*Stereoregular Polymers. VIII. Effects of Various Organic Compounds on the Polymerization of Styrene with Ziegler Catalyst. Part I**

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Much literature has been published in regard to the polymerization of olefins with Ziegler type catalyst. However, only a few of them have given the information as to the polymerization of monomer containing any heteroatom such as oxygen, nitrogen, sulfur or halogen[1]. It is considered that the electron-donating character of these atoms causes strong complex formation between the compound and the catalyst leading to the inhibition of anionic coordination of the double bond of the monomer to the catalyst.

The authors have previously investigated the polymerization of allylchloride[2] with Ziegler catalyst and found that the Friedel-Crafts type reaction caused by compounds containing Al–Cl bond such as Et_2AlCl, $EtAlCl_2$ or $AlCl_3$ formed in the system is essential in the polymerization.

It should be interesting to investigate the effect of the usual organic compound containing heteroatom on the polymerization by Ziegler catalyst using styrene as a monomer. From such experiments any information would be

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[1] J. Lal, *J. Polymer Sci.*, **31**, 179 (1958); E. J. Vandenberg et al., ibid., **41**, 519 (1959); R. F. Heck and D. S. Breslow, ibid., **41**, 520 (1959); G. Natta et al., *Angew. Chem.*, **71**, 205 (1959); W. S. Etlis et al., *Visokomolek. Soed.*, **1**, 1403 (1959); E. J. Vandenberg, Ital. Pat. 571741 (1959); Ger. Pat. 1030562; 1031515 (1958).

[2] S. Murahashi, S. Nozakura and K. Hatada, This Bulletin, **34**, 631 (1961).

expected to be drawn in correlation to the polymerization of any monomer containing heteroatom by this catalyst.

From this point of view, about forty compounds including halides, oxides, carbonyl compounds, amines, nitro compounds, nitriles, sulfides and phosphines, were examined. The stereospecificity of the Ziegler catalyst for the polymerization of styrene was lost by all of them excepting halobenzenes, di-*n*-hexyl ether, triphenylphosphine, thiophene and furan. These exceptions did not destroy the stereospecificity but modified the catalyst system in various extents.

The effects of thiophene and furan were studied in detail. The results indicated that thiophene may not be attacked so strongly by the Ziegler catalyst predicting the possibility of forming stereospecific polymers of vinylthiophenes by this catalyst. However, only amorphous polymers resulted from these monomers.

Experimental

Materials.—*Styrene.*—Commercial styrene was washed with 5% aqueous sodium hydroxide and water, dried over calcium chloride and distilled under reduced nitrogen pressure before use.

2-Vinylthiophene.-This was synthesized according to Emerson[3], b. p. 59.0°C (46 mmHg), n_D^{25} 1.5707. Found: C, 65.15; H, 5.54; S, 28.84. Calcd. for C_8H_6S: C, 65.41; H, 5.49; S, 29.10%.

3-Vinylthiophene.—This was synthesized according to Troyanowsky[4], b.p. 50.5°C (20 mmHg), n_D^{15} 1.5683. Found: C, 66.06; H, 5.73; S, 28.78. Calcd. for C_6H_6S: C, 65.41; H, 5.49; S, 29.10%.

n-Hexane.—A commercial material was shaken with fuming sulfuric acid, washed with 5% aqueous sodium hydroxide and water, dried over calcium chloride, distilled and stored over metallic sodium.

Various Organic Compounds used as Additives.—Most of the compounds were obtained commercially, but ethylene glycol dimethyl ether, di-*n*-butyl sulfide, triethylphosphine and triphenylphosphine were synthesized. All were purified by the usual methods and distilled under dry nitrogen before use.

Triethylaluminum and Titanium Tetrachloride.—Triethylaluminum and titanium tetrachloride were supplied by Mitsui Chem. Ind. Co. and by Osaka Titanium Co., respectively, and both were used as solutions in *n*-heptane.

