



Synthesis and characterization of new diacid monomers and poly (ester-imide) s: a study of thermal property relationship and solubility

Ruaa Jameel Kamel^{*1}, Mohammed Ali Mutar², Farah Safi Khlewee³

¹Department of Pharmaceutical Chemistry, College of Pharmacy, University of Al-Qadisiyah, Iraq,

²Department of Chemical Engineering, College of Engineering, University of Al-Qadisiyah, Iraq

³Department of Chemistry, College of Education, University of Al-Qadisiyah, Iraq



Article History:

Received on: 10.03.2019

Revised on: 20.06.2019

Accepted on: 24.06.2019

Keywords:

pol (esters-imide),
Diols,
pyromellitic anhydride (PMDA)
polycondensation,
dicarboxylic acid

ABSTRACT

Two dicarboxylic acids [2,2'-(((4-hydroxyphenyl) methylene) bis (3-Bromo-4,1- phenylene)) bis (1,3 dioxoisindoline 5 carboxylic acid)) and 2,2 '(((2,4dichlorophenyl) methylene) bis (4,1-phenylene)) bis (1,3-dioxoisindoline-5-carboxylic acid))] were made by the reaction of pyromellitic anhydride (PMDA) with diamine in asolvent of gpyridine/glacial acetic acid at refluxing temperature. The organization of the diacid monomers is defined by FTIR and ¹H-NMR spectroscopy. The sequence of new poly (ester-imide) s are arranged of two di acids and aromatic diols: [Bis (4hydroxyphenyl) 2 furelmethane and 4,4'((1,4phenylene (methanylydene)) bis (azanylyli-dene)) diphenol] by employing the polycondensation in the company of the dibutyltine dilaurate as a catalyst. The PEIs were defined by FTIR, ¹HNMR, and TGA. Poly (ester-imide) s showed excellent solubility in polar aprotic solutions because of the existence of flexible groups in the polymer backbone. Furthermore, they displayed better thermal constancy, and the heat at that 10% loss of weight happened about 700 to 800°C.

*Corresponding Author

Name: Ruaa Jameel Kamel

Phone: +9647826018944

Email: ruaa.kamel@eq.edu.iq

ISSN: 0975-7538

DOI: <https://doi.org/10.26452/ijrps.v10i3.1397>

Production and Hosted by

Pharmascope.org

© 2019 | All rights reserved.

INTRODUCTION

Aromatic polyamide (Zhang *et al.*, 2007) is one of the highly beneficial kinds of polymers that have high performance. These substances were broadly employed in aerospace productions, electronics, automotive, and electrical (Denton *et al.*, 1985). Polyimides are utilized as films, fibres, plastics, foams, coatings, and adhesives (Köytepe *et al.*, 2008). The manufacturing procedure for a polymeric substance

needs which the polymers are soluble in organic solutions for a casting process or melted lower than their decomposition temperature for a molding extrusion procedure. Aromatic polyamides were unsolvable and cannot be fused and hard to manufacture into wanted objects. Most important prepared works have been made to develop the processability without lessening thermal constancy (Ghosh *et al.*, 1996).

Nevertheless, entirely aromatic polyimides have usually insufficiencies solubility, processability, melting or softening behaviour. So, a high volume of study focused on the exploration of new solvable polyimides in entirely iridized shape. Many methods to soluble polyimides containing the combination of malleable links, immense constituents or asymmetric noncoplanar units have been improved (Hamciuc and Hamciuc, 2008). The existence of ester groups into the macromolecular series of a polyimide enhances the solubility that links the benefit of high-temperature stability with the easiness of processability. The general ap-

