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# PLASMA SYNTHESIS OF POLYMERS

## A COMPARISON OF INDUCTIVELY COUPLED RF AND MICROWAVE PLASMAS EXCITED IN THE ISOMERIC DIFLUOROETHYLENES

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**Abstract**—A preliminary investigation of polymers prepared by RF and microwave glow discharge techniques is described. The polymer composition structure as revealed by ESCA is discussed and differences are shown to be subtle rather than major. Microwave prepared polymers are more sensitive to the operating conditions than the corresponding RF prepared polymers.

### INTRODUCTION

The synthesis of thin polymer films by plasma techniques represents an area of considerable current interest in both academic and industrial laboratories [1–4]. The capability of producing films of desirable chemical, physical, electrical and mechanical properties from a wide variety of monomers is becoming increasing apparent; however, the generally cross-linked nature of the films (and consequent insolubility) has posed considerable problems as regards *in situ* investigation of the overall structure and bonding.

In recent papers, we have shown that, with the considerable data base of information derived from ESCA studies of simple well characterized systems, it is now possible to study the gross structural features and compositions of plasma polymer films and that, with the available information levels, it is also possible to derive crude kinetic data for such polymerization [5–7]. The predominant emphasis in the rapidly expanding literature of plasma polymerization has been in the use of RF techniques (both inductively and capacitively coupled) with much less emphasis on microwave instrumentation. Indeed to-date there has been little attempt to compare systematically the results of RF and microwave plasma polymerization under appropriate conditions. We now report such a comparative study of the RF and microwave plasma polymerization of the isomeric difluoroethylenes.

### EXPERIMENTAL

The polymerization by RF excitation of inductively coupled plasmas and the measurement of ESCA spectra have been described previously as has the overall procedure for line shape analysis [2, 5, 8]. Here we present the experimental conditions used in polymerizations in microwave discharges. Microwave excitation was by means of a Microtron 200 mark III microwave power generator and was coupled via a 1″ diameter cavity 2¼″ long and tuned by two tuning stubs at right angles. The reactor itself was a modified version of that described previously [5]. The major modification being the reduction in diameter of the glass reactor to 1″ and the removal of the deposition monitor head. The discharge settings were first optimized using the appropriate monomer. The discharge region was then cleaned using an oxygen discharge followed by one in argon. The discharge region was purged with the monomer for several minutes and the discharge struck to initiate deposition. Short discharge times were employed (*ca.* 15 sec) due to the high rate of deposition at the power loadings involved. The nature of the microwave discharge meant that stable discharge could not be maintained at powers of < 10.0 W at the operating pressures used in this study. The discharge was tuned to give maximum brightness of the discharge zone and was cooled by a stream of compressed air.

### RESULTS AND DISCUSSION

#### (a) *Introduction*

Under comparable conditions of power input and pressure, the average kinetic energy of the electrons which largely dominate reaction processes with the plasmas are very similar for both RF and microwave plasmas; the main difference is associated with the difference in operating frequencies, perhaps a small effect on the ionization rate [9]. Whilst for RF plasmas it is a relatively straighforward matter to operate at extremely low power loadings < 1 W, this is somewhat more difficult for the typical tuned microwave cavity and in practice the typical lower limit in terms of power input is ~ 10 W. The comparison described in this work is for plasmas in the range 10–20 W input power and in the pressure range 0.05–0.2 Torr. The microwave discharge reactor was essentially of the same type as that used in the RF studies as outlined in the experimental section, but the diameter of the microwave reactor was substantially smaller ~ 1″ in the region in which the cavity was mounted. Since the glow region is therefore somewhat more localized, the power density is likely to be somewhat higher (for the same input power) for the microwave set up.

