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Evidence for Molecular Orientation and Residual Charge in the Electrospinning of Poly(butylene terephthalate) Nanofibers

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Received June 15, 2006; Revised Manuscript Received December 20, 2006

ABSTRACT: Poly(butylene terephthalate) electrospun fibers were analyzed by a thermally stimulated current (TSC) technique. In the absence of an electric field, a spontaneous current was released near the glass transition, indicating a dipole relaxation process. A monotonic increase in current generated by dissipation of residual was observed with increasing temperature below the melting point. A peak in the charge dissipation current near the melting point indicates that a substantial amount of residual charge is trapped within or at the interface of the crystalline phase. Molecular orientation was also probed by birefringence analysis. Electrospun fibers showed a high level of birefringence, which extinguished upon melting.

Introduction

Poly(butylene terephthalate) (PBT), a linear polyester of aromatic nature, is a thermoplastic of excellent mechanical properties. Like PET, electrospun fibers of PBT can be used in blood vessel tissue engineering applications as scaffolds for endothelial cells.¹ In this work, PBT electrospun fibers were produced by conventional electrospinning techniques, using a solution of PBT dissolved in trifluoroacetic acid. The dependence of the resulting electrospun fiber on the experimental conditions was examined.

Electrospinning is a process that converts polymer melts or solutions into fibers with diameters in the range of about 20–500 nm. The mechanism of the spinning process involves the injection of charge into a polymer fluid. An external electric field produces a force that is greater than the surface tension of the fluid, causing the ejection and acceleration of a charged polymer fluid jet. The reduction of local charge density is achieved through the creation of surface area as the cylindrical fluid jet extends with the reduction in diameter to form a nanodiameter filament which deposits as a nonwoven mat on a planar, grounded counter electrode. As with conventional spinning techniques, the systematic variation of the extrusion and quench environments in electrospinning leads to the production of nonwoven scaffolds, differing in filament diameter and morphology.^{2,3}

Electrospun fibers were shown to present reduced crystallinity due to rapid solvent evaporation. This is a general phenomenon and has been observed for many polymer systems (see Subbiah et al.² and references therein). Zhou and co-workers⁴ showed that PLLA nanofibers electrospun from the melt were formed with low crystallinity (mostly β), but due to chain orientation a highly crystalline α phase was produced upon annealing.

There is very scarce information on residual charges related to electrospinning process. While polar polymer fibers seem to retain small amount of charges, less polar systems can hold surface charges for long periods.⁵ The temporal behavior of spontaneous charge dissipation on polystyrene and polyacry-

lonitrile electrospun webs was studied by measuring surface charge potential and revealed that very little charge is lost within the first day and decay slowly over 3 months.⁶

Experimental Section

PBT pellets (Celanex 1700A from Ticona) were freeze-ground and dried in a vacuum oven at 110 °C for 4 h. The solvents used were trifluoroacetic acid (Riedel) or hexafluoropropanol (Aldrich). All solutions were prepared by stirring PBT overnight with solvent.

The electrospinning apparatus shown in Figure 1 consisted of (i) a polymer solution delivery system, (ii) a power supply to generate an electrical field, and (iii) a fiber collector device. The delivery system was comprised of a 10 mL syringe fitted with an 18 or 20 stainless steel needle. The plunger of the delivery syringe was connected back-to-back to the plunger of a water filled dual syringe hydraulic system that could be remotely actuated using an infusion pump (Harvard Apparatus, model 975). On the basis of the distance from the needle to the grounded collection plate, a typical electrical field of 1000 V/cm was provided by a dc power supply (Gamma High Voltage Research, model ES30P). The positive lead from the power supply is connected directly to the needle of the delivery syringe. The take-up collector device was a grounded stainless steel plate positioned at a fixed distance, typically 20 cm, from the needle. The delivery syringe apparatus and ground plate were mounted inside a plastic enclosure for solvent exhaust. The infusion pump and power supply were located outside the plastic enclosure. Unless otherwise stated, the standard conditions for electrospinning experiments were as follows: PBT concentration = 4% w/w, applied voltage = 20 kV, needle to target distance = 20 cm, needle i.d. = 34 μ m, solution flow = 20 μ L/min, target is stainless steel flat plate. All electrospun mats were stored in sealed polyethylene bags. The thicknesses of all samples were between 50 and 70 μ m.