proaches utilized in making of the poly(ester imide)s are (a) polycondensation between trimellitic acid or its derivative with a diamine and a diol (Shen, 1982)(b) reaction between a dicarboxylic acid including an imide ring with Diol (Maiti and Das, 1981)(c) polycondensation of a dianhydride comprising ester group with a diamine (Malvaney, 1986) (d) reaction from N-(4-carboxyphenyl)-4-acetoxy phthalimide and 4-acetoxy benzoic acid (Kricheldorf et al., 1989)(e) pyrolytic polymerization of monomers including pre-formed ester links (Kurita et al., 1990)(f) direct polycondensation between a 4-carboxy-N-(p- or m-hydroxyphenyl phthalimide, diacid, and bisphenol A in the existence of an immediate concentration agent (Li et al., 1995). This research including synthesis new poly (ester-imide) (PEIs) from reaction diols such as (M1, M2,) with diimide-dicarboxylic acid such as compounds (M5, M6,) in the existence of dibutyltin dilaurate as Catalyst. Means of FTIR and ¹H-NMR spectroscopy ultimately defined the resulted monomers and polymers, solubility and thermal stability also studied.

MATERIALS AND METHODS

Preparation of monomers

Bis (4-hydroxyphenyl) 2-fuel methane (M1):

A 0.1M solution of H₂SO₄ in methanol (60 %: 40%), phenol (2gm), (21mmol) and Furfural (1.5gm), (12mmol) are joined, and the blend was refluxed at (120) °C for ten hours and the continuous moving. After completing the reaction, the solvent was detached under vacuum (Sarma and Baruah, 2004). The produce was (71%) of brown crystals, m.p= (80°C) crystals.

4,4'-((1,4phenylene(methylidene)) bis(azanylidene)) diphenyl(M2)

This monomer was made by the concentration of one molecule of Terephthalaldehyde (1.34 gm) (10mmol) with two molecules of P-Amino phenol (2.2 gm) (20 mmol) in methanol (5) ml, by boiling defined the blend reflux by (120) °C for 3 hours. Sediment is purified and recrystallized from methanol and desiccated in a vacuum desiccator's (Jarrahpour et al., 2006) to give 2.5 gm (79%wt) of extremely light yellow crystals m.p 205-210°C.

4,4'-((2,4-chlorophenyl) methylene) aniline (M3)

The 0.1M solution of H₂SO₄ in methanol (60%:40%), 1,3dichloroaniline (2gm) (21mmol) and 4-Bromobenzaldehyde (1.5 gm) (12mmol) are joined, and the blend was refluxed at 120°C for 10

hours with the continuous stirring. After completing the reaction, the solution was distanced under vacuum (Sarma and Baruah, 2004). The product is (71%) of brown crystals, m.p= (230 °C) crystals.

The monomer 4-(bis (4-amino-2-bromophenyl) methyl) phenol (M4) made by a similar method that (M3) are shaped, but by utilizing materials such as 3-bromoaniline and 4-hydroxy benzaldehyde in existence of a mixture of methanol and H₂SO₄ as a catalyst. Table 1 Shows as,

Synthesis of dicarboxylic acids:

Synthesis of 2,2'-(((2,4-dichlorophenyl) methylene) bis (4,1-phenylene)) bis (1,3-dioxoisindoline-5-carboxylic acid) [M5]

In 250 mL round-bottomed flask are appended (3.84gm) (20 mmol) of pyromellitic anhydride, (2gm) (4mmol) of DCPMDA, acetic acid (80) mL and pyridine (3:2), and a moving bar at 25 C for 24 hours. The solution was detached under decreased pressure, and the remainder is melted in 100 mL. Later, concerted hydrochloride (5) ml was appended. The solvent is mixed till yellow sediment was made, and sediment was purified and desiccated (M5) (Faghihi and Hagibeygi, 2007).

The diacid 2,2'- (((4-hydroxyphenyl) methylene) bis(3-bromo-4,1-phenylene)) bis (1,3-dioxoisindoline-5-carboxylic acid) (M6) made in similar method above using materials, BABPMP, pyromellitic anhydride acetic acid and pyridine. Table 2 Shows as,

Preparation of poly (ester imide) s:

Dihydroxy monomer and Di-Carboxylic acid, as seen in Table 3 are blended at 120C under continuous moving. When the acid dissolute that contain imide in Dihydroxy monomers, the dibutyltin dilaurate catalyst (0.15 wt. (%)) is joined, and the temperature raised to 160°C for one hour. The constituents were desiccated under vacuum (H.Guimaraesa et al., 2007). Figure 1 and Figure 2 are as following:

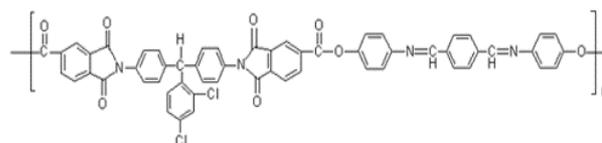


Figure 1: structure of PEI1

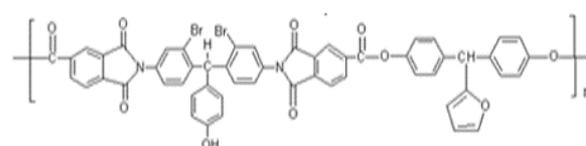


Figure 2: structure of PEI2

Table 1: properties aromatic diamines.

NO	Monomer	Substance	Color	Yield%
1	DCPMDA	2,4dichlorobenzaldehydeAniline 1.5gm(18mmol) 2gm(5mmol)	yellow	51%
2	BABPMP	4-hydroxybenzaldehyde 2-Bromoaniline 2gm(11mmol) 2.5gm(26mmol)	Orange	76%

Table 2: Diacids properties

NO	Diacids	Color	Yield%	M.P/ °c
1	M5	yellow	51%	392oC
2	M6	Orange	76%	395oC

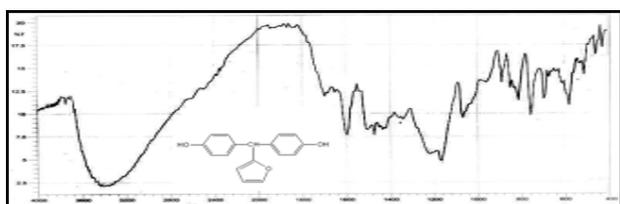
Table 3: Properties of poly (ester-imide) s [PEI₁- PEI₂]

colour	Product (wt%)	Dihydroxy		Diacid		Monomers	Poly(ester-imide)s
		Dihydroxy	Dihydroxy	Diacid	Dihydroxy		
Black	94%	1.1 gm	2.4 gm	M1	M5	PE1	
Yellow	75%	1gm	1.2gm	M2	M6	PE2	

RESULTS AND DISCUSSION

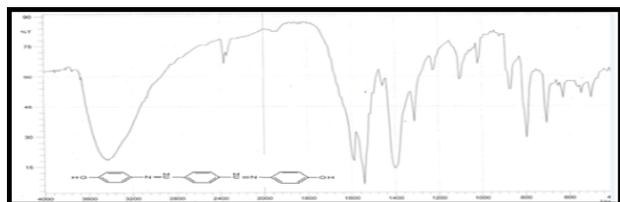
The FTIR spectra of (M1) as displayed in Figure 3 with its absorption band: (Silverstein *et al.*, 2005)

(C=C)_{ar.} 1590; (C-H)_{ar.} 3116 (OH) 3394; (C-H)_{ali} 2947 (C-O) 1218 cm⁻¹

**Figure 3: FTIR spectra of (M1)**

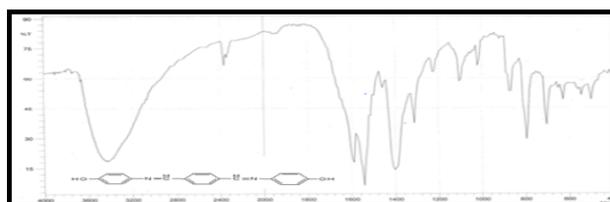
The FTIR spectra of (M2) as revealed in Figure 4 with its absorption band:

(C=C)_{ar.} 1589; (C-H)_{ar.} 3109; (OH) 3425; (C-H)_{ali} 2839 ; (C-N) 1311; (C=N) 1645 Cm⁻¹

