

Synthesis and Proton Conductivity Studies of Methacrylate/ Methacrylamide-Based Azole Functional Novel Polymer Electrolytes

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ABSTRACT: Anhydrous polymer electrolytes based on azole functional methacrylates and methacrylamides have been produced for use in proton exchange membrane fuel cells (PEMFCs). Poly(methacryloyl chloride) (PMAC) was prepared first by free-radical polymerization of methacryloyl chloride, followed by side chain functionalization with 5-aminotetrazole (ATet), 3-amino-1,2,4-triazole (ATri) and 1H-1,2,4-triazole (Tri). Finally, the obtained polymers were doped with triflic acid (TA) at stoichiometric ratios of 1.0, 2.0 and 4.0 with respect to azole units, and the anhydrous polymer electrolytes were obtained. The membranes were characterized by FT-IR, ¹³C-NMR, and elemental analysis. Thermal behaviour of polymers was explored by TGA and DSC. The samples were thermally stable up to approximately 200 °C. Proton conductivity was measured by impedance spectroscopy. Triflic acid doped poly(methacryloyl aminotetrazole) (PMAATet-(TA)₄), poly(methacryloyl-3-amino-1,2,4-triazole) (PMA-Tri-(TA)₄), and poly(methacryloyl-1,2,4-triazole) (PMA-ATri-(TA)₄) showed maximum proton conductivities of 0.01 Scm⁻¹, 0.02 Scm⁻¹ and 8.7x10⁻⁴ Scm⁻¹, respectively, at 150 °C and anhydrous conditions. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39915.

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INTRODUCTION

Quite recently, proton exchange membrane fuel cells (PEMFCs) have attracted a great deal of interest due to their high energy conversion efficiency and their ability to address the environmental concerns related to current energy production.¹ Perfluorosulfonic acid membranes, such as Nafion, have been commonly used as the polymer electrolyte in PEMFCs. In these systems, the proton conduction is mainly dependent on the water content, which limits their usage to above 100°C. However, the operation of fuel cells at higher temperatures, above 100°C, provides benefits such as, improvement of CO tolerance of platinum catalyst, improve mass transportation, increase reaction kinetics and simplify the water management and gas humidification.^{2–5} Therefore, it is essential that alternative anhydrous membranes be developed that have high proton conductivity at elevated temperatures.⁶

A common technique used in the synthesis of anhydrous proton conducting materials is the doping of the polymer matrix with heterogenic compounds such as imidazole, benzimidazole, and triazole.^{7–14} Since these azole groups have high melting points (100–200 °C), they successfully substituted water and provided

high proton conductivity. Furthermore, several polymer systems involving chemical immobilization of protogenic solvents into polymers have been reported in the literature. For example, Ozden et al. synthesized poly(vinylbenzyl chloride) based polymer electrolyte membranes via immobilization of various protogenic solvents, such as Tri, ATri, and ATet. Upon subsequent doping with triflic acid, the cast membranes were obtained.^{11,15} Li et al. tethered 5-amino-1H-benzotriazole on polysulfone backbone and prepared its blends with acidic sulfophenylated poly(ether ether ketone).¹⁶ Celik et al. reported on the preparation of several poly(glycidyl methacrylate) (PGMA) based polymer electrolyte membranes via immobilization of Tri, ATri, and ATet, followed by subsequent doping with triflic and phosphoric acids.^{17,18}

Polymers bearing triazole and tetrazole moieties have been the focus of much attention because of their powerful energetic usage, biological activity and high thermal stability.^{19–21} In both poly(vinyl tetrazole) and poly(vinyl triazole), the aliphatic chain improves its fabrication property, and the triazole and tetrazole side groups may act as proton donors and acceptors. The proton transport occurs between hydrogen bonds of neighboring heterocyclic units through structure

