

Polyparaxylylene Electrets Usable at High Temperatures

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Synopsis

Thin coatings of various polyparaxylylenes were transformed into electrets by corona charging them and then overcoating with more polyparaxylylene to protect the charge layer. For such electrets, the extrapolated ten-year use temperature depended on the thermo-oxidative stability of the polyparaxylylene layer and was greater than 100°C for the most stable electrets. The voltage levels and surface charge densities were always greater than or equal to those of charged Teflon electrets, similar to those used in commercial devices.

Although electrets can be made from almost any organic polymer, electrets made from poly(tetrafluoroethylene) (Teflon) and related materials¹ and poly(vinylidene fluoride)² (PVF₂), have shown the necessary long-lived charge or polarization retention properties to be considered for most commercial devices. However, the high-temperature decay of the charge or polarization of these two polymers has limited their upper-use temperature. Furthermore, the methods of fabricating these two polymers into electrets have limited them to thin-film applications.

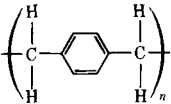
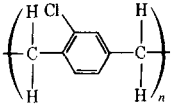
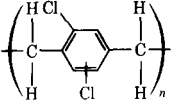
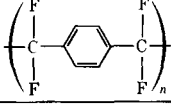
We found that certain vapor-phase deposited polyparaxylylenes can be fabricated into electrets that have higher use temperatures than either Teflon or PVF₂. Because they are made from polyparaxylylene which was conformally deposited on a metal surface, the shape of the electret depends only on the shape of the metal substrate. This ease of fabricating them into complicated shapes means they could be used in non-thin-film applications such as electrostatic filters.

The polyparaxylylenes used in this study are given in Table I. The electrets were made in the following way: (1) the desired polyparaxylylene was deposited from the vapor phase to the desired thickness³ on a metal substrate, which formed an electrode for charging the polymer; (2) the polyparaxylylene layer was charged, either positively or negatively, with a simple dc air corona⁴; (3) additional polyparaxylylene was sometimes deposited over the charge layer to protect it; and (4) the voltage across the electret was monitored, as a function of temperature and time, with a noncontact vibrating electrode electrometer.⁵

Although it is the surface charge density σ which is the best measure of the electret material properties, it is the voltage V across the electret which enters into any device operation and is the quantity which is measured physically. The two quantities are related by the formula $V = \sigma t/k\epsilon_0$, where t is the thickness of the electret layer, k is the electret material dielectric constant, and ϵ_0 is the permittivity of free space.

The electrets were always stored in normal laboratory air under open-circuit conditions. This maximized both the internal field in the electret and the se-

TABLE I
 Halogen-Containing Poly-*p*-Xylylenes

Polymer	Polyparaxylylene designation ^a
	Polyparaxylylene
	Poly(chloro- <i>p</i> -xylylene)
	Poly(dichloro- <i>p</i> -xylylene)
	Poly($\alpha, \alpha, \alpha', \alpha'$ tetrafluoro- <i>p</i> -xylylene) "Polymer AF-4"

^a This family of poly-*p*-xylylenes prepared by the Gorham method is presently marketed by Union Carbide Corporation. AF-4 is not commercially available.

verity of the storage conditions. If they had been stored with short-circuited electrodes, as is often done, the lifetimes would undoubtedly have been even longer.

