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Towards Polymer Diagnostic Agents − Copolymers of *N*-(2-Hydroxypropyl)-methacrylamide and Bis(2-pyridylmethyl)-4-vinylbenzylamine: Synthesis, Characterisation and $Re(CO)_3$-Labelling

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Diagnosis of early stage angiogenic tumours is fundamental for cancer therapy. In this study we present the synthesis and characterisation of functionalised HPMA-copolymers with optimal molecular weights that meet the demands of the enhanced permeability and retention (EPR) effect. Rhenium tricarbonyl complexes of the tripodal ligands bis(2-pyridylmethyl)benzylamine (**1a**) and bis(2-pyridylmethyl)-4-vinylbenzylamine (**1b**) were prepared and characterised by ^{1}H NMR and IR spectroscopy, mass spectrometry and X-ray diffraction. Ligand **1b** was copolymerised with *N*-(2-hydroxypropyl)methacrylamide (HPMA), and the resulting copolymer was treated with $(nBu_4N)_2[Re(CO)_3Br_3]$ to yield a $Re(CO)_3$-labelled copolymer.

Introduction

Polymer–drug conjugates are an interesting concept in medicinal chemistry. The conjugation of prodrugs to hydrophilic polymers provides an opportunity to solubilise poorly water-soluble drugs, improve tumour targeting and reduce drug toxicity.[1] Several polymer–drug conjugates have already entered phase-I/II clinical trials as anticancer agents.[2] The improved tumour targeting is due to the so called enhanced permeability and retention (EPR) effect, which concerns the passive accumulation of macromolecules in solid tumours because of the high vascular density in tumours, the increased permeability and defective architecture of tumour vessels, as well as suppressed lymphatic drainage from the tumour interestitium. The molecular weight (M_w) of macromolecular systems is more important than their nature (proteins, lipids or synthetic polymers) for the EPR effect. Macromolecules with molecular weights above 40 kDa are found to remain at high levels in circulating blood.[3] On the other hand, nephritic excretion is restricted to macromolecules with molecular weights below about 50 kDa.[4]

Although polymers are now widely used in therapeutic approaches, only a few examples of diagnostically used polymer conjugates exist.[5] We are interested in developing organometallic polymer-based tumour diagnostic agents. *N*-(2-Hydroxypropyl)methacrylamide (HPMA) was chosen as a copolymer base since its copolymers are water-soluble, biocompatible and non-immunogenic macromolecular carrier systems.[5a] Furthermore, the molecular weight of HPMA copolymers can be easily varied. Organometallic and coordination chemistry with relation to biological and medicinal chemistry is an increasingly important field. The use of technetium is of particular interest due to the short half-life of ^{99m}Tc ($T_{1/2}$ = 6 h, E_γ = 140 keV), which makes this isotope one of the workhorses of diagnostic nuclear medicine.[6] The chemistry of this element is closest to its heavier congener rhenium, which itself has become interesting for therapeutic purposes as the isotope ^{188}Re ($T_{1/2}$ = 16.9 h, E_β = 2.1 MeV). Since the development of new, simple routes for the synthesis of *fac*-$[^{99m}Tc(H_2O)_3(CO)_3]^+$ and *fac*-$[^{188}Re(H_2O)_3(CO)_3]^+$, several groups have begun to develop ligand systems for these $M(CO)_3$ fragments.[7] Therefore, a macromolecule that is able to bind $M(CO)_3$ (M = Tc, Re) would be interesting for diagnostic as well as therapeutic approaches.

Here, we report the synthesis and characterisation of HPMA-co-bis(2-pyridylmethyl)-4-vinylbenzylamine copolymers with different average molecular weights and the coordination of the $Re(CO)_3$ fragment to these copolymers.

Results and Discussion

The ligand bis(2-pyridylmethyl)benzylamine (**1a**) was prepared from picolyl chloride and benzylamine by modifying a synthesis originally reported by Dick.[8] This ligand serves as a model for the coordination environment of the $Re(CO)_3$ moiety in the polymer. The co-monomer ligand

