Studies on *p*- and *m*-Vinylbenzylmagnesium Chlorides as Initiators and Monomers—Preparations of Macromers and Poly(Grignard reagent)s

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ABSTRACT: *p*- and *m*-Vinylbenzylmagnesium chlorides (VBzMgCl) were prepared in diethyl ether from the corresponding chloromethylstyrenes, and used as initiators in the polymerizations of MMA and styrene. PMMAs with a variety of tacticities were obtained in toluene and THF by these initiators, and highly syndiotactic ($S > 96\%$) PMMA of low polydispersity ($\bar{M}_w/\bar{M}_n = 1.19$) could be prepared with *m*-VBzMgCl in THF at -110°C . It was found by the totally deuterated monomer technique that the polymer molecule thus obtained had one vinylbenzyl group at the beginning of the chain (α -end). The PMMAs could be used as macromers, which were polymerized and copolymerized with styrene by a radical initiator. *p*-VBzMgCl polymerized styrene in THF at 0°C , and the resulting polystyrene can also be used as a macromer. *m*-VBzMgCl and benzylmagnesium chloride did not give polystyrene. Spontaneous polymerizations of VBzMgCl to poly(Grignard reagent)s were also studied.

KEY WORDS Grignard Reagent / Macromer / Polystyrene / Tacticity / Highly Syndiotactic Poly(methyl methacrylate) / Vinylbenzylmagnesium Chloride / Narrow Molecular Weight Distribution / Totally Deuterated Methyl Methacrylate / Graft Copolymer / Poly(Grignard reagent) /

Many papers have been published on the polymerizations of vinyl monomers with Grignard reagents. However, very few report polymerizations with the Grignard reagent containing a vinyl group, which appear to be well suited to the synthesis of macromers containing exactly one polymerizable double bond at the chain end. Tomoi *et al.*¹ synthesized a highly branched polystyrene using a mixture of *m*- and *p*-vinylbenzylmagnesium chlorides (VBzMgCl) as an initiator in toluene in the presence of hexamethylphosphoramide (HMPA). Asami and his coworkers² attempted to prepare a macromer by polymerizing MMA with *p*-VBzMgCl, but they found the resulting polymer to contain much more than one vinylbenzyl group per polymer chain.

In this work MMA and styrene were polymerized with VBzMgCl and the polymers obtained at low temperatures were found to contain one vinylbenzyl group at the chain end (α -end) by ^1H NMR spectroscopy. The structure of PMMA was also studied by the totally deuterated monomer technique.³⁻⁹ The PMMA macromer thus obtained was polymerized or copolymerized with styrene in toluene at 60°C using AIBN as an initiator. The tacticity of PMMA macromer depended on the isomeric structure of VBzMgCl, the type of solvent and the temperature. The PMMA prepared with *m*-VBzMgCl in tetrahydrofuran (THF) at -110°C showed syndiotacticity (96.6% in triad) which was higher than those reported so far. It was also found that VBzMgCl polymerized to linear poly-

mers by itself in THF at 0°C.

EXPERIMENTAL

MMA and styrene were obtained commercially. MMA- d_8 was prepared according to the procedure reported previously.⁵ All these monomers were purified by fractional distillation under reduced nitrogen pressure, dried over calcium hydride and distilled under high vacuum just before use. *p*- and *m*-VBzMgCl and benzylmagnesium chloride (BzMgCl) were prepared in diethyl ether from magnesium and the corresponding chlorides. *p*-Vinylbenzyl chloride was synthesized by the method of Miyake and Tanimoto.¹⁰ *m*-Vinylbenzyl chloride was prepared in the following way. Acetophenone was chloromethylated by chloromethyl methyl ether at 60–70°C in the presence of $AlCl_3$ and the *m*-chloromethylacetophenone obtained was reduced with $LiAlH_4$ in THF at 0°C. The resulting alcohol was dehydrated with $KHSO_4$ at 190–200°C to yield *m*-vinylbenzyl chloride. bp 54–5°C/0.68 mmHg. 1H NMR; 4.48 ppm (s, 2H, $-CH_2Cl$), 5.22 ppm (d, 1H, $=CH_2$), 5.69 ppm (d, 1H, $=CH_2$), 6.66 ppm (q, 1H, $=CH-$), 7.18–7.40 ppm (m, 4H, aromatic-H).

