

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

**WEB OF SCIENCE™**Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Synthesis of Thermally Stable Polyesters

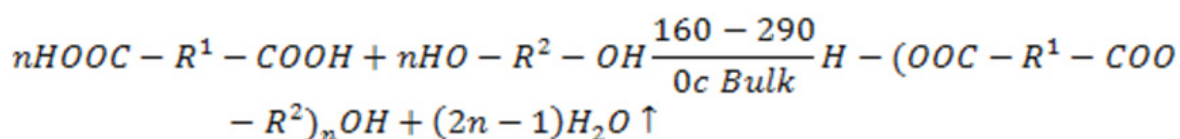
Hossein Mighani

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/39224>

1. Introduction (Roger, 2003)

Polyesters are defined as polymers containing at least one ester linking group per repeating unit. They can be obtained by a wide range of reactions, the most important being polyesterifications between dibasic acids and diols or their derivatives (Scheme 1).



Scheme 1.

Many other reactions have been reported for the synthesis of polyesters, such as reactions between dicarboxylic acid salts and dialkylhalides, reactions between chlorocarbonyloxy-terminated monomers and diacids, or reactions between diketenes and diols. These reactions, however, cannot be applied to the synthesis of high molar mass polyesters under economically viable conditions and are limited to very specific laboratory scale syntheses. Two notable exceptions are the ringopening polymerization of lactones and lactides for the production of degradable polyesters and the biosynthesis of aliphatic polyesters by bacteria or genetically modified plants during the last few years, a number of companies have put biodegradable polymers on the market. Almost all these polymers are polyesters or copolyesters: aliphatic polyesters such as poly (ϵ - caprolactone), poly (butylene-co-ethylene succinate), poly (lactic acid) and microbial poly (hydroxyalkanoic acid), copolyesters of terephthalic acid with various aliphatic diols and diacids and polyesteramides .

1.1. Structure property relationships (Roger, 2003)

The nature- aliphatic or aromatic- of the bivalent - R¹- and - R²- radicals in polyester chains (Scheme 1) exerts a profound influence on the properties of polyesters and define four main classes of linear polyesters.

1.1.1. Aliphatic polyesters are low melting (40 - 80 °C) semicrystalline polymers or viscous fluids and present inferior mechanical properties. Notable exceptions are poly (α -hydroxyacid)s and poly (β -hydroxyacid)s.

1.1.2. Aromatic-aliphatic polyesters, in which R^1 or R^2 is aromatic, are generally high melting (150-270 °C) semicrystalline materials that find applications as engineering thermoplastics, films, or fibers.

1.1.3. Wholly aromatic polyesters, in which both R^1 and R^2 are aromatic, are either high- T_g amorphous polymers or very high melting semicrystalline polymers that often exhibit liquid crystalline properties.

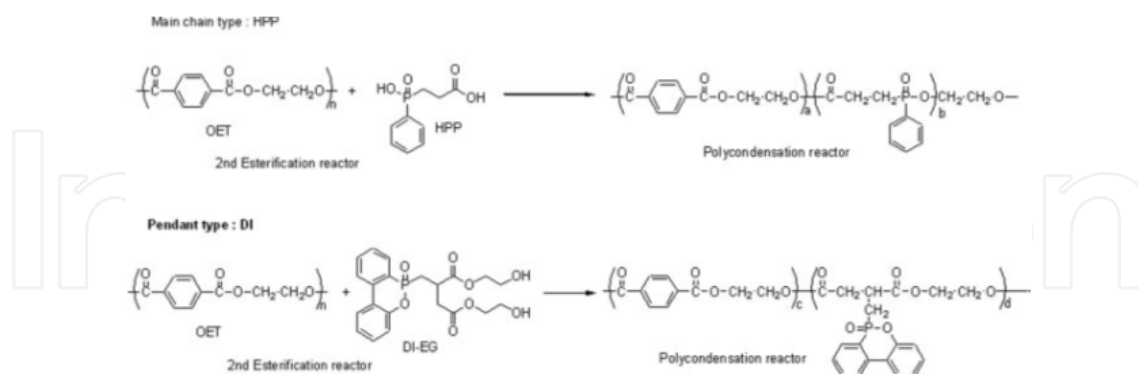
1.1.4. Polyester thermoplastic elastomers, which are obtained by replacing a part of the R^2 diol by dihydroxy polyether macro monomer, present biphasic morphology and rubberlike properties.

2. History of thermally stable polyesters

Polyester resin is attractive in different ways. This material is being used efficiently as folding resin, blend forming, film, fiber, surface covering, rubber and plasticizer. The common factor in these different materials is that all of them contain some joint in their main chain. Different methods for preparation of thermally stable polyester are shown below.

2.1. Flame retardant polyesters

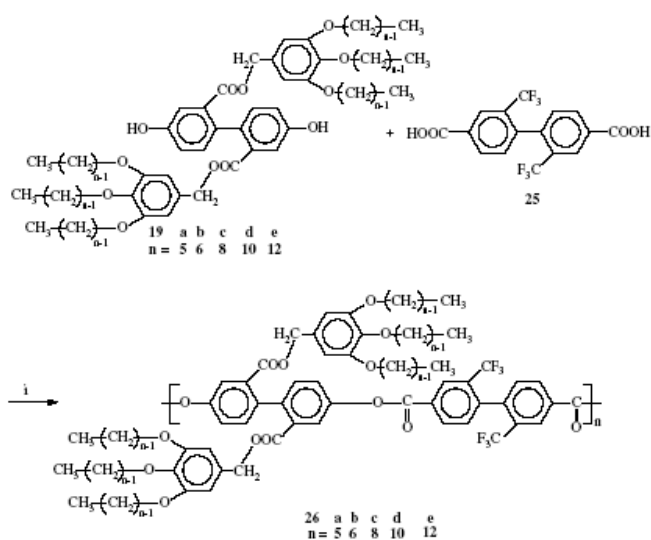
Kim & Yang (Kim & Yang, 2001, 2003, 2008) used phosphorous compounds and copolymerized together to produce polyesters which are resistant to flame and because of their suitable properties (Scheme 2).



