

The Effects of the Branching Structures of Amphoteric Polyacrylamide on the Paper Properties

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1. Introduction

In the pulp and paper industry, waste paper is utilized as a pulp-fiber source in papermaking process for the purpose of environmental protection and efficient use of resources. Repetitive recycling of pulp reduces the fiber length (fibers are partially broken as they are reprocessed) and decreases the quantity of fibrils on the surface of the pulps. Consequently, the strength of the obtained paper, the retention, and the drainage of the pulp slurry get worse.

Paper strength additives can be added to the recycled pulps to compensate for the decrease in paper strength. Paper strength additives can also improve the retention and the drainage of the pulp slurry making them indispensable for the papermaking processes. Paper strength additives are classified into starch-based and polyacrylamide (PAM)-based chemicals, and the latter is more effective in improving paper strength. PAMs are further subcategorized into the anion types, the

Hoffmann types, the Mannich types, and the amphoteric types. At present, the amphoteric PAMs are the most popular among these types (The molecular structure is shown in Figure 1).

The amphoteric PAM is synthesized by radical copolymerization of acrylamide, cationic monomers, and anionic monomers in water and is sold as aqueous solution. In papermaking process, the amphoteric PAM is diluted with additional water before being added to the pulp slurry where the PAM is adsorbed onto the pulp to strengthen the paper. The amide moiety is believed to contribute to improving the paper strength while the cationic and the anionic groups are relevant to the adsorption of PAMs onto the pulp. Compared to other types of PAMs, the molecular weight, molecular structure, distribution of ionic groups in the amphoteric PAMs can be controlled easily. For this reason, amphoteric PAMs can be customized depending on different papermaking conditions.

This review presents our understanding of the structures of some amphoteric PAMs and their physical properties, followed by the evaluation of the performance as paper strength additives.

2. Structural and Physical Properties of Amphoteric PAMs

Amphoteric PAM samples A-F synthesized by the same monomer composition but under different reaction conditions are listed in Table 1. Their B-type viscosity and intrinsic viscosity were measured by Brookfield viscometer and Ubbelohde viscometer, respectively.

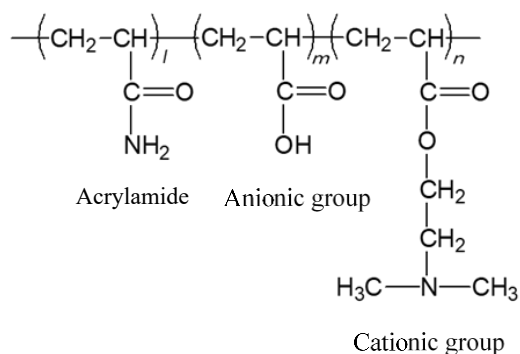


Figure 1. Molecular structure of amphoteric PAM

Table 1. Physical properties of amphoteric PAMs

Sample	Concentration (%)	B-type viscosity (mPa·s/25°C) 20%/10%	Mw	Radius of gyration (nm)	Intrinsic viscosity (dL/g)
A	10	- / 50,000	280 x10 ⁴	67	3.5
B	20	7,000 / 440	260 x10 ⁴	55	1.5
C	20	18,000 / 1,100	380 x10 ⁴	65	2.0
D	20	73,000 / 4,900	590 x10 ⁴	76	2.6
E	20	3,500 / 210	330 x10 ⁴	55	1.2
F	20	7,000 / 400	560 x10 ⁴	64	1.9

Their weight-average molecular weight (Mw) and radii of gyration were determined by GPC equipped with multi-angle light scattering (MALS) as the detector (GPC-MALS).

The plot describing the relationship between the molecular weight and B-type viscosities of the 10% aqueous solutions is shown in Figure 2. Although the Mw of **A** and **B** are very similar, their viscosities are significantly different. Also, the comparison of **B** and **F** reveals that they have different Mw despite their similar viscosities. These differences originate from the structural differences in the amphoteric PAMs, which can be characterized by GPC-MALS. Figure 3 shows the molecular weight distributions and their radii of gyration for **A** (orange) and **B** (blue). It was found that

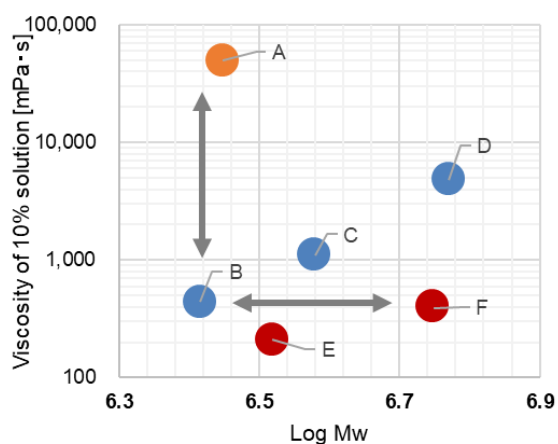


Figure 2. Plot of logarithm of the Mw of amphoteric PAMs A-F versus the corresponding B-type viscosities of 10% aqueous solution

their radii of gyration are substantially different although their molecular weight distributions are very similar. The results show that introducing some branches in the amphoteric PAMs leads to reduction in the radius of gyration provided that their molecular weight is in the same level. By increasing the degree of branching in amphoteric PAM, the radius of gyration can be even smaller.

