Macromolecules **2008,** *41,* 493−496

Poly(ionic liquid)s as Optically Transparent Microwave-Absorbing Materials

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Received August 6, 2007
Revised Manuscript Received November 8, 2007

Introduction

Microwave-absorbing materials are applicable to reducing electromagnetic interference from personal computers, stealth-aircraft technology, microwave cookware, and microwave darkroom protection.[1−5] Microwave absorption is usually achieved by combining dielectric and magnetic loss. Most microwave-absorbing materials are polymer composites with conductive fillers, such as graphite, carbon black, and metals, or magnetic fillers, such as ferrites and carbonyl iron powders. These fillers make the microwave-absorbing materials black and hard to fabricate, for example, into precise parts or thin films.[6,7] Conductive polymers such as polyaniline, polypyrrole, poly-alkylthiophenes, and poly(4,4′-diphenylene diphenylvinylene) were also reported as microwave-absorbing materials.[8−12] However, all these polymers are not optically transparent, which poses a problem for many applications. For example, the microwave darkroom windows and microwave cookware require the microwave-absorbing material to be transparent. In addition, many microelectronic applications call for easy fabrication into precise pieces.

Recently, poly(ionic liquid)s, the polymers made from ionic liquid monomers, have received much research interests for their potential applications such as gas separation materials,[13−16] catalytic membranes,[17] polymer electrolytes,[18−22] and ionic conductive materials.[23−33] Poly(ionic liquid)s contain anion−cation pairs and therefore have a relatively high density of strong dipoles, which makes them promising candidates for microwave absorption. Furthermore, these materials are optically transparent. Their physical properties can be tuned to specific design criteria by adjusting their chemical structure including the cation, anion, or their combination. Therefore, the goal of this work is to characterize the microwave absorption properties of several model poly(ionic liquid)s containing either imidazolium or ammonium cations.

Results and Discussion

The structures of poly(ionic liquid)s studied in this work are shown in Figure 1. Except for P[VBBI][$FeCl_4$], they are synthesized from ionic liquid monomers and characterized by ^{1}H NMR and elemental analysis as previously reported.[13,14] P[VBBI][$FeCl_4$] is prepared from P[VBBI][Cl] by a macromolecular reaction with $FeCl_3$ as follows: P[VBBI][Cl] (1.5 g) is dissolved in 6 mL of methanol, and then 0.453 g of $FeCl_3$ in 1 mL of methanol is added to this solution. Yellow polymer precipitates out. The polymer is isolated, washed with methanol, and dried under vacuum. Elemental analysis (C, N, H) is conducted by Midwest Microlab, LLC, Indianapolis, IN. The Fe content is measured by inductively coupled plasma mass spectrometry (ICPMS). The analysis shows that the polymer anions still contain 17% chloride. The incomplete replacement of Cl^- with $FeCl_4^-$ is due to the rapid precipitation of the polymer after adding $FeCl_3$. Anal. Calcd for $(C_{16}H_{21}N_2)(FeCl_4)_{0.83}(Cl)_{0.17}$: C, 46.60%; H, 5.10%; N, 6.80%; Fe, 11.28%. Found: C, 46.57%; H, 5.09%; N, 6.77%; Fe, 11.30%.

The poly(ionic liquid)s are soluble in DMF. Their number-average molecular weights (M_n) and polydispersity (PDI) measured by gel permeation chromatography (GPC) with a laser light scattering detector (Precision Detectors Inc.) using DMF as eluent[13,14] are 380 kDa (PDI, 1.5) for P[VBBI][Sac], 270 kDa (1.8) for P[VBBI][$FeCl_4$], and 190 kDa (2.0) for P[VBBI][BF_4]. P[VBTMA][BF_4] has a strong interaction with the GPC columns, and thus its M_n cannot be measured accurately by the same method. The X-ray diffraction (XRD) and differential scanning calorimetry (DSC) experiments indicate that these polymers are amorphous at room temperature.[13,14] The glass transition temperatures of P[VBBI][Sac], P[VBBI][$FeCl_4$], P[VBBI][BF_4], and P[VBTMA][BF_4] are 40, 47, 78, and 235 °C, respectively. P[VBBI][$FeCl_4$] is yellowish but transparent. P[VBBI][BF_4], P[VBBI][Sac], and P[VBTMA][BF_4] are colorless and transparent. A piece of transparent P[VBTMA][BF_4] film is shown in Figure 2. As shown in Figure 3, the transmission of visible light through the P[VBTMA][BF_4] film with thickness of 0.43 mm is about 90% at wavelengths from 400 to 800 nm.

