*The Stereoregularity of Poly-p-bromostyrene Polymerized by the Ziegler Catalyst**

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(Received January 10, 1962)

Since stereospecific polymerization was discovered by Natta(1) in 1955, many crystalline structures have been investigated and determined on a number of stereoregular polymers. Crystallizability is not always dependent on the stereoregularity of the polymer, and some of the polymers polymerized by the so-called stereospecific catalysts appear to be amorphous, it not being certain whether they are stereoregular or not(2). For instance, poly-*p*-methylstyrene and poly-*m*-methylstyrene polymerized by the Ziegler catalyst were originally considered to be amorphous. Later it was found, from the infrared spectroscopic study of these polymers, that the polymers might have stereoregularity(3). This led to the preparation of effectively oriented samples of the polymers and to the determination of their crystalline structures(4).

Natta and his coworkers found that poly-*p*-chlorostyrene polymerized by the stereospecific catalyst was amorphous, but the polymer was proved to be stereoregular by its giving of crystalline polyvinylcyclohexane as the result of catalytic hydrogenation. They ascribed the noncrystallinity of the original poly-*p*-chlorostyrene to the steric effect of the chlorine atom in crystalline orientation(5). Poly-*p*-chlorostyrene polymerized by the Ziegler catalyst was found by Nagai to contain a small fraction of the polymer insoluble in cold xylene; this fraction gave an infrared spectrum different from that of the amorphous fraction soluble in cold xylene(6).

For the present work, the authors investigated the stereoregularity of poly-*p*-bromostyrene polymerized by the Ziegler catalyst and were led to the conclusion that the polymer was, in this particular case, not stereoregular, this conclusion being different from Natta's for poly-*p*-chlorostyrene.

Experimental

Materials. — *p-Bromostyrene*. — *p*-Bromoacetophenone was prepared from bromobenzene and acetic anhydride using aluminum chloride as the catalyst(7) and was purified by recrystallization from methanol-water to make it free from the ortho isomer. The pure *p*-bromoacetophenone (m. p., 49.5~50.0°C) was reduced to the corresponding carbinol by the Meerwein-Pondorf method(8). The carbinol was

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* Paper X in a series on "Stereoregular Polymers". Presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960. For paper IX, see This Bulletin, **34**, 1673 (1961).

1) G. Natta, *J. Polymer Sci.*, **16**, 143 (1955).

2) G. Natta, F. Danusso and D. Sianesi, *Makromol. Chem.*, **28**, 253 (1958).

3) H. Tadokoro, S. Murahashi, T. Kitazawa, Y. Yasuhara and S. Nozakura, This Bulletin, **32**, 313 (1959).

4) S. Murahashi, S. Nozakura and H. Tadokoro, ibid., **32**, 534 (1959).

5) G. Natta, P. Corradini and I. W. Bassi, *Makromol. Chem.*, **33**, 247 (1959); G. Natta, ibid., **35**, 94 (1960).

6) K. Nagai, M. Kobayashi and E. Nagai, This Bulletin, **32**, 771 (1959).

7) R. Adams and C. R. Noller, "Organic Synthesis", Coll. Vol. I (1956), p, 109.

8) A. L. Wilds, "Organic Reactions", Vol. II, John Wiley & Sons, Inc., New York (1944), p. 178.

dehydrated to *p*-bromostyrene by potassium bisulfate[9]. The product was dried over calcium chloride and distilled under reduced pressure. A fraction boiling at 69~92°C/13 mmHg was collected and fractionally crystallized several times, about one-sixth of the product being discarded each time as an unfrozen liquid. Pure *p*-bromostyrene was obtained by redistillation of the residue of the final crystallization; b. p., 90.5~91.0°C/13 mmHg, n_D^{20} 1.588.

n-Heptane.—Commercial *n*-heptane was purified in the usual manner[10], dried, and stored over metallic sodium.

Aluminum Triethyl.—Aluminum triethyl was supplied by the Mitsui Chem. Ind. Co. and was used without further purification.

Titanium Tetrachloride.—The titanium tetrachloride was a product of the Osaka Titanium Co.

Titanium Trichloride.—A commercial product (Staufer Chem. Co.) was washed three times with *n*-heptane before use.

n-Butyllithium.—A benzene solution was prepared according to Ziegler's method[11] from *n*-butylchloride and lithium.

