

# Photo-Induced Protonation and Conductivity of Polyaniline/ Poly(ethylene glycol) and Polyaniline/[Poly(ethylene glycol)-grafted Polyaniline] Composites

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**ABSTRACT:** Composites of polyaniline in its emeraldine base form (PANI-EB) and photo-acid generators (PAG) show an increase in conductivity upon photo-irradiation due to the protonation of PANI-EB. Such materials may be utilized to fabricate conducting patterns by photo-irradiation. However, the conductivity obtained by direct irradiation of PANI-EB/PAG composites was normally quite low ( $<10^{-3}$  S/cm) due to aggregation of highly loaded PAG. In this work, poly(ethylene glycol) (PEG), which is a proton transfer polymer, was added to PANI-EB/PAG. Results showed that addition of low  $M_w$  (550) PEG significantly enhance the photo-induced conductivity. Conductivities as high as  $10^{-1}$ – $10^0$  S/cm were observed after photo-irradiation. This conductivity is comparable to that of PANI-salt synthesized by oxidizing aniline in the presence of an acid. High  $M_w$  (8000) PEG is much less effective than PEG 550, which is attributed to its lower compatibility with PANI. PEG-grafted PANI (N-PEG-PANI) was also studied as an additive. Composites of PANI-EB and N-PEG-PANI showed conductivity as high as  $10^2$  S/cm after treatment with HCl vapor. The photo-induced conductivity of the N-PEG-PANI/PANI-EB/PAG composite reached  $10^{-2}$ – $10^{-1}$  S/cm. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3546–3550, 2013

**KEYWORDS:** conducting polymers; photochemistry; composites

Received 5 November 2012; accepted 2 February 2013; published online 28 February 2013

**DOI:** 10.1002/app.39122

## INTRODUCTION

Polyaniline (PANI) is a conducting polymer discovered in the late 19th century.<sup>1</sup> PANI has been of great interest to scientists for the past few decades due to the ease of synthesis, low cost, tunable properties and good stability. It has been studied for a wide variety of electrical devices and functional materials,<sup>2–5</sup> such as novel biosensors<sup>6,7</sup> and energy storage.<sup>8</sup> The oxidation and protonation state dictate PANI's electrical conductivity. The insulating emeraldine base (EB) form of PANI becomes conductive when protonated. The conductivity can be as high as  $10^2$  S/cm.<sup>9–11</sup>

Composites of photo-acid generators (PAGs)<sup>12–18</sup> and PANI-EB has been of interest for photo patterning since early 90s.<sup>19–26</sup> When irradiated the PAG produces a Bronsted acid that can protonate the insulating PANI-EB to the conductive salt form.<sup>19–21</sup> However, conductivities of the composites made of PANI and PAG have been limited to  $\sim 10^{-4}$ – $10^{-6}$  S/cm after irradiation.<sup>23,27</sup> Only after vapor doping with HCl have conductivities higher than  $10^{-3}$  S/cm been observed. Strong acid treatments not only add a processing step, but also may be harmful to other parts of the devices. Therefore, the most desirable pro-

cess to achieve high conductivities is to use photo-irradiation alone. Our group recently reported that poly(vinyl alcohol) (PVA) is an effective additive that improves photo-induced conductivity and reproducibility. Conductivity of the composites of PANI-EB, PAG, and PVA increased from  $<10^{-9}$  S/cm to  $10^{-3}$ – $10^{-2}$  S/cm after irradiation.<sup>26</sup> The enhanced conductivity was attributed to a hydrogen bonding network of PVA and PANI.<sup>28</sup> Herein, we report that conductivity of  $10^{-1}$ – $10^0$  S/cm can be achieved using low molecular weight poly(ethylene glycol) (PEG) as the additive. This conductivity is comparable to that of PANI-salt synthesized by oxidizing aniline in the presence of an acid.

