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Propylene Sulfide를 *o*-Sulfobenzoic Anhydride 개시제로 중합시킬때 반응속도의 연구

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아주공과대학 화학공학과

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The Knetic Study of Propylene Sulfide Polymerization Initiated by *o*-Sulfobenzoic Anhydride

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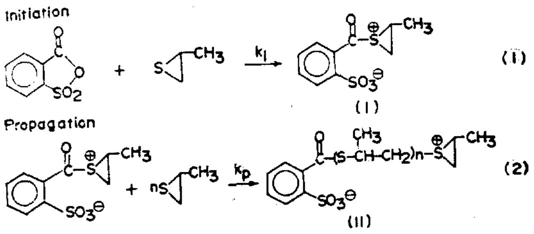
요 약. Propylene sulfide 를 *o*-sulfobenzoic anhydride 로 중합시키면 양성이온 메카니즘에 의하여 중합이 진행되며, 이 반응의 속도를 연구하였다. 반응계중의 단위체와 개시제의 농도는 IR와 NMR를 이용하여 측정하였다. 성장반응속도가 개시반응속도보다 10^3정도 빠르며 이러한 결과는 양성이온 메카니즘에 의하여 생긴것으로 사료된다.

ABSTRACT. The kinetics of the bulk polymerization of propylene sulfide initiated by *o*-sulfobenzoic anhydride were investigated, which proceeded by a zwitterionic mechanism. The instantaneous concentrations of monomer and initiator were determined by means of ir- and nmr-spectroscopy. The rate constant of propagation was found to be about three order of magnitude higher than that of initiation and this should be caused by a zwitterion mechanism.

INTRODUCTION

In the previous paper[1] we reported that macrozwitterions were formed by the polymerization of propylene sulfide initiated by *o*-sulfobenzoic anhydride. The initiator reacted directly with the monomer without any participation of a cocatalyst to form a zwitterion (I) and the propagation proceeded at the cationic end, resulting a macrozwitterion (II): The crucial and rate-determining step in this process of producing zwitterionic poly(propylene sulfide) seems to be the initiation step, which may be hampered by two factors: First, the initiator has relatively low reactivity in comparison with the other conventional initiators



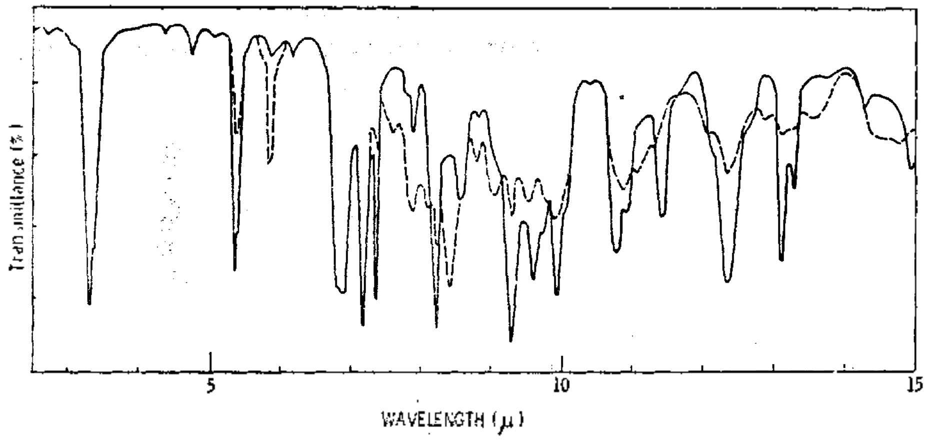


Fig. 1. Ir-spectra during the bulk polymerization of propylene sulfide initiated by 2.88 mole % *o*-sulfobenzoic anhydride at 37 °C. The solid line is after 22 min and the dotted line is after 120 min of polymerization time.

Table 1. δ-Values of proton resonance in monomer and polymer.

Protons	Propylene sulfide[2]	Poly (propylene sulfide)[1]
Methyl	1.43	1.39
Methine	2.93	2.97
Methylene	2.01 (*cis* relative to CH_3) 2.38 (*trans* relative to CH_3)	2.73

Fig. 3.