Lithium Aluminum Hydride.—The lithium aluminum hydride was a commercial product of Metal Hydride Inc.

Tetrahydrofuran.—Tetrahydrofuran was refluxed and distilled over sodium before use.

Polymerization.—The polymerization was carried out in a method similar to that described in a previous paper[12]. After the vessel had been flushed by dry nitrogen, 20 ml. of *n*-heptane and 0.38 g. of titanium tetrachloride were introduced into the vessel. While the solution was boiled gently, 0.225 g. of triethylaluminum was added slowly; the heating was continued for a further 5 min. and then the solution was cooled. After the precipitation of a solid complex, the supernatant liquid was removed by a syringe under dry nitrogen. The solid was washed three times with 20 ml. of *n*-heptane, and 20 ml of *n*-heptane and 0.225 g. of triethylaluminum were added. The monomer was then added to the catalyst suspension and polymerized.

When the catalyst was prepared from titanium trichloride and aluminum triethyl, 0.20 g. of triethylaluminum was added to 1.5 g. of titanium trichloride suspended in 20 ml. of *n*-heptane at room temperature.

The polymer produced was precipitated by pouring the reaction mixture into methanol containing hydrochloric acid, washed thoroughly with methanol, and dried in vacuo at 130~150°C.

Reaction of Poly-*p*-bromostyrene with *n*-Butyllithium.—A three-necked flask was fitted with a reflux condenser, a separatory funnel and a glass tube equipped with a rubber cap. After the flask had been flushed by dry nitrogen, 20 ml. of benzene and a benzene solution of *n*-butyllithium (600 mg.) were introduced with a hypodermic syringe through the rubber cap. While the solution was stirred with a magnetic stirrer and maintained at the reaction temperature, a solution of about 200 mg. of poly-*p*-bromostyrene in 20 ml. of benzene was slowly added, drop by drop, over a period of from 2 to 4 hr. After the addition was complete, stirring was continued for 2 hr.; then the mixture was poured into a large amount of methanol to hydrolyze the lithiated polymer. After the mixture had stood overnight, the polymer was collected, washed with methanol, and dried in vacuo at 70~100°C.

Reduction of Poly-*p*-bromostyrene by Lithium Aluminum Hydride.—A mixture of about 300 mg. of poly-*p*-bromostyrene and 0.5 g. of finely powdered lithium aluminum hydride in 300 ml. of tetrahydrofuran was brought to solution by warming; the solution was then refluxed under dry nitrogen for about 6 days. In the course of the reaction, two portions of 5 ml. of benzene each were added to the reaction mixture in order to solubilize the partially debrominated polymer and to complete the reaction. The reaction mixture was poured into 300 ml. of methanol containing a small amount of hydrochloric acid to decompose the excess lithium aluminum hydride and to precipitate the polymer. The product was then purified by reprecipitation from toluene and methanol.

Measurements of Softening Points and Viscosities.—Softening points were measured using a hot-stage microscope. Intrinsic viscosities are measured in benzene at 20°C using a Ubelhode-type dilution viscometer.

Results and Discussion

It was reported in a previous paper that bromobenzene does not impair the isotactic polymerization of styrene with the Ziegler catalyst[12]. This fact prompted us to prepare the isotactic polymer of *p*-bromostyrene with the catalyst.

p-Bromostyrene was easily polymerized with the catalyst to give a high polymer in good yields. The results of the polymerization are summarized in Table I. Polymerization with the addition of thiophene to the catalyst system gave almost the same results. The addition of thiophene was tried since a good stereospecificity was observed with it in the case of the polymerization of styrene[12]. The polymer showed an amorphous X-ray pattern and the same infrared spectrum as that of the polymer obtained by radical polymerization.

In order to determine the stereoregularity of poly-*p*-bromostyrene, the polymer was reduced to polystyrene and the properties of the resulting polystyrene were compared with those of isotactic and amorphous polystyrenes. Debromination was attempted by two methods, i. e., halogen-metal conversion with butyllithium, followed by hydrolysis (Braun's method)[13] and reduction with lithium aluminum hydride.

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[9] C. Walling, *J. Am. Chem. Soc.*, **70**, 1537 (1948).

[10] A. Weissberger et al., "Organic Solvents", 2nd. Ed., Interscience Publishers, Inc., New York (1955), p. 311.

