Unusual oxygen affinity of linear polyvinyl amine–cobalt complexes with hydroxyl counter ions: an efficient way of separation and chemical storage of molecular oxygen

Ahmet Ince, Baris Gure and Niyazi Bicak
Department of Chemistry, Istanbul Technical University, Istanbul, Turkey

ABSTRACT
Methylated poly(vinyl amine) and its copolymer with diallyldimethylammonium chloride (DADMAC) were prepared by polymerization of N-vinyl formamide (NVF) or copolymerization with DADMAC. Acid hydrolysis of the polymers and subsequent methylation yielded corresponding polyamines. Co(II) complexes of the polyamines were demonstrated to be reasonably fast in molecular oxygen binding, when counter anions of cobalt are exchanged with hydroxyl ions. The oxygenation tests performed with oxygen sensor, FT-IR, and gas-volumetric methods revealed that complexes either with 4/1 or with 2/1 [amine]/[Co] ratios give 1:1 molecular oxygen adducts. Fast oxygenation (c.a. 2–4 min), high storage capacity, and smooth oxygen releasing within 70–120 °C are typical characteristics of the oxygenation–deoxygenation. The system seems to be useful for harvesting and chemical storage of air oxygen.

1. Introduction

Discovery of reversible oxygenation of salicylaldimine–cobalt complex by Tsumaki in 1938 [1] has found considerable attention in academia and industry. Investigations showed that aeration of the complex solution at room temperature results in binding of the molecular oxygen between two cobalt centers. The oxygen is driven off by heating the solution around 100 °C. This system was largely employed as fresh air source in airplanes, mines, and submarines. Oxygen binding characteristics of various derivatives of salicylaldimine-Co (II) complexes have been investigated. [2] Those investigations showed that an additional electron donating ligand so-called ‘axial ligand’ is essential for efficient binding of oxygen. Later investigations revealed that reversible oxygenation behavior is not confined to Co(II) complexes of salicylaldimine, but many other Co(II) complexes such as ethylenediamine-bridged bis-β-diketones,[3] porphyrins,[4] and cyclams [5] can bind molecular oxygen to give 1:1 or 2:1 oxygen adducts depending on nature [6] and steric effects [7] of the ligating groups.

In the continued studies, polymer-based cobalt complexes have been found attractive for storage or separation of air oxygen. Tsuchida et al. reported oxygen selective polymer membranes constituting with supported CoSalenes and poly (vinyl imidazole) as axial ligand.[8] Cosalene bounded epoxidized styrene-butadiene-styrene terpolymers have been employed for preparing oxygen-permeable membranes.[9] It is fact that the most common ligand used for polymer supported oxygen binding group is salicylaldimine. The other ligands are less common. Oxygenation of polymer-bound tetraazaporphirine–cobalt complexes has been studied by Shinohara group. [10] According to their report, oxygenation takes place at subzero temperatures, but the oxygen adduct decomposes above 50 °C as in the case of low molecular weight porphirine complexes. Polystyrene-bound 2,2′-bipyridyl–cobalt complexes have been reported as excellent reversible oxygen binding materials.[11]

In a recent work, Reye and coworkers reported design of CoSalen bearing silica with covalently bound imidazole and pyridine axial ligands for efficient oxygen trapping.[12] However, hydrophobicity of the carrier polymers and low thermal stability of the oxygen-bound metal complexes are the most common drawbacks of the systems described so far.[13]

In the present work, we have investigated reversible oxygen binding ability of water-soluble methylated linear polyvinylamine (PVAm)–cobalt complexes. Since cobalt complexes derived from low molecular weight cyclic multi-amine ligands (cyclams) are known to give more stable oxygen adducts,[5] methylated polyvinylamine function was preferred as ligand for generating thermally stable oxygen adducts via their cobalt complexes.
Moreover, diallyldimethylammonium chloride (DADMAC) was also added as chain expanding comonomer to inspect its effect on the oxygenation kinetics. Interestingly, a remarkable increment in the oxygenation velocity was observed when counter ions of Co(II) were exchanged with hydroxyl ions. Structural characteristics of the polymers were investigated using 1H-NMR and FT-IR techniques. Gas-volumetric method and oxygen sensor technique were employed in investigation of oxygenation–deoxygenation behaviors of the polymers.

