

***o*-Sulfobenzoic Anhydride 로 개시된 Propylene Sulfide 의 양이온중합시 고분자양성이온의 생성**

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Formaton of Macrozwitterions in the Cationic Polymerization of Propylene Sulfide Initiated with *o*-Sulfobenzoic Anhydride

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요 약. *o*-술포벤조산 무수물을 개시제로 사용하여 프로필렌설피드를 괴상 중합시킨 결과 양성이온 메카니즘에 의하여 중합한다는 것이 판명되었다. 생성된 폴리머를 분석한 결과 이 폴리머는 술포늄양이온과 술포산음이온을 폴리머 사슬에 가지고 있다는 것이 판명되었다. 음이온과 양이온의 농도가 거의 같으며 이것은 고분자양성이온임을 나타낸다. 중합제중에 존재하는 수분이 조촉매로 이용되었을 가능성은 없으며 말단기 분석을 이용하여 중합메카니즘을 규명하였다.

ABSTRACT. Bulk polymerization of propylene sulfide with *o*-sulfobenzoic anhydride as initiator was carried out and the polymerization proceeded by a zwitterionic mechanism. Chemical and spectroscopic investigation of the purified polymer revealed that the polymer contained two end groups -thiolester of benzoic acid *o*-sulfonate anions and acyclic *tert*-sulfonium ions which were formed by termination of episulfonium ions with sulfide groups in the polymer chains.

The concentration of sulfonate anions was nearly the same as the concentration of acyclic *tert*-sulfonium ions, as expected for macrozwitterions. The cocatalysis mechanism by a trace of water was excluded and the other possible mechanisms were discussed on the basis of end group analysis.

1. INTRODUCTION

The zwitterion mechanism in the ionic polymerization can be divided in two groups: a zwitterion is formed during the initiation step

and the propagation is proceeded continuously either at cationic or at anionic active center to form the macrozwitterions¹.

In contrast with this mechanism, two different monomers in the copolymerization system

are reacted to form zwitterions, and reactions of the opposing ions between zwitterions gives a macromolecule having a cation at the one end and an anion at the other and². The former mechanism has been repeatedly proposed in the cationic polymerizations of numerous heterocyclic or vinyl monomers³⁻¹⁰. However, this mechanism has not been proven unambiguously, whereas it was successful in the anionic polymerization¹.

The difficulties in proving the cationic zwitterion mechanism and in synthesizing macrozwitterions in cationic polymerization are rooted in the following reasons:

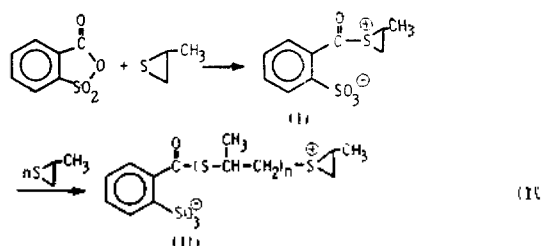
(1) Most cationic initiators (*i. e.* Lewis acid) require a third substance (cocatalyst) in order to start the polymerization⁸, so that the initiation product is not a zwitterion, but an ion pair.

(2) Some cationic initiators, such as TiCl_4 and SnCl_4 , which can start polymerization without a cocatalyst, disproportionate in the polymerization system into anions and cations which initiate the polymerization.¹¹

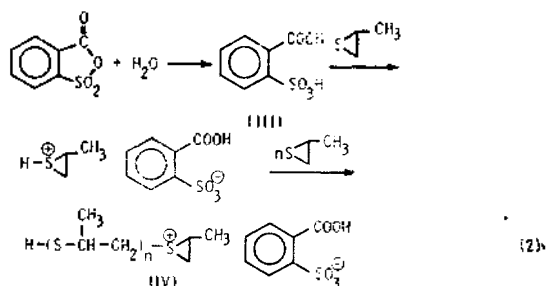
(3) Even if zwitterions were formed in a polymerization system, most of the cations (carbonium or oxonium ions) are too unstable to be proven experimentally. Also, proton or hydride transfers occur frequently on the active species in a cationic polymerization, so that zwitterion structures are destroyed during the polymerization.

