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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 bisketenes 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 ring opening 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 prejudicial 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).

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 mit $C_5 - C_{10}$ are amorph and more than $C_{10}$ are crystalline, its film is totally sleek (Scheme 3).
Scheme 3.

\[ \text{IIIa: } X = \text{--CH}_2\text{--} \]
\[ \text{IIIb: } X = \text{--O--} \]
\[ \text{IIIc: } X = \text{--SO}_2\text{--} \]

\[ \text{IVa: } R = \text{--(CH}_2\text{)_2--} \]
\[ \text{IVb: } R = \text{--(CH}_3\text{)}_3-- \]
\[ \text{IVc: } R = \text{--CH}_3\text{--} \]
\[ \text{IVd: } R = \text{--C--} \]

\[ 1 + \text{III} \rightarrow \]

\[ \text{II} + \text{IV} \rightarrow \]

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.](image)

### 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
Polyester chloride. High solubility in polar solvents 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 \( \text{N}_2 \) atmosphere. Their Young's modulus is about 40 MPa and their elongation at break is about 4 % (Scheme 10).
2.10. Aromatic fluoro polyester

This polymer produced by Hahn & Zhu (Hahn & Zhu, 2007). This polymer is not soluble in organic solvents while soluble in polar solvents such as dimethylsulfoxide (DMSO), dimethylformamide (DMF) and dimethyacetamide (DMAC). This polymer is crystalline (Scheme 11).
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](image)

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 benzoyle 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 benzoylechloride (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, sebacyl 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 NaHCO$_3$. 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.](image)

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 form carbontetrachloride 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-introbenzoylchloride (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-Ethoxycarbonly-4-(4-introphenyl) 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 solutions was cooled and filtered. The solution was cooled at 5 °C and then charged dropwise with a mixture of ethylhydrazin carboxilate (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 hourse 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 with 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 (Urazole) (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 organe 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. Benilbisthisosemicarbazone diamine LH6 (Arquero et al., 1998)

The thiosemicabazide (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).

3.3.1.2. Benilbisthisosemicarbazone diol

To a 250 ml. three –necked flask equipped with a mechanical stirrer and an addition funnel were added Benilbisthisosemicarbazone 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 organe 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).
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