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Structural Changes of Compounds Containing Cyano Groups by Hydroxylamine Treatment

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The reactivities of four kinds of the compounds containing cyano groups, i.e. glutaronitrile, polyacrylonitrile (PAN), PAN-grafted polyethylene (PE) fiber and poly(acrylonitrile(AN)-*co*-methacrylic acid(MAA))-grafted PE fiber, with hydroxylamine were investigated by means of ^{1}H-NMR, ^{13}C-NMR, ^{13}C CP/MAS NMR. As a result, it was suggested that amidoxime group reacted with an adjacent cyano group to form imidedioxime group by the hydroxylamine treatment of the polymer containing cyano groups. And the uranium adsorbent having amidoxime group as a main binding site is prepared via hydroxylamine treatment of the PE fiber containing cyano groups in the solvent of methanol.
Key words: Amidoxime group, Imidedioxime group, Cyano groups, Hydroxylamine, NMR

1. INTRODUCTION

There are various and a great deal of useful metal ions in seawater [1]. Uranium utilized as an energy source is one of them. The formation of uranium is a tricarbonate complex, $[UO_2(CO_3)]^{4-}$ in seawater which is alkaline at pH 8 [2]. The concentration of uranium in seawater is extremely low at 3.3 mg/m^3. However the total amount of uranium dissolved in the world's oceans is 4.5 x 10^9 tons, which is a 1000-fold lager than the estimated amount of uranium under the ground. Japan largely depends on foreign countries for the energy source and the other underground resources. Therefore, it is important for us to improve separation technologies of valuable resources such as uranium from seawater in order to obtain constantly.

A study of separation of uranium from seawater was began in England in early the 1960's [3]. Later many methods of separation were examined. The adsorption method using a stable solid adsorbent promises for separation of uranium from seawater in the viewpoint of economy and environment. Extensive investigations of adsorbents which consist of inorganic or organic materials has been carried out [4~9]. Among the various organic adsorbents, the chelating ion-exchange resin containing amidoxime groups was selected because it was easy to synthesize it and to elute uranium adsorbed. The form of the uranium adsorbent has to be suitable for the system of adsorption using natural energy such as ocean current and wave for reduction of the cost of uranium separation from seawater. Various forms of uranium adsorbents such as spheres [10], membranes [11] and fibers [12~15] have been prepared. Among them, the fibers were selected as the most appropriate form to contact with a large amount of seawater by ocean current.

We have used nonwoven fabric as the base polymer and prepared the uranium adsorbent by using radiation-induced grafting technic [16]. The uranium adsorbent was synthesized via 3 steps as the followings:

(a) acrylonitrile (AN) and methacrylic acid (MAA) were cografted on nonwoven fabric by radiation-induced grafting, so that cyano group and carboxylic acid were introduced onto the base polymer.

(b) the cyano group in the grafted chain was changed to the binding site of uranium by hydroxylamine (NH_2OH) treatment.

(c) the fabric treated with NH_2OH was swelled by alkali treatment with potassium hydroxide (KOH).

Hydroxylamine treatment aims at changing cyano group into amidoxime group as the binding site of uranium. However, in addition to amidoxime group, various functional groups such as imidedioxime group, hydroxamic acid and amide were given by NH_2OH treatment according to Astheimer's report [17]. The condition under which amidoxime group is obtained as a main functional group has to be studied because it is thought that the formation of the various functional groups attribute to reduction of the amount of uranium adsorbed in the adsorbent. The chemical structure of the absorbent has been analyzed by IR spectroscopy, pH titration and other indirect measurements [18]. But these information were not enough to clear the structure of the adsorbent in detail.

In this paper, we investigated the reactivities of four kinds of the compounds containing cyano groups, that is, glutaronitrile, ployacrylonitrile (PAN), PAN-grafted polyethylene (PE) fiber and poly(acrylonitrile(AN)-*co*-methacrylic acid(MAA))-grafted PE fiber, with hydroxylamine by means of ^{1}H-NMR, ^{13}C-NMR, ^{13}C CP/MAS NMR.

