

Preparation of poly(styryl-1,8-naphthyridine) and some of its metal complexes

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Introduction

Polymers containing chelating ligands have found numerous applications in solid phase and organic syntheses^{1,2}. When coordinated to the appropriate metal ions, these systems can function as 'immobilized' homogeneous catalysts which possess the activity of their soluble analogues with the added advantage of ease of recovery from the reaction mixtures. Polymer-bound chelates have also been shown to recover selectively specific metal ions from metal ion mixtures³. Such polymers thus combine the selectivity characteristic of liquid-liquid extractions with the mechanical convenience and flexibility inherent in solid-liquid systems.

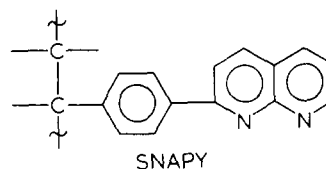
Chelating resins employing phosphine ligands have been widely investigated in several catalytic studies during the past decade^{4,5}. Little work has been done using nitrogen heterocycles, which are some of the most versatile chelating systems known. Neckers and Card have reported⁵ the attachment of 2,2'-dipyridine to an insoluble polystyrene support and demonstrated its potential as a polymer-bound chelate by preparing a wide variety of transition metal complexes⁶. To increase the number of available polymer-based chelating nitrogen heterocycles, we have attached 1,8-naphthyridine to polystyrene-2% divinylbenzene copolymer beads. A number of transition metal and lanthanide ions were coordinated to the poly(styryl-1,8-naphthyridine) to demonstrate its versatility as a polymer-based chelating ligand.

Experimental

The polystyrene-2% divinylbenzene copolymer beads were purchased from Eastman Laboratories. 1,8-Naphthyridine was synthesized according to the method of Hamada and Takeuchi⁷. All other chemicals and solvents were reagent-grade and used without further purification. Reactions involving *n*-butyllithium were carried out under inert atmosphere. Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories. Metal ion loadings of the modified polymer beads were determined by titrating the metal ion solutions before and after exposure to the polymer with 0.01 M EDTA using murexide (ammonium purpurate acid) as the indicator. Infra-red spectra were obtained by use of a Digilab FTS-20 Fourier transform spectrophotometer modified to record spectra by diffuse-reflectance⁸. Samples for i.r. analyses were prepared by grinding the polymer beads with KCl in a ball mill.

Brominated polystyrene (SBr). Brominated polystyrene was prepared using procedures suggested by Farrall and Fréchet⁹. PS-2% DVB copolymer beads (50 g, 0.4 mol phenyl residues) in carbon tetrachloride were treated with bromine (6 ml, 0.1 mol) to afford bromination of 25% of the phenyl residues of polystyrene.

Poly(styryl-1,8-naphthyridine) (SNAPY). 8 g brominated beads (SBr) were swollen in 100 ml of benzene. 20 ml of a 2.2 M solution of *n*-butyllithium in hexane was added and the suspension stirred at 60°C for 3 h. The colour of solution changed from pale yellow to salmon pink at this point.



Solid naphthyridine (8.0 g, 0.062 mol) was added and the resulting purple suspension was heated to reflux for 3 h. The mixture was cooled to room temperature and bubbled with air for 12 h. The golden brown poly(styryl-1,8-naphthyridine) (SNAPY) beads were recovered by filtration, washed with tetrahydrofuran, benzene, and ethyl acetate and dried at 60°C under reduced pressure for 24 h. Anal. found: C, 85.41; H, 7.40; N, 4.61.

Polymer-bound metal complexes. In a typical experiment, 500 mg of the SNAPY beads were soaked in 50 ml of ethyl acetate containing 0.05 M metal ion for 2 h with occasional shaking. The resulting polymer-bound metal complexes were isolated by filtration, washed with ethyl acetate and tetrahydrofuran, and dried at 60°C under reduced pressure for 24 h.

Results and discussion

NAPY was attached to the free phenyl residues of PS-2% DVB by modifying the methods developed by Neckers and Card⁶. The extent of bromination was limited to about 25% of the phenyl residues of polystyrene by stoichiometrically controlling the amount of bromine. Employing tetrahydrofuran instead of benzene as a solvent in the lithiation step prevents synthesis of SNAPY. Tetrahydrofuran and benzene are both excellent swelling solvents. However, the presence of ionic repulsions in the more polar solvent, tetrahydrofuran, limits the accessibility of the brominated sites of polystyrene towards the butyllithium reagent by causing the lithiation reaction to stop once a fraction of the brominated sites have been lithiated⁹.

From elemental analysis, the amount of NAPY attached to the polymer beads may be inferred. Results indicate the presence of 1.63 mmol of NAPY/g of polystyrene or roughly one NAPY group for every five phenyl residues. This represents an 80% conversion of the brominated phenyl residues to naphthyridine-phenyl residues which is a significant improvement over the 50% conversion reported for the formation of poly(styryldipyridine) (SDIPY)⁶.

The diffuse-reflectance infra-red spectrum of SNAPY shows new bands at 1020 and 810 cm^{-1} , which are indicative of NAPY¹⁰. Further evidence of the attachment of NAPY to polystyrene was obtained by computerized Kubelka-Munk spectral subtractions between SNAPY and PS-2% DVB. Several band shifts in the subtraction spectrum suggestive of polymer bound NAPY were observed¹¹.

