



In Based on Amino Acid Compounds Synthesis of New Poly(Ester-Imide)s and Poly(Imide-Urethane)s Derivatives

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ABSTRACT

20 new poly(ester-imide)s and poly(imide-urethane)s structures were synthesized using low temperature solution condensation polymerization. These compounds were optically active, capable of emitting circularly polarized light. The results indicated that the efficiency of the compounds much higher under this synthesis method. Cost effectiveness and short process were other advantages of this synthesis method. The result of the thermal gravimetric analysis (TGA) revealed that heat resistance of some of these compounds was higher than 300°C. Characterization of the synthesized structures was carried out by ¹H-NMR, FT-IR, TGA, and elemental analysis.

Key words: FT-IR, NMR, Poly(amide-imide)s, TGA, Synthesis.

INTRODUCTION

Polymers are useful compounds which are utilized in various industries. Generally, they are composed of monomeric units joined together by polymerization. Polyamides, polyimides, polyesters, and polyurethanes are polymer. Polyimide is known as one of the best and most useful heat resistant, photo resistant, and chemically stable polymers. These polymers are so versatile that can be employed in production of various objects such as semi conductive materials, parts of vehicles and airplanes, coats of electrical wires and electronic circuits, electrical conductive adhesives¹, foams, and composites. There are

many approaches in production of polyesters by low temperature solution condensation polymerization²⁻⁵. Polyimide production methods can be arranged under two general categories: condensation and addition⁶. Fibred poly-imides are excellent alternatives to metals and, due to their high thermal, chemical and mechanical stability, are employed in making the body of airplanes and propulsion systems and vehicles such as automobiles, tanks and missiles⁷. These polymers are also utilized as gas separation membranes, optical and electrical conductive materials, ion exchange membranes, and anti-corrosion layers for metals such as iron. Polyesters are composed of aliphatic and aromatic components. Initially

simple polyesters were synthesized but in the late 1970s and early 1980s aromatic polyesters with liquid crystalline behavior were also synthesized. Although the heat resistance and chemical stability of the fibers originated from these polymers were not favorable but they had a high modulus and good strength. Aromatic polyester was introduced about 90 years ago by Fisher in the form of polyester synthesized from *para*-hydroxybenzoic acid (HBA)⁸. Then, aromatic polyesters with high molecular weight were synthesized⁹⁻¹⁹. Normally, polyesterification reactions develop slowly and, therefore, achieving a sample with high molecular weight is very difficult. Even under high temperatures, such reactions normally took a long time to perform and sometimes initiate only in presence of a catalyst. There are four major polymerization methods for synthesis of polyesters: solution, melt, interfacial, and slurry polymerization. One of the most important polyesters is Vectran. However, there are various methods for synthesis of polyester imides²⁰⁻²⁵.

Polyurethanes are polymers which contain urethane groups in their molecular structure. Such polymers are generally synthesized from reaction between monomers containing two groups of isocyanate and materials containing hydroxyl groups such as glycols, glycerol, castor oil, polyesters, and polyethers. Tendency of isocyanate group toward reaction with hydrogenous compounds such as amines or water results in variety in structure and properties of polyurethanes. Therefore, in addition to urethane groups and hydrocarbon bases, polyurethanes may also have etheric, esteric, amidic, or uric factors²⁶. Segmented thermoplastic polyurethane elastomers (STPUEs) which have both soft and hard segments are considered among important and valuable polymers. The soft parts are normally composed of polyesters or polyethers with high molecular weight which have high flexibility at room temperature and highly affect the properties of the polymer. The hard parts are composed of di-isocyanate and diol with low molecular weight²⁷. Thermostable polyurethanes have numerous properties which result in their wide applications in manufacturing decorative and structural materials, flexible foams for mattress and pillow, rigid foams for insulation, solid or micro foams for dyeing tools, painting rollers, hydraulic stamps,

and oil-resistant elastomers. They are also employed in manufacturing vibrational muffles, rollers, seat belts, covering materials, and etc²⁸. Depending on the reaction method, urethanes may be flexible, rigid, or moldable and can take the form of elastomers, adhesives, or protective covers²⁹. Recently, the application of urethanes has increased automobile industry³⁰. The commonest methods of producing polyurethanes are pre-polymerization and one-step process methods³⁰⁻³⁴. This study is conducted to synthesize new compounds from polyester imide and polyimide urethane derivatives via condensation solution reaction.

EXPERIMENTAL

General method

All the materials were bought from Merck of Germany and purified prior to use. Infrared (IR) spectra were recorded using a Shimadzu 435 IR Spectrometer. IR spectra were obtained from samples as KBr plate and thin-film on NaCl polished crystals. Vibrational frequencies were represented as wave number unit (cm^{-1}) and intensities of absorption bands were displayed as weak, medium, sharp, strong, and broad. Thermal gravimetric analysis (TGA) of the polymers was carried out using Mettler TGA-50 under nitrogen atmosphere at the scanning rates of 10, 30, and 40 °C/min. Elemental analysis of the prepared samples was performed using a Heraeus CHN rapid analyzer. Polymerization reactions were developed in a Samsung domestic microwave oven (2450-MHz and 900-W). Hydrogen Nuclear Magnetic Resonance (¹H-NMR) spectra of 90 and 300-MHz magnet were recorded by Varian EM-390 and Bruker Avance 500, respectively. Multiplicities of NMR peaks are displayed as singlet, doublet, double of doublet, and multiplet. Tetramethylsilane (TMS) was employed as the internal reference signal in measuring NMR spectra.

