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A New Initiator System for the Living Thiiranes Ring-Opening Polymerization: A Way toward Star-Shaped Polythiiranes

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Star-shaped polymers may be prepared by using multifunctional initiators. However, multifunctional initiators are exotic compounds, and only a few star-shaped polymers were obtained in such a way. Representative examples are three-arm star poly(ethylene oxide)s from trimethylolpropane,[1] three-arm star polymers of isobutyl vinyl ether from tris(trifluoroacetate) type initiators,[2] and eight-arm polyisobutylene from calix[8]arenes.[3] Living processes were involved in these syntheses to control arm molecular weight and obtain narrow dispersity.

Thiolate ions are well-known initiators in thiirane polymerization,[4,5] and trithiols and tetrathiols such as 1,2,3-trimercaptopropane, trimethylolpropane tris(3-mercaptopropionate), and pentaerythritol tetrakis(3-mercaptopropionate) are readily accessible which would afford three- and four-arm polythiiranes if their salts were used as initiators. Star-shaped polythiiranes bearing thiol as end groups could be used in the synthesis of previously unknown sulfur-rich networks.

Under usual anhydrous (and aprotic) anionic ring-opening polymerization conditions, it has been demonstrated that thiirane polymerization is not a living process because active center deactivation occurs rapidly at the end of the polymerization. We have established that livingness character may appear when thiolate ions are less reactive through bonding with weakly acidic hydrogens.[6,7] Sulfur atoms are generally not involved in strong hydrogen bonding, but intramolecular H-bonds between S atoms and hydroxyl groups may be important, particularly with thiolate ions. For example, the presence of weak intramolecular H-bonding has even been assumed to explain the fine coupling in ^{1}H NMR spectra of 2,4,6-trimercapto-1,3,5-trithianes in which H atom acidity is quite low.[8] These observations were emphasized by the synthesis of block copolymers comprising unprotected poly(hydroxymethylthiirane) as a first sequence and poly(methylthiirane) as a second sequence;[7] the inverse order of polymerization did not give block copolymers. Intramolecular hydrogen bonding between the hydroxyl group and thiolate ion was assumed to stabilize the active center, thus lowering the thiolate nucleophilicity to avoid rapid deactivation.

Then, we have assumed that a thiolate/thiol system could afford a similar active center stabilization through rapid proton exchange to produce living anionic ring opening polymerization of thiiranes. We have chosen 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base to provide the thiol/thiolate equilibrium in strictly stoichiometric amounts as this amine initiates thiirane polymerization. Some preliminary attempts to prepare star polymers from the polythiols/DBU initatiors were successful, but in order to control accurately the size and the branching of the stars, a more detailed study of a monofunctional initiator system was needed. We report here some results concerning the polymerization of methylthiirane (propylene sulfide) initiated by hexanethiol/DBU, methylthioglycolate/DBU, cyclohexanethiol/DBU, 1,6-hexanedithiol/DBU, 3-mercapto-1,2-propanediol/DBU, and data which confirm the living character of these polymerizations.

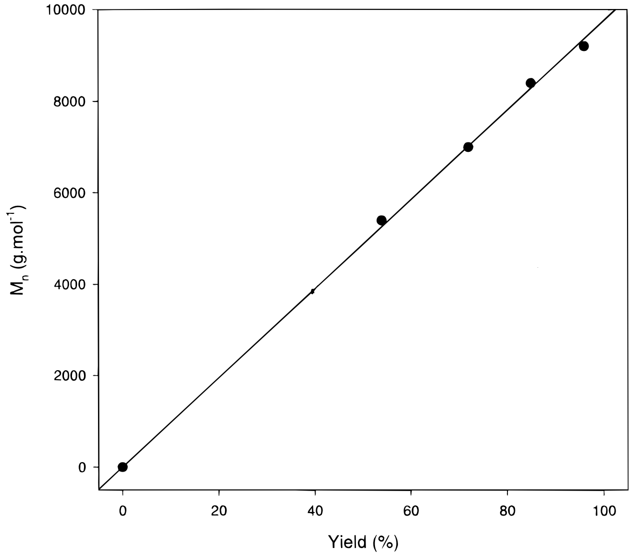
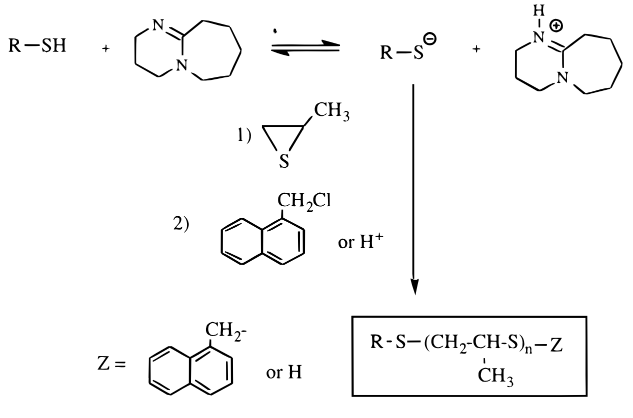


