

# Plasma polymerization of selected organic compounds

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Plasma polymerization reactions and plasma polymers of xylene/air, xylene/argon, xylene/air/argon, toluene/air/argon, dioxane and allyl cyanide were compared with respect to discharge power (between 50 and 500 W), where all other plasma operational parameters were kept constant. In plasma polymerization, the glow characteristics are known to play an important role depending on the factor  $W/F$ , where  $W$  is the discharge power and  $F$  is the monomer flow rate. In plasma polymerization reactions, it is known that decomposition of the monomer and/or polymer produced competes with polymer formation. Above a certain power level, polymer decomposition may become the predominant reaction, and hence polymer deposition rates decrease with increasing discharge power. The plasma polymer films were characterized by Fourier transform infra-red spectroscopy, elemental analysis and thermogravimetric analysis. Infra-red spectra of the plasma polymers obtained indicated that when the discharge power was increased, the absorption intensities of all the functional groups decreased. The deposition rates and chemical structures of the plasma polymers prepared appeared to depend strongly on the structure and characteristics of the monomer used and on the conditions of discharge and other operational parameters.

(Keywords: plasma polymerization; deposition rate; organic monomers)

## INTRODUCTION

There has been an increase of interest in the use of glow discharge for the polymerization of a number of organic and organometallic compounds<sup>1–4</sup>. Glow discharge polymerization of various monomers in the vapour phase has been studied many times<sup>5–7</sup>. The parameters which define the plasma system (such as the monomer flow rate, pressure of the reactor and discharge power) are obviously the most important basic parameters necessary to describe and control the experimental conditions of plasma polymerization. Results obtained in terms of polymer deposition rates are often examined as a function of these parameters. The rate of plasma polymerization and the structures of the plasma polymers produced certainly depend strongly on the nature of the monomer employed. In addition, parameters such as monomer flow rate, reactor pressure, discharge power, reactor configuration, carrier gas and so on can also influence the polymerization rate. The utilization of the composite parameter  $W/F$  (power/flow rate) was first stimulated by Yasuda and coworkers<sup>8–11</sup> since discharge power by itself is not sufficient to describe plasma polymerization phenomena satisfactorily. They concluded that the monomer is subject to vigorous fragmentation upon increasing  $W/F$ , yielding plasma polymers which are usually rich in crosslinks and poor in organic residues. On the other hand, in a separate study the

effects of various gaseous additives on the deposition of a plasma polymer (of methyl methacrylate) were investigated using oxygen, water, argon and ammonia<sup>12</sup>. The results showed that the additives are incorporated into the plasma polymer. Yasuda and Lamaze<sup>13</sup> reported the effects of hydrogen, nitrogen, helium and argon on the polymerization rate of styrene in glow discharge. Their results indicated that argon and nitrogen had the largest effects on the increase in plasma deposition rate.

Plasma techniques are also used extensively for other purposes, i.e. to introduce thermal stability<sup>14</sup>, to change surface energies<sup>15,16</sup>, to improve wettability<sup>17,18</sup> and to produce functional groups<sup>19,20</sup> on the substrate surfaces to enhance adhesion and so on, in addition to their common use in polymer production. One of the main advantages of the plasma processes in these applications is certainly the limitation of their effects to only the top few molecular layers (about 10–30 nm), so that neither the appearance nor the bulk properties of the material are affected.

One of our main interests is to use plasma for surface modification of carbon fibres to improve the match with the matrix polymer in epoxy composite systems. The mechanical properties of these materials are described in a separate publication<sup>21</sup>.

In this paper, our interest is focused more on the nature of the plasma polymer products and the kinetics involved. The effects of discharge power and certain additives (argon and air) on the structures of the plasma polymers obtained were investigated. The monomers used had certain functional groups (like C=O, COOH, COH, NH<sub>2</sub> and C≡N), and since their effects were

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considered very important in the modification of surface properties, it was of prime interest to observe their concentrations in the products prepared under different plasma conditions. The polymeric films with reactive functional groups adhered well to the substrates and they had superior thermal stability and low solubility as a result of their expected crosslinked nature. For this study, four different compounds—xylene, toluene, dioxane and allyl cyanide—were selected as monomers for plasma polymerization. Air and argon were used separately in experiments to function as the reactive gas and carrier gas, respectively. The plasma polymers were examined by Fourier transform infra-red (FTi.r.) spectroscopy, elemental analysis and thermogravimetric analysis.

## EXPERIMENTAL

### Materials

The monomers used—xylene, dioxane, allyl cyanide and toluene—were pure and were purchased from Fluka. All monomers were kept in liquid form at standard temperature and pressure, and they were fed to the reactor tube under vacuum.

### Plasma system

A radio frequency (r.f.) (13.56 MHz) power generator of 1.5 kW capacity was used for the plasma polymerization reactions (Figure 1). The r.f. power was capacitively coupled to the plasma reactor. Rotary and diffusion pumps were used to evacuate the system to about  $4 \times 10^{-5}$  mbar (1 bar =  $10^5$  Pa). The pressure in the reaction chamber was controlled by an ionization gauge. The flow rate of the monomer vapour was regulated by a needle valve. The flow rate of the carrier gas (argon) and the reactive gas (air) was controlled by flow meters.

### Experimental procedure

Glass slides and KBr powder were used as the substrates onto which the plasma polymer films were deposited. To simplify the procedure, a small glass slide was fixed onto a larger one. Deposition rates were followed gravimetrically. The larger coated slide was used to determine the thickness of the polymer film,

measured by multiple-beam interferometry according to Tolansky's method<sup>22</sup>. Polymerizations were carried out for xylene under different plasma conditions with a mixture of air (reactive gas) and argon (carrier gas) and with only argon or air; for toluene with a mixture of air and argon; and separately for dioxane and allyl cyanide in the plasma state. Different discharge powers were used and all other operational parameters were kept constant.

### Characterization

FTi.r. spectra of the plasma polymers deposited on KBr were recorded using an IFS88 spectrometer. Thermogravimetric analyses were obtained using a DuPont 2000 and a Netzsch thermal analyser. In the Netzsch thermal analyser, samples were degraded in an argon atmosphere at a constant heating rate and in a nitrogen atmosphere at different heating rates ranging from 5 to  $20^\circ\text{C min}^{-1}$ . The plasma polymers obtained were tested for their C, H and N contents using an HP 185 elemental analyser.