The amphoteric PAMs **A-F** can be classified into three types based on the structural characterization by GPC-MALS: linear type (**A**), low branched types (**B-D**), and highly branched types (**E-F**). Figure 4 is a plot of **A-F** with a model of their structures. The vertical axis represents the radii of gyration of each sample while the horizontal axis represents the logarithm of Mw. Thus far, it has been shown that the Mw and the structures of the amphoteric PAMs are controllable and characterizable.

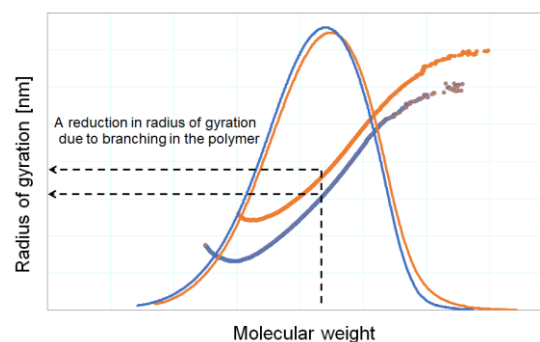


Figure 3. Results of GPC-MALS measurements of amphoteric PAMs

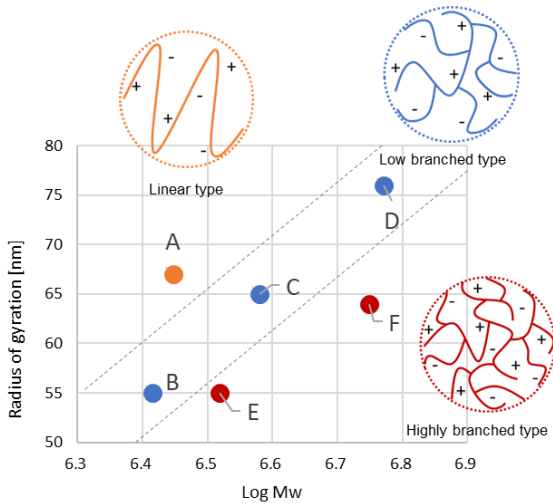


Figure 4. Molecular weight and radii of gyration of amphoteric PAMs

In the following section, the evaluation of their performance related to papermaking process will be shown when the amphoteric PAMs are employed as paper strength additives.

3. Evaluation of Paper Strength Additives by their Paper Strengthening Effect

3-1. Evaluation Methods and Conditions

The pulp slurry (CSF350) was prepared from old corrugated cardboard. The slurry was then adjusted to concentration of 2.4%(w/w) and electrical conductivity of 150 mS/m. To the slurry were added aluminum sulfate (1%) and an amphoteric PAM under stirring to prepare a paper sheet at pH7. The drainage was evaluated using a dynamic drainage jar (DDJ) by the filtering time required to obtain 100mL of the filtrate. The paper sheets were stored at 23°C and a humidity of 50% over 24 hours, and were measured for their paper strength properties thereafter. The degree of adsorption of the amphoteric PAM was calculated based on the nitrogen content in the paper measured by a nitrogen analyzer.

3-2. Drainage

The results of drainage test are shown in Figure 5. The bars represent the drainage test results of PAMs as evaluated via time (vertical axis on the left) while the dashed line represents the intrinsic viscosity as described in the right vertical axis. The shorter the time to collect a certain volume of the filtrate is, the faster the drainage. A performed the best. For the B, C and D, the drainage was improved as the molecular weight estimated from the intrinsic viscosity becomes large. A similar trend was observed between highly branched PAMs E and F. Overall, drainage rate was found to have an inverse correlation to the value of intrinsic viscosity of each sample. Intrinsic viscosity represents the volume occupied by the polymer in solution per unit weight, as its unit (dL/g) indicates. We believe that the amphoteric PAMs having higher intrinsic viscosities take the stretched conformation in the pulp slurry, which makes it possible to efficiently flocculate the pulp fibers to improve the drainage. However, overly viscous amphoteric PAMs tend to hamper the smooth flow of the solution in pipelines and makes its use unfeasible. Therefore, F is the most desirable paper additive of among them.

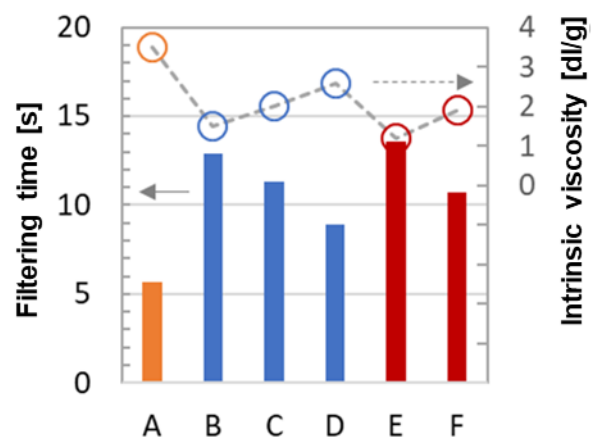


Figure 5. Evaluation of drainage and intrinsic viscosity of PAMs

3-3. Comparison of Paper Strength

Figure 6 shows the relationship between the degree of adsorption of the amphoteric PAMs onto the paper sheet and the paper strength (dry burst index).

