

## On Glow Discharge Polymerizations of Polyfluoroarenes

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### Abstract

Glow discharge polymerizations of fluorobenzenes, perfluoromethylbenzenes, polyfluorostyrenes, and perfluorinated benzocycloalkenes have been studied. The reactivity of these compounds depends on the number and position of fluorine atoms in the ring and on the type of substituent. High reactivity is inherent in compounds with a fluorinated vinyl group and in *ortho*-substituted compounds (perfluoro-*o*-xylene, perfluorobenzocyclobutene). The polymer products were identified by IR spectroscopy and element microanalysis. Film growth rates on metallic supports have been determined. Suggested mechanisms underlying polymerizations are discussed; these include double bond polymerization, condensation of fluoroaromatic rings via elimination of substituent, and ring cleavage that forms aliphatic segments in the polymer chain. Introduction of chlorine atoms in the starting compound decelerates polymer formation. The polymerizations are accompanied by oxidations, leading to oxygen-containing groups in the polymers. Polymerizations of oxygen-containing compounds  $C_6F_5OR$  ( $R = CH_3, CF_2H, CF_3$ ) and  $C_6F_5C(O)CH_3$  have been investigated, and film growth rates have been determined; routes of transformations of oxygen-containing substituents are suggested. For a number of polymers, hydrophobicity and thermal stability are assessed.

### INTRODUCTION

Traditional procedures for the preparation of polymers are known to employ a multitude of solvents during synthesis and subsequent stages, when polymers are isolated, purified, and prepared as thin films. Plasma polymerization is absolutely devoid of these disadvantages. Moreover, as is known, as substrates in plasma polymerizations one can use not only monomers, but also any other organic or organoelement compounds; *i.e.*, the presence of a multiple bond is not an essential condition [1].

Polymerization is initiated by reaction of the substrate with active components of plasma: electrons, ions, excited neutral particles, and vacuum UV radiation. The energy of the active components of plasma may be 0.01–100 eV or higher; *i.e.*, the energy is high enough

for bond cleavage in organic molecules. Due to their inherent reticular structure, plasma synthesized polymers are insoluble in organic solvents, acids, and alkalis. They are useful as coatings for parts designed for operation in aggressive media and at elevated temperatures at which other polymers are inoperative. Moreover, coatings obtained from polyfluorinated compounds in plasma possess high friction properties. The plasma polymerization technique yields very thin coatings on supports of varied (sometimes complicated) form directly placed in a reaction chamber. The thickness of the coating is closely monitored. This is an ecologically clean technique because it avoids using solvents and the substrate is completely exhausted. This work deals with plasma polymerizations of fluorine-containing compounds from various classes, most of which are not polymerizable by traditional methods of polymer chemistry.

## EXPERIMENTAL

Plasma polymerization was conducted in glow discharge conditions (alternating current, frequency 1 kHz); this method was described in detail in our previous paper [2]. Polymers were deposited as films on metallic electrodes (supports) in a cap type reactor in a flow mode with identical parameters of discharge: current density 0.2 mA/cm<sup>2</sup>, vapor pressure in the gas phase ~10 Pa, electrode voltage ~400 V. The thickness of the deposited films was determined by microinterferometry. Film growth rates were calculated from interferometry data and film growth times. The structure of the resulting polymers was investigated by IR spectroscopy, and the composition was studied by the element microanalysis techniques. IR spectra were recorded on a Perkin Elmer 580 spectrophotometer. The spectra of liquid monomers were measured in a KBr cell, while the spectra of insoluble powders were recorded for KBr and CsI pellets or vaseline oil suspension.

