

^1H - and ^{13}C -NMR Analyses of Aqueous Polyamideamine–Epichlorohydrin Resin Solutions

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ABSTRACT: More accurate signal assignment for ^1H - and ^{13}C -NMR spectra of aqueous solutions of polyamideamine-epichlorohydrin (PAE) resin and its related compounds was achieved by using distortionless enhancement of polarization transfer (DEPT) and C-H correlation spectroscopy (COSY) methods. On the basis of the assignment, we developed new methods to determine the content of four-membered azetidinium ring (AZR) and number-average degree of polymerization (DP_n) of the repeating unit of PAE by using NMR. Degree of introduction of epichlorohydrin into

polyamideamine chains at the initial stage was 75–80%, and the resultant AZR content per one repeating unit in the PAE sample prepared in this study was about 72%. DP_n of the initial polyamideamine was 32, and this value decreased to about 18 during the PAE preparation process. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1847–1854, 2004

Key words: NMR; polyamide; polyamine; DP; water-soluble polymers

INTRODUCTION

Water-soluble polyamideamine-epichlorohydrin (PAE) resin, which has been developed and commercialized at the end of the 1950s, nowadays occupies over 90% of the market of wet-strength agents for paper because of its excellent performance. PAE is used as a wet-end additive in the papermaking process to make commodities such as tissue paper, paper towels, milk cartons, photographic base paper, hamburger wrappers, bank notes, waterproof liner boards/corrugated medium, and others.

PAE is synthesized by the following three steps: condensation between adipic acid and diethylenetriamine to form polyamideamine, addition of epichlorohydrin at the secondary amino group in polyamideamine to form *N*-(3-chloro-2-hydroxypropyl)polyamideamine, and formation of four-membered azetidinium ring (AZR) from the 3-chloro-2-hydroxypropyl group. Crosslinking between polyamideamine chains occurs in part during the AZR formation, and this brings about an increase in molecular weight of PAE. Eventually, aqueous 10–30% PAE solutions are obtained. The AZR group is necessary for improving wet strength of paper by PAE, and partial ester formation between the AZR groups in PAE and carboxyl groups in pulp fibers during the papermaking process have been believed to cause the efficient

wet-strength improvement. Shelf-life of the AZR group in PAE is several months at room temperature. Degrees of polymerization and crosslinking, contents of AZR and tertiary amino groups, and amounts of byproducts in PAE solutions are controlled by each manufacturer to improve wet-strength performance as well as papermaking runnability.

Some reports concerning NMR analyses of PAE have been published so far. Carr et al.¹ and Devore et al.² reported signal assignment of ^1H -NMR spectra of PAE. The method the authors used to isolate the PAE for NMR analysis was precipitation by pouring its aqueous solution into acetone and re-dissolving the dried precipitate in dimethylsulfoxide- d_6 (DMSO- d_6). However, isolation of PAE from its aqueous solutions should be avoided, because the AZR group in PAE is unstable and easily crosslinked among PAE molecules. Kricheldorf³ reported signal assignment of ^{13}C -NMR spectrum of an aqueous PAE solution by comparing with a model compound, 1,1-diethyl-3-hydroxyazetidinium chloride. However, no ^1H -NMR spectra of aqueous PAE solutions have been reported so far.

In this study, we report more accurate signal assignment of ^1H -NMR spectra of aqueous PAE solutions prepared in our laboratory, using distortionless enhancement by polarization transfer (DEPT) and C-H correlation spectroscopy (COSY) methods. On the basis of the obtained results, new methods to determine AZR content and number-average degree of polymerization (DP_n) of PAE in aqueous solutions are proposed.

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EXPERIMENTAL

Materials

Dimethyladipate, diethylenetriamine, and epichlorohydrin used were commercial products of laboratory grade (Aldrich Co., USA) and were used without further purification. Other reagents and solvents were also commercial products (Wako Pure Chemicals, Co., Tokyo, Japan).

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. Dimethyladipate (1.0 mol) and diethylenetriamine (1.0 mol) were placed in a four-necked flask fitted with a stirrer, a thermometer, and a condenser, and the mixture was heated at 130–140°C for about 5 h. During this condensation, liberated methanol was trapped in the condenser. The molten polyamideamine obtained was diluted with water to about 55% solution, where the pH was 10.7. The intrinsic viscosity of the polyamideamine prepared was 0.117, when measured by using a capillary viscometer and 1N NH₄Cl as the solvent.

