ON THE REACTIVITY OF SOME POLYFLUORINATED ORGANIC COMPOUNDS IN
A GLOW DISCHARGE

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SUMMARY

The polymerizing reactivity of fluorobenzenes $C_6H_nF_{6-n}$
(n = 1-6), perfluoromethylbenzenes, polyfluorostyrenes, perfluor-
inated cyclo- and benzocyclo-alkenes has been studied in a glow
discharge. The reactivity of each of these compounds is found
to be dependent on the number and position of fluorine atoms
in the ring and on the kind of substituent, the highest
reactivity being exhibited by compounds with the fluorinated
vinyl group and by o-substituted compounds (perfluoro-o-xylene,
perfluorocyclobutene). The discussion of possible ways of poly-
merization is based on kinetic data, infrared spectra, the
amount of fluorine atoms and other groups in polymers.

INTRODUCTION

The substitution of hydrogen atoms in hydrocarbons by
fluorine is known to impart new properties to a molecule, this
being manifested most clearly in polyfluorinated substances.
In particular, the accumulation of fluorine atoms in the benzene
ring leads to a lowering of the order of the π -bonds of a
compound with respect to that of benzene, to diminishing the
aromatic nature of the ring and, consequently, to a change of

the reactivity of a compound [1]. A study of reactions with the participation of nucleophilic, electrophilic, and radical reagents makes it possible to come to certain conclusions about the changes in the reactivity of fluoroaromatic compounds [2,3]. However, other processes, say, polymerization reactions, have been studied insufficiently. In this connection we thought it expedient to investigate polymerization of fluoroaromatic compounds with the aim of elucidating the effect of the accumulation of fluorine atoms, their position and the presence of other substituents in the aromatic ring, on the polymerization process. A glow-discharge plasma was used as a means of initiating reaction on fluoroaromatic compounds [4] The treatment of many different types of organic substances gives rise to polymeric products. The mechanism of this process is not completely understood. However, according to numerous investigations [4] it involves the formation of reactive particles (radicals, ions, excited molecules, etc.), this may be indicative of the reactivity of the initial compound. It should be emphasized that the plasmochemical method enables one to obtain polymeric products from practically any organic and elemento-organic compounds which are not monomers in the normal sense of the word. Polymers are obtained as thin films on a metal or some other substrate from vapours of the initial compounds in the atmosphere of which a discharge is initiated.

EXPERIMENTAL

The experimental technique and vacuum reaction chamber have been described in our earlier publication [5]. In the present investigation, polymers were obtained in a 1-KHz a.c. glow-discharge plasma. The main characteristic determining the kinetics of transformation of polyfluorinated compounds in a glow-discharge is the thickness of a polymeric film formed on the electrode, which was measured microinterferometrically [5]. Polymers obtained were identified by infrared spectroscopy. A film removed from the electrode was divided finely and then pressed in potassium bromide tablets. Infrared spectra were registered with a UR-20 Tseiss spectrophotometer. The fluorine

and hydrogen content of monomers and polymers was determined
by elemental microanalysis. Data on the composition of invest-
igated compounds are listed in Table 1, physicochemical cons-
tants of the compounds being in agreement with the literature
values.

RESULTS AND DISCUSSION

The polymerization process was studied for various groups
of polyfluorinated compounds containing a benzene ring. The
simplest compounds are fluorobenzenes containing 1-6 fluorine
atoms. It was of interest to compare polymerization of benzene
and fluorobenzenes and evaluate the effect of accumulation of
fluorine atoms in the benzene ring. Polymerization of CF_3-homo-
logs of hexafluorobenzene and that of polyfluorostyrenes were
compared with polymerization of hexafluorobenzene. It was par-
ticularly interesting to investigate the behaviour of polyfluoro-
benzocycloalkenes (perfluorinated benzocyclobutene, indane and
tetraline) with the aim of ascertaining the effect of the size
of the fused fluorinated alicyclic ring on their reactivity and
comparing the latter with the reactivity of perfluoro-o-xylene.
Consider polymerization of hexafluorobenzene (II). Figure 1
illustrates the infrared spectra of compound II and its polymer.
A characteristic feature of the polymer spectrum is a broad and
complicated absorption band in the region of 1100-1300 cm^{-1},
being the most intense in the spectrum. As is known [6], the
bands characteristic of the aliphatic bonds C-F are also posit-
ioned in this region. It was proposed [7] that the formation of
such structures was likely to proceed through destruction of the
aromatic ring under the action of a discharge. Using ESCA we
have established that the plasmochemical treatment of compound
II results in the formation of polymeric chains including the
fragments CF_3, CF_2, CF and C-CF.
Absorption bands at 1570, 1360 and 730 cm^{-1} were found in
the polymer II spectrum (Fig. 1). The first three bands can be
identified with the corresponding bands in the compound II spec-
trum, whereas the band at 730 cm^{-1} was not observed in the mono-

TABLE 1

Elemental composition of monomers and polymers

Compound	Weight percentage of elements[a]				F/C	H/C	Empirical formula
	C	F	H	O[b]			
Benzene I	92.25	-	7.75	-	-	1	C_6H_6
	88.89	-	7.10	4.02	-	0.95	$C_6H_{5.7}O_{0.2}$
Hexafluoro-benzene II	38.74	61.26	-	-	1	-	C_6F_6
	40.18	54.02	-	5.80	0.85	-	$C_6F_{5.10}O_{0.65}$
Fluorobenzene III	74.98	19.78	5.24	-	0.176	0.833	C_6H_5F
	70.15	5.87	3.86	20.12	0.053	0.66	$C_6H_{3.93}F_{0.32}O_{1.29}$
meta-Difluoro-benzene IV	63.16	33.31	3.53	-	0.333	0.667	$m\text{-}C_6H_4F_2$
	64.44	19.53	2.58	13.45	0.192	0.478	$C_6H_{2.86}F_{1.15}O_{0.94}$
para-Difluoro-benzene V	63.16	39.31	3.54	-	0.333	0.667	$p\text{-}C_6H_4F_2$
	62.63	20.49	2.48	14.40	0.206	0.478	$C_6H_{2.84}F_{1.24}O_{1.04}$
1,3,5-Trifluoro-benzene VI	54.56	43.15	2.26	-	0.5	0.5	$C_6H_3F_3$
	55.54	32.44	1.58	10.44	0.368	0.34	$C_6H_{2.03}F_{2.21}O_{0.84}$
1,2,3,5-Tetra-fluorobenzene VII	48.01	50.65	1.34	-	0.667	0.333	$C_6H_2F_4$
	50.50	38.54	1.13	9.81	0.482	0.226	$C_6H_{1.59}F_{2.88}O_{0.88}$

