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Propagation Mechanism of Radical Copolymerization of Sulfur Dioxide and Vinyl Chloride

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ABSTRACT

Radical copolymerization of sulfur dioxide and vinyl chloride (VC) has been studied by the comparison of the composition of copolymers obtaining from different reaction conditions, i.e., reaction temperatures, feed compositions, and total monomer concentrations. The composition of VC in copolymer is independent of comonomer composition except at high concentration of VC in feed; it increases with increasing reaction temperature or decreasing total monomer concentration. At lower temperature, the composition of copolymer becomes independent of total monomer concentration. The overall rate of polymerization is proportional to $[VC]^{1.7}$ and $[SO_2]^{-0.5}$. These results were compared with those obtained in our previous study on the SO_2 -styrene copolymerization. A propagation mechanism for radical copolymerization of SO_2 and VC is also proposed.

INTRODUCTION

Although the copolymerization of sulfur dioxide with various olefins and vinyl monomers to form polysulfones has long been known, its propagation mechanism, which may involve participation of monomer complexes, penultimate unit effects, or depropagation, is still a controversial problem [1-4]. In previous papers [4-6], we have proposed a propagation mechanism for radical copolymerization of sulfur dioxide and styrene. In this mechanism, a novel reaction step, elimination of sulfur dioxide from a growing sulfonyl radical under the attack of styrene monomer, was assumed, and the propagation mechanism involving the participation of a charge-transfer complex of sulfur dioxide and styrene proposed by Barb [1] was ruled out.

In continuation of our earlier investigation, in the present paper we have taken VC as a vinyl monomer to test our previously proposed mechanism for SO_2 and styrene, and we compare the compositions of copolymers obtained under different reaction conditions and investigate the overall rate of copolymerization. VC was chosen since its Alfrey-Price Q - e values and homopropagation rate constant (k_{MM}) are quite different from those of styrene. Furthermore, Marvel et al. [7] have reported the preparation of a 1:2 copolymer of SO_2 and VC, in the presence of peracetic acid as a catalyst but did not discuss the mechanism of copolymerization. It has been shown that, in the SO_2 -VC copolymerization by γ -radiation [8-9], copolymer compositions vary considerably with reaction temperature. A mechanism in which the monomer complex of SO_2 and VC participates in the propagation step has been proposed by Schneider et al. [8]. Recently, Cais and O'Donnell have reported on the formation of SO_2 -VC and $(\text{SO}_2)_2$ -VC complexes [3], and the determination of the microstructure of poly(vinyl chloride sulfone) by NMR [10].

EXPERIMENTAL

Vinyl chloride was purified by distillation and stored in a large bulb attached to a vacuum line. Sulfur dioxide was dehydrated with phosphorus pentoxide and vacuum-distilled. 2,2'-Azobisisobutyronitrile (AIBN) and toluene were purified by the usual methods. For copolymerization at 28°C and above, AIBN was used as a catalyst; for the experiment at 0°C cumene hydroperoxide was used.

The polymerization was carried out in a pressure-resistant glass vessel which was closed by means of a stainless-steel needle valve. In a degassed glass vessel containing the required quantities of

catalyst and diluent, liquid SO_2 was charged by a dropping apparatus and VC gas was introduced by means of a vacuum line. The polymerization proceeded in a heterogeneous system and was stopped at times as desired by cooling in a precooled methanol bath (-85°C) and adding hydroquinone. For all experiments the conversion was not allowed to exceed 5 wt %. The copolymers were obtained either by evaporating the unreacted monomers or by precipitating in methanol. The overall rate of copolymerization was deduced from the weights of copolymers. The compositions of the copolymers were determined from elemental analyses for sulfur. Molecular weights of copolymers below 15000 were determined by vapor-pressure osmometry; molecular weights higher than 15000 were measured by a high-speed membrane osmometer.

