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The soluble and insoluble product of diphenylzinc-water systems as initiator in styrene polymerization

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SUMMARY

The solution resulting from reaction between Ph_2Zn and H_2O in benzene was used by itself and separated in soluble and insoluble fractions to initiate styrene polymerization. The soluble fraction produced the largest polymer conversion while the insoluble was reponsible of the highest molecular weights. Resulting polystyrenes were atactic but up to 80-85% syndiotactic triads were detected by ^1H-NMR analysis. Polystyrene obtained using benzene as solvent showed a low crystalline content while the polymer obtained using dichloromethane did not produce any crystalline fraction.

INTRODUCTION

Systems resulting from combination of diphenylzinc, Ph_2Zn, with water, H_2O, have been used as polymerization initiator of several cyclic ethers, viz.: ethylene oxide [1], propylene oxide [2a,b], epiclorhydrine [3], styrene oxide [4] and lactide [5]. Furthermore, these binary systems by thenselves and also including t-butyl chloride, t-BuCl, as third component have been employed to induce the polymerization of monomers such as: methyl methacrylate[6a,6b] and styrene [7a,7b] in various solvents and temperatures.

The polystyrenes obtained showed multimodal SEC chromatograms, indicating the presence of more than one active species. This fact is in concordance with the various polyoxides propossed for diphenylzinc hydrolysis [1]. Such polyoxides are insoluble or parcially soluble in the reaction media.

For styrene polymerization the effect of conditioning variables for diphenylzinc-water interaction prior to start up of polymerization has been studied qualitatively and quantitatively [8]. It was also observed that the systems are influenced by dispersing the precipitate originated by Ph_2Zn-H_2O interaction.

In the present paper we polymerized styrene by both the soluble and the insoluble portion of the reaction product between Ph_2Zn-H_2O. According to previous results [7a] a molar ratio of H_2O/Ph_2Zn = 0.75 was employed.

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EXPERIMENTAL

A vacuum line (10^{-5}mbar) technique was used for filling the polymerization vessels, of ~20 ml Pyrex-glass bulbs. First the Ph_2Zn solution in benzene and then the required amount of water were transferred by syringe under a positive pressure of argon. The reaction mixture was left to react for 1 hour at 0°C (ageing). After separating the soluble and insoluble fractions, solvent and monomer were added to both of them by syringe. The vessel was sealed off from the vacuum line and left at the corresponding temperature for the established length of time. Polymerizations were terminated by precipitation in HCl-acified methanol. The polymers were recovered (after washing several times with methanol) by filtration and dried in vacuum at 60°C.

Polymers were characterized by molecular weights, molecular weight distributions, crystalline contents[9a,b] and aproximate distribution of chain configuration [10].

RESULTS AND DISCUSSION

When Ph_2Zn-H_2O initiator systems were studied for styrene polymerization it was found that the polymerization was much influenced by how the initiator system is prepared including the order the components are mixed, the temperature and aging time which they are left to react before monomer addition [7,8. Water addition to Ph_2Zn generates a precipitate whose appearance changes with temperature and ageing time [8].

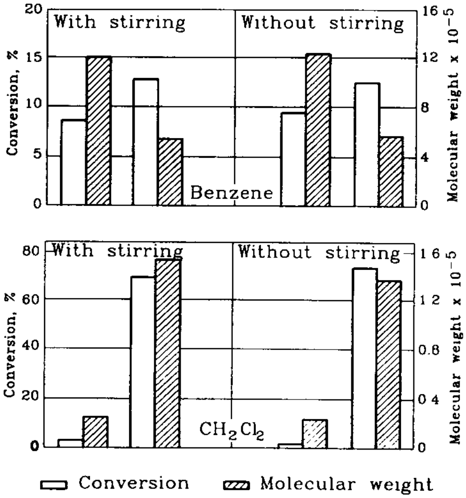

Figure 1. Agitation and solvent effect on styrene polymerization using Ph_2Zn-H_2O systems. Polymerization conditions: 13 days, 60°C, $[Ph_2Zn] = 0.022$ mol/L; $St/Ph_2Zn = 200$ mol/mol; $H_2O/Ph_2Zn = 0.75$ mol/mol.

Figure 1, shows the results of styrene polymerization performed with and without agitation. From these results it can be appreciated that there were almost no changes between them and that the activity of the species were not influenced by agitation.