Polymerization was carried out in a sealed glass ampoule under a dry nitrogen atmosphere. The reaction was initiated by adding the monomer slowly with a hypodermic syringe to the initiator solution cooled to the polymerization temperature. The polymerization was terminated by adding methanol containing HCl equivalent to the Mg^{2+} at the reaction temperature. The reaction mixture was poured into a large amount of methanol to precipitate the high molecular weight polymer. The precipitate was collected by filtration, washed with methanol several times and dried under vacuum. The combined filtrates were concentrated under reduced pressure. The residue was dissolved in benzene and a small amount of insoluble fraction was removed by filtration. The methanol soluble

fraction was recovered from the benzene solution by reprecipitation in hexane.

A syndiotactic and methanol-soluble PMMA macromer prepared with *p*-VBzMgCl in THF at $-78^\circ C$ was polymerized in toluene at 60°C for 24 h using AIBN as an initiator. The reaction mixture was poured into a large amount of methanol to precipitate the poly-(PMMA macromer) formed. The collected methanol-insoluble product was extracted with boiling methanol for 2 h in order to remove the unreacted macromer. Copolymerization of the PMMA macromer with styrene was carried out in a similar manner.

1H NMR spectra were recorded on a JNM-FX100 or a JNM-MH100 spectrometer. The spectra of PMMA and polystyrene were measured in $CDCl_3$ at 55 or 60°C using TMS as an internal standard. Those of P(MMA- d_8) and poly(VBzMgCl) were measured in nitrobenzene- d_5 at 110 and 120°C, respectively, using HMDS as an internal standard. The amount of vinylbenzyl group in the undeuterated PMMA was evaluated from the intensity ratio of vinyl proton signals to methoxy proton signal in the 1H NMR spectrum. The numbers of initiator fragments and terminal methine proton in P(MMA- d_8) were determined as reported previously.^{3–9}

GPC was recorded with a JASCO FLC-A10 chromatograph with Shodex GPC columns A-80M (50 cm $\times$ 2) and KF-802.5 (30 cm) with maximum porosities of 5×10^7 and 4×10^4 , respectively, using tetrahydrofuran (THF) as an eluent. The chromatogram was calibrated against standard polystyrenes. The number-average molecular weights of the polymers were also determined in toluene at 60.0°C with a Hitachi 117 vapor pressure osmometer (VPO).

RESULTS AND DISCUSSION

1. Polymerization of MMA with *m*- and *p*-VBzMgCl

In Table I are shown the results of polym-

Table I. Polymerization of MMA with *p*- and *m*-vinylbenzylmagnesium chlorides and benzylmagnesium chloride in toluene^a

Initiator	Temp °C	Time h	MeOH-insoluble						MeOH-soluble %	CH ₂ =CH- per chain
			Yield %	Tacticity/%			$\bar{M}_n$	$\bar{M}_w/\bar{M}_n^c$		
				<i>I</i>	<i>H</i>	<i>S</i>				
<i>p</i> -VBzMgCl	-78	24	55	33	26	41	11600 ^b	1.84	23	0.99
	0	3	16	48	22	30	12400 ^b	2.25	16	3.08
	30	3	10 ^d	54	21	25	11200 ^b	3.10	6	3.76
	60	1	12 ^e	88	3	9	15000 ^b	5.65	4	6.12
	110	1	12 ^f	—	—	—	—	—	0	—
<i>p</i> -VBzMgCl ^g	-78	24	29	38	24	38	6100 ^c	3.83	25	—
	0	3	17	76	12	12	6100 ^c	13.7	28	—
<i>m</i> -VBzMgCl	-78	24	43	30	24	46	16300	2.67	32	0.92
	0	3	25	57	18	25	8900 ^b	17.6	21	1.02
BzMgCl	-78	24	56	25	32	43	6600 ^c	1.90	37	—
	0	1.5	25	25	33	42	10500 ^c	8.27	24	—

^a MMA 10 mmol, initiator 1.0 mmol, toluene 10 ml.

^b Determined by VPO.

^c Determined by GPC.

^d Contains THF-insoluble polymer (60%).