The concentration of the above aqueous polyamideamine solution was then adjusted to 45% with water, and epichlorohydrin (1.1 mol) was added dropwise to the polyamideamine solution below 30°C for 0.5 h. 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% 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, viscosity of the solution increased with an increase in the reaction time. Two PAE solutions with different viscosities, PAE-I and PAE-II, were prepared in this study. When the Gardner scale viscosity of the 15% PAE solution reached A (low viscosity) level for PAE-I and E–F (high viscosity) level for PAE-II (it took about 2 and 5 h, respectively), water and sulfuric acid were added to each mixture to stop further crosslinking reaction. Properties of the aqueous PAE-II solutions thus prepared were as follows: total solid content, 15.5%; Gardner scale viscosity, E³–F; and pH 2.7. These values for PAE-II are close to those of commercial aqueous PAE solutions.

Analyses

¹H- and ¹³C-NMR spectra of aqueous solutions of PAE and its related compounds were recorded at 20°C by using a Bruker AC 300. A small amount of D₂O was added to the solutions for obtaining an NMR-lock

signal. Solid contents in the solutions for NMR measurements were about 5% for ¹³C-NMR and C-H COSY and about 2–5% for ¹H-NMR. Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3,-d₄ acid (Aldrich) was used as an internal standard for 0 ppm. The DEPT and C-H COSY methods were used to assign ¹H- and ¹³C-NMR signals of PAE and its related compounds.

RESULTS AND DISCUSSION

C-H COSY analysis of PAE and its related compounds

When adipic acid is used as one of the starting materials, high temperatures around 170°C are generally required for polyamideamine synthesis. These severe conditions often give relatively large amounts of by-products in the polyamideamine solutions. In this study, therefore, dimethyladipate was used as the starting material to reduce the reaction temperature. The scheme of PAE synthesis is shown in Figure 1. The AZR content in PAE and DP_n of polyamideamine main chains especially are significant factors influencing the properties of PAE. Furthermore, changes in DP_n of polyamideamine main chains during the PAE preparation process, degree of introduction of epichlorohydrin at the initial stage, degree of crosslinking, and the amount of tertiary amino group in PAE are also significant for understanding of PAE synthesis as well as characterization of PAE. Carbons and protons in the repeating unit of PAE and intermediate *N*-(3-chloro-2-hydroxypropyl)polyamideamine are alphabetically labeled as shown in Figure 2 for convenience.

C-H COSY spectrum of the PAE-II solution prepared in our laboratory and the resultant assignment of each signal are depicted in Figure 3. The DEPT analysis revealed that the methine carbon *h* of AZR in PAE was assigned to the signal at 61.0 ppm, which appeared in between the two signals because of methylene carbons *f* and *f'* at 60.5 and 62.2 ppm. All chemical shifts of PAE carbons obtained in this study were almost equal to those reported by Kricheldorf.³ On the other hand, assignment of some proton signals of PAE in Figure 3 are clearly different from those for PAE/DMSO solutions reported by Carr et al.¹ and Devore et al.² Their results may be wrong, or chemical shifts of PAE protons in DMSO are remarkably different from those in water.

C-H COSY spectra of the intermediate compound, *N*-(3-chloro-2-hydroxypropyl)-polyamideamine solutions at pH 8 and 3, are shown in Figures 4 and 5, respectively. The pH of the original solution of the above intermediate compound just after preparation was about 8. However, the solution at pH 3 was prepared for NMR analysis by adding diluted sulfuric acid for comparison with NMR spectra of PAE solu-

