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Fast space charge behavior in heat-treated polypropylene films

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ABSTRACT: In this study, the characterization of the short-circuit current within hundreds of nanoseconds is proposed to study the effect of heat treatment on fast space charge behavior in the polarized biaxially oriented polypropylene (BOPP) films. The BOPP films were cooled either quickly or slowly during the sample preparation. The damped oscillating feature was found in the short-circuit current of all the polarized film samples, but the periods of the oscillating current for the samples prepared by fast cooling rate decrease faster. Bipolar space charge injection in the polarized BOPP films was observed by the thermal pulse (TP) measurement. The variation feature of the short-circuit current was considered to be associated with the varying fast space charge behavior, which depended on the varying structural traps modified by the heat treatment during the sample preparation. The sample subjected to fast cooling process was with relatively shallow trap level revealed by the thermally stimulated current method, which led to higher mobility of the escaping charge in the sample. The TP measurements were utilized to analyze space charge features in the polarized BOPP films. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42235.

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INTRODUCTION

Space charge is widely considered to be closely associated with materials aging and breakdown in polymer dielectrics.[1–4] Many works report space charge behavior in neat polymer or polymer/filler composites thin film or sheet samples with thickness from about 100 μm to 2 mm under AC or DC field.[5,6] Both the sample preparing procedures by the control of the cooling rate and the filler, micro or nano particles, would change the micromorphology of the polymer dielectrics.[7,8] High applied electric field can also induce the variation of the polymer microstructure.[9] The microstructure in the polymer dielectrics is found to be of great influence on the space charge transport in these materials. Electrons move in the low-density intermolecular regions while holes shift via tunneling between the molecular chains.[9] Considering micromorphology-related charge trap density and trap level, the microstructure would inevitably influence the accumulation and migration of space charge.[10] The polymer films used as the capacitor dielectrics may be subjected to high applied field to meet the downsizing requirement for the equipment in modern electronics and electric power system, which would lead to space charge injection and accumulation.[11–13] On the other hand, part of the injected charge may be released accompanying with the release of free charge at the electrodes during the discharge procedure of capacitors. The duration of the discharge is often <1 ms, especially on the occasion of the capacitor used as impulse power source.[14,15] The frequently rapid release of space charge during the capacitor discharge can bring about the frequent damage to the polymer matrix,[16] which would finally shorten the life of the capacitor.[11] The variation of the micromorphology should have significant impact on the fast space charge behavior. However, the observation of space charge dynamics is often performed by pressure wave propagation (PWP) method,[17] pulsed electro-acoustic method,[18] or thermal pulse (TP) method.[19,20] The minimum measuring interval of the mentioned methods is normally more than 1 ms.[21–23] These methods for measuring space charge are evidently not suitable to monitor the fast space charge behavior. It may be the reason that the rapid space charge behavior in thin polymer films is seldom reported.

The transient discharge current method proposed in our previous work has been demonstrated to be an effective tool for semi-quantitatively analyzing fast space charge phenomenon, which is based on the measurement of the transient short-circuit current of the polarized thin polymer films.[24] The transient short-circuit current was typically with the damped oscillating feature. The applied-field-dependent period of the oscillating current was demonstrated to be related to space charge. The accumulation and migration of space charge in the sample bulk would change the film's equivalent capacitance and, therefore, the period of the damped oscillating current cycles. Analysis of the transient damped oscillating short-circuit current can be greatly helpful to understand the fast space charge behavior. However, there are some difficulties to obtain space charge distribution by the transient discharge current method. Despite of the relatively slow measuring procedure, the TP method has good spatial resolution of space charge distribution for thin polymer films. Therefore, it is thought to be a good way to take the advantages of both these methods to characterize the influence of the micromorphology on fast space charge behavior in thin polypropylene films. The thermally stimulated current (TSC) method was also utilized to study the features of the sample charge traps, which eventually influenced the fast space charge behavior in this investigation.