Polymerization of Styrene.—A 50 ml. five-necked flask[5] was fitted with a thermometer, a nitrogen gas inlet tube and rubber caps, and was flushed by dry nitrogen. Then 20 ml. of *n*-hexane and 0.25 g. (0.00132 mol.) of titanium tetrachloride were charged. While boiling the mixture gently, 0.15 g. (0.00132 mol.) of triethylaluminum was added slowly, and heating was continued for further five minutes and cooled. After precipitating the solid catalyst complex the supernatant liquid was removed by a hypodermic syringe equipped with a long needle under dry nitrogen. The catalyst was washed three times in the flask with 20 ml. of *n*-hexane and then 20 ml. of *n*-hexane and 0.15 g. of triethylaluminum was added. The catalyst mixture was heated to about 60°C and 0.01 mol. of additive compound was added. After the mixture was kept at 60°C for fifteen minutes with occasional shaking, 5 ml. (4.54 g.) of styrene were charged. The polymerization was performed at 60°C for 4 hr. All the procedures were carried out under a stream of dry nitrogen. The polymerization was stopped by adding 10 ml. of methanol and 1 ml. of concentrated hydrochloric acid. The polymer was precipitated by pouring the mixture into about 300 ml. of methanol. After standing overnight, the polymer was collected and washed throughly with methanol and dried in vacuo. The polymer obtained was extracted with a hundred times amounts of methyl ethyl ketone under reflux for three hours. After standing overnight at room temperature the isotactic polymer remained insoluble was collected and washed with methyl ethyl ketone and dried in vacuo at 100°C. The stereospecificity (%) of the polymer was determined as 100×(weight of isotactic part)/(weight of total polymer).

Because of the poor reproducibility of Ziegler type polymerization the conditions and procedures were kept carefully as constant as possible for all over the runs.

Results

Styrene was polymerized by Ziegler catalyst under the same conditions described in the experimental part but without additive compound. The results of the four runs were shown in Table I. The stereospecificity of this catalyst was lower than that of the catalyst[5] prepared in boiling *n*-heptane in a similar manner. This is probably due to the lower temperature at the catalyst formation and also the ageing of the catalyst caused by fifteen minutes time interval before the introduction of monomer.

TABLE I. STEREOSPECIFICITY OF POLYSTYRENE POLYMERIZED BY ZIEGLER CATALYST

	Polymer yield, %		Stereospecificity, %
	Total	Isotactic part	
	12.3	4.3	34.8
	13.4	4.5	33.5
	13.1	5.1	38.9
	11.6	5.6	48.0
Average	12.6	4.9	38.8

The results obtained from the experiments with additive compounds were summarized in Table II.

Halides.—When *n*-butyl chloride was added, the catalyst solid was completely dissolved with a violent evolution of hydrogen chloride.

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[3] W. E. Emerson and T. M. Patrick, "Organic Synthesis" Vol. 38, (1958), p. 86.

[4] C. Troyanowsky, *Bull. soc. chim. France*, 1955, 424.

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

TABLE II. EFFECTS OF VARIOUS ORGANIC COMPOUNDS ON THE STEREOSPECIFIC POLYMERIZATION OF STYRENE BY ZIEGLER CATALYST

Type of compound	Compound	Conversion, %	Stereospecificity %	Change of catalyst
	None	12.6	38.8	
Halide	n-C_4H_9Cl	82.6	0	Dissolved, HCl evolved
	C_6H_5Cl	9.7	45.4	Unchanged
	C_6H_5Br	8.5	39.5	Unchanged
	CCl_4	79.2	0	Dissolved, HCl evolved
Ether	$CH_3OCH_2CH_2OCH_3$	2.0	0	Unchanged
	$(n\text{-}C_4H_9)_2O$	7.1	0	Unchanged
	$(n\text{-}C_6H_{13})_2O$	5.0	33.9	Unchanged
	Tetrahydrofuran	2.3	0	Unchanged
	Dioxane	2.8	0	Unchanged
	$(CH_3CHO)_3$	0.5	0	Unchanged
Acetal	$CH_2(OCH_3)_2$	24.8	0	Unchanged
	$CH_3CH(OC_2H_5)_2$	11.4	0	Unchanged
Ketone and aldehyde	CH_3COCH_3	0.3	0	Dissolved
	$CH_3COC_2H_5$	0.7	0	Dissolved
	$C_6H_5COCH_3$	0.2	0	Dissolved
	C_6H_5CHO	0.2	0	Dissolved
Ester and acid anhydride	$CH_3COOC_2H_5$	4.3	0	Gradually dissolved
	$CH_3COOC_4H_9(n)$	5.2	0	Gradually dissolved
	$(CH_3CO)_2O$	5.7	0	Unchanged
Amine	$C_6H_5NH_2$	2.6	0	Dissolved, gas evolved
	C_5H_5N	0.3	0	Gradually dissolved
	$(C_2H_5)_3N$	1.3	0	Unchanged
Acid amide	CH_3CONH_2	1.4	0	Partly dissolved, gas evolved
	$HCON(CH_3)_2$	1.0	0	Dissolved
Nitro compound	$CH_3CH(NO_2)CH_3$	0.7	0	Dissolved
	$C_6H_5NO_2$	0.2	0	Color changed[a]
Nitrile and azobenzene	C_6H_5CN	1.5	0	Dissolved
	$C_6H_5N{=}NC_6H_5$	0.2	0	Color changed[b]
Sulfur compound	n-C_3H_7SH	0.1	0	Dissolved, gas evolved
	$(n\text{-}C_4H_9)_2S$	6.7	0	Dissolved
	CS_2	5.3	0	Unchanged
	S	2.0	0	Gradually dissolved
	$(CH_3)_2SO$	16.8	0	Dissolved
	Thiophene	5.7	67.3	Unchanged
Furan	Furan	8.2	85.7	Unchanged
Phosphorus compound	$(C_2H_5)_3P$	1.0	0	Dissolved
	$(C_6H_5)_3P$	4.4	35.0	Unchanged