## RESULTS AND DISCUSSION

### Deposition rate of plasma polymers

The rates of plasma polymer deposition from xylene/air, xylene/argon, xylene/air/argon, toluene/air/argon, dioxane and allyl cyanide were determined as a function of discharge power between 50 and 500 W (see Figures 2 and 3). The results obtained show the expected effect of discharge power on the rate of deposition. The deposition rates for all plasma polymers tested seemed to increase first upon increasing the discharge power up to around 200 W. Above this power, all deposition rates decreased gradually down back to approximately their initial values. The highest and lowest deposition rates were obtained for the toluene/air/argon system and for dioxane monomer, respectively, with certain characteristic differences for the systems in between. The deposition rate of the plasma polymer of xylene was about twice that of the plasma polymer of dioxane at all power levels (Figure 2). Interestingly, when the effects of the reactive (air) and carrier (argon) gases alone and their mixture on the deposition rates were examined, no appreciable differences between them were seen. Allyl

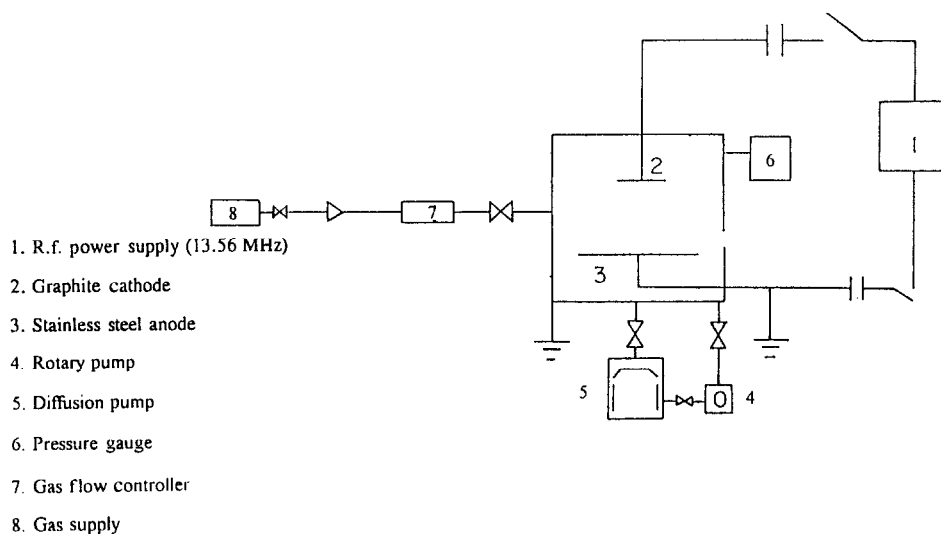


Figure 1 Schematic representation of the experimental set-up

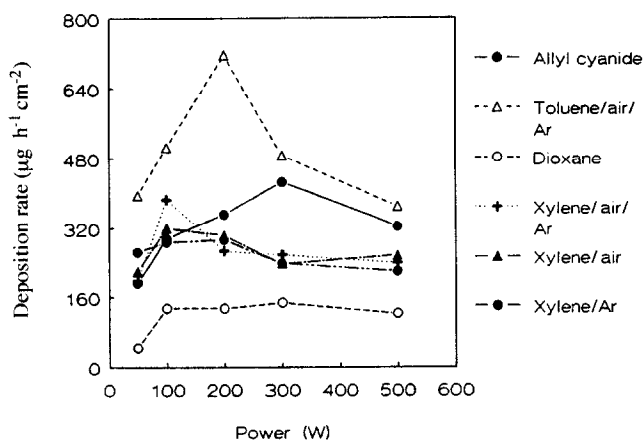


Figure 2 Deposition rates of plasma polymers as a function of r.f. power

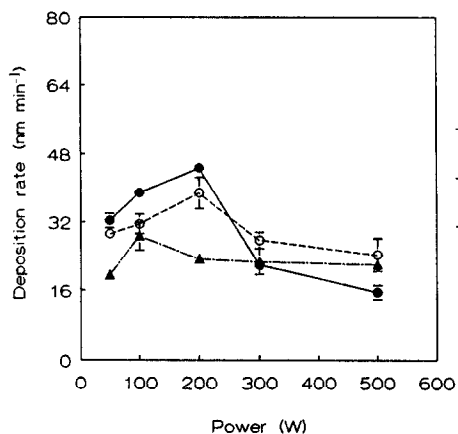
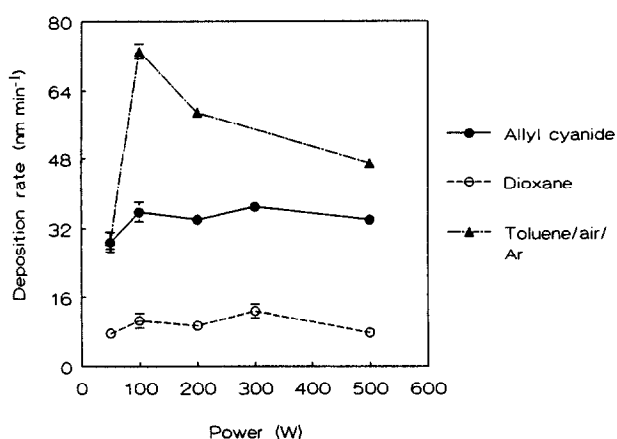


Figure 3 Deposition rates of plasma polymers as a function of r.f. power

cyanide showed similar behaviour to the other systems, except that its maximum deposition rate was observed at a 300 W power level. The increase in deposition rate with increasing discharge power can be explained simply in terms of the increase in available energy that can be used for polymerization<sup>23,24</sup>.

It is obvious that the minimum power necessary to initiate and run the plasma polymerization can differ appreciably from monomer to monomer. The deposition rate also appears to depend strongly on the structure and characteristics of the monomer. Hence, the results presented in this study are unique and are applicable

only for the parameters selected and for the geometry and size of the system used. However, since for most of the monomer systems these parameters were the same, the information obtained about the kinetics and behaviour of these systems in the plasma state is still expected to be valuable. It is believed that it should be possible to predict the behaviour of a monomer under certain plasma conditions by comparison with the behaviour of a similar monomer under the same plasma conditions; however, the general performances of both monomers would have to be known in advance.