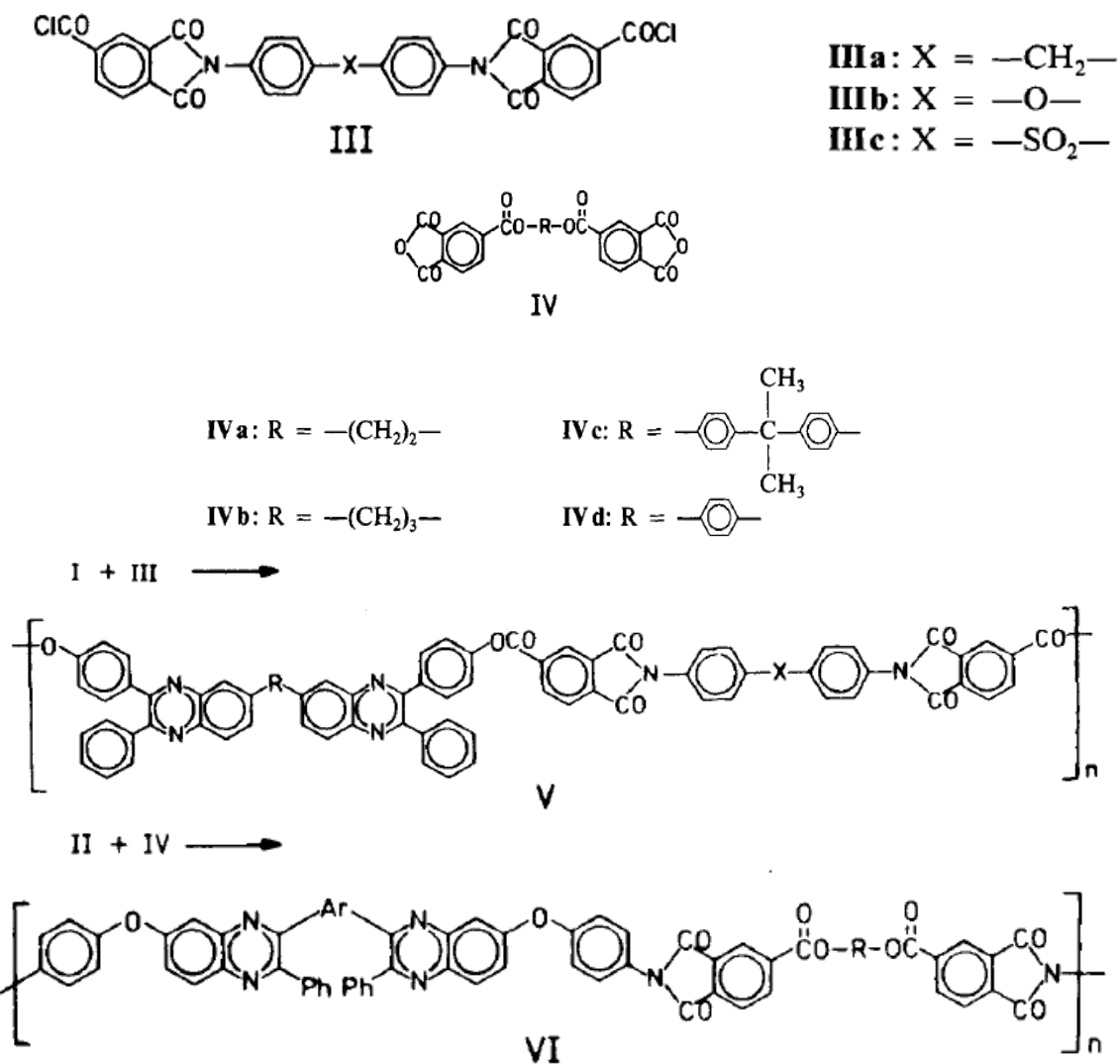
Scheme 2.

2.2. Polyester with alkyl group in the addition chain

Wang et al. (Wang, 2008) produced polyesters in which substituents have many alkyl groups. These polyesters have better solubility than polyesters with one alkyl group; however they are less thermo resistant. Polymer with $C_5 - C_{10}$ are amorphous and more than C_{10} are crystalline, its film is totally sleek (Scheme 3).



Scheme 3.



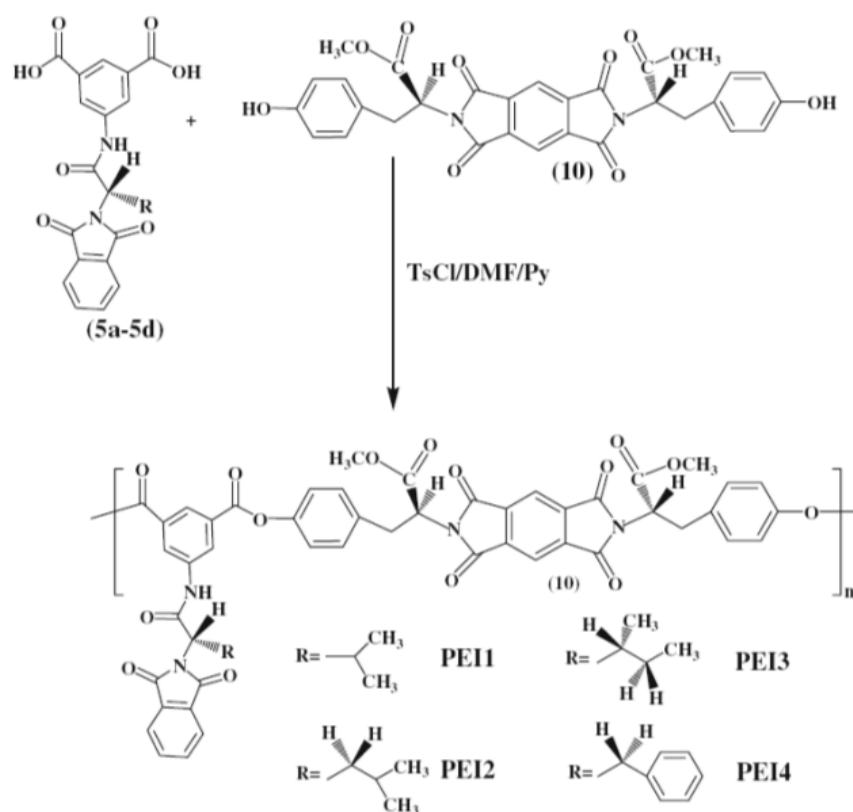
Scheme 4.

2.3. Polyester with quinoxaline ring in the main chain

This type of polyesters (Akutsu et al., 1985, 1987, 1990, 1998, 1999) are produced with heterocyclic groups in their main chain by addition of quinoxaline cycle into the polymer main chain and reaction of quinoxaline hydroxyl compound with diacids and quinoxaline amine compound with dianhydrides. Existence of these groups causes high thermoresistance of the polymer where they will not show any mass depreciatory until 300 °C. They have suitable electrical properties and have capability to form film. These groups are also used in production of pigments (Scheme 4).

2.4. Polyester-imide

This kind of polyester is formed by solution (dilution) condensation polymerization. This polyester has been produced from aromatic diols with aromatic and aliphatic diacidchlorides in high efficiency (Asadi & Shadpour, 2010). These polymers are capable of forming film and semi-cristalline aromatic polyester-imides. The aromatic-aliphatic polyester-imides are amorphous due to their structure (Scheme 5).