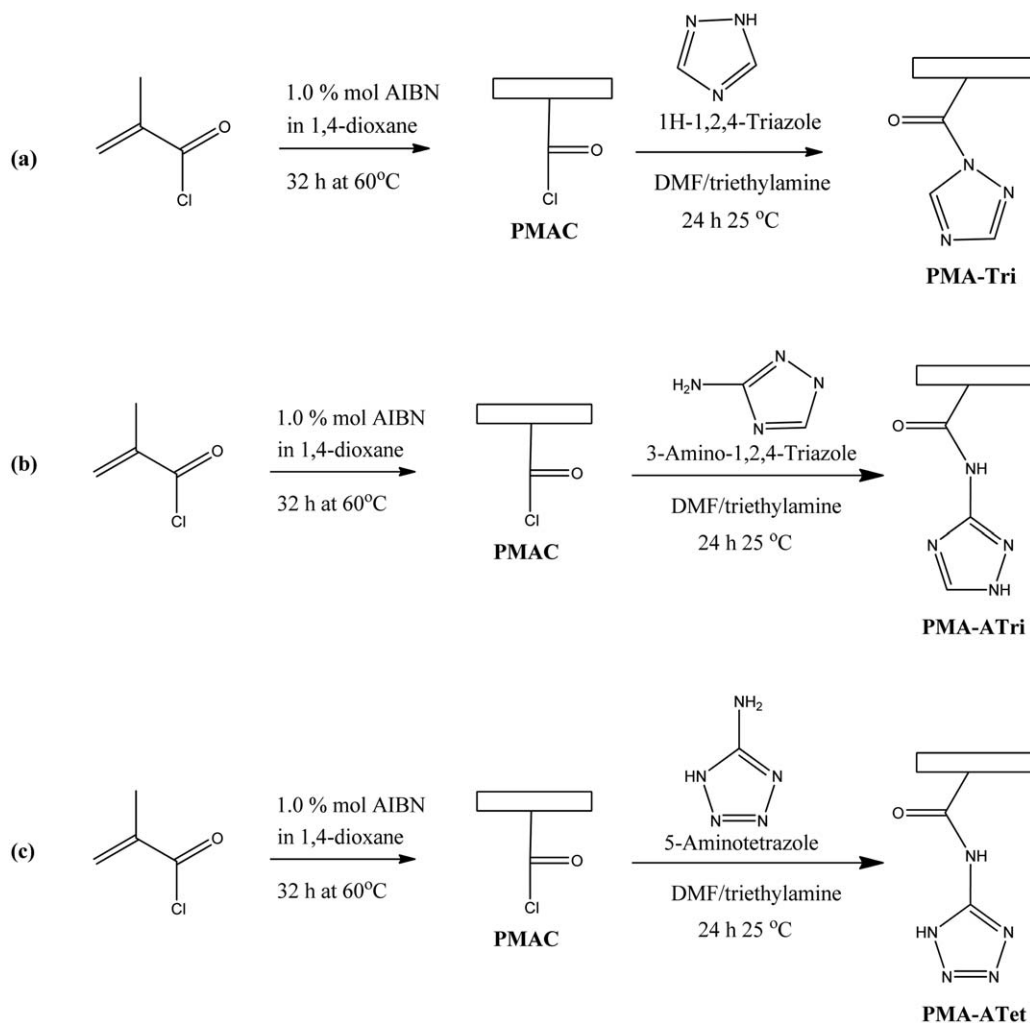


Figure 1. Synthesis scheme of (a) PMA-Tri, (b) PMA-ATri, (c) PMA-ATet.

diffusion. (Tri) and 1H-tetrazole (Tet) are aromatic heterocycles with three and four N atoms, respectively, on the rings that have more configuration than imidazole ring. The pK_a value of 5-vinyl-1H-tetrazole is much lower than that of 5-vinylimidazole.²² Thus, Tri- or Tet-based polymers may exhibit different proton transport ability from imidazole-based polymers.

In this work, anhydrous polymer electrolytes based on azole functional methacrylates and methacrylamides have been produced for use in proton exchange membrane fuel cells (PEMFCs). To the best of our knowledge, this contribution is the first to report on the preparation of methacrylate/methacrylamide based triazole and tetrazole functional polymer electrolytes via post-polymerization functionalization. PMAC was synthesized by free radical polymerization of methacryloyl chloride, followed by covalent attachment of ATet, ATri and Tri distinctly onto PMAC. The reaction was confirmed via elemental analysis, FT-IR and ¹³C-NMR spectroscopies. Functional polymers were doped with TA at several stoichiometric ratios, and the resulting materials were characterized by FT-IR, TGA, and DSC. Proton conductivities were measured by impedance spectroscopy.

EXPERIMENTAL

Materials and Preparation

Methacryloyl chloride (>97%) was purchased from Alfa Aesar and distilled prior to use. Azobisisobutyronitrile (AIBN; Merck) was recrystallized in THF prior to use. 5-aminotetrazole (>98%, Alfa Aesar), 1H-1,2,4-triazole (>97%), and 3-amino-1,2,4-triazole (95%) were obtained from Aldrich Chemical Company. 1,4-dioxane (Merck), trifluoromethanesulfonic acid (>98, Fluka), *N,N*-dimethylformamide (Merck), triethylamine (Merck) and hexane (Merck) were used without further purification.

Poly(methacryloyl chloride) (PMAC) was prepared via conventional free radical polymerization of methacryloyl chloride in 1,4-dioxane using azobisisobutyronitrile, AIBN (1% mol) as initiator (yield: 65%). The mixture was purged with nitrogen and the polymerization reaction was performed at 60°C for 32 h.²³ The synthesis of homopolymer and reaction of PMAC with ATet, ATri, and Tri were carried out as depicted in Figure 1. 1.3 g of PMAC was dissolved in 10 mL DMF, and triazole solutions (1.03 g Tri or 1.25 g ATri in 10 mL DMF) were added to PMAC solution together with 1.3 mL triethylamine. And in

another vessel, 1.3 g PMAC and 1.27 g ATet were dissolved in 10 mL DMF separately and the solution was mixed after adding 2 mL triethylamine. The reaction mixture was purged with nitrogen and the polymerization reaction was performed at 60°C for 24 h, separately. The resulting polymers were dialyzed against water to remove unreacted ATet, ATri, and Tri and then dried under vacuum.

Polymer membranes were obtained by doping with TA of the triazole and tetrazole functional polymers at stoichiometric ratios of 1.0, 2.0, and 4.0 (TA/ATri, TA/Tri, TA/ATet). A stoichiometric amount of PMA-ATet, PMA-ATri, PMA-Tri was admixed with TA in DMF, and homogeneous solutions of PMA-ATet-(TA)_x, PMA-ATri-(TA)_x, and PMA-Tri-(TA)_x were produced, respectively. The solutions were cast in polished polytetrafluoroethylene (PTFE) plates, and the solvent was evaporated in vacuum oven for several days at 50°C. The films were stored in glove box for characterizations.

Methacryloyl chloride is a clear liquid that is miscible in methanol, water, and 1,4-dioxane. ATri is soluble in water, methanol, ethanol and chloroform, and sparingly soluble in ethyl acetate. It is insoluble in ether and acetone. ATet has good solubility in water and ethanol. Tri is soluble in formamide, water and alcohols such as ethanol, butanol and propanol. The homopolymer, PMAC, is a colorless solid that can be dissolved in water, DMF, DMSO and NMP. Modification of PMAC with Tri, ATri, and ATet yields brownish membranes that are soluble in solvents such as DMF, DMSO, and NMP.

