



Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in : <http://oatao.univ-toulouse.fr/>
Eprints ID : 4667

To link to this article : DOI :10.1007/s11664-010-1414-y
URL :<http://dx.doi.org/10.1007/s11664-010-1414-y>

To cite this version :

Diaham, S. and Bechara, M. and Locatelli, M.L. and Tenailleau, Christophe (2011) *Electrical conductivity of parylene F at high temperature*. Journal of Electronic Materials, vol. 40 (n° 3). pp. 295-300. ISSN 0361-5235

Any correspondance concerning this service should be sent to the repository administrator: staff-oatao@inp-toulouse.fr.

Electrical Conductivity of Parylene F at High Temperature

S. DIAHAM,^{1,2,4} M. BECHARA,^{1,2} M.-L. LOCATELLI,^{1,2} and
C. TENAILLEAU³

1.—UPS, INPT, LAPLACE, Université de Toulouse, 118 route de Narbonne - Bât. 3R3, 31062 Toulouse Cedex 9, France. 2.—CNRS, LAPLACE, 31062 Toulouse, France. 3.—Laboratoire CIRIMAT/LCMIE, UPS, Université de Toulouse, 118 route de Narbonne - Bât. 2R1, 31062 Toulouse Cedex 9, France. 4.—e-mail: sombel.diaham@laplace.univ-tlse.fr

The electrical conductivity of both as-deposited and annealed poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) (PA-F) films has been investigated up to 400°C. The static conductivity (σ_{DC}) values of PA-F measured between 200°C and 340°C appear to be ~ 2.5 orders of magnitude lower for annealed films than for as-deposited ones. This change is attributed to a strong increase in the crystallinity of the material occurring above 340°C. After annealing at 400°C in N₂, the σ_{DC} value measured at 300°C, for instance, decreased from $3.8 \times 10^{-12} \Omega^{-1} \text{cm}^{-1}$ to $7.5 \times 10^{-15} \Omega^{-1} \text{cm}^{-1}$. Physical interpretations of such an improvement are offered.

Key words: Parylene F, PA-F, insulating films, electrical conduction, high temperature, crystallization

INTRODUCTION

New high-temperature semiconductor devices able to operate up to 350°C need suitable passivation and encapsulation packaging materials for surface electrical insulation.¹ To date, polyimides (PIs) deposited by spin-coating have been used for passivation of power devices; however, they do not appear to be appropriate conformal encapsulation coatings for three-dimensional (3D) multichip modules. Moreover, long-term use of PIs at 300°C and above is limited due to degradation of properties.²

Polyparaxylylene (PPX) films, usually referred to as parylene (PA), are semicrystalline polymeric materials widely used in microelectronics as interlayers due to their low dielectric constant, high thermal stability, and low gas and moisture permeability.^{3,4} They therefore appear to be potential candidates for surface electrical insulation of power electronic components due to their physical properties and the compatibility of their deposition process. Indeed, contrary to PIs deposited by spin-coating, the most prominent advantage of PAs is the solventless room-temperature vapor deposition

polymerization (VDP) process, which allows deposition of conformal submicron and micron (from 100 nm to 75 μm) films without formation of pinholes.^{5,6} Among the PAs (Fig. 1), poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) (parylene F, PA-F) exhibits the best physical properties for high-temperature applications. It shows low dielectric constant between 2.2 and 2.4 depending on the deposition conditions,^{7–10} and both high melting and decomposition temperatures, above 520°C.^{11,12} PA-F can operate at 350°C in the long term and up to 450°C in the short term, even in air atmosphere. The high thermal stability of PA-F is mainly due to incorporation of C–F bonds into the monomer structure, which have stronger oxidation resistance than the C–H bonds present in classic PA-N.¹²