Predried PBT pellets were melt-pressed into films 50–60 μ m thick at 260 °C and thermally relaxed at 120 °C for 20 min in an oven. Alternatively, 40–50 μ m thick films were prepared by casting TFA solutions of predried PBT, the solvent evaporated in vacuum oven at RT for 1 h and at 80 °C overnight.

Conventional and modulated differential scanning calorimetry (MDSC) experiments were performed on a TA Instruments Q100 DSC. Conventional DSC analysis was performed using a heat-cool-heat program. Samples were heated at 10 °C/min from ambient temperature to 250 °C, followed by cooling at –5 °C/min to 0 °C, followed by heating at 10 °C/min to 250 °C. MDSC analysis was performed using a heating rate of 1 °C/min from 0 to 250 °C with a ± 1 °C modulation amplitude over a period of 60 s.

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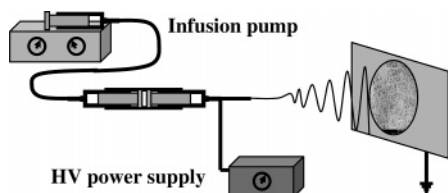


Figure 1. Electrospinning setup.

Table 1. Results from Modulated DSC^a of PBT Samples

sample	T_g (°C)	T_m (°C)	ΔH_f (J/g)
ground	47.9	230.1	84.4
electrospun ^b	47.4	224.7	56.5
melt-pressed	45.9	223.6	44.2
cast ^b	46.7	223.8	47.9

^a Conditions used: ramp 1 °C/min from 0 to 250 °C, modulate ± 1.00 °C every 60 s. ^b Samples prepared from TFA solutions.

Scanning electron microscopy was performed on a Leo-Zeiss model 1525 microscope with 1 kV as accelerating voltage and using noncoated samples. Optical microscopy was performed on an Olympus BX50 with polarizer lens attached to a Mettler Toledo FP82HT heater. Near the PBT melting point, the heating rate of the hot stage was set to 5 °C/min.

X-ray diffraction (XRD) analysis were performed on a Rigaku Miniflex diffractometer coupled with a Fe K α radiation source, with the tube set at 30 kV and 15 mA current, with Mn K β filter, and collected using $2\theta/\theta$ mode.

Thermally stimulated current (TSC) experiments were carried out using a TherMold TSC 9000 TSC/RMA. Two TSC methods were used to probe the behavior of these materials. Both methods involved the ramping of temperature from 10 to 250 °C in the absence of an externally applied field at 7 °C/min. In the first method, the electrospun mat sample was sandwiched between two pieces of Teflon film with a thickness of 0.243 mm. This method was used to probe displacement current occurring entirely within the sample specimen in the vicinity of the glass transition (T_g). In the second method, the electrospun mat sample was placed in direct contact with the TSC instrument electrodes in order to probe the conduction current that occurs across the boundary of the sample and the electrode as a consequence of the dissipation of residual charge. In all cases, TSC measurements of the electrospun mats were performed within the period of 30–45 days after preparation.

Results and Discussion

Like other aliphatic polyesters, the PBT macromolecule contains polar structures such as the carbonyl dipole and nonpolar structures such as the aliphatic butylene moiety. The flexibility of butylene segments allows this polymer to have a high rate of crystallization. From the technical literature for this material, the typical range for the glass transition, T_g , is 45–55 °C. The melting point, T_m , is around 230 °C, and the extent of crystallinity is at about 32%.⁷ Our own determination of T_g and T_m correlate quite well with the literature, as shown in Table 1. All measurements were taken from modulated differential scanning calorimetry (MDSC) experiments. T_g values were determined from the reversing C_p signal vs temperature, where C_p is the complex heat capacity, whereas T_m values were taken from heat flow signals vs temperature.

