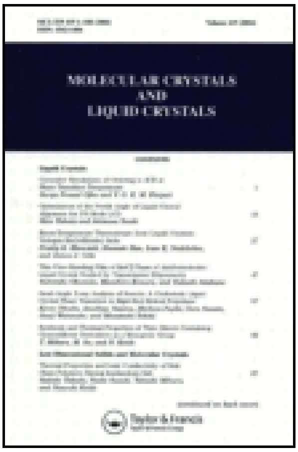

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Comparative Study of Branched and Linear Polymers for the Regulation of Clay Dispersion Stability

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Two series of Dextran-graft-Polyacrylamide copolymers with Dextran backbone of different molecular masses and different numbers of PAA grafts have been synthesized and characterized. Their abilities for the stabilization or destabilization have been examined for a kaolin suspension of moderate concentration within the nephelometric method. The analyzed copolymers have been found to be stabilizers of the suspension when applied in low doses and to be flocculants when applied in moderate or high doses. The mentioned properties are dependent on both molecular mass of a copolymer, as well as on its molecular architecture.

Keywords Branched polymers; internal structure; kaolin suspension; stability of suspension; turbidity

Introduction

Branched copolymers are known to have unique properties both in solutions and in solid state. Meantime, the structure-properties correlations for such polymers have been rather less studied up to now. This is not surprising, since the number of variable parameters becomes almost overwhelmingly large, namely, the initial polymer architecture, average degree of polymerization, solubility properties, changing the solvent composition, distance between grafts, nature and flexibility of backbone and grafts, etc. [1]. All these factors can influence the formation of a nanostructure and determine the final properties of such compounds.

In our previous paper [2], it has been proved that the flocculation abilities of dextran-graft-polyacrylamide copolymers depend on both the dextran backbone length and the PAA-grafts length.

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In the present study, a series of dextran-graft-polyacrylamide copolymers with dextran backbone of different molecular masses and different numbers of PAA grafts has been synthesized and applied for the stabilization or destabilization of kaolin suspensions.

We used namely these copolymers, because many investigations are focused now on replacing the non-biodegradable and costly polyacrylamide flocculants with natural-based polymers. Many authors proves that graft copolymers of polyacrylamide possess a better flocculation efficiency than that of linear polyacrylamide because of peculiarities of their macromolecular structure in solution which results in a better approachability of the side-chains to suspension particles [3–7]. Moreover, the copolymers obtained by grafting the acrylamide chains on natural polymers are easily biodegradable [3,8].

Experimental

Materials and Synthesis of Branched Copolymers

Dextrans with different molecular weights were purchased from Serva (Sweden) with $M_w = 2 \times 10^4$ (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 an initiator. Dextran samples and the ceric salts were used without further purification. Acrylamide (AA) was obtained from Reanal (Hungary) and was twice re-crystallized from chloroform and dried in vacuum at room temperature for 24 h.

Two series of Polyacrylamide grafted to Dextran backbone (D20 and D70), designated as D20-*g*-PAA and D70-*g*-PAA, respectively, were synthesised by the radical polymerization using the Ce(IV)/HNO_3 redox system.

The mechanism of ceric ion initiation and the reaction path were described in our previous paper [8]. The average number of grafting sites per backbone molecule depends on the ratio of molar concentrations of ceric ions to Dextran [8]. The ratio of mol Ce(IV) to mol Dextran was equal to 5, 10, 15, and 20. The amount of monomer AA was kept the same for all syntheses.

The calculated amount of Dextran ($M_w = 20\ 000$ and $M_w = 70\ 000$) was dissolved in 100 ml of distilled water. This solution was stirred while the removal of dissolved oxygen was achieved by bubbling a gentle flux of argon for about 20 min. The calculated amount of a Ce(IV)/HNO_3 initiator (0.125 N HNO_3) was then added. The argon flux was left for another 2 min. Then the acrylamide monomer was added, and the polymerization proceeded in the argon atmosphere for 24 h. Eventually, the copolymer was precipitated into an excess of acetone which gave chiefly two fractions: a fraction totally insoluble (the copolymer) and a remaining turbid suspension. The latter was discarded, while the insoluble fraction was re-dissolved in water and finally freeze-dried.

