

Natalia KUTSEVOL^{1*} and Tetiana BEZUGLA¹

INFLUENCE OF STRUCTURE PECULIARITIES OF DEXTRAN SULPHATE-*g*-POLYACRYLAMIDE ON FLOCCULATION PHENOMENA

WPLYW WŁAŚCIWOŚCI STRUKTURY SIARCZANU DEKSTRANU-*g*-POLIAKRYLAMIDOWEGO NA ZJAWISKO FLOKULACJI

Abstract: Brush-like copolymers of Polyacrylamide grafted onto Dextran Sulphate backbone were tested as flocculation aids in polydisperse kaolin suspension. It was shown that flocculation efficiency of these copolymers is significantly dependent upon their internal structure. Both the kinetics of flock sedimentation and supernatant clarification of suspensions are the function of macromolecule conformation of copolymers in water solution. The most efficient flocculants are copolymers with high molecular mass but low value of R_z^2/M_w .

Keywords: graft copolymers, polyacrylamide, dextran sulphate, flocculation, kaolin suspension

Flocculant-assisted processes are commonly used in mineral industry, ceramic manufacturing, wastewater treatment, etc. Water-soluble polymers such as high-molecular-weight non-ionic and ionic *Polyacrylamides* (PAA) are known to be effective flocculation aids. The flocculation phenomena are affected by a bundle of factors such as flocculant characteristics, dosage, dilution and slurry properties (pH, ionic strength of solution, temperature, solid content, particle concentration, their size, etc.) [1]. But the most important factors are the conformation and adsorption of polymeric flocculants. These two characteristics of polymers and polymer-surface interaction substantially determine a mechanism of flocculation: a) depletion flocculation [2] is caused by the exclusion of the free polymer from the antiparticles region; b) bridging flocculation [3] is caused by a polymer adsorbed on the surface of a particle in an extended conformation. PAA chains adsorb on kaolin particle surface, so being in expanded conformation in water solution PAA-grafted copolymers may act as bridging agent.

Copolymers obtained by grafting Polyacrylamide chains onto polysaccharide backbone are thought to improve the flocculation efficiency of linear PAA due to their branched

¹ Department of Chemistry, Kiev National Taras Shevchenko University, 60 Volodymyrska St., 01601 Kiev, UA,

* Corresponding author: kutsevol@ukr.net

architecture. Moreover, these copolymers seem to be perspective as task-oriented materials because they can be undergone controlled transformations through the variation of numerous parameters such as initial polymer architecture, average degree of polymerization, nature and flexibility of backbone, distance between grafts, their lengths, etc [4].

To obtain polymer systems corresponding to the theoretical model of cylindrical polymer brushes [5] we have synthesized water-soluble branched polymers by grafting of flexible synthetic Polyacrylamide chains onto Dextran Sulphate backbone. Dextran Sulphate molecule due to strong repulsion of charged functional groups of polyion chain (2,3 sulphate groups per one polysaccharide ring) has extremely extended conformation in aqueous solution [6]. This study is aimed to investigate the effect of copolymer internal structure of branched polymers Dextran Sulphate-*graft*-Polyacrylamide, which corresponds to the theoretical model of cylindrical brushes on their flocculation efficiency in kaolin polydisperse suspension.

Materials and methods

The samples of graft copolymers of Polyacrylamide grafted to Dextrane Sulphate backbone ($M_w = 500\,000$), designated as DS-*g*-PAA, were synthesised by radical polymerization using Ce(IV)/HNO₃ redox system. Dextran Sulphate (Leuconostoc, $M_w = 500\,000$) was purchased from Fluka, Cerium(IV) ammonium nitrate from Aldrich (CAN), Acrylamide from Aldrich.

The average number of grafting sites per backbone molecule depends on the ratio of concentration of ceric ions to Polysaccharide [7]. The ratio of mol Ce(IV) to mol Dextrane Sulphate was equal to 25 and 50. The length of grafted chains was regulated by amount of monomer AA added to the reactive mixture (Table 1). To obtain the copolymers with “short” and “long” PAA-grafting chains the amount of monomer Acrylamide was double increased (Table 1). All PAA-*g*-DS copolymers were synthesized and purified according to the procedures described in detail in [4].

