Reactivities of Grignard's Reagent/Hexamethylphosphoramide Systems as Initiators for the Polymerization of α -Methylstyrene

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ABSTRACT: The behavior of the polymerization of α -methylstyrene with the alkyl-magnesium bromide (RMgBr)/hexamethylphosphoramide (HMPA) system was found to be similar to that of the usual anionic equilibrium polymerization. The reactivities of RMgBr as initiators decreased in the order: R=benzyl > allyl > aryl $\approx$ s-alkyl > n-alkyl. This result was explained in terms of both the ease of carbanion formation from RMgBr and the activity of the anion formed. In the case of benzylmagnesium bromide/HMPA catalyst, it is suggested that the reactive species in the initiation is a complex formed by the coordination of four HMPA molecules with the magnesium ion.

KEY WORDS Anionic Polymerization / α -Methylstyrene / Grignard's Reagent / Hexamethylphosphoramide / Carbanion / Coordination /

In the previous paper,¹ it was shown that the reactivities of Grignard's reagent (RMgX) increased very much in the presence of hexamethylphosphoramide (HMPA), and hence this reagent could initiate the polymerization of styrene. A similar phenomenon was recognized in the metalation of fluorene with the diethylmagnesium/HMPA system.² In this paper the polymerization of α -methylstyrene with the RMgX/HMPA system was investigated in order to determine a relation between the reactivity of the reagent as an initiator and the structure of the alkyl group of RMgX. The relative reactivities of structurally different organo-lithium compounds as initiators for the polymerization of styrene in tetrahydrofuran were determined by Waack, *et al.*³ However, there is very little information relating to the effect of structure on the reactivity of organo-magnesium compounds. It is interesting to compare the relationship between the structures and the reactivities of organomagnesium compounds and those of organo-lithium compounds.

EXPERIMENTAL

Reagents

α -Methylstyrene (α -MeSt) was purified by con-

ventional methods, refluxed, and distilled over calcium hydride *in vacuo* just before use. HMPA was refluxed and distilled over CaH₂ *in vacuo*. The alkyl and aryl halides were purified by conventional methods and distilled over CaH₂ under a nitrogen atmosphere or *in vacuo*. The Grignard's reagents were prepared by use of diethyl ether as a solvent under a purified nitrogen atmosphere. The concentration of Grignard's reagents was determined by acid-base titration.⁴

Polymerization Procedure

The polymerization was carried out under a nitrogen atmosphere. In a 30-ml polymerization tube equipped with a self-sealing rubber cap, the monomer and a toluene solution of HMPA were charged and the mixture was brought to a polymerization temperature. The polymerization was initiated by introducing an ether solution of a catalyst with a syringe through the rubber cap. After a given time the polymerization mixture was poured into methanol. The precipitated polymer was collected by filtration, washed with methanol, and dried *in vacuo* at 40°C.

Measurements

Reduced viscosities were measured in a toluene solution at 25°C. The NMR spectra of the polymer solution in chlorobenzene were recorded

at 140°C on a JNM C-60H spectrometer. The electronic spectra of the polymerization mixture were recorded at room temperature by means of a Shimadzu UV-200 spectrophotometer, using 0.2-cm optical cells provided with a 0.18-cm spacer.

RESULTS AND DISCUSSION

Influence of Monomer Concentration and Temperature on Polymerization of α -MeSt

It is known that the solution of "living" poly- α -MeSt has a red color.⁵ In the case of each RMgX/HMPA catalyst system, the polymerization mixture also became red, except in the cases where no polymer formed. The typical spectra of the reaction solution are shown in Figure 1. The 340-nm and 346-nm peaks could be assigned to the poly(α -methylstyryl) anion from analogy with the spectra of poly(α -methylstyryllithium) in tetrahydrofuran.⁶ It has been reported that in the latter case, the wavelength of the absorption maximum is 340 nm at room temperature, but increases by up to 10 nm as the temperature decreases. Moreover, the absorption at about 480 nm increases markedly at temperatures below -70°C. These changes are usually attributed to the formation of a solvent-separated ion-pair.⁷ In the case of the RMgX/HMPA catalyst also, the 340-nm peak is shifted to 346 nm at higher HMPA concentration; moreover, the intensity of

the absorption near 480 nm increases (spectrum B). This result indicates that the solvent-separated ion-pair may be formed in this polymerization system.