Characterizations

Before FTIR spectra measurements, samples were dried under vacuum and stored in a glove box. FTIR spectra were obtained using a Bruker Alpha-P in ATR in the range of 4000–400 cm⁻¹. ¹³C-NMR spectra were recorded using a 400 MHz Bruker Avance spectrometer. Chemical shifts are reported in ppm relative to TMS as internal standard. Thermal stabilities of the polymer electrolytes were examined by a Perkin Elmer STA 6000 Thermal Analyzer. The samples (~10 mg) were heated from room temperature to 750°C under N₂ atmosphere at a scanning rate of 10°C/min. Perkin Elmer 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 composition of carbon, hydrogen and nitrogen in the polymers was measured by using Thermo Scientific Flash 2000 Organic Elemental Analyzer. The proton conductivity studies of the samples were performed using a Novocontrol dielectric-impedance analyzer. The samples were sandwiched between platinum blocking electrodes and the conductivities were measured in the frequency range 1–3 MHz at 10°C intervals. The temperature was controlled with a Novocontrol cryosystem, which is applicable between –150 and 250°C.

RESULTS AND DISCUSSION

The homopolymer of PMAC was obtained by free radical polymerization of methacryloyl chloride in 1,4-dioxane. Then, triazole, aminotriazole, and tetrazole functional groups were

Table I. Azole Content of PMA-ATet, PMA-ATri, and PMA-Tri Calculated from Elemental Analysis Results

Sample	C (%)	H (%)	N (%)	Azole (%)
PMA-ATet	41.35	6.94	23.30	41
PMA-ATri	40.73	6.88	21.20	48
PMA-Tri	42.06	6.92	20.86	38

immobilized by reaction with PMAC as depicted in Figure 1. The composition of the polymer was verified by elemental analysis. Aminotetrazole, triazole, and aminotriazole contents of the samples were calculated through nitrogen analysis, and the results are summarized in Table I. It is verified that ATet, ATri, and Tri are about 41%, 48%, and 38% accessible to PMAC, respectively.

NMR Studies

The ¹³C-NMR spectra of PMA-ATri, PMA-ATet, and PMA-Tri are shown in Figure 2(a–c) together with spectral assignment, respectively. Carbon atoms of the aliphatic chain groups appear at around 18 and 44 ppm. The peaks between 155 and 162 ppm belong to carbon of the triazole rings and triazole rings attached to NH sites in the PMA-ATri, respectively. The peak located at around 180 ppm belongs to carbon of the carbonyl group.

The ¹³C-NMR spectra of PMA-ATet is shown in Figure 2(b). Signals corresponding to the methyl and methylene groups appear between 18 and 44 ppm, respectively. The peak located at around 180 ppm belongs to carbon of the carbonyl group. Additionally, the azole ring carbon gives a peak around 155 ppm of the NH sites in the aminotetrazole ring.^{11,15,17}

The ¹³C-NMR spectra of PMA-Tri is represented in Figure 2(c). Carbon atoms of the aliphatic chain groups (methyl and methylene carbons) appear between 17 and 45 ppm region, respectively. The peak located at around 180 ppm belongs to carbon of the carbonyl group. In addition, the azole ring carbons give a peak around 150 ppm in triazole ring.

FTIR Studies

In the IR spectrum of PMAC, there is a strong band due to the stretching vibration of halide attached to C=O groups at 1698 cm⁻¹. The aliphatic C-H stretchings were observed at 2800–3000 cm⁻¹ regions. There is a broad band due to the stretching vibration of carbonyl group attached to C-Cl groups at 760 cm⁻¹ (Figure 3a). PMA-ATet exhibited several medium or strong peaks at 1689 cm⁻¹ and 1465 cm⁻¹ due to amide bond and tetrazole ring vibrations, respectively.^{11,15,24} The triazole units show several medium or strong peaks at 1692 cm⁻¹ and 1445–1550 cm⁻¹ range due to the amide bond and C=N, C-N ring vibrations, respectively. The aliphatic C-H stretchings were observed at 1380–1470 cm⁻¹ and 2800–3000 cm⁻¹ regions. Figure 3(b–d) shows the FTIR spectrum of acid-doped PMA-ATet, PMA-ATri, and PMA-Tri. Triflic acid gives several absorptions between 1000 cm⁻¹ and 1250 cm⁻¹. The strong bands at 1155 and 1229 cm⁻¹ are attributed to SO₂, and a strong absorption peak at 1026 cm⁻¹ most probably belongs to -SO₃⁻[H⁺]. The formation of a peak at around 3170 cm⁻¹ shows the

