

Reactions of Trithiocyanuric Acid with Oxiranes. IV. Analysis of the Initial Stages of the Synthesis of Polyetherols

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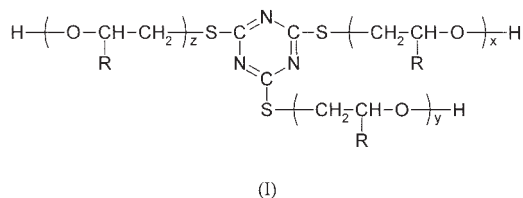
ABSTRACT: The course of the reaction of trithiocyanuric acid (TTCA) with oxiranes, propylene oxide (PO), and epichlorohydrin in a dimethyl sulfoxide solution was monitored by the acid number and epoxy number. The involvement of one of the tautomers of TTCA was postulated on the basis of the studied reaction between TTCA and 3 equiv of oxirane. It was also evidenced that the use of a catalyst was

necessary for the reaction between TTCA and an excess of PO. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4917–4920, 2006

Key words: catalysts; heteroatom-containing polymers; ring-opening polymerization

INTRODUCTION

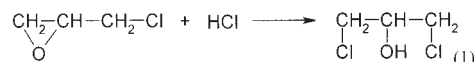
Reactions of trithiocyanuric acid (TTCA) with an excess of ethylene oxide (EO) and propylene oxide (PO) in the solvent dimethylformamide or dimethyl sulfoxide (DMSO) in the presence of triethylamine (TEA) as a catalyst give polyetherols containing an *s*-triazine ring:¹



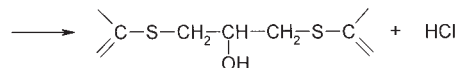
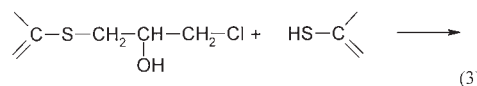
where R is —H or —CH₃ and 6 ≤ x + y + z ≤ 12.

Products have good thermal resistance and can be used as components of polyurethane foams of improved thermal stability.¹

Polyetherols of such properties can be obtained from the reactions of TTCA with an excess of epichlorohydrin (ECH).² These reactions should be conducted without a solvent or catalyst (unlike reactions with EO and PO); otherwise, crosslinking of the products takes place. Moreover, in products of these reactions, some amount of 1,3-dichloropropan-2-ol can be found. This indicates the addition of HCl to ECH according to the following reaction:



The presence of HCl in the reaction mixture is due to the substitution of a chlorine atom in ECH [in reaction (2)] or in a chlorohydroxypropyl derivative [reaction (3)]² by the sulfur atom of the thiol group:



In previous articles, the kinetics and mechanism of the addition of TTCA to oxiranes have been described.³ In this article, only the initial stages of the reaction of TTCA with PO and ECH are described.

EXPERIMENTAL

Monitoring of the reaction between TTCA and oxiranes

To a glass pressure reactor (250 cm³), 17.7 g (0.1 mol) of TTCA (pure; Aldrich, Steinheim, Germany) in 75 cm³ of DMSO (pure; Sigma-Aldrich, Steinheim, Germany) was added. The contents were heated until TTCA dissolved. Then, the appropriate amount of oxirane was added to a cold solution of TTCA (see note 1), and in some cases, TEA (pure; Fluka, Buchs,