## EXPERIMENTAL

### Materials Characterization

PANI-EB ( $M_w = 20,000$ ), triphenylsulfonium triflate, PEG methyl ether tosylate and PEG monomethyl ether (PEG  $M_w$  550) were purchased from Aldrich. PEG 8000 was purchased from Fisher. All of the solvents were used without further purification. Film thickness was measured by a profilometer. ATR-IR spectroscopy was conducted on a Perkin Elmer Spectrum One spectrometer equipped with a Universal ATR Sampling

Accessory (single reflection, Diamond/ZnSe). IR spectra were collected in a range of 1000–4000  $\text{cm}^{-1}$  with resolution of 1 datum every 2  $\text{cm}^{-1}$ . Elemental analysis was conducted at Micro-Analysis Inc., Wilmington, DE.

### Preparation and Irradiation of the Thin Films

PANI and PEG were dissolved in *N*-methylpyrrolidinone (NMP) and mixed with a solution of triphenylsulfonium triflate (PAG) in NMP. The overall solid to solvent ratio (weight) was  $\sim 1 : 10$ . The resulting solution was filtered through cotton. Thin films of the composites were prepared by spin casting on glass substrates with gold electrodes. Each thin film was placed in a vacuum oven at room temperature for 24 h to remove the solvent. The average film thickness was  $\sim 1 \mu\text{m}$ , which was measured by a profilometer. These samples were irradiated in a RPR-100 Photochemical reactor equipped with 254 nm UV lamps. The conductivity before and after irradiation was measured by *I*-*V* scan using a Keithley 2400 source meter. Given that the conductivity of the materials is relatively low and the major application of this type of material is patterning conducting circuits on thin films, *I*-*V* scan is a suitable method. Some samples were tested using the four point probe method. The conductivities of these samples were in the same order of magnitude as the values obtained by *I*-*V* scan.

### Syntheses of PEG Grafted PANI Derivatives

The PEG grafted PANI derivatives were synthesized following literature procedures with some modifications.<sup>29,30</sup> PANI-EB (50 mg) was reacted with (20 mg) sodium hydride in (5 mL) anhydrous dimethyl sulfoxide and allowed to stir for 6 h at 45°C. One molar equivalents of PEG methyl ether tosylate [PEG(1000)tosylate] was added and allowed to stir at room temperature overnight. The product was precipitated out using a brine solution and washed several times with water and dried overnight. Elemental analysis: %C: 56.7, %H: 7.32, %N: 4.88.

## RESULTS AND DISCUSSION

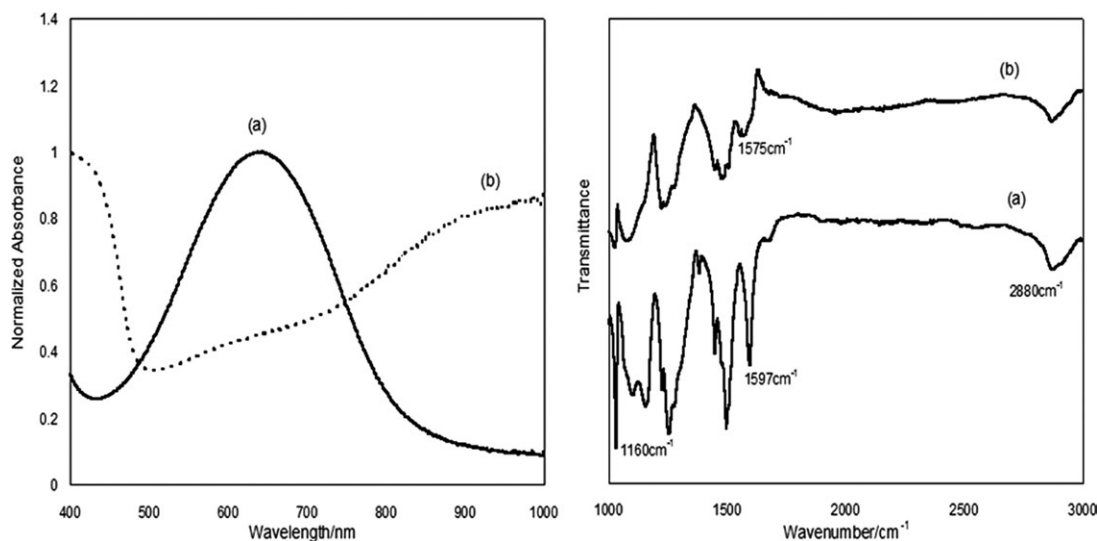
Composites of PANI-EB/PAG often result in low increases in conductivity upon photo-irradiation. The main factors that cause low conductivities are low proton transfer efficiency from the PAG to the PANI-EB and film quality. In a previous study, we found that adding PVA can increase the final conductivity by introducing a hydrogen bonding network that assist proton transfer and by improving film quality.<sup>26,28</sup> This work shows that addition of proton transfer polymer to PANI/PAG is an effective way of improving conductivity. Polyethylene glycol (PEG) is a well-known cationic conducting polymer and has been used for protonic conduction.<sup>31–34</sup> The weak basic ether groups of PEG can bind to protons. Protons can move from the binding oxygen to an adjacent ether oxygen and/or to the oxygens on a nearby chain segment. If there is sufficient segmental mobility the proton can migrate downfield with an applied external field.<sup>35</sup> Therefore, PEG may have the ability to increase the efficiency of protonating PANI with a PAG by increasing the mobility of the proton from the PAG. It should also be noted that PEG is commonly added as a plasticizer to avoid phase separation due to hydrogen bonding with the glycol groups.<sup>31,36–38</sup>