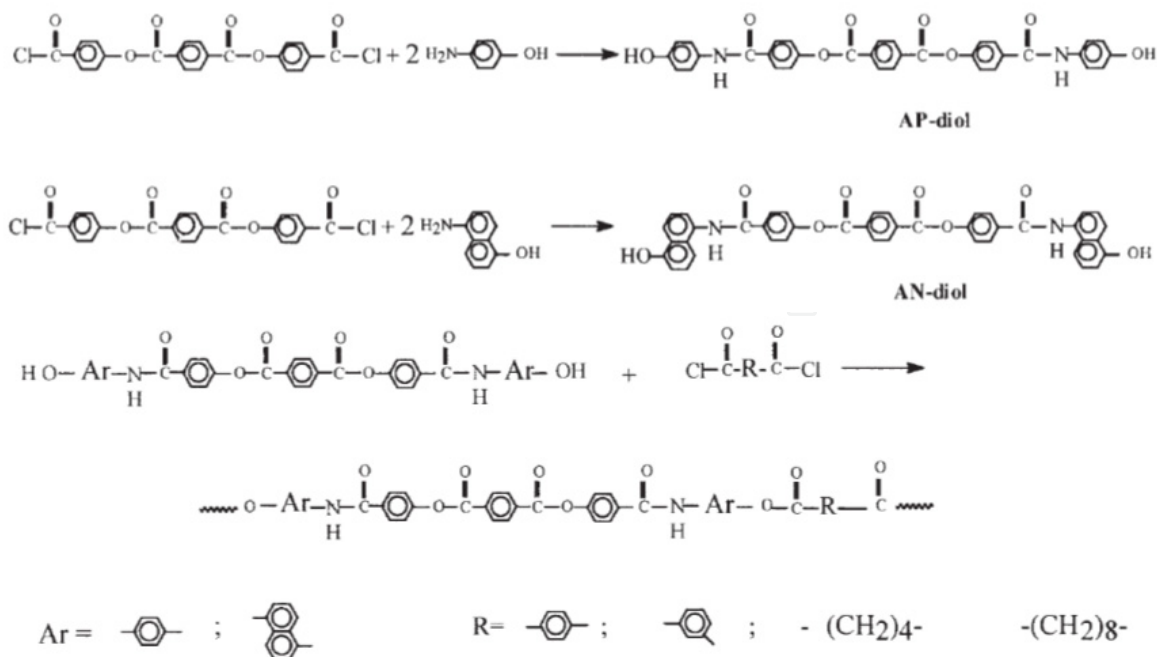


Scheme 5.

2.5. Polyester –Amide – Ester

Polyester-amide-esters are produced by reaction of diols which contain ester-amide-ester groups with aromatic and aliphatic diacidchlorides (Einollahi & Mehdipour, 2004). Totally,

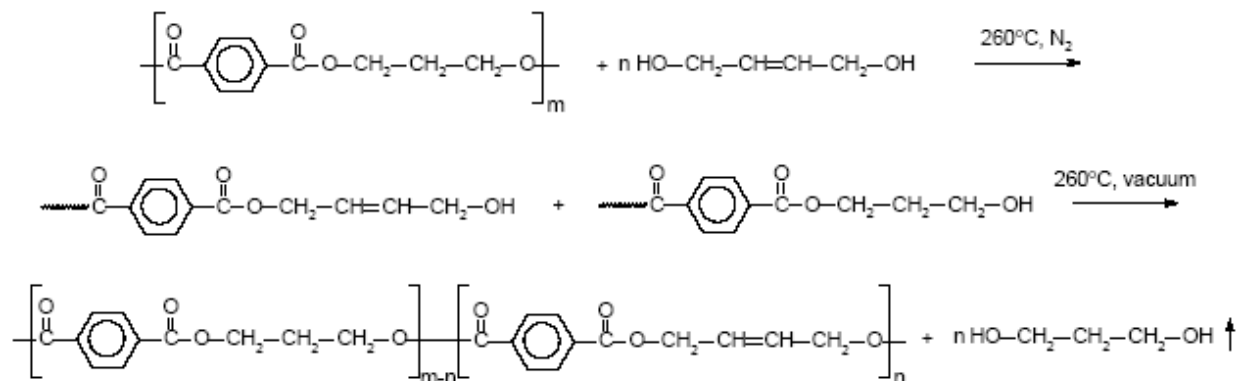
aromatic polymers have a minimum thermoresistance and maximum solubility. Films from these polymers are brittle (Scheme 6).



Scheme 6.

2.6. Unsaturated polyester

Aromatic unsaturated polyester is produced by solid state polymerization of glycolized diol (Boehme et al., 2006). Continuous glycolization is done by an extruder that unsaturated bonds appears as conjugated (Scheme 7).

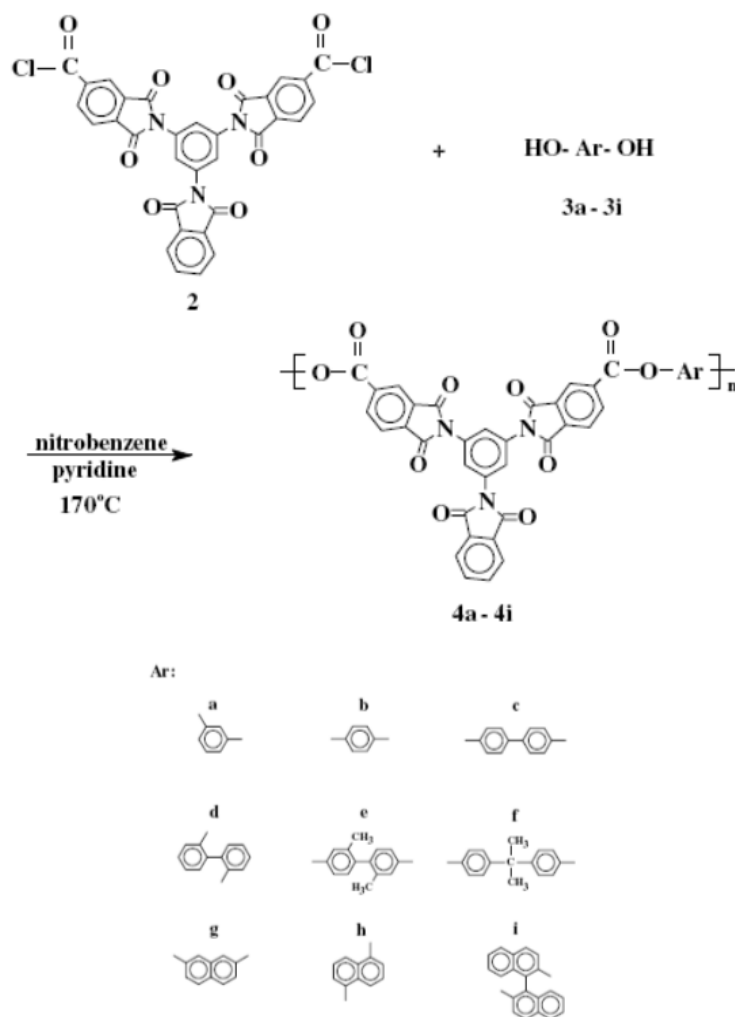


Scheme 7.

2.7. Aromatic polyester-imide

Aromatic polyester-imide is produced by soluble condensation polymerization in high temperature (Behniafar et al., 2005). Pyridine is used as absorbent of produced hydrogen

chloride. High solubility in polar solvent such as dimethylformamide and tetrahydrofuran, T_g about 300 °C and mass reduction about 10 % in 450 °C have been proven (Scheme 8).



Scheme 8.

2.8. Polyester with sulfur in the main chain

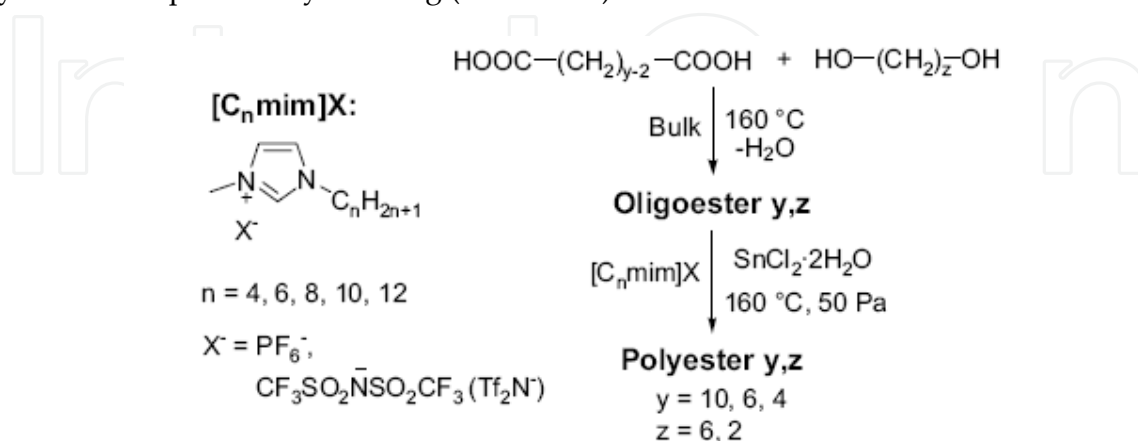
This type of polyesters are produced by from sulfonic diols with sulfur in the main chain with aliphatic diacidchlorides possessing methylene groups from 2 to 10 groups (Hirano, 2004). They have high molecular weight and crystalline structure and also high thermo resistance (Scheme 9).

