Star-Like Dextran-*graft*-(polyacrylamide-*co*-polyacrylic acid) Copolymers

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Summary: Star-like dextran-*graft*-(polyacrylamide-*co*-polyacrylic acid) (D-*g*-(PAA-co-PAAc) copolymers in a salt form were obtained by alkaline hydrolysis of Dextran-graft-Polyacrylamide (D-*g*-PAA) samples. The internal structure of D-*g*-PAA in solution predetermined the reaction course and the conversion degree depended upon the initial architecture of macromolecules. It was shown that macromolecules of D-*g*-(PAA-*co*-PAAc) acquired extended conformation because grafted chains became greatly straightened when charged functional groups appeared. No polyelectrolyte effect for synthesized D-*g*-(PAA-*co*-PAAc) samples was registered. Star-like polyelectrolytes were proved to be more efficient matrices in comparison with linear anionic Polyacrylamide for silver nanoparticle *in situ* synthesis.

Keywords: nanoparticles; non-linear polymers; polyelectrolytes

Introduction

Polyelectrolytes with non-linear architecture of macromolecules attract a warm interest due to their unusual properties arisen from peculiarities of their internal structure in solution. This structure depends on chemical nature of polymer, length of branches and distance between them, amount and distribution of functional groups along chains, construction mode of branched molecule. A lot of variable parameters (pH, ionic strength, chemical nature and charge of counterions, temperature, etc.) affect the properties of polyelectrolyte solution so they have to be taken into account when non-linear ionic polymers are applied as task-oriented materials.

Nowadays linear Polyacrylic acid (PAAc) and Polyacrylamide (PAA) in nonionic and anionic forms are widely used in water treatment, biotechnology, medicine, pharmacology.[1,2] Cognate branched polyelectrolytes with controlled structure seem to be a good substitution of these materials. The local concentration of functional groups in branched polymers is higher than in linear ones [3–4] so they are perspective in nanochemistry and nanotechnology, particularly as polymer matrices for metal ion reactions.

Experimental Part

Source Nonionic Polymers

D-*g*-PAA copolymers were synthesized by grafting Polyacrylamide chains onto Dextran backbone. Two Dextran samples were purchased from Fluka and their molecular weights estimated by the manufacturer were $M_w = 7 \times 10^4$ and $M_w = 2 \times 10^4$ (designated as D70 and D20, respectively). The syntheses were carried out using "grafting from" method. Acrylamide monomer was purchased from Aldrich. It was twice recrystallized from chloroform and dried under vacuum at room temperature. The theoretical number of PAA grafts (n) depend on the ratio of cerium(IV)-initiator concentration to Dextran.[5] For synthesized copolymers n was equal 5 or 20, so non-ionic samples D70-*g*-PAA5; D70-*g*-PAA20; D20-*g*-PAA5, D20-*g*-PAA20 (Table 1) as well as linear PAA ($M_w = 1.40 \times 10^6$) were source polymers for further transformation.

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Table 1.
Molecular parameters of D-*g*-PAA copolymers.[6]

Sample	$M_w \times 10^{-6}$ g · mol^{-1}	$R_g^2/M_w \times 10^{21}$ m^2·mol · g^{-1}
D70-g-PAA5	2.15	3.36
D70-g-PAA20	1.43	2.85
D20-g-PAA5	1.60	2.81
D20-g-PAA20	0.77	2.75

The content of Dextran component in D-*g*-PAA copolymers was less than 5%, thus synthesized samples were star-like polymers with Dextran core and PAA arms.

Synthesis of Star-Like Polyelectrolytes

Star-like D-*g*-PAA copolymers were saponified in order to obtain polyelectrolyte samples.

NaOH was purchased from Aldrich and all solutions for alkaline hydrolysis were prepared with distilled water. Alkaline hydrolysis of D-*g*-PAA and linear PAA samples was carried out as follows: 2 g of D-g-PAA (or PAA) was dissolved in 200 ml of water then 10 ml 5M NaOH was added to it. The mixture was placed in water bath at 50 °C. The probes were taken in 7.5; 15; 30 min and precipitated by acetone. All samples were freeze-dried and kept under vacuum.