Compound							Formula
Pentafluorobenzene VIII	42.87	56.52	0.61	-	0.833	0.167	C_6HF_5
	43.36	47.05	0.54	9.05	0.687	0.148	$C_6H_{0.89}F_{4.12}O_{0.94}$
Octafluorotoluene IX	35.6	64.4	—	-	1.14	—	$C_6F_5CF_3$
	37.6	57.0		5.40	0.96		$C_6F_{5.78}O_{0.66}$
Pentafluorobenzotrichloride X [c]	29.4	33.3	—	-	0.71	—	$C_6F_5CCl_3$
	31.4	29.7		5.00	0.59		$C_6F_{3.58}Cl_{2.2}O_{0.72}$
Perfluoro-α-chlorostyrene XI [c]	36.3	50.3	—	-	0.875	—	$C_6F_5CCl=CF_2$
	36.0	48.2		2.7	0.850		$C_6F_{5.08}Cl_{0.74}O_{0.34}$
Perfluorostyrene XII	38.7	61.3	—	-	1.00	—	$C_6F_5CF=CF_2$
	38.9	53.4		7.7	0.87		$C_6F_{5.2}O_{0.9}$
Perfluoromesitylene XIII	32.14	67.86	—	-	1.34	—	C_9F_{12}
	35.98	58.56		5.46	1.04		$C_9F_{9.14}O_{0.99}$
Perfluorobenzocyclobutene XIV	38.73	61.27	—	-	1.00	—	C_8F_8
	39.96	47.62		14.41	0.79		$C_8F_{6.34}O_{2.28}$
Perfluoroindan XV	36.23	63.74	—	-	1.11	—	C_9F_{10}
	37.19	51.88		10.93	0.88		$C_9F_{7.92}O_{2.03}$
Perfluorotetraline XVI	34.50	65.50	—	-	1.20	—	$C_{10}F_{12}$
	37.53	52.61		9.86	0.89		$C_{10}F_{8.9}O_{0.197}$

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TABLE 1 (cont.)

Compound	Weight percentage of elements [a]				F/C	H/C	Empirical formula
	C	F	H	O[b]			
Perfluoro-o-xylene XVII	$\dfrac{33.56}{38.43}$	$\dfrac{66.44}{49.48}$	$\dfrac{-}{-}$	$\dfrac{-}{13.09}$	$\dfrac{1.25}{0.82}$	$-$	$\dfrac{C_8F_{10}}{C_8F_{6.45}O_{1.87}}$
Perfluoro-cyclopentene XVIII	$\dfrac{28.32}{34.60}$	$\dfrac{71.68}{59.69}$	$\dfrac{-}{-}$	$\dfrac{-}{5.71}$	$\dfrac{1.60}{1.09}$	$-$	$\dfrac{C_5F_8}{C_5F_{5.45}O_{0.62}}$
Perfluoro-cyclohexene XIX	$\dfrac{27.50}{33.04}$	$\dfrac{72.50}{60.04}$	$\dfrac{-}{-}$	$\dfrac{-}{6.92}$	$\dfrac{1.67}{1.15}$	$-$	$\dfrac{C_6F_{10}}{C_6F_{6.9}O_{0.94}}$
Perfluoro-decaline XX	$\dfrac{25.99}{33.82}$	$\dfrac{74.01}{61.46}$	$\dfrac{-}{-}$	$\dfrac{-}{4.72}$	$\dfrac{1.80}{1.15}$	$-$	$\dfrac{C_{10}F_{18}}{C_{10}F_{11.5}O_{1.05}}$

[a] Numerator - for monomers, denominator - for polymers. [b] Oxygen content is determined from the difference 100 - F, Cl, H, C. [c] Weight percentage of Cl (Cl/C): X - $\dfrac{37.3}{33.9}$ ($\dfrac{0.43}{0.37}$); XI - $\dfrac{13.4}{13.1}$ ($\dfrac{0.125}{0.123}$).
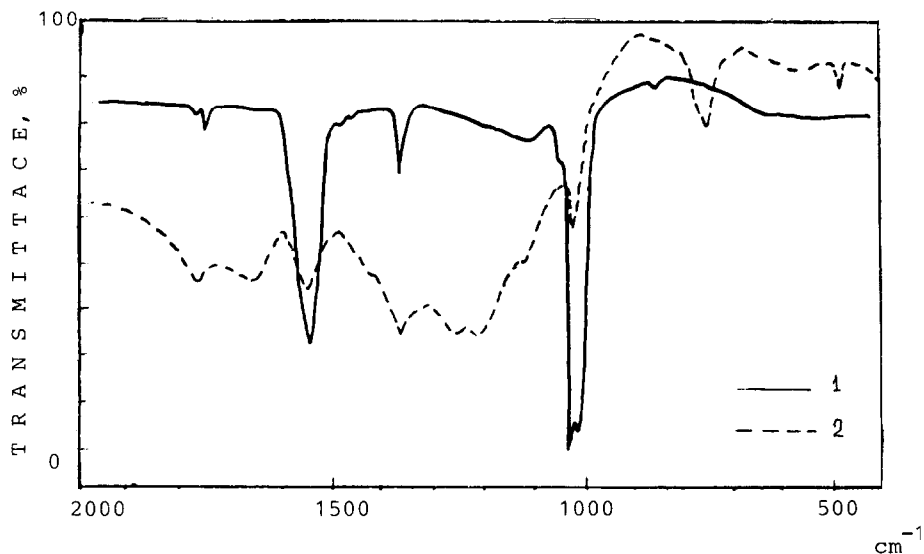
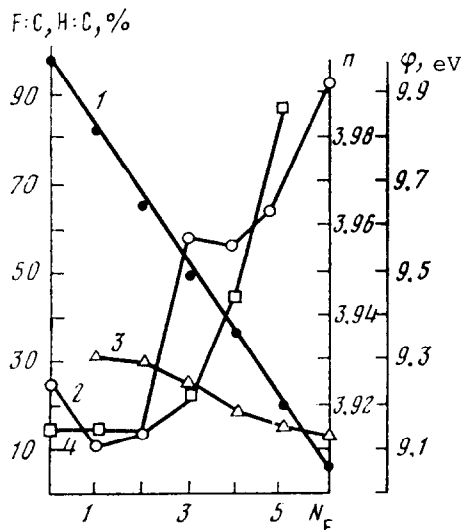Fig. 1. Infrared spectra of hexafluorobenzene (1) and its polymer (2).