#### (b) *Comparison of data for the isomeric difluoroethylenes*

The core level ($F_{1s}$,$C_{1s}$) spectra for the plasma polymers prepared under the same conditions of pressure (0.2 Torr) and input powers of 10 W for the microwave and 1.0 W for the RF plasmas are shown

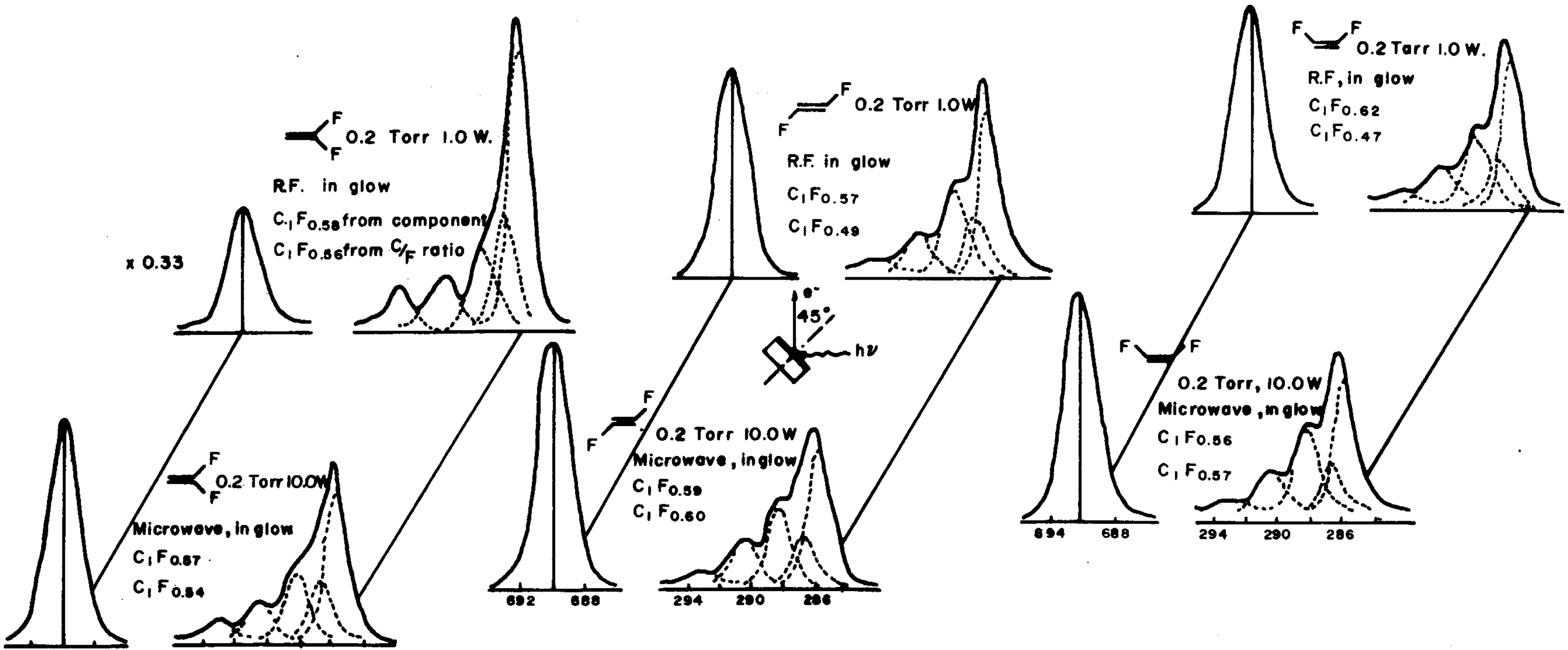

Fig. 1. $F_{1s}$ and $C_{1s}$ levels for plasma polymers prepared at 0.2 Torr in RF and microwave discharges.