## RESULTS AND DISCUSSION

We have investigated how the introduction of fluorine atoms in the benzene ring [benzene, fluorobenzene, *m*- and *p*-difluorobenzenes, 1,3,5-trifluorobenzene, 1,2,3,5-tetrafluorobenzene, pentafluorobenzene, hexafluorobenzene (HFB)] affects film growth rates in

plasma and how the film structure and composition depend on fluorination. The results of these studies are summarized in Table 1. Kinetic studies indicated that the compounds form two groups according to film growth rate: one group characterized by ~90 Å/s (benzene, fluorobenzene, pentafluorobenzene, and HFB) and the other, by ~130 Å/s (di-, tri-, and tetrafluorobenzenes). All of the resulting polymers contained less fluorine and hydrogen compared to the monomers. The loss of hydrogen was especially significant for mono- and difluoro-substituted benzenes. The maximal loss of fluorine was observed for higher ring fluorine-substituted compounds; this can be attributed to the decreased aromaticity of the fluorine-substituted ring [3], which can result in predominant ring cleavage [2] and isomerization reactions. Moreover, the decreased contents of fluorine and hydrogen in polyfluorinated benzenes may also be due to cross-linking of the forming polymer chains. Polymerization can also occur by reactions other than ring cleavage, namely, by ring condensation [2], or by grafting to the polymer chain [4].

Element analysis data are supported by structural data obtained by IR spectroscopy. The spectra of the polymers contained a broad and intense absorption band in the region 1100–1300 cm<sup>-1</sup> and intense bands at 1700–1750 and 1500–1640 cm<sup>-1</sup>, while the narrow intense bands of the monomer in the range 650–900 cm<sup>-1</sup> (ring substituted type) vanished. These

TABLE 1

Glow discharge polymerization of benzene and its fluorinated derivatives

Monomer	Film growth rate, Å/s	Monomer		Polymer		
		F/C	H/C	Formula (based on C <sub>6</sub> )	F/C	H/C
Benzene (C <sub>6</sub> H <sub>6</sub> )	90	—	1	C <sub>6</sub> H <sub>5.7</sub> O <sub>0.2</sub>	—	0.95
Fluorobenzene (C <sub>6</sub> H <sub>5</sub> F)	90	0.167	0.833	C <sub>6</sub> H <sub>3.93</sub> F <sub>0.32</sub> O <sub>0.2</sub>	0.053	0.66
<i>m</i> -Difluorobenzene (C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> )	130	0.333	0.667	C <sub>6</sub> H <sub>2.88</sub> F <sub>1.15</sub> O <sub>0.94</sub>	0.192	0.478
<i>p</i> -Difluorobenzene (C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> )	130	0.333	0.667	C <sub>6</sub> H <sub>2.84</sub> F <sub>1.24</sub> O <sub>1.04</sub>	0.206	0.478
1,3,5-Trifluorobenzene (C <sub>6</sub> H <sub>3</sub> F <sub>3</sub> )	130	0.5	0.5	C <sub>6</sub> H <sub>2.03</sub> F <sub>2.21</sub> O <sub>0.84</sub>	0.386	0.340
1,2,3,5-Tetrafluorobenzene (C <sub>6</sub> H <sub>2</sub> F <sub>4</sub> )	130	0.667	0.333	C <sub>6</sub> H <sub>1.59</sub> F <sub>2.88</sub> O <sub>0.88</sub>	0.482	0.266
Pentafluorobenzene (C <sub>6</sub> HF <sub>5</sub> )	90	0.833	0.167	C <sub>6</sub> H <sub>0.89</sub> F <sub>4.12</sub> O <sub>0.94</sub>	0.687	0.148
Hexafluorobenzene (C <sub>6</sub> F <sub>6</sub> )	90	1	—	C <sub>6</sub> F <sub>5.1</sub> O <sub>0.65</sub>	0.850	—

data indicate that the polymers retained some of the fluorinated benzene rings, while others opened to form aliphatic fluorine-containing chains [5]. The films had cross linkages, as indicated by the broadening of the absorption bands typically observed for plasma-synthesized polymers [6].

Formation of the valence isomers of aromatic compounds, in particular, of Dewar structures under glow discharge conditions may be represented as one of the routes leading to the aliphatic chain in the polymerization products of aromatic hydrocarbons and their fluorinated derivatives. The band at  $\nu = 1300 \text{ cm}^{-1}$  is due to absorption of the fluorinated aliphatic polymer chain and is not observed in the spectra of the monomers.