^e Contains THF-insoluble polymer (67%).

^f Insoluble in usual organic solvents.

^g *p*-VBzMgCl was prepared from Mg and *p*-vinylbenzyl chloride in the presence of 1,2-dichloroethane (*p*-vinylbenzyl chloride/1,2-dichloroethane = 1.0/1.2). Grignard reagent solution thus obtained was found to contain excess MgCl₂ (MgCl₂/*p*-VBzMgCl = 0.2/1.0).

erizations of MMA with *m*- and *p*-VBz-MgCl₂ in toluene at several temperatures together with the results with BzMgCl. In all cases, the products consisted of methanol-soluble oligomer and methanol-insoluble polymer. The tacticities of the polymers obtained at -78°C were stereoblock-like. The isotacticities of the polymers were enhanced by polymerizations in the presence of excess MgCl₂ or at higher temperatures. It is well known that Grignard reagents exist in the Schlenk equilibrium;

and that RMgX species prevail at higher temperatures. Matsuzaki and his coworkers¹¹ suggest that in the polymerization of MMA with C₆H₅MgBr, the active species for iso-

tactic polymer is "C₆H₅MgBr" and that for syndiotactic rich polymer is "(C₆H₅)₂Mg." Isotactic polymerizations have never been observed with dialkylmagnesium initiators except Bz₂Mg.¹² Our results indicate that "VBz-MgCl" species is more isotactic-favoring than "VBz₂Mg" species.

Table II shows the results of polymerizations in THF at low temperatures. All the polymers and oligomers obtained were syndiotactic. The PMMA prepared with *m*-VBzMgCl showed higher syndiotacticity than that prepared with *p*-VBzMgCl. The syndiotacticity increased with a decrease in the polymerization temperature, and the polymer prepared with *m*-VBzMgCl at -110°C showed extremely high syndiotacticity (96.6% in triads) and low polydispersity ($\bar{M}_w/\bar{M}_n = 1.19$).

Table II. Polymerization of MMA with *p*- and *m*-vinylbenzylmagnesium chlorides and benzylmagnesium chloride in THF for 24 h^a

Initiator	Temp °C	MeOH-insoluble						MeOH-soluble %	CH ₂ =CH- per chain
		Yield %	Tacticity/%			$\bar{M}_n$	$\bar{M}_w/\bar{M}_n^c$		
			<i>I</i>	<i>H</i>	<i>S</i>				
<i>p</i> -VBzMgCl	−78	13	6	19	75	12000 ^b	1.91	87 ^d	1.07
<i>m</i> -VBzMgCl	−78	35	0.8	8.6	90.6	13500 ^b	1.30	65	0.95
<i>m</i> -VBzMgCl	−98	40	0.4	5.2	94.4	17300 ^b	1.20	58	1.01
<i>m</i> -VBzMgCl ^e	−110	19 ^f	0.3	3.1	96.6	14000 ^b	1.19	25 ^g	0.87
BzMgCl	−78	50	1	15	84	10500 ^c	1.37	48	—

^a MMA 10 mmol, initiator 1.0 mmol, THF 10 ml.^b Determined by VPO.^c Determined by GPC.^d Tacticity/% *I*:*H*:*S* = 6:19:75, $\bar{M}_n$ = 3500, $\bar{M}_w/\bar{M}_n$ = 1.45.^e MMA 20 mmol, THF 20 ml.^f Fractionation of the polymer by a benzene-hexane mixture (10:1) gave a more syndiotactic polymer (*I*:*H*:*S* = 0:2.4:97.6, yield 30%, $\bar{M}_n$ = 9800, $\bar{M}_w/\bar{M}_n$ = 1.17) as an insoluble fraction.^g Tacticity/% *I*:*H*:*S* = 0.2:3.2:96.6, $\bar{M}_n$ = 4000, $\bar{M}_w/\bar{M}_n$ = 1.43.

