Functional polythiiranes: 1. Comparative study of the anionic polymerization of mercaptomethylthiirane and hydroxymethylthiirane initiated by quaternary ammonium dithiobenzoate

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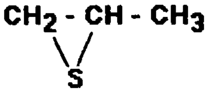
The occurrence of chain transfers has been studied during the anionic polymerization of protic thiiranes in dimethylformamide initiated by tetramethylammonium dithiobenzoate. Results on polymer molecular weights and ^{13}C nuclear magnetic resonance spectra as well as polymerization rates have been used in a comparative study of hydroxymethylthiirane and mercaptomethylthiirane polymerizations. We have demonstrated that chain transfers occur significantly with mercaptomethylthiirane while they may be considered as non-existent with hydroxymethylthiirane. This is due to the equilibrium between 'thiolate' and 'olate' ions being more favourable to thiolate because of the relative acidity of thiols and alcohols.

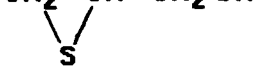
(Keywords: thiirane anionic polymerization; chain transfers; hydroxymethylthiirane; mercaptomethylthiirane; (benzylthio)-methylthiirane)

INTRODUCTION

Many works have been devoted to the anionic polymerization of thiiranes[1] and living polymers can be obtained using numerous nucleophilic and basic initiators. These initiators and the active sites formed are extremely reactive and anionic living polymerization requires high purity and aprotic conditions to avoid termination and transfer reactions[2]. Accordingly the synthesis of functional polymers by direct anionic polymerization of functional monomers is rarely described.

We have previously[3,4] reported on a new type of initiator for thiirane anionic polymerization, namely the crystallized, stable quaternary ammonium salts of carbothioic and dithioic acids. They are much more nucleophilic than basic and allow direct polymerization and copolymerization of methylthiirane (MT) 1 and unprotected 2-(hydroxymethyl)thiirane (HMT)[5] 2:


1 MT


2 HMT

The homo- and copolymer structures have been well established[5] but the occurrence of transfers on hydroxyl groups was difficult to study because of the very low solubility of the homopolymer and copolymers with high HMT contents. Anionic polymerizations of MT in the presence of water or alcohols are known to give only low-molecular-weight polymers[1]. Our previous results[5] seemed to confirm that chain transfers to hydroxyl groups act as a limiting factor for molecular weights.

In the present paper, we report on supplementary results about poly(HMT) molecular weights and on a comparative study of the polymerization of HMT and 2-(mercaptomethyl)thiirane (MMT) 3. The very different behaviours observed for each monomer have led us to conclude that there is a slight occurrence of chain transfer in HMT polymerization, while chain transfer is largely predominant in MMT polymerization. We have also studied the polymerization of (benzylthio)methylthiirane (BMT) 4, which occurs without chain transfer:


3 MMT


4 BMT

EXPERIMENTAL

Spectra were recorded on a Varian EM 390 spectrometer for ^{1}H n.m.r. and on a Brucker AC 300 spectrometer for ^{13}C n.m.r. at 75 MHz. Size exclusion chromatography (s.e.c.) was performed on Styragel columns (Waters) in tetrahydrofuran as solvent. Molecular weights are reported as the molecular weights of equivalent elution

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volume polystyrene. Light-scattering measurements have been done on a Malvern 4700 apparatus.

Tetramethylammonium dithiobenzoate was prepared as previously reported[3]. Monomers were obtained according to known methods: HMT from 3-mercaptopropane-1,2-diol[6], MMT from 2,3-dimercaptopropanol[7] and MT from propylene oxide[8], stored at −30°C and distilled just before use. BMT was obtained according to ref. 9, from MMT and benzyl bromide in the presence of 1,8-diazabicyclo[5.4.0.]undec-7-ene (DBU), with a yield of 95%. BMT decomposes during distillation; E(5 mbar) = 150°C. So, just after filtration on a silica column, the crude product was analysed by h.p.l.c. Its purity was correct and BMT was then polymerized.

Polymerizations

Polymerizations were carried out under nitrogen in small Erlenmeyer flasks equipped with a magnetic stirring bar and a septum: initiator in anhydrous spectroscopic-grade dimethylformamide (DMF) was introduced. These solutions were repeatedly degassed and flushed with nitrogen. Then the monomer(s) in DMF solution was added with a syringe. If necessary, temperature was maintained constant by use of a thermostatic bath during the reaction time.