2. Experimental

2.1. Materials

N-vinyl formamide (Aldrich), styrene (E. Merck), and divinyl benzene (E. Merck) were redistilled under diminishing pressure, prior to use. Diallyldimethylammonium chloride (DADMAC) (65% aqueous solution, Aldrich), morpholine (Aldrich), bromoacetyl bromide (Aldrich), mercury (II) acetate (E. Merck), carbon disulfide (E. Merck), dibenzoyl peroxide (Aldrich), and all the other chemicals were used as purchased, unless otherwise stated. PS-DVB microspheres were obtained by crosslinking copolymerization of styrene with divinyl benzene (with 9/1 M ratio) in aqueous suspension polymerization methodology using Gum Arabic as stabilizer as described before.[14] The resulting bead product was sieved and 210–420 μm size of fraction was used as support for surface-initiated photo-polymerization of the monomers, NVF, and DADMAC.

2.2. Polymerization of NVF and hydrolysis of the polymer

Homopolymerization and copolymerization of NVF was carried out in 25% aqueous monomer solution. In a typical procedure, 10 g (0.14 mol) NVF, 1.85 g DADMAC (65% aqueous solution) (7.4 mmol), and 30 mL of distilled water were charged to 100 mL volume of two-necked flask. Then, 0.4 g 2,2′-azobis(2-methyl propiondiamidine dihydrochloride) (1.475 × 10⁻³ mol) was added under nitrogen stream and the mixture was heated at 70 °C under reflux condenser for 6 h in an oil bath. The mixture was cooled and poured into 100 mL acetone and the polymer precipitated was filtered, washed with acetone (2 × 20 mL), and dried at 60 °C under vacuum for 16 h. The polymer, poly(NVF-co-DADMAC) weighed 11 g.

Hydrolysis of the homo and copolymers was performed with 5 M HCl solution. Thus, 10 g of the polymer sample was dissolved in 150 mL of 5 M HCl solution and heated at 110 °C for 16 h. For the case of the copolymer with DADMAC (10% mol/mol), the hydrolysis product precipitated during the reaction. The product was filtered and dissolved in 120 mL of water. The polymer was precipitated by adding drop wise to 250 mL of NaOH solution (15%), filtered, and dried at 40 °C under vacuum for 16 h. The yield was 5.2 g.

The hydrolysis product of PNVF homopolymer was isolated by a slightly different manner, in which the solution of the hydrolysis product was concentrated by evaporation of water using rotavapor and 40 mL of HCl (37%) was added and HCl salt of the polymer was separated by ultra-centrifugation. The free poly(vinyl amine) was obtained by precipitation from its aqueous solution (100 mL) using 250 mL of NaOH solution (15%). The product was dried at the same conditions. Occurrence of the hydrolysis was confirmed by comparison of 1H-NMR and FT-IR spectra of the initial and final products.

2.3. Methylation of linear poly(vinyl amine) and its copolymers

This was carried out by Eschweiler–Clarke methylation (Reductive Methylation) method, in which the hydrolyzed samples were reacted with 4 mol formaldehyde and 10.8 mol of formic acid per mole of amine content. In a typical procedure, to a solution of 10 g of poly(vinyl amine-co-DADMAC) (10%) (containing 0.164 mol amine) in 100 mL of water were added 53.2 g of formaline solution (37%) and 83.2 g of formic acid (98%) and the mixture was refluxed for 24 h while stirring. Then, two-thirds of the solution was removed by rotavapor and the product was precipitated in 300 mL of cold NaOH solution (5 M) and filtered. To remove acid residues, the crude product was dissolved in 100 mL of distilled water and reprecipitated in a fresh 5 M NaOH solution (300 mL). Finally, the product was dissolved in 80 mL of hot water (80 °C). After cooling, the solution was poured into 300 mL of isopropanol and the polymer precipitated was obtained by decanting of the solvent and dried under vacuum for 24 h at 50 °C.

