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Preparation of PMMA macromers by o-vinylbenzylmagnesium chloride and their polymerization

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Summary

Polymerization of MMA with o-vinylbenzylmagnesium chloride was examined in toluene and in tetrahydrofuran (THF) at various temperatures. The polymer formed in toluene at -78°C was highly isotactic (mm=94%) and containing one vinylbenzyl group at the α-end of the chain, although the methanol-soluble fraction concomitantly formed in an appreciable amount was less isotactic. The PMMAs formed in THF at -78 and -98°C were mostly methanol-soluble and highly syndiotactic (rr=88% at -78°C and 96% at -98°C), and also contained one vinylbenzyl group. The methanol-soluble, isotactic and syndiotactic PMMA macromers were polymerized or copolymerized with styrene by AIBN in toluene at 60°C. The isotactic macromer exhibited slightly higher reactivity than the syndiotactic one.

Introduction

Many papers have been published on the polymerizations of vinyl monomers with Grignard reagents. However, very few were reported on the polymerization with the Grignard reagents containing vinyl group (1-3). Tomoi et al. (1) synthesized a highly branched polystyrene using a mixture of m- and p-vinylbenzylmagnesium chlorides (VBzMgCl) as an initiator. Asami and his coworkers (2) attempted to prepare the PMMA macromer with p-VBzMgCl, but they found the resulting polymer to contain much more than one vinylbenzyl group per polymer chain. In our previous work (3), MMA and styrene were polymerized to the macromers with p- or m-VBzMgCl, and the polymer molecules formed at low temperatures were found to contain one vinylbenzyl group at the beginning of the chain (α-end).

In this work, MMA was polymerized with o-VBzMgCl to PMMA macromers with a variety of tacticities. The polymers prepared at -78°C were found to contain one vinylbenzyl group at the α-end. The resulting PMMA macromers were radically polymerized and copolymerized with styrene to a comblike polymer and a graft copolymer, respectively.

Experimentals

o-VBzMgCl was prepared from o-vinylbenzyl chloride and magnesium in diethyl ether. o-Vinylbenzyl chloride was prepared from o-methoxymethylstyrene according to the procedure reported by Monteard et al. (4). Polymerization procedure and purification of MMA and solvents were the same as those reported previously (3).

^{1}H NMR spectra of the polymers were recorded on a JNM-FX100 or a JNM-MH-100 spectrometer in $CDCl_3$ at 55°C. GPC chromatogram was obtained with a JASCO FLC-A10 chromatograph equipped with Shodex GPC column A-80M (50cm 2) using THF as an eluent. The chromatogram was calibrated against standard polystyrene samples. The number average molecular weight of polymer was also determined in toluene at 60°C with a Hitach 117 vapor pressure osmometer.

Results and Discussion

Polymerization of MMA with o-Vinylbenzylmagnesium Chloride

MMA was polymerized by o-VBzMgCl in toluene and in tetrahydrofuran (THF) at various temperatures. The results are summarized in Table 1. Most of the reaction products were composed of methanol-insoluble polymer and methanol-soluble oligomer. The tacticities and molecular weights of the oligomers distinctively lower than those of the polymers (Table 1), particularly in the polymerization in toluene, indicating the coexistence of two different propagating species in the polymerization.

Table 1 Polymerization of MMA with o-Vinylbenzylmagnesium Chloride[a]

Solvent	Temp. (°C)	Time (hr)	Fraction	Yield (%)	Mn[b]	Mw[c]/Mn	Tacticity(%)			f[d]
							mm	mr	rr	
Toluene	0	3	MeOH-insol.	24.1	11200	3.05	61	17	23	0.92
			MeOH-sol.	32.8	2400	1.34	49	28	23	1.04
Toluene	-78	24	MeOH-insol.	35.1	14500	2.10	94	4	2	0.95
			MeOH-sol.	37.1	2280	1.38	64	22	14	1.00
Toluene	-89	90	MeOH-insol.	41.3	16400	1.77	95	5	2	1.19
			MeOH-sol.	21.1	2540	1.33	55	24	21	1.10
THF	0	3	MeOH-insol.	10.2	8800	1.28	3	18	79	0.94
			MeOH-sol.	70.5	2840	1.60	3	20	77	1.08
THF	-78	24	MeOH-insol.	0.9	9780	3.20	—	—	—	—
			MeOH-sol.	86.0	2440	1.51	0	12	88	1.09
THF	-98	48	MeOH-insol.	6.0	9930	1.12	1	4	95	0.93
			MeOH-sol.	90.6	4360	1.37	0	5	95	1.15

[a] MMA 40mmol, initiator 4.0mmol, solvent 40ml.