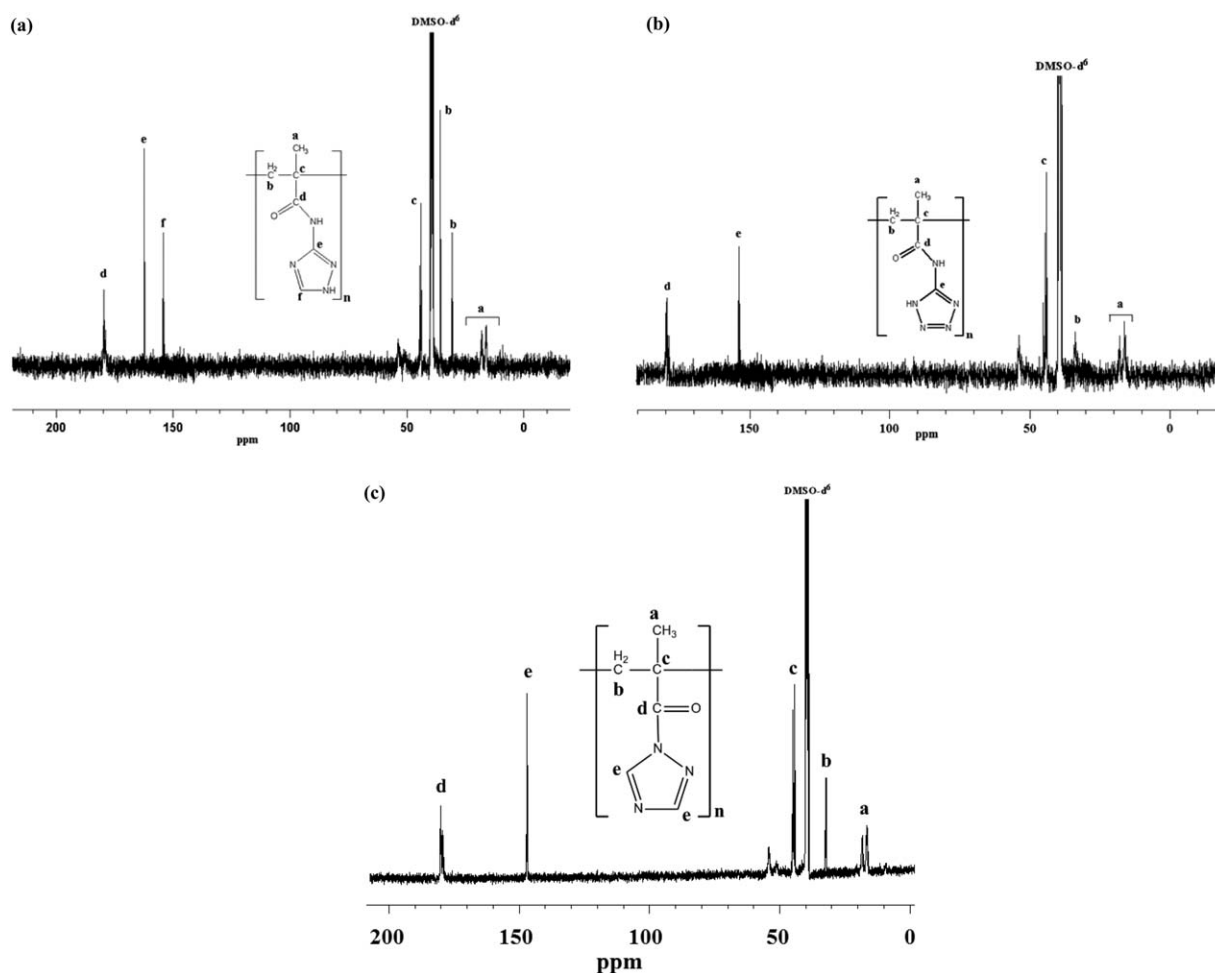


Figure 2. ^{13}C -NMR spectrum of (a) PMA-ATri, (b) PMA-ATet, (c) PMA-Tri recorded in DMSO-d_6 .

protonation of the triazole and tetrazole rings, in addition to the broad peaks around 3480 cm^{-1} .^{11,15,17,25}

Thermal Analysis

The thermal stability of PMA-ATri-(TA)_x and PMA-Tri-(TA)_x ($x=1$ and 4) electrolytes were studied by TGA and depicted in Figure 4(a,b), respectively. The homopolymer, PMAC, is thermally stable up to 210°C beyond which it degrades via two stages. Decomposition of PMAC is represented at 210°C and 365°C [Figure 4(a)]. After the modification of PMAC with 3-aminotriazole, the thermal stability decreases to 195°C as depicted in Figure 4(a). About 30% of the PMA-ATri decomposes between 195 and 350°C because of degradation of aminotriazole units and after 360°C, second weight loss region occurs because of decomposition of the polymer backbone. Since the functional polymers were doped with TA, the thermal stability shifts to 300°C.

Figure 4(b) shows the TGA of triazole functional samples. The sample PMA-Tri is thermally stable up to 200°C. Approximately, 30% of the PMA-Tri decomposes between 200 and 350°C because of degradation of triazole units, and after 360°C, second weight loss region occurs because of decomposition of the polymer backbone. As the functional polymer was doped

with triflic acid, the thermal stability increases. All of these doped samples are thermally stable up to around 325°C. In these doped samples, the weight loss starts at higher temperatures compared with pure polymer as nearly single step. This may be due to the hydrogen bonding between triflic acid and triazole units, which delays the triazole unit degradation.^{11,15}

The thermal stability of PMA-ATet and PMA-ATet-(TA)_x ($x=1$ and 4) electrolytes were studied by thermogravimetric analysis (TGA) and depicted in Figure 4(c). PMA-ATet functional polymer exhibited a thermal stability up to 196°C. The doped samples are also thermally stable up to at least 210°C. 25% of PMA-ATet decomposes between 210 and 340°C because of degradation of aminotetrazole units and after 365°C, second weight loss region occurs because of decomposition of the polymer backbone. After doping the polymer, 10% of the samples, PMA-ATet-(TA)_x ($x=1.0, 2.0, \text{ and } 4.0$), decompose up to 250°C and major weight loss occurs between 250 and 440°C which presumably derives from the decomposition of the polymer electrolyte main chain.^{11,15,17,23}

Table II shows the glass transition temperature, T_g , of PMA-ATet, PMA-ATri, PMA-Tri, and triflic acid-doped samples, PMA-ATet-(TA)_x, PMA-ATri-(TA)_x, PMA-Tri-(TA)_x ($x=1.0,$