2.4. Preparation and oxygenation of the polymer–cobalt complexes

In preparing cobalt complexes of the resins with methylated poly(vinyl amine) brushes, molar ratio of the amine content to Co (II) was kept constant at 2/1 to attain high oxygen binding capacities. In a typical procedure, 0.2 g of the resin sample with 1.5 mmol of amine content was swelled in 15 mL of distilled water in 100 mL of canonical flask for 15 min. To the mixture, there was added a solution of 0.22 g Co(NO₃)₂·6 H₂O (0.75 mmol) in 5 mL of water under nitrogen atmosphere and 7.5 mL of 2 M KOH solution and stirred for 30 min. The mixture was filtered, washed with water (100 mL) and acetone (20 mL) under nitrogen atmosphere. The resin products complexes with cobalt are very sensitive to air oxygen as visually followed
by change of their colors in few minutes. For this reason, all the manipulations should be carried out under nitrogen atmosphere. The product was dried under vacuum at 40 °C for 24 h and stored in tightly closed vial.

For the oxygenation, the complex product was transferred in 20 mL of water and air was passed through (30 mLs⁻¹) for 30 min. Color of the product turned to dark green. The resulting product was washed with water (40 mL), acetone (10 mL) and dried at 30 °C for 24 h under vacuum.

2.5. Tests for oxygen binding characteristics of the polymer complexes
A sample of the oxygenated polymer complex (ca. 0.2–0.5 g) and 25 mL of diethyleneglycol was placed in a 100 mL volume of two-necked flask equipped with a digital thermometer temperature probe which was immersed into the mixture.

The second neck of the flask was connected to the inlet of another flask attached to the oxygen sensor via plastic tube. The third neck of the second flask was connected with an inverted burette immersed into tap water in a glass reservoir. The first flask was placed in a temperature controlled silicone oil bath. The temperature of the oil bath was increased by 10 °C in each measurement step and kept constant for 10 min. Volume of the oxygen evolved was measured via changing level of water in the burette.

2.6. Preparation and oxygenation of polymer–cobalt complexes
The complexes were prepared by combination of the Co (NO₃)₂ and polymer solutions either in water or in ethylene glycol. The cobalt solution was obtained by mixing 10 mol of ammonia solution (25%). Thus, in 50 mL volume of Erlenmeyer flask, 0.466 g of (2 mmol) Co (NO₃)₂ 6H₂O was dissolved in 10 mL of ethyleneglycol and 2.0 mL of ammonia solution (25%) was added to this solution under nitrogen atmosphere. In another vessel, an ethylene glycol solution (15 mL) of 0.57 g polyvinylamine-co-DADMAC solution was mixed and stirred with the above solution under nitrogen atmosphere. Then, a solution of 0.08 g (0.02 mol) NaOH in 5 mL of ethylene glycol was added to the mixture and a nitrogen flow was introduced for 30 min to remove excess of ammonia. The resulting solution was stored in tightly closed bottles.

2.7. Oxygenation and deoxygenation of linear polymer–cobalt complexes
In order to visually follow oxygenation of the polymer–cobalt complex, 2.0 mL of the above solution was taken and charged to closed vials. Then, air (30 mLs⁻¹) was passed through for 5 min. The color of the solution turned from pink to dark brown in ethylene glycol solution.

The oxygenation was monitored either with UV or oxygen sensor techniques. In the UV monitoring, 8 × 10⁻⁴ M solution of the polymer–cobalt complex was prepared and charged to quartz holders (approx. 3 mL) and aerated for 5, 15, 25, and 90 min. UV spectrum of each sample was recorded using ethylene glycol as reference solution.