[11] K. Ziegler and H. G. Gellert, *Ann.*, **567**, 179 (1950).

[12] S. Murahashi, S. Nozakura and K. Hatada, This Bulletin, **34**, 939 (1961).

[13] D. Braun, *Makromol. Chem.*, **30**, 85 (1959).

TABLE I. POLYMERIZATION OF *p*-BROMOSTYRENE WITH ZIEGLER TYPE CATALYSTS
Solvent: *n*-Heptane, 20 ml.

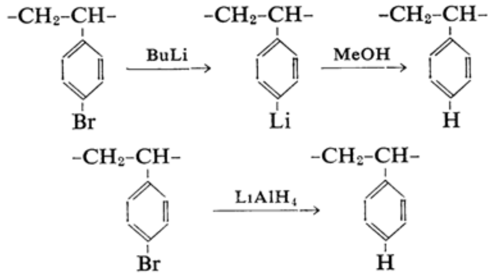
Catalyst g.	Monomer g.	Polymerization Temp. °C	Polymerization Time hr.	Polymer Conv. %	M. p.[b] °C	Elemental anal.[c], % C	H	Br	Ash	[η] dl./g.
$AlEt_3$-$TiCl_4$	7.0	70	6	92.2	218∼224	52.73	3.77	43.41	0.63	0.259
$AlEt_3$-$TiCl_4$[a]	6.3	60	6	87.2	214∼219	52.29	3.91	43.49	0.53	0.244
$AlEt_3$-$TiCl_3$	4.2	10	75	72.0	192	53.11	3.98	43.34	0	0.167
$AlEt_3$-$TiCl_4$	3.5	−35	36	0	—	—	—	—	—	—

a) Thiophene (0.46 g.) was added.
b) The softening point of poly-*p*-bromostyrene prepared by thermal polymerization was 215°C. $[\eta]=0.280$ dl./g.
c) Calcd. for $(C_8H_7Br)_n$: C, 52.49; H, 3.86; Br, 43.65%.

TABLE II. REDUCTION OF POLY-*p*-BROMOSTYRENE WITH *n*-BUTYLLITHIUM
n-BuLi, 600 mg.; Solvent, Benzene 40 ml.

Exp. No.	Polymer g.	Reaction Temp. °C	Reaction Time hr.	Reduced polymer Yield g.	Elemental anal., % C	H	Br	Ash
H-2[a]	0.203	20	3.3	0.133	75.25	6.21	17.62	0.59
H-1	0.206	20	2.2	0.137	69.17	5.46	24.27	0.35
H-4[b]	0.112	20	5.8	0.087	85.43	7.11	6.34	0.89
H-7[c]	0.070	20	6.0	0.063	88.06	7.29	3.49	1.32
H-3[d]	0.200	80	5.3	0.110	91.81	7.68	0.73	0
H-8	0.156	43	5.0	0.065	82.08	7.08	9.09	0.51

a) The polymer was polymerized thermally.
b), c) Specimens H-4 and H-7 were obtained by successive reductions of H-1.
d) Elemental analysis was given for the soluble part of the reduction product.



Braun demonstrated the recovery of an isotactic polystyrene from an amorphous iodinated product which had been derived by the iodination of isotactic polystyrene[14]. He attempted to apply the method to the determination of the stereoregularity of poly-*p*-chlorostyrene and poly-*p*-bromostyrene, resulting in incomplete dehalogenation.

In the present work it was also ascertained that the lithiation of poly-*p*-bromostyrene with butyllithium could not be accomplished satisfactorily. The results of the reduction of poly-*p*-bromostyrene by butyllithium are shown in Table II. When the reaction temperature of 20°C was employed, only a half of the bromine of the polymer was removed. The three successive reactions at the same temperature gave a product still 3.49% bromine. When the reaction was carried out at the boiling point of benzene, the debromination was almost complete, but 90% of the product was insoluble and infusible. This must be a cross-linked polymer produced by the Wurtz-Fittig coupling between the lithiated phenyl group and the bromophenyl group in the polymer chains.

Prolonged reduction of poly-*p*-bromostyrene using lithium aluminum hydride as a reducing agent gave a polystyrene containing a negligible amount of bromine, although in this reaction a large excess of lithium aluminum hydride was required[15]. The results of the reduction are shown in Table III. Elemental analysis of the product showed a good agreement with that of polystyrene except that a trace of ash could not be removed from the samples.

