

## Functional polythiiranes

### 2. Polymers of methyl (2,3-epithiopropyl-thio) ethanoate

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#### Summary

The synthesis of a new monomer holding a carboxylate function and a thiirane ring, is described in this study. Its homopolymerization through thiirane ring opening, using as initiator, tetramethylammonium (di)thiobenzoate in DMF and affording polysulfides with pendent carboxylate groups is investigated. The copolymers with methyl thiirane are identified by <sup>13</sup>C NMR spectroscopy. The corresponding polyacids can be easily obtained through saponification.

#### Introduction

Polymers with functional groups have become of major interest in polymer science and technology. A lot of functionalized side-chain polymers are described for a wide range of uses (1). Numerous polymers have been chosen to constitute the main chain among which vinylic polymers are the most usual. If poly(alkyl)thiiranes have been intensively studied (2), only few papers are devoted to the polymers of functional thiiranes. In fact two problems arise when functionalized polythiiranes are needed: although numerous substituted thiiranes are known (3), the monomer synthesis is often quite difficult in account of the high reactivity of thiiranes through ring opening. Moreover, the ionic initiators commonly used for thiiranes polymerization are themselves highly reactive and inconsistent with the presence of most functional groups. Some polymerizations of protected functional thiiranes have also been investigated but the releasing of the protective groups may lead to polymers with limited conversion and sometimes with isomerized structures (4).

We recently demonstrated the possibility to obtain poly(hydroxymethyl)thiirane using quaternary ammonium salt of dithiobenzoic acid as initiator in DMF (5). Such a salt exhibits an interesting chemoselectivity towards thiirane ring opening and allows anionic polymerization of hydroxymethylthiirane without any protection of the hydroxyl group. In the previous publication (6), we have studied the occurrence of transfers in the polymerizations of hydroxymethylthiirane and mercaptomethylthiirane **MMT**.

In the present paper, we describe the synthesis of a new monomer: methyl (2,3 epithiopropyl-thio) ethanoate **METE**, its homopolymerization and copolymerization with methylthiirane **MT**, using tetramethyl ammonium thio and dithiobenzoate as initiators. A new class of polymers may be easily obtained with this compound by ring opening polymerization: a polythiirane backbone with regular, three atoms-spaced side chains bearing carboxylate functions. The presence of the large C-S bonds in the main chain should enhance its flexibility while the spacer between main chain and the carboxylate function should also enhance the mobility of the side chain in comparison with poly(acrylates). Numerous applications could be investigated about these new polymers.

#### Experimental

##### *Monomers and catalysts synthesis*

**MMT** is prepared according to (7), from commercial 2,3-dimercaptopropanol. **METE** is prepared according to (8) with nearly quantitative yields: **MMT** and methylbromoacetate in stoichiometric amounts are dissolved in benzene; the solution is cooled with an ice bath and

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stirred ; the stoichiometric amount of DBU dissolved in an equivalent volume of benzene is slowly added to the mixture (half an hour) ; at the end of the addition , the ice bath is removed and the mixture is left during a night ; the salt of DBU is then filtered off ; the organic phase is washed with water and dried over sodium sulfate ; benzene is removed in a rotary evaporator ; METE decomposes during distillation (E 0,05 mB: 150 °C) and is purified by chromatographic separation on silica gel (elution with petroleum ether/ ether) to afford an oil : HPLC purity >99,5%

IR (film):  $\nu = 1736 \text{ cm}^{-1}$  ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS,ppm)  $\delta = 3.78$  (3H), 3.36 (2H), 3.00-2.90 (2H), 2.85-2.40 (2H), 2.29 (1H) ; Anal., calc.% for  $\text{C}_6\text{H}_{10}\text{O}_2\text{S}_2$  M = 178.27: C: 40.45, H: 5.61, S: 35.95; found C: 40.28, H: 5.47, S: 35.59

Commercial MT(Janssen) is used in this study and carefully distilled just before use. Tetramethylammonium thio and dithiobenzoates are prepared as previously reported (9,10).