Synthesis

Synthesis of 2-(1-carboxy-2-methylbutyl)-1,3-dioxoisindoline-5-carboxylic acid structure

Into a 25 mL balloon equipped with a magnetic stirrer, trimellitic anhydride dioxo-1,3-dihydroisobenzofuran-5-carboxylic acid-1,3 (0.150 g, 7.806 mol⁻⁴), isoleucine amino-3-methylpentanoic

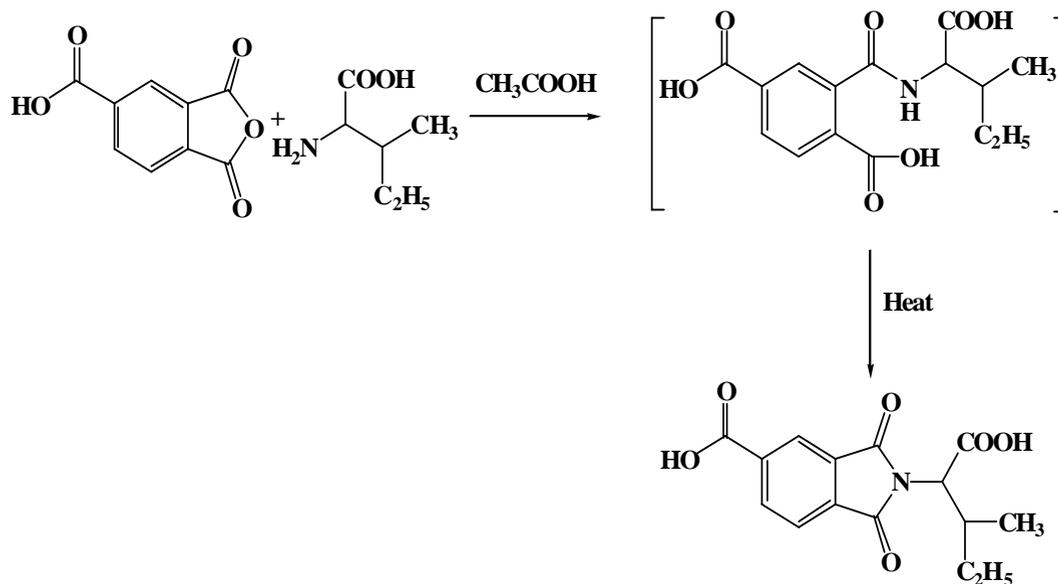


Fig. 1: Synthetic route for the synthesis 2-(1-carboxy-2-methylbutyl)-1,3-dioxoisindoline-5-carboxylic acid structure