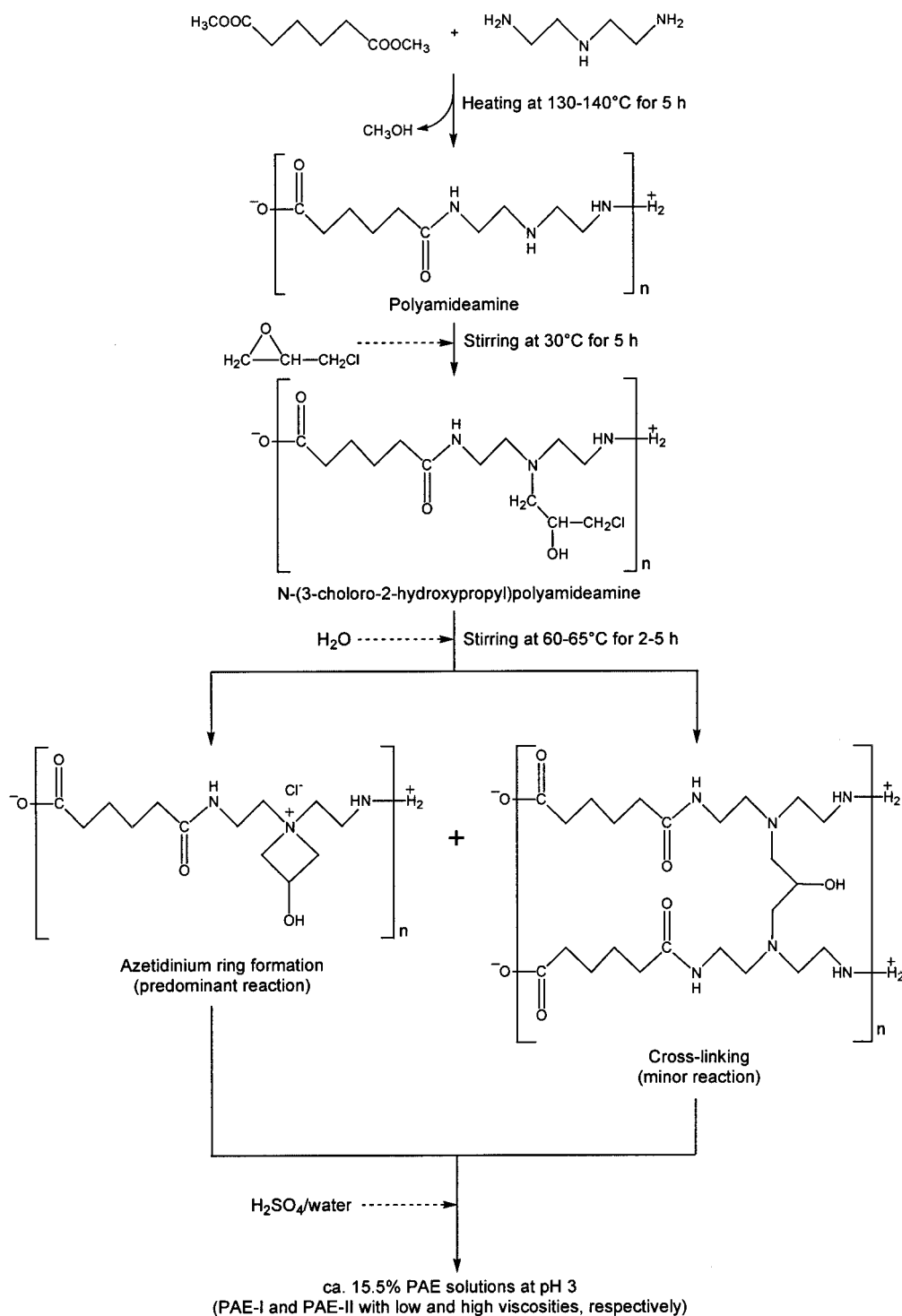


Figure 1 Scheme of preparation of PAE.

tions, whose pH values were always about 3. The methine carbon *h* of the 3-chloro-2-hydroxypropyl group in Figure 2 was assigned by the DEPT analysis. Chemical shifts due to the methylene carbons *e* and the methine carbon *h* were clearly shifted to higher magnetic fields by acidification of the solution, while

all the methylene protons *f*, *g*, and *e* and the methine proton *h* were shifted to lower magnetic fields. However, the shifted values for the *f* and *g* protons were about 0.8 ppm, while those for the *e* and *h* protons were 0.4 ppm. Thus, if 3-chloro-2-hydroxypropyl group is present to some extent in PAE samples, the

