

Polymerization of styrene with diphenylzinc-cocatalyst systems

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SUMMARY

The diphenylzinc-H₂O and diphenylzinc-H₂O-Bu^tCl systems were used as catalysts for styrene polymerization in solution at various temperatures and solvents. The systems are greatly influenced by the molar ratio H₂O/Ph₂Zn, and the maximum catalyst activity, in both cases, was found at a molar ratio of 0.75. GPC results strongly suggest the presence of more than one active species. For Ph₂Zn-H₂O-Bu^tCl system, in dichloromethane at -78°C with the molar ratio of H₂O/Ph₂Zn = 0.75, the reaction is first order with respect to monomer with $k_p = 2.45 \times 10^{-3} \text{ Lmol}^{-1}\text{sec}^{-1}$.

INTRODUCTION

Styrene, St, has been polymerized by combinations of titanium or zirconium compounds with methyl alumoxane, MAO, as catalysts (1-7). In most cases the obtained polystyrene, PSt, was highly stereoregular with syndiotactic placements.

Current literature reports that mixtures of metal alkyl-H₂O systems (where the metal alkyls are triethylaluminium, Et₃Al, or diethylzinc, Et₂Zn) with or without cocatalysts are effective catalyst for St polymerization. (8,9)

We have been working in epoxide polymerization using the diphenylzinc-H₂O system (10-12), which effectively catalyzes ethylene oxide, EO, propylene oxide, PO, and styrene oxide, SO, polymerization. The catalyst activity of the systems markedly depend on the amount of water added. With PO and SO a fraction of isotactic polymer was produced. We reported (12) on the similarity of SO and St for polymerizations initiated by Ph₂Zn-H₂O systems. A coordinative-ionic process was suggested where the ionic character changes from cationic to anionic as the molar ratio H₂O/Ph₂Zn increases from 0 to 1.

The present communication reports preliminary results on the polymerization of St initiated by Ph₂Zn-H₂O and by Ph₂Zn-H₂O-Bu^tCl.

EXPERIMENTAL

A vacuum line (10⁻⁵ mbar) technique was used for filling the polymerization vessels, which consisted of 10 cm lengths of tubing of 2 cm bore. The Ph₂Zn solution in benzene and the required amount of additives and monomer were transferred by syringe under a positive pressure of argon. The reaction mixtures were degassed and then the vessel sealed off from the

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vacuum line and left at the adequate temperature for the required length of time. Polymerizations were terminated by addition of benzene and a small excess of methanol over that required to precipitate the catalyst. Catalyst residues were removed centrifugally, and the polymers were isolated by precipitation with methanol or by freeze-drying.

Intrinsic viscosities, $[\eta]$, were measured at 25°C in chloroform. Viscosity-average molecular weights, M_v , were calculated according the equation (13)

$$[\eta] = 1.12 \times 10^{-4} M_v^{0.73}$$

valid for the molecular weight range 7-150x10⁴.

RESULTS AND DISCUSSION

The results of the polymerization of styrene by the Ph₂Zn-H₂O system, at various molar ratios H₂O/Ph₂O, at 60°C and 120°C in benzene and at 60°C in dichloromethane, are listed in Table 1. When comparing the benzene solution polymerizations, it can be noticed that the polymerization at 120°C produced

Table 1. Polymerization of styrene initiated by the Ph₂Zn-H₂O system at various H₂O/Ph₂Zn molar ratios.

