Bull. Chem. Soc. Ethiop. **2018**, 32(3), 523-530. ISSN 1011-3924
© 2018 Chemical Society of Ethiopia and The Authors Printed in Ethiopia
DOI: https://dx.doi.org/10.4314/bcse.v32i3.11

# SYNTHESIS AND CHARACTERIZATION OF NEW AROMATIC HYDROXY ACID COMPOUNDS

P. Thiruvasagam*

School of Chemical and Biotechnology, SASTRA Deemed University, Thanjavur-613401, India

(Received June 23, 2017; Revised June 27, 2018; Accepted July 12, 2018)

**ABSTRACT**. Four novel aromatic hydroxy acid (HA) compounds N-(4-hydroxyphenyl)-4'-trimellitimide, N-(3-hydroxyphenyl)-4'-trimellitimide, N-(5-hydroxynaphthyl)-4'-trimellitimide and N-{4'-[2-(4-hydroxyphenyl) isopropyl phenyl]}-4''-trimellitimide are synthesized through nucleophilic substitution reaction of trimelitic dianhydrides with the corresponding aminophenol/aminonaphthol using polar aprotic solvents. The hydroxy acid compounds are characterized by FT-IR and $^1$H-NMR spectroscopy.

**KEY WORDS**: Bifunctional molecule, Hydroxy acid, AB-molecule, Imide ring, Nucleophilic substitution reaction

## INTRODUCTION

Bifunctional molecule has properties of two different types of functional groups. Some common functional groups are –COOH (carboxylic acids), –CHO (aldehyde), –$CONH_2$ (amide), –CN (nitrile), –OH (alcohol), –$NH_2$ (amino), –X (halo), etc. The functional groups determine the chemical and biological behavior of the compounds. Many of bifunctional molecules are used to produce medicine, catalysts and also used in condensation polymerization to synthesize polyester, polyamide, etc. [1-3]. Biological molecules such as proteins are made up of bifunctional amino acids. Bifunctional molecules having –COOH and –$NH_2$ are used to synthesize polyamides by self polycondenzation reaction [4, 5] and the molecules having active –$NO_2$ and –OH group are used to make polyether by nucleophilic displacement reaction [6, 7]. Bifunctional molecules having the combination of –COOH and –F, –CHO and –F, –$CONH_2$ and –F, –CN and –F, –COOH and –$NO_2$, –CHO and –$NO_2$, –$CONH_2$ and –$NO_2$, –COOH and –Cl, –CHO and –Cl, –$CONH_2$ and –Cl, etc. are used to synthesize numerous organic compounds that are used to prepare medicines, polymers, etc. [8, 9]. Among the bifunctional molecules, hydroxy acids (HAs) represent a class of compounds which have been widely used in a number of cosmetic, therapeutic formulations and polymer synthesis. Salicylic acid, a most important hydroxy acid is used as a starting material for synthesizing drugs etc. Even though the hydroxy acids are commercially important, the available compounds are less, particularly aromatic hydroxy acids are very limited. This prompted me to synthesize stable imide containing hydroxy acid. In this research work four novel imide containing hydroxy acid compounds are synthesized through two step process and the structures are characterized by spectroscopic analysis.

## EXPERIMENTAL

### *Materials and instruments*

$^1$H-NMR spectra were recorded in DMSO-$d_6$ solution using Bruker 300 MHz instrument and FT-IR spectra were obtained on spectrum one (Perkin Elmer, USA). Aniline, bisphenol-A, 4-aminophenol, 3-aminophenol, 5-amino-1-naphthol and trimellitic anhydride were purchased

---

*Corresponding author. E-mail: thiru_mek@yahoo.com from Sigma-Aldrich Chemicals India and they were used without further purification. N-methyl pyrolidone (NMP) was distilled under reduced pressure before using. All the reagents used were analytical grade. The compound 2-(4-aminophenyl)-2-(4'-hydroxyphenyl) propane was prepared in the laboratory starting from bisphenol-A and aniline as per the procedure reported in our previous publications [10-12].