However, even though development of PA-F started as early as 1963 with the work of Hertler,¹³ followed by Gorham between 1965 and 1967,^{14–16} little work has been dedicated to its physical properties. The main reasons are the difficulty encountered in film synthesis (process, cost) and the only recent availability of commercial films (since 2004). The work reported in the literature deals mainly with film synthesis and the resulting chemical structure (CF₂ formation, crystallization kinetics, and oxygen impurity content),^{8,9,17–19} and

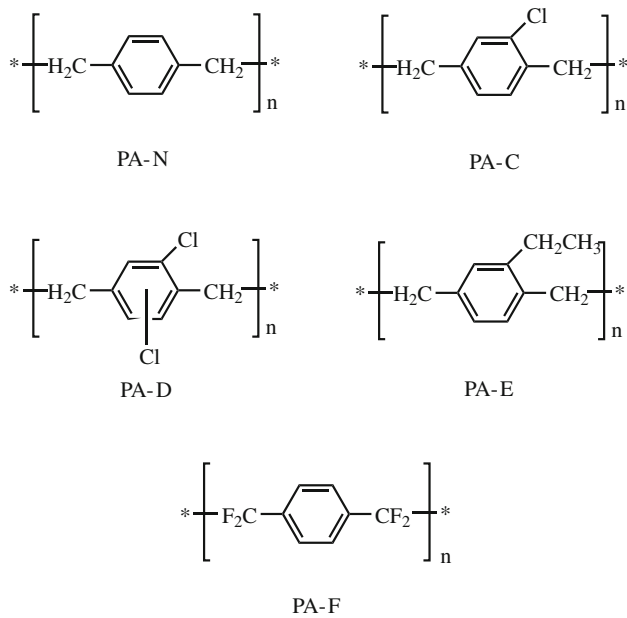


Fig. 1. Different parylene monomers: PA-N, PA-C, PA-D, PA-E, and PA-F.

sometimes with thermal properties.^{11,12} In fact, studies regarding the electrical properties of PA-F are almost nonexistent. Indeed, except for dielectric constant characterization at 25°C^{7–10,20} and surface potential measurements,^{21,22} to date, no data have been reported on the intrinsic electrical properties of PA-F and their temperature dependence. So, this paper deals for the first time with the temperature dependence of the electrical conductivity of PA-F up to 400°C. Moreover, the influence of exposure to high temperature on film properties is studied too.

EXPERIMENTAL PROCEDURES

Material

Electrical conduction of PA-F was studied on poly[(2,3,5,6-tetrafluoro-1,4-phenylene)(1,1,2,2-tetrafluoro-1,2-ethanediyl)] films with a thickness of 10 μm.²³ PA-F films were obtained by VDP at 25°C through the Gorham method (Fig. 2),^{14–16} on stainless-steel substrates (9 cm²). For electrical measurements, circular gold upper electrodes of 5 mm diameter were evaporated in vacuum onto the film surface.

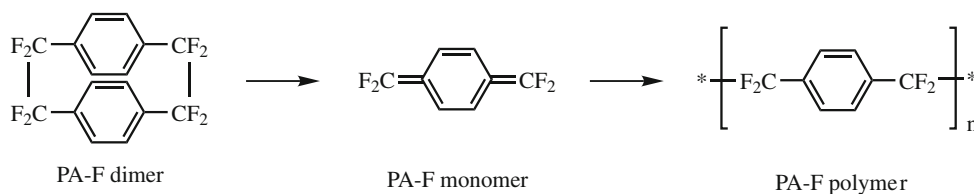


Fig. 2. Synthesis steps of poly(α,α,α',α'-tetrafluoro-p-xylylene).

