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Preparation and characterization of poly(thiirane) block copolymers with pendent hydroxy groups

C. Bonnans-Plaisance*
Laboratoire de Synthèse de Polymères Fonctionnels, URA CNRS 509, Université du Maine, Avenue O. Messiaen, 72017 Le Mans, France

and P. Guerin
Laboratoire de Chimie Biologique et Macromoléculaire, URA CNRS 1467, ENSCR, Avenue du Général Leclerc, 35700 Rennes, France

and G. Levesque
Laboratoire de Chimie des Polymères et Interfaces, URA CNRS 480, Université de Caen, Boulevard du Maréchal Juin, 14050 Caen, France
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^{13}C n.m.r. spectroscopy was used to differentiate between block and statistical copolymers of hydroxymethylthiirane and methylthiirane. Block copolymers could be exclusively obtained if hydroxymethylthiirane constituted the first sequence; however, if the first sequence consisted of methylthiirane, the synthesis of block copolymers failed because of a termination reaction. We demonstrate that the termination reaction is partially avoided in a protic medium.

(Keywords: poly(hydroxythiirane)s; anionic polymerization; protic medium)

INTRODUCTION

The living character of the anionic polymerization of thiiranes under extreme conditions of reagent purity has been known for many years[1,2], especially for methylthiirane (MT), and no monomer transfer was suspected to occur. We have previously studied the anionic polymerization of 2-hydroxymethylthiirane (HMT)[3] and demonstrated that no internal chain transfer occurs in the active site between the thiolate ion and the hydroxy groups owing to the difference in acidity between thiols and alcohols; in contrast, mercaptomethylthiirane (MMT) gives rise to very frequent internal chain transfers as well as a large decrease in the polymerization rate, showing the obvious proton exchange between thiol and thiolate ion in the growing chain-end[4]. The comparison of MMT and HMT monomers has clearly established the different behaviour of hydroxy and thiol groups. In this way, the presence of a hydroxy group in the polymer chain-end does not affect the living character of the active centre, and thus the synthesis of block copolymers is likely.

In this paper, we report the synthesis of such HMT/MT block copolymers using tetramethylammonium dithiobenzoate (TMTB) as an initiator in dimethylformamide (DMF) and their characterization by high resolution ^{13}C n.m.r. spectroscopy. We have also observed that if a first poly(MT) sequence is prepared, it is not possible to add a second MT sequence in DMF to give block polymers on account of a 'killing' reaction; but in a protic medium consisting of DMF with some absolute ethanol, a second MT sequence can be added to some initial chains.

EXPERIMENTAL

The ^1H and ^{13}C n.m.r. spectra were recorded on a Brucker AC 400 spectrometer. The u.v. spectra were obtained on a Varian DMS 100 spectrometer. Molecular weights were determined by size exclusion chromatography (s.e.c.) on Styragel columns (Waters) calibrated with standard polystyrene samples. Light-scattering measurements were performed on a 4700 Maleverne apparatus. The methylthiirane and hydroxymethylthiirane monomers and the initiator tetramethylammonium dithiobenzoate were prepared as previously described[3–5]. The block and statistical copolymers were also obtained as previously described[3–5] but in a special polymerization kit which gave the different polymerization samples in the same experiment. For statistical copolymers, both monomers in determined ratios (total amount 1.6×10^{-2} mol) were mixed and dissolved in DMF. Vacuum and flushing with nitrogen were applied successively and several times. Under nitrogen flow, initiator (1.45×10^{-5} mol) dissolved in DMF was added; the total amount of DMF was 3 ml. For sequential copolymers the same procedure was used, but MT was added 8 min after the addition of the initiator; the purple colour of the initiator had then completely disappeared, proving its whole consumption. All the copolymers were

* To whom correspondence should be addressed

processed with benzyl chloride at the end of the reaction (1 h).

The same apparatus was used to conduct the MT polymerizations with ethanol. Four experiments were then carried out: two samples in pure DMF, one terminated with 1-chloromethylnaphthalene for u.v. measurements; and two samples in DMF/ethanol mixtures, one terminated with 1-chloromethylnaphthalene for u.v. measurements. In these experiments the amount of MT was 0.5×10^{-2} mol; the initiator amounts are given in *Table 2* and the total volume of DMF was 2 ml.

All the copolymers were precipitated in methanol or diethyl ether and the liquid was decanted twice; the copolymers were then washed twice with benzene over 6 h. No poly(MT) was recovered in this process.

