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Branched Dextran-*graft*-Polyacrylamide Copolymers as Perspective Materials for Nanotechnology

Nataliya Kutsevol,[*1] *Tetiana Bezugla,*[1] *Mykola Bezuglyi,*[1] *Michel Rawiso*[2]

Branched dextran-*graft*-polyacrylamide copolymers (D-*g*-PAA*n*) with different number of PAA-grafts have been synthesized for further conversion them to polyelectrolytes dextran-*graft*-(polyacrylamide-co-polyacrylic acid). It is shown that D-*g*-PAA*n* internal structure in water solution is more compact in comparison with linear polyacrylamide and depends upon the distance between PAA grafts. The branched polyelectrolytes are obtained by alkaline hydrolysis of synthesized D-*g*-PAA*n* samples. The conversion of nonionic polymers to partial anionic form depends upon the macromolecular internal structure of D-*g*-PAA*n*. The degree of transformation of amide groups to carboxylate ones is higher for branched copolymers than for linear PAA at the same condition. The synthesized branched copolymers are shown to be perspective as flocculation agents and the matrices for synthesis of the stable Ag nanosystems.

Keywords: branched copolymers; flocculation; nanoparticles; polyelectrolytes

Introduction

Branched polymers become of special interest because of their controlled internal molecular structure. There is now a good evidence that such polymers possess unique properties since the number of variable parameters are overwhelmingly large, namely, initial polymer architecture, average degree of polymerization, solubility properties, distance between grafts, nature and flexibility of backbone and grafts, etc.[1–3] The additional factors affecting the internal structure appear for branched polyelectrolytes: charge density or pH, nature of the charge distribution (static or dynamic), valence and nature of counterions, ionic strength, solvent quality.[4–7]

Due to the structure peculiarities the local concentration of functional groups in branched polymers is notably higher than in linear ones, therefore they should be perspective materials for nanochemistry and nanotechnology (as nanoplatforms or matrices for metal nanoparticle preparation); for biomedical (drug delivery) and technological applications (pollution problems solving: sorption of toxic metal ions from water medium or regulation of stability of disperse systems).

This work is devoted to the synthesis and study of multifunctional materials – water-soluble branched polymers of control internal structure with charged functional groups capable to trap polyvalent metal ions.

Experimental

Materials

Dextrans with different molecular weights were purchased from Fluka which characteristics given by the manufacturer are $M_w = 2 \times 10^4$ (designated as D20 throughout) and $M_w = 7 \times 10^4$ (designated as D70 throughout). Cerium (IV) ammonium nitrate (CAN) from Aldrich was used as

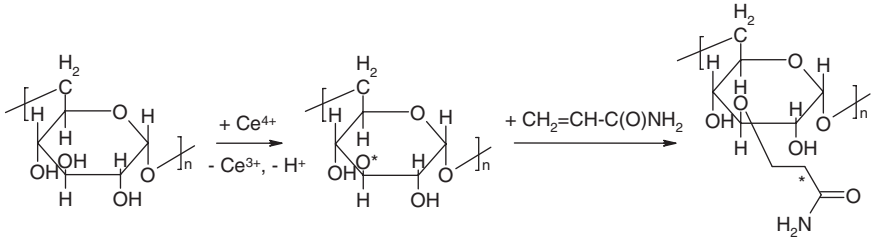
[1] National Taras Shevchenko University of Kyiv, Volodymyrska, 60, 01601 Kyiv, Ukraine
E-mail: kutsevol@ukr.net
[2] Institut Charles Sadron, CNRS UPR22-SC, 23 rue du Loess BP 84047, 67034 Strasbourg Cedex 2, France

initiator. Dextran samples and the ceric salt were used without further purification. Acrylamide (AA) obtained from Aldrich was twice re-crystallized from chloroform and dried under vacuum at room temperature for 24 h. NaOH from Aldrich was used for alkaline hydrolysis of polymer samples.

