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PLASMA POLYMERIZATION OF ORGANIC MONOMERS WITH ADDITION OF I_2

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Key Words: Plasma Polymerization, Organic Compounds, Iodine, Polymer Deposition Rates, Activation Effects

ABSTRACT

Plasma polymerization of several organic compounds under a low pressure was carried out in the presence of a small amount of vaporized iodine (I_2), and the effects were investigated. The polymer deposition rates increased significantly by the addition of I_2, and the promotion of plasma polymerization was indicated. The effects of I_2-addition on the polymerization were evaluated from the deposition rates, which were obtained from the weight increasing profiles of the deposits with the reaction time. Degree of the polymer deposition rate was dependent on the monomer type, and the activation was more prominent for the inherently less reactive monomers in glow discharge plasma;

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e.g., non-polymerizable compounds of ethanol and acetone become polymerized with I_2. The similar activation effects were observed in the plasma polymerization with CH_2I_2 added as an iodine source instead of I_2. Judged from the polymer deposition behaviors and also the changes in the polymer properties, the function of iodine in the plasma polymerization was considered from the two aspects; i.e., the effective activation of polymerization and the incorporation in the polymer deposits.

INTRODUCTION

The process of plasma polymerization of organic compounds, which is carried out under the vacuum condition, is quite different from those of conventional vinyl and condensation polymerization [1, 2]. Electron bombardments to monomer gas molecules take place in a low pressure plasma at first, and the activated species take part in the plasma polymerization. The fact that the dense radicals remain in the polymeric products as detected by ESR [3-6] supports the participation of radicals in the polymer forming steps. The similarities to radiation polymerization have been mentioned, although the process is not feasible under the vacuum condition where plasma polymerization is carried out [7].

Since the ultra-thin polymer membranes with the useful chemical functions are produced by a simplified step in a dry state, much interest has been directed toward such application as the polymer films with electric functions. The electric conductivity of the plasma polymers thus prepared is generally very small, but the polymers become more conductive after doping of a suitable acidic species like iodine. The work on the preparation and the characterization of electrically conductive polymer films by plasma polymerization has been done by many researchers [8-20]. We have also attempted the preparation of conductive polymer films through the simultaneous plasma polymerization of pyrrole (Pyr) with I_2 instead of the I_2-doping after the polymerization [21]. The simultaneous polymerization procedure was employed, being intended to avoid the oxidation of plasma polymers in air before I_2-doping.

During the work, it was interesting to observ that the deposition rates were sometimes much higher than those expected from the formation of the simple polymer adduct structure with iodine. The activation effects by I_2 on the plasma polymerization of monomers were presumed. In other words, the energy transfer to the organic compounds from the activated iodine should take place effectively to lead to the hydrogen extraction from the monomers, which is the initiation step of plasma polymerization. The reaction was attempted with various organic compounds, and the effect of added iodine was investigated to confirm the above presumption.

EXPERIMENTAL

Materials

Three types of organic monomers were used in the present work, i.e., hydorcarbons, N-containing cyclic compounds, and Si-containing monomers with the hexamethyl silyl component. Hydrocarbons included n-hexane (C_6H_{14}, nHex), cyclohexane (C_6H_{12}, cHex) and benzene (C_6H_6, Bz). N-containing monomers included pyrrole (C_4H_5N, Pyr), pyridine (C_5H_5N, Py), pyrrolidine (C_4H_9N, Pyd), and piperidine ($C_5H_{11}N$, Ppd). Si-containing compounds included hexamethyldisilane ($C_6H1_8Si_2$, HMS), hexamethyldisiloxane ($C_6H_{18}Si_{2O}$, HMSO) and hexamethyldisilazane ($C_6H_{19}Si_2N$, HMSZ). Iodine (I2) and diiodomethane (CH_2I_2) were the additive of the plasma polymerization of these compounds.

All the chemicals were purchased from Kanto Chemicals Co. Inc., Tokyo, Japan. The organic monomers were of the reagent grades, and subjected to plasma polymerization as supplied. They were fully degassed in vacuum to remove the dissolved air to prevent oxidation during polymerization.