In order to avoid these difficulties and to synthesize a stable macrozwitterion by a cationic polymerization, we chose propylene sulfide as a monomer and *o*-sulfobenzoic anhydride as an initiator. The monomer, propylene sulfide, should react with the initiator to form a zwitterion, which would start the polymerization of propylene sulfide;

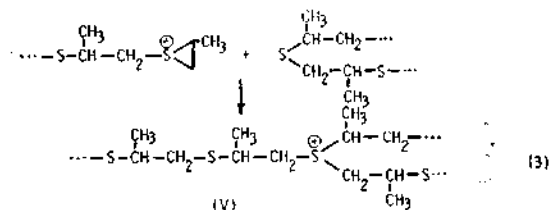
In contrast with other cationic initiators, such as TiCl_4 , this initiator was not expected to



disproportionate. Furthermore, during the ring opening of episulfonium ions no carbonium ion was observed as an intermediate¹², so that transfer reactions resulting from proton or hydride transfer could not occur. The thiolester of benzoic acid-sulfonate anion (TBASA) formed by the initiation step is very weakly basic and nucleophilic, as a result it was expected that the sulfonate anion could not react with episulfonium ion spontaneously. Therefore, the mutual destruction of opposing ions could be avoided during the polymerization. As an alternative mechanism, the initiator could be hydrolysed by a trace of water present in the polymerization system to form a dibasic acid, which can start the polymerization. In this case the initiation is the same as the usual cocatalysis mechanism:



Since episulfonium ions react irreversibly with sulfide to form acyclic *tert*-sulfonium ions¹³, intramolecular or intermolecular termination was expected as follows; this kind of termination was found in the cationic polymerization of 3,3-dimethyl thietane¹⁴.



Because the salt of the acyclic *tert*-sulfonium ion and the anion end group, TBASA, should be stable, the mutual destruction of formed ions is very improbable.

In this work we investigated the problem using end group analysis by spectroscopy as a main tool and the polymerization mechanisms were discussed on the basis of this end group analysis.

2. EXPERIMENTAL

2-1. Synthesis and Purification of Monomer and Initiator.

Propylene sulfide (20ml) were dried over 5g of calcium hydride at 0°C for 1 day and distilled over calcium hydride at 0°C at reduced pressure. *o*-Sulfobenzoic anhydride was synthesized from saccharin¹⁵ and distilled in vacuo (5 torr): m. p 127°C.

2-2. Polymerization

Initiator was weighed into a round bottom flask which had been previously dried by flaming i. vac. Monomer was fed into the flask with the aid of a syringe and the initiator was dissolved in this monomer.

2-3. Synthesis of Model Compounds

Triethylammonium Benzoic Acid Ethyl Thiolester-sulfonate(VII). *o*-Sulfobenzoic anhydride (0.6g) were dissolved in 5 ml of ethyl mercaptan and this solution was stirred under reflux at 20°C for 4 hrs. The excess mercaptan was evaporated under reduced pressure and the residue (yellow oil) was dissolved in 5 ml of methanol. After adding 2 ml of triethyl amine the mixture was stirred at room temperature for

30 min. and the excess amine was evaporated under reduced pressure at room temperature. The salt was dissolved in chloroform and precipitated with ether: yield 80%, m. p 131°C.

Anal. Calc.: C 51.90, H 7.21, O 18.44, N 4.03, S 18.44%

found: C 51.49, H 7.04, O 18.21, N 3.87, S 17.76%

Triethylammonium Benzoic Acid-*o*-sulfonate(VIII). *o*-Sulfobenzoic anhydride(4 m mole) were dissolved in 10 ml water and boiled under reflux for 2 hrs. To this solution 4 m mole of triethyl amine were added and stirred for 30 min. Water was evaporated under reduced pressure at 60°C. The residue was dissolved in methanol and precipitated with ether: yield 85%, m. p 89°C.

Anal. calc.: C 51.50, N 4.62, H 6.94, S 10.56

found: C 51.23, N 4.35, H 6.61, S 10.60

2-4. Spectra

(1) The infrared spectra were taken with the infrared spectrometer IRA-2 (JASCO). The viscous poly(propylene sulfide) was coated as a thin layer on the surface of a NaCl-plate, and the IR-spectra of all model compounds were taken with KBr pellets.

(2) NMR-spectra were taken with the NMR-Spectrometer EM-360A (Varian).