EXPERIMENTAL

Biaxially oriented polypropylene (BOPP) films with thickness 9.8 μm and melting point 169°C were obtained from Bollore plastic films division company. In order to change the degree of crystallinity of the BOPP films, all of the samples with the size 5×5 cm^2 were first heated at 135°C for 10 min. The temperature 135°C is about 25°C higher than the viscous flow temperature of the BOPP used in this investigation. Considering different cooling rates can lead to different degrees of crystallinity during the polymer samples preparation; therefore, half of the samples were subsequently sandwiched by two warm slabs at 60°C to be slowly cooled down and the other half were sharply cooled down by pouring liquid nitrogen directly onto one of the film surfaces. Their corresponding crystallinities are 50.4 and 41.2% measured by the X-ray diffraction (XRD) method. All of the samples subjected to the heat treatment were coated with 150-nm-thick aluminum as the electrodes with diameter 25 mm. In order to reduce the thermal effect by the heated aluminum evaporating source, as far as possible, on the thin sample morphology during the coating process, a reduced low evaporating rate 1.5 nm/s was adopted by HHV Auto 306. Subsequently, the films were subjected to various negative DC high-voltage stress from 1 to 5 kV for 1 min.

Immediately after the high electric field stress, the samples were directly short-circuited by a minimized short circuit to reduce the unexpected interference. The closed short circuit with the polarized film was thought to be equivalent to an RLC series circuit where damped oscillating current is the typical feature. The original capacitance of the BOPP films is about 1 nF. The typical parameter's values of resistance R and self-inductance L in the closed short circuit were about 0.5 ohm and 50 nH, which should be constants for the given short circuit. The short-circuiting current was measured by the pulse current probe (Tektronix P6022) based on the electromagnetic coupling principle. More details about the experiment can be found in Ref. [24. The space charge distributions in the films were detected by the TP method. After the measurements of the short-circuit current, the charge trap features of the heat-treated BOPP films were analyzed by the short-circuit TSC method. The polarized samples were then heated from room temperature to about 170°C. The temperature increasing rate was about 3°C/min.

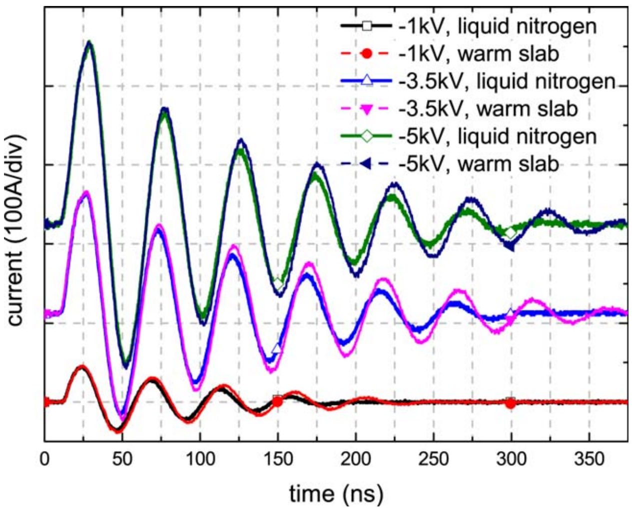

Figure 1. The curves are the oscillating discharge current immediately after the BOPP samples being polarized under various applied fields. The changing duration of the oscillating periods shows the distinct characteristics of applied field intensity and heat treatment dependence. For clear show, the offsets are used for negative 3.5 and 5 kV cases. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Formation of Damped Oscillating Current

For the ideal RLC series circuit, the quasi-period of the discharge oscillating current is a constant and independent of the applied field on the capacitor. For the polarized BOPP films, the quasi-period of the damped oscillating current is partly applied field dependent as shown in Figure 1. Longer duration of the initial oscillating period can be found in the discharge current of the films polarized under high electric field. The feature of changing duration of the oscillating periods is thought to be due to the changing capacitance of the film samples, since the other two parameters R and L are constants for the given circuit. The film capacitance can be expressed as $C=\varepsilon_0\varepsilon_r S/d$. There are two possible main reasons for the initial change of the film capacitance under applied field.

