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Further studies on styrene polymerization using diphenylzinc-additive systems

C. A. Terraza [*], **F. M. Rabagliati** [**]

Grupo de Polímeros, Departamento Ciencias Químicas, Facultad de Química y Biología,
Universidad de Santiago de Chile, Casilla 307, Correo 2, Santiago, Chile

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SUMMARY

Diphenylzinc-water-organic monochloride systems, Ph_2Zn-H_2O-RCl, with n-, sec- and tert-butyl chloride (t-BuCl) and benzyl chloride (BzCl), were used to induce styrene polymerization. Improvement in polymer conversion is in concordance with the enthalpy of dissociation of the organic chloride employed. Polymerization results suggest that systems with t-BuCl and BzCl proceed by coordinate cationic propagation. Obtained polystyrene was atactic with up to 75% syndiotactic triads detected by ^{1}H-NMR spectroscopy.

INTRODUCTION

In the early sixties it was reported that combined systems such as Et_2Zn-H_2O-t-BuCl and Et_3Al-H_2O-t-BuCl, at -78°C in dichloromethane (CH_2Cl_2), were active initiators of styrene polymerization by a cationic mechanism [1,2]. The conversion to polymer was much influenced by the amount of water, the initiator was effective at molar ratios of H_2O/Et_2Zn lower than one, while no polymer was obtained at $H_2O/Et_2Zn = 1$ [2].

Systems such as Ph_2Zn-H_2O-t-BuCl behave similarly for styrene polymerization. At -78°C in dichloromethane, conversion to polymer increases as the ratio H_2O/Ph_2Zn moves from 0.25, to 0.50 and 0.75. Almost no polymer was produced at a molar ratio of unity [3].

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[*] *Present address:* Departamento de Química Orgánica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile

[**] Corresponding author

The present communication reports on the results of using n-BuCl, s-BuCl, t-BuCl or BzCl as third component of Ph_2Zn-H_2O-RCl systems.

EXPERIMENTAL

The polymerization vessels, which consisted of Pyrex-glass bulb of approximately 20 mL capacity were charged using an all glass vacuum line accordingly the techniques described previously [3]. Ph_2Zn solution and the appropriate amount of water were transferred to the polymerization vessel and aged for 3 hours at 0°C. Afterwards, the measured amount of cocatalyst, styrene and solvent were added. After sealing off the reactor was placed at -78°C for 96 hours. Polymerizations were terminated by the addition of benzene and a small excess of acidified methanol over 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 [4]:

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

valid for the molecular weight range: $7\text{-}150\text{x}10^4$.

^{1}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

Table 1 shows the results of the polymerization of styrene when using various combination of Ph_2Zn with water and an organic monochloride. These results show that t-BuCl and BzCl were effective cocatalyst reaching polymer conversions up to 55.6 and 45.1%, respectively. The use of polar solvent and low temperature favors ionic processes. The presence of t-BuCl and also of BzCl enhance cationic propagation. Primary and secondary chloride did not improve the effectiveness of the initiator system when using tertiary butanol as cocatalyst.

Figure 1 shows SEC chromatograms of the various PSts obtained. Systems containing t-BuCl or BzCl gave multimodal signals indicating the presence of more than one active species. PSt obtained using sec- or n-butylchloride gave only one narrow signal suggesting the presence of only one active species.

Table 1. Polymerization of styrene by Ph_2Zn-H_2O-Cocatalyst systems in dichloromethane after 96 hours at -78°C.[a]

Initiator System	Convn[b] %	M_v*10^{-5} [c] g/mol	M_w/M_n [d]	Tacticity[e]		
				II	IS	SS
none	0.0	----	----	--	--	--
Ph_2Zn alone	0.1	nd	nd	nd	nd	nd
Ph_2Zn-H_2O-Bu^nCl	0.1	0.53[f]	2.14	nd	nd	nd
Ph_2Zn-H_2O-Bu^sCl	1.5	0.33[f]	1.47	9	16	75
Ph_2Zn-H_2O-Bu^tCl	55.6	1.08	9.93	8	15	77
Ph_2Zn-H_2O-BzCl	45.1	1.70	3.11	9	16	75
Ph_2Zn-H_2O-Bu^tOH	0.0	----	----	--	--	--

[a] Ph_2Zn/H_2O = 0.75 mol/mol; St/Ph_2Zn = 33.3 mol/mol; Cocat/Ph_2Zn = 1 mol/mol; Ph_2Zn = 0.057 mol/L.
[b] Based on initial St. [c] From intrinsic viscosity.
[d] SEC, THF room temperature. [e] Calculated from ^1H-NMR spectra
[f] From SEC, THF room temperature. nd, not determined.

The reactivity of the systems are related to the easiness of ionizing alkyl halides and the stability of the resulting carbenium ions. It is well known that the order of carbenium ion stability is: benzyl > tertiary > secondary > primary. However, the enthalpy of dissociation for t-BuCl and BzCl are 157 and 166 kcal/mole respectively [5]. For s-BuCl we calculate an approximate value of 179 kcal/mole.

Accordingly to our results initiation of styrene polymerization is critically influenced by both the stability of the resulting carbenium ions and the dissociation enthalpy of the corresponding chloride. Lower values of enthalpy of dissociation of t-BuCl and BzCl produced larger conversions than n-BuCl and s-BuCl.

