Vinyl Polymerization. XLIII. Polymerization of Styrene with Vinylmagnesium Chloride

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(Received September 21, 1959)

It was reported by Beaman[1] and others that Grignard reagents could polymerize some vinyl monomers. Recently, a synthetic method of Grignard reagent from vinyl chloride was published[2]. In this paper the authors prepared vinylmagnesium chloride after Ramsden[2] and carried out the kinetic study of the polymerization of some vinyl monomers.

Experimental

Materials. — Commercial tetrahydrofuran (THF) was refluxed over potassium hydroxide and then over sodium. After distillation it was stored in the presence of lithium aluminum hydride. Before, use, it was redistilled in a stream of nitrogen. Commercial vinyl chloride was dried with potassium hydroxide, calcium chloride and then with phosphorus pentoxide.

Vinylmagnesium Chloride. — Vinyl chloride gas was passed into THF (507 g.) until 144 g. were absorbed. Ethyl bromide (2 ml.) was dropped into a mixture of 44 g. of magnesium turnings and 15 ml. of the vinyl chloride-THF solution was then added as rapidly as possible. After the reaction was completed, excess vinyl chloride was distilled out and the unreacted magnesium was filtered off. The homogeneous solution of vinylmagnesium chloride was stored in a brown bottle. The Grignard solution thus obtained had a concentration of 2.07 mol./l. by Gilman's titration[3] (81% yield). After a month, the concentration decreased to 2.01 mol./l. From these values it was considered that the concentration of the reagent might be kept constant throughout the experiment.

Change of Vinylmagnesium Chloride into Acrylic Acid. — A solution of vinylmagnesium chloride in THF was added into a large excess of powdered dry ice. After being acidified, the organic layer was distilled to give an acid, having a stimulus odor, and boiling at $84\sim88$°C/82 mmHg, ($n^{20}=1.4223$). The acid could be polymerized easily. From these facts, it was confirmed that the acid was acrylic acid (in literature 4, b.p.$_{88}=81$°C, $n^{20}=1.4224$) and the Grignard reagent was vinylmagnesium chloride.

Polymerization.—Styrene and methyl methacrylate were polymerized in a sealed glass tube, and acrylonitrile in a 3-necked flask equipped with a stirrer and a nitrogen inlet tube.

In the case of glass tube method, the tube was first substituted with dry nitrogen and fed with Grignard reagent from a burette, into which the reagent had been fed with the aid of nitrogen pressure. Then, the monomer and solvent were charged. The usual degassing procedure followed. These tubes were set in a water bath at constant temperature and shaken during polymerization. The reacted mixture was poured into methanol, containing excess hydrochloric acid. Polystyrene and polymethyl methacrylate were purified by reprecipitation from benzene solution by methanol. To obtain a sample of polymethyl methacrylate for infrared absorption spectrum, a freezing technique was used.

When acrylonitrile was contacted with the Grignard reagent, so much heat was evolved that the following procedure was used. To a cold mixture of Grignard reagent and a large volume of solvent (THF), the monomer was added through a long glass tube surrounded by dry ice. These operations were carried out under the atmosphere of dry nitrogen.

The intrinsic viscosities shown in Table I are the values at 30°C measured in benzene solution, using a Ubberohde viscometer.

Results and Discussion

Polymerization of Vinylmagnesium Chloride. —As shown in Table I, vinylmagnesium chloride could not be polymerized by the usual methods.

TABLE I. PORYMERIZATION OF VINYLMAGNESIUM CHLORIDE

Initiator	VMgCl* ml.	THF** ml.	T°C	Time hr.	Polymer
AIBN***	50	0	60	10	None
BPO****	50	0	60	10	None
None	50	0	60	10	None
UV 3600 A	50	0	30	10	None

* Vinylmagnesium chloride
** Tetrahydrofuran
*** 2, 2′-Azobisisobutylonitrile
**** Benzoylperoxide

Copolymerization of Vinylmagnesium Chloride with Styren or Methyl Methacrylate.—The white polymers obtained from the systems consisting of styrene and vinylmagnesium chloride had the same analytical results with styrene or methyl methacrylate homopolymer within the limit of experimental error (Table II). To introduce carboxyl groups to the copolymer, the polymerization mixtures were poured onto a large

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[1] R. G. Beaman, *J. Am. Chem. Soc.*, **70**, 3115 (1949).
[2] H. E. Ramsden, *J. Org. Chem.*, **22**, 1602 (1957).
[3] H. Gilman, *J. Am. Chem. Soc.*, **51**, 1676 (1929).

