

# Optimizing Poly(chloro-*p*-Xylylene) or Parylene C Synthesis

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## Synopsis

Current interest for implantable insulating biomaterials has resurrected a class of polymers synthesized from *p*-xylylene and its derivative dimers. Important kinetic aspects for the synthesis of the polymer are derived from measurements of chamber pressure and total weight of film deposition. Reduction of peak chamber pressure during polymer deposition was found to improve film quality, uniformity of deposit, adhesion, and transparency. A low-cost reactor design is proposed which simplifies the deposition characterization steps needed for producing high quality films.

## INTRODUCTION

The Parylenes® are a class of polymers synthesized by pyrolytic vapor decomposition polymerization of *p*-xylylene and its derivative dimers.<sup>1</sup> The most common in industry is the unsubstituted form known as Parylene N, and, in biomedicine, the monochlorinated form Parylene C, synthesized from di(*p*-xylylene) and dichloro-di(*p*-xylylene), respectively. These polymers possess a remarkable combination of physical, chemical, thermal, and electrical properties which make them ideal for numerous engineering applications. The process of polymer formation is also unique and results in conformal coatings on almost any solid substrate exposed to the dimer vapor at ambient temperatures.

Parylene N, because of its simple structure and also because it is the first member of the family, has received maximum attention in the past.<sup>2-5</sup> However, the best performance properties of Parylene N are realized only from depositions at low substrate temperatures that make the polymerization reactor design cumbersome and commercially unattractive.<sup>6</sup> Parylene C, on the other hand, demonstrates its best properties when it is deposited at ambient temperatures.<sup>6</sup> For use in implantable devices, Parylene C has been reported to be biocompatible,<sup>7,8</sup> which is one of its desirable characteristics currently exploited for implantable applications requiring insulating biomaterials.

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In this paper we discuss some new kinetic aspects of Parylene C deposition which allows one to characterize the synthesis independent of reactor geometry. We also present the design of a simple, low-cost, benchtop Parylene C reactor for research and engineering applications.

### EXPERIMENTAL

A schematic of the Parylene reactor used in our study is presented in Figure 1. It consisted of a sublimation chamber, a pyrolysis chamber, a polymer deposition chamber, a cold trap, and a vacuum pump. In contrast to most other reactors described in the literature,<sup>6</sup> the cold trap in our reactor was placed perpendicular to the flow of the active monomer species in the pyrolysis tube which resulted in a much higher polymer deposition efficiency in the main deposition chamber. We also preferred to build the cold trap and other vacuum parts from stainless steel vacuum flanges with copper gaskets. The cooling of the cold trap was done from a liquid nitrogen dewar placed outside the cold trap. Since the amount of polymer deposited in the cold trap was much smaller than in conventional reactors, cleaning of the cold trap after each run was not necessary. The design of the deposition chamber was also unique and allowed maximum space utilization. The pressure in the deposition chamber was monitored with a thermocouple pressure gauge (Varian Model 801). The advantage of this type of gauge over conventional capacitance manometers is that pressure in the deposition chamber can be monitored during synthesis because the Parylene C polymer does not deposit on the heated element of the thermocouple. The 9 in. pyrolysis zone in our reactor was shorter than recommendations in the literature.<sup>6</sup> Placed at both ends of the pyrolysis tube were baffles to control the dimer flow. The sublimation tube was completely enclosed in the sublimation furnace and was attached to the pyrolysis tube with a ground glass joint to allow a better heat transfer and thus prevent undesirable cooling of the dimer vapors in the interfurnace zone. The entire system was attached to a mechanical vacuum pump of 5.6 cfm capacity.