Synthesis of Polymer Samples

Cerium-ion-induced redox initiation method was used for the synthesis of the branched copolymers Dextran-*graft*-Polyacrylamide.[8] Polyacrylamide was grafted to Dextran backbone (D20 and D70) and two series of copolymers with different number of grafts were synthesized. A theoretical number of grafting sites per backbone depends on the ratio of Ce(IV) concentration to Dextran[8]: $n = \frac{[molCe(IV)]}{[molDextran]}$. For both series $n = 5$; 10; 15 and 20. The amount of monomer AA was kept the same for all syntheses. The samples were designated as D20-*g*-PAA*n* and D70-*g*-PAA*n*.

The mechanism of Ce(IV) initiation involves the formation of a chelate complex,[9] which while decomposing generates free radical sites on the polysaccharide backbone. These active free radicals trigger PAA chains growth in the presence of acrylic monomer. The reaction path is shown below:



Calculated amount of Dextran (D20 or D70) was dissolved in 100 ml of distilled water. This solution was stirred while removal of the dissolved oxygen was achieved by bubbling a gentle flux of argon for about 20 min. Then Ce(IV)/HNO_3 initiator (0.125 N HNO_3) was injected to obtain desirable *n* value. Acrylamide monomer was added and the polymerization proceeded at room temperature under argon atmosphere for 24 h. The synthesized copolymers were precipitated into an excess of acetone, re-dissolved in water and finally freeze-dried.

Three samples of linear Polyacrylamide (PAA) were synthesized for comparative investigations.

Alkaline hydrolysis of synthesized D-*g*-PAA*n* and linear PAA samples was carried out as follows: 2 g of D-*g*-PAA*n* (or PAA) was dissolved in 200 ml of distilled 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; 60 min and precipitated by acetone. The hydrolyzed samples were obtained in the salt form. 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 eluent.

The polymer concentrations used for the SEC analysis were below overlap concentration $\boldsymbol{C} = *1/[\eta]$, therefore the intermolecular interactions can be neglected. Thus, the molecular parameters of graft copolymers D-g-PAA*n* correspond to the individual macromolecules in water solution.

Viscosimetry

Viscosity measurements were performed for dilute solutions in a bath kept at 25.0 ± 0.1 °C, using an Oswald type viscometer. The data were analyzed through [10]:

$$\eta_{sp}/C = [\eta] + k_H[\eta]^2C + k'_H[\eta]^3C^2,$$

where η_{sp} is the specific viscosity, $[\eta]$ the intrinsic viscosity and k_H and k'_H being Huggins constants.

All polymer solutions for viscosimetry were prepared using distilled water without salt adding. For non-ionic samples pH of solution corresponds to pH of distilled water and for ionic samples pH were in the range 7,8–8,2.

Potentiometry

Potentiometric titration was performed using a pH meter pH-340 (Russia). Solutions of HCl (0.2N) and NaOH (0.2N) as titrants were used. Polymer concentration was $0.2\,g \cdot dl^{-1}$. The polymer solutions were titrated with HCl up to pH 2 and then with NaOH up to pH 12. Previously a fine blank titration (titration of non hydrolyzed polymer) was made. From the titration curves the absorption of OH- and H+ ions were calculated and the limits of these values were used for determination of conversion degree of amide groups into carboxylate ones.[11] All measurements were performed at 25.0 °C under nitrogen, with constant stirring.

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 μm). The films were cast from aqueous solutions.

Test of Flocculation Ability

Flocculation tests were performed in 50 ml graduated cylinders. Kaolin KOM (Poland) with high content of 2 μm particles was applied in $30\,g \cdot l^{-1}$ suspensions. Polymer concentrations were varied from $1 \cdot 10^{-4}$ to $1 \cdot 10^{-1}\,g \cdot l^{-1}$. The cylinders were inverted 12 times in order to mix the Kaolin suspension with a desired dose of flocculant solution. The Kaolin sedimentation was measured by observing the height of clarified liquid vs time. The sedimentation rate (V_s) and the supernatant clarity by measuring the absorbance at 540 nm (D) in 20 min of flocculation were analyzed.

