The Effects of the Properties of Trunk Polymers on the Flocculating Action of Graft Copolymers

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Acryl amide (AM) was graft copolymerized onto hydroxy ethyl cellulose(HEC), polyvinyl alcohol (PVA), amylose (AL), and amylopectin (AP), whose molecular extensions in an aqueous solution are different. The graft copolymers were then purified by means of fractional precipitation. The effects of the properties of the trunk polymers of the graft copolymers on their flocculating action for kaolin suspensions were examined. It was found that: 1) when the molecular weights ($\bar{M}_n$) of the copolymers were equal, their flocculating action was much influenced by the kind of trunk polymer (HEC, AL, PVA, and AP) and decreased in that order; 2) the differences in their flocculating action are due to the differences in their molecular extensions in an aqueous solution; and 3) the flocculating action of the copolymers increased with an increase in the $\bar{M}_w$ of the branched poly AM (PAM), but was, however, scarcely affected by a small number of grafted PAM per trunk polymer molecule.

High-molecular polyacrylamide (PAM) is now used in large amounts as a flocculant for the treatment of waste water; however, it has some disadvantages, *e.g.*, the abscission of its molecular chains easily occures in a dissolution process because of its high molecular weight. Consequently, the development of flocculants whose molecular weight is relatively low and whose flocculating action is superior to that of high-molecular PAM has been attempted.

It seemed, therefore, that it would be interesting to study the graft copolymers of cellulose, starch, *etc.*, as flocculants. Up to now, in some studies[1] of water-soluble graft copolymers as flocculants, the flocculating action of a reaction mixture composed of graft copolymers, homopolymers, and unreacted trunk polymers has been examined, but that of pure graft copolymers has not yet been investigated. Previously, the present authors[2] proved that the flocculating action of the fractionated water-soluble hydroxyethyl cellulose (HEC)-AM graft copolymers was superior to that of PAM because of the rigid molecular chains and the large molecular extension of HEC.

In this paper, in order to make the relation clearer between the flocculating action of the copolymers and their molecular extensions in an aqueous solution, the flocculating action of the fractionated graft copolymers of the trunk polymers, polyvinyl alcohol (PVA, flexible), amylose (AL), amylopectin (AP, branched) and HEC (rigid), which have different molecular chains, was studied. Moreover, the effects of the molecular weight and the number of the grafted PAM on the flocculating action of the copolymers were examined. Graft copolymerization was carried out by means of the Ce (IV) salt method.[3]

Experimental

Materials. PVA, AL, AP, and HEC: Commercial PVA, AL, AP, and high-molecular HEC (*h*-HEC) were used without further purification. Their molecular weights ($\bar{M}_n$) were 8×10^4, 7×10^4, 1.9×10^5, and 1.8×10^5 respectively. The degree of the hydroxyethylation of HEC was 1.2 as the molar substitution (MS).[4] Low-molecular HEC ($\bar{M}_n$ of *l*-HEC: 7×10^4) was synthesized as has been described in a previous paper.[2] Ammonium cerium(IV) nitrate, AM, CCl_4, and kaolin: they were described in a previous paper.[2]

Graft Copolymerization and Fractionation of Graft Copolymers. Graft Copolymerization: Graft copolymerization was carried out by the Ce(IV) salt method[3] under a stream of N_2 at 40 °C for 30—220 min. In a polymerization apparatus, 0.4 g of the trunk polymers, 2.0—2.5 g of AM, the fixed Ce salt, and HNO_3, and 40 ml of water were added. The concentrations of Ce salt for grafting onto PVA, HEC, AL, and AP were 1.3×10^{-4}—4.0×10^{-4} mol/l, 8.0×10^{-4}—2.2×10^{-2} mol/l 1.8×10^{-3}—2.2×10^{-2} mol/l, and 3.7×10^{-3}—2.2×10^{-2} mol/l respectively, while those of HNO_3 were 0.05—0.07 mol/l (PVA) and 0.014—0.28 mol/l (others). For the preparation of the graft copolymers with low-molecular grafted PAM, a 2—4 ml portion of CCl_4 was added to serve as a regulator.