RESULTS AND DISCUSSION

HMT/MT block copolymers

Copolymers of HMT and MT were prepared using TMTB as the initiator in DMF according to two synthetic routes: in one route, HMT (30 or 15 mol%) and MT (70 or 85 mol%) were mixed to give statistical copolymers; in an identical experiment, HMT and MT were introduced successively in order to prepare diblock (HMT-15/MT-85, HMT-30/MT-70) and triblock (HMT-15/MT-70/HMT-15) copolymers. A careful fractionation in benzene of both types of copolymers did not afford any homopoly(MT). The compositions of the statistical and block copolymers were determined by ^{1}H n.m.r. as previously described[3] and found to be nearly identical to the initial monomer compositions. The analysis was based on the integration data for proton signals (in d_5-pyridine) at 1.50 ppm for $\underline{CH}_3$ groups of MT units and 4.25 ppm for $\underline{CH}_2OH$ groups of HMT units (*Figure 1*). Block copolymers were much less soluble than the statistical copolymers even in aprotic polar solvents and it was not possible to elucidate their structures by an increase in the average molecular weights using s.e.c. or other methods. As previously observed[3,4], the molecular weights of the 15/85 statistical copolymer determined by s.e.c. were inconsistent and not in accordance with those obtained by light scattering (LS). From s.e.c., $M_n = 41\,410$, $M_w = 137\,600$ and $I = 3.3$ (*Figure 5*). From LS, $M_w = 63\,100$.

Acylations of the hydroxy groups with acetyl chloride were performed in DMF, as previously described[4], in order to obtain better solubilities of the block copolymers in tetrahydrofuran (THF) for size exclusion chromatography (s.e.c.) measurements. Several attempts did not enhance the solubility of these polymers in THF; however, this process gave good results with the statistical copolymers[4]. Thus, this weak reactivity of the block copolymers can be understood by assuming that they have a micellar structure, customarily observed with block copolymers[6], and that the hydroxylated sequences could not be easily reached by the reagents. Furthermore, owing to the poor solubility of the block copolymers, the stability of the active centres could not be evaluated by u.v. determination of the end-group concentrations after reaction with 1-chloromethylnaphthalene, as customarily used for this purpose[1].

High resolution ^{13}C n.m.r. was used to study the unit distributions in the copolymers and to differentiate between block and statistical copolymers. Deuterated

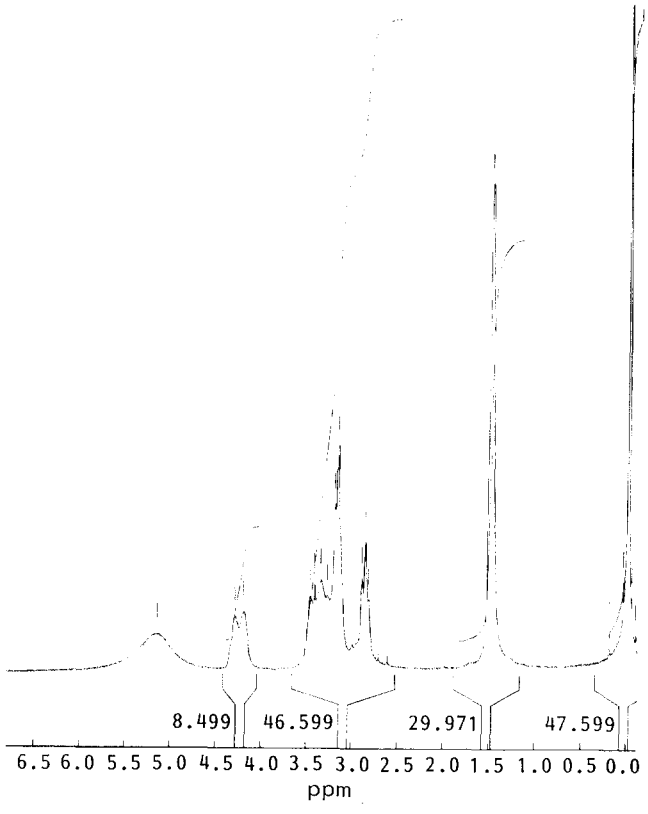

Figure 1 ^{1}H n.m.r. spectrum of an HMT-30/MT-70 statistical copolymer (in d_5-pyridine–TMS)

pyridine was used as n.m.r. solvent because of important stereosensitivity effects on the different carbon atoms of the polymer chain. At first, this study confirmed the absence of signals corresponding to C–O–C bonds resulting from possible transfer reactions. *Figures 2–4* and *Table 1* display ^{13}C n.m.r. spectra and data for some copolymers. The spectrum (*Figures 2b* and *4*) corresponding to a copolymer prepared by mixing HMT and MT in a 15/85 ratio is more complex compared to that for the copolymer prepared by successive introduction of HMT and MT in an identical 15/85 ratio (*Figures 2a* and *3*). At first, tacticity effects appear in block and statistical copolymers, but these effects are more obvious for block copolymers: the methine carbon of each monomer unit is stereosensitive as previously observed in poly(MT)[7] and in other poly(thiirane)s[8,9]. The methine carbon signal displays four peaks corresponding to a triad effect in the racemic polymer. These four peaks (*Figure 3b*) in the case of HMT units are of equal intensity corresponding to a Bernoullian triad distribution: the incorporation of the monomer is not controlled by the configuration of the previous unit. On the contrary, the four signals corresponding to the methine carbon atom of the MT units (41.66, 41.57, 41.52 and 41.49 ppm) are approximately in the ratio 4/2/1/1, indicating a large stereosensitivity effect (*Figure 3c*). A sample of homopoly(MT), prepared with the same initiator in the same conditions, exhibits strictly the same distribution for the four signals corresponding to the methine carbon atom. The assignments of dyads have been made previously[7] for CCl_4/C_6D_6 mixtures; however, for d_5-pyridine the corresponding assignments are not known. For a sample of high tacticity ($\sigma = 0.87$), the methine carbon presents only the signal at 41.67 ppm. This

