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Synthetic Resins as Designable Supports for Metal-Based Chemistry: the Issue of Their Nanomorphology and Molecular Accessibility

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SUMMARY: Macromolecular cross-linked ligands containing pyridyl pendant groups are characterized by a combination of inverse steric exclusion chromatography, ESR and NMR spectrometries in water and methanol. On the basis of the relevant results, methanol is seen to be clearly the best swelling agent and it is chosen as medium for Cu^{II} coordination.

Introduction

The nanochemical technology of the dispersion of metal centres inside the polymer network of macro- and microporous resins goes back to the seminal proposal of Haag and Whitehurst in the late sixties[1)]. The contemporary commercial availability of these technologically very promising materials soon made clear the possibility of their "upgrading" with a variety of functional groups, thus rendering them actual *solid macromolecular ligands* able to co-ordinate numerous metal centres of varying oxidation state. The resulting availability of a

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virtually unlimited number of *macromolecular solid metal complexes* [2)] started a sort of "rush to the perfect catalyst" (hybrid phase catalysis) [3)].

Although the synthesis of organic resins is a mature chemical methodology and the skill of synthetic chemists can provide virtually any desired macromolecular ligands and corresponding macromolecular metal complexes, the issue of the nanostructural features of these functional networks in terms of *textural properties* at the nanometer level (nanomorphology) and of *molecular accessibility*, is still a rather open question, especially when these resins are of the gel-type[4)].

In this paper we will present an *integrated* physico-chemical evaluation approach[5)] based on Inverse Steric Exclusion Chromatography (ISEC)[6)] and on ESR[5)] and Field Gradient-Spin Echo NMR[7)] spectrometries and we will illustrate in a sort of simple case history how these spectrometries do account for the ligating behaviour of a microporous (gelular) resin bearing pyridyl pendant groups.

Results and discussion

ISEC, ESR and Field Gradient Spin Echo NMR as integrable tools for the evaluation of resins nanostructure and molecular accessibility

Macroporous (MaR) and microporous (MiR) resins (mostly polystyrene cross-linked with divinylbenzene) differ significantly in their chemical composition and largely in their micro- and nanostructure. MiR are usually 2-8 % cross-linked, while MaR are 8-20 % cross-linked materials and are normally synthesized in the presence of porogenic components[8)]. In the dry state MiR materials do not possess any porosity in the solid state, but they develope an extensive nanoporosity in the swollen state. On the contrary, MaR do possess a permanent microporosity even in the dry state, which supplements in the swollen state the nanoporosity developed by the swelling process. In chemical applications they are used as beads (0.2 to 1.25 mm) or powders, in fixed-bed reactors or suspension reactors (often operated batchwise) or more frequently in flow-through reactors. Working temperatures range from room temperature up to about 120°C. The mechanical strength of these solids is relatively poor, but this drawback can be managed by means of various technical solutions [8b)].

Our approach is particularly applicable to MiR materials, which are attractive as they offer, in principle, the totality of their functionalized swollen polymer network to the dispersion of co-ordinated metal centers and to the ingress and egress of reagents and products, respectively. The active surface area of MiR can be as high as 2000 m^2g^{-1} [4)]. MiR acidic resins are currently utilized industrially for the synthesis of bisphenol A[4)].

Inverse Steric Exclusion Chromatography : ISEC. This analytical technique is a version of the well known and practiced size exclusion chromatography, which does not aim at the analysis or separation of analytes of expected different sizes, but, on the contrary, aims at defining the nanomorphology of a given gelular matrix on the basis of its behaviour towards analytes of well defined size (solvated-dynamic radii). ISEC was independently proposed by Halasz$^{9)}$ and Freeman$^{10)}$ in the late seventhies and it turns out to be particularly suited for analyzing microporous resins under operational conditions, i. e. in their swollen state. On the basis of Ogston's model$^{11)}$ which considers polymer chains as rigid rods characterized by a fixed diameter and, after the methodological improvement introduced more recently by Jerabek$^{6)}$, ISEC analysis provides for any gelular resin a) its gel volume as seen by the molecular probes employed, b) the internal distribution of its domains in terms of polymer densities and c) its (weighed) average polymer chain concentration (c_c, nm^{-2}, from 0.1 to 2.0 nm^{-2}) a figure which provides a sort of picture "in negative" of the nanoporosity of the polymer network (Fig. 1).