Plasma Polymerization

(a) Apparatus

Plasma was generated with an inductively coupled discharge of a radio frequency at 13.56 MHz in a reactor made of Pyrex glass tubing (4.4 cm-diameter, 26 cm-length), that was connected to the vacuum line. The configuration of the plasma reactor was designed after the model of the Yasuda's system [e.g., Figure 1 in Reference 22], and the glow was developed into the reactor from the squeezed porting of glass tubing (2.2 cm-ϕ, 22 cm) covered by an RF-coil. Plasma polymers were deposited at the center position of the reactor to obtain the polymer deposition rates. The geometry of a plasma reactor should affect the deposition characteristics.

In the case of the I_2 and CH_2I_2-addition experiments, the additives were introduced from the independent valve, which was located between the main reactor and the squeezed portion of a reactor for RF-discharge generation. The mixing ratio is small, and therefore, the flow condition of the monomers should not be affected principally by the addition of the chemicals.

Vapor pressure of a monomer gas was controlled by the opening of vacuum valves (SS-4BMG, Nupro Co., Ohio). In the experiments of plasma polymerization of organic monomers with I_2- and CH_2I_2-addition, the vapors were introduced through the other valve separated from the monomer supply valve.

(b) Polymerization Procedure

Plasma polymerization of the monomers was carried out generally as follows except otherwise noticed. The hydrocarbons and N-containing monomers were supplied at the flow pressure of 5.0 Pa, which was corresponding to the flow rate of 3.8-3.9 cm^3 (STP)/min. The monomer vapor of Si-monomers, that are more polymerizable for the -Si-coupling effects, were polymerized at the rate of 1.34 cm^3 (STP)/min (or at the pressure of 2.0 Pa). Here, the monomer flow rate (cm^3(STP)/min) was calculated from the pressure-time relationship, which was obtained after closing the stopcock of the pumping site.

The additives of I_2 and CH_2I_2 were introduced at the flow rate of 0.1 cm^3 (STP)/min, and the polymerization was carried out in the mixture systems. Plasma polymerization of these monomer mixtures was carried out at 50 W except for the power dependence experiments.

(b) Polymer Deposition Rate

Plasma polymers were formed on a cover glass plate (2.2 cm × 2.2 cm) placed on the reactor wall. The deposits were weighed after a fixed period of, 20, 40, and 60 minutes, respectively, and the polymer deposition rates ($mg/cm^2/min$) were calculated from a slope of the weight increasing profile plotted against the reaction time. The degree of plasma polymerization was judged from the polymer deposition rates.

Evaluation of Plasma Polymers

Plasma polymers were deposited on KBr discs, and infrared spectroscopy was taken with a FT-IR apparatus (Paragon-1000, Perkin-Elmer). Thermal degradation behaviors of the polymers were evaluated under N_2 with a TG-DTA apparatus (Themo Plus TG8120, Rigaku, Tokyo).

RESULTS AND DISCUSSION

Plasma Polymerization in the Presence of I_2

The vapor of I_2 itself provided a strong glow with yellow color running through the whole space of the reactor even at the low applied power of discharge. When plasma polymerization of an organic monomer was carried out in the mixture with I_2-vapor, the polymer deposition took place effectively and the dark films were obtained. The appearance as well as the increase in the weight of deposits suggests the incorporation of iodine in the plasma polymers. The weight increase was, however, sometimes much greater than that expected from the simple adducts with iodine. Plasma polymerization was carried out with several types of monomers of different reactivity in plasma, and the effect of iodine during polymerization was investigated.

(a) Hydrocarbons

The reactivity in plasma is much influenced by the unsaturation number of a monomer [23]. Hydrocarbons with the similar size of molecular weight but with the different unsaturation number were selected, and the addition effects of I_2 on plasma polymerization were investigated. Figure 1-(a) and (b) show the reaction time dependence of the deposited weight of the C_6-hydrocarbons (nHex, cHex, and Bz) by plasma polymerization with and without I_2-addition. The

