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Cyano and Analogous Groups in Plasma Polymers from Nitrogen Monomers

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ABSTRACT

Some nitrogen-containing monomers with different unsaturation numbers were polymerized in glow discharges, and the formation of cyano and analogous groups was investigated with infrared spectroscopy. In these monomers, even if they do not necessarily contain cyano groups as acrylonitrile or propionitrile, comparatively stronger peaks for these groups rearranged from the carbon-nitrogen bondings were observed. The reason for the formation of the groups is considered via kinetics, and it is suggested that the carbon-nitrogen single and/or double bonds which are feasibly fragmented in plasma are stabilized by forming cyano groups.

INTRODUCTION

Plasma polymerization carried out in glow discharges has some unusual characteristics compared to vinyl and condensation polymerizations. It is conducted at reduced pressure, and the irradiation energy per unit molecule is tremendously high. Therefore, the reaction is very radical and the organic molecules are fragmented at first. Then the resulting activated species will have two possibilities: degradation and polymerization. Hydrogen, carbon dioxide, etc. are degradation products from oxygen-containing monomers. Most of the remaining carbonic radicals will be recombined in the gaseous phase and/or on the surface to form thin films with a cross-linked structure.

Plasma polymerization has been investigated for its reaction behavior as well as for the physical properties of the products. One of the interesting features in plasma polymerization is that the monomer does not participate in the polymerization as itself, but it works as an atomic supply unit. Therefore, if the starting monomers have an analogous composition such as acetylene (C_2H_2) and benzene (C_6H_6), i.e., the elemental ratio C:H is 1.0 in both cases, the resulting polymers are more or less similar in their polymerization behavior and in their physical properties [1]. For the above reason, the elemental ratio and unsaturation in the monomer are important in plasma polymerization. Additionally, it is interesting to see if the monomer contains hetero atoms such as nitrogen, oxygen, silicone, and halogens. There is the feasibility of deposition in these polymers. For instance, in the plasma polymerization of some silyl amines it has been observed that the atoms existing in the polymers increase in amount in the order $N < C < Si$ [2]. This suggests that nitrogen is more easily fragmented in plasma, and silicone participates much more in polymerization.

Hetero atoms contained in a monomer play important roles in the physical and chemical properties as well as in polymerization. For example, fluorine or silicon plasma polymers are hydrophobic. On the other hand, plasma polymers from nitrogen-containing hydrocarbons are usually hydrophilic, and some of them are used for reverse osmosis membranes [3]. The hydrophilicity of the polymers is mainly due to the amino-like groups which are formed by rearrangement and incorporation in the course of polymerization.

Incidentally, another interesting feature in the polymerization of nitrogen compounds is that the cyano and analogous groups can be formed even when the monomer does not contain the cyano group. Although the formation of new C–C and C–H bondings in plasma polymers has been investigated and some theories have been given [4], not so much work has been done on the chemical structures of plasma polymers from nitrogen-containing monomers in spite of their usefulness. In this study the formation of cyano and analogous groups is investigated by means of IR spectroscopy, and some effects of plasma on carbon-nitrogen bonds are considered.

EXPERIMENTAL

Monomers

The nitrogen-containing monomers used in this study are listed in Table 1. They were the reagent grades and were used as supplied, but were fully degassed under reduced pressure before the experiments.

TABLE 1. Nitrogen-Containing Monomers Used for Plasma Polymerization and Their Unsaturation Number

Monomer	Formula and molecular weight	Unsaturation number
(1) Morpholine	C_4H_9NO (87.12)	1
(2) Propionitrile	C_3H_5N (55.08)	2
(3) 2-Methyloxazoline	C_4H_7NO (85.11)	2
(4) 2-Methylisoxazoline	C_4H_7NO (85.11)	2
(5) 2-Methylthiazoline	C_4H_7NS (101.17)	2
(6) N,N-Dimethylacrylamide	C_5H_9NO (99.13)	2
(7) Acrylonitrile	C_3H_3N (53.06)	3
(8) Pyrrole	C_4H_5N (67.09)	3
(9) N-Methylpyrrole	C_5H_7N (81.12)	3
(10) Pyridine	C_5H_5N (79.1)	4
(11) Aniline	C_6H_7N (93.13)	4
(12) N-Methylaniline	C_7H_9N (107.16)	4
(13) 2-Furanonitrile	C_5H_3NO (93.09)	5

Procedure for Plasma Polymerization

Details about the plasma polymerization procedure have been reported previously [2].

