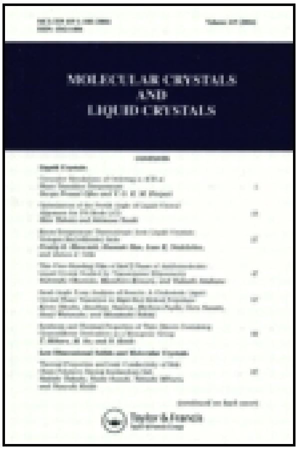

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Flocculation Behaviour of Polymer Brushes of Various Nanostructure

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Dextran-graft-polyacrylamide copolymers with different backbone lengths and graft numbers have been tested as flocculation aids in model kaolin suspensions. According to the sedimentation rate and the final sediment volume the graft copolymers proved to be rather similar to the linear acrylamide homopolymer having similar molecular weight. According to the supernatant liquid clarity the copolymers are more effective flocculants than the linear polyacrylamide. The supernatant clarity is inversely related to the length of backbone between the grafts. Apparently, conformation of grafted chain is somewhat more expanded in the cases where the grafts are closely disposed. Due to an expanded macromolecular conformation the functional groups of these copolymers are more capable of capturing solid particles than those of linear acrylamide polymers.

Keywords: graft length; kaolin; macromolecule conformation; sedimentation rate

INTRODUCTION

Flocculation of suspensions aided with water-soluble polymers is a quite complicated process and depends on several factors including the chemical nature of a polymer and the dispersed particles as well as the concentrations of both flocculant and particles. The macromolecular architecture of the flocculant plays an important role as well. In particular, brush-like and star-like polyacrylamides have been reported as being very effective flocculants for water clarification

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[1–5]. The reason is that non-linear macromolecules have a more expanded macromolecular structure in solution than linear ones [6,7]. The macromolecular structure in aqueous media depends on both the number and length of the grafted chains. In the present work four dextran-graft-polyacrylamide copolymers with the same number of grafts but different backbone lengths and numbers of grafts have been characterized with regard to their flocculation ability as well as their macromolecular structure in water solution.

EXPERIMENTAL

Copolymer Synthesis

Two dextran samples (Serva, Sweden) with different molar mass averages ($M_w = 20000\,g\,mol^{-1}$ and $M_w = 70000\,g\,mol^{-1}$ designated as D20 and D70, respectively) have been used as backbones for polyacrylamide grafting. The grafting reaction was carried out via the red-ox initiation method mediated by cerium (IV) ions [8–11]. This synthetic procedure has been described in detail elsewhere [12]. The molar amounts of cerium initiator (0.12 mmol) and dextran (0.02 mmol) have been kept constant in all the syntheses in order to provide the same number of the grafts (on average six) in the copolymers. The acrylamide monomers were applied in amounts of 0.1 mol and 0.2 mol with the aim of obtaining copolymers with different graft lengths (designated as D-PAA1 and D-PAA2, respectively).

Physical Measurements

The ^1H and ^{13}C NMR spectra (GEMINI-200BB; 200 MHz; D_2O) and size exclusion chromatograms (three coupled Shodex OH-pack columns; a multi-angle light scattering detector WYATT TECHNOLOGY DAWN F; a differential refractometer WATERS R410; 0.1 M $NaNO_3$ water solution) confirm the synthesized polymers are true copolymers and are not mixtures of the initial polysaccharide and an acrylamide homopolymer [11,12]. Dilute solution viscosity measurements have been performed at $25 \pm 0.05°C$ using an Ostwald type viscometer. Static light scattering measurements were made in the angle range of 30 to 150° using a SEMATECH apparatus with a He-Ne laser ($\lambda = 632.8\,nm$). The light scattering data 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 and the z-average radius of gyration R_z [11,12]. The molecular characteristics of the copolymers are presented in Table 1 [11,12]. Linear polyacrylamide (designated as

TABLE 1 Molecular Parameters of the Acrylamide Copolymers

Copolymer sample	$M_w \times 10^{-5}$, g/mol	R_z, nm	$[\eta]$, dl/g	Dextran content, %
D20-PAA1	8.7	60	2.3	2.3
D70-PAA1	9.2	52	1.8	7.6
D20-PAA2	69	182	8.5	0.3
D70-PAA2	47	168	8.3	1.5

PAA1) with average molar weight $M_v = 1 \times 10^6$ was also synthesized using the cerium initiation method.