To begin an experiment, a known mass of dimer was placed in the sublimation tube. The pyrolysis zone had previously been heated to the desired temperature. Substrates were then placed in the deposition chamber and the system evacuated to about 10 mtorr. This usually took about 10 min. The cold trap was then activated by placing a dewar filled with liquid nitrogen around it. The chamber pressure then dropped to about 1–2 mtorr in the next 1–2 min. When the low pressure had been reached, the sublimation furnace was then started. The polymer deposition began within a few minutes and continued for 15 min to several hours, depending on the mass of dimer charge and the conditions of polymerization. After all the dimer had sublimed, the sublimation furnace was turned off as was the pyrolysis furnace. Liquid nitrogen was removed from around the cold trap, and the cold trap was allowed to come to room temperature. A rise in chamber pressure was noticed during the rewarming process.

Precleaned glass microscope slides were used, as received, to study the kinetics of polymer deposition.<sup>9</sup> After each run, the polymer which had been deposited on the walls of the deposition chamber was removed and used for

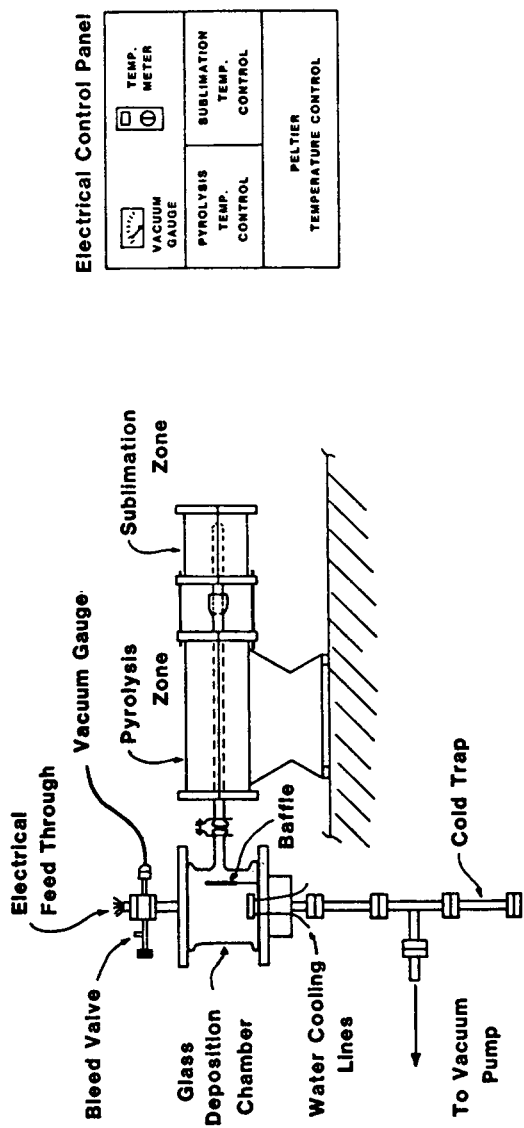


Fig. 1. A schematic diagram of the Parylene reactor as described in the text.

TABLE I  
The Effect of Pyrolysis Temperature on Film Quality for an Unfilled Pyrolysis Tube

Sublimation temperature (°C)	Pyrolysis temperature (°C)	Extractables (%)	IR peak?
160	625	3.6	Yes
160	650	2.3	Yes
160	675	0.1-0.3	No

extraction studies and for IR spectroscopy. Material deposited on the microscope slides was used for the study of the adhesion properties of the polymer.

### RESULTS AND DISCUSSION

Since a complete decomposition of dichloro-di(*p*-xylylene) dimer to active monomer species is desired for obtaining chemically stable Parylene C films, the initial emphasis of our study was placed on determining pyrolysis conditions that would result in a film with the lowest dimer or oligomer content. A wide range of configurations and furnace temperatures were tried for optimizing the dimer decomposition process. We began with a pyrolysis tube randomly filled with  $1 \times 0.5$  cm quartz tubes, followed by a linearly filled tube. The intent of this was to increase the residence time of the sublimed dimer in the pyrolysis zone and thereby improve the probability of splitting the dimer material. We found that while the randomly filled tube produced a polymer with no detectable dimer when operated at 625°C, it placed tremendous restriction on the flow of the dimer into the deposition chamber and effected the deposition process by leaving a fraction of the dimer mass unsublimed. The linearly filled tube was an improvement over the randomly filled tube in terms of the rate of polymer deposition, but even this was abandoned when it was realized that, at a 675°C pyrolysis temperature, an unfilled tube produced a polymer film of equal quality. The results of these experiments are presented in Table I. The dimer peak in the range of 708–724  $\text{cm}^{-1}$  was noticed in the IR spectra of these samples when recorded in the expanded range of 400–1000  $\text{cm}^{-1}$ . This peak disappeared after the polymer films were extracted with xylene at its boiling point for 30 min.