### *Synthesis of aromatic hydroxy acid*

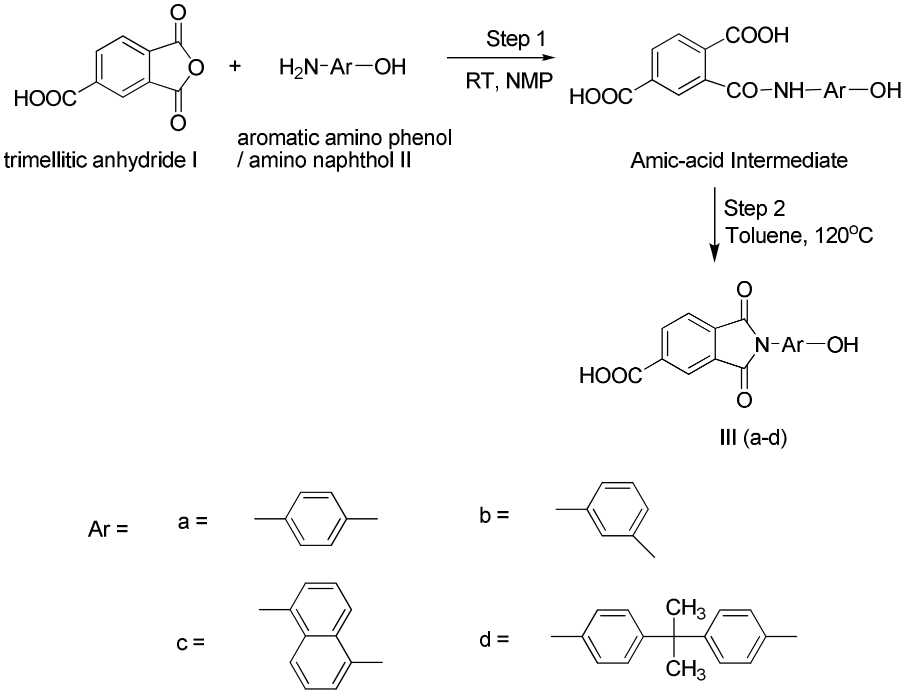
*N-(4-hydroxyphenyl)-4'-trimellitimide (IIIa)*. The stable aromatic hydroxy acids (**IIIa-IIId**) were prepared by the nucleophilic substitution reaction of trimellitic anhydride with aromatic amino phenol/amino naphthol [13-19]. The typical procedure adopted for the synthesis of the compound **IIIa** was as follows: in the first step, trimellitic anhydride (**I**) (0.02 mol) was added slowly under nitrogen atmosphere into the solution of 4-aminophenol (**IIa**) (0.04 mol) in polar aprotic solvent NMP (25 mL), and was stirred at room temperature for 6 h to form amic acid intermediate. In the second step, toluene (15 mL) was added into the amic acid intermediate and the resulting mixture was refluxed at 120 $^{o}$C for 10 h to afford the cyclic diiimide **IIIa**. The water formed during this conversion was removed azeotropically using Dean-Stark trap (Scheme 1). After removing the water, the temperature of the reaction mixture was raised to distilled off the residual toluene. The reaction mixture was cooled, poured into water and the precipitated hydroxy acid compound **IIIa** was filtered, washed with excess of dil. HCl to remove the unreached 4-aminophenol and washed with excess of water, finally dried in vacuum oven at 80 $^{o}$C. Yield: 93%, FT-IR (KBr): 3600-2500 cm$^{-1}$ (–COOH and –OH), 1779 cm$^{-1}$ (imide C=O symmetrical stretching), 1724 cm$^{-1}$ (imide C=O asymmetrical stretching), 728 cm$^{-1}$ (imide ring deformation) and 1371 cm$^{-1}$ (imide C–N stretching). $^1$H-NMR (300 MHz, DMSO-d$_6$, ppm): δ 9.81 (s, –OH, Ar ), δ 8.41–8.38(d, J = 9.0 Hz, H, Ar), δ 8.28 (s, H, Ar), δ 8.06–8.03 (d, J = 9.0 Hz, H, Ar), δ 7.23–7.20 (d, J = 9.0 Hz, 2H, Ar) and δ 6.89–6.86 (d, J = 9.0 Hz, 2H, Ar).

