Polymer Bulletin 13, 349-352 (1985)

Polymer Bulletin

Plasma Polymerization

Preparation of Carboxylate Groups-Containing Thin Films by Plasma Polymerization

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SUMMARY

Plasma polymerization in a mixture of acrylic acid and carbon dioxide (CO_2) gas was investigated. The polymer deposition rate in plasma polymerization of acrylic acid increased by admixing CO_2 gas, and polymers containing carboxyl groups were formed. The amount of carboxyl groups alterable to carboxylate anions by treating with 0.1 N KOH solution or NH_3 gas reached twice of that formed in plasma polymerization without CO_2 gas.

INTRODUCTION

Plasma polymerization is a polymer-forming process different to conventional polymerization processes such as radical and ionic. In plasma polymerization polymer-formation and degradation of monomers occur simultaneously in the discharge state, and the balance between the two processes depends on the nature of monomers as well as on the operating conditions such as rf power, monomer flow rate, and pressure. This model named CAP (Competitive Abration and Polymerization) mechanism has been proposed by Yasuda (1978). In plasma polymerization of oxygen-containing monomers such as carboxylates and carboxylic acids abration process is enhanced compared with in that of hydrocarbon monomers without oxygen (YASUDA 1978). And cross-linked polymers are formed because of decarboxylation (YASUDA 1981). Therefore, in order to obtain polymers with carboxyl and carboxylate groups by plasma polymerization special techniques are required. For example, to get thin films plasma-polymerized from methyl methacrylate (MMA) for lithography of LSI devices MMA has been activated by very weak electron in an afterglow region (MORITA, 1981).

This study focusses on plasma polymerization in a mixture of acrylic acid (AA) and carbon dioxide (CO_2) gas to obtain plasma-polymers containing carboxylate groups. The effects of CO_2 gas in plasma polymerization of AA are evaluated.

EXPERIMENTAL

The apparatus of Pyrex glass (35 mm i. d., 400 mm long) and the experimental procedures used in this study are the same as reported elsewhere (INAGAKI and YAMAZAKI 1984). The glow discharge was initiated at a pressure of 1.3 Pa, at a constant flow rate of monomers (3 cm^3(STP)/min for AA and 2 cm^3(STP)/min for AA/CO_2 mixture), and at a given rf power (13.56 MHz), and continued for a given duration. AA and CO_2 gas were purchased

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from Tokyo Kasei Kogyo Co. and Matheson, respectively. Infrared spectra of the polymers were recorded using KBr discs with a Nihon Bunko spectrometer A-3.

RESULTS AND DISCUSSION

Plasma polymerizations in an AA/CO_2 mixture yields polymeric films soluble in weak alkali solution. Their aspect depended strongly on the CO2 concentration in the mixture as well as on the W/FM value, where W, F, and M are the rf power, the flow rate and the molecular weight of the monomer, respectively. In operation at W/FM values below 100 MJ/kg, colorless and very hygroscopic films were formed, whereas at W/FM values above 130 MJ/kg light-yellow fims were formed. Increase in CO_2 concentration caused similar changes in the polymer aspect. Such operating conditions influenced the polymer deposition rate too. Fig. 1 shows typical polymer deposition rate curves in the AA system with and without CO_2 gas as a function of the W/FM value to elucidate effects of CO_2 gas addition. In the AA system the polymer deposition rate increased first slightly with increasing the W/FM value, then decreased rapidly at W/FM values above 140 MJ/kg, and finally no polymer deposite was observed at the W/FM value of 200 MJ/kg. In the AA/CO_2 mixture system the rate being higher than in the AA system decreased gradually with increasing the W/FM value, and polymer formation extended upto a W/FM value of 300 MJ/kg. This indicates significant influences of CO_2 on plasma polymerization by the retardation of abration reactions by CO_2 gas.

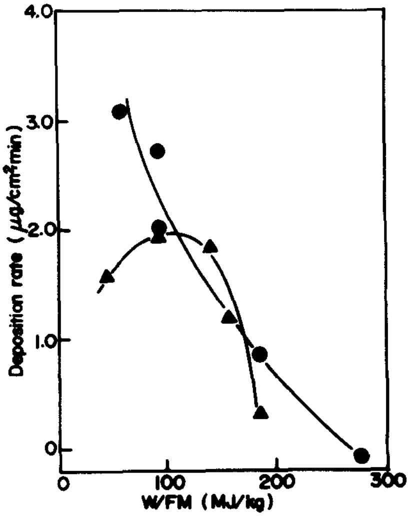


Fig. 1 Polymer Deposition Rate as a Function of W/FM Value; ▲ , AA System; ● , AA/CO_2 (1/1 molar ratio) Mixture System.

Fig. 2 shows typical infrared spectra of plasma-polymerized polymers of AA and of the AA/CO_2 mixture (50 mol% CO_2). The two polymers show similar spectra. On these spectra strong absorption appears at 2970 (ν_{as} CH_3), 2940 (ν_{as} CH_2), 2880 (ν_s CH_3, CH_2), 1720 ($\nu C{=}O$), 1460 (acissoring of CH_3), 1385 (δ_s CH_3), and 1180 cm^{-1} (rocking of $CH(CH_3)_2$ and $(CH_3)_2C$). No absorption related to vinyl groups (at 3070, 3000, 1640, 1440, 990, and 920 cm^{-1}) is observed. These spectra indicate the formation of analogous polymers from both the AA and the AA/CO_2 mixture, which contain carbonyl and/or carboxyl groups and branched methyl groups.