Measurement of Infrared Spectroscopy

Infrared spectra were taken with an IR spectrophotometer, Model IR-430, Shimadzu Seisakusho, Kyoto, Japan.

Polymers deposited on the wall of the reaction chamber were gathered by scratching, and a KBr disk was prepared for the spectrum. When the polymerization rate was high, the polymer layer was deposited directly on the KBr disk.

RESULTS AND DISCUSSION

Reaction Behavior in Glow Discharges

Of the factors related to plasma polymerization, chemical structure, composition, and molecular weight are important for the

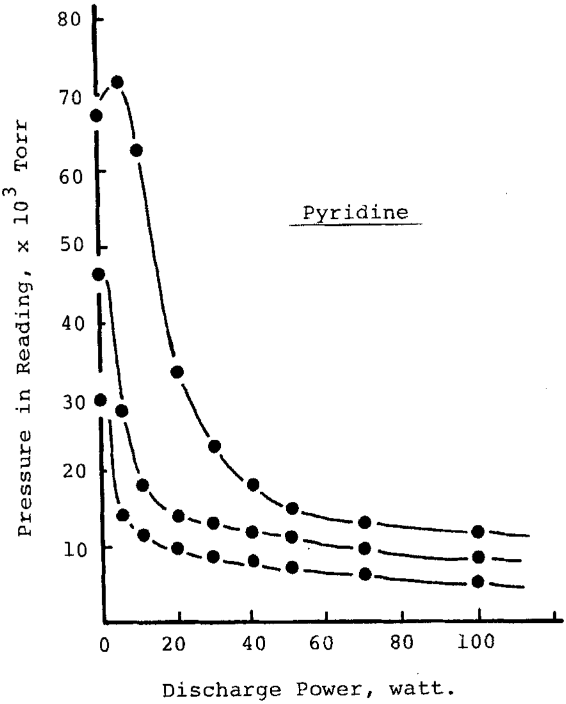

FIG. 1. Dependence of discharge power on the pressure in the reading which shows the reaction behavior of pyridine in plasma.

reactivity. The unsaturation number derived from the olefinic double (or triple) bonds and the cyclic bonds plays an important role [5]. This is because the olefinic and cyclic bonds can form the radically activated species which is easily produced in plasma. Also, the production of hydrogen, which will cause a reduction of reactivity through the consumption of additional energy, will be lowered. The unsaturation numbers of the monomers are listed in Table 1.

The pressure in glow discharges is one of the parameters which directly affects reaction behavior because the pressure is related to the number of particles existing in the system. Figure 1 shows the relation between the pressure and the discharge power in the reaction of pyridine. It was found that the pressure decreases greatly with the applied discharge power and reaches a plateau over certain wattages. This suggests that most of the activated species in plasma participate in polymerization and that the number of fragmented particles is relatively small. In the case of saturated amines such as diethylamine, the pressure increases in plasma and the polymerization proceeds only partially.

