Water Soluble Dextran-Polyacrylamide Graft Copolymers for Capturing Metal Ions

N. Kutsevol,[*1] J.-M. Guenet,[2] N. Melnyk,[1] D. Sarazin[2]*

Summary: The graft copolymers of Polyacrylamide (PAA) to Dextran ($M_w = 20000$ and $M_w = 70000$) have been synthesised by ceric-ion-reduced redox initiation method. Molecular characteristic of graft copolymers were determined from light scattering, SEC, and viscometry data. It was established that the increase of molecular weight of Dextran component up to 3.5 times do not influence essentially organization at molecular level of these copolymers in aqueous solution. Thet D-g-PAA copolymers capable of binding the heavy metal ions.

Keywords: Graft copolymer; Dextran; Polyacrylamide; Polymer-Metal Complex

Introduction

Heavy metals, due to their high toxic effect on living organisms, are highly harmful to human health and to ecological systems. Chemical precipitation, electrodialysis, solvent extraction, and ion exchange are some of the methods used for removal of heavy metals from wastewaters [1]. However they are relatively expensive; therefore, there is research interest in using alternative low-cost effective methods for water clearing process. Water-soluble synthetic and natural macromolecules are among the most efficient materials used as flocculants in the process of water clarification [2]. The attempts have been made in the past decades to combine by grafting the best properties of synthetic and natural polymers [3]. It was concluded that by grafting flexible PAA chains onto the polysaccharide backbone it is possible to develop efficient and shear stable polymers for water treatment in industrial effluents and mineral processing. PAA as well as polysaccharides have on their chains ligands capable to coordinate the metal ions; thus these compounds have attracted our interest.

The aim of the present work is the preparation of graft copolymers consisting of Polyacrylamide chains grafted to a poly-Dextran using $M_w = 20000$) and $M_w = 70000$ backbone, and of determining the influence of polysaccharides main chain length on their molecular structure in aqueous solution and functional properties with special emphasis on the possibility to capture heavy metal ions.

Experimental

Materials

Dextran-graft Polyacrylamide (D-g-PAA) copolymers were synthesized by ceric-ion-reduced redox initiation method [4]. Dextran (Leuconostoc) with $M_w = 20\,000$ (D20) and $M_w = 70\,000$ (D70) (Serva, Sweden), acrylamide (AA) (Reanal, Hungary) and ammonium cerium (IV) nitrate (Aldrich, USA) were used. The amount of initiator, of AA and the molar ratio of Ce^{4+}/ Dextran were the same during the synthesis of D20-g-PAA and D70-g-PAA in order to obtain comparable number and length of grafts chains in copolymers.

The analytical grade hydrated cobalt, nickel, aluminum and iron sulfate were used for preparing the stock solution for

---

[1] Kyiv Taras Shevchenko National University, Department of chemistry, 60 str. Volodymyrska, KYIV 01033, Ukraine
E-mail: kutsevol@ukr.net
[2] Institut Charles Sadron, ULP-CNRS, rue Boussingault, STRASBOURG, 67083, Cedex, France

experiment on complex formation in the systems D-g-PAA/Me^{2+}.

Instruments and Methods

The *FT-IR* spectra were obtained by Spectrophotometer Nicolet NIXUS-475 (USA) in the range 4000–400 cm^{-1} using thin copolymer films ($l = 6–9\ \mu m$). The films were cast from aqueous solutions.

Viscosity measurements were performed for dilute solution using an Ostwald type viscometer kept in a bath at $25 \pm 0.05\,^\circ C$,. The data were analyzed through the equation [5]:

$$\eta_{sp}/C = [\eta] + k_H[\eta]^2 C.$$

The *light scattering* experiments were carried out by using the commercial apparatus (SEMATECH) working with a laser source He-Ne at $\lambda = 632{,}8$ nm. The scattering angle, θ, range investigated was between 30 and 150°. We made conventional static light scattering analysis of the Zimm-plots using the following equation relating the excess Rayleigh ratio $R(q)$, weight-average molar mass M_w, the radius of gyration R_g and the second virial coefficient A_2[6] :

$$KC/R(q) = 1/M_w[1 + q^2/3] + 2A_2C$$

All solutions and solvent after dilution were filtered using 0.45 μm Millipore filters directly in the measurement cells.

