A Solid-State ^{13}C and ^{15}N NMR Study of Plasma Polymerized Acrylonitrile

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ABSTRACT: Solid-state NMR techniques were applied for structural analyses of the plasma polymerized acrylonitriles. Secondary ($-\text{CH}_2-\text{C}\equiv$) and tertiary carbons ($=\text{CH}-\text{C}\equiv$) were formed in the plasma polymerization of acrylonitriles. In addition to the formation of carbon double bonds ($-\text{CH}=\text{CH}-$), amide bonds ($-\text{CONH}-$) were also formed. The film formed at 100 W had a higher cross-linking structure than that formed at 20 W. The film produced from acrylonitrile with nitrogen gas contained carbons adjacent to nitrogen atoms ($=\text{CH}-\text{N}=\text{}$). Near the electrode, nonprotonated carbons adjacent to nitrogen atoms ($\equiv\text{C}-\text{N}=\text{}$) were formed in the plasma polymers. These structural analyses contributed to elucidation of the plasma polymerization mechanism.

KEY WORDS Plasma Polymer / Solid-state NMR / Acrylonitrile /

Plasma treatment and plasma polymerization are known as effective methods for such surface modification, as control of the angle of water contact.¹ The angles of contact of plasma polymers are expected to depend on the chemical structures at the surface. The physical property and the chemical structure of the film are influenced by various conditions of the plasma polymerization, for example, the kind of monomer, coexisting gas, pressure in the chamber, input high frequency power, position of the sample, and so on. Especially, the kind of monomer remarkably changes the chemical structure and angle of contact. For instance, the plasma polymers prepared from nitrile compounds (acrylonitrile and acetonitrile) and alcohols (methanol and ethanol) have hydrophilic surfaces. Hydrophobic surfaces are

formed from aromatic, organosilicon, and fluoro compounds (benzene, tetramethylsilane, and perfluorobenzene).

The spectroscopic studies of chemical structures of hydrophobic plasma polymerized hydrocarbons^{2,3} and siloxanes^{4,5} were reported. The water contact angle at the hydrophilic surface of the plasma polymerized acrylonitrile (AN) is in the ranges of 50–60 degrees. For the plasma polymer of acrylonitrile with nitrogen gas (AN-N), this angle becomes 40–50 degrees. The difference in surface character suggests that the chemical structure of the plasma polymerized acrylonitrile varies depending on polymerization conditions.

In this work, the surface structures of plasma polymerized acrylonitriles are investigated by solid-state NMR spectroscopy.⁶

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EXPERIMENTAL

Plasma Polymerization

A bell-jar type reactor (dimensions: 260 mm diameter, 260 mm in height) was used in the plasma polymerization. Into the chamber evacuated to 0.13 Pa monomer vapor was introduced. Plasma excitation was carried out by a radiofrequency generator operated at 13.56 MHz through a matching box which allowed the reflected power to be minimized. The input power was controlled between 20 W and 100 W at a pressure of 13 Pa. The plasma polymers produced on the glass substrates inside the plasma reaction chamber were removed with a knife and collected.

Nuclear Magnetic Resonance Measurement

NMR spectra of the polymers were measured with a Fourier transform NMR spectrometer (Bruker MSL-300WB) at 7.0 Tesla, measuring both ^{13}C (75.47 MHz) and ^{15}N (30.15 MHz) by the CP/MAS and CPDD/MAS (Cross Polarization with Delayed Decoupling/Magic Angle Spinning) methods at 20°C.^{2,3} The contact time was varied from 0.5 ms to 5 ms. The Hartmann-Hahn condition and the magic angle were carefully adjusted by using $\text{NH}_2\text{CH}_2\text{COOH}$ (for ^{13}C) and NH_4NO_3 (for ^{15}N) samples.

RESULTS AND DISCUSSION

Figure 1 shows ^{13}C -CP/MAS-NMR spectra of plasma polymers prepared at input powers of 20 W, 50 W, and 100 W. NMR spectra were measured under conditions of contact time 1 ms, rotary speed 4500 Hz, 90° pulse 4.5 μs and, pulse interval 6 s. The signals in Figure 1 are very broad, probably reflecting the complexity in chemical structure of the plasma polymers. A quantitative analysis was not possible, but only spectral differences in these samples are discussed. Methyl signal intensities (signals (d): 20 ppm) of the plasma polymers at 20 W and 50 W are larger than the secondary

Figure 1. ^{13}C CP/MAS-NMR spectra of plasma polymerized acrylonitriles by different input powers.

and tertiary carbon signal intensities (signal (c): 40 ppm). However, the NMR spectrum of the polymer at 100 W shows strong intensities of the secondary and tertiary carbon signals. The formation of a cross-linked structure at the secondary and tertiary carbons was detected at high input power. A ^{13}C NMR signal belonging to the amide bond (signal (a): 177 ppm) was also observed in each polymer at 20 W, 50 W, and 100 W. The SSB (spinning side bands) were characterized by measuring the polymers at rotation speeds of 3000 Hz and 3750 Hz. The plasma polymers prepared at 20 W and 50 W resemble each other, while the polymer prepared at 100 W has a signal assigned to double bonds (signal (b): 140 ppm). This suggests that the cross-linked structure of polymer is formed at a high input power.

