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Spontaneous Block-Copolymer Formation by Cationic Polymerization of a Vinyl Ether in the Presence of a Cyclic Sulfide

Nancy H. Haucourt, Libing Peng, and Eric J. Goethals*

Institute of Organic Chemistry, Polymer Division, University of Ghent, Krijgslaan 281 (S4-bis), B-9000 Ghent, Belgium

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ABSTRACT: The acid-initiated cationic polymerization of isobutyl vinyl ether (IBVE) with thietane as nucleophilic moderator at −40 °C in dichloromethane leads to star-shaped poly(vinyl ether)–poly-thietane block-copolymers. The block-copolymer structure is obtained because the vinyl ether polymerization is terminated when the active species (α-alkoxythietanium ion) is attacked at its endocyclic methylene group by a thietane molecule. This reaction is a termination reaction for the vinyl ether polymerization but is an initiation reaction for the thietane polymerization. The star-shaped structure of the block-copolymers is a consequence of the (predominantly) intermolecular termination in the cationic polymerization of thietane. With a bifunctional initiating system the end result is a polymer network consisting of linear poly-IBVE segments interconnected by branched polythietane segments. These findings support the sulfonium ion structure of the active species in the cationic polymerization of vinyl ethers initiated by the acid–sulfide system.

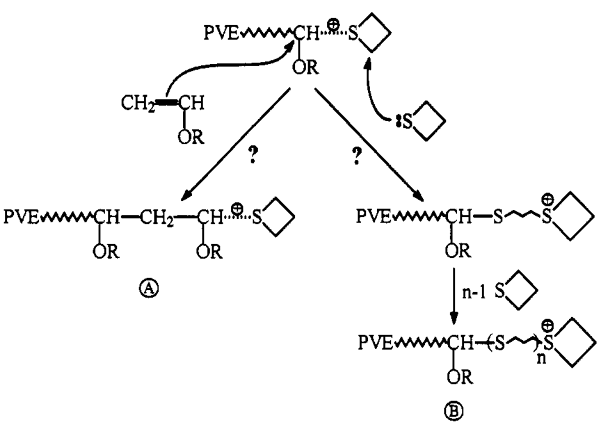
Introduction

One of the most interesting initiating systems which has been found to produce living polymerization of alkyl vinyl ethers is the combination of a strong proton acid and an electron donating "moderator". The most suitable moderator was found to be a dialkyl sulfide such as dimethyl sulfide or thiolane.[1,2] The role of this moderator is to decrease, but not entirely suppress, the reactivity of the active species. The mechanism by which this moderation is obtained has been a matter of discussion for some time. The two opposed theories are on one hand the sulfonium–carbenium ion equilibrium[3] and on the other hand the pseudocationic mechanism.[4] According to the first theory, the active species exist as an equilibrium between a highly reactive carbenium ion species that is capable of propagation and a nonreactive (dormant) sulfonium ion. The pseudocationic theory says that the propagation reaction occurs via a noncharged ester type of active species that is stabilized by the electron donor and describes the reaction as a concerted mechanism with participation of the sulfide in the transition state. Recently, several papers have appeared in which strong evidence was presented for the ionic mechanism, among them ^{1}H-NMR evidence of the presence of sulfonium ions at low temperatures.[1]

In the present paper we describe the use of a four-membered cyclic sulfide as moderator for the vinyl ether polymerization. In contrast to the usually employed five-membered thiolane, the four-membered thietane has enough ring strain to be polymerized and the activation energy of this polymerization is low enough to let it take place at the low temperatures which are generally used for the vinyl ether polymerizations with this kind of initiating systems.[5]

The question that we tried to answer is whether the thietane would act as a moderator only or whether it would be copolymerized. In the latter case this would give definite proof that the active species is at least temporarily, present as a sulfonium ion. Copolymerization would be expected to lead to block-copolymers according to Scheme 1. In this reaction scheme two sulfonium ions with quite different reactivities can be distinguished: the α-alkoxysulfonium ion structure A which is active for the vinyl ether propagation and the "simple" four-membered sulfonium ion B that is formed if the former one is attacked by another molecule of thietane on its endocyclic methylene. Sulfonium ion B would be expected to be no more active for the vinyl ether polymerization but to be an active species for the thietane propagation thus leading to segmented copolymer structures.