Self-exclusion chromatography (SEC) analysis was carried out by using a multi-detection device consisting of a *LC-10AD SHIMADZU* pump (throughput 0.5 ml/mn), an automatic injector *WISP 717+* from *WATERS*, 3 coupled *30cm-Shodex OH-pak* columns (803HQ, 804HQ, 806HQ), a multi-angle light scattering detector *DAWN F* from *WYATT TECHNOLOGY*, a differential refractometer *R410* from *WATERS*. Distilled water containing 0.1 M $NaNO_3$ was used as eluent. The solutions for the SEC analysis with concentration were prepared.

The samples of graft copolymers were dissolved at room temperature. The measurements carried out in 24 hours after preparation of solution for balance achievement.

Results and Discussion

FT-IR and ^1H NMR spectroscopy confirmed that we are dealing with graft copolymers [4]. One narrow peak on the SEC chromatograms testify that the product of grafting process is only graft copolymer. The molecular characteristics of D-g-PAA copolymers calculated from SEC, LS and viscometry are reported in the Table 1.

Unfortunately we could not calculate the number and molecular weight of grafts in D-g-PAA copolymers as during the process of degradation of Dextran chains of the graft copolymers by acid hydrolysis [7] the cross-links of PAA chains occurred [8]. Therefore for graft copolymer characterization we used only total M_w of D-g-PAA (Table 1).

The value of M_w and R_z, determined by SEC and LS methods are in good agreement. The second virial coefficient value $(A)_2$ testify that water is good solvent for D-g-PAA. Increase of Dextran chain length in 3.5 times (70000/20000 = 3.5) do not influence essentially the copolymers macromolecule state in solution. It follows from the comparable values of M_w, R_z and $[\eta]$ for D20-g-PAA and D70-g-PAA samples.

Table 1.
Molecular characteristics of D-g-PAA copolymers calculated from SEC, LS and viscometry

Sample	$M_w \times 10^{-5}$ (SEC)	M_w/M_n (SEC)	R_z,nm (SEC)	$M_w \times 10^{-5}$ (LS)	A_2,cm^3/g (LS)	R_z, nm (LS)	$[\eta]$, ld/g	Content of Dextran component in GC, %
D20-PAA	8,5	1,7	47	8,7	3,1	60	2,3	3
D70-PAA	7,9	2,7	35	10	3,37	52	2,0	9

Table 2.
The value of reduced viscosity change of D-g-PAA solution at metal ions presence. $C_{polymer} = 0.01$ g/dl; $C_{Me}{}^{n+} = 0.06$ g-ion Me^{n+}/l

Metal ion	D20-g-PAA	D70-g-PAA
	$\Delta\eta$, dl/g	$\Delta\eta$, dl/g
Ni^{2+}	2,5	2,4
Co^{2+}	1,5	1,6
Al^{3+}	7,3	6,3
Fe^{3+}	2	2

The graft copolymers ability to bonding heavy metal ions was studied by viscometry and FTIR spectroscopy. For FTIR investigation we used the thin films prepared by drying of aqueous polymer solution with addition of Ni^{2+}, Co^{2+}, Al^{3+} and Fe^{3+} ions. Table 2

Fig. 1 (a; b) shows as example the change of reduced viscosity of the graft copolymer solution in the presence of metal ions. The increase of reduced viscosity observed with increase in ions concentration. The most drastic changes $\Delta\eta$ in comparison with solution of individual copolymers are observed for the most dilute solution (Table 3).

The increase in reduced viscosity is connected with the formation of donor-acceptor bonds between metal ions and functional groups of two or more macromolecules.