Fractionation of Graft Copolymers: In order to obtain the fractionated graft copolymers, the precipitation properties of the trunk polymers and PAM in an aqueous acetone sytem were examined, as is shown in Fig. 1. It can be seen from Fig. 1 that the respective graft copolymers of HEC, PVA, AP, and AL are precipitated when the concentrations of acetone in a solution are 40—70%, 40—48%, 28—36%, and 23—36% respectively. The graft copolymers were precipitated fractionally at the above concentrations of acetone. These fractionated products were confirmed respectively by IR, turbidimetric titration in an aqueous acetone system, and the determination of the nitrogen by means of the Kjeldahl method.

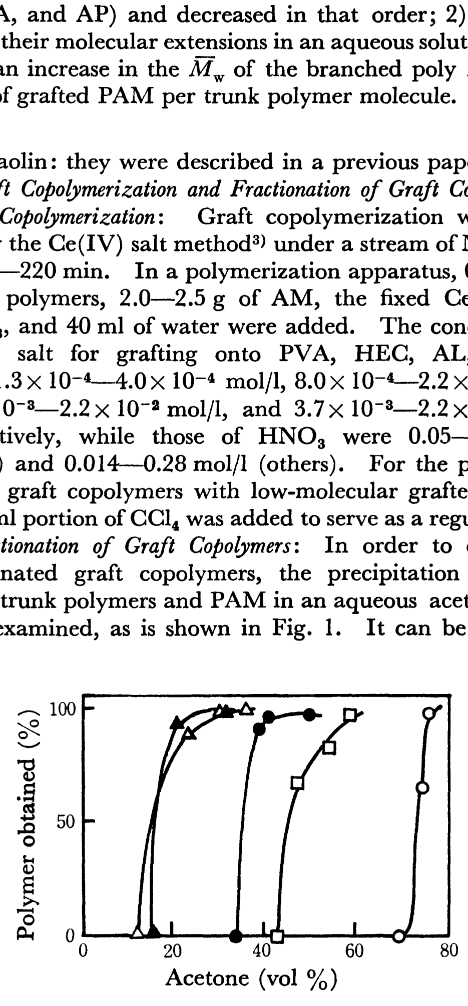

Fig. 1. The precipitation properties of the trunk polymers and PAM in an aqueous acetone system.
●: PAM, ○: HEC, □: PVA, △: Amylopectin, ▲: Amylose. 0.5% aqueous polymer solution at 30 °C.

Determination of the Molecular Weight and Intrinsic Viscosity ([η]). The molecular weight ($\bar{M}_n$) of the graft copolymers was measured with a 502-type high-speed membrane

