

Characterization of Polyamideamine-Epichlorohydrin (PAE) Resin: Roles of Azetidinium Groups and Molecular Mass of PAE in Wet Strength Development of Paper Prepared with PAE

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ABSTRACT: Polyamideamine-epichlorohydrin (PAE) resin is a crosslinked heteropolymer having cationic charges, and has been widely used as a wet strength agent of paper in the papermaking process. In this study, more accurate molecular mass values of PAE were determined by size exclusion chromatography attached with a multi angle laser light scattering detector (SEC-MALS). The obtained weight average molecular mass (M_w) values of commercial and laboratory-made PAE samples were 1,140,000 and 494,000, respectively, and these values were much higher than those reported so far. SEC-MALS analysis also revealed that PAE molecules had highly crosslinked structures and extremely

wide molecular mass distributions. Molecular mass values and content of 3-hydroxy-azetidinium (AZR) groups in PAE and PAE intermediates during the course of PAE synthesis were also determined by the SEC-MALS and ^1H NMR methods, and the relationships between these values and the wet strength development of handsheets prepared with these PAE samples were studied. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2249–2255, 2005

Key words: azetidinium group; molecular mass; PAE; paper; polyamideamine-epichlorohydrin; SEC-MALS; wet strength

INTRODUCTION

Aqueous solutions of polyamideamine-epichlorohydrin (PAE) resin have widely been used as wet strength agents for making tissue paper, paper towels, base paper for liquid packaging, and so on. Generally, 0.1–1% (of dry weight of pulp) PAE is added to pulp slurries as a wet-end additive in papermaking, and sufficient wet strength appears on the PAE-treated paper after the thermal drying process of the wet webs. PAE molecules have the unique four-membered 3-hydroxy-azetidinium groups (AZR) in 70–80% of the polyamideamine repeating units.¹ Crosslinkages between polyamideamine chains through 2-hydroxypropyl bridges as well as ester-linkages formed between AZR groups at the polyamideamine units and carboxyl groups at the end of the polyamideamine main chains are present in PAE as minor structures.² Thus, PAE is one of the crosslinked three-dimensional heteropolymers, and it is empirically well known that both factors, the molecular mass and the

AZR content of PAE, strongly influence the resultant wet strength performance of PAE-added paper.^{3,4}

In our previous article,² we reported new analytical methods of AZR content and number average molecular mass of the polyamideamine main chains of PAE, where ^1H and ^{13}C NMR spectra of aqueous PAE solutions were used. However, when polyamideamine main chains are crosslinked in PAE, real molecular mass values of PAE must be evaluated by some methods other than NMR. Measurements of weight and number average molecular mass values (M_w and M_n , respectively) of commercial PAE samples using size-exclusion chromatography (SEC) have already been reported, and these M_w values were in the range from 6,700 to 230,000.^{5–7} However, these values were calculated on the basis of SEC elution patterns of PAE using water soluble and linear standard polymers, such as poly(ethylene oxide) and dextran. Therefore, the reported values are not necessarily accurate, because there must be some discrepancies between such linear standard polymers with no ionic groups and crosslinked PAE having cationic groups in terms of molecular conformations in aqueous solutions.

In this study, more accurate molecular mass values of commercial and laboratory-made PAE samples were measured by a SEC system attached with a multi angle laser light scattering detector (MALS), where

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determination of accurate refractive index increment (dn/dc) values of the PAE samples were required. Reaction intermediates of PAE were also picked up from the reaction mixture during the course of PAE synthesis, and these PAE intermediates were also subjected to molecular mass and AZR content determinations by SEC-MALS and ^1H NMR, respectively. Handsheets were made from pulp slurries with the PAE intermediates, and wet tensile strength development and PAE retention behavior of the handsheets were studied in terms of molecular mass values and AZR contents of the PAE intermediates added.