Experimental Methods

Size-Exclusion Chromatography

SEC analysis was carried out by using a multidetection device consisting of a *LC-10AD SHIMADZU* pump (throughput 0.5 ml·mn^{-1}), an automatic injector *WISP 717+* from *WATERS*, 3 coupled *30 cm-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 0.1M $NaNO_3$ was used as elluent.

FTIR Spectroscopy

FTIR spectra were obtained on a Nicolet NEXUS-475 (USA) Spectrophotometer in the range 4000–400 cm^{-1} using thin polymer films ($l = 6–9\ \mu m$) that were cast from aqueous solutions.

Potentiometry

Potentiometric titration of polyelectrolyte samples with HCl (0.2 N) and NaOH (0.2 N) solutions was performed using a pH meter pH-340 (Russia). Polymer concentration was 0.2 g · dl^{-1}. All measurements were carried out at 25.0 °C under nitrogen, with constant stirring.

Viscosimetry

Viscosity measurements were performed at 25.0 ± 0.1 °C, using an Oswald type viscometer. All polymer solutions were prepared using distilled water without salt adding. pH of solutions for polyelectrolyte samples were in the range 7,8–8,2.

Transmission Electron Microscopy

The identification of Ag NPs and their size analysis were performed using high-resolution transmission electron microscopy (TEM) and selected area electron diffraction (JEOL (Japan) Jem-1000CXII). The samples were prepared by spraying diluted dispersion onto carbon-coated copper grids and were analyzed.

UV-Vis Spectroscopy

UV-Vis spectra were recorded using Varian Cary 50 Scan UV-Visible Spectrophotometer in the range 190–1100 nm (step 2 nm). Original silver colloids were diluted 50 times before spectral measurements.

Results and Discussion

Star-like D-*g*-PAA copolymers were transformed into polyelectrolytes when some of amide groups of PAA chains convert into carboxylate ones under saponification. In

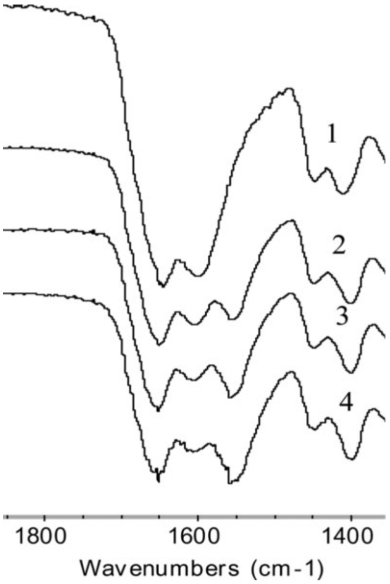

Figure 1.
FTIR spectra of D20-g-PAA5 in nonionic (1) and ionic forms (time of hydrolysis was 7.5 (2); 15 (3) and 30 (4) min).

contrast to nonionic D-*g*-PAA copolymers FTIR spectra of the partly hydrolyzed samples have peaks of Amide 1 (1650–1660 cm^{-1}) and Amide 2 (1615 cm^{-1}) as well as peak of COO^{-}-groups at 1570 cm^{-1}. The increase of hydrolysis time resulted in an increase of the band intensity of COO^{-} groups at 1570 cm^{-1} with respect to that of Amide I and Amide II bands (Figure 1).

Alkaline hydrolysis of D-*g*-PAA was not attended by irrelevant processes (destruction or cross-linking of macromolecules). The chromatograms of non-ionic and anionic samples show peaks at the close eluent volumes demonstrating that molecular weights of hydrolyzed samples do not change drastically and that the small variations observed depend only upon the number of functional groups that were transformed changing their own weight (Figure 2).

Conversion degrees (A) of amide groups into carboxylate ones were calculated from the potentiometric titration data.[6,7] Different times of hydrolysis ensure various A values (Figure 3). In comparison with linear polyacrylamide all branched polymers show higher values of conversion for all times of hydrolysis. Star-like D-*g*-PAA copolymers have higher local concentration of functional groups so their conversion is more efficient.

Alkaline hydrolysis of all source polymers D-*g*-PAA was carried out under the same condition thus the degree of conversion depended only on the time of reaction and on the peculiarities of macromolecule internal structure in solution. Due to different size of Dextran backbones the samples D70-*g*-PAA*n* and D20-*g*-PAA*n* with the same *n* have unequal distance between PAA grafts.[5,6] In addition, the length of PAA arms in different samples is unlike. So, D-*g*-PAA polymers in solution have different internal structure that is determined by architecture of macromolecules. The peculiarities of internal structure affect the course of hydrolysis process.