Measurements

Alternating-current (AC) conductivity σ_{AC} was measured by broadband dielectric relaxation spectroscopy (BDRS) using a Novocontrol Alpha-A spectrometer. Measurements were performed from 200°C to 400°C in N₂ atmosphere and in the frequency range from 0.1 Hz to 100 kHz. σ_{AC} values were derived from their relation with the imaginary part of the dielectric permittivity ϵ'' :²⁴

$$\sigma_{AC}(\omega) = \omega \epsilon_0 \epsilon''(\omega), \quad (1)$$

where ω is the angular frequency and ϵ_0 is the vacuum permittivity. The static (DC) conductivity σ_{DC} was obtained in the low-frequency (frequency-independent) region of the σ_{AC} curves as described by the “universal” power law:²⁵

$$\sigma_{AC}(\omega) = \sigma_{DC} + A\omega^n, \quad (2)$$

where A is an empirical parameter and n is the exponent of the power law ($n \approx 1$).

The thermal stability of the films was investigated by thermal gravimetric analysis (TGA) using a PerkinElmer analyzer in the range from 25°C to 1000°C (heating slope 10°C/min) under air and nitrogen atmospheres.

To identify the thermal transitions in PA-F, differential scanning calorimetry (DSC) measurements were performed using a DSC Netzsch 204 on approximately 5 mg of peeled film. The temperature ranged from 25°C to 420°C in He atmosphere during both heating and cooling cycles at a heating rate of ±10°C/min. To observe changes in the PA-F crystalline phase, x-ray diffraction (XRD) was performed at 25°C on planar 10-μm-thick films using a D5000 Bruker diffractometer with Cu K_α radiation ($\lambda = 1.5418$ Å) using a 1° grazing incidence angle over 2θ values of 10° to 80° with 0.02° step size and 10 s/step scans.

RESULTS AND DISCUSSION

PA-F Conductivity

Figure 3 shows the frequency dependence of the AC conductivity σ_{AC} of as-deposited PA-F films between 200°C and 400°C for both heating and cooling measurements. The AC conductivity consists of a region linear in frequency at high frequency following the “universal” power law, and a frequency-independent region (plateau region) at low frequency corresponding to σ_{DC} . During the

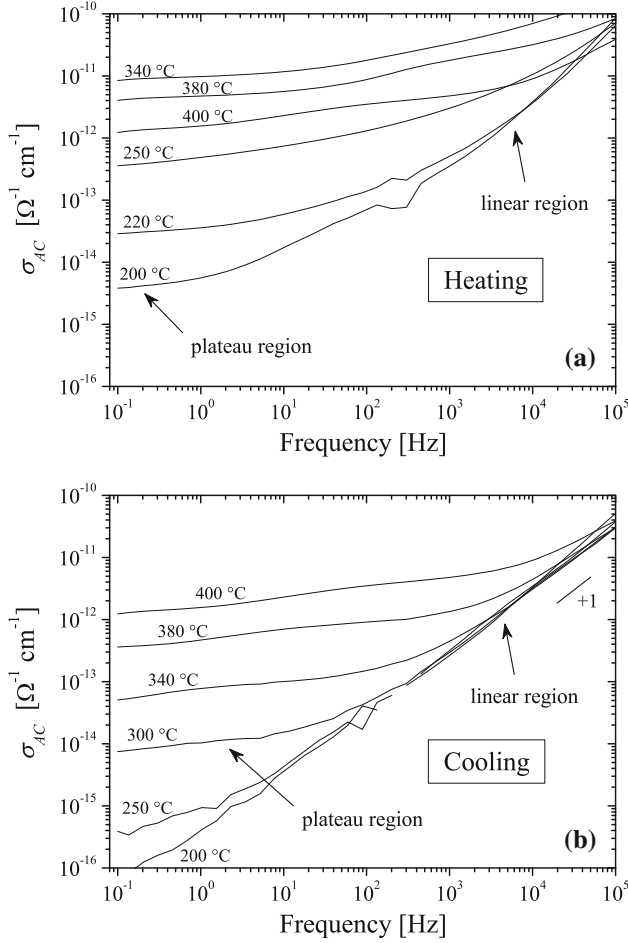


Fig. 3. Frequency dependence of the AC conductivity σ_{AC} of PA-F films between 200°C and 400°C: (a) heating, and (b) cooling measurements.