One is the deformation of the film sample under the pressure of the applied electrostatic field force. However, due to high Young's modulus 2 GPa of the polypropylene film, the strain of the film under an applied field 400 MV/m is as low as 0.0016, which can be neglected in contrast to the large change of the film capacitance during the discharge. The highest variation of the capacitance can be more than 50%.[24] In addition, visible damage to the deposited electrodes during the fast discharge tests was not observed, which meant that the area of the deposited electrodes did not change.

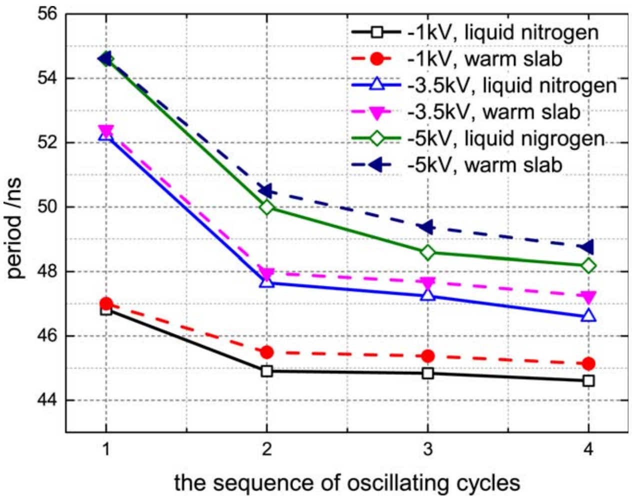

Figure 2. The decaying periods during the sequent cycles of oscillating current in the polarized BOPP films with the different heat histories. The curves are obtained from the data shown in Figure 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The other reason is attributed to space charge polarization, which could nominally modify the relative dielectric coefficient of the polarized film. Space charge injection and migration would therefore lead to the varying capacitance of the film, which has been demonstrated by the stepwise heat treatment experiments.[24] Charges at the electrodes are induced by the injected space charge and then the modification of the sample capacitance Q/V is decided by the density distribution of the injected space charge density. The migration of space charge could induce the change of the equivalent capacitance of the sample. The quasi period T of the damped oscillating current would therefore show the corresponding change, considering the relation

$$T = 2\pi / \sqrt{(1/LC) - (R/2L)^2}. \tag{1}$$

Because space charge injecting rate is applied field dependent, higher field results in more charge injection and consequently may cause longer initial oscillating quasi-period. Bipolar space charge injection and accumulation were observed in this kind of BOPP films under high DC stress.[20] During the film samples being short-circuited, the bipolar space charge accumulating in the sample bulk would shift toward the adjacent electrodes under the electrostatic force and then be recombined at the electrodes, which would therefore reduce the equivalent capacitance of the polarized BOPP films. This is thought to be the reason that the duration of the quasi-periods gradually decrease in the subsequent cycles, which is more distinct in the case of higher applied field as shown in Figure 2. Suppose that all of the samples subjected to the same heat treatment history have the same charge trap levels, according to the isothermal discharge current theory, the initially more space charge injection in the sample bulk polarized under higher applied field may result in faster space charge decaying rate in the measuring duration. It is believed to be the reason that one observes the faster decaying rate of the duration of the quasi-periods in the case of higher applied field. However, in spite of the faster decaying rate in the case of higher applied field, the duration of the last period of the observable oscillating current waveform is longer than that in the case of lower applied field. The results indicate that there was more residual space charge at the end of the discharge tests for the film samples previously subjected to higher applied fields. The results also indicate that only part of the injected space charge was released during the samples being short-circuited. This deduction would be demonstrated by the TP measurement for space charge distribution in the following part.