Thermogravimetric analysis (TGA) traces for these poly(ionic liquid)s are obtained from a Perkin-Elmer TGA 7 instrument. The experiments are conducted under N_2 at a heating rate of 20 °C/min. The results are shown in Figure 4. The poly(ionic liquid)s have good thermal stability. They decompose in two steps. The onset of degradation is at about 350 °C for all the poly(ionic liquid)s, except for P[VBBI][Sac]. It starts to decompose at about 300 °C.

Microwave absorption may result from dielectric loss, conduction loss, and magnetic loss.[1] Since the poly(ionic liquid)s exhibit no magnetic loss and are insulators (the reported ionic conductivity of a poly(ionic liquid) with a similar structure to the polymers reported here is about 10^{-8} s m^{-1} [34]), their

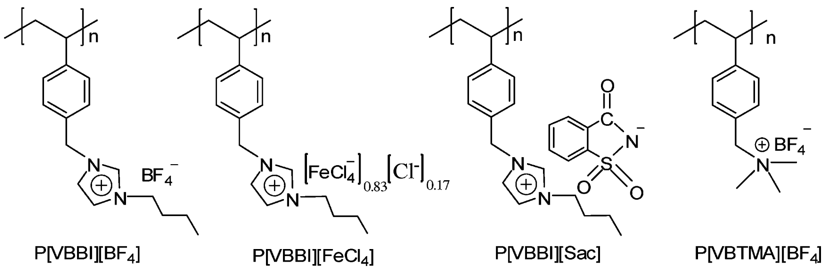

Figure 1. Structures of poly(ionic liquid)s: poly[1-(*p*-vinylbenzyl)-3-butylimidazolium tetrafluoroborate] (P[VBBI][BF_4]), poly[1-(*p*-vinylbenzyl)-3-butylimidazolium tetrachloroferrate] (P[VBBI][$FeCl_4$]), poly[1-(*p*-vinylbenzyl)-3-butylimidazolium o-benzoicsulphimide] (P[VBBI][Sac]), and poly[*p*-vinylbenzyltrimethylammonium tetrafluoroborate] (P[VBTMA][BF_4]).

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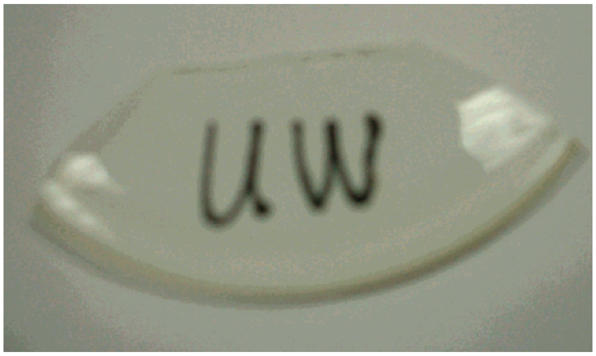

Figure 2. Photo of P[VBTMA][BF_4] film.

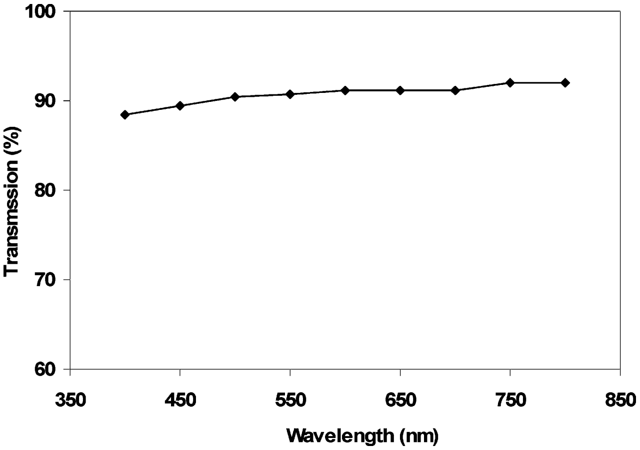

Figure 3. Transmission (%) of visible light through a P[VBTMA]-[BF_4] film (0.43 mm).

