BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 500—505 (1970)

Polymerization of Vinyl Chloride and Copolymerization of Vinyl Chloride with Styrene by Alkylmagnesium Chlorides

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(Received July 29, 1969)

t-Butylmagnesium chloride was found to initiate the polymerization of vinyl chloride efficiently at -22—30°C. The best solvent was diethyl ether, but the degree of polymerization was the highest when no solvent was used ($\bar{P}_n=1940$ at 20°C). The apparent activation energy for the rate of polymerization was 13.2 kcal/mol and the frequency factor was 9.06×10^4. The rate of polymerization, R_p, was equal to const. $\times[\mathrm{VC}]^{3.90}\times[t\text{-BuMgCl}]^{1.98}$. Isopropylmagnesium bromide initiated the polymerization with less efficiency, and phenylmagnesium bromide was completely ineffective. Vinyl chloride and styrene were copolymerized in ether by *t*-butylmagnesium chloride at 30°C. The mole % styrene included in the copolymer was considerably different from those obtained by benzoyl peroxide at 48°C or by di-*t*-butylperoxy oxalate at 30°C.

Guyot and Tho investigated the polymerization of vinyl chloride in tetrahydrofuran with *t*-butylmagnesium chlorde, and suggested that the polymerization was anionic.[1-3] Their study was of great interest, since there have been no other papers on the anionic polymerization of vinyl chloride. However, their evidence did not seem convincing, and there was a paper reporting that the polymerization of vinyl chloride with Grignard reagents was of free radical nature.[4] Thus a more detailed study seemed to be desirable. This paper will describe the results of the investigation.

Experimental

Materials. Diethyl ether was shaken with one-tenth volume of a 10% sodium hydrogen sulfite solution for one hour, washed with a saturated sodium chloride solution containing 10% sodium hydroxide, then with a saturated sodium chloride solution containing some sulfuric acid, and twice with a saturated sodium chloride solution, dried over calcium chloride and then over sodium wire, and finally distilled over sodium under a nitrogen atmosphere at 34.5°C.

A *t*-butylmagnesium chloride solution was prepared in a 300 m*l* three-necked, round-bottomed flask from 1.46 g of magnesium turnings, 6.5 m*l* of *t*-butyl chloride and 150 m*l* of absolute ether under a nitrogen atmosphere. The supernatant solution was titrated and then used. The concentration was usually 1.5—2.0×10^{-4} mol/*l*. Other Grignard solutions were prepared in a similar manner from halides and magnesium in absolute ether under a nitrogen atmosphere.

Styrene was distilled under reduced pressure before use. Vinyl chloride was passed through a silver nitrate solution and a calcium chloride tube, and then collected

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1) A. Guyot and Pham Quang Tho, *C. R. Acad. Sci. Paris*, **256**, 165 (1963).

2) A. Guyot and Pham Quang Tho, *J. Polymer Sci.*, *C*, **1964**, No. 4, 299.

3) A. Guyot and Pham Quang Tho, "Chemistry of Polymerization Processes," ed. by Society of Chemical Industry, London (1966), pp. 69—81.

4) K. Yoshida and T. Morikawa, *Sci. and Ind.*, **27**, 80 (1953).

in a pressure-tube cooled with a dry ice-methanol bath in a vacuum system.

Polymerization of Vinyl Chloride by *t*-Butylmagnesium Chloride. A pressure tube containing *t*-butylmagnesium chloride dissolved in ether was connected to a vacuum system under a nitrogen atmosphere, and cooled with a dry ice-methanol bath. A measured amount of deaerated vinyl chloride was distilled into the pressure tube, which was then sealed under a nitrogen atmosphere. Tubes were placed in a constant temperature bath and shaken by hand occasionally. After the polymerization was over, the ampoule was opened, and the polymer was washed with 6 N hydrochloric acid, water and methanol, and then dried under reduced pressure.

For the runs containing no ether, the ethereal solution of a Grignard reagent was evaporated to dryness in a vacuum, and then vinyl chloride was added to the residue. The mixture was then polymerized by the same procedure as described above.