From Table 1, it is quite clear that PBT samples prepared by various methods show the same temperature for glass transition, with very subtle differences. Also, T_m seems to remain the same, with a decrease on heat of fusion for the electrospun sample. The drop in heat of fusion, and hence crystallinity, is expected in view of the rapid solidification of the fiber perhaps driven by rapid cooling due fast solvent evaporation.

These results seem to be consistent with XRD measurements on PBT materials. The pattern for the ground PBT pellets,

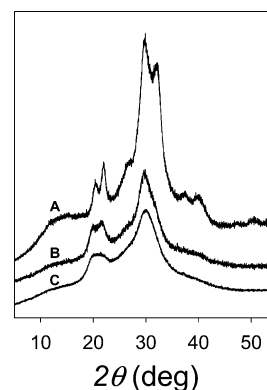


Figure 2. Diffractograms of PBT: (A) ground; (B) electrospun mat from TFA solution after 2 h annealing at 100 °C; (C) electrospun mat from TFA solution before annealing.

indicated by trace “A” in Figure 2, is similar to that previously published for this material.⁸ The diffraction pattern for the PBT mat electrospun from TFA is shown in trace “C”. After annealing the electrospun mat for 2 h at 100 °C, as indicated in trace “B”, there are only minor changes observed in the diffraction pattern. The similarity of this pattern with the ground PBT pattern provides an indication that the filaments that make up the nonwoven, electrospun mat are themselves semicrystalline.

PBT was successfully electrospun from trifluoroacetic acid or hexafluoropropanol as solvent. Figure 3 shows an example of a nonwoven mat produced.

Final fiber diameter was shown to be dependent on polymer concentration (Figure 4A), solution flow, needle diameter, electrical field (Figure 4B), distance between spinneret and take-up, solvent, etc. This behavior is typical of what is observed in other electrospinning processes.^{2,9}

We have also attempted to analyze molecular features of the electrospun fibers. PBT is known to produce two types of crystalline phases: the α phase, where the butylene group sits on a gauche–trans–gauche conformation (found on relaxed samples), and the β phase, where the butylene group presents an extended all-trans conformation (found on stressed samples).⁷ PBT electrospun fibers showed a high level of birefringence (Figure 5), which extinguished upon melting. Direct measurement of the birefringence was precluded by the small size of the fibers. This behavior has only been observed in wet-spun fibers¹⁰ as a dependence of network drawn ratios, but with no relation on the proportion of the two predominant α and β crystalline phases, suggesting that the birefringence emerges as a consequence of amorphous phase orientation.

Thermally stimulated current (TSC) was used to probe for dipole orientation and free charge mobility. As implemented in these experiments, current is measured without the application of an electric field as a function of temperature under two conditions: (i) the sample specimen was placed between two pieces of Teflon film, and (ii) the sample specimen was placed in contact with the instrument electrodes. In both these cases, the driving force for any current that is observed is the movement of charge in or on the sample to restore electrical neutrality. In the case of the specimen between Teflon film, the effect of the film is to block any conduction of current from the sample to the electrode, with the consequence that any observed current must arise from neutralization processes within the specimen. With the specimen in contact with the instrument electrodes, observed current can arise from conduction through the specimen.