*N-(3-hydroxyphenyl)-4'-trimellitimide (IIIb)*. The hydroxy acid compound **IIIb** was synthesised using trimellitic anhydride and 3-aminophenol using the same procedure as adopted for the synthesize of **IIIa**. Yield: 95%, FT-IR (KBr): 3400–2550 cm$^{-1}$ (–COOH and –OH), 1780 cm$^{-1}$ (imide C=O symmetrical stretching), 1722 cm$^{-1}$ (imide C=O asymmetrical stretching), 725 cm$^{-1}$ (imide ring deformation) and 1373 cm$^{-1}$ (imide C-N stretching). $^1$H-NMR (300 MHz, DMSO-d$_6$, ppm): δ 9.82 (s,–OH, Ar), δ 8.42–8.39 (d, J = 9.0 HzH, Ar), δ 8.30(s, H, Ar), δ 8.08–8.05(d, J = 9.0 Hz, H, Ar), δ 7.34–7.28(t, H, Ar) and δ 6.87–6.84(m, 3H, Ar).

*N-(5-hydroxynaphthyl)-4'-trimellitimide (IIIc)*. The hydroxy acid compound **IIIc** was synthesised using trimellitic anhydride and 5-amino-1-nahthol using the same procedure as adopted for the synthesize of **IIIa**. Yield: 95%, FT-IR (KBr): 3450–2850 cm$^{-1}$ (–COOH and –OH), 1782 cm$^{-1}$ (imide C=O symmetrical stretching),1724 cm$^{-1}$ (imide C=O asymmetrical stretching), 726 cm$^{-1}$ (imide ring deformation and 1375 cm$^{-1}$ (imide C-N stretching). $^1$H-NMR (300 MHz, DMSO-d$_6$, ppm), δ 10.45 (s, –OH,Ar), δ 8.47–8.44 (d, J = 9.0 Hz, H,Ar), δ 8.36 (s, H, Ar), δ 8.32–8.29 (d, J = 9.0 Hz, H, Ar), δ 8.14–8.11 (d, J = 9.0 Hz, H, Ar), δ 7.64–7.55 (m, 2H, Ar), δ 7.34–7.20 (t, H, Ar), δ 7.20–7.17 (d, J = 9.0 Hz, H, Ar) and δ 6.95–6.92 (d, J = 9.0 Hz, H, Ar).

*N-{4'-[2-(4-hydroxyphenyl) isopropylphenyl]}-4''-trimellitimide (IIId)*. The hydroxy acid compound **IIId**, was synthesised using trimellitic anhydride and 2-(4-aminophenyl)-2-(4'-hydroxyphenyl)propane using the same procedure as adopted for the synthesize of **IIIa**. Yield: 97%, FT-IR (KBr): 3400–2800 cm$^{-1}$ (–COOH and –OH), 1780 cm$^{-1}$ (imide C=O symmetrical stretching), 1723 cm$^{-1}$ (imide C=O asymmetrical stretching), 726 cm$^{-1}$ (imide ring deformation) and 1380 cm$^{-1}$ (imide C–N stretching). $^1$H-NMR (300 MHz, DMSO-d$_6$, ppm) δ 9.26 (s, H, -OH), δ 8.42–8.39 (d, J = 9.0 Hz, H, Ar), δ 8.30 (s, H, Ar), δ 8.08–8.05 (d, J = 9.0 Hz, H, Ar), δ

7.34 (s, 4H, Ar), δ 7.08–7.05 (d, J = 9.0 Hz, 2H, Ar), δ 6.70–6.67 (d, J = 9.0 Hz, 2H, Ar) and δ 1.6 3 (s, 6H, $-CH_3$).



Scheme 1. Synthesis of hydroxyl acid.

