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Polymerization of styrene with diphenylzinc-butanone systems*

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SUMMARY

In the present work we report the results of the polymerization of styrene using diphenylzinc-butanone, Ph_2Zn-MeCOEt. Our results indicate that these systems induce the polymerization of styrene reaching a larger conversion when the molar ratio MeCOEt/Ph_2Zn = 1,0. According to size exclusion chromatography, SEC, studies of the polystyrene obtained using the Ph_2Zn-MeCOEt showed unimodal curves and have molecular weight distribution narrower than those obtained using the Ph_2Zn-H_2O system, suggesting a more simple reaction system.

INTRODUCTION

Styrene polymerization has been carried out using various initiator systems producing stereoregular polystyrene. Titanium and zirconium compounds combined with methylalumoxane promote syndiotactic polymerization of styrene (1-7). Furthermore, some metalalkyl systems combined with water, with or without a cocatalyst, were also used to polymerize styrene (8-9).

We have been working with combined systems diphenylzinc-cocatalyst, Ph_2Zn-cocat, (cocat = H_2O, ketone) in the polymerization of oxiranes (10-12), styrene (13), and methyl methacrylate (14). In all cases, it has been established that there is a very determinant dependence of conversion to polymer on the molar ratio cocatalyst/Ph_2Zn employed. Furthermore, in oxirane polymerization it was established that the formation of a variable amount of stereoregular polymer is obtained as the molar ratio, cocat/Ph_2Zn, is changed in the range 0 to 2.00.

In the present work we report the results of polymerization of styrene using Ph_2Zn-MeCOEt.

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 Ph_2Zn 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 vacuum line and left at 60°C for the required length of time. Polymerizations were terminated by addition of benzene and a small excess of

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methanol over that required to precipitate the catalyst. Catalyst residues were removed by centrifugation, and the polymers were isolated by precipitation with methanol or by freeze-drying.

Intrinsic viscosities, $[\eta]$, were measured at 30°C in chloroform. Viscosity-average molecular weights, M_v, were calculated according to equation (15):

$$[\eta] = 4.9\text{x}10^{-5}M_v^{0.794}$$

valid for the molecular weight range $19\text{-}373\text{x}10^4$.

RESULTS AND DISCUSSION

Continuing our works on styrene, St, polymerization with combined systems, diphenylzinc, Ph_2Zn, and a cocatalyst, the present paper relates the results when using Ph_2Zn combined with butanone, MeCOEt. These systems already have been reported by us in oxirane polymerization (16) with production of poly(ethylene oxide), PEO, and poly(propylene oxide), PPO. When polymerizing PO, the obtained polymers contained a fraction of isotactic PPO the amount of which was in relationship with the molar ratio, MeCOEt/Ph_2Zn. We have obtained polystyrene, PSt, by using the systems $Ph_2Zn\text{-}H_2O$ and $Ph_2Zn\text{-}H_2O/Bu^tCl$ (13), at different conversions depending on the molar ratio H_2O/Ph_2Zn, the solvent and the polymerization temperature. According to multimodal SEC, the systems $Ph_2Zn\text{-}H_2O$ and $Ph_2Zn\text{-}H_2O/Bu^tCl$, were complex with more than one active species capable of initiating St polymerization.

Table 1. Polymerization of styrene initiated by the Ph_2Zn-MeCOEt system at various MeCOEt/Ph_2Zn molar ratios, after 144 hours[a].

$\frac{\text{MeCOEt}}{Ph_2Zn}$	60°C, PhH				60°C, CH_2Cl_2			
mol/mol	Yield[b] %	$[\eta]$[c] dLg^{-1}	M_v $\text{x}10^{-5}$	$\frac{M_w}{M_n}$[d]	Yield[b] %	$[\eta]$[c] dLg^{-1}	M_v $\text{x}10^{-5}$	$\frac{M_w}{M_n}$[d]
0.00	9.54	1.08	2.95	2.05	7.76	1.01	2.71	2.62
0.50	12.03	2.02	6.50	2.07	7.92	2.06	6.66	1.99
0.75	14.77	2.11	6.87	1.94	8.94	2.79	9.76	2.51
1.00	16.38	1.58	4.77	1.88	8.69	3.22	11.69	5.88
1.50	9.10	2.23	7.36	2.78	6.46	3.58	13.36	2.07
2.00	7.77	2.60	8.93	2.65	3.74	2.65	9.15	1.87

a) $[Ph_2Zn]$ = 0.037 M, [St] = 7,39 M, St/Ph_2Zn = 200 mol/mol.
b) Based on initial St.
c) Measured in chloroform at 30°C.
d) From SEC, chloroform at 40°C.