The i.r. spectra of the polymer-bound complexes are similar to each other and to the original SNAPY polymer. This behaviour may be attributed to conditions approach-

Table 1 Metal ion loadings

Metal salt	Quantity bound (mmol of metal/g of SNAPY)*	% of available NAPY complexed*
Copper (II) nitrate	0.46	28
Copper (II) chloride	0.81	49
Iron (III) chloride	0.95	58
Europium (III) nitrate	0.55	34
Nickel (II) nitrate	0.57	35

* 1 g SNAPY polymer beads contains 1.63 mmol NAPY. Computation made assuming a metal to NAPY ratio equal to unity. If more than one NAPY per metal is involved, this value would be markedly increased

ing infinite dilution of the metal ions. In the case of the polymer-bound nitrates, increased band intensities in the region of 1400–1000 cm^{-2} which are assigned to nitrate modes superimposed on the skeletal vibrations of the polymer are observed¹². The intensities of these bands are observed to diminish proportionally as the nitrate salt loadings are reduced. The chloride complexes do not exhibit these bands.

Due to its ability to swell the polymer support reasonably well and to dissolve a large number of metal salts, ethyl acetate is a convenient solvent in which to study metal loading. The results of such studies (Table 1) demonstrate that SNAPY is capable of binding to a wide variety of metal ions. The amount of metal complexed per mol SNAPY beads (g polymer^{-1}) is similar to that obtained using SDIPY⁶. Assuming that each metal ion is coordinated to one ligand, iron (III) chloride is found to occupy 58% of the NAPY residues in SNAPY compared with all of the BIPY residues in SDIPY⁶. This difference may result from the increased functionalization of SNAPY (22% compared with SDIPY (14%) which would allow more than one NAPY

to coordinate to a single metal ion. It is also known that NAPY, which forms a four-membered ring on chelation, is a much weaker field ligand than DIPY, which forms a five-membered ring, and hence does not bind as strongly to metal ions¹³. With copper (II) nitrate and copper (II) chloride, NAPY forms 1:2 and 1:1 complexes respectively^{14,15}. The large difference in amount of loading observed for these two salts of copper(II) reflects the known coordination chemistry and supports the suggestion that the polymer is flexible enough to allow more than one NAPY group to coordinate to a metal ion.

References

- Hodge, P. *Chem. Br.* 1978, 14, 237
- Hodgkin, J. H. *Chem. Ind., London* 1979, 153
- Melby, L. R. *J. Am. Chem. Soc.* 1975, 97, 4044
- Carraher, Jr., C. E., Sheats, J. E. and Pittman, Jr. C. U. *'Organometallic Polymers'*, Academic Press, New York, 1978
- Tsutsui, M. and Ugo, R. *'Fundamental Research in Homogeneous Catalysis'*, Plenum Press, New York, 1977
- Card, R. J. and Neckers, D. C. *J. Am. Chem. Soc.* 1977, 99, 7733
- Hamada, Y. and Takeuchi, I. *Chem. Pharm. Bull.* 1971, 19, 1857
- Fuller, M. F. and Griffiths, P. R. *Anal. Chem.* 1978, 50, 1906
- Farrall, M. J. and Fréchet, J. M. J. *J. Org. Chem.* 1976, 41, 3877
- Armarego, W. L. F., Barlin, G. B. and Spinner, E. *Spectrochim. Acta* 1966, 20, 117
- Fuller, M. F. and Griffiths, P. R. *Am. Lab.* 1978, 10, 69
- Foster, R. J. and Hendricker, D. G. *Inorg. Chim. Acta* 1972, 6, 371
- Bodner, R. L. and Hendricker, D. G. *Inorg. Chem.* 1973, 12, 33
- Emerson, K., Emad, A., Brookes, R. W. and Martin, R. L. *Inorg. Chem.* 1973, 12, 978
- Foster, R. J. and Hendricker, D. G. *Inorg. Chem.* 1973, 12, 349

Graft polymerization from glass surfaces

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An area of debate in the field of reinforced and filled polymers is the nature and importance of adhesion between the phases. Simple theories predict differences between the mechanical properties of filled polymers having poor adhesion and those having perfect adhesion between the phases¹. Variations in the properties of filled polymers have been attributed to differences in interfacial adhesion^{2,3}. Organochlorosilanes are widely used to promote adhesion between the phases in glass-filled polymers⁴; these agents have one or more groups which condense with the silanol groups on the glass to give covalent bonds between the organic groups and the glass. Often the organic groups are unsaturated, polymerizable groups which may be incorporated into chains of the surrounding matrix when that polymer is prepared or cured with treated glass *in situ*. Such reactions rely on chance encounters of active radicals with the un-

saturated groups on the glass surface, and quantitative control of such processes is inherently difficult.

Our approach is to study glass-filled polymers with a controlled interface by growing polymer chains, ideally of known molecular weight and number per unit area of the surface, from specific sites incorporated on the glass surface. This method should provide positive attachment of a known quantity of polymer to the glass. The polymer-coated glass can then be incorporated into a matrix of polymer, chemically identical with the chains attached to the glass. Interfacial adhesion will rely on entanglements between the chains in the matrix and the bound chains and will depend on the molecular weight and number of such chains per unit area of the interface.

In this preliminary communication we describe a process by which suitable reactive sites are introduced on to the surfaces of glass beads and are subsequently used, in an established reaction, to initiate polymerization of vinyl

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