Journal of Fluorine Chemistry 131 (2010) 776–779

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Proton conductivity properties of acid doped fluoroalkylated 1,2,3-triazole

Sedat Coşgun [a], Sevim Ünügür Çelik [a], Şehmus Özden [a], Suat Tüysüz [a], Ayhan Bozkurt [a,*], Christine Gérardin-Charbonnier [b]

[a] Department of Chemistry, Fatih University, 34500 Büyükçekmece-İstanbul, Turkey
[b] Université Henri Poincaré - Nancy - Faculté des Sciences et Techniques -LERMAB BP 70239, 54506 Vandoeuvre-lès-Nancy Cedex, France

ARTICLE INFO

Article history:
Received 4 January 2010
Received in revised form 23 March 2010
Accepted 24 March 2010
Available online 1 April 2010

Keywords:
Triazole
Cycloaddition reaction
Intrinsic proton conductivity
Organic electrolyte

ABSTRACT

Novel proton conducting organic electrolyte containing fluoroalkylated 1,2,3-triazole was synthesized via intramolecular cyclisation of vinyl azides. FT-IR, elemental analysis and NMR methods were used for the characterization of the resulting organic molecule. Triazole containing sample was doped with triflic acid to obtain proton conducting organic electrolytes. Thermal stability of these materials was analyzed with thermogravimetric analysis (TGA) and the melting temperatures were measured by differential scanning calorimetry (DSC). The effect of acid content on the proton conductivity was investigated with impedance spectrometer and the maximum proton conductivity was measured as 10^{-2} S/cm at 150 °C.

1. Introduction

During the last decade, research activities in polymer electrolyte membranes have increased due to their potential application in advanced electrochemical devices such as polymer electrolyte membrane fuel cells (PEMFCs). Hydrated perfluorosulfonic acid membranes such as Nafion have been successful in fuel cell applications where these materials are typically segregated into hydrophobic and hydrophilic phases, and conductivity occurs through the latter phase via dissociated protons by the dynamics of water [1,2]. However, these membranes have some disadvantages including complex external humidification, high material cost and high methanol crossover, which have slowed down their widespread industrial application [3,4]. In order to overcome these limitations, a number of studies have been performed to produce novel polymer-based materials that can transport protons under anhydrous conditions. Kreuer et al. [5,6] has demonstrated the proton-conducting properties of nitrogen containing aromatic heterocycles such as imidazole, pyrazole, and benzimidazole. Their basic nitrogen sites act as strong proton acceptors with respect to strong acid groups, such as sulfonic acid and phosphonic acid group. The rather isometric molecules are advantageous for extended local dynamics, and their protonated and unprotonated nitrogen functions may act as donors and acceptors in proton transfer reactions while the ring itself is non-polar, avoiding strong solvent effects.

Recent investigations on this area is based on immobilization of the solvent on polymer backbones where proton transport can only occur via structure diffusion between protogenic groups, without vehicular diffusion of small molecular weight compounds [7,8]. While the high proton mobility has been observed in imidazole-based materials, including ionic liquids, oligomers and polymers, the electrochemical stability of imidazole appears to be inadequate for fuel cell applications because of the high electronic density of imidazole ring [9,10]. 1*H*-1,2,3-Triazole (mp 23 °C, bp 203 °C/752 Torr) has a molecular structure similar to that of imidazole and, thus, may conduct a proton via a similar mechanism as in imidazole [11,12]. There are studies about proton conductivity of pure 1*H*-1,2,3-triazole and polymers tethered with 1*H*-1,2,3-triazole [11–13]. They all proposed it as a good proton transferring molecule.

