Polymerization of Styrene with the Ziegler-Natta Catalysts in the Presence of Molecular Hydrogen[*]

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It appears very important matter to have measures of controlling the molecular weight of isotactic polystyrenes in the polymerization with the Ziegler-Natta catalysts. Isotactic polystyrenes hitherto obtained in this laboratory according to the usual way[1] had the molecular weight of the order of several millions. In the course of this study, polymers having lower molecular weight was needed for the study of solution properties.

Among various factors affecting on molecular weight, such as the concentration of monomer, that of catalysts, and that of transfer agents, molecular hydrogen was chosen in the present work as one of the possible transfer agents, which had been known to be effective for controlling the molecular weight of polyethylene[2].

Recently, Natta has revealed in a paper the effectiveness of molecular hydrogen as controlling agents of molecular weight of polypropylene[3].

It has been found in the present work that isotactic polystyrenes of the low molecular weight could actually be obtained in the presence of hydrogen, although in addition to this there has been found another reaction which is competitive to the polymerization reaction, i. e. hydrogenation of styrene to ethylbenzene.

Polymerizations were carried out in an stainless steel autoclave of 200 ml. capacity. After the autoclave was flashed with nitrogen, $TiCl_3$ (3.0 g., the product of Stauffer Chemical Co.) washed with *n*-heptane was poured in with 30 ml. of *n*-heptane, and $AlEt_3$ (0.6 to 0.7 g.) was injected into the bottom of the autoclave

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[1] S. Murahashi, S. Nozakura, M. Sumi and K. Hatada, This Bulletin, **32**, 1094 (1959).

[2] G. Natta, *Chem. & Ind.*, **1957**, 296

[3] G. Natta, *J. Polymer Sci.*, **34**, 531 (1959).

from an injection syringe, and then styrene that was placed in a glass bottle was set in the autoclave. Dry hydrogen was charged to the desired pressure, the temperature was raised to 70°C, and then the shaking was commenced to make styrene contact with the catalyst suspension. Isotactic polymer was purified by the usual extraction procedure with methyl ethyl ketone.

It was found that both yields of total polymer and isotactic fraction in total polymer decreased markedly with increasing hydrogen pressure under the condition otherwise unaltered. As expected, however, intrinsic viscosities of isotactic fractions in toluene at 70°C also decreased as illustrated in Fig. 1.

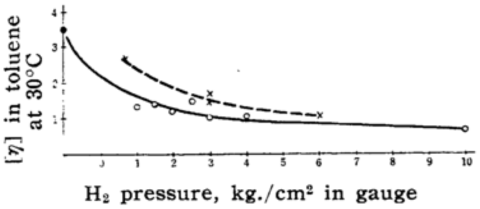

Fig. 1. Variation of intrinsic viscosities of isotactic polystyrenes with hydrogen pressure.

○: Polymerization time, 5 hr.

×: Polymerization time, 21 hr.

●: Polymerization for 5 hr. under a nitrogen atmosphere.

It was also found that the decreasing yields of polymer with increasing hydrogen pressure was mainly attributable to the occurrance of the competitive reaction, i. e. hydrogenation of styrene catalysed by the Ziegler catalyst. In one run, where styrene (9.1 g., 0.087 mol.) was heated with the catalytic system ($AlEt_3$, 0.71 g.; $TiCl_3$, 3 g.) at the constant hydrogen pressure of 8.9 kg./cm^2, 0.068 mol. of hydrogen was absorbed and gave a product, in which 3.7 g. of ethyl benzene was identified together with 0.474 g. of a pasty polymer and 0.499 g. of a solid polymer.

A modified catalyst system, $AlEt_3$-$Ti(OBu\text{-}n)_4$, produced no appreciable amount of polymer, but smoothly catalyzed the hydrogenation of styrene. Styrene alone, styrene and $AlEt_3$, and styrene and $TiCl_3$ did not show any absorption of hydrogen at the similar conditions.

From the above results, the observed decrease of molecular weight of isotactic polystyrenes with increasing hydrogen pressure may be considered to be due to following two reasons: the first is the effect of hydrogen as a chain transfer agent. Hydrogen probably cleaves a growing carbon-metal bond giving a metal-hydrogen bond and a saturated dead polymer, and the former would be still capable of initiating a new polymer chain. The second is the early lowering of monomer concentration due to the consumption of monomer by the hydrogenation reaction. Dependence of molecular weight on monomer concentration had been definitely demonstrated in the polymerization of propylene with the Natta catalysts[4] and hence the similar feature might be held in this case.

Propylene and butene-1 did not suffer such a hydrogenation reaction and the molecular weights of their polymers were found to be effectively controlled by the hydrogen pressure.

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