MECHSNISMS OF GAS PHASE CONVERTION AND POLYMERIZATION IN NONEQUILIBRIUM PLASMA

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Mechanisms of chemical gas phase and heterogeneous reactions leading to polymerization are suggested based on experimental data and simulation of fluorocarbons conversion in nonequilibrium electric discharge plasma.

Introduction

Gas phase conversion and polymerization of fluorocarbons in nonequilibrium plasma of low pressure electrical discharges were investigated and reviewed in ref.[1]. Some neutral stable C_1-C_4 products C_1-C_4 composition, C_1- C_5 ions composition were measured with mass-spectrometry and concentration of fluorine atoms and CF, CF_2, CF_3 radicals were measured with optical actinometry [2-8]. Some conclusions about mechanism of reactions were based on these results. Large amount of C_1-C_8 products were discovered in our laboratory, using gas-chromatography and chromato-mass-spectrometry [9,10]. Detailed studying kinetic curves of all discovered products in line with kinetics of unstable active particles (atomics fluorine, CF_x -radicals) and kinetics of polymerization under controllable plasma parameters fullfilled in our laboratory in recent time [9-13] allowed to make more precise these mechanisms. Particularly initiation of polymerization is shown to be due to free bonds creation at the growing polymeric film surface under ions bombardment. Some contribution of ion-electron recombination is possible near by plasma flowing potential of surface. Destruction of polymeric growing films takes place too due to ionic bombardment.

Growing of polymeric film is connected with combination of radicals formed in gas phase with surface free bonds [11-12]. Polymerization rate does not correlate with CF_2 radicals flux, but correlates with the sum of C_5 - C_8 product concentrations [13]. Polymeric film composition depends sufficiently on conditions. It differs strongly from composition of standard teflon in wide range of residual time of molecules in steady state discharge.

But sharp variation of the film composition is observed at modulation of discharge power by square pulses with duration less than 20ms and large pause duration (τ_p>200ms). Under these conditions the film composition is close to teflon one [12].

The purpose of this paper is studying heavy radicals formation due to gas phase reactions and their role in polymerization. To do these it is necessary to develop the model of gas phase and heterogeneous reactions.

Methodic of mechanisms analyses and results.

Methodic based on mathematical simulation of chemical reaction kinetics under nonequilibrium plasma of complex composition is used developed before in our laboratory [14]. Comparison of the calculation results with experimental data is used for matching elemental stages rate coefficients.

The analysis is fulfilled for decomposition of c-C_4F_8 molecules in RF discharge. In this case most complete experimental data are obtained [10-12] keeping in the mind that chemical reactions kinetics are very similar for other fluorocarbons (C_2F_4, C_3F_6) under the same conditions.

Initial step of mathematical simulation of chemical kinetics is compiling of trial mechanisms which are corrected and completed after comparison of results with experimental data.

In the first variant of primery decay of molecules due to electronic impact is tested which play the main role at the small convertions. The final variant of electron impact initiation is shown to consist of following reactions:

$$\text{c-}C_4F_8 + e \rightarrow 2C_2F_4 + e \qquad (k_1 n_e = 2\ s^{-1}) \qquad (1)$$
$$\rightarrow C_2F_4 + 2CF_2 + e \qquad (k_2 n_e = 1.3\ s^{-1}) \qquad (2)$$
$$\rightarrow C_3F_6 + CF_2 + e \qquad (k_3 n_e = 1.3\ s^{-1}) \qquad (3)$$
$$\rightarrow C_4F_8 + e \qquad (k_4 n_e = 1.6\ s^{-1}) \qquad (4)$$
$$\rightarrow \text{c-}C_4F_7 + F + e \qquad (k_5 n_e = 1.0\ s^{-1}) \qquad (5)$$
$$\rightarrow C_2F_3 + C_2F_5 + e \qquad (k_6 n_e = 1{,}3\ s^{-1}) \qquad (6)$$
$$\rightarrow C_2F_4 + C_2F_3 + F + e \qquad (k_7 n_e = 1.3\ s^{-1}) \qquad (7)$$
$$\rightarrow CF_3 + C_3F_5 + e\ , \qquad (k_8 n_e = 1.0\ s^{-1}) \qquad (8)$$

where n_e - electron density in discharge plasma. The every products are observed experimentally excluding C_2, C_3, C_4 - radicals. The rate coefficients of the reactions (1-8) and other ones are determined at standard regime: mean electric power W = 0.26 W/cm^2; gas pressure p=40 Pa, gas flow rate Q=20 n·cm^3/min; gas temperature T_g=500K.