Flocculation tests were performed in 50 mL graduated cylinders (Fig. 1). Kaolin from Glukhovets (Ukraine) with an average particle

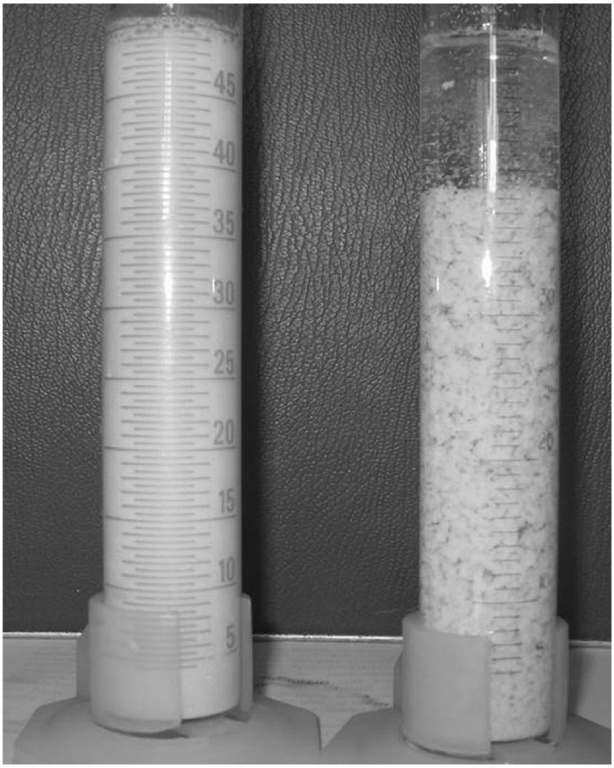

FIGURE 1 Photograph of the sedimentation cylinders in 1 min since the test beginning. Left – blank kaolin suspension; right – the suspension with the dextran-acrylamide copolymer added.

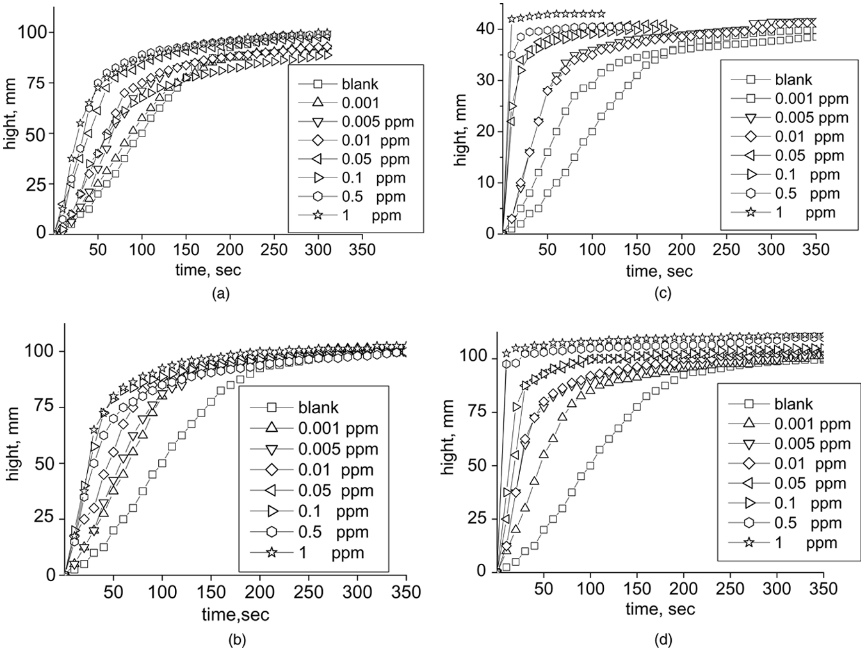

FIGURE 2 (a–d). The height of clarified liquid versus sedimentation time with the indicated flocculant concentration (ppm). The flocculants applied: D20PAA1 (a); D70PAA1 (b); D20PAA2 (c); D70PAA2 (d).

size of 6.5 μm was applied in $30\,g \cdot L^{-1}$ suspensions. 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 sample plots are presented in Figure 2. The cotangent of the steep part of the plot gives in velocity of sedimentation, v_s, and the cotangent intercept with the time scale gives the induction time of sedimentation, τ_0. The precipitate volume, V_p, was measured in 1 min after the onset flocculation. The supernatant clarity was evaluated by measuring the absorbance at 540 nm, A_{540}, 20 min after the start of flocculation.

RESULTS AND DISCUSSION

The flocculation tests clearly indicated that all the polymers studied have good flocculation abilities to be added in very small concentrations. For example, the blank kaolin suspension contains small particles with rather low sedimentation rates (Fig. 1 – left). In the presence of the acrylamide copolymers the kaolin particles are aggregated in visible flocks and the sedimentation rate is significantly increased (Fig. 1 – right). The plots of suspension interface motion (Fig. 2) show that the flock sedimentation rates depend on the flocculant concentration applied. The sedimentation plots in Figure 2 also suggest that the copolymers with longer grafts are more effective flocculants. Some of the quantitative results of the flocculation experiments are summarized in Table 2 in order to compare the flocculation properties of the copolymers in question.