RESULTS

Composition of Copolymer

The dependence of copolymer composition obtained at various reaction temperatures on the feed composition is shown in Fig. 1. Since these results were obtained from the bulk polymerization, the effect of the total monomer concentration on the copolymer composition is negligible. At any given temperature, the copolymer

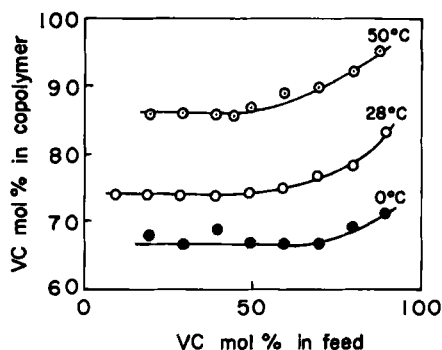


FIG. 1. Dependence of the copolymer composition on the feed composition at various polymerization temperatures (bulk polymerization): (\odot) 50°C ; (\circ) 28°C ; (\bullet) 0°C .

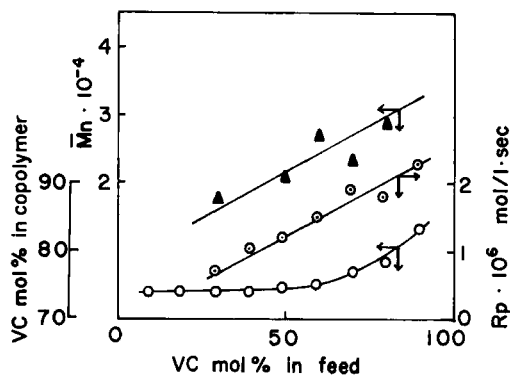


FIG. 2. Relationships between feed composition and (○) overall rate of copolymerization R_p , (○) composition of copolymer, and (▲) molecular weight. Polymerization temperature 28°C; [AIBN] = 5×10^{-2} mole/liter; bulk polymerization.

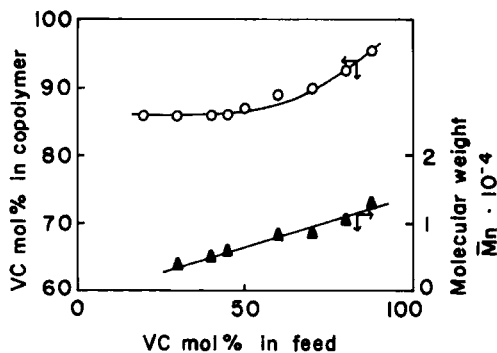


FIG. 3. Relationships between feed composition and (○) composition of copolymer and (▲) molecular weight. Polymerization temperature 50°C; [AIBN] = 5×10^{-2} mole/liter; bulk polymerization.

composition is independent of feed composition, except at high VC concentration in feed. The content of VC in the copolymers increases with increasing temperature. The dependence of the copolymer composition on feed composition in the higher region of the VC concentration becomes stronger at higher reaction temperatures.

The relationships between feed composition, overall rate of polymerization, molecular weight, and composition of copolymers in Figs. 2 and 3 show that both the overall rate of copolymerization and the molecular weight increase as the VC concentration in the feed increases. It is also noted that molecular weights of the copolymers decrease considerably with increasing temperature.

Dilution Effects

The results of the dilution effects in toluene at constant molar ratio of SO_2 to VC in feed ($[\text{SO}_2]/[\text{VC}] = 1$) are shown in Fig. 4. The amount of sulfur dioxide incorporated into the copolymer and the molecular weights of the copolymer obtained at 28°C decrease on dilution of total monomer concentration. However, these dilution effects were not observed at low temperature (0°C).

Overall Rate of Copolymerization

The dependence of the overall rate of copolymerization on the monomer concentration is shown in Figs. 5 and 6. The overall rate

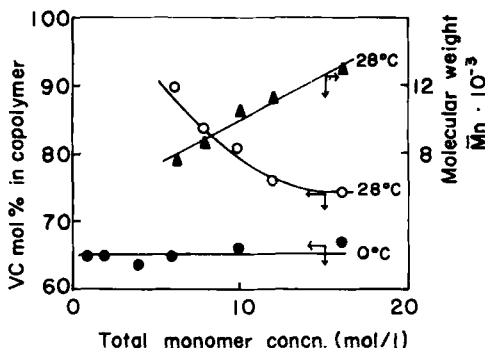


FIG. 4. Relationships between total monomer concentration and (\circ , \bullet) composition of copolymer and (\blacktriangle) molecular weight: (\circ) polymerization temperature 28°C ; (\bullet) 0°C . Molar ratio of VC/ SO_2 in feed 1.0; diluent toluene.