These experiments also showed that the adhesion of the Parylene C film varied with the pyrolysis tube configuration. The films prepared using the randomly filled tube were invariably nonstrippable<sup>6</sup> from the glass slides.

The film thickness was found to vary linearly with the weight of the dimer material in the sublimation tube. Figure 2 depicts this variation in thickness of Parylene C films as a function of dimer mass. The film thickness was determined gravimetrically by weighing the Parylene C film deposited on the glass slide and calculating the thickness by substituting into the formula a density of 1.29  $\text{g}/\text{cm}^3$  for the polymer. The thickness of Parylene films has been found to vary with the configuration and the surface area of the substrates relative to the deposition chamber surface area.<sup>6</sup> For example, if the total substrate surface area is increased, the thickness on any sample decreased and vice versa. Therefore, the substrate surface area was kept constant in these experiments. The variation in thickness as a result of

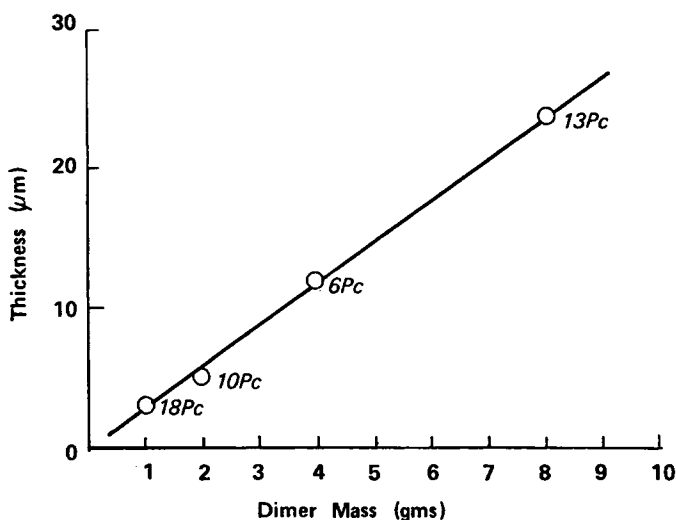


Fig. 2. A plot of Parylene C thickness as a function of dimer mass. All samples were from the same location in the reactor.

horizontal and vertical substrate positions in the reactor was determined. A standard run carried out at  $160^{\circ}\text{C}$  sublimation temperature and  $675^{\circ}\text{C}$  pyrolysis temperature with a dimer charge of 4.0 g was used for each of the experiments to determine positional substrate dependence. Due to the small diameter (6 in.) of the deposition chamber, the maximum horizontal deviation in thickness across the midline of the reactor was 11%. The maximum thickness variation through the vertical midline of the reactor was 26%. The vertical variation in thickness is approximately twice as large as the horizontal, as is the vertical dimension (14 in.).

Substrate shape, morphology, and substrate material also played an important role in determining overall film thickness. The thickness of Parylene C film on wires was found to exceed the thickness on flat substrates when coated together.<sup>10</sup> The effect of surface morphology was determined from the measurement of total thickness on the smooth vs. frosted portions of the micro slides. The higher surface area of the frosted portion gave rise to approximately 60% more polymer deposition in this area than on the polished area of the slide. The physicochemical nature of the substrate material also influenced the polymer thickness, although in a complex manner. If the substrate material was permitted to act as a heat sink, with mechanisms such as a cooling block to dispose of the accumulated heat, the result was increased thickness. In the absence of such cooling mechanisms, the metal substrates showed lower polymer deposition because of higher heat capacity (warmer substrates). In our experiments with aluminum and glass substrates (where no cooling block was used), we observed approximately 25% less polymer deposition on aluminum than on the glass substrate.

