Polymer Bulletin 33, 295–300 (1994)

Polymer Bulletin

The polymerization of propargyl halides (Cl, Br) using $M(CO)_5PPh_3/R_xAlCl_{3-x}$ (M=Mo,W) as catalysts

Michael G. Siskos*, Georgia Kyriakakou, and Antonios K. Zarkadis

University of Ioannina, Department of Chemistry, Section of Organic Chemistry and Biochemistry, 45110 Ioannina, Greece

SUMMARY

Propargylchloride (PCl) and propargylbromide (PBr) were polymerized in good yields using $M(CO)_5PPh_3/R_xAlCl_{3-x}$ as catalysts (M=W, Mo). Mo was found to be more effective than W. The presence of chlorine atoms in co-catalyst was important for the activation of the catalyst. The obtained polymers were coloured, insoluble in all organic solvents and stable until 150°C. From their IR and ESR spectra is concluded that the polymers have highly conjugated structures. The oligomeric products were constituted mainly from cyclotrimers. In the case of Mo-catalyst only 1,2,4-cyclotrimer was obtained; a mixure of 1,2,4 and 1,3,5-derivatives were formed using W-catalysts.

INTRODUCTION

In recent years the polymerization of acetylene and its derivatives has attracted a great attention due to the very interesting physical properties and potential technological applications of the corresponding polymers (1). A great number of catalysts were used for the polymerization: eg. ionic, radical, Ziegler-Natta, whereas quite recently metathesis catalysts based on transition metals of the group VI (Mo,W) were found to be more effective (2-4). It is also known that the combination of the zerovalent complexes of the type $M(CO)_5L$ (M=Mo,W, L = PR_3) with R_xAlCl_{3-x} Lewis acids affords active catalysts either for the metathesis of acyclic olefines or the polymerization of cyclic ones (5-9). However, the above catalytic systems have not been used for acetylenes polymerization.

The polymerization of PCl and PBr and the physical properties of the resulting polymers have been studied by several workers (10-17). In all cases the polymers were black and brown powders and completely insoluble in organic solvents.

The main purpose of the present paper is to investigate the polymerization activity of the $M(CO)_5PPh_3/R_xAlCl_{3-x}$ (M=W, Mo) catalytic system with PCl and PBr as monomers, and to examine the influence of individual reaction parameters (catalyst compositions, monomer concenration, temperature, solvent etc.) on these polymerizations.

EXPERIMENTAL

Materials: PCl and PBr (Aldrich) were distilled under argon. $M(CO)_5PPh_3$ were prepa-

*Corresponding author

red and characterized by standard literature procedure (18). Organoaluminium compounds were purchased from Aldrich Chemicals and used without further purification. All solvents were purified by distillation under argon from drying agent (CaH_2 or Na).

Polymerization: The polymerizations were carried out in Schlenk glassware under dry deoxygenated argon. In a typical experiment 58.6 mg (0.10 mmol) of $W(CO)_5PPh_3$ was added to the flask, followed by injection of 7.97 ml of chlorobenzene and 0.66 ml (0.60 mmol) of $Et_3Al_2Cl_3$ (0.91 M solution in hexane). The clear homogeneous solution was stirred for 3 hours at 30°C and gradually turned light red. After injection of 1.37 ml (20 mmol) of $Cl\text{-}CH_2C{\equiv}CH$ the reaction mixure instantly turned dark brown and became viscous. The polymer was precipitated with exess methanol, filtered, washed with cold methanol and hexane and dried under vacuum to yield 0.91 g (65 %) of a brown amorphous solid. The methanolic solution was concentrated on a rotary evaporator, dissolved in $CHCl_3$ and extracted with 10 % HCl, dilute $NaHCO_3$ solution and finally with distilled water. The organic layer was dried over $MgSO_4$ and the solvent was evaporated leaving the oligomeric product.

Measurements: ^{1}H-NMR Spectra were obtained on a Varian EM-390A spectrometer in CCl_4 (10%). Infrared spectra were recorded on a Perkin-Elmer 783B spectrometer. Differential thermogravimetric analyses (DTG) were carried out with a Chyo Balance Co. RDA3 thermal analyser at a heating rate of 10° C/min under nitrogen atmosphere. ESR measurments were performed on a Varian E-109 spectrometer at room temperature. The g values were estimated using 1,1-diphenyl-2-picrylhydrazyl (DPPH) as a reference.

RESULTS AND DISCUSSION

The catalytic system: Influence of the reaction parameters.