a) The brownish black color of the solid catalyst almost disappeared.
b) The color of the solid catalyst was slightly faded.

Styrene was polymerized by the dissolved catalyst to give polystyrene in high yield. At the addition of the monomer, however, a red coloration and a remarkable temperature rising of the reaction mixture were observed. These signified cationic polymerization of styrene by aluminum chloride, and the resulted polymer was shown to be completely amorphous. The behavior of carbon tetrachloride was similar to that of n-butyl chloride.

Ethers and Acetals.—By the addition of di-n-hexyl ether the catalytic activity was fairly decreased, but the stereospecificity was retained invariably. The isotactic part of the polymer obtained was swollen in methyl ethyl ketone and showed rather lower melting point (215~217°) than ordinary isotactic polystyrene (m. p. 230~233°).

By the additions of the other ethers and acetals the appearance of the catalyst solid remained unchanged but the stereospecificity was completely lost.

Ketones, Aldehydes, Esters, Acid Anhydride, Amides and Amines.—Triethylamine did not affect the catalyst in appearance, but completely diminished the stereospecificity of the polymerization. The catalyst solid was dissolved by the addition of each of all the other compounds listed. The dissolved catalyst showed low activity and gave no stereospecific polymer.

Nitro Compounds, Nitrile and Azobenzene.—Upon adding 2-nitropropane the catalyst was dissolved immediately. Nitrobenzene and azobenzene changed the color of the catalyst solid, but did not dissolved it, while cyanobenzene dissolved the catalyst. These four compounds strongly lowered the catalytic activity, and no stereospecificity resulted.

Sulfur Compounds and Furan.—Sulfur, mercaptane, thioether and sulfone, all these sulfur compounds examined dissolved the catalyst and destroyed the stereospecificity.

Contrary to most of the compounds of this group thiophene and furan did remarkably improve the stereospecificity of the catalyst for the polymerization of styrene. A number of additional polymerizations were carried out by varying the amount of these additives, where the catalyst was prepared as mentioned in the experimental part but without washing. The results were given in Figs. 1 and 2, both of which showed the same trend. The yield of atactic polystyrene decreased rapidly by the addition up to one-fourth molar ratio of the additive compound to titanium tetrachloride and remained almost constant at the higher ratios. On the other hand, the yield of isotactic polymer was unchanged almost constant.

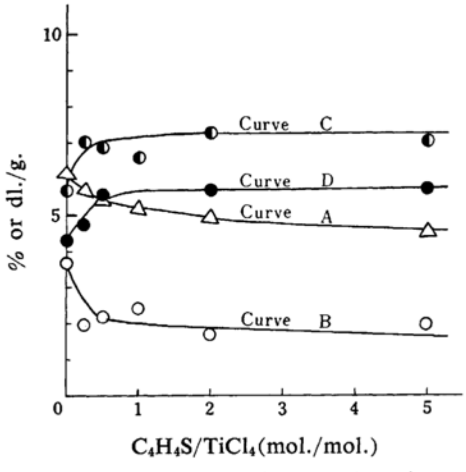

Fig. 1. Effect of thiophene on the polymerization of styrene with Ziegler catalyst.
Curve A: yield of isotactic polystyrene
Curve B: yield of atactic polystyrene
Curve C: stereospecificity $\times 10^{-1}$
Curve D: intrinsic viscosity of the isotactic polystyrene in toluene at 30.0°C