### Polymerizations and copolymerizations

These reactions and the polymerization rate evaluations are carried out as previously reported in references (6,9) . Benzyl chloride in excess is added at the end of the reaction. Polymers are isolated after precipitation in methanol, purified by dissolution / reprecipitation and dried under vacuum.

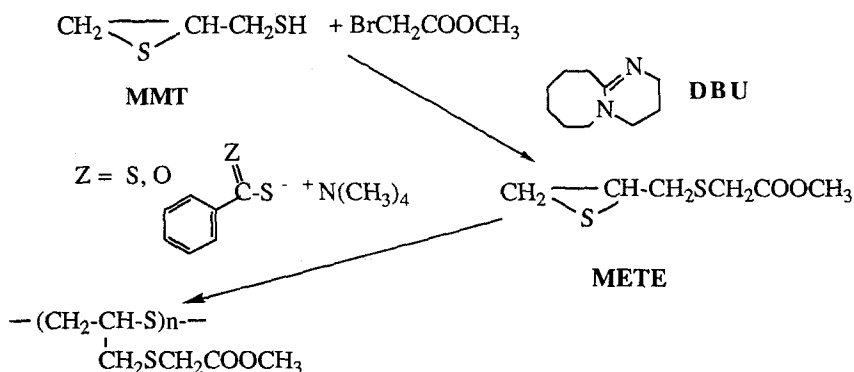
Poly(METE): IR (film):  $\nu = 1737 \text{ cm}^{-1}$   $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS, ppm)  $\delta = 3.83$  (3H), 3.40 (2H), 3.12 (5H) ; Copol(METE/MT): IR (film):  $\nu = 1737 \text{ cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$  TMS,ppm)  $\delta = 3.80$  (3H), 3.40 (2H), 3.11 (8H), 1.40 (3H).

### Saponification

(Co)polymers samples are dissolved in THF. A titrated (1N or 2N) aqueous solution of NaOH is added in a stoichiometric excess (20%) . These mixtures are refluxed three hours and stirred at room temperature one night. The solutions are evaporated under vacuum. The  $^1\text{H-NMR}$  spectrum of the polysalt clearly shows the disappearance of the methoxy signal near 3.80 ppm ( $\text{D}_2\text{O}$ , DSS, ppm)  $\delta = 3.42$  (2H), 3.30-2.9 (5H). In the same experimental conditions a poly(MT) sample (  $M_n = 87\ 200$  ;  $I = 2.6$ ) does not undergo degradation ( $M_n = 82\ 200$  ;  $I = 2.6$ ) . The polysalts are dissolved in water and titrated with an aqueous solution of hydrochloric acid ; the polyacids precipitate ; they are washed with water, dried under vacuum and analyzed . IR (film)  $\nu = 1710 \text{ cm}^{-1}$ , broad band near  $3300 \text{ cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ , TMS,ppm)  $\delta = 5.05$  (OH), 3.30 (2H),3.30-2.9 (5H) ; in copolymers: 1.40 (CH<sub>3</sub>).