The deposition rates presented in Figures 2 and 3 show a strong dependence on the power applied in a rather complex manner, as explained above. This dependence can easily be split into two regions: (1) an increase in deposition rate with increasing power (where polymer formation predominates) and (2) a decrease (or no change) in deposition rate with increasing power (where obviously ablation or degradation predominates, or is at least equal to the polymer formation rate).

Since the characteristics of the polymer formation reactions were our main interest, the first of these two regions was used to evaluate the activation energies of the polymer formation reactions of the monomers tested. For this purpose, modified Arrhenius-type plots<sup>25</sup> were drawn for deposition rate versus discharge power for all of the monomer systems (Figure 4). The Arrhenius-type expression used was

$$\text{deposition rate (DR)} = A e^{-E_a/KW}$$

In this equation,  $K$  is a constant which includes time such that the product  $KW$  can be compared with the product  $RT$  in the standard Arrhenius expression. The  $K$  values were calculated from the monomer flow rates given in Table 1. The  $K$  values were in the range 29.8–56 for the plasma conditions employed. The calculated activation energies of the plasma polymer formation reactions are also presented in Table 1. The activation energies obtained were very small. It appears that formation of an active species is the rate-determining step for the reaction and that polymer formation is quite rapid. It is interesting to note that the highest activation energy was found for dioxane plasma polymerization, which had the lowest rate of deposition. Xylene systems with intermediate rates of deposition yielded the lowest energies of activation, while the toluene system, which had the highest

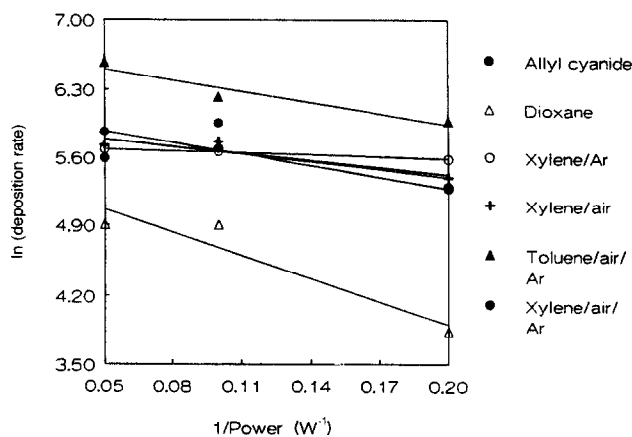


Figure 4 Modified Arrhenius-type plots of kinetic data

**Table 1** Activation energies of plasma polymerization for different monomer

	Xylene/ air/argon	Xylene/air	Xylene/argon	Dioxane	Toluene/ air/argon	Allyl cyanide
Flow rate of monomer (relative scale units)	600	600	600	400	400	750
$K$	37.3	37.3	37.3	56	56	29.8
$E_a$ (kJ mol <sup>-1</sup> )	0.99 ± 0.33	0.90 ± 0.20	0.26 ± 0.05	4.23 ± 0.62	2.12 ± 0.30	1.18 ± 0.30

**Table 2** Elemental analyses of plasma polymers produced under different plasma conditions

System	C content (% w/w)	H content (% w/w)	N content (% w/w)	O content (% w/w)	Formula
Toluene monomer	91.3	8.6			C <sub>7</sub> H <sub>8</sub>
Toluene/air/argon (50 W)	63.72	5.95	3.10	27.23	C <sub>4</sub> H <sub>4.5</sub> N <sub>0.16</sub> O <sub>1.16</sub>
Toluene/air/argon (100 W)	77.1	6.79	0.67	15.44	C <sub>4</sub> H <sub>4.2</sub> O <sub>0.6</sub>
Toluene/air/argon (200 W)	33.46	3.57	1.56	61.41	C <sub>4</sub> H <sub>5.1</sub> N <sub>0.14</sub> O <sub>5.42</sub>
Toluene/air/argon (300 W)	46.35	5.52	2.58	48.13	C <sub>4</sub> H <sub>5.6</sub> N <sub>0.18</sub> O <sub>3.1</sub>
Toluene/air/argon (500 W)	47.09	5.09		47.85	C <sub>4</sub> H <sub>5.1</sub> O <sub>3</sub>
Xylene monomer	90.5	9.4			C <sub>8</sub> H <sub>10</sub>
Xylene/air/argon (100 W)	70.85	6.78	1.33	21.67	C <sub>4</sub> H <sub>4.58</sub> N <sub>0.1</sub> O <sub>0.9</sub>
Xylene/air/argon (200 W)	53.63	5.88	1.34	39.15	C <sub>4</sub> H <sub>5.26</sub> N <sub>0.9</sub> O <sub>2.2</sub>
Xylene/air/argon (300 W)	70.20	6.16		23.64	C <sub>4</sub> H <sub>4</sub> O
Allyl cyanide monomer	71.6	7.4	20.8		C <sub>4</sub> H <sub>5</sub> N
Allyl cyanide (50 W)	44.41	5.71	16.72	33.16	C <sub>4</sub> H <sub>6.2</sub> N <sub>1.3</sub> O <sub>2.2</sub>
Allyl cyanide (100 W)	45	4.04	7.87	43.09	C <sub>4</sub> H <sub>4.3</sub> N <sub>0.6</sub> O <sub>0.6</sub>
Allyl cyanide (200 W)	34.02	3.73	6.09	56.16	C <sub>4</sub> H <sub>5.2</sub> N <sub>0.7</sub> O <sub>4.7</sub>
Allyl cyanide (300 W)	19.32	4.07	7.6	69.10	C <sub>4</sub> N <sub>4.3</sub> NO <sub>10.7</sub>

rate of deposition, showed the second highest activation energy. This discrepancy was probably due to the existence of other effects that were not included in the assumptions and equation given above. In the case of xylene, the system with argon carrier gas had the lowest activation energy by a factor of approximately 3. Hence, it may be suggested that argon gas activates the polymerization of xylene in the plasma state.

#### Results of elemental analysis

The plasma products obtained at different discharge powers were quite different in elemental composition from the starting monomers, which indicates enhanced fragmentation of the monomers in the plasma state.