In this work, composites of PANI-EB, PAG and PEG were studied first. The PAG chosen for these studies was triphenylsulfonium triflate ( $\text{Ph}_3\text{S}^+ \text{OTf}^-$ ) because of its high quantum yield of 50%.<sup>39</sup> Theoretically to achieve maximum conductivity, at least 0.5 molar equivalents of PAG to the aniline unit of PANI-EB must be added. However, at this ratio the weight of the PAG is more than that of the PANI-EB. The heavily loaded low  $M_w$  PAG tends to form macrophases, which lowers the film quality, reproducibility as well as the photo-induced conductivity.<sup>23</sup> Previous work by Chiang and MacDiarmid showed that the conductivity does not increase significantly when the protonation of PANI increases from 25 to 50%.<sup>11</sup> We found that lowering the molar ratio of PAG : PANI-EB to 25% significantly improved the film quality and reproducibility, and in most cases gave higher photo-induced conductivity than the samples with 50% ratio (molar ratio of the polymers mentioned in this article refers to that of the corresponding monomers).

The effects of PEG with different  $M_w$  were studied by adding different ratios of PEG to a fixed 4 : 1 molar ratio of PANI-EB : PAG. Low molecular weight PEG ( $M_w = 550$ ) is a viscous liquid. However, thin films with good quality and stability in air can be prepared from NMP solutions of the PEG, PANI-EB, and PAG. No pasty form was observed even when the weight ratio of PEG : PANI-EB is as high as 1 : 1. SEM did not show any clear feature of phase separation. These results indicate that the low  $M_w$  PEG has good compatibility with PANI-EB, which, as described in the IR analysis below, is at least partially due to the hydrogen bonding between PEG and PANI-EB.

Five different weight ratios of PEG550 : PANI-EB (1 : 10, 1 : 6, 1 : 4, 1 : 2, and 1 : 1) were tested and the thin-film conductivity of the materials was studied. They all have very low conductivity ( $< 10^{-9}$  S/cm) before irradiation. After irradiation at 254 nm, samples with 1 : 10 ratio showed conductivity of  $10^{-4}$ – $10^{-3}$  S/cm, which is not substantially different from the composite with no PEG. When the ratio was increased to 1 : 6, the conductivity significantly increased to  $10^{-2}$  S/cm. Samples with a ratio of 1 : 4 had the conductivity in the same range as that of 1 : 6. Samples with a ratio of 1 : 2 gave the best result, which was  $10^{-1}$ – $10^0$  S/cm after irradiation. The photo-induced conductivity is comparable to the conductivity of common PANI-salt synthesized by oxidizing aniline in the presence of an acid. The value is also approximately two orders of magnitude higher than that of the previously reported composite with PVA as the proton transfer additive.<sup>26</sup> A high PEG loading with 1 : 1 ratio resulted in significant decrease of conductivity, which was  $10^{-4}$ – $10^{-3}$  S/cm. After irradiation, the conductivity of the films was quite stable at ambient temperature and humidity in air. It was in the same order of magnitude after months.