Samples Characterization

Self-exclusion chromatography (SEC) has been used for the characterization of samples. The SEC analysis was carried out by using a multidetection device consisting of an LC-10AD SHIMADZU pump (throughput 0.5 ml/min), an automatic injector WISP 717 + from WATERS, 3 coupled 30-cm Shodex OH-pak columns (803HQ, 804HQ, 806HQ), a multiangle light scattering detector DAWN F from WYATT

Table 1. Characteristics of polymers used for the sedimentation experiments

Series	Notation	Number of grafts	M_w/M_n	$M_w \cdot 10^{-6}$ g/mol	R_g nm	$(R_g^2/M_w) \cdot 10^3$
PAA	PAA-a	–	2.40	1.40	68	–
	PAA-b	–	2.24	1.22	60	–
	PAA-c	–	1.98	0.87	49	–
	PAA-d	–	1.91	0.61	38	–
D20	D20-PAA5	5	1.63	1.60	67	2.8
	D20-PAA10	10	1.62	0.95	51	2.7
	D20-PAA15	15	1.81	0.94	50	2.7
	D20-PAA20	20	1.67	0.77	46	2.7
D70	D70-PAA5	5	1.72	2.15	85	3.4
	D70-PAA10	10	1.66	1.70	71	3.0
	D70-PAA15	15	1.81	1.57	67	2.9
	D70-PAA20	20	1.98	1.43	64	2.8

TECHNOLOGY, and a differential refractometer R410 from WATERS. Distilled water containing 0.1 M $NaNO_3$ was used as an eluent. The solutions for the SEC analysis (3 g/L) were prepared.

Molecular parameters of the synthesized copolymers, i.e., the average molecular mass (M_w), macrocoil radius of gyration (R_g), and their polydispersity (M_w/M_n) are presented in Table 1. Linear polyacrylamides with different molecular weights (Table 1) have been used as reference flocculants.

The copolymers D-g-PAA can be considered as spherical brushes [1] with Dextran core and PAA-corona [9]. As it was reported earlier for systems D20-*g*-PAA and D70-*g*-PAA with 6 long grafts [8], the scattering curve (X-Ray diffraction) in case of D20-*g*-PAA resembles closely that of a worm-like chain. For D70-*g*-PAA, the behavior 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

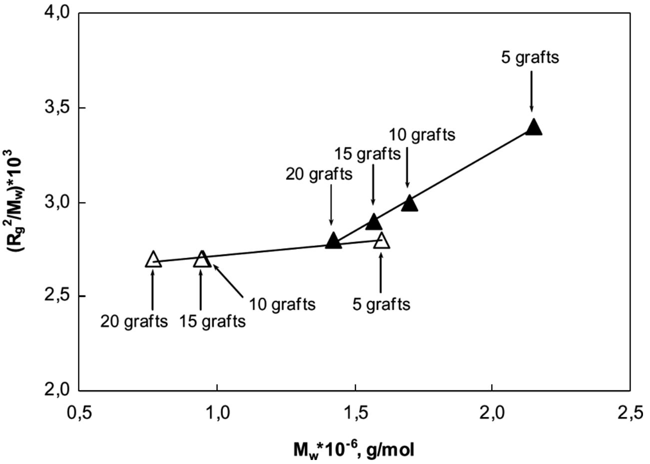

Figure 1. Dependence of R_g^2/M_w for branched copolymers of D20 (△) and D70 (▲) series.

recover a random conformation far from this point. The distance between grafts determines the copolymer internal structure, namely their compactness. Compactness can be expressed in terms of R_g^2/M_w (Table 1). When a value of R_g^2/M_w is lower, the compactness is higher.