When $-CONH_2$ groups transform into the $-COONa$ ones the charges appear on the polymer arms of star-like D-*g*-PAA macromolecules. Dextran-g-(Polyacrylamide-co-Polyacrylic acid) in a salt form acquired extended conformation because grafted chains became greatly straightened when charged functional groups repulsed. The viscometry data showed the drastic growth of intrinsic viscosity for hydrolyzed polymer samples in comparison with non-ionic ones (Table 2).

The absence of polyelectrolyte effect [7] that is registered for all ionic samples is caused by the extremely extended structure too.

Star-like ionic polymers with similar chemical nature, but different internal molecular structure were used as matrices for silver nanoparticles (Ag NPs) preparation. $AgNO_3$ in polymer solution was reduced by $NaBH_4$. The dark reddish brown colloids were obtained as a result of *in situ* synthesis of Ag NPs. Microscopy data show the formation of spherical or roughly spherical Ag NPs with grain size 10–20 nm (Figure 4, a). Indexing process of diffraction pattern (Figure 4, b) is done and Miller Indices (h k l) to each peak is assigned in first step. Obtained diffraction data confirm the face-centered cubic (fcc)

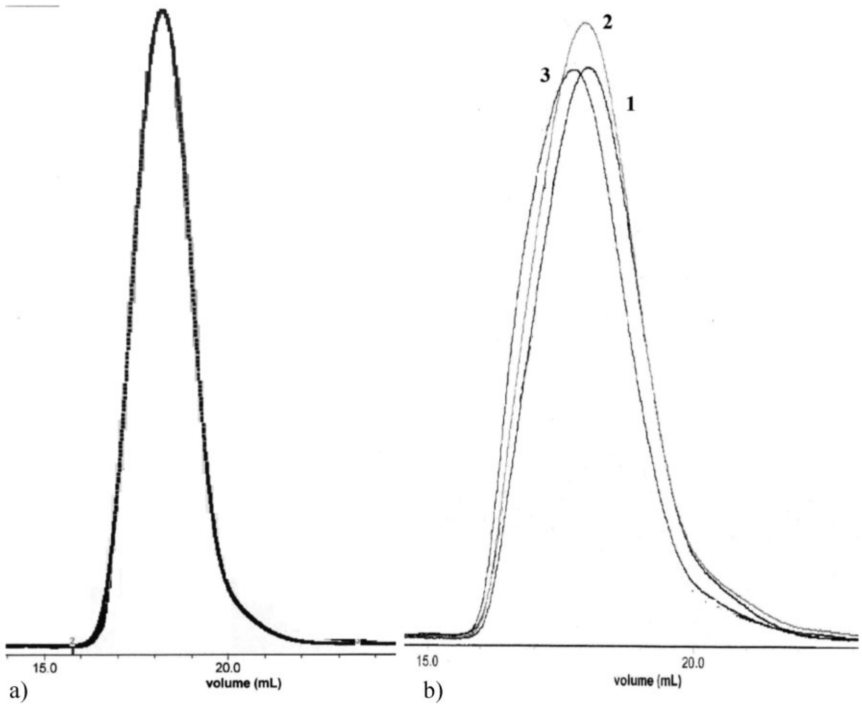

Figure 2.
Chromatograms of D20-g-PAA5 in nonionic (**a**) and ionic (**b**) forms. Time of hydrolysis was 7.5 (1); 15 (2) and 30 (3) min).

form of Ag NPs (JCPDS 04-0783, sp.gr. $Fm\bar{3}m$, $a = 4.077$ Å).

The UV-Vis spectra of silver colloids revealed a surface Plasmon absorption band with a maximum at 400 nm indicating the presence of Ag NPs (Figure 5).

The UV-Vis spectroscopy data show that D-g-PAA samples in ionic form are essentially more efficient as polymer matrices in comparison with ionic linear PAA. For anionic derivatives of star-like D-g-PAA copolymers the maxima of optical density of Ag colloids are rather higher in comparison with anionic PAA and Ag NPs are more stable.