Fig. 2. Sum "n" of the orders of C–C bonds (1) [1], ionization potentials φ for fluorine-containing benzene derivatives (2) [12], and F/C (3) and H/C (4) ratios for corresponding polymers as functions of the number of fluorine atoms N_F in the aromatic ring.

mer spectrum. We compared the infrared spectra of polymer II
and those of the fluoroaromatic compounds obtained as reported
in [8-10] and containing the completely fused fluorinated rings
(Table 2). The spectra of these compounds exhibit, in the region
of 650-900cm^{-1}, intense absorption bands whose location is
dependent on the place of attachment of the fluorinated rings.
In particular, the absorption bands in the region of 720-730 cm^{-1}
were observed in the case of ring monosubstitution and para-
orientation of rings. The presence of such absorption in conjunc-
tion with the bands characteristic of a polyfluorinated aromatic
ring makes it possible to assume that polymeric structures may
also be formed from compound II by fusion of aromatic rings
with the formation of polyphenyls.

The bands observed in the polymer spectrum in the region
of 1700-1850 cm^{-1} may be due to the presence of carbonyl groups
formed as a result of the interaction of atmospheric oxygen
with free radicals in the film [11]. This is consistent with
the elemental analysis data on the presence of oxygen in the
polymer (see Table 1). Besides, this region may also contain
absorption bands corresponding to the vibrations of the -CF=CF-
bond formed due to transformations (isomerization) of a fluor-
inated aromatic ring.

Thus, two types of transformation of the polyfluoroaromatic
ring are likely in the course of polymerization of compound II:
fusion with the formation of a polyphenyl chain, and transform-
ations leading to the appearance of aliphatic fluorine-contain-
ing residues.

A study was conducted of the effect of the number and posi-
tion of fluorine atoms introduced into the benzene ring on the
behaviour of compounds I-VIII in the discharge (Table 1). Kine-
tic investigations showed that in terms of the polymeric film
growth rate these compounds may be divided into 2 groups: group
I includes compounds I, II, III and VII (∞ 90 Å/s); group II
includes compounds IV, V, VI and VII (∞ 130 Å/s).

Figure 2 illustrates the literature data on ionization
potentials measured by the photoionization method [12] and on
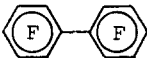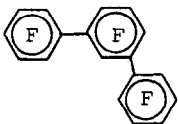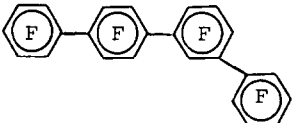the sum of the orders of the C-C bonds [1] for the compounds

investigated. It also presents the fluorine and hydrogen contents of polymers as compared to monomers. It can be seen that on poly- merization the loss of hydrogen is large for compounds with a high hydrogen content, and it becomes significantly smaller for compound VIII.

We note that in spite of the rise in the ionization poten- tials with an increase in the number of fluorine atoms in the benzene ring, the fluorine content of corresponding polymers decreases by approximately a factor of 2. This is likely to be connected with a decrease in the aromaticity of polyfluorinated benzenes [1] resulting in a more significant role of processes leading to the aromatic ring break. Processes involving a break of the aromatic ring have been considered above for compound II. A decrease in the amount of fluorine and hydrogen in the poly- mers obtained from polyfluorobenzenes can also be explained by the presence of secondary processes of cross-linking of the formed polymeric chains. Polymer formation without a break of rings is possible - by fusion of rings or by grafting to the formed polymeric chain, such being the case with monochloro- and monofluoro-benzenes [13].

TABLE 2

Frequencies of absorption bands for multi-ring perfluoroaromatic compounds in the region of 650-900 cm^{-1}

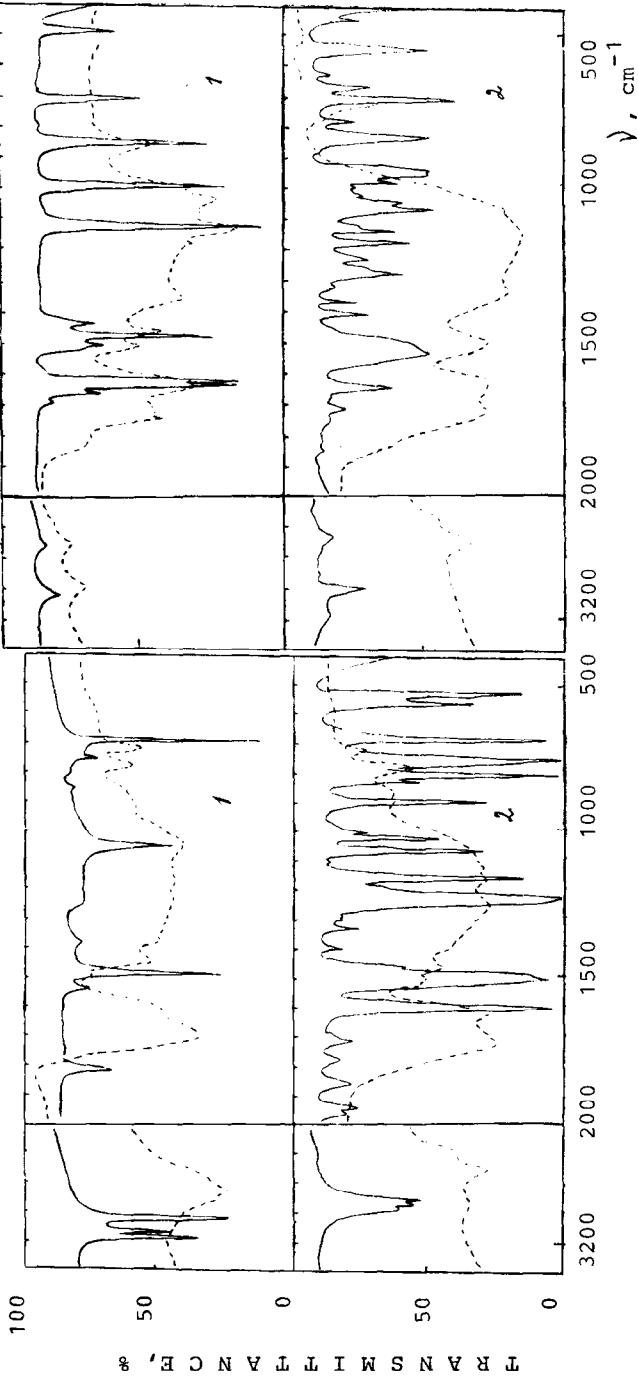| Compound	Frequency, cm^{-1}	Reference
	730(s)	[8]
	720(s)	[9]
	780(s), 650(s)	[9]
	780(s), 720(s), 650(m)	[10]