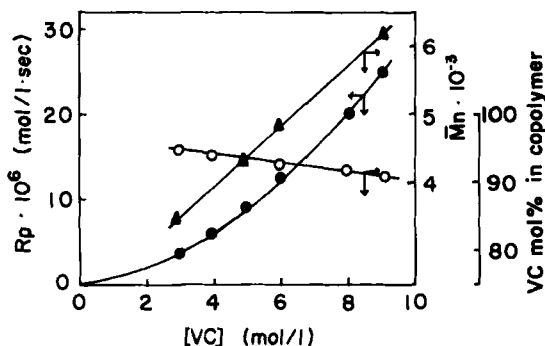


FIG. 5. Dependence of (●) overall rate of copolymerization, (○) composition of copolymer, and (▲) molecular weight on the concentration of vinyl chloride. Polymerization temperature 50°C; [AIBN] = 0.1 mole/liter; [SO₂] = 5.23 mole/liter; diluent toluene.

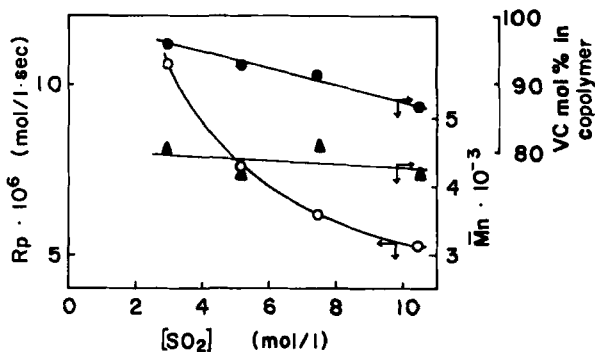


FIG. 6. Dependence of (○) overall rate of copolymerization, (●) composition of copolymer, and (▲) molecular weight on the concentration of sulfur dioxide. Polymerization temperature 50°C; [AIBN] = 6.7×10^{-2} mole/liter; [VC] = 5.05 mole/liter; diluent toluene.

is proportional to $[VC]^{1.7}$, but surprisingly, it is proportional to $[SO_2]^{-0.5}$. It is noted that the molecular weights of the copolymers increase with the increase in the initial VC concentration. The unexpected decreasing trend of the VC content in the copolymers with the increase in the initial concentration of VC can be explained

by the fact that, in this case, the effects of the initial VC concentration on copolymer composition is not as great as that of the total monomer concentration.

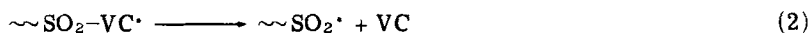
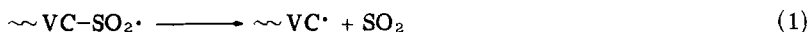
DISCUSSION

Dilution Effects

Exclusion of Participation of Monomer Complex Propagation. Schneider et al. [8] proposed the participation of SO_2 -VC complex in SO_2 -VC copolymerization initiated by γ -radiation. The evidence of the formation of SO_2 -VC and $(\text{SO}_2)_2$ -VC complexes in liquid mixtures of SO_2 and VC has been reported by Cais and O'Donnell [3]. In order to ascertain whether monomer complexes are necessarily involved, we investigated the dilution effects on copolymer composition. As shown in Fig. 4, at first sight the dilution effects at 28°C can be interpreted in terms of the participation of monomer complex or depropagation. From the viewpoint of a complex participation, it is expected that the composition of the copolymer will depend on the total monomer concentration, because the monomer complex concentration increases with increasing the total monomer concentration. However, the absence of dilution effects at 0°C (the copolymer composition is independent of total monomer concentration) indicates that the monomer complex may play no direct part in the copolymerization.