Then for HMT, MT and BMT polymerizations and copolymerization an excess of benzyl chloride was added. For MMT polymerization a slight excess (10%) of sodium methylate was added and the mixture was left for 2 h. Benzyl chloride in excess is then added and the mixture was left for 12 h. We have verified that residual MMT does not give polymers in these conditions: only low-molecular-weight products were obtained.

Polymers were isolated after precipitation in a suitable solvent, MeOH for poly(MT) and ether for poly(HMT), copoly(HMT/MT) and poly(MMT), and purified by dissolution/reprecipitation in solvents. Polymers were then dried under vacuum.

The analysis for protected poly(mercaptomethylthiirane) is as follows. ^{1}H n.m.r. ($CDCl_3$, δ, TMS): 2.60–3.10 (m, 5H), 3.75 (m, 2H, CH_2-ϕ), 7.40 (5H, aromatic protons).

Acylations

Poly(HMT) and copoly(HMT/MT) were dissolved (0.25 g) in DMF in a dried flask: acetyl chloride or benzoyl chloride (in excess of three-fold the stoichiometric amount) was added and also poly(vinylpyridine) (PVP). The suspensions are stirred for 48 h at room temperature for acetyl chloride and refluxing for benzoyl chloride. At the end of the reaction PVP is filtered off and solutions were precipitated in methanol; polymers were purified by dissolution/precipitation in suitable solvents.

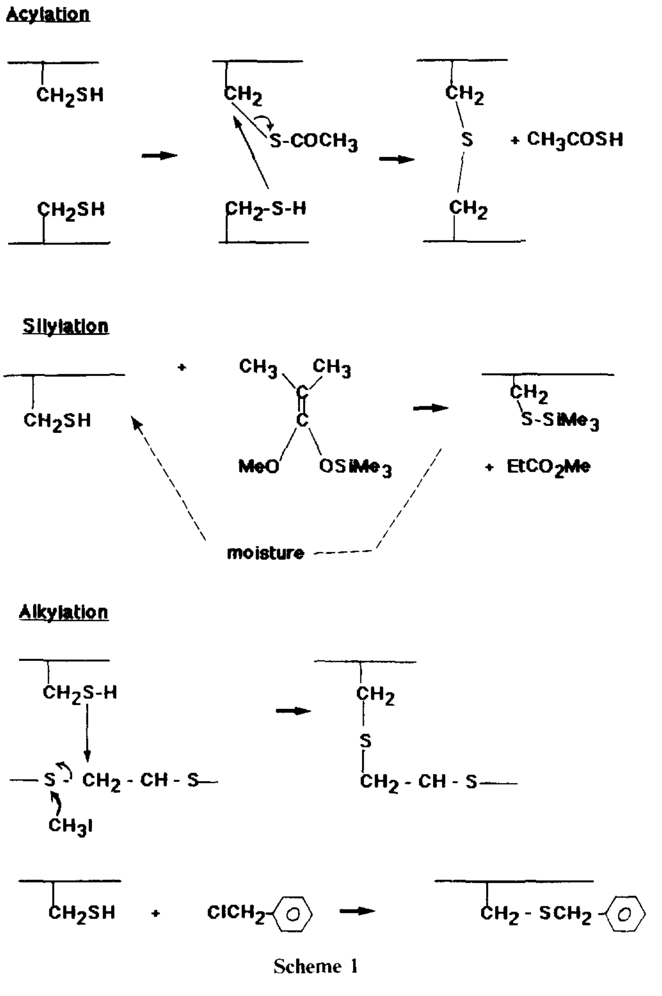
Polymerization rates

Polymerization rates were evaluated by ^{1}H n.m.r. spectroscopy in DMF-d_7. The n.m.r. tubes were prepared in a glove-box, filled with nitrogen: 0.002 mol monomer and 0.3 ml of DMF. Initiator (0.5×10^{-5} mol in 0.1 ml DMF-d_7) was then added through a septum just before spectrum recording; the reaction was monitored by the decrease of the characteristic thiirane doublet at 2.3 ppm.

RESULTS AND DISCUSSION

In DMF solution, tetramethylammonium dithiobenzoate also promotes homopolymerization of MMT but, on contact with air, crosslinking rapidly occurred, leading to insoluble products. It was therefore necessary to protect thiol functions at the end of polymerization in order to prevent coupling reactions through thiol oxidation.