Copolymerization of Vinyl Chloride with Styrene or Methyl Methacrylate by *t*-Butylmagnesium Chloride. A measured amount of deaerated vinyl chloride was distilled into the pressure tube containing *t*-butylmagnesium chloride and styrene or methyl methacrylate. The tubes were sealed under a nitrogen atmosphere, and placed in a constant temperature bath at 30.0°C. After appropriate intervals, the tubes were removed from the bath, cooled to −20°C, opened, and the content was poured into methanol. The polymer precipitated was filtered and washed with methanol until the filtrate formed no precipitates with a silver nitrate solution. The copolymer was dried and was burned in platinum wire within a flask, and chloride ions produced were titrated with 0.02 N mercuric nitrate solution.5)

Copolymerization of Vinyl Chloride with Styrene by *t*-Butylperoxy Oxalate. *t*-Butylperoxy oxalate was prepared according to the method of Bartlett, Benzing and Pincock.6) Procedures of polymerization and the work-up were the same as described above.

Results and Discussion

At first, the polymerization of vinyl chloride was attempted in tetrahydrofuran, but both the extent of conversion and the degree of polymerization were always smaller than those reported by Guyot and Tho.3) After various solvents were investigated, diethyl ether was found to be an excellent medium for the polymerization. The degrees of polymerization reported by Guyot and Tho were 66—73, but those of polyvinyl chloride produced in diethyl ether were as large as 1455.7) It was further found that in the absence of diethyl ether,

TABLE 1. POLYMERIZATION OF VINYL CHLORIDE WITH *t*-BUTYLMAGNESIUM CHLORIDE

Run	*t*-BuMgCl mol/*l*	$[VC]_0$ mol/*l*	Temp. (°C)	Time (hr)	Conversion (%)	Degree of Polymerization	Remarks
1	0.0286	14.44	−22.0	490	19.3	1530	no ether
2	0.040	12.64	10.0	2	1.4	165	
3	0.040	12.64	10.0	19	7.5	780	
4	0.040	12.64	10.0	42	30	986	
5	0.040	12.64	10.0	120	39	1250	
6	0.040	12.64	10.0	350	48	1455	
7	0.0253	12.64	20.0	46	30.7	780	
8	0.0289	14.44	20.0	46	26.6	1940	no ether
9	0.0253	12.64	30.0	46	50.8	640	
10	0.0289	12.64	30.0	46	18.5	840	no ether
11	0.090	11.23	30.0	22	66	212	
12	0.045	11.23	30.0	22	55	360	
13	0.023	11.23	30.0	22	21	710	
14	0.090	11.23	20.0	22	39	237	
15	0.045	11.23	20.0	22	29	450	
16	0.023	11.23	20.0	22	14	610	
17	0.090	11.23	30.0	22	22	254	
18	0.0735	9.20	30.0	22	22	181	
19	0.0540	6.75	30.0	22	23	159	
20	0.0506	12.64	20.0	22	29	470	
21	0.0450	11.23	20.0	22	30	380	
22	0.0368	9.20	20.0	22	29	280	

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5) K. Ono, *Ann. Sankyo Res. Lab.*, **18**, 51 (1966).

6) P. D. Bartlett, E. R. Benzing and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).

7) Recently a detailed investigation on the composition of Grignard compounds has been published, which has established that RMgX (X=Cl, Br, or I) exists as monomeric form in tetrahydrofuran, whereas in diethyl ether RMgCl exists as a dimer in both dilute and concentrated solutions and RMgBr and RMgI are monomeric at low concentrations (0.1 mol/*l*) and polymeric at higher concentrations. (F. W. Walker and E. C. Ashby, *J. Amer. Chem. Soc.*, **91**, 3845 (1969)).

i.e., with a solid Grignard reagent in liquid vinyl chloride, the degree of polymerization was as large as 1940. The results of polymerization are summarized in Table 1.