It was interesting to study the effect of chlorination of the starting fluoroaromatic compounds on their plasma polymerization. Glow discharge polymerization was investigated for octafluorotoluene (OFT), pentafluorobenzotrachloride (PFBTC), perfluoro- $\alpha$ -chlorostyrene (PFCS), and perfluorostyrene (PFS). The introduction of chlorine atoms was shown to decrease the film growth rate. For polyfluorostyrenes, the polymerization rate was appreciably higher than for compounds containing no vinyl bond (Table 2). This indicates that plasma polymerization occurs with participation of the exocyclic double bond. The higher polymerization rate of PFS compared to PFCS agrees with the higher polymerization rate reported for tetrafluoroethylene compared to trifluorochloroethylene [7]. At the same time, the higher polymerization rate of OFT compared to

PFBTC may be explained by the predominant role of the aromatic ring in the process [8].

The polymers had lower contents of fluorine and chlorine compared to the starting monomers, and they also had some oxygen. This is typical for plasmachemical polymerizations and is due to the peculiarities of the mechanism of discharge polymerization [1]. Chain propagation in the course of polymer formation occurs through stepwise recombination of active particles and every time requires a new act of initiation to keep the process going. This is possible through excitation of molecules, radicals, and ions arising from plasma reaction with monomers and their transformation products [6]. Some radicals are trapped by the polymer in the course of its propagation. Moreover, in the polymer, radicals are obviously continuously formed to the end of the period during which the polymer stays in the discharge zone; that is, film growth occurs with plasma etching the polymer (destruction and cross-linking take place). Oxygen is believed to enter the polymer when films come in contact with air due to the interaction of atmospheric oxygen with the free radicals of the film, forming oxygen-containing groups [6].

The  $[F]/[C]$  ratio is an important characteristic of fluoropolymers. The largest value of the ratio obtainable for a polymer is two. This value is typical for monomers with a single double bond, for example, for tetrafluoroethylene or for cyclic compounds without multiple bonds. The ratio decreases (while the rate of polymer formation increases) when the monomer contains additional double bonds.

TABLE 2

Glow discharge polymerization of octafluorotoluene, pentafluorobenzotrachloride, perfluoro- $\alpha$ -chlorostyrene, and perfluorostyrene

Monomer	Film growth rate, Å/s	Monomer			Polymer				
		Mass fraction of elements, %			Formula (based on C <sub>6</sub> )	Mass fraction of elements, %			
		C	F	Cl		C	F	Cl	O
Octafluorotoluene (C <sub>6</sub> F <sub>5</sub> CF <sub>3</sub> )	130	35.6	64.4	—	C <sub>6</sub> F <sub>5.76</sub> O <sub>0.66</sub>	37.6	57.0	—	5.4
Pentafluorobenzotrichloride (C <sub>6</sub> F <sub>5</sub> CCl <sub>3</sub> )	95	29.4	33.3	37.3	C <sub>6</sub> F <sub>3.58</sub> Cl <sub>2.22</sub> O <sub>0.72</sub>	31.4	29.7	33.9	5.0
Perfluoro-α-chlorostyrene (C <sub>6</sub> F <sub>5</sub> CCl=CF <sub>2</sub> )	170	36.3	50.3	13.4	C <sub>6</sub> F <sub>5.08</sub> Cl <sub>0.74</sub> O <sub>0.34</sub>	36.0	48.2	13.1	2.7
Perfluorostyrene (C <sub>6</sub> F <sub>5</sub> CF=CF <sub>2</sub> )	250	38.7	61.3	—	C <sub>6</sub> F <sub>5.2</sub> O <sub>0.9</sub>	38.9	53.4	—	7.7

Among the compounds under study, the largest  $[F]/[C]$  ratios were found for OFT (1.14), HFB, and PFS (1.0). For polymers, this value decreased to 0.96, 0.85, and 0.87, respectively. For chlorine-containing monomers, the  $[Cl]/[C]$  ratio decreased concurrently, especially in the case of PFBTC (from 0.43 to 0.37).