The flocculation of Kaolin/Cu^{2+}/polymer systems were performed by the same technique and the test of Cu^{2+} ions removing was carried out. The atomic absorption spectroscopy (''AAS-1N'' Carl Zeiss Jena (Germany), λ = 324.7 nm) was used for analysis of Cu^{2+} ions content in the supernatant.

Synthesis of Ag Nanoparticles

10 ml of aqueous solution containing 0.005 g of D-g-PAA*n* and 0.51 g $AgNO_3$ was stirred during 20 min and 5 ml of 0.1 M $NaBH_4$ was added. The solution turned dark reddish brown immediately after adding of $NaBH_4$, thus particle formation was indicated. The stability of nanosystems obtained was being controlled during 6 months. Absorption spectra were observed in UV-vis region using Varian Cary 50 Scan UV-Visible Spectrophotometer. Original products solutions were diluted before spectral measurements. All samples were tested by transmission electron microscopy (TEM) for nanoparticles size analysis.

Results and Discussion

Molecular parameters of synthesized polymers are shown in Table 1. The content of polysaccharide component in graft copolymer was calculated as:

$$Cont_{Dex} = \frac{M_{wDex}}{M_{copo}} \times 100\%,$$

where M_{wDex} – molecular weight of Dextran component in the copolymer; M_{copo} – molecular weight of graft copolymer obtained by LS.

According to high values of M_w and R_g for branched copolymers and also taking into account the low content of polysaccharide component in copolymer (Table 1) we can assume that these copolymers are star-like ones.

Table 1.
Molecular parameters of polymers determined by SEC-LS-Rf and viscosimetry in water

Sample	$M_w \times 10^{-6}$ g · mol^{-1}	R_g nm	M_w/M_n	$R_g^2/M_w \times 10^{21}$ m^2 · mol · g^{-1}	$[\eta]$, dl · g^{-1}	$Cont_{Dex}$ %
D70-g-PAA5	2.15	85	1.72	3.36	4.77	3.36
D70-g-PAA10	1.70	71	1.66	2.97	3.68	4.29
D70-g-PAA15	1.57	67	1.81	2.86	3.39	4.67
D70-g-PAA20	1.43	64	1.98	2.85	2.50	5.15
D20-g-PAA5	1.60	67	1.63	2.81	2.25	1.27
D20-g-PAA10	0.95	51	1.62	2.74	1.78	2.15
D20-g-PAA15	0.94	50	1.67	2.69	1.62	2.67
D20-g-PAA20	0.77	46	1.81	2.75	1.46	2.17
PAA1	1.20	60	2.24	–	–	–
PAA2	1.40	68	2.40	–	–	–
PAA3	2.70	112	2.90	–	–	–

LS, light scattering; SEC, size-exclusion chromatography; Rf, refractometry.

All samples have high molecular weights but $M_{w\text{D-g-PAA5}} > M_{w\text{D-g-PAA10}} > M_{w\text{D-g-PAA15}} > M_{w\text{D-g-PAA15}} > M_{w\text{D-g-PAA20}}$ for both series of copolymers with D20 and D70 backbone (Table 1). This is an expected result because CAN is an initiator of copolymerization and an interrupt agent concurrently.[12] So, the increase of its amount in system (for increase the grafts number) changes the balance of two opposite radical polymerization processes: growth of polymer chain and its rupture.

While comparing the samples with D20 and D70 backbone (Table 1), it is revealed that values of M_w for D20-g-PAA*n* copolymers are lower than for D70-g-PAA*n* ones. It confirms an assumption that the accessibility of OH-groups of Dextran macromolecules for Ce(IV) ions is different inside and outside of polysaccharide macrocoil.[13] Size of macrocoil is less for D20 in comparison with D70 hence the amount of OH-groups on the coil ''surface'' is less for D20.