The color of the thin film showed obvious signs of protonation of the PANI-EB by changing from blue before irradiation to green after irradiation. A UV spectrum of the PANI-EB/PAG/PEG mixture shows the characteristic peaks of PANI in EB form before irradiation with a peak at 650 nm attributed to an intermolecular and/or intramolecular charge-transfer process from the benzenoid to quinoid ring. After the thin film was irradiated with 254 nm light this peak at 650 nm disappeared indicating



**Figure 1.** UV-Vis (left) and ATR-IR (right) spectra of a PEG550/PANI-EB/PAG thin film (PEG550 : PANI-EB = 1 : 2). (a) Before irradiation and (b) after irradiation at 254 nm.

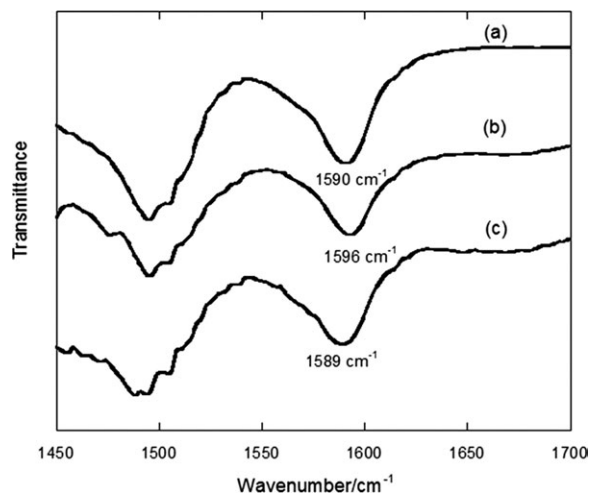
the absence of the exciton in the polaron lattice formed with protonation of the imino groups.<sup>40</sup> (Figure 1) Two new absorption bands appeared with the short-wavelength one centered at  $\sim 400$  nm and the long-wavelength one above 800 nm. These absorption bands are due to the polaron- $\pi^*$  and  $\pi$ -polaron transition.<sup>41</sup>

ATR-IR spectroscopy was used to study the hydrogen bonding and the proton transfer in the material (Figures 1 and 2). The peak at  $1258\text{ cm}^{-1}$  appears due to the partial overlap of C—N stretching vibration from the PANI and the methyl end of the PEG chain. A new peak appears at  $2880\text{ cm}^{-1}$  also representing the C—H stretch of the PEG chain. A peak at  $1160\text{ cm}^{-1}$  is attributed to the ether bonds of the PEG. The characteristic peak located around  $1590\text{ cm}^{-1}$  represents the quinoidal ring stretches of C=C and C=N. The hydrogen bonding and proton transfer occurs on the quinoidal nitrogen should affect this peak the most. A film of PANI-EB alone showed a peak of  $1590\text{ cm}^{-1}$ , which shifted slightly to  $1596\text{ cm}^{-1}$  with the addition of PEG. This slight shift is similar to the shift of  $6\text{ cm}^{-1}$  that was observed with the addition of methanol to PANI, which was attributed to the hydrogen bonding.<sup>42,43</sup> Therefore, the  $6\text{ cm}^{-1}$  observed in this work is attributed to the hydrogen bonding between PANI and the hydroxyl ends of PEG. Once the composite thin film was irradiated, a classic shift to  $1575\text{ cm}^{-1}$  was observed indicating the protonation of PANI.<sup>44</sup>