Electron Spin Resonance : ESR. A given stable radical (e. g. a nitroxide species like TEMPONE, 2,2,6,6-tetramethyl-4-oxo-1-oxyl-pyperidine) dissolved in a given solvent rotates relatively freely under ordinary (bulk) conditions. When this solution is confined inside a microporous network (Fig. 1), the rotational mobility of the probe is more or less reduced and its rotational correlation time, τ, was found by us to quantitatively correlate with $c_c$$^{5)}$.

Static Gradient Spin Echo Nuclear Magnetic Resonance : SGSE-NMR. A liquid sample containing a set of magnetically active nuclei of the same type is exposed to a fixed, homogeneous magnetic field. Then, a second magnetic field is applied and finely varied according to a known linear gradient G, such that the intervention produces a perfectly controlled non-homogeneous magnetic field. The response of the nuclei (echo amplitude A) after a pulse sequence 90°-t_p-180°-t_p is quantitatively correlated with the molecule self-diffusion coefficient$^{7)}$. Obviously, a solvent confined inside a dense polymer network (Fig. 1) will experience a defined reduction of mobility as expressed by Fick's coefficient D, which we find to correlate with c_c and $\tau$$^{13)}$.

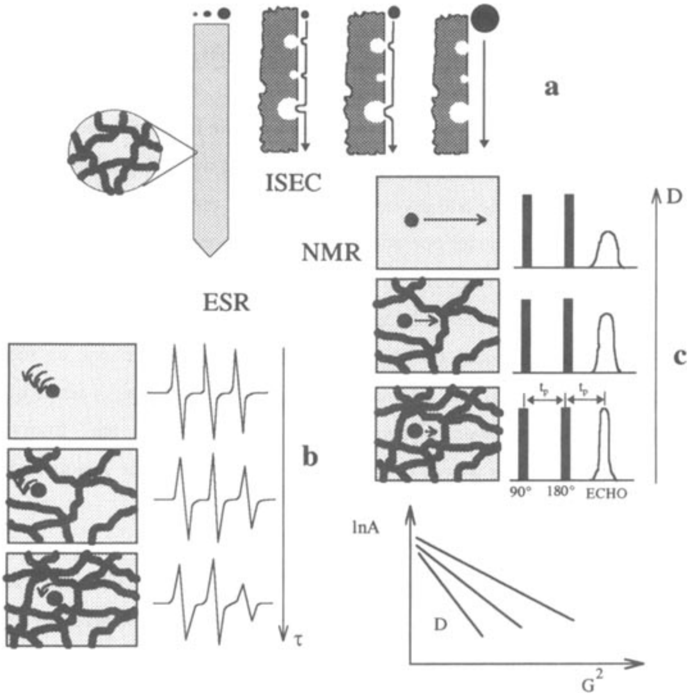

Fig. 1. a) Solutes with different solvated-dynamic radii are featured by different retention volumes after flowing through a given microporous material, from which values ISEC analysis is performed; b) the values of t derive from the geometrical features of the ESR lines; c) D is obtained from the slope of the lnA vs G^2 experimental plots.

Reactivity of poly-4-vinylpyridine-hydroxoethylmethacrylate-divinylbenzene (Poly-VIPY-HEMA-DVB) with Cu^{2+} (aq).

