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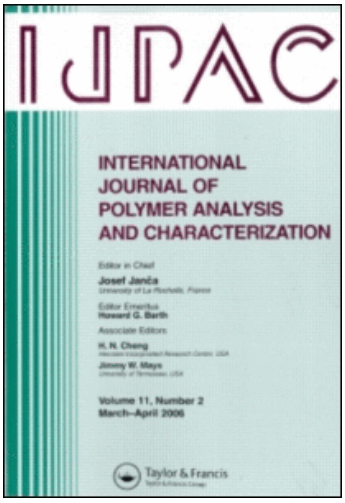

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Koji Miyauchi[a]; Yoshiyuki Sumiyama[a]; Kazuya Jinda[a]
[a] UBE Scientific Analysis Laboratory Inc., Ichihara City, Japan

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Determination of Graft Structure and Graft Ratio of Polyoxyethylene-Grafted Nylon 6 by Chemical Degradation Followed by Nuclear Magnetic Resonance and Electrospray Ionization Mass Spectroscopy

Koji Miyauchi, Yoshiyuki Sumiyama, and Kazuya Jinda
UBE Scientific Analysis Laboratory Inc., Ichihara City, Japan

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Hydrobromic acid (HBr) hydrolysis was effective in the identification of the graft structure of polyoxyethylene-grafted nylon 6 (PGN). One of the degradation products reflecting the graft structure was shown by nuclear magnetic resonance (NMR) analysis and electrospray ionization mass spectrometry (ESI-MS) analysis to be N-bromoethyl-6-aminocaproic acid (NBA). The formation of NBA in HBr hydrolysis of PGN was found to be proportional to the graft ratio (degree of substitution to amide group, x) of PGN. Quantification was carried out via NMR analysis of the degradation products and PGN.

Keywords: Polyoxyethylene-grafted nylon 6; HBr hydrolysis; Graft structure; NMR; ESI-MS

INTRODUCTION

Polyoxyethylene-grafted nylon 6 (PGN) has the properties of nylon and hydrophilicity, which homopolymers of nylon do not have. This polymer has some excellent properties and is widely used as a functional material[1–3].

Dr. K. Saito is gratefully acknowledged for ESI-MS measurements.

Address correspondence to Koji Miyauchi, UBE Scientific Analysis Laboratory Inc., 8-1 Goi minamikaigan, Ichihara City, Chiba, 290-0045, Japan. E-mail: 29687u@ube-ind.co.jp

The polyoxyethylene chain of PGN is supposed to bond to the N atom of the amide group of the main chain. The ratio of the graft structure to the original amide group influences the properties of PGN. Qualitative and quantitative analysis of the graft structure of PGN is highly desirable, but difficult. The existence of extra polymeric components, other than those arising from the homopolymers of nylon 6 and polyoxyethylene, is suggestive of the graft structure of PGN. Direct identification of the graft structure is not easy because of the small amount of the graft structure compared to the large amount of the repeating structures of the main chains and because of structural isomerism at the substituted amide group. Okushita et al.[3] reported the quantitative analysis of the graft ratio (degree of substitution to amide group, x) of PGN by ^{1}H nuclear magnetic resonance (NMR) spectroscopy. They used the amide proton of nylon 6 and PGN. However, the NMR peak of the amide proton is broad, and exact quantification is difficult. Except for this report, as far as we know, no other study of PGN identification has been reported.

Chemical degradation analysis[4,5] is one of the known methods for the analysis of polyamides and polyoxyalkylenes. The polymer (e.g., nylon 6) is degraded to respective monomers by acid hydrolysis, followed by an appropriate method to identify the degradation products. This method has not been previously used for the analysis of PGN. If the degradation products from this method reflect the graft structure, then this can be an easy method for the characterization of PGN.

In this work, polymers of PGN were chemically degraded by hydrobromic acid (HBr)[6] and the degradation products were analyzed by NMR and electrospray ionization mass spectroscopy (ESI-MS).