Fractionation of this polymer by a benzene-hexane mixture (10:1) gave the PMMA with triad syndiotacticity of 97.6% and $\bar{M}_w/\bar{M}_n$ of 1.17. As far as we are aware of, the fraction of syndiotactic triad of the PMMA thus obtained is the highest one reported so far. Several investigations were carried out on the preparation of highly syndiotactic PMMAs using initiators such as triphenylmethylcalcium chloride^{13,14}, bis(pentamethylenimino)magnesium¹⁵ and (C₂H₅)₃Al-TiCl₄ catalysts.^{16,17} Among these initiators the (C₂H₅)₃Al-TiCl₄ catalyst has been frequently used for preparing highly syndiotactic PMMA whose syndiotacticity is more than 90% in triad. However, the molecular weight distribution (MWD) of the polymer obtained is usually very broad. So *m*-VBzMgCl is the first example of an effective initiator for the preparation of highly syndiotactic PMMA with narrow MWD.

In the polymerizations described in Tables I and II the efficiencies of the initiators were generally less than 20%. Since a reaction of the initiator with carbonyl group of MMA hardly occurred in the polymerization

with *m*-VBzMgCl in THF at −78°C as will be described later, most of the VBzMgCl used should remain unreacted in the reaction mixture, and a part of them would coordinate with the propagating chain ends affecting stereoregulation. This may be one of the reasons why tacticity of the polymer greatly depends on the structure of a Grignard reagent.

2. Structural Analysis of PMMA Prepared with VBzMgCl as a Macromer

The polymer prepared with VBzMgCl should contain one vinylbenzyl group at the beginning of the chain (α -end). All the PMMAs obtained with VBzMgCl_s showed the characteristic ¹H NMR signals of vinylbenzyl protons. As a typical example, the ¹H NMR spectrum of PMMA prepared with *p*-VBzMgCl in toluene at −78°C is shown in Figure 1. Intensity measurements of vinyl proton signals indicated that most of the PMMAs polymerized with VBzMgCl at −78°C contained about one vinylbenzyl group at the α -end (Tables I and II).

In the polymerization of MMA with C₄H₉MgCl, the initiator reacts with the

Figure 1. ^1H NMR spectrum of PMMA prepared with *p*-VBzMgCl in toluene at -78°C (CDCl_3 , 55°C , 100 MHz).

Figure 2. ^1H NMR spectra of $\text{P}(\text{MMA}-d_8)$ prepared with *m*-VBzMgCl in THF at -78°C (nitrobenzene- d_5 , 110°C , 100 MHz).

carbonyl group of MMA and the resulting butyl isopropenyl ketone copolymerizes with MMA monomer.⁹ If this type of reaction occurs in the polymerization with VBzMgCl,

some of the polymer molecules should have more than one vinylbenzyl group and thus not usable as a macromer. In order to clarify the problem more precisely, $\text{MMA}-d_8$ was po-

Table III. Numbers of initiator fragments per molecule of P(MMA-*d*₈) prepared with *m*-VBzMgCl in THF at -78°C for 24 h^a

	Yield	$\bar{M}_n^b$	Amount mol/mol					ω -end ^c methine
	%		CH ₂ =	-CH=	Phenyl	Benzyl	Ketone benzyl	
Polymer	44.4	18500	1.01	1.01	1.02	1.01	0.00	0.38
Oligomer	44.5	5200	1.06	1.05	1.06	1.03	0.04	0.29

^a MMA-*d*₈ 10.0 mmol, *m*-VBzMgCl 1.0 mmol, THF 9.0 ml.^b Determined by VPO.^c These values indicate that 62% and 71% of the polymer and oligomer molecules, respectively, have the end groups other than methine proton at their ω -ends as in the polymerization with *n*-butylmagnesium chloride.⁹ Further investigation is now under way to clarify this problem.

lymerized with *m*-VBzMgCl in THF at -78°C and the resultant polymer and oligomer were analyzed for the initiator fragments by ¹H NMR spectroscopy. The spectra of the polymer and oligomer are shown in Figure 2. The resonances due to benzyl methylene, vinyl methylene, vinyl methine and phenyl protons of the initiator fragment appear clearly at 2.28–2.66, 5.05–5.71, 6.44–6.78, and 6.84–7.21 ppm, respectively. The signal due to the methine proton attached to the terminal MMA unit (2.45 ppm) overlapped with the quartet of the benzyl methylene protons. In the spectrum of the methanol-soluble oligomer, a very weak signal due to the benzyl methylene protons of *m*-vinylbenzyl isopropenyl ketone unit was observed at 3.08 ppm. The ketone should be formed through the carbonyl attack of the initiator onto the monomer and incorporated into the oligomer chain. Small shoulders on the upfield side of the signals due to the vinyl methylene and vinyl methine protons of the initiator fragment are attributable to those of the ketone unit, respectively. No signals due to the ketone unit could be observed in the spectrum of methanol-insoluble polymer. Absolute signal intensities of the initiator fragment were measured by the method reported previously^{3–9} and the number of fragments per polymer or oligomer chain