Scheme 1



Results and Discussion

Before the results of the vinyl ether polymerization experiments carried out in the presence of thietane are described, the mechanism of the polymerization of this cyclic sulfide should be remembered. It is presented in Scheme 2. The special characteristic of this polymerization is that the active species, the four-membered sulfonium ion, is attacked not only by monomer to give a propagation reaction but also by the sulfide functions of the formed polymer. The result of the latter reaction is a noncyclic and therefore unreactive sulfonium ion and, consequently, this reaction is a real termination.[5–7] From kinetic measurements the ratio of the rate constants for propagation over that of the termination was found to be ~5. This means that the polymerization stops before all

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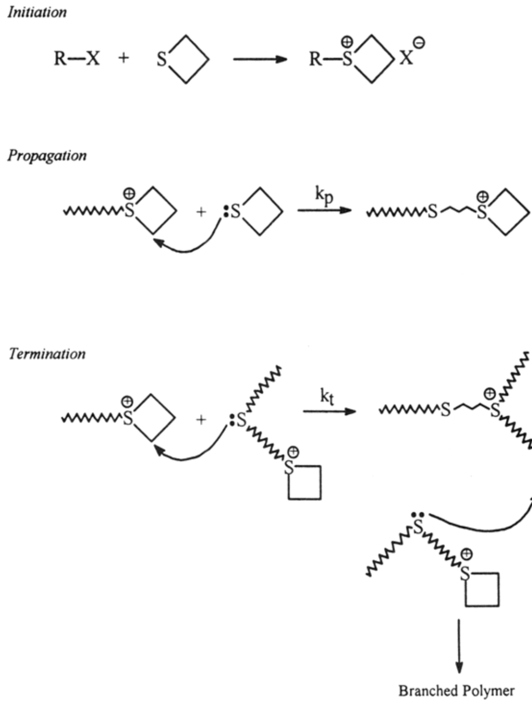
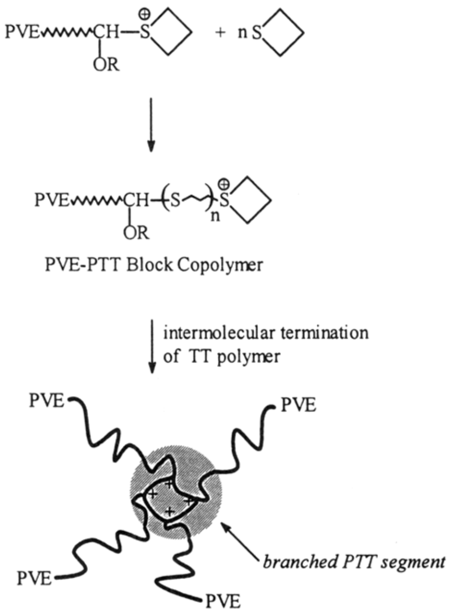
Scheme 2



Scheme 3



monomer is consumed. An important feature of the termination reaction is that it occurs predominantly intermolecularly. This means that by such a reaction two polymer molecules are connected to each other. Since several polymer chains react with their active chain end as well as with their sulfide functions in their chain, the end result is the formation of a branched polymer structure.

If in the polymerization of a vinyl ether in the presence of thietane a block-copolymer is formed, the growing polythietane blocks are expected to form the same kind of branched structures so that in that case the end result is expected to be a star-shaped block-copolymer (Scheme 3). The polymerizations were performed with isobutyl vinyl ether (IBVE) using triflic acid as initiator and were carried out at −40 °C in dichloromethane. In a typical experiment the monomer was used in 1 M concentration, the initiator in 0.011 M, and the thietane in 0.33 M concentration. For comparison, a polymerization with thiolane as the moderator under the same reaction conditions was carried out. According to the concentrations used, the molecular weight of the pure IBVE polymer at complete conversion, in the absence of transfer or termination, should be 9000. The polymerizations were monitored by taking samples after different reaction times and analyzing them by gel permeation chromatography. Figure 1 shows the results obtained after 6 min of polymerization time. It can be seen that in the thiolane case, the molecular weight of the polymer is already close to the expected maximal value and that the molecular weight distribution is narrow. In the thietane case, the molecular weight distribution is still narrow but the molecular weight is markedly lower.