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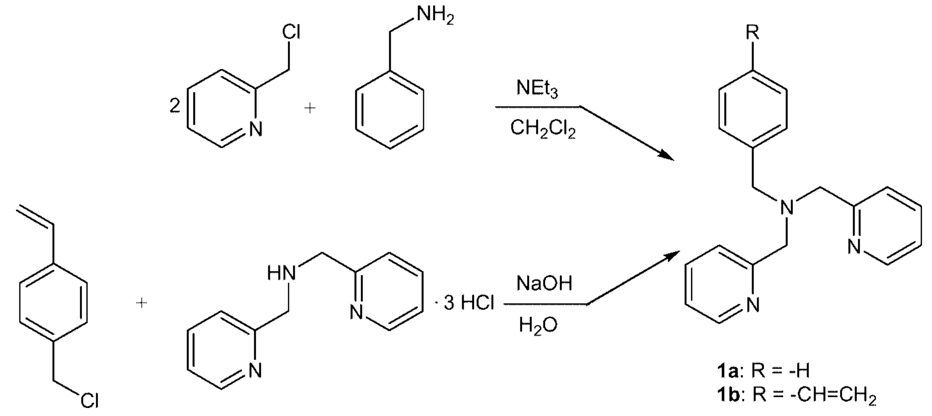
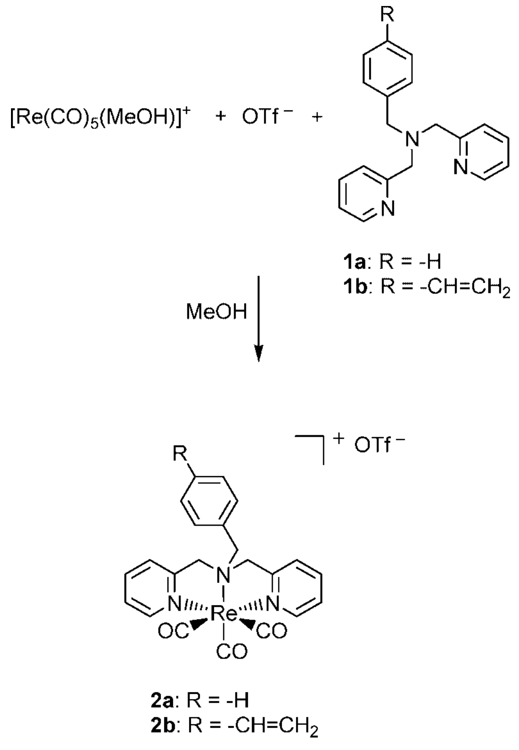


Scheme 1. Synthetic routes to the ligands **1a** and **1b**.

bis(2-pyridylmethyl)-4-vinylbenzylamine (**1b**) was prepared by the reaction of bis(2-pyridylmethyl)amine with 4-vinylbenzyl chloride (Scheme 1).

In the ^{1}H NMR spectra in deuteriochloroform both ligands show singlets at $\delta = 3.7$ and 3.8 ppm in a 2:4 ratio for the CH_2 groups attached to the amine. The aromatic protons of the phenyl ring and the protons of the pyridyl rings (H3, H4 and H5) appear in the region $\delta = 7.1$–7.9 ppm, whereas $H6_{py}$ is at a lower field of $\delta = 8.6$ ppm. In addition, **1b** exhibits signals for the three vinyl protons at $\delta = 5.23$, 5.75 and 6.72 ppm, with the characteristic splitting pattern of two doublets ($^{3}J_{cis} = 11$, $^{3}J_{trans} = 18$ Hz) for the terminal protons and a doublet of doublets for the α-proton of the vinyl group. The FAB^{+} mass spectra of **1a** and **1b** exhibit peaks for the molecular ion at the expected *m*/*z* value together with a characteristic fragmentation pattern.



Scheme 2. Formation of complexes of **1a** and **1b** with $[Re(CO)_5Br]$ in the presence of AgOTf.

Both **1a** and **1b** form complexes of the composition $[LRe(CO)_3]OTf$ when $Re(CO)_5Br$, AgOTf and ligand are mixed in an equimolar stoichiometry in refluxing methanol (Scheme 2).

Upon coordination, the signals of the CH_2 groups directly bound to the amine nitrogen atom are shifted by about 1 ppm towards lower field. Additionally, the methylene protons of the 2-pyridylmethyl groups at $\delta = 4.8$ ppm are no longer chemically equivalent due to the C_s-symmetry of complexes **2a** and **2b** and form an AB spin-system. The aromatic protons of the phenyl and pyridyl rings as well as the protons of the vinyl group in **2b** do not shift upon coordination. The IR spectra of **2a** and **2b** show the characteristic bands of the ligands and the two bands of a nearly C_{3v}-symmetrical $Re(CO)_3$ fragment, with the doubly degenerate *E* band slightly split (**2a**: 2028, 1922 cm^{-1}; **2b**: 2028, 1920 cm^{-1}). This splitting has also been observed in the $Mo^{I}(CO)_3$ complex of **1a**.[9] The FAB^{+} mass spectra of **2a** and **2b** exhibit peaks for the molecular ion at the expected *m*/*z* values (both 100%) together with the characteristic $^{187/185}Re$ isotope pattern.