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EXPERIMENTAL

Samples and Reagents

Two samples of polyoxyethylene-grafted nylon 6 were used: Sample 1 (Lurotex® A25 from BASF, Parsippany, NJ, USA) and Sample 2 (G1039,[3] provided by Ube Laboratory, Ube Industries, Ube, Japan). A control sample was designated Sample 3, which is a mixture of nylon 6 and polyoxyethylene (both commercial products). Hydrobromic acid (47.0–49.0%, special grade chemical) purchased from Wako Pure Chemical Industries (Osaka, Japan), was used as the hydrolysis reagent.

Procedure for HBr Hydrolysis

About 0.1 g of the polymer sample and about 3 g of the HBr were placed in a 30 mL Teflon container in an autoclave, and the autoclave

was sealed. Acid hydrolysis of the polymer was carried out at 150°C. After hydrolysis for a specified time, the autoclave was cooled and opened, most of the contents were collected in a glass container, dried under nitrogen flow, and dissolved in 0.8 mL of D_2O (henceforth called hydrolysis product A). The remainder of the contents in the Teflon container was extracted with 0.8 mL of $CDCl_3$ (hydrolysis product B).

Analyses of Polymers and Hydrolysis Products

Both solutions of the hydrolysis product A in D_2O and the hydrolysis product B in $CDCl_3$ were transferred to NMR tubes and analyzed at ambient temperature on a JEOL (Akishima, Japan) EX400 FT-NMR spectrometer. 3-(Trimethylsilyl) propionic acid-d_4 sodium salt (TSP) was used as the chemical-shift standard in D_2O solution. $CHCl_3$ was used as a chemical-shift standard in $CDCl_3$ solution. The NMR spectra of Sample 1, Sample 2, and Sample 3 were measured at ambient temperature using 10% (g/mL) CF_3COOD solution with polyoxyethylene as a secondary chemical-shift standard. The hydrolysis product A was also analyzed by ESI-MS (JEOL 700QQ mass spectrometer). The ESI-MS spectrometer is a kind of LC-MS without a column.

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RESULTS AND DISCUSSION

The ^{13}C–^{1}H heteronuclear chemical-shift correlation (HETCOR) spectrum of the hydrolysis product A of Sample 1 degraded by HBr hydrolysis at 150°C for 14 h is shown in Figure 1. Under this hydrolysis condition, the cleavage of amide bonds is considered complete[4–6]. Two degradation products have been identified from the spectrum through chemical shifts, peak areas, distortionless enhancement by polarization transfer (DEPT) measurements, and ^{1}H–^{1}H and ^{13}C–^{1}H correlations. One product (peak h-l) is 6-aminocaproic acid (ACA), which is the monomer of nylon 6; the other product (peak a–g) is considered to be N-bromoethyl-6-aminocaproic acid (NBA). The peaks c–g are the main structure of nylon 6. The peaks a, b arise from N-bromoethyl because the chemical shift of peak a is at the low field (3.7 ppm) in ^{1}H and at the high field (29 ppm) in ^{13}C, and this observation indicates the heavy atom effect[7] characteristic of a bromine atom. Thus, the peaks a–g arise from NBA. Figure 2 shows the ESI-MS spectra of the hydrolysis product A of Sample 1 measured by NMR spectroscopy. NBA was observed with the isomer pattern of bromide. Consequently, it was proved that two degradation products were ACA and NBA.

As the N-bromoethyl of NBA group could be formed by the complete HBr hydrolysis of the polyoxyethylene chains grafted onto the amide

