

A STUDY OF THE POLYMERIZATION MECHANISM OF ACETONITRILE IN GLOW DISCHARGE

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ABSTRACT

Plasma polymerization of acetonitrile was carried out by a capacitively coupled RF plasma apparatus with external electrodes under some different reaction conditions such as discharge power. By investigating the informations provided by the polymer deposition regularities, IR spectra and elementary analysis results, the polymerization mechanism of acetonitrile in glow discharge have been investigated. The results show that acetonitrile polymerized in glow discharge mainly through hydrogen detachment for initiation at lower energy levels and the role that opening $C \equiv N$ triple bond played in polymerization became more important at higher energy levels.

INTRODUCTION

Recently, it is found that the plasma polymer membranes prepared from nitrogen-containing monomers have many functional properties. A lot of research works has been done on the potential applications of this kind of polymers. Moreover, the works on the plasma-polymerized acetonitrile membranes have achieved some interesting results. For example, Yasuda et al.^[1] prepared a kind of hydrophilic reverse osmosis membranes from acetonitrile and Suzuki Shinichi et al.^[2] have obtained the semiconducting films by annealing the plasma-polymerized acetonitrile membranes and used them to prepare rectifier with high rectification ratio. As a kind of saturated nitrogen-containing organic compound, acetonitrile is not easy to polymerize by using conventional methods. So it is a representative monomer to be used for investigating the plasma polymerization mechanism. The study on the polymerization mechanism have great practical significance for controlling the structure and properties of the polymerization products and no report has been found by the authors on this aspect. In this paper, the plasma polymerization of acetonitrile was carried out in a capacitively coupled RF plasma apparatus with external electrodes and the polymerization mechanism was investigated through the studies on the polymer deposition rates and chemical structures.

EXPERIMENTAL

Acetonitrile used was produced by the first Shanghai Chemical Plant with analytical reagent grade. It was dried by molecular sieve before used. The purity of hydrogen, nitrogen, oxygen and argon gas used is higher than 99.97%.

The reactor used was a capacitively coupled 13.56-MHz radio-frequency plasma apparatus with

external electrodes^[3] and the discharge power could be adjusted from 0 to 300W in succession. The ratio of plasma gas to monomer was regulated by controlling the partial pressure of gas. Acetonitrile was frozen two times before introduced into the reactor. The position of monomer inlet was assigned as zero, and the direction of the monomer current as positive, the reverse direction as negative. The rate of the polymer deposited on the glass substrate was calculated by weighting. The polymer sample for IR determination was deposited directly on the NaCl disc which is located at 8.5cm from the monomer inlet. The specimen for elementary analysis was gathered by scratching and mixing the polymers which had been deposited on the wall of the reaction chamber in the position of 0 to 7.5cm away from monomer inlet.

Infrared spectra were obtained on an IR spectrophotometer, Model Pekin-Elmer 599B. Elementary analyses were taken with an Automatic Elementary Analysis meter, Model 1160, produced by CARLO ERBA corporation.

RESULTS AND DISCUSSION

The IR spectrum of plasma-polymerized acetonitrile is shown in Figure 1 and the assignments of the absorption bands are listed in Table 1. From Figure 1, we could observe that a lot of $C \equiv N$

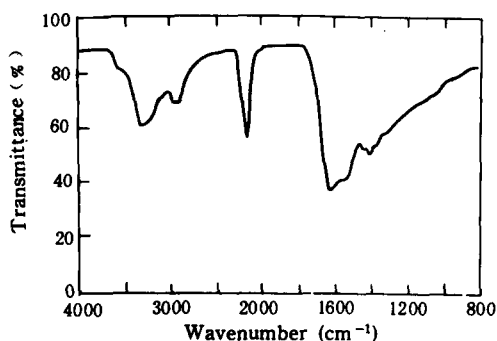


Fig.1 IR spectrum of plasma-polymerized acetonitrile.
Pressure, 6.67Pa. Power, 70W.