Solid-State Structures of $2a·CH_2Cl_2·H_2O$ and $2b·CH_2Cl_2$

For a better understanding of the $Re(CO)_3$ binding in the functionalised polymer we determined the structures of the molecular "model" complexes **2a** and **2b** by X-ray analysis. Both complexes can be crystallised by slow diffusion of *n*-hexane into a solution of the corresponding complex in dichloromethane. Complex $2a·CH_2Cl_2·H_2O$ crystallises in the triclinic space group $P\bar{1}$ (Figure 1). The co-crystallised water molecule is disordered. Interestingly, the achiral complex $2b·CH_2Cl_2$ crystallises in the chiral space group $P2_1$ (Figure 2). The rhenium centre in both structures is in a slightly distorted octahedral coordination environment, with the *N*,*N*,*N* ligands and the three carbonyl ligands coordinating facially. As expected, both structures are very similar at first glance. In the structure of **2a** the angles between the carbonyl ligands are close to 90° and the maximum deviation of the Re1–C_n–O_n (n = 1–3) angles from 180° is less than 1.5°. Interestingly, the $Re(CO)_3$ fragment in **2b** shows significant distortion: the carbonyl groups are slightly bent towards each other and the C1–Re1–C3 angle is only 85.7°. In addition, the Re1–C_n–O_n angles deviate significantly from 180°. The maximum deviation is found for the Re1–C3–O3 angle, which is 174.8°. Selected bond lengths and angles are summarised in Tables 1 and 2.

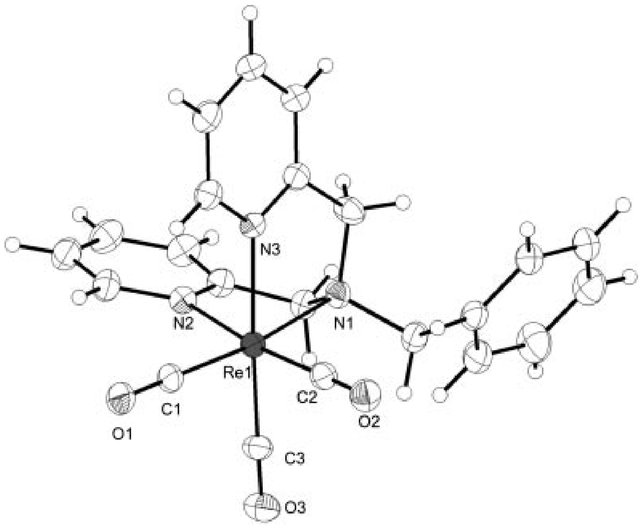


Figure 1. Structure of the cation $[(\mathbf{1a})Re(CO)_3]^+$ in $\mathbf{2a}\cdot CH_2Cl_2\cdot H_2O$. Displacement ellipsoids are shown at the 30% probability level.

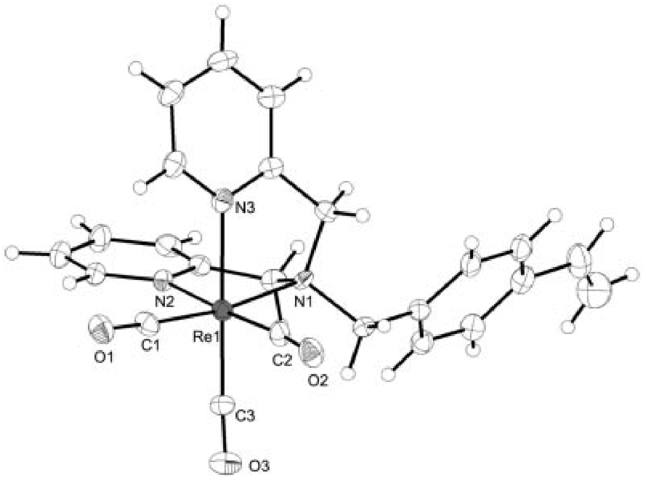


Figure 2. Structure of the cation $[(\mathbf{1b})Re(CO)_3]^+$ in $\mathbf{2b}\cdot CH_2Cl_2$. Displacement ellipsoids are shown at the 30% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for $\mathbf{2a}\cdot CH_2Cl_2\cdot H_2O$.

Re1–N1	2.228(4)	Re1–C1	1.915(5)
Re1–N2	2.162(5)	Re1–C2	1.917(6)
Re1–N3	2.157(4)	Re1–C3	1.940(5)
C1–O1	1.151(6)	C2–O2	1.145(8)
C3–O3	1.133(7)		
N1–Re1–N2	72.12(18)	N1–Re1–N3	78.43(16)
N2–Re1–N3	82.08(18)	C1–Re1–C2	88.7(2)
C1–Re1–C3	89.2(2)	C2–Re1–C3	89.7(3)
Re1–C1–O1	179.3(5)	Re1–C2–O2	179.3(5)
Re1–C3–O3	178.6(5)		

Table 2. Selected bond lengths [Å] and angles [°] for $\mathbf{2b}\cdot CH_2Cl_2$.

