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Effect of Additives and Solvents on Polymerization of Styrene by $CuCl_2 + AlEt_2Br$ Catalyst System

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Summary

Effect of electron-donor additives, solvents of varying dielectric constants, and halogenated aliphatic solvents are studied for the polymerization activity of the catalyst system $CuCl_2+AlEt_2Br$.

Results obtained can be summarized as follows:

1) Radical polymerization is completely absent.
2) Tetrahydrofuran and triphenylphosphine decrease the activity of the catalyst.
3) Anisole decreases the activity in small amounts and activates the catalyst when present in large quantities.
4) Triethylamine and pyridine inhibit polymerization.
5) Activity of the catalyst decreases with increase in the dielectric constant of the polymerization medium.
6) Aliphatic halogenated solvents react with the catalyst to increase the catalytic activity.

Introduction

Activity and stereospecificity of the Ziegler-Natta type catalyst systems are modified by addition of a third-component. The most commonly known additives are electron-pair donors. These affect the catalyst activity by reacting either with catalyst or co-catalyst and in many cases with both components. In literature both enhancement and lowering of the catalyst activity is reported, for various catalysts when a third-component is added.

Effect of solvents on Ziegler-Natta catalyst system is not widely studied. The dielectric constant of the polymerization medium is shown to play

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an important role, in determining activity of the catalyst.

In this communication, effect of hydroquinone, tetrahydrofuran (THF), triphenylphosphine (PPh_3), anisole (MPE), triethylamine (TEA) and pyridine (Py) as additives is reported for polymerization of styrene. Benzene, toluene, chloro and bromobenzene are used as solvents of varying dielectric constant. Methylene and ethylene dichloride are used as aliphatic halogenated solvents.

Experimental

All solvents and additives were purified by following the standard procedures used in study of the Ziegler-Natta catalyst system. PPh_3 was AR grade and was used as received.

All the catalyst preparations and polymerizations were carried out at a temperature $30 \pm 0.05^\circ C$, [Al]/[Cu] ratio of 2.5, an aging time of 4 hrs was used for the studies reported. These reaction conditions being reported optimum in previous communication (PANDYA, 1980). Additives were added after the aging time and allowed to react with the catalyst for further 10 minutes. To obtain maximum conversion and better contrast, 0.005 moles/lit of the catalyst was used, since it was shown that conversion is inversly proportional to the catalyst concentration. In case of various solvents, the catalyst was prepared in particular solvents using 0.01 moles/lit of the latter and the conditions for polymerization are as reported above.

Results and Discussions

Effect of Additives

It can be seen from fig.1 that THF and PPh_3 decrease the catalyst activity. THF and PPh_3 are found to form a complex with copper-compounds. This may be the main cause of the observed decrease. THF also reacts with diethylaluminum bromide and hence the decrease in case of THF is gradual compared to sharp decrease in case of PPh_3.

Results obtained with MPE are presented in Table I. CUNNINGHAM (1968) and GIPPIN (1970) studied the effect of ethers on the Ziegler-Natta catalyst system and attributed the results to the various products formed from reaction of organoaluminum compound and the ether. The observed decrease and increase can be said due to the various products formed, which can have retarding as well as enhancing capacity depending on concentration of anisole.

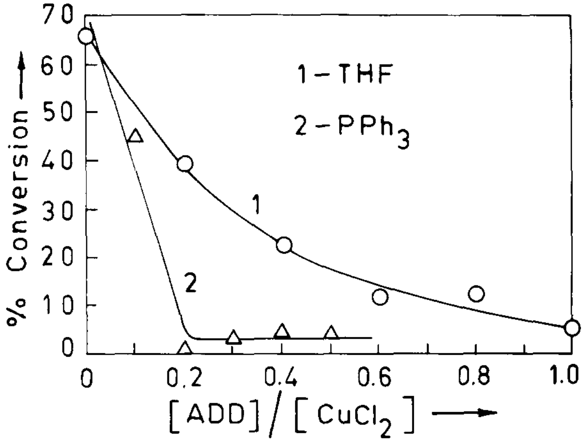

Fig.1 Effect of THF and PPh3 on the catalyst activity. Reaction time 24 hrs.