Figure 2 shows the situation after 110 min of polymerization time. The thiolane-moderated polymerization has reached the expected molecular weight and the distribution is, as expected, narrow. The thietane-moderated polymerization shows a completely different picture: the molecular weight is markedly higher than the theoretical value and the distribution is broad.

An interesting observation was the behavior of the two reaction mixtures upon warming up to room temperature. In the thiolane case, the solution turned yellow and then dark brown. This is due to the presence of the highly reactive α-alkoxysulfonium ions which, above −10 °C, rapidly decompose to form colored reaction products formed probably by a number of elimination reactions. In sharp contrast to this is the behavior of the thietane-moderated polymerization; even at temperatures above room temperature, the reaction mixture remained completely colorless, proving that the ionic species present at the end of the polymerization are different from those present in the thiolane-moderated polymerization.

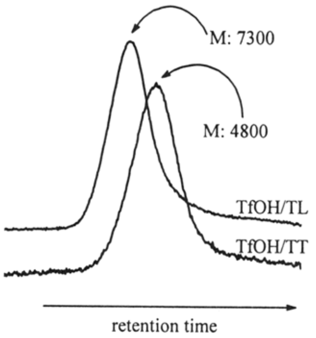


Figure 1. GPC analysis of PIBVE obtained with TL and with TT as moderator after 6 min of polymerization. Polymerization conditions: temperature, −40 °C; solvent, CH_2Cl_2; [IBVE] = 1 M; [TfOH] = 0.011 M; [TL] = [TT] = 0.33 M; $M_{\text{th},100\%\,\text{VE-conv}}$ = 9000 g/mol.

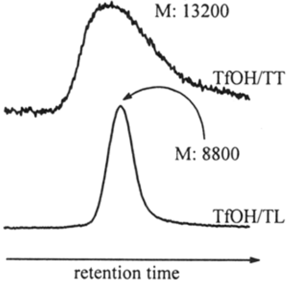


Figure 2. GPC analysis of PIBVE obtained with TL and with TT as moderator after 110 min of polymerization. Polymerization conditions: temperature, −40 °C; solvent, CH_2Cl_2; [IBVE] = 1 M; [TfOH] = 0.011 M; [TL] = [TT] = 0.33 M; $M_{\text{th},100\%\,\text{VE-conv}}$ = 9000 g/mol.