temperatures rise, the plateau occurs at temperature above 200°C and its magnitude increases by more than three orders up to 340°C. From 340°C to 400°C, the magnitude of the plateau decreases by one order, indicating conductivity diminution. During the cooling measurements, the σ_{AC} values are nonreversible in the same temperature range. Thus, the magnitude of σ_{AC} decreases continuously with decreasing temperature, and the σ_{DC} plateau values appear lower in magnitude than during heating. This behavior confirms the improvement of the electrical properties of PA-F films (i.e., higher resistivity) after heating compared with the as-deposited state. Figure 4 shows the temperature dependence of the DC conductivity σ_{DC} (at 0.1 Hz) of PA-F films derived from heating and cooling measurements according to Eq. 2.

During the heating, nonlinear behavior of σ_{DC} is observable, reaching a maximum of $8.4 \times 10^{-12} \Omega^{-1} \text{cm}^{-1}$ at 340°C. It decreases to $1.2 \times 10^{-12} \Omega^{-1} \text{cm}^{-1}$ at 400°C. Subsequent heatings showed the same values as during the cooling measurements (data not shown). From 200°C to 340°C, it is possible to observe an improvement of ~ 2.5 orders

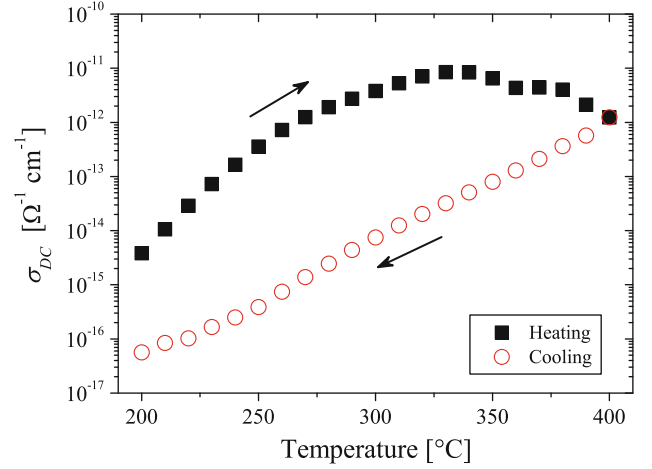


Fig. 4. Temperature dependence of the DC conductivity of PA-F films (estimated using Eq. 2 at 0.1 Hz) for heating and cooling measurements.

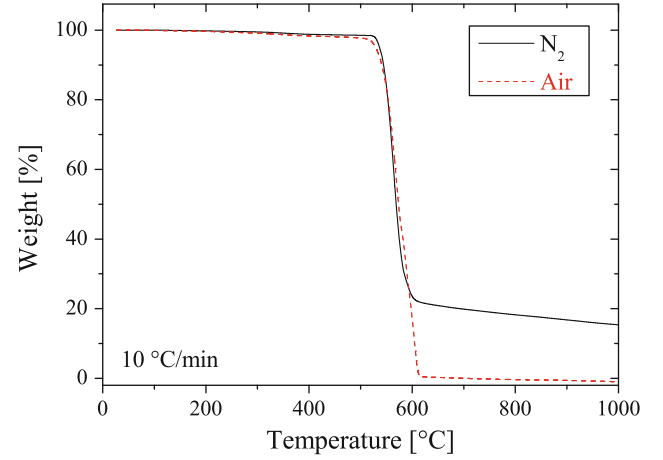


Fig. 5. TGA measurements on as-deposited PA-F films in air and nitrogen atmospheres.