Fig. 2 reports as example the FTIR spectrum of D70-g-PAA. In the spectrum in addition to the characteristic vibrations of α-glycoside rings of Dextran in the range of 750–1040 cm^{-1}, also the characteristic Amide I (CO stretching at 1730–1580 cm^{-1}) and Amide II (NH deformation at 1730–1580 cm^{-1}) vibration of $-CO-NH_2$ groups of the grafted PAA-chains are observed. The correct spectrum analysis in the range of 3500–3000 cm^{-1} is impossible as the stretching vibrations of hydroxyl groups of to dextran overlap the stretching vibrations of $-NH_2$ groups of PAA chains and of –OH groups of bond water present in the graft copolymers. Moreover, for all copolymers the characteristic stretching vibration of Dextran component is poorly resolved due to low content of the Dextran constituent (Table 1).

The analysis of the FTIR spectra for D-g-PAA/Me^{n+} systems was carried out in particular in the 1500–1700 $cм^{-1}$ region (Amide I and Amide II). Table 3 reports the Amide I and Amide II characteristic vibration of D-g-PAA/Me^{n+} systems and D-g-PAA.

D-g-PAA copolymers can form H-bonds of different types (Fig. 3) which are less probable in solution but presents in the bulk state. It is known that the H-bonds formation between functional groups causes the decrease of frequencies of stretching vibration and increase of frequencies of deformation vibration. Table 4

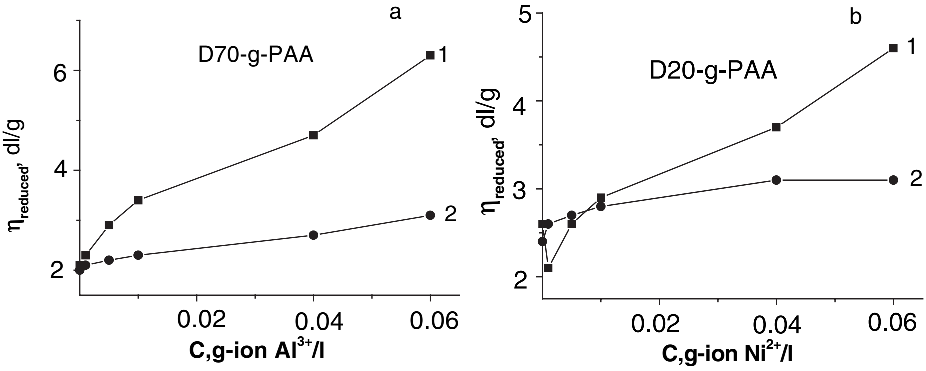

Figure 1.
Dependence of reduced viscosity of D70-g-PAA (a) and D20-g-PAA (b) vs Ni^{2+} and Al^{3+} ions concentration. $C_{polymer} = 0.01$ (1); $C_{polymer} = 0.05$ (2) g/dl.

Table 3.
Amide I and Amide II characteristic vibrations of D-g-PAA/Me^{n+} systems and D-g-PAA.

Metal ion	D20-g-PAA		D70-g-PAA	
	Amide I (ν_1, cm^{-1})	Amide II (ν_2, cm^{-1})	Amide I (ν_1, cm^{-1})	Amide II (ν_2, cm^{-1})
—	1662	1618	1661	1618
Co^{2+}	1657	1615	1663	1615
Ni^{2+}	1656	1609	1655	1603
Al^{3+}	1665	1601	1656	1598
Fe^{3+}	1649	1575	1653	1577

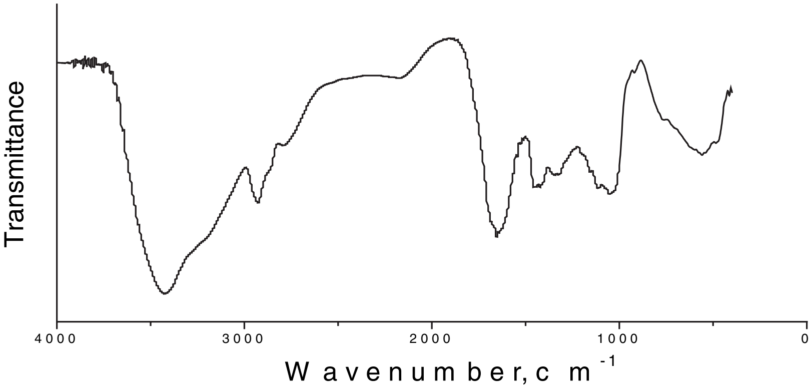

Figure 2.
FTIR spectrum of D70-g-PAA.