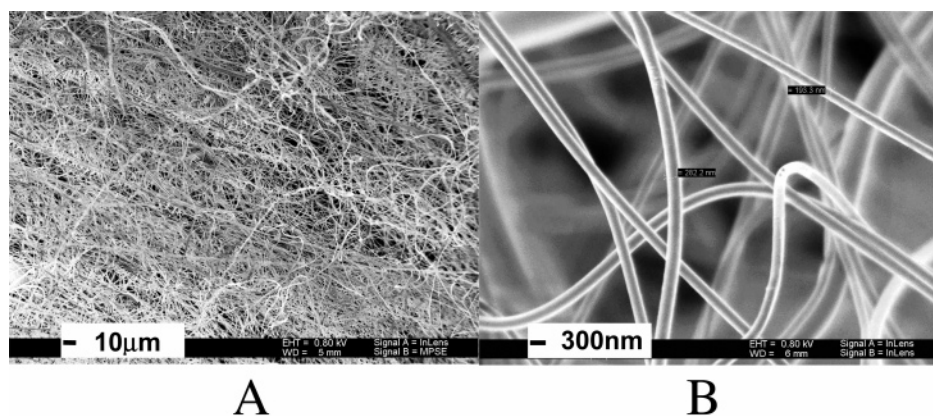


Figure 3. SEM pictures of PBT fibers electrospun from TFA solution: (A) magnification = $\times 1000$; (B) magnification = $\times 40\,000$.

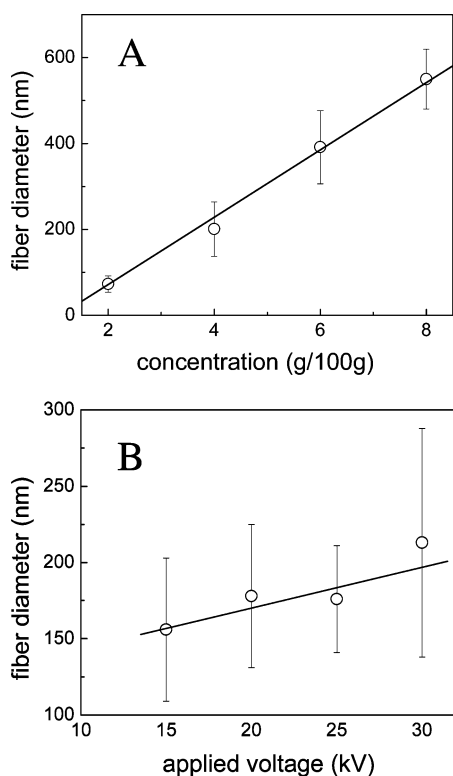


Figure 4. Fiber diameter dependence on concentration of PBT in TFA solution (A) and on the applied voltage (B), using standard conditions unless parameter is varied (see Experimental Section).

In Figure 6, the results are shown for current generated when PBT samples held between two pieces of Teflon film are heated using a linear temperature program in the region of the T_g . For the electrospun mat, a spontaneous current was released near the glass transition which was not observed in control melt-pressed and cast film specimens. Teflon film blocks the conduction of any charge from the sample to the electrodes. The current that is observed must be the result of the relaxation of charges that were displaced within the specimen during the electrospinning process. When a dielectric material is placed between two electrodes with a voltage applied between them, the effect of the field is to displace charged structures by dipole orientation and/or free charge separation. This process is often called polarization. By heating a material polarized in such a manner, a displacement current can be observed when a temperature is reached where the charges become mobile. In polymeric materials, dipoles can relax and free charges can diffuse at the glass transition and, under these conditions, a displacement current can be observed. The results in Figure 6

suggest that there is a polarization process occurring in the electrospun mat during electrospinning.

Orientation of dipoles and/or the separation of free charges have a directionality imposed on it by the orientation of the external field present during the polarization process. In order to examine whether the current is the consequence of charges displaced by an electric field, the orientation of the electrospun mat between the TSC instrument electrodes was flipped. By flipping the orientation of the mat, current arising from charges that have been displaced by the same electric field should have an opposite sign. Figure 7 shows time-dependent decay of this displacement current when the temperature was ramped from 20 to 55 °C and held constant at 55 °C. The TSC signal of this relaxation current is indeed dependent on the orientation of the mat between the TSC electrode pair. By flipping the faces of the samples, a current of opposite sign is observed. This behavior is consistent with the electrospun PBT mat being polarized relative to the ground plate take-up on which it is collected.