Influence of the Microstructure on Fast Discharge Current

As discussed above, it is the initial space charge accumulation that decides the initial change of the film capacitance, which can modify the duration of the oscillating current cycles. The subsequent change of the duration of the oscillating periods can therefore be expected during the release of the injected space charge. For the semicrystalline polymer such as polyethylene, due to the negative affinity, the injected charges mainly transport in the amorphous region. This means that the charges in the samples with more amorphous phase can be with higher mobility.[9] This theory has been demonstrated by some experiments. For example, Diego reported that the recrystallization by the annealing treatment would make the cross-link polyethylene (XLPE) to approach perfect crystal and possible larger dimensions that result in a reduction of conductivity.[25] Polypropylene is also a kind of semicrystalline material, where the crystallization course greatly decides the samples crystallinity. In this study, considering about 110°C viscous flow temperature of the BOPP films, the BOPP films were therefore first subjected to 135°C and then cooled down fast or slowly to control the recrystallization process. It should be noted that the heat treatment temperature, 135°C, is not high enough to completely melt the original crystal spherulite in the BOPP samples with the melting point 169°C. However, the boundaries between crystal spherulites, some secondary crystals, or imperfect crystals could melt at 135°C and then these kinds of regions would change into amorphous phase when being subjected to quenching process. This is thought to be the reason that the samples subjected to fast cooling process have lower crystallinity as the results measured by XRD, which means that there are more amorphous regions, which are the preferring transporting paths of the injected charge as discussed above. Consequently, faster decaying rate of the injected space charge in the samples subjected to fast cooling process can be expected. From Figure 1, we can find that the changing features of the damped oscillating current are influenced not only by applied electric field intensity but also by the heat treatment history. For the three cases of the various applied voltages 1, 3.5, and 5 kV, there are common characteristics for the two kinds of samples with different heat treatment histories. The duration of the oscillating current initial period for the film samples heat-treated by fast cooling rate and by the slow cooling rate is almost the same, and then the duration of the subsequent periods for the samples heat treated by fast cooling rate decrease faster than that for the samples heat treated by slow cooling rate in the case of the same applied field intensity (Figure 2). As discussed above, for the given film

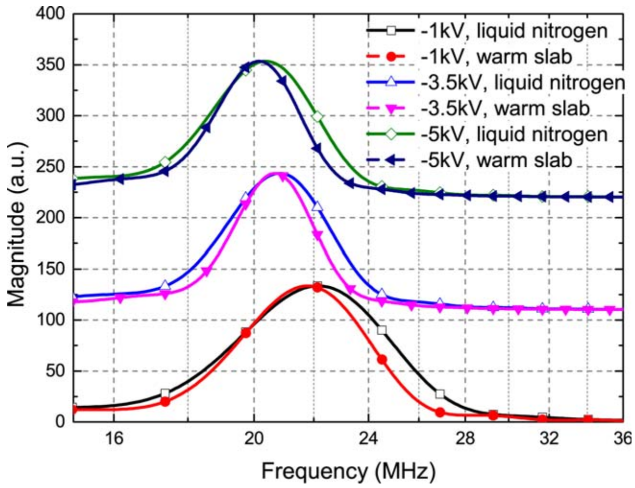

Figure 3. The frequency spectrum characteristics of the discharge oscillating current for the BOPP samples cooled by liquid nitrogen and warm slab after being subjected to various voltage from 1 to 5 kV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

samples, the duration of the oscillating current initial period is determined by the sample's initial equivalent capacitance, which depends on the initial space charge accumulation. From the data in Figures 1 and 2, one could therefore envisage the similar initial space charge accumulation for the two kinds of film samples in spite of their being subjected to the different heat treatment histories. The following change in the subsequent oscillating periods depends on the releasing process of the injected space charge. Faster release of the space charge results in faster decay of the equivalent capacitance and therefore faster decrease of the period, which is corresponding to the case of the film samples cooled by liquid nitrogen. The abovementioned variation is similar for all the three applied field cases. The fast migrating phenomenon of space charge in dielectrics was also reported in several literatures.[16,26,27] The fast migration of space charge layer caused tree-like breakdown within 100 ns.[27] It is clear that the samples' microstructure, which can be changed during the heat treatment process, has great impact on the migration of space charge. Space charge in the samples with more amorphous component may show more movability. It should be the cause that space charge decayed faster in the sample subjected to fast cooling rate during the sample preparation. Actually, the migration of space charge in the dielectrics is trap-modulated. In the semicrystalline polymer, the interfaces between amorphous region and crystalline region are often thought to act as physical traps. The samples with different crystallinity would have different features of the physical traps. The characterizations of the charge decay in the heat-treated BOPP samples should be related to physical traps in nature.