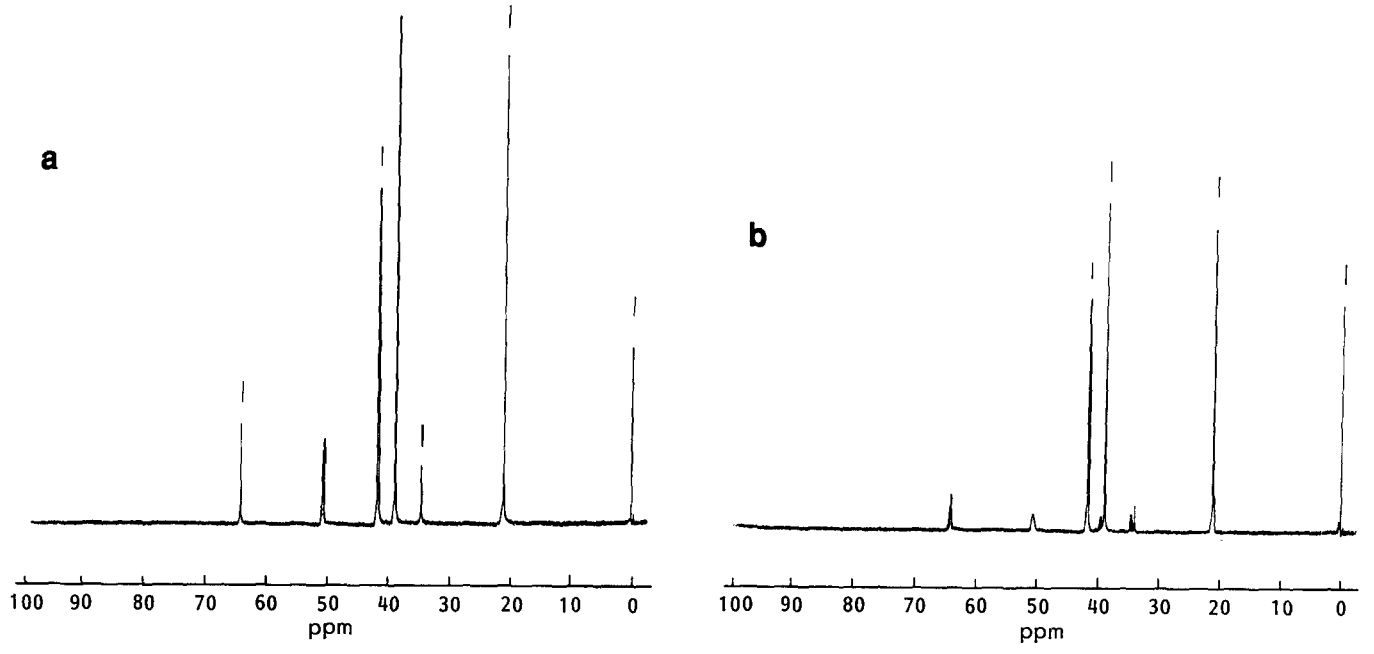

Figure 2 ^{13}C n.m.r. spectra of HMT/MT copolymers (in d_5-pyridine–TMS): (a) 15/85 block copolymer; (b) 15/85 random copolymer

Table 1 ^{13}C n.m.r. data[a] for block and random copolymers in d_5-pyridine

	MT			HMT		
	$\underline{C}H_3$	$\underline{C}H_2$	$\underline{C}H$	$\underline{C}H_2$	$\underline{C}H$	$\underline{C}H_2OH$
Random copolymer (30/70)	20.77[b]	38.80[c]	41.50 41.53 41.59 41.67	38.84–34.74 (multiple lines)	50.23–50.85 (multiple lines)	63.94 64.02 64.11 64.21 64.23 64.35
Block copolymer (15/85)	21.04	38.79	41.49 41.52 41.58 41.66	34.40 34.55	50.37 50.49 50.64 50.79	64.02
Block copolymer (15/70/15)	21.04	38.79	41.49 41.52 41.58 41.66	34.40 34.54	50.37 50.49 50.64 50.79	64.02
Random copolymer (15/85)	20.73[b]	38.77	41.47 41.50 41.46 41.65	33.82–34.80 (multiple lines)	50.11–51.02 (multiple lines)	63.99 64.00 64.10 64.19 64.22 64.31

[a] Chemical shifts in ppm from tetramethylsilane
[b] Four additional small signals between 20.78 and 21.05 ppm
[c] Three additional small signals at 39.37, 39.54 and 39.61 ppm not visible for smaller proportions of HMT

complexity is also observed for the methyl and methylene carbon atoms in the MT units. In order to assign all of the signals in d_5-pyridine, poly(MT) samples of different tacticities have been prepared and are under study. In the block copolymer spectra a dyad tacticity effect on the methylene carbon in the HMT unit is also observed (two identical peaks at 34.40 and 34.54 ppm) which has not been observed in the ^{13}C n.m.r. spectrum of poly(glycidol)[10].