(3) UV-spectra were taken with the Recording Spectrophotometer model Superscan-3 (Varian).

3. RESULT AND DISCUSSION

3-1. Polymerization

In order to avoid any side reactions and terminations, a bulk polymerization was chosen. Since the initiator and polymer were soluble in monomer, the polymerization proceeded in a homogeneous phase. To facilitate end group

analysis we made a low molecular weight polymer, by starting the polymerization with a high concentration of initiator. The polymerization was carried out under a N_2 -atmosphere. The polymer was purified by dissolving in chloroform and precipitating with methanol repeatedly so that the unconverted initiator was excluded. Spectroscopic analysis confirmed that no initiator was included in the purified polymer. The result of several polymerizations are seen in Table 1.

Polymer A was a very viscous colorless oil. Since low molecular weight poly(propylene sulfide) was a viscous oil and high molecular

weight poly(propylene sulfide) an elastomer according to Sigwalt¹⁶, polymer A seemed to have a low molecular weight.

For the purpose of comparing the end groups, a normal poly(propylene sulfide) of high molecular weight was synthesized with $TiCl_4$ and KOH as initiators in a similar manner to Sigwalt¹⁶.

3-2. Spectra of the Polymers and Model Compounds

Spectroscopic investigations on the end groups of polymers were suitable for the elucidation of polymer structures and polymerization mechanisms, because the end groups in II and anions in IV had many characteristic bands in IR-spectra, episulfonium ion and acyclic sulfonium in NMR-spectra and substituted benzene ring in UV-spectra.

Fig. 1 shows the IR-spectra of polymer A prepared by *o*-sulfobenzoic anhydride (solid line) and of polymer B (dotted line). The spectrum of polymer A had bands; absent in the spectrum of polymer B, at 5.97, 8.32, 10.95, 13.0, 15.35, 16.3, 16.8 and 17.8 μ , which

Table 1. Bulk polymerization of propylene sulfide at 20°C.

PI Initiator	$\frac{[I]}{[M]} \times 10^2$	Polymerization time	Yield (%)	$(\eta)^a$
A <i>o</i> -sulfobenzoic anhydride	6.45	3 hrs	26	0.163
B $TiCl_4$	2.5	5 days	—	—
C KOH	2.0	3 days	—	—

^aViscosity was measured in chloroform 30°C with an Ostwald-viscometer; PI: Polymer.

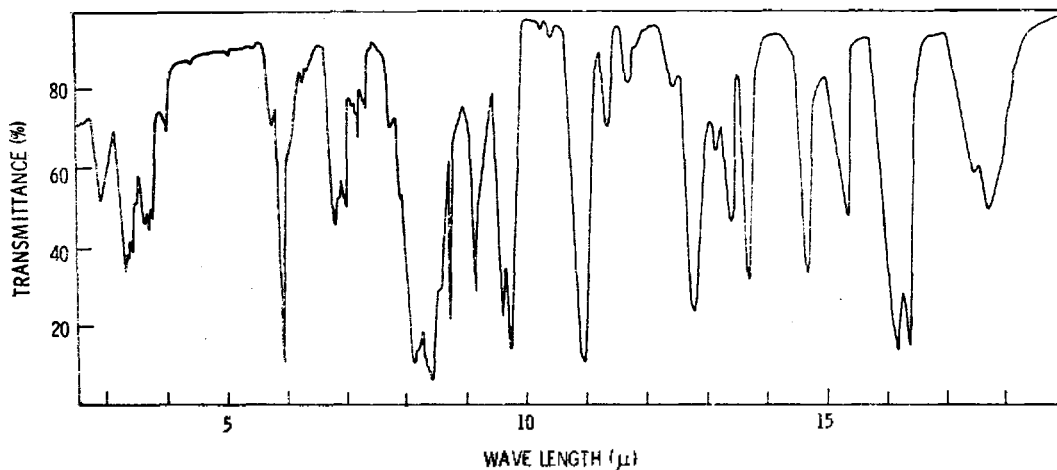


Fig. 1. IR-spectra of poly(propylene sulfide).
Solid spectrum: Polymer A, prepared by initiation with *o*-sulfobenzoic anhydride;
Dotted spectrum: Polymer B, prepared by initiation with titanium tetrachloride.