At the large times (t>10 ms) calculated product concentrations with mechanisms (1-8) are differed strongly from experimental data, and a new products are observed. It is evidence of secondary reactions. The most faster secondary reactions are the reactions of atomic fluorine with nonsaturated fluorocarbons, letter decay being with formation of radicals. Particularly such reaction is very good studied for C_2F_4 [15]:

$$F + C_2F_4 \rightarrow CF_2 + CF_3\ . \qquad (k_9 = 3.5 \cdot 10^{-11} cm^3 s^{-1}) \qquad (9)$$

This value is used for similar reactions of other insaturated fluorocarbons.

The main part of secondary reactions is a combination of radicals, including the saturated radicals giving a saturated fluorocarbons:

$$R_1 + R_2 \rightarrow C_nF_{2n+2} \qquad (n = 2\text{-}11) \qquad (10)$$

$$(k_{10}(n) = 2.3 \cdot 10^{-11} \div 6.3 \cdot 10^{-12}\ cm^3/s)$$

and unsaturated and saturated radicals giving unsaturated flourocarbons:

$$R_3 + R_1(R_2) \xrightarrow{M} C_nF_{2n} \ (n=2\text{-}17) \qquad (11)$$

and unsaturated heavier radicals

$$R_3 + R_1 \xrightarrow{M} R'_3\ . \qquad (12)$$

Mechanism includes 82 reactions of the type (1-12). As rate coefficients for reactions (10-12) the referenced values are used. In the most cases when the values are unknown they are found using analogies and semiempirical calculations. They are corrected up to achievement of satisfactory approximation of experimental kinetic curves.

At this stage a heterogeneous radical recombination reactions are included in mechanism giving stable products desorbed to gas phase and also combination reactions of radicals with free surface bonds (b):

$$R_i + S \rightarrow P(Z_i) \qquad (I=1\text{-}3). \qquad (13)$$

The letter are formed as result of charged particles bombardment of growing polymeric films at surface ($P(Z_i)$):

$$P(Z_i) + i,e \rightarrow R_k + S \qquad (R_k = CF,\ CF_2,\ CF_3,\ F). \qquad (14)$$

Satisfactory approximation of experimental kinetic curves are obtained only in the case of excluding from mechanism all reactions of heterogeneous recombination of radicals giving gas phase products except the only reaction:

$$CF_3 + FS \xrightarrow{W} CF_4 + S. \qquad (15)$$

Final mechanism of gas phase and heterogeneous reactions includes 118 reactions. This mechanism describes satisfactory experimental kinetic curves of formation and decay for more than 30 stable products, atomic fluorine, CF_2 radicals and polymeric film growing. The approximation are good only if the rate coefficients value are varied over narrow limited ranges (fig. 1-5).

Analyses of results and conclusions.

Developed mechanism of gas phase and heterogeneous reactions describes satisfactory the whole experimental data including not only kinetic curves but also other experimental facts, particularly dependencies of film growing rate on the ion and electron fluxes. Besides it allowes to calculate the concentrations and fluxes to surface of all heavy radicals up to $C_{11}F_x$ and evaluates their contribution to polymerization.

Analyses of results shows following:

1. Primer decay of fluorocarbons is due to electron impacts and passes through a number of concurrent channels (1-8).

2. Secondary reactions lead to formation of unsaturated molecules and radicals, kinetic curves passing through a maxima.

3. Formation of saturated fluorocarbons, which give no input to polymerization, is proportional to residual time of gas in discharge zone.

4. Heavy radicals and molecules are synthesized in secondary reactions combination of radicals formed due to decay of initial molecules and in secondary reactions.

5. Main contribution (till 90%) in polymeric film growing rate gives combination of neutral radicals C_4-C_8 with free bonds at $t \geq 50$ ms. Contribution of light radicals C_1-C_3 increases with decreasing of residence time and it is more then 30% at $t \leq 20$ ms.

6. Polymerization is continued during pause, being due to combination of CF_2 radicals. Thickness of film is increased during pause by 20-30% at $t_i = 20$ ms and $\tau_p \geq$ 20ms .