Another approach in the development of proton conducting membranes is to combine the functions of the protogenic group and the proton solvent in a single molecule [1,14]. Such molecules must be amphoteric in the sense that they behave as both a proton donor (acid) and proton acceptor (base), and they must form dynamical hydrogen bond networks [15]. In this work fluorinated organic electrolyte, 5-(perfluoroheptyl)-1*H*-1,2,3-triazole-4-carboxylic acid was synthesized via intramolecular cyclisation of vinyl azides. The characterizations of the samples have been done by elemental analysis, FT-IR, NMR, DSC and TGA. Proton

---

[*] Corresponding author. Tel.: +90 212 8663300.
E-mail addresses: sedatcosgun@fatih.edu.tr (S. Coşgun), sunugur@fatih.edu.tr (S.elik), sehmusozden@gmail.com (Ş Özden), stuysuz@yahoo.com (S. Tüysüz), bozkurt@fatih.edu.tr (A. Bozkurt), christine.gerardin@lermab.uhp-nancy.fr (C. Gérardin-Charbonnier).

0022-1139/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2010.03.015

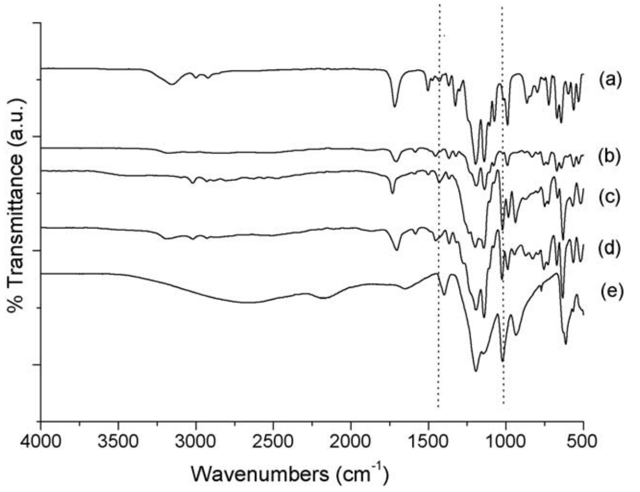


Fig. 1. FT-IR spectra of (a) ethyl 5-(perfluoroheptyl)-3*H*-1,2,3-triazole-4-carboxylate, (b) F7Tri, (c) F7TriTA1, (d) F7TriTA2 and (e) triflic acid.

conductivity of the samples was investigated by dielectric-impedance analyzer using complex dielectric permittivity.

2. Results and discussion

2.1. Characterizations

Fig. 1(a) and (b) shows the FT-IR spectra of carboxylate and acid forms of the sample. Both structures have strong peaks between 1100 and 1300 cm^{-1} due to C–F bonds and 1450–1500 cm^{-1} due to triazole ring. Pure triflic acid and the doped samples give strong and broad absorption bands at 1024 cm^{-1} corresponding to asymmetric O=S=O stretching vibration. In the spectra of F7TriTA1 and F7TriTA2 there are several peaks between 1100 and 1300 cm^{-1} which were attributed to C–F bonds coming from both F7Tri and the dopant (CF_3SO_3). The region between 1250 and 1650 cm^{-1} includes several triazole ring stretchings (~1430 cm^{-1}) and also N–H bending vibrations [18]. There are changes in the intensity of the peaks in this region which may indicate the protonation of the ring. In both the carboxylate and acid forms of the sample the C=O stretching peak is observed around 1710 cm^{-1} which confirms the presence of carboxylic acid group. In addition the absence of an azide peak at 2100 cm^{-1} also indicates the formation of the cyclisation reaction. The protonation of the triazole rings from free nitrogen of the heterocycle is also proved by the N–H stretching around 3100 cm^{-1}.

2.2. Thermal analysis

Fig. 2 shows the thermogravimetry analysis of organic electrolytes. As seen in Fig. 2 pure sample shows minor weight loss between 100 and 150 °C which may be due to absorbed water. Major weight loss occurs after 170 °C due to decomposition of both fluorinated and triazole groups. As the sample was doped with triflic acid the organic electrolytes showed thermal stability up to 170 °C and stepwise decomposition of the molecule and dopant was observed until 300 °C. All samples can be said to be thermally stable up to 170 °C.