The effect of power on the hydrogen content of the plasma polymers can be seen in Table 2. If the hydrogen contents are compared for a fixed number of moles of carbon in the products, an increase in the hydrogen content of the plasma products obtained from toluene/air/argon can be seen, while for the other monomer systems the opposite trend on the average is seen, most

probably because the products are more crosslinked or contain more unsaturated groups. A similar result has been reported by Yasuda *et al.*<sup>26</sup> for plasma polymers produced from other aromatic monomers.

It may be suggested that the hydrogen contents observed can be interpreted as resulting from either chain addition polymerization with crosslinking or polymerization through formation of acetylene derivatives. The latter appears to be corroborated by examination of the i.r. spectra of the plasma polymers obtained (Figures 5–10). It is found that there is a similarity between the i.r. spectra of the plasma polymers of acetylene and toluene prepared at high discharge power levels, as noticed elsewhere<sup>27</sup>.

#### Results of spectroscopy studies

The FT i.r. spectra as a function of discharge power for the plasma polymers prepared under optimized plasma conditions are compared with the spectra of the virgin monomers in Figures 5–10. It can be seen that almost all of the plasma polymers obtained from different

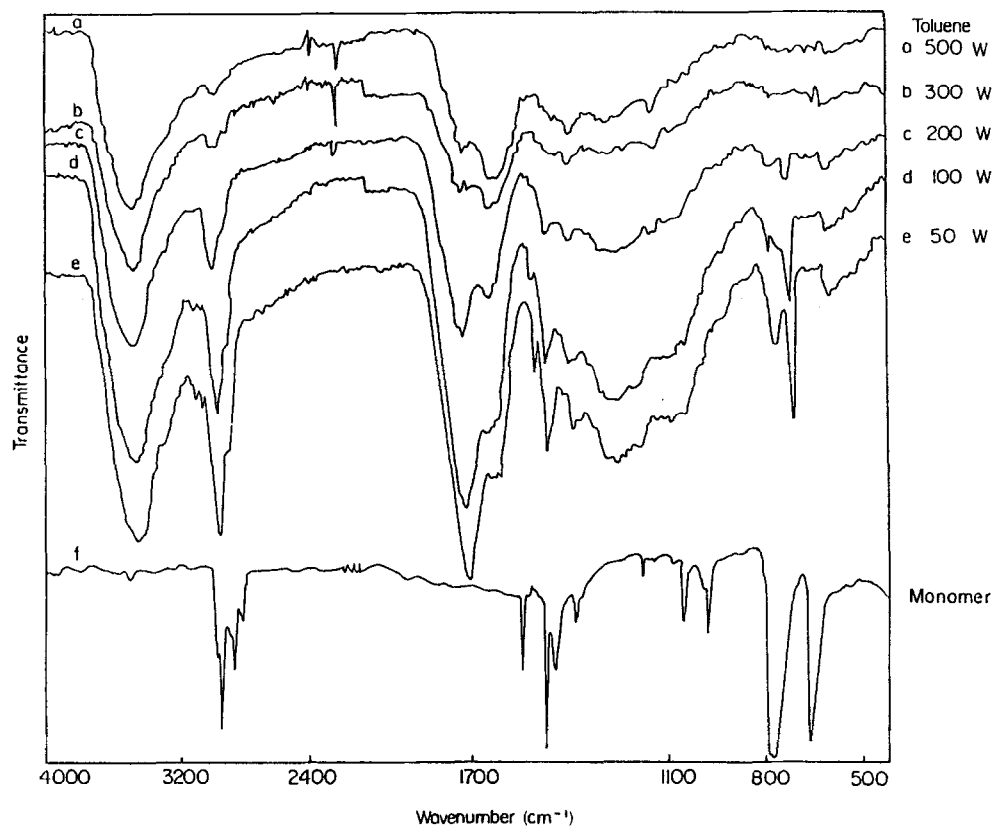


Figure 5 FTi.r. spectra of toluene/air/argon plasma polymers prepared at various r.f. powers

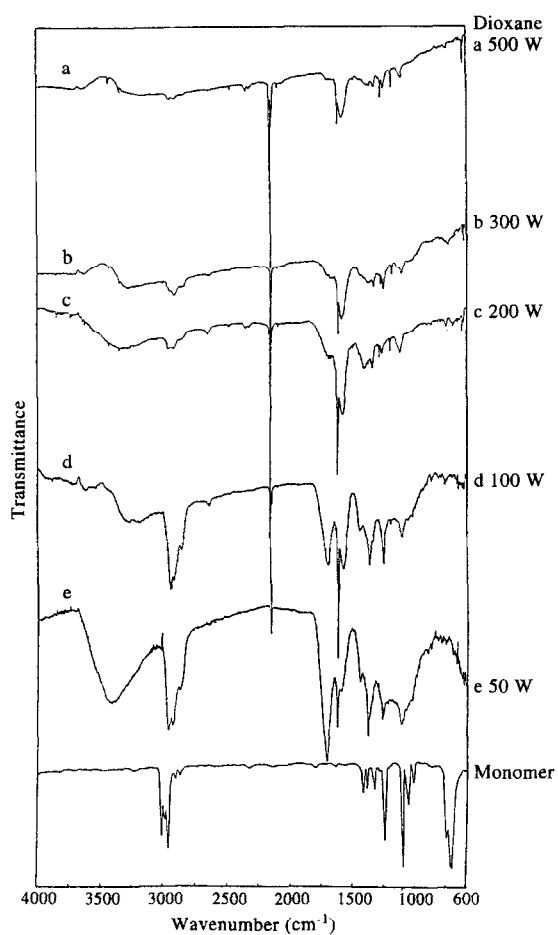


Figure 6 FTi.r. spectra of dioxane plasma polymers prepared at various r.f. powers