Besides stereosensitivity effects, chemical environment effects appear strongly on each carbon atom of the HMT units. At first, the $\underline{C}H_2OH$ signal at 64.02 ppm, which is unique in the case of the block copolymer (*Figure 3a*), displays multiple lines for the random copolymer (*Figure*

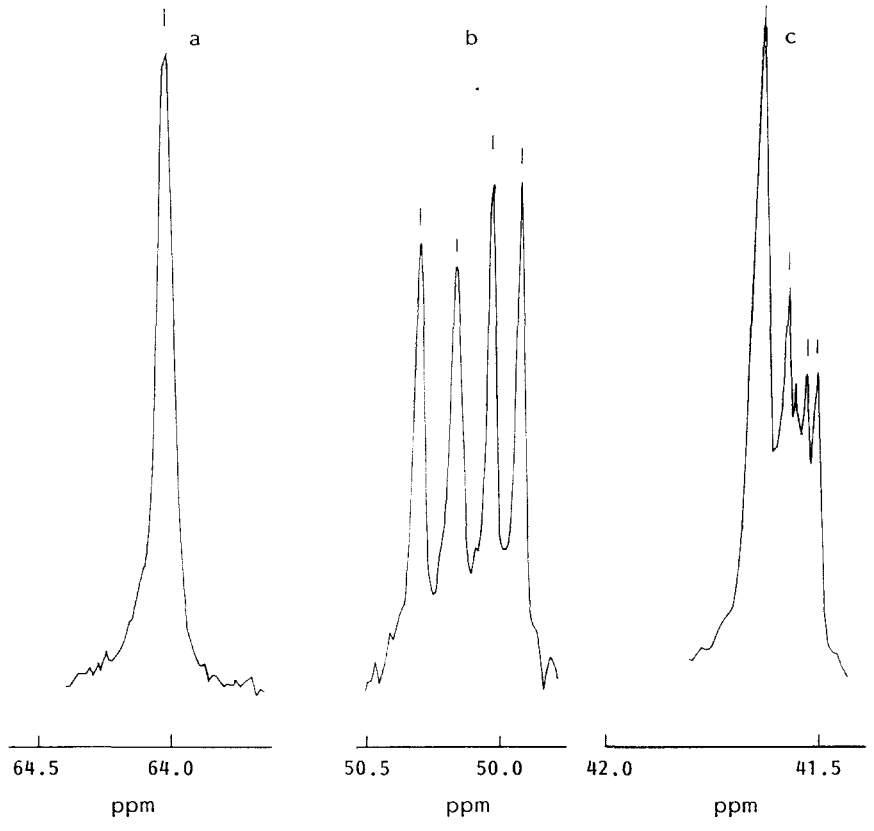

Figure 3 Expanded regions of the ^{13}C n.m.r. spectrum in *Figure 2a* (chemical shifts in ppm from tetramethylsilane): (a) $\underline{C}H_2OH$; (b) $\underline{C}HCH_2OH$; (c) $\underline{C}HCH_3$

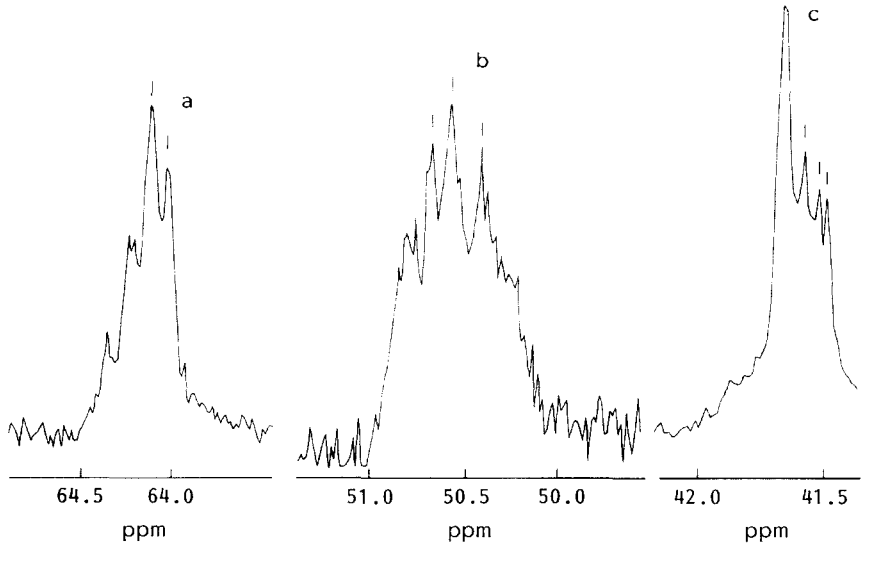

Figure 4 Expanded regions of the ^{13}C n.m.r. spectrum in *Figure 2a* (chemical shifts in ppm from tetramethylsilane): (a) $\underline{C}H_2OH$; (b) $\underline{C}HCH_2OH$; (c) $\underline{C}HCH_3$