Fig. 3 illustrates the DSC measurements of the samples. F7Tri shows a melting point of around 175 °C. The onset of this melting was evaluated as 160 °C. There is also an unapparent melting behavior around 130 °C. After doping this sample with triflic acid, F7TriTA1 showed an endothermic behavior at around 50 °C and a melting behavior at 90 °C. As the acid ratio increased (F7TriTA2), there are two distinctive T_m values around 50 and 85 °C.

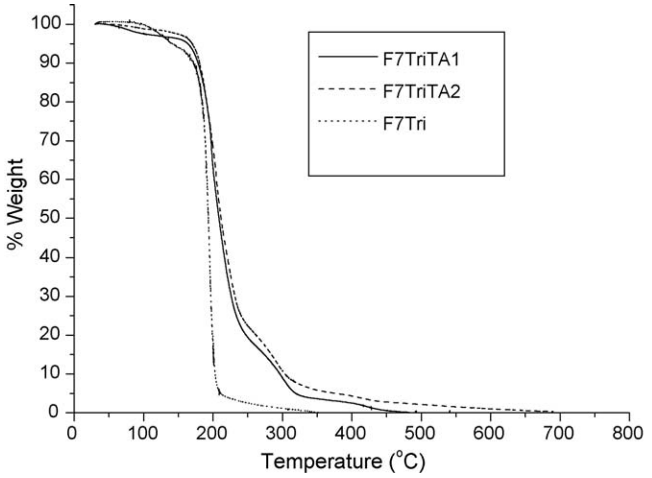


Fig. 2. TG thermograms of F7Tri, F7TriTA1 and F7TriTA2 recorded at a heating rate of 10 °C/min under a nitrogen atmosphere.

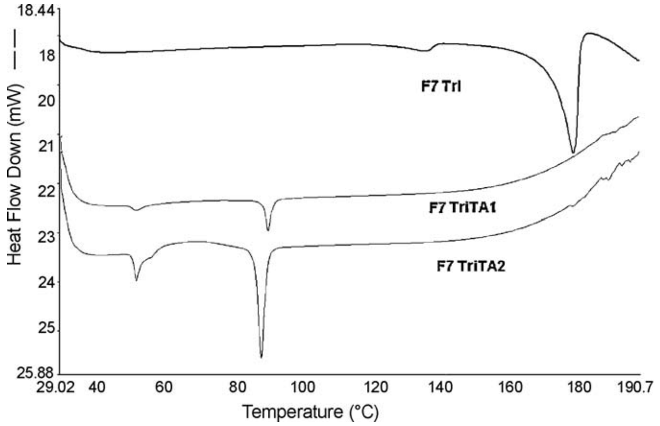


Fig. 3. DSC traces of F7Tri, F7TriTA1 and F7TriTA2 recorded at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.3. Proton conductivity

The proton conductivity studies were performed by sandwiching the organic electrolytes between platin blocking electrodes. The AC conductivities, $\sigma_{ac}(\omega)$ of samples were measured at several temperatures using impedance spectroscopy. The AC conductivity of F7TriTA2 is shown in Fig. 4. Frequency dependent AC

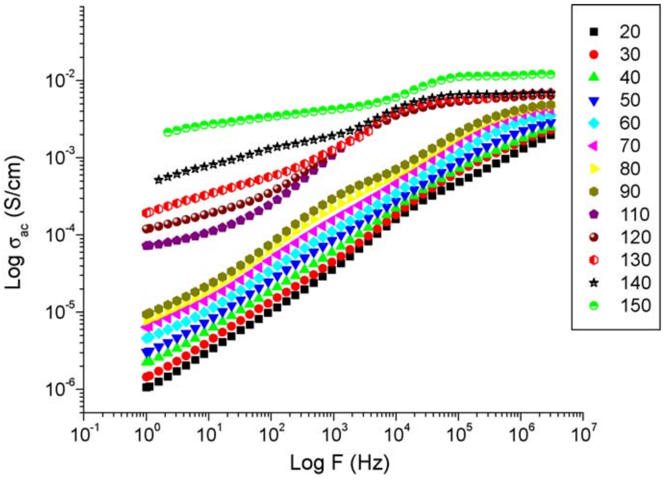


Fig. 4. The σ_{ac} vs. frequency (Hz) for F7TriTA2 at various temperatures.