2. EXPERIMENTAL

2.1. Hydroxylamine treatment

Hydroxylamine treatment of glutaronitrile:

Glutaronitrile was treated with NH_2OH under two different conditions as follows;

(a) 7.4 g of hydroxylammonium chloride was dissolved in 50 ml of water. Potassium hydroxide (KOH) was added to the solution until pH 11.2. 50 ml of methanol was also added to the solution. Then 5.0 g of glutaronitrile was added, and the mixture was stirred for

50 minutes at 353 K. The solvents were removed under a reduced pressure at 333 K. The residue extracted with ethanol, and cooling of the extract afforded 0.3 g of glutardiamidoxime as a colorless crystal in a 3.6 % yield. This product is soluble in ethanol.

IR (KBr, cm^{-1}): 3434 (-NH$_2$), 3175, 3118 (N-H), 2842, 1668 (C=N), 1602, 1400 (C-N), 949, 927 (N-O).

(b) 9.4 g of hydroxylammonium chloride was dissolved in 50 ml of methanol. A methanoic KOH solution, dissolved 7.6 g of KOH in 50 ml of methanol, was mixed with the solution of hydroxylammomium chloride followed by filtration. 5.0 g of glutaronitrile was added to the filtrate, and the mixture was stirred for 16 hours at 353 K. The solvent was removed under reduced pressure at 333 K. The residue extracted with ethanol, and cooling of the extract afforded 0.7 g of 2,6-dihydroxyiminopiperidine as a colorless crystal in a 10.1 % yield. This product is soluble in water.

IR (KBr, cm^{-1}): 3395 (-NH), 3096 (N-H), 2854, 1669 (C=N), 1486, 1388 (C-N), 982, 931 (N-O).

Hydroxylamine treatment of polyacrylonitrile:

Polyacrylonitrile {M_n: 1.43 x 10^4, M_w: 2.64 x 10^4, M_w/M_n: 1.85, IR (KBr, cm^{-1}): 2940, 2244 (C≡N), 1656, 1638 (C=C), 1455} was treated with hydroxylamine under two different conditions as follows;

(a) 0.27 g of hydroxylammonium chloride was dissolved in 25 ml of water. KOH was added to the solution until pH 11.4. Then 25 ml of methanol was added to the solution. 0.20 g of polyacrylonitrile powder was added to the methanoic solution of hydroxylamine, and the mixture was stirred for 1 hour at 353 K. After the mixture was filtered, a residue was washed by methanol. Drying of the residue at 323 K under a reduced pressure afforded 0.20 g of yellow powder. This product is soluble in dimethylformamide (DMF) or dimethylsulfaxide (DMSO). Yield: 61 %. IR (KBr, cm^{-1}): 3181 (N-H), 2938, 2243 (C≡N), 1656 (C=N), 1593 (-NH$_2$), 919 (N-O).

(b) 0.27 g of hydroxylammonium chloride was dissolved in 25 ml of methanol. A methanoic KOH solution, dissolved 0.21 g of KOH in 25 ml of methanol, was mixed with the solution of hydroxylammomium chloride followed by filtration. 0.20 g of polyacrylonitrile powder was added to the filtrate, and the mixture was stirred for 16 hours at 353 K. After the mixture was filtered, a residue was washed by methanol. Drying of the residue at 323 K under a reduced pressure afforded 0.22 g of yellow powder. This product is dissolved in DMF or DMSO. Yield: 61 %. IR (KBr, cm^{-1}): 3181 (N-H), 2938, 2243 (C≡N), 1655 (C=N), 1593 (-NH$_2$), 936 (N-O).

Hydroxylamine treatment of PAN grafted PE fiber and poly(AN-co-MAA)-grafted PE fiber:

PAN-grafted PE fiber (*dg*: 64 %) and poly(AN-*co*-MAA)-grafted PE fiber (*dg*: 71 %)[16] were treated with hydroxylamine under two different conditions as follows;

(a) 4.78 g of hydroxylammonium chloride was dissolved in 75 ml of water. Potassium hydroxide was added to the solution until pH 7. Then 75 ml of methanol was added to the solution. 0.30 g of the PAN-grafted PE fiber and 0.40 g of the poly(AN-*co*-MAA)-grafted PE fiber were soaked for 0 ~ 6 hour in this NH_2OH solution at 350 K. After the hydroxylamine treatment, the fibers were rinsed with a methanol/water solution (1/1 vol. ratio), then were dried at 323 K under a reduced pressure. The weights of the PAN-grafted PE fiber and the poly(AN-*co*-MAA)-grafted PE fiber treated with NH_2OH for 6 hours were 0.33 g and 0.45 g, respectively.