The effect of other process parameters on polymer thickness was less evident. The pyrolysis temperature variation from  $625$  to  $675^{\circ}\text{C}$  did not show any effect on polymer thickness as long as other parameters were kept constant. The sublimation temperature influenced the polymer thickness

TABLE II  
Average Ratio of Parylene C Deposition as a Function of Sublimation Temperature

Sublimation temperature (°C)	Rate <sup>a</sup> ( $\mu\text{m}/\text{min}$ )	$\bar{t}_g$ ( $\mu\text{m}$ )	$\bar{t}_w$ ( $\mu\text{m}$ )
130	0.13	10.5	—
140	0.21	10.0	10.1
160	0.30	10.3	11.4
180	0.36 <sup>b</sup>	9.7	13.7

<sup>a</sup>Rates measured from weight of polymer film deposited on glass slide.

<sup>b</sup>Nonuniform deposition. Dimer mass = 4.0 g. Pyrolysis temp = 675°C.

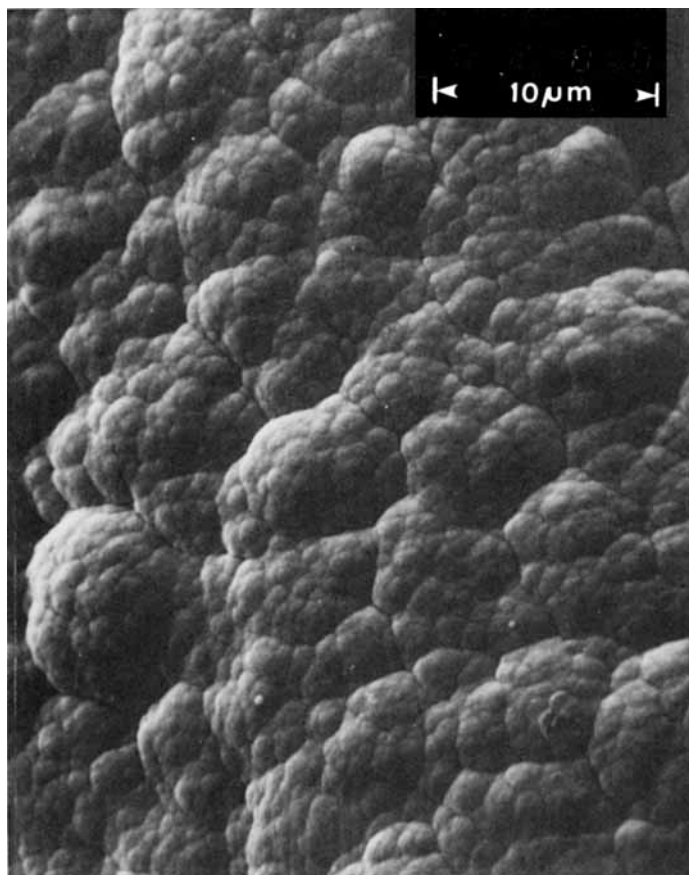
indirectly by changing the uniformity in polymer deposition. As we will show, the mass balance was not affected.

The rate of Parylene C deposition calculated from the film thickness and the length of the experiment also increased with an increase in dimer mass, and reached saturation at 0.20  $\mu\text{m}/\text{min}$  with a 4.0 g dimer mass.