Fig. 3. Infrared spectra: benzene (1) and
monofluorobenzene (2) (solid lines)*.

Fig. 4. Infrared spectra: trifluorobenzene
(1) and pentafluorobenzene (2) (solid lines)*.

Infrared spectra corresponding to polymers = dashed lines.

*

We obtained valuable information on the structures of poly-
mers and processes leading to their formation by comparing the
infrared spectra of polymers with the corresponding spectra of
monomers (Figs. 3 and 4). The most noticeable and general chan-
ges for the entire series of compounds under consideration are
as follows: the appearance of broad and intense absorption in
the region of 1100-1300 cm^{-1} and another intense absorption
band in the region of 1700-1750 cm^{-1} and the disappearance of very
intense and narrow bands typical of a monomer in the region of
650-900 cm^{-1}. It should also be noted that bands characterizing
a fluorinated benzene ring are present in the region of 1500-
1640 cm^{-1}. We observed absorption in the region of 1100-1300 cm^{-1}
in investigating polymerization of hexafluorobenzene and attribut-
ed it to valence vibrations of aliphatic C-F bonds. The same
opinion was expressed in investigating polyvinylfluoride [14],
in this publication the intense absorption bands at 1142 and
1084 cm^{-1} were attributed to vibrations of C-F bonds. Besides,
in studying the action of gaseous fluorine on a polyethylene
film [15], a very broad and intense band was observed in the
region of 1100-1300 cm^{-1}. The comparison of our results with
the literature data testifies to the presence of aliphatic
chains in a polymer. It may be supposed that the appearance of
an aliphatic chain including -C-F groups on plasmochemical
treatment of fluoroaromatic derivatives of benzene may result
from processes involving a break of the ring. This may also be
the result of cross-linking of chains and grafting of aromatic
rings to them. It is known [14] that ultraviolet radiation is
one of the active factors in a glow discharge which participate
in the initiation of the polymerization process. It may be
assumed that one of the ways of the appearance of aliphatic
chains in polymerizates of aromatic hydrocarbons and their
fluorine derivatives is the formation in the discharge of
valence isomers of aromatic compounds, in particular, Dewar's
structures. These compounds are known to be formed from benzene
and its fluorine derivatives under the action of ultraviolet
radiation [16-19]. In this case, isomerization is an inter-
mediate stage leading to the appearance of aliphatic sections in
the polymeric chain.

The spectra of monomers exhibit very intense and narrow absorption bands in the region of 650-900 cm^{-1}, which characterize substitution in the benzene ring. New bands are observed in the spectra of the polymers which are also connected with substitutions in the aromatic rings depending on the way of their inclusion into the polymer structure. We made an attempt to evaluate the behaviour of these absorption bands in the region of 690-770 cm^{-1} and near 860 cm^{-1} depending on the structure of the initial monomer. The bands in the region of 690-770 cm^{-1} characterize a monosubstituted benzene ring, whereas the absorption near 860 cm^{-1} characterizes di- and poly-substitution [20]. In our case, monosubstitution may be connected with grafting of aromatic rings to the polymeric chain, the other kinds of substitution being connected probably with ring fusion. A similar approach was used for determining the structure of a polymer based on monofluoro- and monochloro-benzene [13].

Figure 5 illustrates the relative optical density of the absorption bands at 760 and 850 cm^{-1} in the spectra of polymers as a function of the number of fluorine atoms in the initial monomers. The positions of the absorption bands and their designations are given in Table 3. The relative optical density of each of the above bands calculated as the ratio of the band optical density to the optical density at $\nu = 1300$ cm^{-1} characterizes the absorption of the polymeric aliphatic chain and is absent in the spectra of the monomers (D'_D and D'_E).

TABLE 3

Position of absorption bands in infrared spectra of polymers

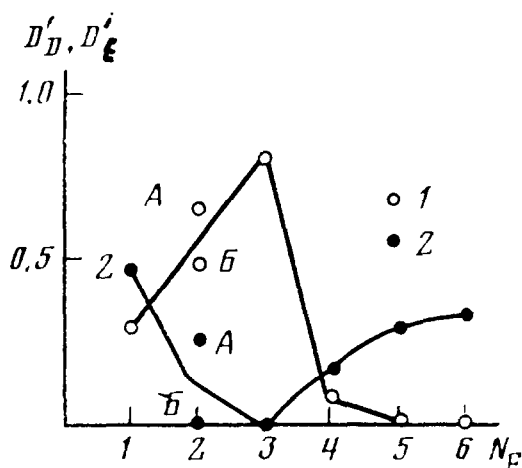| Composition	Position of bands, cm^{-1}				
	A	B	C	D	E
I	1710	1600	–	860	760, 700
II	1730	1640	1530	–	730
III	1730	1620	1500	850	765, 705
IV	1720	1620	1510	860	–
V	1700	1630	1510	860	775
VI	1730	1620	1510	860	–
VII	1730	1640	1520	860	750
VIII	1730	1650	1525	–	730