As is known, the decreased  $[F]/[C]$  ratio considerably decreases hydrophobicity of the polyfluorinated polymer [9]. For discharge-synthesized polymers, this tendency was observed quite distinctly. The measured contact wetting angle for water (bidistillate) was  $95^\circ$  for the OFT polymer (the largest value of  $[F]/[C]$ ) and  $85^\circ$  for the HFB polymer. The wetting angle in the polymers decreased symbatically with the  $[F]/[C]$  ratio.

Plasma-synthesized polymers possess high thermal stability. In the course of thermooxidative destruction, mass loss of 50 % was observed in the temperature range around  $400^\circ\text{C}$  for these polymers versus  $\sim 350^\circ\text{C}$  for polytetrafluoroethylene [10].

The IR spectra of the polymers presented in Table 2 have a wide complex absorption band in the range  $1100\text{--}1300\text{ cm}^{-1}$ , which is the strongest band in the spectrum (aliphatic C–F bonds). Also, there are some bands characteristic of monomers: for example, for PFS, these are absorption bands at  $1787\text{ cm}^{-1}$  (C=C bond stretching vibrations),  $1655\text{ cm}^{-1}$  (stretching vibrations of the C–C<sub>arom</sub> bond of the fluorinated ring), and a doublet at  $1510\text{--}1520\text{ cm}^{-1}$  and  $\sim 1000\text{ cm}^{-1}$  (C–F bond stretching vibrations). All of the synthesized polymers have

bands in the range  $1700\text{--}1850\text{ cm}^{-1}$ . They may be due to the emergence of carbonyl groups, arising from the interaction of the polymer film with atmospheric oxygen. This agrees with element analysis data about the presence of oxygen in the polymers. This region may also contain absorption bands corresponding to the vibrations of the –CF=CF– bond formed by transformations of the fluorinated aromatic ring. The most drastic changes were observed for absorption bands in the range  $700\text{--}900\text{ cm}^{-1}$ : intense bands were present in the spectra of the monomers, but vanished in the spectra of the polymers.

The similarity of the absorption spectra of the polymers in question suggests that there is at least one route of polymerization that is independent of the structure and composition of the substituent in the polyfluorinated ring, namely, ring cleavage and formation of aliphatic C–F bonds. The absorption bands characteristic of these bonds are strong enough in the spectra of all polymers under study.

The higher rate of polymerization in the case of PFS compared to polyfluoroarenes prompted us to study polymerization of other polyfluorostyrenes in an effort to find some general tendencies.

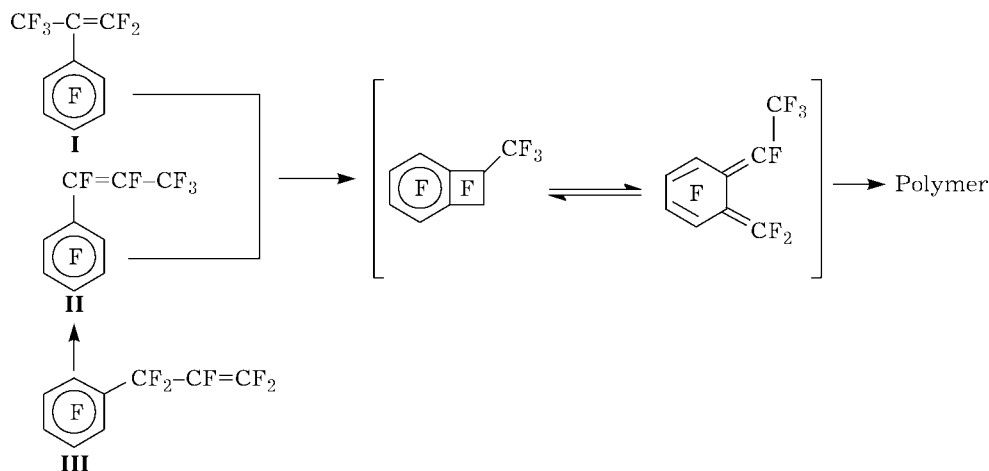
Table 3 lists data on polymerizations of polyfluorostyrenes and some other compounds of interest for the sake of comparison.