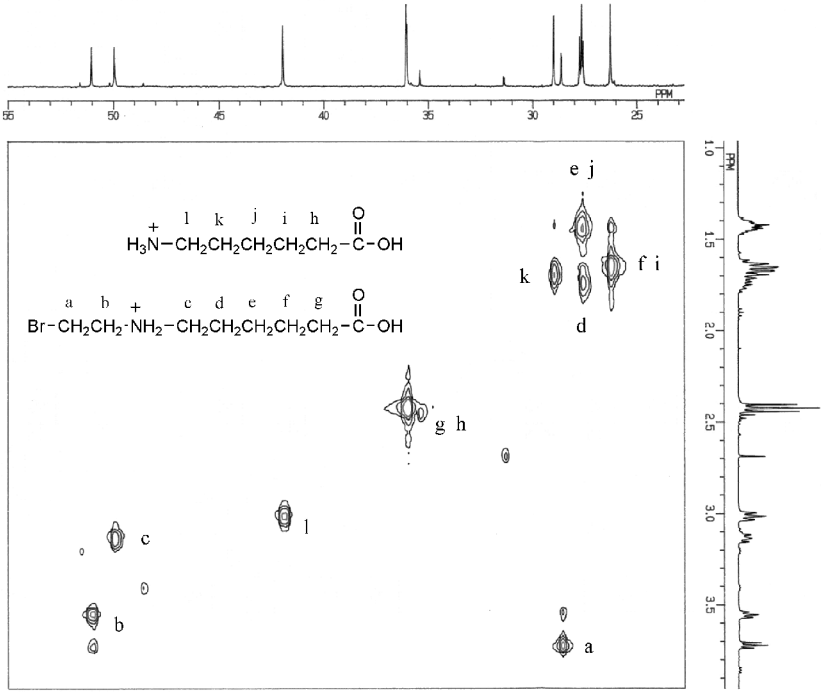

FIGURE 1 ^{13}C–^{1}H HETCOR spectrum of the hydrolysis product A of Sample 1 degraded at 150°C for 14 h.

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group, NBA was thought to be the degradation product resulting from the graft structure. On the other hand, complete HBr hydrolysis of polyoxyethylene would result in dibromoethane. The dibromoethane produced by the hydrolysis of PGN would be vaporized by nitrogen flow after hydrolysis and was removed from the system. (As shown in Figure 3, dibromoethane was indeed observed on the ^{1}H NMR spectra of the hydrolysis product B.) Yet, in Figure 2, only NBA was selectively detected by ESI-MS spectroscopy. The ionization due to the electrospray phenomenon[8] in ESI-MS is affected by factors such as the concentration and pH of the sample solution and molecular weight and electrical factors of the sample compounds[9]. These factors (except the electrical one) might bring about the above selectivity because NBA was observed in both positive and negative ion modes. A major factor is thought to the relative concentration of the degradation products in the system or the molecular size. Further studies of the details of the selective detection mechanisms of NBA by ESI-MS are in progress.