Fig. 5. Dependence of the relative optical density of absorption bands D'_D (1) and D'_E (2) in the infrared spectra of polymers on the amount of fluorine atoms in the aromatic rings of the corresponding monomers (A - compound IV, B - compound V).
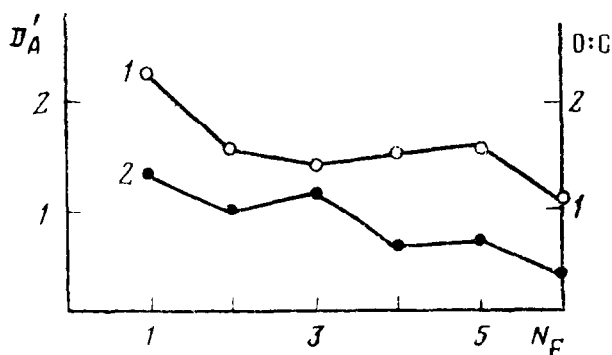

Fig. 6. Dependence of the O/C ratio (1) and relative optical density of absorption band D'_A (2) in infrared spectra of polymers on the amount of fluorine atoms in the aromatic rings of the monomers.

For polymers II and VIII, the relative optical density of the 730 cm^{-1} band was calculated, which characterizes monosubstitution in a polyfluoroaromatic ring (see Table 2). As seen from Figure 5, the main differences in the run of the curves are observed in the region corresponding to an intermediate fluorine content (2-3) of a monomer. In the case of polymer VI, the band at 760 cm^{-1} is practically absent, whereas the band at 850 cm^{-1} is at a maximum. Proceeding from the above, we may suppose that in the case of polymer VI aromatic rings are included into the polymer structure mainly through their fusion, whereas in the case of polymers II and VIII through their grafting to the aliphatic polymer chain. If the fluorine content is small (III), neither fusion nor grafting prevails. Thus, the investigation of fluorinated benzenes has made it possible to evaluate the effect of the number of fluorine atoms and their position in the benzene ring on the behaviour of these compounds in the discharge.

The change in the relative optical density of the absorption bands in the region of 1500-1550 cm^{-1} and 1600-1650 cm^{-1} corresponding to valence vibrations of the fluoroaromatic ring in a polymer (D'_B and D'_C), as a function of the number of fluorine atoms in a monomer, agrees with that presented in Fig. 5.

Elemental analysis results showed the presence of oxygen in all polymers. The oxygen content decreased as the number of fluorine atoms in the initial monomer increased. The presence of oxygen in polymers was supported by the appearance of an absorption band in the region of 1700-1750 cm^{-1}, characterizing vibrations of carbonyl groups (Figs. 3 and 4). Figure 6 illustrates changes in the optical density of such bands in the spectra of the polymers (D'_A) depending on the number of fluorine atoms in the monomers. It can be seen that with an increase in the number of fluorine atoms the optical density decreases, this being in agreement with the elemental analysis data (see Table 1).

Kinetic investigations showed a higher polymerization rate of compounds IV; V, VI, VII with a moderate number of fluorine atoms. Comparison of these findings with the results of studying the polymer structure change by infrared spectra leads to the conclusion that an increase in the polymerization rate is likely

to be connected with an increase in the role of fusion of the fluoroaromatic rings and with a decrease in the proportion of oxidation processes which may contribute to the break of a polymerization chain.

To ascertain the effect of a substituent in the polyfluorinated aromatic ring on polymerization of compounds in a glow discharge, we carried out investigations with toluene octafluoride IX, pentafluorobenzotrichloride X, perfluoro-α-chlorostyrene XI, perfluorostyrene XII and perfluoromesitylene XIII (see Table 1).

The results of kinetic investigations on determining the polymerization rate of these compouns are presented in Fig. 7. As can be seen, the polymerization rate of styrenes is markedly higher than that of compounds not containing vinyl groups. This fact is likely to testify to the participation of the olefinic bond in the polymerization process. The higher polymerization rate of XIII as compared to XI is in agreement with the known data on a higher polymerization rate of tetrafluoroethylene as compared to trifluorochloroethylene [21], as well as with our earlier results on the polymerization of halogenated styrenes [11]. That compound IX exhibits a higher polymerization rate than compound X is evidently connected with the fact that the process occurs mainly due to transformations in the aromatic ring. The break of the C-Hal bond in the benzyl position is not likely to play an essential role (the bond energy of C-Cl and C-F is equal to 339.4 kJ and 448.33-506.99 kJ, respectively [22]. Similarly, in the case of compound XIII, the route involving the detachment of fluorine atoms from CF_3 groups is evidently less important. This may be supported by the value of the polymeric film growth rate and by the composition of the polymer (Table 1). It is likely that in this case the main role belongs to a process similar to that for toluene octafluoride.

An important characteristic of the polyfluorination of polymers is the F/C ratio (see Table 1). The highest possible value of this ratio for polymers is equal to 2. As for monomers, such a value is observed for compounds with one double bond (for example, tetrafluoroethylene), or for cyclic compounds without multiple bonds. The presence of additional double bonds
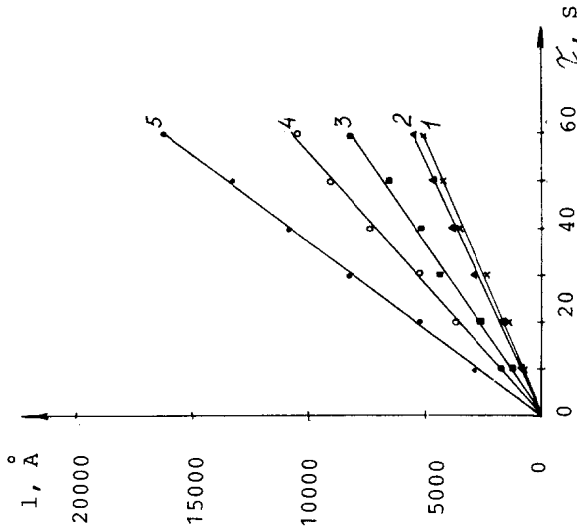
Fig. 8. Infrared spectra of pentafluoro-
benzotrichloride (1) and octafluorotoluene
(2) (solid lines) and corresponding polymers
(dashed lines).