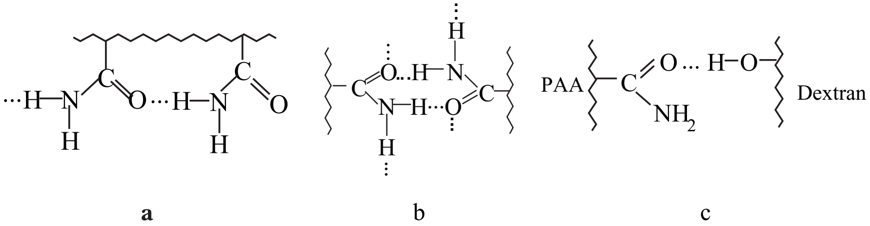

Figure 3.
H-bonds in D-g-PAA (a) and (b) – between functional groups of PAA grafted chains; (c)- between main and grafted chains.

Table 4.
The shift of AmideI and Amide II characteristic vibration of D-g-PAA/Me^{n+} system relatively of amideI and amide II characteristic vibration of different D-g-PAA.

Metal ion	D20-g-PAA		D70-g-PAA	
	Amide I ($\Delta\nu_1$, cm^{-1})	Amide II ($\Delta\nu_2$, cm^{-1})	Amide I ($\Delta\nu_1$, cm^{-1})	AmideII ($\Delta\nu_2$, cm^{-1})
Co^{2+}	5	3	2	3
Ni^{2+}	6	9	6	15
Al^{3+}	3	17	6	20
Fe^{3+}	13	43	8	41

The increase in the frequencies of the stretching as well as of the deformation vibration occurs for the systems D-g-PAA/Me^{2+} in comparison with the individual copolymers. It testify more strong bonding of carbonyl CO groups with metal ions and as results the partial formation of NH_2 groups not involved in H-bonds (Fig. 3, a, b). Thus, the interaction between macroligand and heavy metal ions occurs mainly by formation of donor-acceptor bonds between CO groups of PAA chains and metal ions. The process of complex formation between macroligand and heavy metal ions do not depend on the molecular weight of Dextran component for D20-g-PAA and D70-g-PAA copolymers. The complex formation ability of metal ions with this macroligand is following: $Fe^{3+} > Al^{3+} > Ni^{2+} > Co^{2+}$.

Conclusion

The copolymers Dextran- polyacrylamide based on Dextran of various molecular weight (Mw = 20000 and Mw = 70000) have been synthesised by ceric-ion-reduced redox initiation method. It was shown that increase of Dextran component length in 3,5 times (70000/20000) influences moderately the state of molecules of D-g-PAA in aqueous solution. It was establish that D-g-PAA copolymers are capable of binding the heavy metal ions. The process of complex formation between macroligand and heavy metal ions do not depend on the molecular weight of Dextran component for D20-g-PAA and D70-g-PAA copolymers. The modification of these copolymers will allow one to prepare highly effective flocculants for ecological problems solution.

Acknowledgements: The authors are grateful to NATO (grant N981343) and Ukrainian-French programme DNIPRO for financial support.

[1] I.G. Shibi, T.S. Anirudhan.*Chemosphere.* **2005**, 58, 1117.
[2] T.T. Tripathy, R.P Singh.*Eur.Pol. J.*, **2000**, 36, 1471.
[3] V.D. Athawale, V. Lele.*Carbohyrate Pol.* **2000**, 41, 407.
[4] N. Kutsevol, J.-M. Guenet, N. Melnik, C. Rossi.*Macromol. Symp.* **2005**, 222, 219.
[5] M.C. Delpech, F.M.B. Coutinho, M.E.S. Habibe. *Polym.Test.* **2002**, 21, 155.
[6] see for instance Huglin , M.B. (Ed.) *Light Scattering from Polymer Solutions* **1972** Acad. Press London
[7] V.D. Athawale, M.P. Padwaldesai.*Eur. Pol. J.*, **1999**, 35, 1237.
[8] S. Kiatkamjornwong, W. Chomsaksakul, M. Sonsuk.*Radiat. Phys. Chem.* **2000**, 59, 413.