TABLE 1. CHARACTERIZATION OF GRAFT COPOLYMERS

Sample		$\bar{M}_n$ of copolymer		M.W. of branch of copolymer		Number[a] of branches per one trunk polymer	Chemical composition ratio[b] (wt.) Branch/Trunk polymer
		Obsd ($\times 10^{-5}$)	Calcd[c] ($\times 10^{-5}$)	$\bar{M}_n$ ($\times 10^{-5}$)	$\bar{M}_w$ ($\times 10^{-5}$)		
h-HEC	1	2.3	3.4	2.5	6.1	0.64	0.89
	2	3.4	4.0	3.2	9.0	0.69	1.23
	3	4.2	5.5	3.7	12.8	1.0	2.05
	4	—	16.2	4.5	11.5	3.2	8.00
	5	6.0	6.8	5.6	13.8	0.90	2.80
	6	6.7	7.6	7.2	17.7	0.80	3.22
	7	7.9	9.4	12.6	31.6	0.60	4.18
	8	—	16.7	18.0	45.0	0.83	8.30
l-HEC	1	1.8	2.5	2.2	5.4	0.82	2.58
	2	2.3	3.0	3.0	7.6	0.75	3.21
	3	2.9	3.6	3.4	8.5	0.84	4.08
	4	3.7	4.3	5.0	12.3	0.72	5.14
	5	5.1	5.9	8.1	19.5	0.64	7.41
	6	7.9	8.6	9.8	25.0	0.81	11.3
	7	8.9	9.5	11.0	28.0	0.80	12.6
	8	—	11.4	14.7	36.0	0.73	15.3
	9	—	14.8	18.6	46.0	0.76	20.2
PVA	1	1.3	1.7	1.0	2.9	0.88	1.10
	2	2.7	3.4	3.8	9.5	0.67	3.18
	3	5.9	6.8	8.4	20.5	0.72	7.56
	4	8.5	9.4	9.5	24.0	0.85	10.1
	5	9.2	10.7	11.0	26.9	0.89	12.4
	6	—	15.2	12.0	33.1	1.2	18.0
	7	—	18.9	9.5	24.0	1.9	22.6
	8	—	20.0	19.2	47.4	1.0	24.0
AP	1	3.7	4.5	3.3	8.4	0.79	1.37
	2	5.0	5.4	3.6	9.2	0.97	1.84
	3	5.6	6.0	3.7	9.8	1.1	2.13
	4	—	10.0	3.0	7.8	2.7	4.26
	5	—	7.5	3.5	8.5	1.6	2.96
	6	9.1	10.1	6.8	16.3	1.2	4.29
	7	7.5	8.3	7.5	18.9	0.85	3.36
	8	—	12.9	11.0	27.9	1.0	5.79
AL	1	1.3	1.7	0.9	2.2	1.1	1.41
	2	—	2.7	1.1	2.6	1.9	2.85
	3	3.6	4.2	3.5	8.7	1.0	4.96
	4	5.7	6.4	5.2	12.6	1.1	8.14
	5	7.3	7.9	8.4	20.0	0.86	10.3
	6	1.6	1.8	1.0	2.4	1.1	1.57
	7	—	1.2	0.7	1.5	0.75	0.75

a) ($\bar{M}_n$ of trunk polymer) × (chemical composition ratio)/$\bar{M}_n$ of branch. b) Obtained by Kjeldahl method.
c) $\bar{M}_n$ of trunk polymer + ($\bar{M}_n$ of branch) × (number of branches).

osmometer manufactured by Hewlett Packard Co., while the molecular weights ($\bar{M}_w$ and $\bar{M}_n$) of the grafted PAM were determined from the following viscosity equations as has been described in a previous paper;[2] $[\eta]^{30^\circ\mathrm{C}}_{\mathrm{N\text{-}NaNO_3}}=3.73\times10^{-4}\,\bar{M}_w^{0.66}$ and $[\eta]^{30^\circ\mathrm{C}}_{\mathrm{H_2O}}=6.8\times10^{-4}\,\bar{M}_n^{0.66}$ [5]

Characterization of Graft Copolymers. This is shown in Table 1.

Flocculation Test. The flocculating action of the flocculants was measured by means of the sedimentation rate,[9] with a 25 ml graduated cylinder, and the transmittance of a supernatant solution, with a Shimadzu Bausch and Lomb Spectronic 20 colorimeter, which has been described in a previous paper.[2]

Results and Discussion

Effect of Difference in Kind of Trunk Polymers. Figures 2 and 3 show the effects of the difference in the kind of trunk polymers on the sedimentation rate and the transmittance respectively. Even though the $\bar{M}_n$ of the respective graft copolymers of *h*-HEC, *l*-HEC, AL, PVA, and AP are equal, the sedimentation rate and the transmittance decreased in that order, as is shown in Figs. 2 and 3.

It has been proposed[6,7] that the flocculation of kaolin suspensions with nonionic polymer flocculants is caused by a bridging of kaolin particles with the adsorbed poly-

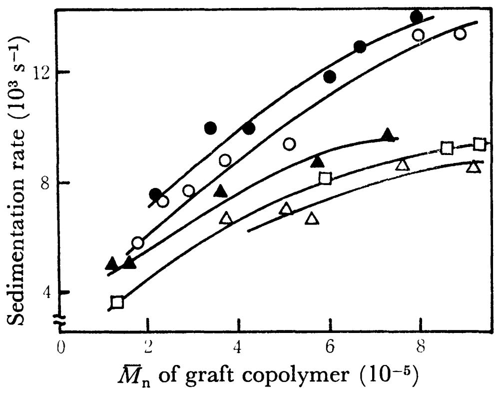

Fig. 2. Effect of the kind of the trunk polymers on the sedimentation rate.
○: *l*-HEC graft copolymer, ●: *h*-HEC graft copolymer, □: PVA graft copolymer, △: AP graft copolymer, ▲: AL graft copolymer.
Dosage of flocculant: 1 mg/l suspension.