According to the difference in the slopes of R_g^2/M_w vs M_w (Fig. 1) for D20-g-PAA and D70-g-PAA series, it can be concluded that the compactness for D70-g-PAA samples depends on two factors simultaneously: the conformation of grafts (mushroom or worm-like) and their number. Whereas the compactness for D20-*g*-PAA ones depends only on the grafts number. With increasing the number of grafts as for D70-PAA15 and D70-PAA20, the conformation become obviously close to the worm-likes [8], as for all copolymers of the D20-PAA series. For all series of D20-*g*-PAA, as well as for D70-*g*-PAA15 and D70-PAA20 copolymers, the values of R_g^2/M_w become low and close. This confirms the theoretical prediction that the compactness of polymer brushes depends on both factors simultaneously: the number of grafts and their conformations.

Sedimentation Experiments

The stabilizing/destabilizing ability of the branched copolymers, as well as of linear PAAs, has been studied using kaolin dispersions of 4 g/dm^3. All the polymers have been applied as freshly prepared stock solutions with a concentration of 100 mg/dm^3. Commercial kaolin KOM manufactured by Surmin-Kaolin (Nowogrodziec, Poland) was used for preparing the suspension. According to the producer, the mineral employed contains 51.5% SiO_2, 34.5% Al_2O_3, 0.63% K_2O, 0.54% TiO_2, 0.53% Fe_2O_3, and small quantities of Ca, Mg, Na and Mn oxides. The dimensions of 99% of the particles did not exceed 15 μm, while the pH of their dispersion in water was 6. Suspensions for the sedimentation tests have been prepared by the thorough mixing of 2 g of kaolin with 300 cm^3 of distilled water during 10 min at 22°C. After the mixing, the suspensions have been put into test cylinders and completed with a certain volume (0, 0.5, 2.5, 5, 10, 20, or 35 cm^3) of the polymer stock solution and distilled water up to a volume of 500 cm^3. The cylinders were turned 10 times by 180^o. Samples for the microscopic investigations have been taken immediately, and the photographs have been obtained after 20 min with a microscope Nikon Eclipse. Samples for the turbidity measurements have been taken from the top layer after 0, 5, 10, and 120 min of the sedimentation. The sample turbidity has been measured by nephelometry at 555 nm, and the obtained results have been presented as the intensity of a signal, I [mV].

Results

Stabilizing/destabilizing properties of branched copolymers and linear Polyacrylamides have been compared using model suspensions with moderate loading of kaolin. Measurements were taken both for short and long periods of sedimentation.

Short Period of Sedimentation

Measurements of turbidity taken for kaolin suspensions containing different doses of a polymer, i.e., linear PAA, copolymer of D20 series, or copolymer of D70 series,