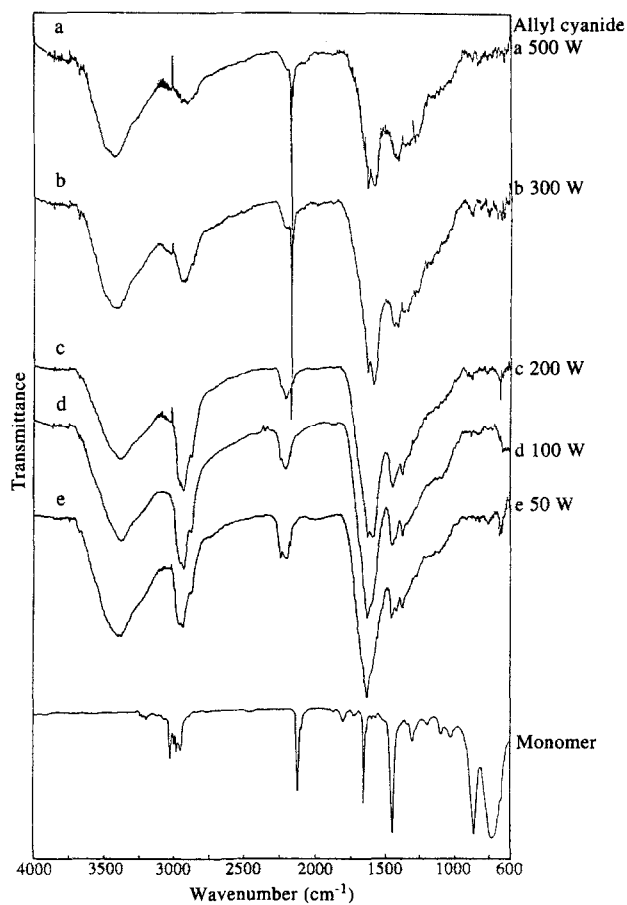


Figure 7 FTi.r. spectra of allyl cyanide plasma polymers prepared at various r.f. powers

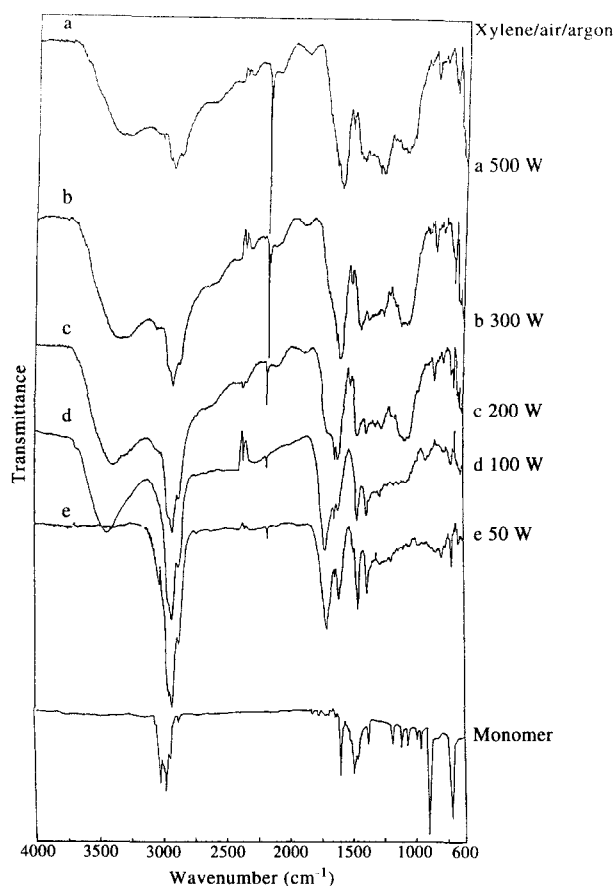


Figure 8 FTi.r. spectra of xylene/air/argon plasma polymers prepared at various r.f. powers

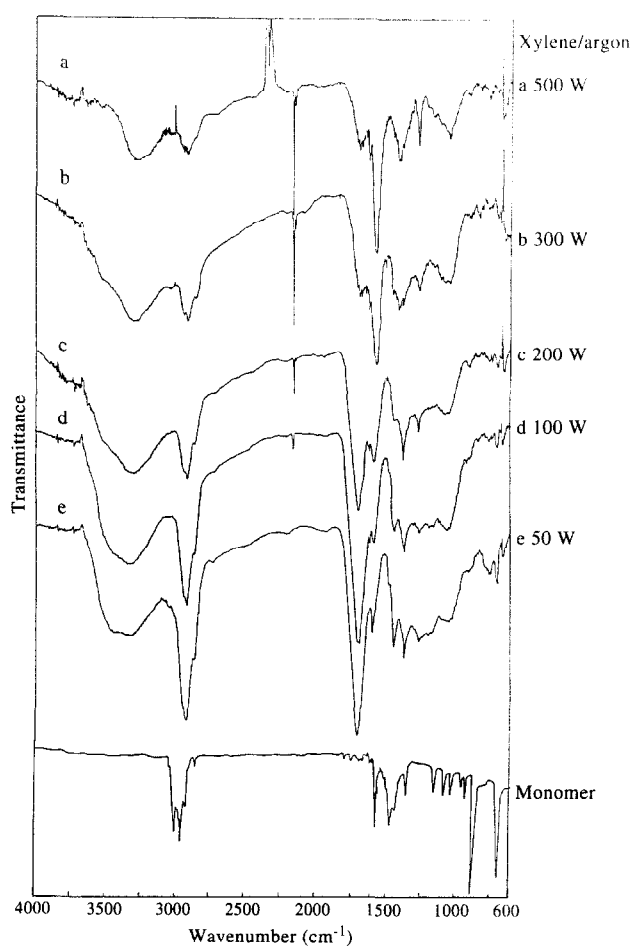


Figure 10 FTi.r. spectra of xylene/argon plasma polymers prepared at various r.f. powers