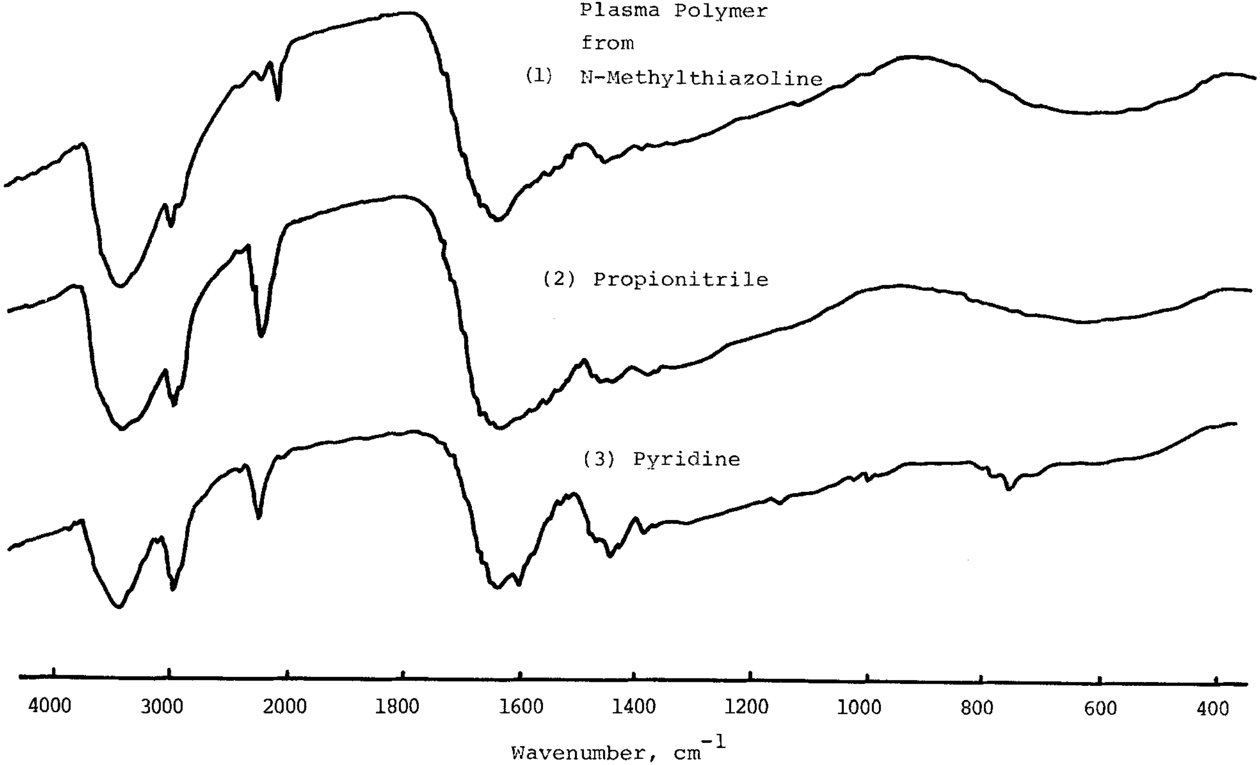

FIG. 2. Infrared spectra of plasma polymers.

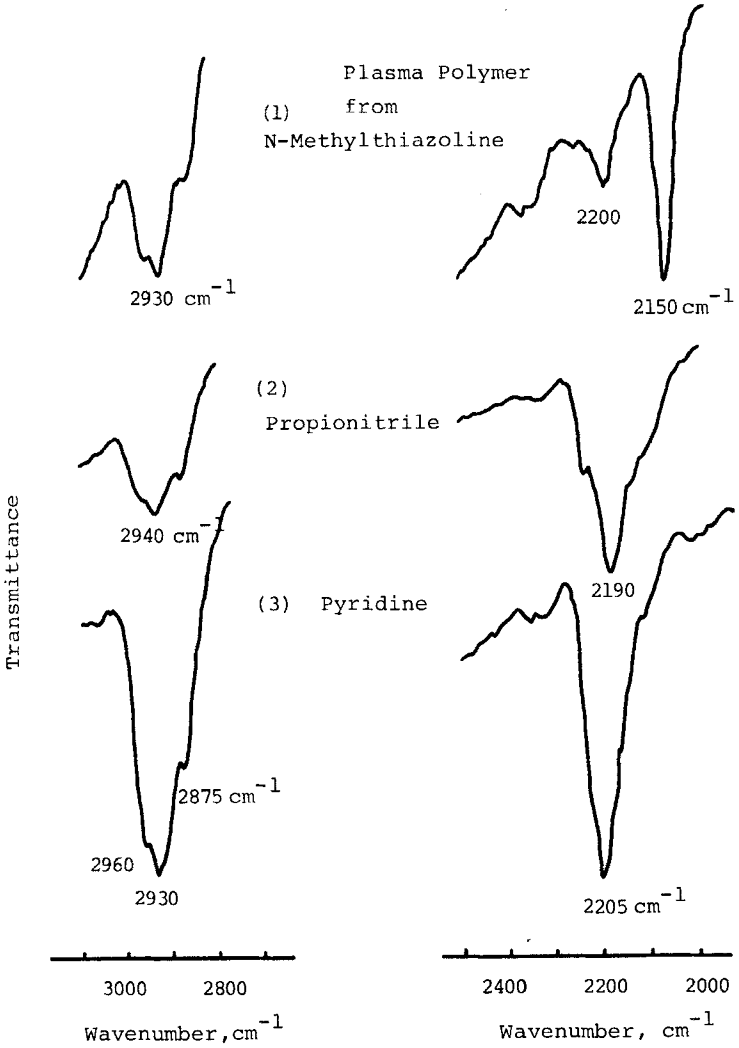

FIG. 3. Infrared spectra expanded around 2900 and 2200 cm^{-1}, respectively, for the C–H and C≡N stretching vibrations.