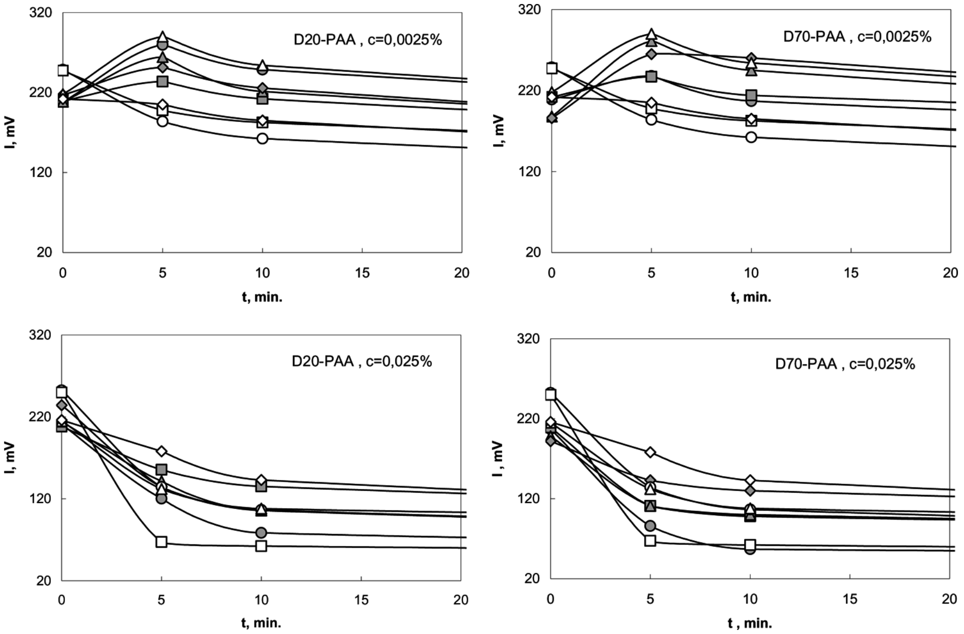

Figure 2. Turbidity of kaolin suspensions in the presence of linear polymers PAA-a (□), PAA-b (○), PAA-c (△), PAA-d (◇) or copolymers with the number of grafts equal to 5 (●), 10 (■), 15 (▲), 20 (◆) at low and medium polymer concentrations. The turbidity values have been registered after 20 min of sedimentation.

have been performed. The turbidity data registered for the first 20 min of experiment have been presented in Figure 2.

At first, the analysis of systems containing a very low dose (i.e., 0.0025%) of a polymer was fulfilled. It was observed that almost all linear Polyacrylamides showed the tendency to destabilize the suspension, but a degree of supernatant clarification was rather low. The only exception is polymer PAA-c with a rather low molecular mass (Table 1) which acted as a fine clay dispersion stabilizer. Branched Dextran-graft-Polyacrylamide copolymers of both D20 and D70 series appear to have a similar ability, when applied at very low concentrations (Fig. 2). Microphotographs taken for the chosen suspensions (Fig. 3) show the reason for the above observation.

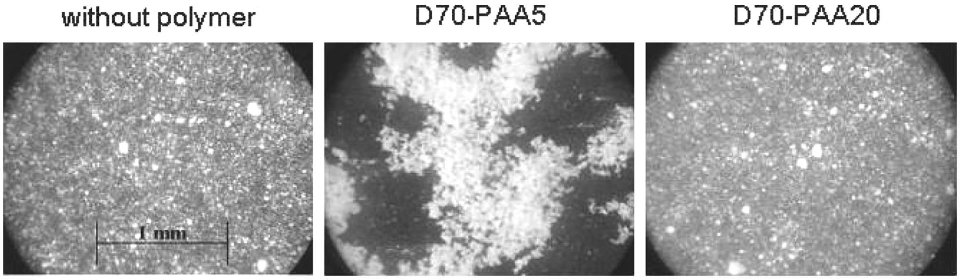
without polymer
D70-PAA5
D70-PAA20

Figure 3. Microphotographs taken after 20 min of the flocculation for a pure kaolin dispersion as well as for flocks created in the systems containing 0.0025% copolymer of series D70.

Copolymers together with kaolin particles create flocks of different dimensions. The biggest flocks were formed, the better clarification was noted.

When higher doses (i.e., 0.025%) of polymers were applied, both linear and branched ones proved as effective flocculants. Flocculating properties of liner PAAs were inversely proportional to their molecular masses (Fig. 2, Table 1). A similar regularity has been also registered in the study [10], where a decrease in the molar mass of starch-graft-polyacrylamide flocculants has led to an increase in the flocculation efficiency. Meantime, in the present study, the best copolymeric flocculant appeared to be D70-PAA5, i.e., the one with the greatest value of molecular mass. Its flocculating abilities were as high as those for the best linear PAA (see Fig. 2). The described observation suggests that the molecular mass of a polymer is not the only parameter conditioning the flocculation properties of polymers. The second important feature is related to the polymer compactness which is dependent on the number of grafted chains and their conformation. It was noted that the flocculation efficiency increases according to an increase in the ratio R_g^2/M_w. The mentioned values for copolymers of D20 series were very similar and lower than those for D70 series. Microphotographs proved that all the copolymers of D20 series, as well as D70-PAA15 and D70-PAA20, create a lot of small flocks (Fig. 3), whereas the D70-PAA5 and D70-PAA10 copolymers with low compactness (Table 1) give visibly bigger flocks. As a consequence, the copolymers of D20 series show somewhat worse flocculation abilities as compared with the copolymers of D70 series (Fig. 2). This way, the suspension clarification efficiency results from flock's size that depends on the polymer compactness.

