Asian Journal of Chemistry Vol. 22, No. 9 (2010), 7227-7234

Copolymerization of Aniline/Acrylonitrile Using Various Oxidants and Solutions

Bahareh Ghobadi Bistouni and Hossein Eisazadeh*
Faculty of Chemical Engineering, Babol Noshirvani University of Technology,
P.O. Box 484, Babol, Iran
Fax: (98)(111)3234201; E-mail: eisazadeh@hotmail.com; bahareh_ghobadi@yahoo.com

An inverted emulsion process was adopted to synthesize conducting copolymer of aniline and acrylonitrile using potassium persulfate, potassium dichromate and benzoyl peroxide as oxidizing agent in different solutions. The chemical structure and morphology of products were characterized by using fourier transform infrared spectroscopy and scanning electron microscope. The results indicate that the morphology, conductivity, homogeneity and particle size are dependent on the type of solution and oxidant. The intensity of peaks related to the type of solution and oxidant.

Key Words: Copolymerization, Aniline, Acrylonitrile.

INTRODUCTION

Polymers are generally used in a wide range of applications often for their low cost, light weight and mechanical properties or for the three characteristics combined. One of the main characteristics required for electrical and or/optical activities to occur in a polymer is a conjugated backbone which can be subject to oxidation or reduction by electron acceptors or donors. Due to delocalization of the π-electrons in conjugated polymers, chain rigidity is very often a predominant property and, as a result of this, an aggregated character of the chains is typical in such material.

This results in intractability which has been one of the drawbacks in the field. During the last decades there has been widespread interest in conducting polymers both for academic purposes and for potential applications. The insolubility in common solvents and infusibility of conducting polymers, in general, make them poorly processable either by solution technique or by melt processing methods[1,2].

Improvement of these material properties can be achieved either by forming copolymers or by forming conductive polymeric composites or blends with commercially available polymers or inorganic materials which offer better mechanical and optical properties, stability and processability[3-6].

From the beginning, interest in conducting polymers has it origins in the possible commercial applications of these materials. Foremost among the current commercial ventures are applications of conducting polymers in energy storage devices such as rechargeable batteries[7], conductive paint[8], removal of heavy metals[9,10], electromagnetic interference shieding[11] and biomedical applications[12], *etc.* Polyaniline has attracted considerable attention because of its unique electrical, optical and electrooptical properties and its numerous potential applications[13].

One of the key problems related to the potential applications of polyaniline is its processability. Processability is an important requirement in conducting polymers for their possible commercial use. Since most of the conducting polymers are not processable, much of the efforts made in this field have been directed towards circumventing this problem. To solve this problem, various approaches have been tried, including addition of side groups to the polymer backbone[14], grafting of polymers to a non-conducting polymer[15], direct polymerization of intractable polymers into the final desired shape, making a composite of blend of conducting polymers[16,17] and copolymerization[18].

In fiber industry, a few of the limitation of polyacrylonitrile due to its high melting point, high viscosity and poor thermal stability have been overcome by the fusion of acrylonitrile with acrylates and acetate through copolymerization technique[19-21].

On the other hand polyacrylonitrile is an outstanding engineering material generally used in textile applications owing to its good mechanical and thermal properties and is available cheaply. Summan[22] prepared polyacrylonitrile complexes with copper halides and studied their electrical conductivity at different temperatures. Lee *et al.*[23] have prepared polyacrylonitrile/polypyrrole composites by post polymerization of pyrrole on polyacrylonitrile matrix.

Park *et al.*[24] have prepared conducting polyaniline-polyacrylonitrile composite films by electrochemical polymerization technique. Electrochemical method has a merit of easy control of morphology and electrical properties of the resulting composites, but has a problem in mass production. Whereas the chemical method is more effective for a mass production of blends/composites or copolymers.

The oxidizing agent traditionally employed in the polymerization of aniline has been ammonium persulphate. The ammonium persulphate being a strong oxidizing agent and aniline polymerization being exothermic, controlling the reaction temperature is rather difficult.

In this study, aniline/acrylonitrile copolymer was prepared in aqueous and aqueous/non-aqueous solution by copolymerization of acrylonitrile and aniline using mixture of potassium dichromate/potassium persulfate and potassium dichromate/ benzoyl peroxide as an oxidant.