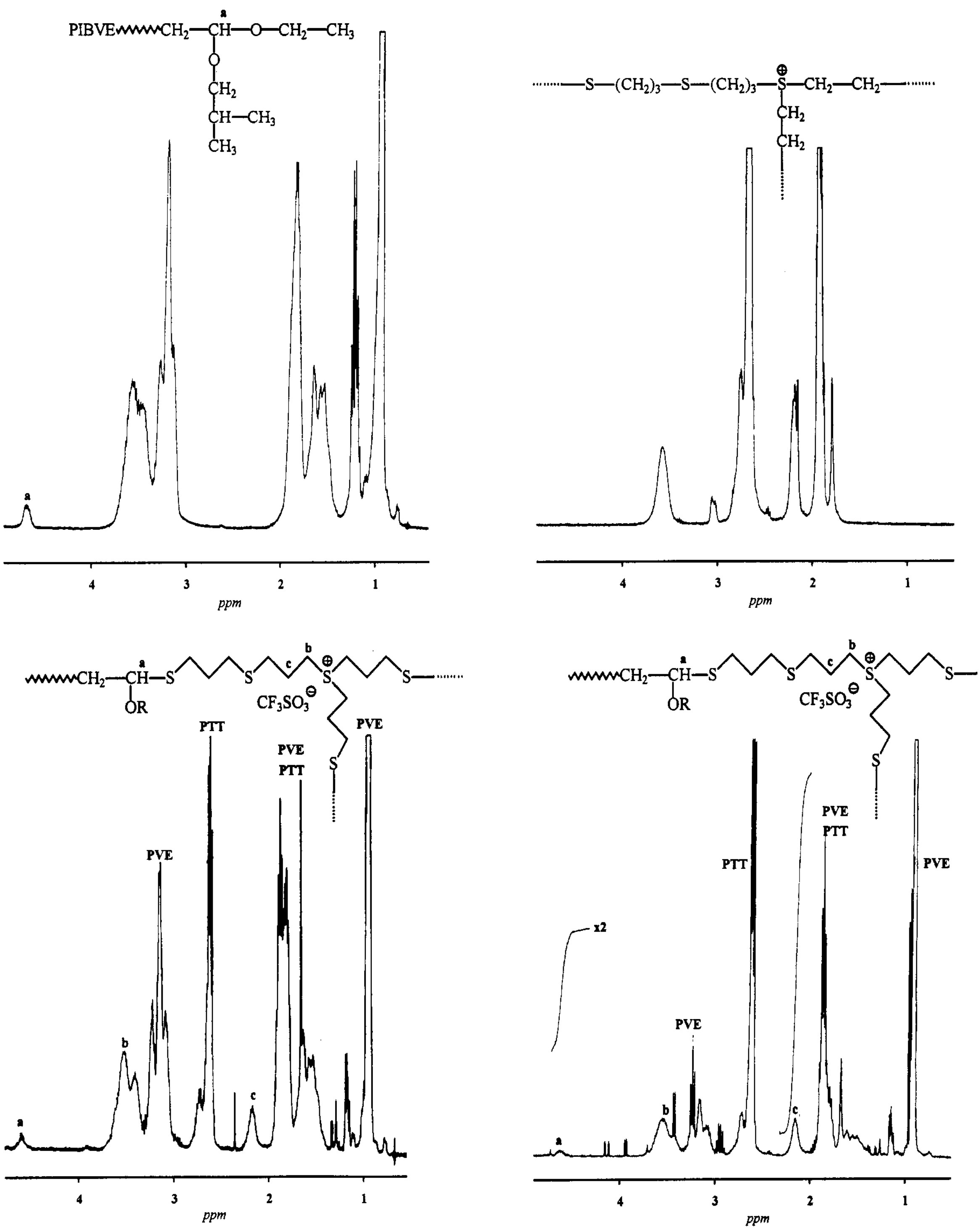


Figure 3. 360-MHz ^{1}H-NMR spectrum of (A, top left) pure poly-IBVE, (B, top right) polythietane, (C, bottom left) polymer obtained with TfOH/TT as initiating system, and (D, bottom right) polymer obtained with TfOH/TT as initiating system and isolated by evaporation of unreacted monomers without termination. For the last polymer, [IBVE] = 1 M, [TfOH] = 0.03 M, and [TT] = 0.9 M.

In Figure 3 (A, B, and C) the ^{1}H-NMR spectra of pure poly-IBVE, polythietane, and the end product of the polymerization of IBVE in the presence of thietane are compared. It can be seen that the last spectrum is a superposition of the first two proving that the end product contains both polymer segments. The most important information from this spectrum, however, is the small peak at 4.65 ppm which is a typical chemical shift value for a thioacetal function. These observations are in agreement with the formation of a poly(vinyl ether)–polythietane block-copolymer structure since, as depicted in the reaction scheme, the junction between the two blocks is indeed a thioacetal.