4a). This remark is valid for the four $\underline{C}H$ signals (near 50.5 ppm), leading to peak splitting in the case of the random copolymer (*Figures 3b* and *4b*). The methylene carbon atom of the HMT unit shows the same phenomenon (*Figures 2a* and *2b*). Moreover, additional peaks are present in the spectra of the random copolymers (39.57 and 39.58 ppm, 34.82 and 34.70 ppm). These peaks, assigned respectively to $\underline{C}H_2$ (MT) and $\underline{C}H_2$ (HMT) are present for different HMT/MT compositions and their intensities are sensitive to the copolymer composition; they can be attributed to the effects of neighbouring units. Furthermore, these random copolymers are probably composed of large sequences of MT units and short sequences of HMT units because of the monomer feed composition and the different reactivities of the monomers. Comparison between the different copolymer spectra allows us to conclude that HMT-30/MT-70 and HMT-15/MT-70/HMT-15 have the block structure and demonstrate living character in this copolymerization.

Table 2 Methylthiirane polymerizations in protic and aprotic media (monomer content 0.5×10^{-2} mol; 2 ml solvent; 20°C)

	First sequence (DMF)				First sequence (DMF/ethanol)			Second sequence		
Sample	Initiator content ($\times 10^{-5}$ mol)	$DP_{n,th}$[c]	$DP_{n,obs}$[d]	I_1[e]	EtOH concentration ($\times 10^{-3}$ mol l^{-1})	$DP_{n,obs}$	I_2	$DP_{n,obs}$	I_3	$DP_{n,th}$
173[a]	0.70	715	620		0			690	2.3	1240
181	0.36	1390	1340	1.7	0			790	2.3	2680
177	0.75	660	606	2.5	0.17	490	2.6	740	2.8	1220
181-3	0.40	1250	1130	1.7	0.85	670	1.8	925	2.2	2260
176 bis	0.45	1110	1060	2.1	1.70	770	1.8	990	2.2	2120
178	0.39	1280	1190	2.1	3.4	730	1.6	925	1.9	2380
180	0.48	1040	969	1.9	5.1	690	1.6	1030	1.7	1940
181	0.36	1390	1340	1.7	8.5	445	1.7	956	1.8	2680
176	0.5	1000	970	2.1	1.7	555	1.6	635	2.2	1940

[a] In 50/50 DMF/THF
[b] With methanol instead of ethanol
[c] The average degree of polymerization calculated for a living polymerization
[d] The average degree of polymerization obtained by s.e.c.
[e] The polydispersity index

Termination reaction in the synthesis of MT/MT block polymers in DMF

Obtaining block copolymers with a hydroxylated monomer was an unexpected result, all the more because the synthesis of MT block polymers in identical conditions has failed. In the MT polymerization in DMF with an $[M_0]/[I_0]$ ratio of over 600 (for complete consumption of the monomer before the end of the polymerization), the DP_n values obtained with a first sequence of MT are in accordance with the calculated values for polymerization without termination (*Table 2*). However, by addition of a second sequence of MT no increase in the DP_n values could be obtained. A decrease was then observed while the polymer yield was increasing (*Table 2* and *Figure 6*). U.v. measurement of the active centre concentrations at the end of the polymerization in DMF after reaction with 1-chloromethylnaphthalene showed a fast disappearance of these active centres; this effect was slower in a less polar medium (50/50 DMF/THF; *Table 3*).

To explain these results, we have assumed that a fast 'killing' reaction occurs just at the end of the propagation step followed by a reinitiation step. Termination reactions in anionic MT polymerizations with quaternary ammonium salt initiators in THF have been previously described[11]. Tersac *et al.*[11] have observed a very slow nucleophilic substitution of thiolate ions on quaternary ammonium ions which takes place long after the end of the propagation step. Several facts suggested to these authors that another reaction was occurring, leading to different and less active end-groups, but this second reaction was not identified. In our polymerization study in THF[12], we almost certainly observed the second termination reaction. Owing to the very high nucleophilicity in DMF of the thiolates often used in organic chemistry[13], three termination reactions must be considered in the polymerizations run in this medium.

1. The accelerated reaction of thiolates on quaternary ammonium ions which, on the contrary, should be slowed down in the polar DMF owing to the partial neutralization of charges in the transition state of the reaction[14]

$$\sim\!\!\sim S^- + N^+(CH_3)_4 \rightarrow \sim\!\!\sim SCH_3 + N(CH_3)_3$$

This reaction does not lead to anionic species which could give reinitiation after addition of a second sequence.