Figure 4 shows the dependence of the suspension turbidity on both the copolymer dose and the copolymer structure.

One can see that the turbidity of a kaolin suspension is decreased when the flocculant dose is increased. In one's turn, the number of PAA chains influences the flocculation efficiency of copolymers of series D70. The best results were obtained for copolymers with low compactness (Fig. 4, Table 1). Microphotographs

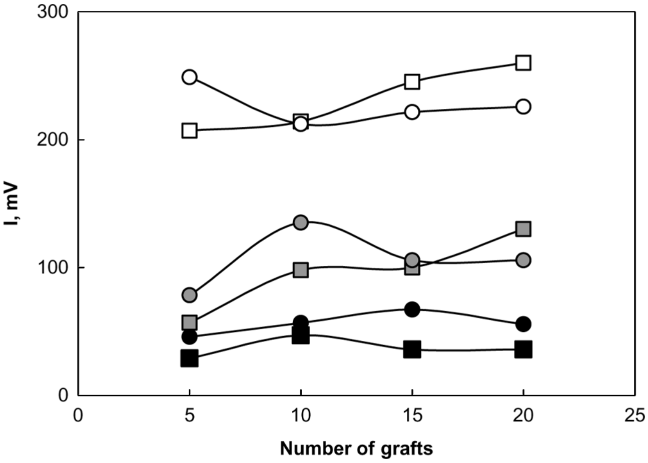

Figure 4. Clarity of kaolin suspensions in the presence of 0.0025% (white marks), 0.025% (gray marks), and 0.1% (black marks) copolymer of series D20 (circles) and D70 (squares), measured after 10 min of flocculation.

(Fig. 5) confirm this observation – when the compactness of a macrocoil decreases, the sizes of flocks increase.

Long Period of Sedimentation

Measurements of the suspension turbidity taken after 120 min of sedimentation have been performed in the presence of all analyzed polymers at different doses. The obtained results are shown in Table 2.

As one can see, an increase of the polymer dose improves the clarity of a suspension in the most cases. The only exception is linear polymer PAA-b, for which a minimal value of turbidity has been registered at an intermediate dose of the flocculant (0.025%). Flocculation abilities of linear polyacrylamides depend nonmonotonically on their molecular masses. The polyacrylamide of the lowest M_W (PAA-d) appeared to have the most efficient flocculating ability at low and medium polymer doses. On the other hand, the PAA-c polymer has the worst flocculating ability at these doses. The polyacrylamide with the highest M_w (PAA-a) has shown the best flocculation abilities at high polymer doses.

