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An Attempt at the Preparation of Macrocyclic Polymer

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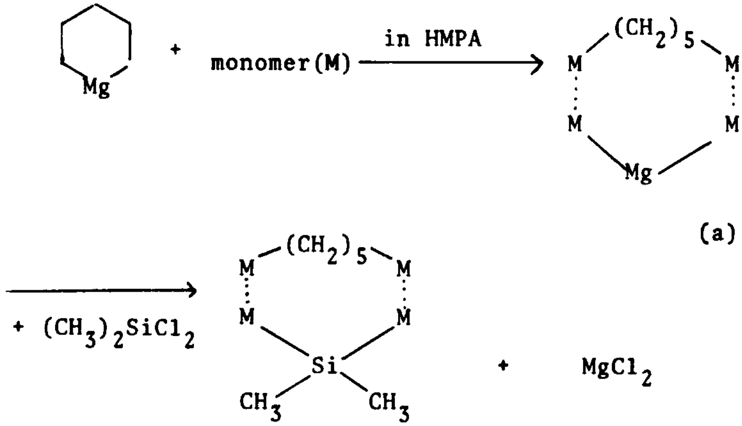
ABSTRACT

Syntheses of cyclic oligomer and polymer were attempted with magnesiacyclohexane as the initiator in HMPA. The oligomer of α-methylstyrene, initiated by magnesiacyclohexane, was treated with dimethyldichlorosilane in order to obtain a stable cyclic oligomer. The products were investigated by GPC, IR, NMR, and elemental analysis. It was found that magnesiacyclohexane could not be activated enough by HMPA, that the magnesium-carbon bond was not stable in HMPA, and that the chain transfer reaction might occur repeatedly during the polymerization. Consequently, the yield of cyclic oligomer was so low that cyclic compounds could not be discriminated from the linear oligomer.

INTRODUCTION

Recently the application of hexamethylphosphortriamide (HMPA) to organic reactions has been extensively investigated, and characteristic features of this compound concerning necleophilic reactions have been demonstrated [1]. Studies on anionic polymerizations of styrene derivatives with organomagnesium compounds using HMPA as an additive or a solvent have been also reported by Sigwalt [2] and Tomoi et al [3]. It has been proposed on the basis of spectroscopic studies that the polymerizations of styrene and α-methylstyrene are essentially of the living type.

The present study was aimed at synthesizing cyclic oligomers and polymers by using the living nature of the polymerization with an organocyclic magnesium compound as the initiator in HMPA. Until now there have been little knowledge on the properties of the cyclic polymers in bulk as well as in solution, though the "cyclic structure" of the polymer appears to be fantastic. In order to obtain useful polymers, the reactive magnesium-carbon bonds present in the macrocycle should be stabilized after the propagation reaction. For this purpose, it was desired to substitute the dimethylsilyl group for the divalent magnesium, a member of the cyclic polymer chain, without destroying the cyclic structure of the polymer. These reactions may be described as



(1)

In this paper we refer to some details on the synthesis of cyclic polymers of styrene and α-methylstyrene and the stabilization of the active polymers obtained. The reaction mechanism is also discussed.

EXPERIMENTAL

Materials

α-Methylstyrene was dried over calcium hydride and purified by distillation.

HMPA, purchased from Japan Oilseal Co., was dried over calcium hydride. It was fractionated twice on a spinning-band column at 98 to 99°C/6 Torr.

Tetrahydrofuran (THF) was refluxed and distilled over fresh sodium wire and was redistilled over $LiAlH_4$.

Dimethyldichlorosilane was distilled twice under nitrogen atmosphere. All the monomers and reagents used were sealed into small ampules individually via the trap-to-trap method in a high vacuum system. Dibenzylmagnesium and magnesiacyclohexane were prepared within a high vacuum system according to the procedures described by Schlenk [4] and Holtkamp [5], respectively.

Oligomerization

The reaction was carried out under vacuum ($< 10^{-5}$ Torr) in a sealed glass reactor to minimize contamination by moisture and oxygen. All the ampules, including the monomers and reagents, were connected separately to a reactor via break-seal. The solvent, initiator, and monomer were transferred to the reactor in this order by smashing the break-seal with a magnetic rod.