(b) 4.78 g of hydroxylammonium chloride was dissolved in 75 ml of methanol. A methanoic KOH solution, dissolved 4.4 g of KOH in 75 ml of methanol, was mixed with the solution of hydroxylammomium

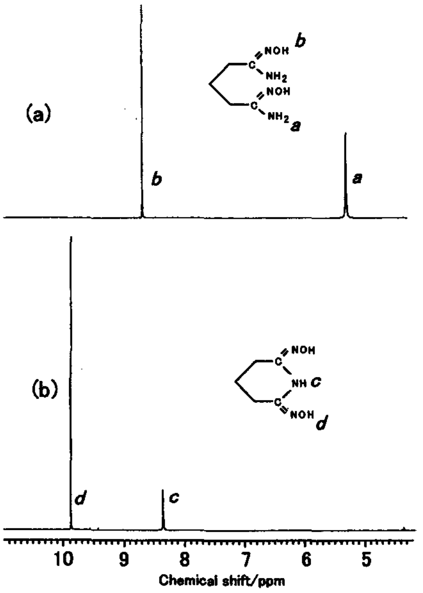

Fig.1 ^{1}H-NMR spectra of (a) glutardiamidoxime and (b) 2,6-dihydroxyiminopiperidine

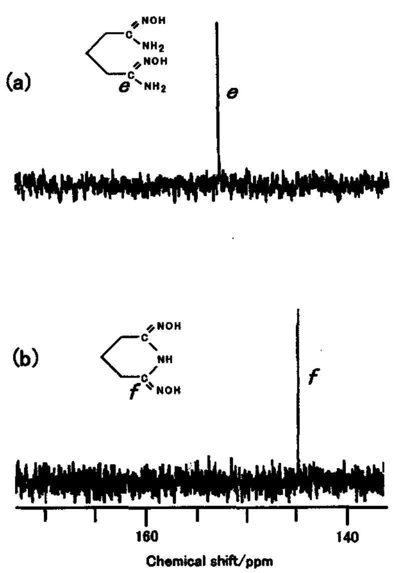

Fig.2 ^{13}C-NMR spectra of (a)glutardiamidoxime and (b) 2,6-dihydroxyiminopiperidine

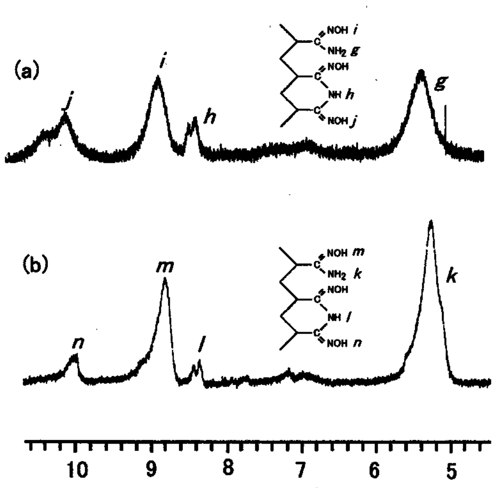

Fig.3 ^{1}H-NMR spectra of polyacrylonitrile treated with NH_2OH
(a) solvent: water/methanol = 1/1 (volume ratio)
(b) solvent: methanol

chloride followed by filtration. 0.30 g of the PAN-grafted PE fiber and 0.40 g of the poly(AN-*co*-MAA)-grafted PE fiber were soaked for 0 ~ 6 hour in the filtrate at 343 K. After the NH_2OH treatment, the PE fibers were rinsed with methanol and then were dried at 323 K under a reduced pressure. The weights of the PAN-grafted PE fiber and the poly(AN-*co*-MAA)-grafted PE fiber treated with NH_2OH for 6 hours were 0.35 g and 0.48 g, respectively.