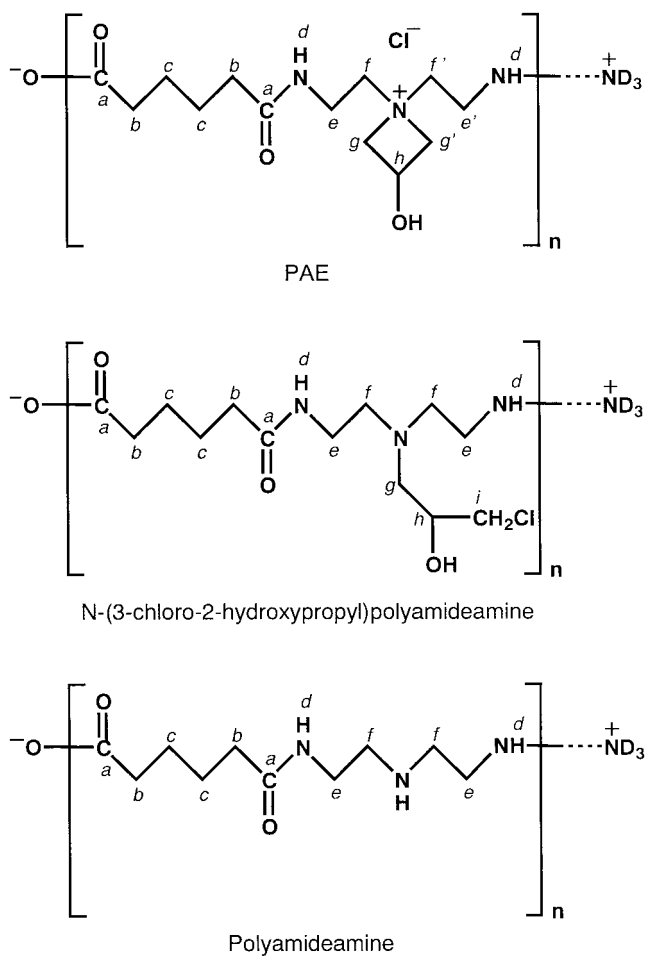


Figure 2 Alphabetical labeling to each carbon or proton in PAE, the intermediate *N*-(3-chloro-2-hydroxypropyl)polyamideamine, and polyamideamine.

signal at 49.2 ppm due to the methylene carbon *i* in Figure 2 should be detected in their ¹³C-NMR spectra.

¹³C-NMR analysis of PAE and its related compounds

Figure 6 illustrates ¹³C-NMR spectra of aqueous solutions of polyamideamine, *N*-(3-chloro-2-hydroxypropyl)polyamideamine, and two PAE samples, PAE-I and PAE-II, which had low and high viscosities, respectively. Degree of crosslinking of PAE-II, which occurs as minor reaction during the reaction of AZR group formation, is higher than that of PAE-I.

The addition of epichlorohydrin to polyamideamine led to a remarkable change in the ¹³C-NMR spectrum. Acidifying the *N*-(3-chloro-2-hydroxypropyl)polyamideamine solution to pH 3 allows the comparison of its ¹³C-NMR spectrum with that of PAE. A small signal due to the methine carbon *h* of AZR was detected in the ¹³C-NMR spectrum of the

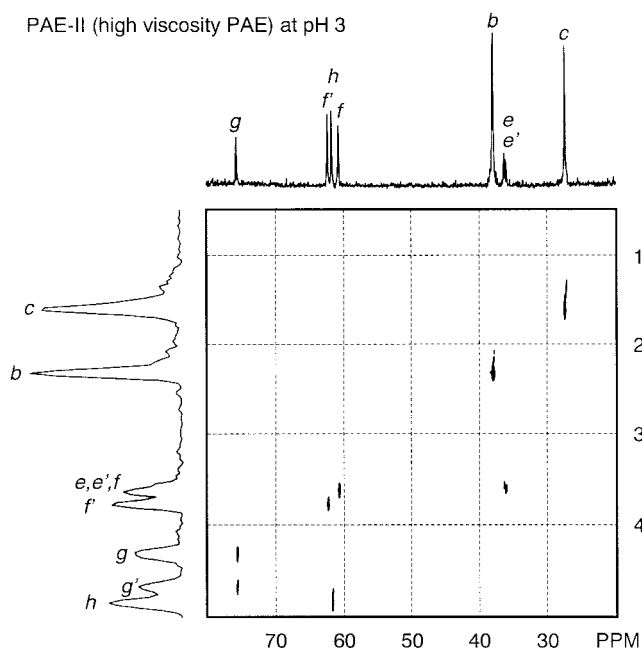


Figure 3 C-H COSY spectrum of PAE-II (high-viscosity PAE) in water at pH 3.

