

# Method of Determination of Transient and Steady-State Conductivity in Polyethylene Terephthalate Ultrathin Films

A. THIELEN,<sup>\*1</sup> J. VANDERSCHUEREN,<sup>1</sup> J. NIEZETTE,<sup>1</sup> and G. FEYDER<sup>2</sup>

<sup>1</sup>Laboratory of Physical Chemistry, University of Liège, Sart-Tilman, B-4000 Liège, Belgium and

<sup>2</sup>Du Pont de Nemours (Luxembourg) S.A., L-2984, Luxembourg

## SYNOPSIS

The determination of transient and/or steady-state conductivity of polyethylene terephthalate (PET) ultrathin films by means of electrode configurations involving any load or stress imposed on the measuring area during measurement usually leads to anomalous behaviors of the charging current and thus prevents a good evaluation of the electrical properties of the samples. This can be avoided by the use of a two-electrode system with lateral contacts, to obtain reproducible results without any requirement for previous mechanical, thermal, or electrical treatments (as is often recommended in the literature), and that permits the characterization of industrial films down to 1.5- $\mu\text{m}$  thick in true storage conditions after production. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

As a first approximation, the application of a step voltage to a polymer far below its glass-transition temperature,  $T_g$ , results in a long-term transient current that decays, at least in some decades of time, approximately according to a  $t^{-n}$  law, where  $n$  is a constant characteristic of the material, often observed to be close to unity. There are numerous interpretations of this phenomenon in the literature. However, the most important mechanisms that have been proposed are dipolar relaxation (with distribution of relaxation times), charge injection forming trapped space charge, tunneling, hopping of charge carriers, or electrode polarization.<sup>1-6</sup>

Measuring such types of transient currents generally involves the use of a three-electrode configuration including a guard ring around the low potential electrode in order to define accurately its area and to prevent surface leakage currents. Such a system (Fig. 1) is considered as a standard for determining the material conductivity (see for example ASTM D-257<sup>7</sup>). For thin films (some microns), the proper use of a guard system is somewhat delicate

because the recommended condition  $g \leq 2t$ , where  $g$  is the gap width and  $t$  the film thickness, is obviously not practical. However this fact is not really critical because the variations in conductivity determination caused by changes of the effective area of the guarded electrode are small and usually negligible with regard to the variations observed from sample to sample. For ultrathin films of polyethylene terephthalate (PET) down to 1.5  $\mu\text{m}$ , a more drastic problem arises because of the necessary connections between the evaporated electrodes and the external circuit. Because of the extreme fragility of the films, any external pressure exerted on the samples (by means of a spring electrode, for example) can lead to spurious and noisy currents, unexpected current jumps during the charging process and/or electrical breakdown at the highest field strength values. Similar irregularities can even be observed by simply connecting thin copper wires to the evaporated electrodes with the help of conductive silver paste and improving the contacts with a thin coat of epoxy resin. It thus appears that any load or stress imposed to the sample in the measuring area prevents a proper evaluation of the electrical properties. It has also been often reported in the literature, especially for polyester Mylar<sup>®</sup> films, that unless a careful annealing procedure at high temperatures is previously used, the reproducibility of charging and discharging

\* To whom correspondence should be addressed.

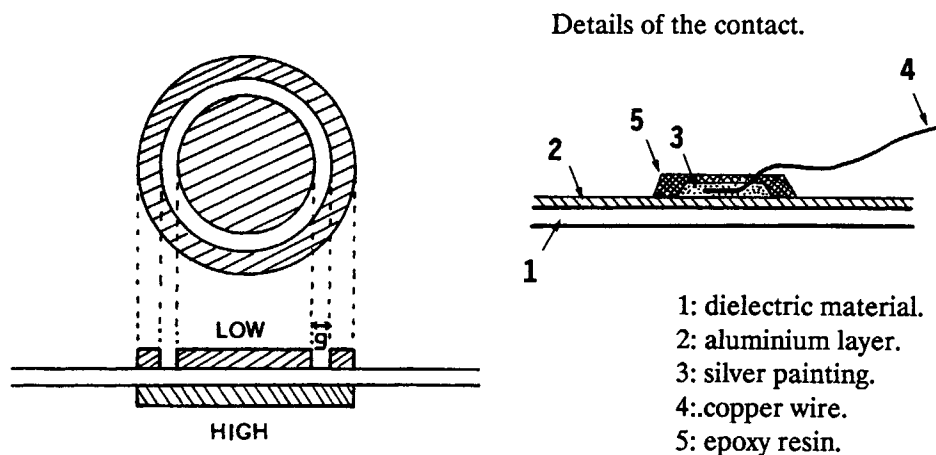


Figure 1 ASTM D-257 standard for the measurement of conductivity of polymers.

currents for a given sample is usually poor with large fluctuations occurring from sample to sample.<sup>8-11</sup> Lilly and McDowell,<sup>12</sup> noticed that the samples had to be previously conditioned near the highest temperature to be employed and relatively high field strengths had to be applied for periods up to 3 weeks before measurements in order to obtain nearly reproducible steady-state currents (to  $\pm 2.5\%$ ). Such procedures are obviously not practical for characterizing industrial films in true storage conditions after production. Anomalies in insulating polymers, like anomalous discharge currents, reversal of current flow during TSC (thermally stimulated current), or charging current increasing with time have been encountered. Most of these phenomena were reviewed and summarized by Wintle.<sup>13</sup>

In this paper, we show that good reproducibility can be obtained for ultrathin PET films under realistic conditions of temperature, electrical field strength, and relative humidity by using a two-electrode system with lateral contacts.