Run 1 shows that this polymerization proceeds even at $-22°C$ though the rate is small. Runs 2—6 show that the degree of polymerisation increases with the extent of conversion; this behavior is not what is expected for free-radical polymerization. Runs 7—10 indicate that in the absence of ether the degree of polymerization is larger though the rate of polymerization is somewhat smaller. Runs 11—16 show that the larger the catalyst concentration the smaller the degree of polymerization. Runs 17—22 indicate that upon dilution of a mixture with ether the extent of conversion is unaltered, but the degree of polymerization decreases.

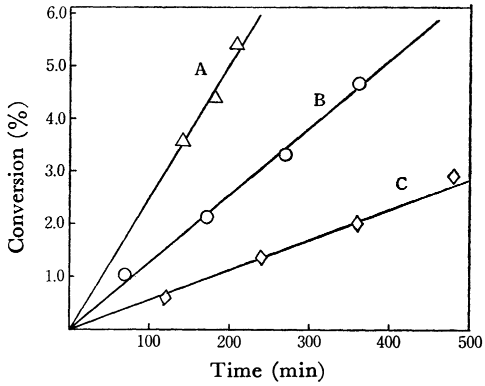

Fig. 1. Rates of polymerization of vinyl chloride at different temperatures.
A, 40.0°C; B, 30.5°C; C, 20.1°C; $[VC]_0=12.64$ mol/*l*, $[t\text{-BuMgCl}]_0=2.50\times10^{-2}$ mol/*l*

Figure 1 shows the rates of polymerization at different temperatures with solutions of the same composition. R_p was 1.25, 2.73, and 5.33×10^{-5} mol/*l* sec at 20.1, 30.5, and 40.0°C, respectively. Plots of log R_p *versus* $1/T$ yielded a straight line, and R_p was expressed as follows.

$$R_p = 9.06\times10^4 e^{-\frac{13200}{RT}} \tag{1}$$

The relationship between R_p and the initial concentration of *t*-butylmagnesium chloride is shown in Fig. 2. With $[VC]_0=11.23$ mol/*l* and at 30.1°C, R_p was 0.333, 3.85 and 9.76×10^{-5} mol/*l* sec when $[t\text{-BuMgCl}]_0$ was 0.0128, 0.0428 and 0.0711 mol/*l*, respectively. From the slope of the straight line, R_p was expressed as follows.

$$R_p = \text{const.} \times [t\text{-BuMgCl}]^{1.98} \tag{2}$$

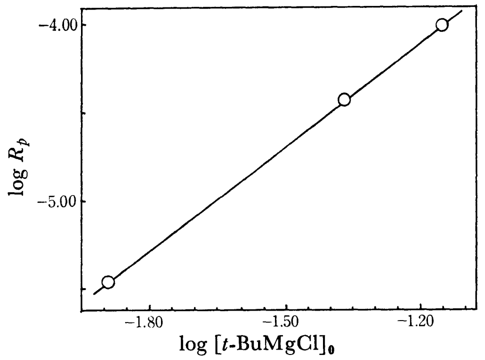

Fig. 2. Rates of polymerization of vinyl chloride with different catalyst concentration at 30.1°C. ($[VC]_0=11.23$ mol/*l*)

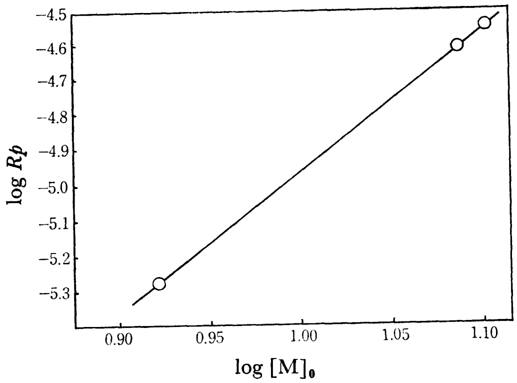

Fig. 3. Rates of polymerization of vinyl chloride with different monomer concentrations at 30.1°C.
($[t\text{-BuMgCl}]_0=2.50\times10^{-2}$ mol/*l*)