Table 1 Assignment of IR absorption bands of plasma-polymerized acetonitrile^[4,5]

Absorption band (cm ⁻¹)	Assignment
3600—3200	N—H stretch in amine and imine O—H stretch
2900	C—H stretch
2185	C≡N stretch
	C=C stretch in olefin
1640	C=N stretch C=O stretch
1550	N—H bend
1450	C—H bend in methylene group
1430	C—H bend in methyl group

groups remained in the polymer because the $C\equiv N$ stretch band is very strong. It is obvious that acetonitrile was initiated to polymerize only through the step of hydrogen detachment if $C\equiv N$ triple bonds were not opened. Simultaneously, we also noted that there were strong spectra peaks of $C=N$ (1640 cm^{-1}) and $N-H$ (1550 cm^{-1} and $3600-3200\text{ cm}^{-1}$) which showed that the $C\equiv N$ triple bonds were opened and participated in the polymerization.

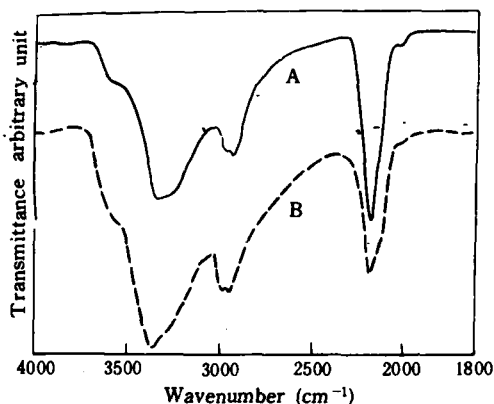


Fig.2 IR spectrum of plasma-polymerized acetonitrile prepared at 70W(A) and 210W(B). Pressure, 6.67Pa.

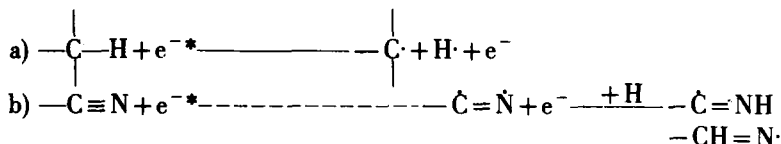
Table 2 The elementary analysis of the plasma-polymerized acetonitrile

Reaction conditions		%wt.			Elementary ratio	
Plasma gas	power, W	C	N	H	H/C	N/C
	70	57.15	34.04	4.01	0.836	0.510
	210	60.39	31.15	5.37	1.060	0.442
H	70	56.23	33.30	4.41	0.934	0.508
N	70	55.70	33.54	4.54	0.926	0.516
O	70	55.93	33.73	4.54	0.967	0.517
Ar	70	54.65	28.79	6.29	1.370	0.452

* Pressure, 6.67 Pa. Plasma gas/Monomer ratio, 1/2.

The elementary analysis results of the plasma-polymerized acetonitrile are listed in Table 2 and the ratios of H/C and N/C have also been obtained by calculating. The ratio of H/C and N/C in acetonitrile monomer is 1.5 and 0.5 respectively. From the results in Table 2, we can observe that H/C ratio of the polymer is in the range of 0.836—1.37 and much lower than that of the monomer, but the N/C ratio between them has little difference. This indicated that acetonitrile polymerization in glow discharge is mainly due to the hydrogen detachment.

According to the above discussion on the results of IR spectrum and elementary analysis of the acetonitrile polymerization product, we could infer that the initiation and reinitiation in the polymerization may be divided into two types as follows:



As for the two courses listed above, we could imagine that the high energy level might be in favor of the b) course to go on because the bond energy of C—H single bond (98.7Kcal/mol) is much lower than that of C≡N triple bond (212.6Kcal/mol)^[6].