## EXPERIMENTAL

Specimens  $4 \times 4 \text{ cm}^2$  were cut from rolls of Mylar® films ranging in thickness from 1.5 to 12  $\mu\text{m}$  (1.5, 3, 6, and 12  $\mu\text{m}$ ) supplied by Du Pont de Nemours (Luxembourg). Whatever the configuration used (see below), the primary electrodes were obtained by evaporating 45-nm thick aluminum layers (occasionally gold) in vacuum ( $P = 2 \cdot 10^{-5} \text{ mbar}$ ). Before and after metallization, the samples were kept at room temperature in a controlled atmosphere of 52% constant relative humidity obtained by means of a saturated salt solution ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , ASTM E-104), which is close to the usual storage conditions

of the industrial film rolls. They were then enclosed at the same RH value (52%) in a grounded brass screen cell in a thermostatic bath whose temperature was controlled at  $23 \pm 0.1^\circ\text{C}$ . Well stabilized field strengths ranging from 3 to 40  $10^6 \text{ V/m}$  were supplied by dry cells. This latter value is the highest one currently used for testing metallized films for capacitors. Charging and discharging currents were measured by a programmable Keithley electrometer, model 617.

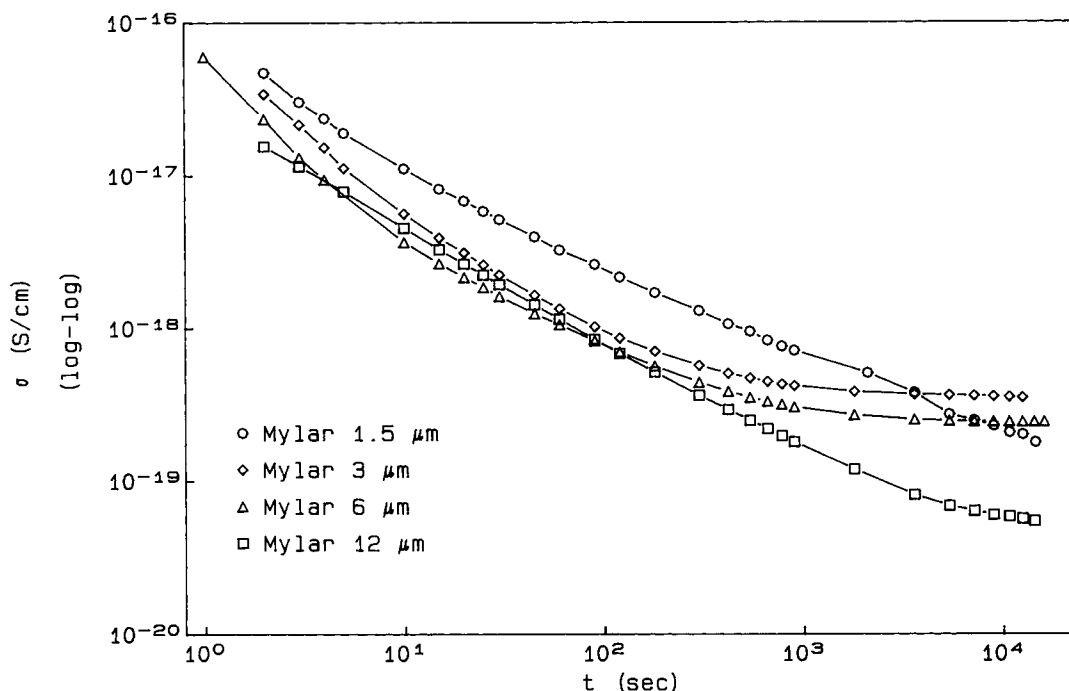
## RESULTS

### Classical Electrode Configurations

A series of charging and discharging experiments were carried out on Mylar® films with a classical three-electrode system connected to the external circuit by means of thin copper wires fixed with silver paste and epoxy resin (Fig. 1). Typical charging currents obtained for an applied field of 30  $10^6 \text{ V/m}$  with 12, 6, 3, and 1.5  $\mu\text{m}$  thick films are shown in Figure 2.

In agreement with different works on PET,<sup>9-12,14-19</sup> for the 12- $\mu\text{m}$  thick films, the results agree fairly well with a  $t^{-n}$  dependence up to  $10^3 \text{ s}$ , after which the steady-state conductivity progressively prevails, but this is no longer true for the thinner samples, except in very limited periods of time. In addition, in the case of 6- and 3- $\mu\text{m}$  thick films, the steady-state conductivity is more rapidly reached and is approximately one order of magnitude higher than in the 12- $\mu\text{m}$  thick specimens.

It is also important to note that the thinner the films, the more important was the number of experiments failing for unexplained reasons. In the



**Figure 2** Transient conductivity observed in Mylar® films of various thicknesses (12, 6, 3, and 1.5  $\mu\text{m}$ ) with the three-electrode configuration for times ranging from 1 to  $10^4$  s.  $T = 23^\circ\text{C}$ ; RH = 52%;  $E_p = 3 \cdot 10^7$  V/m.

current profiles, the manifestations of the failure problem were complex and manifold (high level noise, sudden current jumps during the charging process, dielectric breakdown at the highest field strength values, etc.) and could not be unambiguously related to a given origin for a given thickness. In fact, for the thinnest films, the main problem lies in their increasing fragility that unavoidably leads to increasing manipulation and connection difficulties and thus to increasing possibilities of damaged film (see discussion below). Because the aim of our work was precisely to avoid such troubles, no statistical study of the phenomena has been carried out. With the 1.5- $\mu\text{m}$  thick films, in particular, it was found necessary to test more than 20 samples before obtaining a complete curve such as represented in Figure 2.

The variation of the exponent  $n$ , calculated in limited portions of curves close to the linearity (10–300 s), is shown in Figure 3 as a function of field strength for different thicknesses. The evolution observed is rather complex and seems to disagree with the generally accepted opinion that the slope of the  $\log I - \log t$  plots must be independent of the experimental conditions because  $n$  is a parameter characteristic of the material.