## RESULT AND DISCUSSION

### *Structural characterization of hydroxy acid compounds by FT-IR spectroscopy*

The hydroxy acid compounds were prepared by the nucleophilic substitution reaction of trimelitic dianhydrides with the corresponding aminophenol/aminonaphthol under nitrogen atmosphere using NMP as solvent in a two step process. In the first step intermediate amic acid was prepared through the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group. In the second step, the imidization was accompanied through nucleophilic attack of the amide nitrogen on the acid carbonyl carbon with the elimination of water. The complete cyclisation of the intermediate amic acid was achieved by toluene-water azeotropic distillation (Scheme 1). The FT-IR spectrum of the monomer **IIIa** (Figure 1) showed a characteristic absorption band for the imide ring at 1779 $cm^{-1}$ (imides C=O symmetrical stretching), 1724 $cm^{-1}$ (imides C=O asymmetrical stretching), 728 $cm^{-1}$ (imide ring deformation). The stretching of –COOH group merged with penolic –OH stretching and showed a broad and strong absorption band at 3600–2500 $cm^{-1}$. The C-H ($sp^2$) absorption band (at 3330 $cm^{-1}$) merged into the absorption band of –COOH and –OH group. The FT-IR spectrum of the compound **IIIa** confirmed the formation of imide ring between the trimellitic anhydride and 4-aminophenol. Similarly the FT-IR spectral data of the hydroxy acid compounds **IIIb**, **IIIc** and **IIId** (Figure 2) supported the proposed structures.

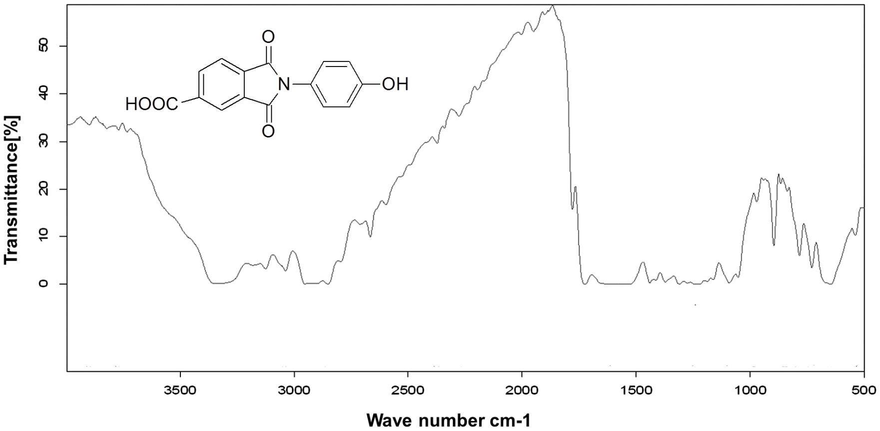


Figure 1. FT-IR- spectrum of N-(4-hydroxyphenyl)-4-trimellitimide (**IIIa**).

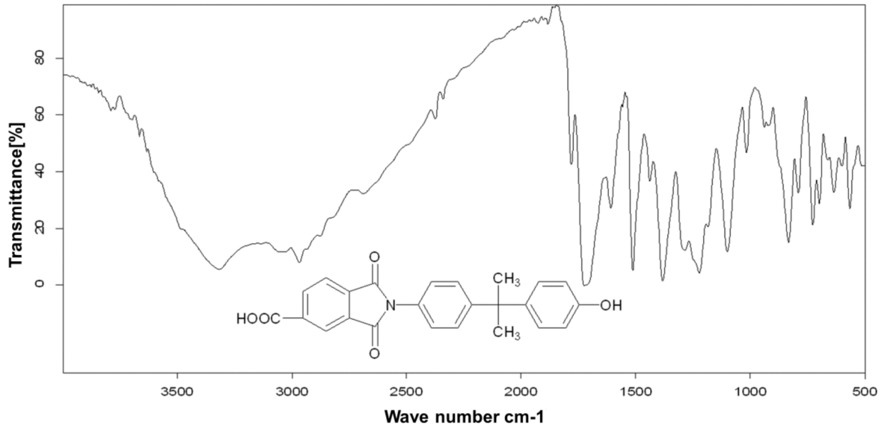


Figure 2. IR spectrum of N-{4’-[2-(4-hydroxyphenyl) isopropylphenyl]}-4’’’-trimellitimide (**IIId**).