Since the normal poly-IBVE contains a peak at 4.8 ppm due to the presence of a terminal acetal function, it could be argued that the peak at 4.65 ppm in Figure 3B could also be ascribed to an acetal instead of a thioacetal. This terminal acetal is obtained when an alcohol is added as a terminator in the usual polymerization procedure. Therefore, another NMR spectrum obtained from a copolymer that was isolated without the addition of any terminator is shown in Figure 3D. After the polymerization at −40 °C, the mixture was allowed to warm up to room temperature, all volatile compounds were evaporated under reduced pressure, and the residue was dissolved in deuteroform for NMR analysis. As can be seen the peak

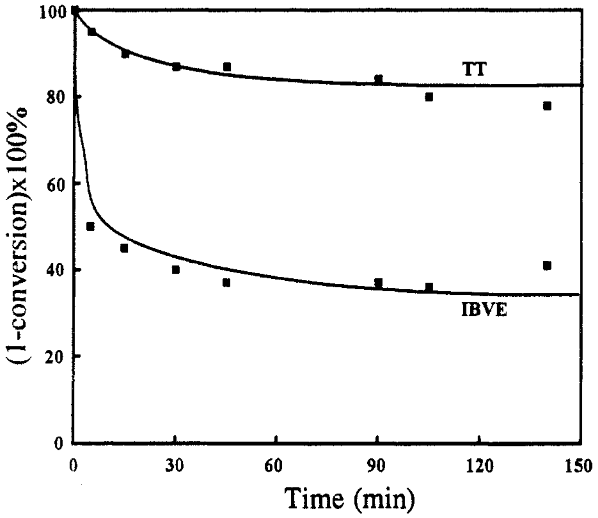


Figure 4. (1-conversion) × 100% for IBVE and TT as a function of time for the polymerization of IBVE initiated by TfOH/TT. Polymerization conditions: temperature, −40 °C; solvent, CH_2Cl_2; [IBVE] = [TT] = 0.33 M; [TfOH] = 0.011 M.

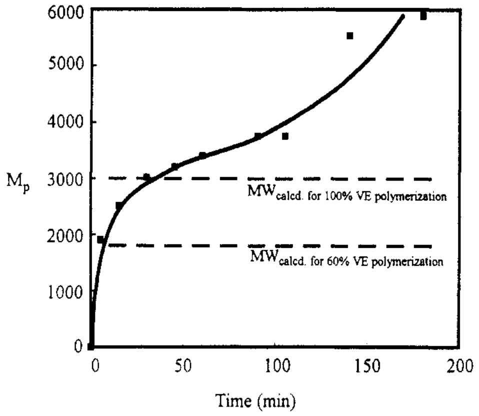


Figure 5. Peak molecular weight (M_p) as a function of time for the polymerization of IBVE initiated by TfOH/TT. Polymerization conditions: temperature: −40 °C; solvent, CH_2Cl_2; [IBVE] = [TT] = 0.33 M; [TfOH] = 0.011 M.

at 4.65 ppm is still present. Thus, it cannot be due to an acetal end group and can only be attributed to a thioacetal proton, proving the presence of a block-copolymer. If the proposed reaction mechanism is correct, the end product should contain equal concentration of thioacetal and sulfonium ion. The protons in α position to the positively charged sulfur are partially overlapping with protons from the polyether and can therefore not be integrated accurately. The methylene protons in β position of the positively charged sulfur, however, are clearly visible as an isolated peak at 2.1 ppm (peak c in the figure). Since each acetal function carries one proton and each sulfonium ion has six β protons, the ratio of the area under peak a (4.65 ppm) to that of peak c (2.10 ppm) should be equal to 6. Experimentally, a value of 6.05 was found, thus confirming that the thioacetal and sulfonium ion are present in the same concentration.

In another experiment, the concentrations of both IBVE and thietane were taken equal to 0.33 M and the initiator concentration to 0.011 M. The concentrations of both reagents were followed as a function of time by GLC, and in the same experiment, polymer samples were isolated and analyzed by GPC. The time–conversion curves for both monomers are shown in Figure 4, and the evolution of the peak molecular weight of the polymers as a function of time is shown in Figure 5. It is clear that under the reaction conditions used, the vinyl ether polymerization stops at limited conversion which is in contrast to the behavior with thiolane as moderator. In this particular experiment, the theoretical molecular weight at quantitative conversion was 3000. Since the final conversion of the IBVE was 60%, the expected molecular weight, in absence of transfer, was 1800. It can be seen from Figure 5, that the molecular weight at the end of the polymerization is considerably higher than that calculated for a "simple" vinyl ether polymerization, which is in agreement with the formation of star-shaped block-copolymers due to the intermolecular termination of the polythietane segments.