Therefore, the dilution effect is attributed to the depropagation.

The copolymer compositions vary with total monomer concentration since the propagation, a second-order reaction, is expected to decrease relatively faster than the first order depropagation on the dilution. Further, two kinds of first-order depropagation processes should be considered:



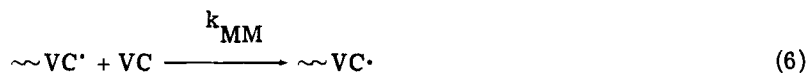
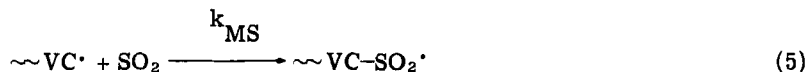
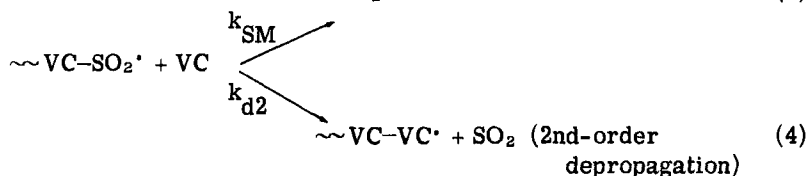
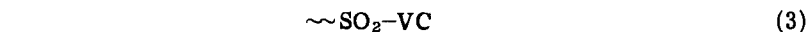
However, the absence of dilution effects at 0°C implies that the rate of these processes must be either negligible or exactly equal at this temperature. The former implication seems to be more reasonable. At 28°C , sulfur dioxide content of copolymer decreases significantly with diluting total monomer concentration. This indicates that the

first-order depropagation of the type shown in Eq. (1) is predominant here. This depropagation involving a scission of C-S bond, seems to be associated with a relatively high activation energy ($E_d - E_p \approx 20$ kcal/mole for the olefin-SO₂ system [11]). It can be negligible at 0°C, but becomes more significant as the temperature increases.

The decrease in sulfur dioxide in copolymer with increasing temperature in Fig. 1 can be also explained by the enhancement in such first-order depropagation with the rise in temperature.

Propagation Mechanism Proposed for Radical Copolymerization of Sulfur Dioxide and Vinyl Chloride. The above results indicate that the dilution effects and the effect of temperature on the copolymer composition observed in the SO₂-VC system are similar to those obtained in the SO₂-styrene system [4]. These results lead to a conclusion that the previously proposed propagation mechanism [4] for the SO₂-styrene system is also applicable for the SO₂-VC copolymerization.

At Low Temperature. It is recalled that the first-order depropagation having a relatively high activation energy may be negligible at low temperature. However, the second-order depropagation, in which an addition of VC to the growing sulfonyl radical occurs concurrently with an elimination of SO₂, still operates even at low temperature, since an electron donor-acceptor interaction between the growing sulfonyl radical and VC may provide the energy



for eliminating a sulfur dioxide unit. We introduce the second-order depropagation step into the reaction scheme to explain the results at low temperature as follows. The composition equation at low temperature was derived from Eqs. (3)-(6) by using the usual steady-state assumption for the growing polymer radicals:

$$n = (\text{VC}/\text{SO}_2)_{\text{copolymer}}$$

$$= 1 + \frac{k_{d2}}{k_{SM}} + \frac{(k_{SM} + k_{d2}) k_{MM} [\text{VC}]}{k_{SM} k_{MS} [\text{SO}_2]} \quad (7)$$