The IR spectra of plasma-polymerized acetonitrile prepared at the discharge power of 70W and 210W are shown in Figure 2. Comparing them, we could find that a higher C≡N group content remained in the polymerization product at lower discharge power while the strength of C≡N absorption band (2185cm⁻¹) weakened obviously and N—H stretch band (3600—3200cm⁻¹) strengthened simultaneously at higher discharge power, that indicated much more C≡N triple bonds to take part in the polymerization. From Table 2, we also observed that the N/C ratio of the polymer prepared at higher discharge power is lower than that of acetonitrile monomer. This case probably resulted from the strong ablation at high energy reaction systems and a few nitrogen-containing groups was broken away from the reactor. In addition, the role of hydrogen detachment should increase with increasing discharge power, however, the elementary analysis results in Table 2 showed that hydrogen content in the polymerization product prepared at higher discharge power was higher than that at lower discharge power. The two courses of initiation and reinitiation proposed above could explain this result very well. When the a) course played a chief role in polymerization, H· radicals formed by the hydrogen detachment from monomer or propagation chain could combine mutually to form the by-product H₂ which was removed from the system by pumping. As the role of the b) course became more important, much more C≡N triple bonds would be opened and it might be possible that more H radicals participated into the polymer structure. This situation seems to be just the H conversion macroscopically.

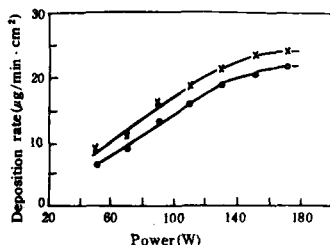


Fig.3 Dependence of plasma-polymerized acetonitrile deposition rate on the discharge power.

Pressure, 6.67Pa. Deposition position, 0 cm(x) and 3.75cm(o)

The deposition rate of plasma-polymerized acetonitrile at different discharge powers are shown in Figure 3. It is found that the polymer deposition rate increases linearly with increasing discharge power in the range of 50—130W. One reason is that the increase of energy is in favor of activating more monomer molecules to join polymerization and another is that much more C≡N triple bonds would be opened and more of the activated species being produced as the discharge power raised. As the discharge power exceeded 150W and continued to raise, the increase of deposition rate become slow gradually and it might result from the strong ablation at high energy level.

The IR spectra of plasma-polymerized acetonitrile prepared at different ratios of plasma gas to

monomer are shown in Figure 4. It is observed that the $C\equiv N$ group content in the polymer tended to decrease as long as the plasma gas concentration increased in the system. Besides changing monomer concentration plasma gas mainly plays a role of transferring energy in the system. So the increase of the plasma gas concentration would be in favor of the monomer molecules to get more energy.

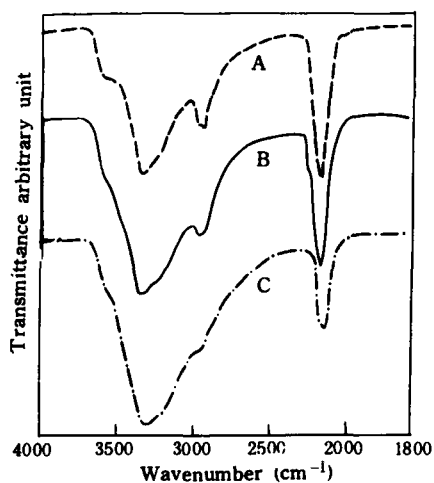


Fig.4 IR spectra of plasma-polymerized acetonitrile prepared at different ratios of plasma gas to monomer. Power, 70W. Pressure, 6.67Pa. N_2 /monomer, 1/2(A), 1/1(B), 2/1(C)

