NOTES

Polymerization of Propylene Oxide Diethylberyllium–Water

A number of metal alkyl compounds, notably those of zinc, aluminum, and magnesium,[1,2] have been reported to be active catalysts for the polymerization of propylene oxide. The zinc and aluminum alkyls have been studied most extensively. In conjunction with water or other chelating agents as catalysts, they polymerize propylene oxide into polymers containing a crystalline fraction of very high molecular weight.

We have studied the alkyl compounds of beryllium and have found that the diethylberyllium–water system is also an outstanding initiator for propylene oxide polymerization. At an optimum water to beryllium ratio, high molecular weight polymers containing a large crystalline fraction could be obtained in high yields. The results are shown in Table I.

TABLE I
Polymerization of Propylene Oxide by Diethylberyllium–Water[a]

No.	$BeEt_2$ concn.[b] wt-%	$BeEt_2$ concn.[b] mol-%	Reaction time, hr	H_2O/$BeEt_2$ ratio	Yield, %	Crystalline polymer,[c] %	$[\eta]$[d]
1	6.2	5.4	20	0	7	0	—
2	6.2	5.4	20	0.1	32	0	4.18
3	6.2	5.4	20	0.2	36	53	—
4	6.2	5.4	20	0.3	46	48	—
5	6.2	5.4	20	0.4	63	53	5.39
6	6.2	5.4	20	0.5	81	51	6.93
7	6.2	5.4	20	0.6	81	51	6.55
8	6.2	5.4	20	0.7	43	33	—
9	6.2	5.4	20	0.8	38	0	1.87
10	6.2	5.4	20	1.0	52	0	0.42
11	6.2	5.4	20	1.2	51	0	Very low
12	1.1	0.9	42	0.6	12	—	1.46
13	2.1	1.8	65	0.5	40	35	6.78
14	3.2	2.8	65	0.5	91	50	6.85
15	4.2	3.6	65	0.5	60	48	5.75

[a] Prepared according to the method of Von Goubean and Rodewald.[7]

[b] Carried out in heptane at 70°C in a sealed tube.

[c] Determined as the acetone-insoluble fraction at 0°C. The crystalline polymer has a mp of 67°–69°C, determined by Fisher-Johns melting point apparatus.

[d] Measured in benzene at 30°C.

Experiments 1 to 11 show the effect of the H_2O/Be ratio on the polymerization. Experiments 12 to 15 show the effect of initiator concentration. The optimum H_2O/Be ratio is in the range of 0.5 to 0.6, below which the yields are lower and above which the molecular weight of the polymer decreases sharply. Best results are obtained with an initiator concentration of 2.8% or greater.

The crystalline fractions in these polymers were higher than in those initiated by the dialkylzinc–water or trialkylaluminum–water systems under similar conditions. The diethylzinc–water-catalyzed polymerization has been reported[3] to be 16% crystalline, and a trimethylaluminum–water-catalyzed polymerization was reported[4] to be 30% crystalline. The stereoregular polymerization of propylene oxide has been proposed to be a coordination propagation mechanism[5] which involves the coordination of the epoxide monomer with the metal atom in the network of metal oxide as the catalyst site prior to the propagation step. The higher stereospecificity of the beryllium catalyst may possibly be attributed to its smaller atomic size, which provides a higher degree of stereoselection of the incoming monomer. A similar phenomenon of the effect of the size of the metal atom on the yield of stereoregular polymer has been observed earlier by Natta[6] in propylene polymerization using a metal–alkyltitanium trichloride catalyst system.

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