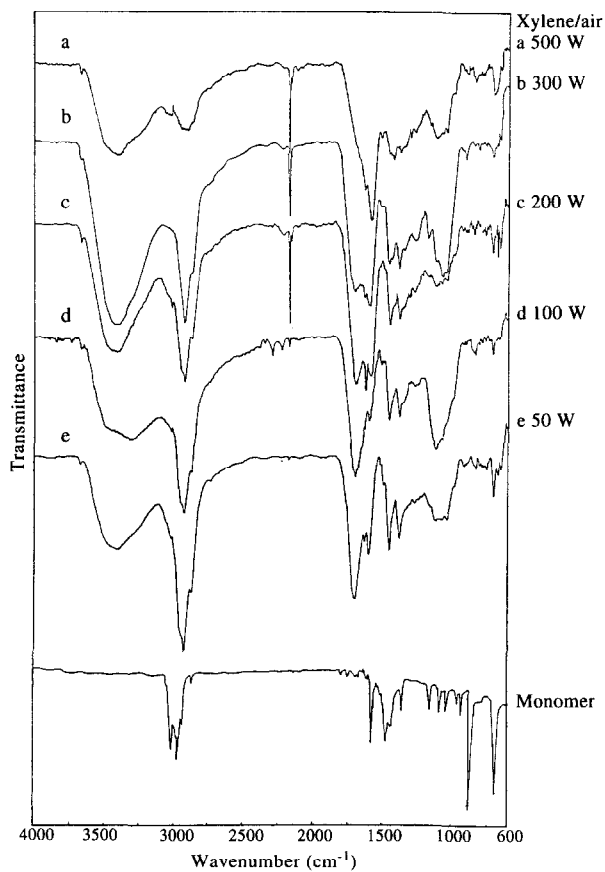


Figure 9 FTi.r. spectra of xylene/air plasma polymers prepared at various r.f. powers

monomers under different reaction conditions gave similar characteristic peaks, indicating the existence of common, similar structural groups in the final products. However, in general the relative intensities of these peaks varied with increasing discharge power.

One of the major peaks observed for all polymers was obtained around  $3430\text{ cm}^{-1}$ , which is most probably due to OH stretching vibrations of intermolecularly bonded OH groups. In particular, the strong peak at  $2965\text{ cm}^{-1}$  and the rather weak peak at  $1370\text{ cm}^{-1}$  can be assigned to the stretching and deformation of methyl groups on aromatic rings, suggesting a significant amount of branching in the plasma polymers. The peak at  $1700\text{ cm}^{-1}$  can be assigned to the carbonyl vibration ( $\text{C}=\text{O}$ ), which could arise from aldehydes or ketones. The absorption at  $1630\text{ cm}^{-1}$  may be identified as an olefinic ( $\text{C}=\text{C}$ ) stretching band. The presence of a  $\text{CH}_2$  or  $\text{CH}_3$  deformation band at  $1450\text{ cm}^{-1}$  indicates that additional branching and crosslinking are present. The strong peak at  $1100\text{ cm}^{-1}$  is due to the COC asymmetric stretching of aliphatic ethers and/or C–O stretching for saturated ethers. Bands between  $900$  and  $600\text{ cm}^{-1}$  indicate CH deformations of substituted benzenes. In addition, in the FTi.r. spectrum of the allyl cyanide plasma polymer, there is a characteristic sharp peak at  $2166\text{ cm}^{-1}$  from the  $\text{C}\equiv\text{N}$  group, most likely in the form of an aliphatic isonitrile, with a second characteristic peak found for nitriles at  $1592\text{ cm}^{-1}$ . The important difference between the allyl cyanide plasma polymer and

the other plasma polymers is also apparent: the distinct peak at  $1700\text{ cm}^{-1}$  due to C=O stretching is not observed for the allyl cyanide plasma polymer. The FTi.r. spectra of xylene and the polymers prepared from xylene/argon at different discharge powers are presented in Figure 10. In general, the same bands are present in these spectra as were observed for films prepared from xylene/air/argon and xylene/air, showing that the carrier or reactive gas had no substantial influence on the resulting structure of these polymers. The formation of new groups in the plasma polymer is mainly caused by the fragmentation of monomers under plasma conditions to give hydrogen and methyl radicals, or by the opening of double bonds in cyclic structures.

The peak intensities in the FTi.r. spectra of the plasma polymers confirmed the strong dependence of the plasma polymer film structure on discharge power. The absorption bands at  $2932\text{ cm}^{-1}$  ( $\text{CH}_3$ ),  $1700\text{ cm}^{-1}$  (C=O) and  $1376\text{ cm}^{-1}$  ( $\text{CH}_3$ ) decayed markedly upon increasing the discharge power, probably because of the thermal scission of carbon-hydrogen bonds during film growth. Moreover, the absorption bands at  $1630\text{ cm}^{-1}$  (C=C) and  $1100\text{ cm}^{-1}$  (COC) increased gradually with increasing discharge power because of the double-bond opening of aromatic rings. In fact, ion sampling of r.f. discharges for benzene<sup>26</sup> has shown that significant fragmentation of the benzene ring occurs for low pressure discharges under conditions similar to those considered in this study.

When the discharge power is increased, the intensities of all peaks decrease. This decrease may be due to increased decomposition of the deposited polymers with increasing power. It is clear from the presence of only a few broad absorption peaks that substantial degradation of the plasma polymers occurs under these conditions. Therefore, all the structural observations regarding the plasma polymers suggest that a high discharge power probably corresponds to severe fragmentation of each molecule in the discharge state and consequently to the production of a tightly crosslinked structure for the plasma polymer.

#### Thermogravimetric analyses

The thermal stabilities of the plasma polymers are compared in Figures 11–14. The results of thermogravimetric analysis (t.g.a.) clearly show the decomposition trends of the synthesized plasma polymers as a function of temperature up to  $1500^\circ\text{C}$ . The plasma polymers began to lose weight at rather low temperatures ( $250\text{--}300^\circ\text{C}$ ). Weight losses were initially observed with a slow rate above this temperature range, probably owing to the high degree of crosslinking<sup>14</sup>. In our case here, the possibility of crosslinking was also confirmed by the insolubility of the plasma polymers in common solvents and by the data from the i.r. spectra, as well as by the data from differential thermal analysis. The plasma polymers of toluene obtained in the presence of argon as the carrier gas and air as the reactive gas appeared to be the most stable (Figure 11) with a weight loss not more than 20%, whereas the corresponding plasma polymer of xylene lost 60% of its weight within the same period of time in the same temperature interval.

The thermal stabilities of the allyl cyanide plasma polymers prepared at different discharge powers are compared in Figure 12. There seems to be no obvious correlation between thermal stability and discharge power of preparation. Plasma polymers of allyl cyanide prepared at 100 and 200 W are more stable than those formed at 50 and 300 W. It can be seen from the FTi.r. spectra of these polymers that their structure changes considerably upon increasing the discharge power.