Gas-volumetric method was combined with oxygen sensor technique for simultaneous measurement of oxygenation and deoxygenation of the polymer complexes. For this purpose, a sample of the polymer–cobalt complex (0.5 g) and 25 mL of diethyleneglycol was placed in a 100 mL volume of three-necked flask equipped with a digital thermometer, a nitrogen inlet, and a delivery tube connected to a flask containing the oxygen sensor. The outlet of the middle flask was connected to an inverted burette which was immersed into water cylinder. The first flask was placed in a silicone oil bath. First, nitrogen was flushed through the system until measuring zero oxygen. Then, an air flow (30 mL) was introduced from the nitrogen inlet for 30 min. The oxygen percentage was monitored by the sensor. Thereafter, the first flask was immersed in temperature-controlled silicone oil bath. The temperature was increased gradually (10 °C in each step) and volume of evolved oxygen was measured from the burette.

2.8. Characterizations
¹H-NMR spectra of linear poly(vinyl amine) derivatives were taken in D₂O solvent, using Bruker 250 MHz NMR spectrometer. UV–vis spectra of the cobalt complex of methylated poly(vinyl amine)'s were recorded using Chebios Optimum–One UV–vis spectrophotometer. Percentage oxygen contents of the gas mixtures were measured using ALMEMO MA2390-3 oxygen meter with Ahlborn Fy 9600-O₂ oxygen sensor which was connected to the gas volumetric setup for simultaneous monitoring of the oxygen. FT-IR spectra were taken by a Perkin Elmer FT-IR Spectrum One B spectrometer.

3. Results and discussion
3.1. Synthesis and characterization of PVAm
Preparation of PVAm by hydrolysis of PNVF has been described in the literature. The reports, however, are somewhat controversial. Although Yamamoto et al. [15] reported full hydrolysis of PNVF by NaOH in aqueous solution, detailed investigation of Witek group [16] revealed that base hydrolysis results in ammonia evolution and formation of considerable amounts of vinyl alcohol segments.
Therefore, poly (vinyl amine-co-vinyl alcohol) is final product of the base hydrolysis. In this work, the starting polymers, linear PNVF, and its random copolymer with DADMAC (10%) were prepared by polymerization in aqueous solutions (Scheme 1).

Molecular weight of the NVF homopolymer was estimated as 246.5 KDa by viscosimetric method using Mark-Houwink parameters (K = 5.43 x 10^{-4} dL/g, α = 0.715, in 0.1 M NaCl solution at 30 °C).[17]

To avoid deamination reaction, NVF homo and copolymer was first subjected to acid hydrolysis (5 M HCl) and neutralized with NaOH solution (5%). Primary amine functions of the hydrolysis product were methylated using Eschweiler–Clarke methylation procedure using formaldehyde-formic acid mixture.

{1HNMR spectra shown in Figure 1} represent structural changes of the copolymer in each modification step.

Thus, disappearance of the C–H proton signal of formamido group at 8 ppm and upfield shift of the methyne group proton signal from 3.9 to 2.1 ppm implies a successful hydrolysis of PNVF segments of the copolymer, P(NVF-co-DADMAC 10%). Strong signal emerged at 1.8 ppm in Figure 1c must be due to methyl protons. Presence of weak signals in 2.1–3.2 ppm range indicates incorporation of DADMAC into the copolymer structure in the first step.

FT-IR spectra of the hydrolysis and methylation products in Figure 1(right) confirm the expected structural changes. The carbonyl vibration of amid group at 1680 cm\(^{-1}\) disappears and a new band originating from N–H plane bending vibration of the amino groups appears at 1600 cm\(^{-1}\) in addition to C–N vibration band at 1190 cm\(^{-1}\).

After methylation, these bands become considerably weak and a new strong band associated with the C–H deformation vibration of the introduced methyl groups is observed at a peak of 1438 cm\(^{-1}\).

Amine contents of the hydrolyzed polymers determined by conductometric method are in consistent with the theoretical values implying successful hydrolyses of the starting polymers (Table 1).

