Cationic Polymerization of Isobutene in Liquid Sulfur Dioxide. Role of Water of Cocatalyst[1]

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Cationic polymerization of isobutene in liquid sulfur dioxide has already been proposed by Elwell and Meier[2a], and has been examined by Furuya and Honda[2b], who reported on the formation of high molecular weight polyisobutene when it was polymerized with alminum chloride at low temperature, but no suggestion has been made on the mechanism of the polymerization.

It is widely recognized that when a Friedel-Crafts catalyst was used in a cationic polymerization, a cocatalyst was necessary to initiate the polymerization[3-5]. Among such cocatalysts, water has lately been known as important proton releasing substance[3,4,6].

On the other hand, the solvents used for the polymerization such as alkyl halides or alkylene dihalides[6-8] have often been regarded as useful cocatalysts in cationic polymerization. However, a recent publication[9] is opposing the proposal.

Dainton[10] has carried out polymerization of isobutene in a gas phase at room temperature using boron trifluoride as a catalyst together with D_2O as a cocatalyst. The polymer obtained (DP, 10) was investigated by infrared spectral analysis in order to elucidate the mechanism of the initiation as well as the termination of the polymerization, though no decisive result was obtained concerning the mechanism of the initiation of the polymerization.

Liquid sulfur dioxide has been found to be a peculiar solvent by us and by others[11] in some organic reactions involving polymerization and a small amount of water in it is very difficult to eliminate within the order of 100 p. p. m. by ordinary method[12]. Therefore, water remaining in liquid sulfur dioxide will often act as a cocatalyst. On the other hand, liquid sulfur dioxide is reported to be able to dissociate as follows[13],

$$2SO_2=SO^{2+}+SO_3{}^{2-}$$

Thus sulfur dioxide seems likely to play a part as a cocatalyst via the sulfite cation.

This paper aims at the elucidation of the role of water, when the comparable amount of water is present in the cationic polymerization of isobutene in liquid sulfur dioxide by using stannic chloride.

The liquid sulfur dioxide used for the present investigation was dehydrated according to Hata and Asano's method[14] of this Institute, whereby water content in liquid sulfur dioxide was reduced to as low as 30 mg./l., that is calculated from the infrared absorption in 3675 cm^{-1} of the vibration of OH.

The participation of heavy water was examined by adding it to this dried sulfur dioxide in the polymerization of isobutene with stannic chloride as the catalyst.

To obtain polymers having the degree of polymerization (DP) of 2 to 4, an experimental condition has been chosen so as to polymerize the monomer at 35°C and stop at the conversion of 2~3%. The products were examined by their infrared spectral absorptions to determine the possibility of the participation of D_2O or sulfur dioxide as the catalyst in the polymerization reaction.

Experimental

Materials.—Isobutene was prepared by dehydration of *tert*-butyl alcohol with acetic acid anhydride containing a small amount of concentrated sulfuric acid. The purity of the isobutene was analyzed by gas chromatography, no contaminant being found in this material. Commercial stannic chloride was dehydrated with phosphoric acid anhydride

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3) C. G. Overberger, R. J. Ehrig and R. A. Morcus, *J. Am. Chem. Soc.*, **80**, 2456 (1958).

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7) D. C. Pepper, ibid., **45**, 404 (1949).

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10) F. S. Dainton and G. B. B. M. Sutherland, *J. Polym. Sci.*, **4**, 37 (1949).

11) See Ref. 1 and the preceding papers of this series.

12) D. Murakami and N. Tokura, This Bulletin, 33, 431 (1958).

13) G. Jander and K. Wichert, *Z. phys. Chem.*, **178**, 57 (1937).

14) T. Hata and T. Asano, *Hisuiken Hokoku* (*Bull. of Inst. of Non-Aqueous Soln.*), **9**, 79 (1960).

and distilled in dry nitrogen atomosphere. Heavy water of 99.8 mol. per cent, $d_4^{25}=1.1043$, made at the Asahi Kasei Industries Ltd. (Nobeoka) was used.