TABLE II. POLYMERIZATION OF SOME VINYL MONOMERS WITH VINYLMAGNESIUM CHLORIDE

VMgCl	Monomer		THF	Temp.	Time	Polymer		
ml.	ml.		ml.	°C	hr.	g.	Yield, %	[η]*
60	Vinylchloride	10**	50	30	20			
90	Styrene	50	0	50	6	48	100	0.136
5	Styrene	10	0	50	6	8.7	96	
0	Styrene	10	5	50	6	0.16	1.7	2.9
0	Styrene	15	0	50	6	0.1	0.7	4.7
6	Styrene	5	0	50	5	2.9	65	0.26
30	Methylmethacrylate	20	50	−60	18	6.8	36	2.2
30	Methylmethacrylate	20	50	10	18	1.3	7.0	2.6
								N %***
20	Acrylonitrile	50	50	30	****	9.3	23	19.49
10	Acrylonitrile	10	0	30		4.4	55	16.83
30	Acrylonitrile	20	50	−10		8.4	52	13.07

* [η] was measured in benzene at 30°C using a Ubberohde viscometer.

** Under UV irradiation, the mixture gave needle crystals gradually but no polymer.

*** By the Kjeldahl method. Calcd. value is 26.40%.

**** Dropping acrylonitrile into Grignard mixture, yellow polymer precipitated immediately.

Polystyrene Found: C, 92.09; H, 8.12.
Calcd. for C_8H_8: C, 92.27; H, 7.74%.
Polymethylmethacrylate Found: C, 59.78; H, 8.27.
Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.05%.

excess of dry ice, acidified with hydrochloric acid and the polymer was reprecipitated. But the infrared absorption spectra of the polymers had no absorption characteristic of the hydroxyl group in carboxylic acid and were identical to those of each homopolymer.

Polymerization of Vinyl Chloride Initiated by Vinylmagnesium Chloride. — The mixture of vinylmagnesium chloride and vinyl chloride was sealed in a glass tube and irradiated by ultraviolet ray of 3600 Å but no polymer was obtained.

Polymerization of Acrylonitrile Initiated by Vinylmagnesium Chloride. — Acrylonitrile polymerized vigorously to yellow powder which contained a much smaller quantity of nitrogen than polyacrylonitrile.

Polymerization of Styrene Initiated by Vinylmagnesium Chloride.—In the presence of vinylmagnesium chloride styrene hardly polymerized at room temperature, but did so easily above 40°C. Fig. 1 shows the process of polymerization. As the concentration of vinylmagnesium chloride increased, the rate of polymerization also increased. Figs. 2—4 are the time-conversion curves at 50, 60 and 70°C, respectively. Fig. 5 shows the dependence of rate on monomer concentration. At a monomer concentration, the rate becomes maximum but the reason is not clear.

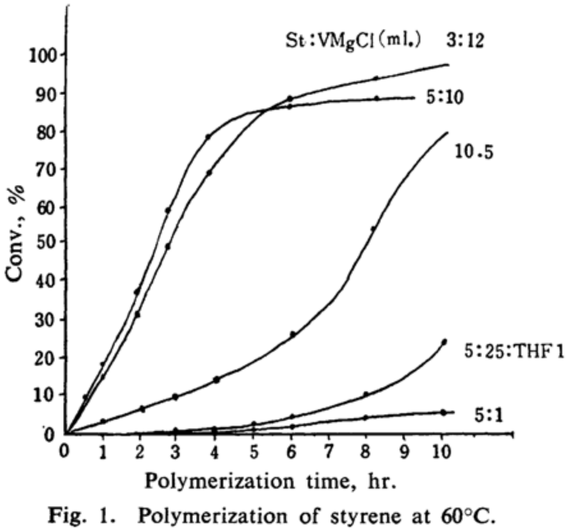

Fig. 1. Polymerization of styrene at 60°C.

