

Poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene)

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Synopsis

Poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) was prepared by the pyrolysis of cyclo-di($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) and by the pyrolysis of α,α' -bis(alkylsulfonyl)- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene. The pyrolysis of α,α' -dibromo- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene also gave the polymer, but the method is less satisfactory. Poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) shows remarkable thermal and oxidative stability at elevated temperatures. Useful mechanical and electrical properties are retained after aging for 3000 hr at 250° in air. After initial change due to crystallization, tensile strength remains near 10,000 psi, elongation above 5%, and dielectric constants and dissipation factors at approximately 2.4 and .001, respectively.

INTRODUCTION

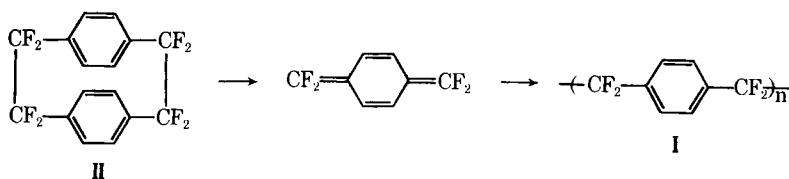
The vacuum pyrolysis of *p*-xylylene to yield the reactive intermediate, *p*-xylylene, which spontaneously polymerized to poly(*p*-xylylene) was first reported by Szwarc¹⁻³ and, since then, has been studied extensively by a number of laboratories.⁴⁻⁶ A particularly notable contribution in this area was that reported by Gorham,⁷ who developed a general technique for the preparation of an entire family of substituted *p*-xylylene polymers. The method was based on the observation that cyclo-di(*p*-xylylene) cleaves quantitatively to the monomeric *p*-xylylene. Since the reaction reported by Gorham occurred at relatively lower temperatures than that reported by Szwarc and produced no by-products, the polymers obtained were free from contamination and crosslinking. Although these polymers possess an outstanding combination of physical, electrical, and chemical properties, the benzylic C—H bonds present are potential sites for thermal and oxidative degradation. Since fluorine is known to impart thermal and oxidative stability, it became of interest to prepare poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) (I). We wish to report the synthesis of this polymer.

Preparation of Polymer

The method of choice for the preparation of poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) was the vapor deposition technique described by Gorham, which not only produced poly(*p*-xylylene) free from crosslinking and contamination, but also gave polymers in film form. Since these polymers were very high melting and slightly soluble only at high temperatures, fabrica-

tion by conventional methods such as molding or solution casting was virtually impossible. Therefore, the technique of preparing the polymer in usable form is of considerable importance if practical applications are considered. The key intermediate needed for the preparation of poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) was the corresponding cyclic dimer, cyclo-di($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) (II), also known as 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane. The synthesis of compound II will be reported elsewhere.⁸

Cyclo-Di($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) was sublimed into a pyrolysis chamber maintained at 600–750°C and the pyrolyzate was led into a cooled deposition chamber, where the polymer I was deposited as a tough and transparent film. The entire system was maintained at 10–100 μ Hg during this operation. The reaction by analogy to *cyclo-di(p*-xylylene) is depicted in the equation below.

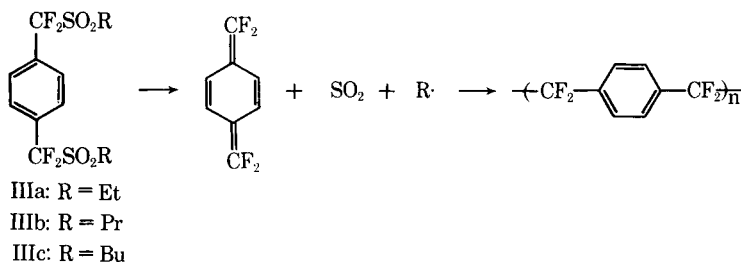


The question whether *p*-xylylene is better represented by a diradical or a quinoid structure has been the subject of some discussion. (For references, see Errede and Szwarc.⁴) While in this paper, *p*-xylylene is depicted as quinodimethane, it is recognized that the diradical structure may be important in providing rational explanation for its high chemical reactivity and free radical behavior.

