Polymer Bulletin 9, 349–354 (1983)

Polymer Bulletin

Polymerization of Benzyl Halides Catalyzed by VIB Metal Carbonyls

Christos P. Tsonis

Chemistry Department, University of Petroleum & Minerals, Dhahran, Saudi Arabia

SUMMARY

The group VIB metal carbonyls were found to promote the polycondensation of benzyl halides when induced by heat. Their catalytic activity decreases in the order: Mo >> W > Cr. Phosphine ligands attached to the metal poison the catalytic activity of the system. Species such as $(CO)_3M(PhCH_2^+)Cl^-$ are considered to be active in promoting polymerization. The final polybenzyls have a branched, polycondensed structure of moderate molecular weight.

INTRODUCTION

Arene metal tricarbonyls have been extensively investigated for their catalytic properties as hydrogenating agents of olefins[1], or their ability to polymerize alkenes[2] and alkynes[3,4]. Studies have also shown that $ArMo(CO)_3$(Ar:toluene[5], polystyrene[6]) are effective homogeneous catalysts for Friedel-Crafts alkylation and acylation reactions and that the tricarbonyl-molybdenum group remains loosely attached to the arene during the course of catalysis. In a related report it was found[7] in this laboratory that arene chromium tricarbonyls were effective homogeneous catalysts for the polymerization of benzyl chloride when they are thermally activated. The catalytic activity on polymerization and induction period were controlled by the nature of the arene attached to the metal.

Since the arene ligand plays an important role on the Friedel-Crafts reactions catalyzed by arene metal tricarbonyls, it was of interest to examine the effect of replacing the arene group by other ligands on the catalytic properties of group VIB metal carbonyls. Therefore, in the present study the polymerization of benzyl halides and their substituted derivatives was investigated using several group VIB metal carbonyls and derivatives as potential homogeneous catalysts.

EXPERIMENTAL

Benzyl chloride and benzyl bromide, purchased from Fluka Chemical Company, were distilled before use. Also obtained from Fluka in highest available purity and used as received were 2-chloroethylbenzene; chloromethyldurene and benzyl alcohol. Molybdenum, chromium and tungsten hexacarbonyls were purchased from Pressure Chemical Company and sublimed before use. Metal complexes of triphenylphosphine molybdenum pentacarbonyl, cis-bis(triphenylphosphine)molybdenum tetracarbonyl, tris (triphenylphosphine) molybdenum tricarbonyl, and tris (acetonitrile) molybdenum tricarbonyl were all prepared from literature methods.

All polymerization reactions were performed in the same manner as described previously[7], except the work up of the polycondensation of chloromethyldurene was different and was carried out as follows. The reaction product was stirred vigorously with hexane to remove the unreacted monomer and the insoluble material was recrystallized from ethanol to give a beige crystalline product which melted at 260-262°C and had molecular weight of 890.

Infrared spectra of polybenzyls were recorded on a Perkin-Elmer model 180 IR spectrophotometer. The molecular weights were determined by Vapor Pressure Osmometry with the exception of polychloromethyldurene which was determined from end group chlorine analysis.

RESULTS AND DISCUSSION

After it was established that VIB metal carbonyls were effective in polymerizing benzyl halides, studies were carried out to determine optimum conditions. Tables I and II show that thermal activation of the catalyst is required. The minimum temperature needed for $Mo(CO)_6$ to possess catalytic activity for the polymerization of benzyl chloride is 60°C, whereas $Cr(CO)_6$ and $W(CO)_6$ require temperatures higher than 100°C. Benzyl bromide is polymerized under milder conditions than benzyl chloride. The catalytic effectiveness for the polymerization of benzyl halides decreases in activity in the order: Mo $>>$ W $>$ Cr.

In general, the percent conversions increased with increasing reaction temperature. The polymer yields and the number average molecular weights increased with conversion but at high temperatures both yield and molecular weight drop off significantly. Apparently, the side reactions become predominant and compete effectively with the growth of the polymer chains. All polybenzyls were insoluble in aliphatic hydrocarbons and alcohols. In other solvents such as methylene chloride, chloroform, chlorobenzene, benzene and toluene solubility was good to moderate. Their texture and color were different from one sample to another and all softened in the 60-80° range.

A number of substituted benzyl halide derivatives were also investigated using $Mo(CO)_6$ at 100°C without solvent. The monomers benzyl chloride, benzyl bromide and 2-methylbenzyl chloride gave branched, amorphous, low melting polybenzyls. The chloromethyldurene, where all except the para position are blocked with methyl substituents, produced a high melting product with very low D.P.($\sim$ 4). This probably is attributed to steric hindrance or due to the fact that the growing chains become insoluble in the molten monomer and precipitate out of solution before having a chance to grow further. The two monomers, 2-chloroethylbenzene and benzyl alcohol were inert to polymerization indicating that the metal carbonyls are more selective less reactive than the conventional Lewis acid catalysts of the $AlCl_3$ type.