The kinetic study of film growth showed that for compounds I–III, the polymerization rate was  $250\text{--}350\text{ \AA/s}$ . The lowest rates ( $\sim 200\text{ \AA/s}$ ) were observed for chlorine-containing fluo-

TABLE 3

Glow discharge polymerization of polyfluorinated styrenes

Monomer	Film growth rate, $\text{\AA/s}$	$D'$	Molecular formula (based on $C_6$ ) of monomer/polymer
Perfluoro- $\alpha$ -methylstyrene (I)	250	0.1	$C_6F_5C(CF_3)=CF_2 / C_6F_{5.22}O_{1.14}$
Perfluoro- $\beta$ -methylstyrene (II)	300	0.12	$C_6F_5CF=CF_2 / C_6F_{5.28}O_{1.21}$
Perfluoroallylbenzene (III)	350	0.16	$C_6F_5CF_2CF=CF_2 / C_6F_{5.28}O_{1.2}$
Perfluoro- $\alpha$ -chlorostyrene (IV)	180	0.8	$C_6F_5CCl=CF_2 / C_6F_{5.08}Cl_{0.74}O_{0.34}$
$\alpha,p$ -Dichlorohexafluorostyrene (V)	200	1.8	$C_6F_4Cl-CCl=CF_2 / C_6F_{4.08}Cl_{1.38}O_{0.46}$
Perfluoro- $\alpha,\beta$ -dichlorostyrene (VI)	200	1.17	$C_6F_6CCl=CF_2 / C_6F_{3.6}Cl_{1.2}O_{0.54}$
Perfluorostyrene (VII)	270	1.25	$C_6F_5CF=CF_2 / C_6F_{5.2}O_{0.9}$
Perfluorobenzocyclobutene (VIII)	750	0.4	$C_6F_4C_2F_4 / C_6F_{4.75}O_{1.68}$



Scheme 1.

rostyrenes IV-VI. Table 3 gives element microanalysis data on the composition of the polymers. It can be seen that the polymers contain less chlorine and fluorine than the corresponding monomers. All of the polymers had oxygen, which is typically observed for plasma-synthesized polymers [6]. Comparison of the relative intensities  $D'$  of the IR absorption bands at  $1540\text{ cm}^{-1}$  (stretching skeletal vibrations of the fluoroaromatic ring) of the polymers *vs* monomers (see Table 3) indicated that the greatest number of aromatic rings is preserved in the structures of polymers IV-VI, characterized by lower rates of film growth. As can be seen, monomer VII and isomers I-III have close rates of polymerization, but the number of fluoroaromatic rings in polymers from monomers I-III is one order of magnitude smaller than in PFS polymer. Po-

lymerization of PFS (VII) apparently occurs by cleavage of the vinyl bond and also by formation of perfluorobenzocyclobutene as an intermediate and cleavage of this rather strained four-membered cycle. The polymerization rates of I-III and VII being similar, one would expect similar routes of polymerization. However, as mentioned above, the number of fluoroaromatic rings in polymers I-III is one order of magnitude smaller than in PFS polymer (see Table 3). Therefore, for compounds I-III we suggested a sequence of polymer formation (Scheme 1).

To verify this scheme we synthesized perfluoro-1-methylbenzocyclobutene [11] and established that the growth rate of a polymer film from this compound was  $400\text{ Å/s}$ , and  $D'$  was  $\sim 0.17$ .