H ₂ O Ph ₂ Zn mol/mol	13 ds. 60°C PhH ^a			3 ds. 120°C PhH ^a			13 ds. 60°C CH ₂ Cl ₂ ^b		
	Yield ^c %	$[\eta]^d$ dLg ⁻¹	M_v x10 ⁻⁵	Yield ^c %	$[\eta]^d$ dLg ⁻¹	M_v x10 ⁻⁵	Yield ^c %	$[\eta]^d$ dLg ⁻¹	M_v x10 ⁻⁵
0.00	9.32	1.31	3.75	100	0.62	1.34	38.1	0.218	0.32
0.25	8.88	1.65	5.14	97.8	0.69	1.55	48.9	0.143	0.18
0.50	9.60	1.68	5.25	94.0	0.64	1.40	53.0	0.128	0.16
0.75	-----	-----	-----	-----	-----	-----	76.8	0.096	0.10
1.00	7.76	3.42	13.93	90.5	0.77	1.81	24.3	0.573	1.20
1.50	10.36	3.11	12.20	-----	-----	-----	11.2	0.735	1.70

a) [Ph₂Zn] = 0.022 M, [St] = 4.35 M, St/Ph₂Zn = 198 mol/mol.

b) [Ph₂Zn] = 0.05 M, [St] = 1.64 M, St/Ph₂Zn = 32,8 mol/mol.

c) Based on initial St.

d) Measured in chloroform at 25°C.

very high conversions after only three days of polymerization. Conversions diminish as water is incorporated to the system. For polymerizations at 60°C polymer yield is only about 10% after 13 days, with almost no difference between the various molar ratios H₂O/Ph₂Zn used. Comparison between both sets of experiments also shows different molecular weights of the PSts obtained; the 60°C process produced the higher MW polymers. It can be assumed that the 120°C process is mainly due to the thermal polymerization of St. GPC chromatograms of PSts obtained at 120°C (Fig. 1) were bi or multimodal indicating the presence of more than one active species. The multiplicity of the modes of chromatograms changes according with the amount of added water. It can be concluded that not only a thermal

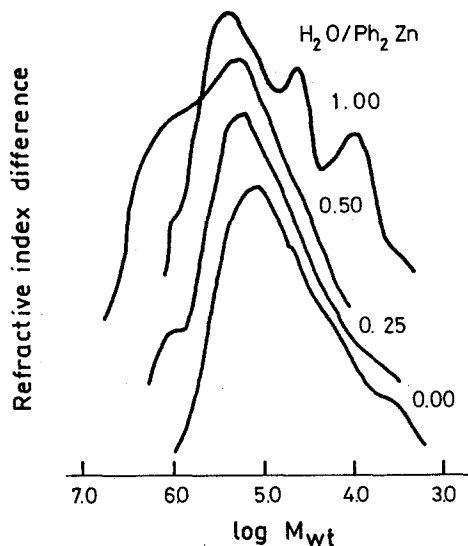


Figure 1. GPC chromatograms of PSTs obtained using $\text{Ph}_2\text{Zn-H}_2\text{O}$ systems at various molar ratios $\text{H}_2\text{O}/\text{Ph}_2\text{Zn}$ in benzene solution after 3 days at 120°C .

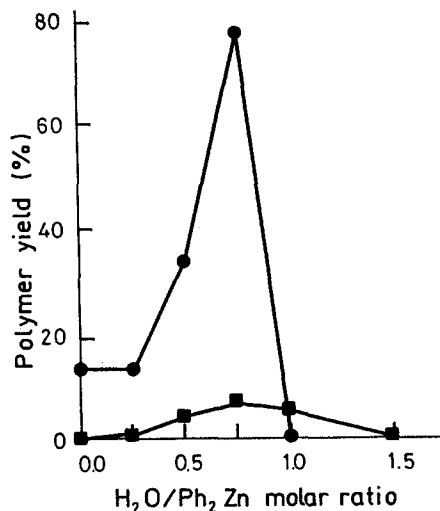


Figure 2. Polymerization of St by $\text{Ph}_2\text{Zn-H}_2\text{O-Bu}^t\text{Cl}$ at -78°C , (●) 5.7 days in CH_2Cl_2 , (■) 6 days in PhMe.

process is occurring but St also polymerizes by species generated by the $\text{Ph}_2\text{Zn-H}_2\text{O}$ reaction. The third set of experiments reported in Table 1, the ones using CH_2Cl_2 as solvent, clearly indicate that water has a specific role particularly when CH_2Cl_2 is used. Evidently the polymerization occurs by a coordinative-ionic process where the monomer coordinates to the active species and propagates by an ionic pathway, as was suggested for the $\text{Ph}_2\text{Zn-H}_2\text{O}$ system to polymerize EQ (10), PO (11), and SO (12).