Re1–N1	2.228(6)	Re1–C1	1.902(8)
Re1–N2	2.156(7)	Re1–C2	1.917(7)
Re1–N3	2.177(7)	Re1–C3	1.918(8)
C1–O1	1.148(11)	C2–O2	1.159(10)
C3–O3	1.158(11)		
N1–Re1–N2	78.7(2)	N1–Re1–N3	78.0(2)
N2–Re1–N3	79.0(3)	C1–Re1–C2	89.6(4)
C1–Re1–C3	85.7(3)	C2–Re1–C3	87.1(4)
Re1–C1–O1	175.8(8)	Re1–C2–O2	177.1(8)
Re1–C3–O3	174.8(7)		

$Re(CO)_3$-Labelled HPMA-Copolymer

In order to obtain HPMA-co-bis(2-pyridylmethyl)-4-vinylbenzylamine copolymer (**3**), freshly synthesised ligand **1b** and HPMA were dissolved in dry acetone and azobis(isobutyronitrile) (AIBN) added as initiator.[10] The reactions were carried out at 50 °C for 24 h. The resulting polymeric product was precipitated from a mixture of acetone and diethyl ether.

The ^1H NMR spectrum of **3** (Figure 3) exhibits signals of the ligand as well as of HPMA. These signals are broadened due to the polymeric character of the examined molecules. Fortunately, there is almost no signal overlap and all signals can be assigned. The signals at δ = 3.8 and 3.9 ppm arise from the protons of the CH_2 groups attached to the amine, and the resonances deriving from the aromatic protons of the phenyl ring and the protons of the pyridyl rings appear in the region δ = 7.1–8.5 ppm. The other broad resonances can be assigned to HPMA and to the CH_2 group in the polymer backbone.

In the IR spectrum, the two $\nu_{C=C}$ bands of the aromatic pyridyl and phenyl rings occur at 1597 and 1572 cm^{-1} and the carbonyl vibration deriving from the HPMA occurs at $\nu_{C=O}$ = 1730 cm^{-1}. Furthermore, the three aliphatic CH_2 and CH_3 vibrations are found in the region between 2980 and 2800 cm^{-1}. With monomer ratios of 10:1, 20:1 and 40:1 (HPMA:ligand) an average molecular weight of between 13.5 and 52 kDa can be obtained, as confirmed by size exclusion chromatography in DMF (Table 3).

The copolymer was labelled with $Re(CO)_3$ by refluxing $(nBu_4N)_2[Re(CO)_3Br_3]$, AgOTf and copolymer in methanol. The IR spectrum clearly shows the vibrational bands of the copolymer as well as the two characteristic carbonyl bands from the pseudo C_{3v}-symmetrical $Re(CO)_3$ fragment.

In order to determine whether the $Re(CO)_3$ fragment is coordinated to the ligand system in the copolymer chain or whether it is non-specifically bound to the copolymer, the same reaction was carried out with poly-HPMA. In this case, the two bands of the carbonyl vibration can also be seen in the IR spectrum, thus indicating that $Re(CO)_3$ fragments are present in this sample as well. A Soxhlet extrac-