After methylation, these bands become considerably weak and a new strong band associated with C–H deformation vibration of introduced methyl groups is observed at 1438 peak cm\(^{-1}\).

The amine content of the hydrolysis product of P(NVF-co-DADMAC) was found to be 15.8 mmolg\(^{-1}\) very close to the theoretical value of 16.4 mmolg\(^{-1}\). The difference might be due to exchange of chloride anions of DADMAC component with hydroxyl ions while treating with concentrated NaOH solution. Amine contents of the methylated PVAm (13.6 and 10.9 mmolg\(^{-1}\)) with and without DADMAC segments, respectively, which are also in good agreement with those of the expected values.

Thus, 22.1 mmolg\(^{-1}\) of amine content of the hydrolysis product of PNVF is slightly lower than the theoretical amine content (23.2 mmolg\(^{-1}\)) of pure poly(vinyl amine).

### 3.2. Oxygenation of linear PVAm–cobalt complexes

The addition of one mole of CoCl\(_2\).6H\(_2\)O per 4 mol of repeating units of methylated PVAm in ethyleneglycol solution gives a soluble pink complex which turns brownish-green after exposure to air for a short period of time implying its high oxidation susceptibility. After heating for 5 min at 100 °C, green color of the solution fades and the pink color is restored, which indicates reversibility of the oxygen binding. No gelation or precipitation was observed during the complexation of methylated PVAm with Co (II). In another words, reaction of PVAm with Co (II) ion does not result in crosslinking, most probably due to mobility of the coordination bond and outer-sphere complex formation.

| Polymer | Amine content\(^{a}\) (mmolg\(^{-1}\)) | Amine content\(^{b}\) (mmolg\(^{-1}\)) | Oxy time (min) | O\(_2\) evol.\(^{c}\) Temp °C | Evolved\(^{d}\) O\(_2\) | O/L[Co(II)] (mol/mol) |
|---------|----------------------------------|----------------------------------|----------------|----------------------------|----------------|----------------------|
| PNVF (246.5 KDa) | 22.1 (23.2) | 13.6 | 15 | 70–120 | 20 ± 2 mL | 0.9 ± 0.1 |
| P(NVF-co-DAD-MAC) | 15.8 (16.4) | 10.9 | 15 | 70–120 | 18.4 ± 2 mL | 0.8 ± 0.1 |

\(^{a}\)The amine content the polymer before methylation (assigned by conductometric titration.

\(^{b}\)Amine content of the polymer after methylation.

\(^{c}\)The temperature at leveling of the deoxygenation curve was assigned as the final temperature.

\(^{d}\)Evolved O\(_2\) volume per 0.8 mmol of the cobalt complex at 0 °C.
Intensities of the two bands remain unchanged after 15 min of air exposure, implying saturation of the oxygenation. To release absorbed oxygen, the aerated polymer complex solutions were heated up to 130 °C in ethyleneglycol, at a heating rate of 2 °C per min. The oxygen released was monitored by gas-volumetric method. Figure 2b and 2c show 70–120 °C of temperature interval for the deoxygenation and 20 and 18.4 mL of oxygen evolution per 0.8 mmol of Co (II) ion for the homo and copolymer complexes, respectively, at STP (standard temperature pressure conditions). This corresponds to nearly 1 mmol per mole of cobalt (Table 1), implying nearly 1:1 oxygen adduct formation in both cases.

Formation of 1:1 molecular oxygen adducts is less common,[18] but these form from the ligands constituting with high electron donating atoms.[19] In this case, oxygen binding occurs to give ‘superoxo’ structure in which two oxygen atoms bind to the same cobalt atom. Considering stability of Co(III) ion in basic medium, highly basic nature of the polyamine ligand (pH 9.5) makes the superoxo cobalt complex stable up to 70 °C.

Good solubility of the polymer complex in water (i.e. 0.1–0.2 M) must be due to positive charge on cobalt center providing high hydrophilicity.