*Structural characterization of hydroxyl acid compounds by $^1$H-NMR spectroscopy*

The $^1$H-NMR spectrum of N-(4-hydroxyphenyl)-4’-nitrophthalimide (**IIIa**) is shown in Figure 3. The phenolic proton appeared as a singlet at 9.81 δ ppm. The two aromatic protons *ortho* to the hydroxyl group appeared as a doublet at 6.89–6.86 δ ppm and the two aromatic protons *meta* to the hydroxyl group appeared as a doublet at 7.23–7.20 δ ppm. The two aromatic proton *meta* and *ortho* to the carboxylic group and flanked between by imide carbonyl and carboxyl group appeared as a doublet at 8.06–8.03 δ ppm and 8.41–8.38 δ ppm, respectively. The aromatic proton flanked by imide carbonyl and carboxyl group appeared as a singlet at 8.28 δ ppm. The protons designated in Figure 3 as “d”, “e” and “f” appeared in the farthest downfield in the range 8.41–8.03 δ ppm because of the electron withdrawing –COOH and imide groups. The peaks at 2.5 δ ppm and at 3.4 δ ppm are due to DMSO and water in DMSO. Similarly the $^1$H-NMR spectrum of the hydroxyl acid compounds **IIIb** (Figure 4), **IIIc** (Figure 5) and **IIId** (Figure 6) supported the proposed structures.

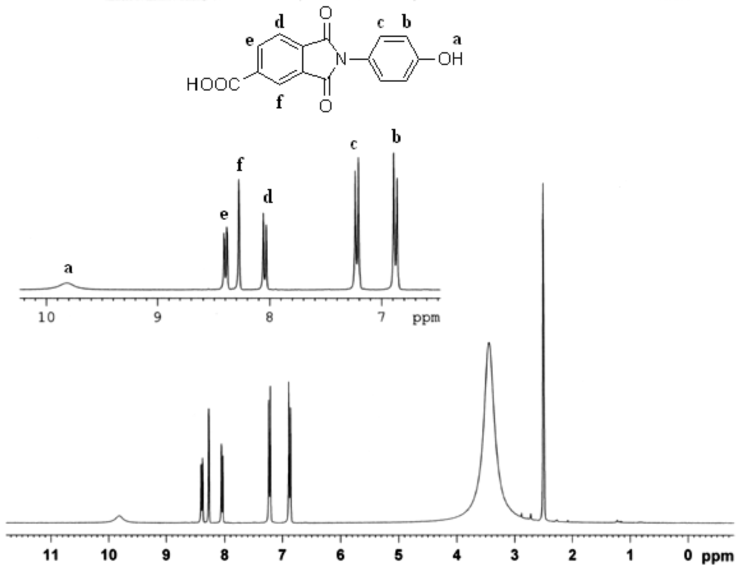


Figure 3. $^1$H-NMR spectrum of N-(4-hydroxyphenyl)-4'-trimellitimide (**IIIa**).

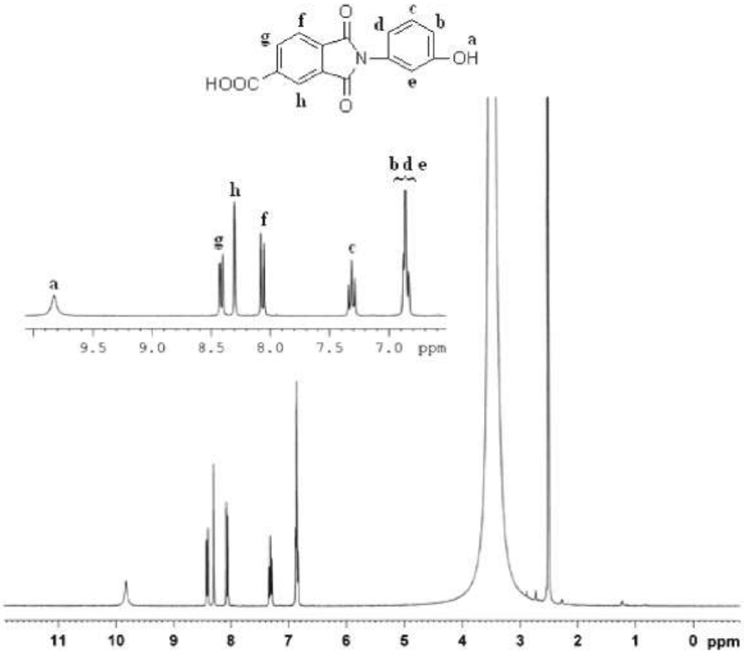


Figure 4. $^1$H-NMR spectrum of N-(3-hydroxyphenyl)- 4'-trimellitimide (**IIIb**).

