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Polysulfone Formation and *cis–trans* Isomerization of Olefins over Manganese Dioxide

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The *cis–trans* selective isomerization of various olefins, induced by adsorbed SO_2 over MnO_2, and the copolymerization of SO_2 and olefins have been studied under the same conditions. The results of a study of the temperature dependence of the two reactions show a good correlation between the occurrence of isomerization and the formation of polysulfone and support the previously proposed mechanism that the *cis–trans* isomerization proceeds by elimination of the olefin molecule from the terminal of polysulfone during the progress of the copolymerization. It is hypothesized that the very high catalytic activity of MnO_2 for the two reactions may be caused by a strong electrostatic field on the surface brought about by the formation of SO_4^{2-}.

INTRODUCTION

In a previous report (*1*), it was shown that SO_2 adsorbed onto various metal oxides or zeolites causes the *cis-trans* isomerization of 2-butenes without enhancing the rate of double-bond migration. This selective *cis–trans* isomerization has been explained by means of a mechanism by which the addition and elimination of *cis-* or *trans*-2-butene molecules at the terminal of the polysulfone formed from SO_2 and 2-butenes cause the isomerization (*1*). However, further studies are needed to confirm this mechanism, and, in this report, we examine a correlation between polysulfone formation and geometrical isomerization which supports the proposed mechanism. It has been found that in the presence of adsorbed SO_2, MnO_2, and PbO_2 have the highest catalytic activities for isomerization among all the catalysts examined (*1*). Furthermore, polysulfone formation from 2-butenes has been confirmed with these two oxides (*1*). Hence, in the present work, we intend to clarify the general feature of the copolymerization of SO_2 with olefins in a gas–solid heterogeneous catalysis system using MnO_2. Then, by studying the correlation between copolymerization and *cis–trans* isomerization for various olefins, we will verify the mechanism of the latter reaction. Finally, the nature of the active site on MnO_2 will be discussed briefly.

EXPERIMENTAL METHODS

Catalyst. Commercial MnO_2 prepared from the reduction of $KMnO_4$ was used as the catalyst. The catalyst (14–22 mesh) degassed at 100°C has a BET surface area of 113 m^2/g.

Materials. The reagent SO_2 gas, anhydrous grade, was supplied by Matheson Chemical Co. The *cis*-2-butene was a high-purity product of Phillips Petroleum Co. Ethylene, propylene, *trans*-2-butene, and 1-butene were purchased from Takachiho Chemical Industry. 1-Pentene, 2-pentenes,

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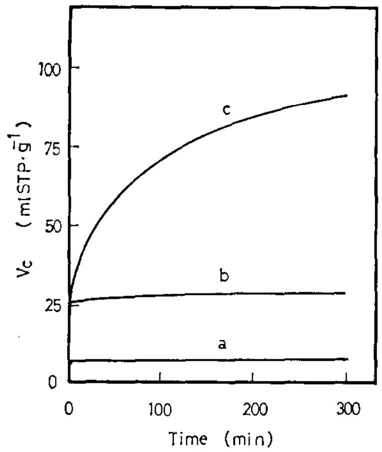


FIG. 1. The time dependence of the amounts of gas consumption at 0°C ($MnO_2 = 0.30$ g): (a) 1-butene, 1.54×10^{-3} mol has been added to the system; (b) SO_2, 1.54×10^{-3} mol; (c) 1-butene + SO_2, 1.54×10^{-3} mol for each compound.

1,3-pentadienes, and 1,2-dichloroethylenes were products of Tokyo Kasei Co., Ltd. Each compound was purified by trap-to-trap distillation in a vacuum apparatus. The *cis*-1,2-d_2-ethylene was a product of Merck Sharp and Dohme Co., Ltd. and was used without further purification.

Apparatus. The apparatus employed was a conventional gas circulating system with a volume of 207 ml, capable of achieving a vacuum of 10^{-6} Torr.

Procedure. Prior to every run, the MnO_2 in the reactor was degassed under vacuum at 0°C, unless otherwise stated. After the addition of SO_2, the two reactions, isomerization and copolymerization, were started by feeding *cis*-2-butene and circulating the gas mixture through the catalyst bed. A small amount of the reacting gases was periodically collected for analysis by gas chromatography, and the conversion of the olefin by isomerization was determined. The copolymerization of olefins with SO_2 was tested by measurement of the decrease in pressure of the equimolar gas mixture of SO_2 and olefin and by measurement of the infrared absorption spectra of the polysulfone formed on the MnO_2 used for the reaction.

