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FLOCCULATION PROPERTIES
OF DEXTRAN-*graft*-POLYACRYLAMIDE
OF VARIOUS INTERNAL STRUCTURE

WŁAŚCIWOŚCI FLOKULACYJNE
DEKSTRANU-*graft*-POLIAKRYLOAMIDOWEGO
O RÓŻNYCH STRUKTURACH WEWNĘTRZNYCH

Abstract: Two series of Dextran-*graft*-Polyacrylamide copolymers (D-*g*-PAA) with polysaccharide backbone having different molecular weights ($M_w = 20\ 000$ and $M_w = 70\ 000$) and with 5, 10, 15 or 20 PAA-grafts per one Dextran macromolecule were tested as flocculation aids in the model kaolin suspensions. These copolymers have shown high flocculation efficiency significantly dependent upon their internal structure. The flocculation ability of D-*g*-PAA samples with the same number of PAA-grafts inversely relates to the spacing of the grafts (ie the length of backbone between the grafts).

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

It is well known that Polyacrylamide flocculants in non-ionic, cationic and anionic form are widely used in wastewater treatment [1]. The flocculation performance of flocculants depends on the chemical nature of flocculants, their molecular weight, the suspension solid content in the wastewater, etc [2]. The solution properties of polymer-flocculant have strong influence on the flocculation process, namely, the more expanded polymer chain, the better its flocculation ability. The shape of polymer chain in solution mainly depends on the concentration of the linear polymer in solution for given polymer/solvent system [3]. But for polymers of non-linear architecture the number of variable parameters become overwhelmingly large, namely, initial polymer architecture, average degree of polymerization, solubility properties, changing the solvent composition, distance between grafts, nature and flexibility of backbone and grafts, etc [4–7]. All these factors can influence the formation of nanostructure,

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determining the final properties of such compounds. We synthesized non-linear biohybrid water-soluble polymers of controlled nanostructure by grafting of synthetic polymers Polyacrylamide onto Polysaccharide backbone. It seems to be a promising approach for obtaining polymers with non-linear architecture, namely, spherical polymer brushes [8], containing Polyacrylamide corona.

This study is aimed to investigate the effect of internal structure of Dextran-*graft*-Polyacrylamide (D-*g*-PAA) on its flocculation efficiency in kaolin polydisperse suspension for optimization of the fine particle setting.

Materials and methods

Two series of Polyacrylamide grafted to Dextran backbone copolymers (M_w = 20 000 and M_w = 70 000), designated as D20-*g*-PAA and D70-*g*-PAA correspondingly, were synthesised by radical polymerization using Ce(IV)/HNO$_3$ redox system. Dextrans were purchased from Serva (Sweden), Cerium (IV) ammonium nitrate from Aldrich (CAN), Acrylamide from Reanal (Hungary).

The average number of grafting sites per backbone molecule depends on the ratio of ceric ion concentration to dextran [9]. The ratio of mole Ce(IV) to mole Dextran was equal to 5, 10, 15 and 20. The amount of monomer Acrylamide was kept the same for all synthesis. All D-*g*-PAA copolymers were synthesized and purified according to procedures described in detail in [10].

The molecular parameters of D-*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 λ = 632.8 nm and the scattering angle range between 30 and 150°. Light scattering (LS) results were analyzed in terms of the excess Rayleigh ratio R(q) by using a classical Zimm-plot which yields the weight-average molar mass M_w, the z-average radius of gyration R_z and the second virial coefficient A_2 [11].

The specific viscosity [η] was determined by viscometry measurements performed for dilute solution at 25.0 ± 0.1 $^{\circ}$C, using an Oswald type viscometer. The critical concentration C* introduced by de Gennes [12], at which the polymer coils start to overlap is expressed as:

$$C* \quad 1/[\eta]$$

The D-g-PAA samples were tested as flocculant agents in kaolin polydisperse suspensions (3 g/dl*). Flocculation process parameters were determined for a wide range of flocculants concentrations. All procedures were strongly standardized and carried out as described in [13]. Polymer solution was added in a single step to a cylinder with kaolin powder and mixed by moving a cylinder up and down six times to ensure that the suspension was well homogenized and the dispersion level was visually checked. All tests were carried out at 20 $^{\circ}$C. The initial settling rates of