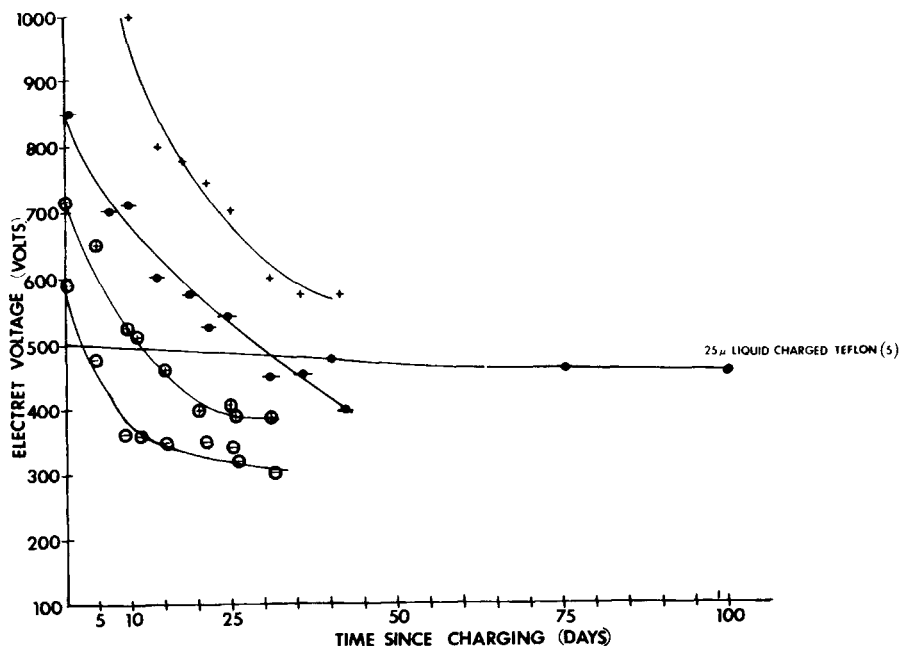


Fig. 1. Voltage across electrets vs. time after charging. (Electrets charged, stored, and measured at ambient temperature.) (+) $-17\text{-}\mu\text{m}$ poly(chloro-*p*-xylylene) \oplus charge; (●) $-17\text{-}\mu\text{m}$ poly(chloro-*p*-xylylene) \ominus charge; (⊕) $-17\text{-}\mu\text{m}$ poly(chloro-*p*-xylylene) \oplus charge, $7\text{-}\mu\text{m}$ overcoat; (⊖) $-17\text{-}\mu\text{m}$ poly(chloro-*p*-xylylene) \ominus charge, $7\text{-}\mu\text{m}$ overcoat.

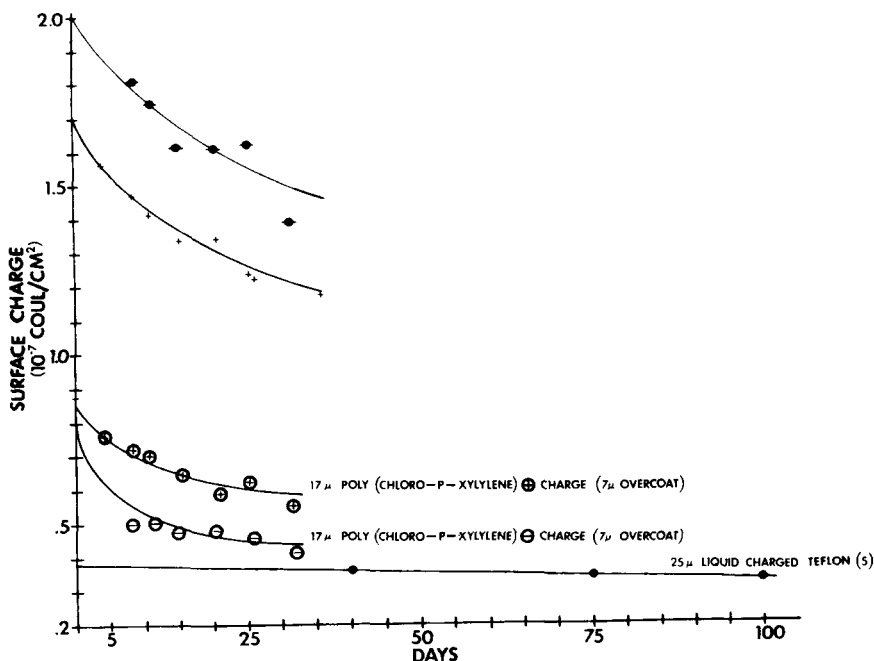


Fig. 2. Electret surface charge density vs. time after charging. (Electrets charged, stored, and measured at ambient temperature.) 6- μ m poly(dichloro-*p*-xylylene (\ominus) charge (no overcoat) and (+) \oplus charge (no overcoat); 17- μ m poly(chloro-*p*-xylylene (7- μ m overcoat) (\oplus) \oplus charge and (\ominus) \ominus charge.

Figure 1 is a plot of the voltage across corona-charged layers of poly(chloroparaxylylene) as a function of time after charging at room temperature for both overcoated and nonovercoated layers. The voltage levels were similar to those published for "liquid charged" Teflon electrets.⁵ Clearly, the vapor-phase-deposited overcoating did not drastically affect the charged layer on the polyparaxylylene.

Figure 2 shows data on the surface charge densities for poly(chloroparaxylylene) and poly(dichloroparaxylylene) electrets, where the preceding formula was used to convert voltage to surface charge. Since the polyparaxylylene electrets supported voltages similar to the Teflon electrets, but across thinner layers, the surface charge densities were higher.