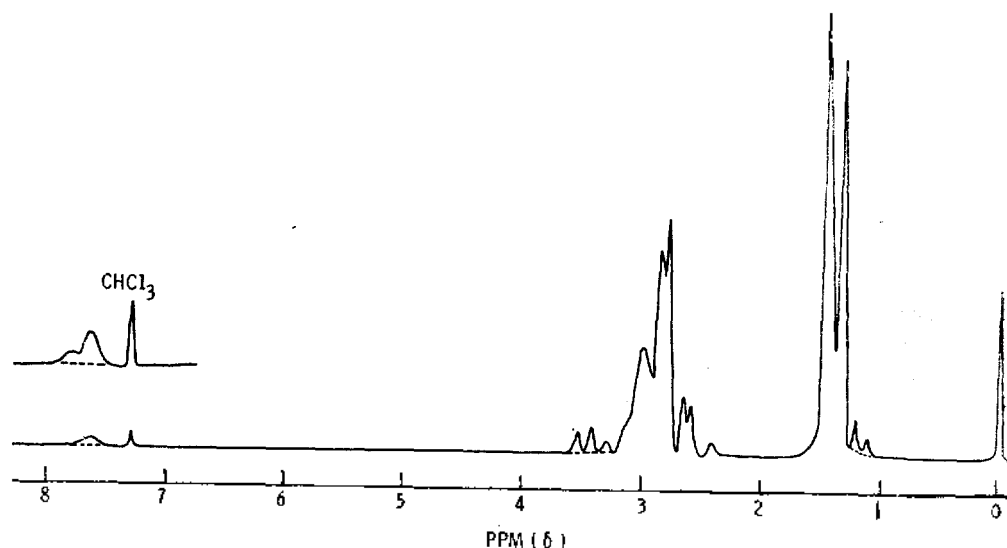


Fig. 2. NMR-spectra of poly(propylene sulfide). Solid spectrum: polymer A, prepared by initiation with *o*-sulfobenzoic anhydride. Dotted spectrum: Polymer C, prepared by initiation with potassium hydroxide.

were associated with the end groups of polymer A.

Fig. 2 shows the NMR-spectra of polymer A (solid line) and of polymer C (dotted line). Polymer A had additional bands at $\delta=7\sim 8$ and $3.2\sim 3.8$ ppm. The signals at $\delta=1.39$ and 3.00 were the absorption peaks of CH_3 - (lit. : $\delta=1.36^{17}$) and CH -protons (lit. : $\delta=2.93^{18}$) in the polymer, respectively. According to Ivin¹⁷, CH_2 -protons of isotactic and syndiotactic poly (propylene-2- d_1 sulfide) showed different chemical shifts in the region of $\delta=2.8\sim 3.0$ ppm. Since the CH -protons were coupled with CH_3 -protons in polymer A, the tacticity of polymer A could not be determined. However, the signals at $\delta=2.42, 2.64,$ and 2.85 originated from CH_2 -protons in polymer A.

In order to identify the band positions of the different end groups in the spectra, the following model compounds were prepared; trieth-

ylammonium benzoic acid ethyl thiolester-*o*-sulfonate (VII) as a model compound for the anionic end group in II, triethylammonium benzoic acid-*o*-sulfonate(VIII) for the anion in IV, and methyl cyclooctenyl episulfonium picrylsulfonate (IX) and methyl diethyl sulfonium iodide (X) for the cationic end groups in II and V. Fig. 3 shows the IR-spectrum of triethylammonium benzoic acid ethyl thiolester-*o*-sulfonate (VII) and Table 2 shows the model compounds and their spectral data. Only some selected IR-band positions are given in Table 2.

3-3. Investigation of the End Groups and Polymerization Mechanisms by Spectroscopy

With the aid of spectra of model compounds the additional bands in the spectra of polymer A can be assigned, so that polymer structure and the polymerization mechanism can be consequently elucidated.