The polymerization of PCl and PBr by $M(CO)_5PPh_3/R_xAlCl_{3-x}$ catalytic system is belived to follow a metathesis mechanism through metal carbene complexes (8,19,20).

TABLE 1: The Influence of the [W]/[Al] Ratio and Temperature on the Polymer Yield of PCl.

No	Catalyst	Cocatalyst	[W]/[Al]	Temperature	Polymer Yield (%)
1	$W(CO)_5PPh_3$	$Et_3Al_2Cl_3$	1/1	30	trace
2	#	#	1/3	30	6
3	#	#	1/6	30	65
4	#	#	1/12	30	87*
5	#	—	1/0	30	—
6	—	#	0/6	30	—
7	#	#	1/6	0	29
8	#	#	1/6	60	78*

[W] = 10^{-2} mol/l, [PCl]/[W] = 200/1, Solvent: Chlorobenzene

* The mixture starts to heterogenize

Table 1 (exp. 1-6) shows the results for the polymerization of PCl in various catalyst/co-catalyst ratios. It was found that the polymer yield steadily increases with the concentration of the organoaluminium compound. The maximum polymer yield was obtained when the $W(CO)_5PPh_3$ to $Et_3Al_2Cl_3$ molar ratio was $^1/_{12}$, but at this ratio a polymer precipitate was started to appear from the reaction mixure (so we choosed the lower ratio 1/6 for the other experiments). At this point we must mention that there is a discrepancy to the results of the metathesis reactions where the best ratio was found to be 1/4. This fact could be attributed to the greater concentration of the $Et_3Al_2Cl_3$ which exhibit high catalytic activity (Lewis acid) for the addition of alkylhalides to olefines. Consequently, this fact is responsible for polymer crosslinking through intra- and intermolecular proccesses (16). It is also useful to note that $M(CO)_5PPh_3$ and $Et_3Al_2Cl_3$ alone are inactive as polymerization catalysts, so that cooperation of both is required.

From table 1 (exp. 3,7,8) is concluded that the polymer yield increases with the polymerization temperature, but at 6O°C the homogeneous solution starts to became heterogeneous.

Table 2 shows the effect of the monomer concentration and the influence of metallo-carbonyl compound and various organoaluminium co-catalysts by the polymerization of PBr. The $Mo(CO)_5PPh_3$ complex was found to be more reactive than the $W(CO)_5PPh_3$. It is also obvious that the polymer yield is increased according to the co-catalyst acitity (increasing the number of chlorine atoms). In the case of Et_3Al no polymer was obtained.

TABLE 2: The Influence of the Monomer Concentration, Organometallic Compound and R_XAlCl_{3-X} on the Polymer Yield of PBr.

No	Catalyst	Cocatalyst	[M]/[W]	Polymer Yield (%)
1	$W(CO)_5PPh_3$	$Et_3Al_2Cl_3$	50/1	64
2	#	#	200/1	59
3	#	#	500/1	24
4	$Mo(CO)_5PPh_3$	#	200/1	73
5	$W(CO)_5PPh_3$	Et_2AlCl	200/1	35
6	#	Et_3Al	200/1	Trace

[W] = 10^{-2} mol/l; [W] /[Al] = 1/6,; Temperature: 30°C; Solvent: Chlorobenzene

TABLE 3. The Influence of Solvent on the Polymer Yield of PBr.

No	Solvent	Polymer Yield (%)
1	Chlorobenzene	59
2	1,2-Dichloroethane	37
3	Dichloromethane	75
4	Toluene	Oligomer
5	Cyclohexane*	48

[PBr] = 2 mol/l; Catalyst = $W(CO)_5PPh_3$; Co-catalyst = $Et_3Al_2Cl_3$; [W] = 10^{-2} mol/l; [W]/[Al] = 1/6; Temperature 30°C; * Polymerization time: 10 min

Table 3 shows the solvent effect on the polymerization of PBr by $W(CO)_5PPh_3$ /$Et_3Al_2Cl_3$. The polymerizations were performed in various organic solvents, giving always good yields. Aromatic and chlorinated hydrocarbon solvents were especially good for this polymerization. In the case of toluene only a oligomeric product was obtained.

Polymer Characterization

The resulting poly(PCl) and poly(PBr) were completely insoluble in common organic solvents. The insolubility of the above polymers, as already mentioned, can be attributed to the polymer crosslinking through an inter- and intramolecular addition proccess of the side group CH_2-X into resulting conjugated double bonds, following by a dehydrohalogenation reaction (16). The poly(PCl) and poly(PBr) were brown and dark brown powders respectively, regardless of the polymerization conditions.

