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Polymerization of styrene with diphenylzinc-water systems previously aged *

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SUMMARY

Diphenylzinc-water systems, Ph_2Zn-H_2O, were aged at various temperatures and for various lengths of time. These systems by themselves and those to which t-butyl chloride was added, $Ph_2Zn-H_2O-Bu^tCl$, were used as initiator for styrene polymerizations. For Ph_2Zn-H_2O systems, both conversion and molecular weight of the polymers were much affected by ageing. $Ph_2Zn-H_2O-Bu^tCl$ systems, after ageing at various temperatures, did not improve their capability to induce styrene polymerization at -78°C in dichloromethane, confirming their ionic nature.

INTRODUCTION

Ph_2Zn-H_2O systems produce various species of zinc polyoxides and have been used as initiators of oxirane and vinyl polymerizations.

We have been working with styrene, St, and methyl methacrylate, MMA, polymerizations using Ph_2Zn-H_2O at various molar ratios [1-3]. Experiments with tert-butyl chloride, Bu^tCl, as a third component were also performed. Results indicate the presence of more than one active species capable of initiating the polymerization. It was postulated that the polymerization was initiated by coordination of monomer to the active species followed by propagation through an ionic pathway [1].

Heterogeneity of the polymerization, due to the formation of a precipitate resulting from the interaction between Ph_2Zn and H_2O, was observed [3]. Recent experiments indicate that heterogeneity as well as the temperature and time of aging determine the efficiency of the initiating systems. These observations agree with results obtained with propylene oxide [4] and methyl methacrylate [5] polymerizations using other heterogeneous initiator systems.

In the present communication we report the results for styrene polymerizations using Ph_2Zn-H_2O and $Ph_2Zn-H_2O-Bu^tCl$ initiator systems previously aged.

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EXPERIMENTAL

A vacuum line (10^{-5}mbar) technique was used for filling the polymerization vessels, which consisted of a Pyrex-glass bulb of approximately 30 mL capacity. The Ph_2Zn solution in benzene and the required amount of additives were transferred by syringe under a positive pressure of argon. The reaction mixtures were degassed and then the vessel sealed off from the vacuum line and left at the corresponding temperature for the established length of time (ageing). Afterwards, the reactor was sealed again to the vacuum line. The measured amount of styrene, solvent and t-BuCl were transferred by syringe. The polymerization mixtures were degassed and then the vessel sealed off from the vacuum line and left at an adequate temperature for the required length of time. Polymerizations were terminated by addition of benzene and a small amount of acidified methanol in excess of that required to dissolve the catalyst. Polymers were isolated by precipitation with methanol.

Intrinsic viscosities, $[\eta]$, were measured at 25°C in chloroform. Viscosity-average molecular weights, M_v, were calculated according to the equation [6]:

$$[\eta] = 1.12x10^{-4}M_v^{0.73}$$

which is valid for the molecular weight range $7\text{-}150x10^4$.

H-NMR experiments were run at 25°C in 1,2-dichlorobenzene in a Bruker AMX-300 spectrometer.

SEC chromatograms were obtained at 25°C in THF in a Bruker LC21/31 apparatus.

RESULTS AND DISCUSSION

When $Ph_2Zn\text{-}H_2O$ systems and $Ph_2Zn\text{-}H_2O\text{-}Bu^tCl$ systems were studied as initiators for St polymerizations, it was established that conversion to polymer is very dependent on the molar ratio H_2O/Ph_2Zn as well as on the solvent (polar or non-polar) employed. Temperature also played a determinant role and the largest conversion to polystyrene was obtained with $Ph_2Zn\text{-}H_2O\text{-}Bu^tCl$ in dichloromethane at -78°C with a molar ratio $H_2O/Ph_2Zn = 0.75$. The obtained PSt showed multimodal SEC chromatograms indicating the presence of more than one active species toward St polymerization [1].

It was also found that the polymerization is much influenced by how the initiator system is prepared including the order in which components are mixed. The temperature and length of time at which they are left to react before the incorporation of monomer also affected the course of polymerization.

Addition of water to Ph_2Zn generates a bulky white precipitate. The aspect of the precipitate changes according to treatment after mixture of the components. Table 1, shows the observed changes for mixtures where the molar ratio H_2O/Ph_2Zn was 0.5.