of magnitude in the σ_{DC} values between the heating and cooling measurements. Indeed, after exposure to 400°C, the σ_{DC} value at 300°C, for instance, decreases from $3.8 \times 10^{-12} \Omega^{-1} \text{cm}^{-1}$ to $7.5 \times 10^{-15} \Omega^{-1} \text{cm}^{-1}$. Although one of the advantages of PA-F is its room-temperature deposition process, which does not require *a priori* an additional curing step, it seems that annealing above 340°C leads to improvement in its insulating electrical properties. Thus, PA-F films present lower σ_{DC} values than PIs over the same temperature range.²⁶

Correlation Between Conductivity and Crystallization

As a preliminary structural study, TGA measurements were performed on as-received films to verify the thermal stability of PA-F. Figure 5 shows the weight stability versus temperature under air and nitrogen atmospheres. While the TGA

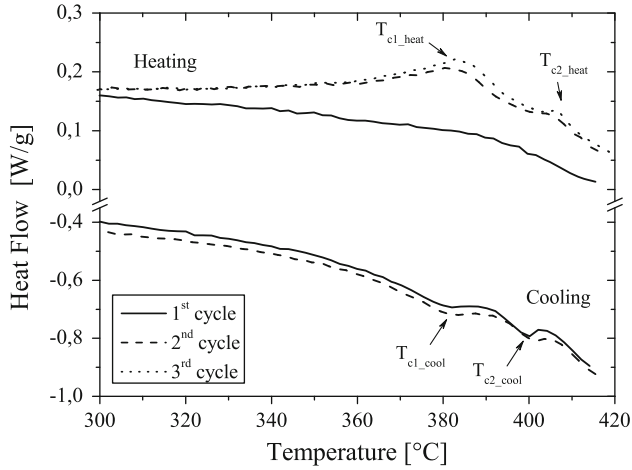


Fig. 6. DSC cycles of PA-F films between 300°C and 420°C. T_c peaks are labeled 1 and 2, respectively, for the primary and secondary crystallization phase transitions, and “heating” and “cooling” for heating and cooling measurements. $T_{c,heat}$ and $T_{c,cool}$ peaks are naturally opposite: *endo* is up during heating and down during cooling.

thermogram in air exhibits slight weight loss below 500°C (more than 1.5% at 400°C), almost no loss is observed under nitrogen (around 1% at 400°C). Simultaneously, the thickness decreased by 8% when the films were annealed at 400°C (data not shown). Therefore, the film density increases with annealing. These results highlight that the evolution of the electrical results is mainly due to density change. The origins of such a change will be discussed below. However, a slight contribution of outgassing of organic impurities should also be considered, even if it appears negligible.

To identify the origin of these electrical changes, complementary measurements were realized using DSC and XRD before and after exposure of PA-F films to high temperature. Figure 6 shows heating and cooling DSC cycles of PA-F between 300°C and 420°C. During the first heating, no thermal event is observed for as-deposited films. After exposure to 420°C, the DSC data of both the first cooling and the second heating exhibit two reversible, endothermic peaks related to two crystalline phase transitions, with the main crystallization temperature (T_{c1}) observed at 382°C and the secondary one (T_{c2}) around 405°C. These peaks are identical for subsequent heating or cooling cycles. These results are consistent with the works of Morgen et al., where T_c was found in the range from 395°C to 403°C.¹⁹

Figure 7 shows XRD measurements of PA-F films before and after annealing at 400°C for 1 h in N_2 . The as-deposited film presents a wide, low-magnitude diffraction peak (centered at $2\theta = 19.14^\circ$) characteristic of a poorly crystallized structure. After annealing, the main PA-F diffraction peak (shifted to $2\theta = 20.36^\circ$) increases strongly, reflecting an increase in the crystallinity of the film. As reported in the literature for PA-N, recrystallization could be accompanied by a possible change in the