The same conclusions can be raised from the pattern of SEC chromatograms. Figure 2, shows SEC chromatograms of polystyrenes obtained using Ph_2Zn-H_2O systems in benzene and in dichloromethane solution with and without stirring. Fig. 2 shows that polymers obtained using benzene have higher molecular weights than the ones obtained when using CH_2Cl_2 as solvent.

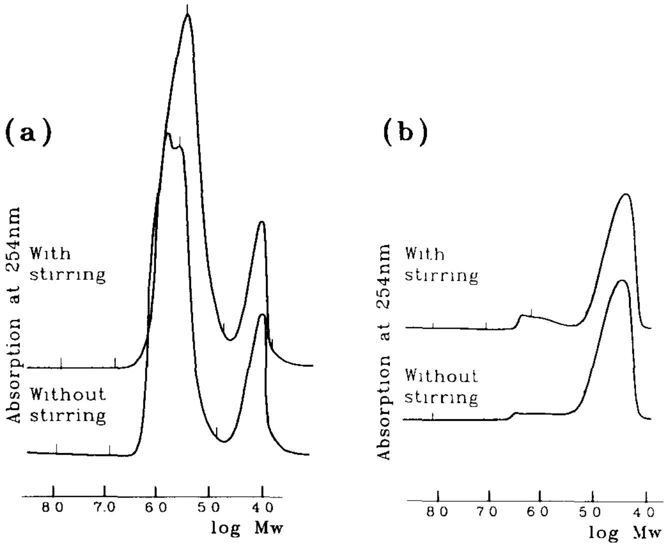

Figure 2. SEC traces of polystyrenes obtained using Ph_2Zn-H_2O systems at 60°C, a) in benzene, b) in dichloromethane; with and without agitation.

Figure 3 shows SEC traces of polystyrenes obtained using the soluble or the insoluble product of the reaction between Ph_2Zn and H_2O. The same patterns were also obtained when moving from benzene to a polar solvent such as dichloromethane.

Table 1 shows the results of styrene polymerization using various initiator systems, for benzene and dichloromethane. The polymerization initiated by Ph_2Zn alone and the one initiated by Ph_2Zn-H_2O soluble fraction produced more polystyrene than the one initiated by the Ph_2Zn-H_2O insoluble fraction. According to SEC results, the polystyrenes obtained using the Ph_2Zn-H_2O insoluble fraction showed the highest molecular weights. This behaviour is much noticeable when using dichloromethane as solvent (Fig. 3b). This finding can be attributed to the ionic nature of the propagation process.

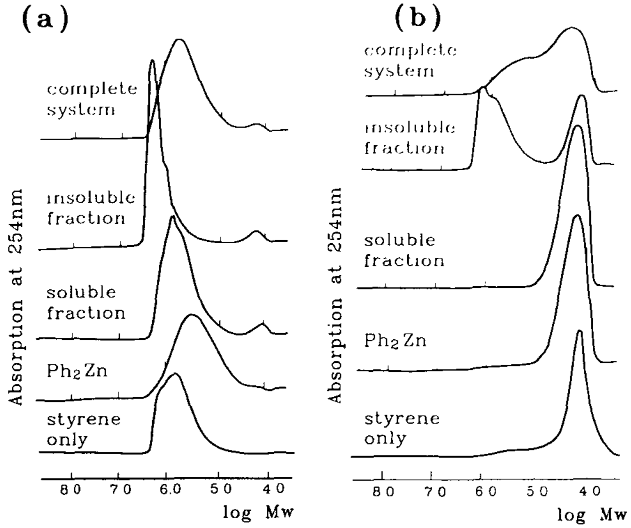

Figure 3. SEC traces of polystyrene obtained using, as indicated, various initiator systems at 60°C, a) in benzene, b) in dichloromethane.

When the initiator system was the complete Ph_2Zn-H_2O both fractions contribute and there is a synergetic effect which produces the highest conversion, particularly in presence of a polar solvent. This effect was not noticed for polymerizations run in benzene. SEC results showed that independently of the solvent, polymers obtained using the complete Ph_2Zn-H_2O system, present a broad MWD in concordance with participation of both, soluble and insoluble fractions. The highest molecular weights were obtained when benzene was the solvent.

^1H-NMR analysis indicates that the polymers obtained are predominantly syndiotactic with an 85% and 80% syndiotactic content for polymerization performed respectively in benzene and in dichloromethane (Table 1).