EXPERIMENTAL

Materials

A commercial aqueous PAE solution (solid content 12.5%) was kindly provided by a supplier. Dimethyladipate, diethylenetriamine, epichlorohydrin, and a poly(diallyldimethylammonium chloride) (PDAD-MAC, M_w 400,000–500,000) solution were commercial products of laboratory grade (Aldrich Co., Milwaukee, WI) and used without further purification. A commercial bleached hardwood sulfate pulp was used in handsheet making after beating to 550 mL Canadian Standard Freeness in a PFI mill. Other chemicals and solvents used were of laboratory grade (Wako Pure Chemicals Co., Japan) and used without further purification.

Preparation of PAE

Aqueous polyamideamine, N-(3-chloro-2-hydroxypropyl)polyamideamine, and PAE solutions were prepared stepwise in our laboratory according to the scheme in Figure 1.² The polyamideamine prepolymer was synthesized as follows: dimethyladipate (1.0 mol) and diethylenetriamine (1.0 mol) were placed in a four-necked flask, and the mixture was heated at 130–140°C for about 5 h.² To a 45 mass % aqueous solution of the polyamideamine prepolymer, epichlorohydrin (1.1 mol per one amideamine repeating unit) was added dropwise below 30°C for 0.5 h, and the mixture was kept at 30°C for 4.5 h to prepare N-(3-chloro-2-hydroxypropyl)polyamideamine. The solution was then diluted to 20 mass % with water, and heated at 60–65°C to convert the 3-chloro-2-hydroxypropyl group to AZR for preparing PAE. Because crosslinking among polyamideamine chains occurred during this reaction, the viscosity of the solution increased with increasing the reaction time. When the Gardner scale viscosity of the 17.5 mass % PAE solution reached the F-G level, water and sulfuric acid were added to the mixture to stop further crosslinking reaction. During the course of this PAE synthesis, a part of the reaction mixture was picked up several times

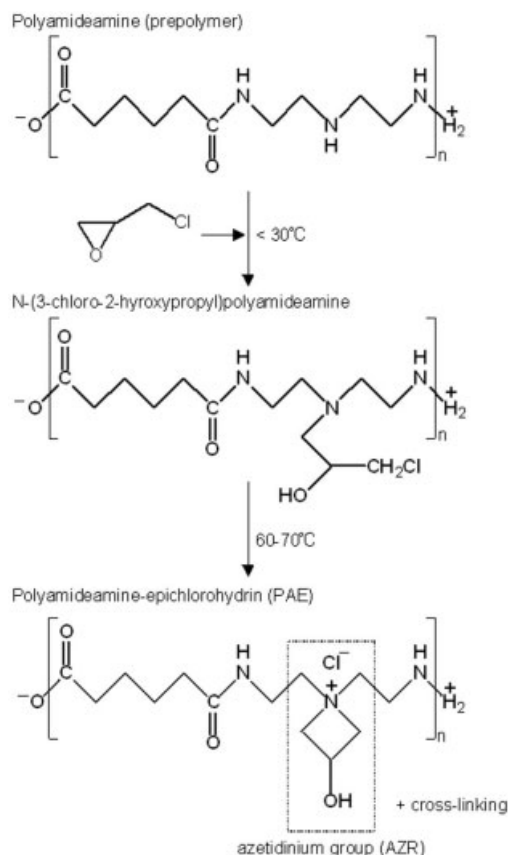


Figure 1 Preparation scheme of PAE.

for sampling of the PAE intermediates. These intermediate samples were immediately diluted with water, adjusted to pH 3 with sulfuric acid, and then stored at 4°C. Details about sampling are described in the Results and Discussion section. Properties of the final PAE solution thus synthesized were as follows: total solid content 14.6%, Gardner scale viscosity E-F, and pH 3. These values are close to those of a commercial aqueous PAE solution.

Handsheet making

An aqueous solution of one of the picked-up PAE intermediates was added to a 0.15% pulp slurry at pH 6.8–7.3 with continuous stirring at 750 rpm. The addition level of the PAE intermediates was fixed to 0.3 mass % of the dry weight of the pulp. The pulp slurry was then subjected to handsheet making with a basis weight of 60 g/m², according to the TAPPI Test Method.⁸ “Noncured” handsheets were prepared by drying the wet webs at 23°C and 50% relative humidity for one day after pressing. On the other hand, “cured” handsheets were prepared by drying the wet webs directly at 100°C for 2 min using a drum dryer after pressing, followed by additional heating at 110°C for 10 min in an oven. These handsheets were condi-

tioned at 23°C and 50% relative humidity for more than one day before evaluation.