TABLE I

Polycondensation of Benzyl Chloride by $M(CO)_6$(M = Cr, Mo,W) Catalysts[a]

Metal	Temp (°C)	Time	Conversion %	Yield %	Color	$\overline{Mn}$
Cr	100	70 hr	4.6	1.4	Grey-yellow	-
"	120	45 hr	66.3	57.2	Brown-yellow	7000
"	140	50 min	78.6	13.8	Orange-yellow	4600
Mo	50	102 hr	6.3	4.0	Grey	-
"	60	65 hr	39.8	32.1	Light-green	3200
"	75	18 hr	46.4	37.1	Light-green	3450
"	85	10 hr	54.5	40.2	Lemon	4380
"	100	3 hr	61.8	38.8	Green-yellow	5000
"	120	30 min	68.7	26.7	Green-beige	2800
"	140	10 Min	82.6	17.0	Light-yellow	1800
W	100	48 hr	9.2	6.4	Light-green	-
"	120	24 hr	70.7	66.3	Beige	5200
"	140	40 min	85.4	54.8	Light-yellow	4100

[a] Conditions: 160 mmoles $PhCH_2Cl$ and 1.0 mmole catalyst.

Monosubstituted benzenes generally show two strong absorption bands in the 675-700 cm^{-1} and 725-775 cm^{-1} regions, whereas para-substituted derivatives show a strong peak in the 800-860 cm^{-1}range. Model[8] compounds of O-, m-, and p-dibenzylbenzene give infrared peaks at 1050, 1090 and 1023 cm^{-1}, which are specific for ortho, meta and para dibenzylbenzene isomers respectively. The band at 1032 cm^{-1} is characteristic of monosubstituted benzyl pendant groups. The polybenzyls isolated in this work showed infrared absorption bands at 1019, 1028, 1070 and 1100 cm^{-1}, indicating that their backbone structure is not linear but a great deal of branching has occurred.

To obtain information and insight into the mechanism by which polymerization occurs several experiments were performed. In one experiment variations in the structure of the catalyst were made by replacing carbon monoxide with various ligands. The results of this study(Table III) indicate that substituent variation on the molybdenum metal by phosphorous compounds has a detrimental effect on the polymerization of benzyl chloride.

TABLE II

Polycondensation of Benzyl Bromide by $M(CO)_6$(M = Cr, Mo,W) Catalysts[a]

Metal	Temp (^{o}C)	Time (hrs)	Yield (%)	Color	$\overline{Mn}$
Cr	80	46	5.4	Grey-yellow	-
"	100	38	38.5	Yellow-green	4300
"	120	7	47.1	Yellow-brown	4100
Mo	50	72	7.6	Beige	-
"	60	64	71.2	beige	4200
"	80	9	40.5	Beige	3800
"	100	2	46.4	Light-green	4600
"	120	1	54.9	Yellow	3100
W	60	66	2.6	Green	-
"	80	6	67,3	Green-yellow	5200
"	100	3	74.5	Orange	6000
"	120	2	79.7	Yellow	4800

[a] Conditions: 168 mmoles $PhCH_2Br$ and 1.0 mmole catalyst.

TABLE III

Effect of Varying Ligands of Catalyst on the Polycondensation of Benzyl Chloride[a]

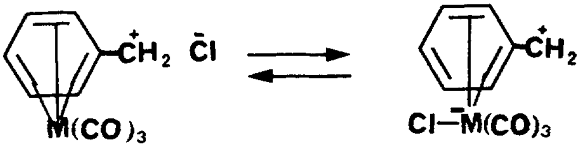
Catalyst	Time(hrs)	Conversion(%)	Yield(%)
$Mo(CO)_6$	3	61.8	38.8
$Mo(CO)_3(CH_3CN)_3$	24	66.4	48.7
$Mo(CO)_3(PPh_3)$	24	0	-
cis-$Mo(CO)_4(PPh_3)_2$	24	0	-
$Mo(CO)_3(PPh_3)_3$	24	0	-

[a] Conditions: 160 mmoles $PhCH_2Cl$; 1.0 mmole catalyst; 100°C; no solvent

The $Mo(CO)_3(CH_3CN)_3$ was an active catalyst or catalyst precursor for the polymerization of benzyl chloride. Acetonitrile is a labile ligand and can be easily dissociate to provide metal vacant sites for catalysis.