Figure 2 shows the ^{13}C -CP/MAS-NMR spectra of plasma polymerized acrylonitrile (AN and AN/E produced near the electrode) and acrylonitrile with nitrogen gas (AN-N and AN-N/E produced near the electrode). The spectra were measured at a rotation speed of

Figure 2. ^{13}C CP/MAS-NMR spectra of plasma polymerized acrylonitriles: AN, poly(acrylonitrile); AN/E, poly(acrylonitrile) near the electrode; AN-N, poly(acrylonitrile-nitrogen gas); AN-N/E, poly(acrylonitrile-nitrogen gas) near the electrode.

4500 Hz. In the spectrum of AN, the signal (a) of amide bonds ($-\text{CONH}-$) appears at 177 ppm. It is supposed that the amide group is formed by a reaction of radical species generated in the film with oxygen in the air. The signal (c') is due to carbons adjacent to the nitrogen atoms ($=\text{CH}-\text{N}=$ and $\equiv\text{C}-\text{N}=$) formed by a cross-linking reaction of the cyano group. The peak intensity of the methyl group [$-\text{CH}_3$; signal (d)] in the plasma polymer is larger than that of the secondary and tertiary carbons [$-\text{CH}_2-$, $=\text{CH}-$; signal (c)]. The peak intensity of signal (c) is high in the plasma polymer (AN/E), suggesting that the polymer (AN/E) has a relatively high cross-linking structure compared with AN. The intensity of the amide signal of AN-N is larger than that of AN and AN/E. The spectrum of

Figure 3. ^{13}C CPDD/MAS-NMR spectra of plasma polymerized acrylonitriles.

AN-N/E is dramatically different from those of the other samples. Signals due to various types of amide bonds [$-\text{CO}-\text{NH}-$, $-\text{CO}-\text{N}=$; signals (a) and (a')] appear, signal (c) increases remarkably, and signal (d) decreases. These results suggest that various radical species (carbon and nitrogen radicals) are generated in the vicinity of electrode in nitrogen gas, giving highly cross-linking polymers. Oxidation of the plasma polymer successively occurs in the air.

In the vicinity of the electrode, highly cross-linking polymers are produced and contain nonprotonated carbons. The cross polarization by the delayed decoupling/magic angle spinning (CPDD/MAS) method was used to measure signals due to nonprotonated carbons. The ^{13}C CPDD/MAS-NMR spectra of the plasma polymerized acrylonitriles are shown in Figure 3. The AN/E and AN-N/E polymers give rise to signals due to cross-

Figure 4. ^{15}N CP/MAS-NMR spectra of plasma polymerized acrylonitriles.

linking carbon double bonds (signal (b)) and nonprotonated quarternary carbons adjacent to nitrogen atoms (signal (c')) in addition to amide (signals (a) and (a')) and methyl carbons (signal (d)).

The CPDD/MAS-NMR spectra indicate that a radical species near the electrode in the air produces polymers including highly cross-linking structure and various types of amide bonds.

^{15}N NMR measurements are useful to confirm the presence of amine and amide nitrogens.⁷ Figure 4 shows ^{15}N CP/MAS-NMR spectra of plasma polymers from acrylonitrile. The difference between AN and AN/E is not detectable but signals of amines are observed at 80–90 ppm (signal (α)). On the other hand, the spectra of AN-N show relatively low ^{15}N chemical shifts at 80–160 ppm (signal (β)).

This suggests that the plasma polymers contain various types of amides and especially the polymer formed near the electrode contains heterocyclic nitrogen compounds (signal (γ): 350 ppm). The existence of nitrogen gas near the electrode induces the formation of a heterocyclic ladder structure in polyacrylonitrile.⁸

The structural analyses of these plasma polymers suggest a polymerization mechanism. The polymerization of acrylonitrile is initiated by the carbon radical species (e.g., $\text{CH}_2=\text{C}-\text{C}\equiv\text{N}$) and nitrogen radical species (e.g., $\text{CH}_3-\text{CH}=\text{C}=\text{N}\cdot$) generated in the plasma reaction chamber. These radical species are stabilized by oxidation in the air after polymerization. In the vicinity of the electrode, carbon and nitrogen radical species react with monomer and cross-linking structures are formed. The plasma polymerization of acrylonitrile with nitrogen gas promotes the formation of nitrogen radical species and, therefore, preparation of various types of amines and amides. It is considered that the carbons adjacent to nitrogen atoms ($=\text{CH}=\text{N}=\text{}$ and $\equiv\text{C}-\text{N}=\text{}$) and the amide groups modify the surface properties of polyacrylonitrile produced by plasma polymerization.

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