

## CHEMISTRY

### Tetrakis (Triphenyl Phosphite) Nickel (0) as an Initiator of Polymerization at Room Temperature

ORGANO-METALLIC compounds in which the metal is in a low (preferably zero) oxidation state, in the presence of a suitable organic halide, can initiate the free-radical polymerization of vinyl monomers<sup>1</sup>. The metal carbonyls and their derivatives, and the hexaphenylisocyanato<sup>2</sup> complexes of group VI metals have been most studied from this point of view. Recently we have studied the compound tetrakis (triphenyl phosphite) nickel (0) (TTPN), described in the literature earlier this year<sup>3</sup>; our observations on this material, which shows unusually high activity as an initiator, are reported here. From a practical point of view this derivative has the advantage of possessing a comparatively high stability in the solid state (it melts fairly sharply at 146° C)—an unusual attribute for a material which is an effective initiator at room temperature.

As a ligand, triphenyl phosphite belongs to the same class as carbon monoxide and phenyl isocyanide; however, the double-bond character of the phosphorus to metal bond arising from the back-donation of electrons from the *d* orbitals of the metal to the ligand is much less and consequently the ligand is more readily displaced.

Tetrakis (triphenyl phosphite) nickel (0) was prepared by the reaction of the pure ligand and freshly sublimed nickelocene in boiling benzene under a nitrogen atmosphere, according to the method of Olechowski, McAlister and Clark<sup>3</sup>, and purified as described by these authors.

The derivative alone is not an effective initiator of the polymerization of methyl methacrylate at 25° C, but it initiates readily in the presence of a low concentration of a suitable organic halide such as carbon tetrachloride. The dependence of rate of polymerization on carbon tetrachloride concentration is remarkably similar to that observed with the metal carbonyl<sup>1</sup> and phenyl isocyanide derivatives<sup>2</sup>; the rate, almost zero for [CCl<sub>4</sub>] = 0, at first rises rapidly with increasing [CCl<sub>4</sub>] but ultimately reaches a plateau value, so that for [CCl<sub>4</sub>] > 0.02 mole l.<sup>-1</sup> it is independent of [CCl<sub>4</sub>]. With nickel carbonyl the limiting rate is reached only at higher values of [CCl<sub>4</sub>] (ref. 4).

In bulk methyl methacrylate at 25° C the rate of polymerization is given by:

$$-\frac{d[M]}{dt} = 1.02 \times 10^{-2} [\text{TTPN}]^{1/2} \text{ mole l.}^{-1} \text{ sec}^{-1} \quad (1)$$

(*M* represents the monomer). The free-radical nature of the reaction is indicated by the half-order in initiator concentration in (1) and also by the fact that the kinetic parameter  $k_p k_t^{-1/2}$  ( $k_p$ ,  $k_t$  being propagation and termination coefficients, respectively) calculated from mean rates and degrees of polymerization has the normal value for the free-radical polymerization of methyl methacrylate at 25° C. The order in monomer concentration is 1.5 (with benzene as diluent), showing that the monomer enters into the initiation step; this has been found with some carbonyls, for example, molybdenum carbonyl<sup>5</sup>. We believe that a similar mechanism holds in all these systems—the metal derivative reacting with monomer to form a complex which afterwards yields radicals on reaction with the halide.

Tetrakis (triphenyl phosphite) nickel (0) does not show the marked inhibition observed with nickel carbonyl<sup>1</sup>, so that the relationship (1) is obeyed over the whole range of concentrations investigated (up to  $2.9 \times 10^{-3}$  mole l.<sup>-1</sup>). Initiation at 25° C is much more rapid under comparable conditions of concentration than with nickel carbonyl particularly at high initiator concentrations when inhibition in the nickel carbonyl system is very marked. Even at low concentrations the difference amounts to a factor

of nearly 100 in the rate of initiation. These results, therefore, are consistent with the view that triphenyl phosphite is a more labile ligand.