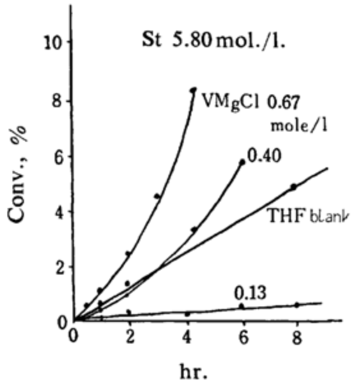

Fig. 2. Polymerization of styrene at 50°C.

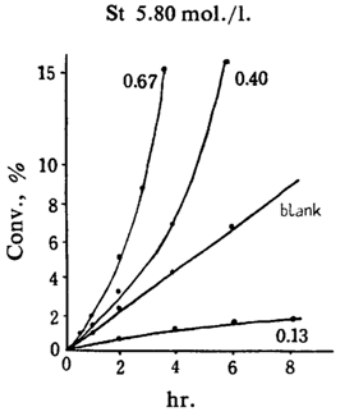

Fig. 3. Polymerization of styrene at 60°C.

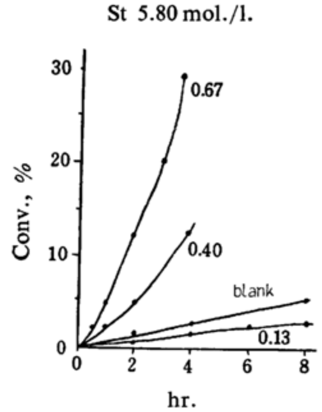

Fig. 4. Polymerization of styrene at 70°C.

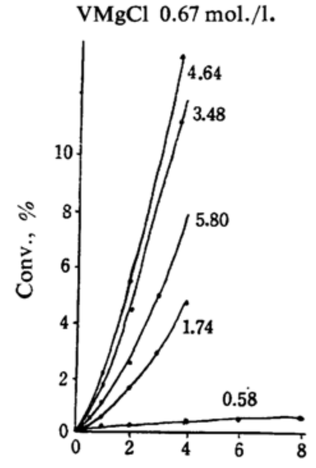

Fig. 5. Polymerization of styrene at constant initiator concentration at 50°C.

The rate of the polymerization of styrene in the absence of vinylmagnesium chloride was abnormally large, as shown in Figs. 2—4, as "blank test". The rapid rate was caused by the addition of THF instead of vinylmagnesium chloride solution. It may be considered that THF included THF-peroxide. In order to testify to this consideration, the THF above used was compared with oxygen absorbed THF. Oxygen was bubbled into THF under the irradiation of ultraviolet ray at room temperature for three days. The effects of the treatment was shown in Fig. 6. When the quantity of vinylmagnesium chloride was small, the rate decreased greatly. This was due to the consumption of the activities of Grignard reagent and peroxide by the mutual reaction.

Observation on the relation between the rate of polymerization and the concentration of vinylmagnesium chloride was carried out. As the curves for time vs. conversion were not straight, the conversions after two hours were plotted against the concentration of vinylmagnesium chloride. Straight lines were obtained as shown in Fig. 7. From the slope of these lines the following equation was derived.

$$Rp = k[C]^{1.4}$$

The overall activation energy of polymerization was about 12 kcal./mol. (Fig. 8).

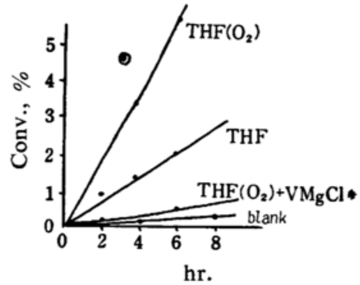

Fig. 6. Polymerization of styrene with O_2 treated tetrahydrofuran.

Double circle shows one carried out with the oily residue which was obtained by evaporation of THF treated with O_2.

* About 0.5 ml. VMgCl to 5 ml. THF(O_2).