When the polyparaxylylene and poly(chloroparaxylylene) electrets were stored at temperatures much above ambient, their charges drained away in a matter

TABLE II
Comparison of Polyparaxylenes and Poly(Tetrafluoroethylene)

Polymer	Glass transition temperature (T_g) ($^{\circ}$ C)	Melting temperature (T_m) ($^{\circ}$ C)	Temperature of rapid weight loss in air (ref. 6) ($^{\circ}$ C)
Polyparaxylylene	60	400	250
Poly(chloroparaxylylene)	90	280	250
Poly(dichloroparaxylylene)	110	300	320
Polymer AF-4 (ref. 7)	95	500	470
Poly(tetrafluoroethylene) (ref. 8)	-113	330	—

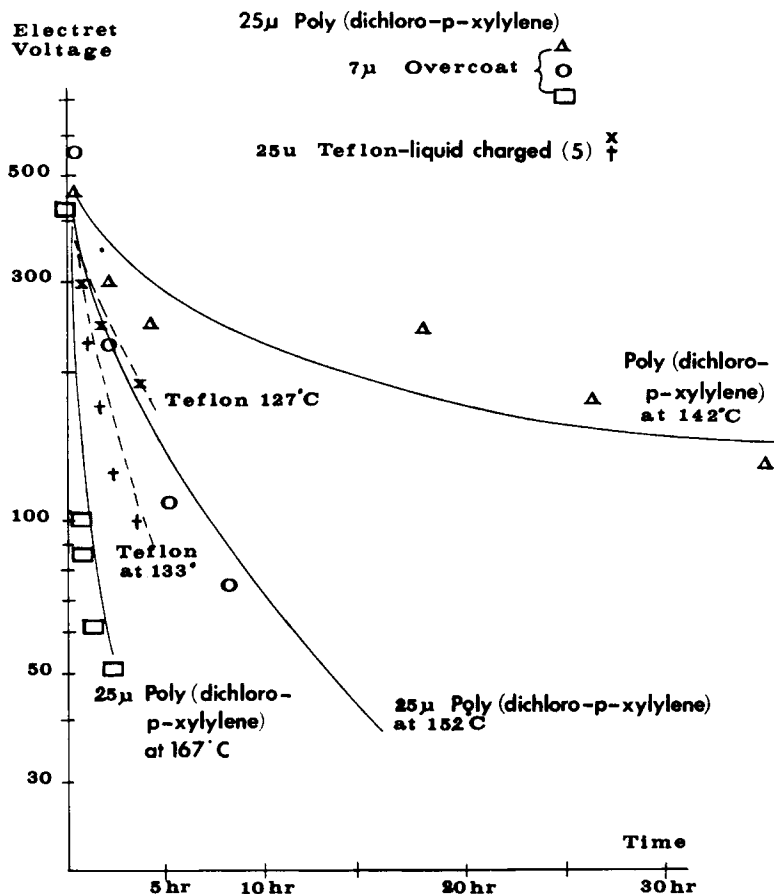


Fig. 3. Voltage across electrets vs. time after charging at various elevated temperatures. (Electrets charged and measured at ambient temperature, but stored at elevated temperature.)

of hours. Electrets made from poly(dichloroparaxylylene) and polymer AF-4 (see Table I), however, showed exceptional high temperature stability. Figure 3 is a plot of the voltages across 25- μ m poly(dichloroparaxylylene) electrets, with a 7- μ m overcoat, at various temperatures and it compares them with published curves of Teflon electrets.⁵ For a given rate of decay, the poly(dichloroparaxylylene) electret had to be raised to a temperature 20°C above that for Teflon.

Since the electrets display a nonexponential decay of voltage, we chose as a measure of the lifetime the time for electrets charged to 500 V to decay to 200 V. Figure 4 is a plot of this lifetime as a function of reciprocal temperature for the poly(dichloroparaxylylene), polymer AF-4, and Teflon electrets.⁵ Extrapolating to a lifetime of 10⁵ hr (11.4 years), the poly(dichloroparaxylylene) and polymer AF-4 electrets have use temperatures of 90 and 170°C, respectively, well above the 60°C use temperature of Teflon.

