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Anchored macromolecular catalysts

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

1983

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Verlaan, J. P. J. (1983). *Anchored macromolecular catalysts: oxidative coupling of phenols catalyzed by polymer-copper complexes*. s.n.

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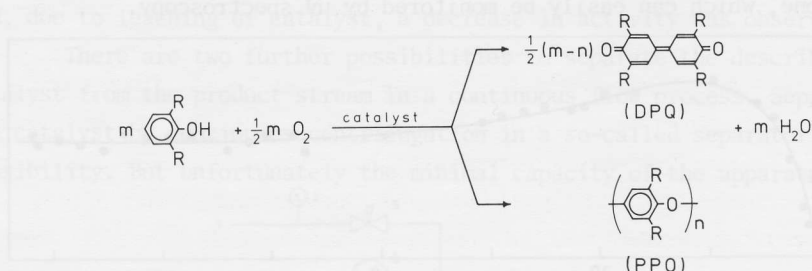
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SUMMARY

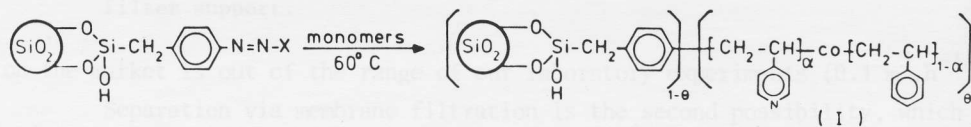
Application of linear macromolecular amines -anchored or not- as ligands for copper redox catalysts to improve the reaction of 2,6-disubstituted phenols to C-C and or C-O coupled products was the main object of this investigation (Scheme 1).



Scheme 1.

In Chapter I a description is given of some general aspects concerning metal catalysis followed by some general remarks on anchorage of low molar mass catalysts. Apart from that the application of linear macromolecules in relation to metal catalysis is discussed. Also a short survey is given of the state of affairs concerning the catalysts and the mechanism of the reaction of 2,6-disubstituted phenols. The catalysts best known so far are homogeneously soluble low molar mass copper amine complexes. However, these catalysts can only be used once in a batch-like operation. The fixation of these ligands in a macromolecule is the first step in the anchoring process. Subsequently these macromolecular catalysts can be anchored on a support to make easy separation possible.

Anchorage of the already known macromolecular pyridine-like catalysts on a support (I) is one method of making batch-like re-use possible. This possibility was thoroughly investigated and is described in Chapter II, III, IV. The most important result was that it was found that, anchorage of pyridine-like macromolecular catalysts to silica via one chain end by copolymerization from the SiO_2 -surface (Scheme 2), was possible, the intrinsic activity being preserved (Chapter II). An increasing θ of the silica with polymer, anchored

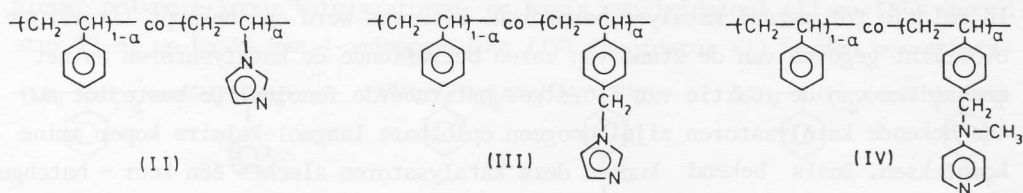


Scheme 2.

or unanchored, positively influenced the substrate complexation to the active sites. Moreover batch-like re-use with complete preservation of activity appeared to be possible. At first application of these catalysts in a continuous process gave some problems (Chapter II) but at a later stage these problems were solved by using a new type of membrane-reactor (Appendix).

The combination of polarities of support and macromolecule strongly influenced the adsorption behaviour of both anchored and unanchored macromolecular catalysts (Chapter IV). Adsorption occurred with pyridine-like polymers, when the silica surface was hydrophobic in combination with styrene as a comonomer and also when the surface was hydrophilic in combination with methylmethacrylate as a comonomer, in the (anchored) macromolecular ligand. Besides the amount of adsorbed polymer was higher when more surface area was offered.

A second way of improving the process was the development of new, better macromolecular catalysts. New low molar mass ligands were used for the copper complexation and they were built in in linear macromolecules. These new polymeric copper catalysts, on the basis of imidazole (II and III) (Chapter V) or on the basis of 4-aminopyridine (IV) (Chapter VI), were synthesized



Scheme 3.

(Scheme 3) and tested on their catalytic activity and then compared to their low molar mass analogues. The binding of these ligands to the nonpolar polystyrene resulted in an enhancement of the reoxidation rates of the active copper sites. Moreover the application of a spacer proved to favourably affect the attainableness of the sites. It was found that these catalysts had rates much higher than those of other amine-copper catalysts. After carrying out a kinetic analysis these higher rates could be ascribed to an intrinsic activity of the sites that was at least ten times higher than is usual.

