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Studies on Macromolecular Complexing Agents. II. Effects of Polypropylene Oxide on the Copolymerization Reaction between Butadiene and Styrene

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LETTER TO THE EDITOR

Studies on Macromolecular Complexing Agents. II. Effects of Polypropylene Oxide on the Copolymerization Reaction between Butadiene and Styrene

It was widely known that copolymerization reactions between diene and styrene in hydrocarbons with alkyllithium catalyst only resulted in the formation of block-type copolymers, the relative reactivity of styrene monomer in early stages of copolymerization being very small. The reactivity of styrene was indeed increased by using some ethers as "randomizer," but significant changes of microstructure in diene units were unavoidable.

As reported previously [1], styrene can be randomly copolymerized with isoprene using a Ziegler catalyst ($AlEt_3$-$TiCl_4$) in the presence of a macromolecular complexing agent. Little change in the microstructure of isoprene unit in the copolymer is observed when styrene content in the copolymer does not exceed about 10-15 mole %.

For example, analyses of the microstructure of isoprene unit in a styrene-isoprene copolymer containing 15.1 mole % styrene showed the following results: cis-1, 4, 90.4; trans-1, 4, 4.8; 1, 2, 0; and 3, 4, 4.8%. The intrinsic viscosity, $[\eta]$, of the copolymer was 1.03 (dl/g 30°C in toluene).

This paper is concerned with an extended study of the effects of the macromolecular complexing agents on the copolymerization reaction between butadiene and styrene with $AlEt_3$-$TiCl_4$($Al/Ti = 1.08$) as catalyst.

The mixture of polypropylene oxide (PPO), $AlEt_3$, and $TiCl_4$ ($Al/Ti = 1.08$ molar ratio) as a catalyst was prepared in a closed, nitrogen-filled vessel. Then a mixture of butadiene and styrene (7/3 molar ratio) was added. After the mixture was allowed to stand at room temperature for 4 hr, methyl alcohol was poured to stop polymerization. Polymers were separated, dried, and analyzed.

As shown in Fig. 1, the rate of polymerization was observed to increase in the presence of propylene oxide (PPO, m.w. = 100, 000). There is little gel formation. The macromolecular ether also enhanced the reactivity of styrene in the copolymerization reaction when the mole ratio of ether oxygen to the aluminum alkyl, —O—/ $AlEt_3$, is 0.5-1.0.

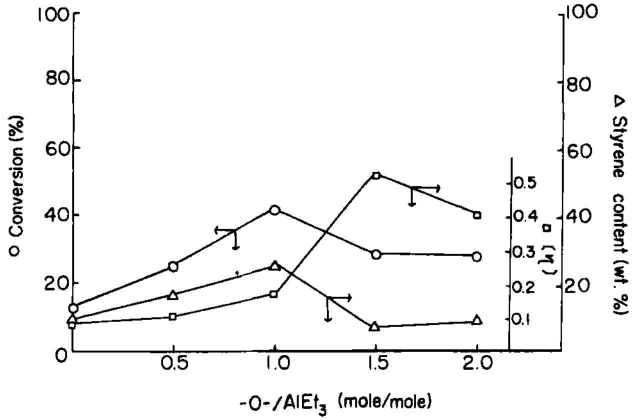

Fig. 1. Effects of polypropylene oxide on copolymerization reactions between butadiene and styrene with $AlEt_3$-$TiCl_4$ (Al/Ti = 1.08) catalysts: butadiene = 0.0459 mole; styrene = 0.0196 mole; toluene = 15 ml; $TiCl_4$ = 1.21 mmole; $AlEt_3/TiCl_4$ = 1.08; polymerization time, 4 hr (at room temperature).

There are no significant changes in the microstructure of the diene units of the copolymer formed, the cis-1, 4 unit content of the copolymer being higher than that of the commercial lithium alkyl-catalyzed styrene-butadiene rubber (SBR), as shown in Table 1.

By oxidizing decomposition [2] of the copolymer, the percentage of random styrene in total styrene unit content was determined. Surprisingly, all styrene units in the copolymer formed in the presence of PPO as complexing agent were randomly distributed along the polymer main chain (Table 2).

Meanwhile, the effects of macromolecular complexing agents on the homopolymerization of butadiene or styrene were also investigated. The rate of butadiene polymerization is found to increase without any changes in the microstructure of polybutadiene formed (Fig. 2, Table 3). The rate of styrene polymerization was also elevated with the aid of the macromolecular ether (Fig. 3).

Ethyl ether and tetraethyleneglycol dimethyl ether do not exhibit effects similar to the high molecular weight PPO in both copolymerization and homopolymerization of butadiene and styrene (Figs. 2 and 4).

More extensive work showed similar effects of macromolecular ethers to be operative also in copolymerizations between other monoolefins (ethylene, propylene, butene-1, etc.) and dienes.