SEC-MALS analysis of PAE and its intermediates

Weight and number average molecular mass (M_w and M_n , respectively), polydispersity (M_w/M_n), and radius-of-gyration of PAE and its intermediates were collected by a SEC-MALS system. A 0.5M acetic acid/0.2M sodium nitrate solution was used as the eluent. The SEC system used consisted of an on-line degasser (DGU-12A; Shimadzu, Japan), a high-pressure pump (LC-10ADVP; Shimadzu, Japan), a stainless steel inline filter with a 0.1 μm polytetrafluoroethylene (PTFE) membrane (Millipore, Billerica, MA), a manual injector (Model 7725; Rheodyne, Rohnert Park, CA), a column oven (CTO-10ACVP; Shimadzu), a SEC column packed with polyhydroxymethacrylate-based gel (OHpak SB-806M; Shodex, Japan), a postcolumn filter with a 0.5 μm stainless steel frit (A-310; Upchurch Scientific, Oak Harbor, WA), a MALS detector (DAWN EOS, λ 690nm; Wyatt Technologies, Santa Barbara, CA), a refractive index detector (RID-10A; Shimadzu), and a UV-vis detector (SPD-10A, Shimadzu, Japan). Data acquisition and processing were carried out using the ASTRA software (Wyatt Technologies).

SEC conditions were as follows: sample concentration of 0.1% (w/V), injection volume of 100 μL , flow rate of 0.5 mL/min, and column temperature of 40°C. The detector cells of MALS and RI were kept at ambient temperature. Before injection, the sample solutions were filtered through a 0.45 or 0.2 μm PTFE disposable membrane. The eluent was filtered through a 0.1 μm PTFE membrane before use.

The value of the refractive index increment (dn/dc) of each sample was measured by using an Optilab DSP (Wyatt Technology, Co., Santa Barbara, CA). The refractive index of the eluent itself was obtained by using an Abbe-type refractometer.

Other analyses

AZR content of the PAE intermediates was determined from their ^1H NMR spectra collected using a Bruker AC 300.² Nitrogen content of the handsheets prepared with the PAE intermediates was determined by an elementary analyzer (FLASH EA1112, Amoco Co., Italy), and the content of the PAE intermediates retained in the handsheets was calculated from the nitrogen contents on the basis of chemical formulae of the PAE intermediates added to pulp slurries.³ Wet tensile strength of the handsheets was measured according to the TAPPI Test Method.⁹ Soaking time of the specimen strips of the handsheets in water for the wet tensile test was set to 30 min.

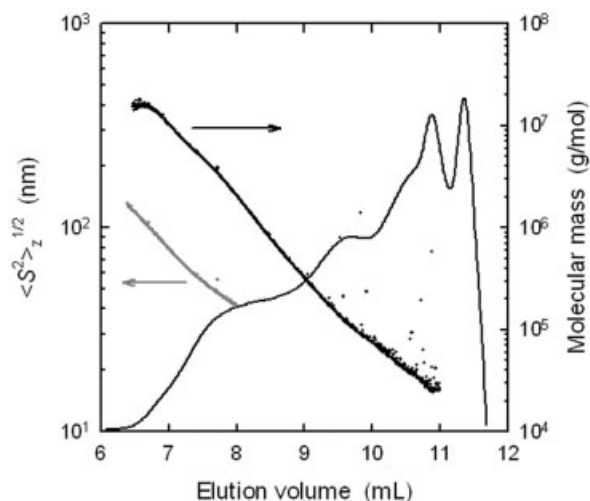


Figure 2 Relationships between elution volume and either SEC elution pattern, radius-of-gyration ($\langle S_z^2 \rangle^{1/2}$), or weight average molecular mass (M_w) of commercial PAE.