N-(3-chloro-2-hydroxypropyl)polyamideamine solution, and thus, a small amount of AZR was formed during the reaction between epichlorohydrin and polyamideamine even below 30°C. On the other hand, quite small signals due to some of the 3-chloro-2-hydroxypropyl group were detected in

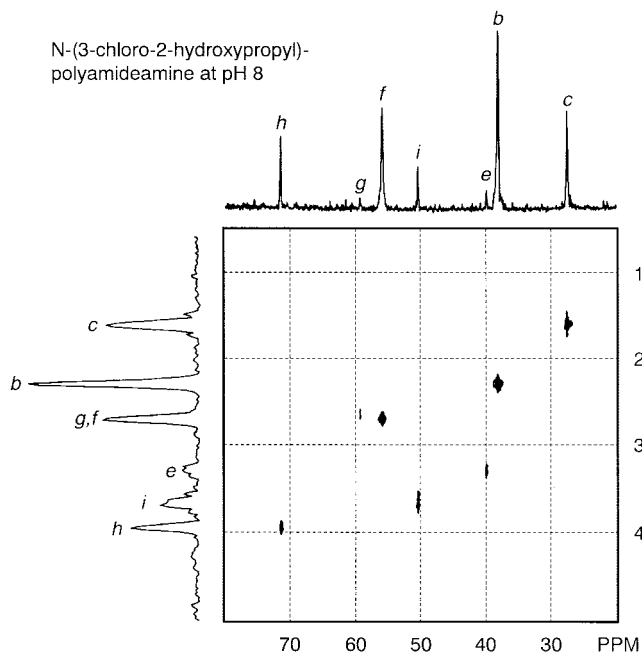


Figure 4 C-H COSY spectrum of *N*-(3-chloro-2-hydroxypropyl)polyamideamine in water at pH 8.

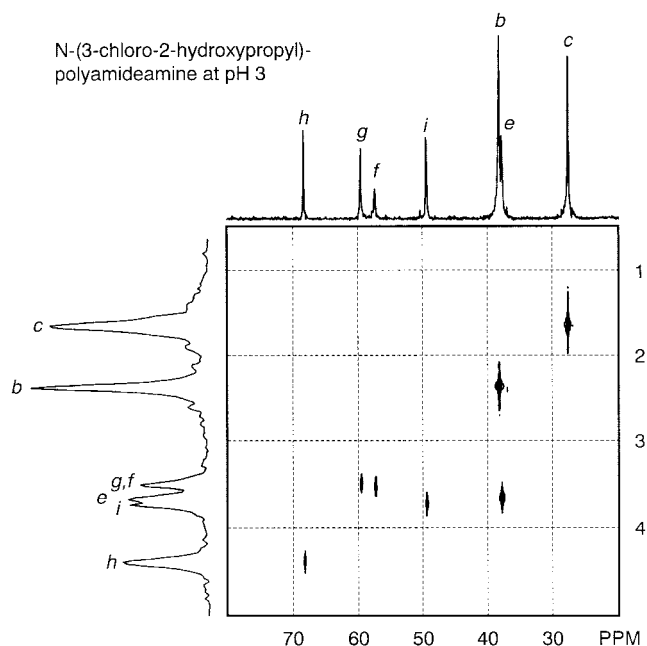


Figure 5 C-H COSY spectrum of *N*-(3-chloro-2-hydroxypropyl)polyamideamine in water at pH 3.

the two PAE samples. A small amount of the pendantlike 3-chloro-2-hydroxypropyl group may have remained in the PAE samples even after heating the *N*-(3-chloro-2-hydroxypropyl)polyamideamine solution at 60–65°C for 2–5 h. Typical ^{13}C -chemical shifts of PAE and *N*-(3-chloro-2-hydroxypropyl)polyamideamine obtained in this study are summarized in Table I.

The Gardner scale viscosities were clearly different between the two PAE samples, PAE-I and PAE-II, at 20% solid content, A (low) level for PAE-I and G (high) level for PAE-II. Although patterns of small signals at 40–70 ppm were slightly different between PAE-I and PAE-II because of crosslinking, no clear differences were observed for the main signals, suggesting that chemical structures detectable at ^{13}C -NMR level were nearly the same between the two PAE samples. Thus, the crosslinking reactions occurring even in quite small quantities during the AZR formation reaction bring about remarkable increases in viscosity of the PAE solutions.