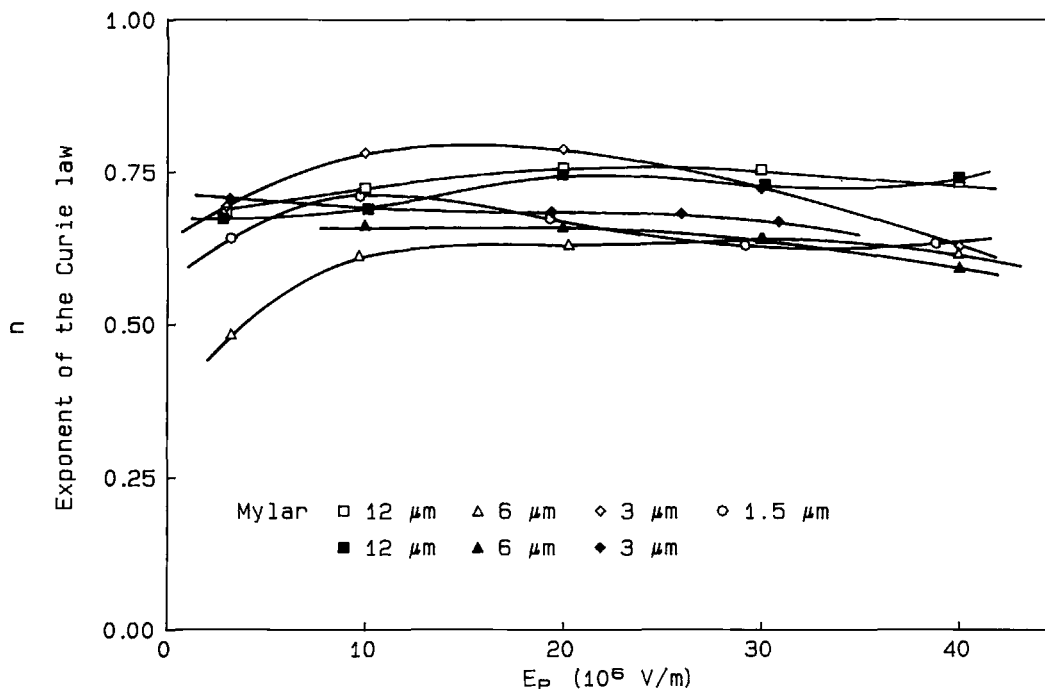
With the 1.5- $\mu\text{m}$  thick films, similar intriguing results were obtained by connecting the evaporated

electrodes to the external circuit through lightly spring-loaded aluminum plates, polished to better than 0.3  $\mu\text{m}$  (Fig. 4). As a matter of fact, even for times lower than  $10^3$  s, pronounced curvatures and/or irregularities were observed in the absorption currents, whatever the applied voltage (Fig. 5).

Because of the high field strengths used, noisy and/or spurious currents are not necessarily surprising and could in principle result from charge injection and/or prebreakdown phenomena. However, it seems that these processes can be ruled out as the possible origin of the irregularities obtained on the basis of the following observations:

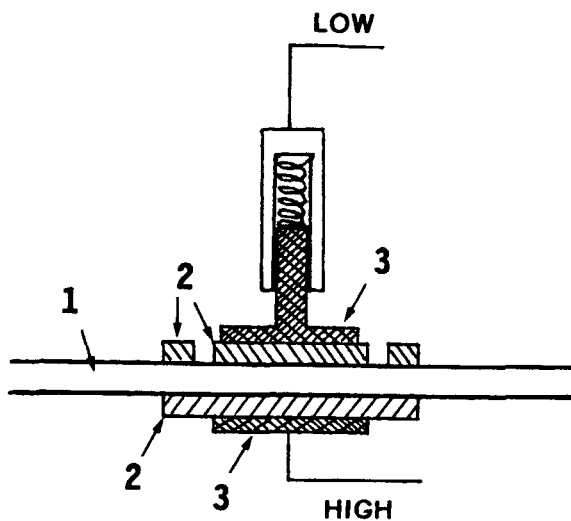
1. even for the highest field strength values used, the absorption and resorption currents are mirror images of one another;
2. applying the highest voltage repeatedly to a particular sample leads to well reproducible results; and
3. the noise level is not directly related to the applied voltage.

On the other hand, in the case of ultrathin films, it appears that the way of connecting the electrodes to the external circuit strongly determines the obtained results whatever the electrode configuration used (with or without guard ring). It thus seems



**Figure 3** Field dependence of the exponent of the Curie-Von Schweidler relationship observed in Mylar® films of various thicknesses (12, 6, 3, and 1.5  $\mu\text{m}$ ). Two samples of each thickness are presented, except for the thinnest film.  $T = 23^\circ\text{C}$ ; RH = 52%.

probable that unexpected electrical effects could be directly related to the type of mechanical contacts in the measuring area. This could explain that sev-



- 1: dielectric material.
- 2: aluminium layer.
- 3: bright aluminium plates.

