Polymer Bulletin 22, 15–20 (1989)

Polymer Bulletin

Plasma polymerization of fluorobenzenes/SO_2 mixtures

N. Inagaki*, S. Tasaka, and T. Kurita

Laboratory of Polymer Chemistry, Faculty of Engineering, Shizuoka University,
3-5-1 Johoku, Hamamatsu, 432 Japan

Summary

Plasma polymerization of mixtures of fluorobenzenes (perfluorobenzene (PFB), pentafluorobenzene (PnFB), and tetrafluorobenzene (TFB)) and sulfur dioxide (SO_2) is carried out for preparation of plasma polymers containing both fluorine and sulfur moieties. The chemical composition of the polymers is inspected by FT/IR and XPS, and the ion-exchange capacity and the electrical conductivity are measured. Plasma polymers prepared from these mixtures are fluro polymers with either of sulfonic acid or sulfinic acid groups. The ion-exchange capacity is 0.49 (for polymers from the PFB/SO_2 mixture), 0.94 (for those from the PnFB/SO_2 mixture), and 1.31 meq/g-polyer (for those from the TFB/SO_2 mixture). The electrical conductivity at a relative humidity of 70 %RH is 8.3 x 10^{-9}, 3.6 x 10^{-7}, and 4.3 x 10^{-5} S/cm, respectively.

Introduction

Fluoropolymers are distinguished from polyolefines in hydrophobicity, temperature and chemical resistance, dielectric constant, index of refraction, coefficient of friction. These properties mainly result from the electronic state of fluorine atom [1]. When hydrogen atoms of carboxylic acids and sulfonic acids are substituted with fluorine atoms the large electron negativity (inductive effect) of fluorine atom accelerates the ionization and makes them strongly acidic. For example, the ionization constant (1.8 x 10^{-5}) of CH_3COOH increases to 2.2 x 10^{-3} for CH_2FCOOH, 5.7 x 10^{-2} for CHF_2COOH, and 5.9 x 10^{-1} for CF_3COOH [1].

Plasma polymerization is one of thin-film processes. Thin films are directly deposited on substrate surfaces without fabrication. Molecules introduced into plasma are activated and fragmented by action of electrons, radicals, and ions, and then two activated fragments recombine stepwise to form a larger molecules. The repetition of the activation, fragmentation, and recombination brings about the polymer deposition. Essentially all the elements present in the plasma are able to be polymerized. This concept suggests that when a mixture of two different molecules is introduced into the plasma the deposited polymers will contain the elements of the two molecules.

An aim of this study is to prepare plasma polymers which contain both fluorine and sulfur moieties and which behave as strong acids. Plasma polymerization of mixtures of fluorocarbons and sulfur dioxide is investigated.

---

*To whom offprint requests should be sent

Experimental

The reaction system used in this study for plasma polymerization was an inductively coupled system where a glow discharge was operated at a frequency of 13.56 MHz. The detail of the reaction chamber made of Pyrex glass (100 mm inner diameter, 400 mm long) and the experimental procedures for plasma polymerization have been given in a literature [2]. Plasma polymerizations were conducted at an electric power (13.56 MHz) of 100 W at a monomer flow rate of 4 cm^3(STP)/min, at a system pressure of 1.3 Pa for 0.5 - 1.0 h. Perfluorobenzene (PFB), pentafluorobenzene (PnFB), tetrafluorobenzene (TFB) (purchased fro Fluorochem Ltd., U.S.A., more than 97 % purity), hexafluoropropene (HFP), and sulfur dioxide (SO_2) (purchased from Takachiho Trading Co., Japan, 99.9 % purity) were used as monomers. Prior to the plasma polymerization PFB, PnFB, and TFB were degassed three times by evaporation under liquid nitrogen cooling.

IR spectra were recorded with a Nihon Bunko fourie transform spectrometer FT/IR-3. 1000 Scans were recorded on each sample and the spectral resolution for the IR measurement was 2 cm^{-1}. XPS spectra (C_{1s} and S_{2p} core levels) were recorded with a Shimadzu electrospectrometer employing Mg Kα exciting radiation and were deconvoluted with a Shimadzu ESCAPAC 760 data system.

The C and H content of the plasma polymers were determined with a Yanagimoto CHN analyzer MT-2. The F and S contents were determined by the alizarine complex method [3] and the Shoniger's flash combustion method [3], respectively. The O content was the difference between the sample weight and the sum of the C, H, F, and S content determined.