^1H -NMR analysis of PAE and its related compounds

Figure 7 shows ^1H -NMR spectra of aqueous solutions of polyamideamine, *N*-(3-chloro-2-hydroxypropyl)polyamideamine, and two PAE samples, PAE-I and PAE-II, with low and high degrees of crosslinking. The signal at 8.1–8.3 ppm is due to amide proton *d*. Because these amide protons are exchangeable to deu-

terium in the presence of D_2O , these protons do not appear quantitatively. No amide protons were detected in the ^1H -NMR spectrum of polyamideamine by the complete deuterium exchange. The methine proton *h* of the 3-chloro-2-hydroxypropyl group was located at 4.0 and 4.4 ppm for the solutions at pH 8 and 3, respectively, as isolated signals in the ^1H -NMR spectra of the intermediate compounds. Thus, degree of introduction of epichlorohydrin into the polyamideamine chains can be calculated from the signal areas of the methine proton *h* and methylene protons *c* of the adipic acid unit.

Furthermore, a pair of the methylene protons *g* in AZR was located at 4.3 ppm as an isolated signal in the ^1H -NMR spectra of PAE samples, and thus, AZR content per one repeating unit in PAE can be calculated from the signal area of the methylene protons *g*. Because the chemical shift of the methine proton *h* of the 3-chloro-2-hydroxypropyl group is close to that of the methylene protons *g* of AZR, the presence of residual 3-chloro-2-hydroxypropyl group in PAE may lead to somewhat inaccurate AZR content, when the above AZR determination method is used.

The difference in ^1H -NMR spectra between PAE-I and PAE-II is little, suggesting that the amount of crosslinking clearly occurring in PAE-II is too low, compared with the AZR group, to detect the protons of the bridge parts. Typical ^1H -chemical shifts of PAE and *N*-(3-chloro-2-hydroxypropyl)polyamideamine obtained in this study are summarized in Table II.

AZR content and number average degree of polymerization (DP_n) of PAE and its related compounds

As shown in Figure 6, the amide carbonyl carbons *a* in the PAE repeating unit appeared at 179.6 ppm, whereas the carboxyl carbons *a'* at the end groups of polyamideamine chains appeared at 180.2 ppm. Thus, DP_n of the repeating unit can be calculated from signal areas of these carbonyl and carboxyl carbons *a* and *a'*, respectively, when quantitative inverse-gated decoupling mode is used in ^{13}C -NMR analysis. However, the differences in signal areas between these carbonyl and carboxyl carbons *a* and *a'*, respectively, are so large that accurate determination of DP_n might be difficult. DP_n values calculated by this method are depicted in Figure 8 and have relatively large fluctuations, depending on the measuring process of the signal areas. The result in Figure 8 indicates that the initial polyamideamine has DP_n of about 16.7, and that this DP_n value decreased to about 8.5 during the process of PAE preparation. Alkaline hydrolysis of the polyamideamine chains may occur to some extent during the reaction of AZR formation at 60°C and pH 8.