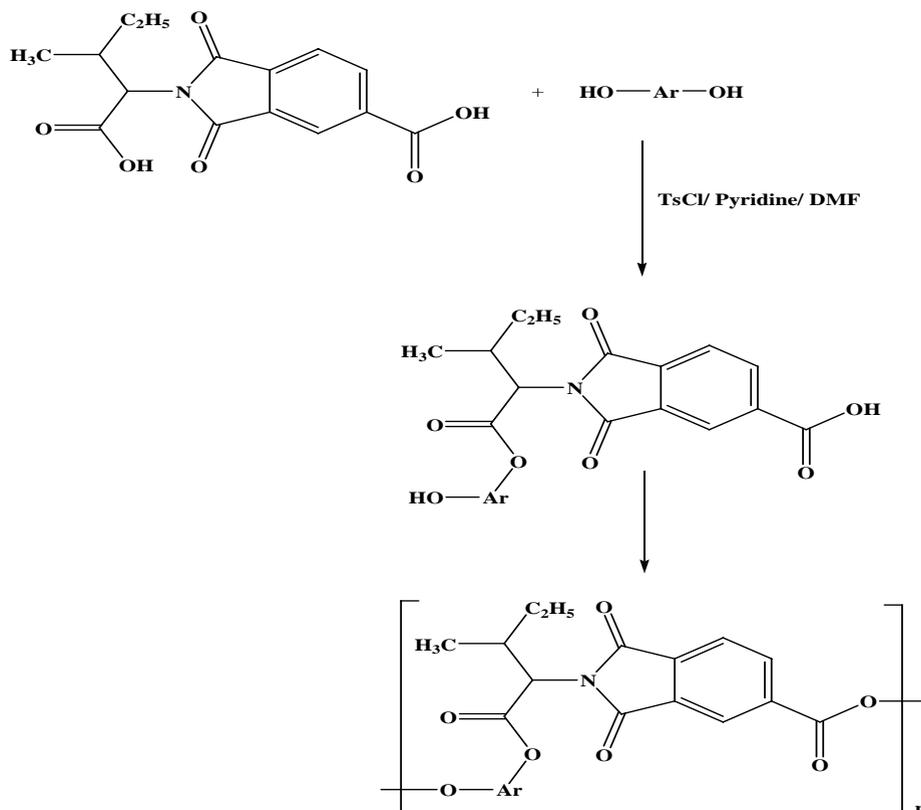


Fig. 2: Synthetic route for the synthesis poly(ester-imide)s derivatives

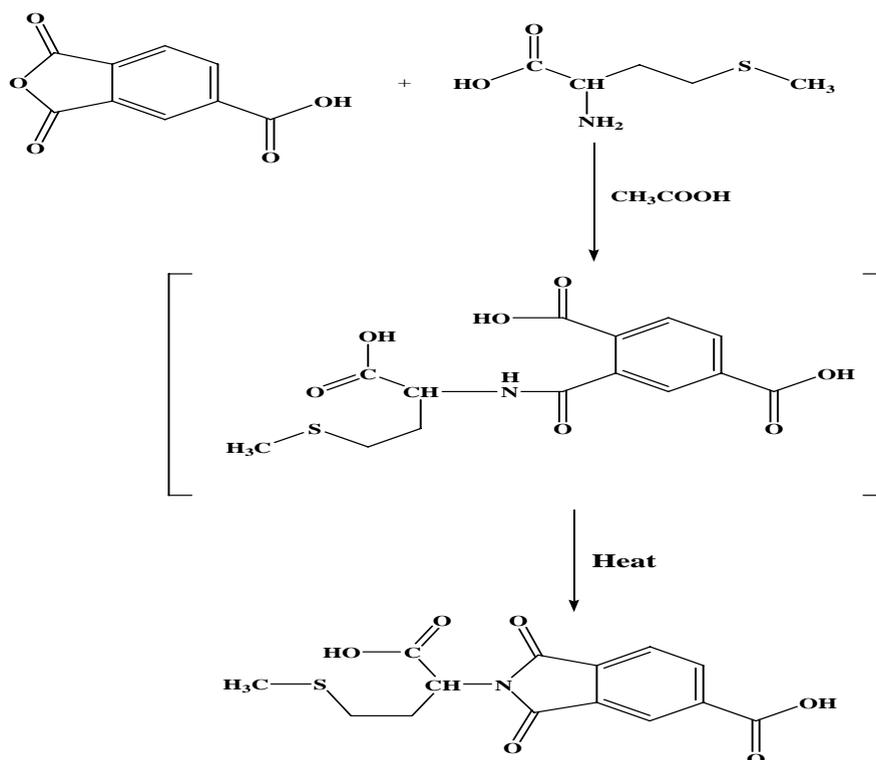


Fig. 3: Synthetic route for the synthesis 2-(1-carboxy-3-(methylthio)propyl)-1,3-dioxisoindoline-5-carboxylic acid structure

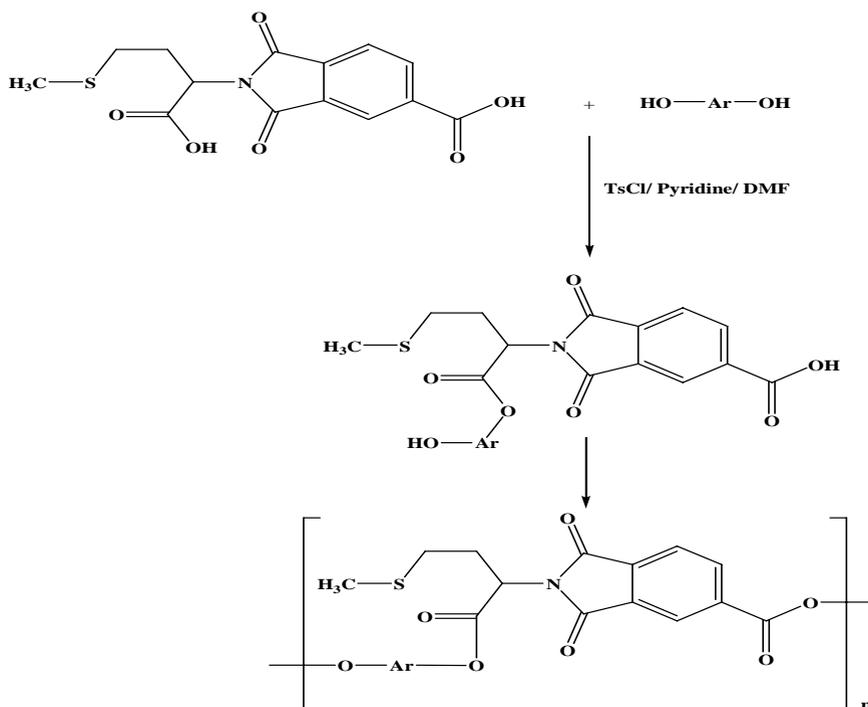


Fig. 4: Synthetic route for the synthesis other poly(ester-imide)s derivatives

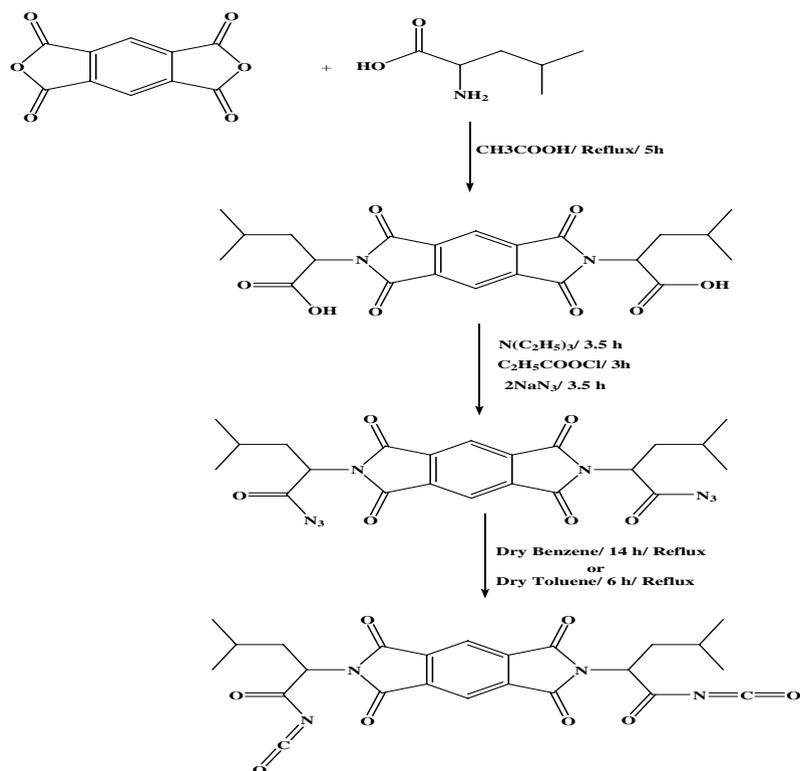


Fig. 5: Synthetic route for the synthesis *N,N*-(pyromellitic)bis(4-isobutyl-2-oxo-1,2,3,4-tetrahydro-1H-imidazole-5-carbonyl diisocyanate) structure