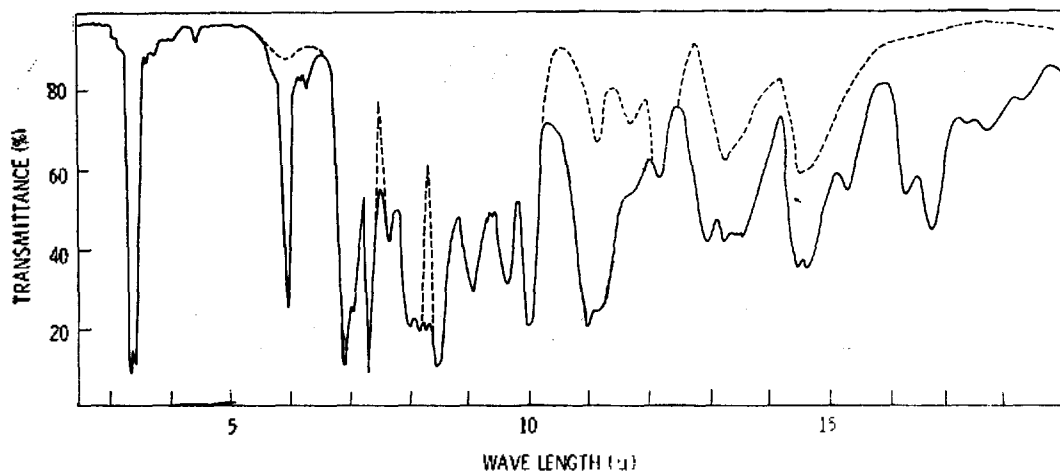


Fig. 3. IR-spectrum of triethylammonium benzoic acid ethyl thioester-o-sulfonate (model compound VII).

Table 2. Model compounds and spectral data.

No.	Model compound	IR(KBr pellet)		NMR	
		Wave length (μ)	Assignment	δ-Value (ppm)	Assignment
VI		5.45	CO	8.02	phenyl in chloroform-d ₁
VII		5.97	CO	7.45, 7.77	phenyl
		10.95	CS in -C-S-	3.05	a, c
		12.9	phenyl	1.25	b, d in dimethylsulfoxide-d ₆
VIII		5.81	CO	7.85, 7.53	phenyl
IX		3.32	CH-stretching in episulfonium ion	2.63	a, b
				1.53	cyclooctane
				8.25	phenyl
X		—	—	2.91	a
				3.40	b
				1.46	c in D ₂ O

3-3-1. Mechanism of Initiation and Propagation.

As stated in the introduction, two quite different mechanisms of chain initiation and propagation are feasible; 1) initiation by direct reaction between monomer and initiator with formation of zwitterions, 2) cocatalysis by an

ionizable cocatalyst such as water.

Direct Initiation without Cocatalyst. In case of that the initiation and propagation proceed *via* reaction (1), the polymer should contain TBASA as anionic end groups. As shown in the Table 2 carbonyl groups of initiator(VI) and model compound VII gave

sharp bands at 5.45 and 5.97 μ , respectively (Fig. 3). A sharp band at 5.97 μ is seen in the spectrum of polymer A and is absent in the spectrum of polymer B (Fig. 1). Since this band position is exactly same as the carbonyl band of model compound VII, it seems clear that TBASA is present in polymer A. A strong band at 10.95 μ assigned to CS-band in thiolester according to Nyquist⁹ was found in the IR-spectra of model compound VII (Fig. 3) and polymer A (Fig. 1), whereas it was absent in the IR-spectrum of polymer B (Fig. 1). Owing to the same positions as well as intensities of the CS-band of thiolester in model compound VII and in polymer A, it is obvious that TBASA is also present in polymer A.

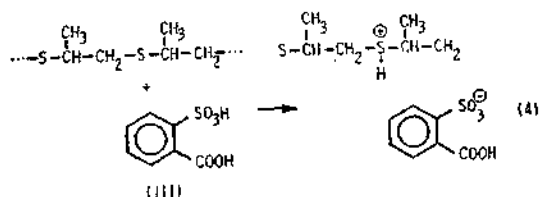
By a direct initiation (1) an *o*-disubstituted benzene ring should be present at the end of polymer A. The *o*-disubstituted benzene ring gave a strong band at 13.0~13.6 μ .²⁰ Polymer A (Fig. 1) and the model compound VII (Fig. 3) give bands at 13.0 and 12.9 μ , respectively, which was not found in the spectrum of polymer B (Fig. 1). It was therefore confirmed that a disubstituted benzene ring is present in polymer A. The additional bands in polymer A at 8.32, 15.35, 16.3, and 17.8 μ which do not occur in polymer B are due to sulfonate anions, since the sulfonate group of the model compound VII (Fig. 3) gives absorption bands at 8.32, 15.35, 16.3 and 17.8 μ . The coincidence of the absorption bands of the carbonyl, benzene ring, CS-band in O=C-S- group and sulfonate anion in polymer A with the bands in model compound VII was taken as proof that TBASA are present in polymer A as end groups and that direct initiation occurred without a cocatalyst.