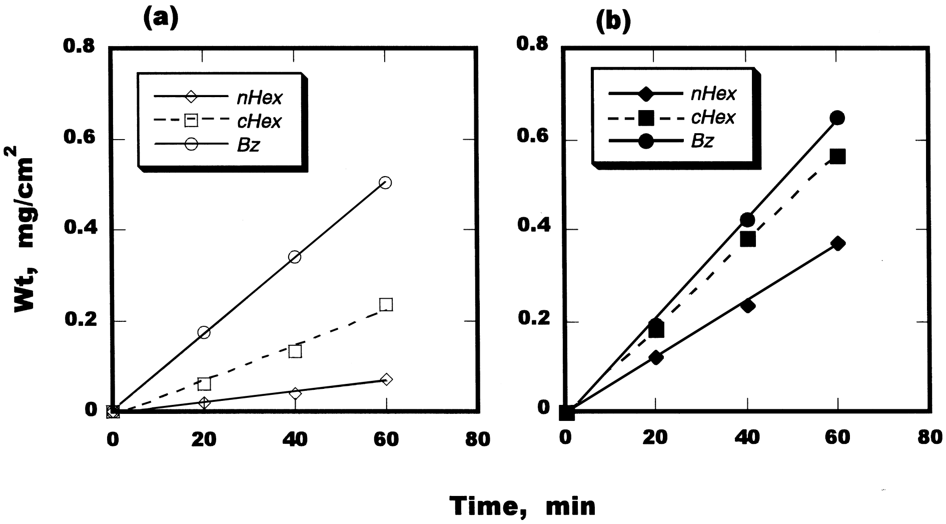

Figure 1. Polymer deposition of nHex, cHex and Bz by plasma polymerization at 50 W, respectively without (a) and with I_2-addition (b). Monomers were supplied at the flow rate of 3.8 cm^3 (STP)/min, and I_2 at 0.1 cm^3(STP)/min.

amount of polymer deposition increased linearly with the reaction time, and the polymer deposition rate calculated from the slope was, 1.1 x 10^{-3}, 3.7 × 10^{-3} and 8.5 × 10^{-3} mg/cm^2/min for nHex, cHex and Bz, respectively. When the polymerization was carried out in the presence of I_2, the rates increased to 6.1 x 10^{-3}, 8.5 × 10^{-3} and 10.7 × 10^{-3} mg/cm^2/min, respectively.

The deposition rate was the highest for the unsaturated aromatic compound of Bz in both cases of plasma polymerization with and without I2-addition. However, from the aspect of the increasing degree of the deposition rates, the effect was more prominent on the reaction of nHex, which is originally less reactive in plasma. The rate was about 5.54 (= 6.1 × 10-3 /1.1 × 10-3) times greater for nHex by the plasma polymerization with I2, while that was 1.26 (= 10.7 × 10-3 /8.5 × 10-3) times greater for Bz.

Polymer deposition rate of a monomer should be related with the mass of a gas molecule, which is determined by both the flow rate and the molecular weight. Although the molecular weight of I_2 (254) is much greater than those of C_6-hydrocarbons (78–86), the supplied rate of I_2-vapor was small and therefore the mass flow rate was still smaller. The deposition rates of these compounds were higher than those expected from the copolymerization by iodine, and the deposition behaviors could not be explained solely by the incorporation of iodine in the polymers.

In order to clarify the activation effects, the amount of I_2 was changed and the influences on the plasma polymer deposition rates were investigated. Figure 2 shows the results with these hydrocarbons. Monomer vapors were supplied at the flow rate of 3.8 cm^3 (STP)/min, and plasma polymerization was run at 50 W. The vapor pressure of I_2 is low by nature, so that the flow rate into the reactor could not be increased so much. The addition range of I_2 to the system was therefore restricted, but the effects of I_2 on plasma polymerization could be pointed out. The result indicates that the deposition rate increased with the increasing flow rate of I_2, and then reached a certain level beyond the flow rate of ca. 0.1 cm^3 (STP)/min.

(b) Discharge Power Dependence

The phenomenon suggests the activating effects of I_2 during plasma polymerization of these hydrocarbons, besides the formation of the adduct structure. In order to see the effects from the quantitative view, the discharge power dependence was studied. Discharge power is, of course, related with the energy applied to the system. Monomers with the higher reactivity can be polymerized