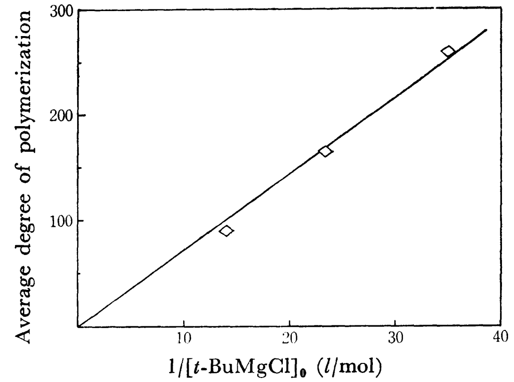

Fig. 4. Relationship between average degree of polymerization and catalyst concentration.
$[VC]_0=11.23$ mol/*l*, Conversion=3.0%, 30.1°C

Figure 3 shows the relationship between the rates of polymerization and the concentration of vinyl chloride. From the slope of the straight line, R_p was expressed as follows.

$$R_p = \text{const.} \times [VC]^{3.90}[t\text{-BuMgCl}]^{1.98} \tag{3}$$
$$(\text{const.} = 2.08 \times 10^{-6} \text{ at } 30°C)$$

The relationship between the average degree of polymerization and $1/[t\text{-BuMgCl}]_0$ is shown in Fig. 4.

As for other Grignard reagents, isopropylmagnesium bromide was found to initiate the polymerization with less efficiency and phenylmagnesium bromide initiated no polymerization. With $[i\text{-PrMgBr}]_0=0.058$ mol/*l* and $[\text{VC}]_0=12.51$ mol/*l* at 25.0°C, a polymer with $\bar{P}=625$ was obtained with 13% yield after 16 hr of polymerization. With $[\text{PhMgBr}]_0=0.288$ mol/*l* and $[\text{VC}]_0=7.30$ mol/*l*, no polymer was formed after 20 hr at 20.0°C or after 3 hr at 60°C.

The possible mechanisms of the initiation of the polymerization are (1) monomolecular homolytic decomposition of RMgX, (2) production of free radicals by the reaction between RMgX and vinyl chloride, (3) anionic polymerization, (4) polymerization by an anion-radical, and (5) polymerization by a complex involving magnesium.

The possibility of (1) was definitely excluded from the observation that an ethereal solution of *t*-butylmagnesium chloride underwent no decomposition when it was kept under a nitrogen atmosphere at room temperature for 25 days.

The frequency factor obtained from the Arrhenius plots was 9.06×10^4 which was smaller than the values found for ordinary radical polymerizations (10^6—10^8). Equation (3) is quite different from the equation applicable to ordinary radical polymerizations ($R_p=\text{const.}\times[\text{VC}]\times[\text{Initiator}]^{0.5}$).

In an attempt to clarify the mechanism of the initiation of polymerization by *t*-butylmagnesium chloride, copolymerization of vinyl chloride and styrene was investigated. The results are summarized in Table 2, and are compared with the results of a free radical polymerization in acetone by benzoyl peroxide at 48°C in Fig. 5. The mol % styrene included in the copolymer obtained by use of *t*-butylmagnesium chloride is considerably different from that obtained by use of benzoyl peroxide.[8] Since the difference in temperatures and solvents might be the cause for such discrepancy, styrene and vinyl chloride were copolymerized in ether at 30°C by use of di-*t*-butylperoxy oxalate. Results are summarized in Table 3 and Fig. 5. These findings indicate that the polymerization initiated by *t*-butylmagnesium chloride is different from ordinary radical polymerization.

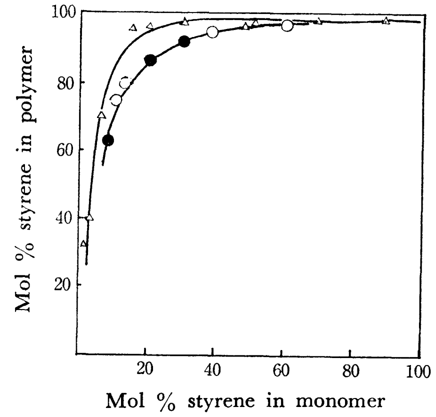

Fig. 5. Copolymerization of vinyl chloride and styrene.

