isomerization of photochromic molecules within restricted locations and that these molecules are only a small fraction of the total concentration of photochromic compound present. The photomechanical response can therefore be thought of as being produced by molecules occupying certain 'sites' within the polymer matrix.

Further evidence in support of this hypothesis was obtained from a computer curve fitting exercise. This produced an equation which closely describes the photomechanical response occurring during dark recovery of the polystyrene system. This equation is:

$$\mathrm{Log}_e\,(\mathrm{stress}) = K_\alpha\left(\frac{1}{\mathrm{time}}\right) - K_\beta\left(\frac{1}{\mathrm{time}}\right)^2 + K_\gamma$$

The lines drawn in *Figure 3* are described by the equation shown above. The constants calculated for each line are tabulated in *Table 1*.

The implication of this equation is that the curves obtained are the resultant of two opposing logarithmic functions. It is therefore suggested that the observed contraction with polystyrene is the net result of a larger contraction opposed by a smaller and more rapid expansion.

Table 1 5% w/w Photochrome in polystyrene dark recovery

Initial stress (grams)	K_α	K_β	K_γ
4	−1.43	−0.572	1.49
7	−1.63	−0.815	1.92
9	−1.69	−0.845	2.14
14	−1.31	−0.786	2.62
19	−0.916	−0.549	2.92
30	−0.540	−0.324	3.66
45	−0.429	−0.257	3.78

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Effect of additives and solvents on polymerization of styrene using $CuCl_2$+$AlEt_2Cl$ catalyst system

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The effect of additives and solvents is reported on the rate of polymerization of styrene by the catalyst system ($CuCl_2$+$AlEt_2Cl$). The electron donating additives triphenylphosphine, anisole and diphenyl ether decreases the rate but hydroquinone has no effect on the rate. Increasing dielectric constant of solvents decreases the percentage conversion but chlorinated hydrocarbons do not obey the trend.

Keywords Insertion; polymerization; styrene; additives; solvents; catalyst

INTRODUCTION

We have reported in our previous communications[1-3] the use of Ziegler–Natta catalyst systems with copper-chloride as a transition metal component. A detailed study of the effect of electron donors and solvents was reported for the system $CuCl_2 + AlEt_2Br$[2]. In this communication we present some observations made on $CuCl_2 + AlEt_2Cl$ catalyst system.

EXPERIMENTAL

Purification of monomer, solvent, additives and the polymerization procedure are the same as reported earlier[2].

The following reaction conditions were used: $[CuCl_2] = 0.01$ mol l^{-1} [Al]:[Cu] = 1.6, ageing time = 4.0 h, styrene = 1.743 mol l^{-1}, total volume = 25.0 ml, temperature = 30°C.

RESULTS AND DISCUSSION

Effect of various additives and solvents are summarized in *Tables 1* and *2*.

It can be seen that with increasing amount of triphenylphosphine (PPh_3) the catalyst activity decreases. This has been already observed in case of

Table 1 Effect of additives on system $CuCl_2/AlEt_2Cl$ for styrene polymerization

Additive	[Additive] mol l^{-1}	Rate (R_p) mol l^{-1}	Reaction time (hours)
–	–	37.57×10^{-5}	00.5
–	–	1.08×10^{-5}	40.0
PPh_3	2×10^{-3}	2.95×10^{-5}	08.0
	4×10^{-3}	1.30×10^{-5}	08.0
	6×10^{-3}	1.43×10^{-5}	08.0
	8×10^{-3}	1.91×10^{-5}	08.0
	100×10^{-3}	0.04×10^{-5}	08.0
Anisole	18×10^{-3}	4.599×10^{-6}	30.0
	72×10^{-3}	0.498×10^{-6}	30.0
	144×10^{-3}	1.680×10^{-6}	30.00
	180×10^{-3}	1.460×10^{-6}	30.0
DPE	12×10^{-3}	1.43×10^{-5}	40.0
	50×10^{-3}	1.38×10^{-5}	40.0
	99×10^{-3}	1.25×10^{-5}	40.0
	120×10^{-3}	1.45×10^{-5}	40.0
Hydroquinone	6×10^{-4}	38.5×10^{-5}	00.5

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Table 2 Effect of solvents on $CuCl_2/AlEt_2Cl$ catalyst system for styrene polymerization

Solvent	ϵ	% Conversion	Reaction time (hours)
n-Hexane	1.89	38.8	0.5
Benzene	2.28	43.0	0.5
Toluene	2.37	36.5	0.5
Bromobenzene	5.40	29.7	0.5
Chlorobenzene	5.62	24.4	0.5
$C_2H_4Cl_2$	10.36	47.9	0.5

$CuCl_2 + AlEt_2Br$ catalyst system for the polymerization of styrene[2]. The rate does not become constant after adding the specific amount of PPh_3 as was seen previously[2]. Hence the conclusion can be drawn, that PPh_3 forms a complex with copper chloride and inhibits the polymerization.

Ethers as additives were studied in detail by Cunningham[4] and Gippin[5]. Different products have been identified in the reactions of ether with Ziegler–Natta type catalysts. The effect of these products mainly govern the reaction rate. The efect of anisole can be explained on the basis of its reaction with $AlEt_2Cl$ which may give various products which retard the polymerization. Gippin[6] observed no change in the rate at optimum catalyst ratio when diphenylether (DPE) was added as an additive. The present study also confirms the same observations.

Pyridine and triethylamine totally inhibit the polymerization as in the case of $CuCl_2 + AlEt_2Br$ system[2]. Hydroquinone also did not effect the rate indicating absence of free radicals.

As can be seen from *Table 2*, the results obtained in solvents of varying dielectric constant indicate a decrease in conversion with increase in dielectric constant. The halogenated aliphatic solvents again indicate higher yields than expected on the basis of their dielectric constants. This has also been observed and explained earlier[2].

CONCLUSIONS

Above studies indicate that the mechanism of polymerization of styrene by $CuCl_2 + AlEt_2Cl$ catalyst system is of the anionic coordinated type, though the activation energy is low.

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