Table 1
Molar proportion of initiator and polysaccharide ($[Ce^{4+}]/[DS]$), amount of acrylamide monomer (AA) and Dextrane Sulphate (DS) in graft copolymer syntheses

Sample	$[Ce^{4+}]/[DS]$	AA [mol/dm ³]	DS [mmol/dm ³]
DS- <i>g</i> -PAA, 25 grafts (short)	25	0.1	0.2
DS- <i>g</i> -PAA, 25 grafts (long)	25	0.2	0.2
DS- <i>g</i> -PAA, 50 grafts (short)	50	0.2	0.2
DS- <i>g</i> -PAA, 50 grafts (long)	50	0.4	0.2

The molecular parameters of DS-*g*-PAA in water solution were determined by the static *light scattering* (LS) experiments carried out by using SEMATECH apparatus with laser source He-Ne of wavelength $\lambda = 632.8$ nm and the scattering angle range between 30 and 150°. Light scattering results were analyzed in terms of the excess Rayleigh ratio $R(q)$ by using a classical Zimm-plot which yielded the weight-average molar mass M_w and the z-average radius of gyration R_z [8].

All samples were tested as flocculants in kaolin polydisperse suspensions (3 g/dl). Flocculation process parameters were determined for a wide range of flocculant concentrations. All procedures were strongly standardized and were carried out as described

in [9]. For the characteristic of supernatant clarification the optical density (D) of supernatant liquid was determined by spectrometer (Varian, Cary 50) at $\lambda = 540$ nm.

Results and discussion

In accordance with the synthesis conditions the DS-g-PAA copolymers have theoretically 25 or 50 PAA-grafts per Polysaccharide backbone (Table 1). The increase of AA monomer amount results in the more high macromolecular weight of copolymers. Some differences in expected M_w values, according to the amount of monomer AA added to the reaction mixture (Table 1), can be accounted for the fact that ceric initiator can form the radicals on the polysaccharide backbone and is an interrupter of polymerization simultaneously.

The molecular parameters obtained by light scattering for the copolymers synthesized are reported in Table 2. These molecular parameters have characterized the properties of individual macromolecules in water solution because the concentrations used for LS ($C \leq 8 \times 10^{-4}$ g/dl) are less in three orders of magnitude than the critical "overlap" concentration $C^* = 1/[\eta]$ ($[\eta]$ - intrinsic viscosity) [6]. Thus the intermolecular interaction can be neglected.

Table 2

Molecular parameters of graft copolymers determined by LS

Sample	$M_w \cdot 10^{-6}$ [g/mol]	R_z [nm]	$R_z^2/M_w \cdot 10^3$ [nm ² ·mol/g]
DS-g-PAA, 25 grafts (short)	1.31	145	16.05
DS-g-PAA, 25 grafts (long)	2.85	142	7.08
DS-g-PAA, 50 grafts (short)	1.89	108	6.17
DS-g-PAA, 50 grafts (long)	3.83	110	3.16

According to the experimental results all copolymers are characterized by high values of the radii of gyration R_z (Table 2), that indicates the extended conformation of copolymer macromolecules in solution. The samples with 25 grafts have close R_z values in spite of the fact that their molecular weights M_w are practically differ twice. The same tendency is observed for samples with 50 grafts. Comparing the samples with different number of grafts one can see that R_z values for samples with 25 grafts are essentially higher than R_z values of samples with 50 grafts (Table 2). It is obvious that the conformation of the samples with 25 grafts is rather more extended than the conformation of copolymers with 50 grafts. So, these data show that the increase of the PAA-grafts number causes the decrease of macromolecule size in solution.