The t.g.a. results certainly offer an indication of the thermal stability of the plasma polymers obtained. The t.g.a. results confirm the results of FTi.r. spectroscopic analysis, indicating that aromatic compounds polymerize mainly through the formation of acetylene derivatives<sup>26,27</sup>.

The thermogravimetric (t.g.) and derivative thermogravimetric (d.t.g.) traces were obtained for plasma polymers of toluene (with air and argon) and allyl cyanide at different heating rates ranging from  $5$  to  $20^\circ\text{C min}^{-1}$  (Figures 13 and 14). In order to calculate the activation energy from the t.g. curves and also to get

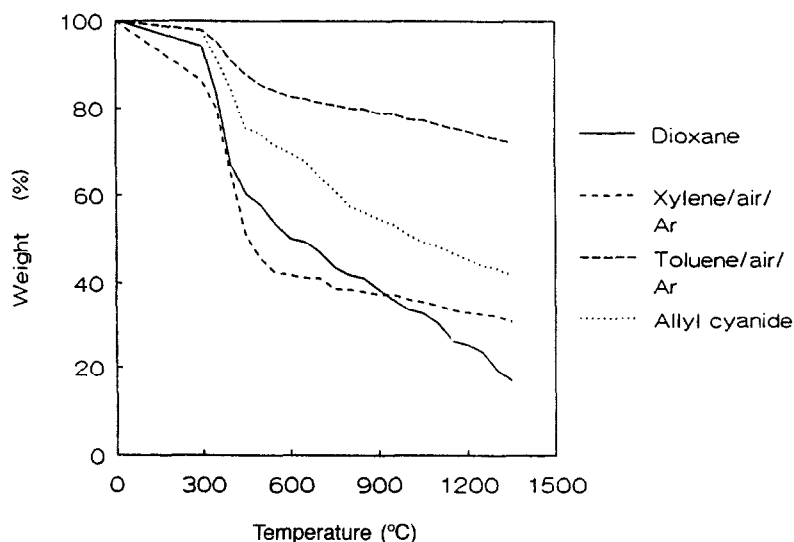


Figure 11 T.g.a. traces of plasma polymers

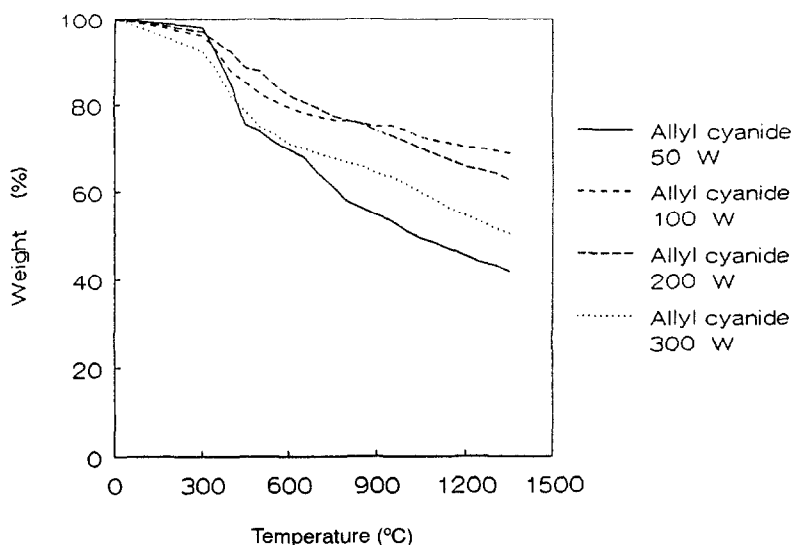


Figure 12 T.g.a. traces of allyl cyanide plasma polymers

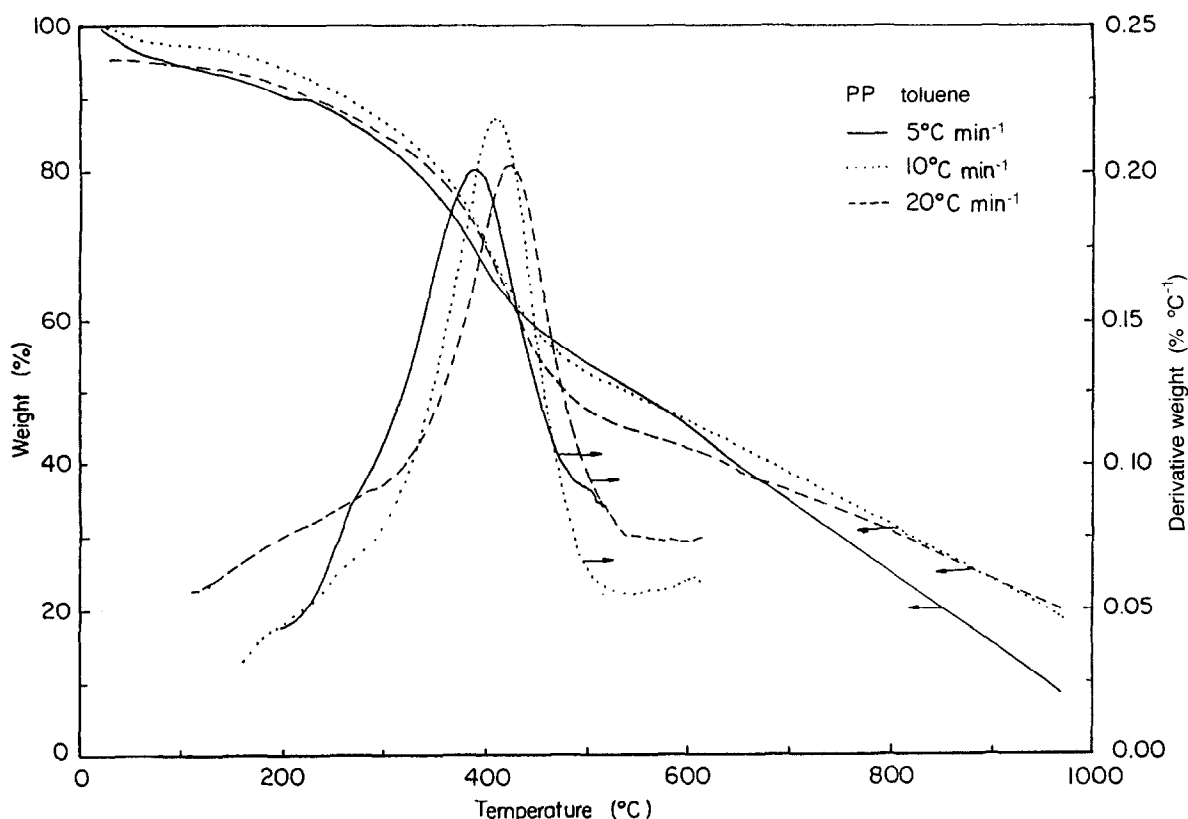


Figure 13 T.g.a. curves of a toluene/air/argon plasma polymer at different heating rates