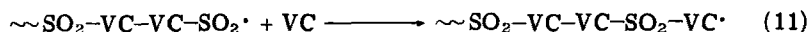
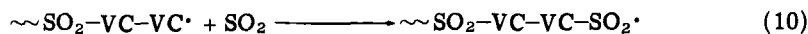
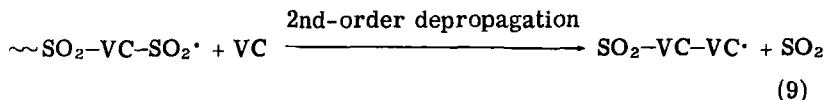
The dependence of the copolymer composition on feed composition at higher VC concentration in the feed (see Fig. 1) is expressed by the last term in Eq. (7). At lower VC concentration ($[\text{VC}] < 70\%$), Eq. (7) becomes approximately

$$n = 1 + (k_{d2}/k_{SM}) \quad (8)$$

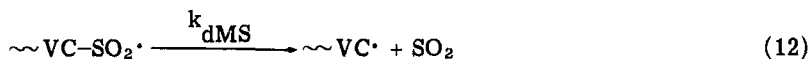
The absence of dilution effect at 0°C can be explained by the composition equation [Eq. (8)] in which n is independent of the total monomer concentration.

Schneider [8] and Suzuki [9] prepared poly(vinyl chloride sulfones) with a wide range of compositions ($n = 3.6-1$) by lowering the reaction temperature from 0°C to -196°C . Their results can be explained by the expected temperature dependence of the ratio k_{d2}/k_{SM} in Eq. (8).

Further, Cais and O'Donnell reported [10] that the poly(vinyl chloride sulfone) prepared at 0°C , $[\text{VC}]$ in feed = 40 mole % contained $> 95\%$ of $\text{SO}_2\text{VCVCSO}_2$ sequence. At the VC concentration in feed used, the reaction expressed by Eq. (6) is negligible. Adding the assumption of the antepenultimate unit effect for growing sulfonyl radical, we can explain their results by the second-order depropagation as follows:



At Room Temperature and Above. The first-order depropagation [Eq. (12)] must be taken into account here.



The composition equation was derived from Eqs. (3)-(6) and (12).

$$\begin{aligned} n &= (\text{VC}/\text{SO}_2)_{\text{copolymer}} \\ &= 1 + \frac{k_{\text{d2}}}{k_{\text{SM}}} + \frac{k_{\text{dMS}}k_{\text{MM}}}{k_{\text{SM}}k_{\text{MS}}[\text{SO}_2]} + \frac{(k_{\text{SM}} + k_{\text{d2}})k_{\text{MM}}[\text{VC}]}{k_{\text{SM}}k_{\text{MS}}[\text{SO}_2]} \quad (13) \end{aligned}$$

At lower VC concentration ($[\text{VC}] < 60$ mole %) Eq. (13) reduces approximately to

$$n = 1 + (k_{\text{d2}}/k_{\text{SM}}) + (k_{\text{dMS}}k_{\text{MM}}/k_{\text{SM}}k_{\text{MS}}[\text{SO}_2]) \quad (14)$$

We can explain the observed dilution effects at 28°C (Fig. 4) by the last term in Eq. (14) because the SO_2 concentration is proportional to the total monomer concentration.

Molecular Weights of Copolymers

It is noted that the molecular weights of copolymers in Figs. 2 and 3 fall off markedly with the rise in the reaction temperature. This can be expected, since the molecular weights of copolymers are decreased not only by the enhancement of depropagation but also by the increase in the rate of the initiation or termination steps. The molecular weights of copolymers also depend on each monomer concentration (See Figs. 2, 5, and 6). They increase with decreasing initial SO_2 concentration or with increasing initial VC concentration. The results are in accord with the fact that the rate of copolymerization is proportional to $[\text{VC}]^{1.7}$ and inversely proportional to the square root of the SO_2 concentration. Finally, the molecular weights of copolymers decrease on dilution (see Fig. 4). This may be attributed to both chain transfer to toluene and the depropagation.