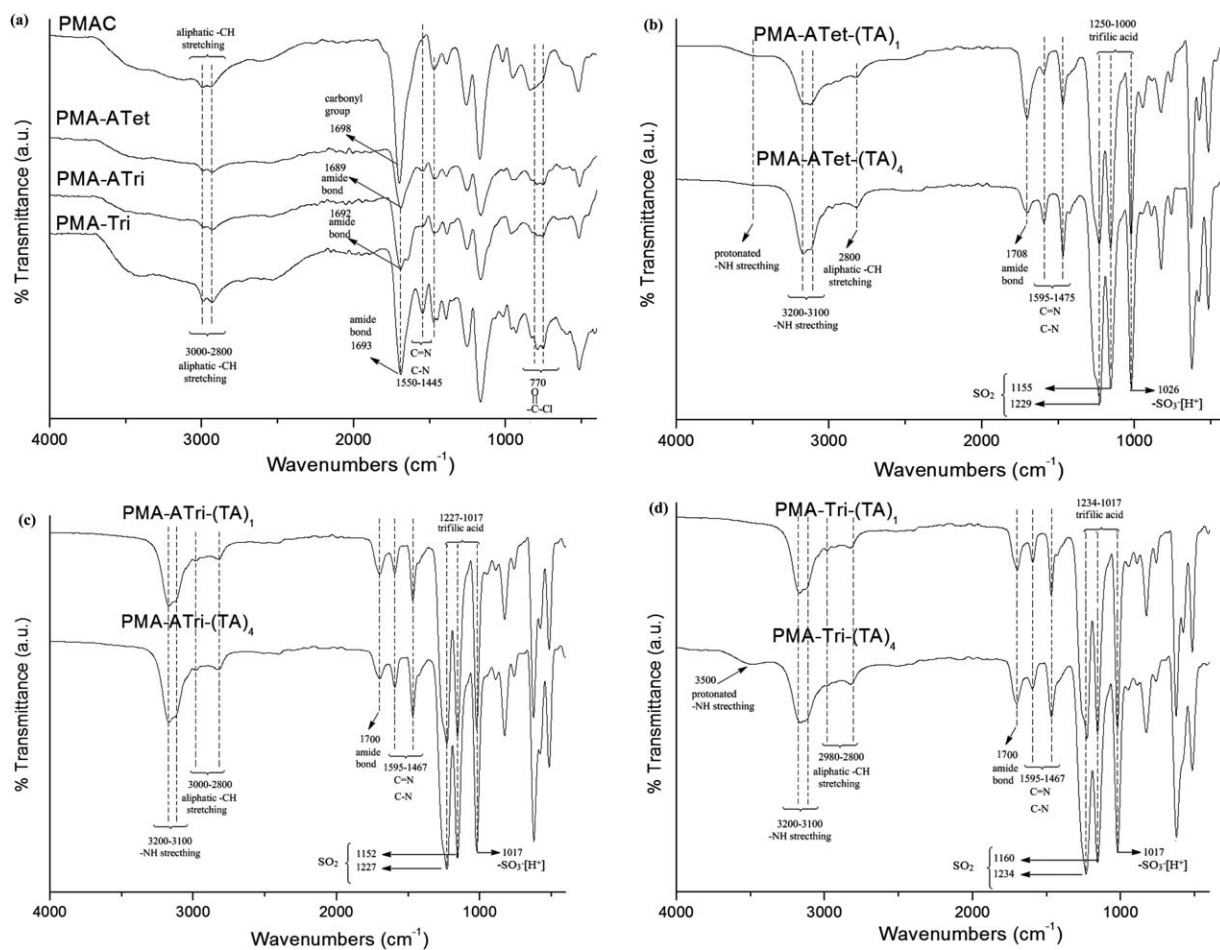


Figure 3. FTIR spectra of (a) PMAC, PMA-ATet, PMA-ATri and PMA-Tri, (b) PMA-ATet-(TA)₁ and PMA-ATet-(TA)₄, (c) PMA-ATri-(TA)₁ and PMA-ATri-(TA)₄, (d) PMA-Tri-(TA)₁ and PMA-Tri-(TA)₄.

2.0, and 4.0) under inert atmosphere at a scan rate of 10°C / min, respectively. The second heating curves were evaluated. The glass transition temperature, T_g of the homopolymer is measured at approximately 120°C. While the tetrazole functional polymer, PMA-ATet, has a T_g of 98°C. The glass transition temperatures of PMA-ATet-(TA)₁, PMA-ATet-(TA)₂, and PMA-ATet-(TA)₄ were shifted to 79°C, 67°C, and 56°C, respectively. While the aminotriazole functional polymer, PMA-ATri, has a T_g of 107°C. The glass transition temperatures of PMA-ATri-(TA)₁, PMA-ATri-(TA)₂, and PMA-ATri-(TA)₄ were shifted to 78°C, 74°C, and 66°C, respectively. Also, triazole functional polymer has a T_g of 112°C. The glass transition temperatures of PMA-Tri-(TA)₁, PMA-Tri-(TA)₂, and PMA-Tri-(TA)₄ were shifted to 96°C, 91°C, and 84°C, respectively. Clearly, the T_g values indicate a pronounced effect of the TA content on the softening behavior of the materials. The presence of single T_g confirms the homogeneity of the materials.

Proton Conductivity

The proton conductivity studies of the samples were performed using a Novocontrol dielectric-impedance analyzer. For conductivity measurements, the samples were sandwiched between platinum blocking electrodes and measurements were performed at 20–150°C temperature range and in the frequency range 1–3

MHz at 10°C intervals. The AC conductivities, $\sigma_{ac}(\omega)$ of the polymers were measured at several temperatures using impedance spectroscopy. Frequency dependent AC conductivities ($\sigma_{ac}(\omega)$) were measured using the following equation;

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \varepsilon''(\omega)\omega\varepsilon_0$$

where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ is the angular frequency, ε_0 is the vacuum permittivity ($\varepsilon_0 = 8.852 \times 10^{-14}$ F/cm), and ε'' is the imaginary part of complex dielectric permittivity (ε^*). The proton conductivities of anhydrous nano-composite polymer electrolytes were measured from 20°C to 150°C.