The pyrolysis temperature at which quantitative conversion of II to I occurs depends on contact time in the pyrolysis zone. At an average feed rate of about 0.065 g/min and pyrolysis tube of 2 in. in diameter and 24 in. in length, the optimum temperature was 720–730°C. The deposition efficiency was shown to be a function of deposition temperature. At -25°C and -35°C , deposition efficiency was 61% and 72%, respectively, and under these conditions uniform and transparent films of 1.2–1.7 mils were obtained. At -45°C , deposition efficiency was 80% but films were hazy. The results are summarized in the experimental section. It is interesting to note that the pyrolytic decomposition of II requires somewhat higher temperatures than cyclo-di(*p*-xylylene), which is quantitatively cleaved at 600°C at similar feed rate.⁷

Since sulfones are known to undergo pyrolytic decomposition with the loss of sulfur dioxide and formation of new C—C bonds,^{9,10} the pyrolysis of α,α' -bis(alkylsulfonyl)- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene (III) was also studied as an alternate route to poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene). Indeed, bis-sulfones III on vacuum pyrolysis decomposed with the evolution of sulfur dioxide and other gaseous products. The pyrolysis was observed by the pressure changes accompanying the reaction. As the decomposition

began, the evolution of gaseous by-products caused an increase in pressure of the system which returned to the initial point when the reaction reached completion. The pyrolyzate on cooling polymerized instantaneously. Clear, transparent film was deposited on the walls of the cooled receiver. That the polymer is poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) was shown by its infrared spectrum which was superimposable with that of the polymers obtained by pyrolysis of II. However, the polymer prepared by the sulfone pyrolysis probably contained trace amounts of as yet unidentified impurities, as shown by elemental analysis. Variation of the alkyl groups from ethyl to butyl in bis-sulfones III showed no significant difference in pyrolysis conditions.



α,α' -Dibromo- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene (IV) was also pyrolyzed by a similar technique at 800–950°C. Polymeric films were deposited in the deposition chamber. The by-product was bromine, which was observable by its characteristic color and odor. However, the films were hazy and opaque. The polymer obtained by pyrolysis of IV at 850°C had an infrared spectrum superimposable with that of poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) obtained from II and III.

Polymer Properties

Poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) is a highly crystalline polymer possessing a crystalline melting point at about 500°C. Its mechanical properties resemble closely those of poly(*p*-xylylene), and these together with those for poly(*p*-xylylene) are summarized in Table I.

TABLE I
Mechanical Properties of Poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) (I)

	I	Poly(<i>p</i> -xylylene)*
Tensile modulus	360,000	350,000
Tensile strength	6,200	6,100
Elongation, %	100	200
Density	1.506	1.103–1.120
Coefficient of friction	0.2	0.25
T _g	90°C	80°C

* Poly(*p*-xylylene) is a member of a family of polymers given the generic name "parylene" that is currently being marketed by Union Carbide Corporation. Properties were obtained in UCC Laboratories.

Attempted dissolution of the polymer in a variety of solvents was not successful; for example, heating a strip of film of the polymer in concentrated nitric acid or ~40% sodium hydroxide to reflux showed no apparent decomposition. However, the polymer decomposed in hot concentrated sulfuric acid. Other solvents tried, both at room temperature and at reflux, were α -chloro- and, α -bromonaphthalene, 40:60 *s*-tetrachloroethane-phenol, *s*-tetrachloroethane, diphenyl ether, and *p*-cresol.

Poly($\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylylene) showed remarkable sun lamp stability. The polymer remained flexible and showed no change after 3600 hr under the sun lamp, whereas poly(*p*-xylylene) became brittle after 575 hr.

One of the outstanding features of poly($\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylylene) was its thermal stability. The polymer maintained useful properties for at least 3000 hr at 250°C in air.

When heated to 250°C, the polymer annealed and increased in density from 1.506 to 1.60. Along with the increased density, due undoubtedly to increased crystallinity, the modulus increased from 360,000 to 423,000. The initial decrease in elongation was probably also the result of increased crystallinity. The percentage elongation at break decreased immediately from 119% to 11% and then gradually tapered off to 5%. The tensile strength of this polymer increased after heat aging at 250°C for a short period of time. It then decreased after long-term heat aging, although the value never dropped below the initial value. The heat-aging data are summarized in Table II.