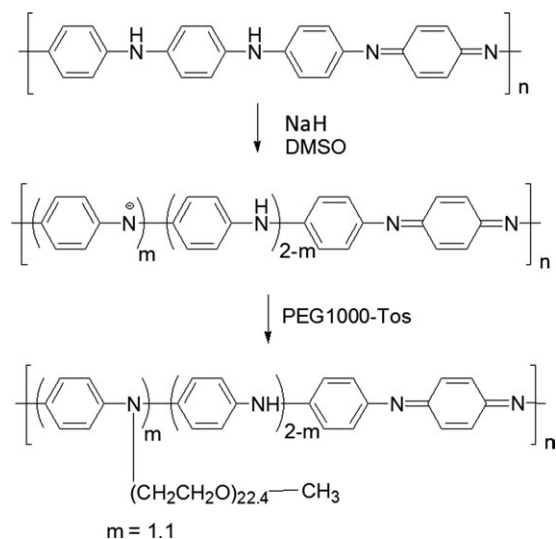
PEG with a  $M_n$  of 8000 was also studied as a proton transfer additive. Thin films of PANI-EB/PAG/PEG 8000 were prepared, in which the ratio of PEG : PANI was 0.5. After irradiation with 254 nm UV light, the conductivity was  $10^{-3}$ – $10^{-2}$  S/cm which is much lower than that of the composite with low- $M_w$  PEG. It is well known that ion mobility in polymers is related to the segmental motions of the polymer.<sup>31,35,45</sup> Chains of the High- $M_w$  PEG are expected to be less mobile in the thin film than that of the low- $M_w$  PEG, which may lower the proton transfer efficiency. In addition, we noted that the film quality and reproducibility of the composite with PEG 8000 are worse than both

the composite with PEG 550 and the composite with PVA, which indicate that the compatibility between PEG 8000 and PANI-EB is not good. As described above, compatibility between PEG and PANI relies on the hydrogen bonding between them. Hydrogen bonding between the hydroxyl ends of PEG and the imino groups of PANI is much stronger than the one between the ether groups of PEG and the amino groups of PANI. PEG 550 has  $\sim 15$  times more hydroxyl groups than PEG 8000, which makes it more compatible with PANI, and thus a better proton transfer additive. In fact, IR of the PEG 8000/PANI-EB composite did not show any positive shift of the quinoidal ring stretch at  $1590\text{ cm}^{-1}$  in contrast to that of PEG 550/PANI-EB (Figure 2).

Previous studies have shown that grafting short PEG chains to a polymer can increase its ion conductivity.<sup>31,35,46,47</sup> Grafting PEG to PANI can avoid the potential compatibility issue.<sup>29,31</sup>



**Figure 2.** ATR-IR spectra of (a) PANI-EB, (b) PANI-EB/PEG 550, and (c) PANI-EB/PEG8000 thin films.



**Scheme 1.** Synthesis of PEG grafted PANI.

Therefore, a PEG grafted PANI was synthesized by attaching short PEG chains ( $M_n$  1000) to the nitrogen atoms of PANI-EB (*N*-PEG-PANI) following a literature method. The only modification is that PEG(1000) tosylate instead of PEG halide was used due to availability. A 1 : 1 molar ratio of PANI(aniline unit) : PEG(1000)tosylate was used in the synthesis of this *N*-PEGPANI. The synthesized polymer has an oxygen/nitrogen ratio of 6.37 based on elemental analysis, which indicated that approximate 1.1 out of every four nitrogen in the PANI was linked to a PEG chain (Scheme 1). To estimate the maximum conductivity of the polymer after being fully protonated, thin films of the polymer were treated with HCl vapor. Consistent with previous reports the doped *N*-PEGPANI showed a lower conductivity than PANI salt.<sup>29,48,49</sup> After vapor doping with HCl, the conductivity of *N*-PEGPANI was only  $10^{-2}$  S/cm. However, when the *N*-PEG-PANI polymer was mixed with PANI-EB at a weight ratio of 1 : 2, the composite showed a conductivity as high as  $10^2$  S/cm after treatment with HCl vapor. Therefore, thin films of PANI-EB/PAG/*N*-PEG-PANI composite were prepared for studying photo-induced conductivity. The weight ratio of PANI-EB : *N*-PEG-PANI was 2 : 1 and the molar ratio of PANI-EB : PAG was 2 : 1. After irradiation at 254 nm, a change in conductivity from  $<10^{-9}$  S/cm to  $10^{-2}$ – $10^{-1}$  S/cm was achieved. Although the value is relatively high, it is lower than that of the composite with PEG 550. Given that *N*-PEG-PANI can also be protonated, we doubled the amount of PAG in the composite. However, the photo-induced conductivity was lowered by approximately an order of magnitude, which is attributed to phase separation of the heavily loaded PAG.

