

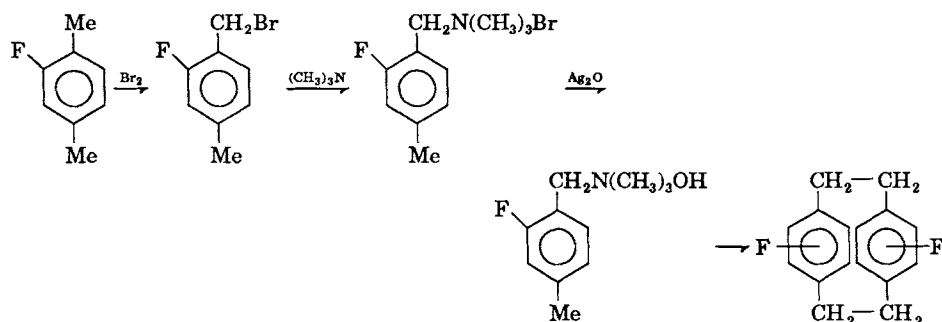
NOTES

*Some Mechanical and Electrical Properties of Polyfluoro-*p*-Xylylene Films Prepared by Chemical Vapor Deposition*

The methods of synthesizing poly-*p*-xylylene (PPX) and polychloro-*p*-xylylene and their properties have been extensively studied.¹⁻⁶ The group of PPX has now become a well-known material because it possesses good mechanical and electrical properties and thermal stability, which may lead to many industrial applications. In fact, this material is outstanding for use as a barrier to gas or moisture penetration. Furthermore, this material can be easily polymerized by pyrolysis or thermolysis without catalyst.

Polyfluoro-*p*-xylylene is one of the homologous material of poly-*p*-xylylene. We believe that the polyfluoro-*p*-xylylene will have better mechanical and electrical properties than some other PPX since the C-F bond has a higher bonding energy than other chemical bonds. In this article, we shall report some mechanical and electrical properties of polyfluoro-*p*-xylylene films.

Prior to the fabrication of polyfluoro-*p*-xylylene films, we first produced the monomers, which are dimers. The dimer (difluoro [2,2] papracyclophane) was synthesized by thermolysis of 2-fluoro-4-methylbenzyltrimethyl ammonium hydroxide in a 34% yield. This synthetic procedure is shown in the following scheme⁷:



The dimer can also be synthesized by pyrolysis of 2-fluoro-1,4-dimethylbenzene in 12% yield.⁸ The dimer is a white solid powder with a melting point of 213°C. The dimers formed by the thermolysis method were then polymerized by high-temperature vacuum pyrolysis at 600°C without using any catalyst. This method is also known as chemical vapor deposition. The procedures and the reaction of the polymerization of polyfluoro-*p*-xylylene are shown in Figure 1. The dimer was cleaved by vacuum vapor-phase pyrolysis at 650°C to form a reactive intermediate, fluoro-xylylene radical in the chamber at a pressure less than 1 mmHg. The fluoro-*p*-xylylene was spontaneously polymerized and deposited on the surface of a stainless steel deposition cylinder whose temperature was maintained at about 20°C. During deposition, the cylinder was rotated so that a uniform film could be deposited on it. The polymerization parameters are listed in Table I. The polyfluoro-*p*-xylylene film is transparent in the visible region. The infrared spectrum of polyfluoro-*p*-xylylene is shown in Figure 2. Assignments of the absorption bands are as follows: 3000–3100 cm⁻¹ (aromatic C-H stretching vibration),^{9,10} 2850–2920 cm⁻¹ (methylene C-H stretching vibration),^{9,10} 1485 cm⁻¹ (aromatic C-C stretching vibration),¹⁰ and 1300–1200, 850 cm⁻¹ (C-F stretching vibration on aromatic ring).⁹

The mechanical properties of the polyfluoro-*p*-xylylene films have been measured on samples with a thickness of 50 μm stripped from the deposition cylinder, and the results are given in Table