[b] Determined by VPO. [c] Determined by GPC.

[d] Number of vinylbenzyl group per chain determined by ^{1}H NMR spectroscopy.

The polymers prepared in toluene at -78 and -89°C were highly isotactic and isotacticity decreased at 0°C. It is well known that Grignard reagent exists in the Schlenk equilibrium. Matsuzaki et al. (5) suggested that in the polymerization of MMA with C_6H_5MgBr in toluene active species responsible for the formation of the isotactic polymer were "C_6H_5MgBr" itself and those for the formation of the syndiotactic polymer were "$(C_6H_5)_2Mg$". Isotactic polymerizations have never been observed with dialkylmagnesium initiators (6) except dibenzylmagnesium (7). Because RMgX species prevails at higher temperatures (8), the isotacticity of the polymer prepared with Grignard reagent is expected to increase with an increase in the polymerization temperature. This is the case for the polymerization of MMA with m- or p-VBzMgCl (3). In contrast to these observations, the o-VBzMgCl behaves differently from m- and p-VBzMgCl's in the polymerization of MMA in toluene as described above (Table 1). The difference may be due to the structural and electronic effects of vinyl group at the ortho position to benzylic carbanion center on the polymerization reaction and the Schlenk equilibrium.

$$2RMgX \rightleftharpoons R_2Mg + MgX_2$$

In the polymerization of MMA with $n\text{-}C_4H_9MgCl$, the initiator reacts with the 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, the resulting PMMA is not suitable for a macromer. The oligomer formed in the polymerization in THF with m-VBzMgCl was found to contain a small amount of m-vinylbenzyl isopropenyl ketone units, which was evidenced by the existence of shouldered ^1H NMR signals at the vinyl methylene signals due to m-vinylbenzyl group at the α-end (3). The numbers of vinyl group in the PMMAs prepared with o-VBzMgCl shown in Table 1 were mostly in the range from 0.9 to 1.1. Whether or not the positive deviation from unity means the existence of the vinylbenzyl isopropenyl ketone unit was checked by close inspection of vinyl proton region in the spectra. Figure 1(A) illustrates the ^1H NMR spectra of the oligomer prepared in toluene at -78°C. An expanded resonance in the figure, due to the vinyl methylene protons, shows no shoulder peaks. For the detailed analysis of the polymer structure, perdeuterated MMA was also polymerized with o-VBzMgCl in toluene at -78°C to suppress the signals due to monomeric units. The polymer also showed the same type of vinyl methylene proton signals as seen in the spectrum of the oligomer. The results indicate that the PMMAs prepared with o-VBzMgCl contain one vinylbenzyl group at the α-end and no other vinylbenzyl group in the molecules. Consequently these PMMAs are