In the NMR-spectrum of model compound VII (measured in dimethylsulfoxide-*d*₆) we found two signals for the benzene protons at δ =7.45 and 7.77ppm, whereas the initiator

gives one signal at δ =8.02ppm in chloroform-*d*₁. In the spectrum of polymer A (measured in chloroform-*d*₁) two signals were found at δ =7.68 and 7.80ppm, which were absent in the spectrum of polymer C. The slight difference in δ -values between model compound VII and polymer A could be caused by the different solvents (compound VII insoluble in chloroform), and from this NMR-study it was ascertained that TBASA was present in polymer A as end groups.

Initiation by Cocatalysis with Water. If initiation [results from cocatalysis with water (reaction 2), we could expect that the polymer should contain benzoic acid-*o*-sulfonate anion as the counter ion. The carbonyl band of the model compound VIII occurred at 5.81 μ and polymer A (Fig. 1) gave also a small band at the same position (5.81 μ). The ratio of the concentrations of anionic end group in II and anion in IV was measured by the ratio of intensities and of extinction coefficients of both carbonyl bands. The concentration of the ions in IV was found to be 12% of the concentration of anionic end groups in II. Since the amount of water in the polymerization system was very small ($[\text{H}_2\text{O}]/[\text{converted initiator}]=0.01$, measured by gas chromatography), it seemed clear that most of the anions in IV were not formed by cocatalysis with water, but during the purification of the polymer; the normal solvents (chloroform and methanol) for the purification of polymer contain a small amount of water which can hydrolyse initiator to form a dibasic acid (III) that can form *sec*-sulfonium ions with the sulfide groups in the polymer chain.

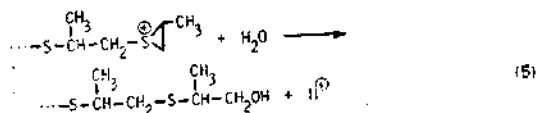
More evidence for the formation of benzoic acid-*o*-sulfonate anions according to reaction (4) was obtained by the fact that the carbonyl band at 5.81 μ did not occur in the IR-spectra



during the polymerization¹¹, which was carried out for the kinetic measurements. The results lead us to conclude that initiation can occur by direct reaction between monomer and initiator in the absence of water and that, in the presence of water, polymerization can be started by both mechanisms, direct initiation or cocatalysis with water.

3-3-2. Chain Transfer

As is usual in the cationic polymerization, the active species (episulfonium ion) could react with a transfer agent, *eg.* water, to form a proton, which can start a new chain;



In this case *pri*-alcohol and mercaptan groups should be formed at the chain ends. The strong absorption band of OH-deformation and CO-stretching of *pri*-alcohols (monomer) occur around 9.52 and 7.41~7.93 μ in the IR-spectrum. Because of the absence of any additional bands in the IR-spectrum of polymer B, transfer with water apparently did not occur.

3-3-3. Termination

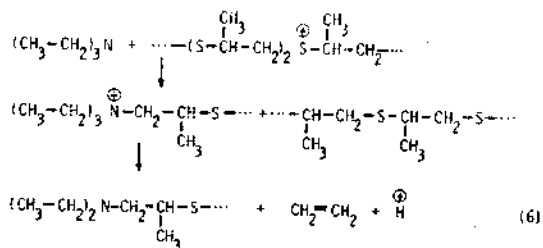
Since episulfonium ions react irreversibly with sulfide to form acyclic *tert*-sulfonium ions¹², the termination may occur intermolecularly or intramolecularly between the active species and sulfide groups in the chain, as discussed in the introduction (reaction 3). The direction and rate of the concurrent reactions of episulfonium ion, whether with poly(propylene sulfide) or with propylene sulfide, are presumably depen-

dent on the steric effects, basicities and nucleophilicities of the sulfides.