**Figure 4: FTIR spectra of (M2)**

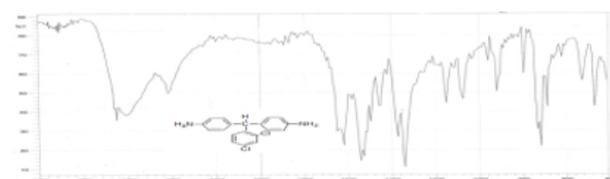
The FTIR spectra of (M3) as displayed in Figure 5 with its absorption band:

(C=C)_{ar.} 1689; (C-H)_{ar.} 3170; (NH₂) 3417; (C-N) 1270; (C-O) 1130; (C-Br) 633 cm⁻¹

**Figure 5: FTIR spectra of (M3)**

The FTIR spectra of (M4) as displayed in Figure 6 with its absorption band:

(C=C)_{ar.} 1650; (C-H)_{ar.} 3093; (NH₂) 3394 ; (C-N) 1288 ; (C-Cl) 771cm⁻¹

**Figure 6: FTIR spectra of (M4)**

The FTIR spectra of (DCPMDA) as displayed in Figure 7 with its absorption band:

(C=C)_{ar.} 1604; (OH) 3200 ; (C-N) 1296 ; (C-O) 1172; (C=O) 1692 ; (C-Cl) 750 cm⁻¹

(DCPMDA) Spectrum is displayed in Figure 8 identifies the subsequent chemical alterations;

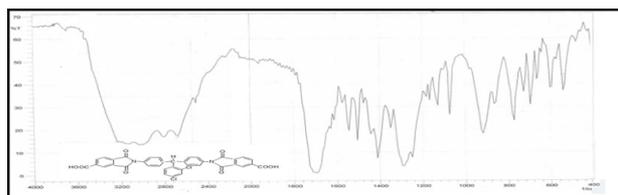


Figure 7: FTIR spectra of (DCPMDA)

DMSO= δ (2.486) ; CH= δ (5.838) (1H); Ar-H group= δ (7.712 -8.982); COOH(2H) = δ (13.536) ppm

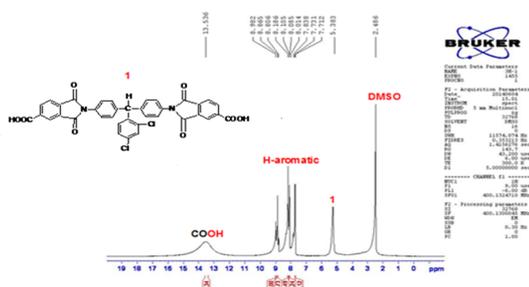


Figure 8: ¹H-NMR spectra of (DCPMDA)

FTIR spectra of (BABPMP) as displayed in absorption band:

Figure 9 shows,

(C=C) ar. (1600) ; (NH₂) 3417; (C-N) 1270; (OH) 3550; (C-O)1130 ; (C=O) 1700 ; C-Br = 633 cm⁻¹

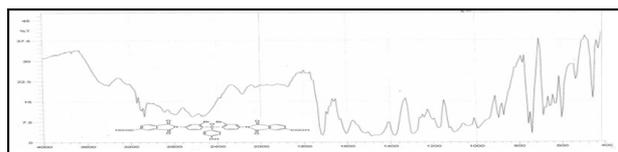


Figure 9: FTIR spectra of (BABPMP).

(BABPMP) Spectrum is displayed in Figure 10 identifies the subsequent chemical alterations;

DMSO = δ (2.476); CH = δ (5.085); Ar-H group = δ (7.495-8.705); COOH = δ (12.014); OH = δ (4.731) ppm

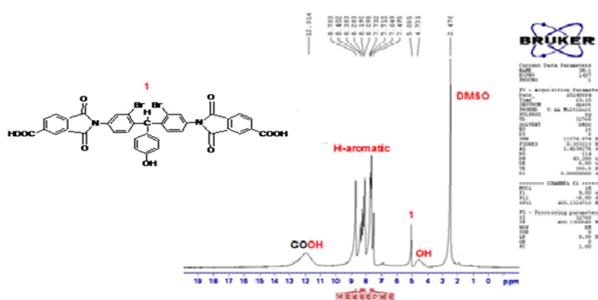
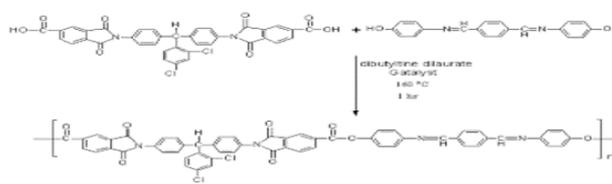