The crystallinity content of the polystyrene obtained were determined by extraction in boiling butanone. The polymerization in benzene gave an insoluble polymer fraction indicating the presence of a syndiotactic polystyrene portion. Figure 4, shows the FTIR-spectra of the butanone-insoluble polystyrene with absortion signals at 1070 and 1217 cm^{-1} which are associated with the syndiotactic configuration and to the α-conformation respectivelly [11a-c]. The intensity of these bands are in concordance with the amount of crystalline polystyrene portion.

Table 1. Styrene polymerization initiated by Ph_2Zn-H_2O soluble and insoluble fractions (after 13 days at 60°C[a]).

	BENZENE						DICHLOROMETHANE					
System	Convn[b]	M_v[c]	M_w/M_n[d]	Tacticity[e]			Convn[b]	M_v[c]	M_w/M_n[d]	Tacticity[e]		
	%	$x10^{-5}$		ii	is	ss	%	$x10^{-5}$		ii	is	ss
Ph_2Zn-alone	10.7	3.77	2.97	5	11	84	14.7	0.41	1.40	9	14	77
Ph_2Zn-H_2O soluble	12.9	10.71	5.25	5	11	85	33.8	0.25	1.36	10	14	76
Ph_2Zn-H_2O insoluble	7.8	36.53	8.06	5	11	85	12.4	8.31	13.75	6	13	81
Ph_2Zn-H_2O complete	11.4	8.93	3.08	4	10	86	73.0	1.89	4.59	6	12	82
none	9.7	12.90	1.75	4	9	87	0.7	0.28	2.67	n.d.[f]		

a) $[Ph_2Zn] = 0.022$ mol/L; styrene/Ph_2Zn = 200 mol/m l; H_2O/Ph_2Zn = 0.75 mol/mol.

b) Based on initial St.

c) From intrinsic viscosity, chloroform, 25°C.

d) From SEC, THF, 25°C.

e) Calculated from H-NMR spectra.

f) n.d. = not determined.

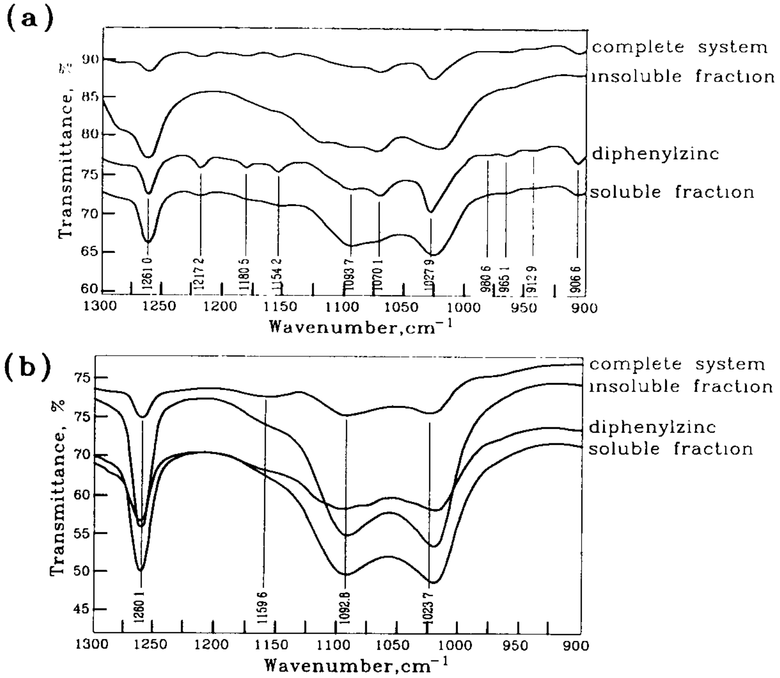

Figure 4. FTIR spectra of polystyrene obtained using, as indicated, various initiator systems at 60°C, a) in benzene, b) in dichloromethane.

CONCLUSIONS

From our results we can conclude that for the Ph_2Zn-H_2O systems under the experimental conditions employed, the nature and conversion are not affected by stirring. This finding can be attributed to the fact that soluble components give the more active species, independent of the solvent used i.e., benzene or dichloromethane.

The Ph_2Zn-H_2O insoluble fraction, produce longer polystyrene chains and broader MWD than those obtained with the Ph_2Zn-H_2O soluble fraction.

Analysis of chain configuration distribution shows little variation due to the nature of the initiator system employed. In benzene there was a larger syndiotactic predominance than with dichloromethane.

According to the butanone insoluble fraction, the polystyrene obtained with dichloromethane did not show cristallinity while those obtained using benzene show a low percentage of crystallinity.

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