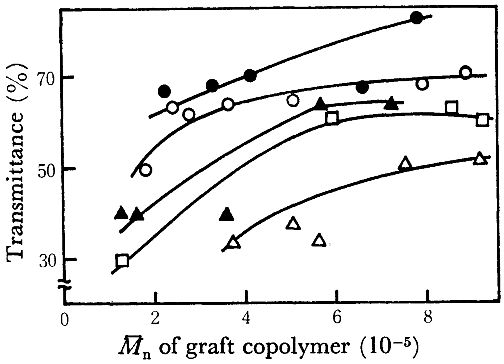

Fig. 3. Effect of the kind of the trunk polymers on the transmittance in 0.8% kaolin suspensions.
Symbols are the same as those in Fig. 2.
Dosage of flocculant: 1 mg/l suspension.

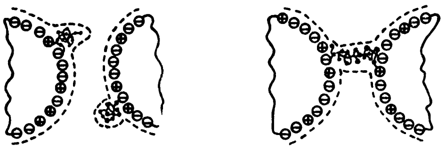

Fig. 4. Schematic representation of flocculation by a bridging of kaolin particles with polymers.
○: Kaolin particle, ••: Polymer.

mers. Consequently, their flocculating action must be determined by two factors. One is the molecular extension, which the molecular chains of the adsorbed polymers can bridge between particles; if the molecular extension of polymers in a solution is small, an interparticle bridging will be unfavorable. This is shown schematically in Fig. 4. The other is the adsorption properties of the flocculants on suspended particles. The adsorption properties of these graft copolymers on the kaolin particles used in this study were not determined. It seems, however, that the adsorption properties are almost identical because of the hydrophilic trunk polymers, which have only hydroxl groups. The difference in the flocculating action of these graft copolymers seems to arise from the difference in their molecular extensions caused by the properties of the trunk polymers. That is, the extension of the HEC graft copolymers seems to be the largest, because of the rigid molecular chains and the large extension of the trunk-polymer HEC. That of the AL graft copolymers appears to be the next largest, because AL has indeed bulky anhydrous glucose groups, just as HEC does, but it is not rigid. That of the PVA graft copolymers seems to be the third largest, because of the flexible and randomly coiled chains of PVA. The smallest one appears to be that of the AP graft copolymers, because of the small extension of AP on the ground of its branching chain structure.

Difference in Molecular Extension in an Aqueous Solution. The difference in the flocculating action of the graft copolymers seems to be due to the difference in their molecular extensions in an aqueous solution caused by the properties of the trunk polymers. In order to make sure of this, the molecular extensions of the graft copolymers were examined. No definitive theoretical equation of the molecular extensions of graft and block copolymers in an aqueous solution has yet been elucidated. It seemed that it would be interesting, however, to compare the extensions of the molecular chains by means of the dimensions (R_e: the radius) of Flory's non-draining equivalent sphere model.8) The relation between R_e, the molecular weight ($\bar{M}$), and ($[\eta]$) is as follows: $[\eta]=KR_e{}^3/\bar{M}$ 8) (K: constant). Consequently, $[\eta]\ \bar{M}_n$ was represented as the evaluation of the molecular extensions of the graft copolymers. When the $\bar{M}_n$ values of the copolymers are equal to each other, the molecular extensions ($\bar{M}_n[\eta]$) of the respective graft copolymers of HEC, AL, AP, and PVA decreased in that order, as is shown in Fig. 5. The order of the flocculating action of the graft copolymers was well in accord with that of their molecular extensions ($\bar{M}_n[\eta]$), except that the graft copolymers of PVA and AP were reversed. The plots of the extensions of the graft copolymers *vs.* the transmittance and the sedimentation rate gave an approximately linear relation regardless of the kind of the flocculants used in this study, as is shown in Fig. 6.