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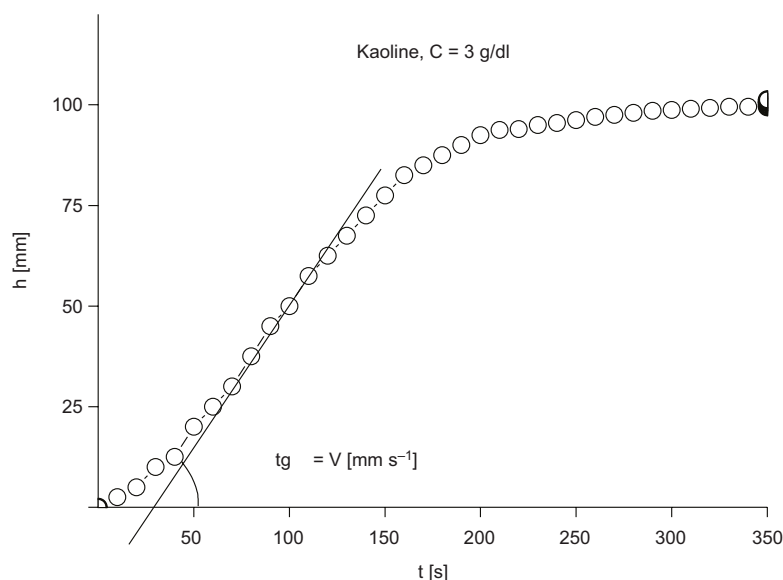
* 1 dl = 0.1 dm^3

Fig. 1. Typical kinetic curve of flocculation process

flocculated suspension were determined by recording the time taken for the "mud line" (solid-liquid interface) in the 50 cm^3 cylinder. The typical kinetic curve of polymer--induced flocculation process is shown in Fig. 1. Using this curve the suspension sedimentation rate was estimated. In 20 minutes after treatment with dose of the flocculants the optical density (A_{540}) of supernatant liquid was determined by spectrometer at λ = 540 nm. It was the characteristic of supernatant clarification.

Results and discussion

The copolymers of D20-*g*-PAA and D70-*g*-PAA series have theoretically 5, 10, 15 or 20 PAA-grafts per Dextran backbone in accordance with the synthesis conditions. All copolymers have high molecular masses but $M_{wD\text{-}g\text{-}PAA,5grafts} > M_{wD\text{-}g\text{-}PAA,10grafts} >$ $> M_{wD\text{-}g\text{-}PAA,15grafts} > M_{wD\text{-}g\text{-}PAA,20grafts}$ for both series of copolymers with D20 and D70 backbone. This is an expected result because CAN is both an initiator of copolymerization and its interrupt agent. So, the increase of its amount in system changes the balance of two opposite radical polymerization processes: growth of polymer chain and its rupture.

The molecular parameters obtained by light scattering and viscometry for different copolymers are reported in Table 1. According to the value of M_w and R_z for graft copolymers and value of M_w for individual dextrans we can assume that these copolymers are star-like. Bearing in mind that the concentrations used for LS is less than the critical "overlap" concentration C* (Table 1), the intermolecular interaction can

be neglected. Thus, the molecular parameters of graft copolymers D-*g*-PAA characterize properties of individual macromolecules in water solution.

Table 1

Molecular parameters of graft copolymers determined by LS (light scattering) and viscometry in water

Sample	$M_w \cdot 10^{-6}$	A_2	R_z [nm]	R_z^2/M_w	C^* [g/dl]
D20-*g*-PAA, 5 grafts	3.65	0	152	6.33	0.433
D20-*g*-PAA, 10 grafts	2.22	0	104	4.87	0.566
D20-*g*-PAA, 15 grafts	1.08	0	59	3.22	0.522
D20-*g*-PAA, 20 grafts	1.07	0	54	2.73	0.704
D70-*g*-PAA, 5 grafts	3.11	0	99	3.15	0.285
D70-*g*-PAA, 10 grafts	2.43	0	78	2.50	0.474
D70-*g*-PAA, 15 grafts	2.29	0	73	2.33	0.790
D70-*g*-PAA, 20 grafts	0.96	0	55	3.15	1.188