Table 2 shows the results of St polymerization using the $\text{Ph}_2\text{Zn-H}_2\text{O-Bu}^t\text{Cl}$ system at -78°C in CH_2Cl_2 , and in toluene, PhMe, for 6 days at various molar ratios of $\text{H}_2\text{O}/\text{Ph}_2\text{Zn}$ and a molar ratio of $\text{Bu}^t\text{Cl}/\text{Ph}_2\text{Zn} = 1$. For both sets of experiments the extent of polymerization reaches its maximum at $\text{H}_2\text{O}/\text{Ph}_2\text{Zn} = 0.75$ (Fig. 2). For experiments in CH_2Cl_2 there is a sharp decrease of conversion when the amount of water in the system is augmented, while in PhMe the conversion gradually diminishes to less than 1% at $\text{H}_2\text{O}/\text{Ph}_2\text{Zn} = 1.5$. These findings can also be attributed to an ionic character of the polymerization which is much enhanced when a polar solvent is used. In all cases the polymerization results showed poor reproducibility. Such situation was also observed when the $\text{Ph}_2\text{Zn-H}_2\text{O}$ system was used to polymerize epoxides (10-12).

Table 2. Polymerization of styrene initiated by the $\text{Ph}_2\text{Zn-H}_2\text{O-Bu}^t\text{Cl}$ system at various $\text{H}_2\text{O/Ph}_2\text{Zn}$ molar ratios.

$\frac{\text{H}_2\text{O}}{\text{Ph}_2\text{Zn}}$ mol/mol	5.7 ds. at -78°C in CH_2Cl_2^a			6 ds. at -78°C in PhMe^b		
	Yield ^c %	$[\eta]^d$ dLg^{-1}	M_v $\times 10^{-5}$	Yield ^c %	$[\eta]^d$ dLg^{-1}	M_v $\times 10^{-4}$
0.00	13.68	0.53	1.07	0.04	nd	----
0.25	13.54	0.21	0.30	1.20	nd	----
0.50	34.02	0.35	0.61	4.76	0.049	0.41
0.75	78.08	0.53	1.08	7.28	0.05	0.43
1.00	1.05	nd	----	6.32	0.046	0.38
1.50	----	----	----	0.66	nd	----

- a) $[\text{Ph}_2\text{Zn}] = 0.05 \text{ M}$, $[\text{St}] = 1.64 \text{ M}$, $\text{Bu}^t\text{Cl/Ph}_2\text{Zn} = 1 \text{ mol/mol}$, $\text{St/Ph}_2\text{Zn} = 32.8 \text{ mol/mol}$.
 b) $[\text{Ph}_2\text{Zn}] = 0.028 \text{ M}$, $[\text{S}] = 0.92 \text{ M}$, $\text{Bu}^t\text{Cl/Ph}_2\text{Zn} = 1 \text{ mol/mol}$, $\text{St/Ph}_2\text{Zn} = 32.9 \text{ mol/mol}$.
 c) Based on initial St.
 d) Measured in chloroform at 25°C .