As it was predicted in the theoretical works the compactness of branched polymers depends on the distance between grafts and their conformation.[14,15] The compactness of branched polymer structure can be estimated as R_z^2/M_w.[16] When the value of R_g^2/M_w is lower, the compactness is higher. According to the data of Table 1 the compactness becomes higher with increasing the number of grafts for both D20-*g*-PAA*n* and D70-*g*-PAA*n* copolymers. But the value of *tan* α of $R_g^2/M_w = f(M_w)$ dependence for D70-*g*-PAA*n* is four times higher comparing with D20-g-PAA*n* (Figure 1). These data are in a good agreement with our previous X-Ray results on copolymer internal structure.[4] As it was reported for similar systems D20-*g*-PAA6 and D70-*g*-PAA6 with 6 long grafts the distance between grafts conditions the conformation of grafts: in case of D20-*g*-PAA6 the scattering curve resembles closely that of a worm-like chain, but for D70-*g*-PAA6 the behaviour differs from that of a worm-like chain, although it is definitely not random, namely, the PAA chains are highly extended near their

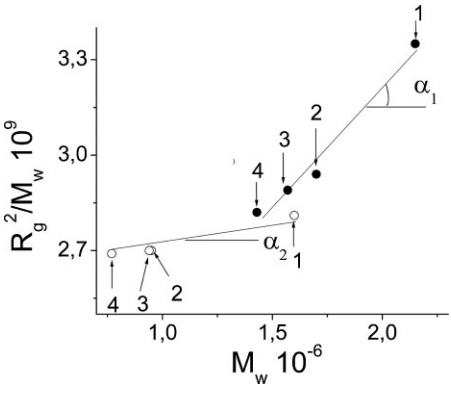
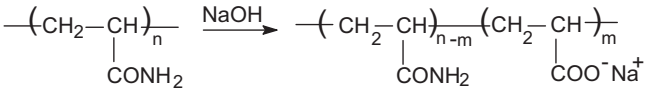


Figure 1.
Dependence of R_g^2/M_w on M_w for D20-*g*-PAA*n* (○) and D70-*g*-PAA*n* (●). *n* =5 (1); 10 (2); 15 (3) and 20 (4).

tethering point and recover a random conformation far from this point.

R_g^2/M_w values are close for all samples D20-*g*-PAA*n*. For series D70-*g*-PAA*n* R_g^2/M_w values decrease from D70-*g*-PAA5 to D70-*g*-PAA20 (Figure 1) but for D70-*g*-PAA15 and D70-*g*-PAA20 these values are close to D20-*g*-PAA*n* copolymers. Obviously, for samples of D70-*g*-PAA*n* series with increasing the number of grafts the conformation of PAA chains becomes worm-like as for D20-g-PAA*n*. Thus, the internal structure of D-*g*-PAA*n* copolymers depends on the grafting ratio as well as the grafted chain conformation.[4]

The synthesized branched and linear samples were saponified. During alkaline hydrolysis the $-CONH_2$ groups of PAA chains are converted to the –COONa groups according to:



FTIR spectra for nonionic and anionic samples of D20-*g*-PAA*n* are represented in Figure 2. Additionally to Amide 1 (1650–1660 cm^{-1}) and Amide 2 (1615 cm^{-1}) region [17] of nonionic samples the peak at 1570 cm^{-1} (COO^-) appears for hydrolyzed ones. This indicates that part of the acrylamide moiety is converted into acrylate ones under the saponification conditions.

The degree of conversion (α) of amide groups of polymers into carboxylate ones at different time of saponification is shown in Table 2. Hydrolysis of D-*g*-PAA*n* is found to be enhanced in comparison with linear PAA. Thus, the macromolecular internal structure affects the degree of the conversion of nonionic polymers to partial anionic form during alkaline hydrolysis.

