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Polymerization of Ethyl and Methyl Vinyl Ethers Catalyzed by Iron Oxide Treatei with Sulfate Ion. Synthesis of Stereospecific Poly. (Methyl Vinyl Ether)[1)]

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A solid catalyst which was prepared by exposing $Fe(OH)_3$, obtained by hydrolyzing $Fe(NO_3)_3$ or $FeCl_3$ with ammonia, to 1 N H_2SO_4 and then calcining in air at 500°C was highly active for the title reaction at 0 — -20°C. This catalyst produced poly (methyl vinyl ether) with the crystalline structure.

Alkyl vinyl ethers are known to be susceptible to cationic polymerization, and the reaction is initiated by Ziegler-type catalysts and alkyl metals.[2)] In a previous paper,[3)] it was reported that calcined iron sulfate was exceedingly active for the polymerization of isobutyl vinyl ether. The maximum activity was shown by the catalyst calcined at 700°C, which gave the crystalline polymer at room temperature. This catalyst was shown to be α-Fe_2O_3, formed by the thermal decomposition of iron sulfate, with a small amount of sulfate ion on the surface as revealed by X-ray photoelectron spectroscopy and X-ray diffraction.[4)] Thus, iron oxide treated with sulfate ion was prepared and it was found to be exceedingly active for the polymerization; the crystalline poly (methyl vinyl ether) was synthesized at -10°C.

The catalyst was prepared as follows. $Fe(OH)_3$ was obtained by hydrolyzing $Fe(NO_3)_3 \cdot 9H_2O$ and $FeCl_3$ with aqueous ammonia, washing the precipitate, drying it at 100°C, and powdering. The dried hydroxide (2 g) was exposed to 1 N H_2SO_4 (30 ml) on a filter paper. After drying, the material was powdered below 100 mesh, calcined in a Pyrex tube in air at 500°C for 3 h, and finally sealed in an ampoule until use. The catalysts thus prepared from $Fe(NO_3)_3 \cdot 9H_2O$ and $FeCl_3$ were referred to Fe_2O_3-I and -II, respectively.

Polymerization was carried out by using these catalysts at 0 — -20°C in bulk or in toluene solution with stirring. After the reaction was stopped by adding methanol into the reaction mixture, the catalyst was separated by filtration or centrifugation. The polymer was obtained by evaporating the unreacted monomer, methanol, and toluene. In the case of ethyl vinyl ether, the reaction mixture was washed with water once and dried over anhydrous calcium chloride after separation from the catalyst. Conversion (%) of ethyl vinyl ether was determined by gas chromatography with benzene as an internal standard. Toluene (guaranteed grade) was purified by distillation over sodium metal. Ethyl and methyl vinyl ethers (Tokyo Kasei's extra pure reagents) were used without further purification.

The present catalyst was surprisingly active for the polymerization of alkyl vinyl ethers. For instance, isobutyl vinyl ether polymerized explosively below 0°C. Thus, less reactive monomers, ethyl and methyl vinyl ethers, were chosen. Table 1 shows the catalytic activities and the product viscosities. The bulk polymerization of ethyl vinyl ether occurred violently at 0°C. In the case of methyl vinyl ether without toluene at -10°C, the reaction immediately started, and difficulty in magnetic stirring of the mixture took place in 2 min. Poly (ethyl vinyl ether) obtained was white

Table 1. Polymerizations of Ethyl Vinyl Ether (EVE) and Methyl Vinyl Ether (MVE).

Monomer	Catalyst	Catalyst (g)	Monomer (ml)	Toluene (ml)	Temp. (°C)	Time (min)	Conversion (%) or Yield (g)	η_{sp}/c[a] (dl/g)	Insoluble fraction[b] (%)
EVE	Fe_2O_3-I	0.6[c]	5	45	RT[d]	5 h	0 %		
		0.3	5	45	0	15	96 %		
		0.6	5	45	-20	10	97 %	0.50	
	Fe_2O_3-II	0.3	5	45	0	15	97 %	0.50	
		0.6	5	45	-20	10	97 %	0.56	
MVE	Fe_2O_3-I	0.4	10[e]	0	-10	30	4.5 g	0.24	7
		0.6	10	60	-10	90	4.9 g	0.41	21
	Fe_2O_3-II	0.2	10	0	-10	30	5.0 g	0.39	2
		0.6	10	60	-10	90	6.0 g	0.34	21

a) Determined with 0.5 g of polymer in 100 ml of benzene at 25°C using a Cannon-Fenske viscometer. b) Water-insoluble portion. About 1 g of poly (methyl vinyl ether) was mixed with 100 ml of water, and the soluble portion was extracted by stirring at room temperature for 1 d. The insoluble portion was separated, washed, and dried in vacuo. c) No treatment with H_2SO_4. d) Room temperature. e) 7.6 g.

and adhesive, while poly (methyl vinyl ether) was less adhesive. The catalyst without the sulfate treatment was inactive. A differently prepared catalyst, which was obtained by treating iron(III) oxide (Wako Pure Chemical Industries, Ltd.) with sulfate ion similarly and calcining at 500°C for 3 h, was also inactive. Other metal hydroxides, $Ni(OH)_2$, $Mg(OH)_2$, $Ti(OH)_4$ and $Zr(OH)_4$, were subjected to a similar treatment, but these substances were completely inactive for the polymerization of the vinyl ethers at room temperature.

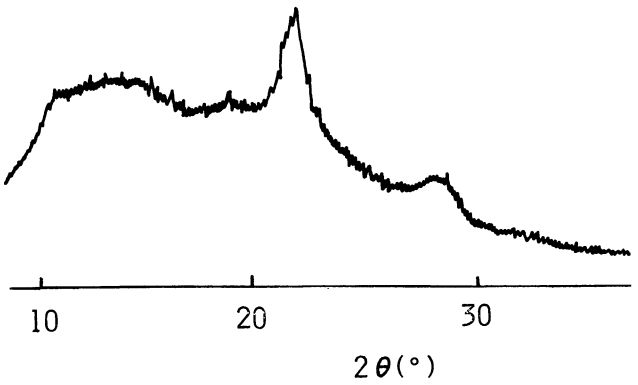

Fig. 1. X-ray scattering of water-insoluble portion of poly (methyl vinyl ether).

A material insoluble in water was obtained from methyl vinyl ether (Table 1). This insoluble fraction is a crystalline polymer as is seen in its X-ray diffraction spectrum (Fig. 1). The crystallinity was also indicated by its IR spectrum, which is in accordance with that of the crystalline polymer reported by Nakano et al.[5]; the characteristic absorption bands appear at 990, 965, and 820 cm^{-1}.

The present catalyst was much more active than the previous one[3] for the polymerization of alkyl vinyl ethers. As for concentration of sulfate ion, the maximum activity was observed when treated with 1 N H_2SO_4.

References

1) Solid catalyst treated with anion V. Part IV: M. Hino and K. Arata, J. Chem. Soc., Chem. Commun., 1979, 1148. 2) K. Tarama, Hannobetsu Jitsuyo Shokubai, Kagaku Kogyosha, Tokyo, 1970, p. 809. 3) M. Hino and K. Arata, J. Polym. Sci., Polym. Lett. Ed., 16, 529 (1978). 4) K. Yabe, K. Arata, and I. Toyoshima, J. Catal., 57, 231 (1979). 5) S. Nakano, K. Iwasaki, and H. Fukutani, J. Polym. Sci. A, 1, 3277 (1963).

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