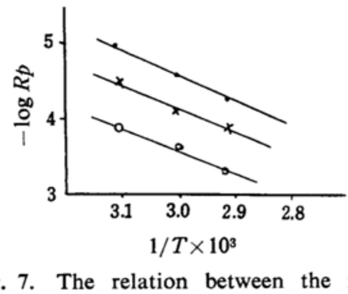

Fig. 7. The relation between the rate of polymerization and the concentration of vinylmagnesium chloride.

● 50°C × 60°C ○ 70°C

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4) C. Moreau, M. Murat and N. Tampier, *Ann. chim.*, [9], 15, 221 (1921).

5) R. Criege, *Angew. Chem.*, 62, 120 (1950).

TABLE III. COPOLYMERIZATION OF STYRENE WITH METHYLMETHACRYLATE

No.	Styrene		Methylmethacrylate		Styrene	Time	Polymer	Styrene mol. % in copolymer
	ml.	mol. × 10^2	ml.	mol. × 10^2	mol. %	min.	g.	
1	10	8.70	0	0	100	710	0.134	100
2	9.5	8.26	0.53	0.49	94.4	570	0.029	70.46
3	9	7.83	1	0.94	89.3	380	0.088	19.75
4	8	6.96	2	1.87	78.8	150	0.141	4.80
5	7	6.09	3	2.80	68.5	70	0.339	4.80
6	6	5.22	4	3.74	58.3	60	0.492	2.50
7	5	4.35	5	4.67	48.2	60	0.612	2.09
8	4	3.48	6	5.61	38.3	50	1.404	0.71
9	3	2.61	7	6.54	28.5	50	1.556	2.47
10	2	1.74	8	7.48	18.9	50	1.108	0.48
11	1	0.87	9	8.41	9.38	20	0.996	1.99
12	0	0	10	9.36	0	20	1.095	1.58

Polymerization temperature ; 10°C.
Grignard concentration ; 0.67 mol./l.
Styrene contents in copolymer were calculated from the carbon contents.

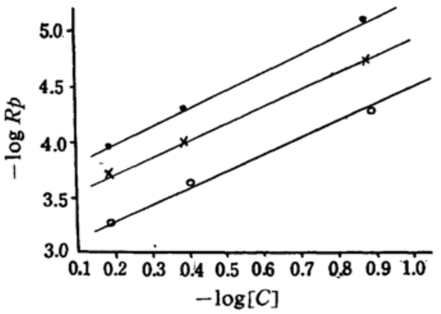

Fig. 8. Overall activation energy of polymerization.

● 50°C × 60°C ○ 70°C

Copolymerization of Styrene with Methyl Methacrylate.—In 1949, Beaman stated that the polymerization initiated by Grignard reagents proceeded through anionic mechanism. This idea has been generally accepted. To confirm the anionic mechanism in these systems, the authors carried out the copolymerization of styrene with methyl methacrylate at 10°C. From the carbon contents of copolymers their composition were calculated and plotted against the compositions in feed (Table III and Fig. 9). It was confirmed from the results in Fig. 9 that the polymerization initiated by vinyl magnesium chloride proceeded by anionic mechanism.

By the Beilstein test, it was found that no chlorine existed in the molecule of copolymer.

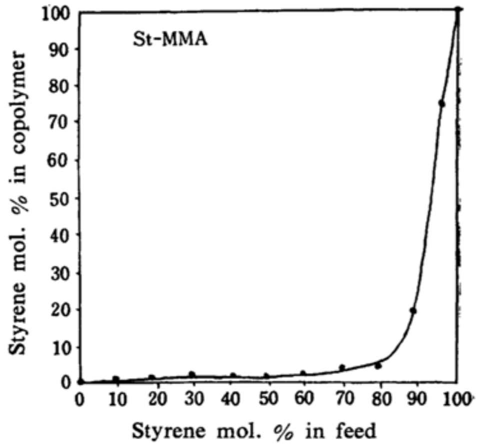

Fig. 9. The composition of styrene-methyl methacrylate copolymer.

From the results stated above, it was possible to state that the order of the rate of polymerization was as follows:

$$\text{acrylonitrile} > \text{methyl methacrylate} \gg \text{styrene} > \text{vinyl chloride} = 0$$

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