2. The reaction of the very nucleophilic thiolate ion in the polar DMF on DMF itself, affording thioformate end-groups and dimethylamide anions which can efficiently reinitiate the polymerization[15] after the addition of a second sequence of MT

$$\sim\!\!\sim S^- + H\text{–}\underset{\displaystyle N(CH_3)_2}{\overset{\displaystyle |}{C}}\!=O \rightarrow \sim\!\!\sim SCHO + \underset{\displaystyle \downarrow MT\ \text{polymers}}{N(CH_3)_2^-}$$

A reaction of this type, acylation of a thiol, has been observed with esters to give thioesters[16], but amides which are less reactive are not customarily used; nevertheless, DMF has been used as a formylating agent in the presence of arylsulfonyl chlorides[17]. We propose that the high nucleophilicity of thiolate ions in DMF as well as the large excess of DMF may explain the unusual formylation of thiolates.

3. The reaction of thiolate ions with small amounts of water which may have been introduced in our experimental conditions, affording thiol end-groups

Table 3 U.v. determination of naphthylmethyl end-group concentrations ($\lambda_{max} = 285$ nm in CH_2Cl_2 for methylthiirane polymerizations

	DMF			DMF/THF (50/50)		
t^a (min)	1	2	3	4	5	6
d^b	0.310	0.250	0.0100	0.380	0.395	0.300

[a] The time between addition of initiator and addition of chloromethylnaphthalene
[b] The optical density obtained from a 50 mg sample of polymer (for chloromethylnaphthalene, $\lambda_{max} = 285$ nm, $\varepsilon = 7950$ in CH_2Cl_2). The theoretical value for a sample without deactivation is 0.530

and hydroxy anions which can give rise to polymerization[15] after the addition of a second sequence of MT

$$\sim\!\!\sim S^- + H_2O \rightarrow \sim\!\!\sim SH + OH^-$$
$$\downarrow MT$$
$$\text{polymers}$$

However, this reaction would be completely avoided in the extreme conditions of purity used by Tersac *et al.* Characterization of the end-groups of the polymers would allow the identification of the deactivation process. The protons of thiol or thioformate end-groups cannot be detected in ^1H n.m.r. spectra owing to the high average molecular weights obtained. Thus, in order to isolate and identify the end-groups we need to react large amounts of a tetramethylammonium thiolate such as dodecanethiolate with DMF; this reaction is being studied at the present time in our laboratory but the practical application is very difficult because the solubility of the dodecanethiolate in DMF is very poor.

MT polymerization in the presence of ethanol

Even if we cannot at the present time accurately identify the termination reaction, it is necessary at this point to explain why this reaction occurs in the MT polymerization and not in the HMT polymerization. Our previous study on mercaptomethylthiirane (MMT) polymerization[4] clearly established the preservation of the active centres for 48 h in the same experimental conditions as used for the MT polymerization. The numerous chain transfers observed during the course of the MMT polymerization probably protected the active centres from being 'killed'. Though no chain transfer could be observed with HMT on account of the different pK_a values of thiols and alcohols, the decrease in the HMT polymerization rate with respect to the MT polymerization rate was attributed to hydroxy group 'assistance'[4]. In order to demonstrate such an 'assistance' of the hydroxy groups in the block HMT/MT copolymer synthesis, we carried out MT polymerizations in the presence of small amounts of absolute ethanol. The effect of adding an alcohol to the anionic polymerization of epoxides has been considered[18]; if the added alcohol is less acidic than the polymer alcohol a broadening of the molecular weight distribution might be expected. The first use of alcoholate initiators in the presence of alcohols in the MT polymerization gave only low molecular weight polymers[19].

Our results are reported in *Table 2*. It appears that the DP_n values obtained in the presence of ethanol are lower than those obtained in pure DMF (*Figure 7*), proving the occurrence of some termination reactions that result in some proton exchanges between thiolates and hydroxy groups; but the addition of a second sequence of monomer induces an increase in the DP_n values (*Figure 8*) which was never obtained in pure DMF, proving the living character of some thiolate end-groups. The u.v. determination of naphthylmethyl end-groups (*Table 3*) shows that the deactivation is very fast in DMF but that it slows down in a less polar medium; the u.v. determination of end-groups also confirms the better preservation of thiolate end-groups in a protic medium (*Table 4*). It would be interesting to obtain a relationship between the amounts of added ethanol and the molecular weight