microwave absorptions are solely due to the dielectric loss. The dielectric loss is characterized with the relative permittivity, ϵ, which consists of a real part, ϵ', commonly known as the dielectric constant, and an imaginary part, ϵ'', commonly known as the dielectric-loss factor, and hence $\epsilon = \epsilon' - i\epsilon''$. The real part, ϵ', relates to phase, and the imaginary part, ϵ'', relates to loss. The loss tangent is defined as $\tan \delta = \epsilon''/\epsilon'$. The dielectric constants and dielectric-loss factors are measured in the NIST lab (Boulder, CO) by a transmission/reflection method using a coaxial line on a HP 8510 Vector Network Analyzer in the frequency range from 0.05 to 10 GHz.[35] Before the measurements, the poly(ionic liquid)s are dried at 60 °C under vacuum. Toroidal samples of 7.0 mm outer diameter, 3.05 mm inner diameter, and about 5 mm length are prepared by compressing polymer powder in a mold with a constant pressure of 280 MPa for 5 min. The samples are molded to fit into a 7 mm air line. There may be some air gaps on the sides of the sample. The effects of these gaps would be to lower the calculated permittivity. Therefore, the results reported in this work are conservative in that they provide lower bounds on the real part of the permittivity. Typical uncertainties in the loss factor are ± 0.02. Because of air gaps, the uncertainty in the real part of the permittivity is $\pm 5-10\%$.[35]

The dielectric constant ϵ' is shown in Figure 5 as a function of frequency. At frequencies lower than 1 GHz, the ϵ' decreases with increasing frequency. At higher frequencies, the ϵ' remains essentially constant. The poly(ionic liquid)s with the imidazolium cations have similar dielectric constants ($\epsilon' \approx 4$). In contrast, P[VBTMA][BF_4] with the ammonium cations has a higher dielectric constant ($\epsilon' \approx 5.2$). This is not surprising because this material is more polar than poly(ionic liquid)s with imidazolium cations, which is in line with results of other ionic liquids.[36]

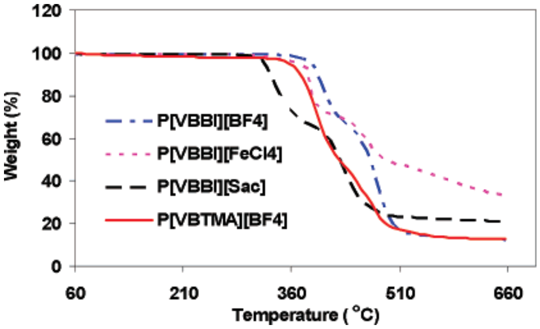

Figure 4. TGA profiles of poly(ionic liquid)s.

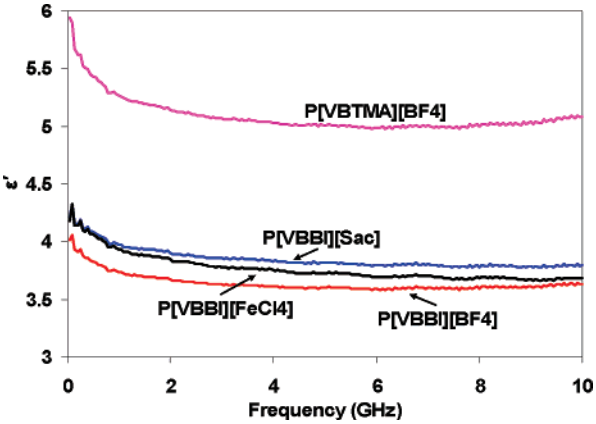

Figure 5. Dielectric constant ϵ' (the real part of complex permittivity) as a function of frequency.

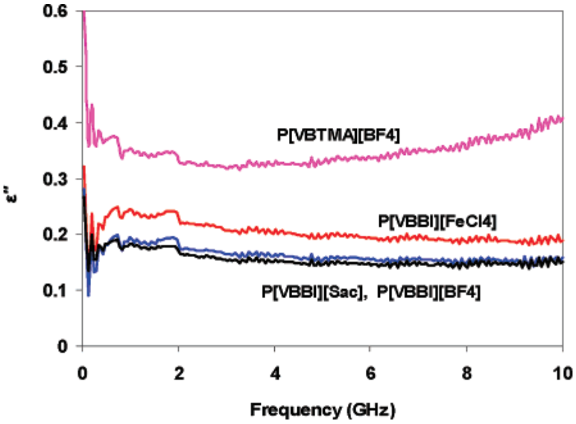

Figure 6. Dielectric loss factor ϵ'' (the imaginary part of complex permittivity) as a function of frequency.