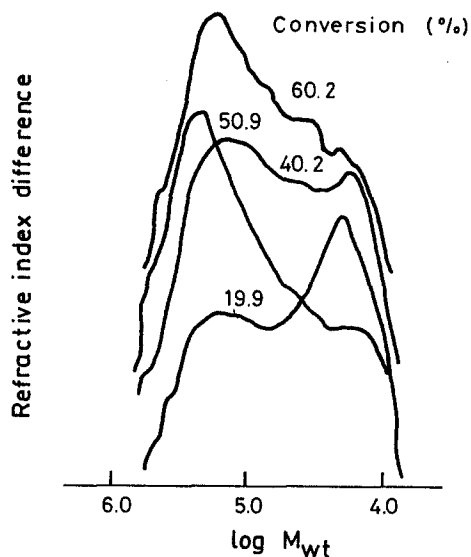
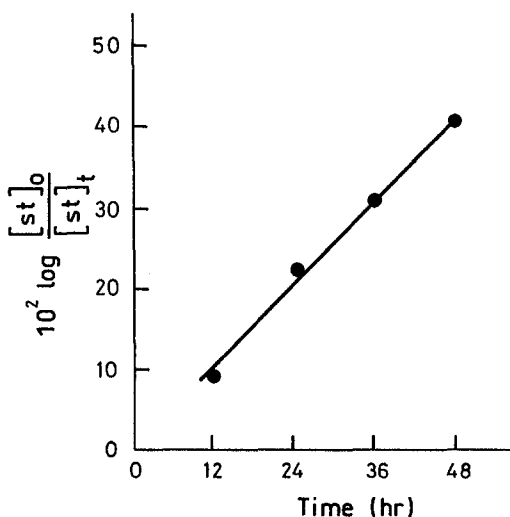


Figure 3. First order plot for St polymerization in CH_2Cl_2 initiated by $\text{Ph}_2\text{Zn-H}_2\text{O-Bu}^t\text{Cl}$ at -78°C . $\text{H}_2\text{O/Ph}_2\text{Zn} = 0.75$, $\text{Bu}^t\text{Cl/Ph}_2\text{Zn} = 1$, $\text{Ph}_2\text{Zn} = 0.048 \text{ molL}^{-1}$

Figure 4. GPC chromatograms of PSt obtained using $\text{Ph}_2\text{Zn-H}_2\text{O-Bu}^t\text{Cl}$, $\text{H}_2\text{O/Ph}_2\text{Zn} = 0.75$, -78°C in CH_2Cl_2 . Various percentages of conversion.

Polymerizations of St by $\text{Ph}_2\text{Zn-H}_2\text{O-Bu}^t\text{Cl}$ in CH_2Cl_2 at -78°C with $\text{H}_2\text{O/Ph}_2\text{Zn} = 0.75$, which yielded the highest conversion to PSt, were performed at various times and the

first order plot shown in Figure 3 was obtained.

It is clear that the polymerization is first order in monomer with $k_p = 2.45 \times 10^{-3} \text{ Lmol}^{-1}\text{sec}^{-1}$ obtained by dividing the slope by the initial Ph_2Zn concentration.

Gel permeation chromatograms of PSts obtained at various conversions are shown in Figure 4. The traces indicate the presence of more than one active species. As the polymerization proceeds the abundance of PSt portions, low and higher molecular weights, move to the higher region centering at around 3.5×10^5 for larger conversions.

According to our results it can be concluded that the system $\text{Ph}_2\text{Zn-H}_2\text{O-Bu}^t\text{Cl}$ at -78°C induces St polymerization, and conversions are greatly influenced by the molar ratio $\text{H}_2\text{O/Ph}_2\text{Zn}$ and the solvent. The present results are in accord with those obtained for epoxide polymerization. In these systems propagation involves a coordinative cationic process when the molar $\text{H}_2\text{O/Ph}_2\text{Zn}$ ratio was less than one, and anionic for molar ratios equal to unity. Recent experiments with methyl methacrylate confirm these findings. No PMMA was obtained for the system $\text{Ph}_2\text{Zn-H}_2\text{O-Bu}^t\text{Cl}$ at $\text{H}_2\text{O/Ph}_2\text{Zn} < 1$ (14). More work is now in progress from which conclusive results are expected.

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