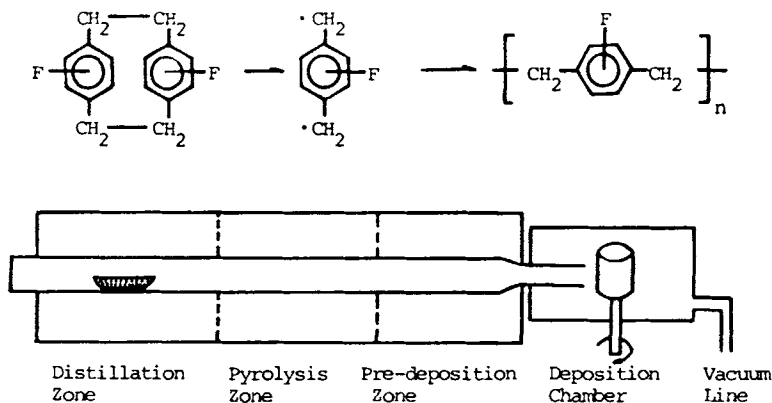


Fig. 1. The procedures and the reaction of the polymerization of polyfluoro-*p*-xylylene.

II. In order to compare the mechanical properties of our films with some other PPX, Table II also includes data of polydichlo-*p*-xylylene, polychloro-*p*-xylylene, polybromo-*p*-xylylene, polymethyl-*p*-xylylene, and polyethyl-*p*-xylylene from other groups.¹ Most of the poly-*p*-xylylenes have a high modulus at room temperature, typically about 28,000 kg/cm². It can be seen that the polyfluoro-*p*-xylylene produced in our laboratory has reasonable tensile strengths and toughness, though the extensibility or elongation at fracture is slightly lower than other PPX. Many investigators have reported^{1,10,11} that poly-*p*-xylylene and some substituted poly-*p*-xylylenes exhibit a high degree of crystallinity, especially poly-*p*-xylylene and halogenated derivatives, which are highly crystalline in nature. From Table II it is clear that the glass transition temperature is higher for halogen-substituted poly-*p*-xylylene than that for poly-*p*-xylylene with ethyl and methyl derivatives. Thus, we can expect that the polyfluoro-*p*-xylylene is also highly crystalline in nature with the glass transition temperature around 80°C. The moisture vapor permeability was measured by a flow method in a standard test cell, which is adequate for the determination of the steady-state permeability as indicated in some studies.^{12,13} The permeability of polyfluoro-*p*-xylylene is low, which is 1.7×10^{-9} g cm/cm² h mmHg, indicating that the polyfluoro-*p*-xylylene is a good material to be used as a barrier to moisture vapor.

All samples for electrical property measurements were made in a sandwich electrode configuration with silver vacuum deposited on one surface as the guard and the guarded electrodes and on the opposite surface as unguarded electrode, the diameter of the guarded electrodes being 1 cm and the width of the guard electrode being 0.2 cm with a separation of 0.1 cm between these two electrodes. The dielectric properties were measured by GR Type 1615-A Capacitance Bridge and Boonton Radio Type 160-A Q meter; the resistance was measured by Keithley 610C electrometer. Figure 3 shows the dielectric constant and the dissipation factor as functions of frequency at the room temperature (20°C). As shown in Figure 3, the dissipation factor of poly-*p*-xylylene is higher

TABLE I
Polymerization Parameters

System pressure	$2-5 \times 10^{-2}$ mmHg
Distillation zone temperature	90-120°C
Distillation rate	0.035 g/min
Pyrolysis zone temperature	650°C
Predeposition zone temperature	150°C
Deposition cylinder temperature	20°C
Deposition rate	0.02 g/min

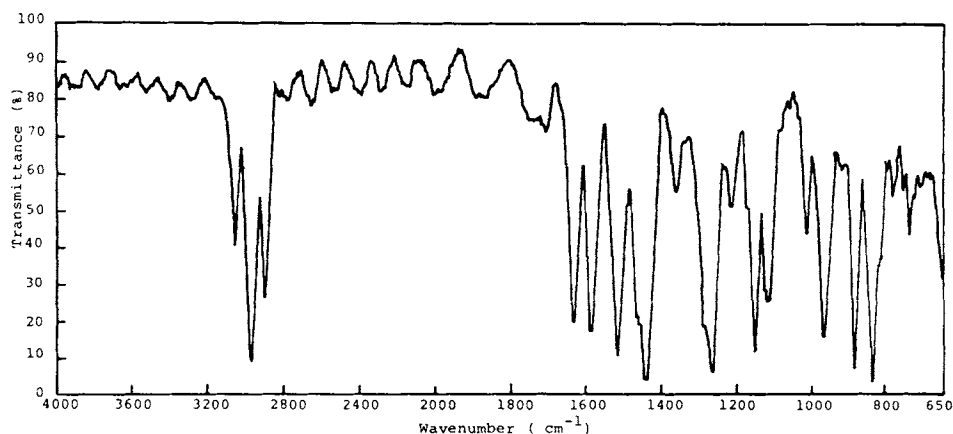


Fig. 2. The infrared spectrum of polyfluoro-*p*-xylylene.