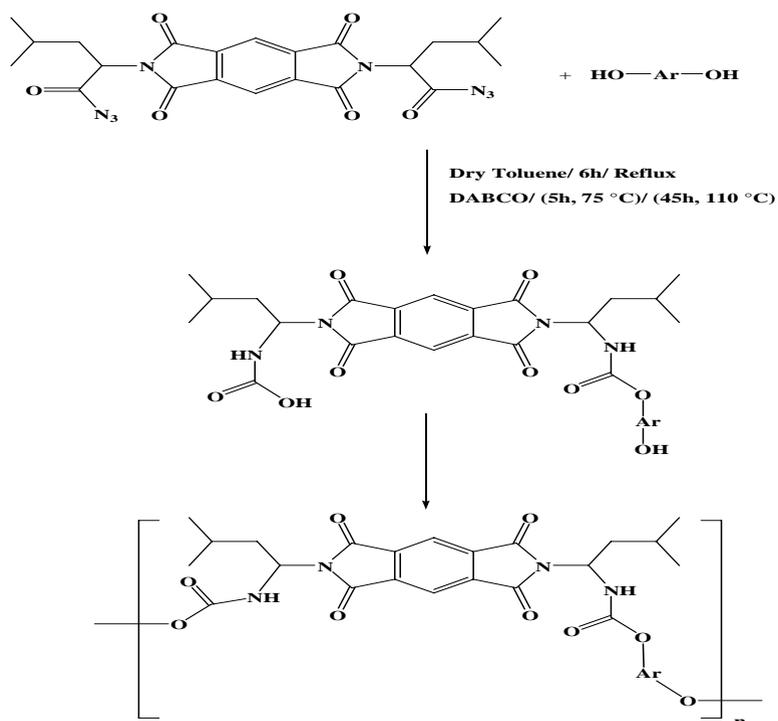


Fig. 6: Synthetic route for the synthesis other poly(imide-urethane)s derivatives

acid-2 (0.102 g, 7.806 mol⁻⁴) and DMF (2 mL) were added and the reaction mixture was refluxed for 4 h. Then, the obtained solution was added to 20 mL of cold, diluted HCl (10%) and 2-(1-carboxy-2-methylbutyl)-1,3-dioxoisindoline-5-carboxylic acid was removed as a white sediment which after being filtered and vacuum dried yielded 0.180 g (76%) of 2-(1-carboxy-2-methylbutyl)-1,3-dioxoisindoline-5-carboxylic acid. 2-(1-carboxy-2-methylbutyl)-1,3-dioxoisindoline-5-carboxylic acid re-crystallized easily in mixture of methanol and water as white crystals and its melting point was 195-97°C.

A white dark compound; Mp 195-197 °C; IR (KBr): 2700-3700 (s, sh), 2800 (s, br), 1780 (s, sh), 1700 (s, br), 1600 (m, sh), 1485 (m), 1460 (m), 1420 (m), 1380 (s), 1340 (s, sh), 1280 (s), 1260 (m, sh), 1200 (m), 1170 (m), 1150 (m, sh), 1090 (m), 1020 (w), 960 (w, sh), 930 (m), 880 (m), 800 (w), 760 (m), 730 (s), 705 (m), 650 (m), 570 (w), 530 (w), cm⁻¹. ¹H-NMR (DMSO-*d*₆, TMS, 90MHz): δ 0.70-1.09 (t, 3H, *J* = 6.0 Hz), 1.10-1.30 (d, 3H, *J* = 6.0 Hz), 1.37-2.70 (m, 3H), 4.55-4.80 (d, 1H, *J* = 6.9 Hz), 8.05-8.25 (d, 1H, *J* = 6.30 Hz), 8.50-8.75 (m, 2H), 8.00- 9.80 (s, 2H) ppm Anal. Calcd for C₁₅H₁₅ON₆: C, 59.01; H, 4.59; N, 4.95; Found: C, 59.22; H, 4.59 N, 5.04.

Synthesis 1a to 6a poly(ester-imide)s derivatives

Synthesis method of 1a to 6a poly(ester-imide)s through direct condensation polymerization is presented in this part. In view of the fact that the procedures are similar only one of these compounds will be explained.

Synthesis 2a poly(ester-imide)s

In a round-bottom 50 mL balloon 0.325 g (1.70 mol⁻³) of tosyl chloride dissolved in 0.30 mL (15.20 mol⁻³) of dry pyridine under room temperature. After stirring for 30 min at room temperature, 0.10 mL (13.00 mol⁻⁴) of pure dimethylformamide (DMF) was added and the solution was stirred for 30 min at room temperature. Then, a solution of 0.200 g (7.8 mol⁻⁴) of di-acid in 0.30 mL of pyridine was added drop wise to it. By adding di-acid solution and stirring for 30 min. the solution became viscous. Subsequently, a solution of 0.094 g (7.8 mol⁻⁴) diol bis phenyl in 0.30 mL of pyridine which was stirred for 35 min. was added

dropwise to it under room temperature and the obtained solution was stirred for 2 h under nitrogen atmosphere at 120°C. After cooling, the obtained transparent viscous solution was poured into 50 mL of cold methanol. The sediment was filtered and vacuum dried for 11 h at 80°C. The yield of the reaction was equal to 0.299 g (92%).

IR (KBr): 2945 (s), 1785 (s, sh), 1743 (s), 1724 (m), 1605 (m, br), 1512 (s), 1468 (s), 1379 (m), 1352 (s, sh), 1291 (s), 1246 (s), 1204 (m), 1165 (s), 1108 (s), 1082 (m), 1061 (s), 1014 (s), 926 (m), 859 (s), 807 (m), 731 (s), 567 (w) cm⁻¹. Anal. Calcd for C₃₀H₂₉NO₇: C, 69.89; H, 5.66; N, 2.68; Found: C, 68.22; H, 5.59 N, 3.01.

Synthesis 1a poly(ester-imide)s

IR (KBr): 3412(H₂O), 2958 (s), 1768 (m), 1730 (s), 1611 (m), 1509 (m), 1466 (s), 1382 (m), 1275 (m), 1243 (m), 1200 (s), 1171 (s), 1108 (m), 1052 (s), 1023 (w), 970 (m), 923 (s), 746 (s), cm⁻¹. Anal. Calcd for C₂₇H₂₁NO₆S: C, 66.45; H, 4.39; N, 2.87; Found: C, 67.91; H, 3.16; N, 4.41.