Results and Discussion

Polymer Deposition Rate

Plasma polymerization of the PFB/SO_2, PnFB/SO_2, TFB/SO_2, and HFP/SO_2 mixtures deposited light-brown films. Figure 1 shows the polymer deposition rate as a function of the SO_2 concentration in the starting mixtures. In the PFB/SO_2 and HFP/SO_2 mixture systems the polymer deposition rate decreased with increasing the SO_2 concentration. Especially, the HFP/SO_2 mixture containing more than 20 mol% SO_2 showed no polymer-deposition. While, in the PnFB/SO_2 and TFB/SO_2 mixture systems the polymer deposition rate increased (at 25 mol% SO_2) and afterward decreased with increasing the SO_2 concentration. This figure indicates that the PFB/SO_2, PnFB/SO_2, and TFB/SO_2 mixture systems are adequate monomers in respect of large polymer-deposition and that hydrogen substituents of fluorobenzenes contribute the formation of plasma polymers. The polymer-deposition rate in plasma polymerization of the PFB/SO_2, PnFB/SO_2, and TFB/SO_2 mixtures containing 75 mol% SO_2 was 2.5, 4.0, and 14.3 μg/cm^2min, respectively.

Elemental Composition of Plasma Polymers

The plasma polymers prepared from the PFB/SO_2, PnFB/SO_2, and TFB/SO_2 mixtures were mainly composed of carbon, fluorine, oxygen, and sulfur atoms. The elemental composition depended on the nature of the used fluorobenzenes and the mixture composition. The atomic ratios (F/C, S/C, and O/C) of the plasma polymers prepared from the PFB/SO_2 mixture remained constant 0.65 - 0.67, 0.21 - 0.27, and 0.10 - 0.13, respectively, independently of the SO_2 concentration, while the ratios of the plasma polymers prepared from the PnFB/SO_2 and TFB/SO_2 mixtures depended on the SO_2 concentration. When the SO_2 concentration of the PnFB/SO_2 mixture changed from 25 to 75 mol% the F/C atomic ratio decreased from 0.57

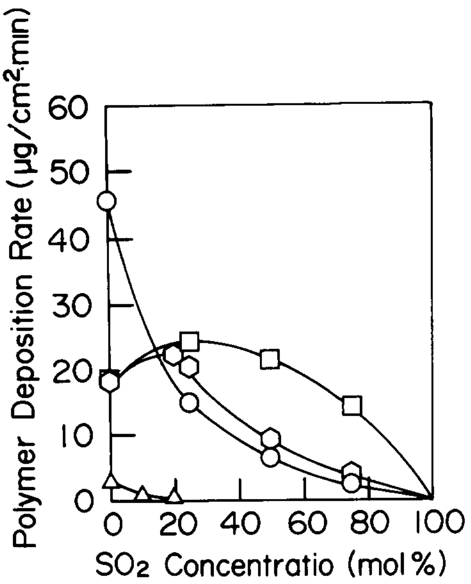

Fig. 1 Polymer deposition rate as a function of SO_2 concentration; ○, in plasma polymerization of PFB/SO_2 mixture; ⬡, in plasma polymerization of $PnFB/SO_2$ mixture; □, in plasma polymerization of TFB/SO_2 mixture; △, in plasma polymerization of HFP/SO_2 mixture.

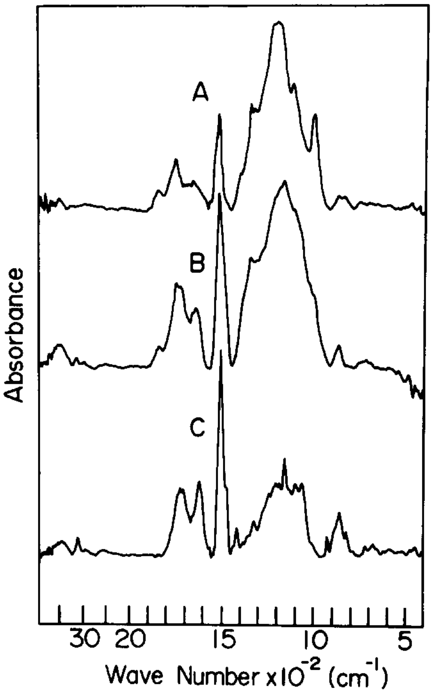

Fig. 2 IR spectra of plasma polymers prepared from PFB/SO_2 (A), $PnFB/SO_2$ (B), and TFB/SO_2 (C) mixtures containing 75 mol%SO_2.

to 0.46, and the S/C and O/C atomic ratios increased from 0.06 to 0.27 and from 0.18 to 0.46, respectively. The plasma polymerization of the TFB/SO_2 mixture also showed similar changes in the F/C, S/C, and O/C atomic ratios. (the F/C atomic ratio changed from 0.49 to 0.13, the S/C ratio from 0.07 to 0.34, and the O/C ratio from 0.03 to 0.36.)