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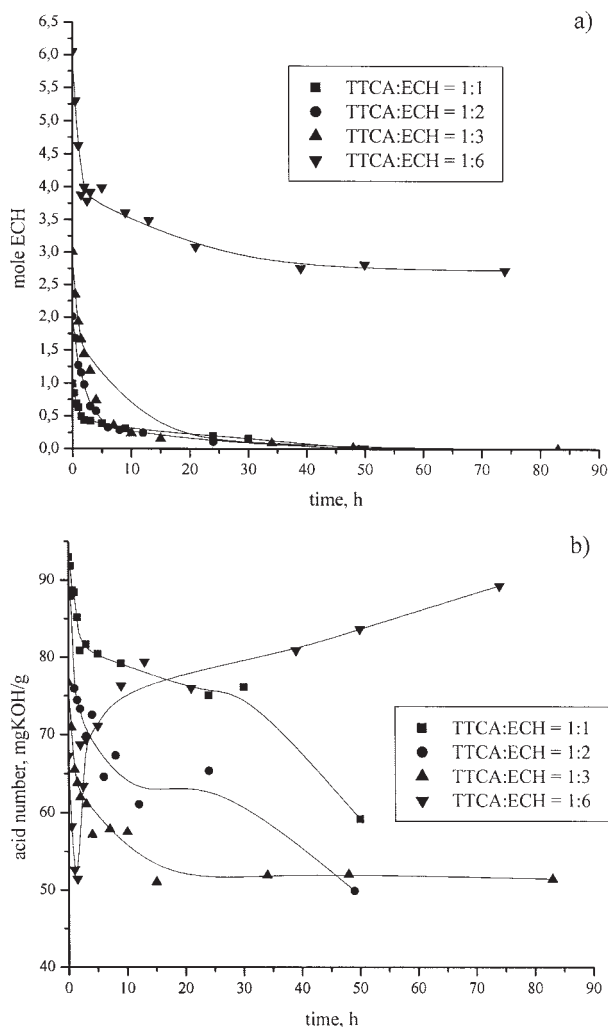


Figure 1 Change in (a) the number of moles of ECH and (b) the acid number for the reaction of TTCA with ECH at 60°C.

Switzerland) as a catalyst was introduced (see note 2). The mixture was stirred and heated to 40 or 60°C (see note 3). During the course of the reaction, 0.1–1.5-g samples were taken for the determination of the epoxy and acid numbers.

Notes

1. The course of the reaction of TTCA with PO (pure; Fluka) and ECH (pure to analysis; H&W, Ltd., Castleford, England) for acid/oxirane molar ratios of 1 : 1, 1 : 2, 1 : 3, and 1 : 6 was investigated.
2. Reactions in the presence of 0.1 mol of TEA/mol of TTCA were studied.
3. The reactions between TTCA and PO and ECH were followed at 40°C, whereas the reaction of TTCA with ECH was additionally studied at 60°C.

Analytical methods

The epoxy number was determined by the titration of a sample with a dioxane solution of hydrogen chlo-

ride.⁴ The acid number was determined by the titration of a sample dissolved in a mixture of 20 cm³ of DMSO and 5 cm³ of H₂O with 0.1M NaOH.

RESULTS AND DISCUSSION

A reaction between TTCA and ECH should be performed under different conditions than those used for a reaction between TTCA and EO or PO. Here the first stages of the reactions of TTCA with oxiranes were investigated through the determination of the acid and epoxy numbers of reaction mixtures. The reactions between TTCA (dissolved in DMSO) and oxirane (ECH or PO) were followed by the determination of the acid and epoxy numbers at 60 (for reactions with ECH) and 40°C (for reactions with PO). The choice of the temperature of the process was related to the volatility of oxiranes. On the basis of the epoxy num-