Table 1 summarizes the results of a number of polymerizations carried out with different concentrations of thietane. When the thietane concentration is low, the polymerization of the vinyl ether is almost not influenced, and the final molecular weight is not much higher than that predicted. Apparently, the termination reaction of the thietane polymerization with such very low monomer concentration is predominantly intramolecular. When the thietane concentration is increased, the conversion of the vinyl ether polymerization decreases and the intermolecular termination of the thietane polymerization becomes dominant, leading to branched polythietane structures and hence to star-shaped polymer structures containing up to approximately four arms per polymer.

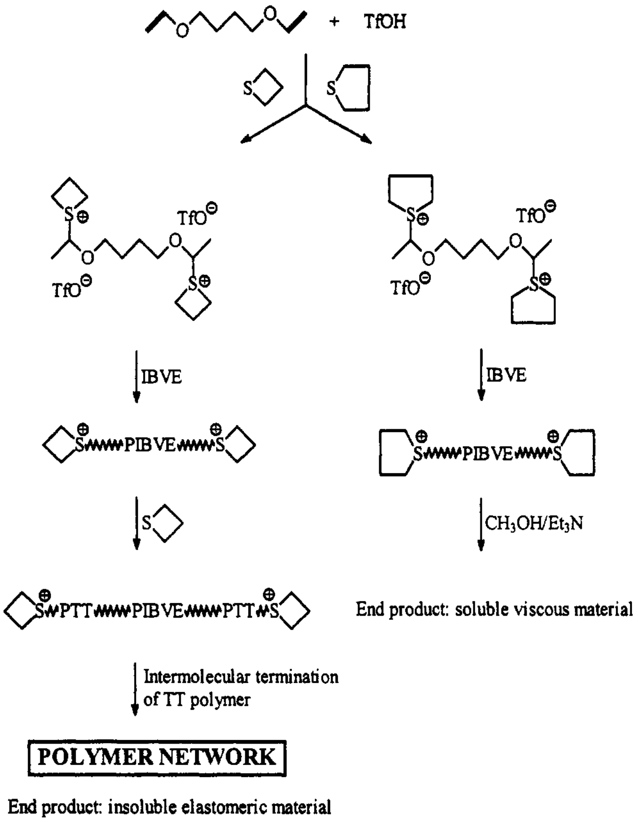
In order to confirm that the bonds between the polyether and the polythietane polymers are indeed stable covalent species, polymerizations of IBVE were initiated with a bifunctional initiating system. If such a polymerization is carried out with thietane as the moderator, then branched polythietane segments should be connected at both chain ends and this should result in a polymer network. The bifunctional initiator was obtained by preparing a bis(α-sulfonium salt) by reaction of 1 mol of butane-1,4-bis(vinyl ether) with 2 mol of triflic acid in the presence of an excess of thietane. For comparison, the reaction was also carried out under the same conditions with thiolane as the moderator. The reaction schemes for the two polymerizations are compared in Scheme 4. The

Table 1. GPC Results of Polymers Obtained from the Polymerization of IBVE with TfOH/TT Initiating System for Different Ratios ([IBVE] = 1 M, [TfOH] = 0.011 M)

	[TT]/[TfOH] = 15		[TT]/[TfOH] = 30		[TT]/[TfOH] = 60	
	MW at peak max	M_w/M_n	MW at peak max	M_w/M_n	MW at peak max	M_w/M_n
reaction time						
6 min	7200	1.1	4800	1.1	3400	1.1
12 min	7800	1.1	5800	1.2	5600	1.3
120 min	9300	1.4	13200	1.4	13000	1.5
conversion of VE (%)	91		50		38	
MW PVE, calcd	8200		4500		3400	
no. of arms in star-shaped block-copolymer[a]	≈1		≈3		≈4	

[a] Estimated from GPC measurements.