The chemical shifts of the phenyl protons in the initiator and in the polymer (II) were found to be $\delta=8.02$ ppm for the former and 7.68 and 7.80 ppm for the latter.[1] The δ-values of the proton signals in the monomer (propylene sulfide) and in the polymer are summarized in *Table* 1. While the δ-values of the methyl and methine protons change little upon polymerization, the signal of the methylene protons is shifted downfield. The changes in the nmr-spectra during the polymerization are shown in *Fig.* 2 (after 3 and 45 min of polymerization time). As the polymerization proceeds, the intensity of the signals at $\delta=7.68$, 7.80 and 2.73 ppm are increased in accordance with the decrease in intensity of the signals at 8.02, 2.01 and 2.38 ppm.

Based on the integration values of the signals from the phenyl protons in the initiator and the zwitterionic polymer (II), the concentration of initiator during the polymerization was evaluated. Since the signal of *trans*-proton of the CH_2-group in the monomer obstructed by the peak of the CH_2-protons in the polymer during the late stage of the polymerization, the instantaneous concentration of monomer was evaluated by means of the change in integration values of the *cis*-proton on propylene sulfide (2.01 ppm). The results of the nmr-measurements are shown in *Fig.* 3 and 4.

Initiation. As shown in *Fig.* 3, the conversion of initiator is very slow as expected. After 50 min of polymerization time, at which time the conversion of the monomer is *ca.* 50 %, only 25% of the initiator was consumed. Since the initiator remains mostly unconverted in the polymerization system, questions are raised as to whether the initiator can react with sulfide groups in the polymer chain to form a zwitterion (IV):

From the result of a model reaction between initiator and diethyl sulfide, the reaction (4) in the cationic polymerization such as Lewis-acids and protonic acids. Secondly, a high energy should be necessary for the heterogeneous ring opening of the initiator to form a zwitterion.

Upon investigation of the polymerization system, characteristic bands of monomer, initiator and polymer were found in the ir- and nmr-spectra, which enabled us to measure the kinetics of polymerization by spectroscopic methods[1]. The rate of initiation was evaluated by ir- and nmr-spectroscopy, while the rate of propagation was measured by means of nmr-spectroscopy.

EXPERIMENTAL

Synthesis and Purification of Monomer and Initiator. Propylene sulfide (20m*l*) was dried over 5 g 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 saccharin and distilled in vacuum (5 torr): m. p 127 °C.

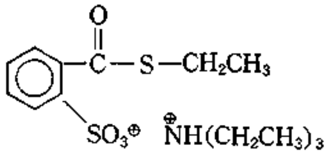
Ir-Spectra Measurements. Initiator (0.5 mmole) was weighed into a round bottom flask which had been previously dried by flaming in vacuum. Monomer (17.4 mmole) was fed into the flask with the aid of a syringe and the initiator was dissolved in this monomer. The polymerization was carried out under a nitrogen atmosphere at 37°C. During the polymerization some drops of polymerization solution were taken out with a syringe at several reaction times and pressed between two KBr-plates. Ir-spectra were recorded with a IRA-2 (JASCO).

Nmr-Spectra Measurements. The polymerization solution was made in the same manner as it was made for the ir-measurements. Then small portion of the reaction mixture was transfered in an nmr-tube and the polymerization was continued in the tube at the constant temperature (37 °C). During the polymerization nmr-spectra were recorded at several reaction times with a Varian EM-360A.

RESULT AND DISCUSSION

Determination of Conversion. In order to avoid any side and termination reactions, a bulk polymerization was chosen. Since the intiator and polymer were soluble in monomer, the polymerization proceeded in a homogeneous phase which was also favorable for the measurements of kinetics.

The carbonyl band of the initiator occurs at 5.45 μ, whereas the carbonyl band in the zwitterionic poly(propylene sulfide) (II) gives a band at 5.97 μ[1]. Ir-spectra of the polymerization solution at 22 and 120 min after onset of the polymerization are shown in *Fig.* 1. As the polymerization proceeds, the extinction of the initiator CO-band decreased in accordance with an increase in the extinction of the CO-band in the zwitterionic polymer (5.97 μ). With the aid of the model compound (III), the ratio between the molar extinction coefficients of the carbonyl bands in initiator (I) and model compound (III) was found to be $\varepsilon_I/\varepsilon_{III}=1.239$.