RESULTS AND DISCUSSION

Molecular mass determination of PAE by SEC-MALS

Molecular mass values of typical commercial PAE and poly(diallyldimethylammonium chloride) (PDADMAC) were determined by the SEC-MALS system using an aqueous eluent, where their dn/dc values of 0.188 and 0.183, respectively, were adopted. Figure 2 depicts the relationships between the elution volume and the SEC elution pattern of commercial PAE, its radius-of-gyration, and M_w plots. The elution pattern of PAE is quite similar to those reported by Swerin and Wågberg.⁵ Both the M_w and radius-of-gyration plots decreased almost linearly with increasing the SEC elution volume, showing that each PAE molecule was adequately separated by the SEC column, depending on radius-of-gyration of each molecule without any agglomeration. Generally, linear synthetic polymers have roughly symmetric SEC elution patterns close to normal distributions. Therefore, the asymmetric and anomalous distribution of PAE must be due to the heterogeneously crosslinked structure of its linear polyamideamine chains.

The SEC elution pattern, radius-of-gyration, and M_w plots of PDADMAC, which is a comparatively linear cationic polymer and used as a coagulant to neutralize anionic substances in the papermaking process, are shown in Figure 3, in which the chemical structure of the typical repeating unit of PDADMAC is drawn. Also in this case, both the radius-of-gyration and the M_w plots decreased almost linearly with increasing the elution volume. The SEC elution pattern of PDADMAC showed a nearly normal distribution.

The relationships between molecular mass and radius-of-gyration of PAE and PDADMAC are plotted

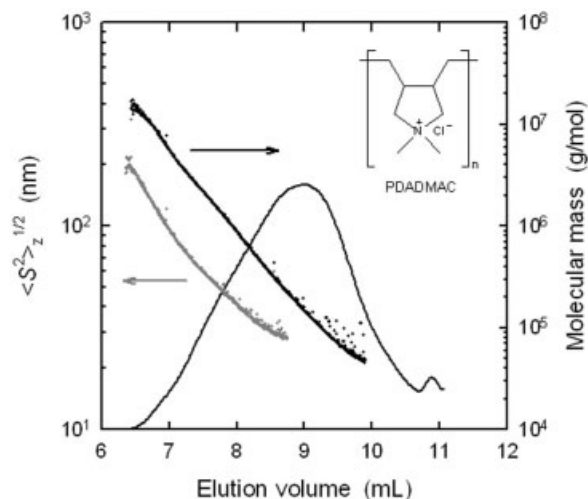


Figure 3 Relationships between elution volume and either SEC elution pattern, radius-of-gyration ($\langle S^2 \rangle_z^{1/2}$), or weight average molecular mass (M_w) of commercial poly(diallyldimethylammonium chloride) (PDADMAC).

in Figure 4. It must be emphasized from these conformation plots that the M_w of PAE is approximately three times as much as that of PDADMAC at the same radius-of-gyration, showing that PAE molecules have highly dense structures in the aqueous solution. This is because PAE molecules have crosslinkages between the polyamideamine main chains, whereas PDADMAC has a comparatively linear structure. Slope values of the plots in Figure 4 give information about molecular conformations of polymers in the solution. The slope value of 0.53 for PDADMAC corresponds to a random-coil conformation of a usual linear polymer in good solvents, while that of 0.43 for PAE does to a highly dense spherical polymer. These slope values also support the difference in chemical structures between PDADMAC and PAE.

M_w , M_n , and M_w/M_n values of PAE and PDADMAC calculated by the SEC-MALS system using each dn/dc value are summarized in Table I. The M_w value of PAE obtained in this study is about 1,140,000, which is far greater than those reported so far using linear standard polymers. Also, M_n and M_w/M_n values of PAE obtained by the SEC-MALS system are remarkably higher than those reported previously. These discrepancies in M_w , M_n , and M_w/M_n values obtained between our SEC-MALS method and the previous SEC/standard polymer systems are due to the highly crosslinked structure of PAE, which is clearly different from those of the linear standard polymers. As a conclusion, it can be regarded that PAE molecules have highly crosslinked structures and extremely wide molecular mass distribution. Thus, the SEC-MALS system allows us to give more accurate molecular mass values and information about the molecular conformations of PAE in aqueous solutions. The M_w value of

PDADMAC was close to that provided by the supplier.