The basicity of cyclic sulfides decrease in the order of ring size as follows: 5>6>4>3²¹. The basicity of a linear sulfide would be the same as a 6-membered ring, so that poly(propylene sulfide) should be more basic than propylene sulfide, whereas the steric hinderance at polymer is larger than that at monomer. However, the relation of reaction rates between two concurrent reactions should depend on the ratio of the concentrations $[\text{monomer}] / [\text{---CH}_2\text{---CH---}]$

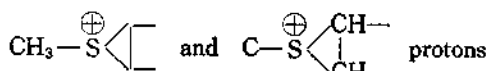
$\begin{array}{c} | \\ \text{CH}_3 \end{array}$ S \cdots). The signals of the protons in acyclic *tert*-sulfonium ions occur at $\delta=3.40$ ppm in the NMR-spectrum (Table 2), as measured with the model compound, methyl diethyl sulfonium iodide (X). NMR-spectra of the reaction mixture during the polymerization showed no signal in the region around $\delta=3.40$ up to 45% conversion of monomer. The fact that the signals of acyclic *tert*-sulfonium ions were, however, found in the NMR-spectrum (Fig. 2) of polymer A, leads us to draw the conclusion that the termination (3) would not occur at a high concentration of monomer, but during the storage of purified polymer or during a late stage of the polymerization. In order to obtain additional information bearing on this problem, we examined polymer A for the presence of *tert*-sulfonium ions with chemical methods. *tert*-Episulfonium or acyclic sulfonium ions react with *tert*-amines to form *quart*-ammonium ions and sulfides^{13, 22}. According to this reaction, *quart*-ammonium ions will be formed in the polymer by treating the polymer with *tert*-amine. Polymer A was stirred with excess of triethyl amine in chloroform at 50 °C for 5 hrs. After purification of the polymer the NMR-spectrum was taken. The signal of acyclic *tert*-sulfonium

ions had disappeared, whereas new peaks at $\delta = 2.42$ and 0.95 had appeared, which are due to $-N-CH_2-$ (lit.: $\delta = 2.42$)²³ and $-N-C-CH_3$ protons (lit.: $\delta = 1.03$)²³. Based on this results we believe that the acyclic *tert*-sulfonium ions react with *tert*-amine to form *quart*-ammonium ions, which should be decomposed by Hofmann degradation (6) under this reaction conditions and that the *tert*-amine groups were consequently attached to the polymer.



Because there are no other functional groups in polymer A, which could react with *tert*-amine and incorporate it in the polymer, the attachment of *tert*-amine to the polymer is further evidence that polymer A contains acyclic *tert*-sulfonium ions.

Though acyclic *tert*-sulfonium ions were found in polymer A, we were unable to determine if episulfonium ions still remained. Methyl cyclooctenyl episulfonium picrylsulfonate (IX, in Table 2) gives a weak band at 3.32μ in the IR-spectrum, which was assigned to the CH-stretching of 3-membered ring by Helmakamp²⁴. The weak intensity of the band and interference by other bands near 3.32μ in the IR-spectrum of polymer A made detection of episulfonium ion impossible.

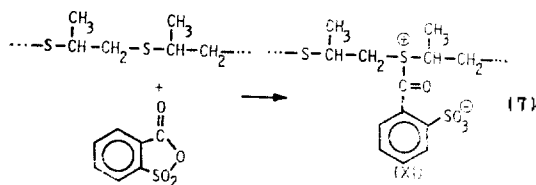


gave signals at $\delta = 2.63$ in the NMR-spectrum (Table 2). Since polymer C, prepared by anionic polymerization, gave signals in this region, episulfonium ions could not be detected

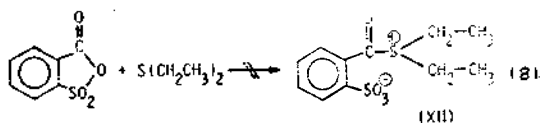
by NMR.