Synthesis 3a poly(ester-imide)s

IR (KBr): 2954 (m), 1783 (s, sh), 1746 (s), 1723 (m), 1629 (m, br), 1512 (s), 1378 (m), 1345 (m, sh), 1276 (s), 1240 (m), 1190 (s), 1162 (s), 1088 (m), 1053 (m), 1003 (s), 816 (m), 729 (s), cm⁻¹. Anal. Calcd for C₂₇H₂₁NO₆S: C, 62.42; H, 4.07; N, 2.70; Found: C, 64.13; H, 3.66; N, 4.31.

Synthesis 4a poly(ester-imide)s

IR (KBr): 3404(m, br, H₂O), 2957 (s), 1784 (s, sh), 1736 (s, sh), 1712 (s), 1567 (s), 1477 (m), 1432 (w), 1354 (m), 1329 (s), 1280 (s), 1232 (m), 1221 (s), 1162 (m), 1084 (s), 1050 (m), 1019 (s), 924 (w), 806 (w), 712 (s), cm⁻¹. Anal. Calcd for C₂₁H₁₇NO₆: C, 66.48; H, 4.52; N, 3.69; Found: C, 67.71; H, 5.19; N, 5.12.

Synthesis 5a poly(ester-imide)s

IR (KBr): 3405(m, br, H₂O), 2956 (m), 1788 (s, sh), 1743 (s), 1726 (m), 1575 (s), 1488 (s), 1389 (s), 1326 (m), 1275 (m), 1238 (s), 1222 (s), 1154 (s), 1111 (m), 1032 (m), 1012 (m), 923 (w), 834 (m, br), 726 (s), 688 (m), 564 (m, br), cm⁻¹. Anal. Calcd for C₃₇H₃₆N₂O₈: C, 71.54; H, 4.29; N, 2.38; Found: C, 71.43; H, 4.03; N, 5.42.

Table 1: Yields and reaction conditions of the synthesized poly(ester-imide)s derivatives.

En	Reactant	Ar	Product	Yield (%)	Color
1a				89	Yellow
2a				92	White
3a				94	Yellow
4a				88	White
5a				91	White
6a				80	Yellow

Synthesis 6a poly(ester-imide)s

IR (KBr): 3406(m, br, H₂O), 2954 (m), 1786 (s, sh), 1754 (s), 1723 (m), 1675 (s), 1646 (s), 1594 (s), 1468 (m), 1427 (s), 1383 (m), 1364 (s), 1322 (m), 1265 (s), 1243 (s), 1212 (s), 1154 (s, sh), 1109 (s), 1095 (m), 1070 (m), 1043 (s), 1022 (m), 863 (m), 788 (m), 720 (s), cm⁻¹. Anal. Calcd for C₃₀H₂₇NO₆: C, 72.42; H, 5.47; N, 2.82; Found: C, 73.69; H, 4.16; N, 5.09.

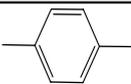
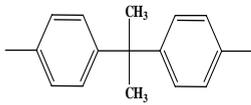
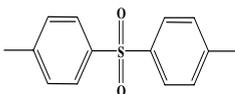
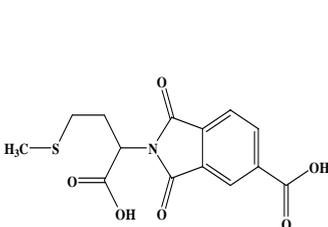
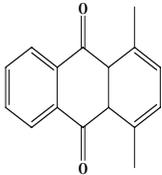
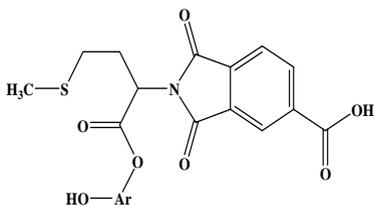
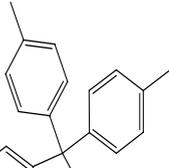
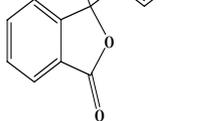
Synthesis 2-(1-carboxy-3-(methylthio)propyl)-1,3-dioxoisindoline-5-carboxylic acid structure

2.00 g (10.40 mol⁻³) of trimellitic anhydride, 1.552 g (10.40 mol⁻³) of methionine, and 50.00 mL

of asetic acid were charged into a round-bottom 50 mL balloon equipped with refrigerant, dryer and magnetic stirrer. The mixture was refluxed for 11 h under solvent boiling point. Then, 40 mL of concentrated HCl (37%) was added to it and the white residue was filtered, washed with water and dried. The yield of the reaction was 2.91 g (91%). This compound re-crystallized in mixture of methanol and water as white crystals. Melting point of this optically active di-acid was 192-93°C.

A white dark compound; Mp 192-193 °C; IR (KBr): 2650-3550 (s,sh), 2803 (s, br), 1784 (s,sh), 1703 (s), 1622 (m, sh), 1485 (s), 1469 (m), 1432

Table 2. Yields and reaction conditions of the synthesized poly(ester-imide)s derivatives.

En	Reactant	Ar	Product	Yield (%)	Color
1b				92	Yellow
2b				95	White
3b				95	Yellow
4b				91	White
5b				86	White
6b				88	Yellow

(m), 1343 (s), 1339 (s,sh), 1273 (m), 1260 (s,sh), 1200 (s), 1170 (m), 1150 (m,sh), 1090 (m), 1020 (w), 960 (w,sh), 930 (m), 886 (m), 802 (w), 765 (m), 734 (s), 705 (m), 657 (m), 578 (w), 539 (w), cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_6\text{S}$: C, 50.48; H, 3.58; N, 4.53; Found: C, 50.01; H, 3.26; N, 4.43.

Synthesis 1b to 6b poly(ester-imide) derivatives

Synthesis of 1b to 6b poly(ester-imide)s are also similar. Therefore, one of these compounds will be explained. It should be mentioned that synthesis of all compounds is based on direct condensation solution polymerization.