In order to further analyze the features of the changing periods, all of the data in Figure 1 are transformed from time domain to frequency domain by Fast Fourier transform. As shown in Figure 3, the central peak frequency decreases from 22 to 20.2 MHz with the increasing applied field, which can be attributed to the increase of the mean durations of the oscillating periods with the increasing applied field. It is noteworthy that the frequency is not intrinsic and partially depends on the shape and area of the used circuit loop. The short-circuit loop always kept the same during the study. It is believed that the applied-field-dependent initial space charge accumulation and the trap-level-dependent space charge attenuation rate should be the decisive factors of this phenomenon. The initial space charge accumulation determines the initial duration of the period as discussed above, and the trap-level-dependent space charge attenuation rate determines the changing rate of the periods with the initial space charge density being taken into account. Comparing the curves' features of the two kinds of film samples previously subjected to the same applied field intensity, one finds that the samples cooled with liquid nitrogen have a wider range of frequency components than samples cooled by warm slab in the three applied field cases. The lower frequency part is almost overlapped, which can be attributed to the similar initial charge accumulation. For the samples cooled by liquid nitrogen, more components in higher frequency part indicate the more reduction of the equivalent capacitance of the polarized sample during the discharge procedure of the film capacitor. Considering space charge accumulation-related equivalent capacitance, it can be deduced that more charge is released from the samples cooled by liquid nitrogen during the procedure of oscillating discharge. This phenomenon indicates that space charge in the samples heat treated by fast cooling rate has relatively high mobility. A similar phenomenon that the different heat treatment leads to the similar initial space charge accumulation and subsequently distinctly different charge dynamics behavior was also found in the sheet polyethylene (PE) samples, which was monitored by the PWP method.[10]

There is a bipolar charge accumulation between the two electrodes in the two kinds of BOPP film samples after the performance of being short-circuited measured by TP method and less residual space charges adjacent to the electrodes are found in the sample cooled by liquid nitrogen as shown in Figure 4. The

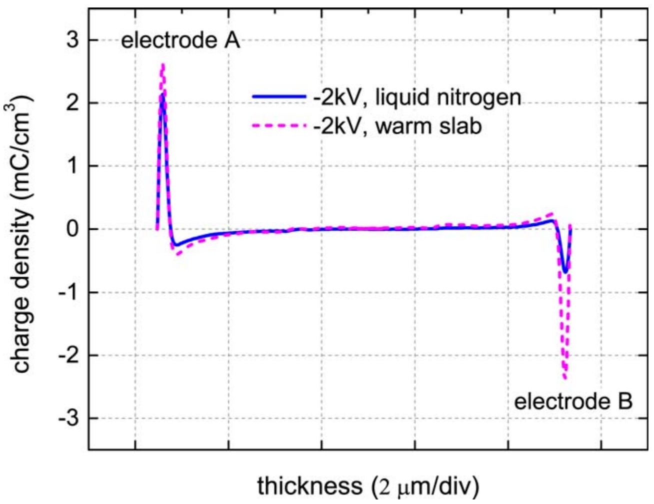

Figure 4. The residual space charge distribution in the polarized BOPP films after being short-circuited was measured by thermal pulse method. The samples heat treated by different cooling rates were previously subjected to negative DC 2 kV for 1 min before being short-circuited. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

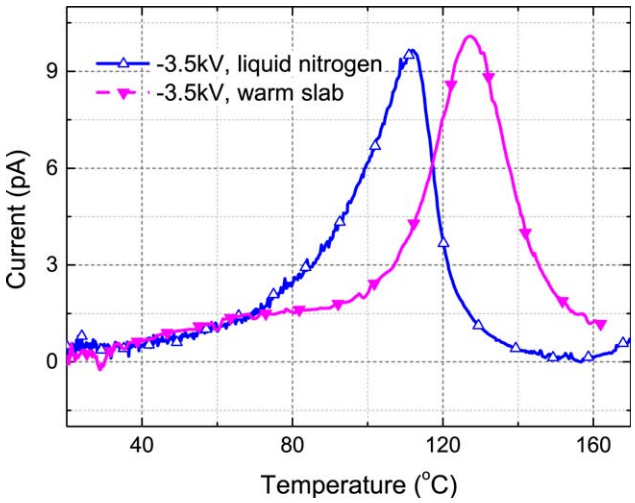

Figure 5. The influence of the heat treatment on TSC results of the BOPP samples being polarized under negative DC 3.5 kV for 1 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