Two modes of polarization in these electrospun mat specimens must be considered. First of all, in molecular structures containing dipoles, under the influence of fields experienced during the electrospinning process, it is possible for dipoles to preferentially orient with respect to those fields. Second, mobile free charges or space charges can be displaced, resulting in charge separation under the influence of these fields. On subsequent heating, as is performed in the TSC experiments, charge neutralization current can be observed from both disorientation of the dipoles and migration of space charge. The current resulting from the disorientation of the dipoles should occur very near the T_g where segmental motion is possible. Space charge also becomes mobile when segmental motion is possible. However, current resulting from space charge neutralization requires the motion of charges over several atomic distances. The consequence of the higher activation energy resulting from the longer distances is that the space charge neutralization peak should be observed at a higher temperature than the dipole disorientation peak at T_g . If both processes are operative, two current peaks should be observed: the peak due to dipole disorientation at T_g and a space charge neutralization peak just above T_g .¹¹ The fact that only a single peak is observed near the T_g in Figure 6 suggests that the current arises from the dipole disorientation. This would mean that dipoles were oriented during the electrospinning process.

By removing the electrospun mat sample from the Teflon sandwich and placing the specimen in direct contact with the TSC instrument electrodes, charge is allowed to conduct directly from the sample to the electrode. Using this technique, any residual charge can flow from the electrospun mat to the

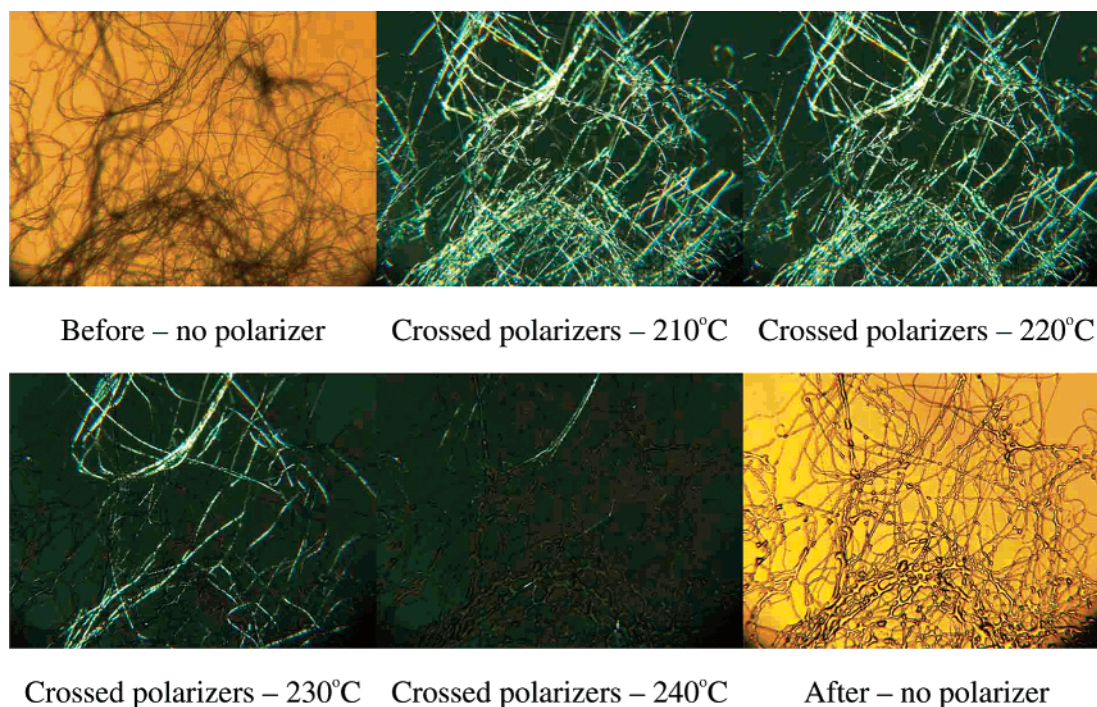


Figure 5. Birefringence observed in PBT electrospun mats from TFA solutions using polarization microscopy.