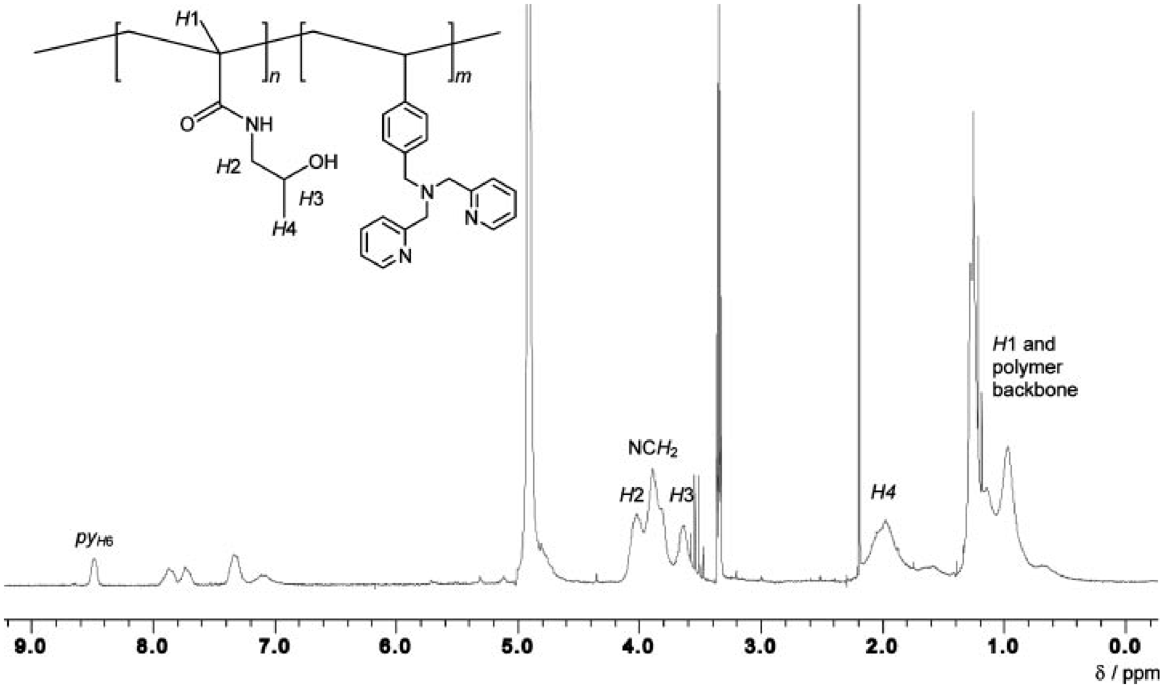


Figure 3. ^{1}H NMR spectrum of HPMA-co-bis(2-pyridylmethyl)-4-vinylbenzylamine copolymer **3a**.

Table 3. Average molecular weights of the copolymers **3** obtained with different monomer and AIBN ratios.

Copolymer	Monomer ratio	HPMA/**1b**/AIBN	M_w [kDa]	Polydispersity
3a	10:1	2 g/440 mg/30 mg	13.5	1.4
3b	20:1	2 g/239 mg/15 mg	20.0	1.2
3c	20:1	2 g/235 mg/20 mg	18.0	1.6
3d	20:1	2 g/253 mg/20 mg	22.5	1.5
3e	40:1	2 g/121 mg/15 mg	52.0	1.8

tion of both labelled polymers was carried out using water as solvent. After extraction, only the IR spectrum of the copolymer sample shows the two carbonyl bands with high intensity (Figure 4); the IR spectrum of the extracted poly-HPMA sample shows the carbonyl bands with very low intensity (Figure 5). This proves that $Re(CO)_3$ is in fact coordinated to **3** and, in addition, that non-coordinated $Re(CO)_3$ can be washed out in order to obtain the pure product.

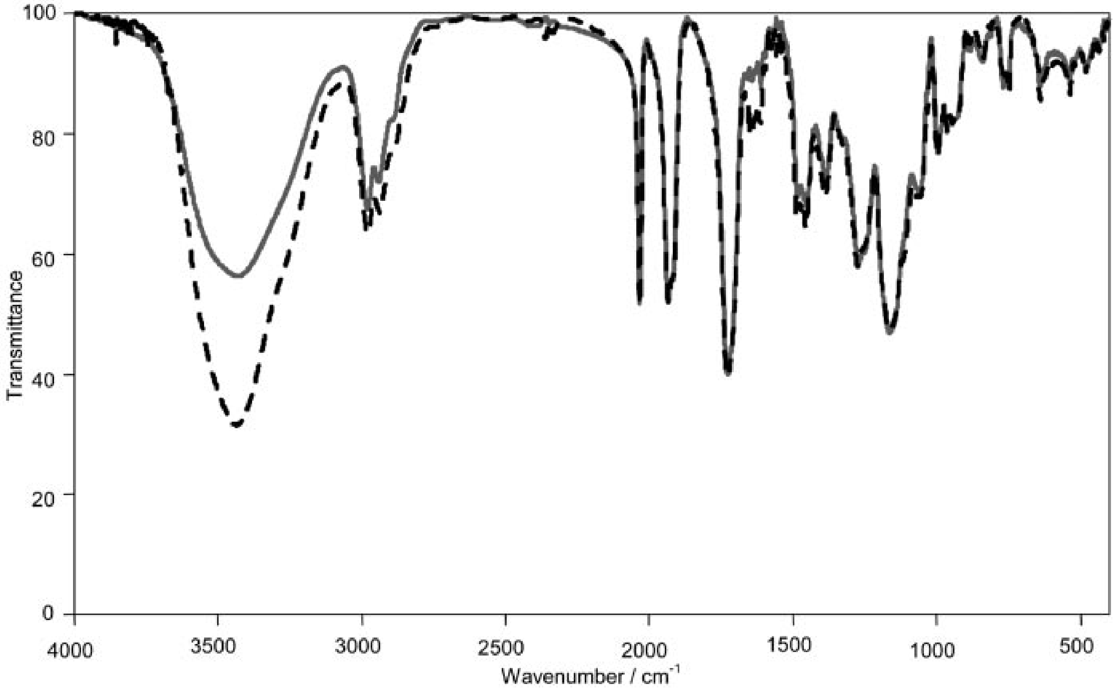


Figure 4. IR spectra of $Re(CO)_3$-labelled HPMA-co-bis(2-pyridylmethyl)-4-vinylbenzylamine copolymer **4a** before (dashed) and after Soxhlet extraction (solid).