EXPERIMENTAL

A magnetic mixer model MK20, digital scale model FR 200, scanning electron microscope (SEM) model XL30 and fourier transform infrared (FTIR) spectrometer model Shimadzu 4100 were employed. A four-point probe method was used to measure the volume resistivity of conducting polymer films.

Materials used in this work were aniline, acrylonitrile, potassium persulfate, potassium dichromate, benzoyl peroxide, ethyl acetate and methanol. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Aniline monomer was purified by simple distillation.

Copolymer preparation: The reaction was carried out in an aqueous and aqueous/non-aqueous media respectively. The conditions for composite formation are summarized in the Table-1.

In a typical experiment 5 mL of acrylonitrile monomer was added to a stirred aqueous solution of 50 mL of sulfuric acid 1 M containing 1.5 g $K_2S_2O_8$ or benzoyl peroxide and heated to 70 ºC for 0.5 h. The solution was cooled using cold water for 10 min. Then 50 mL of sulfuric acid 1 M containing 1 g $K_2Cr_2O_7$ were added to stirred aqueous solution. After few minutes 1 mL aniline monomer was added to the stirred solution. The reaction was carried out at room temperature for 4 h. The product was filtered using filter paper and in order to separate the impurities and oligomers, the resultant product was washed several times with deionized water. It was then dried at room temperature.

RESULTS AND DISCUSSION

The electrical conductivity of various copolymers produced under different reaction conditions were measured on pressed pellets of the copolymer powders. The electrical conductivity of the compressed pellets was measured using four point probe method. As polyaniline is molecular composite containing a cationic polymer backbone, dopant must be incorporated for maintenance of charge neutrality.

As a result, it is expected that the chemical and physical properties of the doped polyaniline will be affected by dopant[25]. Particle size and electrical conductivity of nanocomposite are listed in Table-1. As can be seen, electrical conductivity is dependent on the type of oxidant and solution, since the polarity of solution and type of anion affect the conductivity of product.

TABLE-1
CONDITIONS FOR COPOLYMER FORMATION

Type of solution	Type of oxidant and concentration (g/L)	Average particle size (nm)	Electrical conductivity (S/cm)
Water	$K_2Cr_2O_7$ = 10 $K_2S_2O_8$ = 15	87	1.1×10^{-4}
Water/methanol (75/25 % v/v)	$K_2Cr_2O_7$ = 10 $K_2S_2O_8$ = 15	54	8.0×10^{-6}
Water/ethyl acetate (75/25 % v/v)	$K_2Cr_2O_7$ = 10 $K_2S_2O_8$ = 15	37	5.0×10^{-6}
Water/ethyl acetate (75/25 % v/v)	$K_2Cr_2O_7$ = 10 BPO = 15	61	3.2×10^{-5}

BPO = Benzoyl peroxide.

Morphology plays an important role in determining conductivity and mechanical properties of the materials, because electrical conductivity related to surface morphology. The morphology of the product was studied by using scanning electron microscope.

As can be seen by comparison between Figs. 1, 2 and Figs. 3, 4, particle size and homogeneity of particles are related to the type of solution and oxidant, because the chemical and physical properties of solution influence the rate of polymerization. As can be seen in figures the type of additives affect the homogeneity and size of particles, because ionic and non-ionic additive influence the physical and chemical properties of solution and rate of polymerization.

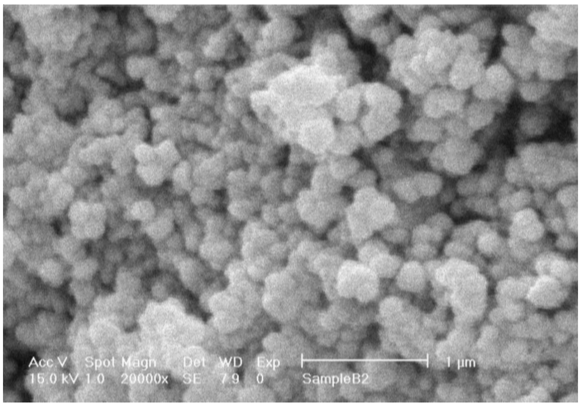

Fig. 1. Scanning electron micrograph of aniline/acrylonitrile copolymer generated in aqueous media. Reaction conditions: ($K_2Cr_2O_7$ = 10 g/L, $K_2S_2O_8$ = 15 g/L, aniline monomer 10.75 × 10^{-2} mol/L, acrylonitrile monomer 7.58 × 10^{-2} mol/L, volume of solution 100 mL, reaction time 4 h at room temperature)