After a desired time of oligomerization, the reaction mixture was poured into a large amount of water. The aqueous mixture was extracted with ether repeatedly and the organic layer was dried over Na_2SO_4. After removing the solvent, the oily products were recovered.

Polymerization

The reaction was carried out similarly to the oligomerization. The reaction mixture was poured into a large volume of methanol containing HCl to isolate the polymer, which was reprecipitated twice with benzene-methanol and then was freeze-dried.

Substitution Reaction of Dimethylsilyl Group for Magnesium Bonded in Cyclic Polymer-Chain

The stabilization was carried out under vacuum in a sealed glass tube with connecting chambers of the reagents via break-seals. Initially, α-methylstyrene was oligomerized for an adequate time and the resulting mixture was divided into two ampules. The oligomer solution in one ampule was terminated with methanol. To another oligomer solution, a THF solution of dimethyldichlorosilane was added dropwise under vacuum through a break-seal at 0°C. The mixture was stirred for 48 hr at 30°C and then refluxed for 1 hr in order to complete the reaction. The products from the two ampules were treated in a similar way to the case of oligomers.

RESULTS AND DISCUSSION

The oligomerization of α-methylstyrene in HMPA was carried out with magnesiacyclohexane (MCH) as a cyclic initiator at room temperature. When the monomer was added to a HMPA solution of MCH, the color of the solution immediately turned from yellow to red and a deep coloration was unchanged for a long duration of the reaction. This reflects the formation of α-methylstyryl anion, which is not killed during the reaction. Table 1 shows the experimental results of the oligomerization. The molecular weight of oligomers obtained were in the range of 300 to 580 as in the anionic polymerizations with alkali metal in THF. The catalyst efficiency, (yield of polymer/mol wt of polymer/MCH) × 100, increased with increasing reaction time and in some cases exceeded 100%. This indicates that the initiation is slow as compared with the propagation, and that the transfer reaction occurs.

TABLE 1. The Oligomerization of α-Methylstyrene in HMPA with Magnesiacyclohexane (MCH)[a]

Run no.	α-Methylstyrene, (mmoles)	MCH (mmoles)	HMPA (ml)	Reaction time (hr)	M[b]	Ef[c] (%)
1	22.0	2.2	10	47	580	51
2	4.9	1.2	1	48	450	42
3	23.0	5.1	11	96	470	77
4	22.9	4.5	18	96	350	94
5	7.8	0.5	9	99	330	95
6	5.7	2.0	3	99	300	99
7	16.5	3.2	10	160	340	127
8	9.7	2.9	15	108	300	110

[a] At room temperature.
[b] Estimated from GPC.
[c] Ef = [yield of oligomer (g)/$\overline{M}$/MCH (mole)] × 100.

TABLE 2. The Polymerization of Styrene in HMPA with Oligo-α-methylstyryl anion[a]

	Oligo-α-methylstyryl anion[b]						
Run no.	MCH (mmole)	α-Methylstyrene (mmoles)	HMPA (ml)	Styrene (mmoles) (solvent)	Yield (%)	M[c] $\times 10^{-3}$	Ef[d] (%)
21	0.88	8.3	3.4	6.7 (THF)	93	8.9	20
22	0.39	1.9	4.4	2.4 (THF)	92	6.3	18
23	1.1	2.5	22	16 (HMPA)	97	13	30
24	1.9	15	21	41 (HMPA)	90	9.7	25

[a] Polymerized at room temperature for 2 to 5 hr.

[b] Magnesiacyclohexane was allowed to react with α-methylstyrene in HMPA for 50 to 100 hr at room temperature.

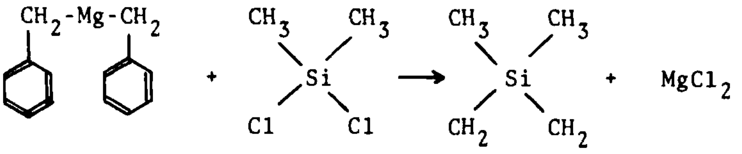
[c] Estimated from GPC.

[d] Ef = [yield of polymer (g)/$\overline{M}$/MCH (mole)] × 100.

In order to obtain high molecular weight cyclic polymers efficiently, the seeding method was employed to overcome the slow initiation. Addition of styrene monomer at room temperature to the red solution, the mixture of α-methylstyrene, HMPA, and MCH, produced the polymer at 20 to 30% catalyst efficiency of polymer formation (Table 2). The discrepancy in the efficiencies of oligomerization and polymerization is discussed later.