In order to determine the strong absorption at 1720 cm^{-1} to be either carbonyl or carboxyl groups these polymers were treated with 0.1 N KOH solution (spectra D in Fig. 2). The treated polymers show new strong absorptions at 1570 and 1400 cm^{-1} which could be assigned to carboxylate (COO^{-}) groups, whereas the absorption at 1720 cm^{-1} still presented although its intensity became weak. Similar modifications could be observed by the treatment of the polymers with ammonia gas. From these modification in infrared spectra it is obvious that the polymers contain both carbonyl and carboxyl groups.

Fig. 3 shows the relative absorption intensities of carbonyl (at 1720 cm^{-1}) and carboxylate groups (at 1570 cm^{-1}) against methylene groups (at 2940 cm^{-1}) (I_{1720}/I_{2940} and I_{1570}/I_{2940}) as a function of the CO_2 content. Both the ratios increased with increasing CO_2 concentration, and then leveled off at a CO_2 concentration of about 50 mol%. The I_{1720}/I_{2940} ratio and especially the I_{1570}/I_{2940} ratio reached twice by admixing 50 mol% CO_2. This indicates the advantage of admixing CO_2 gas during formation of plasma polymers containing carboxylate groups.

Fig. 4 shows the influence of the W/FM value on the formation of carboxylate groups in plasma polymerization of AA and AA/CO_2 mixture (50 mol% CO_2). Changes of the I_{1570}/I_{2940} ratio show gradual

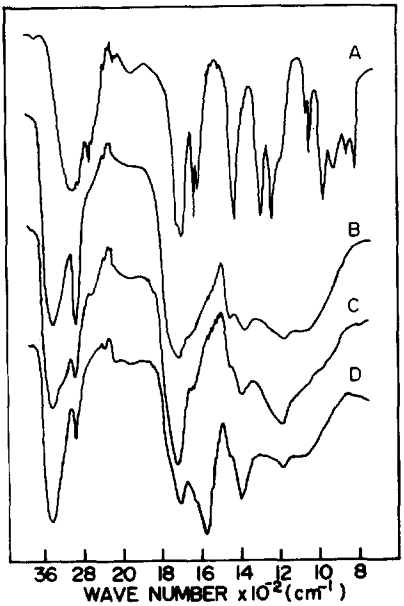
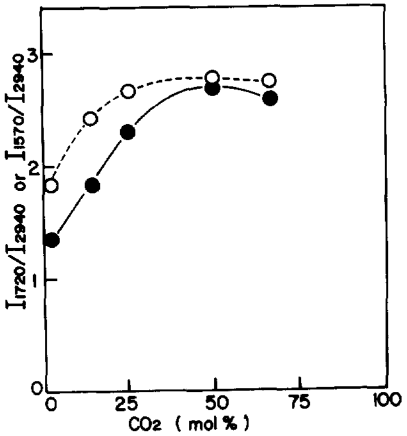


Fig. 2 IR Spectra of Plasma-polymerized Polymers of AA/CO_2mixture; A, monomer; B, plasma-polymerized from AA; C, plasma-polymerized from AA/CO_2 (1/1 molar ratio) mixture; D, plasma-polymer C treated with 0.1 N KOH solution.

Fig. 3 Relative Concentration of Carbonyl Groups (I_{1720}/I_{2940}) and of Carboxylate Groups (I_{1570}/I_{2940}) in Polymers Plasma-polymerized from AA/CO_2 Mixture as a Function of the CO_2 Concentration ;○, I_{1720}/I_{2940} ●, I_{1570}/I_{2940}.



decrease in both the polymerization system with increasing the W/FM value. The ratio was approximately two times higher in the AA/CO_2 mixture system than in the AA system. Similarly, the the I_{1570}/I_{1720} ratio was higher in the AA/CO_2 mixture system than in the AA system.

Conclusively, these results point out an advantage of mixing CO_2 gas and also of operation at low W/FM values to prepared polymers containing carboxylate groups by plasma polymerization.

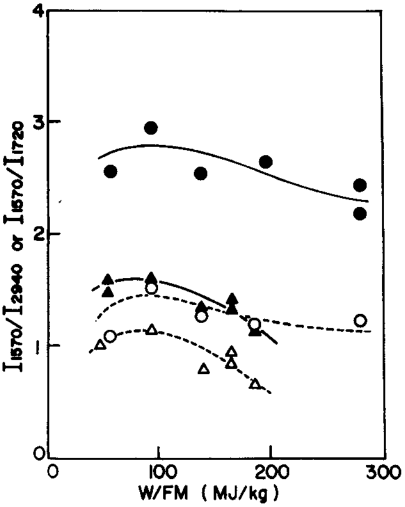


Fig. 4 Relative Concentration of Carboxylate Groups (I_{1570}/I_{2940} and I_{1570}/I_{1720}) in Plasma Films polymerized from AA or AA/CO_2 Mixture (1/1 molar ratio) as a Function of W/FM Value; ▲, I_{1570}/I_{2940} in plasma films from AA; △, I_{1570}/I_{1720} in plasma films from AA, ●, I_{1570}/I_{2940} in plasma films from AA/CO_2 mixture; ○, I_{1570}/I_{1720} in plasma films from AA/CO_2 mixture.

REFERENCES

1. INAGAKI, N. and YAMAZAKI, H. J. Appl. Polym. Sci., 29, 1369 (1984).
2. MORITA, S., HATTORI, S., IEDA, M., TAMANO, J., and YAMADA, M., Kobunshi Ronbunshu, 38, 657 (1981).
3. YASUDA, H., Thin Film Process, VOSSEN, J. L. and KERN, W., Eds., Academic Press, New York, 1978.
4. YASUDA, H., J. Polym. Sci. Macromol. Revs., 16, 199 (1981).

Accepted March 14, 1985

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