In the context of our interest in Cu^{II}-containing resins as potentially useful innovative biocidic (antifouling) materials[14,15)] we became interested in the preparation of expectedly hydrophilic gelular resins stemming from the co-polymerization of 4-vinylpyridine (VIPY) (Aldrich) with a large molar excess hydroxoethylmethacrilate (HEMA) (Aldrich) in the presence of divinylbenzene ca. 3 % mol (DVB) (Aldrich). The reaction of the macromolecular ligand (**P-L**) with Cu^{II} in water was somewhat naively expected to give the facile quantitative incorporation of one Cu^{II} per stoichiometrically available N atom, under appropriate conditions. In fact, the results turned out to be disappointing, in this connection, and a Cu^{II} incorporation far lower than the expected was observed (Tab. 1).

Our ligating resins are prepared by γ-irradiation of the suitable monomer mixture (ca. 10 g) at lower temperature (Tab. 1) up to ca. 100 % polymerization yield[16)]. After grinding of the resin block so obtained, repeated thorough washing with water (3x50 ml) and MeOH (3x50 ml) and drying under vacuum to constant weight, a final yield equal to 95 % was observed. The yellowish powder was sieved to < 212 mm and characterized by elemental analysis and IR spectroscopy (Tab. 1). SEM analysis reveals the expected compact vitreous microstructure typical of dry microporous resins.

Table 1. Collection of experimental data on resins **P-L** and on **P-L-Cu^{II}** complexes

species	**elemental composition (%)**				**remarks**
	C	H	N	Cu	
P-L_1[a]	56.47[c] (58.45)[d]	7.29 (7.61)	1.01 (1.13)		^{60}Co, -78°C, 1 Mrad, 24 h[f] 0.6 meq N g^{-1}
P-L_2[b]	59.97[c] (58.76)[d]	7.95 (7.61)	1.02 (1.13)		^{60}Co, -78°C, 1 Mrad, 24 h[g] 0.7 meq N g^{-1}
					Expansion volume (ml g^{-1}): toluene, **0.0**; water, **0.8**; methanol, **1. 3** 3428 cm^{-1} (s)(OH); 1726 cm^{-1} (s) (C=O); 1156 cm^{-1}(m) and 1077 cm^{-1} (m) (C-O)[h]
P-L_1-Cu^{II}	55.64[e]	7.87	1.00	0.40	Incorporation of Cu^{2+} in water; **Cu/N exp. 0.08**; blue; λ_{max} ca. 660 nm (very broad)[i]
P-L_2-Cu^{II}	50.98[e]	7.21	0.91	2.65	Incorporation of Cu^{2+} in methanol ; **Cu/N exp. 0.57**;dark blue; λ_{max} ca. 660 nm (very broad)[i]

[a] Monomer mixture : a) by weight, g, VIPY (1.04), HEMA (10.91), DVB (0.55); b) mol, VIPY (3.96), HEMA (33.50), DVB (1.00). [b] Monomer mixture : a) by weight, g, VIPY (1.05), HEMA (11.05), DVB (0.55); b) mol, VIPY (4.02), HEMA (34.0), DVB (1.00). [c] Experimental. [d] Calculated on the basis of 100 % polymerization yield. [e] Experimental; 1g of resin is suspended in 10 ml water or methanol for 10 min, under vigorous stirring and an equimolar amount of Cu^{2+} (from $CuSO_4 \cdot H_2O$) in 10 ml water or methanol, is added dropwise for few minutes under stirring; the blue resin is filtered, washed with 3x40 ml water or methanol and dried under vacuum. [f] Polymerization yield = 95 %. [g] Polymerization yield not determined. [h] FT-IR, Biorad FTS7PC. [i] Cary 5 UV-VIS-NIR equipped with DRA (Diffuse Reflectance Accessory).