As can be seen in Table 1, when ageing at 0°C and at 30°C, there were almost no changes in the appearance of the initial precipitate. At 60°C the white precipitate changes from a bulky white to a yellow precipitate and then to yellow granules. These changes suggest that something occurs with the resulting products or species which will initiate polymerization.

Table 1. Time and temperature effect on the Ph_2Zn-H_2O system in benzene at a molar ratio H_2O/Ph_2Zn = 0.50 mol/mol.

Time	Temperature, °C			
h.	0	30	60	120
0.5	bulky white precipitate	bulky white precipitate	bulky white precipitate	white suspension; some yellow ppt.
1.0	bulky white precipitate	bulky white precipitate	yellow ppt.; clear soln.	yellow granules; clear soln.
2.5	bulky white precipitate	bulky white precipitate	yellow granules; clear soln.	yellow granules; clear soln.
14.0	bulky white precipitate	some yellow precipitate	yellow granules; clear soln.	pale brown ppt.; clear soln.
72.0	bulky white precipitate	some yellow precipitate	yellow granules; clear soln.	pale brown ppt.; clear soln.

The effect of conditioning temperature, during a fixed 2 hour period of time, can be seen in Table 2. Aged systems increased the conversion to polymer when the conditioning was done at higher temperatures. On the other hand, the tacticity of the resulting PSt remains almost unchanged, with a syndiotactic abundance, expressed as triad percentage, around 85-86%.

Table 2. Polymerization of styrene initiated by the Ph_2Zn-H_2O system in benzene after 13 days at 60°C[a]. Effect of 2 hours pretreatment at various temperatures.

Ageing	H_2O/Ph_2Zn = 1.00					H_2O/Ph_2Zn = 0.50				
Temperature	Convn[b]	M_V[c]	Tacticity[d]			Convn[b]	M_V[c]	Tacticity[d]		
°C	%	$x10^{-5}$	ii	is	ss	%	$x10^{-5}$	ii	is	ss
nonaged	6.2	4.31	6	13	81	8.2	2.79	4	14	82
0	8.8	7.11	3	12	85	8.5	2.38	3	10	87
30	9.9	9.41	5	12	83	9.7	2.40	5	10	85
60	10.5	9.67	5	14	85	10.5	2.38	5	9	86
120	----	----	-------			11.1	2.39	4	11	86

a) $[Ph_2Zn]$ = 0.057 mol/L; styrene/Ph_2Zn = 33,3 mol/mol.
b) Based on initial St. c) From intrinsic viscosity.
d) Calculated from H-NMR spectra.

When the ageing time was varied at a fixed temperature (Table 3) there was also an increase in conversion with time at 0°C. But when the ageing temperature was 60°C the conversion increased for the one and two hours of ageing and then decreased suggesting that the product of the Ph_2Zn and H_2O reaction changes, possibly in structure or at least in its morphology. This would make difficult the access of monomer to the point of generation of propagating species and consequently a slower polymerization process would result. The tacticity remained almost unchanged, suggesting that active species were almost the same in nature.

Table 3. Polymerization of styrene initiated by the Ph_2Zn-H_2O system in benzene after 13 days at 60°C^a. Effect of pretreatment time.

Ageing Time	$H_2O/Ph_2Zn = 1.00^b$			$H_2O/Ph_2Zn = 0.50^c$		
hours	Convn^d %	M_v^e $x10^{-5}$	Tacticity^f ii is ss	Convn^d %	M_v^e $x10^{-5}$	Tacticity^f ii is ss
non aged	6.2	4.31	6 13 81	8.2	2.79	4 14 82
1	9.9	7.55	2 12 81	10.4	3.79	4 10 86
2	8.8	7.11	3 12 85	10.5	2.38	5 9 86
3	11.8	5.55	6 13 81	8.8	2.23	5 11 84
5	----	----	-------	9.8	----	-------

a) $[Ph_2Zn]$ = 0.057 mol/L; styrene/Ph_2Zn = 33,3 mol/mol.
b) Ageing at 0°C. c) Ageing at 60°C. d) Based on initial St.
e) From intrinsic viscosity. f) From H-NMR spectra.

Table 4. Polymerization of styrene initiated by the Ph_2Zn-H_2O-Bu^tCl system in dichloromethane after 6 days at -78°C^a. Effect of 2 hours ageing at various temperatures.