Analysis. Analysis of the isomers of olefins was performed by means of gas chromatography using a column with a stationary phase of propylene–carbonate or silver nitrate–benzyl cyanide on Celite 545. The isomers of 1,2-d_2-ethylene were analyzed in a Shimazu double-beam infrared spectrophotometer. The absorption peaks at 725 and 987 cm^{-1} are assigned to *trans*-1,2-d_2-ethylene, and the peak at 842 cm^{-1} is assigned to *cis*-1,2-d_2-ethylene (*2*). These peaks were used for quantitative estimation of the conversion.

The sample of MnO_2 used for the polymerization experiment was ground to a fine powder and was mixed with KBr. Infrared spectra of the KBr-supporting sample disk were recorded for estimating the amount of polysulfone formed over MnO_2.

RESULTS

Copolymerization of 1-Butene with SO_2

Adsorption of 1-butene on MnO_2 at 0°C is complete within a few minutes after introduction of the gas. In the case of SO_2, after the fast initial adsorption, a small increase in the amount of adsorption with time was observed. In contrast, in the experiment of co-adsorption of SO_2 and 1-butene, a fairly fast continuous consumption of the gas mixture was observed, suggesting that a reaction between the two adsorbates does occur. The time dependence in the amounts adsorbed are illustrated in Fig. 1.

The infrared spectra of the MnO_2 used for the experiments in Fig. 1 are shown in Fig. 2. The absorption at 710 cm^{-1} observed on every spectrum in the figure is attributed to the Mn–O vibration in the MnO_2 lattice (*3*). The broad band at 1120 cm^{-1} for spectrum 2 is assigned to the S–O unsymmetrical stretching vibration of SO_4^{2-} species (*4*) formed through a reaction of SO_2 with surface oxygen. The formation of SO_4^{2-} has also been confirmed in the case of PbO_2. Spectrum 3 for the MnO_2

sample used in the co-adsorption experiment exhibits the two characteristic absorption bands of a polysulfone, one at 1300 cm^{-1} and the other at 1120 cm^{-1}, due to the symmetrical and the unsymmetrical stretching vibration of the sulfone group, respectively (*5*).

A_p/A_M, the optical density for the band at 1300 cm^{-1} divided by that at 710 cm^{-1}, has been measured for the MnO_2 samples used in the reaction for different running times. This ratio represents the relative amount of polysulfone produced on a unit weight of MnO_2. A plot of A_p/A_M against the amount of the gas mixture consumed, V_c, is indicated in Fig. 3. The good linear correlation, as seen in the figure, suggests that, after the rapid initial adsorption corresponding to the value of the intercept at the abscissa, the SO_2 and 1-butene in the gas phase must be consumed by the copolymerization between the two compounds over MnO_2. By analyzing the products in the gas phase after 5 hr of copolymerization, it has been shown that no other reactions, such as double-bond migration, disproportionation, metathesis, or dimerization of the butene occur. Furthermore, quantitative analysis of the gas-phase composition of SO_2 and 1-butene has indicated that these two compounds are consumed in equal amounts, suggesting that the polymer is a 1:1 copolymer.

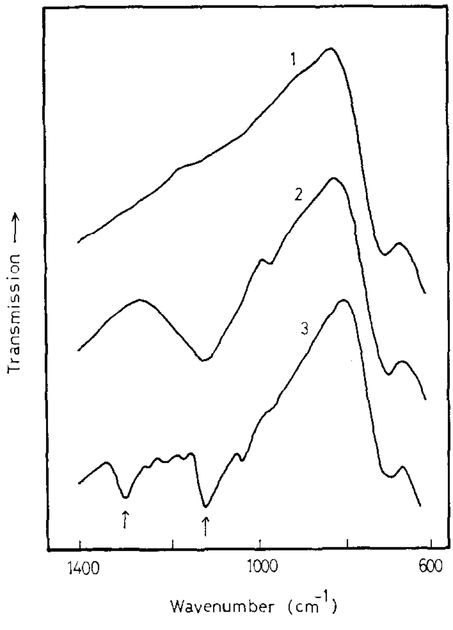


FIG. 2. The infrared spectra of the wafers of MnO_2: (1) background spectrum of MnO_2; (2) after 5 hr of contact with SO_2 at 0°C; (3) after 5 hr of contact with 1-butene and SO_2 (1:1) gas mixture at 0°C.