(III)

From the ratio of the extinctions of the carbonyl bands in initiator and polymer (E_i/E_p) the instantaneous concentration of initiator ($[I]$) was obtained by means of Eq. (3)

$$[I]=[I]_0\left(\frac{E_p}{E_i}\cdot\frac{\varepsilon_I}{\varepsilon_{III}}+1\right)^{-1} \tag{3}$$

where $[I]_0$ is the initial concentration of initiator. The evaluated concentration of initiator during the polymerization, $[I]$, are plotted in

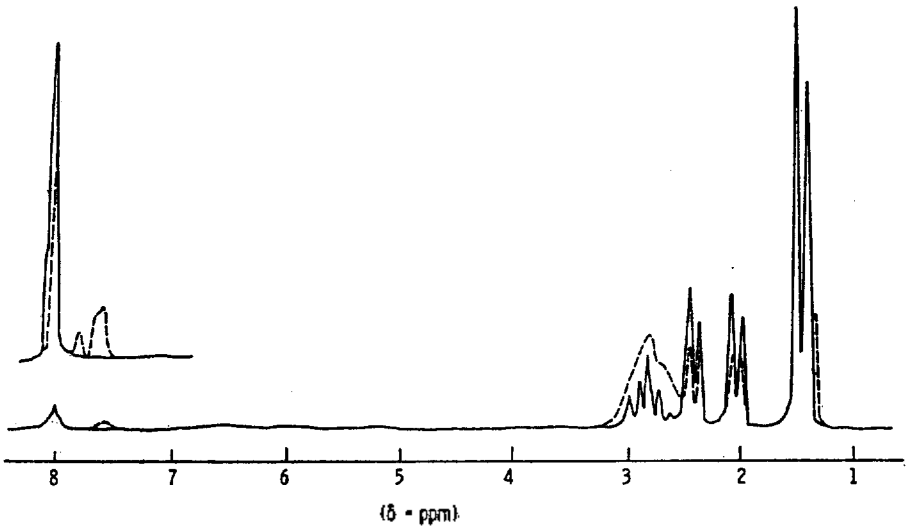
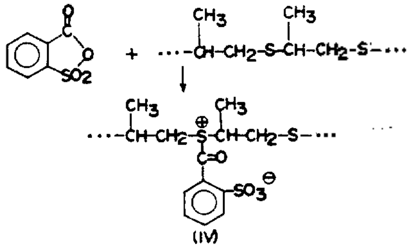


Fig. 2. Nmr-spectra during the bulk polymerization of propylenen sulfide initiated by 2.88 mole% *o*-sulfobenzoic anhydride at 37 °C. The solid line is after 3 min and the dotted line is after 45 min of polymerization time.



(4)

was excluded[1]. The amount of consumed initiator produces an equimolar amount of propagating species as shown by Eq. (1) and therefore:

$$[P^{\oplus}]=[I]_0-[I] \tag{5}$$

The concentration of active species as a function of polymerization time is shown in *Fig.* 5 and it increases continually with the polymerization time from 0 to 0.1 mole/*l* in 50 min.

The rate of initiation gives:

$$-\frac{d[I]}{dt}=K_i\,[I][M] \tag{6}$$

Integration of Eq. (6) gives:

$$\ln\frac{[I]_0}{[I]_t}=K_i\int_0^t [M]dt \tag{7}$$

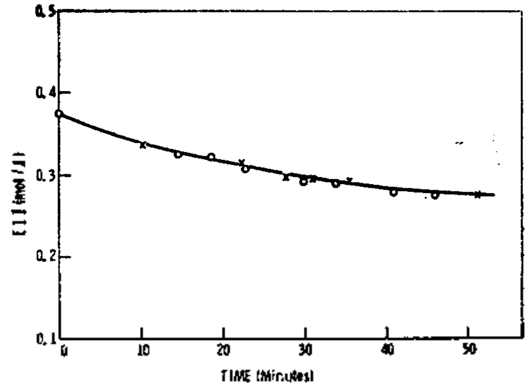


Fig. 3. Bulk polymerization of propylene sulfide initiated by 2.88 mole% *o*-sulfobenzoic anhydride at 37 °C. Initial concentration $[I]=0.366$, $[M]=12.8$ mole/*l*. (o): The values measured by ir-spectroscopy, (×): the values measured by nmr-spectroscopy