## Results and Discussion

### Monomer synthesis

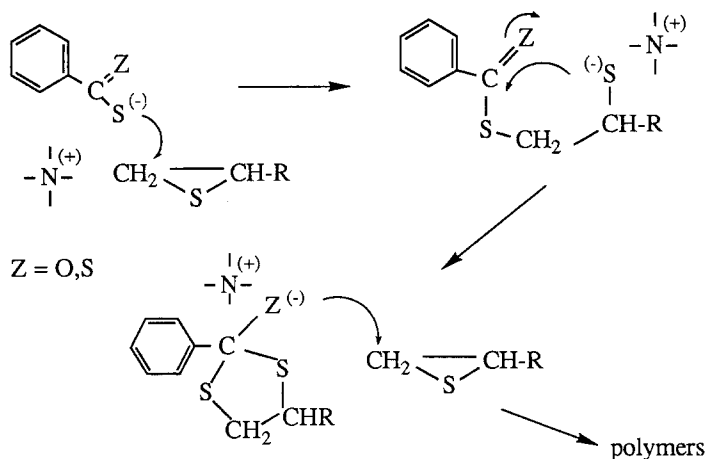


Thiiranes are generally prepared from epoxides but yields are sometimes low in this way. Epoxides with carboxylate substituents are known and may be obtained from epoxidation of methyl alkenoates (11), but yields are significant only from  $\omega$ -alkenoates. To prepare **METE**, we used the well-known nucleophilic character of the thiol function in mercaptomethylthiirane. A convenient and very simple procedure to prepare sulfides is described by Ono *et al.*: thiols are allowed to react with alkylhalides in benzene in the presence of DBU (8). We applied this procedure to **MMT** and methyl bromoacetate. Direct addition of DBU on **MMT** induced ring opening of thiirane ring and fast polymerization. To avoid this reaction, DBU had to be added slowly in the reagents mixture. With "active" bromides such as bromoacetate or benzyl bromide (6), substitution was faster and quantitative yields were obtained. When less "active" halides (chlorides) were used the substitution rate has slowed down and only substituted oligomers were isolated. The very high reactivity of bromo esters and benzyl bromide in  $S_N2$  substitution thus allows simple and rapid synthesis of **METE** and (benzylthio)methyl-thiirane (6).

### Homopolymerization

Polymerization of the purified monomer was managed as previously reported (6,9) with tetramethylammonium dithiobenzoate in DMF. In the polymerization conditions, esters do not react with dithiobenzoate ions. We firstly studied the kinetics of the homopolymerization reaction. For this purpose we looked at the disappearance of the characteristic thiirane doublet at 2.3 ppm in  $^1H$ -NMR spectroscopy in  $d_7$ -DMF; in the experimental conditions previously selected, this signal has completely disappeared one minute after the initiator addition and the NMR spectrum then obtained was the polymer one. An identical result was observed with methylthiirane in the same experimental conditions (6). We may conclude that a quantitative yield was reached and that very few terminations by transfer or deactivation occurred: this polymerization has probably a living character.

The homopolymerization of **METE** gave amorphous polymers, soluble in most organic solvents. Table 1 displays the results for different initiator concentrations; the ratio  $DP_n \text{ exp}/DP_n \text{ theo}$  increases when the initiator concentration increases. A similar result was already observed with methyl thiirane (9), and is consistent with a slower rate for initiation than for polymerization; the whole initiator is not consumed: at the end of the reaction the purple colour of the remaining initiator (dithiobenzoate) is observed. The addition of dithiocarboxylate anion on thiirane methylene carbon generates a thiolate anion which gives a nucleophilic attack on the thiocarbonyl group and the resulting thiolate may be the actual initiator for thiiranes polymerization. This reaction have been very clearly demonstrated with chloromethyl thiirane (10).



Taking account of the high reactivity of the thiiranes, we have failed in pointing out trithioorthobenzoate end groups: even with high concentrations of initiator, high molecular weights polymers have been obtained and their end groups could not be analyzed. At the present time further studies are in progress to accurately analyze the ends groups and to back the assumed initiation mechanism (12). Therefore, we now think that these two steps initiation slows down initiation rate with regard to polymerization rate, increasing the DP<sub>n ex</sub>/DP<sub>n th</sub> ratio. A. Midrak (10) observed that thiobenzoate reaction with chloromethylthiirane had a weaker tendency than dithiobenzoate to give carbonyl group participation on account of the difference of reactivity between carbonyl and thio carbonyl groups. The results of polymerizations run out with tetramethylammonium thiobenzoate are reported on table 1: no noticeable change in the

DP<sub>n ex</sub>/DP<sub>n th</sub> ratio have been observed substituting thiobenzoate with dithiobenzoate.