Chemical Structure of Plasma Polymers

Figure 2 shows typical IR spectra of the plasma polymers prepared from the PFB/SO_3, $PnFB/SO_2$, and TFB/SO_2 mixtures. Characteristic absorption peaks due to fluorine and sulfur moieties can be observed in these IR spectra. The plasma polymers prepared from the PFB/SO_2 mixture containing 75 mol%SO_2 show intense absorption peaks at 1733 (C=O and CF_2=C groups), 1640 (CF=CF groups), 1500 (fluorinated phenyl rings), 1330 (SO_2 asymmetric stretching vibration), 1100 (C-F stretching vibration), and 990 cm^{-1} (unknown), and a broad absorption peak at 1230 - 1150 cm^{-1}. The plasma polymers from the $PnFB/SO_2$ mixture containing 75 mol%SO_2 show intense absorption peaks at 1740 (C=O and CF_2=C groups), 1640 (CF=CF groups), 1500 (fluorinated phenyl rings), and 1335 cm^{-1} (SO_2 asymmetric stretching vibration), and a broad absorption peak at 1250 - 900 cm^{-1}. The plasma polymers prepared from the TFB/SO_2 mixture containing 75 mol%SO_2 show intense absorption peaks at 1720, 1700 (C=O and CF_2=C groups), 1620 (CF=CF groups), 1500 (fluorinated phenyl rings), 1150 (C-F groups), 1090 (S(O)OH groups), 1055 (S=O groups), and 857 cm^{-1} (unknown).

These IR spectra suggest that the plasma polymers prepared from the PFB/SO_2, PnFB/SO_2 and TFB/SO_2 mixtures possess fluorinated phenyl rings, fluoro carbon groups, and sulfur moieties. The relative intensity of the IR absorption peak at 1500 cm^{-1} (fluorinated phenyl rings) is the plasma polymers prepared from the TFB/SO_2 mixture > those from the PnFB/SO_2 mixture > those from the PFB/SO_2 mixture. This indicates that the plasma polymers from the TFB/SO_2 mixture contain much amounts of fluorinated phenyl rings, while the plasma polymers from the PFB/SO_2 mixture contain a little amount of fluorinated phenyl rings. Hydrogen substituents retard the cleavage of phenyl rings in a glow discharge state to be plasma-polymerized.

Empirically, absorption peaks in ranges of 1300 - 1000 cm^{-1} give information of the chemical structure of fluoro carbons and sulfur moieties. Bellamy [4] reported the frequency shift of C-F stretching vibration. The absorption peak appears at 1072 cm^{-1} for CF groups, at 1155 and 1095 cm^{-1} for CF_2 groups, and at 1210 and 1102 cm^{-1} for CF_3 groups. The S=O stretching vibration is shifted by oxidation number of sulfur atoms [4]. The vibration peak appears at 1390 and 1205 cm^{-1} for SO_3 groups, at 1300 and 1135 cm^{-1} for SO_2 groups, and 1190 and 1050 cm^{-1} for SO groups. And SO_3H and S(O)OH groups show the absorption peak at 1175 and 1090 cm^{-1}, respectively. However the details of fluoro carbons and sulfur moieties could not be determined from only the IR absorption inspection because the absorption peaks due to C-F and S=O stretching vibrations overlap and broad IR spectra in ranges of 1300 - 1000 cm^{-1} are too less qualitive to be assigned. The assignment of the fluoro carbons and sulfur moieties in the plasma polymers needs help by other chemical analyses.