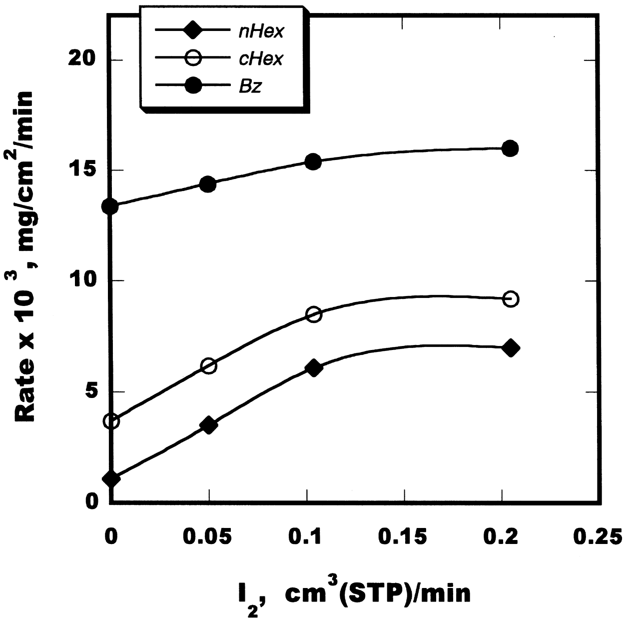

Figure 2. Dependence of the deposition rates of nHex, cHex and Bz on the flow rate of I_2 added for the plasma polymerization; the flow rate at 3.8 cm^3(STP)/min, power at 50 W.

in plasma under the low power condition.

Although the pressure reading should be somewhat changed depending on the system configuration of the pressure meter, the pressure in the reactor during plasma polymerization is the important indication of the reactivity of monomers and reflects the degree of hydrogen release by plasma. For example, when nHex and Bz introduced at the initial pressure of 5.0 Pa, respectively were reacted at 50 W, the system pressure during discharge changed to 12.8 Pa and 2.9 Pa. The higher pressure of nHex is related with the released amount of hydrogen from the more saturated structure. When the monomers were reacted in the presence of small amount (0.1 Pa) of I_2, the system pressure of the mixture changed and reached 15.2 Pa and 6.1 Pa, respectively. At present, the identification of the species of the product gases has not been undertaken, but the increase of the pressure should indicate the effective removal of hydrogen from the hydrocarbons and other supplied monomers. The fact should result in the effective plasma polymerization process of monomers by the addition of I_2.

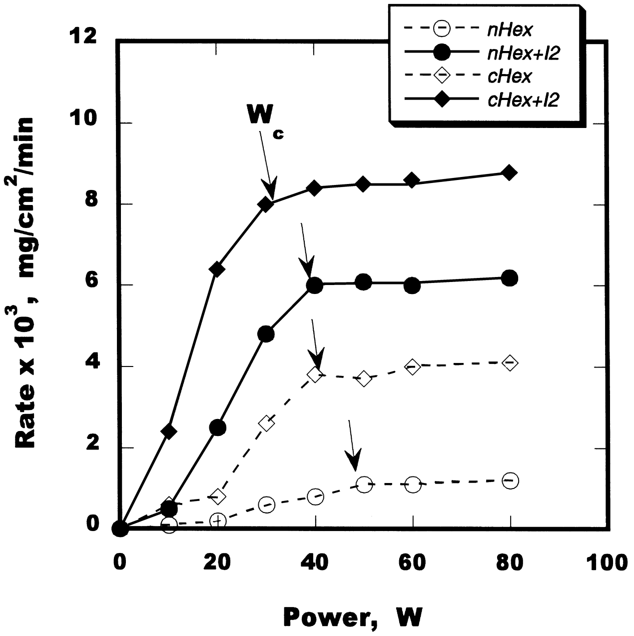

Figure 3. Discharge power dependence of the plasma polymer deposition rates of nHex and cHex (flow rate; 3.8 cm^3 (STP)/min), respectively with and without I_2.

The discharge power dependence of plasma polymer deposition rates is shown in Figure 3, respectively for nHex and cHex (3.8 cm^3 (STP)/min) with and without I_2. The deposition rate increased at first with the increase of discharge power, and then reached a saturated level. (The lower rate at the low discharge power was related with plasma polymerization under the insufficient power condition.) An important point to be noted in the results is that the lowest effective power for plasma polymerization of a monomer decreased with the I_2-addition. In other words, the plasma polymerization was achieved under the lower energy level.

The critical power (Wc) for plasma polymerization is defined as the lowest point of the power for plasma polymerization, which reaches the saturated level of polymer deposition. The activation effect of I_2 may be more clearly seen by Wc, and the plasma polymerization takes place effectively by the I_2-addition under the lower power input; e.g., Wc decreased from 50 W to 40 W for nHex, and from 40 W to 30 W for cHex. It is thus confirmed that the monomers are activated with I_2 in plasma, judged from the power dependence profile.