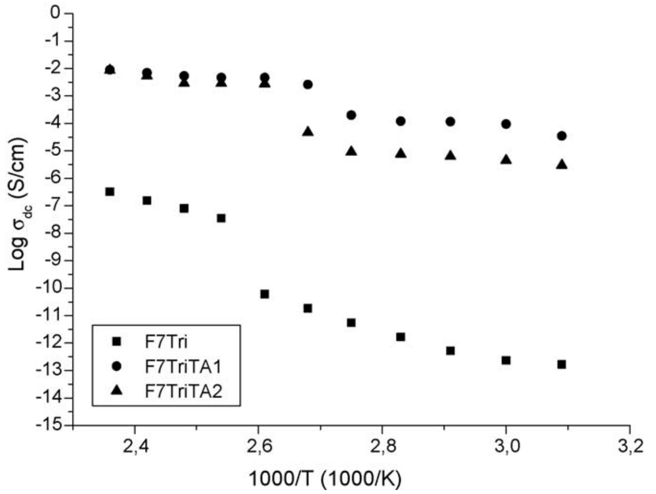


Fig. 5. DC conductivities of F7Tri, F7TriTA1 and F7TriTA2 as a function of reciprocal temperature.

conductivities ($\sigma_{ac}(\omega)$) were measured using Eq. (1):

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \varepsilon''(\omega)\omega\varepsilon_o \tag{1}$$

where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ is the angular frequency, f is frequency (1/time), ε_o is the vacuum permittivity ($\varepsilon_o = 8.852 \times 10^{-14}$ F/cm), and ε'' is the imaginary part of complex dielectric permittivity (ε^*) [19–22]. The decrease in proton conductivity in low frequency region is due to blocking electrode polarization. The DC conductivity (σ_{dc}) of the samples was derived from plato regions of the AC curve (e.g. 10^5 Hz–3×10^6 MHz for 120–150 °C in Fig. 4) by linear fitting of the data. In non-plato regions the middle region was fitted linearly to eliminate the effect of electrode polarization and dispersion.

The DC conductivities of the organic electrolytes were compared in Fig. 5. The conductivity isotherm illustrates that the DC conductivity strongly depends on the temperature. Pure sample shows low proton conductivity and as the sample was doped with triflic acid ($x = 1$) the conductivity increases to 10^{-2} S/cm at 150 °C. The value of the conductivity did not change so much when the acid ratio increased to $x = 2$. In triazole based systems the proton conductivity is expected to occur by transfer of acidic protons along the unprotonated and protonated triazole units, defined as Grotthuss mechanism. As reported in the literature, anhydrous polymer systems facilitate the formation of protonic defects and provide strongly labile proton donor and acceptor functions. In addition, acidic molecules such as sulfonic acid could also act as proton donors and acceptors. Protonated and non-protonated nitrogen in heterocyclic group of F7Tri and sulfonate group of triflic acid may act as proton donors and acceptors in this system. As the acid ratio was increased to $x = 2$, there is not a considerable difference in DC conductivity. This may be due to reaching of the system to threshold point where further increase causes blocking of the defects in heterocycle. Beside that there is an apparent increase in proton conductivity above T_m values (>80 °C) which indicates the effect of molecule mobility on proton transfer.