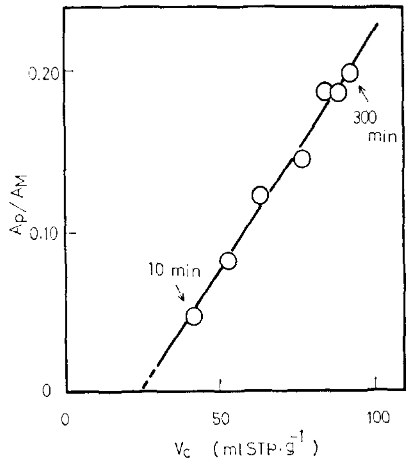


FIG. 3. Plot of A_p/A_M against the amount of the gas mixture consumed (V_c): A_p and A_M are the optical densities for the bands of polysulfone and MnO_2, respectively. The polymerization was carried out at 0°C using 1-butene and SO_2 (1.54×10^{-3} mol for each compound). MnO_2 was degassed at 0°C before running the experiment.

Correlation between Copolymerization and cis–trans Isomerization

The copolymerization and geometrical isomerization of various olefins were tested by feeding the SO_2–olefin (1:1) gas mixture of 3.0×10^{-3} mol onto the MnO_2 bed (0.30 g) maintained at 0°C, and analysis of the products was carried out after the reaction had been run for 5 hr. Formation of the polysulfone has been confirmed for many alkenes, as shown in Fig. 4. The relative amounts of the polymers formed are summarized in Tables 1 and 2. The *cis* and *trans* compositions of the olefins in the gas phase, before and after their use for

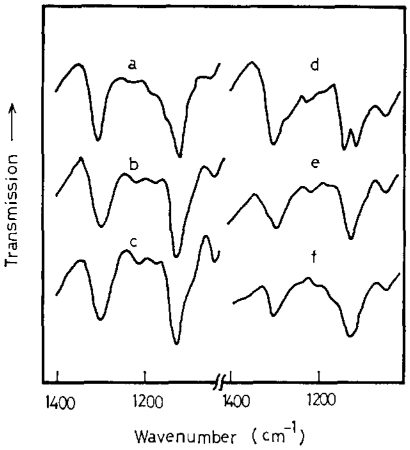


FIG. 4. The infrared spectra of the polysulfones formed from various olefins: (a) ethylene; (b) propylene; (c) 1-butene; (d) 2-butene; (e) 1-pentene; (f) 2-pentene. The copolymerizations were carried out for 5 hr at 0°C, using a 1:1 gas mixture of SO_2 and olefins (3.0×10^{-3} mol). No difference was observed in the spectra between the isomers of 2-butene or between those of 2-pentene.

copolymerization are also shown in Table 2. It is obvious from Table 2 that only the olefins undergoing geometrical isomerization accompany the copolymerization or vice versa.

The effects of temperature on both the rate of geometrical isomerization of *cis*-2-butene and the amount of polysulfone formed from *cis*-2-butene or 1-butene are shown in Fig. 5, where these reactions were carried out under a total initial pressure of 240–250 Torr (SO_2/butene = 1.0). This figure indicates that copolymerization has a ceiling temperature (*5, 6*) of about 20–30°C, and that the rate of geometrical isomerization of *cis*-2-butene reaches its maximum at about this temperature.

The effect of temperature on the geometrical isomerization of *cis*-1,2-d_2-ethylene has also been examined under a total reactant pressure of about 140 Torr (SO_2/ethylene = 1.0) using 0.1 g of MnO_2. Isomerization did not occur at 0°C. However, it proceeded fairly rapidly at 100°C without an accompanying hydrogen-exchange reaction. The percentages of *trans* isomer produced after reaction for 3 hr were 0.7 and 29% at 25 and 100°C, respectively.