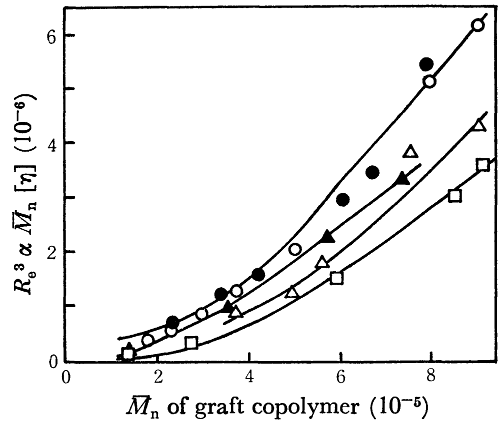

Fig. 5. Relation between the molecular extensions ($\bar{M}_n[\eta]$) and the $\bar{M}_n$ of the graft copolymers.
Symbols are the same as those in Fig. 2.

In conclusion, the difference in the flocculating action of the graft copolymers must be due to the difference in their molecular extensions in an aqueous solution, determined on the basis of the properties of the trunk poly-

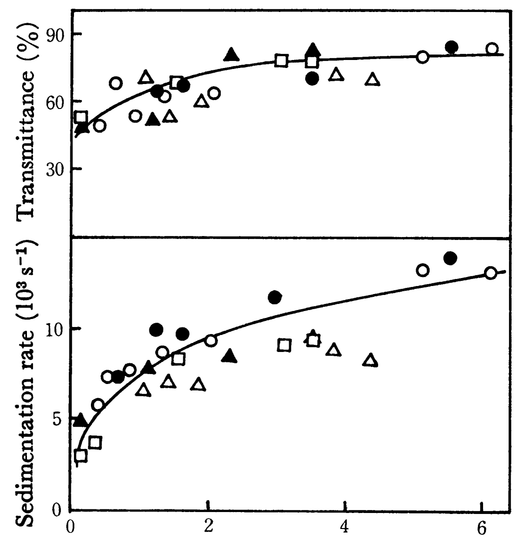

Fig. 6. Relation between the molecular extensions ($\bar{M}_n[\eta]$) and the sedimentation rate and the transmittance of 3% kaolin suspensions.
Symbols are the same as those in Fig. 2.
Dosage of flocculant: 1 mg/l suspension.

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Effects of the Molecular Weight and Number of the Branched PAM of Graft Copolymers. Figures 7 and 8 show the effects of the molecular weight ($\bar{M}_w$) of the branched PAM of the graft copolymers on the sedimentation rate and the transmittance of a supernatant solution respectively. As is shown in Fig. 7, the sedimentation rate increased with an increase in the $\bar{M}_w$ of the branched PAM in all the different trunk polymers. This result suggests that kaolin particles are sedimented by means of the bridging mechanism.$^{6)}$ That is, the higher the $\bar{M}_w$ is, the more effective the bridging flocculation may be. The transmittance also increased with the increase in the $\bar{M}_w$ as well as the sedimentation rate, up to 3.5×10^6 of the $\bar{M}_w$ of the branched PAM. However, at the $\bar{M}_w$ values above that value, there was little effect of the $\bar{M}_w$ on the clarification. This may be because the clarification results from the reduction of the electrostatic repulsion between the colloidal fine particles, which could not be sedimented thoroughly by the bridging alone.

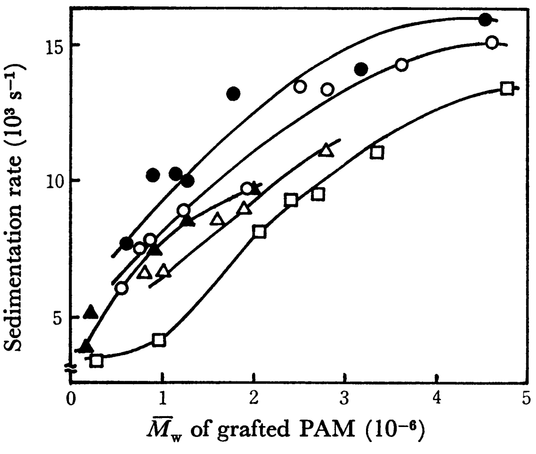

Fig. 7. Effect of the $\bar{M}_w$ of the grafted PAM of the graft copolymers on the sedimentation rate.
Symbols are the same as those in Fig. 2.
Dosage of flocculant: 1 mg/l suspension.