The infrared spectra of poly(PCl) and poly(PBr) showed a broad absoption band centered at 1605 cm^{-1} [poly(PCl)] and 1600 cm^{-1} [poly(PBr)] due to the stretching vibration of the conjugated double bonds. The spectra are also characterized by absorption bands at 3020 cm^{-1}(=C–H streching); 2970, 2930, 2870 cm^{-1}(–C–H streching); 1450 cm^{-1} (CH_2 deformation) for poly(PCl) and at 3015, 2960, 2930, 2870, 1440 for poly(PBr) respectevely. Also bands at 740 cm^{-1} and 1025 cm^{-1} appeared in both polymers are attributed to the out-of-plane deformation vibrations, characteristic for a cis and trans structure. It should be also noted that the acetylene (–C≡C–) and the carbon-hydrogen (≡C–H) streching vibrations of the monomers are absent in the spectra of the polymers.

Thermogravimetric analyses of the poly(PCl) and poly(PBr) reveal that they are stable until 150°C. A notable weight loss was observed in the range of 150-200°C which gradually increased with the temperature.

All the obtained polymers are paramagnetic as one would expect for polyconjugated systems (21-22). The ESR spectra are consisted from a symmetrical single line with peak-to-peak width (ΔH_{pp}) in the range of 8.5-10.7 G for poly(PBr) and 9.0-11.7 G for poly(PCl). The g values were measured and found to be in the range of 2.0027-2.0034 in both polymers. Both linewith and g-value are characteristic for polyconjugated systems (23,24).

Oligomer Characterization

The oligomeric products were constituted mainly from cyclotrimers. The ^{1}H-NMR spectra (fig.1a,b,c) show that these cyclotimers are the 1,2,4- and 1,3,5-trisubstituted benzenes(25,26) [scheme I(A)].

In the case of Mo catalysts the 1,2,4- trisubstituted product was obtained almost exclusively. This cyclotrimer exhibit signals at δ 4.45 and 4.65 ppm, which were assigned to the methylene protons (CH_2-X) at the 4- and 1,2-position of the benzene ring. The aromatic protons appear at 7.35 ppm (5,6 position) and 7.4 ppm (3 position). With W catalysts a mixure of the 1,2,4- and 1,3,5-cyclotrimers were obtained, something which is concluded from the increase of the peak area at 7.35 and 4.45 ppm.

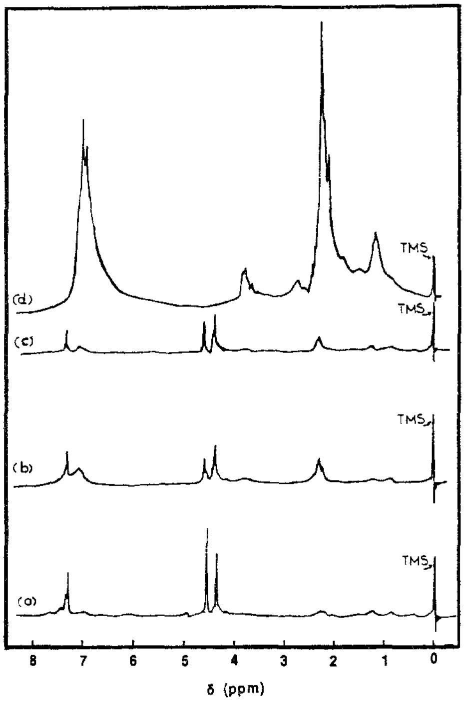
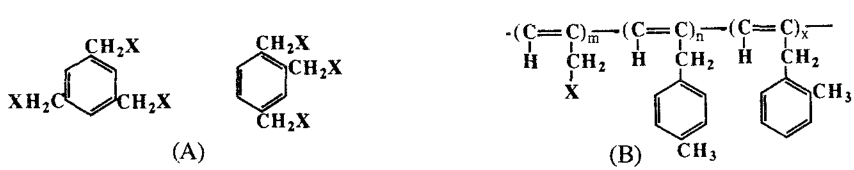