Various compounds (o-xylylene dibromide, dimethyldichlorosilane, sulfur chloride, thionyl chloride, etc.) were reacted with dibenzylmagnesium as a model reaction for the replacement of an inert group for magnesium bonded in the cyclic polymer chain. Of these compounds, dichlorodimethylsilane reacted with dibenzylmagnesium to give dibenzyldimethylsilane in good yield (82 to 91%) in THF, HMPA, and THF-HMPA mixture (Eq. 2). MCH was found to react with dimethyldichlorosilane to yield silacyclohexane, indicating that the cyclic structure was kept during the substitution reaction (Eq. 3).

If α-methylstyrene is incorporated into the carbon-magnesium bond and the carbanion produced has a living nature in HMPA, the cyclic oligomer can be obtained as shown in Eq. (1). For magnesium attached to the cyclic oligomer chain, the dimethylsilyl group can be substituted similarly to Reaction (3). The following experiments were carried out in order to prove the substitution reaction. The results of the reaction are given in Table 3.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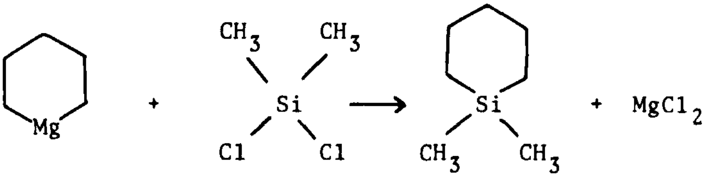

(3)

The reaction mixture, including α-methylstyrene, MCH, and HMPA, was divided into two parts (10A and 10B). They were treated with water (10A) and with dimethyldichlorosilane (10B). The two dead polymers showed gel-permeation chromatograms similar to Fig. 1. As the extention of the cyclic oligomer in the solution is expected to differ from that of the linear oligomer, this result suggests that a significant amount of the oligomer did not react with dimethyldichlorosilane. The observed silicon content of the oligomer (10B) was only 25% of the calculated one, assuming that the reaction proceeds via the mechanism of Eq. (1). This indicates that only a quarter of the oligomer can react with dimethyldichlorosilane, and the residual oligomer might have been dead before addition of dimethyldichlorosilane because the living oligomer reacts easily with dimethyldichlorosilane. These results imply that the oligomerization involves chain transfer and/or termination reactions. Hydrolysis of the cyclic oligomer containing magnesium [(a) in Eq. 1] yielded the linear oligomer (I), which has the $(CH_2)_5$ group in its chain. If the chain transfer reaction occurs, the oligomer (II), without the $(CH_2)_5$ group, may be formed. The aromatic/aliphatic hydrogen ratios of oligomer (I) and (II) are calculated by $5n/(5n + 12)$ and $5n/(5n + 2)$ respectively, where n is the number of α-methylstyrene units incorporated. The calculated carbon per hydrogen ratios for oligomers (I) and (II) were compared with the observed value. The aromatic/aliphatic hydrogen ratio and the carbon/hydrogen ratio of the oligomer measured by NMR and elemental analysis, respectively, agreed with the calculated one for oligomer (II) (Table 4). An absorption band due to the $(CH_2)_5$ group at 720-730 cm^{-1} was not observed in the IR spectrum of the oligomer. These results strongly substantiate the occurrence of chain transfer.

TABLE 3. The Reaction of Oligo-α-methylstyryl Anion with Dimethyldichlorosilane

Run no.	Oligomerization[a]			Dimethyldichro-silane (mmoles)	M[c]	Silicon content (%)
	α-Methylstyrene (mmoles)	MCH (mmole)	HMPA (ml)			
10A	4.0	0.6	7.5	-	310	-
10B[b]	7.6	1.2	14	1.1 (in 14 ml THF)	350	2.0

[a] At room temperature for 92 hr.

[b] Allowed to react at 0°C (1 hr), 30°C (48 hr), and 60 to 70°C (1 hr).

[c] Observed by vapor pressure osmometer.