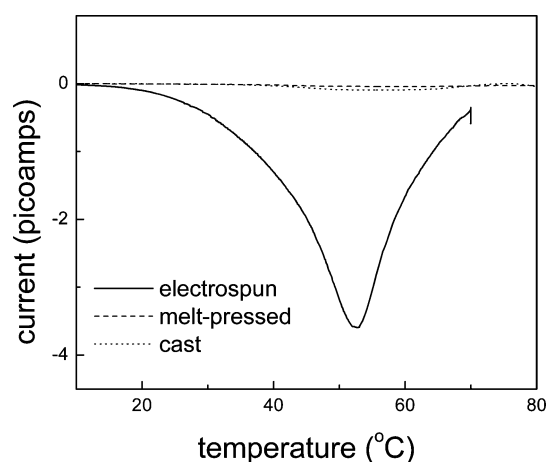


Figure 6. Thermally stimulated relaxation current spectra of PBT near glass transition.

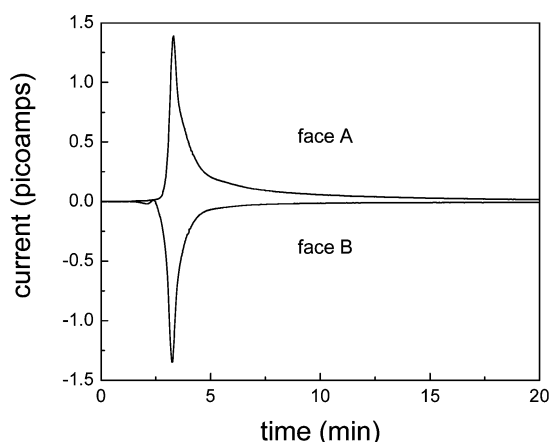


Figure 7. Thermally stimulated relaxation current kinetics of PBT upon heating at 55 °C.

electrode and be detected as a current as a function of temperature in the TSC instrument. Figure 8 shows the results for experiments conducted in this manner on electrospun mat,

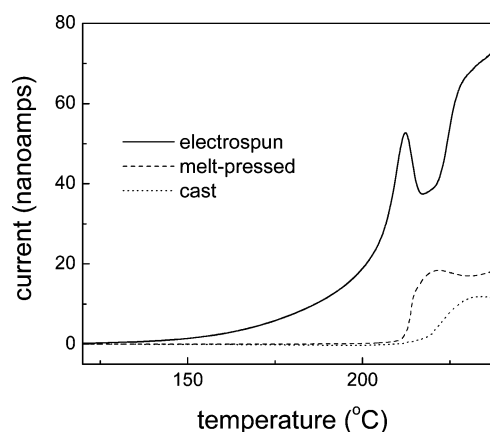


Figure 8. Thermally stimulated relaxation spectra of PBT near melting.

melt-pressed film, and solvent-cast film of PBT over a temperature range of about 125–240 °C. The melt-pressed and solvent-cast films show almost no current until the region of melting is approached, and a small current peak is observed. In contrast, the electrospun mat shows a substantial monotonic increase in current with temperature from 125 °C to the melting point, with a sharp peak at the melting point.

The magnitude of the current observed for the electrospun mat using this technique is up to 40 000 times higher than that previously observed for the displacement current at the glass transition. It should also be noted that this higher temperature current cannot be observed when the specimen is between the two pieces of Teflon film. In addition, there is no directionality to this current. Flipping the specimen with respect to the electrodes does not change the direction of the current. This is consistent with a conduction current resulting from the dissipation of excess charge that resides in or on the sample specimen.