way to sharply cool the heated samples by pouring liquid nitrogen onto one of the film surfaces (electrode B) could make sharply reduce the surface temperature of the sample upside. The quenching process may cause the surface crystallization, which can be the reason that far-less residual space charge is found near the electrode B than that near the electrode A for the sample cooled by liquid nitrogen. Space charge near the electrode by fast cooled down shows higher mobility. The charge density measured by the TP method is in agreement with the residual space charge density in the short-circuited samples based on the deduction by analyzing the transient discharge current. Since there are the similar initial space charge density and the different final residual charge density in the two kinds of samples previously being subjected to completely different heat treatments, it is considered that the injected space charge in the two kinds of samples should have different mobilities. Higher mobility would lead to faster decay of the accumulating space charge. Because the space charge mobility is trap-level-dependent as the following expression:[28]

$$\mu=\mu_0\frac{N}{M}\exp(-U/kT) \tag{2}$$

where μ_0 is the mobility ratio of free carriers that is a constant less sensitive to temperature; N, M, U , and k are the degeneracy (number of vacancies) of the conduction level, the number of traps, the level of traps, and the Boltzmann constant, respectively. According to eq. (2), lower trap level is corresponding to higher charge mobility. Figure 5 shows the short-circuit thermally stimulated current results of the polarized BOPP samples being subjected to fast and slow cooling preparation procedures. The temperature at the peak current at the TSC test means that the process of charge detrapping or depolarization mainly occurs at the temperature, which indicates the charge stability in the charge trap. The charge trap level can be calculated based on the theory for thermally stimulated current. The BOPP film heat treated by faster cooling rate is with lower temperature at the peak current, which indicates the shallower trap level. Therefore, the higher mobility of the injected space charge can be expected for the samples cooled by liquid nitrogen. This is also in accordance with the above deduction based on the analysis of the oscillating current. Based on the above discussion, the effect of the heat treatment on the fast space charge behavior in BOPP films can be qualitatively distinguished by the transient discharge current method. Quantifying the fast space charge properties in the dielectric films by analyzing the transient short-circuit current need further research work.

CONCLUSIONS

Controlling the cooling rate during the sample preparation can change the crystallinity of the BOPP films, which shows great influence on the fast space charge behavior. The changing duration of the periods in the damped oscillating short-circuit current of the polarized BOPP films is attributed to the fast migration of the injected space charge. The space charge in the sample with the lower crystallinity has greater mobility, which leads to the faster decreasing duration of the periods in the damped oscillating short-circuit current. The measuring results of the charge traps by the thermally stimulated current method verify the short-circuit current-based deduction about the influence of the morphology on the space charge mobility in the BOPP films. The damped oscillating current method is successfully utilized to qualitatively compare fast space charge phenomenon in the given material.