Table 2.
Degree of conversion of D-*g*-PAA*n* and PAA samples during hydrolysis

Sample	α, %			
Time of hydrolysis, min	*7.5*	*15*	*30*	*60*
D70-g-PAA5	33	34	37	52
D70-g-PAA20	27	32	35	43
D20-g-PAA5	19	31	35	40
D20-g-PAA20	20	21	36	50
PAA2	–	21	28	34

The viscosimetry data have shown the drastic change of reduced viscosity for

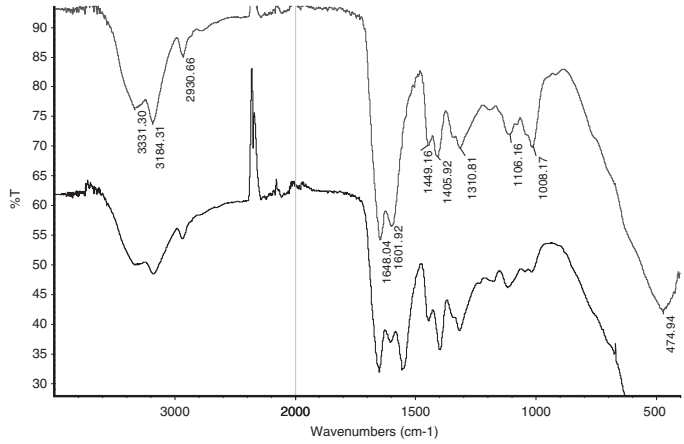


Figure 2.
FTIR spectra of D70-*g*-PAA5 in nonionic (on the top) and ionic (on the bottom) form. Time of hydrolysis was 60 min.

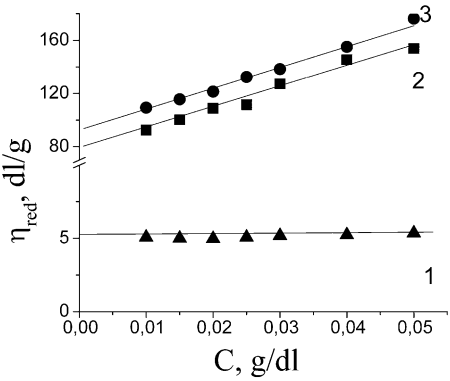


Figure 3.
Dependence of reduced viscosity on polymer concentration for D70-*g*-PAA5 in nonionic (1) and ionic (2, 3) form in salt free solution. Times of hydrolysis were 7.5 min (2) and 60 min (3).

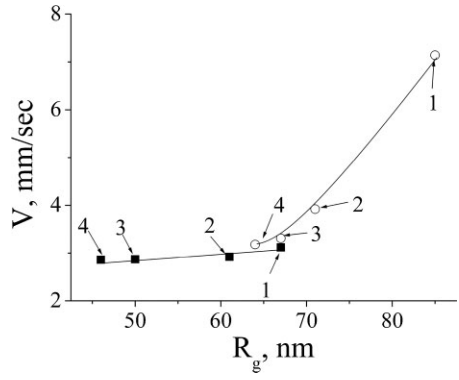


Figure 4.
Kaolin dispersion setting *vs* R_g of macrocoils for D70-*g*-PAA*n* (○) and D20-*g*-PAA*n* (■) (n = 5 (1); 10 (2); 15 (3) and 20 (4)). $C_{polymer} = 10^{-3}$ g/dl.

modified copolymers in comparison with nonionic ones and surprising absence of polyelectrolyte effect for hydrolyzed branched samples (Figure 3). Such behavior can be explained by the extremely extended structure of branched macromolecules of Dextran-*g*-(Polyacrylamide-co-Polyacrylic acid) in solution with charges appearance on grafted chains.

It's known that reduced viscosity of polyelectrolyte solution increases in very dilute regime due to unwrapping of charged polymer chains[18]. As it was shown in our previous work [4] grafted chains in branched polymers even in non ionic form have worm-like or mushroom conformation that is far from random coil. For all hydrolyzed D-g-PAA*n* the PAA chains are extremely straightened therefore their conformation can not be changed when solution dilutes.

Prospects of Application

Flocculation of Kaoline Dispersion by Branched Polymers D-g-PAAn

The flocculation ability tests have shown that internal structure of branched macromolecules D-*g*-PAA*n* affects the sedimentation rate of Kaolin dispersion. The data represented in Figure 4 correlate with the dependence of R^2/M_w on M_w (Figure 1).