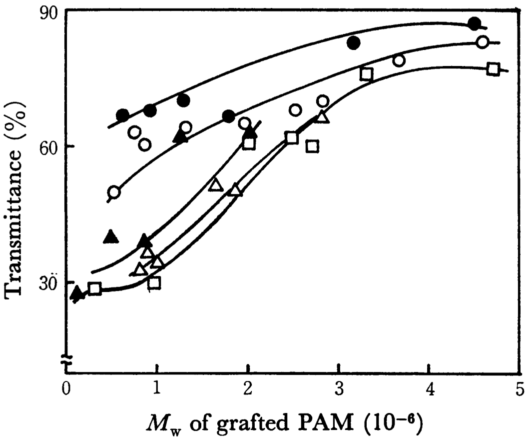

Fig. 8. Effect of the $\bar{M}_w$ of the grafted PAM of the graft copolymers on the transmittance of 0.8% kaolin suspensions.
Symbols are the same as those in Fig. 2.
Dosage of flicculant: 1 mg/l suspension.

When the $\bar{M}_w$ values of the branched PAM were equal to each other, the flocculating action of the respective graft copolymers of HEC, AL, AP, and PVA decreased in that order. The difference in their flocculating action seems to be due to the difference in the molecular extensions caused by the properties of the trunk polymers. This was discussed before. The flocculating action of the *h*-HEC graft copolymers was superior to that of the *l*-HEC graft copolymers even if the $\bar{M}_w$ values of their branched PAM were equal. This must be due to the easier bridging with the former compared with the latter, because the molecular weight ($\bar{M}_n$) of the former was, as a whole, higher than that of the latter.

Figure 9 shows the effect of the number (1—3) of the

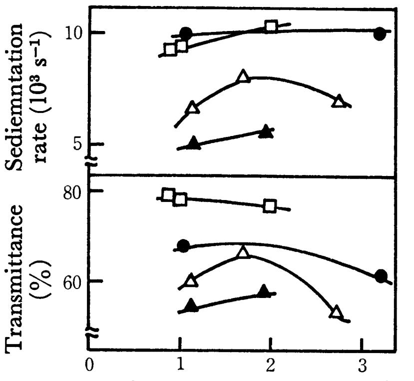

Fig. 9. Effect of the number of the grafted PAM per one trunk polymer molecule on the sedimentation rate and the transmittance of 3% kaolin suspensions.
$\bar{M}_n$ of grafted PAM:
●: *h*-HEC graft copolymer (4.0×10^5)
□: PVA graft copolymer (9.5×10^5)
△: AP graft copolymer (3.5×10^5)
▲: AL graft copolymer (1.0×10^5)
Dosage of flocculant: 1 mg/l suspension.

branched PAM on the sedimentation rate and the transmittance. The flocculating action of the graft copolymers which had two branched PAM was a little superior to that of others. However, on the whole, the flocculating action was scarcely affected by the number of the branched PAM, even if the kind of the trunk polymer was different.

References

1) M. Inano, *Kogyo Kagaku Zasshi*, **72**, 2298 (1969); T. Hirano and T. Hasegawa, *ibid.*, **74**, 91, 456 (1971).

2) N. Miyata, I. Sakata, and R. Senju, *Nippon Kagaku Kaishi*, **1974**, 1782.

3) G. Mino and S. Kaizerman, *J. Polym. Sci.*, **31**, 242 (1958); H. Narita and S. Machida, *Seni Gakkaishi*, **27**, 162 (1971).

4) P. W. Morgan, *Ind. Eng. Chem. Anal. Ed.*, **18**, 500 (1946).

5) "New Product Bulletin," No. 34, 2, American Cyanamide Co., New York (1955).

6) A. S. Michaels, *Ind. Eng. Chem.*, **46**, 1485 (1954).

7) A. S. Michaels and O. Morelos, *ibid.*, **47**, 1801 (1955).

8) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

9) This was represented by the reciprocal of the time required for the solid-liquid boundary to sediment by 10 ml in a 25 ml graduated cylinder. The sedimentation with uniform rate was observed when the height of the solid-liquid boundary fall between 2 ml and 12 ml.