Preparation of PAE and the molecular mass of the PAE intermediates

The reaction scheme of PAE from polyamideamine through N-(3-chloro-2-hydroxypropyl)-polyamideamine is given in Figure 1, where "n" means the degree of polymerization (DP_n) of the repeating polyamideamine unit. Although the outline of the preparation method of PAE has already been reported in our previous paper,² more detailed PAE preparation conditions adopted in our laboratory are illustrated in Figure 5. The reaction temperature and concentration of the mixture were controlled in terms of reaction time during the course of the PAE synthesis, and the corresponding viscosity of the reaction mixture was monitored. We picked up the PAE intermediate samples from the reaction mixture at the seven stages from 0 to 6 shown as "sampling number" on the upper horizontal axis in Figure 5. Samples 0 and 6 correspond to the polyamideamine prepolymer and the final PAE, respectively; and Samples 1–5 are the PAE intermediates. If the reaction in Figure 5 continues over 10.15 h, clear gel formation of the reaction mixture occurs by excess crosslinking, and the gel once formed can no longer be used as a wet strength agent in papermaking. Thus, as soon as the Gardner scale viscosity of the 17.5 mass % PAE solution reached the F-G level, which corresponded to the reaction time of 10.13 h in Figure 5, water and sulfuric acid were added to the mixture to stop further crosslinking reaction. The protonation of the residual tertiary amino groups

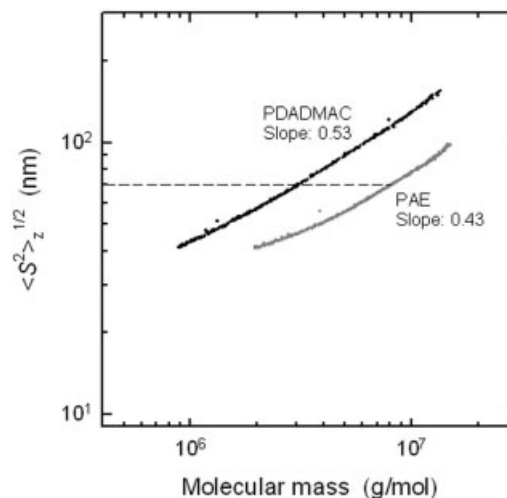


Figure 4 Relationships between weight average molecular mass (M_w) and radius-of-gyration ($\langle S^2 \rangle_z^{1/2}$) of commercial PAE and poly(diallyldimethylammonium chloride) (PDADMAC).

TABLE I
Molecular Mass and Polydispersity of Commercial PAE and PDADMAC^a

	M_w	M_n	M_w/M_n	Method, standard	Reference
PAE	1,140,000	27,000	42	SEC-MALS ^b	This work
PAE	228,000	9,500	24	SEC, PVP ^c	Fischer (1996) ⁷
PAE	11,000	2,100	5.2	SEC, dextran	Guise (1982) ⁶
PAE	6,700	1,970	3.4	SEC, PEO, ^d & PEG ^e	Swerin (1994) ⁵
PDADMAC ^a	663,000	126,000	5.3	SEC-MALS ^f	This work
PDADMAC ^a	400,000–500,000	—	—	—	Supplier's data

^a Poly(diallyldimethylammonium) chloride.

^b The dn/dc value of 0.188 was adopted.

^c Poly(2-vinylpyridine).

^d Poly(ethylene oxide).

^e Poly(ethylene glycol).

^f The dn/dc value of 0.183 was adopted.

present in PAE by sulfuric acid added can suppress further crosslinking reactions.

