydrogen atoms capable of reaction with oxiranes). An effective addition catalyst was also selected. By taking into account the solubility of trithiocyanuric acid^{1,4,46,47} and the reactions of isocyanuric acid with oxiranes,⁴⁹ as well as on the reactions of melamine with oxiranes,^{50,51} THF, DMSO, and DMF were chosen as solvents, and TEA was chosen as catalyst.

In preliminary experiments we found that in THF the addition of thiolic groups to EO or PO takes place

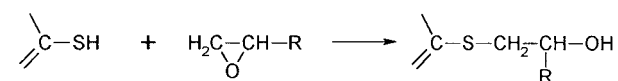
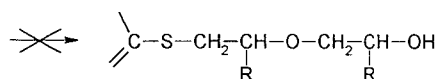
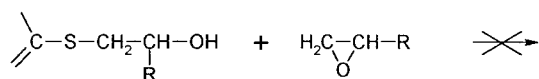


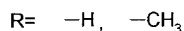
Table I The Conditions of Synthesis of Polyetherols From Trithiocyanuric Acid With Oxiranes

Oxirane	Molar ratios acid : oxirane	Reaction conditions	
		Temperature, °C	Time, h
EO	1 : 6	55–100	12
	1 : 9	65–100	18
	1 : 12	65–100	24
PO	1 : 6	60–100	12
	1 : 9	75–100	20
	1 : 12	75–100	27

and consecutive reactions of hydroxyalkyl groups are practically halted.



where:



The reason seems to be the low temperature in which the reaction was carried out, a result of the relatively low boiling point of THF (65°C).

Further experiments were carried out with DMSO as a solvent. It dissolved trithiocyanuric acid in a way similar to THF, but its boiling point was considerably higher (189°C). Unfortunately, partial decomposition of the solvent, which took

place during distillation after the reaction, led to contaminated products.

DMF (bp 153°C) seems to be free of these disadvantages. It can easily be distilled off after reaction completion without contaminating the products. The synthesis of polyetherols was carried out for the molar ratio acid : oxirane equal to 1 : 6, 1 : 9, or 1 : 12. Trithiocyanuric acid was dissolved in DMF at temperatures about 60–70°C; then the reaction mixture cooled down before a proper amount of TEA was added (about 0.25–0.36 mol TEA per mol acid); and, finally, portions of oxirane (EO, PO) were introduced until the desired molar ratio was reached. It is worth noting that the addition of the first 3 mol of oxirane was very fast (within 2 h), and the addition of further amounts of oxirane was much slower. The reaction conditions are presented in the Table I. Dark brown semisolid resins were obtained in the reactions with EO. The more oxirane was added, the less viscous was the resin obtained.

The structure of the products was studied by using elemental analysis (Table II), infrared spectra, and ¹H-NMR spectra.

In the IR spectrum of solid trithiocyanuric acid (Fig. 1) the following bands, have been identified: N—H stretching vibrations—2900–3150 cm⁻¹; N—H deformation vibrations—1570 cm⁻¹; cyanuric ring vibrations—1535 cm⁻¹; N—H deformation vibrations and C—N stretching ones—1360 cm⁻¹; C=S stretching vibrations—1120 cm⁻¹.

The mentioned bands vanish for the IR spectra of products. Instead, bands characteristic of polyetherols appear (Fig. 2), for example, hydroxy-group stretching vibrations, at about 3300 cm⁻¹, and associated and free hydroxy-group deformation vibrations, at 1420 and 1310 cm⁻¹, respectively; C=N stretching vibrations, at 1600–1700

Table II Elemental Analysis of Products of Reactions of Trithiocyanuric Acid with Oxiranes

Oxirane	Molar Ratios (Acid : Oxirane)	Elemental Analysis							
		C (wt %)		H (wt %)		N (wt %)		S (wt %)	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
EO	1 : 6	40.80	40.00	6.16	7.09	9.52	9.15	21.78	19.29
	1 : 9	43.96	43.54	6.85	8.01	7.32	7.68	16.76	15.60
	1 : 12	45.94	42.36	7.28	8.69	5.95	6.43	13.62	12.06
PO	1 : 6	47.97	43.76	7.48	8.27	7.99	8.48	18.29	18.30
	1 : 9	51.48	47.87	8.21	8.89	6.00	6.41	13.74	12.87
	1 : 12	53.58	47.62	8.65	9.44	4.81	5.19	11.00	10.36

Table III Some Properties of the Products of Reaction of Trithiocyanuric Acid with Oxiranes