Figure 1. Evolution of the average molecular weight (obtained by SEC in polystyrene equivalent) with the polymerization yield. The solid line represents the linear regression (r^2 = 0.9994).

The system used to initiate the polymerization is a thiol and DBU in stoichiometric amounts which give an acid−base equilibrium:



An evaluation of the equilibrium constant thiol/thiolate was attempted for hexanethiol by ^{1}H NMR in d_6-DMF. In the presence of DBU, the complete disappearance of the S−H signal was observed, and a high equilibrium constant was postulated although a quantitative value could not be calculated. This high value suggests a high

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Table 1. Methylthiirane Polymerization Using a Thiol/DBU Initiator in DMF; [Monomer]$_0$ = 6.75 mol L^{-1}

run no.	thiol	temp, °C	[M]/[I]	M_n calcd[a]	M_n SEC[b]	M_n NMR	M_n UV	I_p	termination conditions[d] SA	termination conditions[d] time, h	coupling, % (SEC)
1	hexanethiol	−15	13.5	1000	1280	1330	1330	1.07	4	40	0
2	hexanethiol	−15	134.9	10000	11950			1.21c	6	5	58
3	hexanethiol	−15	134.9	10000	9740			1.15c	30	24	23
4	hexanethiol	−15	134.9	10000	9400	12000	8950	1.09	20	40	0
5	methylthioglycolate	−15	80.9	6000	6250	9400	7622	1.08	30	48	2
6	hexanethiol + cyclohexanethiol	+20	67.5	5000	5000	3830		1.12	20	48	2
7	hexanethiol + cyclohexanethiol	+20	134.9	10000	10530		12000	1.11	40	48	5
8	1,6-hexanedithiol	−15	27.0	2000	2040	2500		1.09	20	40	0
9	1,6-hexanedithiol	+20	674.7	50000	54300			1.27c	40	48e	26
10	3-mercapto-1,2-propanediol[f]	+20	27.0	2000	1800	2220		1.05	40	72	5
11	3-mercapto-1,2-propanediol[g]	+20	67.5	5000	3900	5120		1.1	40	72	5

[a] From DP$_n$ = [monomer]/[initiator]. [b] In polystyrene equivalent in THF. [c] Bimodal distribution due to coupling of thiolate end groups into disulfides. [d] SA = stoichiometric amount - reaction time (room temperature). [e] Aqueous HCl. [f] Yield = 60%. [g] Yield = 40%.

