

Preliminary communication

NEW CATALYSTS FOR ACETYLENE POLYMERISATION

S. CERIOTTI, G. LONGONI and P. CHINI

Istituto di Chimica Generale e Centro del CNR, Via G. Venezian 21, 20133 Milano (Italy)

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Summary

The salts $[\text{NMe}_4]_2[\text{Ni}_5(\text{CO})_{12}]$, $[\text{NMe}_4]_2[\text{Ni}_6(\text{CO})_{12}]$, $[\text{NMe}_4]_2[\text{Ni}_{12}(\text{CO})_{21}\text{H}_2]$ and $[\text{NEt}_4]_3[\text{Ni}_{12}(\text{CO})_{21}\text{H}]$ in acetone are efficient catalysts for the polymerisation of acetylene.

Because of the high electric conductivity of doped polyacetylene [1,2], there is considerable interest in this polymer. We wish to report that several nickel carbonyl anionic clusters are efficient catalysts (20–30 g of polymer per gram of catalyst)* for acetylene polymerisation.

Rapid formation (2–5 h) of a thick slurry of red-violet polyacetylene is observed at atmospheric pressure and room temperature in the reaction of acetylene with an acetone solution of the salts $[\text{NMe}_4]_2[\text{Ni}_5(\text{CO})_{12}]$ [4], $[\text{NMe}_4]_2[\text{Ni}_6(\text{CO})_{12}]$ [4], $[\text{NMe}_4]_2[\text{Ni}_{12}(\text{CO})_{21}\text{H}_2]$ [5], and $[\text{NEt}_4]_3[\text{Ni}_{12}(\text{CO})_{21}\text{H}]$ [5]. Conversions of about 100–200 mol of monomer per mol of nickel present in the catalyst have been obtained with about 0.2–1 g of catalyst per liter. The reaction was usually carried out at room temperature, although $[\text{NMe}_4]_2[\text{Ni}_{12}(\text{CO})_{21}\text{H}_2]$ is active at least at temperatures as low as -40°C . Conversely the platinum clusters [6] $[\text{NBu}_4]_2[\text{Pt}_9(\text{CO})_{18}]$ and $[\text{NBu}_4]_2[\text{Pt}_{12}(\text{CO})_{24}]$ are inactive even near the boiling point of acetone.

The red-violet polymer becomes black on drying, and the IR spectrum shows characteristic absorptions due both to *cis* (740 cm^{-1}) and *trans* (1015 cm^{-1}) polyacetylene [7], usually in similar intensities. The complete insolubility and the extreme sensitivity to air oxidation (fresh, highly divided polymer ignites in air!) have prevented us from characterising the product further. In every case gas-chromatography showed only traces of cyclic oligomers (benzene, styrene and cyclooctatetraene).

Addition of hydrogen or propylene, in 1/1 ratio to the acetylene, or of water (0.5%), had no significant effect on the polymerisation.

*The original catalysts gave about 2 g of polymer per gram of catalyst [3].

Experimental

A solution of $[\text{NEt}_4]_3[\text{Ni}_{12}(\text{CO})_{21}\text{H}]$ (61.5 mg) in acetone (350 ml) is prepared under nitrogen, saturated with acetylene (1 atm, 20°C), and then stirred at 20°C for 5 h as acetylene is slowly bubbled through. The polymer is filtered off, washed with acetone, and dried in vacuum (2.2 g).

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References

- 1 H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang and A.H. Heeger, *J. Chem. Soc. Chem. Commun.*, (1977) 578.
- 2 C.K. Chiang, M.A. Druy, S.C. Gau, A.J. Heeger, E.J. Louis, A.G. MacDiarmid, Y.W. Park and H. Shirakawa, *J. Amer. Chem. Soc.*, 100 (1978) 1013.
- 3 G. Natta, G. Mazzanti and P. Corradini, *Atti Accad. Naz. Lincei, Rend. Clas. Sci. Fis. Mat. Nat.*, 25 (1958) 3.
- 4 G. Longoni, P. Chini and A. Cavalieri, *Inorg. Chem.*, 15 (1976) 3025.
- 5 R.W. Broach, L.F. Dahl, G. Longoni, P. Chini, A. Schultz and J. Williams, *Advan. Chem. Ser.*, 167 (1978) 93.
- 6 G. Longoni and P. Chini, *J. Amer. Chem. Soc.*, 98 (1976) 7225.
- 7 T. Ito, H. Shirakawa and S. Ikeda, *J. Polym. Science*, 13 (1975) 1943.