DISCUSSION

The Mechanism of cis–trans Isomerization

The absence of double-bond migration for any olefins tested here shows that the *cis–trans* isomerization catalyzed by SO_2 adsorbed on MnO_2 does not proceed via the mechanisms generally proposed for normal butene isomerizations over metal oxides, such as the one invoking a carbonium ion, a carbanion, or an alkyl radical as the reaction intermediate. This has been supported by the observation that no deuterium exchange occurs in 1,2-d_2-ethylene (this work), deuterium–butene, C_2D_4–butene, and C_2D_4–C_2H_4 (*1*). The only reaction observed in the present work, other than geometrical isomerization, is copolymerization between SO_2 and olefins. MnO_2 and PbO_2, which have the

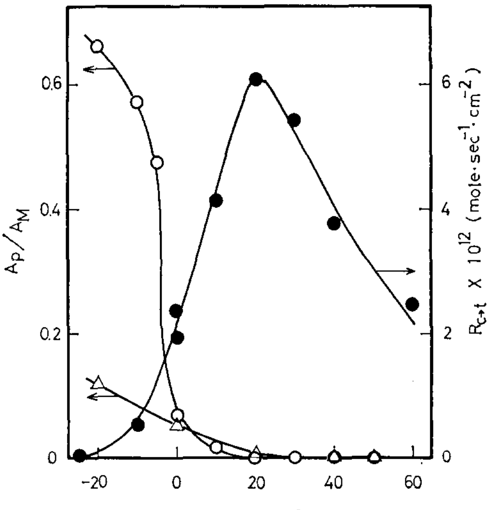


FIG. 5. The rate of geometrical isomerization and the formation of polysulfone as a function of temperature: MnO_2 was degassed at 100°C. (●) The initial rate of geometrical isomerization; (○) the relative amount of the polysulfone formed from *cis*-2-butene; (△) the relative amount of the polysulfone from 1-butene.

TABLE 1

Formation of Polysulfones from Various Olefins at 0°C after Reaction for 5 hr[a]

Olefin	Relative amount of polysulfone formed ($A_p/A_M \times 10^3$)
Ethylene	53
Propylene	79
1-Butene	54
1-Pentene	119
2-Methyl-2-butene	0

[a] MnO_2 was degassed at 100°C before running the experiment.

highest catalytic activities in the geometrical isomerization induced by SO_2, are the only two catalysts producing the polysulfone to a measurable extent, of the 12 catalysts examined in previous work (*1*). This and the clear evidence in Table 2 that geometrical isomerization of olefins always accompanies the formation of their polysulfones strongly support the idea that selective *cis–trans* isomerization of olefins occurs via the following mechanism (*1*, *7*):

$$SO_2 + cis\text{- or } trans\text{-2-olefin} \rightleftarrows \mathrm{CTC}, \tag{1}$$

$$\mathrm{CTC} \rightarrow P_B + P_S, \tag{2}$$

$$P_B + SO_2 \rightarrow P_S, \tag{3}$$

$$P_S + cis\text{- or } trans\text{-2-olefin} \rightarrow P_B, \tag{4}$$

$$P_B \rightarrow P_S + trans\text{-2-olefin}, \tag{5}$$

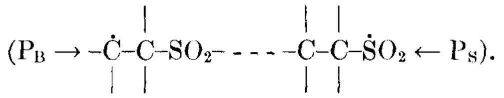
$$\rightarrow P_S + cis\text{-2-olefin}, \tag{6}$$

$$P_S \rightarrow P_B + SO_2 \tag{7}$$

$$P_B \rightarrow \text{stabilized}, \tag{8}$$

$$P_S \rightarrow \text{stabilized}, \tag{9}$$

where CTC is the charge-transfer complex of SO_2 and the 2-olefin interested, and P_B or P_S represents the terminal group of the olefin or SO_2 radical of the corresponding polysulfone, respectively



$$(P_B \rightarrow -\dot{C}-C-SO_2- - - - -C-C-\dot{S}O_2 \leftarrow P_S).$$

The selective *cis–trans* isomerization occurs through the depropagation step [(5) or

TABLE 2

Polysulfone Formation and *cis–trans* Isomerization of Various 2-Olefins at 0°C after Reaction for 5 hr[a]