The values of the radii of gyration (R_z) define the extended conformation of copolymer macromolecules in solution. In spite of zero values of the second virial coefficient A_2 the copolymers of both series are characterized by high value of R_z, especially for D20-*g*-PAA and D70-*g*-PAA with 5 grafts per Dextran macromolecule. The important characteristic for nonlinear polymers is the "factor of compactness" that is expressed as R^2/M [14]. While compare the samples of D70-PAA copolymers with D20-PAA ones having close molecular mass and equal number of grafts, we found the values of R^2/M for D20-*g*-PAA copolymers are higher (Table 1), therefore their compactness is lower. This data is in good agreement with our previous results on copolymer intramolecular structure [10]. X-Ray diffraction experiments have shown that in case of D20-PAA the scattering curve resembles closely that of a worm-like chain. For D70-PAA, the behaviour differs from that of a worm-like chain, although it is definitely not random, namely the PAA chains may be highly extended near their tethering point and recover a random conformation far from this point. So the PAA chains of D20-PAA with a closer spacing between grafts have a more linear and therefore more expanded conformation than those of D70-*g*-PAA (Fig. 2). Thus, the internal structure of D-*g*-PAA copolymers is dependent upon the distance between grafts and the length of PAA-chains.
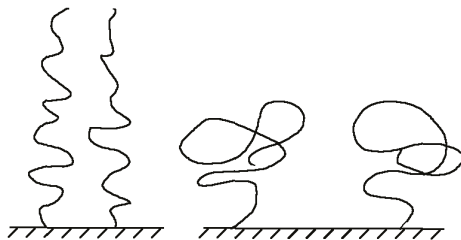

Fig. 2. Scheme of copolymer fragment near tethering points

According to experimental results the flocculation activity of copolymers was revealed to be very high (Table 2). The values of C* (Table 1) testify that the polymer solutions used in flocculation process are very dilute and, thus, an analysis the flocculation parameters using the molecular parameters of copolymers obtained by LS (Table 1) is correct.

Table 2

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

Samples	D70-PAA 5 grafts	D70-PAA 15 grafts	D70-PAA 20 grafts	D20-PAA 5 grafts	D20-PAA 15 grafts	D20-PAA 20 grafts
C [g/dl]	V [mm/s]					
0	0.80	0.80	0.80	0.80	0.80	0.80
0.00001	0.87	0.75	0.75	0.84	0.84	0.86
0.00005	1.38	1.1	1.3	1.56	0.85	1.20
0.0001	1.63	1.42	1.5	1.87	1.01	1.42
0.0005	2.25	2.15	1.97	3.75	1.62	1.60
0.001	3.00	2.50	2.25	4.12	1.97	1.95
0.005	3.50	2.75	2.75	4.30	2.37	2.80
0.01	3.75	3.05	2.8	4.62	2.4	2.90

Polymer-induced flocculation of mineral suspensions is complicated process that involves many steps, namely mixing of polymer molecules among the particles; adsorption of polymer chains on the particles; rearrangement of the adsorbed chains; collisions between polymer-adsorbed particles; and flock formation and also break-up of flocks [15]. It is impossible to single out each step of this process in our investigation but the analysis of flocculation parameters permits to find the relationship between the internal structure and the flocculation efficiency of examined copolymers.

The suspension sedimentation rate (V) that is the kinetic characteristic of flocculation process depends on flocculant dose (Table 2). Flocculant creates bridges between kaolin particles that causes the formation of flocks and their setting. The dimensions of flocks are in direct dependence on flocculant concentrations.

As it resulted from experimental data sedimentation rate is the greatest for samples with the highest values of macromolecular mass and the highest values of R^2/M parameter (less compactness). It is more interesting to compare the samples with close M_w, for instance D20-*g*-PAA, 15 grafts and D20-*g*-PAA, 20 grafts. The kinetic characteristics, namely V, are essentially different in spite of fact that M_w are $1.08 \cdot 10^6$ and $1.07 \cdot 10^6$ respectively. The reason for better effectiveness of the sample D20-*g*-PAA, 15 grafts is the more extended conformation of their macromolecules in water solution (the "factor of compactness" R^2/M is greater than for D20-*g*-PAA, 20 grafts). So the internal structure of D-*g*-PAA copolymers which defines the macromolecule conformation in water solution is very important for flocculation performance.

The degree of water clarification that was estimated by optical density after 20 minutes after treatment with flocculant agent revealed to be greater and the dose can be less when D-*g*-PAA copolymers with 5 PAA-grafts were used (Table 3). Expanded

structure of these copolymers allows them to capture much more solid particles including very small ones.