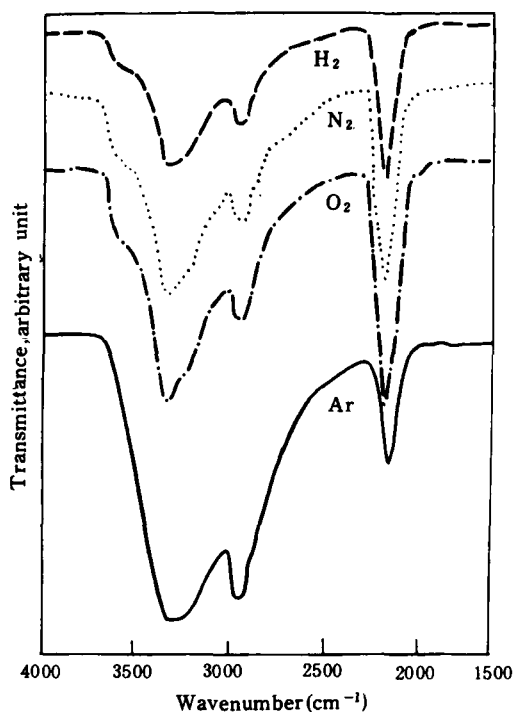


Fig.5 IR spectra of plasma-polymerized acetomitrile prepared in different plasma gas. Pressure, 6.67Pa. Power, 70W. Plasma gas/monomer, 1/2.

Figure 4 shows the IR spectra of plasma-polymerized acetonitrile prepared at different ratios of plasma gas to monomer. Comparing the strength of $C \equiv N$ absorption band (2185cm^{-1}), and $N-H$ absorption band ($3600-3200\text{cm}^{-1}$), we presume that $C \equiv N$ groups participate the polymerization to a certain extent. In Figure 5, We could observe that the order of $C \equiv N$ absorption bands strength is $\text{Ar} \leq \text{O}_2 < \text{N}_2 < \text{H}_2$ roughly which is used as plasma gas. Contrasting the elementary analysis results in Table 2, we could find that the hydrogen content is higher if the $C \equiv N$ group content is lower in the polymers. In this respect, it also justified the above discussion on the hydrogen conversion. The N/C ratio of the polymer prepared in Ar glow discharge is lower than that of the monomer. This situation may be associated with the strong etching ability of argon^[1].

The polymer deposition rates in different plasma gas glow discharge are shown in Figure 6. The polymer deposition rate is in the order of $\text{N}_2 > \text{O}_2 > \text{H}_2 > \text{Ar}$ approximately. Besides Ar, all plasma gases used in this experiment could take part in polymerization in some forms. As we have the discussed above, the hydrogen detachment is an important step for initiation and reinitiation in the plasma polymerization of acetonitrile. It is obvious that the increase of $\text{H}\cdot$ radical content in the system is unfavourable for the hydrogen detachment and even to terminate the activated species produced. In N_2 or O_2 glow discharge system, the $\text{N}\cdot$ or $\text{O}\cdot$ radical could combine with $\text{H}\cdot$ radical to form NH_3 or H_2O and suppressing the $\text{H}\cdot$ radical content in the gaseous phase. In H_2 glow discharge system, however, it is more difficult to conduct the initiation and reinitiation courses through hydrogen detachment. As a result, the polymer deposition rate in H_2 glow discharge becomes smaller than that in N_2 or O_2 glow discharge.

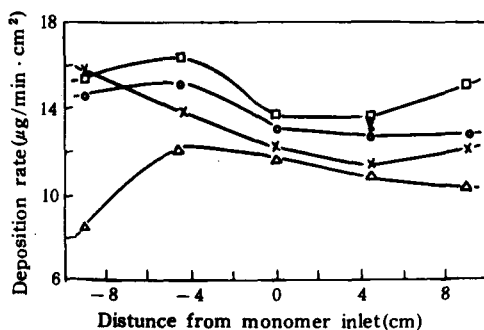


Fig.6 Deposition rate of plasma-polymerized acetonitrile in different plasma gases. Power, 70W.

Pressure, 6.67Pa. Plasma gas/monomer, 1/2.

Plasma gas, N_2 (□), O_2 (○), H_2 (×), Ar(Δ).

Keywords:

Plasma polymerization; Acetonitrile; Glow discharge; Mechanism

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