The DC conductivity (σ_{dc}) of the samples was derived from the plateaus of log scale σ_{ac} versus frequency (F) curves by linear fitting plateau regions and extrapolating to zero frequency of the data. A marked curvature is observed for all samples and the curves are interpreted with the Vogel-Tamman-Fulcher (VTF) equation:

$$\log \sigma = \log \sigma_o - E_v / [k(T - T_o)]$$

where σ_o is the conductivity at infinite temperature, E_v is the Vogel activation energy, and T_o is the Vogel temperature.

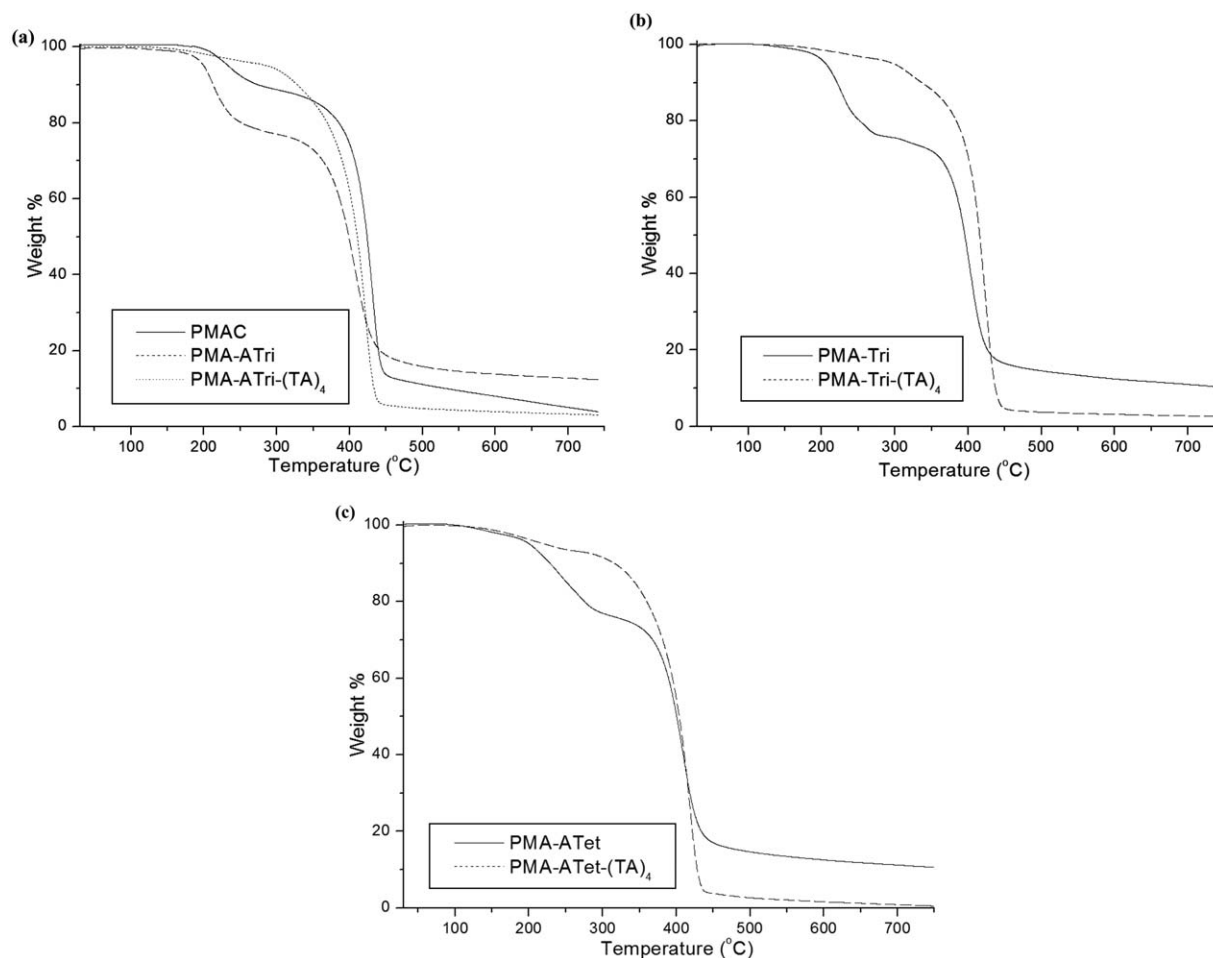


Figure 4. Thermogravimetry (TG) Analysis of methacrylate based azole functional polymers under nitrogen atmosphere at a heating rate of 10°C/min. (a) PMAC, PMA-ATri and PMA-ATri-(TA)₄, (b) PMA-Tri and PMA-Tri-(TA)₄, (c) PMA-ATet and PMA-ATet-(TA)₄.