Table 1, shows the experimental results for the polymerization of St catalyzed by the Ph_2Zn-butanone systems at mole ratios of MeCOEt/Ph_2Zn from 0.00 to 2.00, during 6 days at 60°C, in benzene and also in dichloromethane. It can be appreciated that the added butanone influences both the conversion to polymer and the molecular weigth. The largest amount of polymer was obtained at a molar ratio equal to unity when benzene was the solvent; this was also the case for EO and PO polymerization using water as cocatalyst. Nevertheless, the Ph_2Zn-MeCOEt systems produced PSt, as is shown in Fig. 1, with a molecular weight distribution, MWD, unimodal and narrower than those obtained with Ph_2Zn-H_2O systems (13). This is quite different when water was the other component, and where the formation of several active species were postulated. We therefore think that this is a simpler catalytic system with only one active species responsible for the polymerization; the active species results from an interaction between diphenylzinc and the carbonyl group, through zinc-oxygen coordination.

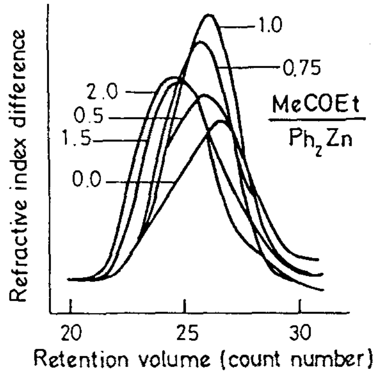

Figure 1. SEC chromatograms of PSts obtained using Ph_2Zn-Butanone systems at various molar ratios MeCOEt/Ph_2Zn in benzene after 6 days at 60°C.

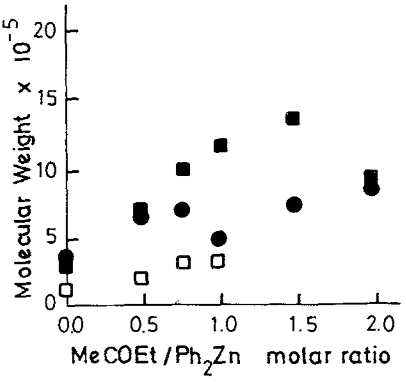

Figure 2. Molecular weights of PSt obtained using Ph_2Zn-Butanone systems during 6 days at 60°C (●) in PhH, (■) in CH_2Cl_2 and (□) at -78°C in CH_2Cl_2.

Table 1, also shows the results of St polymerization at 60°C using dichloromethane solvent; this polar solvent will facilitate ionic polymerization. For EO and PO polymerizations, using MeCOEt-Ph_2Zn systems, it was postulated that the polymerization proceeds by a coordinative-ionic mechanism with a marked ionic character in the propagation step (16,17). The CH_2Cl_2 results showed very slight differences from those for benzene solvent. The conversions, nearly 8%, are lower than those obtained for benzene. The main difference seems to be that the highest conversion was reached at a molar ratio of 0.75 instead of 1.0. This was corroborated by low temperature polymerization experiments.

Table 2 shows the experimental results of low temperature experiments using dichloromethane solvent. From the data it can be appreciated that there is a very low conversion, with no polymer production at a molar ratio larger than 1. The highest conversion was reached at a molar ratio 0.75. Contrary to the

Table 2. Effects of the molar ratio, $MeCOEt/Ph_2Zn$, on the polymerization of styrene initiated by the Ph_2Zn-MeCOEt system in dichloromethane at -78°C for 144 hours.[a]

$\frac{MeCOEt}{Ph_2Zn}$ mol/mol	Yield[b] %	$[\eta]$[c] dLg^{-1}	M_v $x10^{-5}$	$\frac{M_w}{M_n}$[d]
0.00	1.00	0.45	0.98	3.68
0.50	1.87	0.73	1.80	3.20
0.75	4.91	1.04	2.82	2.64
1.00	2.48	1.12	3.09	2.56
1.50	0.00	----	----	----
2.00	0.00	----	----	----

a) $[Ph_2Zn]$ = 0.037 M, [St] = 7.39 M, St/Ph_2Zn = 200 mol/mol.
b) Based on initial styrene.
c) Measured in chloroform at 30°C.
d) From SEC, chloroform at 40°C.

results obtained with the Ph_2Zn-H_2O systems, propagation with the Ph_2Zn-MeCOEt systems do not exhibit a remarkable ionic character. This could be attributable to a Ph_2Zn:OC(Et)Me complex which inhibit the coordination of monomer to the zinc of the active species and subsequent ionic propagation.

The molecular weights of the PSts varied according the molar ratio $MeCOEt/Ph_2Zn$, the solvent, and the polymerization temperature. Fig. 2 shows the molecular weights calculated from intrinsic viscosity values.

Finally, it is of interest that no isotactic PSt was isolated. NMR analysis did not indicate the presence of syndiotactic polymer. Evidently the obtained polymer was mainly atactic PSt.

CONCLUSIONS

Ph_2Zn-MeCOEt systems polymerize styrene to high molecular weight PSt through a process which is greatly influenced by the molar ratio $MeCOEt/Ph_2Zn$; stereoregular polymer was not obtained under the experimental conditions employed.

The systems used behave differently from similar ones with water as cocatalyst. Unimodal MWD PSts are obtained suggesting that only one type of active species is formed.

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