(c) N-containing Cyclic Compounds

The plasma polymerization of N-containing cyclic compounds has been investigated for the application to electrically conductive membranes [18, 19], reverse osmosis membranes [24], etc. DC plasma polymerization of Pyr was also carried, and the product films formed on the anode and the cathode were characterized by van Ooij *et al*. [25, 26]. The polymers of Pyr formed on the anode were less crosslinked than the products on the cathode, and the role of positive ion in modifying the structure of the Pyr plasma polymer has been suggested.

The N-containing monomers of Pyr, Py, Pyd and Ppd were used, and the effects of I_2-addition on the plasma polymerization were investigated. Pyr and Py are composed of the unsaturated structure, and Pyd and Ppd the saturated cyclic structure. The higher reactivity of the compounds with unsaturated structure was evident from the comparison of the deposition rates. The polymer deposition rates were carried out under the same flow rate and power condition. The rate was 8.8×10^{-3} mg/cm^2/min and 14.4×10^{-3} mg/cm^2/min, respectively for Pyr and Pd, while that was 5.7×10^{-3} mg/cm^2/min and 6.7×10^{-3} mg/cm^2/min for Pyd and Ppd. Naturally, the molecular weight of the starting monomer influenced the polymer deposition rates. It should be also noticed that the deposition degree is dependent on the monomer structure, and the unsaturated monomers are more polymerized in glow discharges. The higher polymerization degree of the unsaturated monomers (Py and Pyr) is evident when the rates are compared with those of the corresponding saturated monomers (Pyd and Ppd). Unsaturated monomers of Py and Pyr gave in general the tight polymer films by plasma polymerization composed of the more carbonized structure with dark color.

The formation of the composites with I^- is supposed as the intermediate process in the plasma polymerization of these N-containing monomers. The effect of I_2 is clear when the deposition rate was compared with those of hydrocarbons; e.g., Py vs. Bz. The original deposition rate of 7.0×10^{-3} and 13.5×10^{-3} mg/cm^2/min respectively for Py and Bz, became 14.4×10^{-3} and 15.4×10^{-3} mg/cm^2/min with the plasma polymerization added by I_2. Thus, the accelerating is evident for the N-containing compound of Py, as the increasing degree of the deposition rate was much greater.

According to the discharge power dependence, the effect of I_2-addition was clear again with the experimental results using these N-containing compounds. The Wc value decreased in the polymerization with I_2, and the accelerating effect, that was similar to those for the hydrocarbons as shown in Figure 3, was observed. For example, Wc decreased from 50 W to 40 W for Pyd and 30 W to 20 W for Pyr in the plasma polymerization with I_2. The same trend was observed with the combination of Ppd and Py.

(d) Comonomer System with HMSO

Plasma polymers from the Si-containing monomers have some useful properties in the mechanical and chemical stability, which is advantageous in the application for the various purposes [27-30]. The effects of I_2-addition were investigated with some Si-containing monomers (HMSO, HMS and HMSZ). These Si-monomers were supplied at the flow rate of ca. 1.34 cm^3 (STP)/min, and the polymerization was carried out at 50 W. (The flow rates lower than other cases were taken for the full polymerization of these Si-monomers. As the molecular weight of these monomers was larger than the other compounds investigated in the present work, more energy was necessary for the completion of polymerization. Flow rates were decreased instead of the discharge power increase.)

Under the polymerization condition, the deposition rate of 5.6×10^{-3}, 5.5×10^{-3}, and 5.8×10^{-3} mg/cm^2/min was obtained, respectively. The rate changed to 7.5×10^{-3}, 8.4×10^{-3}, and 8.9×10^{-3} mg/cm^2/min for the polymerization with I_2, which is 30-50% increase. The Si-compounds are originally reactive, and as a result, the polymerization accelerating effects of I_2 should be comparatively smaller.

Next, the plasma polymerization of the comonomer system of HMSO-nHex was carried out and the effect of I_2-addition was examined. The acceleration effects were more clearly confirmed also with this comonomer system. The flow rate of nHex was changed, while that of HMSO was fixed at 1.34 cm^3 (STP)/min. The dependence of polymer deposition rates on the relative flow rate of nHex was investigated at the power of 50 W (Figure 4). The increase of these polymer deposition rates was observed in the plasma polymerization with the addition of I_2, while the deposition rates decreased slightly at the flow rate of nHex higher than 3.0 cm^3 (STP)/min in case of the mixture system of HMSO-nHex.