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REFERENCES

1. Montanari, G. C. *IEEE Trans. Dielectr. Electr. Insul.* **2011**, *18*, 339.
2. Dissado, L. A.; Mazzanti, G.; Montanari, G. C. *IEEE Trans. Dielectr. Electr. Insul.* **1997**, *4*, 496.
3. Mazzanti, G.; Montanari, G. C.; Dissado, L. A. *IEEE Trans. Dielectr. Electr. Insul.* **2005**, *12*, 876.
4. Zhang, Y. W.; Lewiner, J.; Alquie, C.; Hampton, N. *IEEE Trans. Dielectr. Electr. Insul.* **1996**, *3*, 778.
5. Tanaka, T.; Imai, T. *IEEE Electr. Insul. M* **2013**, *29*, 10.
6. Chen, G.; Fu, M.; Liu, X. Z.; Zhong, L. S. *J. Appl. Phys.* **2005**, *97*, 083713.
7. Tanaka, Y.; Chen, G.; Zhao, Y.; Davies, A. E.; Vaughan, A. S.; Takada, T. *IEEE Trans. Dielectr. Electr. Insul.* **2003**, *10*, 148.
8. Zheng, F. H.; Hao, S. J.; Wang, W. Y.; Xiao, C.; An, Z. L.; Zhang, Y. W. *J. Appl. Polym. Sci.* **2009**, *112*, 3103.
9. Jones, J. P.; Llewellyn, J. P.; Lewis, T. J. *IEEE Trans. Dielectr. Electr. Insul.* **2005**, *12*, 951.

10. Zheng, F. H.; Zhao, H.; Xia, J. F.; Zhang, Y. W. In Proceedings of the 2010 IEEE International Conference on Solid Dielectrics, Potsdam, Germany, **2010**; p 375.
11. Reed, C. W.; Cichanowski, S. W. *IEEE Trans. Dielectr. Electr. Insul.* **1994**, *1*, 904.
12. Dissado, L. A.; Montanari, G. C.; Fabiani, D. *J. Appl. Phys.* **2011**, *109*, 064104.
13. Chen, Q.; Wang, Y.; Zhou, X.; Zhang, Q. M.; Zhang, S. *Appl. Phys. Lett.* **2008**, *92*, 142909.
14. Barshaw, E. J.; White, J.; Chait, M. J.; Cornette, J. B.; Bustamante, J.; Folli, F.; Biltchick, D.; Borelli, G.; Picci, G.; Rabuffi, M. *IEEE T. Magn.* **2007**, *43*, 223.
15. Picci, G.; Rabuffi, M. *IEEE Trans. Plasma Sci.* **2000**, *28*, 1603.
16. Blaise, G. *J. Appl. Phys.* **1995**, *77*, 2916.
17. Laurenceau, P.; Dreyfus, G.; Lewiner, J. *Phys. Rev. Lett.* **1977**, *38*, 46.
18. Maeno, T.; Futami, T.; Kushibe, H.; Takada, T.; Cooke, C. M. *IEEE Trans. Electr. Insul.* **1988**, *23*, 433.
19. Collins, R. E. *J. Appl. Phys.* **1980**, *51*, 2973.
20. Zheng, F. H.; Liu, C. D.; Lin, C.; An, Z. L.; Lei, Q. Q.; Zhang, Y. W. *Meas. Sci. Technol.* **2013**, *24*, 065603.
21. Takada, T.; Tanaka, Y.; Adachi, N.; Qin, X. K. *IEEE Trans. Dielectr. Electr. Insul.* **1998**, *5*, 944.
22. Fukuma, M.; Teyssedre, G.; Laurent, C.; Fukunaga, K. *J. Appl. Phys.* **2005**, *98*, 093528.
23. Mellinger, A.; Singh, R.; Gerhard-Multhaupt, R. *Rev. Sci. Instrum.* **2005**, *76*, 1.
24. Zheng, F. H.; Lin, C.; Liu, C. D.; An, Z. L.; Lei, Q. Q.; Zhang, Y. W. *Appl. Phys. Lett.* **2012**, *101*, 172904.
25. Diego, J. A.; Belana, J.; Orrit, J.; Sellares, J.; Mudarra, M.; Canadas, J. C. *J. Phys. D Appl. Phys.* **2006**, *39*, 1932.
26. Fabiani, D.; Montanari, G. C.; Siracusano, E.; Dissado, L. A. IEEE. In CEIDP: 2009 Annual Report Conference on Electrical Insulation and Dielectric Phenomena, Virginia Beach, USA, **2009**; p 31.
27. Noskov, M. D.; Malinovski, A. S.; Cooke, C. M.; Wright, K. A.; Schwab, A. J. *J. Appl. Phys.* **2002** *92*, 4926.
28. Spears, W. E. *J. Non-cryst. Solids* **1969** *1*, 197.