2.9. Polyester with aryl-ether group

This polyester produced (Chern & Huang, 1998) with solution polycondensation in high temperature. These polyesters have good solubility and high molecular weight. Their 5 % mass reduction temperature is about 400 °C in N_2 atmosphere. Their Young's modulus is about 40 MPa and their elongation at break is about 4 % (Scheme 10).

2.11. Aliphatic polyester with high molecular weight

This polyester is produced in two steps in bulk polycondensation. These polyesters are among biopolymer and specifically polymers which are among green chemistry family (Fu & Liu, 2008). They have high molecular weight and to achieve this high molecular weight they have to be purified by washing (Scheme 12).



Scheme 12.

3. Experiments

3.1. Synthesis of polyesters with azaquinoxaline ring (Ghaemy et al., 2009)

3.1.1. Synthesis of the monomer

Synthesis of the monomer 2,3-Bis(4-hydroxy phenyl)-5-azaquinoxaline diol (DIOL) took place in two steps: first, the synthesis of 4,4'-dihydroxybenzil (DHB), and second, the reaction of DHB with 2,3 diamino pyridine. Both steps are described in Scheme 13.

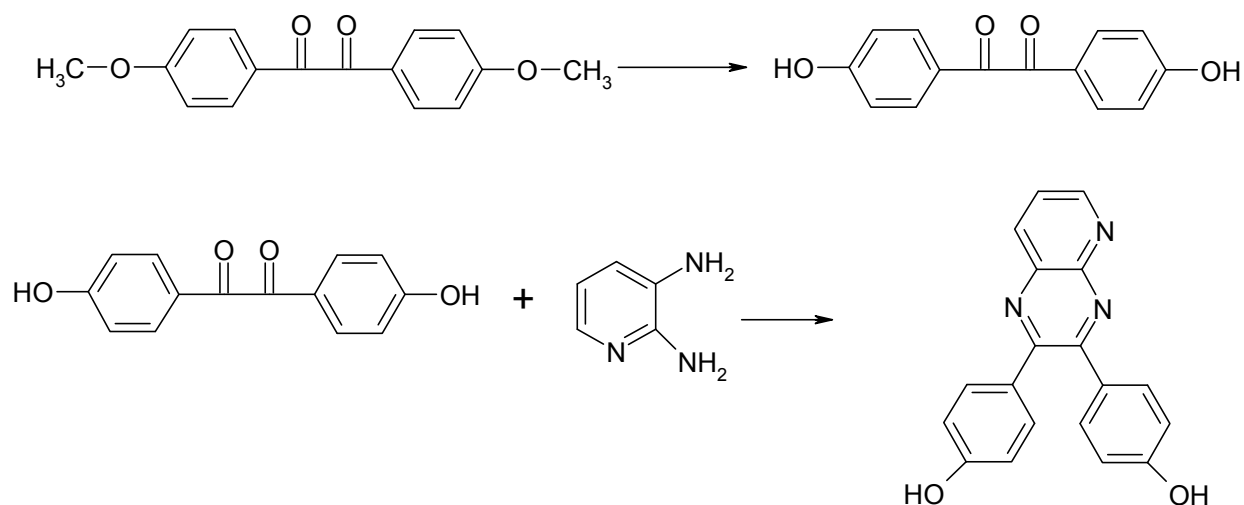
3.1.1.1. 4, 4'-Dihydroxybenzil (Moylan et al., 1993)

In a 1 L, three-necked, round-bottom flask equipped with a reflux condenser, a magnetic stirrer bar, and a nitrogen inlet were placed 6 g (22 mmol) of 4,4'- dimethoxybenzil, 60 ml of acetic acid (HOAc), and 300 ml HBr (68%). The suspension was heated at reflux with stirring for 4 h to become a homogeneous yellow solution which was cooled to room temperature, during which a yellow solid was formed. The solid was filtered, washed with cold water several times, recrystallized in HOAc, and dried in vacuum oven. The yellow needles obtained in a yield of 82% (3.3 g), which starts to melt at 244 °C.

3.1.1.2. 2,3-Bis(4-hydroxy phenyl)-5-azaquinoxaline

A 500 ml, round-bottom flask equipped with a magnetic stirrer bar, a reflux condenser, a Dean-Stark trap and a nitrogen inlet was charged with 0.48 g (2 mmol) of 4,4'-dihydroxybenzil, 0.22 g (2 mmol) of 2,3-diaminopyridine, 50 ml of toluene, and 36 ml of deoxygenated acetic acid. The reaction mixture was stirred at reflux for 12 h, during which the generated water was collected in the Dean-Stark trap. The reaction vessel was let to cool to room temperature, and then poured into 500 ml slurry of ice and water containing 7.2 ml

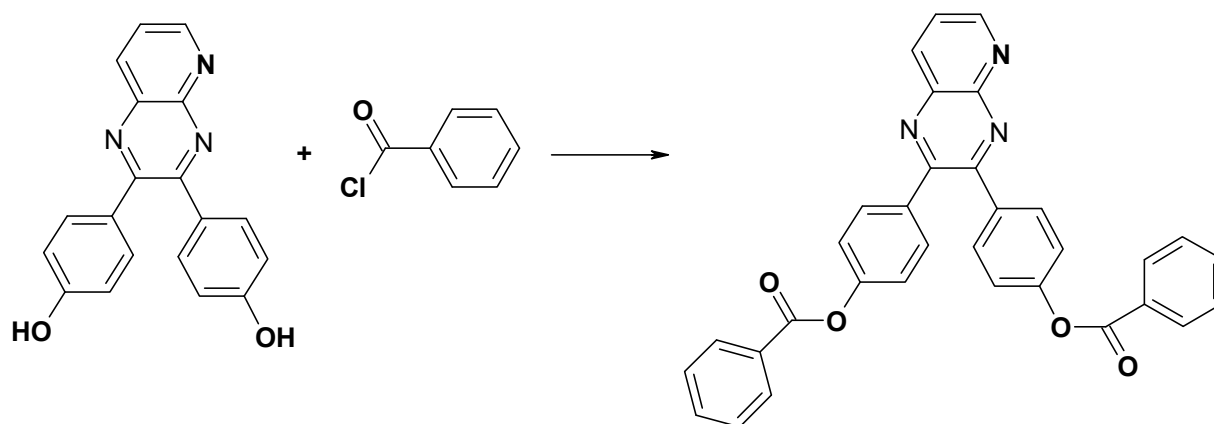
of HCl (37%). The precipitate was filtered and recrystallized in ethanol. The dark yellow powder was obtained with a yield of 85% and melting at 324 °C.