**Figure 4** Experimental system: spring-loaded aluminium plates providing the connections with the external circuit.

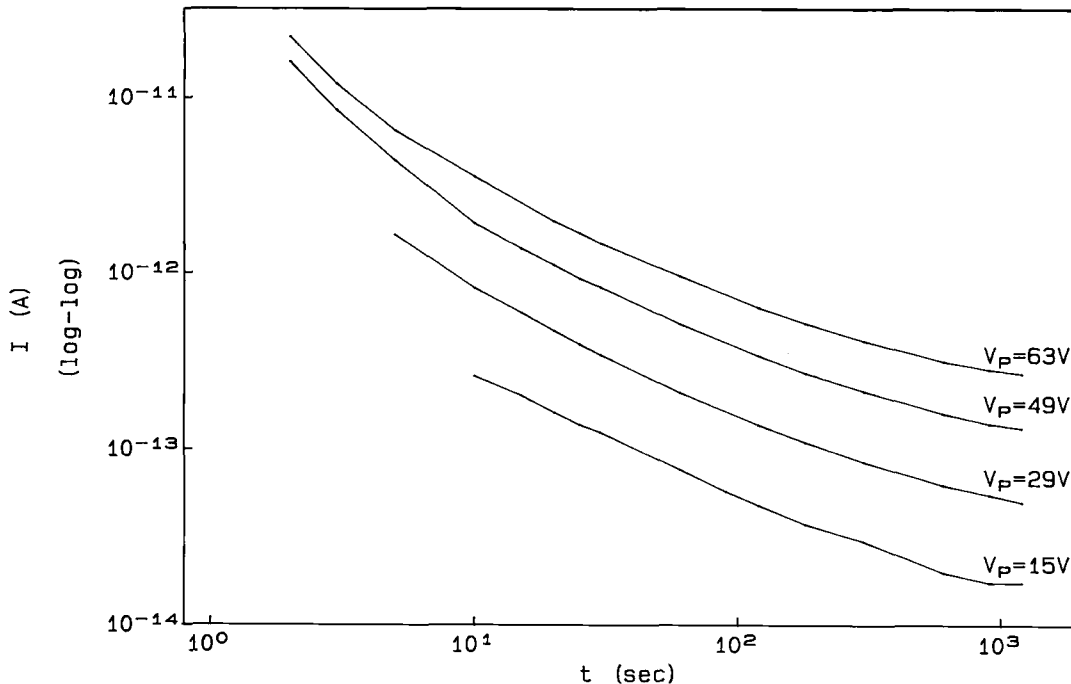
eral authors<sup>8-11</sup> noticed that their samples had to be thermally and/or electrically conditioned for a long time before measurement in order to reduce the contact effects to a minimum.

Such phenomena, inducing mechanical constraints or even damages in the bulk, are obviously expected to have the most dramatic consequences in ultrathin films. With connections involving the use of epoxy resin, this could be caused by the existence of mechanical heterogeneous stresses or even microtears resulting from shrinkage effects induced by the polymerization of the resin. With the spring electrodes, on the other hand, similar microtears or conducting paths could also be created locally by the pressure exerted on the particles of additive providing the surface roughness required for high-speed film winding.

In the light of these experimental evidences, we have used a two-electrode configuration with opposite lateral contacts to overcome these difficulties. The area of the contacts was negligible with respect to the circular measuring area in order to minimize the field distortion (Fig. 6).

#### Two-Electrode Configurations

As shown in Figure 7, a very good agreement between the two-electrode and three-electrode configurations

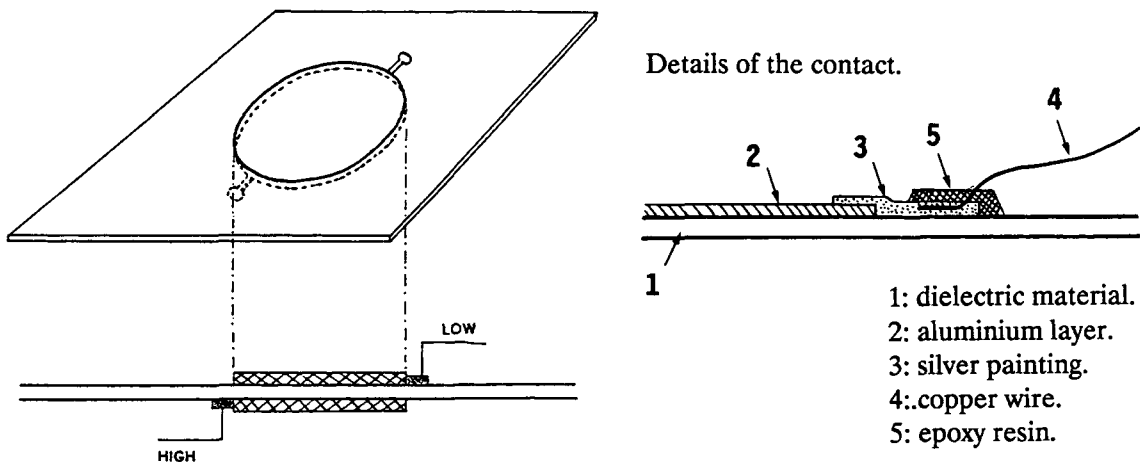


**Figure 5** Transient current observed in nonmetallized 1.5- $\mu\text{m}$  thick Mylar<sup>®</sup> film for different applied voltages and times ranging from 1 to  $10^3$  s;  $T = 23^\circ\text{C}$ ; RH = 52%.