Fig.1: ^{1}H-NMR spectra of oligomeric products a) PBr with $Mo(CO)_5PPh_3$ $/Et_3Al_2Cl_3$ (1/6), 30°, Chlorobenzene
b) PBr with $W(CO)_5PPh_3$ $/Et_3Al_2Cl_3$ (1/6), 30°, Chlorobenzene
c) PCl with $W(CO)_5PPh_3$ $/Et_3Al_2Cl_3$ (1/6), 30°, Chlorobenzene
d)PBr with $W(CO)_5PPh_3$ $/Et_3Al_2Cl_3$ (1/6), 30°, Toluene

The ^{1}H-NMR spectrum of the oligomeric product which was obtained using toluene as solvent (fig.1d) exhibit two broad signals in the range of 2.0-2.4 ppm and 5.8-7.3 ppm (four sharp peaks at 2.10, 2.27, 6.95 and 7.05 ppm). These signals were attributed to the ortho- and para-substituted toluenes on the side polymer chain [scheme I(B)], caused by an electrophilic aromatic substitution, favorable under the reaction conditions ($Et_3Al_2Cl_3$ as Lewis acid and presence of a nucleophilic solvent) (16).



Scheme I

REFERENCES

1. Masuda T, Higashimura T (1987), *Adv. Polym. Sci.*, 81: 121
2. Masuda T, Higashimura T (1984), *Acc.Chem.Res.*, 17: 51
3. Gibson HW (1986), *"Handbook of Conducting Polymers"*, Marcell Dekker, New York, Vol 1, p 405
4. Costa G (1989), In *"Comprehensive Polymer Science"*, G. Allen Ed., Pergamon, Oxford, Vol 4, p 155

5. Basset JM, Coudurier G, Mutin R, Praliand (1974), *J. Catal.*, 34:196
6. Basset JM, Bilhou JL, Mutin R, Theolier A (1975), *J. Am. Chem., Soc.* 97:7376
7. Bilhou JL, Basset JM, Mutin R, Graydon NF (1977), *J. Am. Chem. Soc.*, 99: 4083
8. Leconte M, Basset JM (1979), *J. Am. Chem. Soc.*, 101: 7296
9. Larroche C, Laval JP, Lattes A, Leconte M, Quignard F, Basset JM (1982), *J. Org. Chem.*, 47:2019
10. Trachtman M (1964), *J.Phys.Chem.*, 68:1415
11. Akopyan LA, Grigoryan SG, Zhamkochyan GA, Matsoyan SG (1975), *J. Polym. Sci. USSR*, 17: 2896
12. Deits W, Cukor P, Rubnerand M, Jopson H (1981), *Ind.Eng.Chem.Prod. Res. Dev.*, 20:696
13. Voronkov MG, Pukhnarevich VB, Sushchinskaya SP, Annenkova VZ, Annenkova VM, Andreeva NJ (1980), *J. Polym. Sci., Polym. Chem. Ed.*, 18: 53
14. Furlani A, Russo MV, Carusi P, Licoccia S, Leoni E, Valendi G (1983), *Gazz. Chim. Ital.*, 113: 671
15. Masuda T, Kuwane Y, Yamamoto K, Higashimura T (1980), *Polym. Bull.*, 2:823
16. Kunzler J, Percec V (1990), *J. Polym. Sci., Polym. Chem. Ed.*, 28:1043
17. a) Lee WC, Sohn JE, Gal YS, Choi SK (1988), *Bull. Korean Chem. Soc.*, 9:328 b) Gal YS, Jung B, Cho HN, Lee WC, Choi SK (1992), *Bull. Korean Chem. Soc.*, 13:4
18. Magee TA, Matthews CN, Wang TS, Hotiz JH (1961), *J. Am. Chem. Soc.*, 83:3200
19. Bilhou JL, Smith AK, Basset JM (1978), J. *Organometall. Chem.*, 148:53
20. Bilhou JL, Basset JM (1977), *J. Organometall. Chem.*, 132:395
21. Ranby B, Rabek JF (1977) *"ESR Spectroscopy in Polymer Reacearch"*, Springer-Verlag, Berlin
22. Chien JCW (1984), *"Polyacetylene-Physics, Chemistry and Material Sciences"*, Academic Press, New York
23. Goldberg IB, Crowe HR, Newman PR, Heeger AJ, Mac Diarmid AG (1979), *J. Chem. Phys.*, 70:1132
24. Siskos MG, Bokaris EP, Zarkadis AK, Kyriakakou G (1992), *Eur. Polym. J.*, 28:1127
25. Vögtle F, Zuber M, Lichtenthaler RG (1973), *Chem. Ber.*, 106:717
26. Kanischka G (1986), *"Thesis"*, University of Bayreuth

Accepted June 11, 1994 St