According to the theoretical model of cylindrical polymer brushes [5] and the experimental results for polymer brushes with non-ionic main chain [10], the increase of grafts number causes the increase of the main chain rigidity. Also, it is shown [10] that the size of cylindrical brush-like macromolecules is a superposition of the sizes of the main and grafted chains. Thus, with increasing of the length of grafts the size of macromolecules should increase, but for series of DS-g-PAA the opposite effect is observed. Obviously with increase of the content of PAA-component in DS-g-PAA copolymers the electrostatic repulsion between charged groups of polysaccharide component becomes lesser, so the main chain loses rigidity and becomes more flexible and more compact. So, it seems that

the highest value of R_z of DS-g-PAA samples with 25 short grafts is caused by the more extended conformation of polysaccharide main chain. It is known, that branched polymers have more compact internal structure in comparison with linear ones. The compactness can be estimated by ratio of R_z^2/M_w (Table 2). The less R_z^2/M_w value corresponds to the more compact internal macromolecule structure. So, the compactness of the copolymers increases with the increase of content of PAA-component in graft copolymers.

The flocculation activity of copolymers depends on the macromolecule conformation in water solution, so the internal structure of DS-g-PAA copolymers that defines the macromolecule conformation is very important for the flocculation performance.

To find the relationship between the internal structure and the flocculation efficiency of DS-g-PAA copolymers we tested them in kaolin flocculation process. The polymer solutions used were very dilute, thus the application of the molecular parameters of copolymers obtained by LS (Table 2) for analysis the flocculation process was correct.

The flocculation activity of DS-g-PAA copolymers was revealed to be very high (Tables 3 and 4). The kinetic characteristic of flocculation process is the sedimentation rate (V) of flocks formed after dispersion treatment with flocculation aids. Even low concentrations of copolymers accelerate the aggregation and sedimentation of suspension particles. As usual [11] the sedimentation rate (V) directly depends on the dose of flocculant (Table 3). In accordance with bridging mechanism of flocculation the polymer chains adsorb on the particles and form the flocks [12]. Their dimensions affect their setting. The increase of flocculant concentration causes the formation of the fair-sized flocks those settle faster. Such correlation remains for all copolymers examined.

Table 3

Floc sedimentation rate in kaolin suspensions (C = 3 g/dl*)

Samples	DS-g-PAA 25 grafts (short)	DS-g-PAA 25 grafts (long)	DS-g-PAA 50 grafts (short)	DS-g-PAA 50 grafts (long)
C [g/dl*]	V [mm/s]			
0	0.80	0.80	0.80	0.80
0.00001	1.00	0.80	0.94	0.98
0.00005	1.42	1.60	1.45	1.57
0.0001	1.83	2.11	2.94	3.12
0.0005	2.21	3.25	3.05	4.94
0.001	3.12	4.42	3.17	6.70

* 1 dl = 0.1 dm³

Table 4

Optical density of supernatant liquid

Samples	DS-g-PAA 25 grafts (short)	DS-g-PAA 25 grafts (long)	DS-g-PAA 50 grafts (short)	DS-g-PAA 50 grafts (long)
C [g/dl*]	A ₅₄₀			
0	1.222	1.222	1.222	1.222
0.00001	1.266	1.115	0.328	1.055
0.00005	1.650	1.240	0.470	0.820
0.0001	1.491	0.980	0.759	0.507
0.0005	1.006	0.329	0.417	0.101
0.001	0.447	0.184	0.186	0.121

* 1 dl = 0.1 dm³

It is known that flocculation efficiency of Polyacrylamide rises with increasing of its molecular weight. In contrast to linear Polyacrylamide the non-linear copolymers have not direct relations between their molecular weight and sedimentation rate of kaolin flocks. The increase of their M_w not always causes the improvement of their flocculation efficacy (Tables 2, 3). The linear Polyacrylamide macromolecules are of random coil conformation in water solution, but the DS-g-PAA polymer brushes have the initial complicated architecture that determines the macromolecule conformation in water solution and shows some peculiarities of flocculation behaviour.