The internal macromolecule structure also influences the supernatant clarification. The dependence of the supernatant optical density (D) on R_g of copolymer macrocoil is shown in Figure 5. It is inverted to image of Figure 4 and correlates with macromolecules compactness R^2/M_w (Table 1, Figure 1). The supernatant optical density displays the capability of polymer flocculant to trap the smallest particles of clay suspension. The compact structure of branched macromolecules provides the high local concentration of functional groups accessible for the smallest Kaolin particles. The D-*g*-PAA*n* samples with close values of R^2/M_w demonstrate similar

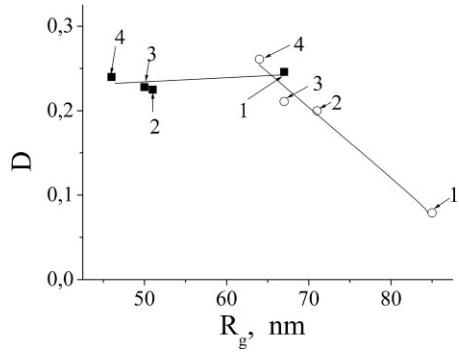


Figure 5.
Supernatant optical density *vs* R_g of macrocoils for D70-*g*-PAA*n* (○) and D20-*g*-PAA*n* (■) (*n* = 5 (1), 10 (2), 15 (3) and 20 (4)). $C_{polymer} = 10^{-3}$ g/dl.

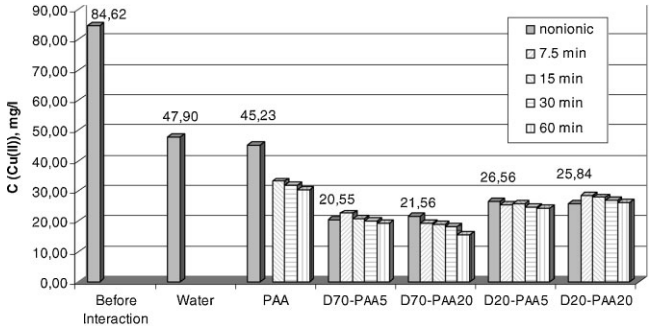


Figure 6.
Content of Cu^{2+} in supernatant after sedimentation of Kaolin dispersion.

flocculation ability for both flocculation parameters, namely sedimentation rate and supernatant clarification. The branched polyelectrolytes Dextran-*graft*-(Polyacrylamide-co-Polyacrylic acid) are less efficient in clarification but rather more effective in sedimentation rate in comparison with nonionic initial copolymers.

Comparative Investigation of Cu^{2+} Ions Removing From Kaoline/Cu^{2+} Dispersion by Linear and Branched Polymers

The study of two-component system Kaoline/Cu^{2+} has shown that Kaoline can remove metal ions from aqueous medium by adsorbing them during the process of clay particles sedimentation (Figure 6). FTIR spectra of polymer/Cu^{2+} system have demonstrated the complex formation between Cu^{2+} ions and functional groups of PAA-chains in nonionic and ionic forms both for linear PAA and D-*g*-PAA*n*.

Removing of Cu^{2+} ions from ternary system Kaolin/Cu^{2+}/polymer in flocculation process was analyzed by atomic absorption of supernatant too (Figure 6). All branched polymers D-*g*-PAA*n* are more efficient for heavy metal ions trapping in comparison with linear PAA, but the branched copolymers in ionic form are also more efficient than their nonionic branched analogues.

Branched Copolymers D-g-PAAn as Matrices for In Situ Synthesis of Nanoparticles

Nanoparticles (NPs) of noble metals attract a great attention due to their unique optical, conduction, catalytic and medical properties. Last years the attempts to find simple methods for synthesis of stable nanosystems have been made. Recent reports have been found on the preparation of metal NPs in aqueous solutions involving the use of poly(ethylene oxide),[19] amine functionalized poly(propylene imine) dendrimeres[20] and block copolymer micelles.[21]

In this work we demonstrate a simple way to generate well-defined monodispersed ''aggregates'' of Ag nanoparticles by using branched D-*g*-PAA*n*. UV-vis absorption spectra of the product solutions contain the peaks at about 460 nm (Figure 7) that correspond the Ag NPs with size <20 nm. The branched samples are more efficient polymer matrices for nanoparticles synthesis in comparison with linear PAA. Ag NPs synthesized in nonionic matrices D-g-PAA*n* were stable in time (without any precipitation during 6 months of the experiment).