Plasma copolymerization was attempted also with some heterocyclic compounds. Monomer mixture of HMSO (1.34 cm^3(STP)/min) with Pyr (3.8 cm^3(STP)/min) was subjected to glow discharge at 50 W, and the plasma polymerization with and without the I_2-addition was compared. The data of the polymer deposition rates are summarized in Table 1, respectively for the polymeriza-

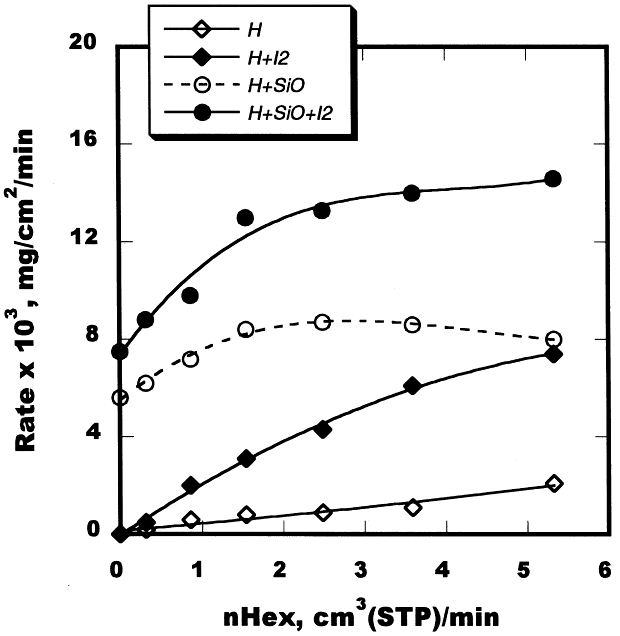

Figure 4. Dependence of the flow rate of nHex (H) on the plasma copolymerization rate of HMSO (SiO) at the flow rate of 1.34 cm^3 (STP)/min with and without I_2 at 50 W.

TABLE 1. Comparison of the Polymer Deposition Rates of HMSO-Pyr at the Power of 50 W

			HMSO+Pyr	
	(1) HMSO 1)	(2) Pyr 2)	(3) calct. 3)	(4) actual
Without I_2	5.6×10^{-3}	8.6×10^{-3}	14.2×10^{-3}	12.8×10^{-3}
With I_2 4)	7.5×10^{-3}	13.7×10^{-3}	21.2×10^{-3}	21.8×10^{-3}

1) At the flow rate of 1.34 cm^3(STP)/min.

2) 3.8 cm^3(STP)/min.

3) Added value of the rates of HMSO (1) and Pyr (2).

4) 0.1 cm^3(STP)/min.

tion with and without I_2-addition. The rates given by the mixture system of HMSO-Pyr are put respectively for the actual data and the calculated data, which were obtained from the summation of the each rate of HMSO and Pyr. The actual polymer deposition rate of the monomer mixture of HMSO+Pyr was 12.8 × 10^{-3} mg/cm^2/min, and the value was somewhat smaller than the calculated value from the sum of the each rate of HMSO and Pyr (14.2 × 10^{-3} mg/cm^2/min). On the other hand, the actual rate was comparable to the value from the polymerization with I_2. The rate of the plasma polymerization of Pyr + SiO with I_2 was 21.8 × 10^{-3} mg/cm^2/min, while the calculated rate for Pyr-I_2 and SiO-I_2 was 21.2 × 10^{-3} mg/cm^2/min. The activation of the plasma polymer deposition by the I_2-addition became evident again in the mixture system.

(e) Alcohol and Ketones

Alcohols and ketones are hard to form polymer deposits, although they contain the useful functional groups of –OH and C=O. Those monomers are apt to decompose through the oxygen detachment in glow discharge plasma. However, when the compounds were reacted with I_2-vapor in plasma, the polymerization proceeded and the dark deposits were formed.

Methanol (Me), ethanol (Et), and acetone (Ac) were used, and the polymer deposition behaviors by plasma polymerization with I_2-addition were investigated (Figure 5). The results were compared with a case of nHex as described previously. The deposition rate with I_2-addition was estimated as 1.2 × 10-3, 2.8 × 10-3, and 3.3 × 10-3 mg/cm^2/min, respectively, for Me, Et and Ac. The order of deposition rate corresponds to the carbon number of the supplied compounds.

Effects of CH_2I_2

Diiodomethane (CH2I2) was used as an iodine source instead of I_2, and the effects of the addition on the plasma polymerization of organic monomers were investigated. Some differences between I_2 and CH_2I_2 in the behavior under glow discharge should be pointed out. The glow discharge was not as strong as that of I_2, but a small amount of polymer deposit was formed from CH2I2 itself.