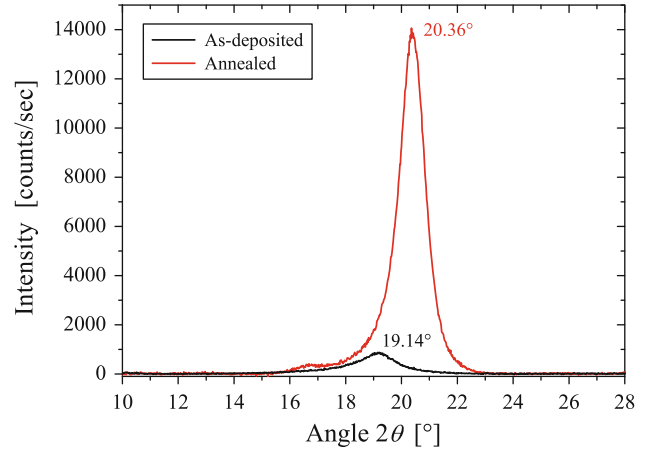


Fig. 7. XRD of as-deposited and annealed (1 h at 400°C in N_2 atmosphere) PA-F films.

PA-F polymorphism, even if this has not been demonstrated to date.¹⁹ The small peak at an angle near $2\theta = 16.4^\circ$ that appears after annealing is due to diffraction of K_β radiation from the same high-temperature crystalline plane that gives rise to the main K_α peak. The length of the repeat units (d -spacing) for both as-deposited and annealed films was calculated using the Bragg equation:

$$2d \sin \theta = k\lambda, \quad (3)$$

where λ is the wavelength of the incident x-ray beam and k is an integer (here $k = 1$). The interplanar d -spacings are 4.64 Å to 4.36 Å for the as-deposited and annealed films, respectively. This decrease shows the space confinement of the amorphous phase between the lamella stacks (crystal-lites). These values are in agreement with those reported by Morgen et al. and Blackwell et al., where the d -spacings in equivalent annealing conditions (400°C and 450°C) were 4.33 Å and 4.4 Å, respectively.^{19,27,28}

As a consequence of progressive crystallization from the glassy state, semicrystalline polymers often exhibit chain arrangements in the form of lamellae (i.e., parallel chain arrangements, ~ 10 nm in thickness), which often organize in spherulites (i.e., spherical semicrystalline regions approximately $1 \mu\text{m}$ to $100 \mu\text{m}$ in diameter inside non-branched linear polymers). Spherulites consist of arrangements of dense lamella stacks consisting of both crystalline lamellae and amorphous regions.²⁹ Figure 8 shows polarized optical microscope images of films before and after annealing. The increase of crystallinity appears through the formation of a low density of spherulites with a maximum diameter around $10 \mu\text{m}$ (not observed on as-deposited films).

The conductivity changes occurring from 340°C after one heating can be explained by the increase of the PA-F crystallinity. The electrical results are consistent with the DSC, XRD measurements, and density changes. Such an improvement in the elec-

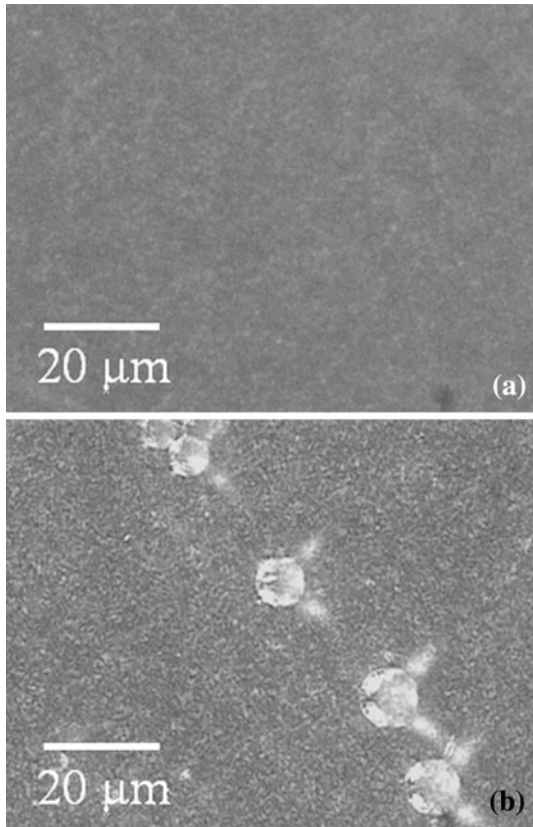


Fig. 8. Optical microscope images of PA-F: (a) as-deposited and (b) annealed films. Bar 20 μm . Spherulites appear after annealing (b), with maximum diameter around 10 μm .