Pyridine gives a brownish black polymeric product which is probably due to partial carbonization. As the unsaturation in the monomer decreases, the polymers formed become less colored. The plasma polymer from morpholine (unsaturation number 1.0) is rather yellow.

TABLE 2. Absorption Bands for Cyano and the Analogous Groups (1) and for Carbon-Hydrogen Bonds (2) in the Infrared Spectra of Plasma Polymers from Nitrogen Monomers

	Absorption band (cm^{-1})	
Plasma polymer from	(1)	(2)
(1) Morpholine	2180 (cyano) 2240	
(2) 2-Methyloxazoline	2150 (s, –O–C≡N) 2210 (cyano) 2237	2876 2938 ($-CH_2-$) 2973
(3) 2-Methylisoxazoline	2220 (cyano)	
(4) 2-Methylthiazoline	2050 (s, –S–C≡N) 2200 (cyano) 2240	2875 2930 ($-CH_2-$) 2970
(5) N,N-Dimethylacrylamide	2160 (s, cyano)	2880 2940 ($-CH_2-$) 2960
(6) Propionitrile	2120 2190 (s, cyano) 2240 (m)	2880 2940 ($-CH_2-$) 2975
(7) Acrylonitrile	2200 (s, cyano)	
(8) Pyrrole	2200 (m, cyano)	
(9) N-Methylpyrrole	2170-2230 (cyano)	
(10) Pyridine	2175 (s, cyano) 2205	2875 2930 ($-CH_2-$) 2960
(11) Aniline	2210	
(12) N-Methylaniline	-	
(13) 2-Furanonitrile	2200 (s, cyano)	

Infrared Spectroscopic Study

As plasma polymeric products are usually insoluble in solvents, investigation on the chemical structure is restricted. The usual spectroscopic medias, such as MNR, which are effective for identification of hydrocarbon structures cannot be used. One popular method is IR spectroscopy which is useful for the detection and identification of functional groups.

Figure 2 shows the IR spectra of plasma polymers form N-methylthiazoline (1), propionitrile (2), and pyridine (3). They were produced

TABLE 3

Type of bonding	D_0 (kcal/mol) [6]
C–N	72.8
C=N	147
C≡N	212.6

under plasma conditions, 50×10^{-3} torr and 50 W, and deposited under a monomer inlet which was designed for uniform deposition. The general features of the spectra peaks are similar, and some interesting bands can be pointed out: 1) strong absorption bands around 3300 cm^{-1} and around 1630 cm^{-1}, respectively, for amines and the C=C (and/or C=N) bonds, 2) medium peaks at the 2800-3000 cm^{-1} wavelength for methyl and methylenes, and 3) relatively stronger absorptions around 2200 cm^{-1}, mainly for nitriles. Almost the same characteristics were observed in other polymers. It is interesting to note that the saturated $-CH_2-$ groups is also observed in pyridine polymers whose initial monomer is fully unsaturated. In addition, the olefinic C–H groups, which usually appear in the region higher than 3000 cm^{-1}, cannot be detected or are negligibly small.

In order to see further details in the state of the functional groups, the band peaks were expanded and are shown in Fig. 3. In these spectra the main peak around 2930 cm^{-1} is assigned to the C–H stretching vibrations of acyclic methylenes and the peak around 2960 cm^{-1} to that of alkylic-CH_3. The peak bands around 2200 cm^{-1} are a little complicated. The peaks at 2200, 2190, and 2205 cm^{-1}, respectively, for the polymers from N-methylthiazoline, propionitrile, and pyridine are assigned to the nitriles. The strong peak at 2050 cm^{-1} in the N-methylthiazoline polymer is assigned to the stretching vibration of the S–C≡N group which is formed by detaching the 2-methyl group from the polymer. There are some peaks in the range higher than 2200 cm^{-1}. Their exact assignment cannot be given at the present time, but they are possibly from the isonitriles and/or isocyanates which are formed by rearrangement in the course of polymerizations.

Analogous phenomena were observed in polymers of other nitrogen monomers. The main band peaks are listed in Table 2 for methyl and methylenes (1) and for nitriles (2) together with their assignments.

Formation of cyano and analogous groups is observed in the plasma polymers of these nitrogen monomers, and this may be related to the mechanism of plasma polymerization or the participation of carbon-nitrogen bonds in the reaction. Bond energies are compared in Table 3. From these data it can be seen that the C–N bonding is much more easily opened and, as a result, C–N and possibly C=N bondings may open to be fragmented or may form tighter bonding of cyano groups.

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