2. NMR spectroscopy

Chemical structures of the compounds obtained via NH_2OH treatments were investigated by ^{1}H, ^{13}C and ^{13}C CP/MAS NMR spectroscopy (Bruker, Avance DRX-400, ^{1}H resonance frequency; 400 Hz) at room temperature. ^{1}H and ^{13}C NMR measurements were managed with DMSO-d_6 as a solvent.

3. RESULTS AND DISCUSSION

3.1. NH_2OH treatment of glutaronitrile

^{1}H-NMR spectra of the products by the NH_2OH treatment were shown in figures 1-(a) and (b). Peak *a* (5.3 ppm) and peak *b* (8.7 ppm) were assigned to amide and oxime of glutarodiamidoxime, respectively. Peak *c* (8.4 ppm) and peak *d* (9.9 ppm) were assigned to imide and oxime of 2,6-dihydroxyiminopiperidine, respectively.

Figures 2-(a) and (b) show spectra of ^{13}C-NMR of glutardiamidoxime and 2,6-dihydroxyiminopiperidine, respectively. Peak *e* (152.6 ppm) and peak *f* (144.6 ppm) were assigned to amidoxime and imidedioxime groups, respectively.

3.2. NH_2OH treatment of polyacrylonitrile

Figures 3-(a) and (b) show spectra of ^{1}H-NMR of the polyacrylonitrile treated with NH_2OH in the solvent of water-methanol and methanol, respectively. According to the spectral data of ^{1}H-NMR of glutardiamidoxime and 2,6-dihydroxyiminopiperidine (fig.1-(a), (b)), peak *g* (5.2 ppm), peak *i* (8.7 ppm), peak *k* (5.2 ppm) and peak *m* (8.7 ppm) were assigned to amidoxime group, and peak *h* (8.3 ppm), peak *j* (10.3 ppm), peak *l* (8.3 ppm) and peak *n* (10.3 ppm) were assigned to imidedioxime group. As shown in figure 3-(a), imidedioxime group was produced by NH_2OH treatment in the water-methanol solvent. This result differs from the case of glutaronitrile under the same condition. The production of imidedioxime group suggests that amidoxime group reacted with an adjacent cyano group because polyacrylonitrile consists of the sequence of 1,3-dicyano dispositions. As shown in figure 3-(b), both of amidoxime and imidedioxime group were obtained by hydroxylamine treatment in methanol though only imidedioxime group was produced by treating glutaronitrile in the same solvent. Integral ratio of amidoxime group was larger than that of imidedioxime group. This result suggests that amidoxime group is obtained prior to imidedioxime group by NH_2OH treatment of polyacrylonitrile contrary to the case of glutaronitrile in methanol.

3.3. NH_2OH treatment of PAN-grafted PE fiber and poly(AN-*co*-MAA)-grafted PE fiber

Figure 4-(a) and (b) show spectra of ^{13}C CP/MAS NMR of the AN grafted PE fiber treated with NH_2OH in the solvents of water-methanol and methanol, respectively. According to the spectral data of ^{13}C NMR of glutardiamidoxime and 2,6-dihydroxyiminopiperidine (figure 2-(a), (b)), peaks *o* and *q* (149 ppm) were assigned to imidedioxime group, and peaks *p* and *r* (157 ppm) were assigned to amidoxime group.

Figures 4-(c) and (d) show spectra of ^{13}C CP/MAS NMR of the poly(AN-*co*-MAA)-grafted PE fiber treat-