Fig. 7. Polymer film thickness as a function
of deposition time for hexafluorobenzene (1),
pentafluorobenzotrichloride (2), octafluoro-
toluene (3), perfluoro-α-chlorostyrene (4) and
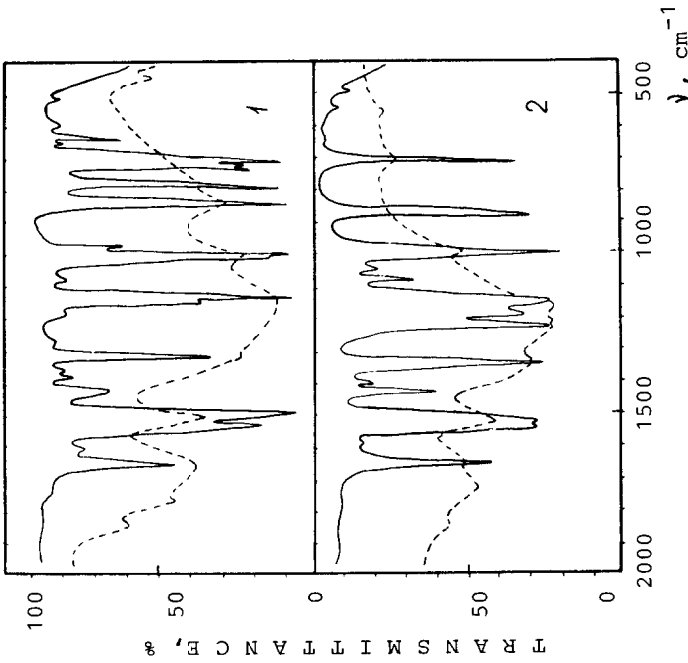perfluorostyrene (5).

in a monomer leads to a decrease in the F/C ratio with a
simultaneous increase in the polymer formation rate [23]. The
largest values of the F/C ratio were observed for compounds
XIII - 1.34, IX - 1.14, XII - 1.0. For the corresponding polymers,
these ratios decreased to 1.04, 0.96 and 0.87 (see Table 1).
Besides, chlorine-containing compounds exhibited a simultaneous
decrease in the Cl/C ratio, which was especially noticeable for
X (from 0.43 to 0.36).

    Infrared spectra of monomers and polymers IX-XII are ill-
ustrated in Figs. 8 and 9. A characteristic feature of all
investigated polymers is that their spectra are similar to the
spectrum of hexafluorobenzene (Fig. 1). Irrespective of initial
monomers, the spectra of the polymers are characterized by a
broad and complicated absorption band in the region of 1100-
1300 cm^{-1}, which is the most intense. It has been mentioned
above that this band corresponds to the aliphatic C-F bonds.
In addition, some bands typical of monomers are observed in the
spectra of polymers. For compound XII, for instance, they are bands
corresponding to valence vibrations of the C=C bond (1787 cm^{-1}),
and the C-C$_{arom.}$ bond of the fluorinated ring (1655 cm^{-1}, a doub-
let 1510-1520 cm^{-1}), and the band near 1000 cm^{-1} corresponding
to valence vibrations of the C-F bond. It is of interest to
note that the absorption bands in the region of 700-900 cm^{-1}
experience the most noticeable changes; in the spectra of mono-
mers IX-XII the bands are intense, whereas in the spectra of
the polymers they are weak. The bands in the region of 1700-
1850 cm^{-1} are typical of all polymers obtained. They may be due
to the presence of carbonyl groups in the polymer formed, or,
as mentioned above, as a result of the interaction of the poly-
meric film with atmospheric oxygen. This is in agreement with
the elemental analysis data on the presence of oxygen in a
polymer. Besides, that same region contains the bands cor-
responding to vibrations of the -CF=CF- bond formed due to
transformations of a fluorinated aromatic ring.

    The similarity of the absorption spectra of all investiga-
ted polymers enables us to consider that there exists at least
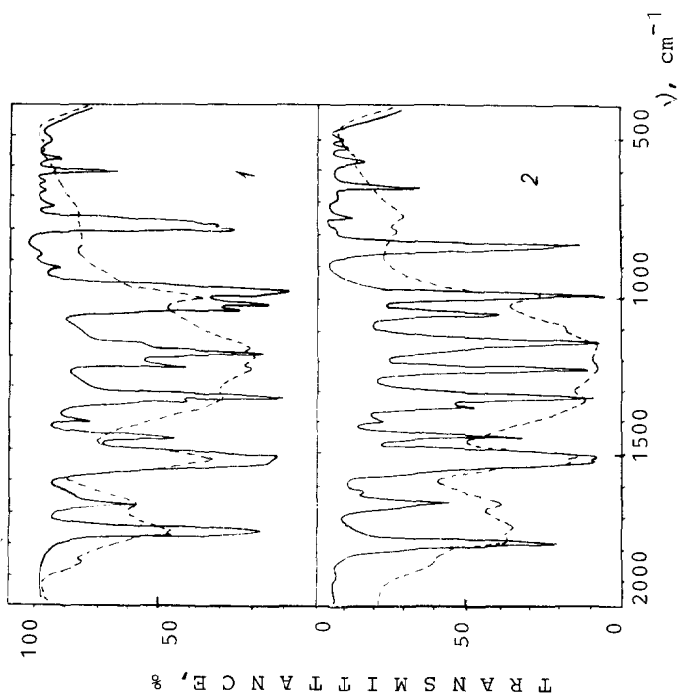one general way in which polymerization proceeds, and which is

Fig. 10. Dependence of the relative optical density of absorption band at 1540 cm⁻¹, D'₁₅₄₀, (1) and polymer film growth rate (2) on the F/C ratio in monomers.