△ with *t*-butylmagnesium chloride in ether at 30°C

○ with benzoyl peroxide in acetone at 48°C

● with di-*t*-butylperoxy oxalate in ether at 30°C

Copolymerization of vinyl chloride and methyl methacrylate by *t*-butylmagnesium chloride was attempted, and the results are shown in Table 4. The rates of polymerization were much greater than those of vinyl chloride and styrene, and the polymer obtained was the homopolymer of methyl methacrylate. Apparently the anionic polymerization of only methyl methacrylate took place. It is reasonable that vinyl chloride could not compete with methyl methacrylate, since methoxycarbonylcarbanion is far more stable than chlorocarbanion.

TABLE 2. COPOLYMERIZATION OF VINYL CHLORIDE AND STYRENE BY *t*-BUTYLMAGNESIUM CHLORIDE AT 30.0°C

Mol % styrene in monomers	Catalyst mol/100 mol monomers	Time (hr)	Conversion (%)	Cl (%) in copolymer	Mol % styrene in copolymer
89.1	0.23	3.0	0.253	0.389	98.8
69.1	0.23	2.3	0.715	0.270	99.2
50.5	0.23	2.8	0.282	0.463	98.5
48.4	0.33	333.5	1.92	1.08	96.9
29.9	0.60	70.5	2.35	0.870	97.4
20.0	0.33	70.5	0.318	1.41	96.0
15.0	0.33	355	0.291	1.76	95.0
7.0	0.60	189	1.15	11.58	70.1
3.3	0.60	186	1.10	27.13	39.6
1.0	0.60	186	0.073	31.75	32.1

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8) E. C. Chapin, G. E. Han and R. G. Fordyce, *J. Amer. Chem. Soc.*, **70**, 538 (1948).

TABLE 3. COPOLYMERIZATION OF VINYL CHLORIDE AND STYRENE BY DI-*t*-BUTYLPEROXY OXALATE AT 30.0°C

Mol % styrene in monomers	Catalyst mol/100 mol monomers	Time (hr)	Conversion (%)	Cl (%) in copolymer	Mol % styrene in copolymer
29.4	0.30	48	4.62	2.57	92.6
20.1	0.30	50	6.45	4.74	86.9
14.8	0.30	50	2.32	7.46	80.0
7.0	0.30	50	1.06	15.0	62.7
2.95	0.30	50	0.525	22.6	47.5

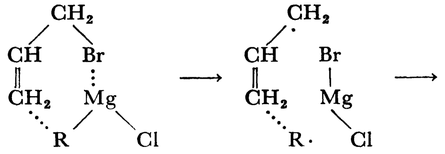
TABLE 4. COPOLYMERIZATION OF VINYL CHLORIDE AND METHYL METHACRYLATE BY *t*-BUTYLMAGNESIUM CHLORIDE AT 30.0°C

Mol % MMA in monomers	Catalyst mol/100 mol monomers	Time (min)	Conversion (%)	Cl (%) in copolymer	Mol % MMA in copolymer
67.2	0.33	3	9.43	0	100
49.5	0.18	5	4.26	0	100
28.7	0.22	5	8.54	0	100
9.95	0.22	5	6.03	0	100
8.01	0.4	15	4.18	0	100
4.87	0.44	5	4.13	0	100
1.97	0.4	20	1.49	1.82	95.0

From the data on the copolymerization of styrene and vinyl chloride shown in Table 2, the monomer reactivity ratios r_1 and r_2 were calculated by means of Fineman and Ross' plots. The values obtained were r_1(styrene)$=56$ and r_2(vinyl chloride)$=0$. The values reported for the copolymerization with benzoyl peroxide were $r_1=35$ and $r_2=0.067$.[8]

Since the rate of conversion in the styrene-vinyl chloride was very low, the rate of polymerization of styrene alone by *t*-butylmagnesium chloride was determined. The initial rate of polymerization of styrene alone was 4.86×10^{-7} mol/*l* sec at 30.0°C when [*t*-BuMgCl]$_0$ was 0.57 mol/*l* and [styrene]$_0$ was 5.46 mol/*l*. The initial rate of polymerization of vinyl chloride alone was 9.76×10^{-5} mol/*l* sec at 30.0°C when [*t*-BuMgCl]$_0$ was 0.63 mol/*l* and [VC]$_0$ was 10.2 mol/*l*.