Scheme 13.

3.1.1.3. Synthesis of the model compound

Model compound was prepared from 2,3-bis(4-hydroxyphenyl)-5-azaquinoxaline and benzoyl chloride by using conventional method, Scheme 14. A two-necked round-bottom flask equipped with a magnetic stirrer bar, a reflux condenser and a nitrogen inlet/outlet tube was charged with DIOL (0.314 g, 1 mmol) in 20 ml DMF and 0.8 ml triethylamine. A solution of benzoyl chloride (0.244 g, 2 mmol) in 10 ml DMF was added drop wise at 0 °C. The reaction was stirred for 5 h at room temperature. The solution was then poured into water, and the precipitate was filtered and washed several times with the solution of NaHCO₃. The solid product was then dried in a vacuum oven at 60 °C (Scheme 14).

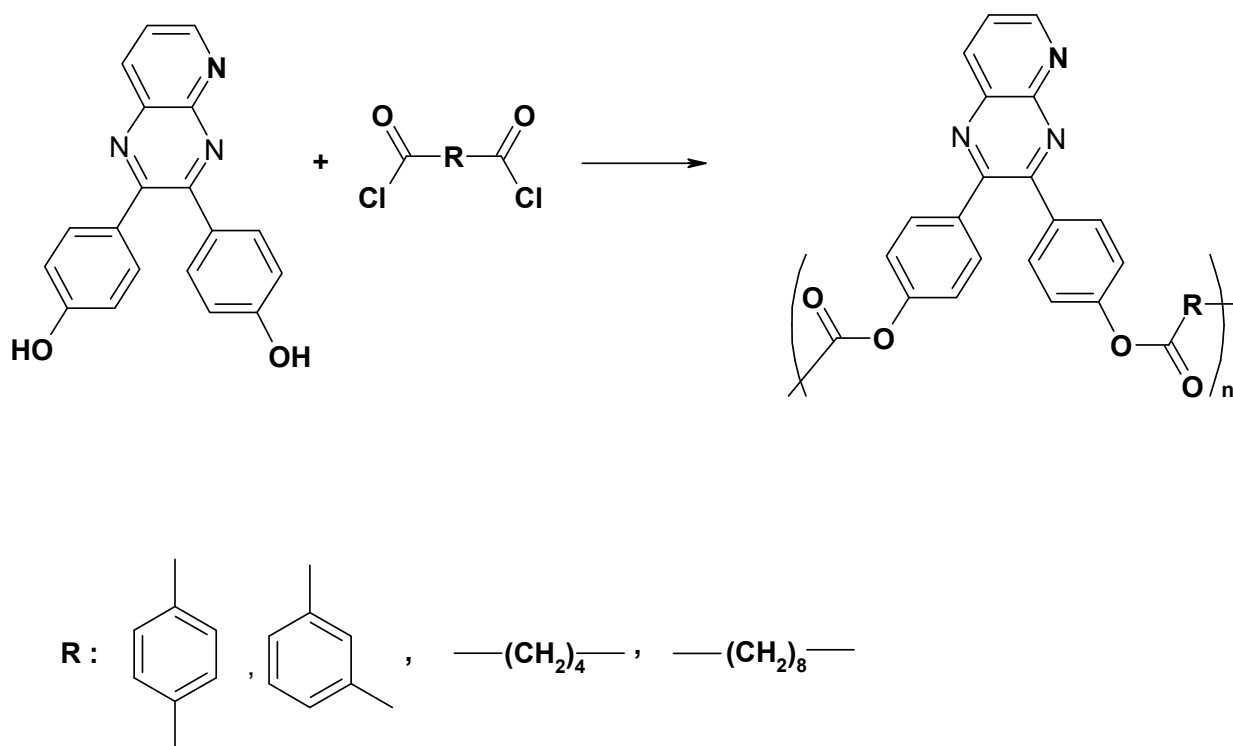


Scheme 14.

3.1.1.4. Synthesis of polyesters

Polyesters were prepared from polycondensation of 2,3-bis(4-hydroxyphenyl)-5-azaquinoxaline with aromatic and aliphatic dicarboxylic dichlorides such as terephthaloyl

dichloride, isophthaloyl dichloride, sebacoyl dichloride and adipoyl dichloride. A typical synthesis procedure for the preparation of polyesters was conducted in three-necked, round-bottom flask equipped with a nitrogen inlet, a condenser and a magnetic stirrer bar. The flask was charged with the diol (0.628 g, 2 mmol) in 20 ml DMF and 0.8 ml triethylamine. A solution of terephthaloyl dichloride (0.406 g, 2 mmol) in 10 ml DMF was added drop wise at 0 °C. The reaction mixture was stirred for 5 h at room temperature. The solution was then poured into water and the precipitate was filtered and washed several times with the solution of NaHCO₃. The solid product was then dried in a vacuum oven at 60 °C. The synthesis procedure and the polymer designations are shown in Scheme 15.



Scheme 15.

3.2. Synthesis of polyesters with urazole ring (Mighani et al., 2011)

3.2.1. Preparation of monomers

3.2.1.1. 4-Nitrobenzoylchloride (Mallakpour & Nasr, 2002)

A 100 ml flask was charged with a mixture of 4-nitrobenzoic acid. (5.00 g, 29.9 mmol), 5 ml thionyl chloride and 20 ml ethylacetate. Subsequently the mixture was stirred at reflux temperature for 2 hours to obtain a transparent solution. Next the additional content of thionyl chloride and solvent was extracted out of solution by using distillation and was poured into cold water. The yellow powder produced was separated by filtration. Then the product dried in vacuum oven at 50 °C. A purified sample was obtained by recrystallization from carbon tetrachloride and obtained in 95% yield (5.436 g) with the melting point of 71-72 °C.

3.2.1.2. 4-Nitrobenzoylazide (Mallakpour & Nasr, 2002)

A 100 ml flask was charged with 4-nitrobenzoylchloride (5.43 g, 29.2 mmol) and 10 ml acetone. The mixture was subsequently stirred at 5 °C temperature and then added dropwise of a sodiumazide solution (1.69 g, 30.1 mmol) in 7 ml water for 30 minutes. The solution was stirred for additional 1 hour and the white precipitate was filtered and dried at air. A purified sample was obtained in a 90% yield (4.95 g) with the melting point of 73-75 °C.

3.2.1.3. 1-Ethoxycarbonyl-4-(4-nitrophenyl) semicarbazide (Mallakpour & Nasr, 2002)

A 250 ml flask was charged with 4-nitrobenzoylazide (4.00 g, 21 mmol) and 75 ml dried toluene. The mixture was subsequently stirred under N₂ at reflux temperature for 6 hours. The solution was cooled and filtered. The solution was cooled at 5 °C and then charged dropwise with a mixture of ethylhydrazin carboxylate (ethyl carbazate) (2.70 g, 21 mmol) and 40 ml dried toluene in 15 minutes. The solution was stirred for 30 minutes in ice bed and for 1 hour at room temperature. The solution refluxed for 3 hours, cooled, filtered and dried at 70 °C for one day. A purified sample was obtained in a 93% yield (4.8 g) with the melting point of 219-220 °C.