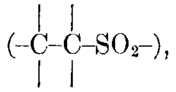
Starting olefin	Relative amount of polysulfone ($A_p/A_M \times 10^3$)	Composition of starting olefin		Composition after the reaction	
		cis(%)	*trans*(%)	*cis*(%)	*trans*(%)
cis-2-Butene	70	100	0	36	64
trans-2-Butene	32	0	100	19	81
cis-2-Pentene	0	98	2	21	79
cis-2-Pentene	63[b]	98	2	48	52
trans-2-Pentene	0	0	100	10	90
trans-2-Pentene	73[b]	0	100	9	91
cis-1,3-Pentadiene	0	100	0	100	0
cis-1,3-Pentadiene	0[b]	100	0	100	0
trans-1,3-Pentadiene	0	0	100	0	100
cis-1,2-Dichloroethylene	0	95	5	95	5
trans-1,2-Dichloroethylene	0	3	97	3	97

[a] MnO_2 was degassed at 100°C before running the experiment.

[b] These reactions were carried out at −16°C.

(6)] of the copolymerization in the adsorption layer. This mechanism explains the results in Fig. 5: (i) With a rise in temperature up to the ceiling temperature of copolymerization, the rate of *cis–trans* isomerization increases sharply, and, accordingly, the polysulfone formation decreases; (ii) above the ceiling temperature, the rate of isomerization decreases as a consequence of the decrease in the number of polysulfone sites necessary for isomerization. It has been suggested that, in the liquid-phase reaction, the ceiling temperature for ethylene is more than 100°C higher than that for *cis*-2-butene (*5*). This implies that the rate of isomerization of *cis*-1,2-d_2-ethylene must be very slow at 0°C; however, it may be considerable at higher temperatures. These considerations have been confirmed in the present study as described above, which also supports the polysulfone-accompanying-isomerization mechanism.

In a homogeneous system under ultraviolet irradiation or with radical initiators, an aliphatic olefin almost invariably gives a 1:1 copolymer of the repeated structure

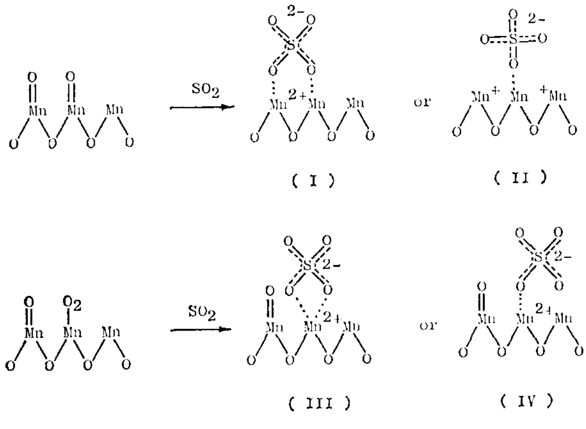


$$(-\mathrm{C}-\mathrm{C}-\mathrm{SO_2}-),$$

independent of the co-monomer composition (*8, 9*). The 1:1 copolymer has also been suggested in the present study.

The Role of Sulfate Ion in the Reactions

The picture of the primary step suggested for the *cis–trans* isomerization of 2-butenes caused by sulfur dioxide is a polarization of the charge-transfer complex (CTC) in the electrostatic field, resulting in formation of the radical ion which initiates copolymerization and, accordingly, isomerization (*7*). Formation of the sulfate ion shown in Fig. 2 (Spectrum 2) may be a result of the reaction of SO_2 with surface oxygen atoms or molecules over MnO_2, according to one or both of the following mechanisms:



where the SO_4 is weekly coordinated to Mn in structures I–IV, since spectrum 2 in Fig. 2 is very similar to that expected from a free sulfate ion (*4*); the surface manganese will be positively charged because of a consequent electron transfer from the surface to sulfate ions. This mechanism suggests that a strong electrostatic field would be formed. Furthermore, it is probable that the CTC, favorably positioned between the manganese cation and the sulfate anion, would be strongly polarized and activated by means of a concerted action of the anion-cation pairs. The action of SO_4^{2-}, as described above, may explain the fact that MnO_2 and PbO_2 have very high catalytic activities in the polysulfone accompanying geometrical isomerization. In order to confirm these points, further studies are in progress.

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