Acetylation by means of acetyl chloride in the presence of poly(vinylpyridine) also gives crosslinks, probably by reaction between thiol and first-formed thioacetate groups (*Scheme 1*). 1-Methoxy-2-methyl-1-trimethylsiloxypropene is a suitable reagent for thiol protection[10], leading to trimethylsilyl sulphides (*Scheme 1*). The silylation of poly(MMT) has given a fraction whose ^{1}H n.m.r. spectrum was in accordance with the expected structure, but a large amount of polymer was crosslinked. The protective reagent is bulky and steric hindrance has probably prevented protection of some thiol groups. Moreover, trimethylsilyl sulphides are readily hydrolysed by atmospheric moisture. Alkylation with methyl iodide (in the presence of sodium methoxide) exclusively gives crosslinked poly(MMT). Alkylation of the polythioether backbone, simultaneously with the thiol group, has certainly occurred, as it was observed by other authors[11] on poly(thio-1-(N,N-dimethylaminoethyl)-ethylene). Alkylation with benzyl chloride (in the presence of sodium methoxide) was finally found to be the best method, and we have obtained benzylated substituted samples that are soluble in most organic solvents.



Scheme 1

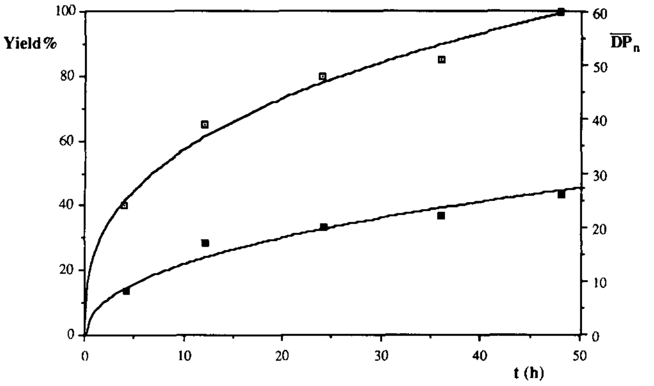


Figure 1 Time dependence of MMT polymerization

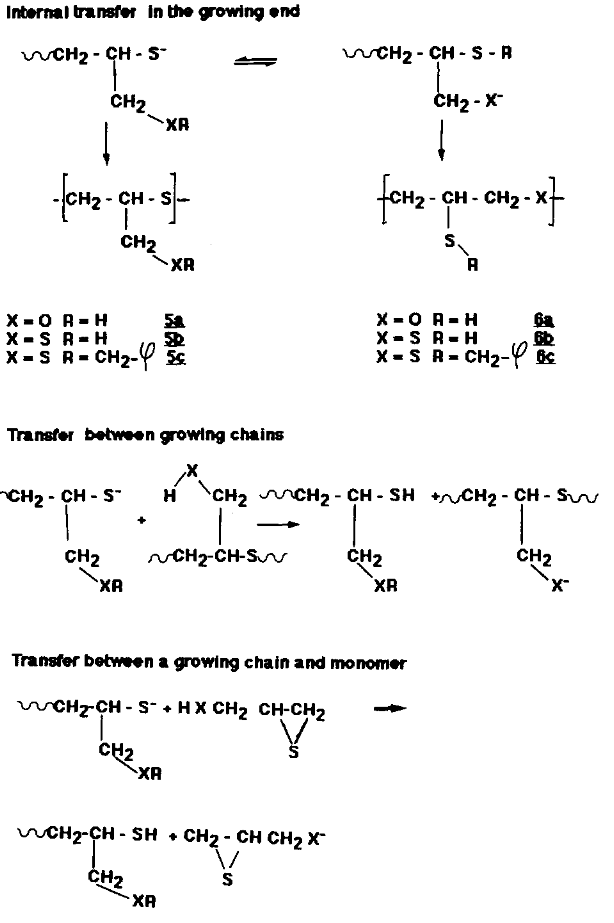
The polymerization reactions of both HMT and MMT monomers have been compared on three points: polymerization rates; molecular weights and $\overline{DP}_n$; and ^{13}C n.m.r. spectra of polymers.

MMT polymerization is slow (*Figure 1*) and quantitative yields are obtained only after 48 h. The yields and the molecular weights increase with time (*Figure 1*). These results are characteristic of an apparently living polymerization. The observed number-average degrees of polymerization are always lower than the theoretical ones ($\overline{DP}_n = 200$) and remain as low as 26 for a quantitative reaction. The polydispersity index is very high at the end of the polymerization, $\bar{M}_w/\bar{M}_n = 33$. This indicates very frequent proton transfers between the growing chains or between a growing chain and monomer, inducing terminations and ramifications (*Scheme 2*).