3.2.1.4. 1-Ethoxycarbonyl-4-(4-aminophenyl)semicarbazide (Mallakpour & Nasr, 2002)

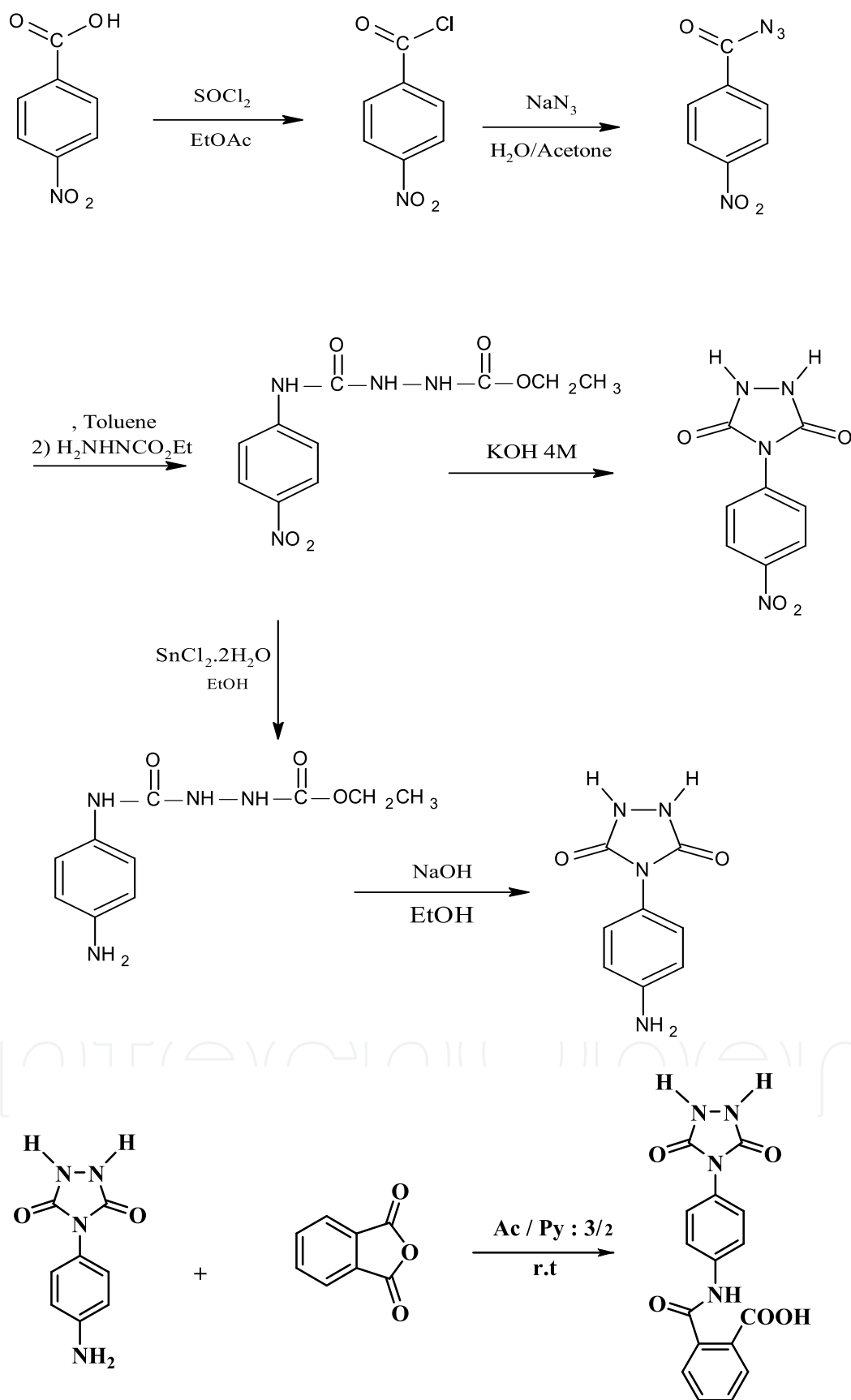
A 250 ml flask was charged with 1-ethoxycarbonyl-4-(4-nitrophenyl) semicarbazide (3.04 g, 11.3 mmol), SnCl₂·2H₂O (9.37 g, 4.3 mmol) and 15 ml ethanol. The mixture was subsequently stirred under N₂ at reflux temperature for 4.5 hours to obtain a transparent solution. The solution was cooled with ice bed and water and stirred for 15 minutes. The pH of solution was raised to 10 with a solution of sodium hydroxide 30%. The mixture was put in 30 ml ethylacetate. Afterward the white powder was filtered and dried at 70 °C for one day. A purified sample was obtained in a 82% yield (2.2 g) with the m.p. >340 °C.

3.2.1.5. 4-(4-aminophenyl)-1,2,4-triazolidyne-3,5-dione (Urazole) (Mallakpour & Nasr, 2002)

A 100 ml round flask was charged with pure sodium (0.23 g, 10 mmol) dissolved in 14 ml absolute ethanol. The solution was under N₂ and added 1-ethoxycarbonyl-4-(4-aminophenyl) semicarbazide (2 g, 8.4 mmol). The mixture was subsequently stirred under N₂ at reflux temperature for 4.5 hours and cooled with ice bed. The solution was neutralized with HCl 30%. The product was filtered (1.38 g, 86%), recrystallized with hot water and dried. A purified sample was obtained in a 86% yield (1.38 g) with the melting point 270-273 °C.

3.2.1.6. 4-(4-phthalimidophenyl)-1,2,4-triazolidyne-3,5-dione (Mallakpour & Nasr, 2002)

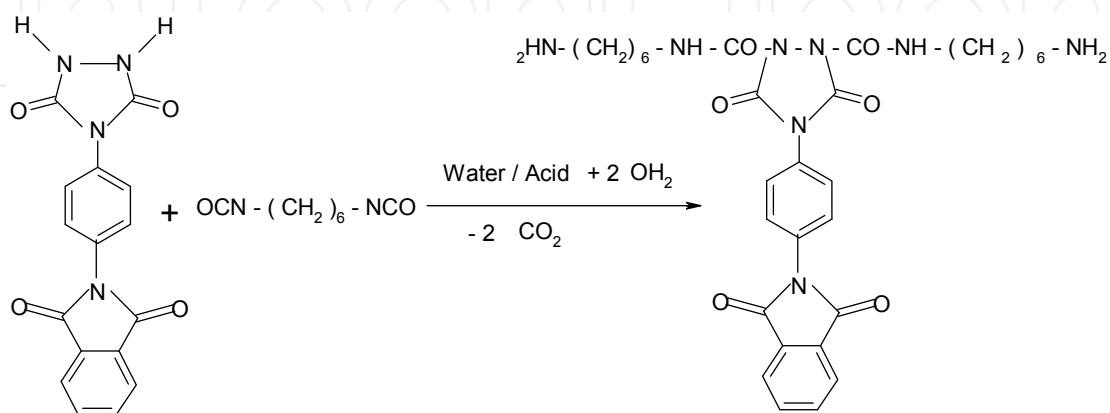
A 25 ml round flask was charged with 4-(4-aminophenyl) urazole (0.2 g, 1.04 mmol) and a mixture of solvents acetic acid/ pyridine (3/2) and anhydride phthalic (0.15 g, 1.04 mmol). The mixture was subsequently stirred at room temperature for 2 days till the amic acid was produced as a white precipitate. The solution was stirred at reflux temperature for 8 hours and then filtered and the white precipitate washed with ethanol, filtered and dried. The white purified sample (1.38 g) was obtained in a 76% yield (0.46 g) with the melting point of 363-365 °C (Scheme 16).