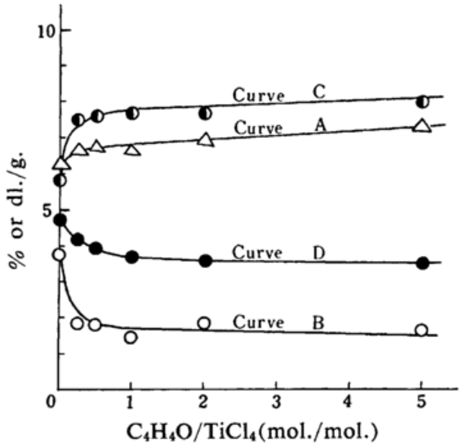

Fig. 2 Effect of furan on the polymerization of styrene with Ziegler catalyst.
Curve A: yield of isotactic polystyrene
Curve B: yield of atactic polystyrene
Curve C: stereospecificity $\times 10^{-1}$
Curve D: intrinsic viscosity of the isotactic polystyrene in toluene at 30.0°C

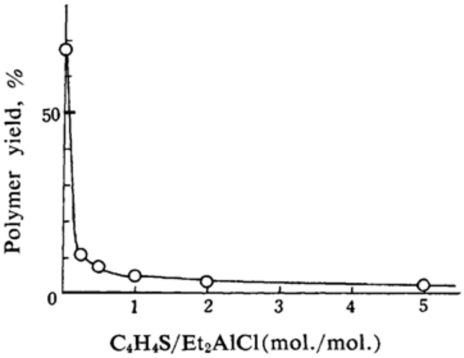

Fig. 3. Effect of thiophene on the polymerization of styrene by Et_2AlCl.
Polymerization temperature: 60°C, polymerization time: 4 hr., styrene; 5 ml., *n*-heptane: 20ml., Et_2AlCl: 1.32×10^{-3} mol.

In an attempt to elucidate the action of these compounds the polymerizations of styrene catalyzed by Et_2AlCl were similarly carried out using thiophene as an additive. The results were shown in Fig. 3. The curve in Fig. 3 closely resembled that of the atactic yield in Fig. 1.

Carbon disulfide did not change the appearance of the catalyst but destroyed the stereospecificity at all.

Phosphorus Compounds.—Triethylphosphine dissolved the catalyst to lose the activity and the stereospecificity, while triphenylphosphine behaved similarly as di-*n*-hexyl ether did and gave isotactic polystyrene having a lower melting point (219∼221°C) but not being swollen in methyl ethyl ketone.

Polymerization of Vinylthiophenes.—2-Vinylthiophene and 3-vinylthiophene were synthesized and polymerized with several catalysts of the Ziegler type. All of the polymers obtained were shown to be amorphous by their X-ray diffractions.

Discussion

The additive compounds examined were found to fall into four groups according to their behavior to the Ziegler catalyst.

Group I.—This group includes alkyl halides and carbon tetrachloride. The compounds dissolve the catalyst solid with a violent evolution of hydrogen chloride. In this case the polymerization shows a sign of cationic process and givesan atactic polystyrene in high yield.

In the case of *n*-butyl chloride the evolution of hydrogen chloride takes place analogously to the reaction between butyl bromide and aluminum bromide[6], as follows:

$$CH_3CH_2CH_2CH_2Cl \xrightarrow{Et_2AlCl\ etc.} CH_3CH_2CH=CH_2+HCl$$

In the first stage, this reaction proceeds very slowly by a catalytic action of small amounts of original species having Al-Cl linkage such as Et_2AlCl, $EtAlCl_2$ or aluminum chloride, then becomes faster owing to a gradual accumulation of these compounds generated by the reaction between triethylaluminum and hydrogen chloride liberated, and is finally led to the violent reaction. These compounds containing Al-Cl linkage may catalyze the polymerization of styrene in a cationic mechanism.

Group II.—The compounds belonging to this group are ketones, aldehydes, esters, amides, primary and secondary amines, pyridine, aliphatic nitro compounds, nitriles, mercaptanes, thioethers and so on. Every compound of this group leads the catalyst to dissolution and destroys its stereospecificity as well as the catalytic activity for the polymerization of styrene. Each of these compounds has a strong electron donor group, an active hydrogen atom or any of the other functional groups, all of which seem to react with organometallic compounds and could probably destroy the activity of the Ziegler catalyst.