trical properties has already been reported in classical semicrystalline polymers, such as poly(ethylene terephthalate) or poly(ether-ether-ketone), however the crystallization transition appears at lower temperature.^{30,31} The strong decrease in the σ_{DC} values for the annealed PA-F films is related to the reduction of the amorphous region free volume (characterized by the d -spacing decrease) and so the crystalline-amorphous interfaces, leading to an interfacial Maxwell-Wagner polarization process (i.e., separation of charges). Compared with pure amorphous materials in which free voids are present, the semicrystalline polymers often organized in lamellar or spherulitic structures show lower conductivity values,³² because the mobility of the chains and the charge carriers under an applied electric field is considerably reduced. In PA-F films, the crystallization temperature has a very high value ($T_c \approx 382^\circ\text{C}$) compared with other semicrystalline materials ($T_c < 165^\circ\text{C}$). Therefore, the structure needs to receive more thermal energy to improve its self-organization. It has been shown that the (100) PA-F plane is parallel to the film surface, and the chain axis is parallel to the draw direction.²⁸ The motion of charges (often controlled by a hopping conduction process) in the direction normal to the film surface is thus more difficult

across organized parallel planes of chains than along them and/or in the free voids of the amorphous phase.

CONCLUSIONS

The electrical conductivity of PA-F films deposited by VDP has been investigated up to 400°C . The effects of thermal annealing have also been studied. The DC conductivity σ_{DC} of PA-F shows two different behaviors in strong relation with the thermal history of the material. σ_{DC} values measured between 200°C and 340°C are ~ 2.5 orders of magnitude lower for annealed films than for as-deposited ones. For instance, after exposure to 400°C , the σ_{DC} value at 300°C decreases from $3.8 \times 10^{-12} \Omega^{-1} \text{cm}^{-1}$ to $7.5 \times 10^{-15} \Omega^{-1} \text{cm}^{-1}$. This change has been attributed to the crystallinity increase occurring above 340°C , which is supported by the occurrence of a crystallization transition in the same temperature range ($T_c \approx 382^\circ\text{C}$) on DSC thermographs, a strong increase in the XRD peak intensity after annealing at 400°C , and low-density spherulite growth. After annealing, the σ_{DC} improvement is mainly explained by the decrease of the charge mobility in free volumes. The d -spacing decrease between two consecutive crystalline planes confirms the reduction of the amorphous regions where charges can move. PA-F demonstrates exceptional electrical properties for high-temperature insulating applications.

ACKNOWLEDGEMENT

The authors would like to thank the Fondation de Recherche pour l'Aéronautique et l'Espace (FRAE) for the financial support of this work.