The direct current (DC) conductivities of the triflic acid-doped PMA-ATri, PMA-Tri, and PMA-ATet which were derived from impedance plots are compared in Figure 5(a–c). The conductivity

isotherm illustrates that the DC conductivity strongly depends on temperature and the doping ratio of triflic acid. In the anhydrous conditions, the highest proton conductivities were obtained for TA

Table II. T_g and Proton Conductivity Values of Azole Containing Polymers

Sample name	Polymer-(TA) ratio	T_g (°C)	Max. proton conductivity (S cm ⁻¹)
PMAC	-	120°C	-
PMA-Tri	-	112°C	-
PMA-ATri	-	107°C	-
PMA-ATet	-	98°C	-
PMA-Tri-(TA) ₁	1 : 1	96°C	0.004 S cm ⁻¹ at 150°C
PMA-Tri-(TA) ₂	1 : 2	91°C	0.007 S cm ⁻¹ at 150°C
PMA-Tri-(TA) ₄	1 : 4	84°C	0.02 S cm ⁻¹ at 150°C
PMA-ATri-(TA) ₁	1 : 1	78°C	1.5 × 10 ⁻⁴ S cm ⁻¹ at 150°C
PMA-ATri-(TA) ₂	1 : 2	74°C	4.8 × 10 ⁻⁴ S cm ⁻¹ at 150°C
PMA-ATri-(TA) ₄	1 : 4	66°C	8.7 × 10 ⁻⁴ S cm ⁻¹ at 150°C
PMA-ATet-(TA) ₁	1 : 1	79°C	0.008 S cm ⁻¹ at 150°C
PMA-ATet-(TA) ₂	1 : 2	67°C	0.009 S cm ⁻¹ at 150°C
PMA-ATet-(TA) ₄	1 : 4	56°C	0.01 S cm ⁻¹ at 150°C

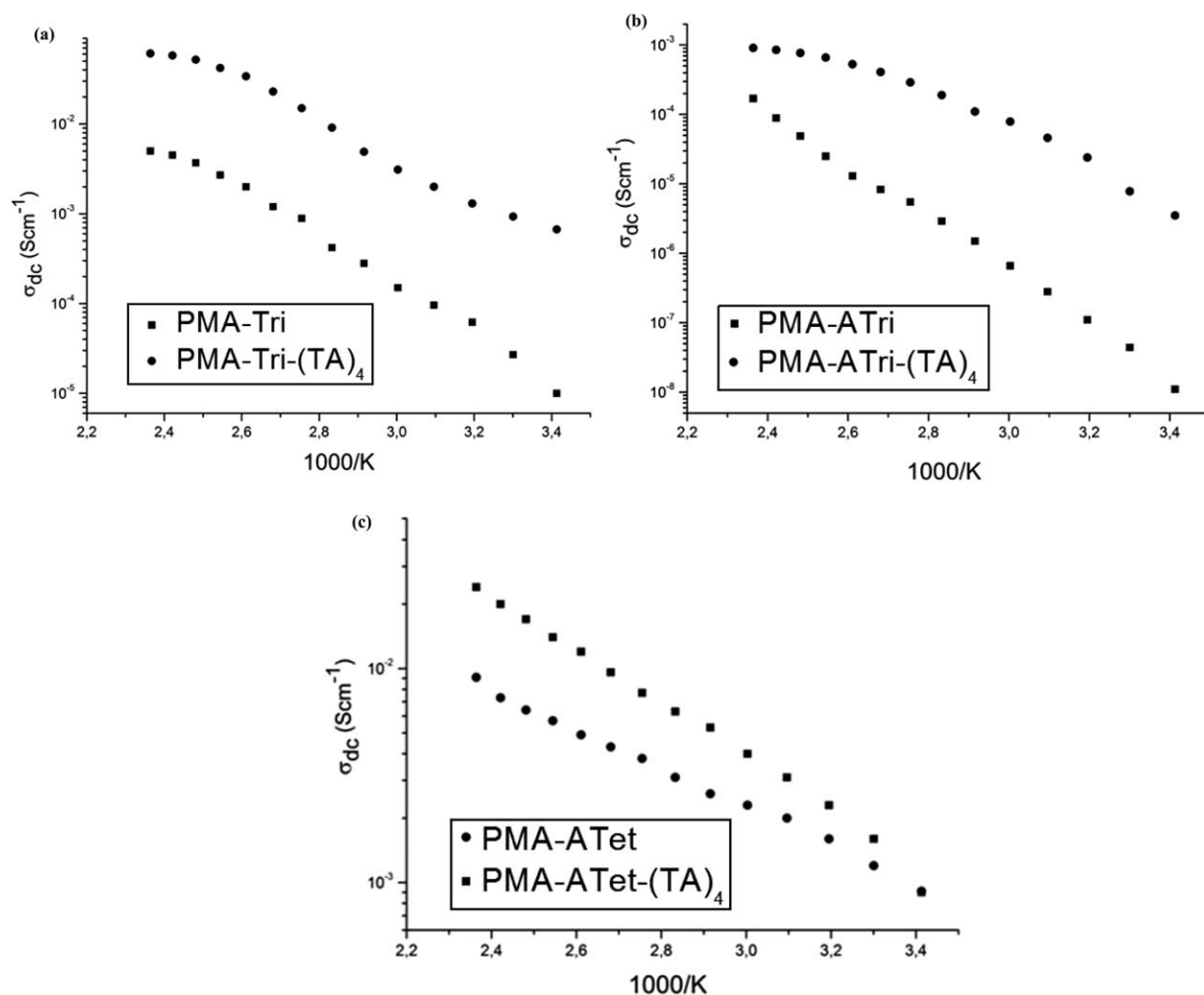


Figure 5. DC conductivity measurements of (a) PMA-Tri-(TA)_x ($x = 1$ and 4), (b) PMA-ATri-(TA)_x ($x = 1$ and 4), (c) PMA-ATet-(TA)_x ($x = 1$ and 4) as a function of reciprocal temperature.

ratio of 4. PMA-Tri-(TA)₄, PMA-ATri-(TA)₄, and PMA-ATet-(TA)₄ membranes gave maximum conductivities of 0.02 S cm^{-1} , $8.7 \times 10^{-4} \text{ S cm}^{-1}$, and 0.01 S cm^{-1} at 150°C , respectively. In the azole functional polymer/acid systems, acid ratio plays a crucial role in proton conductivity. Çelik et al. showed that the proton conductivity decreased as the triflic acid ratio became lower, which was explained with an aggregation scheme of the azole units in the polymer matrix¹⁸. In a similar work, Aslan et al. investigated effect of the TA ratio on azole functional polymers and the proton conductivity reached to 0.012 S cm^{-1} at 80°C .²⁶