The sublimation temperature had perhaps the greatest influence on Parylene C deposition rate since the vapor pressure of the dichloro(*p*-xylylene) dimer at 100°C is less than 1 mtorr. Table II reports the effect of sublimation temperature on the rate of polymer deposition. As expected, polymer deposition rates increased sharply with an increase in sublimation temperature, and although the average thicknesses of the polymer deposited on glass slides ( $\bar{t}_g$ ) and on the walls of the deposition chamber ( $\bar{t}_w$ ) did not change significantly, the difference in the two thicknesses increased with an increase in the sublimation temperature. Thus, the dependence of Parylene C polymer at higher sublimation temperatures leads to nonuniform coatings.

The opacity of the film increased with an increase in the sublimation temperature. The film obtained at 180°C or higher was either opaque or had white specks on the surface. Although the extraction experiments and IR spectroscopy did not show a significant increase in the dimer content of the films deposited at a sublimation temperature of 180°C, scanning electron micrographs revealed marked morphological changes. The films formed at 180°C sublimation temperature showed very rough surfaces and a "globular" structure as shown in Figure 3. Our previous experience with such films indicated that they undergo rapid electrical failure in an ionic medium.<sup>11</sup>

The pressure measured by the thermocouple gauge in the deposition chamber showed nonlinear increases as the polymerization proceeded. Plots of this change as a function of time and at different sublimation temperatures are presented in Figure 4. The zero time refers to the start of the sublimation furnace. It is interesting to note that as the sublimation temperature increased, the pressure curves became narrower, with the maximum pressure in the deposition chamber increasing. Surprisingly, the area under the pressure curve did not change appreciably, indicating that the rate of polymer deposition was directly proportional to the equilibrium monomer pressure in the reactor. Therefore, differentiation of these curves as a function of time can provide rate curves similar to those reported by Kramer et al.<sup>5</sup> Since the total weight of the polymer film did not change during a given run, the equation



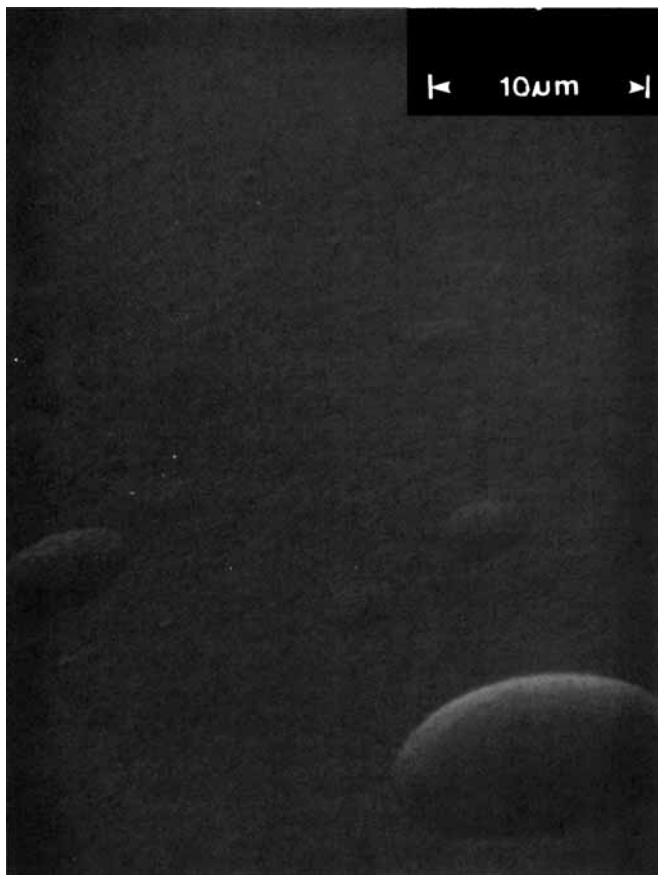
(a)

Fig. 3. (a) A scanning electron micrograph of the surface of the Parylene C film deposited at 180°C. (b) A scanning electron micrograph showing the relatively smooth surface of Parylene C when deposited at 140°C.