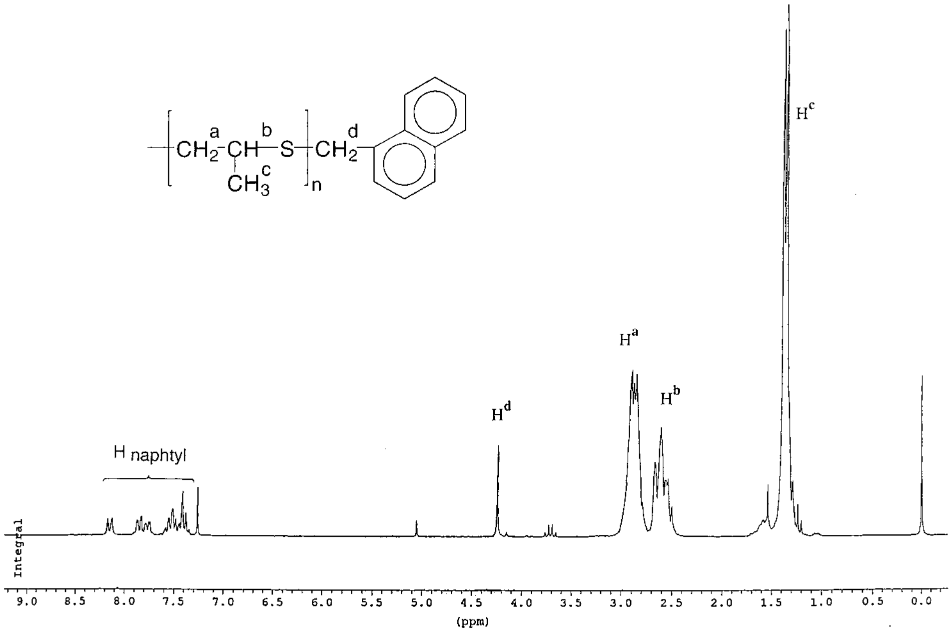

Figure 2. ^{1}H NMR spectrum (CDCl$_3$/TMS) of α-naphthylmethyl end-capped polymethylthiirane.

concentration of thiolate ions in such a solvent. The growing species also give the same equilibrium, which looks like a "dormant" polymerization that was studied by Swarc and Hermans.[9] For such an acid−base equilibrium we can expect that rapid exchange between the thiol and thiolate forms results in a negligible effect on the molecular weight distribution. The initiation and the propagation steps are the same, and for both we can expect the same rate and a nearly "ideal" type of polymerization.[10]

A kinetic study of the polymerization initiated by DBU hexanethiolate in tetrahydrofuran (THF) was carried out using a monomer/initiating system ratio for which theoretical number-average molecular weight is 10 000 g mol^{-1} (theoretical DP$_n$ = 135). The increase of the molecular weight with the yield (Figure 1) demonstrates a living process. Nevertheless, in THF the rate is low, and for practical purposes we carried out other polymerizations in dimethylformamide (DMF). Even at −20 °C in DMF, the rate is very high: the conversion is quantitative in less than 5 min for the same monomer/initiating system ratio, previously used in THF (theoretical DP$_n$ = 135), and an accurate kinetic study is not possible. As previously used to terminate thiirane polymerizations,[11] the active centers were reacted with 1-(chloromethyl)naphthalene at the end of the polymerization time. This reaction must be carried out at room temperature because higher temperatures (such as 40 °C) have led to degradation through chain−thioether group alkylation. Benzyl bromide was also found to be too reactive at room temperature and led to polymer degradation.

Table 1 summarizes the results of polymerizations in DMF (quantitative yields unless stated). Polymers were characterized using size exclusion chromatography (SEC), ^{1}H NMR, and UV−vis determinations of end-capped naphthyl groups. Molecular weights (M_n) estimated from ^{1}H NMR spectra integration are calculated using signals from methylene in the naphthylmethylthio end group and from methylene and methine in the main chain (Figure 2).

For UV−vis determinations (in CHCl$_3$) we took as specific absorption of a naphthalene unit the absorption of 1-[(hexylthio)methyl]naphthalene at 287 nm: ϵ-