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[14] D. Braun, *J. Polymer Sci.*, **40**, 578 (1959).

[15] The necessity of a large excess of lithium aluminum hydride may be explained, according to Bailey[15], as follows: as the reduction proceeds, the produced aluminum tribromide reacts with lithium aluminum hydride and gives aluminum hydride. Both aluminum hydride and lithium aluminum hydride may cause a ring cleavage of the solvent tetrahydrofuran and may thus be consumed. (W. J. Bailey and F. Marktscheffel, *J. Org. Chem.*, **25**, 1797 (1960).)

TABLE III. REDUCTION OF POLY-*p*-BROMOSTYRENE WITH $LiAlH_4$

$LiAlH_4$: 0.5 g.
Solvent : Tetrahydrofuran, 30 ml.
Reaction temp : 66°C (b. p. of tetrahydrofuran)

Exp. No.	Polymer g.	React. time hr.	Reduced polymer				
			Yield	Elemental analysis[b], %			
			g.	C	H	Br	ash
H-11	0.316	6	0.247	60.70	4.54	35.07	0.63
H-12	0.300	145	0.130	91.62	7.69	0	0.67
H-13[a]	0.300	145	0.126	91.11	7.55	0.36	0.80

a) Poly-*p*-bromostyrene obtained by thermal polymerization
b) Calcd. for polystyrene $(C_8H_8)_n$: C, 92.26 ; H, 7.74%

TABLE IV. A COMPARISON OF THE REDUCED POLYMER WITH ISOTACTIC AND ATACTIC POLYSTYRENES

Polystyrene	Reducing agent	M. p. °C	Solubility[d]		X-Ray diffraction
			EMK[e]	Toluene	
Amorph. P. S.[a]	—	110~3	+	+	Amorph.
Isot. P. S.[b]	—	230~3	−	+	Cryst.
From PPBS[c],[f]	*n*-BuLi	120	+	+	Amorph.
From PPBS	$LiAlH_4$	150~5	+	+	Amorph.
From PPBS[g]	$LiAlH_4$	146~9	+	+	Amorph.

a) Amorphous part of the polymer obtained by the polymerization of styrene with the Ziegler catalyst
b) Isotactic part of the polymer obtained by the polymerization of styrene with the Ziegler catalyst
c) PPBS : Poly-*p*-bromostyrene
d) + : Soluble, − : Insoluble
e) EMK : Ethyl methyl ketone
f) The soluble fraction of the polymer reduced at 80°C
g) A specimen obtained by the reduction of a thermally polymerized poly-*p*-bromostyrene

The polystyrene obtained by the reduction was not separated into fractions having different properties with usual organic solvents. The polymer was heat-treated at 100°C for eight hours, but no crystallization by the treatment was detected. It was soluble in ethyl methyl ketone, gave only amorphous X-ray patterns, and showed a softening point of 150~155°C and the same infrared spectrum as that of atactic polystyrene. In the infrared spectrum, no absorption band was observed at 1364 and 1297 cm^{-1}, which bands had been proved to be characteristic of isotactic polystyrene[16]. A comparison of the reduced polymers with isotactic and atactic polystyrenes is shown in Table IV.

It may well be assumed that no change in the steric configuration of the main chain occurred through the reduction process. On the basis of these results, we may draw the conclusion that poly-*p*-bromostyrene polymerized with the Ziegler catalyst is substantially atactic in the steric configuration of the main chain. A major factor in the lack of stereoregularity may be the disturbance of stereoregulation at the site of polymerization by the bulky bromine atom attached to the para position of the benzene ring.

It is also to be noted that the polystyrene obtained by the reduction of poly-*p*-bromostyrene has a softening temperature of about 150°C. This is about 40°C higher than that of the conventional atactic polystyrene (ca. 110°C). Similarly, a polystyrene which was obtained by the lithium aluminum hydride reduction of thermally polymerized poly-*p*-bromostyrene showed the unusual softening point of 146~149°C. Therefore, there may be a possibility that the elevation of the softening point is due to a minor change in the chemical structure during the reduction, to, that is, for instance, a small extent of cross-linking.

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[16] H. Tadokoro, T. Kitazawa, S. Nozakura and S. Murahashi, This Bulletin, 34, 1209 (1959).