The details of the fluoro carbon and sulfur moieties were inspected by XPS. The C_{1S} core level spectra for the plasma polymers distributed widely in ranges of 283 - 296 eV and had four separated peaks. The C_{1S} spectra were deconvoluted into five or six components by the curvefitting procedure. Each of the deconvoluted components is represented in dashed lines in Figure 3. The assignment of the deconvoluted components were made on the basis of substituent effects studied by Clark and Feast [5]. The chemical shifts of the C_{1S} core level are 2.9 and 0. 7 eV for the primary and secondary effect of fluorine substituents at α and β carbon position, respectively. From the chemical shifts the component appearing at 293.7 - 295.1 eV (component I) is assigned to CF_3 groups having a variety of environments ranging from $-CH_2-\underline{C}F_3$ to $-CF_2-\underline{C}F_3$ groups. Similarly, the components from 290.8 - 293.6 eV (component II), from

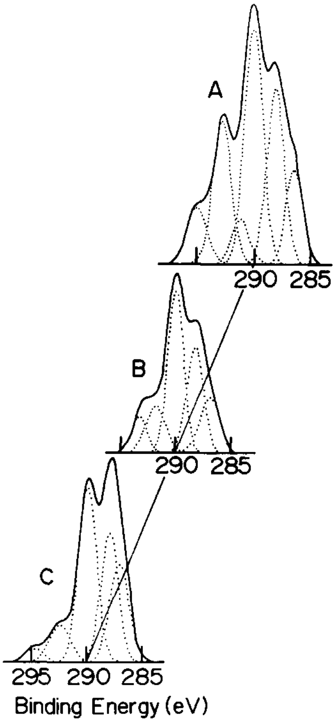

Fig. 3 XPS(C_{1S}) spectra of plasma polymers prepared from PFB/SO_2 (A), PnFB/SO_2 (B), and TFB/SO_2 (C) mixtures containing 75 mol%SO_2.

287.9 - 290.7 eV (component III), and from 285.0 - 287.8 eV (component IV) are assigned to CF_2, CHF, and hydrocarbon-like carbon, respectively. However the component III and IV involve the contribution of C=O and C-S groups, respectively, because the plasma polymers contain oxygen and sulfur moieties. Results of the deconvolution, summarized in Table 1, indicate that the plasma polymers from the PFB/SO_2 mixtur are rich in the highly-fluorinated carbon groups (component I and II), while the plasma polymers from the TFB/SO_2 mixture are rich in the low-fluorinated carbon groups (component III and IV).

Table 1 Relative Concentration of Fluorocarbons of Plasma Polymers prepared from PFB/SO_2, $PnFB/SO_2$, and TFB/SO_2 Mixtures

Starting Mixture	SO_2 Conc. (mol%)	Conc. of Component (mol%) Comp. I	Comp. II	Comp. III	Comp. IV
PFB/SO_2	75	9.9	25.2	53.2	11.7
$PnFB/SO_2$	75	-	21.4	62.7	15.9
TFB/SO_2	75	3.2	9.4	64.7	22.7

The S_{2P} core level spectra for the three plasma polymers showed a single peak with a FWHM value of 2.6 eV (Figure 4). The peak for the plasma polymers prepared from the PFB/SO_2, $PnFB/SO_2$, and TFB/SO_2 mixtures containing 75 mol%SO_2 is 168.2, 166.0, and 166.0 eV, respectively. Lindberg and Hanrin [6] reported the substituent effect of sulfur groups on the chemical shift of S_{2P} core levels. The S_{2P} core level is shifted to high binding energy regions by increasing the oxidation number: 163.7 - 163.9 eV for SH and SCH_3, 165.9 - 166.0 eV for $S(O)CH_3$ and SO_2Na, 168.2 - 168.5 eV for SO_3Na and SO_2OCH_3, and 169.8 - 170.2 eV for SO_2F groups.

From this reference it can be assumed that sulfur moieties of the plasma polymers prepared from the PFB/SO_2 mixture are in a highly oxidized state (SO_3) and that those of the plasma polymers prepared from the $PnFB/SO_2$ and TFB/SO_2 mixtures are in a low oxidized state (SO or SO_2).

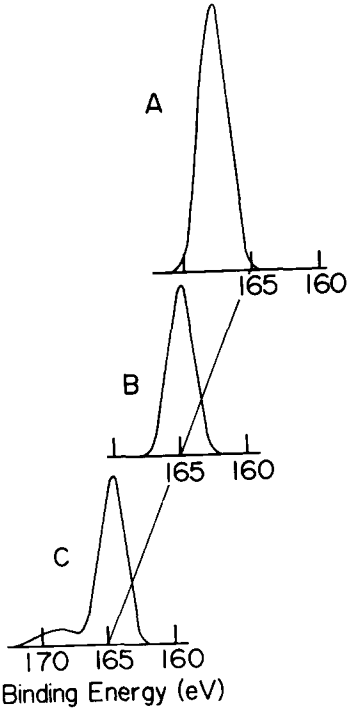

Fig. 4 XPS(S_{2P}) spectra of plasma polymers prepared from PFB/SO_2 (A), $PnFB/SO_2$ (B), and TFB/SO_2 (C) mixtures containing 75 mol%SO_2.