can be formalized as

$$\text{polymer weight} = \int kP dt \quad (1)$$

where  $k$  is an empirically determined constant,  $P$  is chamber pressure, and  $t$  is time. The above relationship was tested by artificially changing the monomer pressure in the deposition chamber. It was noted that while the pressure vs. time curves of Parylene C deposition were sensitive to the geometric factors of the reactor, the area under the pressure-time curve was determined only by the mass of the dimer. Since higher pressure in the deposition chamber led to nonuniform, opaque films which had poor adhesive qualities, attempts were made to artificially depress the pressure effect in the deposition chamber. Two different means of slowing the feed rate of the sublimed dimer were tried; one by modifying the sublimation tube and the other by modifying



(b)

Fig. 3. (Continued from the previous page.)

the pyrolysis tube. The modifications were achieved by placing baffles in the tubes to restrict the dimer flow rates. The sublimation tube baffle (called the external baffle) consisted of a quartz cap with holes at the closed end, and was mounted at the mouth of the sublimation tube. The pyrolysis tube baffle (called the internal baffle) consisted of a permanently drawn glass restriction at the inlet end of the tube. The result of placing these baffles on the kinetics of Parylene C deposition is depicted in Figure 5. In each case, a decrease in the system pressure was noticed. Thus, baffling of the Parylene C reactor led to the same effect as decreasing the sublimation temperature. Interestingly enough, the area under the pressure-time curves remained constant, indicating that baffles simply slow down the rate of polymer deposition without altering the total amount of polymer deposited in the chamber.

Figure 6 depicts the effect of sublimation tube capacity on the pressure curve observed in Parylene C deposition. Although different size tubes may expose a different surface area to the dimer, it was clear from these results that a longer sublimation tube had a depressing effect on the pressure curves; the area under the curve, however, was not affected.

Figure 7 depicts the effect of dimer mass on the pressure curves of Parylene C deposition. Increased dimer mass led to an increase in the maximum



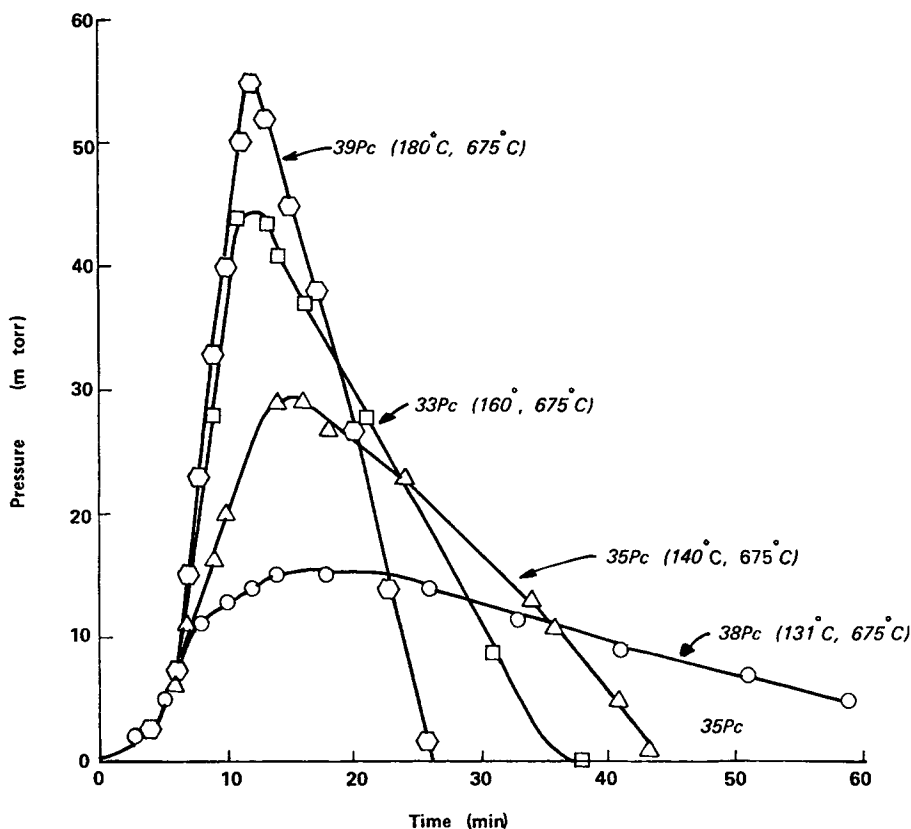


Fig. 4. Pressure in the Parylene deposition chamber as a function of time and different sublimation temperatures.