The dielectric loss factor ϵ'' as a function of frequency is shown in Figure 6. For the imidazolium poly(ionic liquid)s, the ϵ'' slightly decreases with increasing frequency at frequencies lower than 4 GHz. At higher frequencies, the ϵ'' remains essentially constant. For P[VBTMA[BF_4], the ϵ'' decreases with increasing frequency and then slightly increases with increasing frequency. At 10 GHz, ϵ'' for P[VBTMA][BF_4] is 0.4.

As shown in Figure 1, P[VBBI][BF_4] has the same backbone as polystyrene but with ion pair groups. P[VBBI][BF_4] has a dielectric loss 115 times higher than polystyrene. Thus, the ion pairs are the cause of the dielectric loss.

The effect of cation is inferred by comparing the dielectric losses of poly(ionic liquid)s with the same backbone and anions but different cations, P[VBBI][BF_4] and P[VBTMA][BF_4]. The ammonium cation-based P[VBTMA][BF_4] has a dielectric loss

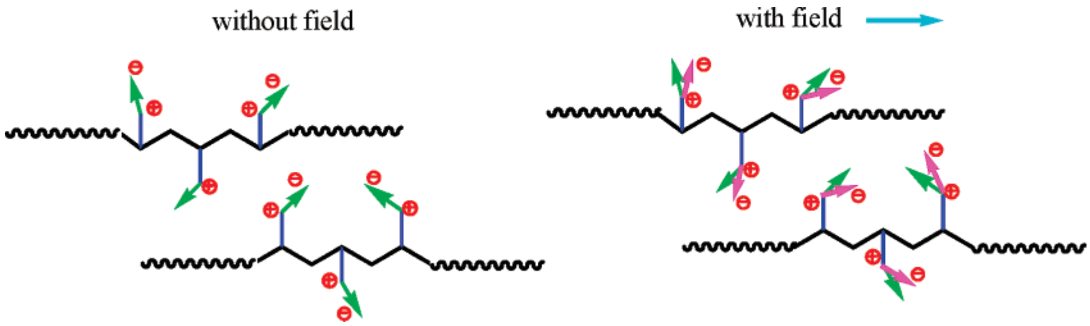

Figure 7. Orientation of ion-pair dipoles in poly(ionic liquid) without and with an electric field (green vector vs purple vector).

Table 1. Comparison of Dielectric Properties for Poly(ionic liquid)s and Other Polymers at 9 GHz and 20 °C Unless Noted Otherwise

material	ϵ'	ϵ''	tan δ
P[VBBI][BF_4]	3.6	0.14	0.039
P[VBBI][Sac]	3.8	0.15	0.039
P[VBBI][$FeCl_4$]	3.6	0.19	0.053
P[VATMA][BF_4]	5.0	0.37	0.074
polystyrene[37]	2.5	0.0012	0.00048 (at 11 GHz)
polycarbonate[37]	2.8	0.0014	0.0005 (at 11 GHz)
polysulfone[37]	3.0	0.026	0.0085 (at 10 .8 GHz)
poly(vinyl chloride)[37]	2.7	0.014	0.005 (at 11 GHz)

about 1.5 times higher than the imidazolium cation-based P[VBBI][BF_4] (Figure 6). This is because the ammonium cation is more polar than the imidazolium cation.

To probe the effect of anion on the dielectric loss, the dielectric losses of three poly(ionic liquid)s, P[VBBI][Sac], P[VBBI][BF_4], and P[VBBI][$FeCl_4$], with the same backbone and cations but different anions are compared. Sac^- is a mostly used organic anion while BF_4^- is a widely used inorganic anion in ionic liquids. A poly(ionic liquid) with $FeCl_4^-$ anions containing transition metal ions Fe^{3+} is also synthesized to test whether such kinds of anions can further increase the loss factor. The three poly(ionic liquid)s, however, have very similar dielectric losses, which indicates that the anions have a minor effect on the dielectric loss compared with the cations of poly(ionic liquid)s.

As summarized in Table 1, poly(ionic liquid)s have much higher dielectric loss factors (ϵ'') than other polymers due to their strong dipole moments. For example, the ϵ'' of P[VBTMA][BF_4] is 25 times higher than that of poly(vinyl chloride) and 263 times higher than that of polycarbonate. Their loss tangents (tan δ) shown in Table 1 are also much higher than those of other polymers.