Sulfur dioxide was dehydrated according to the procedure of Hata and Asano[14]. In a glass pressure vessel, predehydrated sulfur dioxide[12] (200 ml. of liquid sulfur dioxide, which was treated with 30 g. of phosphoric acid anhydride for 24 hr.) was mixed with purified iodine (0.5 g.) and pure pyridine (10 ml.). The mixture was then distilled carefully through a tube packed with copper powders. The water content of the sulfur dioxide thus dehydrated was reported as 30 mg./l.[14]

Polymerization. — A weighed amount of stannic chloride sealed in an ampoule was added to a definite amount of sulfur dioxide in a pressure vessel by breaking the ampoule. This solution after filtration was diluted with a requisite amount of sulfur dioxide to the catalyst of a definite concentration.

The preparation of the normalized D_2O solution of sulfur dioxide was also prepared by a similar manipulation.

The DP of polyisobutene has been reported to be dependent on the temperature of polymerization. If the DP was large, the weak band of C–D stretching vibration derived from the cocatalyst fragment would become difficult to identify by an infrared spectral analysis. The optimum condition to realize the purpose of this project was searched in the ranges, 1.6×10^{-1} to 4.0×10^{-4} mol. per liter for tin(IV) chloride and 1.0×10^{-1} to 9.0×10^{-3} mol. per liter for D_2O respectively and decided as,

$SnCl_4$	3.0×10^{-2} mol./l.
D_2O	6.0×10^{-2} mol./l.

the concentrations being calculated by volume of sulfur dioxide at −10°C. The samples in Figs. 3 and 4 were prepared with catalysts in such concentrations. The specimens in Figs. 1 and 2 were prepared by another recipe, i. e. $SnCl_4$ 7.4×10^{-3} and D_2O 3.3×10^{-2} mol./l., respectively. The polymerization was carried out at 35°C, and the mole ratio of isobutene to liquid sulfur dioxide was 1 to 2. The time for 2∼3% conversion required about 20 min.

To stop the polymerization, liquid sulfur dioxide and isobutene unreacted were evaporated as fast as possible, the temperature of the residue being sustained at −10°C. The polymer produced during this period was so scarce that it should be treated cautiously during the water washing and the separation. The liquid polymer thus obtained, about 1 to 2 g. for each run, was dried with sodium sulfate and fractionated into the respective fractions, dimer (b. p. 104∼105°C)[15], (yield about 50% of the total polymer), trimer (b. p. 181∼183°C)[15] and tetramer (b. p. 120∼121°C/20 mmHg)[15].

The average molecular weight of the liquid polymer obtained was in the range of 138 (DP, 2.5) to 209 (DP, 3.7) which were measured by the cryoscopic method in benzene.

Infrared Spectra. — Infrared spectra were taken by a Perkin-Elmer double beam model 21 spectrometer, the cells being made of sodium chloride of the width, ca. 0.05 to 0.5 mm., respectively.

Results and Discussion

We have obtained a clear evidence to support the participation of water molecule as a cocatalyst in the polymerization. The polymerization in the extremely dried sulfur dioxide did not proceed to an appreciable extent.

As has been pointed out very recently by Kennedy[16], the monomer transfer should be as minimized as possible. So the polymerization was conducted at a higher reaction temperature (35°C) and the reaction was stopped at 2∼3% conversion, thus obtaining the polymer of a lower DP and of a lesser monomer transfer. Another reason for stopping the polymerization at low conversion was to inhibit the further polymerization of the low polymer produced, where the formation of head to head type polymer was expectable.

The C–D bonding of the polymer was observed distinctly by the infrared spectroscopy. The molecular weight of the polymer thus obtained was in the range of 138 (DP, 2.5) to 209 (DP, 3.7) according to the result of cryoscopic measurements in benzene. Figure 1 shows the spectrum of polyisobutene (unfractionated) of DP 2.5.