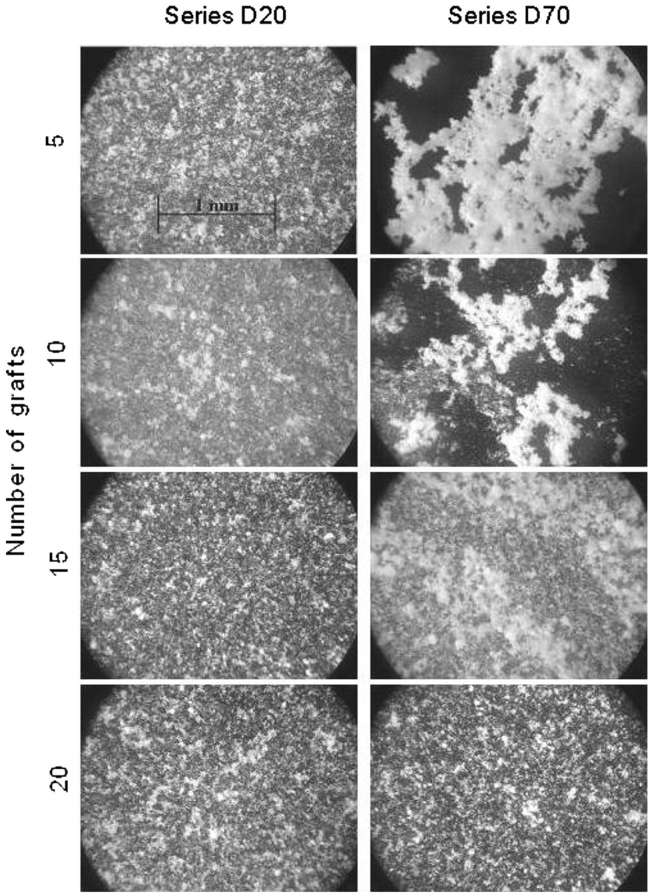

Figure 5. Microphotographs taken after 20 min of the flocculation for flocks created in the systems containing 0.025% copolymer of series D20 or D70.

Table 2. Relative turbidity of suspensions measured after 120 min of sedimentation. Relative turbidity given as the ratio of signals noted for the systems with and without polymer

	Relative turbidity at different polymer concentrations		
Polymer	0.0025%	0.025%	0.1%
PAA-a	0.81	0.44	0.26
PAA-b	0.58	0.41	0.68
PAA-c	0.95	0.76	0.29
PAA-d	0.43	0.33	0.32
D20-PAA5	0.95	0.41	0.30
D20-PAA10	0.79	0.54	0.33
D20-PAA15	0.72	0.38	0.26
D20-PAA20	0.52	0.38	0.24
D70-PAA5	0.91	0.45	0.18
D70-PAA10	0.92	0.41	0.24
D70-PAA15	0.80	0.50	0.23
D70-PAA20	0.78	0.63	0.22

Copolymers D-PAA used at a very low dose appeared generally to have rather poor destabilizing properties as for the kaolin suspension. The increase in the copolymer concentration allowed us to register the suspension clarification comparable to that for linear polyacrylamides. Copolymers of D70 series at high doses appeared to be even more efficient than linear polyacryamides. Especially, D70-PAA5 can be recommended as an efficient flocculant for the acceleration of the sedimentation of a mineral suspension. The results obtained for this copolymer in the case of a long period of sedimentation are in full agreement with those presented for a short time of sedimentation.

Conclusions

In the present study, we have obtained the following results:

1. Dextran-graft-polyacrylamide copolymers used at very low doses (i.e., up to 0.0025% of the mineral mass in a suspension), in contrast to the majority of linear PAAs, are rather good stabilizers of the suspension. Samples of copolymers signed as D70-PAA20, as well as D70-PAA15 and D20-PAA5, have been found as the best stabilizing agents. These copolymers used at low doses practically don't create flocks with kaolin particles.
2. Dextran-graft-polyacrylamide copolymers used at a dose equal or higher than 0.025% of the mineral mass in a suspension possess the ability to destabilize colloidal dispersions and can be used as flocculation agents. The especially efficient flocculant appeared to be copolymer signed as D70-PAA5 which possesses the ability to create big heavy flocks with kaolin particles. Its ability for the destabilization of a dispersion is comparable to that of linear PAA.
3. Flocculation properties of liner PAAs are inversely proportional to their molecular masses. In the case of copolymers D-PAA, their abilities to stabilize or

destabilize a mineral suspension depend on the molecular mass, number of grafted PAA chains, and macromolecule radius. That is why the increase in flocculation abilities of copolymers D-PAA follows the increase in the ratio R_g^2/M_w.

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