Scheme 16.

3.2.1.7. 4-(4-phthalimidophenyl)-1,2,4-triazolidyne-3,5-diamine

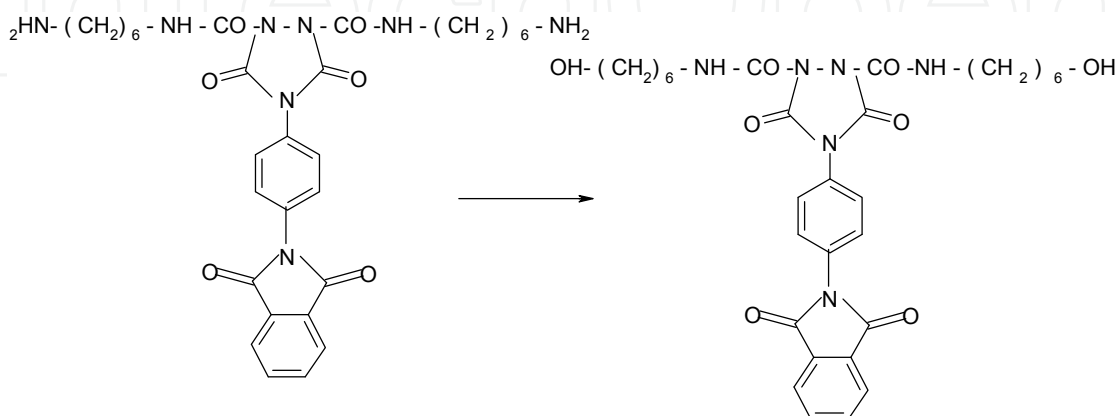
A 10 ml round flask was charged with 4-(4-phthalimidophenyl)-1,2,4-triazolidyne-3,5-dione (2.5 g, 7.7737 mmol), and hexamethylenediisocyanate (0.2615 g, 1.555 mmol) and 3 ml dimethylformamide. The mixture was subsequently stirred at room temperature for 2 days and the precipitate was obtained in a Solution with low concentration of water/acid and filtered and dried. The purified sample was obtained in a 85% yield with the melting point 124 – 125 °C (Scheme 17).



Scheme 17.

3.2.1.8. 4-(4-phthalimidophenyl)-1,2,4-triazolidyne-3,5-diol

To a 250 ml. three-necked flask equipped with a mechanical stirrer and an addition funnel were added 4-(4-phthalimidophenyl)-1,2,4-triazolidyne-3,5-diamine (6.06 g, 0.0100 mol), concentrated hydrochloric acid (22 ml), and water (100 ml). The solution was cooled to 0 °C in an ice bath. A solution of sodium nitrite (1.45 g, 0.0210 mmol) in water (10 ml) was added at 0 - 5 °C. the resulting solution was poured into a cold solution of phosphoric acid (20 ml) in water (1.8 l). After stirring for 5 min. The organic mixture was heated at the boiling point for 10 min. The mixture was cooled and extracted with diethyl ether (3 x 200 ml). The combined organic phase was extracted with 2 N sodium hydroxide solution (2 x 50 ml). The combined aqueous phase was acidified with concentrated hydrochloric acid, extracted with diethyl ether (3 x 100 ml) and dried with magnesium sulfate (Scheme 18).



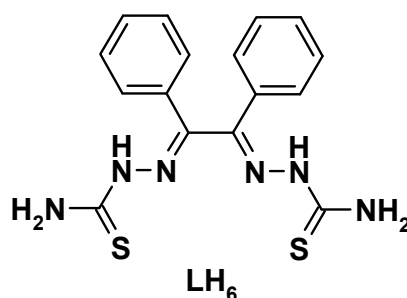
Scheme 18.

3.3. Synthesis of polyesters with thiosemicarbazid ring (Ghaemy et al., 2008)

3.3.1. Preparation of monomers

3.3.1.1. Benilbisthiosemicarbazone diamine LH6 (Arquero et al., 1998)

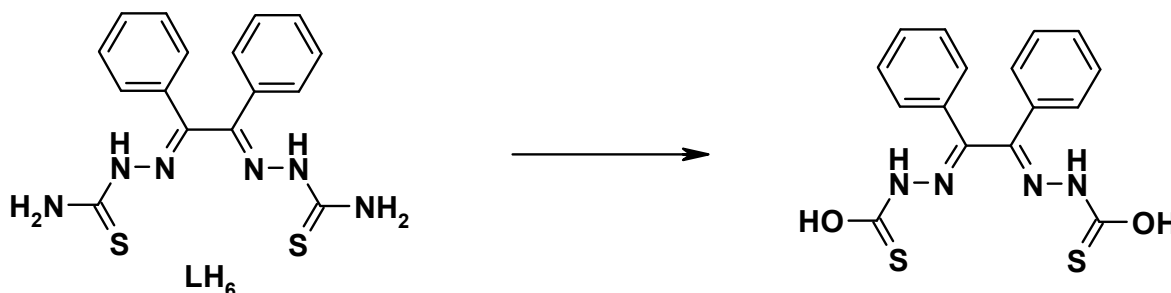
The thiosemicarbazide (3.64 g, 40.30 mmol) was dissolved in 40 ml of 2N HCl and 1ml of conc. HCl and then added to a suspension of benzyl (4,24 g, 20.20 mmol) in 50 ml of methanol and a few drops of conc. HCl. The mixture was stirred for 6 h at room temperature. The yellow solid was filtered off, washed with methanol and dried in a vacuum oven at 70 °C for 2 h. A yellow solid product was obtained in a 75% yield which starts to melt and decompose at 240 °C (Scheme 19).



Scheme 19.

3.3.1.2. Benilbisthiosemicarbazone diol

To a 250 ml. three-necked flask equipped with a mechanical stirrer and an addition funnel were added Benilbisthiosemicarbazone LH6 (3.56 g, 0.0100 mol), concentrated hydrochloric acid (22 ml) and water (100 ml). The solution was cooled to 0 °C in an ice bath. A solution of sodium nitrite (1.45 g, 0.0210 mmol) in water (10 ml) was added at 0-5 °C. The resulting solution was poured into a cold solution of phosphoric acid (20 ml) in water (1.8 l). After stirring for 5 min. The organic mixture was heated at the boiling point for 10 min. the mixture was cooled and extracted with diethyl ether (3 x 200 ml). The combined organic phase was extracted with 2 N sodium hydroxide solution (2 x 50 ml). The combined aqueous phase was acidified with concentrated hydrochloric acid, extracted with diethyl ether (3 x 100 ml) and dried with magnesium sulfate (Scheme 20).



Scheme 20.