Oxirane	Molar Ratios (acid : oxirane in a Product)	Temperature (°C)	Refraction Index	Density (g cm ⁻³)	Viscosity × 10 ³ (Pa s)	Surface Tension ×10 ³ (N m ⁻¹)
1	2	3	4	5	6	7
		20	—	—	—	—
		30	—	—	—	—
		40	1.5642	1.3437	—	81.1
	1 : 6	50	1.5611	1.3352	9071	57.9
		60	1.5574	1.3278	2622	63.0
		70	1.5540	1.3203	801	43.5
		80	1.5510	1.3135	447	37.4
		20	1.5350	1.2909	—	45.0
		30	1.5324	1.2818	3746	43.5
		40	1.5299	1.2743	1659	41.2
EO	1 : 9	50	1.5269	1.2668	493	38.8
		60	1.5239	1.2599	224	39.4
		70	1.5206	1.2517	100	36.4
		80	1.5173	1.2452	63.1	33.6
		20	1.5209	1.2484	—	40.0
		30	1.5179	1.2414	1146	38.4
		40	1.5142	1.2336	410	37.1
	1 : 12	50	1.5121	1.2252	205	36.0
		60	1.5089	1.2173	101	34.4
		70	1.5051	1.2100	53.7	31.4
		80	1.5014	1.2028	36.8	29.8
		20	—	—	—	—
		30	—	—	—	—
		40	1.5439	1.2432	—	45.5
PO	1 : 6	50	1.5395	1.2364	16402	38.4
		60	1.5361	1.2299	5980	38.9
		70	1.5329	1.2228	2158	34.6
		80	1.5296	1.2160	940	33.2
		20	1.5129	1.1830	—	—
		30	1.5086	1.1768	1092	35.0
		40	1.5052	1.1692	421	34.2
	1 : 9	50	1.5022	1.1617	203	33.5
		60	1.4988	1.1544	103	31.9
		70	1.4951	1.1469	58.7	30.4
PO		80	1.4919	1.1397	36.2	29.4
		20	1.4965	1.0924	—	34.3
		30	1.4930	1.0852	486	32.9
		40	1.4899	1.0781	221	31.6
	1 : 12	50	1.4863	1.0713	108	30.1
		60	1.4826	1.0644	60.9	29.1
		70	1.4792	1.0556	36.2	27.9
		80	1.4752	1.0484	25.0	26.5

Some physical properties of polyetherols were determined, such as: refractive index, density, viscosity, and surface tension (Table III). The direction of changes in these properties was as expected. They decreased with increasing amounts of oxirane. The smallest values corresponded to

the molar ratio of trithiocyanuric acid : oxirane equal to 1 : 12.

The thermal stability of polyetherols was determined by thermal analysis (Fig. 5). The process of degradation of the *s*-triazine ring, yielding the only exothermic peak, was observed in a tem-

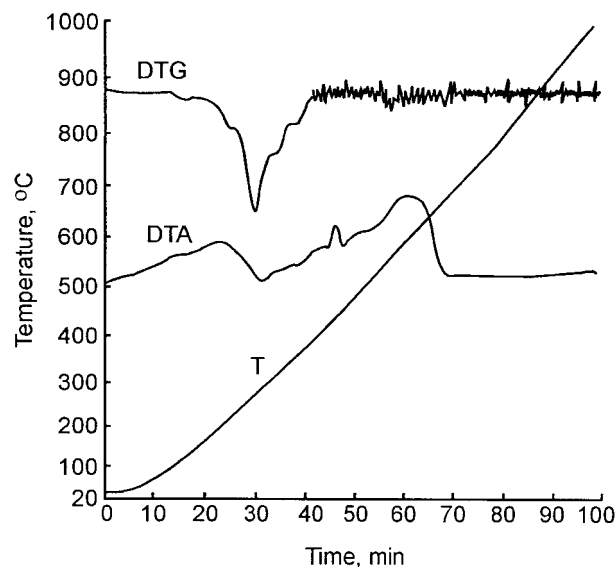


Figure 5 The results of thermal analysis of the reaction product of 1 mol of trithiocyanuric acid with 6 mol of PO.

perature range as high as 280–300°C. The polyetherols were found to be quite resistant to thermal treatment.

Preliminary studies of the applicability of polyetherols as components of polyurethane foams were carried out. They revealed that the polyetherol obtained at the molar ratio of trithiocyanuric acid : oxirane equal to 1 : 9, with pure 4,4'-diisocyanate diphenylmethane and a small amount of water, yielded foams of high thermal resistance. Additional details on the properties and applicability of polyetherols will be published separately.

CONCLUSIONS

Trithiocyanuric acid reacts with an excess of EO and PO in DMF with TEA used as a catalyst. The resulting polyetherols containing an *s*-triazine ring are linked to the etherol chain via sulfur atoms. They have good thermal resistance and can be used as components of polyurethane foams of improved thermal stability.

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