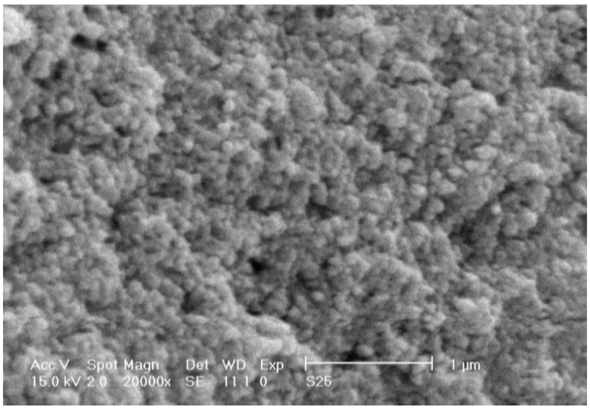

Fig. 2. Scanning electron micrograph of aniline/acrylonitrile copolymer generated in aqueous/ non-aqueous (water/methanol 75/25 % v/v) media. Reaction conditions: ($K_2Cr_2O_7$ = 10 g/L, $K_2S_2O_8$ = 15 g/L, aniline monomer 10.75 × 10^{-2} mol/L, acrylonitrile monomer 7.58 × 10^{-2} mol/L, volume of solution 100 mL, reaction time 4 h at room temperature)

Fig. 3. Scanning electron micrograph of aniline/acrylonitrile copolymer generated in aqueous/non-aqueous (water/ethyl acetate 75/25 % v/v) media. Reaction conditions: ($K_2Cr_2O_7$ = 10 g/L, $K_2S_2O_8$ = 15 g/L, aniline monomer 10.75 × 10^{-2} mol/L, acrylonitrile monomer 7.58 × 10^{-2} mol/L, volume of solution 100 mL, reaction time 4 h at room temperature)

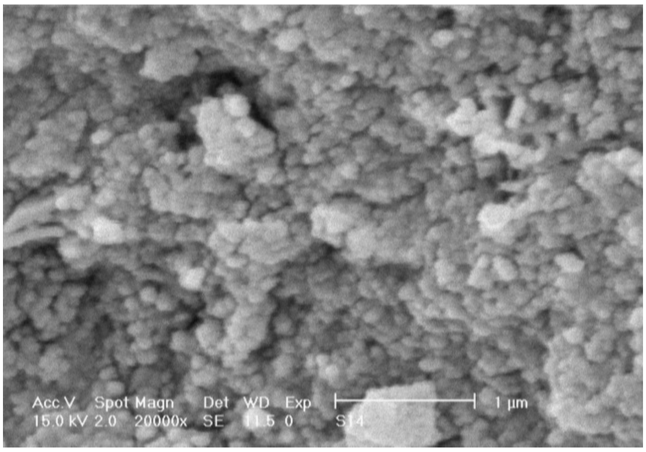

Fig. 4. Scanning electron micrograph of aniline/acrylonitrile copolymer generated in aqueous/non-aqueous (water/ethyl acetate 75/25 % v/v) media. Reaction conditions: ($K_2Cr_2O_7$ = 10 g/L, benzoyl peroxide = 15 g/L, aniline monomer 10.75 × 10^{-2} mol/L, acrylonitrile monomer 7.58 × 10^{-2} mol/L, volume of solution 100 mL, reaction time 4 h at room temperature)

Adsorption of the surface active agent on the aniline/acrylonitrile particles is primarily due to the hydrophobic component in the surfactants, probably *via* a hydrogen bonding mechanism with the aniline N-H group[26]. The chemical structures of the obtained products were determined by FTIR spectroscopy.

The FTIR spectra in the 2000-500 cm^{-1} region for aniline/acrylonitrile copolymer is shown in Figs. 5-7. As can be seen, the FTIR spectrum changes when the copolymer is formed by copolymerization. For instance, pure PAni (Fig. 5a) shows the presence of characteristic absorption bands at 1573 cm^{-1} (C=C stretching vibration of the quinoid ring), 1487 cm^{-1} (stretching vibration of C=C of the benzenoid ring), 1307 cm^{-1} (C-N stretching vibration), 1169 cm^{-1} (C-H in-plane deformation), 817 cm^{-1} (C-H out-of-plane deformation).