Author details

Hossein Mighani
 Uni of Golestan, Iran

4. References

- Acierno, D.; Fresab, R.; Iannelli, P. & Vacca, P. (2000) segmented liquid-crystalline polyesters with allyl groups as lateral substituents, synthesis and characterization, *Polymer*, 41, pp. 4179-4187, ISSN 0032-3861
- Akutsu, F.; Inoki, M.; Sunouchi, K.; Sugama, Y.; Kasashima, Y.; Naruchi, K. & Miura, M. (1998) synthesis and properties of novel polyamides containing 2-methyl-4,5-oxazolidinyl structure, *Polymer*, 39, pp. 1637-1641, ISSN 0032-3861
- Akutsu, F.; Hirata, H.; Hayashi, H.; Miura, M. & Nagakubo, K. (1985) Synthesis of polyamides containing α -diketone moieties and 2,3-quinoxalinediyl units in the main chain, *Macromol.chem.rapid commun* 6, pp. 215-218, ISSN 1521-3927
- Akutsu, F.; Inoki, M.; Inagawa, T.; Kasashima, Y.; Sonoda, Y. & Marushima, K. (1999) Metal adhesive properties of polyamides having the 2,3-bis(1,4-phenylene)quinoxalinediyl structure, *Journal of Appl Polym Science*, 74, pp. 1366-1370, ISSN 1097-4628
- Akutsu, F.; Kuze, S.; Matsuo, K.; Naruchi, K. & Miura, M. (1990) Preparation of polyimides from 2,3-bis(4-aminophenyl)quinoxalines and aromatic tetracarboxylic dianhydrides, *Macromol. chem. Rapid commun.*, 11, pp. 673-677, ISSN 1521-3927
- Akutsu, F.; Hayashi, H.; Miura, M. & Nagakubo, K. (1985) synthesis of polyamides having 2,3-benzog[*g*]quinoxalinediyl units in the main chain, *Macromol. Chem. rapid commun.*, 6, pp. 475-479, ISSN 1521-3927
- Akutsu, F.; Naruchi, K.; Miura, M. & Nagakubo, K. (1987) polyesters with 2,3-quinoxalinediyl units in the main chain, *Macromol. Chem. rapid commun.*, 8, pp. 113-117, ISSN 1521-3927
- Arquero, A.; Cafiadas, M.; Martinez-Ripoll, M.; Mendiola, A. & Rodriguez, A. (1998) Selective access to new semicarbazone and thiosemicarbazone derived from benzyl. Study of their conversion reactions, *Tetrahedron*, 54, pp. 11271-11284, ISSN 0040-4020
- Bruma, M.; Schulz, B.; Koepnick, T.; Stiller, B.; Belomoina, N. & Mercer, F. (1999) Synthesis and study of aromatic polyamides containing silicon and phenylquinoxaline ring in the main chain, *Europ. polymer journal*, 35, pp. 1253-1260, ISSN 0014-3057
- Behniafar, H.; Akhlaghinia, B. & Habibian, S. (2005) synthesis and characterization of new soluble and thermally stable poly(ester-imide)s derived from N-[3,5-bis(trimellitoyl)phenyl]phthalimide and various bisphenols, *European polymer journal*, 41, pp. 1071-1078, ISSN 0014-3057
- Boehme, F.; Komber, H. & Jafari, S.H. (2006) synthesis and characterization of a novel unsaturated polyester based on poly(trimethylene terephthalate), *polymer*, 47, pp. 1892-1898, ISSN 0032-3861
- Bruma, M.; Hamciuc, S.E.; Hamciuc, C.; Belomoina, N.M. & Krongiuz, E.S. (1992) Thermostable polyesters containing imide and phenylquinoxaline units, *Die Angewandte Makromolekulare Chemie*, 194, pp. 179-187, ISSN 1522-9505

- Chern, Y.T. & Huang, C.M. (1998) synthesis and characterization of new polyesters derived from 1,6- or 4,9-diamantanedicarboxylic acyl chlorides with aryl ether, *polymer*, 39, pp. 2325-2329, ISSN 0032-3861
- Fu, C. & Liu, Z. (2008) synthesis of high molecular weight aliphatic polyesters in 1-alkyl-3-methylimidazolium ionic liquids, *polymer*, 49, pp. 461-466, ISSN 0032-3861
- Ghaemy, M.; Mighani, H. & Ziaei, P. (2009) Synthesis and characterization of novel organosoluble polyesters based on a DIOL with azaquinoxaline ring, *Journal of Applied Polymer Science*, 114, pp. 3458-3463, ISSN 1097-4628
- Ghaemy, M.; Mighani, H. & Behmadi H. (2008) synthesis and characterization of novel Schiff-base polyamides from copper/benzilbisthiosemicarbazone complexes, *Journal of Applied Polymer Science*, 109, pp. 2388-2394, ISSN 1097-4628
- Hirano, H.; Watase, S. & Tanaka, M. (2004) Linear polymers with sulfur in the main chain. II. Synthesis of polyesters by interfacial polycondensation of bis(4,4'-hydroxyphenyl)sulfide with several aliphatic acid dichlorides and their properties, *Journal of applied polymer science*, 91, pp. 1865-1872, ISSN 1097-4628
- Mallakpour, S. & Asadi, P. (2010) Novel chiral poly(ester-imide)s with different natural amino acids in the main chain as well as in the side chain: synthesis and characterization, *Colloid polymer science*, 288, pp. 1341-1349, ISSN 0303-402X
- Mehdipour-Ataei, S. & Einollahy, P. (2004) Novel diols containing ester and amide groups and resulting poly(ester-amide-ester)s, *Journal of applied Polymer Science*, 93, pp. 2699-2703, ISSN 1097-4628
- Mighani, H.; Nasr Isfahani, H. & Mighani, S. (2011) Novel organosoluble polyamides with phthalimide pendant group: Synthesis, physical and thermal characterization, *macromolecules, an Indian journal*, 7, pp. 78-84, ISSN 0974-7478
- Moylan, C.R.; Miller, R.D.; Twieg, R.J.; Betterton, K.M.; Lee, V.Y.; Matray, T.J. & Nguyen, C. (1993) Synthesis and nonlinear optical properties of donor-acceptor substituted triaryl azole derivatives, *Chem Mater*, 5, pp. 1499-1508, ISSN 0897-4756
- Rogers, M.E. & Long, T.E. (2003) synthetic Methods in Step-Growth polymers, John Wiley & Sons. Inc, ISBN:0.471-38769-X, New Jersey, USA
- Shadpour-Mallakpour, E. & Nasr-Isfahani, H. (2002) Synthesis of Novel Azo dyes derived from 4-Phenylurazole, *Indian Journal of Chemistry*, 41B, pp. 169-174, ISSN: 0376-4699
- Wang, D.H.; Cheng, S.Z.D. & Harris, F.W. (2008) synthesis and characterization of aromatic polyesters containing multiple n-alkyl side chain, *Polymer*, 49, pp. 3020-3028, ISSN 0032-3861
- Yang, C.P.; Chen, R.S. & Yu, C.W. (2001) Preparation and characterization of organosoluble polyimides based on 1,1-bis[4-(3,4-aminophenoxy)phenyl]cyclohexane and commercial aromatic dianhydrides, *Journal of Applied Polymer Science*, 82, pp. 2750-2759, ISSN 1097-4628
- Yang, C.P. & Su, Y.Y. (2003) properties of organosoluble aromatic polyimides from 3'-trifluoromethyl-3,4'-oxydianiline, *polymer*, 44, pp. 6311-6322, ISSN 0032-3861
- Yang, S.C. & Kim, J.P. (2008) Flame retardant polyesters. III. Fibers, *Journal of Applied Polymer Science*, 108, pp. 2297-2300, ISSN 1097-4628
- Zhu, Q. & Han, C.C. (2007) synthesis and crystallization behaviors of highly fluorinated aromatic polyesters, *polymer*, 48, pp. 3624-3631, ISSN 0032-3861