The top effective matrices are the hydrolyzed star-like polymers D20-*g*-PAA20 and D70-*g*-PAA20. The conversion degree of these polymers with 30 min of hydrolysis is close (36% and 35%,

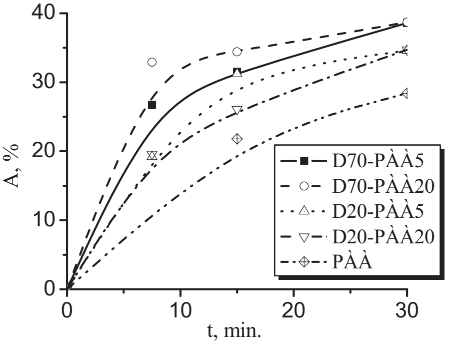

Figure 3.
Conversion degree (A) as function of hydrolysis time.

Table 2.
Intrinsic viscosity of anionic derivatives of D-g-PAA copolymers.

Sample	[η], dl/g			
Time of hydrolysis, min	*0*	*7.5*	*15*	*30*
D70-g-PAA5	4.8	80.6	82.1	85.4
D70-g-PAA20	2.5	81.1	82.7	85.8
D20-g-PAA5	2.2	79.0	82.0	84.0
D20-g-PAA20	1.5	62.3	63.8	65.8

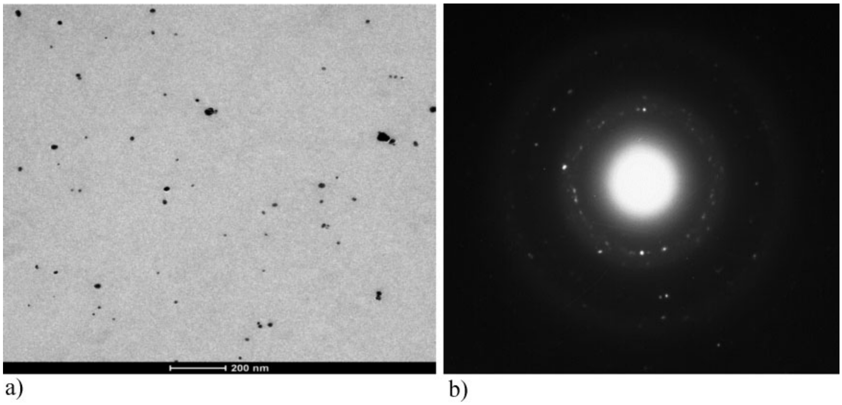

Figure 4.
TEM (**a**) and diffraction (**b**) images of Ag NPs synthesized in hydrolized D70-*g*-PAA20 matrix. Time of hydrolysis was 30 min.

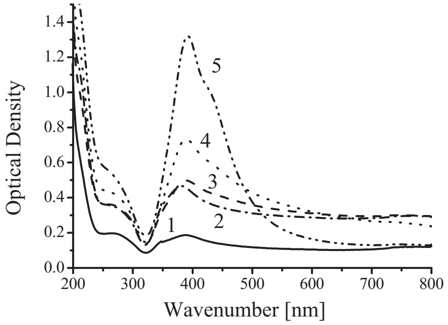

Figure 5.
UV-Vis spectra of Ag nanoparticles prepared in ionic polymer matrices: hydrolyzed PAA (1); D20-g-PAA5 (2); D70-g-PAA5 (3); D70-g-PAA20 (4); D20-g-PAA20 (5). Time of hydrolysis was 30 min. [AA monomer]/[Ag^+]=5.

respectively). They have the same number of grafts, but different distance between them. Thus, the internal structure of non-linear polymers in solution affects the process of Ag NPs formation.

Conclusion

Star-like Dextran-*graft*-Polyacrylamide copolymers are transformed into polyelectrolytes by alkaline hydrolysis when some of amide groups of PAA chains are converted into carboxylate ones. The internal structure of polymers in solution determines the run of the reaction and the conversion degree of samples. The high values of intrinsic viscosity are the result of greatly straightened charged arms of hydrolyzed D-*g*-PAA. No polyelectrolyte effect for D-*g*-(PAA-co-PAAc) samples in a salt form is registered. Synthesized star-like polyelectrolytes are more efficient matrices in comparison with linear anionic Polyacrylamide for silver nanoparticle *in situ* synthesis.

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