For perfluorobenzocyclobutene, the film growth rate was very high given the mean

TABLE 4

Glow discharge polymerization of oxygen-containing functional derivatives of polyfluoroarenes

Monomer	Film growth rate, Å/s	Monomer				Polymer				$\frac{D_{1720}}{D_{1200}}$	$\frac{D_{1510}}{D_{1200}}$
		Formula (based on $\text{C}_1$ )	[F]/[C]	[O]/[C]	[H]/[C]	Formula (based on $\text{C}_1$ )	[F]/[C]	[O]/[C]	[H]/[C]		
(IX)	210	$\text{C}_1\text{F}_{0.6}\text{O}_{0.12}\text{H}_{0.37}$	0.6	0.12	0.37	$\text{C}_1\text{F}_{0.62}\text{O}_{0.29}\text{H}_{0.33}$	0.62	0.29	0.33	1.8	1.8
(X)	220	$\text{C}_1\text{F}_{0.71}\text{O}_{0.14}\text{H}_{0.43}$	0.71	0.14	0.43	$\text{C}_1\text{F}_{0.75}\text{O}_{0.25}\text{H}_{0.29}$	0.75	0.26	0.29	1.0	5.8
(XI)	120	$\text{C}_1\text{F}_{1.14}\text{O}_{0.14}$	1.14	0.14	—	$\text{C}_1\text{F}_1\text{O}_{0.25}\text{H}_{0.22}$	1.0	0.25	0.22	0.5	1.1
(XII)	210	$\text{C}_1\text{F}_1\text{O}_{0.14}\text{H}_{0.14}$	1.0	0.14	0.14	$\text{C}_1\text{F}_{0.85}\text{O}_{0.24}\text{H}_{0.04}$	0.85	0.24	0.04	0.6	0.8
$\text{C}_6\text{F}_6$	90	$\text{C}_1\text{F}_1$	1.0	—	—	$\text{C}_1\text{F}_{0.72}\text{O}_{0.11}$	0.72	0.11	—	0.5	0.6

Note. IX -  $\text{C}_6\text{F}_5\text{C}(\text{O})\text{CH}_3$ , X -  $\text{C}_6\text{F}_5\text{OCH}_3$ , XI -  $\text{C}_6\text{F}_5\text{OCF}_3$ , XII -  $\text{C}_6\text{F}_5\text{OCF}_2\text{H}$ .

number of fluorinated benzene rings in the polymer. It seems that polymerization of VIII occurs via cleavage of the four-membered fluorinated ring, forming a biradical which is then transformed into a polymer.

As shown above, all polymers formed by plasma polymerization contain oxygen. That is why it was of interest to study polymerization of oxygen-containing functional derivatives of polyfluoroarenes  $C_6F_5X$ , where  $X = OCH_3$ ,  $OCF_2H$ ,  $OCF_3$ ,  $C(O)CH_3$ . Polymers obtained by glow discharge polymerization of these compounds are characterized by the presence of carboxyl groups (IR absorption bands at 2500–3600 and 1600–1850  $cm^{-1}$ ). Higher polymerization rates were observed for compounds with a hydrogen atom in the OR function (Table 4). The relative optical density  $D_{1510}/D_{1200}$ , defining the content of fluoroaromatic rings in the polymer, was high for all monomers under study. The values of  $D_{1720}/D_{1200}$ , defining the content of carboxyl groups in the polymer, were also high. Monomers from this series are likely to preferably undergo processes involving substituents, namely, transformations occurring after hydrogen atom elimination, including the formation of carboxyl groups.

## CONCLUSIONS

Investigations of plasma polymerization of polyfluoroaromatic compounds revealed that polymers may be obtained from compounds of various classes, including compounds with-

out vinyl bonds. In these cases, polymerization occurs with cleavage of some aromatic rings and formation of linear fluorinated chains. All of the synthesized polymers typically have high fluorine contents and a hydrophobic surface. The higher thermal stability of these polymers compared to that of polytetrafluoroethylene may be a useful property in articles designed for work at elevated temperatures and in aggressive media. Glow discharge polymerization of polyfluoroarenes retains all the advantages of the plasma polymerization method mentioned in the Introduction. Using plasma polymerization for the preparation of polymers substantially expands the scope of the starting polyfluorinated compounds.

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