Dielectric loss can result from electronic polarization, atomic polarization, or/and orientation polarization of a homogeneous polymer. Electronic polarization is the displacement of the electron cloud of the atoms in the polymer molecule relative to its positive nuclei. Atomic polarization is the distorted arrangement of atomic nuclei in a polymer molecule. The times required for electronic polarization and atomic polarization are around 10^{-15} and 10^{-13} s, respectively.[38] In the frequency range from 1 to 10 GHz, in which the dielectric losses of poly(ionic liquid)s are measured, the dielectric loss caused by electronic polarization and atomic polarization is negligible.[38] Thus, the dielectric loss of a polar polymer comes from the orientation polarization.[38] As sketched in Figure 7, poly(ionic liquid)s have strong dipole moments created by the permanent ion pairs. In the absence of an external field, these dipoles are randomly oriented (randomly point in different directions) and continually jump from one orientation to another as a result of thermal agitation. In an external field, these dipoles orient themselves in the direction of the applied field (Figure 7). When the dipole orientation phase lags the alternating electric field of the microwave energy, a dielectric loss will occur. Its value will depend not only on the dipole strength but also on the dipole concentration and polymer morphology.[38] The high dipole concentrations of poly(ionic liquid)s make their dielectric loss factors much higher than those of other polymers. The dielectric loss of P[VBTMA][BF_4] is higher than those of the other poly(ionic liquid)s studied in this work because of its higher polarity (stronger dipole moments).

Conclusion

Model poly(ionic liquid)s, P[VBBI][BF_4], P[VBBI][Sac], P[VBTMA][BF_4], and P[VBBI][$FeCl_4$], have dielectric constants from 3.7 to 5.3 and dielectric loss factors from 0.18 to 0.37, which are much higher than those of other known polymers. Both the dielectric constants and the dielectric loss factors of poly(ionic liquid)s remain essentially constant in the frequency range of 1−10 GHz. The model poly(ionic liquid) containing ammonium cations, P[VBTMA][BF_4], has the highest dielectric constant and dielectric loss factor among the tested model poly(ionic liquid)s. The TGA, DSC, and XRD data confirm that all these materials are amorphous and thermally stable.

Acknowledgment. The authors are grateful to Dr. James Baker-Jarvis, National Institute of Standards and Technology (NIST), Boulder, CO, for the measurements of the permittivity and to Mr. Ryan Niezgoda and Dr. John Ackerman at General Electric Co. for the preliminary RF-waveguide measurement suggesting a high microwave absorption by one of the poly(ionic liquids) studied in this work.

References and Notes

(1) Petrov, V. M.; Gagulin, V. V. *Inorg. Mater.* **2001** *37*, *93*−98.
(2) Bregar, V. B. *IEEE Trans. Magn.* **2004**, *40*, 1679−1684.
(3) Yoshihiro, K.; Satoshi, S.; Ken-ichi, S.; Nobuki, T.; Toshio, T.; Koichiro, I. *Mater. Trans.* **2002**, *43*, 406−409.
(4) Saib, A.; Bednarz, L.; Daussin, R.; Bailly, C.; Lou, X.; Thomassin, J. M.; Pagnoulle, C.; Detrembleur, C.; Jerome, R.; Huynen, I. *IEEE Trans. Microwave Theor. Tech.* **2006**, *54*, 2745−2754.
(5) Zou, Y. H.; Liu, H. B.; Yang, L.; Chen, Z. Z. *J. Magn. Magn. Mater.* **2006**, *302*, 343−347.
(6) Peng, C. H.; Hwang, C. C.; Wan, J.; Tsai, J. S.; Chen, S. Y. *Mater. Sci. Eng., B* **2005**, *117*, 27−36.
(7) Bosman, Y.; Lau, Y.; Gilgenbach, R. M. *Appl. Phys. Lett.* **2003**, *82*, 1353−1355.
(8) Truong, V. T.; Riddell, S. Z.; Muscat, R. F. *J. Mater. Sci.* **1998**, *33*, 4971−4976.
(9) Chandrasekhar, P.; Naishadham, K. *Synth. Met.* **1999**, *105*, 115−120.
(10) Olmedo, L.; Hourquebie, P.; Jousse, F. *Synth. Met.* **1995**, *69*, 205−208.
(11) Wan, M. X.; Li, J. C.; Li, S. Z. *Polym. Adv. Technol.* **2001**, *12*, 651−657.
(12) Phang, S.W.; Daik, R; Abdullah, M. H. *Thin Solid Films* **2005**, *477*, 125− 130.
(13) Tang, J. B.; Tang, H. D.; Sun, W. L.; Plancher, H.; Radosz, M.; Shen, Y. *Chem. Commun.* **2005**, 3325−3327.