Elemental analysis of resins **P-L$_1$** and **P-L$_2$** especially the nitrogen figure, reveals that VIPY and HEMA exhibit comparable reactivities at 95 % conversion and γ-ray irradiation is confirmed to be an effective tool for vinyl monomer polymerization[16)]. Addition of Cu^{2+} aqueous solutions to equimolar aqueous suspensions of **P-L** provides rapid coordination of the metal center by the macromolecular ligand, according to a visual estimate, but the incorporation degree of Cu^{2+} is remarkably low (Cu/N = 0.08), thus showing that ca. 90 % of the potentially available pyridyl groups are not in fact available to metal coordination, in the hypothesis of a 1 to 1 coordination ratio in the final Cu^{II} "molecular complex". Expansion volume (EV) measurements reveal that in fact, in spite of the large molar fraction of the hydrophilic monomer HEMA, our **P-L** ligands are not particularly hydrophilic materials and water is in fact a poor swelling medium (EV= 0.8 ml g^{-1}), while MeOH is, a better one. This observation is not totally surprising in that poly-HEMA chains are known to give macromolecular entanglements with consequent physical cross-linking effects[17)] which are to be considered in addition to the normal ones produced by the chemical cross-linking. In practical terms, this observation prompted us to reproduce in MeOH the exact reaction conditions utilized in water. The results are impressive and the Cu/N figure reaches 0.57, which means that, on the basis of formation of **P-L**-$Cu(H_2O)_5^{2+}$ molecular species, ca. 50 % of the stoichiometrically available pyridyl groups are involved in metal coordination in practice. Of course, the experimental Cu/N value could fit also with the utilization of 100 % of pyridyl groups to give the prevailing formation of (**P-L**)$_2$-$Cu(H_2O)_4^{2+}$ species. The reflectance spectrum in the VIS range of both **P-L**-Cu^{II} (λ_{max}= ca. 660 nm) is reminiscent in shape of that of $Cu(H_2O)_5^{2+}$ (λ_{max} = ca. 800 nm)[18)] and the significant ipsochromic effect observed fits also with the presence of one or more pyridyl groups in the metal coordination sphere. The ESR spectrum of **P-L**-Cu^{II} materials recorded at room temperature under various conditions are collected in Fig. 2 A. Both in the dry and swollen state, the parallel and perpendicular g components of the Cu^{II} signal, as well as the hyperfine structure, are partially resolved. Apparently, even in the swollen state the paramagnetic centers are trapped in macromolecular meshes small enough to hinder the tumbling of the metal centers and to prevent the consequent averaging of the ESR parameters. Although the values of the ESR spectral parameters as roughly estimated from the spectra of the dry and water- and methanol swollen samples are similar, differences in the spectral resolution are observed. Since line broadening is caused by molecular tumbling and by dipolar interactions, the observed differences have to be related to the different swelling ability of the liquid media, which apparently influences the polymer chain concentration and the Cu-Cu distance in the swollen state.

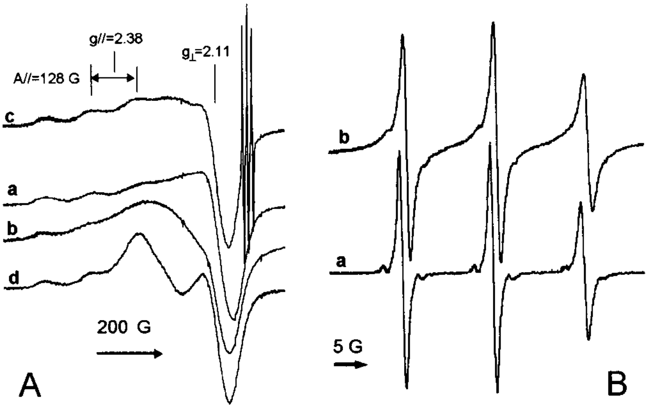

Fig. 2. A : ESR spectra of a) **P-L$_1$-Cu^{II}** dry, b) **P-L$_2$-Cu^{II}** dry, c) **P-L$_2$Cu^{II}** in swollen by a 10^{-4} methanol solution of TEMPONE, d) **P-L$_2$-Cu^{II}** swollen in water. B: ESR spectra of TEMPONE (10^{-4}) inside methanol-swollen **P-L$_2$** (a) and **P-L$_2$-Cu^{II}** (b).