Ageing Temperature °C	Conversion^b %	M_v^c $x10^{-5}$	Tacticity^d ii	is	ss
-78	71.4	0.140	12	17	71
0	73.2	0.235	12	18	70
30	69.8	0.121	11	17	72
60	65.9	0.207	9	15	76

a) H_2O/Ph_2Zn = 0.75; $[Ph_2Zn]$ = 0.057 mol/L; styrene/Ph_2Zn = 33,3 mol/mol; Ph_2Zn/Bu^tCl = 1.0.
b) Based on initial St. c) From intrinsic viscosity.
d) Calculated from H-NMR spectra.

Figures 1 and 2 show the SEC chromatograms of the obtained PSts using aged initiator systems. It can be appreciated that ageing did not change the pattern of the SEC chromatograms.

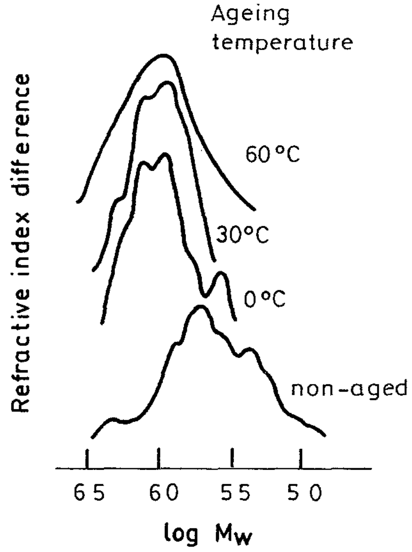

Figure 1. SEC chromatograms of PSts obtained using Ph_2Zn-H_2O systems at molar ratio H_2O/Ph_2Zn = 1 in benzene solution after 13 days at 60°C. Initiator systems aged 2 hours in benzene at various temperatures.

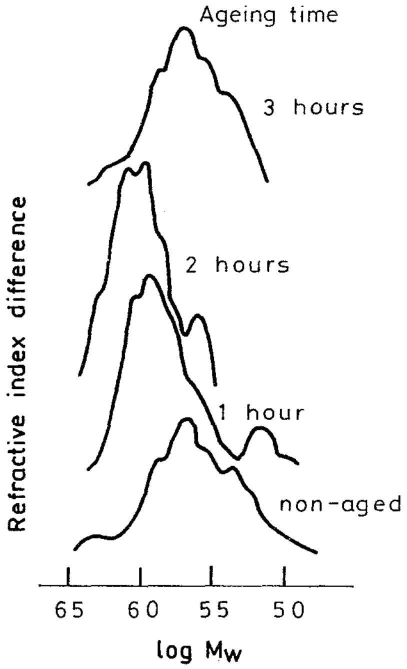

Figure 2. SEC chromatograms of PSts obtained using Ph_2Zn-H_2O systems at molar ratio H_2O/Ph_2Zn = 1 in benzene solution after 13 days at 60°C. Initiator systems aged at 0°C in benzene at various lengths of time.

Moreover, it is clear that the molecular weights of the polymers resulting from aged initiator systems move to higher values. This situation suggests the possibility of increasing the abundance active species which are responsible for high molecular weight PSt.

For the three component Ph_2Zn-H_2O-Bu^tCl systems in dichloromethane at -78°C, the results (Table 4) indicate that there were no improvements in conversion but decreases both in conversion and molecular weights of PSt due to the ageing. These results suggest that for such systems the main contribution to polymerization is centered in ionic species whose abundance or formation did not vary with the ageing time nor with the temperature at which they are previously aged.

CONCLUSIONS

The Ph_2Zn-H_2O and Ph_2Zn-H_2O-Bu^tC systems used in styrene polymerizations are complex in nature. The Ph_2Zn-H_2O system is affected by the conditioning (temperature and time) pretreatment before incorporation of monomer to the reaction mixture.

For the Ph_2Zn-H_2O-Bu^tCl systems, in reaction conditions where an ionic process is favored,there were no improvements by pre-polymerization conditioning suggesting that the polymerization mechanism relies strongly on the ionic nature of the initiating system.

Our experiments revealed that the systems studied present two kinds of initiating substances, soluble and insoluble, in the reaction media.

More work with separate soluble and insoluble products is under way from which conclusive results are expected.

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