The SEC elution patterns of Samples 0–6 are depicted in Figure 6. Sample 0, that is, the polyamideamine prepolymer, had a normal distribution pattern, and this pattern became bimodal and shifted to higher elution volume by the reaction with epichlorohydrin (Sample 1). This shift of SEC elution pattern is not due to depolymerization of the prepolymer but is ascribed to changes in molecular conformation of Sample 1 in the solvent, as described in the next paragraph. Moreover, the SEC elution pattern of Sample 0 indicates that the peak at elution volume of 10.8 mL is due to some polymer components present in Sample 1 (and

also Samples 2–6), and that at 11.3 mL is due to some low-molecular-mass compounds other than polymers.

As for Samples 1–6, the SEC elution pattern spread to lower elution volume as the sample number increased. A remarkable spreading of the SEC elution pattern was observed especially between Samples 2 and 3. The M_w , M_n , and M_w/M_n values of Samples 0–6 were calculated by the SEC-MALS system using each dn/dc value, and are summarized in Table II, together with each AZR content. Here, as described in the above paragraph, the M_w and M_n calculations were carried out for the SEC elution volume up to 11.1 mL to exclude some effects of low-molecular-mass compounds in this study. As shown in Table II, the dn/dc value of Sample 0 was clearly larger than those of Samples 1–6, thus resulting that the M_w and M_n values of Sample 0 calculated from the MALS data were reasonably lower than those of Sample 1. Probably the polyamideamine molecules of Sample 0 having one tertiary amino group in each repeating unit have an

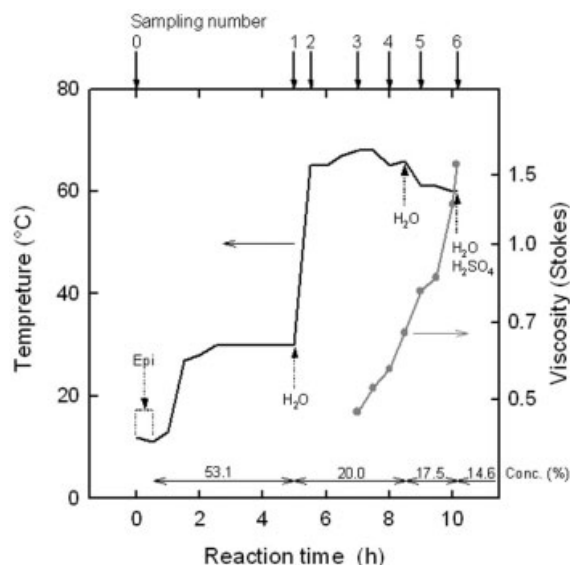


Figure 5 Relationships between reaction time and either temperature or solid concentration, which were controlled during the PAE synthesis in this study. The viscosities of the reaction mixture are also plotted. PAE intermediates were picked up from the reaction mixture at sampling numbers 0–6. Epi: epichlorohydrin.

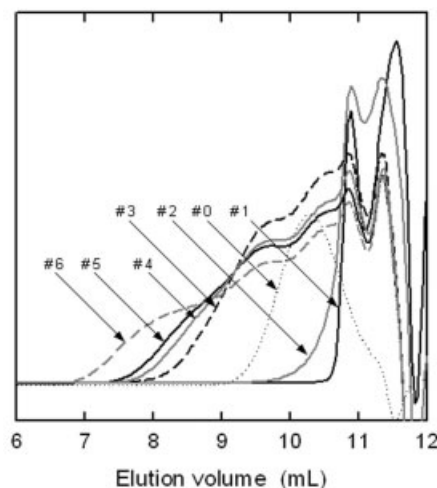


Figure 6 SEC elution patterns of PAE and PAE intermediates. Samples 0–6 correspond to those in Figure 5.

TABLE II
Molecular Mass, Polydispersity, and AZR Content of PAE Intermediates Picked up from the Reaction Mixture During the Course of PAE Synthesis

Sample number ^a (reaction time, h)	M_w	M_n	M_w/M_n	dn/dc ^b	AZR content (%) ^c
0 (0.0)	9,100	3,700	2.5	0.252	0
1 (5.0)	10,600	7,000	1.5	0.158	26
2 (5.5)	11,900	8,700	1.4	0.170	37
3 (7.0)	67,400	12,800	5.3	0.170	73
4 (8.0)	124,000	13,300	9.3	0.168	66
5 (9.0)	159,000	13,800	11	0.170	69
6 (10.1)	494,000	18,700	27	0.172	67

^a See Figure 5.