With both initiators, high polydispersity indexes were obtained for an anionic polymerization: this also results from the difference between initiation rate and polymerization rate: this assumption is now confirmed by the study of methylthiirane polymerization in DMF which leads also to high polydispersity indexes; if the polymerization rate is slowed down using THF instead of DMF (9) or by adding some amounts of ethanol in DMF, better values of polydispersity indexes are observed (13)

Table 1: Homopolymerization of METE; a) tetramethyl ammonium dithiobenzoate % mole/monomer mole; b) tetramethyl ammonium thiobenzoate % mole/monomer mole; METE: 2 mole/l; solvent: DMF; 20°

%init a)	DP <sub>n th</sub>	M <sub>n</sub> *	$\frac{DP_{n\ ex}}{DP_{n\ th}}$	I	%init b)	DP <sub>n th</sub>	M <sub>n</sub> *	$\frac{DP_{n\ ex}}{DP_{n\ th}}$	I
0.40	250	48 000	1.1	2.2	0.50	200	31 300	0.9	1.9
0.84	119	32 900	1.5	1.9	0.83	120	23 400	1.1	2.1
1.16	86	21 100	1.4	1.9	1.00	100	21 700	1.2	1.8
1.54	65	26 200	2.3	2.8	1.50	67	18 300	1.5	1.9
1.90	52	16 400	1.8	3.6	2.00	50	17 500	1.9	1.9

M<sub>n</sub>: number average molecular weight; DP<sub>n ex</sub>: number average degree of polymerization observed; DP<sub>n th</sub>: number average degree of polymerization calculated from the monomer/initiator ratio; I: polydispersity indexes

\* Molecular weights are reported as the molecular weights of equivalent elution volume polystyrene in size exclusion chromatography on Styragel columns (Waters) in THF.

The <sup>1</sup>H and <sup>13</sup>C (off resonance and noise decoupled) NMR spectra (Fig 1A) were consistent with the homopolymers structure, demonstrating the regioselectivity of the ring opening. The methine carbon of the main chain exhibits a diad effect ( $\delta = 46.95, 46.83$ ) often noticed in <sup>13</sup>C NMR of polythiiranes (14). The signal at 37.35 ppm was attributed to the methylene carbon near the carbonyl group; assignment of both other signals at 36.00 and 34.25 ppm to both other methylene carbon is much more difficult and has been accomplished with the 50/50 copolymer spectrum (Fig 1B).

#### Copolymerization with methyl thiirane

The copolymerization of METE with methylthiirane has been studied. The copolymer composition is nearly the monomer composition and yields were nearly quantitative. The copolymer composition has not changed after several reprecipitations and we can assume that we are in the presence of copolymers. Furthermore the <sup>13</sup>C NMR spectrum of a 50/50

	$\delta$ ppm MT			$\delta$ ppm METE						
Homopol.	20.75	41.26	38.40	34.25	36.00	37.35	46.83	46.95	52.54	170.71
Copol.	20.76	41.30	37.24	34.24	35.32	37.39	46.88	46.94	52.54	170.68
			37.34		35.41					
			38.43		36.02					
					36.06					
	CH <sub>3</sub>	CH	CH <sub>2</sub>	CH <sub>2</sub>	CH <sub>2</sub> main chain	CH <sub>2</sub> CO	CH diad	CH diad	CH <sub>3</sub>	C=O