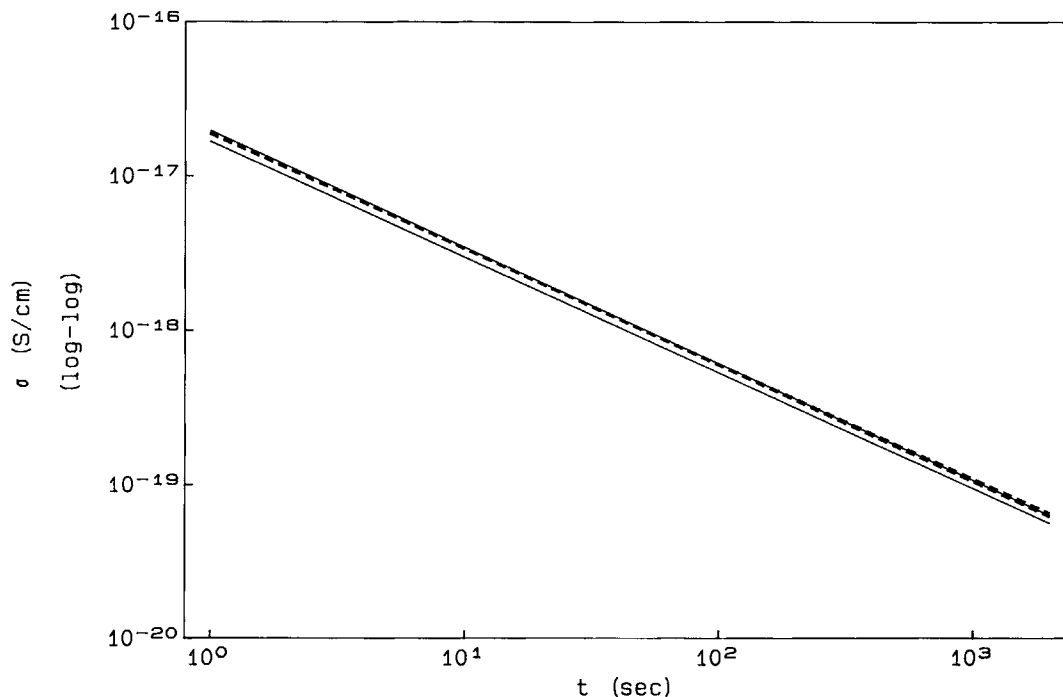
was observed with simultaneously metallized 12- $\mu\text{m}$  thick films, that is, those films expected to be the less sensitive to contact effects. This is not necessarily surprising because pointed out by several authors that measurements with and without guard rings usually give very nearly the same results in PET (for which the surface leakage currents are normally low and not apparent).<sup>12</sup> But it proves the validity of the lateral contact configuration and the possibility to use it with thinner films.

The difference in results obtained with the two

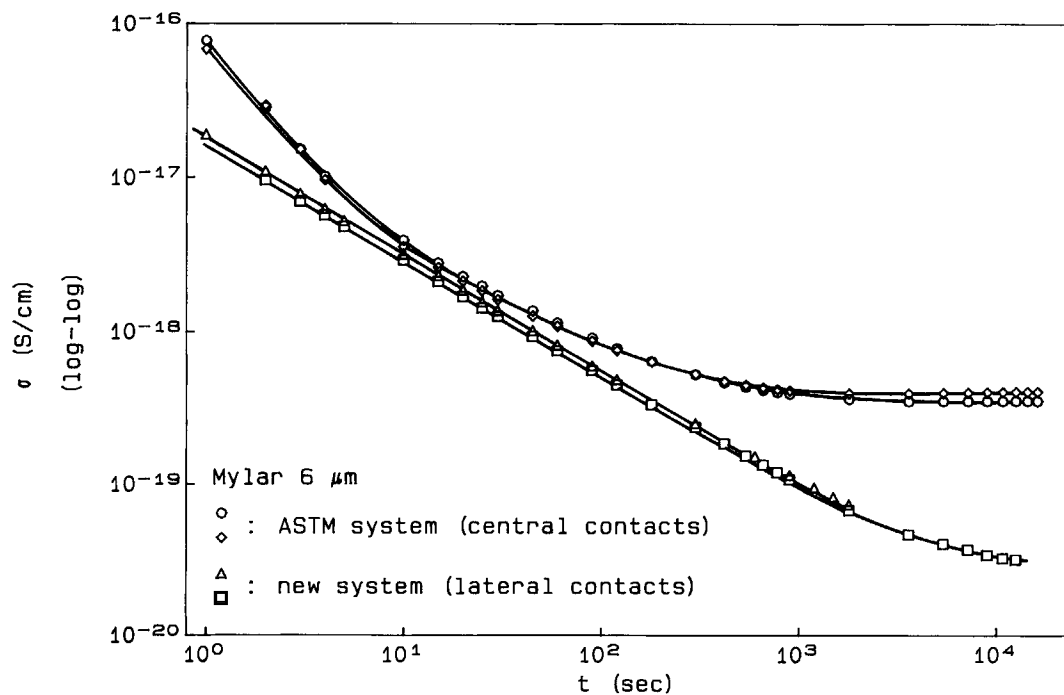
types of electrode configurations for the thinner films (from 6 to 1.5  $\mu\text{m}$ ) is illustrated in Figures 8-10. Typical results obtained with the new system for four thicknesses down to 1.5  $\mu\text{m}$  and a given field strength ( $4 \cdot 10^7$  V/m) are represented in Figure 11. The log-log plots are now all characterized by a good linearity over a time period as long as  $10^3$  s and the absolute values of conductivity are nearly independent of the film thickness. In addition, the transient currents are reproducible from sample to sample to a few percent (Fig. 12) to precisely characterize the