The induction time of sedimentation approaches zero at flocculant concentrations between 0.01–0.1 ppm (Table 2). According to this parameter, the most effective flocculant is the D70-PAA2 sample. The values of sedimentation rate are increased and the values of final sediment volume are progressively decreased as the flocculant concentration increases (Table 2). According to these parameters the D20-PAA1 and D70-PAA1 copolymers are rather similar to the linear PAA1 polyacrylamide. It should be noted that average molecular weights of the copolymers of the PAA1 series and the linear PAA1 sample are nearly the same (Table 1). For this particular case the data

TABLE 2 Characteristics of the Polyacrylamide Flocculants

Sample	C, ppm	τ_0, s	v_s, mm/s	V_p, ml	A_{540}
Blank	–	13	0.5	43	0.276
PAA1 (linear)	0.001	11	0.63	37	0.212
	0.01	4	1.3	23	0.247
	0.1	0	2.2	16	0.105
	1	0	2.6	13	0.099
D20-PAA1	0.001	8	0.65	38	0.268
	0.01	6	1.1	30	0.150
	0.1	0	1.2	31	0.045
	1	0	2.1	18	0.059
D70-PAA1	0.001	7	0.88	32	0.297
	0.01	2	1.1	23	0.255
	0.1	0	1.6	17	0.131
	1	0	2.4	17	0.088
D20-PAA2	0.001	8	0.93	30	0.175
	0.01	5	1.5	20	0.100
	0.1	0	6.3	13	0.011
	1	0	10.5	7	0.048
D70-PAA2	0.001	5	1.1	25	0.180
	0.01	0	2.5	17	0.136
	0.1	0	4.0	12	0.031
	1	0	10.2	7	0.065

suggest that both the sedimentation rate and the final sediment volume are not dependent on the macromolecular structure of a flocculant.

The fastest rates of sedimentation and the lowest sediment volumes have been registered for the D20-PAA2 and D70-PAA2 samples. The apparent cause is that both the samples have longer polyacrylamide grafts than those in the samples of PAA1 series. It should be taken into account that i) the average number of grafts per macromolecule is approximately the same in all the copolymers, as a result of identical synthesis conditions (see Experimental) and ii) the content of polysaccharide backbone in the graft copolymers is insignificant (Table 1). Considering the above and the average molar masses of the PAA2 series copolymers (Table 1), one can estimate that the grafts of the PAA2 series are 5 to 8 times longer than those of the PAA1 one.

The most important parameter of the flocculation efficiency is the supernatant clarity. According to the supernatant turbidity (Table 2) all the graft copolymers are more effective flocculants than the linear acrylamide homopolymer. The apparent cause is that the graft copolymers have a non-linear structure resulting in more expanded conformations of the macromolecules in a solution. The comparison of the supernatant clarity data indicates that the copolymers having longer acrylamide grafts are more effective flocculants (Table 2). This observation agrees well with the data on the z-average radius of gyration (Table 1): the larger the R_z value, the more clarified supernatant liquid is obtained. Among the graft copolymers of similar graft length the more effective flocculants are those having shorter backbones (compare D20 and D70 copolymers in both the series of the Table 2).

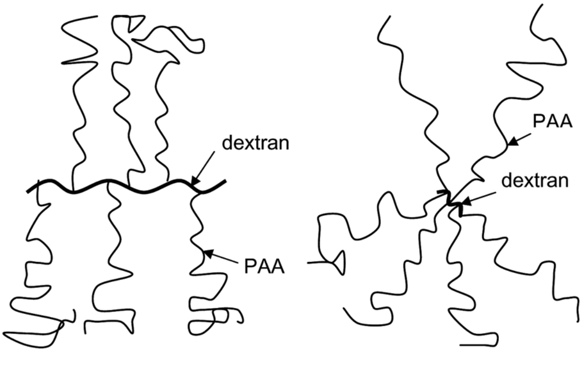

FIGURE 3 Schematic representation of macromolecular structure of the graft copolymers with long and short backbones.

The apparent cause may be that the conformation of the grafted chain is somewhat less expanded in the cases where the grafts are further apart (see Fig. 3). Proximity of the grafted chains to each other may force the chains to adopt a more linear and therefore more expanded structure.

CONCLUSION

The graft copolymers of polyacrylamide to dextran with the same number of grafted chains of comparable length have been synthesized. The flocculation ability of the copolymers in question has been compared with that of linear acrylamide homopolymer having similar molecular weight. Due to an expanded macromolecular conformation the functional groups of these copolymers are more capable of capturing solid particles than those of linear acrylamide polymers. The spacing of the acrylamide grafts (i.e. the length of backbone between the grafts) is inversely related to the flocculation ability because closer spacing of the forces it to adopt a more linear and therefore more expanded conformation.

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