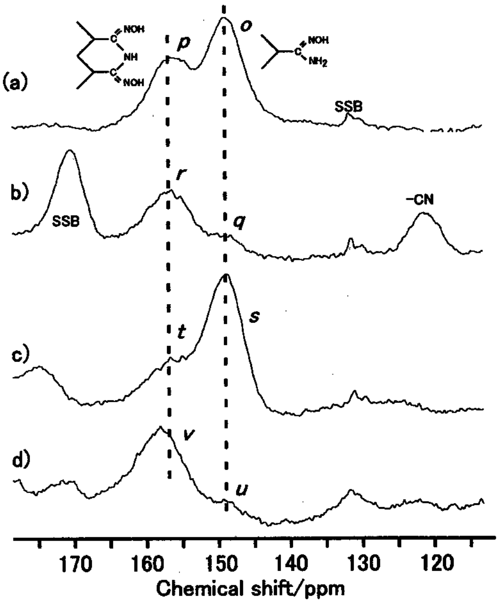

Fig.4 ^{13}C CP/MAS NMR spectra of PE fibers treated with NH_2OH
(a) PAN-grafted PE fiber
solvent: water/methanol = 1/1 (volume ratio)
(b) PAN-grafted PE fiber, solvent: methanol
(c) Poly(AN-*co*-MAA)-cografted PE fiber,
solvent: water/methanol = 1/1 (volume ratio)
(d) Poly(AN-*co*-MAA)-cografted PE fiber, solvent: methanol

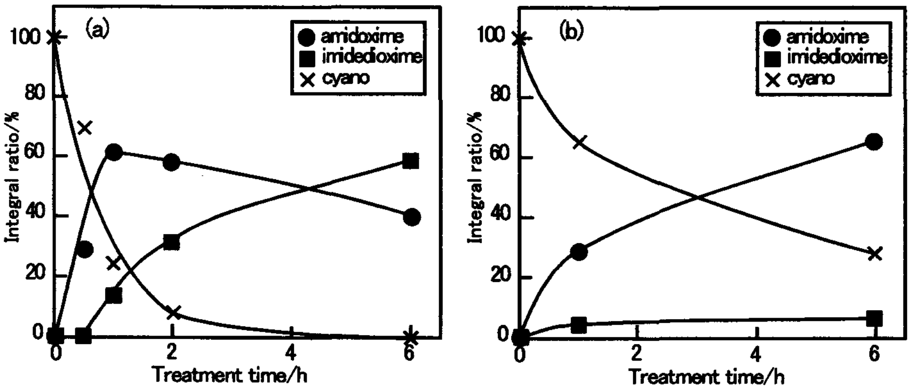

Fig.5 Integral ratio as a function of the treatment time with NH_2OH for PAN-grafted PE fiber
(a) solvent: water/methanol = 1/1 (volume ratio)
(b) solvent: methanol

ed with NH_2OH in the solvent of water-methanol and methanol, respectively. Peaks *s* and *u* (149 ppm) were assigned to imidedioxime group. And peaks *t* and *v* (157 ppm) were assigned to amidoxime group.

Spectra of ^{13}C CP/MAS NMR of the PAN-grafted PE fibers treated with NH_2OH were analyzed by curve-fitting, and the integral ratio of functional groups was calculated. Figures 5-(a) and (b) show the changes of integral ratio of amidoxime and imidedioxime groups as a function of the treatment time with NH_2OH in the solvent of water-methanol and methanol, respectively. As shown in figure 5-(a), Amidoxime group was produced within 1 h then the amount of it decreased. On the other hand, imidedioxime group increased gradually. And cyano group disappeared within 6 h. The production of imidedioxime group and the decrease of amidoxime group suggests that amidoxime group reacted with an adjacent cyano group and hydroxylamine. As shown in figure 5-(b), Amidoxime and imidedioxime groups were produced gradually and slightly, respectively. And cyano group decreased gradually. The reaction of cyano group with hydoxylamine in methanol was slower than the case in the solvent of water-methanol. The ratio of the production of amidoxime group was larger than that of imidedioxime group. These results reveal that the uranium adsorbent having amidoxime group as a main functional group is synthesized by hydroxylamine treatment of the PE fiber containing cyano groups in methanol.

4. CONCLUSION

The reactivities of the compounds containing cyano groups, such as glutaronitrile, polyacrylonitrile, PAN-grafted nonwoven fabric and poly(AN-*co*-MAA)-grafted nonwoven fabric, with hydroxylamine were investigated by means of ^1H-NMR, ^{13}C-NMR, ^{13}C CP/MAS NMR. The following conclusions were derived from the present work.

1. The uranium adsorbent having amidoxime group as a main binding site is prepared via hydroxylamine treatment of the fiber containing cyano groups in the solvent of methanol.
2. Amidoxime group reacted with an adjacent cyano group to form imidedioxime group by the hydroxylamine treatment of the polymer containing cyano groups.

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