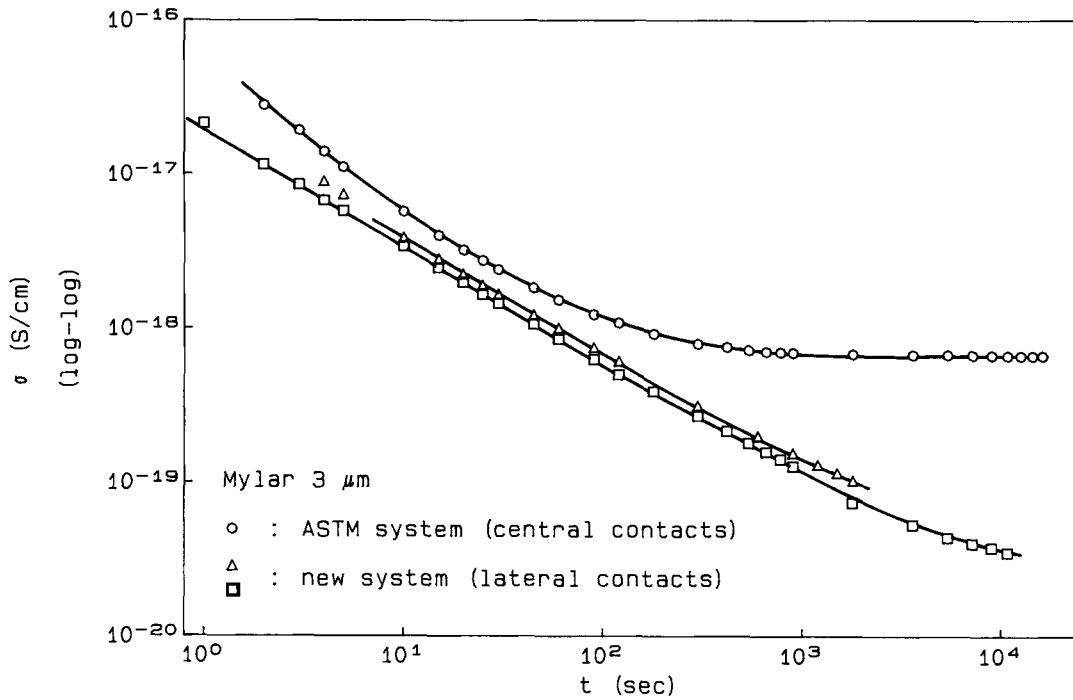
**Figure 6** New experimental contacting system including lateral contacts outside of the measuring area.



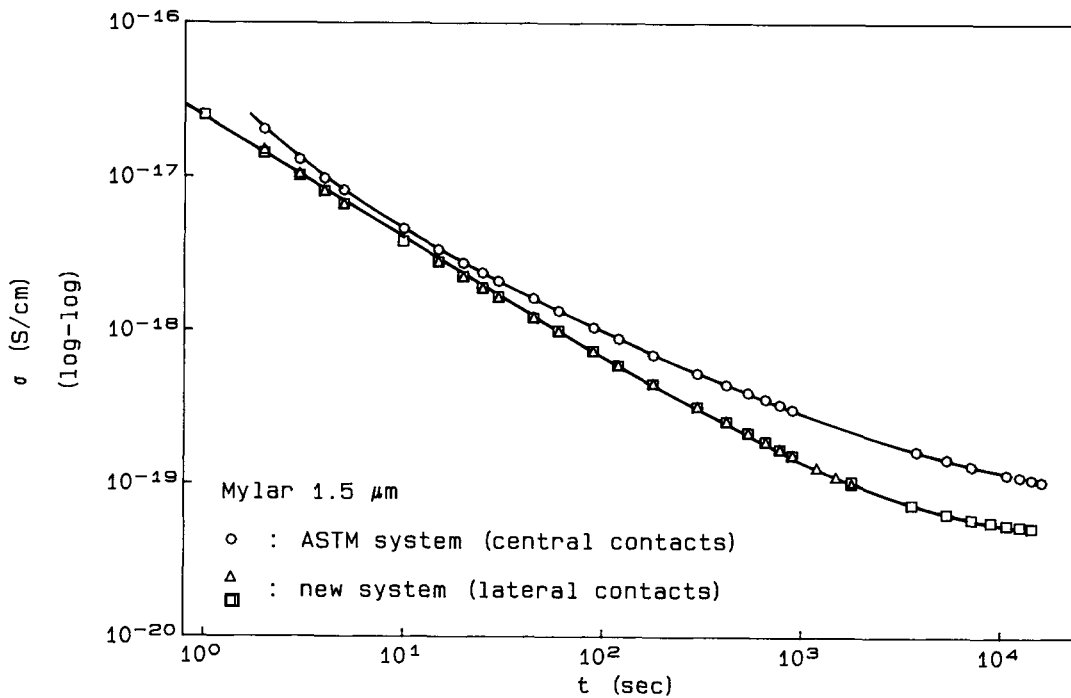
**Figure 7** Transient conductivity observed in four samples of 12- $\mu\text{m}$  thick Mylar<sup>®</sup> film either with the three-electrode system (filled lines) or with the new two-electrode configuration (dotted lines) for times ranging from 1 to  $10^3$  s.  $T = 23^\circ\text{C}$ ; RH = 52%.