On the other hand, HMT polymerization is very fast under the same conditions as observed by ^{1}H n.m.r. spectroscopy: the characteristic thiirane doublet at 2.3 ppm disappears completely within 2 min. In identical experimental conditions the disappearance of the same doublet for MT is over in less than 1 min. It is not possible to measure the poly(HMT) molecular weights directly because of their low solubility in common solvents. The polymers have been processed by acetylation with acetyl chloride or benzoyl chloride. No degradation occurs during this process as applied to a 12/88% HMT/MT copolymer modification (*Table 1*). The molecular-weight determinations on the modified polymers and HMT/MT copolymers show that observed $\overline{DP}_n$ are in the same range as the calculated ones (*Table 1*). For HMT polymers the differences between calculated $\overline{DP}_n$ and observed $\overline{DP}_n$ are smaller than for MMT polymers. The accuracy of these results is certainly limited by the use of polystyrene standards in the g.p.c. determination: these standards are not really adequate for our macromolecules. This is particularly evident in the 50/50% HMT/MT copolymer case: the direct measurement gives a more important deviation than the value obtained on a modified polymer. The more HMT the copolymers contain, the more inadequate the standards are. This has probably given in our previous study[5] an apparent molecular weight decrease with the increase in hydroxyl monomer content.

The n.m.r. studies have also confirmed the different behaviour of both HMT and MMT monomers. Internal chain transfers in HMT polymerization would have given ether units in the polymer in *Scheme 2* (**6a**). ^{13}C chemical shifts for this rearranged unit and for unit **5a** in poly(HMT) have been calculated according to ref. 12. The observed values (in pyridine-d_5, ppm), i.e. 33.11 (CH_2), 48.94 (CH) and 61.78 (CH_2OH), are consistent with the calculated ones for **5a**, i.e. 33.90, 52.40 and 70.50 ppm, except for the hydroxymethyl carbon, for which numerous hydrogen-bonding abilities are not taken into account in the evaluation. No supplementary signal is found to correlate with the postulated isomerized structure **6a**. It would have given peaks near 77.30 ppm (unit **6a**) or 79.90 ppm (units **5a** + **6a**) for carbons bonded with oxygen atoms. The absence of unit **6a** may also result from important rate reduction of the propagation step: the 'olate' anion is a much less active centre than the 'thiolate' ion towards thiirane polymerization. So, we should have observed an important decrease of the polymerization rate and even a cessation of the polymerization reaction.

On the contrary, the protected poly(MMT) n.m.r. spectrum shows evidence for transferred structures. In



Scheme 2

Table 1 Number-average degree of polymerization for poly(HMT) and copoly(HMT/MT)

HMT (%)	$\overline{DP}_n$ (calc)	$\overline{DP}_n$ (obs)	$\overline{DP}_n$ (obs) after acylation
100	45		35[a]
100	40		100[a]
100	105		60[b]
75	100		65[b]
50	100	23	57[b]
10	100	160	330[a] 156[b]