pressure observed. The area under the pressure-time curve was found to be directly proportional to the starting dimer mass.

### CONCLUSIONS

There are many practical applications of controlling operational parameters. As stated earlier, higher pressure led to nonuniform films and also produced opaque films. The opaque films have been shown to be electrically "weak" and may even produce an undesirable reaction on biological implantation. The optical clarity of the films was greatly improved by lowering the pressure in the system, either by baffling or by reducing the sublimation temperature. It was also noted that the films obtained at lower chamber pressures were nonstrippable from a glass slide, while the films obtained at higher deposition pressures were very weakly bonded and could be removed from the substrate easily. Thus, a lower system pressure leads to a structurally more stable polymer due to a slowing of the deposition process.

Thus Parylene C deposition is a highly system dependent process and in this respect resembles plasma polymerization. The good quality Parylene C films were obtained by lowering the rate of polymer deposition. The practice of simply increasing dimer mass to achieve thicker films of high quality would not be supported by our studies. The increased dimer mass would lead to an

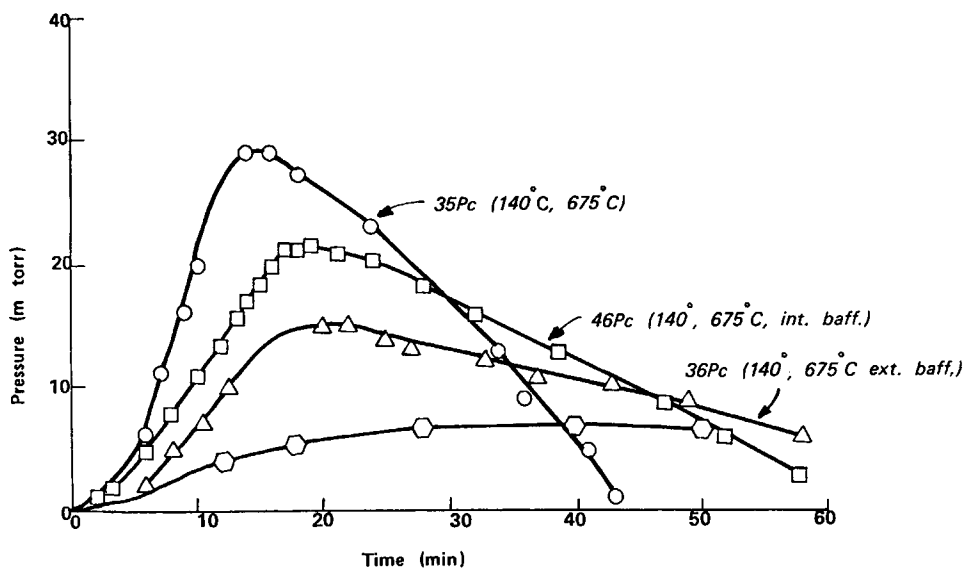


Fig. 5. The effect of baffles on Parylene chamber pressure. The baffles have the same effect as decreasing the sublimation temperature (i.e., the dimer feed rate).

elevation in system pressure, and therefore modification in the sublimation tube geometry would be necessary in order to maintain the quality of the film. The above findings also explain the improved adhesion obtained by using the randomly filled pyrolysis tube where due to the restrictions imposed by the fillings a lower deposition rate was accomplished.