The accelerating effect of plasma polymerization of organic monomers was also observed with the addition. Plasma polymerizations with Et and also Ac confirmed the ability. The flow rate of CH_2I_2 was fixed at the same value as that of I_2 investigated previously, and the behaviors of polymerization was compared under the same monomer supply and power condition. The polymer depo-

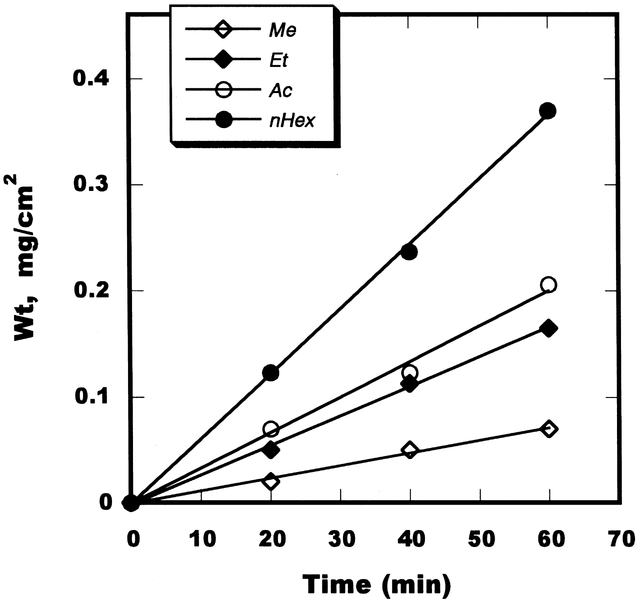

Figure 5. Plasma polymer deposition of methanol (Me), ethanol (Et), acetone (Ac), and nHex with I_2 at 50 W; the flow rate of organic compounds at 3.8-3.9 cm^3 (STP)/min, and that of I_2 at 0.1 cm^3 (STP)/min.

sition rates were estimated as 2.1×10^{-3} and 2.8×10^{-3} $mg/cm^2/min$, respectively for Et-CH_2I_2 and Ac-CH_2I_2.

The activation effect was, however, somewhat smaller compared to that of the polymerization with I_2, even though the additive of CH2I2 contains the carbon portion that can be incorporated in the polymer products through copolymerization. The fact may suggest the other prevailing function of these additives rather than the activity as a simple comonomer.

Deposition Rate vs. Hydrogen Number Ratio in a Monomer

The participation of the activated I_2 on the initiation of plasma polymerization has been described above. The hydrogen detachment from a monomer plays an important role in the excitation [31]. The relationship was taken between the polymer deposition and the hydrogen ratio in a monomer, and the effects of I_2-addition on polymerization were evaluated. The results obtained in the present work are summarized in Figure 6, respectively for the plasma poly-

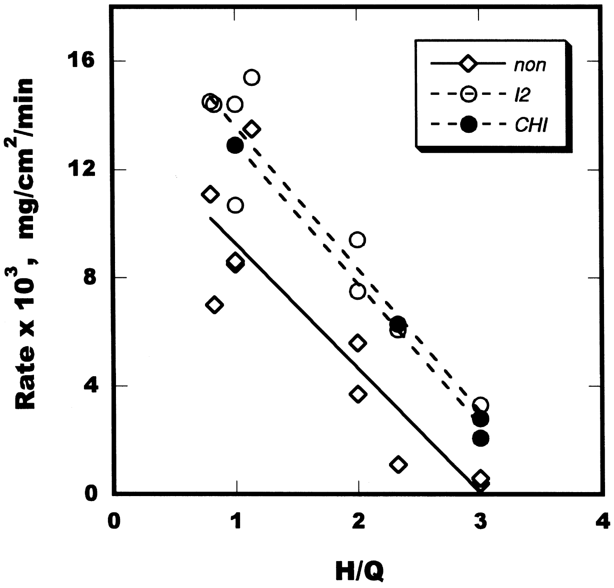

Figure 6. Relationship between the deposition rate and the hydrogen ratio (H/Q) of monomers, respectively for plasma polymerization at 50 W with and without the I_2- and CH_2I_2-addition. The flow rate of organic monomers was ca. 3.8 cm^3 (STP)/min, and I_2 and CH_2I_2 , was added at the rate of 0.1 cm^3 (STP)/min.

merization with and without I_2- and CH_2I_2-addition. In the Figure, H is the number of hydrogen in a monomer molecule, and Q the total number of C, O, and N, which will compose the predominant portion of the polymer deposits. For example, the H/Q value is 6/6 = 1.00 for Bz, and 14/6 = 2.33 for nHex. Thus, the greater value of H/Q of a monomer implies the more saturated structure with hydrogen. It was shown that the polymerization rate of the compounds was reciprocally related with the H/Q values.