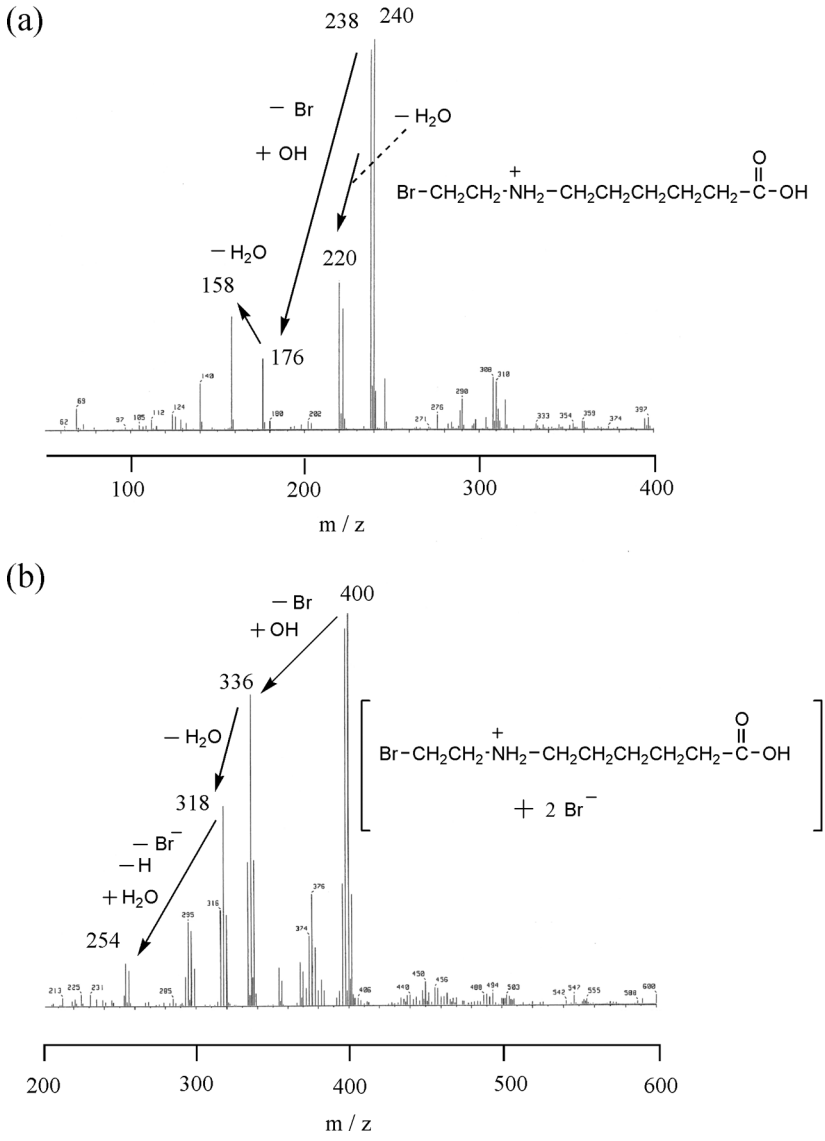

FIGURE 2 Positive (a) and negative (b) ESI-MS spectra of the hydrolysis product A of Sample 1 degraded at 150°C for 14 h.

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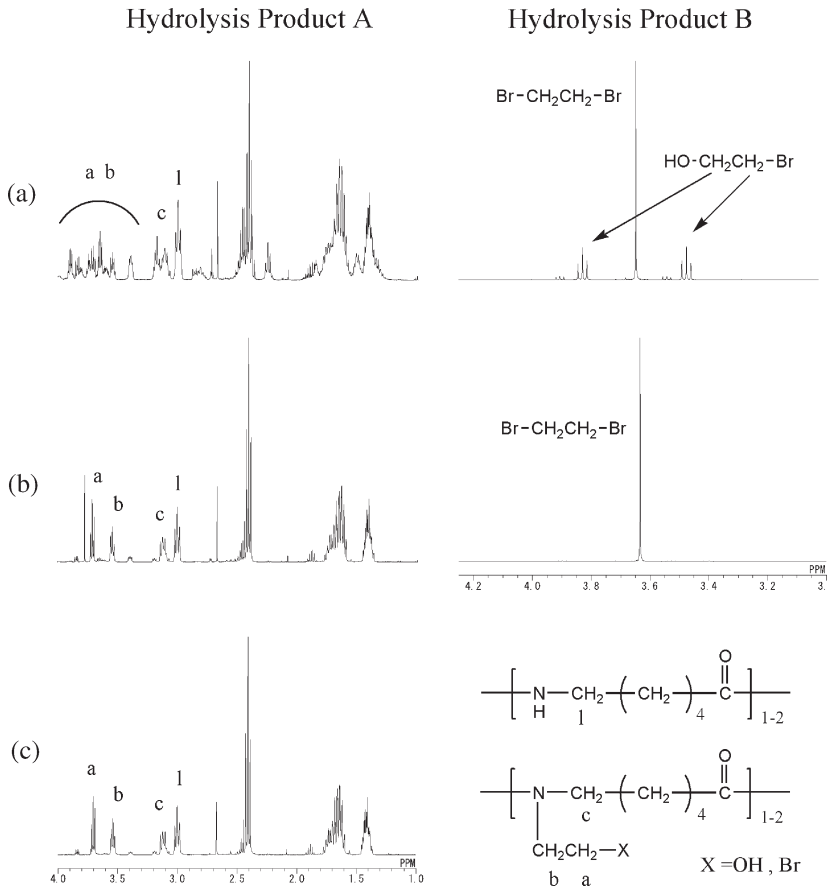

FIGURE 3 ^{1}H NMR spectra of the hydrolysis products A and B of Sample 1 degraded at 150°C for 1 h (a), 4 h (b), and 14 h (c).