The ionic conductivity of pure 1*H*-1,2,3-triazole is about 1.3×10^{-4} S/cm at room temperature [11]. Zhou et al. tethered 1*H*-1,2,3-triazole into a sulfonated polysulfone (sPSU) polymer membrane [11]. The conductivities of the membranes increased with the concentration of 1*H*-1,2,3-triazole and the conductivity reached about 0.01 S/cm at 110 °C under dry conditions. They also synthesized poly(4-vinyl-1*H*-1,2,3-triazole) and compared its proton conductivity with poly(4-vinylimidazole). They reported that the maximum proton conductivity of the triazole containing polymer (~10^{-4} S/cm) is about 10^5 times higher than the imidazole containing one [11]. Martwiset et al. tethered 1*H*-1,2,3-triazole onto several polyacrylates and studied effect of triazole content, T_g and acid doping on proton conductivity. It was reported that continued conductivity improvements were observed up to 100% mol trifluoroacetic acid and further addition decreased proton conductivity [13]. In this work the maximum proton conductivity was obtained as about 10^{-2} S/cm at 150 °C for the sample containing 200% mol triflic acid per mol of triazole unit.

3. Conclusions

In this work fluorinated organic electrolyte with 1,2,3-triazole and carboxylic acid group was synthesized via intramolecular cyclisation of vinyl azides. Characterization, thermal studies and proton conductivity studies were done for resulting organic electrolytes. FT-IR, NMR and elemental analysis results confirmed the structure of the samples. DSC results indicated the crystalline character of the organic electrolytes. TGA studies showed that the samples are thermally stable up to 170 °C. Proton conductivity measurements showed that $x = 1$ is the optimum ratio and maximum proton conductivity was obtained as about 10^{-2} S/cm at 150 °C for F7TriTA1.

4. Experimental

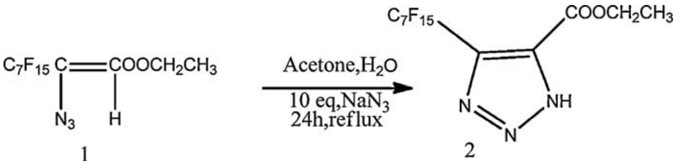
4.1. Synthesis of ethyl 5-(perfluoroheptyl)-3H-1,2,3-triazole-4-carboxylates

The synthesis of the triazole containing molecule was carried out according to literature [16,17] (Scheme 1). Ester derivative of 3-azido-3-(perfluoroalkyl)propenoic acid, **1** (2 mmol) was dissolved in acetone (9 ml) and water (1 ml), and sodium azide (10 equiv.) was then added. The mixture was heated under reflux for 24 h. On cooling to room temperature, ethyl acetate (60 ml) was added, and the organic phase was washed three times with saturated aqueous solution of NaCl, and then with HCl solution. The organic phase was then dried with sodium sulfate, and the solvent was evaporated under vacuum. The resulting triazole containing sample, **2** was a yellow solid with high yield, 90%.

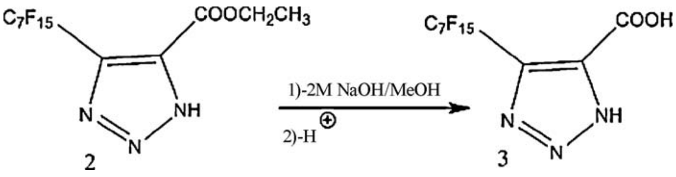
IR: $\tilde{\nu}$ = 1704(C=O), 1100–1300 (C–F) cm^{-1}
^{1}H NMR ($CDCl_3$): δ = 1.35 (t, $^3J_{H-H}$ = 7.0 Hz, 3 H, $-CH_3$), 4.43 (q, $^3J_{H-H}$ = 7.0 Hz, 2 H, CH_2-) ppm.
^{13}C NMR ($CDCl_3$): δ = 15 ($-CH_3$), 63 ($-CH_2-$), 110–120 (CFluor),138, 140 ($C_{triazole}$), 160 (CO) ppm.
^{19}F NMR ($CDCl_3$): δ = −79 (t, $^3J_{F-F}$ = 9 Hz, 3 F, CF_3-), −105.4 (m, 2 F, $-CF_2-C_{triazole}=$), −119 to −124 (m, (2n − 4) F, CF3–(CF_2)n–$_2$–CF2–) ppm.
Elemental analysis: $C_{12}H_6F_{15}N_3O_2$ (509.17): Calc. C: 28.31, H: 1.19, F: 55.97, N: 6.28; Found. C 27.79, H 1.21, F 53.70, N 7.20.