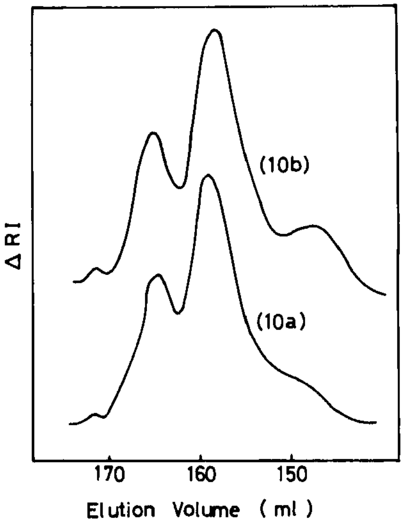


FIG. 1. Gel-permeation chromatogram of the reaction product between α-methylstyrene and magnesiacyclohexane: 10A and 10B correspond to the runs shown in Table 3. Carrier: THF, 1.0 ml/min.

In order to confirm the reaction mechanism further, the reaction mixture (run No. 8 in Table 1) was analyzed as follows. After oligomerization for 108 hr, a small amount of methanol was added to the reaction mixture through a break-seal to terminate the reaction. From the gas chromatographic analysis of the resulting solution, it was found that the quantity of n-pentane produced corresponded to about 80% of the MCH added initially. The catalyst efficiency of MCH as estimated by gas chromatography, 20%, agreed with that estimated by ([polymer yield]/[mol wt of polymer]/[MCH]) × 100 (Table 2). On the contrary, the high catalyst efficiency in the case of oligomerization of α-methylstyrene, over 100% (Table 1), indicates that the chain transfer reaction occurred repeatedly.

In conclusion, the oligomerization of α-methylstyrene by MCH in HMPA proceeds by a mechanism different from a living type as reported by the earlier investigators, and the chain transfer reaction occurs repeatedly as shown schematically in Table 5. Consequently, the synthesis of macrocyclic oligomer and polymer has not succeeded by the method described here.

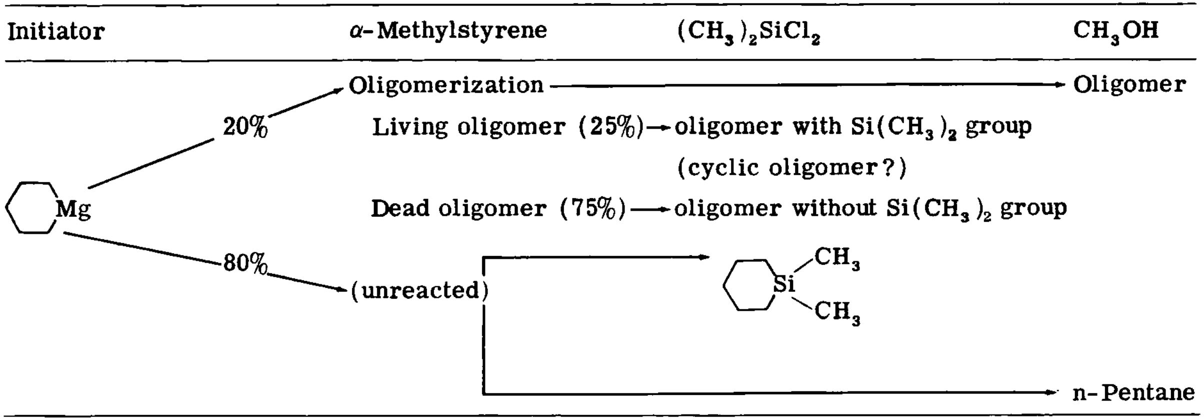
Further details of the mechanism on the oligomerization by organomagnesium compounds will be reported in the near future.

TABLE 4. The Analyses of the Oligomer

Run no.	Molecular weight of oligomer	Aromatic/aliphatic H ratio			Carbon/hydrogen ratio		
			Calc			Calc	
		Obs[a]	(I)[b]	(II)[c]	Obs[d]	(I)[b]	(II)[c]
3	470	0.89	0.59	0.91	10.26	8.63	10.13
6	300	0.82	0.46	0.86	-	-	-

[a] Observed by NMR spectra.
[b] Calculated for the oligomer with the $(CH_2)_5$ group.
[c] Calculated for the oligomer without the $(CH_2)_5$ group.
[d] Calculated from elemental analysis.

TABLE 5. The Reaction Products by the Oligomerization of α-Methylstyrene with Magnesiacyclohexane in HMPA



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