^b The refractive index increment.

^c AZR contents are expressed as percentages per one polyamideamine repeating unit.

extremely expanded conformation due to intramolecular electric repulsions in the solvent for SEC analysis, compared with those of Samples 1–6.

From the M_n values, more than four polyamideamine main chains in number average were crosslinked to form one PAE molecule in the final stage. However, the high M_w/M_n value of 27 for Sample 6 indicates that its molecular distribution is remarkably wide from high to low crosslinked PAE molecules. Table II also shows that the M_n value gradually increased with the reaction time, while the M_w and M_w/M_n values increased more remarkably in the reaction time of 5.5–10.1 h, which corresponded to the reaction at 60–65°C to form AZR groups and crosslinkages (Fig. 5). The formation of AZR groups remarkably increased within 2 h by heating the reaction mixture at 60–65°C, and then reached a plateau level around 66–73%. Probably the formation of AZR groups and their consumption to form intermolecular crosslinkages are in the equilibrium state at the reaction time of 8–10.1 h, thus resulting in a significant viscosity increase (Fig. 5). These results show that the most significant factors influencing wet strength performance of PAE-treated paper can be evaluated by the SEC-MALS and ¹H NMR analyses of PAE and the PAE intermediates.

Roles of molecular mass and AZR content of PAE in wet strength development of paper

Samples 1–6, that is, the PAE intermediates and PAE, were separately added to pulp slurries, and the obtained handsheets were subjected to the wet strength test and determination of nitrogen content for evaluation of retention values of Samples 1–6 in the handsheets. Figure 7 shows the relationships between the reaction time during the course of PAE synthesis and either molecular mass of the PAE intermediates or wet strength of the handsheets prepared thereof. The increasing patterns of wet tensile strength of the cured and noncured handsheets with the reaction time are similar to that of M_w in Figure 7. This result indicates

that the M_w of PAE primarily influences the wet strength development of PAE-treated paper; the higher the M_w of PAE used in papermaking, the higher the wet strength of the PAE-treated paper.

As to the mechanisms of wet strength development of paper by PAE, covalent bond formation between the AZR groups of PAE and the carboxyl groups slightly present in paper pulps and others have been reported so far.^{10–15} Moreover, further intramolecular crosslinkages must be formed in each PAE molecule retained in the PAE-treated paper during the thermal drying process and the post conditioning process in papermaking. Therefore, the actual mechanisms of wet strength development of PAE-treated paper are much more complicated. However, the good correlation observed between the M_w value of the PAE intermediates and the wet strength of the PAE-treated handsheets (Fig. 7) suggests the significance of the M_w

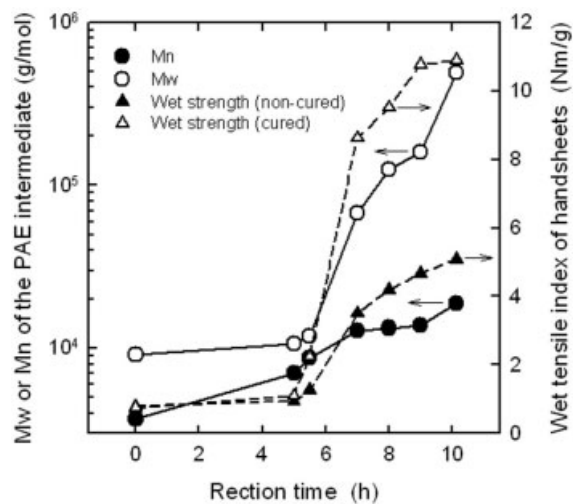


Figure 7 Relationships between reaction time in Figure 5 and either molecular mass of the PAE intermediates or wet tensile strength of the handsheets prepared thereof. Addition level of the PAE intermediates: 0.3% of dry weight of pulp.