The degree of water clarification was estimated by the optical density of supernatant over the kaolin flock sediment in 20 minutes after treatment with flocculant aids. As it resulted from experimental data more fine clarification occurred when we used the DS-g-PAA copolymers having 50 grafts per macromolecule (Table 4). When compare all samples the degree of clarification is in direct dependence on the compactness of DS-g-PAA macromolecules in solution (Fig. 1). The fine purification requires the removal of very small particles so the flocculation process is expected to settle down the most of impurities. As it resulted from experimental data the best clarification (the lowest value of supernatant optical density) was achieved when using the copolymer samples with low R_z^2/M values - copolymers DS-g-PAA, 50 grafts in a proper concentration.

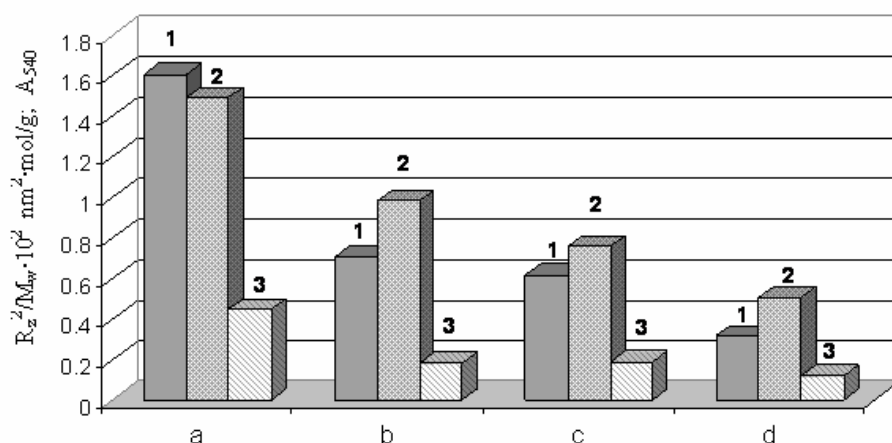


Fig. 1. Molecular parameter R_z^2/M_w (1) and supernatant optical density (A_{540}) after treatment the kaolin dispersion with 0.0001 g/dl (2) and 0.001 g/dl (3) of copolymer flocculants: a - DS-g-PAA, 25 grafts (short); b - DS-g-PAA, 25 grafts (long); c - DS-g-PAA, 50 grafts (short); d - DS-g-PAA, 50 grafts (long)

The brush-like polymers with high compactness of macromolecule structure in water solution has an ability to interact with a great number of suspension particles including very small ones. The best results in flocculation process may be achieved when the optimal dose of flocculant aid ensures both the rate of sedimentation and supernatant clarification of required level. Thus, the better flocculant must have high content and suitable density of functional groups that trap suspension fine particles.

Conclusions

The initial architecture and the internal structure of branched DS-*g*-PAA macromolecules determine the flocculation efficiency against the kaolin polydisperse suspension. The high compactness of DS-*g*-PAA, 50 grafts macromolecules ensures high degree of clarification due to the high concentration of functional groups trapping suspension fine particles. Adding in optimal dose these copolymers ensure the high rate of flock sedimentation and high level of supernatant clarification of kaolin polydisperse suspensions.

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WPŁYW WŁAŚCIWOŚCI STRUKTURY SIARCZANU DEKSTRANU-*g*-POLIAKRYLAMIDOWEGO NA ZJAWISKO FLOKULACJI

Abstrakt: Badano wpływ kopolimeru złożonego z poliakrylamidu szczepionego w strukturę siarczanu dekstranu (o strukturze przypominającej szczotkę) na flokulację polidispersyjnej zawiesiny kaolinu. Wykazano, że skuteczność flokulacji tych kopolimerów zależy od ich struktury wewnętrznej. Zarówno kinetyka sedymentacji osadu, jaki i klarowania się roztworu nad osadem są funkcjami konformacji makromolekuł kopolimerów w roztworze wodnym. Najbardziej efektywnymi flokulantami są kopolimery o dużej masie molekularnej i małej wartości R_z^2/M_w .

Słowa kluczowe: kopolimery szczepione, poliakryloamid, siarczan dekstranu, flokulacja, zawiesina kaolinu