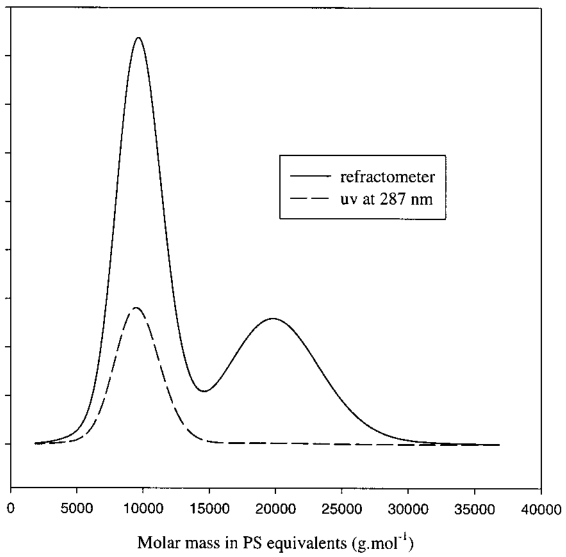

Figure 3. SEC chromatogram of polymer 3 (M_n in polystyrene equivalent = 9740 g mol^{-1}). The solid line corresponds to the refractometric detection, and the dashed line corresponds to the UV detection at 287 nm.

($CHCl_3$) = 7400. This compound was prepared from hexanethiol/DBU and (1-chloromethyl)naphthalene. The relative errors in these measurements are in the range as previously observed.[11] High molecular weight polymers can be obtained (sample 8). Several conclusions may be extracted from these results. The number-average molecular weights are in accordance with the theoretical ones for a living polymerization, $DP_n = [M]_0/[I]_0$, and close to the values from ^1H NMR spectra and UV end group determinations. These results confirm the living character of these polymerizations and imply that the active center's concentration remains constant during the process: the initial thiol is converted to thiolate ion, or rapid exchanges are operating throughout the process. Polydispersity indices (PI) are usually in the range 1.05−1.12, a narrow molecular weight distribution which results from the equivalence of initiation and propagation rates. However, some samples exhibit higher PI. In runs 3 and 8 (Table 1), a bimodal distribution is observed by refractometric detection (Figure 3): both peaks are quite narrow (PI < 1.1), corresponding to number-average molecular weights close to and exactly twice the theoretical one. We think the 2-fold molecular weight peak observed corresponds to oxidative coupling of thiolate species when the mixture is brought to air before the chloromethylnaphthalene reaction is complete, as was previously observed by Boileau et al.[11] Literature data[12] also explain that the reaction conditions (highly polar solvent and large cation) are very propitious to fast oxidation of thiolates on exposure to air. Effectively, the second distribution vanishes when higher reaction time and larger excess of (1-chloromethyl)naphthalene are used for terminations (samples 2−4 in Table 1). SEC−UV detection at 287 nm confirms this assumption: the high molecular peak, free of the naphthyl−methylthio group, is absent from the chromatogram (Figure 3). Owing to the high dilutions of the reactive species, bimolecular termination reactions must be quite slow, and if narrow distribution polymers are wanted, large reaction times are needed. HCl acidification of the reaction medium in order to obtain thiol end groups (as in sample 8) led to a biphasic reaction mixture. Ion-exchange resin seems to be a more reliable and efficient acid reagent to obtain thiol-free terminated polythiiranes.[13]

Thiolate ions from methylthioglycolate are also suitable initiators without any interference of the ester group.[14] Primary and secondary thiols initiate both the polymerization at high rate as is evidenced in samples 5 and 6 where an equimolecular mixture of cyclohexanethiol and hexanethiol gives a polymer of narrow distribution. However, complex equilibriums exist between different thiols and thiolate ions.

Hexanedithiol gives an initiation with both thiolate functions as molecular weight is in accordance with growth by both ends.

For samples 9 and 10 obtained from DBU and unprotected 3-mercapto-1,2-propanediol—a protic initiator—polydispersity indices remain narrow. However, yields are not quantitative after 20 min at room temperature: a slowing down of thiirane polymerization rate was previously pointed out in a protic medium.[6] The SEC molecular weight (in polystyrene equivalents) seems overestimated, and the values obtained by NMR are probably more representative: intermolecular hydrogen bonding between dihydroxy end groups might explain the observed difference between SEC- and NMR-determined molecular weights. Observed yields were lower for these polymers because of their solubility in many solvents.

In conclusion, living thiirane polymerization can be obtained using thiol/DBU as initiator; this system looks suitable to prepare controlled polyarmed star polythiiranes although oxidative coupling of the thiolate end group must be carefully avoided.[13]

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