The value of $\int_0^t [M]dt$ was obtained by a graph integration from the $[M]$-time curve in *Fig.* 4. The plot of Eq. (7) is shown in *Fig.* 6. From the slope of the linear plot the rate constant of initiation is found to be 2.6×10^{-4} $\mathrm{min}^{-1}(\mathrm{mole}/l)^{-1}$. At the later stage of polymerization (after 35 min of polymerization time), a

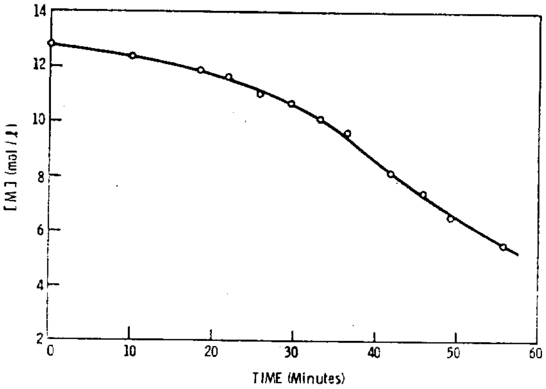


Fig. 4. Monomer concentration as a function of polymerization time, measured by nmr-spectroscopy. The polymerization conditions are the same as in *Fig.* 3.

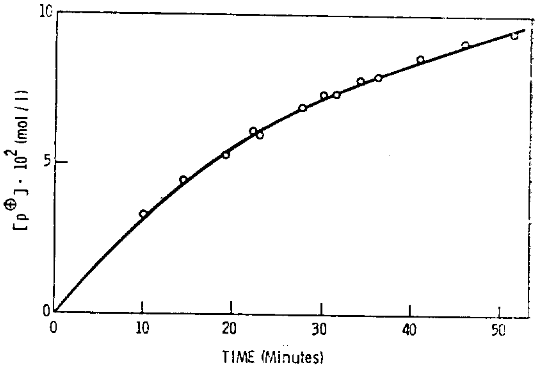


Fig. 5. Time-dependent concentration of active species during the bulk polymerization of propylene sulfide initiated by 2.88 mole% *o*-sulfobenzoic anhydride at 37 °C.

slight deviation, a decrease in the rate constant, is observed, which will be discussed later.

The initiation reaction is first order with respect to the concentration of initiator. If the initiation occurs by cocatalysis with water, *i.e.*, *via* hydrolysis of the initiator by water to form a dibasic acid (*o*-sulfobenzoic acid), which starts the polymerization, the rate of initiation should be conetrolled by the concentration of water. The first order dependence of the initiator concentration is evidence for the direct initiation by means of Eq. (1) without any participation of cocatalyst.

Propagation. The conversion of monomer is very slow at the early stage of polymerization (*Fig.* 4), and it increases with the concentration of propagating species, which is increasing continually with time (*Fig.* 5). This observation is quite different from the conventional ionic polymerizations initiated by active catalysts: At the beginning of the polymerization, apart from the induction period, the most active species are formed which leads to a large increase in the rate of polymerization.

The formation of acyclic *tert*-sulfonium ions by means of the reaction between episulfonium

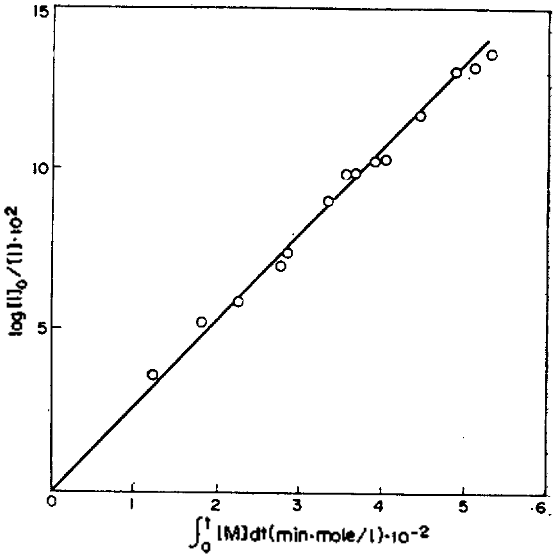


Fig. 6. The plot of Eq. (7) of the polymerization under the same conditions as in *Fig.* 3.