In order to illustrate the quantitative yield of NBA by HBr hydrolysis, ^{1}H NMR spectra of hydrolysis products A and B of Sample 1 degraded at 150°C for 1 h, 4 h, and 14 h are shown in Figure 3. The assignment of the spectra was made from the chemical shifts, the peak areas, ^{1}H-^{1}H correlation, and earlier assignments from Figure 1. The polyether chains were completely degraded to monomer units with OH and Br terminal after one-hour hydrolysis (Figure 3(a)). The polyamide chains were incompletely degraded to monomers and oligomers. The oligomers were identified by the NMR peak numbers, the peak areas, and ^{1}H–^{1}H correlation. After 1 h, NBA has already been observed (peaks a, b, c). At 4 h

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TABLE I Ratios of NBA/(ACA + NBA) obtained at different reaction times in HBr hydrolysis of Sample 1

Reaction time/h	NBA/(ACA + NBA)
1	0.53[a]
4	0.33
14	0.36

[a]Calculated using amounts of ACA and NBA containing each oligomer.

and 14 h, the degradation products consisted of only ACA and NBA (Figure 3(b) and 3(c)). The ratios of NBA/(ACA + NBA) obtained by ^{1}H NMR peak areas at different reaction times are given in Table I. The ratios at 4 h and 14 h are evidently less than that at 1 h. Therefore, the N−EtO bond of the graft structure is also degraded to some extent together with the degradation of the main chains of polyamide and polyether. As the ratio of NBA/(ACA + NBA) at 4 h is similar to that at 14 h within experimental error, the HBr hydrolysis of PGN at 150°C is regarded as complete after 4 h reaction time. NBA is not further degraded even after another 10 h of reaction. Because the amounts of the minor degradation products at 14 h are less than those at 4 h, in subsequent work HBr hydrolysis of PGN was carried out at 150°C for 14 h.

If the amount of NBA is correlated with the graft ratio (x) of PGN, then x can be estimated from the amount of NBA. In order to establish this correlation, HBr hydrolysis of Sample 2 was carried out at 150°C for 14 h. Sample 1 is soluble in water, but Sample 2 is not. Since polyoxyethylene chains are soluble in water, the value of x of Sample 2 is expected to be less than that of Sample 1. The values of x of Sample 1 and Sample 2 were calculated by ^{13}C NMR peak areas (Figure 4) using the following assumption. The complicated peak patterns observed on the ^{13}C NMR spectra are presumed to be due to structural isomerism resulting from the nature of the substituted amide (the anisotropy of the carbonyl group and the restricted rotation of the amide bond) and the distribution of the length of nylon 6 chains and polyoxyethylene chains. The detailed assignment of the ^{13}C NMR peaks is not easy, but an approximate assignment may be possible through consideration of the electronegativity of the amide group and the ether oxygen. We assigned region A (34–45 ppm) to peaks due to $(CH_2)_4-\underline{C}H_2-NCO-\underline{C}H_2-$ and region B (50–58 ppm) to peaks due to $N-\underline{C}H_2\underline{C}H_2-O$. The value of x can be calculated from the equation:

$$x = B/0.5\,A$$

where A and B are ^{13}C NMR peak areas of region A and region B.

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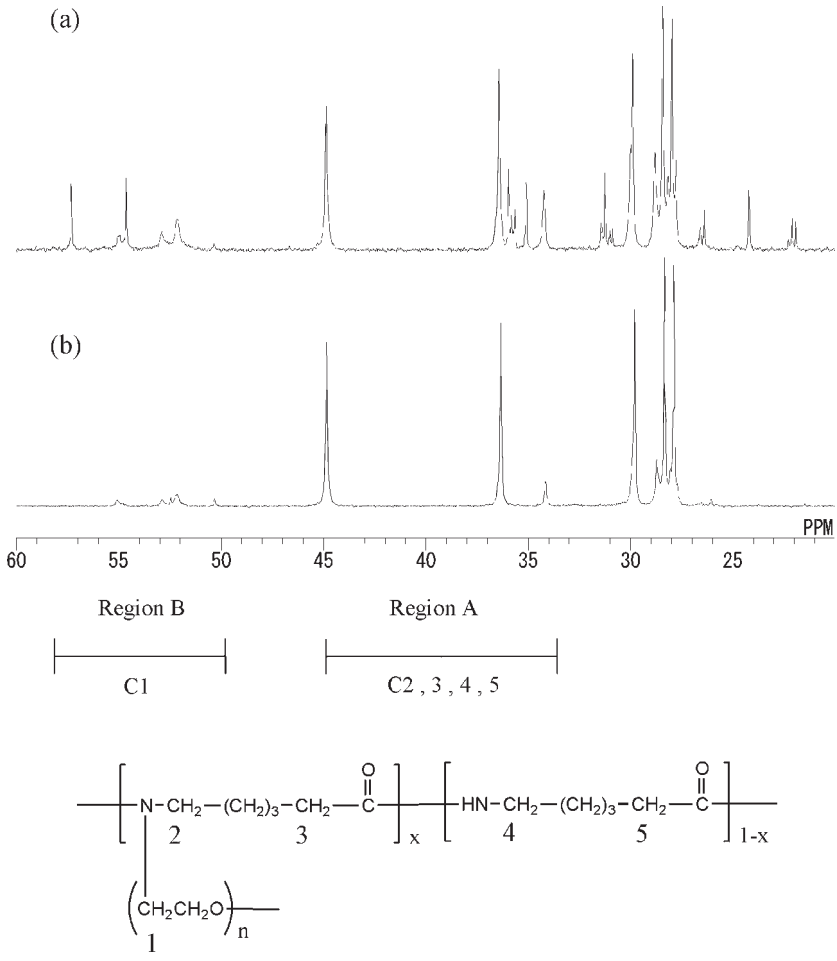