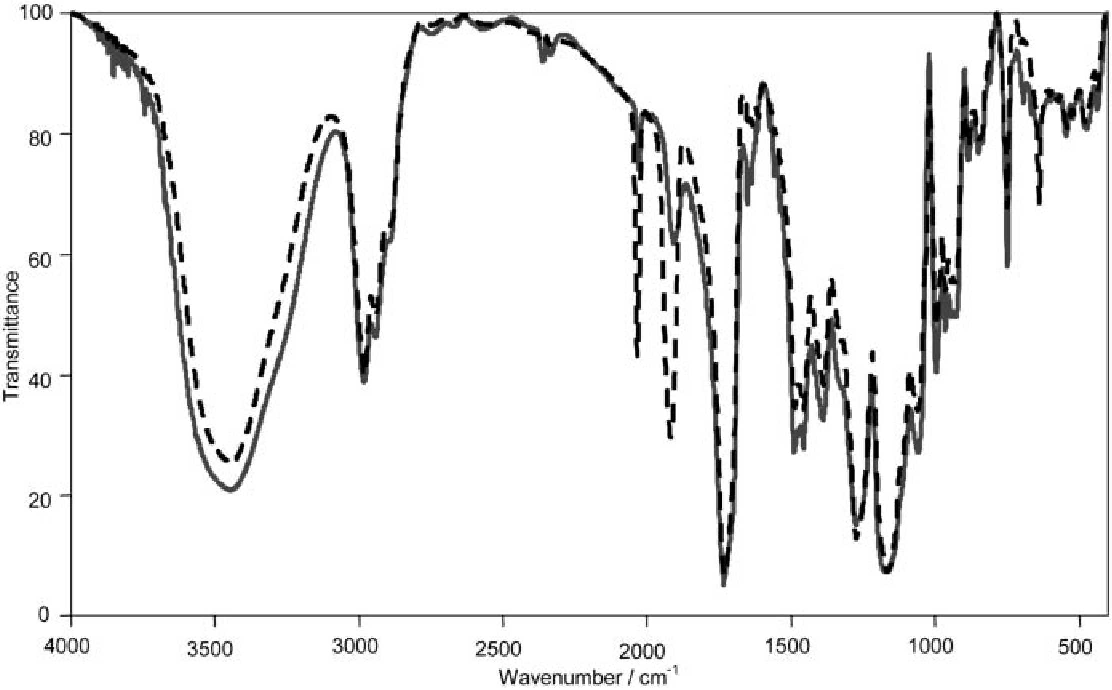


Figure 5. IR spectra of $Re(CO)_3$-labelled poly-HPMA before (dashed) and after Soxhlet extraction (solid).

Conclusions

We have presented a novel, water-soluble co-polymer of HPMA, namely HPMA-co-bis(2-pyridylmethyl)-4-vinylbenzylamine. The average molecular weight can be controlled by variation of the co-monomers and radical starter. With copolymer **3e**, a polymer having a molecular weight (52 kDa) suitable for the EPR effect was obtained. The copolymers can be labelled with $[Re(CO)_3Br_3]^{2-}$ at the bis(2-pyridylmethyl)amine unit and it has been shown that the $Re(CO)_3$ labels are not easily lost in aqueous medium. This makes these copolymers interesting carriers for the diagnostically used ^{99m}Tc.

The solid-state structures of the bis(2-pyridylmethyl)-amine-derived complexes **2a**$\cdot CH_2Cl_2\cdot H_2O$ and **2b**$\cdot CH_2Cl_2$ have been determined by X-ray crystallography. The IR spectra of these complexes and the $Re(CO)_3$-labelled copolymer are identical, they therefore resemble the structure of the binding sites in the labelled copolymer.

Experimental Section

2-Picolyl chloride hydrochloride, benzylamine and 4-vinylbenzyl chloride were used as purchased from Aldrich and Fluka. Bis(2-pyridylmethyl)amine tris(hydrochloride),[11] $Re(CO)_5Br$[12] and $(NBu_4)_2[Re(CO)_3Br_3]$[7a] were prepared according to literature procedures. The preparation of the complexes was carried out in Schlenk tubes under an atmosphere of dry nitrogen using anhydrous solvents purified according to standard procedures. Crystals suitable for X-ray structure analysis were prepared by slow diffusion of *n*-hexane into a solution of the complexes in dichloromethane. ^{1}H NMR spectra were recorded with a Bruker AM 200 and Bruker DRX 500 spectrometer. $^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker DRX 500 spectrometer. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra were calibrated against the residual proton signals and the carbon signals of the solvents as internal references ([D$_1$]chloroform: δ_H = 7.30 ppm and δ_C = 77.0 ppm). The FAB mass spectra were recorded with a Finnigan MAT 8200 mass spectrometer in an NBA matrix. IR spectra were recorded with a Bruker IFS 66 FT-IR spectrometer. Size-exclusion chromatography was performed with a Viskotec GPCmax VE 2001 GPC solvent/sample module with a Viskotec VE 3580 RI detector.