Synthesis 2b poly(ester-imide)

In a round-bottom 50 mL balloon 0.324 g (16.10 mol^{-3}) of tosyl chloride dissolved in 0.30 mL (15.20 mol^{-3}) of dry pyridine under room temperature. After stirring for 30 min. at room temperature, 0.10 mL (13.00 mol^{-4}) of pure dimethylformamide was added and the solution was stirred for 30 min. at room temperature. Then, a solution of 0.200 g (6.18 mol^{-4}) of di-acid in 0.30 mL of pyridine was added drop wise to it. After stirring for 35 min. the solution became viscous. Subsequently, a solution of 0.142 g (6.18 mol^{-4}) diol bis phenyl in 0.30 mL of pyridine which was

Table 3. Yields and reaction conditions of the synthesized poly(imide-urethane)s derivatives.

En	Reactant	Ar	Product	Yield (%)	Color
1c				91	White
2c				87	White
3c				89	White
4c				80	White
5c				85	Yellow

stirred for 40 min was added drop wise to it under room temperature and the obtained solution was stirred for 2 h under nitrogen atmosphere at 125°C. After cooling, the obtained transparent viscous solution was poured into 60 mL of cold methanol. The sediment was filtered and vacuum dried for 9 h at 75°C. 0.302 g of polymer was obtained and the yield of the reaction was equal to 95%. The melting point of 2b polymer was 220-25°C.

A white dark compound; Mp 220-225 °C; IR (KBr): 3484 (m), 3065 (m), 2972 (s), 2925 (m), 1722 (s), 1634 (s), 1605 (m), 1506 (m), 1434 (s), 1385 (s), 1282 (s), 1257 (s), 1211 (s), 1177 (s), 1116 (s), 1089 (m), 1063 (s), 1016 (s), 954 (m), 923 (s), 864 (m), 812 (s), 733 (s), 616 (m), 555 (m), cm⁻¹.

¹. Anal. Calcd for C₁₉H₁₃NO₆S: C, 59.53; H, 3.42; N, 3.65; Found: C, 60.47; H, 2.13; N, 4.07.

Synthesis 1b poly(ester-imide)

IR (KBr): 3485 (m), 3077 (m), 2925 (m), 1723 (s), 1604 (s), 1505 (m), 1465 (sm), 1433 (m), 1388 (s), 1282 (m), 1252 (s), 1205 (s), 1169 (m), 1110 (s), 1088 (m), 1062 (s), 1021 (m), 976 (m), 936 (m), 855 (s), 746 (m), 716 (s), 687 (s), 615 (w), 533 (m), 515 (w), cm⁻¹. Anal. Calcd for C₃₃H₂₁NO₈S: C, 67.00; H, 3.58; N, 2.37; Found: C, 67.98; H, 2.32; N, 3.97.

Synthesis 3b poly(ester-imide)

IR (KBr): 3483 (m), 3113 (m), 2915 (m), 1725 (m), 1573 (s), 1483 (m), 1432 (m), 1382 (s),

1288 (m), 1154 (s), 1114 (s), 1052 (m), 1011 (s), 813 (s), 732 (s), 618 (m), 535 (s), cm^{-1} IR (KBr): 2945 (m), 2900 (m, sh), 2243 (s), 1775 (m), 1732 (s, sh), 1712 (s), 1455 (m), 1409 (m), 1374 (m, sh), 1238 (m), 1114 (m), 1084 (m), 1032 (m), 943 (s), 922 (m), 900 (m, sh), 842 (w), 812 (s), 785 (m), 734 (s), 695 (s), 614 (m), 532 (m) cm^{-1} . Anal. Calcd for $\text{C}_{28}\text{H}_{27}\text{NO}_6\text{S}$: C, 66.52; H, 5.38; N, 2.77; Found: C, 67.61; H, 4.56; N, 3.81.

Synthesis 4b poly(ester-imide)

IR (KBr): 3485 (m), 3100 (m), 2925 (m), 1733 (s), 1626 (m), 1593 (s), 1497 (s), 1433 (m), 1395 (s), 1318 (s), 1285 (s), 1244 (s), 1208 (s), 1144 (m), 1115 (s), 1072 (m), 1051 (m), 1025 (s), 954 (m), 918 (s), 863 (m), 833 (m), 764 (w), 722 (s), 683 (m), 622 (m), 564 (s), cm^{-1} . Anal. Calcd for $\text{C}_{25}\text{H}_{17}\text{NO}_8\text{S}_2$: C, 57.36; H, 3.27; N, 2.68; Found: C, 58.02; H, 2.34; N, 3.24.

Synthesis 5b poly(ester-imide)

IR (KBr): 2923 (m, br), 1784 (m), 1726 (s), 1485 (m), 1373 (s), 1292 (s), 1256 (m), 1135 (s), 1020 (m), 929 (m), 877 (s), 805 (m), 749 (m), 733 (s), 715 (s), 622 (m), 618 (s), 576 (w), 522 (m), 454 (m), cm^{-1} . Anal. Calcd for $\text{C}_{27}\text{H}_{15}\text{NO}_8\text{S}$: C, 63.16; H, 2.94; N, 2.37; Found: C, 64.71; H, 2.46; N, 3.58.

Synthesis 6b poly(ester-imide)

IR (KBr): 3483 (m), 3072 (m), 2925 (m), 1733 (m), 1645 (s), 1612 (m), 1500 (m), 1435 (m), 1384 (s), 1247 (m), 1168 (s), 1108 (s), 1055 (m), 1035 (m), 952 (m), 921 (m), 866 (m), 812 (m), 782 (m), 733 (s), 662 (w), 613 (s), 525 (m), cm^{-1} . Anal. Calcd for $\text{C}_{25}\text{H}_{17}\text{NO}_6\text{S}_2$: C, 61.09; H, 3.49; N, 2.58; Found: C, 62.31; H, 2.86; N, 3.42.

Synthesis N,N-(pyromellitic)bis lous diisocyanate structure

0.25 g (10.12 mol^{-4}) of di acyl azide dissolved in 20 mL of dry benzene. The solution was refluxed for 3 h under nitrogen atmosphere. Then, benzene was removed under reduced pressure and the crude product was re-crystallized in mixture of benzene and dry hexane. 0.407 g of pure diisocyanate was obtained and the yield of the reaction was 92%. In another method, diisocyanate was produced with a lower yield in dry toluene under reflux condition for 5 h. The melting point of this compound was 61-62 °C (its thermal degradation point was 70°C).