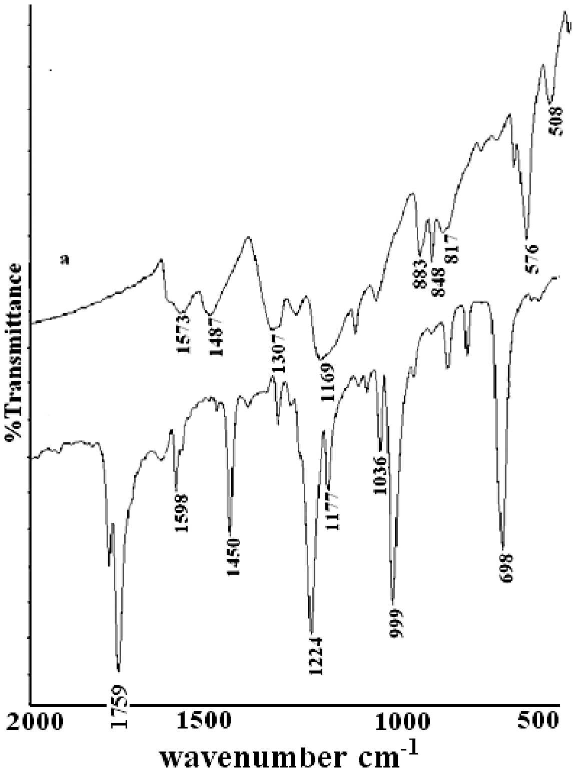

Fig. 5. FT-IR spectra of a) pure polyaniline and b) pure polyacrylonitrile formed in water/ethyl acetate solution

Conclusion

In this work the characteristics of aniline/acrylonitrile copolymer, such as conductivity, morphology, particle size and chemical structure, were investigated. It was found that the type of oxidant and solution have a considerable effect on the conductivity, particle size and morphology. The SEM micrographs show that the type of oxidant and solution play a major role on the surface morphology of products. The type of oxidant and solution also influence the particle size and electrical conductivity. The chemical structure of products was determined by FTIR spectrum. As shown in the figures the intensity of peaks related to the type of oxidant and solution.

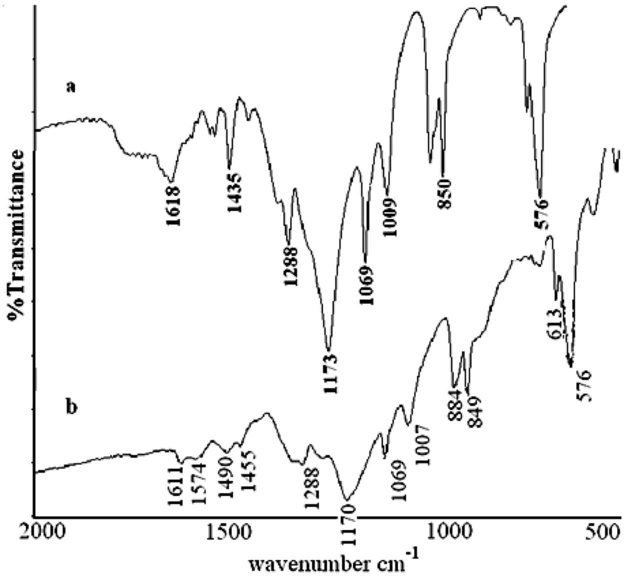

Fig. 6. FT-IR spectra of aniline/acrylonitrile copolymer generated in a) water/methanol and b) in aqueous media