Bis(2-pyridylmethyl)benzylamine (1a): 2-Picolyl chloride hydrochloride (2.05 g, 12.5 mmol) and benzylamine (0.67 g, 6.3 mmol) were dissolved in 15 mL of water and heated to 60 °C. To this solution 5 mL of aqueous NaOH (5 M) were added dropwise over a period of 30 min and the resulting mixture stirred for an additional 60 min. The cooled solution was extracted three times with 20 mL of dichloromethane, the combined organic layers were dried with Na_2SO_4, filtered and the solvent removed in vacuo. The product was obtained as a viscous brown oil (1.51 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.64 (s, 2 H, NC*H$_2$*Ph), 3.76 (s, 4 H, pyC*H$_2$*), 7.1–7.9 (m, 11 H, aromatic *H*), 8.62 ppm (m, 2 H, py*H6*). $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ = 58.9, 60.3, 122.5, 123.3, 127.5, 129.1, 129.4, 127.0, 139.1, 149.4, 160.0 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2819, 1590, 1570, 760, 699 cm^{-1}. FAB$^+$ MS (NBA matrix): *m*/*z* (%) 290 (100) $[(pyCH_2)_2NCH_2Ph + H]^+$, 197 (47) $[pyCH_2NCH_2Ph]^+$, 93 (49) $[pyCH_2]^+$, 91 (60) $[CH_2Ph]^+$.

Bis(2-pyridylmethyl)-4-vinylbenzylamine (1b): Under an inert gas atmosphere, 4-vinylbenzyl chloride (1.3 g, 8 mmol), bis(2-pyridylmethyl)amine trishydrochloride (2 g, 6.5 mmol) and triethylamine (4 mL, 40 mmol) were dissolved in 30 mL of dichloromethane and stirred for 8 h. The white precipitate of triethylamine hydrochloride was removed by filtration. The organic solution was extracted twice with 10 mL of water and dried with Na_2SO_4. The solvent was removed in vacuo to give the product as an orange viscous liquid (1.4 g, 68%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.71

(s, 2 H, NCH_2Ph), 3.84 (s, 4 H, pyCH_2), 5.23 (d, $^3J_{cis}$ = 11 Hz, 1 H, *cis*-CH_2CH), 5.75 (d, $^3J_{trans}$ = 18 Hz, 1 H, *trans*-CH_2CH), 6.72 (dd, 1 H, CH$_2$CH), 7.1–7.9 (m, 10 H, aromatic H), 8.56 ppm (m, 2 H, py$H$6). ^{13}C{^{1}H} NMR (500 MHz, CDCl$_3$): δ = 58.6, 60.4, 113.9, 123.2, 126.6, 129.4, 129.4, 136.9, 136.9, 137.0, 139.0, 149.4, 160.2 ppm. IR (KBr): $\tilde{\nu}$ = 2922, 2821, 1629, 1590, 1569, 825, 760 cm^{-1}. FAB$^+$ MS (NBA matrix): *m*/*z* (%) 316 (59) [(pyCH$_2$)$_2$-NCH$_2$PhCHCH$_2$ + H]$^+$, 223 (45) [pyCH$_2$NCH$_2$PhCHCH$_2$]$^+$, 198 (26) [(pyCH$_2$)$_2$N]$^+$, 117 (100) [CH$_2$C$_6$H$_4$CHCH$_2$]$^+$, 93 (56) [pyCH$_2$]$^+$.

General Procedure for the Preparation of Re(CO)$_3$ Complexes: Under an inert gas atmosphere, AgOTf (129 mg, 500 µmol) and Re(CO)$_5$Br (0.2 g, 0.5 mmol) in methanol were heated to reflux for 60 min. The AgBr precipitate was removed by filtration and 0.5 mmol of the ligand (**1a** or **1b**) dissolved in 5 mL methanol was added. The solution was refluxed for an additional hour. After cooling to ambient temperature the solvent was removed in vacuo and the residue dissolved in a minimum of dichloromethane. *n*-Hexane was added to the solution and colourless crystals deposited after a few days.