Group III.—By the compounds of this group the catalyst is not changed in appearance, but the stereospecificity is destroyed. The compounds may include ethers, acetals, acid anhydride and tertiary amines. All of these have a electron-donor group and may be capable of forming a Lewis acid-Lewis base type complexes with triethylaluminum and/or with titanium trichloride in the catalyst. This complex formation must destroy the suitable site for the isotactic polymerization of styrene in the catalyst.

It should be noted, however, that the stereospecificity of the catalyst is not destroyed by a compound having bulky substituent groups around the hetero atom, such as di-*n*-hexyl ether. Triethylamine causes no dissolution of the catalyst, although it has stronger electronegativity than pyridine, a member of Group II. This may be attributed to the steric hindrance around the nitrogen atom[7].

Group IV.—The stereospecificity of the catalyst is not destroyed by the compounds of this group. These includes halobenzenes, di-*n*-hexyl ether, thiophene, furan and triphenylphosphine.

By the additions of thiophene and furan the stereospecificity is remarkably increased, while the total polymer yield is relatively reduced. This means that the action of these additives is related to an inhibition of the atactic polymerization of styrene by the catalyst. The feature is demonstrated in detail by Figs. 1 and 2, which were obtained from the experiments with varying the amounts of the additives.

When the catalyst is formed by the preparative method used in these experiments, it is considered that more than ninety percent of titanium tetrachloride are reduced to titanium trichloride and triethylaluminum is converted to diethylaluminum chloride, ethylaluminum dichloride and aluminum chloride, all of which are responsible for the formation of atactic polystyrene by this catalyst[5,8].

$$Et_3Al+TiCl_4 \rightarrow Et_2AlCl+TiCl_3+Et\cdot \quad (1)$$

$$Et_2AlCl+TiCl_4 \rightarrow EtAlCl_2+TiCl_3+Et\cdot \quad (2)$$

$$EtAlCl_2+TiCl_4 \rightarrow AlCl_3+TiCl_3+Et\cdot \quad (3)$$

The plots in Figs. 1 and 2 were obtained from the experiments without washing the catalyst. As the molar ratio of triethylaluminum to titanium tetrachloride was higher than unity, diethylaluminum chloride must be the main product among the three aluminum chlorides, and may be present in an approximately equimolar amount to that of titanium trichloride or, accordingly, of titanium tetrachloride used. The similarity of the two curves, Curve B in Fig. 1 and the curve in Fig. 3, indicates evidently the interaction between thiophene and diethylaluminum chloride being

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[6] J. J. Burbage, *J. Phys. Chem.*, **56**, 730 (1952).

[7] W. Gordy et al., *J. Chem. Phys.*, **8**, 170 (1940).

[8] W. M. Saltman, W. E. Gibbs and J. Lal, *J. Am. Chem. Soc.*, **80**, 5615 (1958).

the substantial cause in the inhibition of the atactic polymerization of styrene. Probably diethylaluminum chloride may form an acid-base type complex with thiophene or furan and lose the catalytic activity for the cationic polymerization of styrene. It is remarkable that only one-fourth molar amount of thiophene or furan against diethylaluminum chloride sufficiently inhibits the polymerization. On the other hand, the electronegativities weakened by the conjugate system of these compound are supposed to be not sufficient to affect the active site of the solid catalyst for the isotactic polymerization of styrene.

Between the actions of thiophene and furan some differences are found. The isotactic yield decreased slightly and the molecular weight of the isotactic polymer increased gradually with the increasing amount of thiophene, while the increasing amount of furan gave the reverse tendencies. The explanation of these facts has still not been obtained.

Vinylthiophene gave no isotactic polymer by the Ziegler catalyst. This suggests that the active species of the catalyst for the isotactic polymerization of styrene does not always function as an active site for the isotactic polymerization of any other monomers.

Triphenylphosphine and di-*n*-hexyl ether, which have rather strong electronegativities, do not destroy the activity of the catalyst for the isotactic polymerization of styrene because of the steric effects of the bulky substituent groups on the phosphor and the oxygen atoms. The lower melting point of the isotactic polymer produced in the presences of these additives suggests that the polymer may be constructed by isotactic stereoblocks. This is probably caused by the modification of active center of the catalyst with these compounds.

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