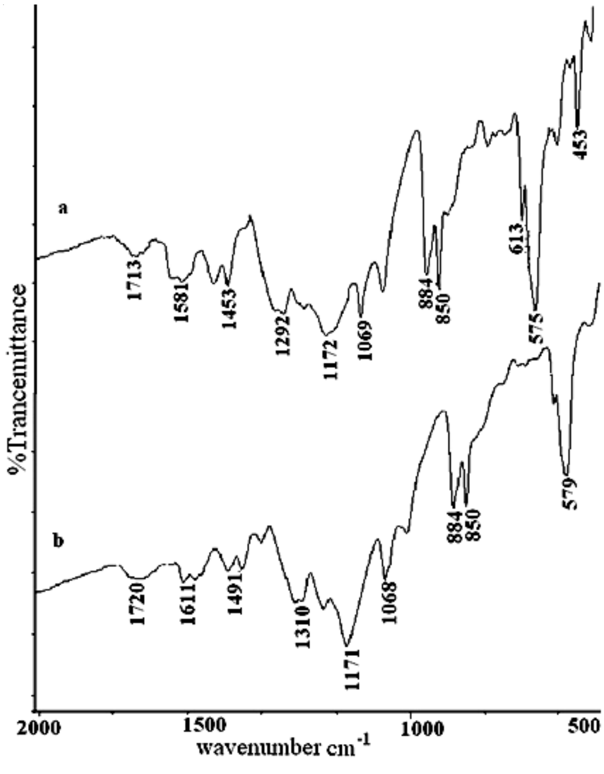

Fig. 7. FT-IR spectra of aniline/acrylonitrile copolymer generated in water/ethyl acetate solution, a) $K_2Cr_2O_7$/Benzoyl peroxide and b) $K_2Cr_2O_7/K_2S_2O_8$ used as oxidant

REFERENCES

1. W. Yin, J. Li, Y. Li, J. Wu and T. Gu, *J. Appl. Polym. Sci.*, **80**, 1368 (2001).
2. J.M. Machado, F.E. Karasz and R.W. Lenz, *Polymer*, **29**, 1412 (1988).
3. M.A.D. Paoli, R.J. Waltman, A.F. Diaz and J. Bargon, *J. Chem. Soc. Chem. Commun.*, **15**, 1015 (1984).
4. S.E. Lindsey and G.B. Street, *Synth. Met.*, **10**, 67 (1984).
5. C. Cassignol, M. Cavarero, A. Boudet and A. Ricard, *Polymer*, **40**, 1139 (1999).
6. N.V. Bhat, A.P. Gadre and V.A. Bambole, *J. Appl. Polym. Sci.*, **80**, 2511 (2001).
7. B. Scrosati, *Polym. Internat.*, **47**, 50 (1998).
8. H. Eisazadeh, G. Spinks and G.G. Wallace, *Mater. Forum.*, **17**, 241 (1993).
9. H. Eisazadeh, *J. Appl. Polym.*, **104**, 1964 (2007).
10. H. Eisazadeh, *Chin. J. Polym. Sci.*, **25**, 393 (2007).
11. S.K. Dhawan, N. Singh and S. Venkatachalam, *Synth. Met.*, **125**, 389 (2001).
12. S. Benabderrahmane, S. Bousalem, C. Mangeney, A. Azioune, M.J. Vaulay and M.M. Chehimi, *Polymer*, **46**, 1339 (2005).
13. W.R. Salanek, I. Lundstrom, W.S. Huang and A.G. MacDiarmid, *Synth. Met.*, **13**, 291 (1986).
14. S.S. Pandey, S. Annapoorni and B.D. Malhotra, *Macromolecules*, **26**, 3190 (1993).
15. A. Andreatta, A.J. Heeger and P. Smith, *Polym. Commun.*, **31**, 275 (1990).
16. A.I. Nazzal and G.B. Street, *J. Chem. Soc. Chem. Commun.*, **13**, 375 (1985).
17. M. Aldissi, *Synth. Met.*, **13**, 87 (1984).
18. H.S. Nalwa, *J. Phys. D: Appl. Phys.*, **23**, 745 (1990).
19. H. Eisazadeh, *J. Vinyle Addit. Tech.*, **13**, 229 (2007).
20. H. Eisazadeh and A. Kavian, *Polym. Compos.*, **30**, 43 (2009).
21. H. Eisazadeh and M. Ghorbani, *J. Vinyl Addit. Technol.*, **15**, 204 (2009).
22. M.J. Saglam, *Appl. Polym. Sci.*, **32**, 5719 (1986).
23. J.A. Shelter, *J. Polym. Sci. B*, **19**, 209 (1963).
24. R. Joseph, S.G. Devi and A.L. Rakshit, *Polym. Sci.*, **23**, 338 (1994).
25. Y. Lee, D. Shin, J. Cho, Y.H. Park, Y. Son and D.H. Baik, *J. Appl. Polym. Sci.*, **69**, 2641 (1998).
26. A.M. Summan, *J. Polym. Sci. Polym. Chem.*, **37**, 3057 (1999).
27. Y.H. Park and C.R. Park, *Synth. Met.*, **118**, 187 (2001).
28. J. Liu and M. Wan, *Synth. Met.*, **124**, 317 (2001).
29. S.P. Armes and M. Aldissi, *Polymer*, **31**, 569 (1990).

(*Received*: 1 February 2010; *Accepted*: 22 June 2010) AJC-8823