Kobayashi *et al.* compared the hydrogen/carbon ratio in the plasma polymers with that in the corresponding monomers, and reported the ratio ranging from 0.52 to 0.95 [32]. Hydrogen was released excessively during the plasma polymerization process, and the higher energy was necessary for the stable glow discharges to sustain the activation of the released hydrogen. The dissociation of C-H is necessary for the effective polymerization of monomers in the plasma. The hydrogen ratio in a hydrocarbon monomer plays an important role in the plasma polymerization.

Polymerization Mechanism of Monomers with I_2

The increase of polymer deposition rate was evident for both the additions of I_2 or CH_2I_2 in the plasma polymerization. It is suggested that the activated iodine, as used in the present experiments, functions to release hydrogen and sustain the plasma during polymerization.

Glow discharge intensity became stronger when smaller amount of I_2 exists in the plasma polymerization field, and this related with the polymer deposition rates becoming higher. The ionization energy level of I_2 is lower than those of the conventional hydrocarbons [33]. The energy transfer from the more easily activated iodine to the supplied monomers was considered for the activation of polymerization. Kruse *et al.* have investigated the plasma polymerization of 2-iodothiophene, and suggested the effects of released iodine from the monomer during the plasma reactions [16]. Iodine attached to thiophene ring is dissociated effectively in plasma, and the activated iodine ions and/or radicals should participate in the propagation of plasma polymerization. Quite the similar effects are expected with the plasma polymerization of organic monomers with I_2.

When the ionization energy of halogen containing ethylene derivatives are compared, the energy for dehalogenation is lower than that for dehydrogenation [7]. Halogen containing compounds such as C_2H_3Cl, C_2H_3F and C_2F_4 were used, and their behaviors on plasma polymerization were investigated [34]. The higher reactivity has been discussed from the aspect of the effective activation of the molecules through the feasible release of halogens in plasma.

The role of the participation of the released halogens in the formation of radical intermediates has also suggested in these reports. The same mechanism should be true in the plasma polymerization of the composite monomers system with I_2 or CH_2I_2.

Some Aspects of the Product Polymers

The polymer network and the morphology should have also been changed by the polymerization of the organic monomers carried out in the presence of I_2. The plasma polymer films prepared in the mixture gas of Pyr-I_2 became electrically more conductive than the Pyr plasma polymer [21]. The fact supports the formation of the ionic complex structure with iodine, which is taking place concurrently with the activation of monomers for polymerization.

Actually, the formation of a chemical bond of C-I, which should appear in the lower wave number range of 600-500 cm^{-1} in the infra-red spectra [35], could not be excluded. It was suggested in the plasma polymer from 2-iodothiophene that iodine is incorporated in the forms of I_3^- and I_5^- ions, or in the covalent bonds [16]. The same structure is expected in the present polymers, although the reaction type is different.

Plasma polymers prepared with the addition of I_2 were thermally stabilized sometimes, according to the thermal gravimetry studies. As stated previously, the effects of I_2 was comparatively smaller in the plasma polymerization of HMSO, but the plasma polymers formed in the presence of I_2 were less degraded under heating. The weight loss of a plasma polymer which was prepared in the composition of HMSO-I_2 was about 6% by the heating up to 500 °C, while that of the plasma polymers of HMSO alone was 26%. This indicates that the polymer network of HMSO was formed with the tighter structure.

CONCLUSION

Plasma polymerization of monomers was carried out with the addition of I_2 or CH_2I_2, and the increase in the polymer deposition rates was observed. Iodine was indeed incorporated in the polymer, and the properties of the product polymer were changed from those of polymers produced without I_2-addition. The increasing degree in the polymer deposition rate was more prominently observed in the plasma polymerization of less polymerizable hydrogen-rich monomers. From the fact, the activation of monomers by the excited states of these additives was indicated to be the effectual factor.

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