was determined as shown in Table III. The polymer and oligomer molecules contained one vinylbenzyl group at the α -end, indicating that the PMMA can be used as a macromer.

As shown in Tables I and II, all the PMMAs prepared by VBzMgCls at -78 – -110°C contain about one vinylbenzyl group in a chain; but those obtained above 0°C contained more than one vinylbenzyl group in a chain. This indicates that the reaction of the initiator with the carbonyl group of MMA occurred at higher temperatures and the resultant isopropenyl ketone copolymerized in the polymer chain. The incorporation of vinylbenzyl isopropenyl ketone units in the polymer chain caused crosslinking at higher temperatures to form the polymer insoluble in usual organic solvents (Table I).

In the polymerization of MMA with C₄H₉MgCl in toluene at -78°C , a fair amount of the polymer or oligomer molecules contained one butyl isopropenyl ketone unit at their terminating chain ends (ω -ends).⁹ As mentioned above, this is not the case in the polymerization with *m*-VBzMgCl and only a few percent of oligomer molecules contained one ketone unit in a chain. The difference in the amount of the ketone incorporated in the polymer or oligomer chain can be related to the selectivity of the 1,2- and 1,4-additions of the Grignard reagents onto α,β -unsaturated

Table IV. Polymerization and copolymerization of PMMA-macromer with AIBN in toluene at 60°C for 24 h^a

Macromer ^b		Styrene mmol	AIBN mmol	MeOH-insoluble			MeOH-soluble %
g	mmol			Yield %	$\bar{M}_n^c$	$\bar{M}_w/\bar{M}_n^d$	
0.55	0.16	0.0	0.004	50	101200	1.72	50
0.67	0.20	2.0	0.022	42	30500	3.41	40

^a Toluene 2 ml.

^b Prepared with *p*-VBzMgCl in THF at -78°C. $\bar{M}_n = 3500$, $\bar{M}_w/\bar{M}_n = 1.45$, *I*:*H*:*S* = 6:19:75 (*cf.* Table II).

^c Determined by VPO.

^d Determined by GPC.

carbonyl compounds. It has been found that benzylmagnesium chloride or bromide reacts with conjugated aldehydes preferentially in the 1,4-manner.¹⁸ Therefore, it is reasonable that VBzMgCls have the same reaction tendency as benzylmagnesium chloride or bromide.

From the results mentioned above, it is concluded that polymerizations with VBzMgCl at low temperatures provide a convenient and useful method for preparing PMMA macromers with various tacticities.

3. Polymerization and Copolymerization of PMMA Macromer

The syndiotactic and methanol-soluble PMMA macromer prepared with *p*-VBzMgCl in THF at -78°C (*cf.* Table II) was polymerized in toluene at 60°C using AIBN as an initiator (Table IV). The yield of poly(PMMA macromer) thus obtained was 50%, and the GPC analysis showed that the polymacromer contained no starting macromer (Figure 3). The UV spectrum of the polymacromer did not show the characteristic absorption of vinylbenzyl group ($\lambda_{\max} = 254.8$ nm, $\epsilon_{\max} = 12000$) which appeared in the spectrum of the starting macromer. The degree of polymerization determined by VPO was 29 and the apparent value of $\bar{M}_w/\bar{M}_n$ determined by GPC was 1.72. The ¹H NMR spectrum and GPC pattern of the methanol-soluble fraction were

Figure 3. GPC curves of poly(PMMA macromer) (A) and of the starting PMMA macromer (B). Detector for GPC, RI.

Figure 4. GPC curves of polystyrene-graft-PMMA (A) and of the starting PMMA macromer (B).

very similar to those of the starting macromer.