Gough and Dixon studied the reaction between allyl bromide and *t*-butylmagnesium chloride, and proposed that a radical mechanism is operative. They formulated the reaction as follows.[9]



RCH_2-CH=CH_2, *etc.*

They found that relative rates of reaction of alkylmagnesium halides with allyl bromide were *t*-BuMgCl 107, *s*-BuMgCl 22.6, *n*-BuMgCl 2.77 and PhMgCl 1.00. This variation in rates is somewhat in parallel with the variation in the efficiency of initiation by *t*-tubyl-, isopropyl-, and phenylmagnesium halides in this investigation. However, as a possible intermediate of the polymerization by *t*-butylmagnesium chloride a free radical is excluded on the basis of the findings that (1) the rate of polymerization was proportional to $[VC]^4\cdot[Cat]^2$ instead of $[VC][Cat]^{0.5}$, (2) the results of copolymerization by *t*-butylmagnesium chloride were different from those by benzoyl peroxide or *t*-butylperoxy oxalate, and (3) the frequency factor obtained from the Arrhenius plots of rates of polymerization was 9.06×10^4 which was smaller than the values found for ordinary radical polymerizations (10^6—10^8).

Another possible intermediate of this polymerization is an anion, but this possibility can be rejected on the basis of the finding that phenylmagnesium bromide failed to initiate the polymerization of vinyl chloride. It is not reasonable that *t*-butylmagnesium chloride initiates an anionic polymerization whereas phenylmagnesium bromide does not.

Other possible propagating species in this polymerization are an anion-radical or a complex involving magnesium.

Russel, Jansen and Strom have shown that butylmagnesium bromide in a tetrahydrofuran solution forms an anion-radical with a variety of nonbenzenoid aromatic compounds of aromatic ketones such as benzophenone of fluorenone.[10]

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[9] R. G. Gough and J. A. Dixon, *J. Org. Chem.*, **33**, 2148 (1968).

[10] G. A. Russell, E. G. Jansen and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964).

$$[\mathrm{Bu{:}}]^- + \mathrm{A} \rightarrow [\mathrm{Bu}\cdot + \mathrm{A}^{\overline{\cdot}}] \rightarrow \mathrm{BuA}^-$$

Maruyama has found that Grignard reagents react with ketones to form an anion-radical.[11]

$$\mathrm{RMgX} + \overset{|}{\underset{|}{\mathrm{C}}}\mathrm{=O} \rightarrow [\overset{|\cdot}{\underset{|}{\mathrm{C}}}\mathrm{-O^-}] \rightarrow \mathrm{R}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{OMgX}$$

Thus it is probable that an anion-radical is the propagating species in the polymerization by *t*-butylmagnesium chloride. Findings in this investigation excluded three other possible initiation mechanisms, namely (1) radical polymerization by monomolecular decomposition of *t*-butylmagnesium chloride, (2) radical polymerization by a reaction between *t*-butylmagnesium chloride and some other substances, and (3) anionic polymerization. At this stage it is not possible to determine whether the propagating species is an anion-radical or a complex involving magnesium.

Though the mechanism of initiation was not completely clarified, the investigation demonstrated that polymerization of vinyl chloride proceeded efficiently in the presence of *t*-butylmagnesium chloride in diethyl ether or in the absence of solvent at −22°—30°C, and the degree of polymerization of polyvinyl chloride thus obtained was as high as 1940.

Grateful acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[11] K. Maruyama, This Bulletin, **37**, 897, 1013 (1964).