Figure 2 shows changing UV–vis spectrum of methylated vinyl amine–DADMAC copolymer complex with Co (II) by air exposure. Thus, increasing air exposure results in red-shift of the charge transfer band of the cobalt–amine complex from 315 to 350 nm. Similarly, d–d transition band at 515 nm shifts to 590 nm and its intensity increases simultaneously.

**Scheme 1.** Preparation of methylated poly (vinyl amine) copolymers in high molecular weights via copolymerization of NVF with DADMAC in aqueous solution.

**Scheme 2.** Proposed scheme for the reversible oxygenation of cobalt complex moieties (with [L]/[M]: 2/1) on the surface brushes.
The results also showed that incorporation of DADMAC segments in the polymer structure does not bring additional advantage in the oxygen binding (Table 1). It is important to note that oxygenation and deoxygenation of the complexes can be cycled up to 10 times as inferred from the color change by aeration and followed heating. This reveals reversibility of the oxygenation and stability of the ligand within the cycle.

We have also investigated counter anion effect on oxygenation of cobalt complexes with chloride, nitrate, and hydroxyl ions. The hydroxyl ions were generated by exchanging the counter anions by KOH addition. It was found that oxygenation is very slow in the cases for chloride or nitrate ions so that volume of the trapped oxygen was only 2.6 mL (per 0.8 mol of cobalt) after 20 min of aeration. Such a phenomenon is not reported so far.

However, in an interesting paper, Marchaj et al. reported pH dependency and kinetics of oxygenation of some cobalt (II) complexes.[20] What they found was little influence of axial ligand on the oxygenation at high pH values. They also reported possibility of dioxygen uptake by cobalt–cyclam complexes in basic solutions without using axial ligand. Later on, such an unusual oxygenation behavior was reported by Ceccanti et al.[21] They proposed that role of the axial ligand is to enhance pH of the medium rather than coordinating. Those observations are in good agreement with the present results. At present, actually we do not know the mechanism of the ‘hydroxyl ion effect’. Presumably, this is due to easy replacing of the hydroxyl anions with molecular oxygen.

In the last part of the work, we have investigated effect of [Amine]/[ Cobalt] ratio. The complexes with 4/1 and 2/1 [Amine]/[ Cobalt] ratios were studied. The oxygenation rate and oxygen uptake capacities were almost the same for both cases. The only difference was slightly low saturation temperature (110 °C) of the deoxygenation profile for the case with 2/1 [Amine]/[Cobalt] ratio. Slightly high thermal stability of the oxygenated tetraaza complex can be attributed to three chelate rings in the coordination, whereas the complex with 2/1 [L]/[ M] ratio has only one chelate ring. This means that, complexes with 4/1 and 2/1 [Ligand]/[ Cobalt] ratios form 1:1 oxygen adducts.

Since oxidation state of oxygenated cobalt is +3, one of the hydroxyl groups must retain around cobalt for the electro neutrality, as reported by Nikon and Martell.[22] According to this scheme, reversible oxygenation of the polymer-bound cobalt complexes with [L]/[ M] : 2/1 ratio can be depicted schematically as shown in Scheme 2.

4. Conclusion
In conclusion, structural aspects of methylated polyvinyl amines and oxygenation behavior of their cobalt complexes can be summarized as follows:

- Co(II) complexes of the polymers are water-soluble and show rapid oxygenation by aeration, in water or ethylene glycol solvent, when counter ions of cobalt are exchanged with hydroxyl ions.
- In these conditions, oxygenation is completed within minutes at room temperature to give 1:1 oxygen-cobalt adducts (superoxo structure) as inferred from gas-volumetric measurements.
- The deoxygenation takes place in a temperature interval, 70–120 °C.
- Presence of DADMAC copolymer segments does not bring additional advantages in the oxygenation.
- The use of 4 and 2 amines per cobalt in complex formation does not change the capacity, so that 1:1 oxygen adduct forms each case.
- The cobalt complex presented seems to be superior to previous oxygen binding system and good candidate for chemical storage of molecular oxygen.

Disclosure statement
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