FIGURE 4 ^{13}C NMR spectra of a CF_3COOD solution of Sample 1 (a) and a CF_3COOD solution of Sample 2 (b).

Figure 5 shows the result of a control experiment with Sample 3 (a mixture of nylon 6 and polyoxyethylene). The hydrolysis product A was only ACA. The region B of ^{13}C NMR spectrum had no peaks.

Figure 6 shows a plot of the ratio (y) of NBA/(ACA + NBA) obtained by ^{1}H NMR peak areas against x of PGN. This plot gave an excellent straight line ($y = 0.44x$, $R^2 = 0.99$). As expected, the value of x for Sample 2 was less than that for Sample 1. The good linear relationship proved that the formation of NBA in HBr hydrolysis of PGN is

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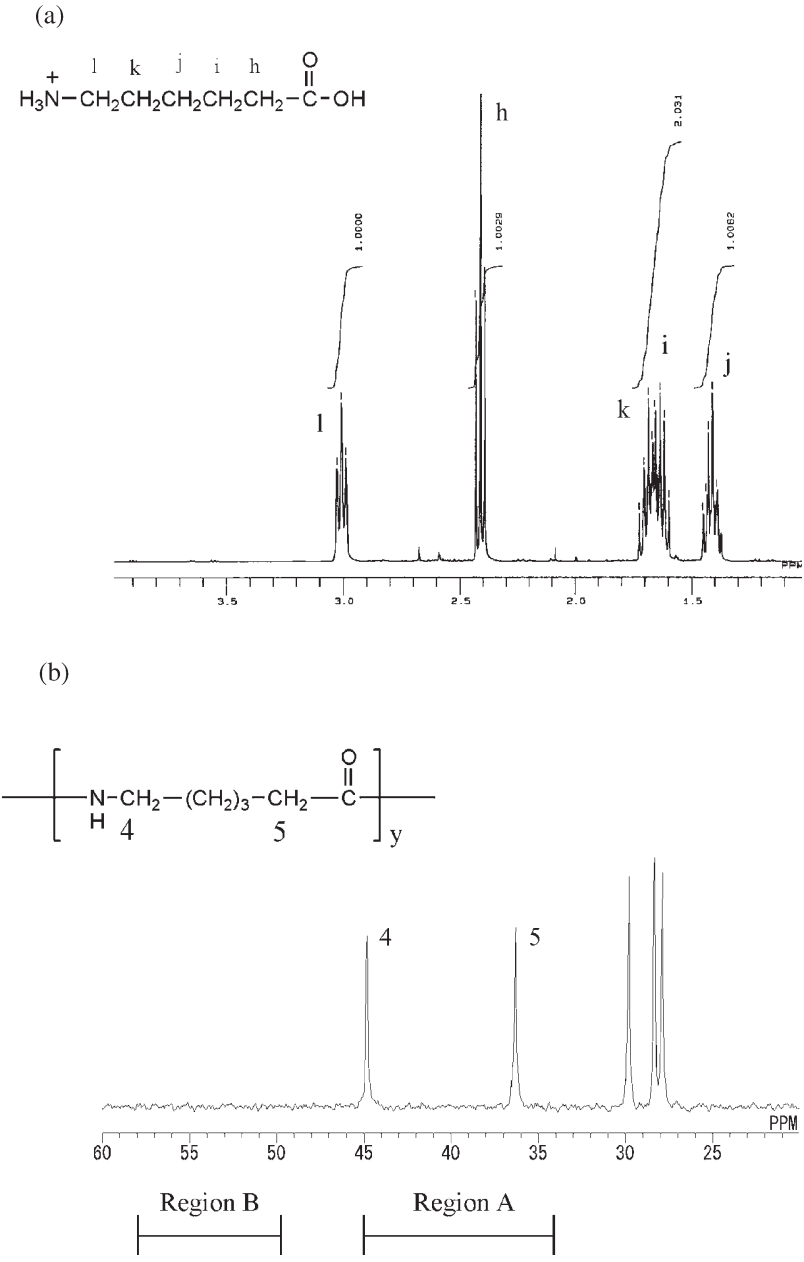