The very marked effect of the swelling medium on the overall reactivity of the macromolecular ligand towards Cu^{II} prompted us to carry out a combined ISEC-ESR-NMR approach on both **P-L** and **P-L-Cu^{II}** materials in water and in methanol (Table 2). ISEC analysis was carried out on **P-L$_1$** in water. The gel volume detected by ISEC is 0.55 ml g^{-1} and turns out to be built up of dense nanodomains with 2.0 nm^{-2} polymer chain concentration. This gel volume is significantly lower than that determined from direct chromatographic data (1.04 ml g^{-1}) 5,6), thus revealing the presence of more dense domains not detected by ISEC.

ESR analysis performed on **P-L$_1$** after swelling in a 10^{-4} M water solution of TEMPONE reveals no freely rotating probe molecules, only immobilized TEMPONE is observed.

NMR analysis in water turns out to be unable to detect appreciable amounts of solvent inside the polymer network, thus fitting with the observed ESR data and with the higher chain density detected by ISEC.

ESR data fit with ISEC information in that the probe of substantial size (hydrodynamic radius 0.32 nm), albeit able to gain access to the gel volume, experiences such a viscous liquid medium that it undergoes full rotation hindrance.

Table 2. ISEC-ESR-NMR results on **P-L** and **P-L-Cu^{II}** materials (room temperature).

material	**ISEC**	**ESR**[a]	**NMR**[b]
P-L	**H_2O**; accessible to steric probes; $c_c = 2.0$ nm^{-2}	**H_2O**; TEMPONE is immobilized	**H_2O**; solvent protons are almost undetectable
P-L	**MeOH** not performed	**MeOH** TEMPONE rotates τ= 366 ps, τ_o= 37 ps	**MeOH**; solvent protons are detected D=0.69 x10^{-5} (cm^2 s^{-1}) D$_o$= 2.4 x10^{-5} (cm^2 s^{-1})
P-L-Cu^{II}	**MeOH** not performed	**MeOH** ; TEMPONE rotates τ=384 ps, τ_o=37 ps	**MeOH**; solvent protons are not detectable (see text)

[a] TEMPONE 10^{-4} M; X-band JEOL JES-RE1X. [b]Bruker SXP 4-100 MHz

ISEC analysis in methanol is not possible owing to the known[6)] occurrence of non-steric interactions of the molecular probes with the polymer network. On the contrary, ESR and NMR analysis are successful. ESR spectra reveal that TEMPONE rotates freely, albeit less rapidly (τ=366 ps vs τ=37 ps in bulk methanol) and the NMR results show that Fick's coefficient for methanol diffusion, D, is reduced to 0.69x10^{-5} cm^{2}s^{-1} from 2.4x10^{-5} cm^{2}s^{-1} observed in bulk methanol. On the basis of these observations, methanol can be rationally indicated as a convenient solvent for exploiting the chemical reactivity of **P-L** ligands with Cu^{II}.

NMR analysis of methanol-swollen **P-L-Cu^{II}** materials reveals that, not unexpectedly, the overal paramagnetism of the polymer network promotes such an efficient spin-spin relaxation of the solvent protons that no overall NMR signal can be observed. On the contrary and most remarkably, ESR works perfectly. Upon swelling resin **P-L$_2$-Cu^{II}** with a 10^{-4} M solution of TEMPONE, the spectrum of the spin probe appears to be substantially unaffected by the matrix paramagnetism and τ results to be quite close to that observed in **P-L$_2$**. (Fig.2B). This apparent lack of interaction between the molecules of the spin probe and the Cu^{II} complexes pendant from the polymer backbone is mainly attributable to the relative immobilization (*vide infra*) of the Cu^{II} spinofores and to the reduced mobility of TEMPONE, which are obviously not allowed to move in the fluid medium as they would be in a conventional solution. This result strongly suggests that the spin probe-based ESR evaluation of the nanomorphology and molecular accessibility proposed by us will be valid for paramagnetic functional resin-metal complexes.

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