## CONCLUSIONS

This work shows that addition of low- $M_w$  PEG to PANI-EB/PAG can significantly increase the photo-induced conductivity to  $10^{-1}$ – $10^0$  S/cm without post-treatment with HCl. The improvement could be due to both good proton transfer ability of PEG and good compatibility between low- $M_w$  PEG and PANI-EB. PEG grafted PANI-EB can also be used as an effective additive. The

high conductivity ( $10^2$  S/cm) of the HCl-vapor doped PANI-EB/*N*-PEG-PANI composite indicates that this is a promising system. Although the photo-induced conductivity of PANI-EB/PAG/*N*-PEG-PANI composite is lower than that of PANI-EB/PAG/PEG550, the system may be improved by developing PAGs with better compatibility, which will be explored in the future.

## ACKNOWLEDGMENTS

Supports from Air Force Office of Scientific Research (FP048956-A) and National Science Foundation Polymers Program are gratefully acknowledged.

## REFERENCES

1. Letheby, H. *J. Chem. Soc. Trans.* **1862**, 15, 161.
2. Zhang, J.; Kong, L.; Wang, B.; Luo, Y.; Kang, L. *Synth. Met.* **2009**, 159, 260.
3. Crompton, R. *Popular Plast. Packaging.* **2011**, 56, 27.
4. Moriuchi, T. *Acc. Chem. Res.* **2012**, 45, 347.
5. Bendrea, A.-D. *J. Biomater. Appl.* **2011**, 26, 3.
6. (a) Virji, S.; Fowler, J. D.; Baker, C. O.; Huang, J.; Kaner, R. B.; Weiller, B. H. *Small* **2005**, 1, 624.
7. Nemzer, L.; Schwartz, A.; Epstein, A. J. *Macromolecules* **2010**, 43, 4324.
8. Murugan, A.; Muraliganth, T.; Manthiram, A. *Chem. Mater.* **2010**, 22, 2692.
9. Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, 48, 91.
10. Lee, K.; Cho, S.; Park, S.-H.; Heeger, A. J.; Lee, C.-W.; Lee, S.-H. *Nature* **2006**, 441, 65.
11. Chiang, J. C.; MacDiarmid, A. G. *Synth. Met.* **1986**, 13, 193.
12. Crivello, J. V. *J. Photopolym. Sci. Technol.* **2009**, 22, 575.
13. Crivello, J. V. *J. Photopolym. Sci. Technol.* **2008**, 21, 493.
14. Ivan, M. G.; Scaiano, J. C. *Photochem. Photophys. Polym. Mater.* **2010**, 479.
15. Ito, H. *J. Poly. Sci. A: Poly. Chem.* **2003**, 41, 3863.
16. Stewart, M. D.; Tran, H. V.; Schmid, G. M.; Stachowiak, T. B.; Becker, D. J.; Willson, G. C. *J. Vac. Sci. Technol. B.* **2002**, 20, 2946.
17. Postnikova, S. V.; Stewart, M. D.; Tran, H. V.; Nierode, M. A.; Medeiros, D. R.; Cao, T.; Byers, J.; Webber, S. E.; Wilson, G. C. *J. Vac. Sci. Technol. B.* **1999**, 17, 3335.
18. Jussila, Salme; Puustinen, Maria; Hassinen, Tomi; Olkkonen, Juuso; Sandberg, Henrik G. O.; Solehmainen, Kimmo. *Org. Electron.* **2012**, 13, 1308.
19. Lee, C. W.; Kim, Y. B.; Lee, S. H. *Chem. Mater.* **2005**, 17, 366.
20. Lee, C. W.; Seo, Y. H.; Lee, S. H. *Macromolecules* **2004**, 37, 4070.
21. Angelopoulos, M.; Shaw, J. M.; Lee, K. L.; Kam, L.; Huang, W. S.; Lecorre, M. A.; Tissier, M. *Polym. Eng. Sci.* **1992**, 32, 1535.
22. Salavagione, H.; Miras, M.; Barbero, C. *Macromol. Rapid Commun.* **2006**, 27, 26.