FIGURE 5 ^{1}H NMR spectrum of the hydrolysis product A of Sample 3 degraded at 150°C for 14 h (a) and ^{13}C NMR spectrum of a CF_3COOD solution of Sample 3 (b).

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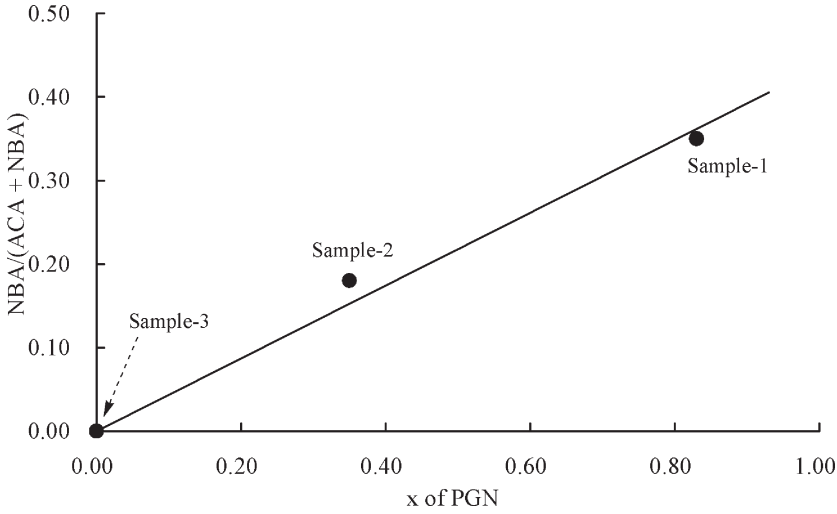

FIGURE 6 Relationship between the graft ratios (x) of PGN and the ratios (y) of NBA/(ACA + NBA) in HBr hydrolysis of PGN.

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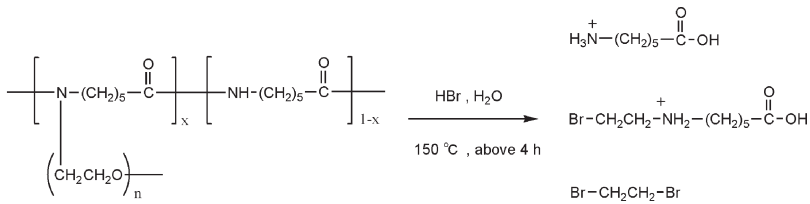
proportional to the graft ratio of PGN. Thus, the value of x calculated by ^{13}C NMR peak areas can be used for the determination of the graft ratio. Further work may be required to establish ^{13}C NMR as a precise and reliable method.

CONCLUSION

HBr hydrolysis of PGN may be summarized in Scheme 1.

The combination of HBr hydrolysis, NMR, and ESI-MS has been shown to be useful for the qualitative and quantitative analysis of the graft structure. This combination is particularly effective if the original polymer has poor solubility in the NMR solvent and low graft ratio. This



SCHEME 1

combination is also useful if the original polymer contains a mixture of nylon 6 and polyoxyethylene. The relative amount of the graft ratio (x) of the original polymers can be determined by utilizing the linear relationship in Figure 6. This method is sufficiently practical to be used for material analysis.

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