TABLE II
Room Temperature Mechanical Properties of
Poly($\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylylene) Heat Aged at 250°C

	Control	24 hr	168 hr	744 hr	2100 hr	3000 hr
Modulus, psi	361,000	398,000	390,000	365,000	338,000	422,900
Tensile strength, psi	6,500	14,700	14,100	13,400	10,700	10,600
Elongation, %	120	11	9	8	6	5
Density, g/r.c.	1.506	1.580	1.590	1.603	1.587	1.597

Electrical properties of this polymer were similar to those of poly(*p*-xylylene); the dissipation factor was slightly higher for I (0.0008) than for poly(*p*-xylylene) (0.0002). However, the values were relatively constant with frequency (Table III). Heat aging of the polymer showed no significant change in electrical properties. The data are summarized in Table IV.

TABLE III
Electrical Properties of Poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene)

	I	Poly(<i>p</i> -xylylene)
Dielectric strength (S/T), V/mil	6,300	6,500
Dielectric strength (S/S), V/mil	5,250	6,000
Volume resistivity (23°), ohms	5.3×10^{16}	1.4×10^{17}
Surface resistivity	1.3×10^{14}	10^{13}
Dissipation factor		
60 cps	0.0008	0.0002
1 kcps	0.0008	0.0002
1000 kcps	0.0007	0.0004
Dielectric constant (23°)		
60 cps	2.36	2.65
1 kcps	2.36	2.65
1000 kcps	2.35	2.65

TABLE IV
Electrical Properties of Poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene)
Heat Aged at 250°C

	Control	24 hr	168 hr	2100 hr	3000 hr
Dielectric strength, V/mil	6,200	4,500	4,500	3,700	3,700
Dielectric constant					
60 cps	2.36	2.23	2.11	2.43	2.50
1 kcps	2.36	2.22	2.11	2.42	2.50
100 kcps	2.35	2.22	2.10	2.41	2.49
Dissipation factor					
60 cps	0.0008	0.0008	0.0011	0.0015	0.0009
1 kcps	0.0008	0.0009	0.0049	0.0017	0.0009
100 kcps	0.0007	0.0008	0.0011	0.0013	0.0010
Volume resistivity	5.3×10^{16}				
Surface resistivity	1.3×10^{14}				

EXPERIMENTAL

Procedure for the Preparation of poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene)

The apparatus used for the preparation of poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) is shown in Figure 1. The unit consists basically of three sections: a *p*-xylylene vapor generator, a deposition chamber, and a pumping system. The generator was composed of a 2 in. \times 44 in. Vycor tube. One portion was used for vaporization of the octafluoro-di(*p*-xylylene) while the center portion was used for pyrolysis (conversion of the di(*p*-xylylene) to the monomeric *p*-xylylene). The pyrolysis section was heated externally by a 24-in. Hevi-Duty furnace. The pyrolysis tube was connected directly to a steel deposition chamber, 6 in. in diameter and 20 in. long. Inside the

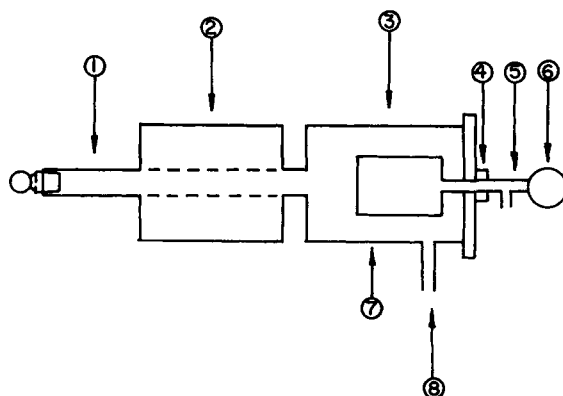


Fig. 1. Deposition apparatus: ①, vaporization section; ②, pyrolysis section; ③, deposition chamber; ④, rotary vacuum seal; ⑤, coolant tube; ⑥, drive motor; ⑦, cooled mandrel; ⑧, vacuum port.

deposition chamber was a hollow steel mandrel which was cooled by circulation of chilled methanol, introduced by means of a hollow shaft. The shaft was rotated during the experiment.