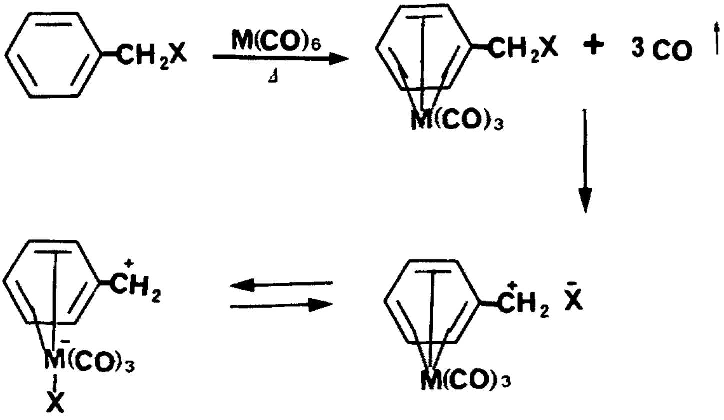
When a mixture of benzyl chloride and $Mo(CO)_6$ was heated while a stream of carbon monoxide was passed through the solution the rate of the polymerization was supressed considerably. No reaction took place under carbon monoxide pressure.

From these experiments, it may be concluded that although $M(CO)_6$ is introduced in the reaction mixture, it is the $(PhCH_2Cl)M(CO)_3$ which acts as the initiator in the polymerization. Group VIB metal carbonyls are known[9] to be thermally converted to $(arene)M(CO)_3$ in the presence of aromatic solvents. The benzyl halide metal tricarbonyl can exist in the following form:

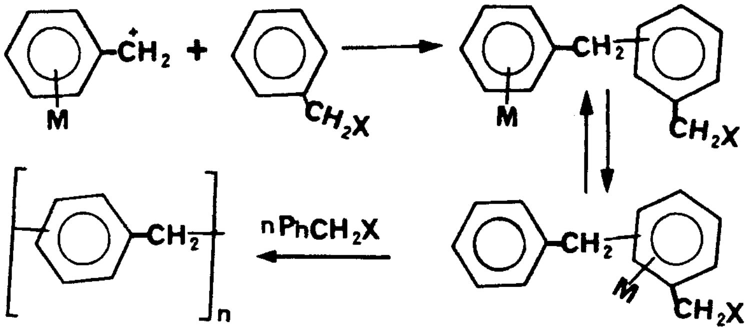


Reports have demonstrated[10] that complexed benzyl carbonium ions generated in solution are several times more stable than uncomplexed benzyl carbonium ions. In fact, the attachment of the $M(CO)_3$ moiety to the benzyl ring stabilizes the benzyl carbonium ion intermediate by back donation of electron density from the metal d-orbital to the non-bonding π-orbital of the benzyl cation ligand[11]. Furthermore, the benzyl carbonium ion may be stabilized via a π-benzyl metal complex, a benzologue of the π-alkyl ligand[12].

Thus, a plausible mechanistic path to account for the catalyzed polycondensation of benzyl halides by group VIB metal carbonyls may be as follows:



The complexed benzyl carbonium ion may then be attacked by a benzyl halide monomer. Propagation can occur via metal ring exchange[13], followed by chain growth:



For the sake of simplication, the metal ligands are not shown in the above scheme.

ACKNOWLEDGEMENT

The author is grateful to the University of Petroleum and Minerals for financial support of this project. Document CY36.

REFERENCES

1. CIAS, M. and REJOAN, A., Inorg. Chim. Acta, 4, 509 (1970)
2. KATAPINKA, G.L. German Patent, 1,949, 574 (1970)
3. WOON, P.S. and FARONA, M.F., J.Polym. Sci. Polym. Chem. Edn. 12, 1749 (1974)
4. SVANDIZE, L.M. et al, Vysokomol. Soedin, Ser. B, 21, 455 (1979)
5. WHITE, J.F. and FARONA, M.F., J. Organometal. Chem., Chem.,63, 329(1973)
6. TSONIS, C.P. and FARONA, M.F., J.Organometal. Chem. 114, 293 (1976)
7. TSONIS, C.P. and HASAN, M.V., Polymer, in press.
8. KUO, and LENZ, R.W., J. Polym. Sci.Polym. Chem. Edn., 14,2749 (1976).
9. NICHOLLS, B. and WHITING, M.F., Proc. Chem. Soc. (London), 152 (1958)
10. HOLMES, J.D., JONES, D.A.K. and PETTIT, R., J. Organometal Chem., 4, 324 (1965)
11. CLACK,D.W. and KANE-MAGVIRE, L.A.P., J. Organometal Chem., 145, 201 (1978)
12. COTTON,F.A. and LAPRADE, M.D., J. Amer. Chem. Soc., 90, 5418 (1968)
13. WERNER, H. and PRINZ, R., J. Organometal Chem., 5, 79 (1966).

Received November 15, 1982, accepted after Revision January 8, 1983

S