The solid line 1 in Fig. 2 shows the spectrum of the dimer fraction (cell width, 0.0496 mm.). If sulfur dioxide reacted as the cocatalyst, there should be absorptions corresponding to SO, SO_2H or SO_2 group in the polymer chain. We could not identify SO group absorption (1060∼1040 cm^{-1})[17] in Figs. 1 and 2. Since the polymer obtained was so low in its DP that the presence of any sulfur atom clinging

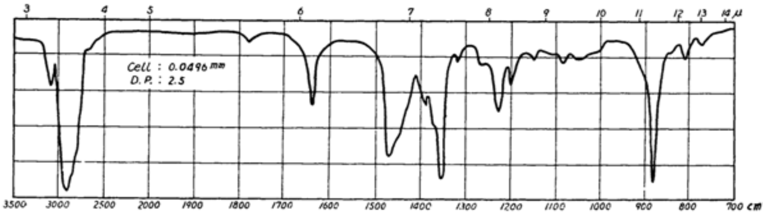

Fig. 1. Infrared spectrum of polyisobutene (DP 2.5).

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[15] a) H. Adkins, F. F. Diwoky and A. E. Broderick, *J. Am. Chem. Soc.*, **51**, 3422 (1929); b) S. W. Lebedev and G. G. Kobliansky, *Ber.*, **63**, 103 (1930).

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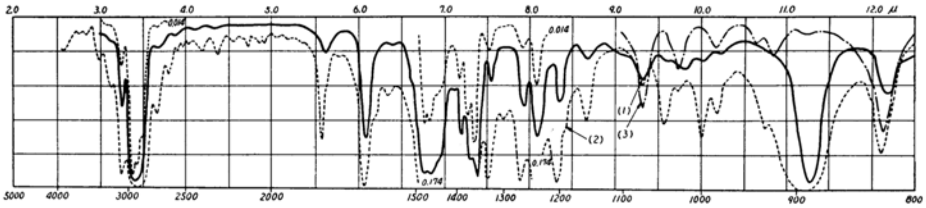

Fig. 2. Infrared spectra of isobutene dimer.

(1) ——— Sample (dimer) (cell, 0.0496 mm.)
(2) ------ 2, 4, 4-Trimethyl-1-pentene (cell, 0.174 and 0.014 mm.)
(3) —·—· 2, 4, 4-Trimethyl-2-pentene (cell, 0.013 mm.)

to the polymer chain may be ruled out. The dotted line 2 in Fig. 2 is the infrared spectrum of authentic 2, 4, 4-trimethyl-1-pentene (one of diisobutenes) cited from the Infrared Spectral Data of A. P. I.[18], which is consistent with that of our dimer except only by a small discrepancy in 1100~950 cm⁻¹.

In Fig. 3, line 1 shows a spectrum of the dimer in the range between 3000~1800 cm⁻¹, polymerized with D_2O in liquid sulfur dioxide. Line 2 in Fig. 3 is that of the dimer obtained with water. If water was playing a role as a cocatalyst, the polymer obtained from the polymerization with heavy water added should have a C–D bond at the end of the chain as shown in the following equations:

$$SnCl_4\cdot D_2O + (CH_3)_2C{=}CH_2$$
$$\rightarrow CH_2D\text{–}\underset{+}{C}(CH_3)_2 + SnCl_4DO^-$$
$$CH_2D\text{–}\underset{+}{C}(CH_3)_2 + (CH_3)_2\cdot C{=}CH_2$$
$$\rightarrow CH_2D\text{–}C(CH_3)_2\text{–}CH_2\text{–}\underset{+}{C}(CH_3)_2$$

Comparing lines 1 and 2 in Fig. 3, we can recognize a sharp band at 2183 cm⁻¹ (C–D stretching frequency) in 1, which evidently proves the participation of water molecule in the polymerization.