In a typical run, 9.0 g of cyclo-di($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) was charged into the vaporization section of the pyrolysis tube. The system

TABLE V
Preparation of Poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene)
From Cyclo-di($\alpha,\alpha,\alpha',\alpha'$ -Tetrafluoro-*p*-xylylene)

Dimer charge	Deposition temp., °C.	Run time, min	Polymer weight, g	Deposition efficiency	Thickness, mil	Polymer appearance
9.0	-25	145	5.5	61.3	1.2-1.35	transparent
9.0	-25	75	5.5	61.3	1.2-1.35	transparent
9.0	-25	65	5.5	61.3	1.2-1.35	transparent
9.0	-35	60	6.5	72.3	1.5-1.7	transparent
9.0	-45	65	7.2	80	1.5-1.7	Hillock-filled opaque
18	-35	117	12.2	67.7	2.5-3.2	transparent
18	-25	108	12.0	66.7	2.5-3.5	transparent

Anal. calc. for $(C_8H_4F_4)_n$: C, 54.55; H, 2.29; F, 43.15; found: C, 54.12; H, 2.40; F, 43.30.

was assembled and evacuated to 58μ at vacuum probe. The pyrolysis section of the tube was heated to $720-730^\circ\text{C}$. The rotating mandrel was cooled to -25°C . When the system was at the desired temperature, heat was applied to the vaporization section to about 100°C . During the run, the pressure increased from 58μ to 160μ , which returned to 58μ when the cyclic dimer II was spent.

The vaporization section was then cooled and the coolant in the rotating mandrel was warmed to 0°C, the system was returned to atmospheric pressure.

Poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) film deposited was 1.3–1.5 mil thick and was weighed to determine the recovery. Typical data for the preparation of the polymer are summarized in Table V.

Pyrolysis of α,α' -bis(Alkylsulfonyl) $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene

The apparatus used for the preparation of poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) by the pyrolysis of the bis-sulfone is a prototype with the essential features of that shown in Figure 1. The deposition chamber consists of a water-cooled and a dry ice-acetone-cooled condenser.

In a typical run, 0.9 g of α,α' -bis(alkylsulfonyl)- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene was charged into the sublimation tube and the entire system was evacuated. When the temperature of the pyrolysis zone reached 650°C, heat was applied to the sublimation tube to about 200°C. The pyrolysis was observed by the pressure change accompanying the reaction. As the decomposition began, the pressure increased from an initial 5 μ to 300 μ , which returned to the initial value as the reaction was completed. Film was deposited on the walls of both the water-cooled and the dry ice-cooled condensers. Films that were deposited in regions where the temperature was between -40°C and +15°C were tough and transparent but those deposited below -40°C were hazy. However, their infrared spectra were superimposable. Data are summarized in Table VI.

TABLE VI
Pyrolysis of α,α' -bis(Alkylsulfonyl)- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene

bis-Sulfone III	Sublimation temp., °C	Pyrolysis temp., °C	Recovery, %
R = Et ^a	200	650	70
R = Et ^b	250	750	14
R = Pr	200	700	72
R = Bu	200	700	68

^a Anal. calc. for (C₈H₄F₄)_n: C, 54.55; H, 2.29; F, 43.15; found: C, 53.72; H, 1.51; F, 45.10.

^b Anal. found: C, 56.04, H, 3.07; F, 41.56.

Pyrolysis of α,α' -Dibromo- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene

The apparatus used for the pyrolysis of α,α' -dibromo- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene is that described for the pyrolysis of sulfones.

α,α' -Dibromo- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene (2.0 g) was charged into the distillation tube and the entire system was evacuated to 50 μ . When the pyrolysis temperature reached 850°, the distillation tube was heated to 50°C. The pyrolyzate was cooled successively with a cold water condenser and a dry ice trap. Film was deposited in both the water-cooled con-

denser and the dry ice trap. The film deposited in the dry ice condenser was quickly washed with thiosulfate solution before allowed to warm to room temperature. The total yield of polymer was 0.24 g (23%). The infrared spectra of polymer so obtained is superimposable with that obtained by pyrolysis of cyclo-di($\alpha, \alpha', \alpha', \alpha'$ -tetrafluoro-*p*-xylene).

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