Fig. 9. Infrared spectra of perfluoro-α-chloro-styrene (1) and perfluorostyrene (2) (solid lines) and corresponding polymers (dashed lines).
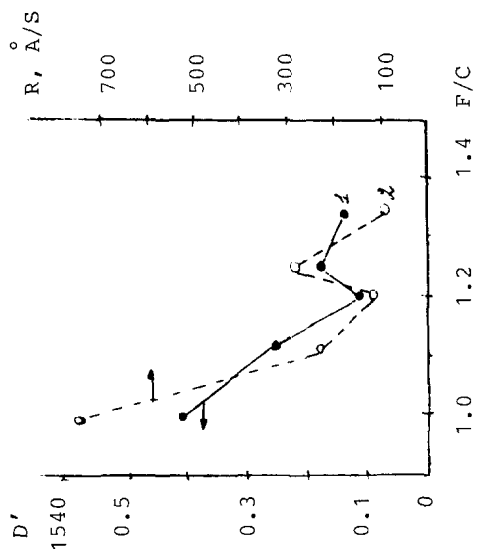
independent of the composition and structure of a substituent
in a polyfluorinated ring. The characteristic feature of this
process is the transformation of a polyfluorinated aromatic
ring with the formation of aliphatic bonds. This process is
likely to occur through the formation, in a plasma, of valence
isomers of aromatic compounds, in particular, of structures
such as Dewar's benzene [16-19], which may be the intermediate
stage in polymerization with ring opening.

The fact that the spectra of polymers obtained from sub-
stituted polyfluoroaromatic compounds contain absorption bands
characteristic of the initial compounds allows one to assume
that polymerization may proceed with the participation of a
substituent. In this case the polymeric film growth rate for
compounds with substituents (Fig. 7) depends considerably on
the nature of substitution and on the kind of substituent. The
maximum growth rate and maximum amount of fluorinated aromatic
rings in polymers were found for perfluorostyrene. It is connect-
ed, evidently, with the run of the polymerization process with
the participation of the vinyl group.

It was shown earlier [24] that irradiation of polyfluorina-
ted styrenes by ultraviolet light gave rise to perfluorobenzo-
cyclobutenes, and that photolysis of polyfluorinated alkenyl-
benzenes, in which the double bond is not conjugated with the
ring, led to the formation of polyfluorinated derivatives of
Dewar's benzene. If a similar process took place for perfluoro-
styrene in the glow discharge, then perfluorobenzocyclobutene
XIV, isomeric to perfluorostyrene, might participate in the
polymerization process.

$CF=CF_2$

glow discharge ⟶ glow discharge ⟶ polymer

It is known that the ability of cyclic compounds to undergo
ring opening depends, in a general case, on the ring strain
which, in turn, is related to the ring order [25]. The relativ-
ely strained fluorinated butene ring in compound XIV may open in
the polymerization reaction, whilst the benzene ring may be
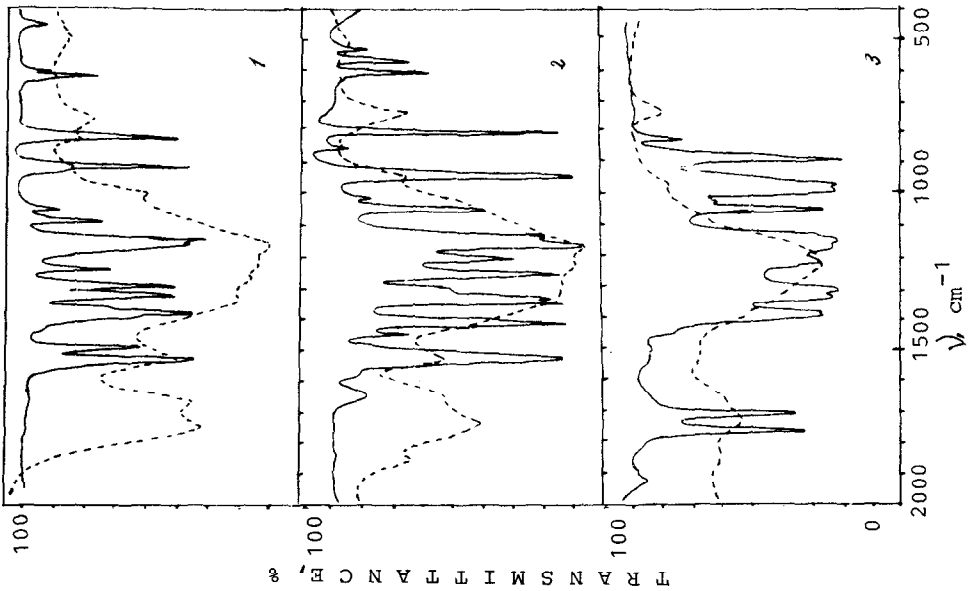retained to a greater extent. Such a viewpoint is quite in agree-

Fig. 11. Infrared spectra of monomers (solid lines) of perfluorobenzocyclobutene (1), perfluoroindan (2), perfluorocyclopentene (3) and corresponding polymers (dashed lines).
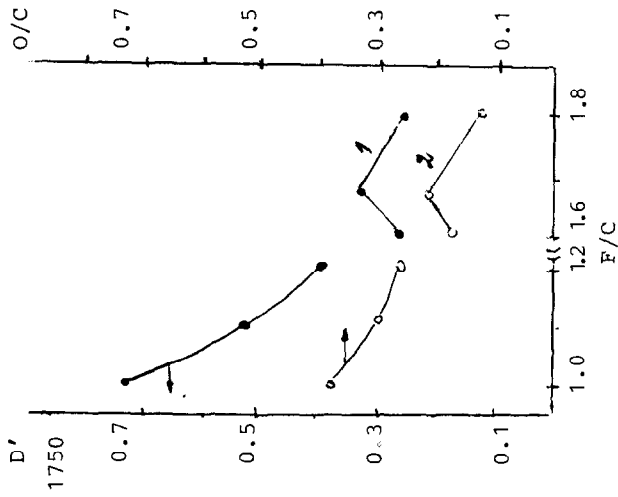
Fig. 12. Relative optical density of absorption band at 1750 cm⁻¹, D1750, (1) and the O/C ratio (2) as functions of the F/C ratio in monomers.

ment with our data: the polymer film growth rate for compound
XIV is very high, and the amount of fluorinated benzene rings
is maximum (Fig. 10).