The line 3 in Fig. 3 is the spectrum of the dimer fraction obtained at a nearly 100% conversion of the polymerization in the same condition with heavy water. In this spectrum, we can recognize the dilution of the C–D band as the result of transfer reaction during the polymerization.

Figure 4 shows the infrared spectrum of the fraction of trimer and the higher polymer of the same product polymerized with D_2O (line 1). Other lines 2 and 3 are those of trimer and tetramer, respectively, which were derived by polymerization with water. However, the absorptions in the line 1 are overlapping and those at 2130 to 1820 cm⁻¹ indicate a slight shift, the presence of C–D band is evidenced by a clear peak at 2183 cm⁻¹. From the result above described, it can be concluded that in the cationic polymerization of isobutene with stannic chloride as catalyst in liquid sulfur dioxide, added water may take part in the polymerization as the cocatalyst.

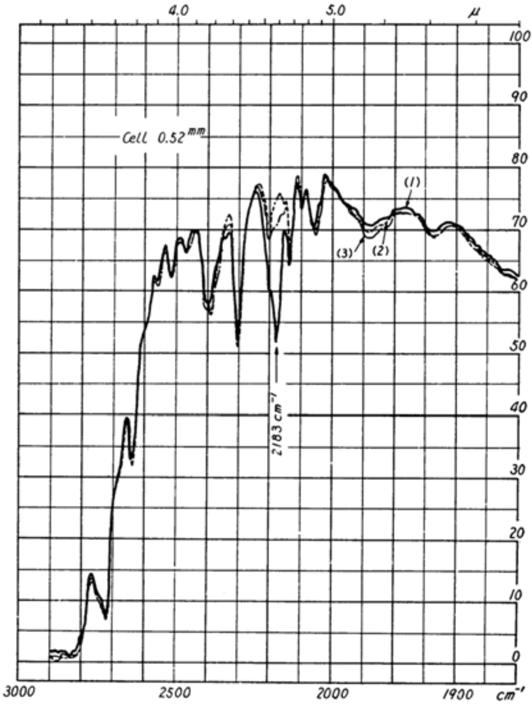

Fig. 3. Infrared spectra of isobutene dimer (3000~1800 cm⁻¹).

(1) ——— with D_2O
(2) ------ with H_2O
(3) —·—· with D_2O (near 100% conversion)

Next, we have to discuss again the spectra in Fig. 3, in which the line 3 is that of authentic 2, 4, 4-trimethyl-2-pentene of A. P. I.[18] The dimer prepared by us had strong absorptions at 1642 and 888 cm⁻¹ of terminal double

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[18] A. P. I., Infrared Spectral Data, I (Pittburgh), No. 276 and 277 (1943—1945).

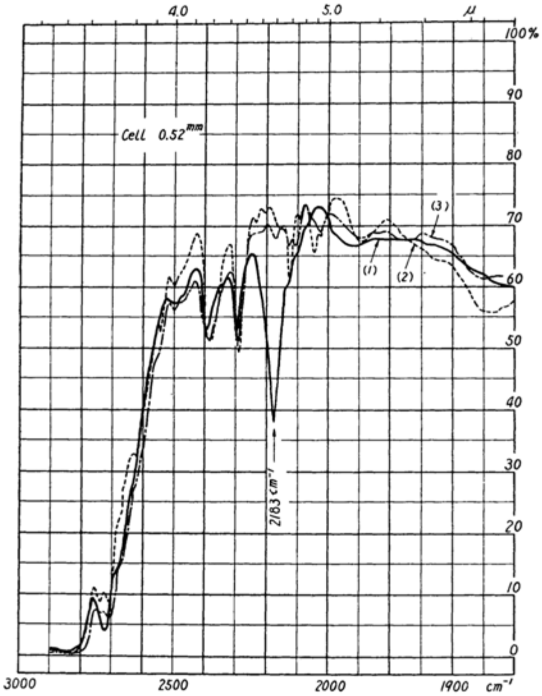
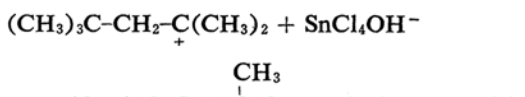