Though the spectra did not change for several hours, it was found that the peaks near 340 nm disappear, and a new peak near 420 nm appears, after about 24 hr. This suggests that an irreversible termination may occur in this system, because Schmitt has recently reported that the aging of living oligomers of α -MeSt with sodium counter-ion in tetrahydrofuran results in an irreversible termination, and the spectra of the solution has a characteristic peak at 425 nm.⁸ It has been reported that such spectral changes occur in the case of the living poly- α -MeSt produced by magnesium-biphenyl in HMPA.⁹ The structure of the propagating species will be considered in a later section.

It is well-known that the anionic polymerization of α -MeSt with an organo-alkali metal compound proceeds to an equilibrium.^{10,11} It is necessary to check the equilibrium polymerization in the case of the polymerization initiated with the RMgX/HMPA system. Table I shows the results of the influence of monomer concentration and temperature on the polymerization initiated with isopropylmagnesium bromide or benzylmagnesium bromide. When the reaction time was longer than 12 hr, the yields of the polymers changed very little and hence it is thought that the polymerization no longer proceeds after this time. In the case of both catalysts, the yields and the molecular weights of polymers increased with an increase in the concentration of monomer. Moreover, when the concentration of monomer was 1.26 M, no polymer was obtained, though the reaction solution became red. This finding can be explained as the equilibrium polymerization, because the concentration of monomer in equilibrium at 20°C has been reported to be 1.69 M in the case of organosodium catalyst.¹⁰ The fact that the yields and the molecular weights of polymers increased with a decrease in the polymerization temperature is in agreement with the usual behavior of equilibrium polymerization. These results suggest that the polymerization of α -MeSt initiated with the RMgX/HMPA system occurs through an equilibrium mechanism. In the case of RMgX catalyst, however, the mono-

Figure 1. Spectra of polymerization mixtures at room temperature: $[M]_0$, 3.0 M; $[CH_2=CHCH_2-MgBr]$, 0.02 M; A (—), [HMPA], 0.1 M; B (---), [HMPA], 0.6 M.

Reactivities of Grignard's Reagent/HMPA Systems

Table I. Effect of monomer concentration and temperature on polymerization of α -MeSt^a

Initiator RMgBr	Initiator concn, 10 ² M	Monomer concn, M	Temp, °C	Time, hr	Yield, %	η_{sp}/c^b , dl/g	α^c
<i>i</i> -Pr	5.30	2.11	20	16	27	0.06	30
<i>i</i> -Pr	5.30	3.17	20	16	59(57) ^d	0.17(0.17) ^d	30
<i>i</i> -Pr	5.30	4.22	20	16	70	0.27	30
<i>i</i> -Pr	7.20	2.05	0	17	75	0.19	21
<i>i</i> -Pr	7.20	2.05	-20	17	91(91) ^d	0.24(0.24) ^d	21
PhCH ₂	1.66	1.26	20	24	0	—	2.5
PhCH ₂	1.66	2.52	20	24	43	0.24	2.5
PhCH ₂	1.66	3.79	20	24	63(64) ^d	0.47(0.46) ^d	2.5

^a Solvent, toluene.

^b Toluene solution at 25°C, $c=0.25$ g/dl.

^c $\alpha=[\text{HMPA}]/[\text{Initiator}]$.

^d The values in parentheses denote the data obtained after 12 hr.

mer concentration in equilibrium is slightly smaller than that in the case of organo-alkali metal catalyst. For example, in the former case it was about 1 M at 15°C, while it has been reported to be 1.4 M in the latter case.¹⁰ The authors cannot yet explain such a difference.

Effect of Structure on Reactivity of Grignard's Reagent

As previously described, the polymerization of α -MeSt by the RMgX/HMPA system could be

roughly treated as a living polymerization of an equilibrium type. In such a case, the molecular weight of the polymer is determined by the ratio of the rate of propagation to that of initiation. The molecular weight of the polymer produced, therefore, is a measure of the reactivity of the initiator compared with that of the propagating anionic polymer species,³ though the yield of the polymers, of course, must also be considered. Table II shows the results of polymerization by

Table II. Polymerization of α -MeSt with various Grignard's reagents^a

Initiator RMgBr	Initiator concn, 10 ² M	Monomer concn, M	Temp, °C	Time, hr	Yield, %	η_{sp}/c^b , dl/g	α^c
Et	6.35	2.72	15	16	68	0.45	32
<i>n</i> -Bu	6.35	2.72	15	16	69	0.36	32
<i>i</i> -Pr	7.20	3.10	10	18.5	50(?) ^d	2.38	11
<i>i</i> -Pr	7.20	2.72	10	18.5	72	0.20	21
<i>i</i> -Pr	7.20	2.72	15	16	62	0.15	32
Cyclohexyl	6.35	2.72	15	14	68	0.20	21
Ph	6.35	2.72	15	16	60	0.14	21
Ph	3.18	2.72	15	16	57	0.14	43
<i>p</i> -Tolyl	6.35	2.72	15	16	58	0.09	21
Allyl	3.65	2.78	15	16	0	—	1.5
Allyl	3.65	2.78	15	16	62	0.18	3
Allyl	3.65	2.78	15	16	65	0.09	6
PhCH ₂	3.65	5.35	15	16	0	—	1.5
PhCH ₂	3.65	5.35	15	16	84	0.29	2.5
PhCH ₂	3.65	2.78	15	16	65	0.09	3
PhCH ₂	3.65	2.78	15	16	63	0.06	6

^a Solvent, toluene.