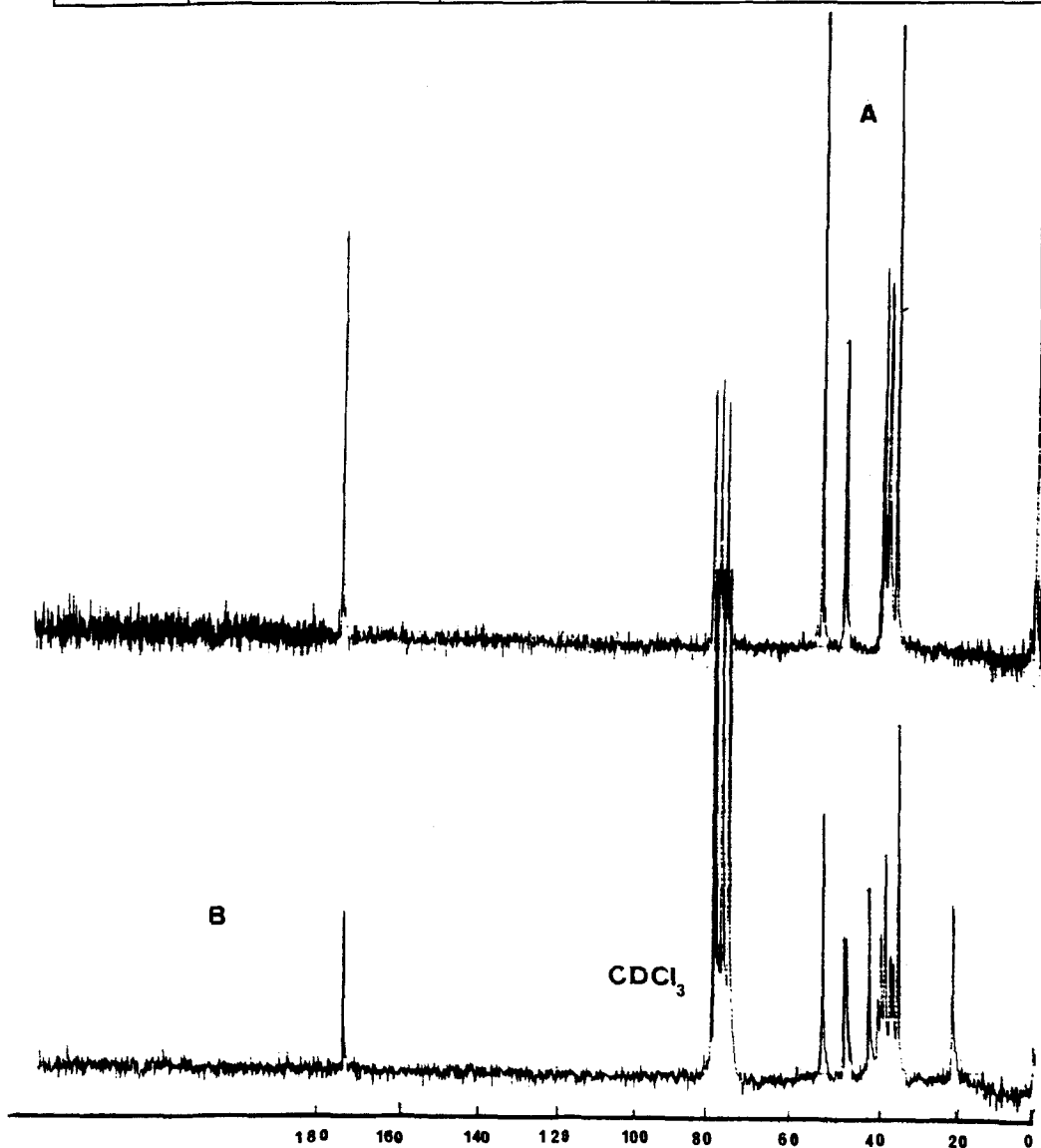


Figure 1  $^{13}\text{C}$  NMR spectra (Varian FT 80A,  $\text{CDCl}_3$ , TMS):  
 A : Homopolymer ; B : Copolymer 50/50