than some other PPX (e.g., the dissipation factor of poly-*p*-xylylene is 0.0002 at 1000 Hz). The high dissipation factor is due to the ring-substituted fluorine, this ring-substituted fluorine converts the poly-*p*-xylylene, which is a highly symmetrical, nonpolar polymer, into an asymmetrical polar polymer. A similar observation has been reported for polychloro-*p*-xylylene,¹ which has a dissipation factor of 0.04. There is one peak for the dissipation factor at 10^5 Hz, and the dielectric constant has a clear decrease at frequencies above 10^5 Hz. In general, there are at least two types of dielectric losses, namely conduction loss and dipole relaxation loss. The conduction loss is characterized by the upturn in dissipation factor at low frequency, which decreases with increasing frequency, while the dipole relaxation loss is characterized by a loss peak. From the experiment data in Figure 3, it can be concluded that the dielectric loss in polyfluoro-*p*-xylylene is mainly due to dipole relaxation loss. The loss peak may indicate that there is a relaxation group, which has an overall resonant frequency as 10^5 Hz. Denote τ as the relaxation time of the polar group in polyfluoro-*p*-xylylene; ω is the frequency of the electric field. The dissipation factor will reach its maximum value when $\omega\tau = 1$. In our case, the dissipation factor has a maximum value at 10^5 Hz, thus τ should be 1.59×10^{-6} s. The slow variation of the dissipation factor with frequency around the peak indicates that the polarization may involve more than one polar group. Figure 4 shows the dielectric constant

TABLE II
Mechanical Properties of Polyfluoro-*p*-Xylylene and Several Other PPX^a

Properties	Polyfluoro- <i>p</i> -xylylene	Polydichloro- <i>p</i> -xylylene	Polychloro- <i>p</i> -xylylene	Polybromo- <i>p</i> -xylylene	Polymethyl- <i>p</i> -xylylene	Polyethy- <i>p</i> -xylylene
Tensile strength (kg/cm ²)	644	420	742	560	665	770
Tensile modulus (kg/cm ²)	20,700	28,000	32,200	28,000	28,000	12,250
Elongation at break (%)	5.57	5-10	220	30	230	275
Glass transition temperature (°C)	80 (expected)	110	80	80	50-60	25
Crystalline melting point (°C)	210-230	300	290	270	200-210	160-170

^a Data from Ref. 1.

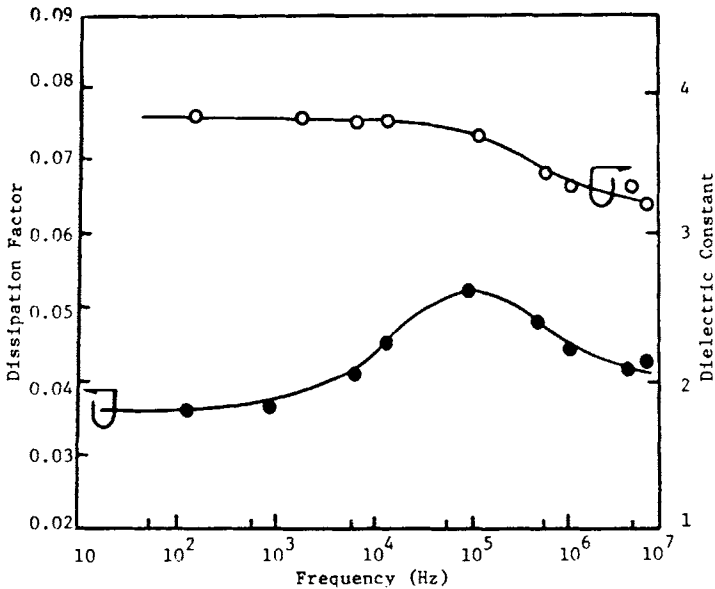


Fig. 3. The dielectric constant and the dissipation factor as functions of frequency at room temperature.