4.2. Ester saponification: preparation of 5-(perfluoroheptyl)-1H-1,2,3-triazole-4-carboxylic acid

To a solution of 2 mmol ester triazole, **2** in methanol (10 ml), 5 eq. of a 2N sodium hydroxide solution in methanol/water (90/10)



Scheme 1. Synthesis of ethyl 5-(perfluoroheptyl)-3*H*-1,2,3-triazole-4-carboxylate.



Scheme 2. Preparation of 5-(perfluoroheptyl)-1*H*-1,2,3-triazole-4-carboxylic acid (F7Tri).

were added (Scheme 2). The mixture was stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure. The residue was dissolved in ethyl acetate (100 ml) and then acidified with HCl (1 M) until pH 1. The aqueous layer was extracted with ethyl acetate (2–100 ml). The combined organic layers were dried over magnesium sulfate and the solvent was evaporated under reduce pressure. The acid triazole, **3** was obtained as a yellow transparent solid. Yield: 95%

^{13}C NMR (CD_3COCD_3): $\delta = 110–120$ (C–F), 138.2 and 160.3 ($C_{triazole}$) ppm.
^{19}F NMR (CD_3COCD_3): $\delta = -80.5$ (t, $^3J_{F-F} = 9$ Hz, 3 F, CF_3–), -106.3 (m, 2F, –CF_2–triazole), -120 to -127 (m, (2n − 4) F, CF_3–$(CF_2)n_{-2}$–CF_2–) ppm.
Elemental analysis: $C_{10}H_2F_{15}N_3O_2$ (481.12): Calc. C: 24.96, H: 0.42, F: 59.23, N: 8.73; Found. C: 24.90, H: 0.56, F: 58.66, N: 8.73.

4.3. Preparation of 1,2,3-triazole containing organic electrolytes

0.5 g 5-(Perfluoroheptyl)-1*H*-1,2,3-triazole-4-carboxylic acid (F7Tri) was dissolved in methanol and triflic acid (TA) was added with molar ratios $x = 1$ and $x = 2$ per mol of triazole unit. The mixture was stirred 1 h and then cast on PTFE plates. The resulting organic electrolytes (F7TriTA1 and F7TriTA2) were dried under vacuum and stored in glove box for measurements.

4.4. Characterizations

The progress of reaction was determined using FT-IR spectra. FT-IR spectra were recorded on a Bruker Alpha-P in ATR.

NMR spectra were recorded on a Bruker AM 400 or an AC 200 instrument. Chemical shifts are reported in ppm relative to TMS as internal standard for the ^{1}H spectra and to $CFCl_3$ for the 19F NMR spectra. Coupling constants (J) are in Hertz.

Elemental analyses were performed by Thermo Flash 2000.

Thermal stabilities of the polymer electrolytes were examined by a PerkinElmer STA 6000 Thermal Analyzer. The samples (∼10 mg) were heated from room temperature to 400 °C under N_2 atmosphere at a scanning rate of 10 °C/min.

PerkinElmer JADE differential scanning calorimetry (DSC) was used to investigate the thermal transitions of the samples. The samples (∼10 mg) were filled into aluminum pans and then heated to the desired temperature at a rate of 10 °C/min under nitrogen atmosphere.