We consider the above findings of the dependency of the polymer deposition kinetics and polymer properties on the system geometry very significant. It suggests that the kinetics of Parylene C deposition are very complex. Factors like sublimation and pyrolysis tube geometry, baffles, and even restrictions imposed by deposited film in the tubes, can significantly change the course of the reaction resulting in poor film quality and reproducibility. The actual

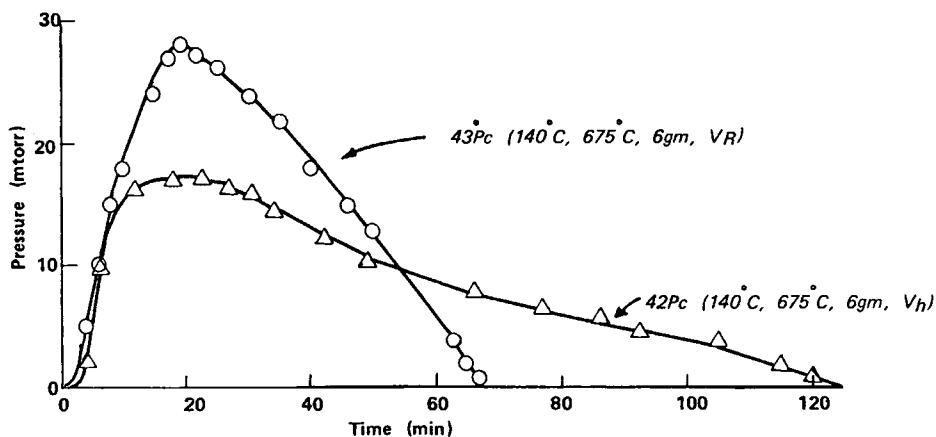


Fig. 6. Effect of sublimation tube capacity on chamber pressure. The longer tube ( $V_h = 24$  in.) depresses the chamber feed rate.

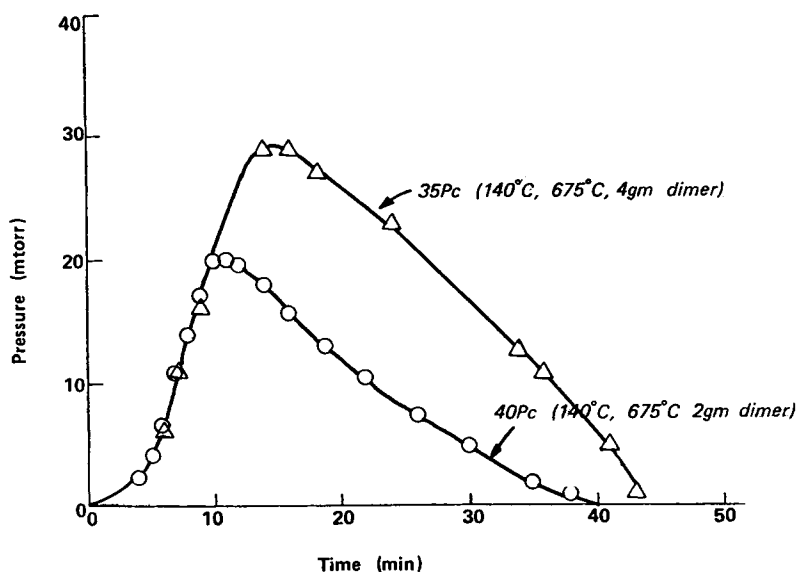


Fig. 7. Effect of dimer mass on pressure in the chamber. The increase in dimer mass leads to an increase in chamber pressure.

effect of these factors is cumulative and may vary from reactor to reactor. We have also demonstrated that at least three observable properties of Parylene C, viz., clarity, dimer content, and adhesion to a substrate can be altered by these equipment factors perhaps as effectively as by varying the more traditional parameters such as sublimation temperature, dimer mass, etc. Since the film changes are at a molecular level, more refined techniques would be required to ascertain the effects of these parameters on structural modifications in these films.

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