A white dark compound; Mp 61-62 °C; IR (KBr): 2945 (m), 2900 (m, sh), 2243 (s), 1775 (m), 1732 (s, sh), 1712 (s), 1455 (m), 1409 (m), 1374 (m, sh), 1238 (m), 1114 (m), 1084 (m), 1032 (m), 943 (s), 922 (m), 900 (m, sh), 842 (w), 812 (s), 785 (m), 734 (s), 695 (s), 614 (m), 532 (m) cm^{-1} . Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_8$: C, 58.30; H, 4.48; N, 11.33; Found: C, 57.95; H, 4.63 N, 11.06.

Synthesis 1c to 5c poly(imide-urethane)s

Synthesis of 3c poly(imide-urethane)s is explained in the next part. The procedure of synthesis of other poly(imide-urethane)s are similar.

Synthesis 3c poly(imide-urethane)s

In a double-neck, round-bottom 25 mL balloon equipped with refrigerant, dryer and magnetic stirrer 0.20 g (4.04 mol^{-4}) of di acyl azide dissolved in 0.10 mL of dried toluene. Reaction mixture was placed under nitrogen atmosphere at solvent boiling point for 6 h. the obtained transparent solution cooled down to room temperature. Then, 0.006 g of DABCO and 0.092 g (4.04 mol^{-4}) of bis phenyl was added to the solution. While stirred intensively under nitrogen atmosphere, the reaction mixture was heated for 5 h at 75°C and for 52 h at 115°C. Then, the solution cooled and deposited 3c polymer. The deposit of 3c polymer dissolved in 0.40 mL of DMF and was poured into 60 mL of methanol. The deposit was filtered and vacuum dried at temperature of 85°C for 12 h. 0.254 g of polymer was produced and the yield of the reaction was 89%.

A white dark compound; IR (KBr): 3345 (m, br), 2934 (m), 1752 (s), 1735 (m, sh), 1712 (s), 1654 (m), 1512 (s), 1454 (m, sh), 1365 (m, sh), 1342 (s), 1263 (m), 1212 (s), 1175 (s), 1155 (m), 1026 (m), 962 (w), 853 (s), 732 (s), 617 (w), 565 (m) cm^{-1} . Anal. Calcd for $\text{C}_{37}\text{H}_{38}\text{N}_4\text{O}_8$: C, 66.62; H, 5.74; N, 8.40; Found: C, 68.97; H, 7.38; N, 6.36.

Synthesis 1c poly(imide-urethane)s

IR (KBr): 3345 (m, br), 2934 (m), 1772 (s), 1751 (m), 1725 (s), 1658 (m, sh), 1512 (m), 1488 (s), 1451 (m, sh), 1366 (m), 1340 (m), 1322 (m), 1284 (m, sh), 1267 (m), 1187 (m), 1133 (s), 1078 (m), 1012 (s), 951 (m), 833 (m), 732 (w), 731 (s), 636 (w), 579(w) cm^{-1} . Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}_9$: C,

59.36; H, 5.34; N, 9.89; Found: C, 59.87; H, 5.23; N, 10.03.

Synthesis 2c poly(imide-urethane)s

IR (KBr): 3355 (m, br), 2946 (m), 1765 (s), 1746 (s, sh), 1722 (m), 1665 (m, sh), 1643 (m, sh), 1527 (s), 1485 (m), 1452 (m, sh), 1368 (s), 1338 (m), 1318 (m), 1272 (s), 1255 (m), 1200 (s), 1154 (m), 1142 (s), 1075 (m), 1020 (w), 1003 (m), 955 (s), 822 (m), 756 (w), 735 (s), 624 (w), 569(w) cm^{-1} . Anal. Calcd for $\text{C}_{34}\text{H}_{32}\text{N}_4\text{O}_8$: C, 65.38; H, 5.16; N, 8.97; Found: C, 64.96; H, 5.32; N, 10.92.

Synthesis 4c poly(imide-urethane)s

IR (KBr): 3352 (m, br), 3112 (w), 2952 (m), 1773 (m), 1743 (s), 1721 (m), 1654 (s), 1612 (s), 1585 (s), 1522 (m), 1454 (s), 1432 (m), 1387 (s), 1356 (m), 1342 (s), 1275 (m), 1235 (s), 1212 (s), 1143 (m), 1073 (s), 1054 (w), 1022 (m), 1002 (m), 884 (m), 843 (w), 782 (m), 725 (s), 627 (w), 613 (w), 580 (w) cm^{-1} . Anal. Calcd for $\text{C}_{36}\text{H}_{30}\text{N}_4\text{O}_{10}$: C, 63.71; H, 4.45; N, 8.25; Found: C, 63.82; H, 4.46 N, 7.21.

Synthesis 5c poly(imide-urethane)s

IR (KBr): 3348 (m, br), 2953 (m), 2847 (m, sh), 1775 (m), 1752 (s), 1711 (m), 1632 (m), 1522 (m, sh), 1503 (m), 1454 (s), 1360 (m), 1332 (s), 1322 (m), 1277 (s), 1245 (m), 1218 (s), 1163 (m), 1152 (s), 1102 (m, sh), 1077 (m), 1022 (s), 1012 (m), 974 (m), 941 (s), 935 (m), 855 (m), 815 (m), 751 (s), 711 (s), 677 (m), 614 (w), 565(w) cm^{-1} . Anal. Calcd for $\text{C}_{42}\text{H}_{36}\text{N}_4\text{O}_{10}$: C, 66.66; H, 4.79; N, 7.40; Found: C, 65.88; H, 5.25; N, 8.47.