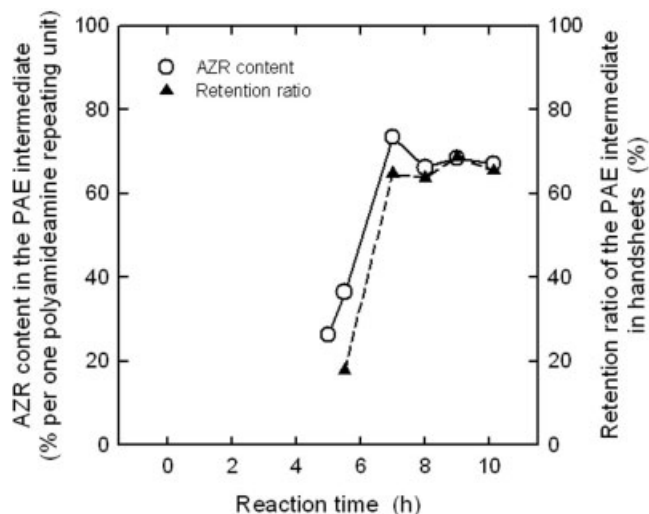


Figure 8 Relationship between reaction time in Figure 5 and either AZR content in the PAE intermediates or their retention ratios in handsheets. Addition level of the PAE intermediates: 0.3% of dry weight of pulp.

values of the PAE added to pulp slurries rather than the relative AZR content in PAE for wet strength development of paper. In this context, lower molecular mass PAE molecules present in commercial PAE resin solutions may not positively participate in the wet strength development of paper. Thus, if these low-molecular-mass regions in PAE ineffective in wet strength development can be removed from PAE resins, the addition levels of PAE to pulp slurries can be reduced, and more efficient wet strength development for PAE-treated paper may be achievable.

On the other hand, the changing pattern of AZR content in the PAE intermediates to the reaction time corresponded well with that of retention values of the PAE intermediates in the handsheets (Fig. 8). Quaternary ammonium groups are formed in the PAE intermediates associated with the formation of the AZR structure (Fig. 1). Thus, the retention behavior of the PAE intermediates in the handsheets in the papermaking process is primarily governed by the amount of AZR groups or cationic quaternary ammonium groups in PAE; electrostatic interactions between anionic pulp fibers and cationic PAE molecules are the primary factor influencing the retention behavior of PAE in pulp slurries. Moreover, the AZR groups in PAE molecules adsorbed on pulp fibers by electrostatic interactions in pulp slurries and retained in wet webs may make it possible to form further intramolecular crosslinkages and/or covalent bonds with the carboxyl groups in pulp fibers during the thermal

drying process of wet webs and the post conditioning process. These structural changes of PAE by the AZR groups remaining in wet webs may also play a significant role in wet strength development of paper.

CONCLUSIONS

More accurate molecular mass values of commercial and laboratory-made PAE samples were determined by the SEC-MALS system. The obtained M_w values were much higher than those reported by SEC systems using linear standard polymers with no cationic groups. Moreover, PAE molecules have extremely large M_w/M_n values or wide distribution of the molecular mass values. Thus, the PAE molecules have highly dense structures by crosslinkages between the polyamideamine main chains, and have spherical conformations in aqueous solutions. During the course of PAE synthesis, molecular mass of the PAE intermediate increased with increasing the reaction time at 60–65°C by crosslinkages through the ring-opened AZR groups. This increase in molecular mass of the PAE intermediates corresponded well with the increase in wet strength of the handsheets prepared thereof, thus indicating that the molecular mass of PAE has a strong influence on the resultant wet strength performance when used as an additive in papermaking. On the other hand, the pattern of AZR content in the PAE intermediates is consistent with that of their retention ratio in the handsheets. Thus, the formation of cationic quaternary ammonium groups in the PAE intermediates directly governs the retention of the additives on anionic pulp fibers in the papermaking process. The AZR groups once formed in the PAE intermediates are partly consumed by the formation of crosslinkages between the polyamideamine main chains during the course of PAE synthesis, resulting in the formation of highly crosslinked PAE.

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