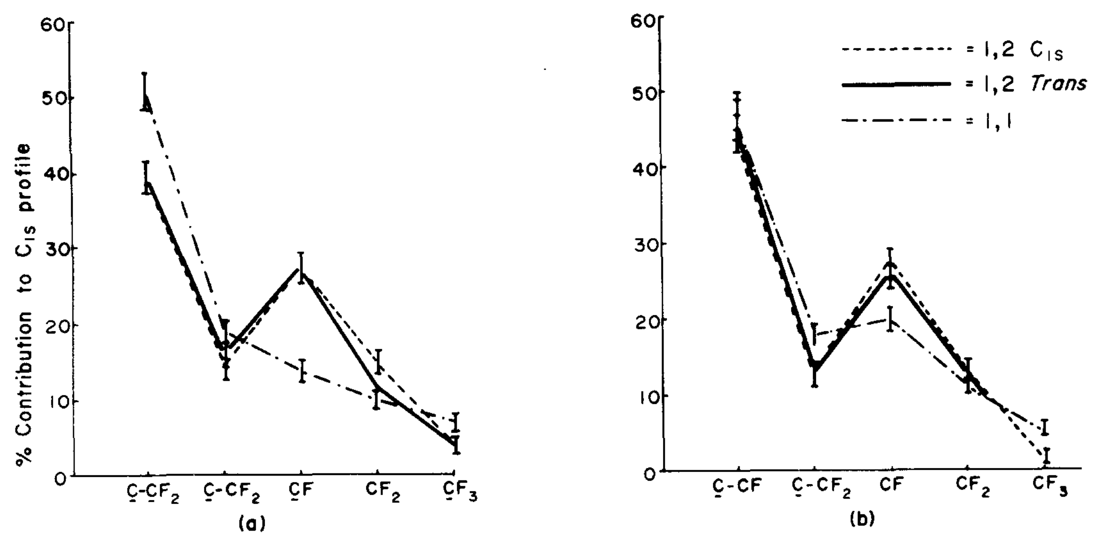

Fig. 2. Percentage contribution to the $C_{1s}$ envelope for C-F functionalities in the plasma polymers. (a) RF; (b) microwave.

in Fig. 1* where the results refer to an electron take off angle of 45°.

A cursory examination of the spectra reveals striking similarities. Thus the overall line shapes and component compositions of the $C_{1s}$ levels are very similar both within a given discharge set and also between the two sets. In each case the assignment of the five components of the $C_{1s}$ levels follows from a comparison with data compiled on model systems and the well established fact that the factors which determine shifts in binding energies are short range in nature [10, 11]. In decreasing binding energy, the components centred ~293.5 eV, 291 eV, 288.5 eV, 286.5 eV and 285.8 eV are assigned to $CF_3$, $CF_2$, $CF$, $—C—CF_2$ and $C—CF$ structural features.

We have previously shown that under a given set of experimental conditions (for the inductively coupled RF plasmas) the compositions and gross structural features (as evidenced by the core level spectra) for the geometric isomers are essentially the same [5, 6]. For the 1,1-difluoroethylene, however, the plasma polymer although of essentially identical composition to that for the isomeric 1,2-difluoroethylenes is distinctively different in terms of the overall functionality. It is clear that this difference also carries over to the microwave plasma polymers; however, the differences between the overall band profile for the 1,1-difluoroethylene and those for the isomeric 1,2-difluoroethylenes is not quite so distinctive. This is readily evidenced from the component line shape analysis displayed in Fig. 2. The error bars represent an upper limit in terms of the line shape analysis and these have been deliberately exaggerated to emphasize the fact that the differences do indeed lie outside the error limits for such an analysis. The noticeable feature in each case is the lower contribution of $CF$ and higher contribution of $CF_3$ structural features for the plasma polymers produced from the 1,1-difluoroethylene.

The stoichiometries of the polymer films are in all cases close to 0.5 (viz. $C_2F_1$). In order to investigate the effect of power loadings and pressure, Fig. 3 shows the $C_{1s}$ and $F_{1s}$ level spectra for microwave plasma polymer films produced at 20 W power loading and 0.1 Torr. For comparison, spectra for the RF plasma polymers at the same pressure but lower power are also included. It is interesting to note that in our previous studies of RF plasma polymers deposited in the glow region, the overall effect of power loading is relatively small [5–7]. It is clear from a comparison of Figs 1 and 3 that this does not apply to the microwave plasma although, as we have already noted, the smaller dimension of the microwave cavity implies a higher power density than for the RF plasma.

At the higher power loading of 20 W, the overall band profiles for the $C_{1s}$ levels for the microwave plasma polymers are closely similar for the isomeric difluoroethylenes. The stoichiometries for the microwave plasma polymer films produced from the isomeric difluoroethylenes at 20 W at 0.1 Torr (100 $\mu$) and at 10 W and pressures of 0.2 and 0.5 Torr are displayed in Table 1.