Scheme 4



results were as follows: in the thiolane case, the end product was a viscous liquid as would be expected for a linear low molecular weight poly-IBVE. In the thietane case the reaction mixture gelled a short time after the start of the polymerization and after evaporation of the solvent an elastomeric material was obtained. This is precisely what would be expected for a cross-linked low T_g polymer, and this result is in agreement with the mechanism proposed above by which several poly-IBVE segments are connected to each other through their end groups by branched polythietane segments.

Conclusions

It has been shown that in the acid-initiated cationic polymerization of IBVE with thietane as moderator, the cationic end groups are α-alkoxy cyclic sulfonium ions. These ions are capable of propagation of the vinyl ether polymerization either as such or after dissociation to a more reactive carbenium ion. The α-alkoxysulfonium ions can also be attacked by a thietane monomer at their endocyclic methylene leading to a ring opening of the four-membered sulfonium ion. This reaction is a termination reaction for the vinyl ether polymerization but is the initiation reaction for the thietane polymerization. As a consequence, the vinyl ether polymerization stops at incomplete conversions. These conversions become lower as the thietane concentrations are increased. By this mechanism, poly(vinyl ether)–polysulfide block-copolymers are formed. Due to the intermolecular termination of the thietane polymerization, the end products have star-shaped block-copolymer structures. When using bifunctional initiating systems, these polymerizations lead to polymer networks consisting of linear poly-IBVE segments connected to each other through their end groups by branched polythietane segments. These findings confirm the sulfonium ion structure of the active species in the polymerization of vinyl ethers initiated by acid/sulfide initiating systems.

Experimental Part

Monomers and Reagents. IBVE was distilled over CaH$_2$, refluxed over CaH$_2$ for 4 h before use, and freshly distilled (bp 82.5 °C). Thiolane (TL) and thietane (TT) were purified by refluxing over CaH$_2$ followed by distillation (bp's 119 and 94 °C). Triflic acid was purified by distillation (bp 162 °C). 1,4-Bis(vinyloxy)butane (BVOB) was purified by distillation over CaH$_2$ (bp 168 °C).

Polymerizations. In a typical polymerization initiated by TfOH/TT ([TfOH]/[TT] = 1/30), 1.3 mL of IBVE (10 mmol) and 240 μL of TT (3.3 mmol) were added to 10 mL of dichloromethane, followed by the addition of 10 μL of TfOH (0.11 mmol) at −40 °C to start the polymerization. After 4 h, 220 μL of MeOH (5.5 mmol) and 0.08 mL of Et$_3$N (0.58 mmol) were introduced to terminate the reaction. The polymerization with the bifunctional initiator system was carried out as follows. For the synthesis of the bis(α-alkoxysulfonium) ion 20 μL of TfOH (0.22 mmol) was added to a solution of 17 μL of BVOB (0.11 mmol) and 480 μL of TT (6.6 mmol) in 2 mL of dichloromethane cooled at −40 °C. After 5 min 2.9 mL of IBVE (22 mmol) was added to the mixture to start the polymerization. After 40 min the reaction mixture started gelling. After 3 h the mixture was warmed up to room temperature and the solvent and unreacted monomers were evaporated under reduced pressure. An elastomeric residue was obtained.

Analytical Methods. ^{1}H-NMR spectra were recorded with a Bruker AM 360 instrument. GPC analyses were performed with a Waters instrument equipped with a 60-cm 500-Å Polymer Laboratories column. Calibrations were made with polystyrene standards.

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References and Notes

(1) Cho, C. G.; Feit, B. A.; Webster, O. W. *Macromolecules* **1990**, *23*, 1918.
(2) Cho, C. G.; Feit, B. A.; Webster, O. W. *Macromolecules* **1992**, *25*, 2081.
(3) Matyjaszewski, K. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 107.
(4) Plesch, P. H. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 11.
(5) Goethals, E. J.; Drijvers, W.; Van Ooteghem, D.; Buyle, A. M. *J. Macromol. Sci. Chem.* **1973**, *A7*, 1375.
(6) Goethals, E. J.; Drijvers, W. *Makromol. Chem.* **1973**, *165*, 329.
(7) Goethals, E. J. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 56*, 27.