Figure 10: ¹H-NMR spectra of (BABPMP)

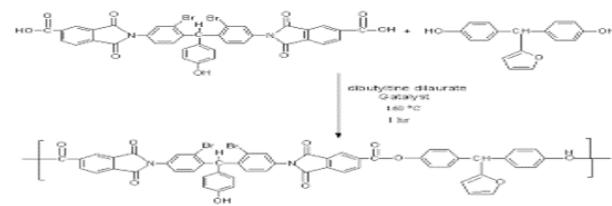
Synthesis of poly (ester amide) s [PE1- PEI2]

This part of the study employed polycondensation way for the preparation of chains of new

polyester from the immediate polycondensation reaction diacids (DCPMDA, BABPMP) with new diverse aromatic di hydroxyl monomer [M1, M2], correspondingly by utilizing the dibutyltin dilaurate as catalyst (0.15 wt (%)). These polymers had a soft section like methylene unit, and pyridine heterocyclic ring in key series to develop solubility in organic solutions. These polyesters are defined through ¹H-NMR spectra. Scheme 1 and Scheme 2 are as follows,



Scheme 1: Synthesis of (PEI)



Scheme 2: Synthesis of (PE2)

poly(ester imide) s [PEI1-PEI2] Characterization:

¹H-NMR spectrum of (PEI1), is displayed Figure 11 identifies the subsequent chemical changes; DMSO = δ (2.488-2.529) ; CH = δ (0.780-1.539); Ar -H group = δ (7.789 -8.255); OH = δ (4.731) ppm

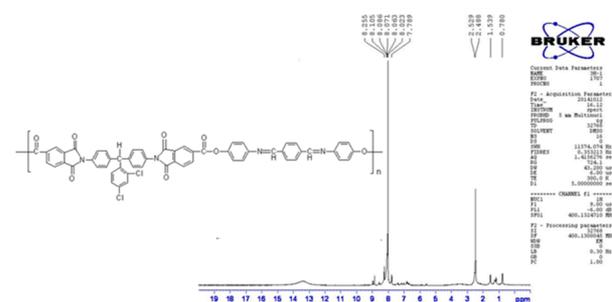


Figure 11: ¹H-NMR spectra of PEI1

(PEI2) Spectrum is displayed in Figure 12 identifies the subsequent chemical alterations: DMSO = δ (2.147); CH = δ (7.789); Ar-H group = δ (8.025-8.255); OH = δ (4.731) ppm

The solubility of poly (ester imide) s:

The solubility of polyesters PEI1-PEI4 is qualitatively examined in organic solutions. The outcomes were briefed in Table 4 . The way which tries to

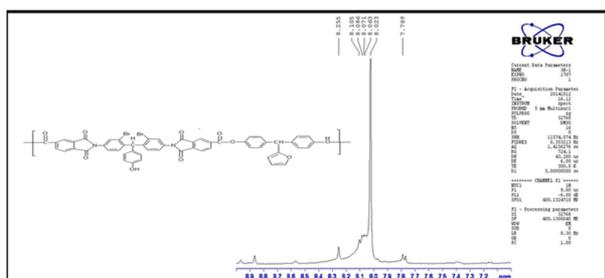


Figure 12: ¹H NMR spectra of PEI2

improve the process capabilities and solubility are through presenting immense groups, elastic connections, or molecular asymmetry into the polymer backbones. The current study, the supplement of immense pendant groups in polymer backbone may not offer an improved solubility due to reduced filling density and crystallinity but similarly would report a rise in T_g by limiting the segmental mobility. Among the main goals of the study is to produce polyesters with better solubility (Zhao *et al.*, 2009). Solubility is examined as (0.01gram) of the polymeric specimen in (2ml) of a solution. All of the recently prepared polyesters have well solvable.