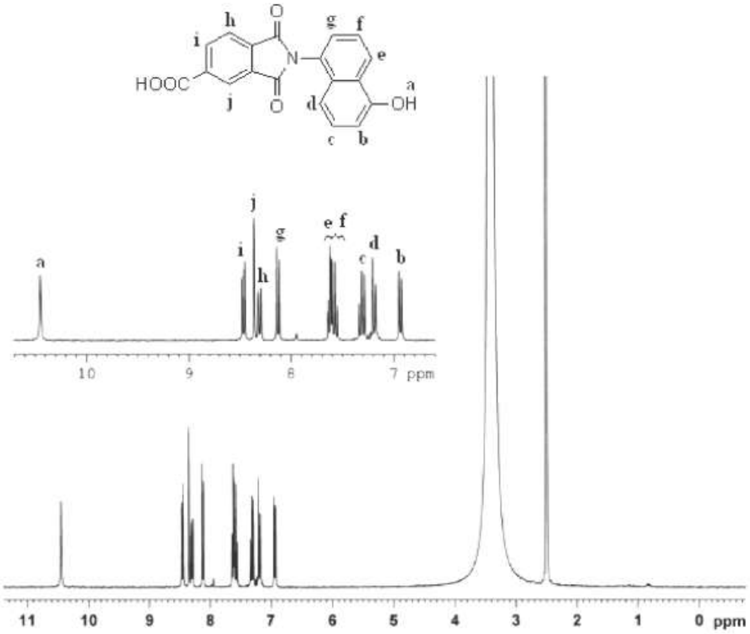


Figure 5. $^1$H-NMR spectrum of N-(5-hydroxynaphthyl)-4'-trimellitimide (**IIIc**).

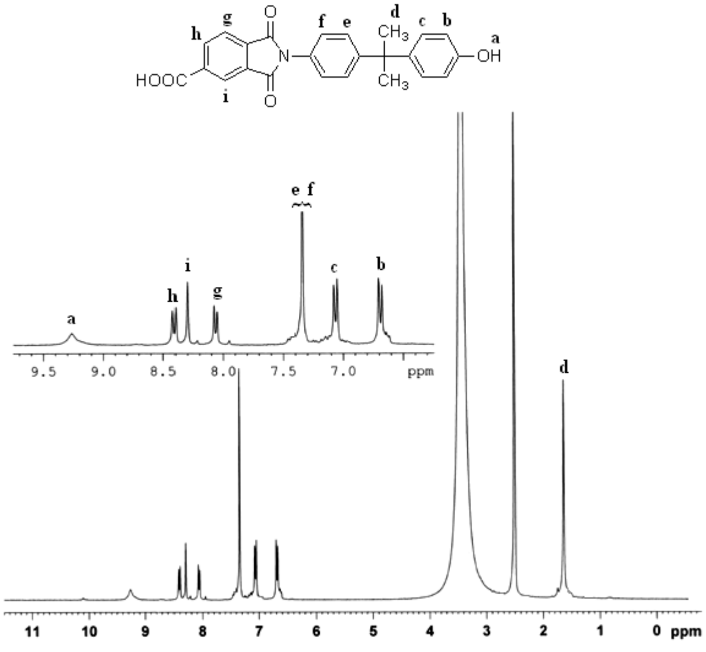


Figure 6. $^1$H-NMR spectrum of N-{4'-[2-(4-hydroxyphenyl) isopropylphenyl]}4''-trimellitimide (**IIId**).

## CONCLUSION

We have successfully synthesised four imide containing hydroxyl acid (HA) compounds through two step process with high yield. The structures of the compounds are confirmed by FT-IR and $^1$H-NMR spectroscopy analysis. These compounds can be used as a starting material for synthesize of new organic compounds and also can be used to synthesise polyesters, polyether, polyamides, etc. Thus, these HAs are considered to be more useful compounds for further applications.