TABLE I

[MPE]$^+$	% Conversion
0.000	66.14
0.040	oily liq.
0.055	traces
0.073	02.61
0.090	84.46

+ Concentration in moles/lit. Reaction time 24 hrs.

TEA and Py are reported to form tight complexes with copper salts(WENDLANDT, 1965). The inhibition of polymerization by these compounds may be due to poisoning of the catalyst by complex formation.

To check whether the polymerizations proceed by free-radicals that might be produced during catalyst formation, hydroquinone containing monomer was polymerized.No change in the conversion shows that the free-radical propagation is absent.

Effect of Solvents

GIPPIN(1966) studied the effect of dielectric constant on the polymerization of butadiene with Co-octoate/ $AlEt_2Cl$ / H_2O catalyst.LIVSHITSIN(1977) studied effect of changing dielectric constant of catalyst solution with varying compositions of the components. Their results indicate that the activity of catalyst system decreases with increase in dielectric constant. This is in accordance with the

Hildebrandt's theory for the effect of dielectric constant on reaction rate. We have obtained similar results with the present system which are presented in Table II.

Methylene and ethylene dichloride when used as solvents gave higher conversions than expected on the basis of their dielectric constant. This can be said mainly due to the reaction of these solvents with catalytic complex.

TABLE II

Solvent	ε	% conversion[+]
n-Hexane	01.89	53.64
Benzene	02.28	32.30
Toluene	02.37	18.50
Bromobenzene	05.40	05.62
Chlorobenzene	05.62	06.89
Methylene-dichloride	10.00	38.78
Ethylene-dichloride	10.36	56.07

[+] Reaction time 30 minutes.

When different compositions of n-hexane and methylene dichloride were used, first a decrease in activity and later an increase was observed(Fig.2).

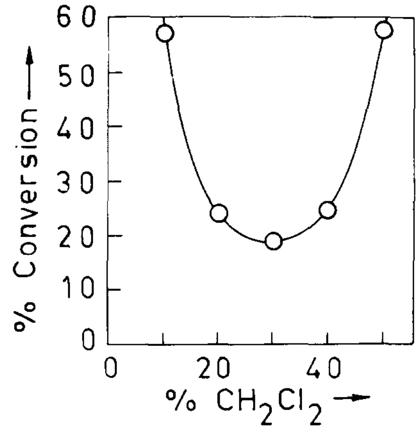

Fig.2 Effect of mixed solvents
Reaction time 30 minutes.

This shows that beyond a specific amount of methylene dichloride(30 % in our studies) the catalyst composition may change.

Conclusions

Electron-donor additives complex with the catalyst system to retard or inhibit the polymerization, depending on their reaction with catalyst components. It was found by using THF, PPh_3, MPE, TEA and Py as additives that the active center for the polymerization is the transition metal-carbon bond. The mechanism of polymerization is reported previously as co-ordinated type. Effect of additives show that this should be bimetallic consisting of Cu and Al atoms.

Effect of solvents, is to decrease the activity with increase in dielectric constant, which is in agreement with reported observations in the literature.

It can be said that the catalyst system $CuCl_2$ + $AlEt_2Br$ polymerizes styrene by a co-ordinated bimetallic mechanism.

References

CUNNINGHAM, R.E. and DOVE, R.A. : J. Polymer Sci., A1, 6, 1751 (1968)
GIPPIN, M. : Rubber Chem. Technol., 39, 508 (1966)
GIPPIN, M. : J. Appl. Polymer Sci., 14, 1807 (1970)
LIVSHITSIN, A.S., KOPYLOV, M.B., KORO'LKOVA, Z.S. and ESTRAIN, A.S. : Zh. Prikl. Khim. (Leningrad) 50, 693 (1977)
PANDYA, M.V., DESHPANDE, D.D. and DESAI, N.M. : Polymer Bulletin in press
WENDLANDT, W.W. and ALI, S.I. : Anorg. Allgem. Chem. 337, 6 (1965)

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