copolymer (Fig 1B ) bears evidence for the actual existence of these copolymers ; signals corresponding to both homopolymers are easily identified in this spectrum ; but supplementary signals appear for the main chain methylene carbon of each unit . According to the increments values given in (15) , the predicted chemical shift for a main chain methylene in homopoly **MT** (unit A-A) is : 37.6 ppm ; the same carbon in a copolymer (unit B-A) is predicted at 37.1 ppm . These predicted values are in accordance with those observed (Fig 1) . The main chain methylene carbon of the **METE** unit is predicted at 33.6 ppm in homopolymer (unit B-B) and at 34.1 ppm in the copolymer (unit A-B) . Although nearly related , the predicted and observed values (Fig 1) don't shift in the same way in this case . But the predicted values don't take in account long range anisotropic effects and the coil conformation effects of macromolecules . The presence of these supplementary signals appears characteristic of sequences of different distribution and then , confirm the existence of copolymers . Owing our previous study (6) and the observed similar polymerization rates, we may assume in **METE** polymerization no carboxylate group participation as in **MT** polymerization . Then an identical reactivity of both anions may be considered , leading to short sequences and giving intense signals . Similar supplementary signals have yet been observed (5) in copolymers of methyl thiirane and hydroxymethylthiirane **HMT** and are being studied at the present time (13) : they are weaker for **HMT** copolymers because the slight difference of reactivity between **HMT** and **MT** resulting of some hydroxyl group participation (6) , give larger sequences . The methylene signal at 34.24 ppm in copolymers is identical with the one at 34.25 ppm in homopolymer and may be definitively attributed to the side chain methylene carbon ; while signal at 36.00 ppm in the homopolymer correspond to the main chain methylene carbon.

### Saponification

% METE	% Hydro	pK <sub>A</sub>	pH at neut
5	89	6.9	4.75
10	63	6.5	4.7
51	90	6.0	3.8
66	66	5.5	3.55
83	82	4.9	3.45
100	66	5.2	3.2

Table 2 Hydrolysis for homo and copolymers and pK<sub>A</sub> of polyacids

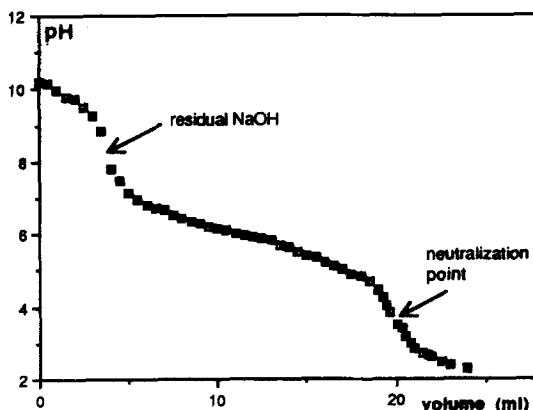


Figure 2 : Hydrolysis curve with 0.1N HCl for a 50/50 copolymer

The modification of polymers in polyacids via saponification and acidification was also studied. Saponification was realized by using an excess of aqueous sodium hydroxyde ; the modification, proved by the disappearance of the methoxy signal in <sup>1</sup>H-NMR, was quantitative in all cases and the polysalts were water soluble except for copolymers with a **METE** content < 5% . Salt titrations were monitored by potentiometry ; a typical curve is described in Fig 2 . The excess of sodium hydroxyde was easily evaluated and then the neutralisation point for the polyacid . A slight decrease of the apparent pK<sub>A</sub>, obtained by a graphic determination is observed (Table 2 ) when the polyacid content increases in the polymer . The polyacids pK<sub>A</sub> values cannot be more accurately correlated to the copolymer composition : important effects owed to sequences distribution may be taken in account . Moreover the medium heterogeneity near the neutralization point has certainly disturbed its evaluation . The modification of

polymers functionality was observed by  $^1\text{H}$  NMR spectroscopy . Molecular weights measurements after saponification and acidification of poly(METE) gave inconsistent results as it can be expected for these polyelectrolytes ; but a poly(methyl)thiirane sample processed in the same conditions displayed no degradation

### Conclusion

We realized the synthesis, the polymerization and the copolymerization of a new monomer methyl (2,3-epithiopropyl-thio)ethanoate leading to a new class of polymers with carbon-sulfur bonds in the main chain and pendent carboxylate functions in side chains . The chemoselectivity of ammonium salt of (di)thiobenzoic acid towards thiirane ring was confirmed since carboxylate functions were found in the polymers without modification ; the new polymers and copolymers afford easily polyacids through saponification . The potential reactivity of these new polymers is very broad and for further applications a study of their chemical and physical properties is also in progress.

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