3-3-4. Side Reaction

Owing to the low catalytic activity of the initiator the initiation reaction occurred very slowly and it was found by kinetic measurements that 70% of the fed initiator remained when half of the monomer was converted¹¹. Under this condition the initiator might react with sulfide groups in the polymer chain to form zwitterions XI;



If the zwitterion XI were formed in the polymer, it would interfere with the spectral analysis for end groups in polymer A because of the similar structures of the zwitterion XI and the end groups. To obtain information bearing on this problem, the following model reaction was chosen; equimolar amounts of diethyl sulfide and *o*-sulfobenzoic anhydride (initiator) were dissolved in acetonitrile and stirred at 40°C for 3 hrs;



After evaporation of solvent and unreacted diethyl sulfide, the NMR-spectrum of the residue was taken. In this spectrum we did not find any signals of *tert*-sulfonium ions, but only the signal of benzene protons of the initiator. From this result we can conclude that the reaction (8) did not occur. Since the sulfonium ion in compound XII is adjacent to a partially positive carbon atom, we can

assume that compound XII is very unstable and its formation should be difficult.

3-4. Concentration of Ions and Degree of Polymerization

On the bases of IR and NMR spectra, the concentrations of ions in the polymer were calculated and shown in Table 3.

The concentration of cation is nearly the same as the concentration of anion, within experimental error, as one would expect for a macrozwitterion. The termination by formation of acyclic *tert*-sulfonium ions (reaction 3) occurred nearly quantitatively either during storage of purified polymer or during a late stage of the polymerization, because the concentration of both ions in polymer A are nearly equal.

The concentration of ions, found in the purified polymer A, is about two orders of magnitude higher than the concentration of water which was originally present in this polymerization system, measured by gas chromatography. Since short chain oligomers should be removed by the purification, the concentration of active species during the polymerization should be higher than this measured ion concentration. This is a further evidence for the direct initiation according to reaction (1).

On the basis of ion concentrations in the polymer, the degree of polymerization and the

number average molecular weight of polymer A were found to be 35.5 and 2800, respectively, assuming that transfer had not occurred.

3-5. Molecular Weight and Polymer Structure

The number average molecular weight (M_n) of polymer A, measured in chloroform by vapour pressure osmometry, was found to be 3800. This was slightly higher than M_n calculated from the concentrations of ions in polymer A. Since the deviations caused by association of ionic molecules were not observed in the measured range of concentration in osmometry, the difference between calculated and measured M_n seems to be due not to association of molecules, but to intermolecular termination (reaction 3). Chain transfer was not considered in this analysis because of the absence of *pri*-alcohol end groups. As the termination can result from both paths, intermolecular or intramolecular reactions, the polymer can have branched structures or ring forms as follow;

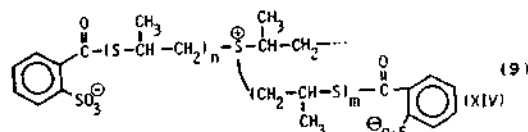
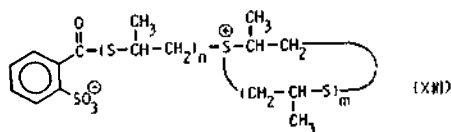


Table 3. Concentrations of the ions in polymer A.

Kinds of ions	Concentration (mole/g polymer)	Method of measurement
$\text{-CH}_2\text{-CH-S}^+(\text{CH}_3)_2\text{(CH}_2\text{-CH-S)}_2\text{-}$	3.84×10^{-4}	NMR
	3.59×10^{-4}	IR
	0.43×10^{-4}	IR

Based on the difference between calculated and measured M_n , the ratio of intramolecular to intermolecular termination would be about three.

4. CONCLUSION

We summarize the important results of this investigation very briefly as follow:

(1) Thiolester of benzoic acid-*o*-sulfonate anion was found as an end group in the polymer.

(2) The concentration of active species during the polymerization was at least 100 times higher than the water concentration present in the polymerization system.

(3) The concentration of sulfonate anion was nearly same as the concentration of acyclic *tert*-sulfonium ion in the polymer.

(4) The absence of *pri*-alcohol groups in the polymer indicated that the transfer reaction was very improbable.

Due to points 1 and 2, it was obvious that the polymerization of propylene sulfide initiated with *o*-sulfobenzoic anhydride proceeded by a zwitterion mechanism (I). After propagation of the polymerization *via* zwitterion (II), the termination (3) occurred during the late stage of polymerization or during storage of isolated polymer. On the basis of points 3 and 4, we may conclude that polymer structures XIII and XIV resulted.

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