The proton conductivity studies of the samples were performed using a Novocontrol impedance spectrometer. The doped samples were light yellow sticky materials and for conductivity measurements they were sandwiched (thickness = 0.5 mm) between Pt electrodes and heated from 20 to 150 °C at 10 °C intervals under dry-nitrogen atmosphere in the frequency range 0.1 Hz to 1 MHz. The temperature was controlled with a Novocontrol cryosystem, which is applicable between −150 and 250 °C.

Acknowledgement

The authors are thankful to the Fatih University Research Project Foundation (Contract no.: P50020801).

References

[1] P. Jannasch, Curr. Opin. Colloid Interface Sci. 8 (2003) 96.
[2] M.F.H. Schuster, W.H. Meyer, Annu. Rev. Mater. Res. 33 (2003) 233.
[3] B. Bae, D. Kim, J. Membr. Sci. 220 (2003) 75.
[4] Y.F.A. Manthiram, M.D. Guiver, Electrochem. Commun. 8 (2006) 1386.
[5] K.D. Kreuer, A. Fuchs, M. Ise, M. Spaeth, J. Maier, Electrochim. Acta 43 (1998) 1281.
[6] W. Munch, K.D. Kreuer, W. Silvestri, J. Maier, G. Seifert, Solid State Ionics 145 (2001) 437.
[7] M. Schuster, W.H. Meyer, G. Wegner, H.G. Herz, M. Ise, K.D. Kreuer, J. Maier, Solid State Ionics 145 (2001) 85.
[8] J.C. Persson, P. Jannasch, Chem. Mater. 15 (2003) 3044.
[9] C. Yang, P. Costamagna, S. Srinivasan, J. Benziger, A.B. Bocarsly, J. Power Sources 103 (2001) 1.
[10] W. Deng, V. Molinero, W.A. Goddard III, J. Am. Chem. Soc. 126 (2004) 15644.
[11] Z. Zhou, S.W. Li, Y.L. Zhang, M.L. Liu, W. Li, J. Am. Chem. Soc. 127 (2005) 10824.
[12] Z. Zhou, R. Liu, J.H. Wang, S.W. Li, M.L. Liu, J.L. Bredas, J. Phys. Chem. A 110 (2006) 2322.
[13] S. Martwiset, R.C. Woudenberg, S. Granados-Focil, O. Yavuzcetin, M.T. Tuominen, E.B. Coughlin, Solid State Ionics 178 (2007) 1398.
[14] K.D. Kreuer, in: J.T. Hynes, J.P. Klinman, H.H. Limbach, R.L. Schowen (Eds.), Hydrogen Transfer Reactions, Wiley, VCH, 2005, pp. 709–736 (Ch. 23).
[15] H. Steininger, M. Schuster, K.D. Kreuer, A. Kaltbeitzel, B. Bingöl, W.H. Meyer, S. Schauff, G. Brunklaus, J. Maier, H.W. Spiess, Phys. Chem., Chem. Phys. 9 (2007) 1764–1773.
[16] E. Mayot, P. Lemiere, C. Gerardin-Charbonnier, Eur. J. Org. Chem. (2008) 2232.
[17] S. Cosgun, C. Gerardin, J. Amos, C. Selve, J. Fluorine Chem. 125 (2004) 55–61.
[18] F. Billes, H. Endredi, G. Keresztury, J. Mol. Struct. [Theochem.] 530 (2000) 183–200.
[19] S.Ü. Çelik, A. Bozkurt, Eur. Polym. J. 44 (2008) 213.
[20] S.Ü. Çelik, Ü. Akbey, A. Bozkurt, R. Graf, H.W. Spiess, Macromol. Chem. Phys. 209 (2008) 593.
[21] S.Ü. Çelik, A. Aslan, A. Bozkurt, Solid State Ionics 179 (2008) 683–688.
[22] N.K. Karan, D.K. Pradhan, R. Thomas, B. Natesan, R.S. Katiyar, Solid State Ionics 179 (2008) 689–696.