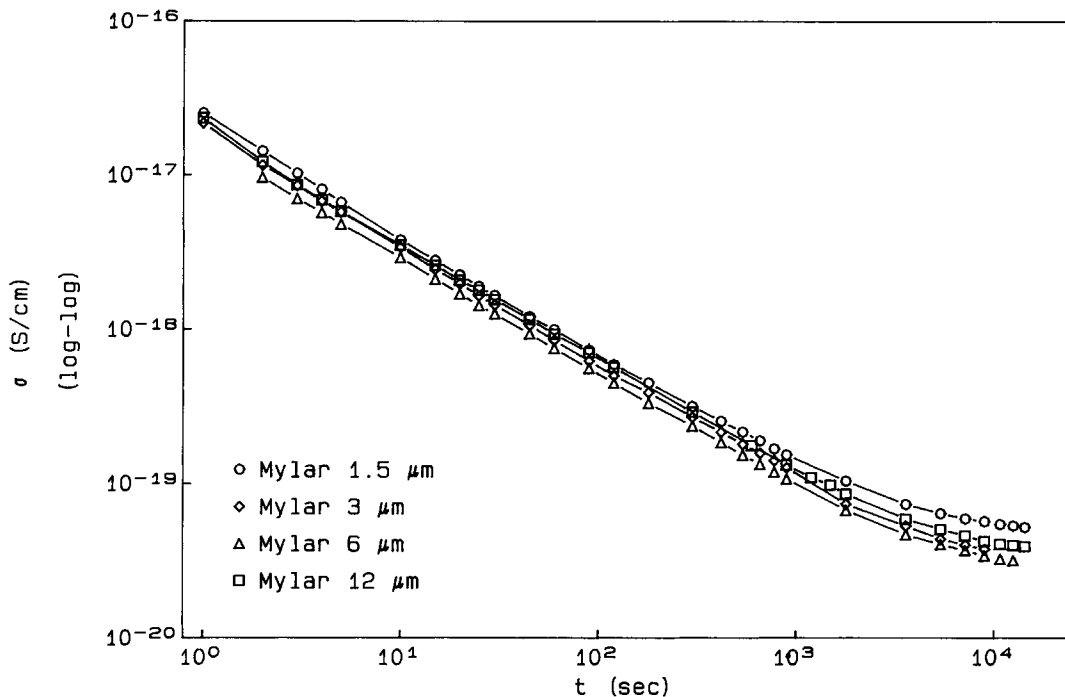
**Figure 8** Transient conductivity observed in four different samples of 6- $\mu\text{m}$  thick Mylar<sup>®</sup> film either with the ASTM configuration or with the new lateral contacting system, for times ranging from 1 to  $10^4$  s.  $T = 23^\circ\text{C}$ ; RH = 52%;  $E_p = 4 \cdot 10^7$  V/m.



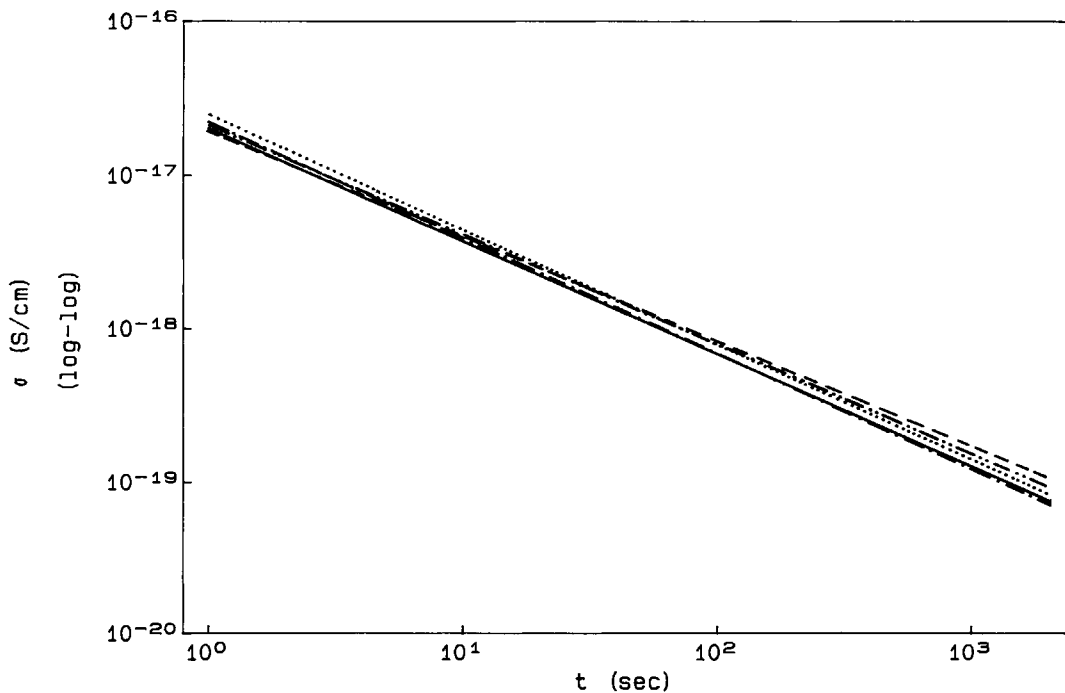
**Figure 9** Transient conductivity observed in three different samples of 3- $\mu\text{m}$  thick Mylar<sup>®</sup> film either with the ASTM configuration or with the new lateral contacting system, for times ranging from 1 to 10<sup>4</sup> s.  $T = 23^\circ\text{C}$ ; RH = 52%;  $E_p = 4 \cdot 10^7$  V/m.



**Figure 10** Transient conductivity observed in three different samples of 1.5- $\mu\text{m}$  thick Mylar<sup>®</sup> film either with the ASTM configuration or with the new lateral contacting system, for times ranging from 1 to 10<sup>4</sup> s.  $T = 23^\circ\text{C}$ ; RH = 52%;  $E_p = 4 \cdot 10^7$  V/m.