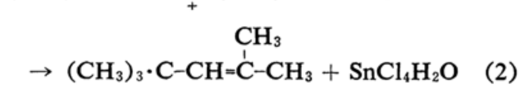
Fig. 4. Infrared spectra of isobutene polymers.

(1)	———	Trimer and higher fraction (with D_2O)
(2)	------	Trimer (with H_2O)
(3)	—·—·	Tetramer (with H_2O)

bond[19,20] and at 1200 and 1237 cm^{-1} of terminal *tert*-butyl group, respectively, which are almost consistent with 3. But there seem some inaccordances in the range of 1100 to 950 cm^{-1} between the two. The authentic 2, 4, 4-trimethyl-pentene has strong absorptions in its spectrum at 1074, 1034 and 983 cm^{-1}, whereas our dimer has weak bands at 1074 and 1030 cm^{-1}, which may be attributed to the presence of a small amount of 2, 4, 4-trimethyl-2-pentene (cf. line 3 in Fig. 2). Accordingly, in the termination step of the polymerization, reaction 1 may be preferred but reaction 2 may also occur in lower frequency.



$$(CH_3)_3C\text{-}CH_2\text{-}\underset{+}{C}(CH_3)_2 + SnCl_4OH^- \rightarrow (CH_3)_3C\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 + SnCl_4H_2O \quad (1)$$



$$(CH_3)_3\cdot C\text{-}CH_2\text{-}\underset{+}{C}\cdot(CH_3)_2 + SnCl_4OH^- \rightarrow (CH_3)_3\cdot C\text{-}CH{=}\overset{CH_3}{\overset{|}{C}}\text{-}CH_3 + SnCl_4H_2O \quad (2)$$

Finally, some comment should be added on the deuterium-hydrogen exchange during the polymerization. If the deuterium hydrogen exchange was proceeding competitively in the polymerization reaction, above conclusion could not be drawn. However, the possible deuterium hydrogen exchange during the polymerization would be rured out by the following reason. The line 3 in Fig. 3, which is the spectrum of the dimer fraction obtained at a nearly 100% conversion of the polymerization with D_2O, shows no strengthening of C–D band absorption as compared with that of 2∼3% conversion. On the contrary, there is marked decrease of C–D absorption in 3. Thus, no deuterium hydrogen exchange is conceivable.

This view may be supported by the experiment of Price and Berti[21], who observed no inclusion of deuterium in the polymerization of *cis*-stilben with boron fluoride and heavy water. The discussions on the same subject associated with the reacting species in the cationic reactions with Lewis acid as catalyst will be found abundantly, among which the works of Levy, Taft, Jr. and Hammett[22], Tauber and Eastham[23], and Hart and Levitt[24] are suggestive.

Water can thus be a cocatalyst in a cationic poymerization in liquid sulfur dioxide. However, the conclusion that sulfur dioxide cannot always be a catalyst or a cocatalyst is premature and should be reserved, because the polymerizations described above were undertaken only in a limited condition. The monomers such as vinyl ethers[25] and formaldehyde[26] can be polymerized cationically in liquid and gaseous sulfur dioxide without an acid catalyst.

Summary

Polymerization of isobutene was carried out in liquid sulfur dioxide with stannic chloride as catalyst containing water or heavy water. It was confirmed with the aid of infrared spectrometry that in liquid sulfur dioxide water was playing a part as a cocatalyst when water was present in a comparable amount.

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[25] W. Reppe, German Pat. 625017, U. S. Pat. 2188778.

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