Copolymerization of PMMA macromer with styrene was carried out with AIBN at 60°C in toluene (Table IV). The GPC curve in Figure 4 indicates that the methanol-insoluble copolymer did not contain the starting macromer. Copolymerization between PMMA macromer and styrene actually took place to form a polystyrene-*graft*-PMMA, since the GPC chromatograms obtained using RI and UV detectors were very similar with each other. The mole ratio of MMA units to styrene units in the graft copolymer was found to be 74:26 by ^1H NMR spectroscopy; thus the copolymer had $\overline{\text{DP}}$ of 80 and 6.7 graft chains per main chain.

4. Polymerization of Styrene with VBz-MgCl

Polymerizations of styrene were carried out in toluene or THF using BzMgCl, *p*-VBzMgCl and *m*-VBzMgCl as initiators in the presence or absence of HMPA. The results are shown in Table V. Among the initiators used, only *p*-VBzMgCl polymerized styrene in THF at 0°C, but did not at -78°C. Grignard reagents including BzMgCl are known to be unable to initiate the polymerization of styrene in toluene or THF.¹⁹ Substitution of vinyl group at the *p*-position of a phenyl ring may stabilize the benzyl anion owing to the delocalization of electrons and favor the ionic dissociation of the C-Mg bond in *p*-VBzMgCl, resulting in an increase in the nucleophilicity of this initiator. This effect seems to be small in the case of *m*-VBzMgCl, which does not initiate the polymerization of styrene. The polystyrene prepared with *p*-VBzMgCl showed the NMR signals of vinyl methylene protons at 5.10 and 5.58 ppm and can be used as an α -(*p*-vinylbenzyl)polystyrene macromer.

Tomoi *et al.*¹ reported that BzMgCl polymerized vinyl monomers such as styrene and α -methylstyrene in the presence of mono- or didentate phosphoryl compounds with dimethylamino substituents, and that the mix-

Table V. Polymerization of styrene with *p*- and *m*-vinylbenzylmagnesium chlorides and benzylmagnesium chloride for 24 h^a

Initiator	Solvent	Temp		Yield	$\bar{M}_n^b$	$\bar{M}_w/\bar{M}_n^b$
		°C	%			
BzMgCl	THF	0	0	—	—	—
<i>p</i> -VBzMgCl ^c	THF	0	81	4800	2.46	—
<i>p</i> -VBzMgCl	THF	-78	0	—	—	—
<i>p</i> -VBzMgCl	Toluene	0	0	—	—	—
<i>p</i> -VBzMgCl	HMPA/ toluene ^d	-78	99	10600	2.90	—
<i>m</i> -VBzMgCl	THF	0	Trace	—	—	—

^a Styrene 10 mmol, initiator 1.0 mmol, solvent 10 ml.

^b Determined by GPC.

^c *p*-VBzMgCl 0.50 mmol.

^d HMPA, hexamethylphosphoramide; [HMPA]/[*p*-VBzMgCl]=2.0 (mol/mol).

ture of *m*- and *p*-VBzMgCls gave highly branched polystyrene ($\bar{M}_w/\bar{M}_n=11.6$) in the polymerization in toluene at 0°C in the presence of HMPA. We found that *p*-VBz-MgCl polymerized styrene to a high molecular weight polymer in the presence of HMPA in toluene even at -78°C (Table V). The reaction mixture showed the deep red color of benzyl anions. The molecular weight distribution of the polymers were broader than that of polystyrene prepared with *p*-VBzMgCl in THF at 0°C. A small amount of unreacted *p*-VBzMgCl was copolymerized into the polystyrene chain and the resulting pendant benzylmagnesium chloride group polymerized styrene to form polystyrene-*graft*-polystyrene, a branched polystyrene.