ions (propagating species) and the sulfide groups in the polymer chains was assumed to terminate the polymerization[1]. In the case where the acyclic *tert*-sulfonium ions were formed by the termination reaction, the resonance signal from the $\mathrm{C-\overset{\oplus}{\underset{\displaystyle |\atop C}{S}}-CH_2-C}$ protons must occur at $\delta=$

3.40 ppm[1]. No signal was observed in this region during the polymerization in the measured time interval (*Fig.* 2, up to 50 % conversion of monomer), suggesting that the rate of reaction of episulfonium ions with monomer is much faster than the rate of reaction of these ions with the sulfide groups in the polymer chain. Accordingly, this termination was neglected in this kinetic calculation.

The rate of monomer consumption is given by:

$$-\frac{d[M]}{dt}=K_i\ [I][M]+K_p\ [P^{\oplus}][M] \quad (8)$$

By substitution of Eq. (5) in (8), we obtain:

$$-\frac{d[M]}{dt}=(K_i-K_p)\ [I][M]+K_p\ [I]_0[M] \quad (9)$$

Integration and rearrangement of *Eq.* (9) gives:[3]

$$\frac{\ln\ [M]_0/[M]_t}{\int_0^t [I]dt}=(K_i-K_p)+K_p\frac{[I]_0 t}{\int_0^t [I]dt} \quad (10)$$

The value of $\int_0^t [I]dt$ was obtained by a graph integration from the $[I]$-time curve in *Fig.* 3.

The plot of Eq. (10) is shown in *Fig.* 7. A strong deviation from this equation is found in the early stage of polymerization (up to 20 min of polymerization time). A similar curvature has been also found in the cationic polymerization of 2-methyl-2-oxazoline initiated by methyl tosylate.[3] The rate constant of the propagation was found from the linear part of plot to be 1.5×10^{-1} min^{-1}(mole/l)$^{-1}$. From the intercept of the plot one should be able to calculate the rate constant of initiation. However, the fact that K_i and K_p differed by more than 2 orders of magnitude made its evaluation impossible.

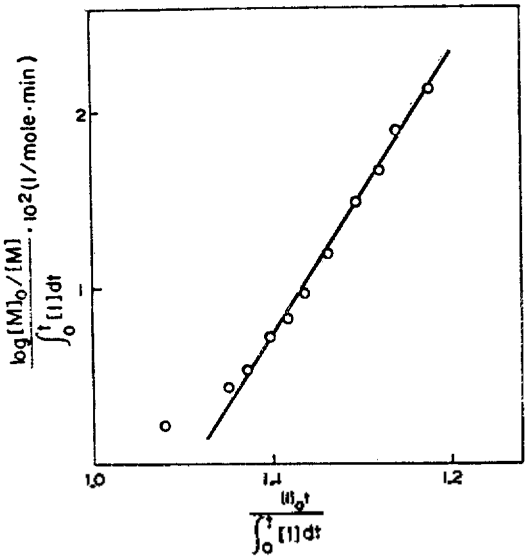


Fig. 7. The plot of Eq. (10) of the polymerization under the same conditions as in *Fig.* 3.

This polymerization system differs from conventional ionic polymerization in such a way that the concentrations of ions (active species and gegenions) are continually increased as the polymerization proceeds. The continual increases in ionic strength and dielectric constant of the polymerization medium, resulting from the increase in ion concentrations, may influence the rate of initiation and propagation.

The high concentrations of ions at the later stage of polymerization seems to hamper the formation of ions from neutral molecules, resulting in a decrease in the rate of initiation. The gradual increase in the rate constant of propagation at the early stage of polymerization might be attributed to the fact that the rise in the dielectric constant of the polymerization medium in accordance with the increase in ion concentrations would affect the ratio of free ions to ion pairs in favor of free ions. However, since the salt effect in organic solvent is complicated, this kind of polymerizaion kinetics should be studied further.

4. CONCLUSION

The rate constant of propagation is about three orders of magnitude higher than that of initiation. Consequently, the overall rate of polymerization at the beginning was very slow and increased slowly in accordance with the increasing concentration of active species. Compared with most ionic polymerizations, this abnormal behavior seems to be caused by the zwitterionic mechanism. The energy barrier for the formation of zwitterion from neutral molecules in the initiation step could be higher than that for the propagation step.

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