The similarity of the infrared spectra of the polymers
from perfluorostyrene (Fig. 9) and from compound XIV (Fig.11)
is likely to testify to the structural similarity of the poly-
mers themselves. Thus, the data obtained do not contradict the
above polymerization scheme for perfluorostyrene, but they do
not exclude the possibility of some other pathway, in particular,
through the formation of a perfluorostyrene dimer.

It seemed interesting to compare the results on the poly-
merization of compound XIV with those of other perfluorobenzo-
cycloalkenes, viz. perfluoroindan XV and perfluorotetraline XVI,
with the aim of evaluating the effect of the order of the fluor-
inated alicyclic ring on the polymerization rate. In this
connection, the behaviour of perfluoro-o-xylene XVII and per-
fluorinated cyclopentene XVIII, cyclohexene XIX and decaline XX
was investigated.

The results of elemental microanalysis and the F/C ratios
in monomers and polymers are summarized in Table 1. Kinetic
investigations revealed the following values of the polymer
film growth rate: XIV-750 $\overset{\circ}{A}$/s, XV-200, XVI-120, XVII-270, XVIII
and XIX-90, XX-70 $\overset{\circ}{A}$/s.

Figure 11 presents the most typical infrared spectra of
monomers and polymers for this series of compounds. These spect-
ra are similar to spectra of polymers from hexafluorobenzene,
perfluorostyrene, octafluorotoluene and other perfluoroaromatic
compounds. Besides the absorption bands at 1100-1300 cm^{-1}, 1520-
1540 cm^{-1}, 1700-1750 cm^{-1} typical of all spectra, an absorption
band at 750 cm^{-1} was also observed. The nature of this band
was discussed in publication [26], devoted to the study of the
polymerization of tetrafluoroethylene in a discharge, and attri-
buted to the presence of the $>CF-CF_3$ fragment in the polymer.

It is shown that a change in the relative optical density
of the absorption band at 1540 cm^{-1} (Fig. 10) is related to a
change in the polymer film growth rate in the series of com-
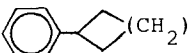pounds XIV-XVI, both quantities correlating with the order of

the perfluorinated ring fused with the fluorinated benzene ring.
In the case of perfluorotetraline XVI, the polymer film growth
rate and the amount of fluorinated benzene rings decreased to
values characteristic of hexafluorobenzene, which may be due to
the minimum strain of the alicyclic ring. These results are in
agreement with the data of work [27] in which a relationship
was found between the size of the ring and its stability against
electron collision, i.e. the activation energy of fragmentation
(E_a) of cyclic compounds of the type ⬡—◁$(CH_2)_n$ increases
in going from the strained phenylcyclobutane derivative to the
nonstrained phenylcyclohexane derivative (Table 4).

TABLE 4

n	Cycle strain, kJ/mole	E_a, kJ/mole
1	6.26	8.24
2	1.55	10.39
3	0	14.93

The question of the polymerization of compound XVII is
complicated. On the one hand, the process may proceed owing to
the detachment of a fluorine atom from CF_3 (transformation to
compound XIV cannot be excluded). On the other hand, the fluor-
inated benzene ring may participate in polymerization, as in
the case of octafluorotoluene. The possibility of the first way
of polymerization is supported by the data on an increase in
the polymer film growth rate as compared to octafluorotoluene,
perfluoromesitylene and by the data on an increase of the amount
of perfluoroaromatic rings (Fig. 10), as well as by a consider-
able decrease of the F/C ratio in the polymer (Table 1).

It is of interest to note that the polymer film growth
rates for compound XVII and perfluorostyrene are equal, and the
infrared spectra of these compounds are identical.

A comparative study of the polymerization of perfluorocyclo
pentene XVIII and perfluorocyclohexene XIX showed that the poly-
mer film growth rate was likely to depend to a lesser degree
on the ring order and was lower than for perfluorocycloalkenes.

In this connection, it seems strange that the presence of the
olefinic bond in XVIII and XIX does not impart a greater tenden-
cy to polymerization in comparison with perfluorobenzocyclo-
alkenes. We also note that the polymerization rate for XVIII and
XIX (90 Å/s) is close to that for such an alicyclic compound as
perfluorodecaline XX (70 Å/s).

Close values of the polymer growth rate for aliphatic and
olefinic compounds were observed in [28]. The authors suggested
3 types of reactions in the course of polymerization of such
compounds: 1) the opening of double bonds, 2) breakage of C-C
bonds, and 3) detachment of hydrogen. For compounds XVIII-XX,
all the three reactions are likely to occur, the third reaction
being the detachment of a fluorine atom. The reality of the
latter reaction is confirmed by the smaller fluorine content of
polymers from these compounds as compared to polymers from
compounds XII-XVI. It should be noted that the infrared spectra
of polymers of compounds XVIII-XIX (Fig. 11) are similar to one
another and to the spectra for perfluorodecaline XX.

Figure 12 compares the results of measuring the relative
optical density of the absorption band at 1750 cm^{-1} for com-
pounds XIII-XV and XVIII-XX, and the elemental analysis data on
the O/C ratio. It should be noted that these results are related
and that the formation of carbonyl-containing compounds is
maximal in the polymerization of perfluoroaromatic derivatives
and less pronounced in the case of perfluoroalicyclic compounds.
In publication [29] it was supposed that oxygen-containing
groups in polymers formed in a glow discharge appeared initial-
ly in the form of peroxides. From this point of view the in-
crease in the oxygen content of the polymers from compounds
XIV-XVI could be explained by a greater stability of aromatic
radicals $Ar_F O^{\cdot}$ as compared to nonaromatic radicals $Alk_F O^{\cdot}$
present in polymeric chains. At the same time, the oxygen
content of the polymer from compound XVIII is not large, which
may be due to a smaller aromatic ring content of the polymer
chain.

The data obtained make it possible to relate, with a
sufficient degree of precision, an increase in the polymer film
growth rate for perfluoroaromatic compounds in a glow discharge
to the presence of <u>ortho</u>-positioned alkyl groups, or to the
possibility of their formation in the course of polymerization.

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