## REFERENCES

1. Scheinberg, R.S. Alpha hydroxy acids for skin rejuvenation. *West. J. Med.* **1994**, 160, 366-367
2. Thiruvasagam, P. Synthesis and characterization of AB-type monomers and polyimides: A review. *Des. Monomers Polym.* **2013**, 16, 197-221
3. Begunov, R.S.; Valyaeva, A.N.; Belomoina. N.M.; Bulycheva, E.G. Synthesis and properties of new poly(benzimidazole) Based on AB-type Monomer. *Dokl. Chem.* **2014**, 454, 1-5.
4. Im, J.K.; Jin, C.J. Synthesis and properties of new AB-type semi-crystalline poly(ether imide). *Polym. Bull.* **1999**, 43, 157-163.
5. Mitsutoshi, J.; Ken, F., Gang,Y.; Masa-aki, K. Synthesis and properties of hyperbranched aromatic polyamide copolymers from AB and $AB_2$ monomers by direct polycondensation. *Macromolecules* **2000**, 33, 6228-6234.
6. Thiruvasagam, P.; Venkatesan, D. Synthesis and characterization of polyetherimides derived from AB monomers. *J. Macromol. Sci. PartA: Pure Appl. Chem.* **2009**, 46, 419-424.
7. Hyo, S.L.; Sang, Y.K. Synthesis of poly(arylene ether amide)s containing $CF_3$ groups by nitro displacement reaction of AB-Type monomers. *Macromol. Rapid Commun.* **2002**, 23, 665-671.
8. Thiruvasagam, P. Characterization of thermally stable AB-type poly(ether-amide)s derived from AB-type monomers by fluoro displacement reaction. *Polym.-Plast. Technol. Eng.* **2014**, 53, 1-7.
9. Lucas, M.; Hedrick, J.L. Poly(aryl ether amides): self polymerization of an AB monomer via amide-activated ether synthesis. *Polym. Bull.* **1992**, 28, 129-133.
10. Thiruvasagam, P.; Venkatesan, D. Synthesis and characterization of processable aromatic polyimides. *High Perform. Polym.* **2010**, 22, 682-693.
11. Thiruvasagam, P.; Siva, C.; Sundararaman, C.; Venkatesan, D. Synthesis and characterization of new diimide diol and processable polyesterimide derived there from. *Polym. Polym. Compos.* **2011**, 19, 763-771.
12. Thiruvasagam, P. Synthesis of new unsymmetrical diamine and polyimides: Structure–property relationship and applications of polyimides. *J. Polym. Res.* **2012**, 19, 1-9.
13. Abd El-Galil, M.K.; Moged, A.B.; Moustafa, A.G. Synthesis and study of some new N-substituted imide derivatives as potential antibacterial agents, *Chem. Papers* **2010**, 64, 637-644.
14. Martin, D.; Matej, M.; Maria, O.; Juraj, B.; Dusan, C. Jr. Spectral characterisation of new organic fluorescent dyes with an alkoxysilane moiety and their utilisation for the labeling of layered silicates. *Chem. Papers* **2013**, 67, 18-28.
15. Mahmoud, F.; Salman, A.A.; Ahamad, I.; Khalid, M.A.; Mohamed, G.; Khalid, A.A.; Salem, E.G.; Mamdouh, A. Facile synthesis of 3-substituted quinazoline-2,4-dione and 2,3-di-substituted quinazolinone derivatives. *Chem. Papers* **2013**, 67, 229-235.

16. Thiruvasagam, P.; Vijayan, M. Synthesis of new diacid monomers and poly(amide-imide)s:study of structure–property relationship and applications. *J. Polym. Res.* **2012**, 19:9845. DOI: 10.1007/s10965-012-9845-1.
17. Thiruvasagam, P.; Vijayan, M. Synthesis of poly(amide-imide)s from new diacid monomers: Study of structure–property relationship and applications. *High Perform. Polym.* **2012**, 24, 210-217.
18. Shahran, M.A.; Shahriar, K. Synthesis and characterization of novel diimide-dinaphthols and resulting poly(urethane-imide)s. *Polym. Int.* **2003**, 52, 1487-1492.
19. Shahran, M.A.; Shahriar, K. Use of new diimide-dinaphthols in preparation of novel thermally stable poly(ester-imide)s. *J. Appl. Polym. Sci.* **2003**, 88, 2168-2172.