The difference in behavior between the electrospun mat and the other films suggests that there is a much higher level of residual charge on the electrospun mat than is observed for melt-pressed or solvent-cast film. The only source of that increased level of charge can be the electrospinning process itself. A

simple rationalization of this high residual charge level is to consider the fate of the charges that are initially injected into the polymer solution. Those charges likely reside on the surface of the filaments that make up the mat. The nonwoven structure of the mat does not allow most of the filaments to be in contact with the ground plate take-up and precludes the dissipation of these injected charges. Owing to the dielectric character of the material, these charges will remain in place. As the temperature is increased in the TSC experiments, the charges can become mobile and find conduction paths to the electrode where they are observed as charge dissipation current. The monotonic increase in current with temperature that is observed is consistent with an increase in this surface charge mobility with temperature.

The peak in current that is observed near the melting point requires some specific consideration. It is well-established that excess charge can accumulate at domain boundaries such as the interface between two phases. For semicrystalline polymers, charges can be trapped at crystalline/amorphous interface and in defects within the crystalline phase.^{12,13} Melting of the crystalline phase will release these trapped charges. The peak in current observed near the melting point for PBT in Figure 8 is consistent with this behavior. A small release in static charge is observed near the melting point for both melt-pressed and solvent-cast film; however, the large peak observed for the electrospun mat reflects a high level of residual charge trapped in or near the crystalline phase as a result of charge injection during the electrospinning process.

Although not shown here, the monotonic increase in current from dissipation of surface charge and the release of trapped charge on melting were quite general phenomena observed in our laboratory for other polymeric systems. This suggests that residual surface charge and excess trapped charge are general factors to be considered in electrospinning systems. The total charge dissipated by the sample will likely depend on two general factors. First of all, those details of the electrospinning experimental conditions that control charge injection will determine how much charge gets injected into the initial dilute polymer solution. These factors can include the electrical properties of the polymer and solvent, the applied voltage, the conducting material used to accomplish charge injection, etc. Second, the prevailing conditions during the electrospinning process that control charge dissipation and/or detachment. While the total charge released by the sample seems to be inherently dependent on thickness and polymer polarity, we believe that the sample storage method used is the most important parameter that regulates the lifetime of residual charges, since ambient humidity and temperature are believed to regulate charge detachment.¹⁴ The practice of storing the samples in sealed polyethylene bags has prevented unwanted instability within the time span between sample preparation and measurement.

Conclusions

Electrospun fibers present unexpected molecular and crystalline orientation. This orientation may to be a result of

electrostatic forces which operate during the forming of the nonwoven fiber structure. Relative to the ground plate take-up, the electrospun mat is polarized. This fact unambiguously demonstrates that electrostatic forces during electrospinning can influence the development of the solid polymer microstructure.

The monotonic increase in current as a result of charge dissipation with increasing temperature below the melting point suggests that residual charge from the charge injection step during electrospinning remains distributed on the high specific surface area of the formed mats generated by the electrospinning process. This charge is immobilized on the surface of the inner fibers that are not in direct contact with the ground plate take-up.

A peak in the measurement of current vs temperature near the melting point of the PBT suggests that residual charge is also trapped at the crystal/amorphous interface and at crystalline imperfections. These charges are also taken to originate in the charge injection step of the electrospinning process.

The presence of these residual charges may represent a problem for some electrospinning applications. However, for some tissue engineering applications, the presence of these charges could be of some benefit in the growth of dipolar cells. Nerve cells, for instance, is known to present a dipolar structure.¹⁵ Spinal implants, typically made of biodegradable polyesters, depend on the ingrowths of such cells through porous materials.¹⁶

Acknowledgment. L.H.C. was supported by CAPES, CNPq, and FAPESP (Brazil).

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MA061342D