There is relatively little variation in stoichiometry with electron take-off angle for the polymer produced from a given monomer at a fixed pressure. This provides strong evidence for the vertical homogeneity of these polymers on the ESCA depth scale. This is also apparent from the near constancy of the $F_{1s}/F_{2s}$ ratio which accords with a vertically homogeneous film extending to a depth $\geq 3\lambda$ where $\lambda$ is the mean free path corresponding to photoemission from the $F_{2s}$ levels. This is of course substantially larger than the corresponding mean free path for electrons photoemitted from the $F_{1s}$ levels since the kinetic energies are so different (~560 eV for the $F_{1s}$ and ~1220 eV for the $F_{2s}$ levels). Application of such an analysis provides the data in Table 1 and stoichiometries as

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* In previous studies we have shown that the compositions and overall features of structure and bonding in the RF plasma polymerized films are essentially constant over the range of power loadings 1–10 Watts input power so that there are no ambiguities in terms of a comparison of data corresponding to these different power loadings [5, 6].

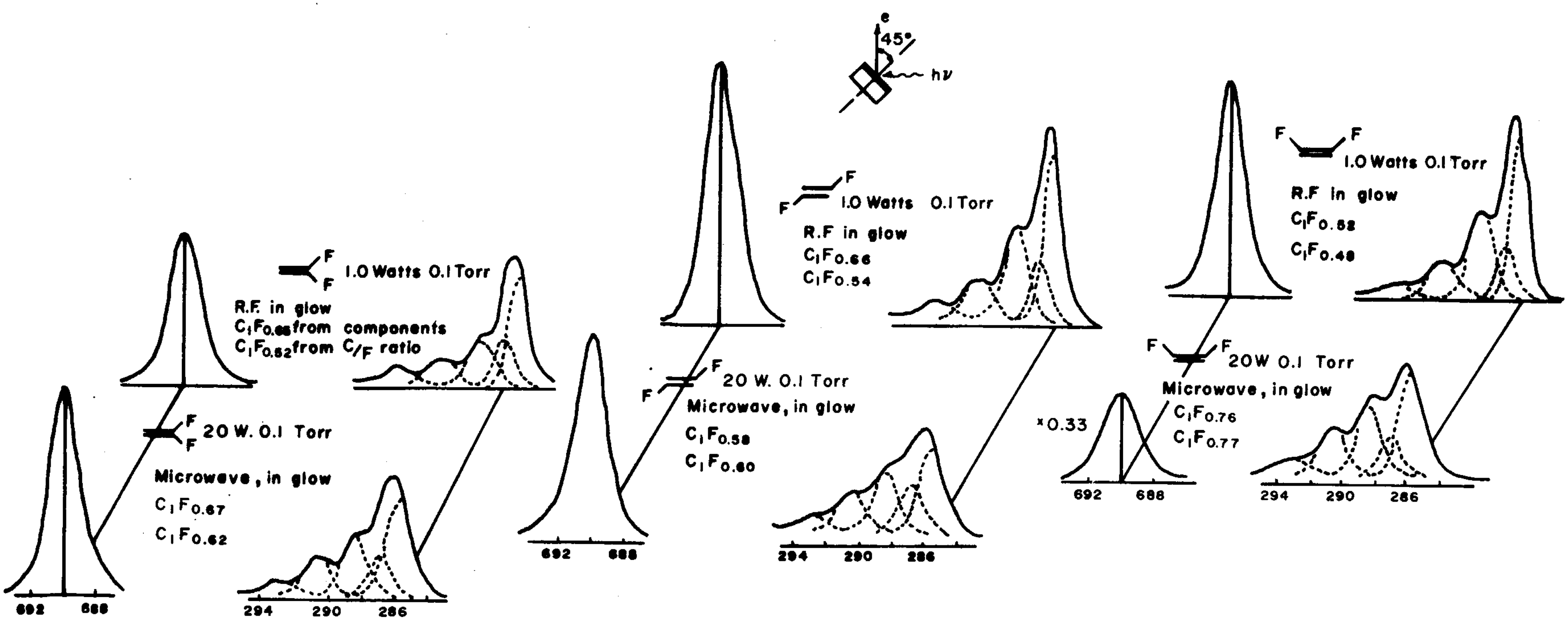

Fig. 3. $F_{1s}$ and $C_{1s}$ levels for plasma polymers prepared at 0.1 Torr in RF and microwave discharges.