Further studies to elucidate the chemical behavior of macromolecular ethers as complexing agent are in progress.

Table 1. Styrene Contents and Microstructure of Styrene-Butadiene Copolymer[a]

—O—/Al, mole/mole	Styrene content in copolymer, wt. %	cis-1, 4	trans-1, 4	1, 2
0	9.10	66.4	30.2	3.4
0.5	16.5	63.7	33.0	3.3
1.0	25.5	64.2	31.6	4.2
1.5	7.6	66.4	29.7	3.9
2.0	9.6	56.6	37.3	6.0
Solprene	25	32	41	27

[a] Catalyst system: $AlEt_3/TiCl_4 = 1.08$; other polymerization conditions are given in Fig. 1.

Table 2. The Content of Randomly Distributed Styrene Units in Copolymer[a]

—O—/Al, mole/mole	Total styrene content in copolymers, wt. %	Recovered, polystyrene, %	Random styrene vs. total styrene	Random styrene content in 1 g of copolymer
0	9.10	7.08	22.2	0.020
0.5	16.5	3.85	76.7	0.129
1.0	25.5	2.25	91.2	0.222
1.5	7.6	1.38	81.7	0.062
2.0	9.6	1.10	88.6	0.086

[a] Catalyst system: $AlEt_3/TiCl_4 = 1.08$; other polymerization conditions are given in Fig. 1.

Table 3. The Microstructure of Polybutadiene[a]

—O—/Al	cis-1, 4	trans-1, 4	1, 2
0	65.6	26.8	7.8
1.0	64.0	32.0	2.8

[a] Polymerization conditions are given in Fig. 2.

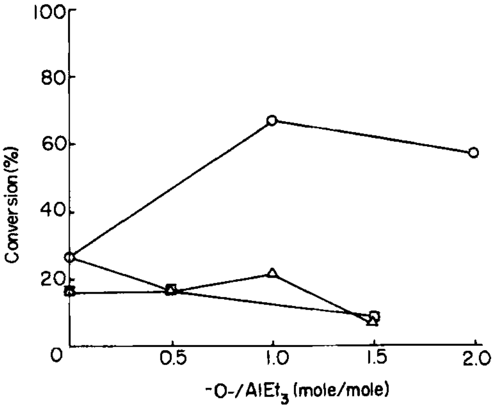

Fig. 2. Effect of PPO, ethyl ether and tetraethyleneglycol dimethyl ether on the polymerization of butadiene with $AlEt_3$-$TiCl_4$ (Al/Ti = 1.08) catalysts: butadiene = 0.063 mole; toluene = 15 ml; $TiCl_4$ = 1.21 mmole; $AlEt_3/TiCl_4$ = 1.08; polymerization time, 4 hr (at room temperature). (○), PPO; (△), ethyl ether; (□), tetraethyleneglycol dimethyl ether.

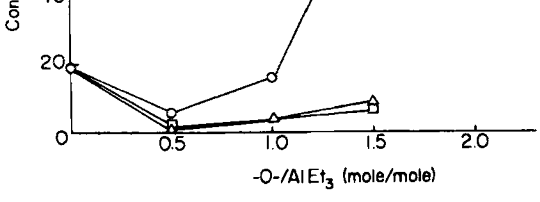

Fig. 3. Effect of PPO, ethyl ether, and diethyleneglycol dimethyl ether on the polymerization of styrene with $AlEt_3$-$TiCl_4$ (Al/Ti = 1.08) catalysts: styrene = 0.059 mole; toluene = 15 ml; $TiCl_4$ = 1.21 mmole; $AlEt_3/TiCl_4$ = 1.08; polymerization time 1 day (at room temperature). (○), PPO; (△), ethyl ether; (□), diglyme.

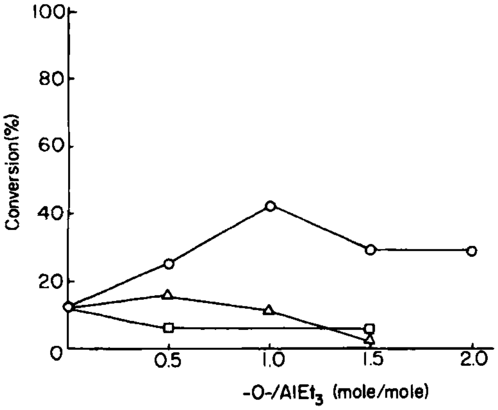

Fig. 4. Effect of various ethers on copolymerization reaction between butadiene and styrene with $AlEt_3$-$TiCl_4$ (Al/Ti = 1.08) catalysts: Experimental conditions are given in Fig. 1. (○), PPO; (△), ethyl ether; (□), tetraethyleneglycol dimethyl ether.

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