The partial precipitation of Ag was observed in present of hydrolyzed D-*g*-PAA*n* matrices, but after some precipitation the Ag colloid remained stable in time. The synthesis of Ag nanoparticles was failed in presence of hydrolyzed PAA (Figure 7).

The synthesized Ag NPs are uniform in size and have spherical shape with smooth morphology (Figure 8). The diameter of the particles is found to be approximately 20 nm, which is in agreement with UV-vis spectroscopy data.

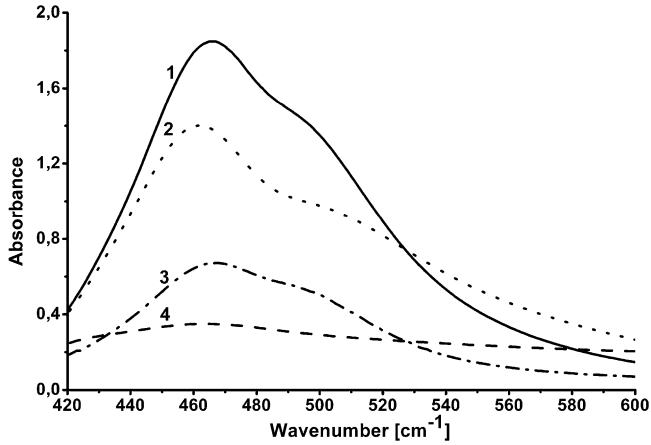


Figure 7.
UV-vis spectra of Ag nanoparticles synthesized in polymer matrices D70-*g*-PAA20 (1), PAA (2), hydrolyzed D70-*g*-PAA20 (3) and hydrolyzed PAA (4). Time of hydrolysis was 60 min.

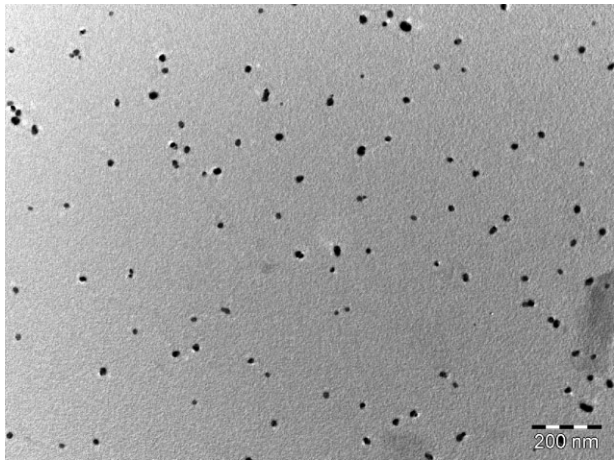


Figure 8.
TEM image of the Ag NPs synthesized in D70-*g*-PAA5 matrix.

Conclusion

Branched copolymers Dextran-*g*-Polyacrylamide with different distance between grafts have been synthesized and modified by alkaline hydrolysis to branched polyelectrolytes. It is shown that D-*g*-PAA*n* samples are star-like copolymers. The internal structure of D-*g*-PAA*n* depends on the grafting ratio as well as the grafted chain conformation. In hydrolysis the degree of conversion of amide groups to carboxylate ones is higher for branched polymers in comparison with linear PAA. The extremely extended structure of branched macromolecules of Dextran-*g*-(Polyacrylamide-co-Polyacrylic acid) in solution has caused the absence of polyelectrolyte effect. It is shown that branched copolymers D-*g*-PAA*n* in non-ionic and ionic forms are perspective materials for removing heavy metal ions

from aqueous clay dispersion and can be efficient matrices for metal nanoparticle preparation.

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