7. Large contribution of CF_2 radicals to pulsed discharge polymerization at $t_i \leq 20$ ms leads to variation of film composition and structure, which approach teflon composition and structure. Decreasing of ion bombardment in this case assists to such structure variation.

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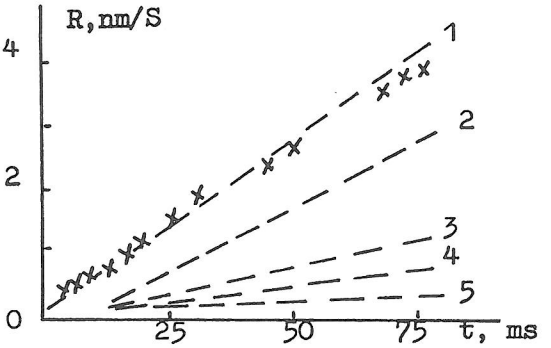

Fig. 1. Kinetic curves of polymeric film growing rate (R). Points represent the experimental data, broken lines are calculated overal film rate (1) and contributions of various radicals ΣC_4-C_8 (2); C_4(3); C_5 (4); C_1(5).

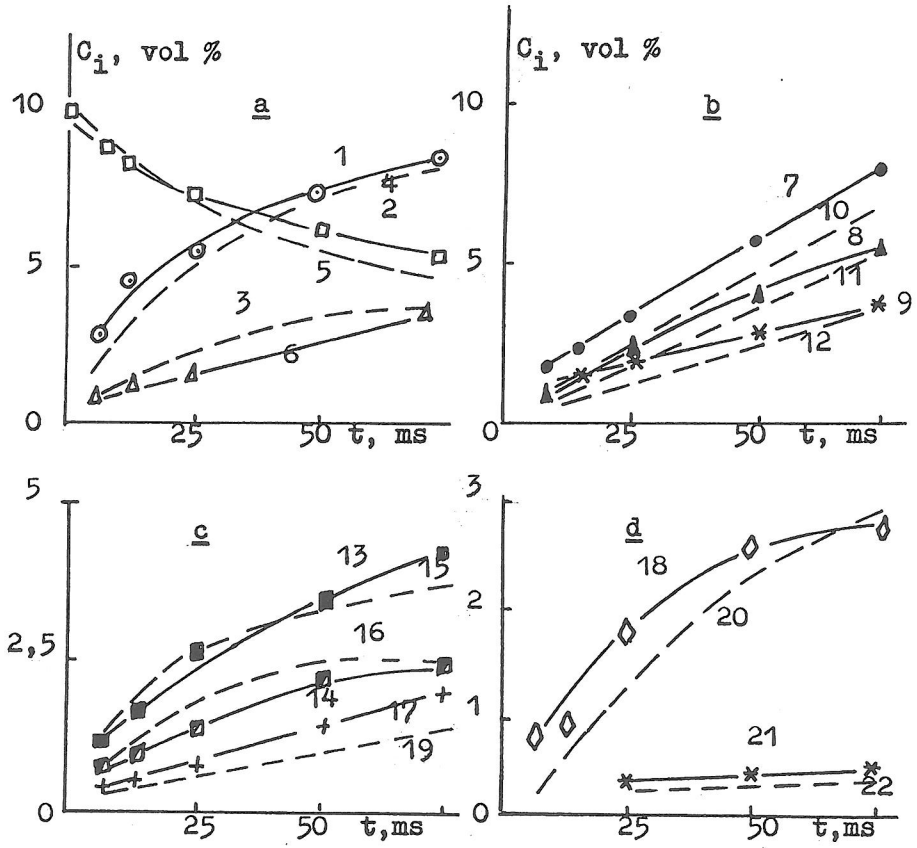

Fig. 2. Kinetic curves of c-C_4F_8 decay and gaseous products formation. Points and solid lines are experimental data; broken lines - calculations.
1,4 - 0.5C_2F_4; 2,5 -0.1 c-C_4F_8; 3,6 - C_3F_6; 7,10 - C_2F_6; 8,11 - C_3F_8; 9,12 - ΣC_6C_7; 13,15 - ΣC_4; 14,16 - C_4F_8; 17,19 - C_5F_{12}; 18,20 - ΣC_5; 21,22 - ΣC_8.