From early experiments using Ph_2Zn-H_2O-t-BuCl, at various molar ratio H_2O/Ph_2Zn and solvents, we postulated the existence of a ion-pair as propagating entity of polymerization[6]. This is in accord with the high color intensity noted during the polymerization [7]. Furthermore, methyl methacrylate did not produce PMMA with the Ph_2Zn-H_2O-t-BuCl system at -78°C in CH_2Cl_2. We concluded that propagation was cationic, at least under the conditions employed [6,8].

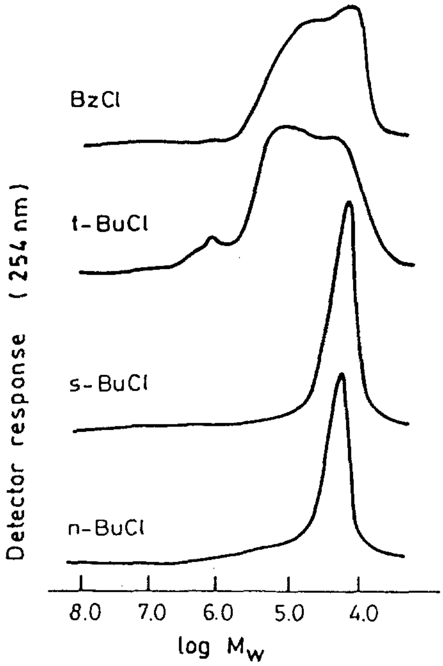


Figure 1. SEC chromatograms of PSts obtained using Ph_2Zn-H_2O-RCl in CH_2Cl_2 after 96 hours at -78°C.

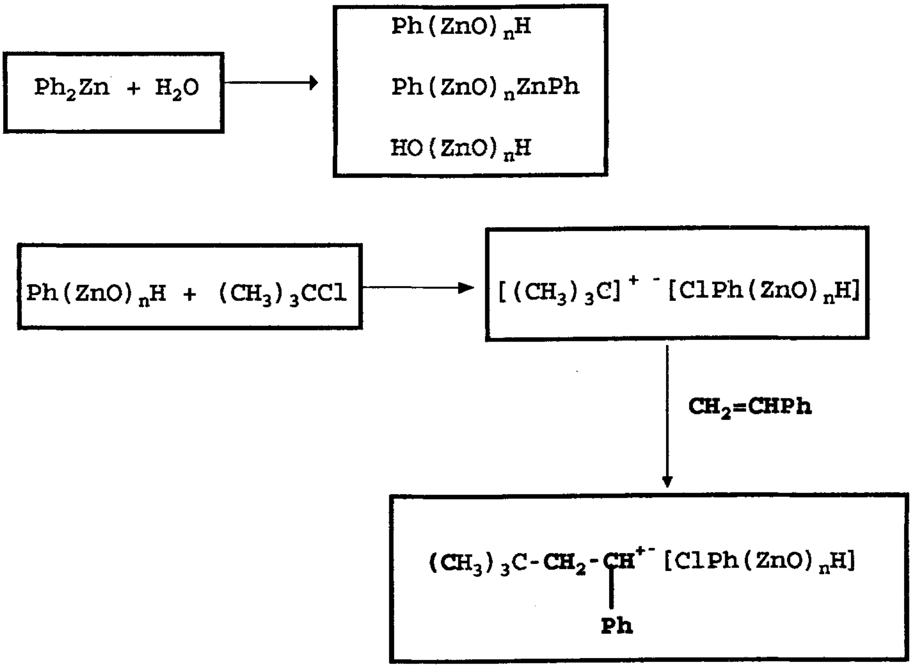
Based on the above facts we postulate that the polymerization proceeds through monomer coordination to active species and propagates cationicaly.

The present results, together with the previous ones, suggest that Ph_2Zn-H_2O-t-BuCl systems initiate styrene polymerization by 3 steps (see scheme):

1.- Formation of poly(zinc oxide)s resulting from reaction of Ph_2Zn with water [9].
2.- Reaction of poly(zinc oxide)s with t-BuCl. The resulting complex ion-pairs are capable of initiating styrene polymerization by $[(CH_3)_3C]^{+}\ ^{-}[ClPh(ZnO)_nH]$.
3.- Insertion of the first monomer.

The hydrolysis of t-BuCl was not considered in the scheme as the system with t-BuOH did not produce polystyrene. Experiments using Ph_2Zn-H_2O-t-BuOH systems at molar ratios of H_2O/Ph_2Zn = 0.25, 0.50, 0.75 and 1.00 were not able to initiate styrene polymerization.

Scheme:



The microstructure by ^1H-NMR analysis of the polymers obtained indicates predominantly atactic polymers. However, up to ~77% of syndiotactic triads have been found. DSC analysis showed only the T_g endotherm.

CONCLUSIONS

Ph_2Zn-H_2O-organic monochloride systems are capable of initiate St polymerization accordingly with organic chloride dissociation.

Initiation seems to proceed in three stages including: formation of poly(zinc oxide) species, reaction of the organic chloride with poly(zinc oxide) to generate ion pairs, and finally monomer insertion in the ionic species.

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