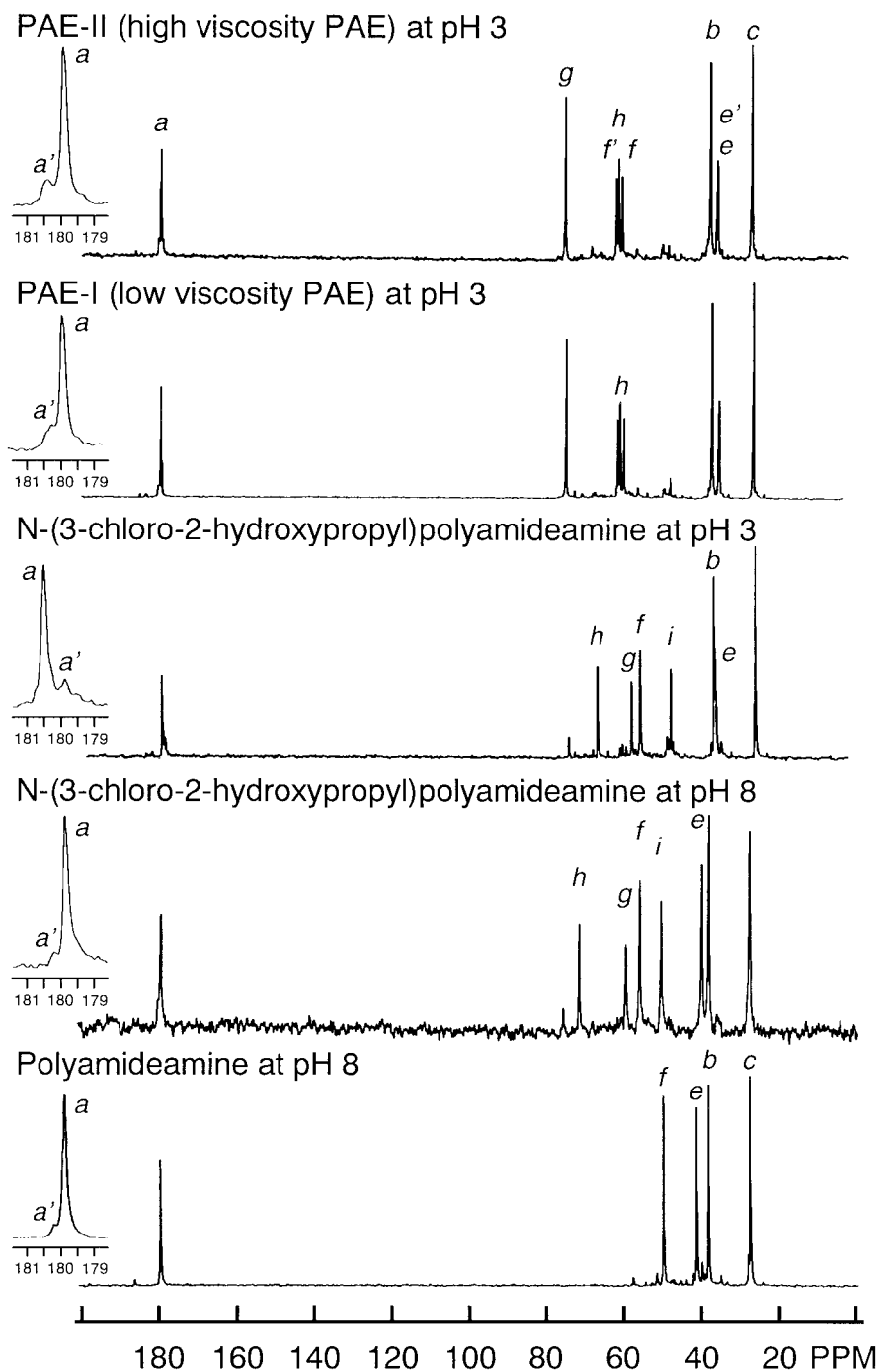


Figure 6 ^{13}C -NMR spectra of PAE and its related compounds.

TABLE I
 ^{13}C -Chemical Shifts of PAE and *N*-(3-chloro-2-hydroxypropyl)polyamideamine in Water at pH 3

	a	b	c	d	e	f	g	h	i
PAE	179.6	38.0	27.4	—	36.1 36.3	60.5 62.2	75.6	61.6	—
<i>N</i> -(3-chloro-2-hydroxylpropyl)polyamideamine	180.7	38.0	27.4	—	37.5	57.1	59.3	68.0	49.2

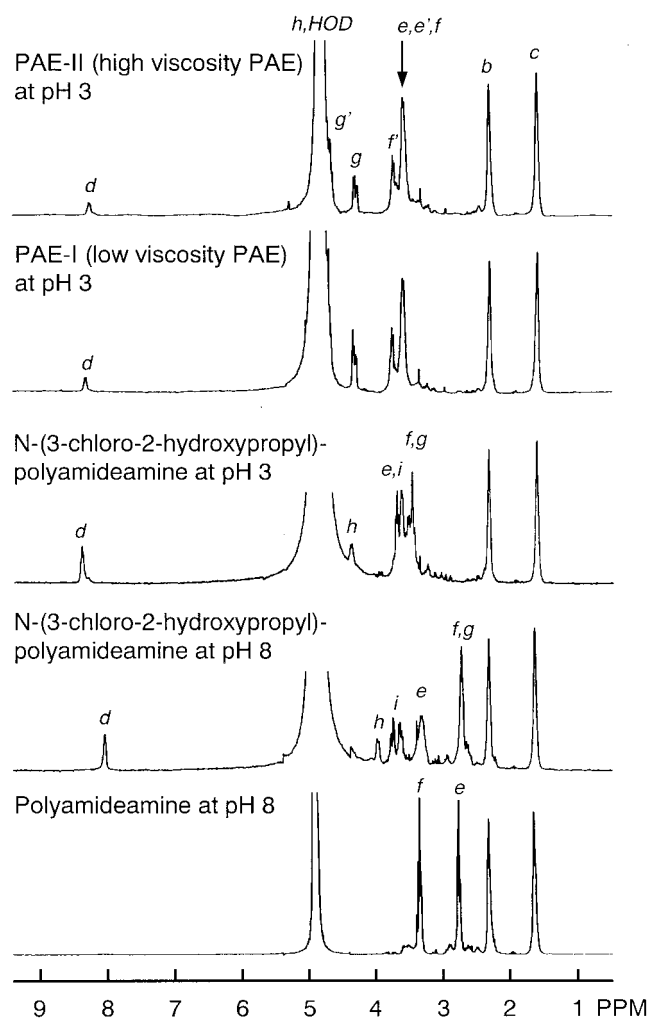


Figure 7 ¹H-NMR spectra of PAE and its related compounds.