[(1a)Re(CO)$_3$]OTf (2a): Yield: 0.28 g (76%). ^{1}H NMR (500 MHz, CDCl$_3$); δ = 4.69 (s, 2 H, PhCH_2), 4.82 (m, 4 H, [AB]$_2$, pyCH_2), 7.1–7.9 (m, 11 H, aromatic H), 8.6 ppm (m, 2 H, py$H$6). IR (KBr): $\tilde{\nu}$ = 2028, 1922, 1612 cm^{-1}. FAB$^+$ MS (NBA matrix): *m*/*z* (%) 560 (100) [(**1a**)Re(CO)$_3$]$^+$. C$_{23}$H$_{19}$F$_3$N$_3$O$_6$ReS·CH$_2$Cl$_2$·C$_6$H$_{14}$ (879.80): calcd. C 39.0, H 2.7, N 5.9; found C 38.6, H 2.7, N 5.8.

[(1b)Re(CO)$_3$]OTf (2b): Yield: 0.27 g (75%). ^{1}H NMR (500 MHz, CDCl$_3$); δ = 4.67 (s, 2 H, PhCH_2), 4.82 (m, 4 H, [AB]$_2$, pyCH_2), 5.31 (d, $^3J_{cis}$ = 11 Hz, 1 H, *cis*-CH_2CH), 5.78 (d, $^3J_{trans}$ = 18 Hz, 1 H, *trans*-CH_2CH), 6.69 (dd, 1 H, CH$_2$CH), 7.1–7.9 (m, 10 H, aromatic H), 8.6 (m, 2 H, py$H$6). IR (KBr): $\tilde{\nu}$ = 2028, 1920, 1560 cm^{-1}. FAB$^+$ MS (NBA matrix): *m*/*z* (%) 585 (100) [(**1b**)Re(CO)$_3$]$^+$. C$_{25}$H$_{21}$F$_3$N$_3$O$_6$ReS·CH$_2$Cl$_2$·C$_6$H$_{14}$ (905.84): calcd. C 40.9, H 2.9, N 5.7; found C 40.1, H 2.6, N 5.6.

General Procedure for the Preparation of HPMA-co-bis(2-pyridylmethyl)-4-vinylbenzylamine Copolymers (3): HPMA and bis(2-pyridylmethyl)-4-vinylbenzylamine were dissolved in 15 mL of acetone in a Schlenk tube under an inert gas atmosphere. After addition of AIBN, the solution was heated to 50 °C and stirred for 24 h. The polymer was then precipitated by pouring the reaction mixture into a mixture of acetone and diethyl ether (1:1), the precipitate was filtered off and dried in vacuo to give **3a** (1.5 g, 67%). ^{1}H NMR (200 MHz, [D$_4$]methanol): δ = 1.0 [CH_2 (polymer backbone), HPMA-H1], 2.0 (HPMA-H4), 3.6 (HPMA-H3), 3.8 (NCH_2Ph), 3.9 (pyCH$_2$), 4.0 (HPMA-H2), 7.1–7.9 (aromatic H), 8.6 ppm (py$H$6). IR (KBr): $\tilde{\nu}$ = 2980, 2800, 1597, 1572, 749 cm^{-1}.

General Procedure for the Preparation of Re(CO)$_3$-Labelled HPMA-co-bis(2-pyridylmethyl)-4-vinylbenzylamine Copolymers (4): Under an inert gas atmosphere, (*n*Bu$_4$N)$_2$[Re(CO)$_3$Br$_3$] (0.1 g, 0.13 mmol) and AgOTf (0.11 g, 0.39 mmol) were heated to reflux in methanol for 60 min. Precipitated AgBr was removed by filtration and 0.458 g of the copolymer **3a** dissolved in 10 mL methanol was added. The solution was refluxed for an additional hour and then cooled to room temperature. The polymer was then precipitated in a mixture of acetone and diethyl ether (1:1), filtered off and dried in vacuo (0.46 g, 93%). ^{1}H NMR ([D$_4$]methanol): δ = 1.0 [CH_2 (polymer backbone), HPMA-H1], 2.0 (HPMA-H4), 3.6 (HPMA-H3), 3.9 (pyCH$_2$), 4.0 (HPMA-H2), 7.1–7.9 (aromatic H), 8.5 ppm (py$H$6). IR (KBr): $\tilde{\nu}$ = 2980, 2800, 2033 (ν_{CO}), 1933 (ν_{CO}), 1612, 1598, 749 cm^{-1}.

X-ray Crystallographic Study: Crystallographic data were collected with a Stoe IPDS diffractometer at 183(2) K using a graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Suitable crystals were covered with Paratone N oil, mounted on a glass fibre and immediately transferred to the diffractometer. 8000 Reflections distributed over the whole limiting sphere were selected by the program SELECT and used for unit cell parameter refinement with the program CELL.[13] Data were collected for Lorentz and polarisation effects as well as for absorption (numerical). Structures were solved by direct methods using SIR97[14] and were refined by full-matrix least-squares methods on F^2 with SHELXL-97.[15]

CCDC-617234 and -617235 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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