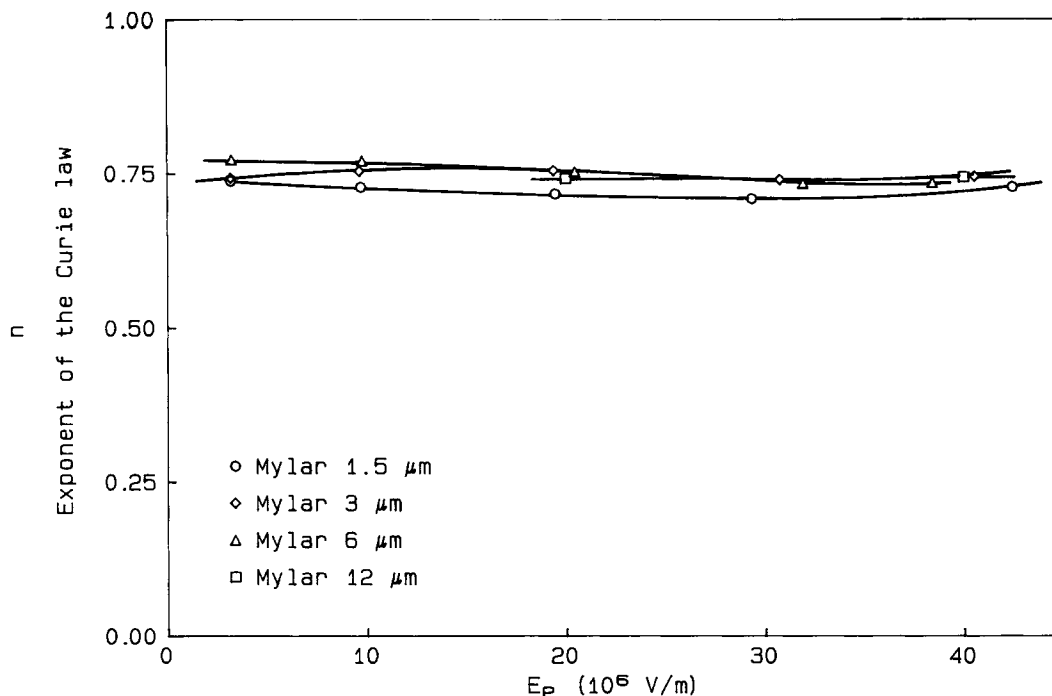


**Figure 11** Transient conductivity observed in Mylar® films of various thicknesses (12, 6, 3, and 1.5  $\mu\text{m}$ ) with the new lateral contacting system for times ranging from 1 to  $10^4$  s.  $T = 23^\circ\text{C}$ ; RH = 52%;  $E_p = 4 \cdot 10^7$  V/m.



**Figure 12** Transient conductivity observed in five different samples of 1.5- $\mu\text{m}$  thick Mylar® films with the new lateral contacting system for times ranging from 1 to  $10^3$  s.  $T = 23^\circ\text{C}$ ; RH = 52%;  $E_p = 2 \cdot 10^7$  V/m.





**Figure 13** Field dependence of the exponent of the Curie-Von Schweidler relationship observed in Mylar® films of various thicknesses (12, 6, 3, and 1.5  $\mu\text{m}$ ) with the new lateral contacting system.  $T = 23^\circ\text{C}$ ; RH = 52%.

intrinsic properties of the films without previous conditioning.

At room temperature and in the considered range of time, the same good reproducibility is also obtained after repeated applications of the field to a given sample (negligible electrification effects). It thus appears that, in untreated PET films, the reproducibility of electrical DC measurements is intrinsically quite satisfactory and that most thermal treatments advocated in the literature for obtaining reproducible results are in fact not required if sufficient care is taken to avoid some damaging or mechanical stress of the films.

As shown in Figure 13, the exponent  $n$  of the Curie-Von Schweidler relationship, calculated from measurements carried out with the two-electrode system, is nearly independent of the film thickness and field strength. Its value can be estimated to  $0.75 \pm 0.03$ , close to that obtained by other authors for thicker films.<sup>14</sup>

## CONCLUSIONS

The present experimental evidence defines a simple procedure using a two-electrode configuration with

opposite lateral contacts for obtaining reproducible and reliable measurements of the transient and steady-state electrical conduction in ultrathin PET films without any previous electrical, mechanical, or thermal treatments. Such treatments, often recommended and even claimed to be necessary to obtain reproducible results, induce in fact pronounced changes in the matrix morphology and/or the size and number of crystallites. This prevents a full characterization of industrial films under realistic storage conditions. It appears from our measurements that the previously encountered difficulties could arise from the existence of mechanical stresses or microtears induced in the films at the level of the connections to the external circuit. We have shown that this can be easily avoided by realizing opposite contacts outside the circular electrode area.

## REFERENCES

1. J. R. Mac Donald, *J. Chem. Phys.*, **54**, 2026 (1971).
2. R. H. Walden, *J. Appl. Phys.*, **43**, 1178 (1972).
3. J. Lindmayer, *J. Appl. Phys.*, **36**, 196 (1965).
4. H. J. Wintle, *J. Appl. Phys.*, **42**, 4724 (1971).
5. H. J. Wintle, *J. Appl. Phys.*, **44**, 2514 (1973).

6. S. Havriliak and S. Negami, *Polymer*, **8**, 161 (1967).
7. Annual Book of ASTM Standards, Part 39, 151 (1980).
8. E. Sacher, *J. Macromol. Sci. Phys. B.*, **19**, 131 (1981).
9. E. Sacher, *J. Macromol. Sci. Phys. B.*, **4**, 441 (1970).
10. A. Y. Ko and J. Hirsch, *Solid State Commun.*, **39**, 215 (1981).
11. D. K. Das Gupta and K. Joyner, *J. Phys. D: Appl. Phys.*, **9**, 829 (1976).
12. A. C. Lilly, Jr. and J. R. McDowell, *J. Appl. Phys.*, **39**, 141 (1968).
13. H. J. Wintle, *IEEE Trans. Elect. Insul.*, **EI-21**, 747 (1986).
14. G. Lengyel, *J. Appl. Phys.*, **37**, 807 (1966).
15. D. M. Taylor and T. J. Lewis, *J. Phys. D: Appl. Phys.*, **4**, 1346 (1971).
16. H. J. Wintle, *J. Non-Cryst. Sol.*, **15**, 471 (1974).
17. J. Vanderschueren and A. Linkens, *J. Appl. Phys.*, **49**, 4195 (1978).
18. H. J. Wintle, *J. Appl. Phys.*, **62**, 2933 (1987).
19. H. J. Wintle, *IEEE Trans. Elect. Insul.*, **25**, 27 (1990).

Received September 25, 1992

Accepted January 23, 1993