TABLE 1. Comparison of the Kinetic Behavior of the SO₂-Vinyl Chloride Copolymerization with that of the SO₂-Styrene System^a

	SO ₂ -VC system	SO ₂ -styrene system	Remarks
k_{MS} (liter/mole-sec)	$k \sim VC \cdot + SO_2$	$k \sim St \cdot + SO_2$	$k_{CH_3 \cdot} + SO_2 \approx 10^8 b$
k_{SM} (liter/mole-sec)	$k \sim SO_2 \cdot + VC$	$k \sim SO_2 \cdot + St$	$k_{RSO_2 \cdot} + St$ <hr/> $k_{RSO_2 \cdot} + VC$
$k_{MM} \approx k_p$ (liter/mole-sec) ^d	11,000 (50°C)	123 (50°C)	$> 125^\circ C$
Order of k's	$k_{MS} \gg k_{MM} > k_{SM} \approx k_{d2}$	$k_{MS'} k_{dMS} \gg k_{MM'} k_{SM'} k_{d2}$	Room temp and above
R_p	$R_p \propto [VC]^{1.7} [SO_2]^{-0.5}$	$R_p \propto [St]^{1.3} [SO_2]^0$	
Alfrey-Price Q-e ^d			
Q	+0.044	+1	
e	+0.20	-0.8	

^aData of Matsuda et al. [4].

^bData of James et al. [15].

^cData of Takahara et al. [13].

^dData of Brandrup and Immergut [14].

Comparison of SO₂ - VC System with SO₂ - Styrene System

The results of the comparison of the two systems are summarized in Table 1. Using the Alfrey-Price Q-e values of these vinyl monomers we will make a qualitative comparison of the rate constants for the elementary steps in the proposed mechanism. The addition of the growing sulfonyl radical to vinyl monomer is an electrophilic reaction [12]. The e value for the arene sulfonyl radical has been reported [13] to be +2.8. The electrophilic attack of the growing sulfonyl radical to vinyl monomer is more favorable for vinyl monomer having a more negative e value, and yielding a radical more stabilized by resonance effects. By this consideration, we conclude that k_{SMst} is larger than k_{SMvc} (where the subscripts st, vc denote styrene and vinyl chloride, respectively). From the extrapolated value in our earlier work [13], it was shown that the rate constant for the addition of sulfonyl radical to styrene is at least 125 times greater than that of the sulfonyl radical to VC [Eq. (3)].

On the other hand, on the basis of the e values, the addition of a growing styryl radical to SO₂ should be more rapid than that of VC radical to SO₂ [Eq. (5)], i.e., $k_{MSst} > k_{MSvc}$.

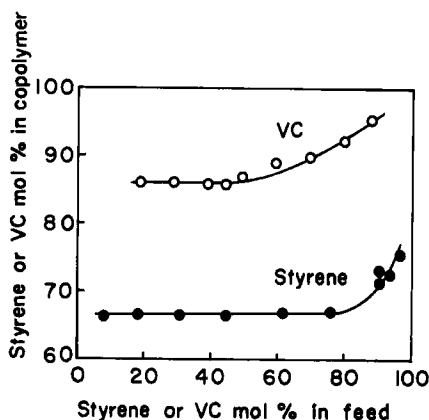


FIG. 7. Dependence of copolymer composition on feed composition for copolymerization: (●) sulfur dioxide-styrene; (○) sulfur dioxide-vinyl chloride. Polymerization temperature 50°C; bulk polymerization.

The growing $\sim\text{VC-SO}_2\cdot$ radical, being unstable due to the electrostatic repulsion between Cl atom and SO_2 group, will release more easily an SO_2 unit, i.e., $k_{\text{dMSst}} < k_{\text{dMSvc}}$. This conclusion is in accord with the result in Fig. 7. Indeed, under the same reaction conditions, poly(styrene sulfone) is richer in SO_2 than poly(vinyl chloride sulfone).

It is also noted that the effect of feed composition on the copolymer composition in high region of the initial vinyl monomer concentration is more significant for SO_2 -VC system (Fig. 7). We can explain these results by the vinyl monomer concentration dependence of the last term in Eq. (13) in which $k_{\text{MMvc}} > k_{\text{MMst}}$.