quantitative information about the thermal decomposition of the plasma polymers, the method of Kissinger<sup>28</sup> was used. The equation involved in the Kissinger method is

$$-d(\ln B/T_m^2)/d(1/T_m) = -E/R$$

The Kissinger method allows one to calculate the activation energy of thermal decomposition from one point (the maximum on the d.t.g. curve) obtained at several heating rates. The activation energy of thermal decomposition can be obtained from the slope of the plot of  $\ln(B/T_m^2)$  versus  $1/T_m$ . According to this method, the

activation energies for plasma polymers of toluene and allyl cyanide were calculated. Table 3 summarizes the maximum pyrolysis temperatures ( $T_m$ ) obtained at different heating rates. The  $T_m$  values obtained increase slightly with increasing heating rate. If the  $T_m$  values obtained at different heating rates are compared, it can be seen that the stabilities of the samples differ slightly, but the  $T_m$  values of the plasma polymers of toluene and allyl cyanide are similar at heating rates of 20 and  $5^\circ\text{C min}^{-1}$ , respectively. The activation energy of decomposition obtained for the plasma polymer of toluene is somewhat higher than that obtained for the plasma



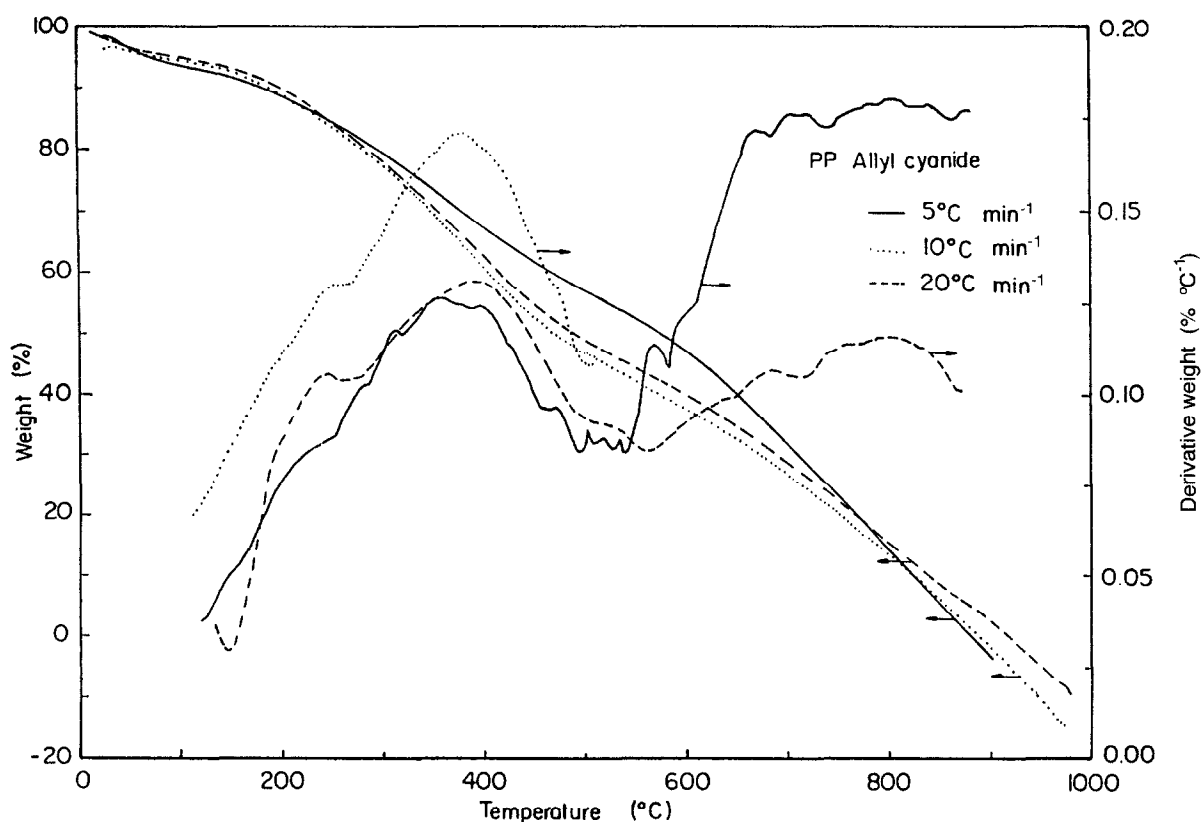


Figure 14 T.g.a. curves of an allyl cyanide plasma polymer at different heating rates

Table 3 Maximum pyrolysis temperatures and activation energies of the plasma polymers of toluene and allyl cyanide

Heating rate (°C min <sup>-1</sup> )	Toluene plasma polymer			Allyl cyanide plasma polymer		
	5	10	20	5	10	20
Maximum pyrolysis temperature $T_m$ (°C)	357	372	395	395.6	409.5	424.8
$E_a$ (kJ mol <sup>-1</sup> )	180 ± 0.65			118 ± 0.65		

polymer of allyl cyanide. From the results shown in Table 3, it can be deduced that the plasma polymer of toluene is the more stable under the plasma conditions employed. This conclusion was confirmed by the results of t.g.a. and FTi.r. spectroscopy.

## CONCLUSIONS

A modified Arrhenius equation was used to compare the activation energies of polymer formation in the plasma state and the decompositions of four different monomers. Polymer formation in the plasma was found to require very small activation energies and the plasma polymers obtained were stable, as shown by the activation energies of thermal decomposition. It was observed from infra-red studies that when the discharge power was increased, the intensities of all the peaks of the plasma polymer decreased owing to decomposition.

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