Table 3

Optical density of supernatant liquid

Sample	D70-PAA 5 grafts	D70-PAA 15 grafts	D70-PAA 20 grafts	D20-PAA 5 grafts	D20-PAA 15 grafts	D20-PAA 20 grafts
C [g/dl]	A_{540}					
0	1.222	1.222	1.222	1.222	1.222	1.222
0.00001	1.117	1.216	1.200	0.909	1.205	1.146
0.00005	1.061	0.826	1.144	0.812	1.208	1.104
0.0001	0.840	0.803	0.735	0.579	1.118	1.098
0.0005	0.507	0.578	0.392	0.431	0.634	0.621
0.001	0.495	0.362	0.376	0.327	0.577	0.461
0.005	0.211	0.262	0.199	0.100	0.291	0.279
0.01	0.121	0.177	0.154	0.078	0.251	0.190

When compare the flocculation efficiency of D20-*g*-PAA and D70-*g*-PAA (Fig. 3a, b) anyone can be convinced of the fact that the flocculation ability is inversely related to the spacing of the PAA grafts (ie the length of backbone between the grafts). Thus, for D20-*g*-PAA and D70-*g*-PAA having 5 grafts per macromolecule (c = $1 \cdot 10^{-2}$ g/dl) the sedimentation rates are 4.62 and 2.88 mm/s and values of optical density are 0.078 and 0.121, respectively. Due to more expanded conformation in water solution the sample of D20-*g*-PAA, 5 grafts is more effective flocculant than D70-*g*-PAA, 5 grafts which has greater distances between grafts and therefore less extended structure.
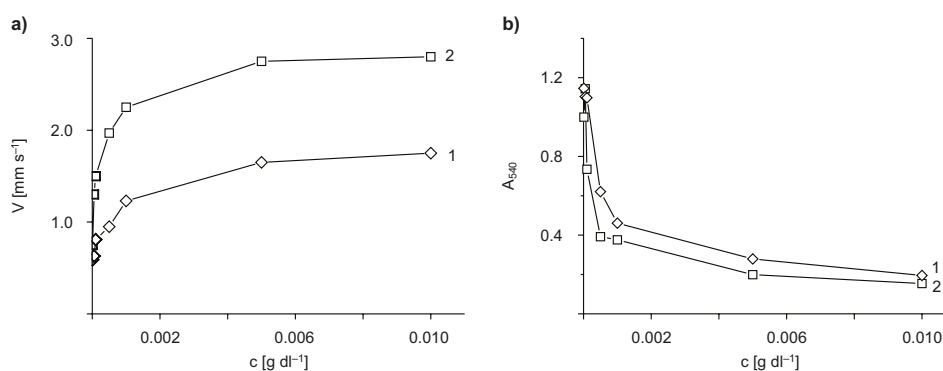

Fig. 3. Suspension sedimentation rate (a) and optical density of supernatant (b) for D70-PAA, 5 grafts (1) and D20-PAA, 5 grafts (2) copolymers

Thus the analysis of flocculation process parameters kinetic and the degree of water clarification has shown that the flocculation efficiency depends on macromolecular conformation directly. When the internal structure of grafted copolymer ensures the

expanded macromolecular conformation in water solution the functional groups of these copolymers are capable to capture pollutants and flocculation process will pass quickly and with high degree of clarification.

Conclusions

The internal structure of branched D-*g*-PAA macromolecules has influence upon the properties of their aqueous solutions. In kaolin suspensions the best flocculation efficiency was registered for copolymers with shorter distance between tethering points. Thus, the conformation of PAA grafts in star-like copolymers D-*g*-PAA, which according to the theoretical model are the spherical brushes with PAA-corona, as well as the copolymer compactness in solution plays a predominant role in the flocculation process.

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WŁAŚCIWOŚCI FLOKULACYJNE DEKSTRANU-*graft*-POLIAKRYLOAMIDOWEGO O RÓŻNYCH STRUKTURACH WEWNĘTRZNYCH

Abstrakt: Badano właściwości flokulacyjne kopolimerów dekstran-*graft*-poliakryloamidowych (DG-PAA) ze szkieletem dekstranowym o dwóch różnych masach molekularnych (M_w = 20 000 i M_w = 70 000) oraz z 5, 10, 15 lub 20 molekułami PAA dołączonymi (zaszczepionymi) do tego makromolekularnego szkieletu. Do pomiarów wykorzystywano zawiesinę kaolinu w wodzie. Kopolimery te miały dużą skuteczność flokulacyjną zależną od ich struktury molekularnej. Zdolność flokulacyjna próbek D-*g*-PAA, z taką samą liczbą zaszczepionych molekuł PAA, jest odwrotnie proporcjonalna do odległości między molekułami zaszczepionymi do szkieletu molekuły dekstranu.

Słowa kluczowe: dekstran, poliakryloamid, kopolimery szczepione, flokulacja, zawiesina kaolinu