Overall Rate of Copolymerization

The overall rate of copolymerization for the SO_2 -styrene system was previously found to be independent of the initial SO_2 concentration. This was interpreted that the addition of the growing sulfonyl radical to styrene and its reverse step are much faster than other processes at room temperature and above ($k_{\text{MS}}, k_{\text{dMS}} \gg k_{\text{MM}}, k_{\text{SM}}, k_{\text{d2}}$). In the SO_2 -VC system, the overall rate is surprisingly inversely proportional to the square root of the SO_2 concentration. It is very difficult to explain this unexpected effect in terms of the initiation and termination steps. If the propagation step is assumed to be responsible for this effect, the following interpretation seems to be most reasonable: since the rate constant for the reaction of methyl radical with SO_2 is about 10^8 liter/mole-sec [15] and that k_{MM} for vinyl chloride is about 11000 liter/mole-sec [14], it is reasonable to assume that $k_{\text{MS}} \gg k_{\text{MM}}$. The increase in initial SO_2 concentration leads to a considerable increase of sulfonyl radical in the total growing radical concentrations. Consequently, the overall rate of copolymerization is slowed for two reasons: (1) the reaction of growing sulfonyl radical with VC radical is very slow ($k_{\text{MM}} > k_{\text{SM}}$); and (2) the propagation of growing vinyl chloride radical to vinyl chloride is hindered, because the concentration of growing VC radical is expected to decrease considerably. Our explanation appears to be consistent with the results presented in Fig. 8. Indeed, when the initial SO_2 concentration increases, the rate of SO_2 disappearance increases slightly, but the rate of VC disappearance falls off significantly due to the above-mentioned reasons. Therefore, the difference in the dependency of overall rate on concentration of SO_2 between these two systems can be considered to be $k_{\text{MMvc}} > k_{\text{MMst}}$ and $k_{\text{SMst}} > k_{\text{SMvc}}$.

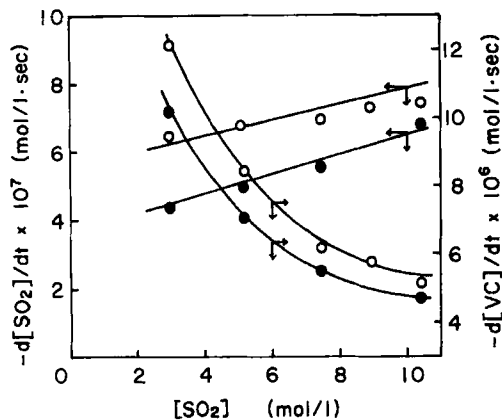


FIG. 8. Relationships between sulfur dioxide concentration and rate of disappearance of sulfur dioxide and of vinyl chloride: (○) $[AIBN] = 1.0 \times 10^{-1}$ mole/liter; (●) $[AIBN] = 6.7 \times 10^{-2}$ mole/liter. Polymerization temperature 50°C ; $[VC] = 5.05$ mole/liter; diluent toluene.

CONCLUSIONS

The previously proposed mechanism for the SO_2 -styrene system is also valid for the SO_2 -VC system, except that the homopropagation [Eq. (6)] must be taken into account even at 0°C .

VC in poly(vinyl chloride sulfone) is richer than styrene in poly(styrene sulfone). This is interpreted by the fact that

$$k_{MMvc} > k_{MMst}, k_{dMSvc} > k_{dMSst} \text{ and } k_{MSst} > k_{MSvc}.$$

The difference in the dependency of the overall rate of copolymerization on the initial SO_2 concentration is due to the fact that $k_{MMvc} > k_{MMst}$ and that $k_{SMst} > k_{SMvc}$.

ACKNOWLEDGMENT

One of the authors (H. H. Thoi) expresses his thanks to the Japanese Ministry of Education for the award of a scholarship for carrying out this investigation.

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DISCUSSION

Dr. Mielke (Hoechst A. G., Gendorf, West Germany): I am interested in the properties of the copolymers obtained by Dr. Matsuda, both the morphology and the thermodynamic properties.

Dr. Matsuda: The purpose of the polymerization experiments was to determine the propagation mechanism. This meant that we carried out the polymerization in small-scale experiments and we did not obtain sufficiently large amounts of polymers to determine the physical properties. I have no data on them.