RESULTS AND DISCUSSION

20 new poly(ester-imide) and poly(imide-urethane) structures were synthesized using low condensation solution mechanism. These compounds were optically active, capable of emitting circularly polarized light. The process of the synthesis of the compounds is displayed in figures 1 to 6. The speed and yield of the reactions are reported in tables 1 to 3. The result of TGA revealed that heat resistance of some poly(ester-imide) derivatives was higher than 300°C, while heat resistance of poly(imide-urethane) compounds was about 70°C. With respect to the fact that synthesis of these polymers was carried out in

solution phase, an important point was that their synthesis conditions were highly depended on some general factors such as physical and special properties of the materials, selected physical conditions of reaction, equivalence of reactants, and appropriate temperature. The synthesis of poly(ester-imide)s based on diacids by direct condensation solution polymerization was carried out by condensation initiators such as DMF/Py/TSCI. Viscosity affected by various factors such as growth time of TSCL/Py, amount of DMF added to TSCL/Py, adding time of diol, and reaction time, was studied in numerous experiments. The most important point was the influence of the amount of DMF. Due to absence of hydrogen bond, no salt was required in the synthesis of polyesters. Since the synthesis of polyesters was difficult, direct condensation polymerization method was employed which could produce polyesters with a higher molecular weight under better conditions and in less time. The reason of selecting this method for synthesis of poly(imide-urethane)s was that, in comparison with similar synthesis methods, direct condensation polymerization produced a higher yield and developed the mechanism more slowly.

CONCLUSION

The polymers were soluble in polar aprotic solvents but not in common organic solvents. In comparison with poly(ester-imide)s, poly(imide-urethane)s had less heat resistance which was resulted from the weakness of urethane bonds against heat. However, both polymers were optically active because of containing a chiral center. Optically active polymers based on amino acids could induce chirality to polymer chain and were biologically degradable. Introduction of amino acid groups resulted in high optical activity in these polymers and increased their solvency in polar solvents. In comparison with similar synthesis methods, direct condensation polymerization produced a higher yield and improved reaction speed. The direct condensation polymerization method employed in synthesis of the

polymers could produce polymers with a higher molecular weight under better conditions and in less time.

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REFERENCES

- J.Y. Jadhav, J. Preston, W.R. Krigbaum, *J. Polym. Chem. Sci*, **27**: 1175 (1989).
- H. Schnell, *Ind. Eng. Chem*, **51**: 157 (1959).
- A.J. Conix, *Ind. Eng. Chem*, **51**: 147 (1959).
- J. Preston, W.L. Hofferbert, *Polym. Symph*, **65**: 13 (1978).
- H. Williams, *Chem. Ind. (London)*, **79**: 900 (1960).
- M.P. Stevens, *Polymer Chemistry*, Oxford Univ. Press, 382 (1999).
- J.Y. Jadhav, J. Preston, W.R. Krigbaum, *J. Polym. Chem. Sci*, **27**: 1175 (1989).
- A. Blumstien, K.N. Sivaramakrishnan, R.B. Blumstein, S.B. Clough, *Polymer*, **23**: 47 (1982).
- J. Blackwell, G.A. Gutierrez, *Polymer*, **12**: 671 (1982).
- G.R. Mitchell, A.H. Windle, *Polymer*, **23**: 1269 (1982).
- J. Blackwell, G. Liezer, G.A. Gutierrez, *Macromolecules*, **16**: 1418 (1983).
- W. Volksen, J.R. Lyerla, J. Economy, B. Dawson, *J. Polym. Chem. Ed*, **21**: 2581 (1984).
- H.R. Dcke, R.W. Lenz, *J. Polym. Chem. Ed*, **22**: 2249 (1984).
- F. Higashi, N. Akiyama, T. Koyama, *J. Polym. Chem. Ed*, **21**: 3233 (1983).
- H.D. Stenzenberger, *Add. Polym. Sci*, **117**: 165 (1994).
- M. Kyotana, H. Kanetsuna, *J. Polym. Chem. Ed*, **21**: 379 (1983).
- J. Asrai, H. Torium, J. Watanabe, W.R. Krigbaum, A. Ciferri, *J. Polym. Phys. Ed*, **21**: 1119 (1983).
- G. Liezer, G. Schwarz, H.R. Kricheldorf, *J. Polym. Phys. Ed*, **21**: 1599 (1983).
- D. Acierno, F.P. Lamantia, G. Polizzotti, A. Ciferri, W.R. Krigbaum, R. Kotek, *J. Polym. Phys*, **21**: 2027 (1983).
- D.R. Patil, *J. Macromol. Soc. Chem*, **27**: 331 (1990).
- S. Malti, S. Das, *Angew. Makromol. Chem*, **86**: 181 (1980).
- S. Sasaki, Y. Hasudu, *J. Polym. Lett. Ed*, **25**: 377 (1987).
- S.K. Douli, D. Pal, S. Maiti, *J. Appl. Polym. Sci*, **30**: 3867 (1985).
- S. Maiti, S. Das, *J. Appl. Polym. Sci*, **86**: 957 (1991).
- Bennabi, Lamia, Belarbi Lahcene, Bousalem Smain and Abederrezak Mesli., *Orient J. Chem.* **27**(2): 537-543 (2011).
- H. Sidney, *Hand book of Thermoset Plastics*, Noyes Publications, New York, (1986).
- H.D. Kim, T.J. Lee, *J. Appl. Polym. Sci*, **73**: 345 (1997).
- J.H. Chief, *Chemical Engineers Hand book*, Forth Edition, (1963).
- N.R. Nardo, *J. Elastomers and Plastics*, **19**: 11 (1987).
- H.D. Kim, J.H. Huh, *J. Appl. Polym. Sci*, **69**: 1349 (1998).
- G. Labbe, *Synthesis*, **6**: 525 (1987).
- R.V. Sreenivasulu, T.M. Aminabhavi, *Polym. Plast. Technol. Eng*, **32**: 15 (1993).
- I. Bechara, *J. Cell. Plast*, **15**: 102 (1979).
- H. Sehovic, A. Sendijarevic, V. Sendijarevic, S. Wong, K.C. Frisch, *J. Coat. Technol*, **59**: 747 (1987).
- M. Bogumila, *J. Appl. Polym. Sci*, **30**: 2731 (1987).