From the combination of IR and XPS inspections we conclude that the sulfur moieties may be sulfonic acid groups (SO_3H) for the plasma polymers prepared from the PFB/SO_2 mixture, and sulfinic acid groups ($-S(O_2)-H \rightleftharpoons -S(O)-OH$) for the plasma polymers prepared from the $PnFB/SO_2$ and TFB/SO_2 mixtures.

Ion-exchange Capacity and Electrical Conductivity

The plasma polymers prepared from the PFB/SO_2, $PnFB/SO_2$, and TFB/SO_2 mixtures containing 75 mol%SO_2 showed the ion-exchange ability of which the capacity was 0.49, 0.94, and 1.31 meq/g-polymer, respectively. The plasma polymers from the TFB/SO_2 mixture are larger in ion-exchange capacity than Nafion (0.5 - 0.9 meq/g-polymer) [1] although the ionization groups of the plasma polymers prepared from the TFB/SO_2 mixture are weak sulfinic acid groups, while those of Nafion are strong sulfonic acid groups.

The three plasma polymers showed less electrical conductivity (10^{-10} - 10^{-15} S/cm) in vacuum, but the conductivity increased in humid atmosphere. The electrical conductivity at a relative humidity of 70 %RH is 8.3×10^{-9} (plasma polymers prepared from the PFB/SO_2 mixture), 3.6×10^{-7} (those from the $PnFB/SO_2$ mixture), and 4.3×10^{-5} S/cm (those from the TFB/SO_2 mixture).

In conclusion we summarize the plasma polymerization of the fluorobenzenes/SO_2 mixtures as follows.

(1) Plasma polymerizations of the PFB/SO_2, $PnFB/SO_2$, and TFB/SO_2 mixtures deposit thin films which contain fluoro carbons and sulfur moieties.
(2) Hydrogen substituents of fluorobenzenes contribute the formation of plasma polymers.
(3) The F/C, S/C, and O/C atomic ratios of the films deposited from the plasma polymerization of the $PnFB/SO_2$ and TFB/SO_2 mixtures depend on the composition of the starting mixtures. However the polymers plasma-polymerized from the PFB/SO_2 mixture show constant F/C, S/C, and O/C atomic ratios independently of the starting mixture composition.
(4) The deposited plasma polymers contain fluorocarbon chains such as fluorinated phenyl rings, CF, CF_2, and CF_3 groups, and sulfonic acid groups (for the plasma polymers prepared from the PFB/SO_2 mixture) or sulfinic acid groups (for the plasma polymers prepared from the $PnFB/SO_2$ and TFB/SO_2 mixtures).
(5) The plasma films show the ion-exchange ability of which is 0.49 (polymers from the PFB/SO_2 mixture), 0.94 (for those from the $PnFB/SO_2$ mixture), and 1.31 meq/g-polymer (for those from the TFB/SO_2 mixture).
(6) The electrical conductivity at a relative humidity of 70 %RH is 8.3 $\times 10^{-9}$, 3.6×10^{-7}, and 4.3×10^{-5} S/cm for the plasma polymers prepared from the PFB/SO_2, $PnFB/SO_2$, and TFB/SO_2 mixtures, respectively.

References

1. T. Satokawa, Functiona Fluoropolymers, Nikkan Kogyo, Tokyo, 1982.
2. N. Inagaki and H. Kawai, Sen-i Gakkaishi, 40, T-377 (1984).
3. K. Hozumi, Ed., Yuki Biryou Teiryo Bunseki (in Japanese), Nankodo, Tokyo, 1969.
4. L. J. Bellamy, The Infrared Spectra of Complex Molecules, Wiley, New York, 1966; Advances in Infrared Group Frequency, Methuen, New Fetter, Florida, 1968.
5. D. T. Clark 'and W. J. Feast, J. Macromol. Sci., Revs. Macromol. Chem., C12, 191 (1975).
6. B. J. Lindberg and K. Hamrin, Acta Chimca Scandinavica, 24, 3661 (1970).

Accepted April 26, 1989 C