23. Venugopal, G.; Quan, X.; Johnson, G. E.; Houlihan, F. M.; Chin, E.; Nalamasu, O. *Chem. Mater.* **1995**, *7*, 271.
24. Falcao, E. L.; Azevedo, W. M. de. *Synth. Met.* **2002**, *128*, 149.
25. Salavagione, H. J.; Miras, M. C.; Barbero, C. J. *Am. Chem. Soc.* **2003**, *125*, 5290.
26. Shi, Z.; Johns, Valentine; Alber, C. Liao, Y. *Synth. Met.* **2011**, *161*, 1420.
27. Potje-Kamloth, K.; Polk, B. J.; Josowicz, M.; Janata, J. *Chem. Mater.* **2002**, *14*, 2782.
28. Foreman, J. P.; Monkman, A. P. *J. Phys. Chem. A.* **2003**, *107*, 7604.
29. Kang, E. T. *Chem Mater.* **2001**, *13*, 581.
30. Hwang, G.-W.; Wu, K.-Y.; Hua, M.-Y.; Lee, H.-T.; Chen, S.-A. *Synth. Met.* **1998**, *92*, 39.
31. Ratner, M. A.; Shriver, D. F. *Chem. Rev.* **1988**, *88*, 109.
32. Tang, Q. *J. Mater. Chem.* **2012**, *22*, 15836.
33. Shukur, M. F. *Adv. Res.* **2012**, *488–489*, 583.
34. Ibrahim, A. C. *New J. Chem.* **2012**, *36*, 1218.
35. Barker, R. E. *Pure Appl. Chem.* **1976**, *46*, 157.
36. Li, Y.; Wu, W.; Lin, F.; Xiang, A. *J. Appl. Polym. Sci.* **2012**, *126*, 162.
37. Hardy, C. L.; Shriver, D. F. *Macromolecules* **1984**, *17*, 975.
38. Hardy, C. L.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 3823.
39. Dektar, J. L.; Hacker, N. P. *J. Am. Chem. Soc.* **1990**, *112*, 6004.
40. Natesan, B.; Karan, N. K.; Katiyar, R. S. *Phys. Rev. E.* **2006**, *74*, 042801.
41. Quillard, S.; Berrada, K.; Louarn, G.; Lefrant, S.; Lapkowski, M.; Pron, A. *New J. Chem.* **1995**, *19*, 365.
42. Zhou, S.; Wu, T.; Kan, J. *Eur. Polym. J.* **2007**, *43*, 395.
43. Patil, R.; Roy, A. S.; Anilkumar, K. R.; Ekhelkar, S. *J. Appl. Polym. Sci.* **2011**, *121*, 262.
44. Entezami, A. Akbar. *Iran. Polym. J.* **2002**, *3*, 159.
45. Fuoss, R. M. *J. Am. Chem. Soc.* **1941**, *63*, 378.
46. Shiver, D. F. *J. Am. Chem. Soc.* **1984**, *106*, 6854.
47. Binks, A. E.; Sharples, A. *J. Polym. Sci. A2.* **1968**, *6*, 407.
48. Li, Z. F. *J. Colloid Interface Sci.* **2004**, *269*, 62.
49. Ma, H.; Guan, J.; Liu, N.; Lu, G.; Yuan, R. *Gaofenzi Xuebao.* **2006**, *1*, 92.