(14) Tang, J. B.; Tang, H. D.; Sun, W. L.; Plancher, H.; Radosz, M.; Shen, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5477–5489.
(15) Tang, J. B.; Tang, H. D.; Sun, W. L.; Radosz, M.; Shen, Y. *Polymer* **2005**, *46*, 12460–12467.
(16) Tang, J. B.; Tang, H. D.; Sun, W. L.; Radosz, M.; Shen, Y. *Macromolecules* **2005**, *38*, 2037–2039.
(17) Carlin, R. T.; Fuller. J. *Chem. Commun.* **1997**, *15*, 1345–1346.
(18) Sato, T.; Marukane, S.; Narutomi, T.; Akao, T. J. *Power Sources* **2007**, *164*, 390–396.
(19) Ricks-Laskoski, H. L.; Snow, A. W. *J. Am. Chem. Soc.* **2006**, *128*, 12402–12403.
(20) Fuller, J.; Breda, A. C.; Carlin, R. T. *J. Electroanal. Chem.* **1998**, *459*, 29–34.
(21) Fuller, J.; Breda, A. C.; Carlin, R. *J. Electrochem. Soc.* **1997**, *144*, L67–L70.
(22) Watanabe, M.; Mizumura, T. *Solid State Ionics* **1996**, *86–88*, 353–356.
(23) Matsumi, N.; Sugai, K.; Miyake, M.; Ohno, H. *Macromolecules* **2006**, *39*, 6924–6927.
(24) Narita, A.; Shibayama, W.; Matsumi, N.; Ohno, H. *Polym. Bull. (Berlin)* **2006**, *57*, 109–114.
(25) Yoshio, M.; Kagata, T.; Hoshino, K.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2006**, *128*, 5570–5577.
(26) Ogihara, W.; Suzuki, N.; Nakamura, N.; Ohno, H. *Polym. J.* **2006**, *38*, 117–121.
(27) Ogihara, W.; Washiro, S.; Nakajima, H.; Ohno, H. *Electrochim. Acta.* **2006**, *51*, 2614–2619.
(28) Nakajima, H.; Ohno, H. *Polymer* **2005**, *46*, 11499–11504.
(29) Ohno, H.; Yoshizawa, M.; Ogihara, W. *Electrochim. Acta* **2004**, *50*, 255–261.
(30) Ogihara, W.; Sun, J.; Forsyth, M.; MacFarlane, D. R.; Yoshizawa, M.; Ohno, H. *Electrochim. Acta.* **2004**, *49*, 1797–1801.
(31) Washiro, S.; Yoshizawa, M.; Nakajima, H.; Ohno, H. *Polymer* **2004**, *45*, 1577–1582.
(32) Hoshino, K.; Yoshio, M.; Mukai, T.; Kishimoto, K.; Ohno, H.; Kato, T. *J. Polym. Sci., Polym. Chem.* **2003**, *41*, 3486–3492.
(33) Ohno, H.; Yoshizawa, M.; Ogihara, W. *Electrochim. Acta* **2003**, *48*, 2079–2083.
(34) Marcilla, R.; Alcaide, F.; Sardon, H.; Pomposo, J. A.; Pozo-Gonzalo, C.; Mecerreyes, D. *Electrochem. Commun.* **2006**, *8*, 482.
(35) Baker-Jarvis, J.; Janezic, M. D.; Riddle, B. F.; Johnk, R.; Kabos, P.; Holloway, C. L.; Geyer, R. G.; Grosvenor, C. A. *Measuring the Permittivity and Permeability of Lossy Matertials: Solids, Liquids, Metals, Building Materials and Negative-Index Materials*; National Institute of Standards and Technology: Boulder, CO, 2005; Tech. Note 1536.
(36) Tokuda, H.; Tsuzuki, S.; Hayamizu, M. K.; Watanabe, M. *J. Phys. Chem. B* **2006**, *110*, 19593–19600.
(37) Riddle, B.; Baker-Jarvis, J.; Krupka, J. *IEEE Trans. Microwave Theory Tech.* **2003**, *51*, 727–733.
(38) Ku, C. C.; Liepins, R. *Electrical Properties of Polymers: Chemical Principles*; Hanser Publishers: New York, 1987; pp 21–101.

MA071762I