The 3-chloro-2-hydroxypropyl or AZR content in the PAE and its related compounds are calculated from ¹H-NMR spectra in Figure 7 and shown in Figure 8. Degree of introduction of epichlorohydrin into polyamideamine chains was 75–80% at the initial stage, and heating of the *N*-(3-chloro-2-hydroxypropyl)-polyamideamine solution at 60–65°C gave a little lower AZR content per one repeating unit for the PAE-I sample with Gardner viscosity of A level. The PAE-II sample with Gardner viscosity of G level had an AZR content of about 72%. Thus, AZR content

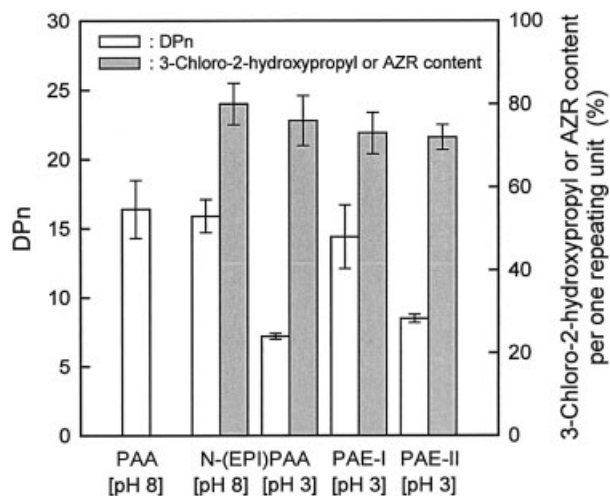


Figure 8 DP_n of polyamideamine chains and 3-chloro-2-hydroxypropyl or AZR content per one repeating unit of PAE and its related compounds. PAA: polyamideamine; EPI: epichlorohydrin; PAE-I: low viscosity PAE; PAE-II: high viscosity PAE.

slightly decreases from the initial value with an increase in the heating time by consuming the AZR group for crosslinking reactions between polyamideamine chains. The AZR content of PAE-II prepared in this study is a little higher than those (60–70%) reported by Carr et al.¹ and Bates.⁴ The value reported by Carr et al.¹ was obtained from ¹H-NMR spectra of once-precipitated PAE samples. A part of AZR group in these PAE samples may have been modified during the precipitation, isolation, and redissolution processes. The value reported by Bates⁴ was obtained for dialyzed PAE by the titration method by using 2-mercaptoethanol/iodine. Some low-molecular-weight fractions of PAE may have been removed during the dialysis process.

CONCLUSION

New ¹H- and ¹³C-NMR methods for determining degree of introduction of epichlorohydrin into polyamideamine chains, AZR content, and DP_n of main chains in PAE samples were developed on the basis of ¹H- and ¹³C-chemical shifts of PAE and its related compounds. Because aqueous PAE solutions prepared

TABLE II
¹H-Chemical Shifts of PAE and *N*-(3-chloro-2-hydroxypropyl)polyamideamine in Water at pH 3

	a	b	c	d	e	f	g	h	i
PAE	—	2.3	1.6	(8.3)	3.6	3.6	4.3	4.9	—
<i>N</i> -(3-chloro-2-hydroxypropyl)polyamideamine	—	2.3	1.6	(8.3)	3.7	3.5	3.5	4.4	3.8

at both laboratory and industrial levels can be subjected to ^1H - and ^{13}C -NMR analysis simply by addition of small amounts of D_2O into the PAE solutions, the new methods allow more accurate and easy determinations compared with the conventional and time-consuming titration methods or precipitation/isolation/redissolution procedures of PAE. The developed NMR methods are applicable to characterization of PAE samples prepared under various conditions for obtaining relationships between structural factors of

PAE and the resultant wet-strength behavior or runnability in practical papermaking process.

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