^b Toluene solution at 25°C, $c=0.25$ g/dl.

^c $\alpha=[\text{HMPA}]/[\text{Initiator}]$.

^d The polymerization system had solidified.

various RMgX/HPMA systems, where the halogen component is bromide. In this Table, the parameter α is defined as the mole ratio of HMPA to RMgX. When the experimental conditions, such as monomer concentration and polymerization temperature, were fixed, the yields of polymers were found to be approximately constant, though there were slight differences, and to be independent of the structure of RMgX and the magnitude of α . On the other hand, the relative viscosities, which are related to the molecular weights of the polymers, were dependent on the structure of RMgX and the magnitude of α . In the case of the same catalyst, the molecular weights of polymers decreased with an increase in the magnitude of α . This behavior is in agreement with that in the polymerization of styrene by RMgX/HPMA systems.¹ This result suggests that the increment of the rate of initiation was larger than that of the rate of propagation, when α was increased.

The molecular weights of polymers obtained by the primary alkyl catalysts were larger than those obtained by the secondary alkyl catalysts, under slightly different conditions. This fact indicates that the latter are more reactive than the former. It was found by a similar comparison that the aryl catalysts are as reactive as the secondary alkyl catalysts. In the case of the benzyl catalyst, the molecular weight of the polymer formed was lower than for all other cases, though the polymerization was carried out at a lower HMPA concentration. Consequently, it was found that reactivities with Grignard's reagents as the initiators decrease in the order: benzyl > allyl > aryl $\approx$ s-alkyl > n-alkyl. Waack, *et al.*, showed that reactivities with organo-lithium compounds as the initiators for the polymerization of styrene in tetrahydrofuran decreased in the order: alkyl > benzyl > allyl > phenyl.³ The order of the reactivities of RMgX found here was in disagreement with the result in the case of organo-lithium compounds.

The reactivity behavior of RMgX could be accounted for by the following mechanism

where K_1 and K_2 are equilibrium constants in reactions 1 and 2, respectively, k_3 is the rate constant of reaction 3, and m represents the number of HMPA molecules interacting with species I to form species II. In the first step, the monomeric species I, in which two HMPA molecules are coordinated with the magnesium atom, is formed by the interaction between the aggregated Grignard's reagent and HMPA. The presence of species I has been suggested by the electronic and the NMR spectra of the RMgX/HPMA system.^{12,13} Moreover, the presence of a similar complex was indicated in the case of dialkyl-magnesium/HPMA system by NMR spectroscopy.^{2,13} Table II shows also that the polymerization with the benzyl- or the allyl-catalysts did not proceed in the case of $\alpha < 2$. This reveals that species I is not reactive enough to initiate the polymerization of α -MeSt. Moreover, the fact that the polymerization proceeds easily when α is slightly larger than two supports the idea that the polymerization is initiated by species II, formed by the interaction of species I with m molecules of HMPA. Such a drastic change of the catalytic activity with the magnitude of α has been found in the polymerization of styrene.¹ This phenomenon could be explained by assuming $K_1 > K_2$ and $K_1 \gg 1$ in reactions 1 and 2. In other words, the formation of species I is almost quantitative, and hence species II is scarcely formed in the case of $\alpha < 2$, as the concentration of free HMPA is almost zero. Actually, it has been indicated that K_1 are much larger than unity in the case of both benzylmagnesium chloride¹² and ethylmagnesium bromide.¹³

The effect of the structure of RMgX on reactions 1 and 2 is given below. At first it could be assumed that the extent of formation of species I is not almost influenced by the structure of RMgX, as a steric hinderance does not seem to be present in reaction 1, at least for the case of RMgX. On the other hand, the extent of formation of species II (probably an ionic species) seems to be highly dependent on

the structure of RMgX , for the ionic character of the carbon—magnesium bond increases to a great extent by the additional coordination of HMPA at reaction 2.¹² Thermodynamic stability of the carbanion is directly related to the acidity of the corresponding hydrocarbon. Relative acidities of the hydrocarbons corresponding to the catalysts used in this study are reported to be in the order: toluene (α -position) > propylene (α -position) > benzene > ethane.¹⁹ This result has been explained as mainly a resonance effect. Therefore, when RMgX is the resonance-stabilized species, such as benzylmagnesium halide or allylmagnesium halide, the equilibrium constant K_2 seems to be larger than that in the case of alkylmagnesium halide or arylmagnesium halide, in which there is no resonance stabilization.