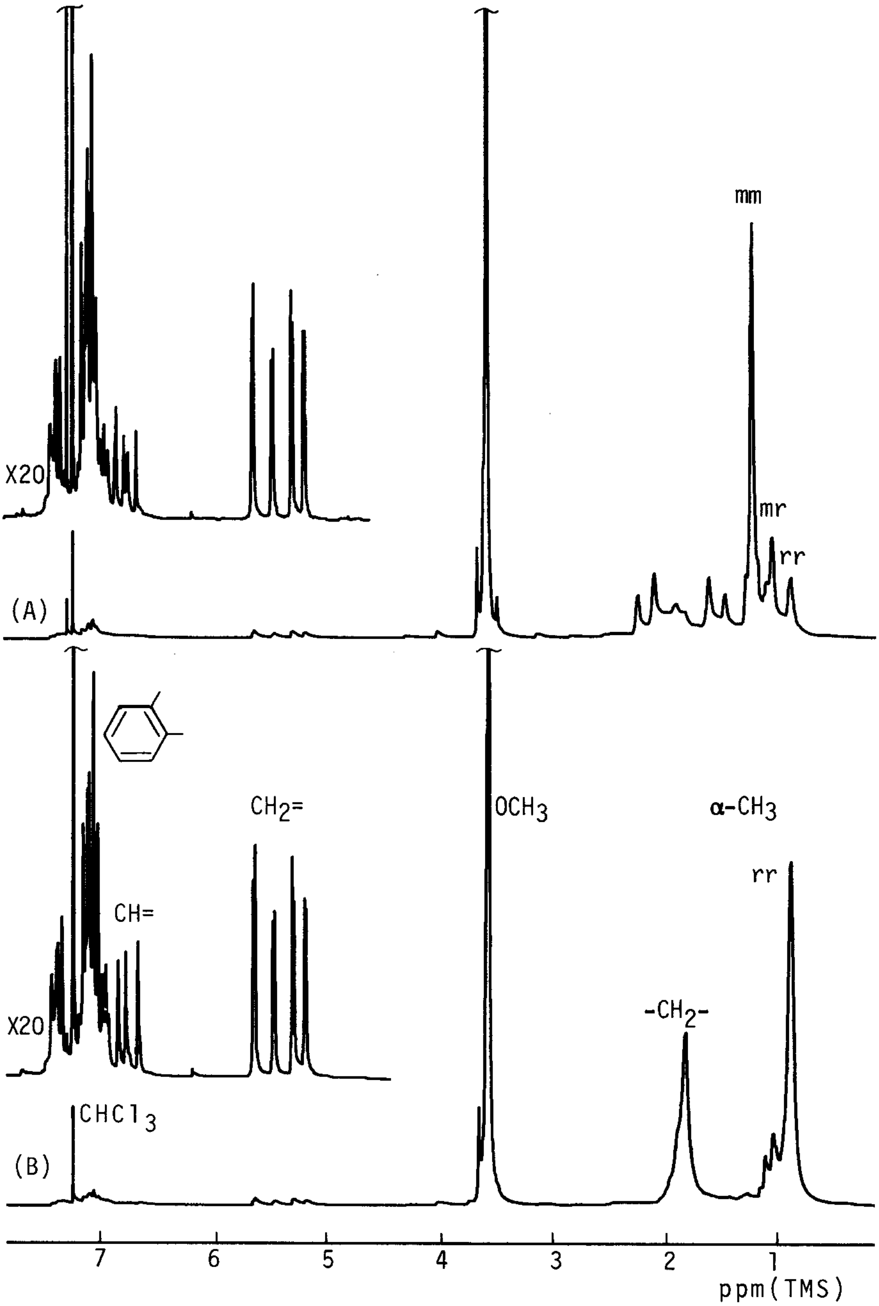

Figure 1 ^1H NMR spectra of isotactic (A) and syndiotactic (B) PMMA oligomers prepared with o-vinylbenzylmagnesium chloride in toluene and in THF, respectively, at -78°C.

usable as a macromer. The attack of the initiator on the carbonyl group of MMA scarcely occurred in the polymerization with o-VBzMgCl, probably owing to steric hindrance around the benzylic carbanion in o-VBzMgCl.

PMMAs prepared in THF at -78 and -98°C were highly syndiotactic and fairly narrow molecular weight distribution as shown in Table 1, and most of the polymers were methanol-soluble. Vinyl methylene proton signals of the methanol-soluble polymer prepared at -78°C (Figure 1B) indicate the existence of single type of vinyl group in the chain as observed for the PMMA prepared in toluene. It is worth noting that a single initiator, o-VBzMgCl, can afford both highly isotactic (mm=94%) and syndiotactic (rr=96%) PMMAs by changing the polymerization medium. So o-VBzMgCl is the most suitable initiator for preparing PMMA macromers of a variety of tacticities.

The rate of polymerization was apparently larger with o-VBzMgCl than with m- or p-VBzMgCl. This may be partly due to the higher initiator efficiency (Table 2) of o-VBzMgCl and partly due to the higher ionic character of $-CH_2-Mg$ bond in o-VBzMgCl. The latter is evidenced by the fact that in the methylene carbon ($-CH_2-Mg$) of o-VBzMgCl resonates at higher magnetic field (22.46 ppm) than those of m-VBzMgCl (23.75 ppm) and p-VBzMgCl (24.99 ppm) in the ^{13}C NMR spectra measured in diethyl ether at 27°C.

Table 2 Initiator Efficiencies[a] of Vinylbenzylmagnesium Chlorides in the Polymerizations[b] of MMA in Toluene and in THF at -78°C for 24hr

Solvent	Initiator Efficiency		
	o-VBzMgCl	m-VBzMgCl	p-VBzMgCl
Toluene	0.19	0.11	—
THF	0.35	—	0.26

[a] Calculated from the yields and Mn's of the polymer and oligomer.

[b] MMA 10mmol, initiator 1.0mmol, solvent 10ml.