Triazole and tetrazole units are promising heterocycles whose molecular structures are similar to imidazole and therefore may conduct protons via structure diffusion mechanism.^{1,6,27} The high conductivities attained for highly doped PMA-Tri, PMA-ATri, and PMA-ATet host matrices imply that conductivity in such systems occurs predominantly via the Grotthuss mechanism. Also tetrazole and triazole are promising in that respect where their basic nitrogen sites act as strong proton acceptors with respect to the acid group in the membranes, thus forming proton charge carriers.²⁸ The proton could travel between protonated azole units and sulfonic acid units of TA.

CONCLUSIONS

In this work, we have prepared methacrylate and methacrylamide based novel proton-conducting polymers. The pristine polymer (PMAC) was prepared by free radical polymerization of methacryloyl chloride and then it was chemically modified with ATet, ATri, Tri, respectively. Elemental analysis showed that PMAC was modified with ATet, ATri, and Tri yielding 41%, 48%, and 38% functionalization, respectively. The structure was confirmed by FTIR and ¹³C-NMR spectroscopy. The functional polymers were doped with TA at several stoichiometric ratios. TG analysis showed that the samples were thermally stable up to $\sim 200^\circ\text{C}$. DSC results illustrated both the homogeneity of the materials and the plasticizing effect of the dopant. The proton conductivity increased with dopant concentration and temperature. At 150°C and anhydrous conditions, PMA-ATet-(TA)₄ and PMA-Tri-(TA)₄ showed maximum proton conductivities of 0.01 S cm^{-1} and 0.02 S cm^{-1} , respectively.

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REFERENCES

1. Celik, S. U.; Bozkurt, A. *Electrochim. Acta* **2011**, *56*, 5961.
2. Bae, B.; Kim, D. *J. Membr. Sci.* **2003**, *220*, 75.
3. Manthiram, Y. F. A.; Guiver, M. D. *Electrochem. Commun.* **2006**, *8*, 1386.
4. Mehta, V.; Cooper, J. S. *J. Power Sources* **2003**, *114*, 32.
5. Shen, Y.; Xi, J.; Qiu, X.; Zhu, W. *Electrochim. Acta* **2007**, *52*, 6956.
6. Celik, S. U.; Bozkurt, A.; Hosseini, S. S. *Prog. Polym. Sci.* **2012**, *37*, 1265.
7. Yamada, M.; Honma, I. *Polymer* **2005**, *46*, 2986.
8. Liu, Y.; Yu, Q.; Wu, Y. *J. Phys. Chem. Solids* **2007**, *68*, 201.
9. Guhathakurta, S.; Min, K. *Polymer* **2009**, *50*, 1034.
10. Göktepe, F.; Bozkurt, A.; Günday, S. T. *Polym., Int.* **2008**, *57*, 133.
11. Ozden, S.; Celik, S. U.; Bozkurt, A. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 4974.
12. Sen, U.; Celik, S. U.; Ata, A.; Bozkurt, A. *Int. J. Hydrogen Energy* **2008**, *33*, 2808.
13. Kim, J. D.; Mori, T.; Hayashi, S.; Honma, I. *Electrochem. Soc.* **2007**, *154*, A290.
14. Boroglu, M. S.; Celik, S. U.; Bozkurt, A.; Boz, I. *J. Membr. Sci.* **2011**, *375*, 157.
15. Ozden, S.; Celik, S. U.; Bozkurt, A. *Electrochim. Acta* **2010**, *55*, 8498.
16. Li, W.; Manthiram, A.; Guiver, M. D.; Liu, B. *Electrochem. Commun.* **2010**, *12*, 607.
17. Celik, S. U.; Bozkurt, A. *Eur. Polym. J.* **2008**, *44*, 213.
18. Celik, S. U.; Akbey, U.; Bozkurt, A.; Graf, R.; Spiess, H. W. *Macrom. Chem. Phys.* **2008**, *209*, 593.
19. Shin, J. A.; Lim, Y. G.; Lee, K. H. *Bull. Korean Chem. Soc.* **2011**, *32*, 547.
20. Pu, H.; Ye, S.; Wan, D. *Electrochim. Acta* **2007**, *52*, 5879.
21. Igrunova, A. V.; Sirotkin, N. V.; Uspenskaya, M. V. *Russ. J. Appl. Chem.* **2001**, *74*, 818.
22. Kizhnyayev, V. N.; Vereshchagin, L. I. *Russ. Chem. Rev.* **2003**, *72*, 143.
23. Stroehriegel, P. *Makromol. Chem.* **1993**, *194*, 363.
24. Levchik, S. V.; Ivashkevich, G. A.; Balabanovich, A. I.; Lesnikov, A. I.; Gaponik, P. N.; Costa, L. *Thermochim. Acta* **1992**, *207*, 115.
25. Bozkurt, A. *Turk. J. Chem.* **2005**, *29*, 117.
26. Aslan, A.; Celik, S. U.; Sen, U.; Haser, R.; Bozkurt, A. *Electrochim. Acta* **2009**, *54*, 2957.
27. Li, S.; Zhou, Z.; Zhang, Y.; Liu, M. *Chem. Mater.* **2005**, *17*, 5884.
28. Kreuer, K. D.; Fuchs, A.; Ise, M.; Spaeth, M.; Maier, J. *Electrochim. Acta* **1998**, *43*, 1281.