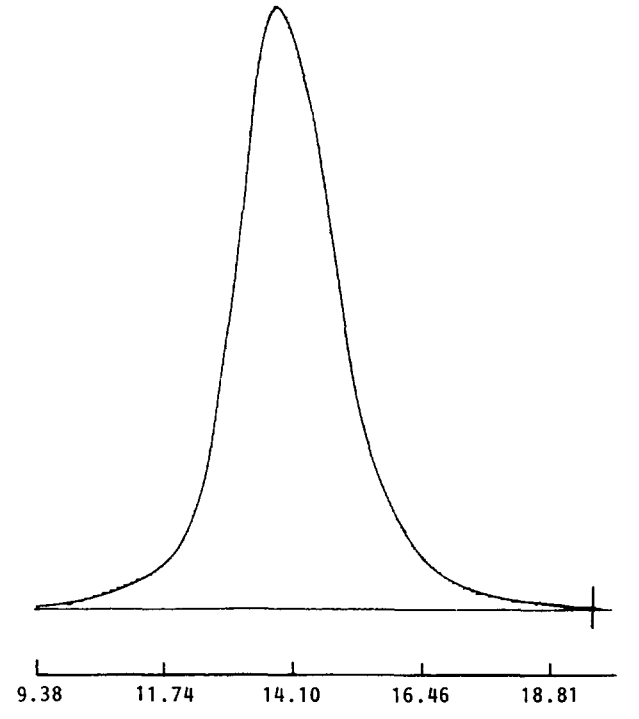

Figure 5 S.e.c. curve for a 15/85 HMT/MT statistical copolymer (elution volume in ml)

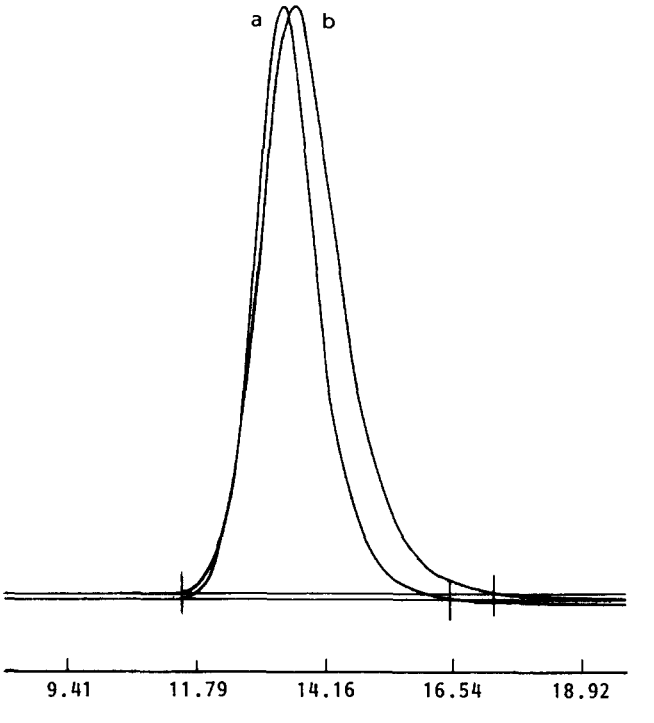

Figure 6 S.e.c. curves for poly(MT) sample 181 prepared in pure DMF: (a) first sequence; (b) after addition of a second sequence (elution volume in ml)

distribution. Mathematical procedures have been developed to deal with either the study of impurity transfer (with instantaneous initiation and reinitiation)[20] or impurity termination ($[\text{impurity}]/[I_0] < 1$)[21] in anionic polymerizations. Our experiment is not related to any of these theoretical treatments as the impurity concentration is larger than the initiator concentration; in the case of transfer the initiation and reinitiation reactions have different rates. Furthermore, the hydroxy group slows

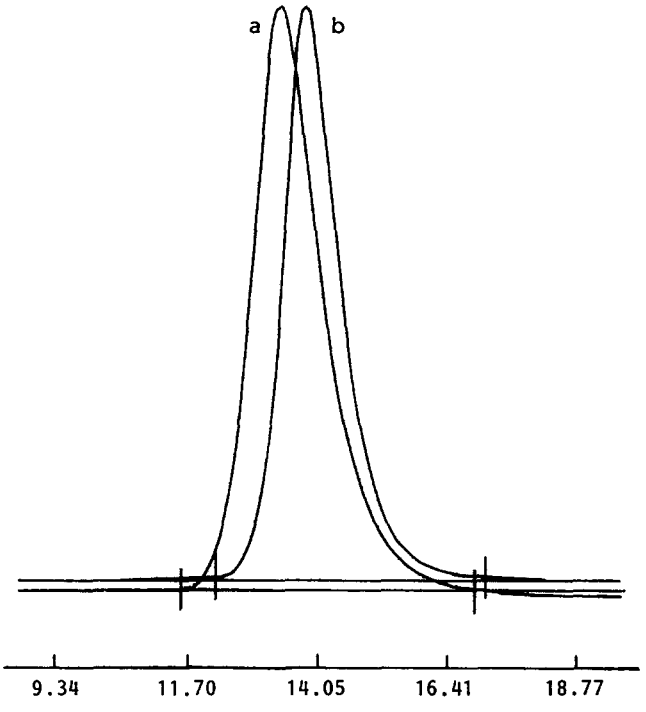

Figure 7 S.e.c. curves for poly(MT) sample 180 first sequence: (a) in pure DMF; (b) in DMF/ethanol (elution volume in ml)