and the dissipation factor as functions of temperature at a constant frequency of 1000 Hz. It can be seen that the dielectric constant and the dissipation factor are practically independent of temperature from room temperature (20°C) to 140°C. The dielectric constant starts to decrease and the dissipation factor starts to increase beyond 140°C as expected. Similar phenomenon has also been observed by other investigators for vapor-phase polymerization poly-*p*-xylylene.^{5,14} Ieda et al.⁵ have reported that poly-*p*-xylylene is temperature resistant up to 250°C and that the dielectric constant starts to decrease and the dissipation factor starts to increase beyond 140°C. By comparing

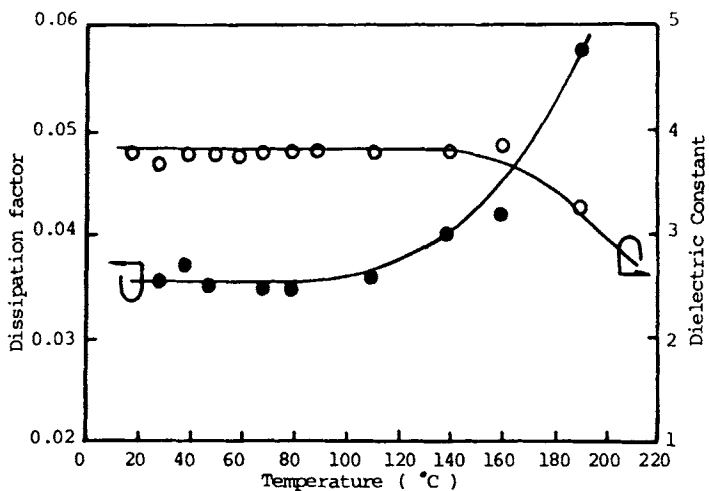


Fig. 4. The dielectric constant and the dissipation factor as functions of temperature at 10³ Hz.

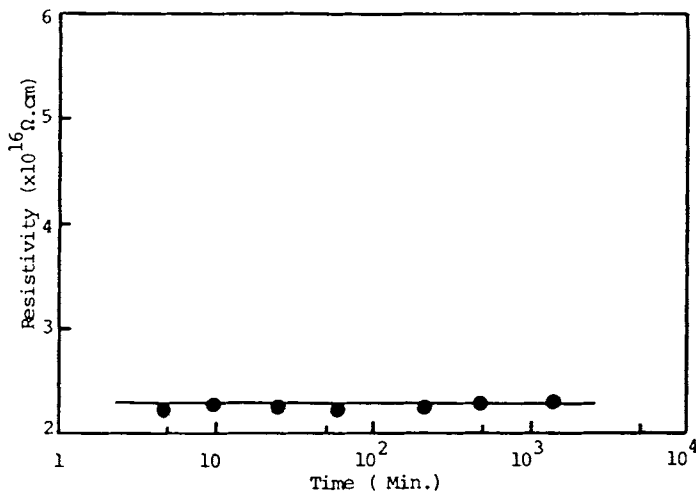


Fig. 5. The resistivity of polyfluoro-*p*-xylylene as a function of the immersion time in water.

the data in Table II, it can be seen that this phenomenon cannot be due to the glass transition because the glass transition temperature T_g is lower than 140°C (T_g for some PPX polymers is around 80°C). It is also not due to the melting temperature T_m , which is much higher than 140°C (T_m for some PPX polymers is higher than 200°C). This phenomenon may be attributed to the temperature dependence of the dielectric relaxation of polyfluoro-*p*-xylylene.

The effect of permeation of water on the resistivity has also been measured. Prior to the measurement the samples were immersed in water for a predetermined period and then taken out and dried with wiper paper. The measured resistivity as a function of immersion time is shown in Figure 5. It can be seen that the immersion time does not have any detectable effect on the electrical resistivity of the polyfluoro-*p*-xylylene sample, indicating that polyfluoro-*p*-xylylene is a good coating material for preventing water from penetration.

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