Radical polymerization and Copolymerization of the PMMA Macromers

The macromers used in the radical polymerization are the methanol-soluble isotactic and syndiotactic PMMAs of similar molecular weights prepared with o-VBzMgCl at -78°C in toluene and in THF, respectively, whose ^{1}H NMR spectra are shown in Figure 1. These were polymerized or copolymerized with styrene in toluene at 60°C for 24hr using AIBN as an initiator. The results are shown in Table 3. The resulting polymers or copolymers were extracted with boiling methanol for 2hr to remove the starting macromers. The GPC analysis showed that the products did not contain the starting macromers. The yields of the poly(PMMA macromer)s were

Table 3 Polymerization and Copolymerization of PMMA Macromer with AIBN in toluene at 60°C for 24hr[a]

PMMA macromer						Styrene	Polymer		
(g)	(mmol)	Tacticity(%)			Mn	(mmol)	Yield (%)	Mn^b	Macromer content(%)[c]
		mm	mr	rr					
0.23[d]	0.10	64	22	14	2280	——	11.8	14100	100
0.24[e]	0.10	1	12	87	2440	——	9.9	14000	100
0.23[d]	0.10	64	22	14	2280	1.00	30.6	36100	6.2
0.24[e]	0.10	1	12	87	2440		32.5	20900	5.3

[a] $[\text{Macromer}]_0/[\text{AIBN}]_0$=40mol/mol and $[\text{Macromer}]_0$/toluene=0.1 mol/l for polymerization, $([\text{Macromer}]_0+[\text{Styrene}]_0)/[\text{AIBN}]_0$=100 mol/mol and $([\text{Macromer}]_0+[\text{Styrene}]_0)$/toluene=1.0 mol/l for copolymerization.

[b] Determined by VPO.

[c] 100×[PMMA macromer unit]/([PMMA macromer unit]+[styrene unit]).

[d,e] Methanol-soluble fractions of PMMAs prepared with o-VBzMgCl in toluene and in THF, respectively, at -78°C.

lower than those of the polymacromers prepared with m- and p-VBzMgCl (3), probably owing to the steric hindrance at the position of vinyl group. The isotactic macromer gave polymacromer in slightly higher yield than the syndiotactic one. In the copolymerization with styrene, the isotactic macromer showed higher extent of incorporation into the copolymer than the syndiotactic one, also indicating higher reactivity of the isotactic macromer. The measurements of ^{13}C and ^1H NMR spin-lattice relaxation times of polymethacrylates indicate that the isotactic polymer chain has a greater segmental mobility than the syndiotactic chain (10). The higher mobility of the isotactic chain is one of the causes of the higher reactivity of the isotactic PMMA macromer. The same trend was observed in the polymerizations of isotactic and syndiotactic PMMA macromers carrying p-vinylbenzyl group at terminal ends prepared by end-capping method (11).

The GPC chromatograms of the copolymers obtained using RI and UV detectors were very similar in the pattern with each other (Figure 2), showing that the copolymers were actually the (polystyrene-graft-PMMA)s. From number average molecular weight determination by VPO and compositional analysis by ^1H NMR, the graft copolymers carrying isotactic and syndiotactic PMMA chains were found to have the degrees of polymerization of 92 and 151 for backbone chain, and 4.8 and 9.3 graft chains per backbone chain, respectively.

The properties of these comblike polymers and graft copolymers with the stereoregular PMMA side chains are our next interest.

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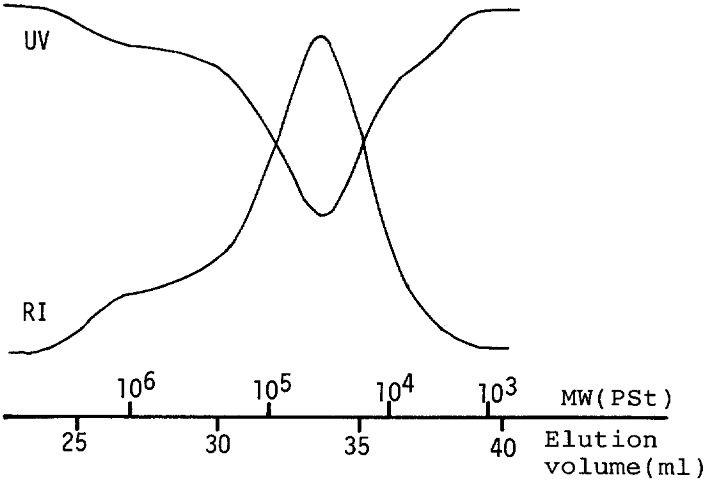

Figure 2 GPC curves of copolymer of styrene and syndiotactic PMMA macromer

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