In practice, however, the overall reactivity must also be dependent on the magnitude of the rate constant of reaction 3. The magnitude of k_3 in the case of benzyl- or allyl-species in which there is resonance stabilization is considered to be smaller than that in the case of alkyl- or aryl-species in which there is no resonance stabilization. That is to say, the dependence of the value of k_3 on the structure of RMgX should be reversed in comparison with that of K_2 . These two factors, *i.e.*, the ease of carbanion formation from RMgX and the activity of the anion formed, affect the reactivity of the RMgX /HMPA system. The experimental data could be explained by assuming that, in determining the reactivity of the RMgX /HMPA system, the former factor plays a principal role rather than the latter. The reactivity of the organo-lithium compound in tetrahydrofuran may be mainly determined by the activity of the carbanion, as the carbon—lithium bond of the organo-lithium compound is more ionic than the carbon—magnesium bond of Grignard's reagent.²⁰

Kennedy¹⁴ has reported that the reactivities with alkyl halide/diethylaluminum chloride systems as the cationic initiators for the polymerization of isobutene decrease in the order: benzyl $\approx$ *t*-alkyl > allyl $\approx$ triphenylmethyl > *s*-alkyl > *n*-alkyl. It is interesting that the order of the reactivity series in the RMgX /HMPA system is similar to that in the alkyl halide/diethylaluminum chloride system. The latter result

has also been explained in terms of both the ease of carbonium ion formation and the stability of the carbonium ion formed.

Structure of Reactive Species

In order to make clear the structure of species II, a polymerization with the benzylmagnesium bromide/HMPA system was carried out by means of a method of continuous variation. The result is shown in Figure 2. When the mole fraction

Figure 2. Polymerization of α -MeSt with the benzylmagnesium bromide/HMPA system: $[\text{M}]_0$, 3.85 M; A, $[\text{PhCH}_2\text{MgBr}] + [\text{HMPA}] = 0.084 \text{ M}$, 20°C, 16 hr; B, $[\text{PhCH}_2\text{MgBr}] + [\text{HMPA}] = 0.168 \text{ M}$, 15°C, 16 hr.

of benzylmagnesium bromide was 0.2, the lowest molecular weight polymer was obtained in the case of both A and B. This finding suggests that the species which is generated by the interaction of benzylmagnesium bromide with four HMPA molecules initiates the polymerization of α -MeSt. That is to say, the value of m in reaction 2 is two, and four molecules of HMPA coordinate with the magnesium ion. It is well-known that the coordination number of the magnesium ion is four or six in the usual case. Moreover, it has been reported that magnesium salts such as perchlorate¹⁵ or halides¹⁶ form complexes with four HMPA by solvation of the magnesium cation. The reactive species, therefore, seems to be represented by the following formula.

The presence of such a complex has already been suggested by the study of the electronic spectra.¹² Consequently, the polymerization is initiated by the benzyl carbanion formed in this way. In the case of other RMgX also, ionic species similar to species III seem to initiate the polymerization of α -MeSt. Moreover, the structure of the propagating end must be similar to species III, because the structure of the poly(α -methylstyryl) anion is analogous to that of the benzyl anion. An ion pair such as species III may be regarded as a solvent-separated ion-pair rather than a contact ion-pair, because the magnesium fluoride—HMPA complex, in which three or four HMPA molecules coordinate to the magnesium ion, exists as a solvent-separated ion-pair.¹⁷ The spectra of the polymerization mixture (Figure 1) seem also to support this concept.

Structure of Polymer

Figure 3 shows the NMR spectrum of poly- α -MeSt obtained by benzylmagnesium bromide at $\alpha=2.5$. The spectra of polymers obtained under various conditions were very similar to

Figure 3. The α -methyl and methylene proton region of the NMR spectrum of poly(α -MeSt): PhCH_2MgBr catalyst, $\alpha=2.5$; temp, 15°C .

the spectrum shown in Figure 3. The polymer was predominantly syndiotactic and heterotactic. The structure of the polymer obtained by the RMgX/HMPA system was similar to that obtained by alkyl-lithium catalyst in tetrahydrofuran.¹⁸

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