These extrapolations are only approximate since a lifetime cannot be rigorously defined, the kinetics of the charge decay are unknown, and the extrapolation is across three orders of magnitude in time. Nevertheless, it serves to emphasize the exceptional high-temperature charge retention properties of electrets made

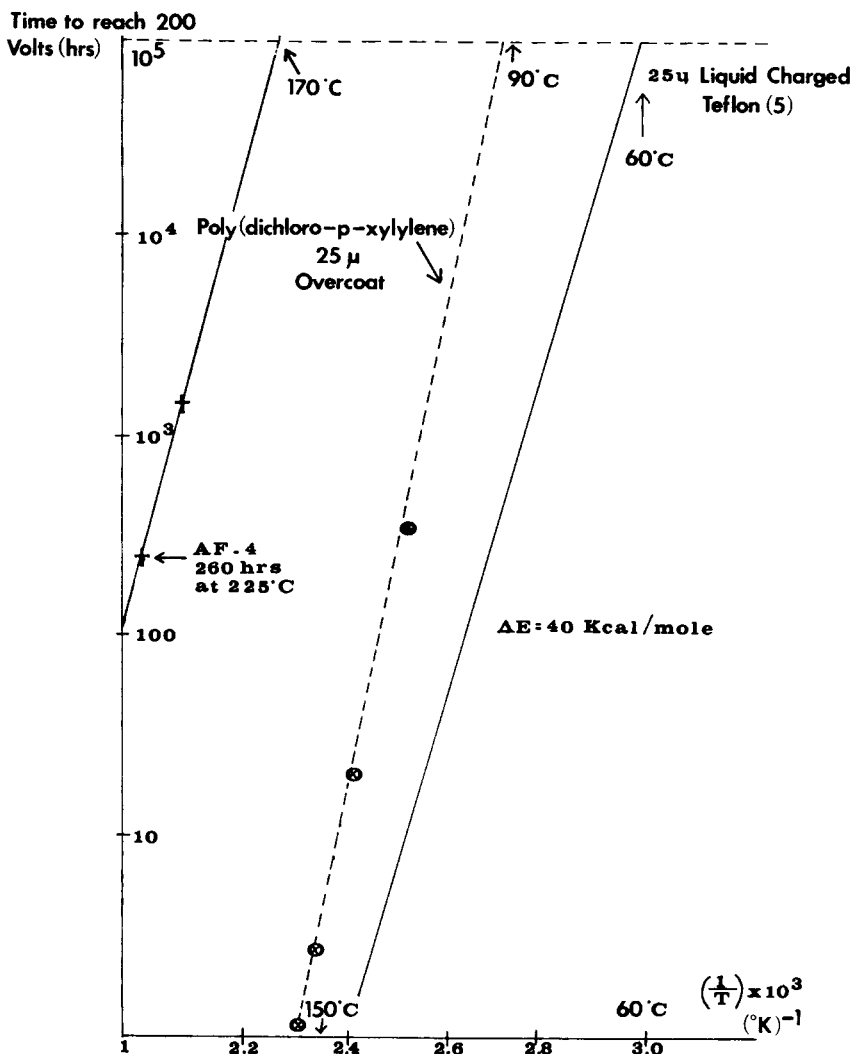


Fig. 4. Time for electret voltage to decay from 500 to 200 V vs. inverse storage temperature. (Electrets charged and measured at ambient temperature, but stored at elevated temperature.)

from poly(dichloroparaxylylene) and polymer AF-4 (see Table I for structures).

Table II compares the polymer properties of the various polyparaxylylenes and poly(tetrafluoroethylene). The only polymer property listed here which correlates with the electret lifetime is the thermo-oxidative stability, as measured by the temperature by which the polymers start to undergo rapid weight loss in air.⁶ Since both poly(tetrafluoroethylene) and poly(vinylidene fluoride) are also thermo-oxidatively stable polymers, this is consistent with previous results.

Charge decay in polymers is usually discussed in terms of charge traps, their density and energy distribution. While such language is good for characterizing a polymer, it has little predictive value since the chemical nature of the traps is unknown. Regardless of the exact kinetics of charge transport through polymers,

it seems qualitatively reasonable that the charge retention properties would be related to the thermo-oxidative stability. Electronic charge transport (as opposed to ion mobility) probably involves unpaired electrons, and unpaired electrons can only be produced by breaking of covalent bonds along the polymer backbone. Since the thermo-oxidative stability is a measure of the difficulty of breaking the bonds, it is perhaps reasonable that this would be related to the charge retention properties of the polymer. In this regard, the polyparaxylylenes were good polymers for study since their electronic structure could be altered without significantly changing the polymer morphology or type of bond along the polymer backbone.

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