REFERENCES

1. R. Kirschman, *High-Temperature Electronics*, Part 8 (Piscataway, NJ: IEEE Press, 1998), p. 727.
2. R.W. Johnson and J. Williams, *Mater. Sci. Forum* 483–485, 785 (2005).
3. S.W. Chow, W.E. Loeb, and C.E. White, *J. Appl. Polym. Sci.* 13, 2325 (1969).
4. M. Szwarc, *Polym. Eng. Sci.* 16, 473 (1976).
5. W.F. Beach, C. Lee, D.R. Bassett, T.M. Austin, and R. Olson, *Xylylene Polymers in Encyclopedia of Polymer Science and Engineering*, 2nd ed., vol. 17 (New York: Wiley, 1991), p. 990.
6. W.R. Dolbier Jr. and W.F. Beach, *J. Fluor. Chem.* 122, 97 (2003).
7. L. Alexandrova and R. Vera-Graziano, *Polymeric Materials Encyclopedia*, ed. J.C. Salamone (New York: CRC Press, 1996), .
8. P.K. Wu, G.R. Yang, L. You, D. Mathur, A. Cocozziello, C.I. Lang, J.A. Moore, T.M. Lu, and H. Bakru, *J. Electron. Mater.* 26, 949 (1997).
9. P.K. Wu, G.R. Yang, J.F. McDonald, and T.M. Lu, *J. Electron. Mater.* 24, 53 (1995).
10. J. A. Moore and Chi-I. Lang, *Fluoropolymers 1: Synthesis*, ed. G.G. Hougham, P.E. Cassidy, K. Johns, and T. Davidson, Chap. 18 (New York: Plenum Press, 1999).
11. K.R. Williams, *J. Therm. Anal.* 49, 589 (1997).
12. B.L. Joesten, *J. Appl. Polym. Sci.* 18, 439 (1974).
13. W.R. Hertler, *J. Org. Chem.* 28, 287 (1963).
14. W.F. Gorham and J.T.C. Yeh, *J. Org. Chem.* 34, 2366 (1965).

15. W.F. Gorham, *J. Polym. Eng. Sci. Part A-1* 4, 3027 (1966).
16. W.F. Gorham, US Patent No. 3,342,754 (19 September 1967).
17. L. You, G.R. Yang, C.I. Lang, J.A. Moore, P.K. Wu, J.F. McDonald, and T.M. Lu, *J. Vac. Sci. Technol. A* 11, 3047 (1993).
18. D. Mathur, G.R. Yang, and T.M. Lu, *J. Mater. Res.* 14, 246 (1999).
19. M. Morgen, S.H. Rhee, J.H. Zhao, I. Malik, T. Ryan, H.M. Ho, M.A. Plano, and P. Ho, *Macromolecules* 32, 7555 (1999).
20. B. Hanyaloglu, A. Aydinli, M. Oye, and E.S. Aydi, *Appl. Phys. Lett.* 74, 606 (1999).
21. R. Raschke and T.E. Nowlin, *J. Appl. Polym. Sci.* 25, 1639 (1980).
22. H.W. Lo and Y.C. Tai, *J. Micromech. Microeng.* 18, 104006 (2008).
23. J.K. Fink, *High Performance Polymers*, Chap. 2 (Norwich, NY: William Andrew, 2008).
24. C.F. Kremer and A. Schönhal, *Broadband Dielectric Spectroscopy* (Berlin: Springer, 2003).
25. A.K. Jonscher, *Dielectric Relaxation in Solids* (London: Chelsea Dielectrics, 1983).
26. S. Diahm, M.L. Locatelli, and T. Lebey, *Appl. Phys. Lett.* 91, 122913 (2007).
27. J. Blackwell, S.-Y. Park, S.N. Chvalun, K.A. Mailyan, A.V. Pebalk, and I.E. Kardash, *Polym. Prep.* 39, 892 (1998).
28. S.-Y. Park, J. Blackwell, S.N. Chvalun, K.A. Mailyan, A.V. Pebalk, and I.E. Kardash, *Macromolecules* 32, 7845 (1999).
29. G.R. Strobl, *The Physics of Polymers* (Berlin: Springer, 1996).
30. T.A. Ezquerra, F.J. Baltà-Calleja, and H.G. Zachmann, *Polymer* 35, 2600 (1994).
31. A. Nogales, T.A. Ezquerra, Z. Denchev, I. Sics, F.J. Baltà Calleja, and B.S. Hsiao, *J. Chem. Phys.* 115, 3804 (2001).
32. K. Ikezaki, T. Kaneko, and T. Sakakibara, *Jpn. J. Appl. Phys.* 20, 609 (1981).