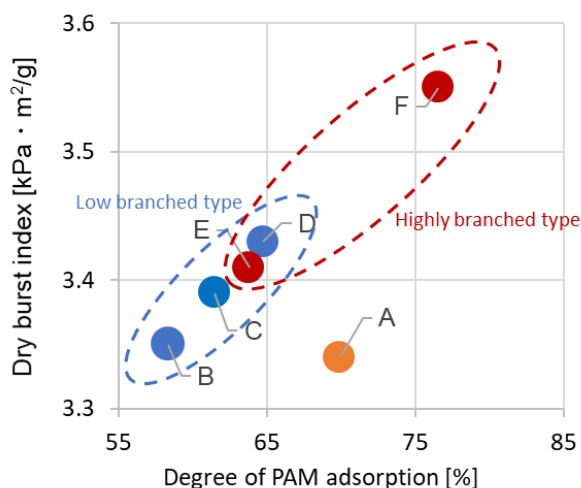


Figure 6. The degree of adsorption of PAMs and paper strength

The order of Mw for **B**, **C** and **D** in Table 1 was found to have strong correlation with their alignment in Figure 6. This means that increasing the Mw of amphoteric PAMs helps them be adsorbed to pulp and strengthen the paper. This trend was observed for **E** and **F** as well. Among these samples, **F** achieved the best paper strength. **A** only showed the same level of paper strength as **B** despite the higher adsorption to the pulp. Presumably, **A** caused a strong flocculation of the pulp fibers resulting in a poor paper sheet formation. We found that introducing branches and higher Mw of amphoteric PAM enhanced their absorption to pulp fibers, which improved the properties of obtained papers.

Figure 7 shows a schematic representation of the amphoteric PAMs that rationalizes how the structure and the Mw of PAM influence its adsorption to fibers and paper strengthening effect. **C** has the equivalent polymer structure as **B** but a higher Mw. The higher the Mw of amphoteric PAM becomes, the more ionic

groups a single polymer possesses, which functions as adsorption sites to the pulp fibers. **E** has the equivalent Mw as **C** but has additional branching. The difference in their charge densities can be clarified by the zeta potential. The zeta potential of **E** (+9.3 mV) was larger than that of **B** (+5.9 mV). In this case, although the number of ionic groups in a single amphoteric PAM does not differ significantly, the density of ionic groups is increased.

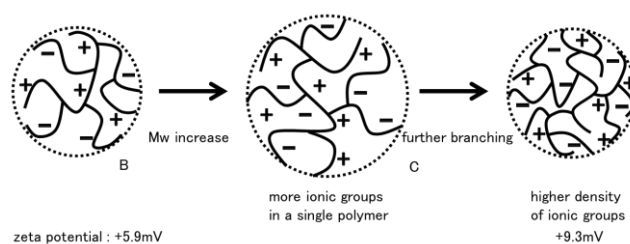


Figure 7. Effect of high Mw and highly branched structures on amphoteric PAM

Table 2. DS series products

Product	Characteristics
DS4433	General-purpose product Excellent effect of enhancing paper strength
DS4434	Excellent effect under high-electrical conductivity condition
DS4431	Excellent effect of enhancing drainage and retention Improve retention of sizing agents and dyes
DS4817	Excellent effect even without alum by introducing a special functional group
DS4356	Excellent effect under acidic condition Improved interaction with alum
DS4424	Excellent effect under neutral condition Excellent paper strength and retention in the presence of calcium carbonate
DS4845	Can spontaneously adsorb to pulp, less likely to be disturbed by calcium carbonate

We offer a variety of DS series products as paper strength additives by the application of the structure control technologies to the synthesis of amphoteric PAMs. Table 2 shows representative DS series products. Choice is made based on the papermaking conditions.

4. Conclusion

We demonstrated that the molecular weight and the structure of the amphoteric PAM can be controlled, and

be characterized by GPC-MALS. By introducing branches to amphoteric PAMs, the viscosity of the aqueous solutions can be significantly reduced, which allows us to serve the amphoteric PAMs at higher concentrations. Moreover, increasing the molecular weight of amphoteric PAMs improved the drainage and paper strength, which indicates that controlling the structure of the amphoteric PAM is the key factor to high quality paper strength additives.

Environmental protection and saving resources are becoming important day by day. Under the papermaking

conditions to fulfil such requirements, the performance of current paper chemicals such as paper strength additives could be weakened. Therefore, further improvement in the performance of the paper strength additives is necessary. With our vision "Explore the Future through Eco-Friendly Technology", we contribute to the development of papermaking industry by making technological breakthrough and supplying high-performance paper chemicals that fulfil our customer's needs.

Profile



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