5. Spontaneous Polymerization of *p*- and *m*-VBzMgCls

VBzMgCls were stable in diethyl ether at room temperature but self-polymerized when the solvent was changed from diethyl ether to THF. When the ether solution of *p*-VBzMgCl evacuated at 25°C for 1 h, a white powdery solid was obtained. Analysis of the product indicated that the solid was the Grignard reagent complexed with two moles of diethyl

Table VI. Polymerization of *p*- and *m*-vinylbenzylmagnesium chlorides^a

Monomer	Solvent	Temp	Time	Yield	$\bar{M}_n^b$	$\bar{M}_w/\bar{M}_n^b$
		°C	day	%		
<i>p</i> -VBzMgCl	Et ₂ O	0	7	0	—	—
	THF	0	3	2.5	7800	3.3
	THF	60	1	11 ^c	—	—
	HMPA/toluene ^d	0	3	78	4900	3.7
<i>m</i> -VBzMgCl	THF	0	3	11	3300	1.8
	THF	60	1	33 ^c	—	—
	Toluene	0	3	0	—	—

^a [Monomer] = 1.0 mol l⁻¹.

^b Determined by GPC.

^c Insoluble in usual organic solvents.

^d HMPA, hexamethylphosphoramide; [HMPA]/[*p*-VBzMgCl] = 2.0 (mol/mol).

ether. Further evacuation at 25°C for 2 h gave the complex with 1 mol of diethyl ether as a glassy, yellow solid. When THF was added to this solid at 0°C, a yellow solution was formed and the polymerization of *p*-VBzMgCl occurred slowly with precipitation of a white solid polymer. The color of the supernatant liquid turned deep green during the polymerization. The results of polymerization are shown in Table VI. The rate of polymerization was low at 0°C. At 60°C the rate became higher but the polymer obtained was not solu-

ble in usual organic solvents.

The polymer prepared at 0°C in THF and precipitated in a large amount of methanol showed the ¹H NMR spectrum very similar to that of poly(*p*-methylstyrene) prepared with C₄H₉Li in THF at -78°C as shown in Figure 5. This indicates that the polymerization of *p*-VBzMgCl proceeded through the vinyl double bonds. The polymer molecule was found to contain 1.1 vinyl double bond at the α-end. In this polymerization, the monomer functioned also as an initiator.

In the presence of HMPA, *p*-VBzMgCl polymerized even in toluene at 0°C in good yield. The color of the reaction mixture was deep red owing to the existence of benzyl anions. The ¹H NMR spectrum of the polymer differed from that of the polymer prepared in

THF in the absence of HMPA (Figure 5). The broad signal at 2.2—2.4 ppm was assigned to the benzyl methylene protons of phenylene-trimethylenephénylene group. The assignment was done by comparing the chemical shift with that of 1,3-diphenylpropane. In the

presence of HMPA, the reactivity of the pendant benzylmagnesium chloride group was enhanced enough to polymerize *p*-VBz-

MgCl, resulting in the formation of a highly branched polymer like the following structure.

Figure 5. ^1H NMR spectra of CH_3OH -quenched poly(*p*-VBzMgCl)s prepared in THF at 0°C (A) and in toluene at 0°C in the presence of HMPA (B), and of poly(*p*-methylstyrene) prepared in THF at -78°C with $\text{C}_4\text{H}_9\text{Li}$ (C) (nitrobenzene- d_5 , 120°C , 100 MHz).

Table VII. ^{13}C NMR chemical shifts (ppm) of *p*- and *m*-vinylbenzylmagnesium chlorides in THF at 27°C

	$\text{CH}_2=$	$=\text{CH}-$
<i>p</i> -VBzMgCl	105.59	138.95
<i>m</i> -VBzMgCl	111.00	140.05

m-VBzMgCl was more reactive than *p*-VBzMgCl as shown in Table VI. Vinyl methylene and methine carbons of *m*-VBzMgCl resonated at a lower magnetic field than those

of *p*-VBzMgCl (Table VII), indicating a lower π -electron density on the vinyl group of the *m*-isomer than that of the *p*-isomer. The results clearly indicate that the polymerization of VBzMgCl proceeds through an anionic mechanism. The polymer of *m*-VBzMgCl was found to contain a large amount of phenylenetrimethylene structure even when the polymerization was carried out in THF at 0°C in the absence of HMPA. The incorporation of phenylenetrimethylene group may be due to the higher steric hindrance of styryl propagating species of *m*-isomer than those of *p*-isomer.

In conclusion, *m*- and *p*-VBzMgCl's self-polymerized to form highly reactive poly-(Grignard reagent)s. Application of these reactive polymers to practical uses is now under investigation.

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