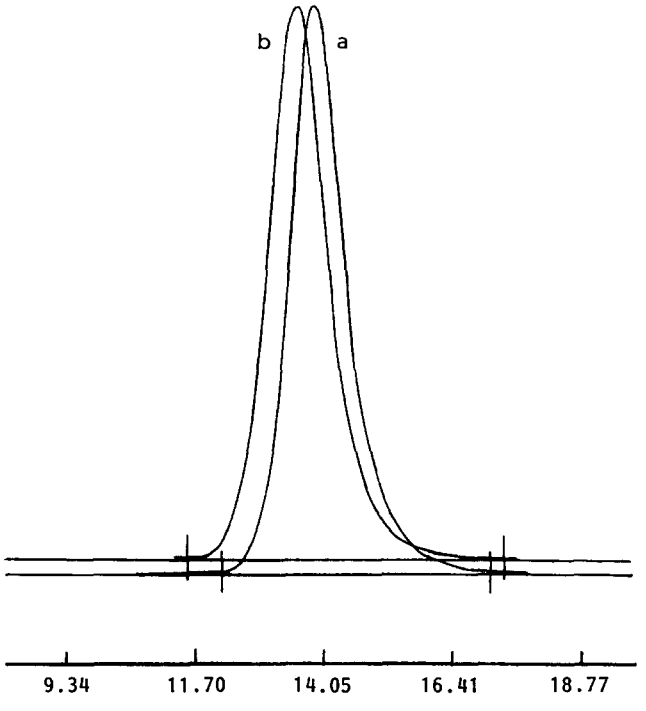

Figure 8 S.e.c. curves for poly(MT) sample 180: (a) first sequence in DMF/ethanol; (b) second sequence in DMF/ethanol (elution volume in ml)

down the polymerization and k_p is not a constant for all measurements. Thus, at the present time the molecular weight distribution cannot be accurately related to the ethanol concentration. The setting up of such a relationship would need a complete kinetic study of the MT polymerization in DMF and in DMF/ethanol mixtures.

Nevertheless, the results described here exhibit clearly the assistance of hydroxy groups in protecting some thiolate end-groups against deactivation. Owing to the respective entropies of both reactions, i.e. internal and bimolecular proton exchange, we can easily understand now why side-chain hydroxy groups of poly(HMT) growing chains (or side-chain thiol groups of poly(MMT) growing chains) are more efficient than the ethanol hydroxy groups.

Table 4 U.v. determination of naphthylmethyl end-group concentrations in protic and aprotic media ($\lambda_{max}=285$ nm in CH_2Cl_2) for methylthiirane polymerizations (polymerization time 10 min; 2 ml solvent; 20°C)

Sample	Initiator content ($\times 10^{-5}$ mol)	EtOH in DMF ($\times 10^{-3}$ mol)	d (50 mg)	d_{th}[c] (50 mg)
173-2[a]	0.70	0	0.060	0.750
181-2	0.36	0	0	0.390
177	0.75	0.17	0.387	0.805
181-3	0.40	0.85	0.233	0.430
176 bis	0.45	1.7	0.358	0.485
178-1	0.39	0	0.150	0.420
178-4	0.39	3.4	0.380	0.420
180-1	0.48	0	0	0.515
180-4	0.48	5.1	0.372	0.515
181-5	0.36	8.5	0.476	0.390
176[b]	0.50	1.7	0.478	0.537

[a] In 50/50 DMF/THF
[b] With methanol instead of ethanol
[c] The optical density calculated for a living polymerization

Broad molecular weight distributions are always obtained with TMTB in DMF. The polymerization rates are probably higher than the initiation rates. A broadening of the molecular weight distribution may be expected in the presence of ethanol. The polydispersity indices reported in *Table 2* are nearly identical in protic and aprotic solvents. A broadening of the molecular weight distribution is not observed in protic solvents. We meet here another effect of ethanol upon polymerization. The equilibrium

$$\sim\!\!\sim S^- + EtOH \rightleftharpoons \sim\!\!\sim SH + EtO^-$$

slows down the polymerization rate so that the initiation rate becomes higher and better values of the polydispersity indices are then obtained.

CONCLUSIONS

Anionic polymerizations of thiiranes are usually carried out in aprotic media in order to avoid termination reactions that occur through chain transfer. However, we have demonstrated in this paper that a protic solvent can display an ambivalent behaviour and can also protect some active centre against deactivation. The occurrence of either behaviour is probably related to the protic solvent concentration, but an accurate connection needs a very full kinetic study of the reaction. This will be considered in future work.

Nevertheless, the present study explains why HMT/MT block copolymers can be synthesized when MT block polymers cannot. In the case of HMT the preventive behaviour of the hydroxy groups leads to the formation of diblock and triblock copolymers; these copolymers have been clearly characterized by their ^{13}C n.m.r. spectra, which are very different from those of statistical copolymers.

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