[a] By acetyl chloride
[b] By benzoyl chloride

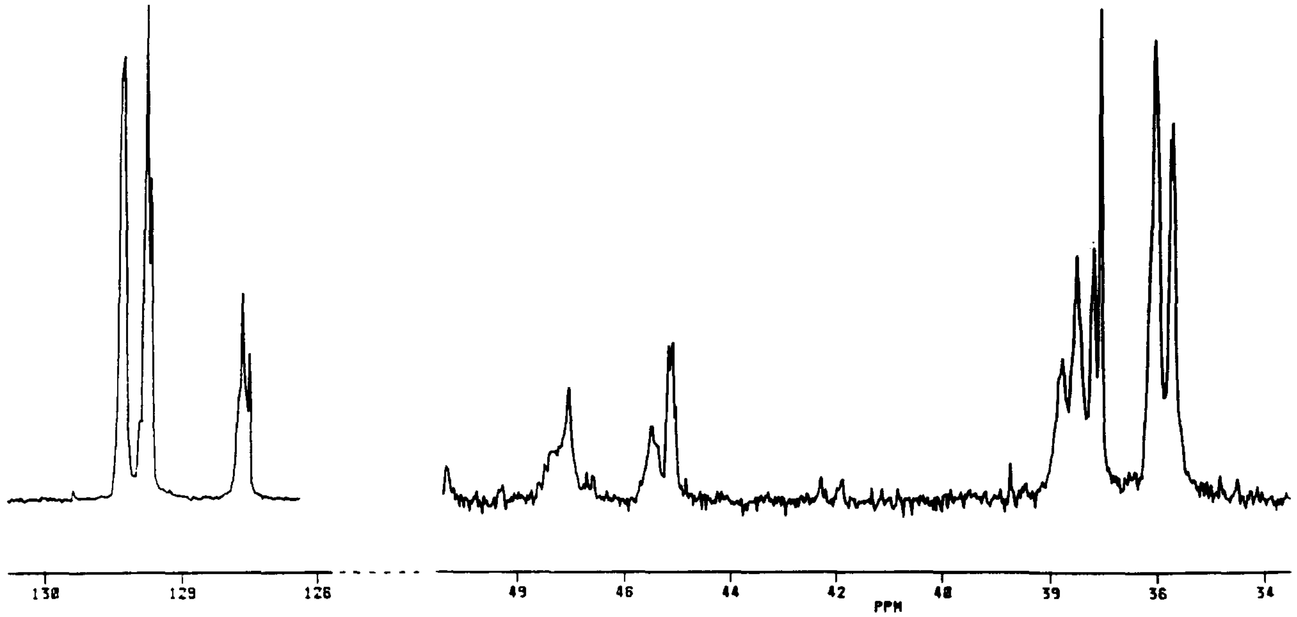


Figure 2 ^{13}C n.m.r. spectrum ($CDCl_3$): poly(MMT) benzylated after polymerization

the ^1H n.m.r. spectrum the benzylic proton gives a very broad signal, nearly a triplet. The ^{13}C n.m.r. spectrum (*Figure 2*) presents numerous signals that are difficult to analyse accurately, owing to the different structures that result from chain transfers (see *Scheme 2*). In order to attribute some of these signals, we have synthesized and polymerized (benzylthio)methylthiirane (BMT) **4**.

The behaviour of BMT towards polymerization with tetramethylammonium dithiobenzoate is similar to that of MT. Polymerization rate is high: the ^1H n.m.r. thiirane doublet at 2.3 ppm has completely disappeared after 1 min. The ^1H n.m.r. spectrum of poly(BMT) is identical to that of protected poly(MMT) but the benzylic proton now gives a sharp singlet. The very simple high-resolution ^{13}C n.m.r. spectrum (*Figure 3*) clearly proves the sole presence of units **5c**. The chemical shifts (ppm) for carbon atoms are observed at: 35.87 and 36.03 for the methylene carbons; 37.21 for the benzyl methylene carbon; 46.97 and 47.03 for the methine carbon; and 127.13, 128.57, 128.95 and 138.08 for aromatic carbons. The chemical shift of the benzylic carbon in **5c** is evaluated as above according to ref. 12 at 37.30 ppm; the chemical shift of the benzylic carbon in the isomerized structure **6c** is calculated similarly at 34.80 ppm. This spectrum also shows a diad effect for methine carbon: this was previously observed by other authors[13]. The signals of poly(BMT) spectrum (*Figure 3*) may be identified in the protected poly(MMT) spectrum (*Figure 2*). There, number-average molecular weights of poly(BMT) obtained by means of g.p.c. are also lower than those calculated by the ratio of concentrations of monomer to initiator. The difference between theoretical and experimental values, however, is smaller than for poly(MMT): calculated values $\bar{M}_n = 25\,000$, $\overline{DP}_n = 125$; experimental values $\bar{M}_n = 7500$, $\overline{DP}_n = 40$, $\bar{M}_w = 13\,300$. This reduction of molecular weights cannot be attributed to the formation of inactive species with impurities since the whole of the monomer has reacted (as for HMT polymerization). A measure of the molecular weight for a poly(BMT) sample (calculated values $\bar{M}_n = 18\,000$, $\overline{DP}_n = 90$) was realized by g.p.c. and also by light scattering (LS). The results clearly show that g.p.c. determinations give a lower value than light scattering: g.p.c., $\bar{M}_w = 5300$: LS, $\bar{M}_w = 15\,000$. Thus standards used in g.p.c. are not very convenient for our macromolecules, as we have assumed above.