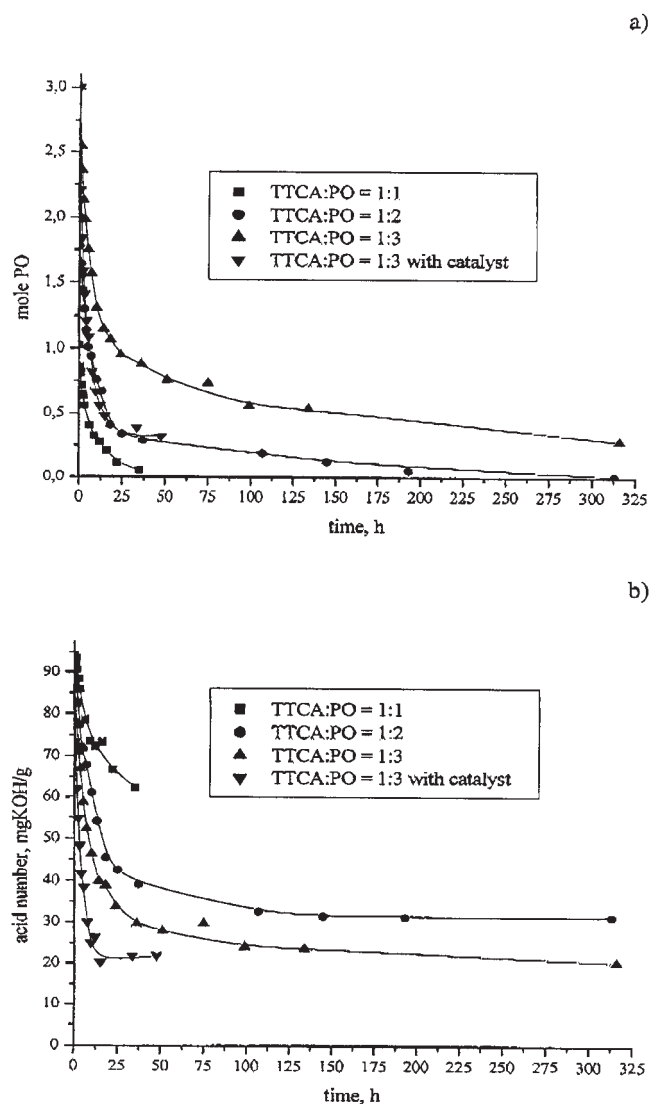


Figure 2 Change in (a) the number of moles of PO and (b) the acid number for the reaction of TTCA with PO at 40°C.

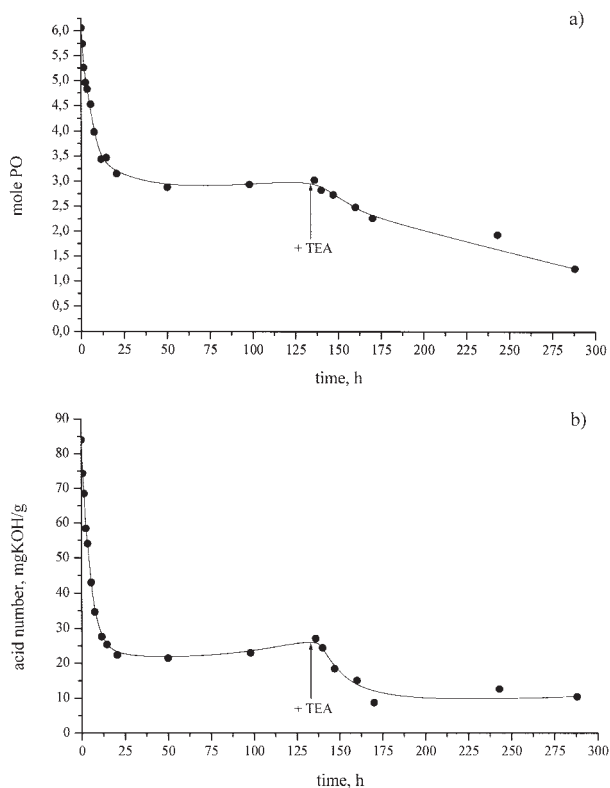
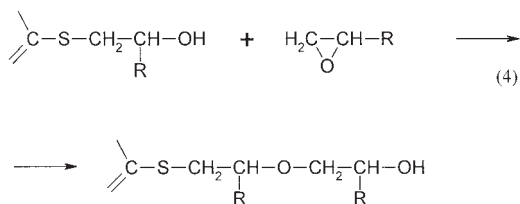


Figure 3 Change in (a) the number of moles of PO and (b) the acid number for the reaction of TTCA with PO in the presence of a catalyst at 40°C.

ber, the amount of unreacted oxirane was calculated (Figs. 1–4).

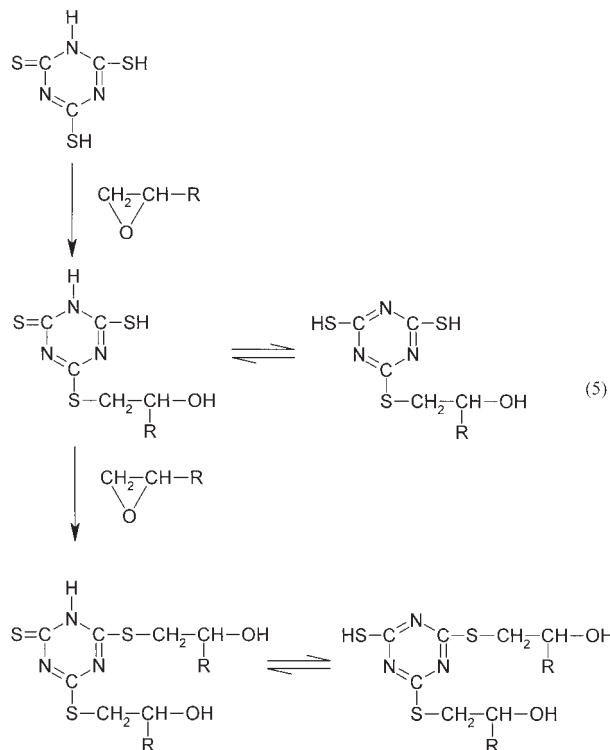
The first 2 mol of oxirane reacts with TTCA considerably faster than the third one (see Figs. 1 and 2). This suggests that TTCA occurs in the dithiol form in DMSO in the presence of oxirane ($-\text{SH}$ groups are more reactive than NH groups and forming OH groups⁵). A consecutive reaction between the formed hydroxyalkyl groups with oxirane,