Table 4: Solubility of poly (ester imide) s.

Poly (ester-imide)s		Solvent
PEI2	PEI1	
++	- +	pyridine
++	++	CHCl ₃
--	--	CH ₂ Cl ₂
++	++	NaOH
--	+++	H ₂ SO ₄
++	++	HNO ₃
++	+++	Acetone
++	++	Benzene
++	++	DMF
++	--	DMSO
+++	--	THF

1- Complete Soluble(+++); 2- Soluble at 25 C (++) ; 3- Semi-complete Soluble (+-)

Poly (ester-imide)s thermal analysis

Thermogravimetric Analysis includes defining variations mass. It is generally employed to investigate degradation temperatures, absorbed content of constituents, levels of inorganic, and organic parts enclosed in a material and analyses solvent residues (Moukhina, 2012). It utilizes a delicate electronic balance from that the sample is suspended in a furnace organized by a temperature programmer. The thermal characteristics of four exam-

ples of this polyester were examined through thermogravimetric analysis (TGA) in Argon atmosphere temperature degree of 10°C/min and the yields like Ti, Top, Tf, T₅₀ %, % sediment at 800 °C, and char produces at (500) °C is briefed in Table 5 . The temperatures of 50% loss of weight of (PEI1-PEI2) as a normal reference for thermal constancy of polymers are all from 700 to 800°C, char produces (PEI1-PEI2) at 500°C are 58% until 79% in Argon atmosphere, that refers to that they can endure extreme temperature resistant needs as some particular substances in modern aerospace. Weight residue of (PEI1-PEI2) at (800) °C are the maximum than Aromatic polyester of this chain, (49% until 58%). Figure 13 and Figure 14 are as following:

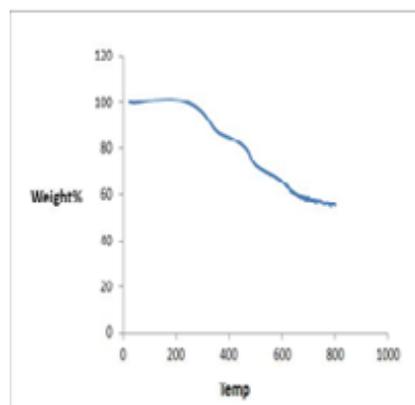


Figure 13: TGA curve of PEI1

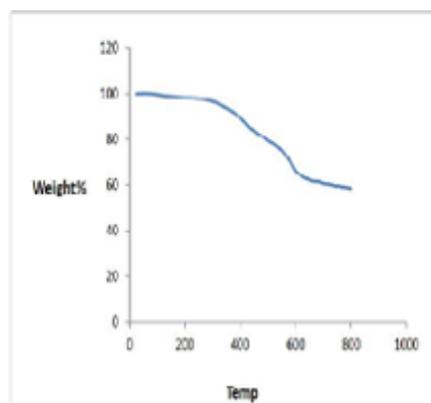


Figure 14: TGA curve of PEI2

CONCLUSIONS

The current study has positively made new dicarboxylic acid 2,2'-(((4-hydroxyphenyl) methylene) bis (3-Bromo-4,1-phenylene)) bis (1,3 dioxoisindoline 5 carboxylic acid)) 2,2'(((2,4dichlorophenyl) methylene) bis (4,1-phenylene)) bis (1,3-dioxoisindoline- 5-carboxylic acid), Diamine [4,4'-((2,4-chlorophenyl) methylene) aniline and 4-(bis (4-amino-2-bromophenyl) methyl) phenol, and

Table 5: Thermal behaviour data of poly(ester-imide) s

Aromatic poly (esterimide) s	DT/°C	DT/°C	DT/°C	DT/°C	T _{50%}	Residue at 800°C	Char % at 500°C
PEI1	200	400	554	800 >	790	49%	72%
PEI2	400	600	—	800 >	789	58%	79%

diols. There is an imide group linked. These polymers have high solubility because of the presence of the ester in the polymer that male (PEIs) have high ability to attract with processed plastics that may be subject of additional studies.