Table 1. Stoichiometries of polymer films produced in microwave plasmas

| Power loading | | 1,1 | | 1,2 *cis* | | 1,2 *trans* | |
|---|---|---|---|---|---|---|---|
| | | C:F 1 | C:F 2 | C:F 1 | C:F 2 | C:F 1 | C:F 2 |
| 20 W | 100μ | | | | | | |
| | 10° | 0.63 | 0.68 | 0.75 | 0.72 | 0.62 | 0.61 |
| | 45° | 0.62 | 0.67 | 0.77 | 0.76 | 0.60 | 0.59 |
| | 70° | 0.64 | 0.63 | 0.68 | 0.76 | 0.63 | 0.67 |
| 10 W | 200μ | | | | | | |
| | 10° | 0.52 | 0.65 | 0.58 | 0.56 | 0.6 | 0.64 |
| | 45° | 0.54 | 0.57 | 0.57 | 0.56 | 0.6 | 0.59 |
| | 70° | 0.53 | 0.49 | 0.54 | 0.56 | 0.59 | 0.5 |
| 10 W | 500μ | | | | | | |
| | 10° | 0.47 | 0.49 | 0.49 | 0.53 | 0.47 | 0.46 |
| | 45° | 0.48 | 0.54 | 0.44 | 0.51 | 0.41 | 0.51 |
| | 70° | 0.46 | 0.41 | 0.46 | 0.40 | 0.41 | 0.43 |

C:F 1 is the $C_1F_x$ stoichiometry obtained from corrected $C_{1s}$ and $F_{1s}$ intensities.
C:F 2 is the $C_1F_x$ stoichiometry obtained from the deconvolution of the $C_{1s}$ profiles.

obtained from the deconvolution of the $C_{1s}$ profile are generally higher than those from the $C_{1s}$ and $F_{1s}$ area ratios. We have previously shown how stoichiometries can be independently derived from an analysis of the component contributions to the $C_{1s}$ levels and from the area ratios for the $F_{1s}$ and $C_{1s}$ levels. The most likely interpretation of this apparent discrepancy is the accidental degeneracy of a shake-up transition for one of the high intensity low binding energy components with the direct photoionization peak originating in photoemission from the $CF_3$ structural features. The typical energy separation for a low energy $\pi \longrightarrow \pi^*$ shake-up satellite of ~7.5 eV would identify the corresponding photoionization peak as that at ~286 eV. We have previously cited evidence [12] for such accidental degeneracies which, if not taken into account, lead to an inflated estimate of the extent of fluorine incorporation as is in fact revealed in a comparison of the appropriate columns of data in Table 1.

There are a few discernible trends in the data displayed in the Table worthy of note. Firstly, the degree of fluorine incorporation decreases as the operating pressure is increased; a trend of this nature is not so apparent in the previously reported data for the RF plasma polymerizations [5, 6]. Speculation as to the most likely cause for this trend is difficult on the data provided by the limited study reported here, but the change in the sweeping rate from the system of the reactive fluorine containing precursors must obviously be relevant. Visual observation of the glow discharge region indicates that it was more extensive at lower pressures. At higher powers the extent of fluorine content increases considerably and the stoichiometries at 20 W and 0.1 Torr are in the range 0.62–0.77. Although the overall $C_{1s}$ band profiles indicate that at higher powers and lower pressure the distribution of structural groups (viz. $CF_3$, $CF_2$ etc.) becomes more nearly similar, the stoichiometries reveal subtle differences with respect to each of the monomers.

## CONCLUSIONS

Although this is only a preliminary investigation of the differences in structure and composition of polymer films produced in microwave and RF plasma, it illustrates that there are likely to be subtle rather than major differences; it is also clear however that these differences are more dependent on the operating parameters for the microwave as compared to RF plasmas.

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