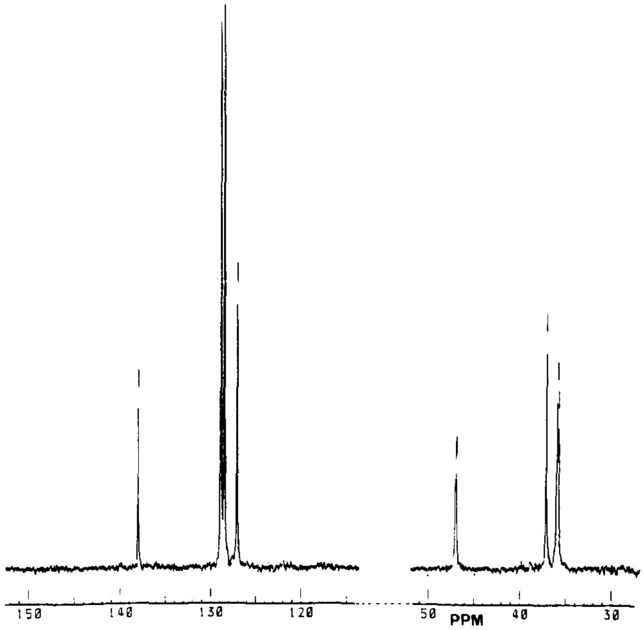
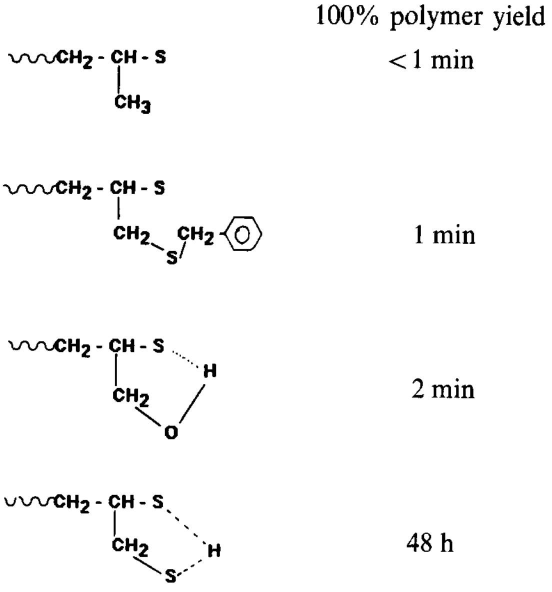


Figure 3 ^{13}C n.m.r. spectrum ($CDCl_3$): poly(BMT)

Chain transfers appear particularly evident during MMT polymerization and correlate with a reduction of the polymerization rate. Because of easy proton transfer, the anionic charge is delocalized on both sulphur atoms and the nucleophilicity of both thiolate anions is then reduced (*Scheme 3*). Consequently the polymerization rate is also reduced. If the anionic charge is well localized on one sulphur atom as in BMT and MT. The high nucleophilicity of thiolate anion in polar DMF accounts for the fast reaction and no transfer occurs. According to the high polymerization rate observed in HMT polymerization, we can now conclude that the anionic



Scheme 3

charge is very slightly delocalized in HMT: thus only few transfers are likely to occur in HMT polymerization.

In order to obtain supplementary proof of the almost complete absence of transfer in HMT polymerization, we have carried out MT polymerization under two different conditions in the same experiment: with pure DMF and in the presence of 50 mol% ethanol. A lower value for number-average molecular weight is effectively observed in the presence of ethanol, i.e. $\bar{M}_n = 101\,600$ (in pure DMF $\bar{M}_n = 152\,200$), but the chain transfer constant calculated according to ref. 14 is small, 1.5×10^{-3}. This reaction is not a perfect living polymerization owing to the experimental conditions of this anionic polymerization, but certainly has an important living character.

CONCLUSIONS

This study has clearly shown the evidence of transfers in the polymerization of MMT. For the other monomers studied, HMT, MT and BMT, few transfers occur during the polymerization. Different factors help chain growth in the polymerization of a protic monomer such as HMT with dithiobenzoic acid quaternary ammonium salts in DMF. First, these salts are weak bases: they remain anionic even in protic medium and retain their high nucleophilicity assisted by the polar DMF. This is not realized for usual anionic initiators, which are often very strong bases and are destroyed in protic medium. Second, the acidity of the hydroxyl group is weaker than that of the thiol group and the equilibrium is shifted to the thiolate as previously reported in molecular chemistry[15]. Both facts account for the higher rates for initiation and growth steps than for the deactivation reaction. On the contrary, if an equilibrium can set up between two anions of equal stability, the rates are lowered and chain transfers occur during the polymerization, as was noted with MMT.

At the present time, investigations are in progress to synthesize HMT/MT block copolymers, proving the conservation of most of the active sites in HMT polymerization, and to study the polymerization of other functional thiiranes.

ACKNOWLEDGEMENTS

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