where R is $-\text{H}$, $-\text{CH}_3$, or $-\text{CH}_2\text{Cl}$, can be neglected because in a mixture of 1 mol of TTCA and 6 mol of PO, only 3 mol of oxirane can react. A further reaction needs the TEA catalyst to occur (Fig. 3).

Because the thioketonal group $\text{C}=\text{S}$ is absent in the products of the reaction (this comes from an analysis of IR spectra¹), the NH groups that could react with oxiranes are absent in the reaction system as well. We conclude that the addition of the acid to oxirane par-

tially shifts the tautomeric equilibrium [eq. (5)] toward the thiol form:



where R is $-\text{H}$, $-\text{CH}_3$, or $-\text{CH}_2\text{Cl}$.

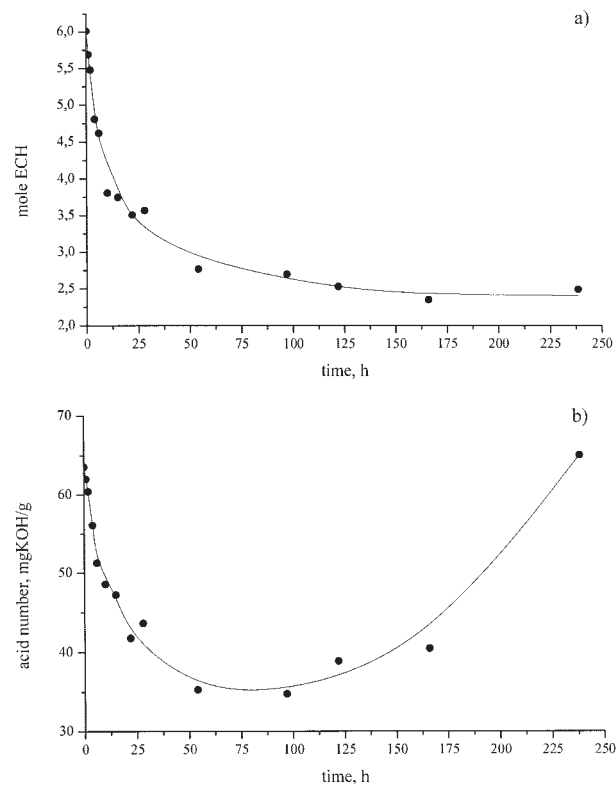


Figure 4 Change in (a) the number of moles of ECH and (b) the acid number for the reaction of 1 mol of TTCA with 6 mol of ECH at 40°C.

The tautomeric equilibrium of TTCA is pH-dependent.⁶ Thus, this shift is probably related to a decrease in the acidity of the system.

An analysis of the reaction course of TTCA with ECH shows that the final acid number is larger than those for reactions with PO (Figs. 1 and 2).

Moreover, the changes in the acid number during the reaction course are irregular (the acid number temporary rises). The reaction course for the larger ECH/TTCA ratio (6 mol of ECH/mol of TTCA) causes a substantial growth of the acid number (Figs. 1 and 4) and thickening of the reaction mixture and, consequently, gelation of the reaction system. It results from the release of hydrogen chloride in the reaction and confirms the possibility of chlorine substitution in ECH in a parallel reaction by thiol groups [eq. (2)]. The lowering of the temperature makes the gelation process slower (Fig. 4).

Using TEA substantially increases the reaction rate of TTCA with PO (Figs. 2 and 3).

CONCLUSIONS

TTCA in a DMSO solution is present in the dithiol form. During the reaction with PO or ECH, the tautomeric equilibrium shifts toward the trithiol form. The addition of TTCA to the first 3 mol of PO can be performed without a catalyst, but a further reaction needs the TEA catalyst to obtain polyetherols.

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