Triphenyl phosphite acts as a mild inhibitor of the polymerization, the effect being very small compared to the inhibition by carbon monoxide encountered in the corresponding carbonyl system. (Triphenyl phosphite is not a retarder in these reactions, nor does it affect the free-radical polymerization of methyl methacrylate initiated by *azo-bis-isobutyronitrile*.) This may indicate that the initial reaction of the nickel derivative with monomer is not readily reversible, or that the greater part of the process involves addition of monomer without scission of a triphenyl phosphite ligand.

Use of polyvinyl trichloroacetate (PVTCA) as the halide in place of carbon tetrachloride leads to very rapid gelation at 25° C. Thus with [PVTCA] =  $3.84 \times 10^{-2}$  base mole l.<sup>-1</sup> (weight average molecular weight 88,000) and [TTPN] =  $6.15 \times 10^{-4}$  mole l.<sup>-1</sup> the gel time is 10 min, approximately. As already shown<sup>6</sup>, this implies that radical formation takes place by abstraction of a halogen atom from the halide by the metal derivative, giving an organic radical (for example,  $\cdot\text{CCl}_2$  from CCl<sub>4</sub>) capable of initiating polymerization.

Work is in progress to investigate the effect of changes in the structure of the organic ligand on the activity of these initiating systems.

We thank Joseph Crossfields and Sons, Ltd., for financial support of one of us (K. H.).

C. H. BAMFORD  
K. HARGREAVES

Department of Inorganic,  
Physical and Industrial Chemistry,  
University of Liverpool.

<sup>1</sup> Bamford, C. H., *J. Polym. Sci.*, Part C, No. 4, 1571 (1964). Bamford, C. H., Eastmond, G. C., and Maltman, W. R., *Trans. Farad. Soc.*, **61**, 267 (1965) and earlier papers quoted.

<sup>2</sup> Bamford, C. H., Eastmond, G. C., and Hargreaves, K., *Nature*, **205**, 385 (1965).

<sup>3</sup> Olechowski, J. R., McAlister, C. G., and Clark, R. F., *Inorg. Chem.*, **4**, 246 (1965).

<sup>4</sup> Bamford, C. H., and Finch, C. A., *Trans. Farad. Soc.*, **59**, 548 (1963).

<sup>5</sup> Bamford, C. H., Denyer, R., and Eastmond, G. C., *Trans. Farad. Soc.*, **61**, 4160 (1965).

<sup>6</sup> Bamford, C. H., Eastmond, G. C., and Robinson, V. J., *Trans. Farad. Soc.*, **60**, 751 (1964).

### Effect of Zinc Chloride on the Velocity Coefficients in the Polymerization of Methyl Methacrylate

It is well known that the reactivity of the propagating species in ionic polymerization is greatly influenced by the proximity and character of the coions and by complex formation. As a rule, free radical reactions are comparatively insensitive to the nature of their environment, although there are references in the literature to changes in the rate of free-radical polymerizations, and the nature of the polymers formed, which have been attributed to the participation of radicals in complexed forms. The investigation of the structure and reactivity of radical complexes in polymerization is a field which has not been surveyed systematically, but which, nevertheless, may contain interesting features. We have embarked on an investigation of the absolute rate coefficients in the free-radical polymerization of vinyl monomers in the presence of possible complexing agents and report here some results for the methyl methacrylate-zinc chloride system. The only measurements of a similar type recorded in the literature appear to be those of Bamford, Jenkins and Johnston<sup>1</sup>, on acrylonitrile in *NN*-dimethylformamide solution in the presence of lithium salts. Kargin, Kabanov and Zubov<sup>2</sup> considered that the presence of zinc chloride during the polymerization of methyl methacrylate affects the microstructure of the polymer, but this finding was not confirmed by Bovey<sup>3</sup>. More recently, Imoto, Otsu and Harada<sup>4</sup> have