REFERENCES

- Denton, D. D., Day, D. R., Priore, D. F., Senturia, S. D., Anolick, E. S., Scheider, D. 1985. Moisture diffusion in polyimide films in integrated circuits. *Journal of Electronic Materials*, 14(2):119–136.
- Faghihi, K., Hagibeygi, M. 2007. New aromatic polyamide with azo and phosphine oxide groups in the main chain. *Turkish Journal of Chemistry*, 31(1):65–73.
- Ghosh, M. K., Mittal, K. L., *et al.* 1996. "Polyimides Fundamentals and Applications" . pages 7–48. Marcel Dekker: New York, .
- Hamciuc, E., Hamciuc, C. 2008. *Advances in functional heterochain polymers*. Nova Science Publishers, Inc, New York.
- H.Guimaraes, M.Brioude, *et al.* 2007. *Materials Research*, 10(4):335–339.
- Jarrahpour, A. A., Jalbout, A. F., Rezaei, S., Trzaskowski, B. 2006. Synthesis and Physical Characterization of 2-((E)-1-(3-((E)-1-(2-hydroxyphenyl) ethylideneamino)-2-methylphenylimino) ethyl) phenol. *Molbank*, 2006(1):455.
- Köytepe, S., Paşahan, A., Ekinçi, E., Alıcı, B., Seçkin, T. 2008. Synthesis, characterization of phosphine oxide-containing polyimides and their use as selective membrane for dopamine. *Journal of Polymer Research*, 15(3):249–257.
- Kricheldorf, H. R., Schwarz, G., Nowatzky, W. 1989. New polymer syntheses: 34. Copoly(ester imide)s of 4-hydroxybenzoic acid and N-(4-carboxyphenyl)-4-hydroxyphthalimide. *Polymer*, 30(5):936–941.
- Kurita, K., Mikawa, N., Koyama, Y., Nishimura, S. 1990. Polymers based on p-aminophenol. 6. Facile synthesis of the simplest wholly aromatic poly (imide-ester) by pyrolytic polymerization of monomers containing preformed ester linkages. *Macromolecules*, 23(10):2605–2609.
- Li, C. H., Jung, A., Liang, A. L., Chang, T. C. 1995. Studies on the synthesis and properties of thermotropic liquid crystalline copoly (amide-ester-imide) derived from N-(hydroxyphenyl) phthalimide-4-carboxylic acid with amino acid. *Journal of applied polymer science*, 56(12):1661–1666.
- Maiti, S., Das, S. J. 1981. *Appl Polym Sci*.
- Malvaney, J. G. J. 1986. *Polym Sci Part A. Polym Chem*, 1986, 24, 613.
- Moukhina, E. 2012. Determination of kinetic mechanisms for reactions measured with thermoanalytical instruments. *Journal of thermal analysis and*, 109(3):1203–1214.
- Sarma, R. J., Baruah, J. B. 2004. Synthesis and characterization of bis-(3, 5-dimethyl-4-hydroxyphenyl)(aryl) methanes as precursor for three state indicator. *Dyes and pigments*.
- Shen, D. C. 1982. U.S. Patent, 4(362).
- Silverstein, R. M., Webster, F. K., D.J. 2005. *Spectrometric Identification of Organic compound 7th*. John Wiley and Sons.
- Zhang, S. J., Li, Y. F., Wang, X. L., Zhao, X., Shao, Y., Ma, T. 2007. Synthesis and Characterization of Soluble Polyimides Derived from the Polycondensation of 2,6-bis(4-amino-2-trifluoromethylphenoxy-4'-benzoyl)pyridine with Some Aromatic Dianhydrides. *High Performance Polymers*, 19(4):462–476.
- Zhao, X., Wang, C., Chen, L., Zhu, M. 2009. Novel poly (fluorinated imide) s containing naphthalene pendant group: synthesis and characterization. *Colloid and Polymer Science*, 287(11):1331.